Photoelectrochemical Water Splitting of Modified Tungsten Oxide Nanostructures via Vapour Deposition

This thesis is submitted in partial fulfilment of the requirements for the Degree of Doctor of Philosophy (Chemistry)

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2020 June
Declaration

I, Xueling Xia, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm this has been indicated in the thesis.
Abstract

Semiconductor photocatalysts have been used for water splitting for several decades. By utilizing solar energy, splitting water into H₂ and O₂ is considered to be a promising way for generating renewable energy. The aim of this project was to synthesize and study different nanostructured photoelectrode materials for photoelectrochemical (PEC) water splitting. Tungsten(VI) oxide (WO₃) is a promising photoanode material which is active under visible light illumination. Flat WO₃ films and nanostructured WO₃ films were deposited via aerosol-assisted chemical vapour deposition (AACVD). The morphology, structure and PEC properties of the films were compared, with nanostructured WO₃ films showing improved performance compared to flat WO₃ films (~ 0.41 mA/cm²) with an average photocurrent density of ~ 0.68 mA/cm² at 1.23 V vs. RHE (reversible hydrogen electrode).

Nanostructured WO₃ modified with Au, Ag and Pt nanoparticles (NPs) were deposited via AACVD on nanostructured WO₃ films, and deposition parameters optimized. The band gap of metal NP-modified WO₃ films appeared narrower than that for WO₃ alone. The size, morphology and density of metal nanoparticles were controlled by deposition temperature and precursor amount with (0.1 mg) Au/WO₃ and (100 µL) Ag/WO₃ both having the highest photocurrent density amongst all samples at 0.96 mA/cm² at 1.23 V (vs. RHE), which was 1.5 times that of undecorated WO₃. Pt/WO₃ showed 1.33 times PEC enhancement.

Highly uniform, dense, amorphous TiO₂ and Al₂O₃ films were synthesized via atomic layer deposition (ALD). Precursor vapour pressure, dose/purge times, gas flow rate and deposition temperature were optimised. The growth rate of TiO₂ deposition was in the range of 0.5 – 0.7 Å/cycle. For Al₂O₃, a stable ALD process with a growth rate of 1 – 1.4 Å/cycle was observed.

Heterojunction films composed of WO₃, metal NPs, TiO₂ and Al₂O₃ thin films were constructed together in specific sequence in order to optimise PEC water splitting
performance. Ag/WO$_3$ films with and without ALD layers had higher PEC performance and were more stable than undecorated WO$_3$ films after 24 h, however the use of ALD layers wasn’t considered to be fully successful, and the parameters need further optimization.
Impact Statement

As the natural resource crisis issue becomes more urgent, using solar energy for providing electricity is getting more popular. This PhD project focused on the fabrication of photoelectrochemical materials, WO$_3$ and its modification with metal nanoparticles and thin film layers via different deposition techniques.

Inside academia:

A new recipe of Al$_2$O$_3$ thin film deposition using a novel Al precursor via ALD has been established. The work of Al$_2$O$_3$ ALD has been published and referenced by other researchers in the field. During doing the PhD project, the ALD system was adapted to enable different precursor deliveries and was also proved having advantages for research. The ALD work was also utilized for collaboration with other research groups.

ALD, CVD and AACVD have all been chosen to prepare nanomaterials with different structures such as nanoneedles, nanoparticles and thin film. They demonstrated a way to produce varies nanostructures using selected methods. The purpose of using different components for photoactive electrode, surface plasmon resonance and passivation protection has been considered, which showed its potential for solar energy application.

The sandwich devices of WO$_3$/Metal/Metal oxide for water splitting have been designed and tested. The systematic study of different deposition parameters for building different nanomaterials provides ideas for future work in this area.

Outside academia:

Some work of TiO$_2$ and Al$_2$O$_3$ deposition using our ALD system has also been done for a commercial company. The new routes of metal nanoparticles AACVD show potentials for industrial CVD for metal nanoparticle coatings as well. The whole device was interested to be tested in gas sensing sector at gas sensor manufacturing companies which our group has collaboration with.
Acknowledgements

First, I would like to thank my supervisor, Professor Chris Blackman. Chris gave me the opportunity to get involved in the world of ALD and CVD which I had zero knowledge before, and he had to taught me everything. Chris has been very supportive through my whole PhD period, not only in research but also in my life.

Special thanks to my colleagues and seniors in the group, Dr. Rachel Wilson, Dr. Yaomin Li and Dr. Yiyun Zhu for their patient guidance and help related to ALD, CVD and my life. Great thanks to Mr. Tom Bridges, Mr. Jim Stevenson, Mr. Jim Percival, Mr. John Cowly, Mr. Tony Bernard, Mr Charles Willoughby, they were always there helping me when I need technical support (laterally fixing everything every day!), I can’t finish this project without them.

I would like to thank people at UCL, Dr. Steven Firth, Dr. Steve Hudziak, Professor Robert Palgrave, Dr. Alaric Taylor, Mr. Martin Vickers, Mr. Jian Guo, Dr. Sanjay Sathasivam, Dr. Caroline Knapp, Dr. Tom Gregory, Dr. Barry Reid, Dr. Jose Marin Beloqui; people from Imperial College, Dr. Ye Ma, Dr. Andreas Kafizas; people from Beijing University of Chemical Technology, Ms. Qi Yan, Ms. Hongwei Wang, Ms. Yingchun Yu and my dear mom-Ms. Shujun Wang for the training, assistance and idea related to SEM, TEM, UV/Vis, AFM, EDS, XRD, XPS, ellipsometer and many other instrument. Thank Professor Jim Anderson, Mr. Tony Field, Mr. Joe Nolan, Ms. Ninik Smith, Dr. JadrankaButorac and all the academic and supportive staff in the department for their kind help.

I would like to thank Mr. Jone-him Tsang, Mr. Ju Hun Shin, Miss Yuting Yao, Miss Xinyue Zhang, Miss Jingyi Xu and Mr. Mingfeng Xu from our group, my colleagues, Miss Manni Yang, Dr. Tingting Zhao, Mr. Jianwei Li, Miss Premrudee Promdet, Mr. Fan Cui, Miss Yu Wang, Dr. Qiushi Ruan, Dr. Guanjie He, Dr. Yongzheng Xing for the help in research and friendship in life.
My lifelong friends, Sidan Bi, Yunhu Peng, Lihui Peng, Wenjin Xu, Bo Zhang, Na Pan, Weijie Wu, Shuhan Jin, Mengting Li and Shenkai Chen now at different time zone, thank you for the company and never give up.

To my fantastic flatmates, Miss Yifan Zhao, the coolest biochemist and Miss Jinwen Chen, the cutest stage manager, you are the best mates I can imagine. Yifan, you are going to be great.

I suffered from mental health issues during my PhD and did have tough time. When I escaped from the work, I spent a lot of time in the theatres and met many friends here and there. Andy, Bing, Cls, Ethel, Gaoxing, Geno, Jing, Jun, Kid A, Mai Mai, Martin, Miranda, Memory, Sherry, Xiaoxi, thank theatres bring us together. We had the best memories and.

Thank to ITA, Barbican and D’haus, my favourite theatres, Ivo van Hove and Miro Rau, my favourite directors and ITA ensemble, the best group of people in the world, my life became colourful and meaningful because of you. I have learned a lot to become a human. Eelco, thank you for your precious friendship.

The most important appreciation to my dearest mom and dad, thank you for your care, help and support in my life. I cannot be anything without you and I love you too.

This thesis was written during quarantine time when I was supposed to have a trip to AMS, our all-time favourite place. However, I had to cancel all the plans for this year and managed to finish this efficiently. Special thanks go to the music from Christian and Woods of Birnam, which I looped and sang everyday while writing.

To everyone I forgot to mention in the acknowledge, thank you.

Finally, the last sentence quoted from Angels in America: “More Life.”
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<th>Description</th>
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<tr>
<td>Ag-AMP</td>
<td>Silver 2-amino-2-methyl-1-propanol</td>
</tr>
<tr>
<td>AIP</td>
<td>Aluminium isopropoxide</td>
</tr>
<tr>
<td>ALE</td>
<td>Atomic layer epitaxy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>AACVD</td>
<td>Aerosol-assisted chemical vapour deposition</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>APCVD</td>
<td>Atmospheric pressure chemical vapour deposition</td>
</tr>
<tr>
<td>ATSB</td>
<td>Aluminium tri-sec-butoxide</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>eV</td>
<td>Electrovolt</td>
</tr>
<tr>
<td>Eg</td>
<td>Bandgap energy</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>GPC</td>
<td>Growth per cycle</td>
</tr>
<tr>
<td>HER</td>
<td>Hydrogen evolution reaction</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>HAuCl₄·3H₂O</td>
<td>Hydrogen tetrachloroaurate(III) trihydrate</td>
</tr>
<tr>
<td>H₂Cl₆Pt·xH₂O</td>
<td>Hydrogen hexachloroplatinate(IV) hydrate</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre for Diffraction Data</td>
</tr>
<tr>
<td>k</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>JCPDS</td>
<td>Joint Committee on Powder Diffraction Standards</td>
</tr>
<tr>
<td>LPCVD</td>
<td>Low pressure chemical vapour deposition</td>
</tr>
<tr>
<td>LSPR</td>
<td>Localized surface plasmon resonance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>MFC</td>
<td>Mass Flow Controller</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal-organic chemical vapour deposition</td>
</tr>
<tr>
<td>n</td>
<td>Refractive index</td>
</tr>
<tr>
<td>NNs</td>
<td>Nanoneedles</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>OER</td>
<td>Oxygen evolution reaction</td>
</tr>
<tr>
<td>OPr</td>
<td>Isopropoxide</td>
</tr>
<tr>
<td>PEC</td>
<td>Photoelectrochemical</td>
</tr>
<tr>
<td>Ra</td>
<td>Roughness (average)</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible hydrogen electrode</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean squared roughness</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard cubic centimetres per minute</td>
</tr>
<tr>
<td>SEA</td>
<td>Spectroscopic ellipsometry analysis</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SPP</td>
<td>Surface plasmon polariton</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface plasmon resonance</td>
</tr>
<tr>
<td>TAS</td>
<td>Transient absorption spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TTIP</td>
<td>Titanium (IV) isopropoxide</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>W(CO)$_6$</td>
<td>Tungsten hexacarbonyl</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

1.1 Overview

On April 22nd 2020, this year’s Earth Day, there was an article posted on The Guardian, “Pandemic side-effects offer glimpse of alternative future on Earth Day 2020”[2]. Since most flights were cancelled, public transportations were stopped, oil price hit zero, and human activities were minimized, significant improvement in air quality was observed. However, despite the Covid-19 pandemic crisis energy demand is generally still increasing rapidly in every industry all over the world. People consume natural resources faster than their formation, resulting in rapid pollution generation and therefore clean alternatives are in urgent demand for slowing down the energy crisis and environmental damage. Semiconductor photocatalysts, starting from TiO$_2$, have been used for water splitting for several decades. By utilizing solar energy, splitting water into hydrogen and oxygen is considered as a promising way for generating renewable energy. Tungsten(VI) oxide, WO$_3$, is a valuable material in this respect because of its low cost, low toxicity, excellent stability and visible light region band gap $^{[3]}$. Modifying pure WO$_3$, for instance by metal catalyst deposition, doping, semiconductor heterojunction formation or micro/nano-structure engineering, are routes to enhance its water splitting photocatalytic performance.

In the introduction, the principle of photoelectrochemical water splitting, the background of the materials used in the project (tungsten(VI) oxide, gold, silver, platinum, titanium oxide and aluminium oxide), complex nanostructure design and their influence on performance, preparation methods for nanostructures (especially aerosol assisted chemical vapour deposition (AACVD) and atomic layer deposition (ALD)) and the motivation and aims of this research project will be introduced.
1.2 Photoelectrochemical water splitting

1.2.1 Energy challenge and renewable energy

The most challenging issue of the 21st century is the energy crisis; how to generate enough energy to meet the desired living standard of an increasing population of over 8 billion? Coal, oil and natural gas, were generated by nature over millions of years, sequestering carbon dioxide. According to BP Statistical Review of World Energy in 2020, the reserves-to-production ratio (years of reserves left) of oil, natural gas and coal are 49.9 years, 49.8 years and 132 years [4]. The oil price was 30.37 US dollars per barrel in 2000, hit 100 US dollars per barrel in 2008 and dropped back to 57 US dollars per barrel in 2019 [4]. Although it dropped significantly at the start of 2020 [5], it is certain it will rise again once economic activity returns to pre-2020 levels, and fossil fuel extraction becomes increasingly difficult. However burning fossil fuels generates greenhouse gases including CO₂, which are starting to have a huge impact on the environment and hence global warming is a more urgent problem than the energy crisis in the near term.

As an alternative, free and renewable energy, solar energy has the second highest power generation capacity of 724.1 TWh (Terawatt-hours) in 2019 [4,6]. In 1972, Fujishima and Honda was the first reporting the photocatalytic water splitting using TiO₂ [7]. Since then, photoelectrochemical water splitting has been seen as an exciting new path for providing energy by converting solar energy into chemical energy [8].

1.2.2 Fundamentals of water splitting

Solar water splitting can be categorized into photocatalytic, thermochemical and photobiological water splitting methodologies [9]. Photocatalytic water splitting was demonstrated by Fujishima and Honda using TiO₂, and later noble metal decorated TiO₂, in a photoelectrochemical cell [7,10]. Figure 1.1 shows a photoelectrochemical cell using TiO₂ as a photoanode and Pt as a cathode. When the photoanode is under sufficient solar
energy illumination, that is with energy above the band gap of the material, electrons from the valence band are excited to the conduction band, resulting in generation of holes in the valence band. In the presence of an external bias, the electrons are transferred to the (Pt) cathode, producing H\textsubscript{2} from water reduction. The holes in the valence band are transferred from the (TiO\textsubscript{2}) photoanode to oxidize water to produce O\textsubscript{2}\textsuperscript{[11]}.

![Figure 1.1](image.png)

**Figure 1.1** a) PEC water splitting using a TiO\textsubscript{2} photoanode and b) a short-circuit model of a PEC cell\textsuperscript{[12]}.

The mechanism of photocatalytic water splitting for this system is shown in equation 1.1\textsuperscript{[11]}.

\[(1) \quad \text{TiO}_2 \xrightarrow{h\nu} e^- + h^+\]

\[(2) \quad 2\text{H}_2\text{O} + 4h^+ \rightarrow 4H^+ + O_2 \quad E_{ox}^0 = -1.229 \text{ V vs NHE}\]

\[(3) \quad 2H^+ + 2e^- \rightarrow H_2 \quad E_{red}^0 = +0.000 \text{ V vs NHE}\]

\[(4) \quad \text{H}_2\text{O} \rightarrow H_2 + \frac{1}{2} O_2, \quad \Delta G^0 = 237 \text{ kJ mol}^{-1} \quad \text{(Equation 1.1)}\]

The Gibbs free energy of overall water splitting reaction at 298 K and 1 mol/L electrolyte concentration is +237 kJ/mol. In acidic environment, a potential more positive than 1.229 V (vs NHE) is needed to oxidize water while a potential more negative than 0 V (vs NHE) is required to reduce water.
1.3 Background of tungsten oxide, gold, silver, platinum, titanium oxide and aluminium oxide

1.3.1 Tungsten oxide and its properties

WO₃ is an important functional material which has wide applications in electrochromic devices [13,14], photocatalysis [15,16], gas sensing [17,18] and photocatalytic water splitting [19,20]. WO₃ is yellow powder, with density ~ 7.16 g/cm³, melting point of 1473 °C and boiling point of 1700 °C. It is insoluble in water and acid (except hydrofluoric acid), and soluble in ammonium hydroxide forming tungstates [21]. The outer electron configuration of tungsten is 5d⁴6s², so it can present five valence states of +2, +3, +4, +5, and +6 in its compound, where the coexistence of different valence states may also occur. WO₃ is highest state of tungsten oxide. Generally, the oxygen ratio in WO₃ is not strictly the stoichiometric ratio of 1:3 and it is typically expressed in the form of WO₃-x, such as WO₂.₉₀, WO₂.₈₃ and WO₂.₇₂. Due to the existence of oxygen deficiency, some W⁶⁺ are reduced into W⁵⁺ and form a mixture of W⁵⁺ and W⁶⁺ [22].

The colour of WO₃ changes with the oxygen content. WO₃ appears yellow, WO₂.₉₀ appears purple, WO₂.₈₃ appears dark blue and WO₂.₇₂ appears blue [23]. The common WO₃ crystal phases include monoclinic II (ε-WO₃) [24], triclinic (δ-WO₃) [25], monoclinic I (γ-WO₃) [26], orthorhombic (β-WO₃) [27] and tetragonal (α-WO₃) [28]. The structure transformation of WO₃ depends on the temperature, tetragonal above 740 °C, orthorhombic between 330 – 740 °C, monoclinic I between 17 – 330 °C, triclinic between -43 – 17 °C and monoclinic II below -43 °C [29]. The monoclinic I structure is the most common one with a space group of P2₁/n. Each phase change of WO₃ is not a structural reconstruction but relates to a certain degree of adjustment and distortion based on the original tungsten-oxygen octahedron. The distortion of the octahedron (twist, tilt, etc.) and the displacement of tungsten atoms from the centre of the octahedron to the edges of the octahedron are the reasons of all phase transformations. The steady-state cubic-WO₃, which is not observed, is a non-twisted ReO₃ type structure with low crystallinity, while
the steady-state monoclinic I WO₃ exhibits a twisted ReO₃ type structure, forming a three-dimensional network of WO₆ octahedron. A schematic of monoclinic-WO₃ crystal structure are shown in figure 1.2.

\[ \text{Figure 1.2 Crystal structure of the monoclinic WO}_3^{[30]} \]

WO₃ is an n-type semiconductor with an indirect band gap of \( \sim 2.5 - 2.9 \) eV, whilst non-stoichiometric WO₃-x has a band gap of \( 2.4 - 2.8 \) eV \( ^{[31]} \), and the oxygen generating performance of WO₃ under visible light is superior than TiO₂ \( ^{[32]} \). The band gap of WO₃ and some other semiconductor materials used as photocatalysts for water splitting are shown in figure 1.3. The conduction band of WO₃ is not negative enough for water reduction but the valence band is very positive of the water oxidation potential and hence is very suitable for water oxidation. Therefore, WO₃ is normally used as a photoanode. WO₃ has an efficiency of \( \sim 4.8\% \) in photoelectrochemical water splitting device with a theoretical photocurrent of \( \sim 4.8 \) mA/cm² maximum under one sun illumination \( ^{[33]} \). WO₃ has low cost, low toxicity, good stability, low photo corrosion possibility, suitable band gap for PEC water splitting and superior electron transport properties comparing to TiO₂ \( (\sim 3.2 \text{ eV}) \), ZnO \( (\sim 3.2 \text{ eV}) \), α-Fe₂O₃ \( (\sim 2.2 \text{ eV}) \) and BiVO₄ \( (\sim 2.4 \text{ eV}) \) \( ^{[34,35]} \).
Figure 1.3 Band edge positions of various semiconductors with the redox potentials for water splitting at pH=0\[36\].

1.3.2 Gold, silver, platinum nanoparticles and SPR effect

Gold nanoparticles (Au NPs) are gold particles with a diameter of 1 to 100 nm which have unique optoelectronic properties. The properties are tuneable by changing size, shape, surface chemistry, or aggregation state of Au NPs. Their broad range of applications include electronics\[37\], sensing\[38\], drug delivery\[39\], disease diagnosis\[40\] and chemical catalysis\[41\]. These are mainly due to surface functionalization ability and surface plasmons.

In surface plasmons, oscillating electric fields of a light wave propagating near the nanoparticles interact with the free electrons causing a concerted oscillation of electron charge. This oscillation is in resonance with the frequency of visible light (figure 1.4)\[42\]. Surface plasmon polariton (SPP) and localized surface plasmon (LSP) are two known types of surface plasmons depending on the geometry. SPP is sustained at a flat metal–
dielectric interface by propagating electromagnetic surface waves which is associated with a collective oscillation of the free electrons in the metal. LSPs are associated with bound electron plasmas in nanoparticles with dimensions much smaller than the incident wavelength.

Figure 1.4 a) surface plasmon polariton (SPP) of Au film and b) localized surface plasmon (LSP) of Au NPs [42].

Figure 1.5 Absorption spectra of UV-visible spectrometry depending on the diameter of gold nanoparticles, 5 to 400 nm [43].

For small Au NPs, the surface plasmon resonance (SPR) causes an absorption of light in the blue range of the visible light spectrum reflecting red light. As the size of Au NPs increases, the wavelength of the SPR related absorption shifts to longer wavelengths.
The wavelength of the Au NPs SPR peak is between 520 nm and 600 nm \[43\]. The SPR can be tuned by controlling the size and shape of the nanoparticles to provide nanoparticles with tailored optical properties.

Au NPs have been utilized in water splitting enhancement. Rayalu et al. \[44\] synthesized Au NPs on commercial TiO\(_2\) powders by a photodeposition method giving hydrogen evolution of 32.4 \(\mu\text{mols} \cdot \text{h}^{-1}\) under purely visible light illumination comparing to 1.9 \(\mu\text{mols} \cdot \text{h}^{-1}\) of TiO\(_2\) P-25. Mi et al. \[45\] dispersed Au NPs on an array of AZO/TiO\(_2\) core/shell nanostructures \textit{via} physical vapour deposition giving photocurrent density of an AZO/TiO\(_2\)/Au electrode of up to 1.1 mA·cm\(^{-2}\) at 1.23 V (vs RHE) under simulated sunlight illumination, which is five times of that of a flat AZO/TiO\(_2\).

Silver nanoparticles have somewhat similar behaviour to gold. The SPR peak of Ag NPs appears from 400 nm (10 nm diameter particles) to 500 nm (100 nm diameter particles) \[46\]. Salimi et al. \[47\] has recently obtained 3 – 4 times photocurrent enhancement from Ag-functionalized CuWO\(_4\)/WO\(_3\) photoanodes compared to CuWO\(_4\) and WO\(_3\) films alone.

\textbf{Figure 1.6} Extinction (scattering + absorption) spectra of silver nanoparticles with diameters ranging from 10-100 nm \[46\].

Unlike the other noble metal nanoparticles which display SPR in the visible range, platinum nanoparticles have a SPR peak in the ultraviolet range at ~ 215 nm with the
spectra for most platinum particles with different sizes being similar. Pt NPs are normally used as co-catalyst in electrocatalysis [48] and photocatalysis [49] including water splitting. Pt has -0.1 eV Gibbs energy and is a very good catalyst for hydrogen production. The drawbacks include the requirement for expensive rare materials, difficulty in shape and size controlling.

1.3.4 Titanium oxide

Titanium oxide is a semiconductor material occurring in nature as rutile and anatase phases, with other crystal structures include brookite, TiO$_2$-II and suboxide phases. [50]. It is a white solid material with a refractive index of 2.5 – 2.6, and is insoluble in water. The most used application of TiO$_2$ is as a pigment in food colours, sunscreen and paint [51]. Another important use of TiO$_2$ is as a photocatalyst.

The band gap of TiO$_2$ is 3.2 eV which is wider than WO$_3$ (figure 1.3) and not excitable under visible light, but TiO$_2$ P 25 has good photocatalytic activity of degrading 60% 1,4-dichlorobenzene in 10 mins under UV irradiation [52]. Biphasic TiO$_2$ (rutile/anatase mixtures) is also considered as photoactive as the interfaces between rutile and anatase facilitate the charge separation [53]. When doped with nitrogen ions or decorated with metal oxide such as WO$_3$ or metal such as Pt, TiO$_2$ can also be excited under visible light [54]. TiO$_2$ in both thin film and nanoparticle form has potential in photocatalysis. For example, Kinato et al. [55] synthesized Pt-loaded TiO$_2$ thin films via radio frequency magnetron sputtering to tailoring it to visible light responsive.

1.3.5 Aluminium oxide

Aluminium oxide occurs naturally in its crystalline polymorphic phase $\alpha$-Al$_2$O$_3$ as the mineral corundum, varieties of which form gemstones ruby and sapphire. Al$_2$O$_3$ also exists in other phases including the cubic phases ($\gamma$-Al$_2$O$_3$ and $\eta$-Al$_2$O$_3$), the monoclinic phase ($\theta$-Al$_2$O$_3$), the hexagonal phase ($\chi$-Al$_2$O$_3$), the orthorhombic phase ($\kappa$-Al$_2$O$_3$) and
the tetragonal phase (δ-Al₂O₃) [56]. It is a white solid material with a refractive index of 1.6 – 1.7, and is insoluble in water. The applications of Al₂O₃ include ceramics, cosmetics, catalysis, abrasive and protection and electrical insulation [57].

Al₂O₃ is an electrical insulator which has an electrical resistivity of \( \sim 1 \times 10^{14} \ \Omega \cdot \text{cm} \) [58] and is responsible for the surface resistance of metallic aluminium. The thin Al₂O₃ passivation layer forms on aluminium quickly after exposure to air to prevent further oxidation. Therefore, Al₂O₃ thin films can be used to enhance corrosion resistance of unstable electrode materials at the potential expense of electron transfer across the interface. For example, Fan et al. [59] confirm that with a thin layer of Al₂O₃ coating on the surface, Si photocathode exhibits a high stability of continuous hydrogen production for more than 100 hours.

1.4 Nanostructures design and strategies of performance improvement based on WO₃

1.4.1 Nanostructuring

The size and morphology of material have great impact on their properties and the structure of WO₃ plays a very important role in the efficiency of photo-catalysis[60]. Semiconductor materials such as WO₃ with different nanostructures usually offer different photoelectrochemical (PEC) properties compared to bulk materials. The nanostructures can be categorized into 0-D nanostructures (nanosphere), 1-D nanostructures (nanorod, nanowire, nanobelt, nanofiber), 2-D nanostructures (nanoplate, nanosheet) and 3-D nanostructures (porous structure, hierarchical structure) [61]. Different nanostructures and their surface area per gram are displayed in figure 1.7. They have specific advantages: the large surface area of nanostructures provides larger area under light irradiation and more interfacial contact between electrode and electrolyte [62]. The band gap is changed by modifying the structures. For example, the longer length of
nanorods legs leads to a narrower band gap \cite{63,64}. The photogenerated charge carrier diffusion length and transportation path are varied due to the designed structures \cite{65,66}.

Figure 1.7 a) Classification of 0-D, 1-D, 2-D and 3-D WO$_3$ and b) the relationship between surface area and nanostructures diameter \cite{67}.

1-D nanostructures with high aspect ratios include nanorods, nanobelts, needles, fibres and wire-like structures. They can orthogonalize the direction of light absorption (along the long axis) and charge transport (across the short radius), leading to both efficient light absorption and charge carrier collection. Wang et al. \cite{68} synthesized WO$_3$ nanorods by a hydrothermal process assembled on indium tin oxide (ITO) glass, as shown in figure 1.8 (a). The WO$_3$ nanorods were electrochromically stable between +3 V and -3 V for more than 3000 CV cycles with colour display from colourless to green, blue and deep blue. Gonçalves et al. \cite{69} prepared a colloidal WO$_3$ nanowire photoanode by using nonhydrolytic media (figure 1.8 (b)) achieving a photocurrent of 1.96 mA·cm$^{-2}$ and 69% photocurrent remained after 3500 s at 1.23 V (vs RHE) in a KCl saturated solution. They identified preferential growth along the (2 0 0) plane as associated with improved photocurrent performance due to better charge transfer from the WO$_3$ surface to water, which decreases the electron transfer recombination. Rao et al. \cite{70} synthesized WO$_3$
nanotubes (figure 1.8 (c)) by a flame vapor deposition method, using a flame to oxidize and evaporate tungsten metal to produce tungsten oxide. The WO₃ nanotubes showed superior PEC water-splitting performance, with photocurrent of 2.2 mA/cm² at 2 V (vs Pt).

Figure 1.8 a) TEM image of WO₃ nanorods [68], b) TEM images of WO₃·H₂O nanowires [69] and c) SEM images of WO₃ nanotubes [70].

2-D nanostructures also have large surface area. Zeng et al. [71] developed a method by reducing and calcining peroxotungstate to prepare a vertically aligned monoclinic WO₃ nanoplate array films (figure 1.9) with preferentially exposed (0 0 2) planes. The film annealed at 500 °C exhibited the highest water splitting current density of ~1.42 mA/cm² at 1.23 V vs RHE in 0.1 M Na₂SO₄ under AM 1.5 G illumination. The photocurrent density of the WO₃ film only decreased from ~1.45 mA/cm² to ~1.26 mA/cm² after 3600s which showed excellent stability. Shown in figure 1.10, Zhou et al. [72] had successfully prepared WO₃ nanosheets with rich oxygen vacancies by a facile solvothermal reaction and hydrogenation method. The hydrogenated nanosheets exhibit remarkable electrochromism and photocatalytic performances. The hydrogenated WO₃ electrode displays a photocurrent of 35 μA·cm⁻² under visible irradiation compared with the non-hydrogenated samples (20 μA·cm⁻²) due to their oxygen vacancies, narrowed band gap coupling with fast charge transfer and enhanced adsorption of visible light.
Figure 1.9 top-view and cross section view SEM images of the WO$_3$ nanoplate array films $^{[71]}$.

Figure 1.10 TEM images and HRTEM images of the annealed and hydrogenated WO$_3$ nanosheets $^{[72]}$.

3-D nanostructures are more like the aggregation of 1-D and 2-D nanostructures or synthesized with the help of frameworks. Complex 3-D structures can also facilitate the PEC performance. Yun et al. $^{[73]}$ prepared 3-D honeycomb-like WO$_3$ nanostructures with assistance of polystyrene bead skeleton via electro-deposition (figure 1.11). The photocurrent density of this WO$_3$ structure was 0.47 mA/cm$^2$ at 1.23 V (vs NHE) illuminated by visible light in 0.1 M KOH solution. The IPCE value was 14% at 377 nm comparing to the value of SnO$_2$ which was 0.5%. Qiu et al. $^{[74]}$ reported a flower-like
nanoplate assembly synthesized from a hydrothermal process using H$_2$WO$_4$ (figure 1.12). It had a photocurrent density of 0.24 mA/cm$^2$, producing 0.23 mmol·g$^{-1}$ O$_2$ in the first 30 min and 0.39 mmol·g$^{-1}$ O$_2$ in 60 min which showed the great potential of the hierarchical structure as an anode material.

![Figure 1.11 TEM images of WO$_3$ inverse opal film](image1)

**Figure 1.11** TEM images of WO$_3$ inverse opal film $^{[73]}$.

![Figure 1.12 SEM images of WO$_3$ nanoflowers](image2)

**Figure 1.12** SEM images of WO$_3$ nanoflowers $^{[74]}$.

### 1.4.2 Heterojunction

Building semiconductor/semiconductor heterojunction structures by combining multi-metal oxide is a popular way to improve photoelectrochemical properties. Heterojunction structures can shift the absorption wavelength and enhance the PEC performance due to the separation of photogenerated carriers between semiconductors of different energy levels. The change of morphologies in heterojunction structures would also enhance the PEC performance comparing to single semiconductor $^{[75-78]}$.

There are five commonly used heterojunction structures for enhancing photocatalytic performance; conventional type-II heterojunctions $^{[79]}$, p-n heterojunctions $^{[80]}$, surface
heterojunctions [81], direct Z-scheme heterojunctions [82] and semiconductor–graphene (SC – graphene) heterojunctions [83]. The schematic illustrations of photocatalytic mechanism of these heterojunctions are shown in figure 1.13. For the type-II heterojunctions (figure 1.13 (a)), the conduction band (CB) and valence band (VB) of semiconductor A are higher than the corresponding band of semiconductor B. Under light irradiation, the photogenerated electrons will transfer to semiconductor B while the photogenerated holes will transfer to semiconductor A leading to a separation of electrons/holes [84]. The common WO$_3$/TiO$_2$ and WO$_3$/BiVO$_4$ structures are type II heterojunctions. P-n heterojunctions and direct Z-scheme heterojunctions are also seen in WO$_3$-related structures.

![Schematic illustration of the photocatalytic mechanism](image)

**Figure 1.13** Schematic illustration of the photocatalytic mechanism. a) type-II heterojunction; b) p-n heterojunction; c) surface heterojunction; d) direct Z-scheme heterojunction and e) semiconductor–graphene heterojunction [84].

Xu *et al.* [85] fabricated a novel type II 2-D ultrathin TiO$_2$/WO$_3$·H$_2$O heterostructure by mixing TiO$_2$ nanosheets and WO$_3$·H$_2$O nanosheets solutions together with the assistance of supercritical CO$_2$. The TiO$_2$/WO$_3$·H$_2$O heterostructures degraded 95.5% methyl orange in an aqueous solution in 150 min. The photocurrent density reached 6.5 μA·cm$^{-2}$ exhibiting a significant enhancement compared to TiO$_2$ and WO$_3$·H$_2$O nanosheets whose
photocurrent response is 0.8 μA·cm\(^{-2}\) and 1.2 μA·cm\(^{-2}\), respectively. (figure 1.14). Liu et al. \cite{86} used a soaking-calcining-hydrothermal process to obtain a BiVO\(_4\)/WO\(_3\) heterojunction film. The obtained BiVO\(_4\)/WO\(_3\) photoanodes showed a high PEC activity of a photocurrent density up to 2.92 mA·cm\(^{-2}\) at 1.81 V (vs RHE), which was attributed to the extended photoresponse range from < 460 nm to < 510 nm and the improved charge separation of 65%.

**Figure 1.14** a) The photocurrent response (1.4 V vs Ag/AgCl) of the TiO\(_2\)/WO\(_3\)·H\(_2\)O heterostructures in 0.5 M Na\(_2\)SO\(_4\) electrolyte under simulated solar light. b) Schematic diagram of charge transfer in TiO\(_2\)/WO\(_3\)·H\(_2\)O heterostructures \cite{85}.

Wu et al. \cite{87} prepared a flake-like NiO/WO\(_3\) p-n heterojunction photocathode by hydrothermal and dip-coating method. The photocurrent density of NiO/WO\(_3\) heterojunction was −23.39 μA/cm\(^2\) at 1.20 V (vs. RHE) under simulated sunlight, much higher than that of NiO which was only −5.93 μA/cm\(^2\).

Gao et al. \cite{88} fabricated a Z-scheme TiO\(_2\)/WO\(_3\)/Pt one-dimensional nanofibers heterostructure by a facile electrospinning technique and annealing. The H\(_2\) production of TiO\(_2\)/WO\(_3\)/Pt nanofibers (128.66 μmol·g\(^{-1}\)·h\(^{-1}\)) was greatly enhanced comparing to pure TiO\(_2\) nanofibers (undetectable) and TiO\(_2\)/WO\(_3\) nanofibers (27.73 μmol·g\(^{-1}\)·h\(^{-1}\)). The enhanced PEC activity was mainly attributed to the Z-scheme heterojunction system with effective charge separation using WO\(_3\) as a hole collector and Pt NPs as electron collectors.
Figure 1.15 (left) The schematic of the energy band structure and electron-hole pair separation and (right) TEM images of the one-dimensional Z-scheme TiO$_2$/WO$_3$/Pt heterostructures $^{[88]}$.

1.4.3 Metal decoration (Schottky junction)

Transition metals such as Pt, Ag, Ir, Au, Ru, Pd and Rh are commonly used for semiconductor metal deposition $^{[89-93]}$. Metal decoration can facilitate the separation of photogenerated electrons and holes on the surface of the semiconductors, thereby improving the photocatalytic activity. When the metal nanoparticles are in contact with the semiconductor surface, the charge carriers are redistributed, and the electrons are transferred from the higher Fermi level semiconductor to the lower Fermi level metal nanoparticles, forming a Schottky barrier until the energy level balanced. The Schottky barrier becomes an effective trap for capturing excited electrons and hence separating photo-generated carriers, therefore suppressing the recombination of electrons and holes. The surface coverage of semiconductors should be controlled within an appropriate range. Overdeposition may cause the metal nanoparticles to become the reaction centre, block active sites, or affect photon adsorption resulting in rapid recombination of electrons and holes $^{[94]}$.

Hu et al. $^{[95]}$ developed an electron-charging and reducing method to prepare Au/WO$_3$ by depositing Au NPs on electron-charged WO$_3$ for plasmonic solar water splitting (figure 1.16). The OER photocurrent of Au/WO$_3$ was improved by 40% at 1.23 V (vs. RHE)
compared to WO₃. The high photoactivity of the photoanode toward OER was ascribed to the plasmon resonance energy transfer enhancement and the catalytic enhancement of Au NPs.

**Figure 1.16** (left) SEM image of Au/WO₃. (right) Current density-potential curves of the WO₃ and different Au concentration Au/WO₃ photoanodes in 0.1 M Na₂SO₄ solution under chopped illumination.⁹⁵

Naseri et al.⁹⁶ synthesized Ag NPs on WO₃ thin film via sol-gel method. Photoanodes containing different concentrations of Ag nanoparticles with 470 nm SPR peak were synthesized by a sol-gel method. The sample with 2 mol% Ag:WO₃ had the highest photoresponse, much higher than WO₃ (figure 1.17) and also produced the highest hydrogen production rate of ~ 3 μmol/h. Widiyandari et al.⁹⁷ used a flame assisted spray pyrolysis method to prepare Pt/WO₃ nanorods used for photodegradation of the dye amaranth using visible light irradiation. Enhanced photocatalytic activity was observed after the addition of Pt. A low Pt concentration (0.12 wt.%) of the Pt/WO₃ nanocomposite had the optimal photocatalytic activity of degrading 50% amaranth in 20 min. The addition of Pt affected neither the morphology nor the crystallite structure of WO₃.
Figure 1.17 (left) SEM image of the Ag:WO$_3$ nanocomposite film for 10 Ag mol%. (right) Photoresponse of Ag:WO$_3$ nanocomposite photoanodes vs time chopping the illumination source at 1 V $^{[96]}$. 

1.4.4 Passivation layer

A surface passivation layer was originally used as a protection for unstable semiconductor materials against photo corrosion or chemical corrosion $^{[98]}$. However, it is claimed that passivation layers could also enhance the photocatalytic ability by (1) preventing the formation of band gap states that promote the recombination of electrons and holes; (2) catalysing the reaction at the surface; (3) shifting the band positions by charge distributions $^{[99]}$. The schematic reaction mechanism and J-V curves of semiconductor with passivation layer are shown in figure 1.18. Passivation layers are usually only several nanometres thick which permits electron tunnelling and hence no band alignment is needed between the semiconductor and passivation layer to allow charge transfer. The most used method for preparing passivation layers is atomic layer deposition $^{[100]}$, but also spin coating $^{[101]}$ and dip casting $^{[102]}$ have been used. The most popular passivation layer materials are TiO$_2$ and Al$_2$O$_3$ thin films.
Figure 1.18 a) Application of a thin noncatalytic surface layer to passivate defect states, strongly suppressing surface recombination for improving water oxidation. b) The schematic I–V curves of a photoanode with and without surface passivation layer [99].

Gui et al. [103] used ALD to coat high-quality Al₂O₃ onto the surface of TiO₂ nanotubes. The modified TiO₂ nanotube film worked as a photoanode. The photocurrent of the photoanode with Al₂O₃ passivation coating (0 – 150 ALD cycles) at 0.5 V (vs Ag/AgCl) were enhanced by 1.8 times comparing to TiO₂ (0.55 mA/cm²). Xie et al. [1] fabricated a TiO₂ thin layer via ALD onto TiO₂ nanorod arrays/CdS quantum dots as a passivation layer for the quantum dots. The degradation rate of methyl orange under visible light was 156% of TiO₂/CdS. The photocurrent and the stability of TiO₂/CdS are enhanced by the ALD TiO₂ coating. In figure 1.19, TiO₂/CdS/TiO₂ with under 60 ALD cycles shows 1.5 times photocurrent density at 0 V (vs Ag/AgCl) comparing to CdS/TiO₂. It suggests that ALD TiO₂ reduces photo-corrosion in the semiconductor-semiconductor heterojunction.

Figure 1.19 a) TEM image of TiO₂/CdS coated with 60 cycles ALD TiO₂; b) I-V curves of TiO₂/CdS coated with different cycles of ALD TiO₂ [1].
1.4.5 Doping

Doping can modify the properties of semiconductors and ionic defects created by doping foreign ions into semiconductors and act as a trap for charge carriers to extend their lifespan. For instance foreign ions with different sizes to the host lattice will cause a certain distortion of the semiconductor crystal structure and encourage the separation of photogenerated electrons and holes\textsuperscript{[104]}.

Kalanur et al.\textsuperscript{[105]} fabricated Ti-doped WO$_3$ thin films on fluorine-doped tin oxide (FTO) utilizing a facile hydrothermal method. Different amounts of Ti-doping were achieved by adding different volumes of titanium tetra-n-butoxide into peroxopolytungstic acid before hydrothermal deposition at 150 \degree C for 2 h. The WO$_3$ photoanode doped with 1.16 at\% Ti produced a maximum photocurrent density of 1.139 mA·cm$^{-2}$ (at 1.23 vs. RHE), which was 3.5 times higher than undoped WO$_3$ (0.335 mA·cm$^{-2}$) under simulated AM 1.5G illumination (figure 1.20). The substitution of W by Ti widened the band gap and shifted the conduction band minimum towards the hydrogen redox potential.

![Figure 1.20](image_url) Linear sweep voltammetry of undoped and 1.16 at\% Ti doped WO$_3$ photoanode under dark and AM 1.5G illumination measured in 0.1 M Na$_2$SO$_4$\textsuperscript{[105]}. 
1.4.6 Surface sensitisation

In surface sensitisation a photoactive compound is adsorbed on the surface of the photocatalyst. If the excited state potential of the photosensitizer used is lower than the conduction band potential of the semiconductor, photogenerated electrons can be transferred to the conduction band of the semiconductor, the excitation wavelength range is expanded and the response to light is enhanced. Commonly used dye photosensitizers include coumarin, eosin, polyaniline, chlorophyll and ruthenium bipyridine \(^{106,107}\).

1.5 Comparison of commonly used preparation methods

Commonly used preparation methods for WO\(_3\) include liquid phase synthesis methods: hydrothermal synthesis, sol-gel and electrochemical synthesis and vapour phase synthesis methods: sputtering (PVD), AACVD (CVD) and ALD. These methods are also reported while fabricating metal nanoparticles. Among them, sol-gel, sputtering and ALD are also reported as preparation methods for passivation layer. The comparison of sample preparation using these methods is shown in table 1.1.

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Table 1.1 comparison of different preparation methods.
1.6 Aerosol assisted chemical vapour deposition (AACVD)

1.6.1 The fundamentals of AACVD technique

Chemical vapour deposition (CVD) has been used as a synthesis technique for nanomaterials with various structures. The majority of the periodic table has been deposition via CVD as elements, oxides, nitrides, sulphides or composites \[1^{23}\]. In recent years, different types of CVD have been studied including aerosol-assisted chemical vapour deposition (AACVD), atmospheric pressure chemical vapour deposition (APCVD), conventional chemical vapour deposition (thermal CVD), laser chemical vapour deposition (LCVD), low pressure chemical vapour deposition (LPCVD), photochemical vapour deposition (PCVD), plasma enhanced chemical vapour deposition (PECVD) and metal-organic chemical vapour deposition (MOCVD) \[1^{24}\]. Among them, AACVD is a variant of the traditional CVD which uses aerosol droplets to transfer precursor to the reactor with the help of carrier gas. AACVD has the advantages of using a wide range of precursors, including low volatility or thermally unstable precursors, high reaction rate, morphology control and low cost \[1^{25,126}\].

A schematic diagram of AACVD process is shown in figure 1.21. The precursor is dissolved in a solvent and atomized to aerosol droplets with a sub-micrometre size by an ultrasonic aerosol generator. The carrier gas helps to transfer the distributed aerosol droplets into a heated reactor. The droplets are evaporated and decomposed, forming the precursor vapour. The desired materials can be deposited via the decomposition of the precursor vapour. If the vapour nucleated via homogeneous reaction at high temperature, powders will be generated. If the vapour decomposed at lower temperature, heterogeneous reaction will take place forming an adhesive film on the heated substrate \[1^{25}\].
1.6.2 Precursors and reaction mechanism

The precursor for AACVD needs to have sufficient solubility in solvent, high chemical purity, stability during evaporation, non-zero vapour pressure at the reaction temperature, decomposition with minimal impurities, and preferably low cost and low toxicity \[^{[124]}\]. Commonly used CVD precursors for metal oxides are metal hydrides, halides and metalorganic compounds. Among them, metalorganic compounds can be deposited at lower temperatures \[^{[126]}\]. AACVD is considered as one precursor reacting with a gas on the substrate surface or only a single-source precursor deposition. For the single-source precursor deposition, a delicate balance must be achieved between the thermal stability of the precursor in the gas phase and the chemical reactivity at the substrate surface \[^{[127]}\].

The type of CVD growth taking place can be examined by scanning electron microscopy. Three different growth models are studied for films growth via CVD (Figure 1.5) \[^{[128,129]}\].
(a) Frank-van der Merwe growth (Layer by layer growth): the atoms in the film are attracted more strongly to the substrate than to each other and grow layer by layer. Flat films are more likely to form.

(b) Stranski-Krastanov growth (Layer + island growth): between (a) and (c), (b) proceeds by a layered growth initially followed by island growth afterwards. Very rough clusters on the film surface will form the morphologies of nanoplates and nanoflowers.

(c) Volmer-Weber growth (Island growth): the atoms are more attracted to each other than the substrate and grow in one direction. These morphologies include nanorods and nanoneedles.

Figure 1.22 WO₃ thin film growth via AACVD with three growth modes: (a) Frank-van der Merwe growth, (b) Stranski-Krastanov growth and (c) Volmer-Weber growth [125]

1.6.3 AACVD of nanostructures

1.6.3.1 AACVD of WO₃ nanostructures

Many different types of W precursors have been reported for fabricating tungsten oxide via AACVD. The recently used precursors include WCl₆ [130], [W(CO)₆] [125], [W(OPh)₆] [118], [n-Bu₄N]₂[W₆O₁₆] and [n-Bu₄N]₄H₃[PW₁₁O₃₉] [129].
Ling et al. \cite{125} studied the growth mechanism of WO$_{3-x}$ thin films deposited via AACVD using [W(CO)$_6$] at 339 – 358 °C on quartz substrate. The morphologies of as-deposited WO$_{3-x}$ varied from planar to nanorod structures from reactor inlet to outlet in figure 1.23. The variation was due to the actual temperature change on the substrate surface which changed the growth mode of WO$_{3-x}$ due to the competition between nucleation rate and growth rate. Thus, the morphology of the film could be controlled by varying the deposition temperature.

![Figure 1.23 SEM images of WO$_{3-x}$ thin films from W(CO)$_6$ showing various nanostructures that from the reactor inlet to the outlet with an increase of substrate surface temperature \cite{125}.](image)

Stoycheva et al. \cite{112} grew WO$_3$ on alumina gas sensor platforms by AACVD using [W(OPh)$_6$] as the precursor at different temperatures in different solvents include acetone, toluene and acetone + toluene (50:50). Corresponding to different temperatures and different solvents, nanoneedle-like and grain-like films were deposited. The obtained films were decorated with gold nanoparticles by radio frequency sputtering. WO$_3$ nanoneedle-like gas sensor showed high selectively towards NO$_2$. Two different nanoneedle-like morphologies are shown in figure 1.24.
1.6.3.2 AACVD of Au, Ag, Pt NPs

Metal decoration can be achieved by AACVD as well. Wet-chemical synthesis methods typically use organic capping agents (polymers and surfactants) to stabilise metal nanoparticles in solution but this can form an organic layer at the interface between the metal particles and the semiconductor, leading to poor interfacial contact which can cause poor charge separation efficiency \[^{[131]}\]. Nanoparticles synthesized \textit{via} AACVD shows good control of particle size, crystallinity, porosity and stoichiometry by adjusting the reaction parameters \[^{[132]}\].

Vallejos \textit{et al.} \[^{[133]}\] synthesized Au nanoparticles functionalized WO\(_3\) nanoneedles on gas sensor substrates \textit{via} AACVD in a single step using HAuCl\(_4\) and [W(OPh)\(_6\)] as precursors (figure 1.25). The gas sensor had higher sensitivity to ethanol at lower concentrations compared with pure WO\(_3\) gas sensors.

**Figure 1.24** SEM image of WO\(_3\) nanoneedles deposited \textit{via} AACVD using W(OPh)\(_6\) in a) acetone + toluene \[^{[112]}\] and b) acetone \[^{[118]}\].

**Figure 1.25** TEM images of WO\(_3\) nanoneedles with dispersed gold nanoparticles on the surface \[^{[133]}\].
Naeem et al.\textsuperscript{[134]} deposited Ag-Mn$_2$O$_3$ composite thin films on FTO glass at 450 °C by AACVD using a mixture of acetatoargentate, Ag(CH$_3$COO) and [Mn(dmae)$_2$(TFA)$_4$] in methanol. The band gap of Ag-Mn$_2$O$_3$ was 1.8 eV, lower than Mn$_2$O$_3$. The Ag-Mn$_2$O$_3$ film showed an enhanced photocurrent of 3 mA·cm$^{-2}$ at 0.7 V (vs Ag/AgCl), which was 1.6 times higher than Mn$_2$O$_3$ under AM 1.5 G illumination. The as-synthesized Mn$_2$O$_3$ and Ag-Mn$_2$O$_3$ had band edges of 270 nm and 325 nm respectively. The recombination lifetime for the Mn$_2$O$_3$ and Ag-Mn$_2$O$_3$ films are calculated to be 11.6 ms and 16.2 ms in the absence of light. The carrier densities of them were calculated to be $1.62 \times 10^{13}$ cm$^{-3}$ and $3.09 \times 10^{13}$ cm$^{-3}$ respectively. The good photocatalytic property was due to the plasmonic effect of Ag nanoparticles, which enhanced the visible light absorption, the separation of electrons and holes and the carrier density.

![Figure 1.26](image.png)

**Figure 1.26** a) SEM image of Ag-Mn$_2$O$_3$ composite thin film. b) Elemental distribution of Ag in Ag-Mn$_2$O$_3$ composite thin film\textsuperscript{[134]}.

Moniz SJ et al.\textsuperscript{[135]} reported the use of H$_2$PtCl$_6$·6H$_2$O precursor to deposit Pt nanoparticles via AACVD. Pt-Bi$_2$O$_3$ composite film was synthesized via co-deposition with [Bi(dbm)$_3$]$_2$ and H$_2$PtCl$_6$·6H$_2$O via AACVD. The Pt-Bi$_2$O$_3$ composite film reduced water and generated H$_2$ at a rate of 3.1 μmol·h$^{-1}$·m$^{-2}$ simulated solar irradiation compared to either Pt or Bi$_2$O$_3$ individually which produced no hydrogen.

### 1.7 Atomic layer deposition (ALD)

#### 1.7.1 The fundamentals of ALD technique
ALD is a thin film deposition technique using sequential pulses of gas phase precursors. The precursors react with the surface in a self-limiting way so the reaction in each pulse terminates when the reaction sites on the surface are saturated \[^{136,137}\]. In an ideal ALD process cycle (the schematic is shown in figure 1.27): (1) precursor A is pulsed into the reaction chamber and reacts with the substrate surface, forming a monolayer on the surface through a self-limiting process, (2) by-products and unreacted precursor are removed by a carrier gas flow, usually N\(_2\) or Ar, (3) precursor B is pulsed into the reactor and reacts with the surface to create another monolayer, (4) and then precursor B and by-products are removed from the chamber \[^{138}\]. These steps are repeated until a uniform film with desired thickness grows on the substrate.

The ALD process is conducted at lower temperatures than CVD, below the precursor decomposition temperature, normally over a specific temperature range called the ‘ALD window’. Temperatures out of this range would result in low or high growth rate due to initiation of a non-ALD process \[^{139}\].

\begin{figure}
\centering
\includegraphics[width=\textwidth]{ald_schema.png}
\caption{A schematic of ALD procedure. (a) Substrate surface; (b) Precursor A is pulsed in and reacts with substrate surface; (c) redundant precursor and by-products are purged by inert gas; (d) precursor B is pulsed in and reacts with precursor A; (e) redundant precursor and by-products are purged by inert gas; (f) repeat (b)-(e) until gaining desired thickness \[^{138}\].}
\end{figure}
ALD is considered as a subclass of CVD. Compared to CVD, the low deposition temperature, conformality and thickness control are the most important advantages of using ALD. Due to its self-limiting characteristic, the reaction is theoretically restricted to form one layer on the surface each cycle under ideal conditions, therefore, the uniformity and conformality can be guaranteed for films deposition on high aspect ratio and 3D structures (e.g. figure 1.28). The thickness of films can be controlled by the number of cycles because of its self-limiting property. Each cycle forms one layer normally less than 1 Å. The whole ALD process can take a long time due to the relatively slow deposition rate compared to competing techniques.

![Cross-sectional SEM image of an Al₂O₃ ALD film with a thickness of 300 nm on a Si wafer with a trench structure](image)

**Figure 1.28** Cross-sectional SEM image of an Al₂O₃ ALD film with a thickness of 300 nm on a Si wafer with a trench structure [140].

### 1.7.2 Precursors and reaction mechanism

Precursors play an important role in the ALD process. They can be gas, liquid or solid but they must be volatile and thermally stable. They need to react rapidly with the substrate surface and each other to form layers quickly. By-products should not react with precursors or the surface. Metal precursors and non-metal precursors are two types of precursors needed for ALD [141]. Non-metal precursors provide O, N, S or H for depositing oxides, nitrides or sulphides. They are usually hydrides, such as H₂O, H₂S, NH₃ and others such as H₂O₂ and O₃ when a highly reactive oxidizing agent is needed. Non-metal precursors typically have no problems with volatility or thermal stability.

ALD precursors require relatively small ligands with low steric hindrance around the metal centre, otherwise the growth rates will be low. Widely used metal precursors include
metal halides (e.g. [TiCl₄] [142], [WCl₆] [143]), metal alkyls (e.g. [Al(CH₃)₃] [144], [Zn(CH₂CH₃)₂] [139]), metal alkoxides (e.g. [Ti(O²Pr)₄] [145], [Al(O²Pr)₃] [143]) β-diketonates (e.g. [Er(thd)₃] [146]) and cyclopentadienyl compounds (e.g. [InCp] [147]). New precursors are still being investigated for large scale ALD.

In a metal oxide ALD process, water is often used as the oxygen source. In this project, Ti and Al alkoxides are used as metal precursors respectively for deposition of TiO₂ and Al₂O₃. For example, the mechanism of TiO₂ ALD synthesis from [Ti(O²Pr)₄] [148,149] is generally identified as:

\[
\begin{align*}
(1) &\quad 2 \cdot \text{OH} (s) + \text{Ti(O²Pr)₄} (g) \rightarrow (-\text{O})_2\text{Ti(O²Pr)₂} (s) + 2 \cdot \text{PrOH} (g) \\
(2) &\quad (-\text{O})_2\text{Ti(O²Pr)₂} (s) + 2 \text{H₂O} (g) \rightarrow (-\text{O})_2\text{Ti(OH)₂} (s) + 2 \cdot \text{PrOH} (g) \\
(3) &\quad \text{Ti(OH)-O-Ti(OH)} (s) \rightarrow (-\text{O})_2\text{Ti} (s) + \text{H₂O} (g) \\
(4) &\quad (-\text{O})_2\text{Ti} (s) + \text{Ti(O²Pr)₄} (g) \rightarrow \text{Ti(O²Pr)-O-Ti(O²Pr)₃} (s)
\end{align*}
\]

Titanium isopropoxide, [Ti(O²Pr)₄] reacts with two OH groups on the substrate surface to produce (-O)₂Ti(O²Pr)₂ in the first half reaction, this species reacts with water in the second half reaction (equation 1, 2). After one cycle, the surface has OH groups again, then the next cycle starts [150]. Aluminium isopropoxide, [Al(O²Pr)₃] is also expected to follow a similar reaction mechanism.

Aluminium tri-sec-butoxide ([Al(O²Bu)₃], ATSB) was used as a metal precursor for Al₂O₃ in this project. Compared to [Al(O²Pr)₃] whose O²Pr groups allow polymerisation, [Al(O²Bu)₃] has longer alkyl groups that enhance its volatilisation characteristics.

1.7.3 ALD of metal oxide thin films

1.7.3.1 ALD of TiO₂ thin films
Many titanium-based chemicals have been discovered to be ALD precursors for TiO$_2$. Commonly used Ti precursors are halides ([TiCl$_4$]$^{[151]}$, [TiI$_4$]$^{[152]}$), alkoxides ([Ti(O$^\text{i}$Pr)$_4$]$^{[153]}$, [Ti(OEt)$_4$]$^{[154]}$ and [Ti(OMe)$_4$]$^{[155]}$), alkylamides ([Ti(NMe$_2$)$_4$]$^{[156]}$) and heteroleptic precursors.

In figure 1.29, deposition using [TiCl$_4$] shows growth rate (growth per cycle, GPC) of ~ 0.5 Å/cycle, which decrease with increasing deposition temperature. Aarik et al. $^{[151]}$ studied ALD of TiO$_2$ from [TiCl$_4$] and H$_2$O at substrate temperatures of 100 – 400 °C. They demonstrated dependence of the growth rate on the temperature and the film structure. The growth rate also depended on the precursor pulse times. For all halides, the reaction by-products are harmful to the deposition instruments and cause corrosion$^{[157]}$.

Among alkoxides, [Ti(O$^\text{i}$Pr)$_4$] is the most popular precursor due to its relatively high vapour pressure and reasonable reactivity towards H$_2$O even below 100 °C. Rittala et al. $^{[158]}$ found that the growth rate of [Ti(O$^\text{i}$Pr)$_4$]/H$_2$O process is ~ 0.15 – 0.6 Å/cycle with an increasing trend with increasing deposition temperature. Annealing only gave a small increase in the film crystallinity and no thickness shrinkage. The temperature for ALD growth was limited by the thermal decomposition of [Ti(O$^\text{i}$Pr)$_4$]. The alkoxide precursors decompose at relatively low temperatures. [Ti(O$^\text{i}$Pr)$_4$] decomposes from 250 °C, whilst [Ti(OEt)$_4$] and [Ti(OMe)$_4$] are slightly more stable.

Due to the low binding energy of Ti-N, alkylamides have high reactivity towards H$_2$O, therefore they are good ALD precursors$^{[159]}$. TiO$_2$ films can be deposited below 100 °C with less corrosive by-products than halides. ALD of [Ti(NMe$_2$)$_4$]/H$_2$O shows a decreasing growth rate with increasing deposition temperature.
Figure 1.29 Growth-per-cycle (GPC) trends as a function of deposition temperature as retrieved from literature. (a) Halides precursors, red: [TiI₄], green: [TiF₄] and black: [TiCl₄]; (b) alkoxide precursors, green: [Ti(OMe)₄]; (c) alkylamides precursors; (d) heteroleptic precursors. The dashed line shows the level of ‘typical’ GPC of 0.5 Å/cycle for TiO₂ ALD [157].

1.7.3.2 ALD of Al₂O₃ thin films

Commonly used aluminium precursors include the most popular alkyls ([Al(CH₃)₃][160]), halides (AlCl₃[144]) and alkoxides ([Al(OiPr)₃][144] and [Al(OEt)₃][161]).

Yun et al [162] reported Al₂O₃ films grown using AlCl₃ and [Al(CH₃)₃] with H₂O as precursors in the temperature ranging from 250 to 500 °C. The Al₂O₃ film grown using AlCl₃ at 500 °C contained ~ 0.5 at. % Cl impurity. The growth rate of the film using [Al(CH₃)₃] change from 1.0 Å/cycle at 250 °C to 0.75 Å/cycle at 400 °C. The Al₂O₃ films grown using [Al(CH₃)₃] showed that the growth rate and the impurity decreased, and the refractive index increased with the growth temperature. The film impurity levels were lowered by increasing the purge time after each [Al(CH₃)₃] pulse.
Räisänen et al. \cite{144} grew Al$_2$O$_3$ films by ALD using reactions between AlCl$_3$ and [Al(OiPr)$_3$] which served as both metal and oxygen source. The film growth rate was 0.8 Å/cycle. The residual contents of hydrogen, carbon and chlorine in the film deposited at 300 °C were 0.7, <0.1 and 1.8 at.%. The chlorine content decreased with increasing growth temperature.

Atomic layer deposition of Al$_2$O$_3$ using dimethylaluminum isopropoxide [(CH$_3$)$_2$AlOCH(CH$_3$)$_2$], (DMAI) and H$_2$O as precursors have also been reported by Cho et al. \cite{163}. DMAI was a new ALD precursor which was stable in nitrogen and argon and not reacting in air. The growth rate of 1.06 Å/cycle was achieved in the temperature range of 120 – 150 °C.

1.7.4 The use of ALD thin film layers

1.7.4.1 Spacer layer in surface plasmon resonance (SPR) enhancement

In the theory of plasmonics, a wave formed by light coupling to electrons in a material (typically a metal) is bound to the surface of the material. This wave is called a surface plasmon polariton (SPP) \cite{164}. Metal nanostructures such as particles, wires, films and apertures can concentrate SPP and enhance light-matter interactions \cite{165–169}. This can benefit aspects such as bioimaging, sensing and lithography \cite{170}. When the structure is based on a metal substrate, changing the distance between the metal substrate and nanostructures will change the surface plasmon resonance (SPR) \cite{171}. ALD-grown overlayers can be used on metallic nanoplasmonic structures as a passivating layer, or as a spacer layer. The spacer layer can enhance the optical transmission, tune the Raman signal and protect the surface \cite{172}. Figure 1.30 shows an example of Al$_2$O$_3$ spacer layer.
Ag and Au are used in most plasmonic devices operating at infrared or visible regions [173]. Ag has better optical properties, higher sensitivity, is cheaper and has stronger interfacial adhesion with a silicon substrate than Au but is less stable and readily oxidized in the air, which causes lower optical intensity in nanoplasmonic structures. An overlayer of 10 – 20 nm can protect the metal surface and improve the SPP performance of Ag and Au. The thickness of the overlayers must be less than the mean decay length of SPPs [174]. These thin films must be pinhole free, coat the whole structure surface and grow at low temperature to avoid the oxidizing of metal underneath [175,176]. Consequently, ALD is an excellent choice for this need.

In surface-enhanced Raman spectroscopy (SERS), the electromagnetic field relies on the distance between the metal and nanostructures in the illuminated nanoplasmonic structures [177]. The enhancement of Raman spectra changes sharply with the distance between the metal surface and the nanostructures above. The dielectric constant of the film, which varies in atomic layer deposition, is considered because it plays an important role in SPR sensors and hence deposition of Al₂O₃ has also been investigated.

Thin Au films are known to form island-like structures with small gaps between the islands, which produce intense electric field "hot spots" under visible illumination [178,179]. These hot spots are not only appearing between nanoparticles (NPs) but also can be generated between nanoparticles and the metal substrate. Changing the distance between
the metal substrate and SPR nanoparticles can lead to the tuning of Raman signal. Taking advantage of these additional hot spots produced by the gap, the signal should be enhanced. A good match between the metal and space layer is required. Figure 1.31 shows a schematic of self-assembled Au NPs\textsuperscript{[180]} on TiO\textsubscript{2}/Au/Si in NaCl solution.

![Image](image1)

Figure 1.31 The schematic of Au/TiO\textsubscript{2}/Au/Si in NaCl solution.

1.7.4.2 Passivation layer in photovoltaics

As mentioned above, ALD-grown thin films can play the role of passivation layer for Ag metal-nanostructure SPPs device. ALD passivation layers also have applications in protecting photovoltaic materials due to the dense and pinhole free films and excellent uniformity typically achieved in ALD. Unlike CVD and PVD, ALD has good ability for making thin passivation films. Many photoelectrodes used in photoelectrochemical processes such as water splitting require stabilization in aqueous electrolytes. An ALD thin film can increase the chemical stability for the electrode material to prevent electrode corrosion. Paracchino et al.\textsuperscript{[181]} developed a method to coat a 20 nm AZO film and a 10 nm TiO\textsubscript{2} film on copper oxide water splitting photocathodes (figure 1.32), the chemical stability remained 62% after 10 hours\textsuperscript{[182]}. Using Al\textsubscript{2}O\textsubscript{3} as a protection layer for a silicon solar cell has also been studied recently\textsuperscript{[183–185]}.

![Image](image2)

Figure 1.32 Cross-sectional SEM image of a sample with TiO\textsubscript{2} deposited at 150°C.
1.8 Motivations and aims

Energy demand is increasing rapidly all over the world. Clean alternatives are in urgent demand for slowing down the energy crisis and environmental damage. Semiconductor photocatalysts have been used for water splitting for several decades. By utilizing solar energy, splitting water into H₂ and O₂ is considered as a promising way for generating renewable energy. This project is aiming to synthesize and study different nanostructured photo electrode materials for photoelectrochemical water splitting.

WO₃ is a promising photoanode material due to its low cost, low toxicity, excellent stability and visible light region band gap. WO₃ with various nanostructures can be prepared by many methods, among which CVD is a reproducible method. Different nanostructures vary the PEC performance and stability. Enhanced water splitting performance can be achieved by modifying the pure WO₃ with metal nanoparticles deposition. Au, Ag and Pt nanoparticles are synthesized via AACVD. These nanoparticles have different SPR wavelength and morphologies which make them behave differently on WO₃. Deposition parameters are studied and discussed.

In recent years, metal oxide thin films deposited via ALD are popular and successfully used to build heterojunctions and passivation layers. In this project, we aim to deposit TiO₂ and Al₂O₃ thin films on electrode materials to avoid delamination of electrode materials during PEC water splitting. Film thickness measurement and properties characterization are demonstrated. Complex nanostructures are designed to study the PEC performance of different structures with different materials.

In summary, this research project focused on the nanostructured WO₃ thin films and their modifications for photoelectrochemical water splitting using AACVD and ALD. Chapter 2 will introduce synthesis and characterization methods. Chapter 3 will focus on synthesis and characterization of nanostructured WO₃ films. Chapter 4 will focus on metal (Au, Ag and Pt) nanoparticles decorated WO₃ nanoneedles and their PEC performance. Chapter 5
will study the ALD of TiO$_2$ and Al$_2$O$_3$ thin films and their properties and also assemble the nanomaterials above and study the PEC performance of the system.
Chapter 2. Methodology

2.1 Introduction

This chapter includes the materials and chemicals used in the project. The setup and operation procedure of thin film deposition methods: atomic layer deposition (ALD), chemical vapour deposition (CVD) and aerosol assisted chemical vapour deposition (AACVD) are described. The characterization techniques used to analyse the samples are also described.

2.2 Materials and chemicals

Materials: Titanium(IV) isopropoxide (TTIP, 97%), aluminium isopropoxide (AIP, 98%+), aluminium tri-sec-butoxide (ATSB, 97%) and tungsten hexacarbonyl ([W(CO)6], 97%) were purchased from Sigma-Aldrich Corporation. Hydrogen tetrachloroaurate(III) trihydrate (HAuCl4·3H2O, 99.99% (metals basis), Au 49.5% min, Alfa Aesar™), hydrogen hexachloroplatinate(IV) hydrate (H2Cl6Pt·xH2O, ca. 40% Pt, ACROS Organics™), acetone (laboratory reagent grade), propan-2-ol (laboratory reagent grade), methanol (HPLC grade) and ethanol absolute (HPLC grade) were received from Fisher Scientific UK. Silver 2-amino-2-methyl-1-propanol (Ag-AMP) was synthesized and supplied by Miss Bhide Malavika and Mr. Ye Zhou from Dr. Caroline Knapp’s group (UCL). The method of synthesising Ag-AMP is described in the literature [186]. Super premium glass microscope slides were purchased from VWR International, LLC. Quartz slides were purchased from Wuxi Crystal and Optical Instrument Co., Ltd. P-doped silicon wafers were bought from Suzhou Crystal Silicon Electronics & Technology Co., Ltd. Silicon wafers covered with Au and Ag layers were provided by Professor Joshua Edel from Department of Chemistry, Imperial College London. Deionized water was obtained from ELGA Purelab Option (ELGA LabWater). Liquid nitrogen and argon gas were provided by BOC. FTO glass (TEC-15) was received from Pilkington NSG.
2.3 Experimental methods

2.3.1 Atomic layer deposition (ALD)

Two ALD systems (home build, flow-type, cold wall) were used for depositing metal oxide thin films (e.g. TiO$_2$ and Al$_2$O$_3$). Both were designed and constructed in house by Prof. Chris Blackman, Dr. Rachel Wilson and me. The photograph and schematic of one ALD system are shown in figure 2.1 and 2.2.

The tubing parts used for building the pipe works were purchased from Swagelok. They are 1/8-inch and 1/4-inch diameter stainless steel pipework, same sized tube fittings and valves for different uses. Solenoid valves (Series 9 miniature calibrant valve) were purchased from Parker. KF flange and clamp kits were purchased from Swagelok. Oil sealed vacuum pumps (TRIVAC D4B and D8B) with vacuum fittings and pressure gauges were purchased from Oerlikon Leybold. A base pressure of $1 \times 10^{-2}$ to $4 \times 10^{-2}$ mbar could be archived while the whole system was under vacuum. Running pressure of the system depended on the gas flow rate during each deposition.
Argon gas (99.998%, BOC) was used as a carrier gas in all depositions to help the precursor vapours transport through the reactor system. By connecting to four mass flow
controllers (MFC, Brooks Instrument, model number GF40), gas flow was split into four routes for purge line, bubbler 1, 2 and 3. Gas flow rate were controlled by MFCs with flow rates varying in a range of 0 – 1000 standard cubic centimetres per minute (sccm). Total gas flow rate used in this project was between 100 sccm and 400 sccm depending on the precursors and reaction conditions, under which the pressure shown in the reactor was ~ 1 – 4 mbar.

Bubblers were constructed between the MFC and reaction chamber as containers for precursors. The photograph and schematic of a bubbler with its inlet and outlet arms are shown in figure 2.3. Lower-volatility metal precursors needed to reach certain temperature to be vaporized. Therefore, the bubbler containing lower-volatile precursors was heated by the surrounding heating block. The bubbler temperature was monitored and controlled by two k-type thermocouples in contact with the heating block and the liquid precursor respectively. The required temperature was calculated from the lowest vapour pressure needed to transport one dose. The inlet pipe reached the bottom of the bubbler, so that Ar-carrier gas would force the precursor vapour to transport into the outlet pipe while inlet valve and outlet valve were opened. The bubbler containing relatively high-volatility water was cooled with the assistance of a cooling water system (4 °C) to keep the vapour pressure at a suitable low level to avoid flooding the system.
Stop valves and solenoid valves (Series 9 miniature calibrant valve, Parker) were installed on both inlet and outlet arms of every bubbler. One-way stop valves were fitted near the bubbler end for maintenance use. Precursor dosing and purging were controlled by solenoid valves. Three-way solenoid valve was used on the inlet arm to switch whether the gas flows into the bubbler or into the purge line. Two-way solenoid valve was used on the outlet arm to control the gas flowed out from the bubbler. One-way check valve was fitted on inlet arm to prevent precursor flow backwards into the inlet pipeline while pressure built up in the bubbler. All solenoid valves were electronically controlled by custom IGI Systems Lab Interface Input control boxes. With all these assistances, the gas flowed in a single direction.

Pipelines can be defined into four parts (figure 2.2). (1) inlet pipeline, which connects from MFCs to bubblers inlet “reaction route”, (2) Reaction pulse pipeline, which connects from bubblers outlet to reaction chamber, (3) Purge pipeline, which included pipework from “MFC purge” to reactor outlet and from bubbler arm inlet “purge route” to reaction chamber outlet, (4) reactor outlet pipeline, connecting from reaction chamber outlet to the
pump. Pulse pipeline and reactor outlet pipeline needed to be heated up to a certain stable temperature (100 – 200 °C). They were heated by several fiberglass heating tapes (Electrothermal, 400 W, 230 V) winding on the pipelines. The temperature should be higher than the bubbler temperature, lower than the precursor decomposition temperature and lower than the substrate deposition temperature in order to prevent precursor vapour from either condensing, decomposing or reacting on the pipeline inner wall. This action prevents the system from building blockages.

The heating block, which is also the sample holder (4 cm × 5 cm) was designed to sit into the middle of the cold wall reaction chamber. The temperature of the heating block was controlled and monitored by two k-type thermocouples inserted into the heating block. The photograph and schematic of this part are detailed in figure 2.4. The temperature range of the heating control was 20 – 600 °C. In this project, substrates were sat on the top of the heating block and grown mainly under 150 – 400 °C (occasionally under 100 °C) according to the nature of the precursors and substrates.

Two control boxes were used to monitor and control the temperature of bubblers, pipelines and heating blocks, all gas flows and all solenoid valves. The ALD system was further controlled by custom IGI Systems LAB Interface software on a computer connecting to the control boxes. By programming ALD recipes and editing heating system, all temperatures, gas flow rates and switching all solenoid valves, the ALD system was manually controlled during maintenance and automatically controlled during reaction from the computer software.

A cold trap was built between the reactor outlet and the pump to capture residual precursor and by-products passing through, protecting the pump from being damaged. While the experiment was running, the cold trap was filled with liquid nitrogen (BOC).
Figure 2.4 Photograph and schematic of the design of ALD reaction chamber.

The substrates used for ALD depositions were super premium microscope slides (VWR International, LLC), quartz (Wuxi Crystal and Optical Instrument Company Limited), silicon (Suzhou Crystal Silicon Electronics & Technology Co., Ltd) and FTO glass (TEC-15, Pilkington). Before deposition, substrates were cut into desired size, cleaned by isopropanol and dried in compressed air. FTO glass were cleaned by acetone, isopropanol, methanol and deionized water for 15 min, respectively, and dried in compressed air. Other depositions were performed on samples which already have single-layered or multi-layered materials on the substrate. The substrate was loaded onto the heating block and fed into the reactor chamber (figure 2.4).

Precursors used in this project include deionized H$_2$O, Titanium(IV) isopropoxide (TTIP, [Ti(O$^{i}$Pr)$_4$], 97%), aluminium isopropoxide (AIP, [Al(O$^{i}$Pr)$_3$], 98%+), aluminium tri-sec-butoxide (ATSB, [Al(O$^{s}$Bu)$_3$], 97%). ALD of TiO$_2$ was carried out using H$_2$O maintained at 5 °C and TTIP maintained at 25 °C. ALD of Al$_2$O$_3$ was carried out using H$_2$O
maintained at 5 °C and AIP maintained at 90 °C or ATSB maintained at 120 °C. Details will be discussed in chapter 5 and chapter 6.

A typical deposition in this ALD system is described. A substrate was first cleaned and sat on the heating block and then fed into the reaction chamber. The system was pumped to vacuum, and the heating block was heated to a desired temperature. Gas flow rate for each MFC was changed to required amount in the software and the ALD recipe built. Parameters needed included dose time of each precursor in one cycle, purge time after each dose, deposition temperature, number of cycles, gas flow rate of each channel and valve timings needed for each dose and purge. Then the deposition was started until it automatically finished. The substrate was cooled down to room temperature in the chamber.

ALD films were deposited by pulsing metal precursor and water precursor into the reaction chamber and reacting on the substrate alternatively. An Ar gas purge was introduced between each dose to prevent CVD-like growth happening. Therefore, the two precursors never interacted in the gas-phase with each other. A full ALD cycle consists of (1) metal precursor dose, (2) Ar purge, (3) water dose, (4) Ar purge. The reaction mechanism of an ALD cycle is described below in equation 2.1:

(1) $x \cdot \text{-OH (s)} + \text{M(OR)}_4 \cdot (g) \rightarrow (\text{-O-})_x \text{M(OR)}_{4-x} \cdot (s) + x \text{RH (g)}$

(2) $(\text{-O-})_x \text{M(OR)}_{4-x} \cdot (s) + (4-x) \text{H}_2\text{O (g)} \rightarrow (\text{-O-})_x \text{M(OR)}_{4-x} \cdot (s) + (4-x) \text{RH (g)}$  \hspace{1cm} (2.1)

This ALD reaction (pose and purge sequences) was repeated for a desired number of cycles to deposit a thin film with a required thickness.

2.3.2 Chemical vapour deposition (CVD) and pulsed CVD

Chemical vapour deposition was achieved in the ALD system. To operate in CVD mode, the inlet valve and outlet valve of metal bubbler were kept open for the entire deposition
continuously dosing metal precursor into the reactor at a constant gas flow. No water precursor was used alongside. The deposition was run for hours. CVD mode was usually operated at a higher deposition temperature than ALD to ensure the metal precursor decomposed on the substrate. CVD mode, which was much easier to achieve, was normally studied prior to ALD recipe optimization.

A deposition mode called “pulsed CVD” was used to mimic the metal precursor half cycle in ALD. A cycle in pulsed CVD mode only contained one metal precursor pulse and one Ar purge. Its purpose was to demonstrate that precursor transport took place under pulse conditions.

2.3.3 Aerosol assisted chemical vapour deposition (AACVD)

The AACVD reactor used was built in house by Prof. Chris Blackman’s group. The photograph and schematic of AACVD system were shown in figure 2.5 and 2.6. \( \text{N}_2 \) (99.99%, BOC) was used as a carrier gas to transport the aerosol into the reactor. An MFC (Brooks Instrument, 0 – 500 sccm) was installed to control the gas flow rate with a flow of 300 sccm. MFC outlet was connected to the inlet pipe of a custom flask (UCL Chemistry) containing liquid precursor (figure 2.6). Precursor aerosol was generated by an ultrasonic humidifier (2 MHz, Johnson Matthey Liquifog). With the help of the humidifier, gas flow and the design of the flask, the precursor aerosol was transported into the reactor inlet pipe. The reaction chamber is a 3 cm × 6 cm × 0.4 cm flat space sat inside the heating block. By adjusting the height and the position of the sample in the reaction chamber, a desired film can be obtained. The heating block was heated by a heating jacket and rod-heater (0 – 600 °C). A thermocouple was used to control and monitor the deposition temperature. The inlet pipe was cooled by a cooling water system (4 – 10 °C) running through the cooling water jacket to prevent the precursor from decomposing on the manifold’s inner wall before it reached the substrate. The precursor aerosol was then evaporated by the high temperature in the reaction chamber and the
precursor then decomposed on the substrate to form a thin film. The residual vapour was exhausted into the fume cupboard.

**Figure 2.5** Photograph of the home-build AACVD system.

**Figure 2.6** Schematic of the home-build AACVD system.
The substrates used for AACVD depositions were super premium microscope slides (VWR International, LLC), quartz (Wuxi Crystal and Optical Instrument Company Limited) and FTO glass (TEC-15, Pilkington). Substrate pre-treatment for AACVD and ALD was the same. Other depositions were performed on samples which already have single-layered or multi-layered materials on the substrate.

Metal precursors used AACVD in this project include tungsten hexacarbonyl ([W(CO)₆], 97%) for preparing WO₃ nanoneedle array, hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, 99.99% (metals basis), Au 49.5% min) for preparing Au nanoparticles, hydrogen hexachloroplatinate(IV) hydrate (H₂Cl₆Pt·xH₂O, ca. 40% Pt) for preparing Pt nanoparticles and Ag-AMP (synthesized by Dr. Caroline Knapp’s group) for preparing Ag nanoparticles. They were dissolved in organic solvents (e.g. methanol, ethanol or acetone) for use in AACVD. Details will be discussed in chapter 3 and chapter 4.

In a typical deposition using this AACVD system, a substrate was first cleaned and sat on the sample holder in the reaction chamber. The reactor was sealed and preheated to a desired temperature. Precursor was prepared in the flask. Gas flow rate was adjusted to the required amount. The ultrasonic humidifier was switched on and adjusted to the position which generated maximum mist to fill up the flask. The heater and the humidifier were switched off once the precursor was finished. The sample was cooled down to room temperature under N₂ atmosphere and taken out. Parameters which have impact on the sample include substrate height and position, precursor concentration, solvent, deposition temperature and gas flow rate. Then the deposition was started until automatically finished. The substrate was cooled down to room temperature in the chamber.
2.4 Characterization techniques

2.4.1 Scanning Electron Microscope (SEM)

Scanning electron microscopy is an imaging technique mostly used to obtain morphology, structure and chemical composition information from the sample surface. The morphologies of all samples were observed by field emission scanning electron microscope (FESEM, JEOL JSM-6700F, JSM-7800F) with a current of 10 mA and an acceleration voltage of 5 – 15 kV. Before examination by FESEM, samples were connected to the analysis stub with carbon tape or copper tape and coated with gold or carbon to increase surface conductivity.

2.4.2 Transmission Electron Microscope (TEM)

Transmission Electron Microscope (TEM) is a microscopy technique using an electron beam transmitting through a specimen to form an image. High resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100) mode operated at 200kV was used to directly image the crystal structure of the samples. Sample preparation included sonicating solid sample to remove it from its substrate and dropping the sonicated solution on 300 mesh carbon film coated TEM grids. Features of nanostructures, grain boundary, lattice parameters and fast Fourier transform (FFT) were analysed through Gatan microscopy suite software (Gatan, Inc.).

2.4.3 Energy-dispersive X-ray Spectroscopy (EDS)

Energy-dispersive X-ray Spectroscopy (EDS) can be used to detect element composition, relative abundance and distribution of the sample to a certain thickness. Element composition and abundance of larger sample area was investigated by energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments) equipped with FESEM. Element distribution and content of single nanostructure was analysed by EDS (Oxford
Instruments) equipped with HRTEM. Different analysis modes, point analysis, line scan and area mapping, were used to achieve the requirement.

2.4.4 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a scanning probe microscopy imaging topography and measuring force. By scanning the sample surface, surface properties and 3D image can be measured. Tapping mode of atomic force microscopy (AFM, Nano Surf Easy Scan 2 AFM, Bruker Dimension FastScan2-SYS and Keysight Technologies 5600LS) with non-contact long cantilever AFM probe was used to investigate the surface structure of the sample. The images were analysed by Gwyddion software. The average roughness (Ra) and the root mean square roughness (Rq or RMS) information can be obtained from the software.

2.4.5 Film thickness measurement via spectral reflectance

It is an optical measurement instrument using spectral reflectance to measure the amount of light reflected from the surface and bottom of a thin film. Reflections from different interfaces interfere with each other and cause wavelength oscillation in the spectrum. The frequency of the oscillations can be calculated to figure out the distance between the interfaces, which is the film thickness. Thicker films will show more oscillation wave features than thinner films. The thickness of the films deposited via ALD and CVD was measured using a visible reflection spectrometer (Filmetrics, Inc., F20). The wavelength of the incident light was between 380 nm and 1050 nm. The refractive index (n) and the extinction coefficient (k) of the tested materials need to be specified beforehand using reference values. Measurements were taken at chosen points across the sample substrate. Average value was used as the film thickness.

2.4.6 Variable Angle Spectroscopic Ellipsometer (VASE)
Ellipsometry is an optical measurement method for characterizing the dielectric properties of thin films. Ellipsometry measures the change of polarization upon transmission or reflection and compares it to models. The two different polarization and multiple incidence angle measurements provide more information for simulation and the flexible parameters changes can provide more reliable results comparing to visible reflection spectrometry. It can be used to investigate film thickness, composition, roughness, refractive index, doping concentration, electrical conductivity and other properties.

TiO$_2$ and Al$_2$O$_3$ films deposited via ALD and CVD were measured by a spectroscopic ellipsometer (SEMILAB SE-2000) with Semilab Sam suite software. The incident light was generated by a 75 W xenon lamp with a wavelength from 185 nm to 2000 nm. Measuring angles were selected in the range of 12 - 90°. The angles were 60°, 65°, 70° and 75° for TiO$_2$ films and 56°, 57°, 58°, 59° and 60° for Al$_2$O$_3$ films. Different models were built for each film depending on the optical constants of each materials. The data was modelled and fitted by Spectroscopic Ellipsometry Analysis (SEA) software.

### 2.4.7 X-ray Diffraction (XRD)

X-ray diffraction (XRD) can be used to study the chemical composition, crystallographic structure, and physical properties of thin films and structured materials by measuring the spacing between atoms. X-ray diffraction of the samples on plain substrates were measured by a Bruker D8 Discover LynxEye diffractometer with copper Kα (\(\lambda=0.1541 \text{ nm}\)) as the X-ray source, a current of 40 mA and a voltage of 40 kV. The data was collected with a scanning rate of 0.05°/s over a 2θ range from 10° to 66° counted at 0.5 second per step. XRD data was analysed using Jade 6.5 software (Materials Data, Inc.). Then XRD patterns obtained were compared with International Centre for Diffraction Data (ICDD, also known as JCPDS) database standards to confirm the phase structure and chemical composition of the samples.
2.4.8 X-ray Photoelectron Spectroscopy (XPS)

As a sensitive surface measurement technique, X-ray photoelectron spectroscopy (XPS) can provide the chemical state and chemical composition information by exciting electrons on the sample surface. An X-ray photoelectron spectrometer (Thermo Fisher scientific, Neslab ThermoFlex1400) with a monochromatic Al Kα x-ray source was used for the measurement. The data was analysed by CasaXPS with charge compensation and carbon calibration. It was also compared to the reference from the NIST XPS database [187]

2.4.9 Ultraviolet–visible spectroscopy (UV/Vis)

Ultraviolet-visible spectrophotometer measures the intensity of light after passing through a sample and compares it to the intensity of incident light. The ratio is transmittance (T%). It can also be configured to measure reflectance (R%). The absorbance (A) can be calculated from %T (equation 2.2):

\[
A = -\log \left( \frac{T\%}{100\%} \right)
\]  
(2.2)

Solid state UV/Vis spectra were collected by an integrating sphere equipped UV/Vis spectrophotometer (PerkinElmer, Lambda 950). The range of the wavelength measured was 200 – 800 nm.

The film thickness can also be calculated using the Swanepoel method [188] by collecting UV/Vis data in the wavelength range of 250 – 2500 nm.

2.4.10 Photoelectrochemical (PEC) measurement

Photoelectrochemical measurement instrument was built in house by Dr. Yaomin Li and me. The tests were done in a three-electrode system in a cubic quartz cell connecting to a potentiostat (Interface 1000, Gamry). The electrolyte was 0.1 M H₂SO₄, the counter
The electrode was a Pt mesh and the reference electrode was a Ag/AgCl electrode (CHI111). The light source was a 75 W USHIO xenon lamp with a Newport AM 1.5 G filter. The light intensity was calibrated to one sun by a photodiode (CPC). Nernst equation was used to convert the as-measured working potential by Ag/AgCl electrode ($V_{Ag/AgCl}$) to reversible hydrogen electrode potential ($V_{RHE}$).

$$V_{RHE} = V_{Ag/AgCl} + 0.0591\text{pH} + 0.1976$$

The linear sweep voltammetry (LSV) was scanned at a speed of 10 mV/s. The samples were measured for several scans for the reproducibility between measurements. The chronoamperometry tests were measured at 1.23 V (vs. RHE) for 24 hours under one sun illumination.

Spectral reflectance measurement, SEM, SEM-EDS, TEM, TEM-EDS, XRD, XPS, UV/Vis, AFM and PEC measurement were mostly carried out at Department of Chemistry, UCL. Ellipsometry was carried out at Department of Chemical Engineering, UCL. Part of SEM, SEM-EDS, PEC measurement and AFM was done at Department of Archaeology, UCL, Department of Chemistry, Imperial College and Analysis and Test Center, Beijing University of Chemical Technology.
Chapter 3. AACVD of WO$_3$ and its photoelectrochemical properties

3.1 Introduction

WO$_3$ is a long-time popular material used in photodegradation and photoelectrochemistry. This chapter describes the preparation of tungsten oxide film by aerosol assisted chemical vapour deposition. Flat WO$_3$ film and nanostructured WO$_3$ film were obtained by altering the precursor solvent. The compositions, structures, morphologies and optical properties were analysed by XRD, SEM, TEM and UV/Vis. Photoelectrochemical (PEC) performance of the films was measured and compared to test the reproducibility of the samples.

3.2 Experimental

3.2.1 Flat WO$_3$ film

FTO glass and quartz were cut into 2.5 cm × 2.5 cm pieces, cleaned by acetone, isopropanol, methanol and deionized water for 15 min, respectively, and dried in compressed air. The substrate was placed inside the reaction chamber of the AACVD reactor. The reactor was heated to 375 °C. 0.06 g (0.17 mmol) tungsten hexacarbonyl \([\text{W(CO)}_6, 97\%, \text{Sigma-Aldrich}]\) was dissolved in 15 cm$^3$ acetone (laboratory reagent grade, Fisher Scientific UK) and sonicated until completely dissolved. The solution was transferred to a glass flask and an ultrasonic humidifier was used to generate an aerosol from the precursor, with the aerosol then transported to the substrate via 300 sccm nitrogen carrier gas. After the precursor was exhausted, the reactor was cooled down to room temperature. The as-synthesized film was annealed in air in a muffle furnace (echml-PD, Carbolite Shfld.) at 530 °C for 2 hours. Deposition parameter details are shown in table 3.1.
<table>
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<th>Type</th>
<th>Substrate</th>
<th>W(CO)₆ /g</th>
<th>Solvent /mL</th>
<th>Temperature/°C</th>
<th>Flow rate/sccm</th>
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<td>WO₃₋ₓ (3.2.1)</td>
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<td>10 cm³ acetone</td>
<td>375</td>
<td>300</td>
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<td>WO₃₋ₓ (3.2.2)</td>
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<td>10 cm³ acetone + 5 cm³ methanol</td>
<td>375</td>
<td>300</td>
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</table>

Table 3.1 Conditions of WO₃₋ₓ deposited via AACVD.

3.2.2 Nanostructured WO₃ film

FTO glass and quartz were cut into 2.5 cm × 2.5 cm pieces, cleaned by acetone, isopropanol, methanol and deionized water for 15 min, respectively, and dried in compressed air. The substrate was placed inside the reaction chamber of the AACVD reactor. The reactor was heated to 375 °C. 0.06 g (0.17 mmol) tungsten hexacarbonyl [W(CO)₆, 97%, Sigma-Aldrich] was dissolved in 10 cm³ acetone and 5 cm³ methanol (laboratory reagent grade, Fisher Scientific UK) and sonicated until completely dissolved. The solution was transferred to a glass flask and an ultrasonic humidifier was used to generate an aerosol from the precursor, with the aerosol then transported to the substrate via 300 sccm nitrogen carrier gas. After the precursor was exhausted, the reactor was cooled down to room temperature. The as-synthesized film was annealed in air in a muffle furnace (echml-PD, Carbolite Shfld.) at 530 °C for 2 hours.

3.3 Result and discussion

3.3.1 Flat WO₃ film

Tungsten hexacarbonyl is a volatile, air-stable, colourless compound used as an AACVD precursor to produce WO₃ [189]. Flat WO₃ film was deposited via AACVD using only acetone as the precursor solvent. The substrate was placed near the outlet part of the reaction chamber with a mask covering one end. In figure 3.1, we can see the colour of the as-synthesized film is translucent grey blue with metallic lustre. After being annealed under air at 530 °C, the film became colourless, still with metallic lustre. The original
colour indicates the formation of sub-stoichiometric $\text{WO}_{3-x}$\textsuperscript{[190]}. After annealing at 530 °C, oxygen was supplied to let $\text{WO}_{3-x}$ become $\text{WO}_3$ (equation 3.1).

\begin{equation}
\text{(1)} \quad \text{W(CO)}_6 + \text{O}_2 \rightarrow \text{WO}_{3-x} + 6 \text{CO}_2
\end{equation}

\begin{equation}
\text{(2)} \quad \text{WO}_{3-x} + \frac{x}{2} \text{O}_2 \rightarrow \text{WO}_3 \quad (3.1)
\end{equation}

Figure 3.1 a) As-synthesized flat $\text{WO}_{3-x}$ and b) $\text{WO}_3$ after annealed at 530 °C on quartz deposited via AACVD. The deposition conditions used are described in section 3.2.1.

XRD patterns of as-synthesized $\text{WO}_{3-x}$ via AACVD and $\text{WO}_3$ after annealing are shown in figure 3.2. Comparing to JCPDS card PDF#36-0103, the peaks of $\text{WO}_{3-x}$ at 23.58 °, 32.07 ° and 48.15 ° are corresponding to (0 1 0), (4 0 4) and (0 2 0) planes. This would be a monoclinic phase $\text{WO}_{2.83}$ ($a = 19.31$ Å, $b = 3.78$ Å and $c = 17.07$ Å). After being annealed at 530 °C for 2 hours, the peaks of $\text{WO}_3$ at 23.13 °, 28.02 °, 33.33 °, 34.18 °, 41.50 °, 47.25 °, 50.45 ° and 53.52 ° are corresponding to (0 0 2), (1 1 2), (0 2 2), (2 0 2), (2 2 2), (0 0 4), (1 1 4) and (0 2 4) planes comparing to JCPDS card PDF#43-1035. This is a monoclinic phase $\text{WO}_3$ with $a = 7.297$ Å, $b = 7.539$ Å, $c = 7.688$ Å). The strongest peak at 23.13 ° shows the crystallinity at (0 0 2) plane. Therefore, there is a growth preference in [0 0 2] direction which helps reach the lowest surface energy\textsuperscript{[191]}. 89
Figure 3.2 XRD patterns of as-synthesized flat WO$_{3-x}$, WO$_3$ via AACVD and JCPDS cards, PDF#43-1035 and PDF#36-0103. The deposition conditions used are described in section 3.2.1.

Figure 3.3 SEM images of flat WO$_3$ films on FTO glass via AACVD after annealing under different magnifications, a) 100k; b) 5k. The deposition conditions used are described in section 3.2.1.

The surface morphology of WO$_3$ films after annealing was observed by SEM. As shown in figure 3.3 (b), this WO$_3$ film could be described as “flat” WO$_3$ film under 5000 times magnification, because only nanoparticle aggregations can be seen in the image. The
image under 100k times magnification (figure 3.3 (a)) shows the detail of the flat WO$_3$ film. From the image we can see the clusters of some much smaller nanoparticles. The size of a single nanoparticle is approximately 20 nm in diameter, a number of which forms the 200 nm cluster. The film follows layer by layer growth and slightly transform to layer + island growth with the rough clusters on the surface. This film structure provides good adhesion on the FTO substrate. Also because of the AACVD process, the uniformity of the film is less than the film deposited by ALD, but it will be called ‘flat film’ when comparing to the other structures mentioned below.

Figure 3.4 UV/Vis spectra of flat WO$_{3-x}$ and WO$_3$ on quartz deposited via AACVD. The deposition conditions used are described in section 3.2.1.

Figure 3.4 shows the UV/Vis absorption spectra of flat WO$_{3-x}$ and WO$_3$ prepared by AACVD. WO$_3$ has weaker absorption than WO$_{3-x}$ in visible light region. WO$_3$ has an indirect band gap, its band gap energy ($E_g$) can be calculated by the following equation (equation 3.2) $^{[192]}$:

\[
(\alpha \nu)^{1/2} = A(\nu - E_g)
\]  

(3.2)
Where $\alpha$, absorption coefficient; $h$, Plank's constant; $\nu$, frequency of radiation. $\alpha = \frac{2.303 \times \text{Absorbance}}{\text{Thickness}}$, $\nu = \frac{c}{\lambda}$, where $c$, speed of light. Tauc plot of figure 3.4 can be plotted between $(\alpha h \nu)^{1/2}$ and $h \nu$ in figure 3.5. Therefore, the band gap of WO$_{3-x}$ is $\sim 2.8$ eV, after annealing, the band gap of WO$_3$ is $\sim 3.0$ eV. The calculated band gap value is in the range of the literature value, $2.6 - 3.0$ eV \[^{193,194}\].

![Graph](image)

**Figure 3.5** Tauc plot of flat WO$_{3-x}$ and WO$_3$ on quartz deposited *via* AACVD. The deposition conditions used are described in section 3.2.1.

### 3.3.2 Nanostructured WO$_3$ film

Nanostructured WO$_3$ film was deposited *via* AACVD using methanol and acetone as the precursor solvent. It can be seen in figure 3.6 that the film near outlet part looks more even than the film near inlet part. Therefore, the substrate was placed near the outlet part of the reaction chamber with a mask covering one end. In figure 3.7, we can see the colour of the as-synthesized film is dark blue. After annealing under air at 530 °C, the colour of the film changes to light yellow. The change of colour indicates the transformation from sub-stoichiometric WO$_{3-x}$ to WO$_3$ \[^{190}\].
Figure 3.6 As-synthesized nanostructured WO$_3$ on FTO glass via AACVD. The deposition conditions used are described in section 3.2.2.

XRD patterns of as-synthesized, nanostructured WO$_{3-x}$ via AACVD and WO$_3$ after annealing are shown in figure 3.8. Comparing to JCPDS card PDF#36-0103, the peaks of WO$_{3-x}$ at 23.46 °, 28.69 °, 33.13 °, 35.55 °, 40.21 ° and 47.90 ° are corresponding to (0 1 0), (6 0 0), (1 1 4), (5 0 4), (6 1 2) and (0 2 0) planes. This would be a monoclinic phase WO$_{2.83}$ (a = 19.31 Å, b = 3.78 Å and c = 17.07 Å). After annealing at 530 °C for 2 hours, the peaks of WO$_3$ at 23.13 °, 28.82 °, 33.33 °, 34.11 °, 41.69 °, 47.25 °, 50.51 ° and 53.52 ° are corresponding to (0 0 2), (1 1 2), (0 2 2), (2 0 2), (1 2 2), (2 2 2), (0 0 4), (1 1 4) and (0 2 4) planes comparing to JCPDS card PDF#43-1035. This is a monoclinic phase WO$_3$ with a = 7.297 Å, b = 7.539 Å, c = 7.688 Å). The strongest peak at 23.13 ° shows the crystallinity at (0 0 2) plane. Therefore, there is a growth preference in [0 0 2] direction which is the same direction as flat film as will be later confirmed by HRTEM. The
transformation of tungsten oxide from WO$_{3-x}$ to WO$_3$ has a good match with the colour changing from dark blue to light yellow.

Figure 3.8 XRD patterns of as-synthesized nanostructured WO$_{3-x}$, WO$_3$ on quartz deposited via AACVD and JCPDS cards, PDF#43-1035 and PDF#36-0103. The deposition conditions used are described in section 3.2.2.

Figure 3.9 Fitted W 4f high resolution XPS spectra of nanostructured a) WO$_{3-x}$ and b) WO$_3$ deposited via AACVD on FTO glass. The deposition conditions used are described in section 3.2.2.
Figure 3.9 displays W 4f XPS spectra of WO$_3$-$\chi$ film and WO$_3$ film deposited via AACVD on FTO glass. W 4f spectra of WO$_3$-$\chi$ shows two doublets. The core peaks of W$^{6+}$ in WO$_3$-$\chi$ was observed at a binding energy of 38.3 eV and 36.2 eV corresponding to W 4f $5/2$ and W 4f $7/2$. The lower intensity peaks at 37.0 eV and 35.0 eV corresponding to W 4f $5/2$ and W 4f $7/2$ are the peaks of W$^{5+}$ (figure 3.9 (a)). The W 4f spectra of WO$_3$ shows only W$^{6+}$ peaks at 37.4 eV and 35.3 eV corresponding to W 4f $5/2$ and W 4f $7/2$, indicating the oxidation of the tungsten oxide and the presence of only WO$_3$ (figure 3.9 (b)).

Figure 3.10 SEM images of nanostructured WO$_3$ films deposited via AACVD on FTO glass under different magnifications, a) 2k; b) 20k. The deposition conditions used are described in section 3.2.2.

The surface morphology of WO$_3$ films after annealing was observed by SEM. As shown in figure 3.10 (b), this WO$_3$ film is formed by a large number of WO$_3$ nanoneedles. The image under 100k times magnification (figure 3.10 (a)) shows the WO$_3$ nanoneedles film under larger scale. From the image we can see the random orientation of these nanoneedles. The size of a single nanoneedle is approximately 150 nm in diameter. Though the crystal structures of WO$_3$ NNs and flat WO$_3$ are similar, the morphology are quite different. The change of the structure from nanoparticle cluster to nanoneedle occurs as a function of precursor solvent from acetone to a mixture of acetone and methanol (2 : 1). Ling$^{[128]}$ found that the solvent used for AACVD deposition affects the thin film formation because the solubility of the precursor varies. [W(CO)$_6$] has high solubility in acetone and low
solubility in methanol resulting in different concentration of precursor in generated aerosols. Depending on the surface tension, viscosity and density of the solvent, the size of aerosols delivered into reactor varies. It is also suspected that solvents were actively participating in the formation of the thin films but finding wasn’t conclusively proven.

![Figure 3.11](image)

**Figure 3.11** a) TEM image and schematic of a WO$_3$ nanoneedle cluster; b) high-resolution TEM image of nanostructured WO$_3$; c) FFT of HRTEM. The deposition conditions they used via AACVD are described in section 3.2.2.

WO$_3$ films were further analysed by TEM (figure 3.11). The diameter of a single nanoneedle changes from 150 nm (thick tip) to 30 nm (thin end connecting to the substrate), the length of the nanoneedle is 3 μm (figure 3.11 (a)). The growth direction which is shown in the schematic is from thick tip to thin end standing on the substrate. It
might be the narrow end cross-section connecting to the substrate that makes the nanoneedle films to be easily delaminated whereas the flat films are more adherent. The d-spacings of WO$_3$ shown in figure 3.11 (b) are 0.38 nm, 0.36 nm and 0.28 nm. The (h k l) planes are (0 0 2), (2 0 0) and (0 2 2), respectively (figure 3.11 (c)). These results calculated from TEM images further indicate this WO$_3$ is in monoclinic phase.

Figure 3.12 shows the UV/Vis absorption spectra of flat WO$_3$ and WO$_3$ nanoneedle films prepared by AACVD. As shown in Figure 3.7 above, WO$_{3-x}$ NNs film is non-transparent. WO$_3$ NNs is also less transparent than flat WO$_3$ which can be proved from the UV/Vis spectrum. The band gap energy ($E_g$) of WO$_3$ NNs is calculated by equation 3.2 and plotted in Tauc plot (figure 3.13). Therefore, after annealing, the band gap of WO$_3$ NNs is ~2.6 eV which is narrower than flat WO$_3$ ~3.0 eV. This is a possibility of light scattering affecting the UV-Vis measurement. Rayleigh scatter happens with nanostructures whose size is smaller than the wavelength of light, and normally has higher intensity below 400 nm$^{[195]}$. For nanorods, the amount of light scattered relates to the diameter of the rod. The transmission of the rods first increases and then decreases after reaching the maximum$^{[195]}$. In this case, the real bandgap would be slightly narrower than that presented.

![Figure 3.12](image.png)

**Figure 3.12** UV/Vis absorption spectra of flat WO$_3$ and WO$_3$ nanoneedles films. The deposition conditions they used via AACVD are described in section 3.2.2.
Figure 3.13 Tauc plot of flat WO₃ and WO₃ NNs. The deposition conditions they used via AACVD are described in section 3.2.2.

WO₃ deposited via AACVD has been widely studied at Department of Chemistry, University College London. S. Ashraf et al. [196] reported WO₃ thin films were produced using [NH₄]₆[W₁₂O₃₉], [NH₄]₁₀H₂[W₂O₇]₆, [nBu₄N]₄[W₁₀O₃2] and [nBu₄N]₂[W₆O₁₉] as W precursors in acetonitrile or water. Morphologies showed in figure 3.14. The WO₃ films functioned as gas sensors showing faster responses to ethanol and nitrogen dioxide vapour in air comparing to screen-printed sensors and at lower temperature (250 °C). R. Palgrave et al. [197] reported using [W(OPh)₆] as an AACVD precursor to deposit crystalline monoclinic WO₃ after annealing. The WO₃ films showed significant photochromism to blue state with UV light radiation. Comparing to these previously used precursors, the W(CO)₆ precursor we used produce less carbon and nitrogen residual. Also, by adjusting the amount and composition of the solvent, the nanoneedle array structured WO₃ we synthesised helps increase the surface area and may provide more active area for application such as photocurrent density measurement.
3.3.3 PEC test, comparison and reproducibility

To evaluate the photoelectrochemical property of these two types of WO$_3$, linear sweep voltammetry was used to investigate the photoelectrochemical performance under visible light (figure 3.15). Because WO$_3$ is an n-type material, both films have a positive slope. The dark current density of both flat WO$_3$ film and WO$_3$ NNs film are nearly zero. The photocurrent density of flat WO$_3$ film at 1.23 V (vs. RHE) is $\sim 0.41$ mA/cm$^2$. The photocurrent density of WO$_3$ NNs film reaches $\sim 0.77$ mA/cm$^2$ at 1.23 V (vs. RHE). The onset potential of both films is 0.48 V (vs. RHE).
Figure 3.15 Chopped I-V curve of flat WO$_3$ and WO$_3$ nanoneedles films. The deposition conditions they used via AACVD are described in section 3.2.2.

The difference in performance may be due to the visible light absorption difference between these two film structures (figure 3.12). In this case, WO$_3$ NNs film has higher visible light absorption and better charge transfer property comparing to flat WO$_3$ film as it generated higher photocurrent. This is probably due to the high surface area and aspect orientation which increase the light absorbing ability.

Subsequently 10 pieces of WO$_3$ NNs film were deposited via AACVD using two AACVD reactors, two humidifiers with the same design while deposition parameters were kept the same to test the reproducibility of the films according to the instruments. Each film was cut into two pieces. Linear sweep voltammetry of each sample was measured and compared to each other. The average photocurrent and standard deviation of these 20 samples was calculated and plotted in figure 3.16. The average photocurrent density of WO$_3$ NNs films is ~ 0.68 mA/cm$^2$ at 1.23 V (vs. RHE) with a standard deviation of 0.1 mA/cm$^2$. 
Figure 3.16 Reproducibility I-V curve of WO$_3$ nanoneedles films. The deposition conditions they used via AACVD are described in section 3.2.2. (Error bar is obtained from standard deviation of 20 samples.)

Comparing to the photocurrent density of nanowires in the same monoclinic phase, the current densities of our WO$_3$ NNs films are much higher (table 3.2). Nanoparticles seems to have best PEC performance among all. However, among various WO$_3$ morphologies, our nanoneedles with PEC performance of $\sim 0.68$ mA/cm$^2$ at 1.23 V (vs. RHE) are competitive with values reported in literature although not the highest, however due to the different crystal structures, morphologies, electrolyte and light source, the photocurrent densities cannot be directly compared.
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<th>Synthesis method</th>
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<th>Electrolyte</th>
<th>Light source</th>
<th>Ref.</th>
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</thead>
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Table 3.2 PEC performance of WO₃ films prepared by various methods in the literature.
**3.4 Conclusions**

WO$_{3-x}$ films were deposited *via* aerosol assisted chemical vapour deposition at 375 °C, using W(CO)$_6$ as precursor, in 15 cm$^3$ acetone (flat WO$_3$) or 10 cm$^3$ acetone + 5 cm$^3$ methanol (WO$_3$ nanoneedles) with 300 sccm N$_2$ flow rate on FTO glass. WO$_{3-x}$ was annealed at 530 °C in the air and transformed to WO$_3$.

Blue grey translucent flat WO$_{3-x}$ was transformed to colourless metallic-lustre WO$_3$. XRD analysis suggests that the crystal structures of WO$_{3-x}$ (WO$_{2.83}$) and WO$_3$ are in monoclinic phase with a growth preference for WO$_3$ in [0 0 2] direction. SEM images show that the flat WO$_3$ film is formed by clusters of small WO$_3$ nanoparticles with 20 nm diameter. Visible light absorption and band gap of the flat as-deposited WO$_{3-x}$ and annealed WO$_3$ can be calculated from UV/Vis spectra and Tauc plot. The band gap of WO$_{3-x}$ is $\sim 2.8$ eV, after annealing, the band gap of WO$_3$ is $\sim 3.0$ eV.

Dark blue WO$_{3-x}$ nanoneedles film was transformed to light yellow WO$_3$ after annealing. XRD analysis suggests that the crystal structures of WO$_{3-x}$ (WO$_{2.83}$) and WO$_3$ are in monoclinic phase with a growth preference for WO$_3$ in [0 0 2] direction. W 4f XPS spectra with 4f$_{5/2}$ and 4f$_{7/2}$ show W$^{6+}$ peaks and W$^{5+}$ peaks in WO$_{3-x}$ and only W$^{6+}$ peaks in WO$_3$ which indicates the oxidation of the tungsten oxide and only the presence of WO$_3$. SEM and TEM images show that WO$_3$ film is formed by a large number of WO$_3$ nanoneedles with random orientation. The diameter of a single nanoneedle changes from 150 nm (thick tip) to 30 nm (thin end), the length of the nanoneedle is 3 μm. D-spacing and (h k l) planes of WO$_3$ were also observed by TEM. Visible light absorption and band gap of the flat WO$_{3-x}$ and WO$_3$ can be calculated from UV/Vis spectra and Tauc plot. The band gap of WO$_3$ is $\sim 2.6$ eV. AACVD precursors, solvents and WO$_3$ film morphologies have been compared and morphology with higher surface area may provide more active area and higher photocurrent density.
PEC measurement of these two types of WO$_3$ gives the photocurrent density of flat WO$_3$ film at 1.23 V (vs. RHE) is $\sim 0.41$ mA/cm$^2$ and that of WO$_3$ NNs film is $\sim 0.77$ mA/cm$^2$ at 1.23 V (vs. RHE). The reproducibility of WO$_3$ NNs film was obtained from 20 samples showing an average photocurrent density of $\sim 0.68$ mA/cm$^2$ at 1.23 V (vs. RHE) with a standard deviation of 0.1.
Chapter 4. AACVD of Au, Ag and Pt NPs on WO$_3$ and its photoelectrochemical properties

4.1 Introduction

To improve the photocurrent of WO$_3$ NNs in water splitting, noble metal nanoparticles were introduced into the system. Au and Ag NPs are normally used as plasmonic materials, Pt NPs are normally used as a catalyst in the reaction.

In this chapter, the deposition of Au, Ag, Pt nanoparticles via AACVD is described. The precursors used were hydrogen tetrachloroaurate(III) trihydrate (HauCl$_4$·3H$_2$O) for Au, silver 2-methyl-2-aminopropan-1-ol (Ag-AMP) for Ag and hydrogen hexachloroplatinate(IV) hydrate (H$_2$Cl$_6$Pt·xH$_2$O) for Pt. The reaction parameters were optimized to obtain the desired nanoparticle size and shape. The composition, structure and morphology of these nanoparticles were characterized by XRD, XPS, UV/Vis, SEM and TEM. After characterization, the nanoparticles were deposited on WO$_3$ NNs films for photoelectrochemical use. The composition, structure and morphology of these metal NPs/WO$_3$ were characterized by XRD, XPS, UV/Vis, SEM, TEM and EDS. Their PEC properties were investigated by linear scan voltammetry.

4.2 Experimental

4.52.3 Synthesis of Au nanoparticles via AACVD

FTO glass and quartz were cut into 6 cm × 2.5 cm pieces, cleaned by acetone, isopropanol, methanol and deionized water for 15 min, respectively, and dried in compressed air. A WO$_3$ NNs film was cut into 0.8 cm × 1.5 cm pieces. The substrate was placed inside the reaction chamber of the AACVD reactor. The reactor was heated to 250 °C, 300 °C, 350 °C or 400 °C. 5 mg, 3.4 mg, 1.7 mg, 1 mg, 0.5 mg, 0.25 mg, 0.1 mg or 0.02 mg HauCl$_4$·3H$_2$O (99.99% (metals basis), Au 49.5% minimum, Alfa Aesar™), Fisher
Scientific UK) was dissolved in 15 cm³ methanol (laboratory reagent grade, Fisher Scientific UK) and sonicated until completely dissolved. The solution was transferred to a glass flask and an ultrasonic humidifier was used to generate an aerosol from the precursor, with the aerosol then transported to the substrate via 300 sccm nitrogen carrier gas. After the precursor was exhausted, the reactor was cooled down to room temperature. Deposition parameter details are shown in Table 4.1.

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<tr>
<th>Substrate</th>
<th>Solvent /mL</th>
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<tr>
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**Table 4.1** Conditions of Au NPs deposited via AACVD.

### 4.2.2 Ag nanoparticles deposition

FTO glass and quartz were cut into 6 cm × 2.5 cm pieces, cleaned by acetone, isopropanol, methanol and deionized water for 15 min, respectively, and dried in compressed air. A
WO₃ NNs film was cut into 0.8 cm × 1.5 cm pieces. The substrate was placed inside the reaction chamber of the AACVD reactor. The reactor was heated to 275 °C. 100 μL or 20 μL silver 2-methyl-2-aminopropan-1-ol (Ag-AMP) was dissolved in 15 cm³ methanol and sonicated until completely dissolved. The solution was transferred to a glass flask and an ultrasonic humidifier was used to generate an aerosol from the precursor, with the aerosol then transported to the substrate via 300 sccm nitrogen carrier gas. After the precursor was exhausted, the reactor was cooled down to room temperature. Deposition parameter details are shown in table 4.2.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solvent /mL</th>
<th>Ag-AMP /μL</th>
<th>Temperature /°C</th>
<th>Flow rate /sccm</th>
</tr>
</thead>
<tbody>
<tr>
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<td>15</td>
<td>20</td>
<td>275</td>
<td>300</td>
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<tr>
<td>FTO</td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WO₃</td>
<td></td>
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<tr>
<td>Quartz</td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.2** Conditions of Ag NPs deposited via AACVD.

### 4.2.3 Pt nanoparticles deposition

FTO glass and quartz were cut into 6 cm × 2.5 cm pieces, cleaned by acetone, isopropanol, methanol and deionized water for 15 min, respectively, and dried in compressed air. WO₃ NNs film was cut into 0.8 cm × 1.5 cm pieces. The substrate was placed inside the reaction chamber of the AACVD reactor. The reactor was heated to 350 °C. 1.5 mg or 0.5 mg H₂Cl₆Pt·xH₂O (ca. 40% Pt, ACROS Organics™, Fisher Scientific UK) was dissolved in 15 cm³ methanol and sonicated until completely dissolved. The solution was transferred to a glass flask and an ultrasonic humidifier was used to generate an aerosol from the precursor, with the aerosol then transported to the substrate via 300 sccm nitrogen carrier gas. After the precursor was exhausted, the reactor was cooled down to room temperature. Deposition parameter details are shown in table 4.3.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Solvent /mL</th>
<th>H₂Cl₆Pt·xH₂O /mg</th>
<th>Temperature /°C</th>
<th>Flow rate /sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO</td>
<td>15</td>
<td>0.5</td>
<td>350</td>
<td>300</td>
</tr>
<tr>
<td>FTO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WO₃</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WO₃</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>0.5</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Quartz</td>
<td>1.5</td>
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</tbody>
</table>

Table 4.3 Conditions of Pt NPs deposited via AACVD.

4.3 Result and discussion

4.3.1 Au nanoparticles and Au/WO₃

4.3.1.1 Au nanoparticles on FTO glass

Au was first deposited on FTO glass rather than WO₃ NNS film to study its properties alone. An Au film was deposited via AACVD at 300 °C, 300 sccm gas flow rate, on FTO glass and other substrates using HauCl₄·3H₂O as the Au precursor and methanol as the precursor solvent. It can be seen in figure 4.1 that the as-deposited film on FTO appears bluish violet with gold reflection. The film colour indicates the formation of nanostructures on the substrate arising from metal surface plasmon resonance (SPR).

![Figure 4.1](image-url) Au NPs deposited at 300 °C on FTO glass via AACVD down (inlet) to up (outlet). Other deposition conditions are described in section 4.2.1.
XRD pattern of as-synthesized Au via AACVD is shown in figure 4.2. Comparing to JCPDS card PDF#04-0784, the peaks of Au at 38.25 °, 44.40 ° and 64.65 ° are corresponding to (1 1 1), (2 0 0) and (2 2 0) planes which have a good match with the JCPDS card. This is a cubic phase Au crystal structure (a = b = c = 4.08 Å).

![XRD pattern](image)

**Figure 4.2** XRD patterns of as-deposited Au on FTO glass using 5 mg HauCl₄·3H₂O in 15 cm³ methanol at 300 °C, as compared to JCPDS cards, PDF#04-0784. Other deposition conditions are described in section 4.2.1.

Figure 4.3 displays Au 4f XPS spectra of Au film deposited via AACVD on FTO glass. The Au spectra have two doublets. These two peaks observed at a binding energy of 87.5 eV and 83.3 eV corresponding to Au 4f ½ and Au 4f ½, respectively. This indicates the presence of Au⁰, which is Au metal from the deposition.
Figure 4.3 Fitted Au 4f high resolution XPS spectra of Au NPs deposited at 300 °C on FTO glass. Other deposition conditions are described in section 4.2.1.

The surface morphology of Au film deposited at 300 °C and 350 °C were observed by SEM in figure 4.4. As shown in figure 4.4 (a), this Au film deposited at 300 °C is formed by many nanoparticles (NPs). They are in sphere or cubic shape separating from each other, with most size of \(~ 10 – 20 \text{ nm}\) (figure 4.5). The image of Au film deposited at 350 °C (figure 4.4 (b)) shows the formation of Au nanoparticles as well. However, the increase of temperature enlarges the NPs to a diameter of \(~ 25 \text{ nm}\). The space among Au NPs decreases, which make them more likely to form Au clusters.

Figure 4.4 SEM images of Au NPs deposited on FTO glass via AACVD under 100k magnifications deposited at a) 300 °C; b) 350 °C. Other deposition conditions are described in section 4.2.1.
Figure 4.5 Size distribution of figure 4.4 (a) with average diameter of 13.6 ± 3.7 nm.

Au NPs were further analysed by TEM (figure 4.6). There is one random shaped, crystallized Au nanoparticle (15 nm × 25 nm) and one Au sphere (~ 15 nm) in this image. Cubic Au with (1 1 1), (2 2 0) and (3 2 2) crystal planes which corresponding to d-spacings, 0.23 nm, 0.20 nm and 0.15 nm can be observed from the high-resolution TEM image. XRD, XPS, SEM and TEM analysis together suggest that the Au film deposited via AACVD was crystallized Au nanoparticles, with uniform size.

Figure 4.6 high-resolution TEM image of Au NPs. The deposition conditions via AACVD are described in section 4.2.1.
Figure 4.7 shows the UV/Vis absorption spectra of Au NPs films prepared by AACVD on FTO glass. As shown in the figure, the Au spectrum has an obvious peak at 580 nm. This could be the plasmon peak of Au nanoparticles which attributes to the surface plasmon resonance (SPR) \[203\]. This absorption peak appearing in the visible light region is responsible for the visible light response.

![UV/Vis spectra of Au NPs and FTO glass](image)

**Figure 4.7** UV/Vis spectra of Au NPs deposited at 300 °C via AACVD on FTO glass comparing to bare FTO glass. Other deposition conditions are described in section 4.2.1.

### 4.3.1.2 Au nanoparticles on WO\(_3\) NNs film

After Au NPs deposited on FTO glass were analysed, they were then deposited on WO\(_3\) NNs films and the deposition parameters were optimized. Au film was deposited at 250 °C, 300 °C, 350 °C and 400 °C respectively via AACVD, 300 sccm gas flow rate using 5 mg, 3.4 mg and 1.7 mg HauCl\(_4\)·3H\(_2\)O as Au precursor and methanol as the precursor solvent. The as-deposited Au/WO\(_3\) can be seen in figure 4.8. Comparing to light yellow WO\(_3\) NNs, Au/WO\(_3\) appears purple. The colour gradient shows that with the temperature rises, the colour of Au/WO\(_3\) deepened from purple (250 °C) to blackish purple (400 °C). The increasing of HauCl\(_4\)·3H\(_2\)O precursor concentration also has impact on the colour of Au/WO\(_3\), which changes from light purple to dark purple. The colour
changes indicate that at least one factor, the amount of Au NPs, the density of Au NPs or the size of Au NPs has changed. As the Au/WO$_3$ are used for water splitting, we want to find out a suitable combination of Au and WO$_3$ which has the best performance. Therefore, the parameters of Au NPs deposition on WO$_3$ NNs need to be optimized.

![Figure 4.8](image)

**Figure 4.8** Photograph of (left) WO$_3$ deposited *via* AACVD on FTO glass and (right) Au/WO$_3$ deposited *via* two steps AACVD on FTO glass at different temperatures and Au precursor concentration. The deposition conditions are described in section 4.2.1.

XRD patterns of as-synthesized Au/WO$_3$ deposited using 5 mg Au precursor in 15 cm$^3$ methanol at 300 °C with a constant flow of N$_2$ at 300 sccm is shown in figure 4.9. All Au/WO$_3$ peaks are matched with JCPDS card WO$_3$ PDF#43-1035 and Au PDF#04-0784. The identical WO$_3$ peaks at 23.05 ° and 33.05 ° which are indexed to (0 0 2) and (0 2 2) and the intensive peak of Au at 38.10 ° corresponding to (1 1 1) show no obvious peak shift comparing with bare WO$_3$ and Au materials. Au peaks are significant in this XRD
pattern due to the “high” concentration of Au precursor. SnO$_2$ peaks from FTO glass were also observed at 35.30 ° and 62.00 °.

![XRD patterns of Au/WO$_3$ NNs on FTO glass using 5mg Au precursor in 15 cm$^3$ methanol at 300 °C with a constant flow of N$_2$ at 300 sccm comparing to standard JCPDS of WO$_3$ PDF#43-1035 and Au PDF#04-0784.](image)

**Figure 4.9** XRD patterns of Au/WO$_3$ NNs on FTO glass using 5mg Au precursor in 15 cm$^3$ methanol at 300 °C with a constant flow of N$_2$ at 300 sccm comparing to standard JCPDS of WO$_3$ PDF#43-1035 and Au PDF#04-0784.

Figure 4.10 shows the XRD patterns of Au/WO$_3$ NNs on FTO glass deposited at different temperatures (250 °C, 300 °C, 350 °C and 400 °C) and different Au precursor concentration (5 mg, 3.4 mg and 1.7 mg). All the WO$_3$ peaks and Au peaks are at the same positions with no shift as those in figure 4.9. There is no obvious variation tendency among the WO$_3$ peak intensities. Au deposited at higher temperatures or using higher Au precursor concentrations shows stronger Au peaks which can be seen at 38.10°. Therefore, Au/WO$_3$ (5 mg, 400 °C) has either larger Au particles which diffract strongly or has a higher amount of Au loading which gives more intense peak.
Figure 4.10 XRD patterns of Au/WO$_3$ NNs deposited via AACVD on FTO glass at different temperatures and Au precursor concentration. The deposition conditions are described in section 4.2.1.

Figure 4.11 displays XPS spectra of Au/WO$_3$ film deposited via AACVD on FTO glass. The Au spectra have two Au peaks which belong to elemental Au observed at a binding energy of 87.6 eV and 83.9 eV are corresponding to Au 4f$_{5/2}$ and Au 4f$_{7/2}$, respectively, and are in good agreement within the literature$^{[204]}$. The W 4f spectra of WO$_3$ shows only W$^{6+}$ peaks at 37.7 eV and 35.6 eV corresponding to W 4f$_{5/2}$ and W 4f$_{7/2}$.

Figure 4.11 a) Fitted W 4f and b) fitted Au 4f high resolution XPS spectra of Au/WO$_3$ (5 mg, 300 °C) deposited via AACVD on FTO glass. The deposition conditions are described in section 4.2.1.
The XPS spectra of W 4f and Au 4f plotted separately according to different deposition temperature are shown in figure 4.12 as a, b) 250 °C; c, d) 300 °C; e, f) 350 °C and g, h) 400 °C. Among them, W 4f peaks of Au/WO₃ deposited at 400 °C show relatively low intensity due to the high Au coverage on WO₃ NNs surface. W 4f peaks of Au/WO₃ deposited lower than 350 °C show reasonable peak intensities. There is no W 4f peak shift or shape change in each temperature group. Due to the individual difference of the measure positions, there is no dependence relationship between Au precursor concentration and W 4f peak intensity.

Au 4f peaks of Au/WO₃ deposited at 400 °C show positive correlation between Au precursor concentration and Au 4f peak intensity. We also suspect as the deposition temperature grows, the Au coverage on WO₃ NNs surface (surface Au:W ratio) changes. If so, the colour changes of Au/WO₃ could also be explained. There is no obvious Au 4f peak shift or shape change in each temperature group.
Figure 4.12 W 4f and Au 4f high resolution XPS spectra of Au/WO₃ deposited via AACVD using different amount of Au precursor on FTO glass at a, b) 250 °C; c, d) 300 °C; e, f) 350 °C and g, h) 400 °C. Other deposition conditions are described in section 4.2.1.
By plotting all W 4f and Au 4f XPS spectra together into figure 4.13, we can observe a Au peak shift of 0.4 eV from lower binding energy to higher binding energy while the deposition temperature increases. The shift to higher binding energy may due to the electronic interaction of Schottky junction formed between Au NPs and WO$_3$ NNs and the electron transfer is from WO$_3$ to Au. While the deposition temperature and concentration of precursor increase, the intensity of W 4f peaks decrease consistent with an increase of Au on the WO$_3$ nanorod surface.

![XPS spectra](image)

**Figure 4.13** a) W 4f and b) Au 4f high resolution XPS spectra of Au/WO$_3$ deposited via AACVD on FTO glass using different Au precursor concentrations and temperatures. Data plotted in the rainbow colour from red to violet. The deposition conditions via AACVD are described in section 4.2.1.
The atomic ratio of Au:W on Au/WO₃ surface is calculated from XPS spectra and displayed in table 4.4. Au/WO₃ deposited at 400 °C has extremely high Au at% of more than 80% which means that Au NPs may shield the WO₃ NNs from illumination and decrease the intrinsic properties of WO₃ for water splitting. Lower deposition temperatures and lower Au precursor concentrations provide lower Au:W ratio. For example, doing deposition at 350 °C using 5 mg Au precursor shows Au:W = 1.60, doing deposition at 300 °C using 5 mg Au precursor shows Au:W = 1.11 while doing deposition at 300 °C using 1.7 mg Au precursor shows an Au:W = 0.81. From experience, we assume that lower temperature and lower concentration without overdeposition will give better PEC performance, this hypothesis will be discussed later.

<table>
<thead>
<tr>
<th>Element ratio</th>
<th>W (at%)</th>
<th>Au (at%)</th>
<th>Au:W</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7 mg, 250 °C</td>
<td>57.2</td>
<td>42.8</td>
<td>0.75</td>
</tr>
<tr>
<td>3.4 mg, 250 °C</td>
<td>53.5</td>
<td>46.5</td>
<td>0.87</td>
</tr>
<tr>
<td>5 mg, 250 °C</td>
<td>51.2</td>
<td>48.8</td>
<td>0.95</td>
</tr>
<tr>
<td>1.7 mg, 300 °C</td>
<td>55.3</td>
<td>44.7</td>
<td>0.81</td>
</tr>
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<td>3.4 mg, 300 °C</td>
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<td>66.9</td>
<td>1.80</td>
</tr>
<tr>
<td>5 mg, 300 °C</td>
<td>47.5</td>
<td>52.5</td>
<td>1.11</td>
</tr>
<tr>
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<td>52.9</td>
<td>1.12</td>
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<tr>
<td>3.4 mg, 350 °C</td>
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<td>63.2</td>
<td>1.72</td>
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<tr>
<td>3.4 mg, 400 °C</td>
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<td>86.4</td>
<td>6.35</td>
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<tr>
<td>5 mg, 400 °C</td>
<td>18.8</td>
<td>81.2</td>
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Table 4.4 Surface atomic ratio of Au:W of Au/WO₃ deposited via AACVD at different temperature and Au precursor concentration calculated from XPS data in figure 4.13.

Figure 4.14 shows the UV/Vis absorption spectra of Au/WO₃ prepared by AACVD on FTO glass plotted in rainbow colour. The 400 °C group shows totally different curves
comparing to other temperature groups due to the light absorption by the blackish colour. Using WO\textsubscript{3} UV/Vis as a reference, Au/WO\textsubscript{3} deposited at 250 °C, 300 °C, and 350 °C have plasmon peaks at 550 nm, 540 nm and 525 nm respectively. The red shift of the SPR peak indicates that the size of Au NPs becomes smaller while the deposition temperature decreases \[^{43}\].

There is also a shift in bandgap from $E_g$(WO\textsubscript{3}) = 2.6 eV to $E_g$(Au/WO\textsubscript{3}) = 2.4 eV. Because the Fermi level of WO\textsubscript{3} is lower than the work function of Au \[^{205}\], a Schottky barrier is expected to be formed between the interface of Au and WO\textsubscript{3} with electron transfer from the WO\textsubscript{3} to Au (as seen in XPS, Figure 4.14) which would cause a reduction in bandgap as observed. As the Fermi level of WO\textsubscript{3} is lower than work function of Au, the interaction between Au and WO\textsubscript{3} might be expected to promote the separation of electrons and holes and hence provide more e\textsuperscript{-}/h\textsuperscript{+} pairs during water splitting by reducing recombination in the WO\textsubscript{3}. This indicated Au/WO\textsubscript{3} as a promising material for PEC water splitting.

**Figure 4.14** UV/Vis spectra of WO\textsubscript{3} and Au/WO\textsubscript{3} deposited via AACVD on FTO glass using different Au precursor concentrations and different temperatures. Data plotted in the rainbow colour from red to violet. The deposition conditions are described in section 4.2.1.

The surface morphology of Au/WO\textsubscript{3} deposited on FTO glass at 300 °C were observed by SEM in figure 4.15. The morphology of Au/WO\textsubscript{3} using 1.7 mg Au precursor under low
magnification shows no change comparing to WO₃ itself (figure 4.15 (a) and (d)). Images (b) and (c) show two WO₃ NNs using 1.7 mg and 5 mg Au precursor, respectively. Au NP on top of the nanoneedle in (b) has a size of 20 nm, however Au NPs on top of the nanoneedle in (c) have a size of 80 nm with little gap between each other, the NPs away from the top are smaller. This confirms Au NPs’ size is related to the concentration of Au precursor. Even though the conditions used for depositing Au on FTO glass and on WO₃ NNs are similar, due to the different surface structures of FTO glass and WO₃ nanoneedle film, the size and shape of Au NPs did not appear similar. The highly roughness and shielding of WO₃ NNs structure lead to larger and more irregular NPs on the thick tip, but smaller and more spherical NPs on the surface of the lower part.

![SEM images of Au/WO₃ deposited via AACVD on FTO glass at 300 °C, a) using 1.7 mg Au precursor under 5k magnification; b) using 1.7 mg Au precursor under 200k magnification and c) using 5 mg Au precursor under 200k magnification. SEM images of WO₃ d) under 1k magnification and e) under 100k magnification. The deposition conditions are described in section 4.2.1.](image)

**Figure 4.15** SEM images of Au/WO₃ deposited via AACVD on FTO glass at 300 °C, a) using 1.7 mg Au precursor under 5k magnification; b) using 1.7 mg Au precursor under 200k magnification and c) using 5 mg Au precursor under 200k magnification. SEM images of WO₃ d) under 1k magnification and e) under 100k magnification. The deposition conditions are described in section 4.2.1.

By putting SEM and TEM images following the trend of deposition temperature and Au precursor concentration (figure 4.16, 17, 18 and 19), the information become clear. High deposition temperature and high Au concentration will reflect in large Au NP with random...
shape including sphere, rod, cube, octahedron, tetrahedron, cuboctahedron, truncated tetrahedron and more. Low deposition temperature and Au concentration provide 10 – 20 nm diameter nanoparticles with uniform spherical morphology. This size and shape are considered better to obtain a strong plasmonic effect [206–208]. Still, due to the WO₃ NNs orientation, Au NPs at the top of the NN’s are larger than those on the sides of the NNs, whilst the bottom part of the needle has no Au NP. AACVD cannot solve this problem while keeping the size and shape at the same time while doing two-step deposition. However, co-deposition in one step was somehow unsuccessful with no metal NPs deposited under these conditions.

Figure 4.16 SEM images of Au/WO₃ deposited via AACVD on FTO glass at different temperature using 1.7 mg Au precursor. The deposition conditions are described in section 4.2.1.
Figure 4.17 SEM images of Au/WO$_3$ deposited via AACVD on FTO glass at 300 °C using different Au concentration. The deposition conditions are described in section 4.2.1.

Figure 4.18 TEM images of Au/WO$_3$ deposited via AACVD on FTO glass at different temperature using 1.7 mg Au precursor. The deposition conditions are described in section 4.2.1.
Figure 4.19 TEM images of Au/WO₃ deposited via AACVD on FTO glass at 300 °C using different Au concentration. The deposition conditions are described in section 4.2.1.

HRTEM images of Au/WO₃ deposited on FTO glass at 300 °C with 1.7 mg Au precursor are shown in figure 4.20. WO₃ NNs and Au NPs are all crystallized and easily observed in the figure. (0 0 2) plane (d = 0.38 nm) of WO₃ can be seen. The diameters of Au NPs are ~ 8 – 10 nm. Au d-spacings of 0.23 nm and 0.20 nm can be observed and confirmed as (1 1 1) and (2 2 0) crystal planes, these are confirmed as Au metal. Au nanoparticles have spherical and icosahedral morphologies.

Figure 4.20 HRTEM images of Au/WO₃ deposited via AACVD on FTO glass at 300 °C with 1.7 mg Au precursor. The deposition conditions are described in section 4.2.1.
Linear sweep voltammetry was used to investigate the photoelectrochemical performance of Au NPs on FTO glass in 0.1 M H₂SO₄ electrolyte under one sun illumination (figure 4.21). The photocurrent densities of Au NPs under illumination and under dark condition are similar. The photocurrent density of Au NPs under illumination at 1.23 V (vs. RHE) is 0.07 mA/cm². The photocurrent density of Au NPs in the dark at 1.23 V (vs. RHE) is 0.06 mA/cm². Therefore, bare Au NPs didn’t provide any significant photocurrent, as expected for a metal.

Figure 4.21 I-V curve of Au NPs deposited via AACVD on FTO glass at 300 °C with 5 mg Au precursor. The deposition conditions are described in section 4.2.1.

To evaluate the photoelectrochemical property of Au/WO₃ deposited using different precursor concentrations at different deposition temperature, linear sweep voltammetry was used to investigate the photoelectrochemical performance under visible light (figure 4.22). To reduce the impact of the difference between samples, the WO₃ NNs substrates were always cut from the same piece of sample before AAVCD of the metal NPs. The dark current densities of Au/WO₃ in all conditions are nearly zero. The photocurrent densities at 1.23 V (vs. RHE) of Au/WO₃ films deposited at different temperature using different Au precursor amount are shown in table 4.8. For films deposited at 250 °C,
300 °C and 400 °C, lower precursor amounts generally give higher photocurrent at 1.23 V. Comparing the similar precursor amount, lower deposition temperature leads to higher photocurrent density at 1.23 V. Among all samples, most samples with lower Au:W ratio (< 1.0) generate higher photocurrent than samples with higher Au:W ratio which probably means lower Au loading can provide better PEC performance in Au/WO₃ system. From the I-V curves we can see no matter 1.7 mg, 3.4 mg or 5 mg Au precursor has been used, nearly all photocurrent densities of Au/WO₃ are lower than WO₃. Higher Au concentration (5 mg) normally gives worse photocurrent density. As the deposition temperature increases, the onset potential of Au/WO₃ becomes higher from 0.55 V (vs. RHE) for 250 °C to 0.60 V (vs. RHE) for 300 °C to 0.68 V (vs. RHE) for 350 °C and to 1.0 V (vs. RHE) for 400 °C. I-V curve of Au/WO₃ deposited at 400 °C shows no photoelectric hydrolysis stage comparing to the other samples deposited under 400 °C. This is probably due to the high deposition temperature increasing the Au loading and particle size which doesn’t provide obvious SPR but shield the WO₃ surface. Au/WO₃ deposited at 300 °C also gives the smallest gap between photocurrent densities of Au/WO₃ and bare WO₃. Combined with the above analysis, 300 °C is more suitable as deposition temperature although the amount of Au precursor needed further adjustment to see if any enhancement was possible.
Figure 4.22 I-V curve of Au/WO$_3$ deposited via AACVD on FTO glass at a) 250 °C; b) 300 °C; c) 350 °C and d) 400 °C using 1.7 mg, 3.4 mg and 5mg Au precursor comparing to bare WO$_3$. The deposition conditions are described in section 4.2.1.
Table 4.5 Photocurrent density at 1.23 V (vs RHE), onset potential and Au:W ratio of Au/WO$_3$ films deposited via AACVD under different deposition conditions described in section 4.2.1.

<table>
<thead>
<tr>
<th>AACVD condition</th>
<th>Photocurrent density at 1.23 V (vs. RHE)/ (mA/cm$^2$)</th>
<th>Onset potential / V</th>
<th>Au:W</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7 mg, 250 °C</td>
<td>0.55</td>
<td>0.55</td>
<td>0.75</td>
</tr>
<tr>
<td>3.4 mg, 250 °C</td>
<td>0.58</td>
<td>0.55</td>
<td>0.87</td>
</tr>
<tr>
<td>5 mg, 250 °C</td>
<td>0.51</td>
<td>0.55</td>
<td>0.95</td>
</tr>
<tr>
<td>1.7 mg, 300 °C</td>
<td>0.51</td>
<td>0.60</td>
<td>0.81</td>
</tr>
<tr>
<td>3.4 mg, 300 °C</td>
<td>0.51</td>
<td>0.60</td>
<td>1.80</td>
</tr>
<tr>
<td>5 mg, 300 °C</td>
<td>0.42</td>
<td>0.60</td>
<td>1.11</td>
</tr>
<tr>
<td>1.7 mg, 350 °C</td>
<td>0.45</td>
<td>0.68</td>
<td>1.12</td>
</tr>
<tr>
<td>3.4 mg, 350 °C</td>
<td>0.50</td>
<td>0.68</td>
<td>1.72</td>
</tr>
<tr>
<td>5 mg, 350 °C</td>
<td>0.40</td>
<td>0.68</td>
<td>1.60</td>
</tr>
<tr>
<td>1.7 mg, 400 °C</td>
<td>0.34</td>
<td>1.0</td>
<td>4.26</td>
</tr>
<tr>
<td>3.4 mg, 400 °C</td>
<td>0.26</td>
<td>1.0</td>
<td>6.35</td>
</tr>
<tr>
<td>5 mg, 400 °C</td>
<td>0.51</td>
<td>1.0</td>
<td>4.32</td>
</tr>
</tbody>
</table>

Up to this point, 300 °C is selected as deposition temperature, 1.7 mg is selected as Au precursor amount for Au step when depositing Au/WO$_3$ via AACVD. These parameters help prepare more even size and shape of Au NPs with Au:W ratio of 0.81 which means Au NPs didn’t shield most surface area. PEC measurement in section 4.3.4 will further prove this optimisation.

The amount of Au precursor was further scaled down, with 1mg, 0.5 mg, 0.25 mg, 0.1 mg and 0.05 mg Au precursor tried when depositing Au/WO$_3$ via AACVD on FTO glass at 300 °C. The pictures of the as-deposited samples are shown in figure 4.23. As the amount of Au precursor became less, the sample colour changed from light purple (1 mg) to orange brown (0.5 mg), dark yellow (0.25 mg) and light yellow (0.1 mg and 0.05 mg). It could still be distinguished from bare WO$_3$. The deposition temperature of Au is much

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lower than that of WO$_3$, so the only reason for the colour change is likely to be the Au NPs surface reflection rather than any structural change in the WO$_3$ nanorods themselves.

**Figure 4.23** Photograph of Au/WO$_3$ deposited *via* two steps AACVD on FTO glass at 300 °C using 1 mg, 0.5 mg, 0.25 mg, 0.1 mg and 0.05 mg Au precursor and bare WO$_3$ (from left to right). Other deposition conditions are described in section 4.2.1.

UV/Vis spectra of Au/WO$_3$ with lower amount of Au precursor appear closer in form to a WO$_3$ UV/Vis spectrum (figure 4.24). 0.1 – 1 mg precursor can still provide enough Au NPs to show SPR peaks at ~ 520 – 530 nm. The band gap of 0.1 – 1 mg appears slightly narrower than WO$_3$ (band edge to higher wavelength). Au/WO$_3$ with 0.05 mg Au precursor would be considered as no difference to bare WO$_3$ in terms of spectral shape (no SPR visible) although the band edge still appears shifted.

**Figure 4.24** UV/Vis spectra of Au/WO$_3$ deposited *via* AACVD at 300 °C using 1mg, 0.5 mg, 0.25 mg, 0.1 mg and 0.05 mg Au precursor and bare WO$_3$. Other deposition conditions are described in section 4.2.1.
The atomic ratio of W and Au in Au/WO$_3$ samples of different Au amount are calculated from XPS and EDS data (table 4.5). Au:W (EDS) is the ratio of whole selected area while Au:W (XPS) is the ratio of surface layer (5 nm depth) of the selected area. Both Au:W ratio of bulk material and surface layer show the relationship between Au precursor amount and Au%. The surface Au% is much higher than the bulk Au% for all Au precursor amount. There is no obvious ratio difference for 0.1 mg and 0.05 mg showing from the data below.

<table>
<thead>
<tr>
<th>Element ratio</th>
<th>EDS – bulk</th>
<th>XPS – surface</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>W (at%)</td>
<td>Au (at%)</td>
</tr>
<tr>
<td>0.05 mg Au precursor</td>
<td>99.2</td>
<td>0.8</td>
</tr>
<tr>
<td>0.1 mg Au precursor</td>
<td>99.1</td>
<td>0.9</td>
</tr>
<tr>
<td>0.25 mg Au precursor</td>
<td>98.6</td>
<td>1.4</td>
</tr>
<tr>
<td>0.5 mg Au precursor</td>
<td>97.7</td>
<td>2.3</td>
</tr>
<tr>
<td>1 mg Au precursor</td>
<td>94.4</td>
<td>5.6</td>
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</tbody>
</table>

**Table 4.6** Atomic ratio of W and Au of Au/WO$_3$ deposited via AACVD at 300 °C and different Au precursor amount calculated from XPS data and EDS data. The deposition conditions are described in section 4.2.1.

SEM and TEM images (figure 4.25) of Au/WO$_3$ deposited at 300 °C using 1 mg, 0.5 mg, 0.25 mg, 0.1 mg and 0.05 mg Au precursor (from top to bottom) show the same tendency observed from Au:W ratio. From the images we can see even lowest Au precursor amount (0.05 mg) produced many Au NPs on WO$_3$. The size of Au NPs drops down from ~ 15 nm (1 mg) to ~ 5 nm (0.1 mg) and remains no change. The density of Au NPs also decreases as Au precursor concentration drops.

Based on the above analysis of Au/WO$_3$ nanostructure system, we will pick 0.5 mg and 0.1 mg from this section which deposits 10 nm and smaller Au NPs as Au precursor amount for further investigation and as a reference for Pt and Ag nanoparticles deposition.
Figure 4.25 SEM and TEM images of Au/WO₃ deposited via AACVD at 300 °C using 1 mg, 0.5 mg, 0.25 mg, 0.1 mg and 0.05 mg Au precursor (from top to bottom). Other deposition conditions are described in section 4.2.1.
On decreasing the amount of Au precursor, all Au/WO₃ films deposited at 300 °C show better PEC performance (figure 4.26) than samples with higher Au loading (figure 4.22 (b)). The photocurrent densities of all Au/WO₃ with ≤ 1 mg Au precursor at 1.23 V (vs. RHE) reach ~ 0.8 – 0.9 mA/cm² which are slightly higher than the photocurrent density of bare WO₃. This indicates that lower amount of Au precursor, which deposits smaller and lower coverage Au NPs gives Au/WO₃ with better PEC performance. The mechanism could be because the SPR effects is stronger when the NPs are 10 nm sphere with suitable spacing between each other, or because less shielding of the WO₃ NN surface makes absorption of light relatively more efficient.

**Figure 4.26** I-V curve of Au/WO₃ deposited on FTO glass deposited at 300 °C using less amount of Au precursor comparing to bare WO₃. The deposition conditions are described in section 4.2.1.

### 4.3.2 Ag nanoparticles and Ag/WO₃

#### 4.3.2.1 Ag nanoparticles on glass and FTO glass

Ag-AMP (figure 4.27) is composed of two alkanolamine groups which coordinate to an Ag⁺ cation in the centre. The long carbon backbone may increase the stability of the
precursor and prevent the decomposition of thermally sensitive precursor before entering the reaction chamber, facilitating the transportation of aerosol into the reaction chamber via AACVD. The deposition parameters were adapted from previous work in the group.

Ag was first deposited on microscope glass slide in figure 4.28. Since Ag is easier to be oxidized than Au, the deposition temperature is set to be lower. Ag NPs were deposited via AACVD at 275 °C, 300 sccm gas flow rate on glass and other substrates using Ag-AMP as Ag precursor and methanol as the precursor solvent. The as-deposited film on glass appears light yellow brown.

Figure 4.27 Chemical formula of silver 2-amino-2-methyl-1-propanol (Ag-AMP).

Figure 4.28 Ag film deposited at 275 °C on glass via AACVD. Left (inlet) to right (outlet). The deposition conditions are described in section 4.2.2.

No obvious peaks are found in XRD patterns at 275 °C (figure 4.29). It could be because of the small particle size, low concentration or non-crystallinity. From the film colour, we can say the reason could be the combination of particle size and concentration.
Figure 4.29 XRD patterns of as-deposited Ag film via AACVD on glass using at 275 °C using 100 μL Ag-AMP, as compared to JCPDS cards, PDF#41-1402. The deposition conditions are described in section 4.2.2.

Ag film on glass is analysed by XPS, Ag 3d and O 1s spectra are shown in figure 4.30. The two Ag peaks at binding energy of 374.0 eV and 368.1 eV are corresponding to Ag 3d$_{3/2}$ and 3d$_{5/2}$ respectively, which match to the value of Ag metal in NIST XPS database [209]. The only state of Ag in the measurement is Ag$^0$, which indicates the presence of only silver metal. Therefore, Ag was not oxidized at 275 °C.

Figure 4.30 Fitted Ag 3d and high resolution XPS spectra of Ag NPs deposited via AACVD on glass at 275 °C using 100 μL Ag-AMP. The deposition conditions are described in section 4.2.2.
The surface morphology of an Ag-film deposited at 275 °C shows that the film is formed of nanoparticles (figure 4.31). A large number of nanoparticles are uniformly distributed on the substrate. The size seems to be around 10 nm. Due to the charging of the surface, the sample is poorly focused.

![SEM image of Ag NPs](image)

**Figure 4.31** SEM images of Ag NPs deposited via AACVD on glass at 275 °C using 100 μL Ag-AMP. The deposition conditions are described in section 4.2.2.

Ag NPs were further analysed by TEM (figure 4.32). The size of these Ag NPs ranges from 4 nm to 10 nm. D-spacings of 0.25 nm, 0.20 nm and 0.15 nm can be observed from the high-resolution TEM image. These values are representing (1 0 0), (1 0 3) and (1 1 0) crystal planes. XPS, UV/Vis and TEM analysis together suggest that the Ag NPs deposited via AACVD are crystallized nanoparticles.
Figure 4.32 HRTEM images of Ag NPs deposited via AACDV on glass at 275 °C using 100 μL Ag-AMP under different magnification. The deposition conditions are described in section 4.2.2.

Figure 4.33 shows the UV/Vis absorption spectra of Ag NPs films prepared by AACVD on glass (microscope slide). As shown in the figure, Ag spectrum has a weak absorption peak at 420 nm. This could be attributed to the surface plasmon resonance (SPR) of Ag NPs. Comparing to the peak of Au NPs at 580 nm, the peak of Ag NPs is nearer to the band gap of WO₃ and probably will have different PEC properties from Au/WO₃.

Figure 4.33 UV/Vis spectra of Ag NPs deposited via AACVD on microscope slide. The deposition conditions are described in section 4.2.2.
4.3.2.2 Ag nanoparticles on WO₃ NNs film

Ag NPs were then deposited on WO₃ NNs still at 275 °C. Figure 4.34 shows (a) bare WO₃, (b) Ag/WO₃ using 20 μL Ag-AMP and (c) Ag/WO₃ using 100 μL Ag-AMP. Comparing to light yellow WO₃ NNs, Au/WO₃ appears more brownish yellow. The colour of Ag/WO₃ deepened with the rise of Ag-AMP concentration.

![Figure 4.34](image)

Figure 4.34 Photograph of Ag/WO₃ deposited via two steps AACVD on FTO glass, a) WO₃; b) Ag/WO₃ using 20 μL Ag-AMP and c) Ag/WO₃ using 100 μL Ag-AMP. The other deposition conditions are described in section 4.2.2.

XRD pattern of Ag/WO₃ (figure 4.35) shows sharp and strong crystallized WO₃ peaks with no evidence of Ag peaks comparing to standard JCPDS card WO₃ PDF#43-1035 and Ag PDF#41-1402. This is likely due to the low concentration of Ag-AMP which caused low Ag NPs coverage. The identical WO₃ peaks at 23.05 ° and 33.20 ° which are indexed to (0 0 2) and (0 2 2) show no obvious peak shift comparing with bare WO₃.
Figure 4.35 XRD patterns of Ag/WO$_3$ NNs deposited via AACVD on FTO glass using 100 μL Ag precursor in 10 cm$^3$ methanol at 275 °C with a constant flow of N$_2$ at 300 sccm comparing to standard JCPDS of WO$_3$ PDF#43-1035 and Ag PDF#41-1402. The deposition conditions are described in section 4.2.2.

Figure 4.36 shows the UV/Vis absorption spectra of Ag/WO$_3$ prepared by AACVD on FTO glass using different amount of Ag-AMP. Using WO$_3$ UV/Vis as a reference, Ag/WO$_3$ deposited using 100 μL Ag precursor and 20 μL Ag show no obvious peak. It is hard to say the 480 nm peak is a plasmon peak. The SPR peak of Ag NPs is probably merged with the curve of WO$_3$ band gap.
Figure 4.36 UV/Vis spectra of WO$_3$ and Ag/WO$_3$ deposited *via* AACVD on FTO glass using different amount of Ag precursor. The deposition conditions are described in section 4.2.2.

Figure 4.37 displays the XPS spectra of Ag/WO$_3$ film deposited *via* AACVD on FTO glass. By using 20 μL Ag-AMP, the two Ag$^0$ peaks at binding energy of 374.3 eV and 368.4 eV are corresponding to Ag 3d$_{3/2}$ and 3d$_{5/2}$ respectively. By using 100 μL Ag-AMP, binding energy of Ag 3d$_{3/2}$ and 3d$_{5/2}$ move to 374.1 eV and 368.1 eV respectively. The only state of Ag in the measurement is Ag$^0$, which indicates the presence of only silver metal. Therefore, Ag was not oxidized at 275 °C. The intensity of the Ag peaks increases as the amount of precursor increased. The peak position of W 4f$_{5/2}$ and W 4f$_{7/2}$ also remain unchanged at ~ 37.7 eV and 35.5 eV. All W elements are W$^{6+}$. 

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**Figure 4.36** UV/Vis spectra of WO$_3$ and Ag/WO$_3$ deposited *via* AACVD on FTO glass using different amount of Ag precursor. The deposition conditions are described in section 4.2.2.

**Figure 4.37** XPS spectra of Ag/WO$_3$ film deposited *via* AACVD on FTO glass. By using 20 μL Ag-AMP, the two Ag$^0$ peaks at binding energy of 374.3 eV and 368.4 eV are corresponding to Ag 3d$_{3/2}$ and 3d$_{5/2}$ respectively. By using 100 μL Ag-AMP, binding energy of Ag 3d$_{3/2}$ and 3d$_{5/2}$ move to 374.1 eV and 368.1 eV respectively. The only state of Ag in the measurement is Ag$^0$, which indicates the presence of only silver metal. Therefore, Ag was not oxidized at 275 °C. The intensity of the Ag peaks increases as the amount of precursor increased. The peak position of W 4f$_{5/2}$ and W 4f$_{7/2}$ also remain unchanged at ~ 37.7 eV and 35.5 eV. All W elements are W$^{6+}$. 

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Figure 4.37 high resolution XPS spectra of a) Ag 3d and b) W 4f of Ag/WO₃ deposited via AACVD on FTO glass using 100 μL and 20 μL Ag-AMP. The deposition conditions are described in section 4.2.2.

The atomic ratio of W and Ag in Ag/WO₃ samples of two different Ag amount are calculated from XPS and EDS data (table 4.7). Ag:W (EDS) is the ratio of whole selected area while Ag:W (XPS) is the ratio of surface layer (5 nm depth) of the selected area. Both W:Ag ratio of bulk Ag/WO₃ and surface show the relationship between the amount of Ag-AMP and Ag (at%). The surface Ag% is higher than the bulk Ag% for both 20 μL Ag-AMP and 100 μL Ag-AMP. An increase in Ag (at%) is demonstrated as the amount of Ag-AMP increase.

<table>
<thead>
<tr>
<th></th>
<th>EDS</th>
<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W (at%)</td>
<td>Ag (at%)</td>
</tr>
<tr>
<td>20 μL Ag precursor</td>
<td>99.7</td>
<td>0.3</td>
</tr>
<tr>
<td>100 μL Ag precursor</td>
<td>97.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Table 4.7 Atomic ratio of W and Ag of Ag/WO₃ deposited via AACVD at 275 °C using 100 μL and 20 μL Ag-AMP calculated from XPS data and EDS data. Other deposition conditions are described in section 4.2.2.

The surface morphology of Ag/WO₃ deposited using (a) 100 μL Ag-AMP and (b) 20 μL Ag-AMP are observed by SEM in figure 4.38. The Ag NPs are so small that it is hard to
distinguish the size difference between using 100 μL and 20 μL Ag-AMP. From the TEM images of these two samples in figure 4.39, we can see the size and density change of the Ag NPs. All NPs are sphere and of uniform size. Ag NPs of ~ 10 nm diameter were deposited by 100 μL Ag-AMP. Ag NPs of ~ 6 nm diameter were deposited by 20 μL Ag-AMP. There are less Ag NPs adhering on WO₃ NNs when the precursor concentration is lower.

**Figure 4.38** SEM images of Ag/WO₃ deposited via AACVD on FTO glass at 275 °C with a)100 μL Ag precursor and b) 20 μL Ag precursor. Other deposition conditions are described in section 4.2.2.

**Figure 4.39** HRTEM images of Ag/WO₃ deposited via AACVD on FTO glass at 275 °C with a)100 μL Ag precursor and b) 20 μL Ag precursor. Other deposition conditions are described in section 4.2.2.
HRTEM images of Ag/WO₃ deposited on FTO glass at 275 °C with 100 μL Ag precursor are shown in figure 4.40. The lattice fringes are easily observed in the figure which means WO₃ NNs and Ag NPs are all crystallized. D-spacing of 0.38 nm is attributed to (0 0 2) crystal plane of WO₃. Ag d-spacings of 0.25 nm and 0.20 nm can be observed and confirmed as (1 0 0) and (1 0 3) crystal planes, they are confirmed as Ag metal. Ag NPs are in nice spherical morphologies with a diameter of 10 nm.

![HRTEM images of Ag/WO₃ deposited via AACVD on FTO glass at 275 °C with 100 μL Ag precursor.](image)

**Figure 4.40** HRTEM images of Ag/WO₃ deposited via AACVD on FTO glass at 275 °C with 100 μL Ag precursor. Other deposition conditions are described in section 4.2.2.

4.3.3 Pt nanoparticles and Pt/WO₃

4.3.3.1 Pt nanoparticles on glass

Inorganic chemical H₂Cl₆Pt·xH₂O was used as Pt precursor for depositing Pt film on microscope glass slide. Pt NPs were deposited via AACVD at 350 °C, 300 sccm gas flow rate on glass and other substrates using H₂Cl₆Pt·xH₂O as Pt precursor and methanol as the precursor solvent. The as-deposited film on glass appears dark brown (figure 4.41).

![Pt NPs deposited at 350 °C on glass via AACVD.](image)

**Figure 4.41** Pt NPs deposited at 350 °C on glass via AACVD. Left (inlet) to right (outlet). The deposition conditions are described in section 4.2.3.
XRD pattern of as-synthesized Pt via AACVD is shown in figure 4.2. Comparing to JCPDS card PDF##04-0802, the weak peaks at 39.70 ° and 46.30 ° are corresponding to (1 1 1) and (2 0 0) crystal planes of Pt in the JCPDS card. This is a cubic phase Pt crystal structure (a = b = c = 3.92 Å). There is no sharp peak due to the low crystallinity or the low concentration of Pt.

Pt film on glass is analysed by XPS, Pt 4f and O 1s spectra are shown in figure 4.3. The core peaks of Pt⁰ at binding energy of 74.5 eV and 71.4 eV are corresponding to Pt 4f₅/₂ and Pt 4f₇/₂ respectively. Pt metal is expected to have asymmetric peak shape and the peak values match to the values in NIST XPS database [210]. The chemical state of Pt⁰ indicates that the Pt here is pure Pt metal.

**Figure 4.42** XRD patterns of as-deposited Pt film via AACVD on glass using at 350 °C using 1.5 mg H₂Cl₆Pt·xH₂O, as compared to JCPDS cards, PDF#04-0802. The deposition conditions are described in section 4.2.3.
Figure 4.43 Fitted Pt 4f and high resolution XPS spectra of Pt NPs deposited via AACVD on glass at 350 °C using 1.5 mg Pt precursor. The deposition conditions are described in section 4.2.3.

TEM images of Pt NPs deposited on glass at 350 °C using 1.5 mg Pt precursor in figure 4.44 (a) show clusters of Pt NPs in low magnification. The morphology of Pt NPs is more irregular than Ag NPs and Au NPs though the size of Pt is smaller. The diameter of Pt NPs is ~ 3 – 5 nm. From the high-resolution TEM image, lattice fringe d-spacings of 0.24 nm and 0.20 nm can be observed from many Pt NPs. These d-spacing represent (1 1 1) and (2 0 0) crystal planes. Therefore, Pt NPs deposited via AACVD are crystalline, and hence the low XRD peak intensity is likely due to the small size of nanoparticles or low loading.
Figure 4.44 TEM and HRTEM images of Pt NPs deposited via AACVD on glass at 350 °C using 1.5 mg Pt precursor under different magnification. The deposition conditions are described in section 4.2.3.

According to literature [211], the SPR peak of Pt is ~ 215 nm which is not possible to be detected on a glass substrate due to strong substrate absorption in this region. UV/Vis of Pt NPs has been reported at below 300 nm by several literatures [212–214]. Therefore in figure 4.45, the peak at 300 nm may not relate to an SPR peak of Pt but could also be due to residual PtCl₆²⁻ although XPS does not indicate presence of any such species [215].

Figure 4.45 UV/Vis spectra of Pt NPs deposited via AACVD on microscope slide. The deposition conditions are described in section 4.2.3.
4.3.3.2 Pt nanoparticles on WO$_3$ NNs film

Pt NPs were then deposited on WO$_3$ NNs still at 350 °C. Figure 4.46 shows (a) bare WO$_3$, (b) Pt/WO$_3$ using 0.5 mg Pt precursor and (c) Pt/WO$_3$ using 1.5 mg Pt precursor. Comparing to light yellow WO$_3$ NNs, Pt/WO$_3$ appears brown. The colour of Au/WO$_3$ deepened with the rise of H$_2$PtCl$_6$ concentration.

![Image of Pt/WO$_3$ deposition](image.png)

**Figure 4.46** Photograph of Pt/WO$_3$ deposited via two steps AACVD on FTO glass, a) WO$_3$; b) Pt/WO$_3$ using 0.5 mg Pt precursor and c) Pt/WO$_3$ using 1.5 mg Pt precursor. The deposition conditions are described in section 4.2.3.

XRD pattern of Pt/WO$_3$ (figure 4.47) shows sharp and strong crystallized WO$_3$ peaks with no evidence of Pt peaks comparing to standard JCPDS card WO$_3$ PDF#43-1035 and Pt PDF#04-0802. The crystallized Pt NPs are likely too small, or the amount is not enough to provide XRD signal. The identical WO$_3$ peaks at 23.10 ° and 33.30 ° which are indexed to (0 0 2) and (0 2 2) show no obvious peak shift compared with bare WO$_3$. 
Figure 4.47 XRD patterns of Pt/WO₃ NPs deposited via AACVD on FTO glass using 1.5 mg Pt precursor in 10 cm³ methanol at 350 °C with a constant flow of N₂ at 300 sccm compared to standard JCPDS of WO₃ PDF#43-1035 and Ag PDF#04-0802. The deposition conditions are described in section 4.2.3.

Figure 4.48 shows the UV/Vis absorption spectra of Pt/WO₃ prepared by AACVD on FTO glass using 1.5 mg Pt precursor and 0.5 mg Pt precursor. Pt NPs has no identical peak in UV/Vis. Using WO₃ as a reference, both 0.5 mg Pt/WO₃ and 1.5 mg Pt/WO₃ show higher light absorbance in visible range which also related to figure 4.46 that 1.5 mg Pt/WO₃ showed darker sample colour.
Figure 4.48 UV/Vis spectra of WO₃ and Pt/WO₃ deposited via AACVD on FTO glass using different amount of Pt precursor. The deposition conditions are described in section 4.2.3.

Figure 4.49 displays the XPS spectra of Pt/WO₃ film deposited via AACVD on FTO glass. By using 0.5 mg Pt precursor, the two Pt⁰ peaks at binding energy of 75.0 eV and 71.9 eV are corresponding to Pt 4f₅/₂ and 4f₇/₂ respectively. The intensity of the Pt peaks increases as the amount of precursor increased. All W elements are W⁶⁺.

Figure 4.49 high resolution XPS spectra of a) Pt 4f and b) W 4f of Pt/WO₃ deposited via AACVD on FTO glass using 1.5 mg and 0.5 mg Pt precursor. The deposition conditions are described in section 4.2.3.
The atomic ratio of W and Pt in Pt/WO$_3$ samples of two different Pt amount are calculated from XPS and EDS data (table 4.8). Pt:W (EDS) is the ratio of whole selected area while Pt:W (XPS) is the ratio of surface layer of the selected area. Both W:Pt ratio of bulk Pt/WO$_3$ and surface show the relationship between the amount of Pt precursors and Pt (at%). The surface Pt% is higher than the bulk Pt% for both 0.5 mg Pt precursor and 1.5 mg Pt precursor. An increase in Pt (at%) is demonstrated as the amount of Pt precursor increase. The surface coverage of Pt NPs remains high for both concentrations.

<table>
<thead>
<tr>
<th>Element</th>
<th>EDS</th>
<th>XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>W (at%)</td>
<td>Pt (at%)</td>
</tr>
<tr>
<td>0.5 mg Pt precursor</td>
<td>98.4</td>
<td>1.4</td>
</tr>
<tr>
<td>1.5 mg Pt precursor</td>
<td>98.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 4.8 Atomic ratio of W and Pt of Pt/WO$_3$ deposited via AACVD at 350 °C using 1.5 mg and 0.5 mg Pt precursor calculated from XPS data and EDS data. The deposition conditions are described in section 4.2.3.

The surface morphology of Pt/WO$_3$ deposited using (a) 1.5 mg Pt precursor and (b) 0.5 mg Pt precursor are observed by SEM in figure 4.50. The Pt NPs are extremely small but still can be distinguished on WO$_3$ NNs. However, it is hard to distinguish the size difference between two different Pt amounts. From the TEM images of these two samples in figure 4.51, we can see that the densities of Pt NPs on WO$_3$ NNs are very high. All NPs appear spherical and of uniform size and no obvious difference can be observed between these two samples. In some areas, Pt NPs appear to aggregate together and form multi layers outside the nanoneedle, which may be undesirable for PEC water splitting due to shielding of the surface of the WO$_3$ NNs.
Figure 4.50 SEM images of Pt/WO$_3$ deposited via AACVD on FTO glass at 350 °C with a) 1.5 mg Pt precursor and b) 0.5 mg Pt precursor. The deposition conditions are described in section 4.2.3.

Figure 4.51 HRTEM images of Pt/WO$_3$ deposited via AACVD on FTO glass at 350 °C with a) 1.5 mg Pt precursor and b) 0.5 mg Pt precursor. The deposition conditions are described in section 4.2.3.

HRTEM images of Pt/WO$_3$ deposited on FTO glass at 350 °C with 0.5 mg Pt precursor are shown in figure 4.52. Pt NPs are in spherical morphologies with a diameter of ~ 2 – 4 nm. The lattice fringes are easily observed in the figure which means WO$_3$ NNs and Pt NPs are all crystallized. D-spacing of 0.38 nm is attributed to (0 0 2) crystal plane of WO$_3$. 
D-spacings of 0.23 nm and 0.20 nm can be observed and confirmed as (1 1 1) and (2 0 0) crystal planes of Pt.

![HRTEM images of Pt/WO_3 deposited via AACVD on FTO glass at 350 °C with 0.5 mg Pt precursor.](image)

**Figure 4.52** HRTEM images of Pt/WO_3 deposited *via* AACVD on FTO glass at 350 °C with 0.5 mg Pt precursor. The deposition conditions are described in section 4.2.3.

### 4.3.4 Comparison of AACVD synthesised modified materials and their applications

In the past decade, many AACVD works relating to metal oxide and metal nanoparticles have been done by researches. Table 4.10 displays some of the AACVD synthesised materials, their deposition precursors and solvents and their applications. For example, R. Palgrave *et al.*[^197^] studied undoped WO_3 and Ti doped WO_3 film by using [Ti(OiPr)_4] and [W(OPh)_6] precursors dissolving in acetone. The films showed photochromism of reversible colour change from yellow to blue, after UV irradiation at 254 nm with 30% increase in optical density for Ti:WO_3 (W:Ti = 92:8) comparing to undoped WO_3. WO_3 with higher Ti dopant showed no photochromism due to the incorporation of Ti into the WO_3 lattice. Vallejos *et al.*[^133^] synthesized Au nanoparticles functionalized WO_3 nanoneedles on gas sensor substrates *via* AACVD in a single step using HAuCl_4·3H_2O and [W(OPh)_6] as precursors. The gas sensor had higher sensitivity to ethanol at a six-fold increase in response to low concentrations compared with pure WO_3 gas sensors.
C. Crick et al. [216] reported a AACVD process of TiO₂ NPs decorated polymer matrix using polydimethylsiloxane polymer precursor with oleic acid functionalised TiO₂ NPs in chloroform. The resazurin dye was completely discolored by NP embedded superhydrophobic film after 90 min UV irradiation. Higher NP loadings gave greater photocatalytic activity with dye degradation. C. Chew [217] described a one pot AACVD process of Au NPs decorated SnO₂ using [CH₃CH₂CH₂SnCl₃] and HAuCl₄·xH₂O with the assistance of auric acid in methanol as transparent conducting oxide (TCO). In these two cases, capping agents were used to prevent the nanoparticles from aggregation.

From examples above and in the table, we can see that most decorated or doped metal oxide deposited via AACVD are used for gas sensing, TCO and photocatalysis related applications. There were several literatures exploring AACVD deposited materials for water splitting but using slightly different methods (e.g. spray CVD). Till now, there is little research on using metal NPs decorated metal oxide deposited via AACVD for water splitting, especially metal/WO₃.

Among the AACVD literatures listed below, both one step and two steps deposition have been used by researchers. Some of the research used capping agents to prevent the nanoparticles from aggregation. However, organic shells were more likely to remain on the nanoparticles which were confirmed by SEM. Most literature showed the decoration and dopant preparation using only one condition which makes it harder to know if it is the amount, size or coverage of the materials is optimized. In our research, two steps AACVD reaction was performed to deposit WO₃ decorated evenly with Au, Ag and Pt NPs without the use of capping agent.
<table>
<thead>
<tr>
<th>Materials</th>
<th>Precursors, agent and solvent</th>
<th>Step</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti doped WO$_3$ film</td>
<td>[Ti(OiPr)$_4$] and [W(OPh)$_6$] in acetone</td>
<td>One step</td>
<td>Photochromism</td>
<td>197</td>
</tr>
<tr>
<td>PdO NPs/WO$_3$ NNs</td>
<td>W(CO)$_6$ in acetone and methanol [Pd(acac)$_2$] in methanol</td>
<td>Two steps</td>
<td>Gas sensing</td>
<td>218</td>
</tr>
<tr>
<td>Au NPs/CeO$_2$ film</td>
<td>[Ce(dbm)$_3$] and NH$_4$AuCl$_4$ in acetone</td>
<td>One step</td>
<td>--</td>
<td>219</td>
</tr>
<tr>
<td>Au, Cu and Pt NPs/WO$_3$ NNs</td>
<td>[W(OPh)$_6$] in acetone with H$_2$PtCl$_6$·xH$_2$O in methanol</td>
<td>One step</td>
<td>Gas sensing</td>
<td>220</td>
</tr>
<tr>
<td>Ag/Ag$_2$O NPs/WO$_3$ NNs</td>
<td>W(CO)$_6$ in acetone and methanol and AgNO$_3$ in acetone and methanol</td>
<td>Two steps</td>
<td>Gas sensing</td>
<td>221</td>
</tr>
<tr>
<td>AuNP/SnO$_2$ nanocomposite</td>
<td>[CH$_3$CH$_2$CH$_2$SnCl$_3$] and H$_2$PtCl$_6$·xH$_2$O with auric acid in methanol</td>
<td>One step</td>
<td>TCO</td>
<td>222</td>
</tr>
<tr>
<td>Al, Ga and In doped ZnO film</td>
<td>[Zn(acac)$_2$] with AlCl$_3$/GaCl$_3$/InCl$_3$ in methanol</td>
<td>One step</td>
<td>TCO</td>
<td>223</td>
</tr>
<tr>
<td>N-modified TiO$_2$ film</td>
<td>[Ti(OiPr)$_4$] in ethanol</td>
<td>One step</td>
<td>Photocatalysis</td>
<td>224</td>
</tr>
<tr>
<td>TiO$_2$-polymer matrix film</td>
<td>polydimethylsiloxane polymer with oleic acid functionalised TiO$_2$ NPs in chloroform</td>
<td>One step</td>
<td>Superhydrophobicity and photocatalysis</td>
<td>216</td>
</tr>
<tr>
<td>WO$_3$ NNs</td>
<td>W(CO)$_6$ in acetone and methanol</td>
<td>One step</td>
<td>Water splitting (predicted)</td>
<td>202</td>
</tr>
<tr>
<td>Au, Ag and Pt NPs/WO$_3$ NNs (this work)</td>
<td>W(CO)$_6$ in acetone and methanol with H$_2$PtCl$_6$·xH$_2$O, Ag-AMP and H$_2$PtCl$_6$·xH$_2$O in methanol</td>
<td>Two steps</td>
<td>Water splitting</td>
<td>--</td>
</tr>
</tbody>
</table>

**Table 4.10** Comparison of AACVD synthesised modified materials in the literature and their application.
4.3.5 PEC test for Au, Ag and Pt

To discuss the water splitting of using Au/WO$_3$, Ag/WO$_3$ and Pt/WO$_3$, the I-V curves obtained by linear sweep voltammetry are shown in figure 4.53, 54 and 55. Photocurrent density of them at 1.23 V (vs. RHE) and correlated metal/W at% ratio is listed in table 4.9. The photocurrent densities of Ag/WO$_3$ are slightly higher than the photocurrent densities of Au/WO$_3$ and higher than the photocurrent densities of Pt/WO$_3$. For Au/WO$_3$ and Ag/WO$_3$, it seems that “higher” precursor amount helps to have stronger upward trend and gain better photocurrent. For Pt/WO$_3$, low precursor amount seems better. We cannot say Pt NPs help improve the PEC performance of Pt/WO$_3$. Generally, lower metal/W ratio (<0.5), which is lower metal loading, provides higher photocurrent at 1.23 V. Also, for the Au NPs, it is found that while the amount of Au precursor increases, the photocurrent density of Au/WO$_3$ first increases and then decreases with higher precursor amount.

![Figure 4.53 I-V curve of Au/WO$_3$ deposited via AACVD on FTO glass at 300 °C comparing to bare WO$_3$. The deposition conditions are described in section 4.2.1.](image)

Figure 4.53 I-V curve of Au/WO$_3$ deposited via AACVD on FTO glass at 300 °C comparing to bare WO$_3$. The deposition conditions are described in section 4.2.1.
Figure 4.54 I-V curve of Ag/WO₃ deposited via AACVD on FTO glass at 275 °C comparing to bare WO₃. The deposition conditions are described in section 4.2.2.

Figure 4.55 I-V curve of Pt/WO₃ deposited via AACVD on FTO glass at 350 °C compared to bare WO₃. The deposition conditions are described in section 4.2.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photocurrent density at 1.23 V (vs. RHE)/ (mA/cm²)</th>
<th>metal/W ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃ dark</td>
<td>0.03</td>
<td>--</td>
</tr>
<tr>
<td>WO&lt;sub&gt;3&lt;/sub&gt; light</td>
<td>0.64</td>
<td>--</td>
</tr>
<tr>
<td>------------------</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>0.1 mg Au/WO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.96</td>
<td>0.027</td>
</tr>
<tr>
<td>0.5 mg Au/WO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.87</td>
<td>0.397</td>
</tr>
<tr>
<td>20 μL Ag/WO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.90</td>
<td>0.003</td>
</tr>
<tr>
<td>100 μL Ag/WO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.96</td>
<td>0.024</td>
</tr>
<tr>
<td>0.5 mg Pt/WO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.85</td>
<td>0.081</td>
</tr>
<tr>
<td>1.5 mg Pt/WO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.62</td>
<td>0.101</td>
</tr>
</tbody>
</table>

Table 4.9 Photocurrent density of samples shown in figure 4.52, figure 4.53 and figure 4.54 at 1.23 V (vs. RHE) and the metal/W ratio of the samples.

By plotting the bare WO<sub>3</sub> NNs and WO<sub>3</sub> NNs with Au, Ag and Pt NPs deposition in the same graph (figure 4.56), we can compare them together. Pt/WO<sub>3</sub> has no advantage comparing to Au and Ag. From above discussion we know that though the exact amount of precursor for Au, Ag and Pt are close, the as-deposited metal particles show quite different morphologies and properties. Pt NPs are small and have less gap between each other. What’s more, Pt NPs sometimes form multi-layers outside WO<sub>3</sub> NNs. As a plasmonic material, the plasmonic peak of Pt is at ~ 215 nm which is not like that of Au and Ag in visible region. This may be why Pt enhancement under illumination is uncompetitive compared to Ag or Au. Ag/WO<sub>3</sub> shows better water splitting ability and increasing photocurrent dentistry across the whole voltage range comparing to Au/WO<sub>3</sub> which makes it a promising material structure. Ag is also cheaper than Au.
Figure 4.56 I-V curve of Metal/WO₃ deposited via AACVD on FTO glass comparing to bare WO₃. The deposition conditions are described in section 4.2.

Table 4.11 displays the comparison of photocurrent densities of metal/WO₃ and WO₃. Few publications were found specifically for the water splitting of metal NPs supported on WO₃. No literature was found using AACVD or CVD as the method to synthesize metal NPs. Of our samples Au/WO₃ and Ag/WO₃ performed an average photocurrent density with an enhancement of 1.50 times of WO₃. However in the literatures, the films with enhancement rate higher than this work have relatively low photocurrent densities of both WO₃ and Metal/WO₃. The films reported with high photocurrent density has an enhancement rate lower than this work. Therefore, our Au/WO₃ and Ag/WO₃ are comparable to those prepared by other methods. The PEC enhancement rate of Pt/WO₃ is lower than the one reported by the literature. Due to the lack of literature, only one reported Pt/WO₃ was found with a photocurrent density lower than this work.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Synthesis method</th>
<th>Photocurrent density of WO$_3$ at 1.23 V vs RHE</th>
<th>Photocurrent density of modified WO$_3$ at 1.23 V vs RHE</th>
<th>Enhancement /times</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/WO$_3$</td>
<td>Electro-deposition</td>
<td>1.15 mA/cm$^2$</td>
<td>1.6 mA/cm$^2$</td>
<td>1.39</td>
<td>95</td>
</tr>
<tr>
<td>Au/WO$_3$</td>
<td>Electro-deposition</td>
<td>0.3 mA/cm$^2$ at 1.0 V vs SCE</td>
<td>0.53 mA/cm$^2$ at 1.0 V vs SCE</td>
<td>1.77</td>
<td>226</td>
</tr>
<tr>
<td>Au/WO$_3$</td>
<td>Photo-reduction</td>
<td>0.75 mA/cm$^2$ at 1.0 V vs Ag/AgCl</td>
<td>1.15 mA/cm$^2$ at 1.0 V vs Ag/AgCl</td>
<td>1.53</td>
<td>227</td>
</tr>
<tr>
<td>Au/WO$_3$</td>
<td>AACVD (this work)</td>
<td>0.64 mA/cm$^2$</td>
<td>0.96 mA/cm$^2$</td>
<td>1.50</td>
<td>--</td>
</tr>
<tr>
<td>Au/WO$_3$</td>
<td>Sol-gel</td>
<td>1.25 mA/cm$^2$ at 0.2 V vs MSE</td>
<td>1.80 mA/cm$^2$ at 0.2 V vs MSE</td>
<td>1.44</td>
<td>199</td>
</tr>
<tr>
<td>Ag/WO$_3$</td>
<td>Sol-gel</td>
<td>0.06 mA/cm$^2$ at 1.0 V vs Ag/AgCl</td>
<td>0.22 mA/cm$^2$ at 1.0 V vs Ag/AgCl</td>
<td>3.67</td>
<td>96</td>
</tr>
<tr>
<td>Ag/WO$_3$</td>
<td>UV irradiation</td>
<td>0.08 mA/cm$^2$</td>
<td>0.17 mA/cm$^2$</td>
<td>2.13</td>
<td>228</td>
</tr>
<tr>
<td>Ag/WO$_3$</td>
<td>AACVD (this work)</td>
<td>0.64 mA/cm$^2$</td>
<td>0.96 mA/cm$^2$</td>
<td>1.50</td>
<td>--</td>
</tr>
<tr>
<td>Pt/WO$_3$</td>
<td>UV irradiation</td>
<td>0.08 mA/cm$^2$</td>
<td>0.21 mA/cm$^2$</td>
<td>2.63</td>
<td>228</td>
</tr>
<tr>
<td>Pt/WO$_3$</td>
<td>AACVD (this work)</td>
<td>0.64 mA/cm$^2$</td>
<td>0.85 mA/cm$^2$</td>
<td>1.33</td>
<td>--</td>
</tr>
</tbody>
</table>

**Table 4.11** PEC performance of Metal/WO$_3$ compared to WO$_3$ in the literature.
4.4 Conclusions

Au NPs were deposited using HAuCl₄·3H₂O + methanol at different concentration (5 mg, 3.4 mg and 1.7 mg) at different deposition temperature (250 °C, 300 °C, 350 °C and 400 °C) with 300 sccm N₂ flow rate, first on FTO glass and then on WO₃ NNs film via AACVD. The as-deposited film on FTO appears bluish violet with gold reflection, the film colour changes with the change of Au precursor amount and deposition temperature. XRD patterns show that it is cubic Au. UV/Vis of Au NPs and Au/WO₃ show an SPR peak which shifts with deposition temperature. The morphology and structure of Au/WO₃ were observed from SEM and TEM images showing the size, shape and density different of each deposition condition. After that 300 °C was selected as deposition temperature and the amount of Au precursor was further reduced to 0.05 – 1 mg. The ratio of Au:W (at%) for the surface and as a bulk ratio shows that the metal NPs segregate at the surface. SEM and TEM images show that when the amount of Au precursor used become less, the size and density of Au NPs become smaller and lower, and the shape of Au NPs become more spherical. The size of Au NPs on Au/WO₃ (1.7 mg, 300 °C) is ~ 8 – 10 nm. The deposition of Au NPs was used as a reference for Ag and Pt AACVD.

Ag NPs deposited using 20 μL and 100 μL Ag-AMP + methanol at 275 °C with 300 sccm N₂ flow rate, first on glass and then on WO₃ NNs film via AACVD. The as-deposited film on glass appears light yellow/brown. The XPS spectra and HRTEM images confirmed the presence of cubic structure Ag⁰. The calculation from XPS and EDS data provide the Ag:W (at%) of the surface and the whole material, again showing surface segregation of the NPs. UV/Vis of Ag NPs shows lower SPR peak at 400 nm which is not seen in the UV/Vis of Ag/WO₃. The morphology and structure of Ag/WO₃ were observed showing the crystallized 10 nm spherical Ag NPs and the coverage on WO₃ NNs.

Pt NPs deposited using 0.5 mg and 1.5 mg H₂Cl₆Pt·xH₂O + methanol at 350 °C with 300 sccm N₂ flow rate, first on glass and then on WO₃ NNs film via AACVD. The as-deposited film on glass appears dark brown. XRD patterns show that it is cubic Pt.
HRTEM images confirmed the size of Pt NPs is ~ 2 – 4 nm. The morphology and structure of Pt/WO₃ were observed from SEM and TEM images showing the crystallized Pt NPs which are highly covering and sometimes aggregating on WO₃ NNs.

Linear sweep voltammetry was used to investigate the photoelectrochemical performance of all samples. Firstly, bare Au NPs were confirmed not to provide any significant photocurrent. The dark current densities of Au/WO₃, Ag/WO₃ and Pt/WO₃ in all conditions are nearly zero. For the Au NPs, it is found that while the amount of Au precursor increases (0.05 – 1.5 mg), the photocurrent density of Au/WO₃ first increases comparing to WO₃ and then decreases with higher precursor amount (1.7 – 5 mg). The photocurrent densities of Ag/WO₃ and Au/WO₃ under their optimized deposition conditions showed 1.5 times enhancement compared to WO₃ while Pt/WO₃ showed 1.33 times PEC enhancement. Because the as-deposited metal particles show quite different morphologies and properties, Pt/WO₃ is not a good material for water splitting. The mechanism of the enhancement in Au/WO₃ and Ag/WO₃ films for PEC water splitting could be because of the SPR effect, more efficient light absorbing of the less shielded WO₃ or a Schottky barrier formed between the interface of metal NPs and WO₃.
Chapter 5. Deposition of ultrathin film layers via ALD with metal/WO\textsubscript{3} heterojunctions: the construction of complex nanostructures and their photoelectrochemical properties

5.1 Introduction

In previous chapter, we discussed the preparation of WO\textsubscript{3} films, Au, Ag and Pt NPs and metal/WO\textsubscript{3}. As we want to further improve the metal/WO\textsubscript{3} heterojunctions, either improving water splitting ability or protect the materials from corrosion, ALD thin film was introduced into the nanostructures. As mentioned in the literature review, the use of ALD thin film layer includes spacer layer in SPR enhancement and passivation layer in photovoltaics. The spacer layer can enhance the hot spots and change the surface plasmon resonance. These thin films must be pinhole free, coat the whole structure surface and grow at low temperature to avoid the oxidization\textsuperscript{[170]}. As a passivation layer, ALD film can also protect photocatalytic materials. An ALD thin film can increase the chemical stability for the electrode material to prevent electrode corrosion and may also enhance the PEC performance. For example, by depositing 3.5 nm TiO\textsubscript{2} ALD layer on plain WO\textsubscript{3}-Au film, Akbari et al\textsuperscript{[229]} gained photocurrent of 11 mA at 1 V comparing to the value of plain WO\textsubscript{3}-Au film of 5 mA.

This chapter will introduce ALD of TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, two classical ALD material, their characterisation and their properties. The method of constructing these individual components in different order via ALD and AACVD will also be introduced. The structures, morphologies, optical properties and compositions of the complex structures were characterized by XRD, XPS, UV/Vis, SEM, TEM and EDS. Their PEC properties were investigated by linear scan voltammetry and chronoamperometry.

5.2 ALD of TiO\textsubscript{2} thin films on different material
This section discusses atomic layer deposition (ALD) of titanium oxide (TiO$_2$) thin films using titanium isopropoxide and water as precursors. ALD of TiO$_2$ on different substrates have been studied. The reaction parameters, including precursor vapour pressure (bubbler temperature) and deposition temperature, were investigated. Thin film thickness, quality and conformity were analysed by various characterization techniques, XRD, SEM, AFM, XPS, spectral reflectance and ellipsometer.

Titanium(IV) tetraisopropoxide [Ti(O$i$Pr)$_4$, TTIP] is a colourless to pale yellow liquid commonly used as a precursor for preparing TiO$_2$. The structural formulas of (a) TTIP is shown in figure 5.1. It is a volatile and moisture sensitive precursor which is suitable for ALD and has been reported in publications \cite{230,231}. TTIP decomposes at 300 °C to TiO$_2$ (equation 5.1) \cite{232}:

\[
\text{Ti(OC}_3\text{H}_7)_4 \rightarrow \text{TiO}_2 + 4 \text{C}_3\text{H}_6 + 2 \text{H}_2\text{O} \quad (5.1)
\]

![Figure 5.1 The structural formulas of TTIP.](image)

The mechanism of TiO$_2$ ALD synthesis from TTIP \cite{148,149} is generally identified as equation 5.2

(1) \(2\cdot\text{OH (s)} + \text{Ti(O$i$Pr)$_4$ (g)} \rightarrow (-\text{O-})_2\text{Ti(O$i$Pr)$_2$ (s)} + 2 \cdot\text{iPrOH (g)}\)

(2) \((-\text{O-})_2\text{Ti(O$i$Pr)$_2$ (s)} + 2 \text{H}_2\text{O (g)} \rightarrow (-\text{O-})_2\text{Ti(OH)$_2$ (s)} + 2 \cdot\text{iPrOH (g)}\)

(3) \(\text{Ti(-OH)-O-Ti(OH) (s)} \rightarrow \text{Ti(-O-)$_2$Ti (s)} + \text{H}_2\text{O (g)}\)
(4) \[ \text{Ti}(-\text{O})_2\text{Ti} \ (s) + \text{Ti}(\text{OiPr})_4 \ (g) \rightarrow \text{Ti}(\text{OiPr})_2\text{-Ti}(-\text{O})\text{Ti}(\text{OiPr})_3 \ (s) \] (5.2)

TTIP reacts with two OH groups on the substrate surface to produce (-O-)\text{Ti}(\text{OiPr})_2 in the first half reaction, this species reacts with water in the second half reaction. After one cycle, the surface has OH groups again, then the next cycle starts.

To prevent the CVD-like reaction causing by thermal decomposition, precursor temperature and ALD growth temperature should be lower than decomposition temperature of the precursor ( < 300 °C). In this work, standard ALD reaction of TTIP was carried out at 200 °C.

Precursor vapour pressure depends on the precursor temperature in the bubbler. The vapour pressure of TTIP can be manipulated by varying the temperature. The relationship between vapour pressure and temperature can be described as equation 5.3

\[
\lg \ (P_{\text{Torr}}) = a - \frac{b}{T} \tag{5.3}
\]

where T is the precursor temperature (K), \( P_{\text{Torr}} \) is the vapour pressure (Torr), a and b are specific parameters of the material.

According to the vapour pressure data in the literature \([233–235]\), a function can be simulated as equation 5.4 and plotted in figure 5.2.

\[
\lg \ (P_{\text{Torr}}) = 9.835 - \frac{3191.5}{T} \tag{5.4}
\]

By manipulating the bubbler temperature, and hence the vapour pressure, the volume of vapour transported to the reaction chamber during each dose can be controlled. A bubbler temperature of 25 °C could provide 0.133 Torr vapour pressure which was found sufficient to pulse TTIP vapour through our ALD system. Overdosing leads to excessively long purge times in order to maintain ALD-like growth, whilst underdosing causes low growth rates and non-uniform growth.
5.2.1 Experimental

5.2.1.1 Synthesis of TiO$_2$ films on glass microscope slides

TiO$_2$ films were grown on glass substrates in a homemade ALD reactor using titanium isopropoxide (TTIP) and water as precursors. Prior to deposition, substrates were cut into ~4.0 cm x 2.5 cm pieces, cleaned by iso-propanol and dried by comprised air.

TiO$_2$ films were grown with 100, 300, 600 and 1000 deposition cycles, respectively. Each cycle consisted of a 2 s TTIP pulse, a 1 min argon purge, then followed by a 2 s water pulse and a 3 min argon purge. The gas flow rate was set to 70 sccm. The precursor bubbler temperature of TTIP was 25 °C, the temperature of water was 5 °C. The substrate was heated to 200 °C for films deposition. To prevent condensation in the pipework, the lines were heated to 130 °C. Deposition parameter details are shown in table 5.1.

<table>
<thead>
<tr>
<th>Deposition mode</th>
<th>Substrate</th>
<th>Deposition recipe</th>
<th>Cycle</th>
<th>Substrate temperature/°C</th>
<th>Flow rate/sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD</td>
<td>Glass</td>
<td>TTIP 2 s purge 1 min H$_2$O 2 s purge 3 min</td>
<td>100</td>
<td>200</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1 Parameters of the TiO$_2$ films deposition on glass using TTIP as metal precursor. Repeated works are not included.
5.2.1.2 Synthesis of TiO$_2$ films on Au/Si and Ag/Si

Au deposited on silicon (Au/Si) and Ag deposited on silicon (Ag/Si) were used as substrates. Both Au and Ag were 100 nm thick, they were fabricated by sputtering at Imperial College. Prior to deposition, substrates were cut into ~ 1.0 cm x 2.5 cm pieces, cleaned by iso-propanol and dried by comprised air. The deposition parameters are described above. The films deposited on Au/Si and Ag/Si substrates were deposited at 80 °C, 150 °C and 200 °C for 300 reaction cycles. The gas flow rate was set to 70 sccm for 150 °C and 200 °C, 100 sccm for 80 °C. Deposition parameter details are shown in table 5.2.

<table>
<thead>
<tr>
<th>Deposition mode</th>
<th>Substrate</th>
<th>Deposition recipe</th>
<th>Cycle</th>
<th>Substrate temperature/°C</th>
<th>Flow rate/sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD</td>
<td>Silicon+Au</td>
<td>TTIP 2 s purge 1 min H$_2$O 2 s purge 3 min</td>
<td>300</td>
<td>200</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>150</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Silicon+Ag</td>
<td>TTIP 2.5 s purge 2 min H$_2$O 2 s purge 3 min</td>
<td>300</td>
<td>80</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 5.2 Parameters of the TiO$_2$ films deposition on Au/Si and Ag/Si using TTIP as metal precursor. Repeated works are not included.
5.2.2 Result and discussion

5.2.2.1 The growth of TiO$_2$ films on microscope slides via ALD

The synthetic method used in this report was based on a method previously developed in the group $^{[236]}$. 100, 300, 600 and 1000 cycles of reaction were carried out on glass to investigate the relationship between number of cycles and film thickness and hence, growth rate (equation 5.5).

$$\text{growth rate} = \frac{\text{film thickness}}{\text{reaction cycles}} \quad (5.5)$$

The film thickness and growth rate are listed in table 5.2. The as-synthesised films (figure 5.3) had a brownish colour which becomes darker as the number of cycles increased indicating that the film thickness had changed, this is the quickest and simplest way to determine the formation of a TiO$_2$ film. The thickness had an approximately linear relation with number of cycles after an induction period which is commonly observed in ALD$^{[124]}$ (figure 5.4). This relation can be used as a reference when a desired thickness is needed. The ALD growth rate observed was 0.5 – 0.7 Å/cycle. Using TTIP and water as precursor, others reported a growth rate of 0.3 – 0.6 Å/cycle at 300 °C $^{[150,158]}$. The bond length of Ti-O bond is ~ 1.89 – 2.07 Å which is almost 3 – 4 times of the growth rate $^{[237]}$. The growth rate is lower than that expected for ‘one atomic layer’ per cycle, which is thought to be due to the steric hindrance of TTIP molecules.

<table>
<thead>
<tr>
<th>Reaction cycles</th>
<th>100</th>
<th>300</th>
<th>600</th>
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</thead>
<tbody>
<tr>
<td>Film thickness (nm)</td>
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<td>21</td>
<td>34</td>
<td>47</td>
</tr>
<tr>
<td>Growth rate (Å/cycle)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Table 5.3** TiO$_2$ thin film thickness and growth rate of different reaction cycles. The conditions of them deposited via ALD are described in section 5.2.1.1.
Figure 5.3 TiO$_2$ film on glass slide (from left to right, 100, 300, 600 and 1000 cycles). The conditions of them deposited via ALD are described in section 5.2.1.1.

Figure 5.4 The relationship between TiO$_2$ film thickness and number of reaction cycles with film growth rate. The conditions of them deposited via ALD are described in section 5.2.1.1.

The morphology of a film deposited for 600 reaction cycles is shown in the SEM image (figure 5.5), but the structure details are difficult to observe by SEM. The sample was also analysed by AFM (figure 5.6) with the roughness ($R_a$) of the analysed area being 1.1 nm and the root mean square roughness ($R_q$) being 1.4 nm.
Figure 5.5 SEM image of 600 cycles TiO$_2$ film on microscope glass slide. The conditions of it deposited via ALD are described in section 5.2.1.1.

Figure 5.6 AFM 3D image of a) microscope slide substrate and b) TiO$_2$ film surface after 600 cycles ALD growth on microscope slide. The conditions of it deposited via ALD are described in section 5.2.1.1.

No sharp peak was observed from the XRD pattern (figure 5.7), either because the film was too thin to provide significant diffraction, or the as-synthesised material was amorphous. XPS spectra in figure 5.8 shows two peaks at 464.0 eV and 458.3 eV corresponding to Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$, respectively. These indicate the Ti$^{4+}$ peaks in TiO$_2$. 
Figure 5.7 XRD pattern of TiO$_2$ film after 300 cycles ALD growth. The conditions of it deposited via ALD are described in section 5.2.1.1.

Figure 5.8 XPS spectra of Ti 2p in TiO$_2$ film after 300 cycles ALD growth. The conditions of it deposited via ALD are described in section 5.2.1.1.

5.2.2.2 The growth of TiO$_2$ films on Au/Si substrate and Ag/Si substrate via ALD

Ag-coated silicon substrate (Ag/Si) and Au-coated silicon substrate (Au/Si) were used for TiO$_2$ thin film deposition. An initial target of 20 nm was set as a desired TiO$_2$ film thickness, and hence the number of reaction cycles was set to 300 cycles. The temperature used for TiO$_2$ growth on glass substrates was 200 °C, however, the ideal temperature on
the metal coated substrates was unknown and hence the attempts were varied from 80 °C to 150 °C and to 200 °C.

Part of the measurement of the film thickness is shown for example in figure 5.9. The film thickness of TiO$_2$/Au/Si formed at 150 °C is 16.1 nm (figure 5.9 (a)), which also shows a good fit (goodness of fit = 0.99). The thickness of TiO$_2$/Ag/Si formed at 150 °C is 20.3 nm (figure 5.9 (b)). The goodness of fit is 0.87 which might indicate the deviation of film thickness from the measured value on Ag/Si. The thickness of TiO$_2$/Au/Si formed at 200 °C is 15 nm (goodness of fit = 0.99), but for TiO$_2$/Ag/Si deposited at 200 °C, the thickness rises to 24.5 nm which is even higher than that on glass and the goodness of fit was poor (0.79). After the temperature goes down to 80 °C, thickness of film on both the TiO$_2$/Au/Si and TiO$_2$/Ag/Si is approximately 6 nm (goodness of fit = 0.94). It indicates that the low deposition temperature restricts the growth rate of the film.
Figure 5.9 Spectral reflectance measurement of the film thickness of a) TiO$_2$ deposited on Au/Si and b) TiO$_2$ deposited on Ag/Si at 150 °C. The conditions of them deposited via ALD are described in section 5.2.1.2.

The AFM scan and 3D images (figure 5.10 and figure 5.11) show the surface morphologies of TiO$_2$/Ag/Si and TiO$_2$/Au/Si films synthesised at different temperatures. For the silicon wafer coated with Au layer, there is little structure difference before and after the ALD process on Au/Si. The roughness of Au/Si is 0.3 nm with a root mean square roughness of 0.4 nm. After deposition at 80°C, the roughness increases slightly to 0.5 nm with an RMS roughness, 0.6 nm. There is no obvious difference in surface roughness between deposition temperatures of 80 °C, 150 °C and 200 °C.
Figure 5.10 AFM scan and 3D images of a, b) Au/Si substrate; c, d) TiO$_2$ film deposited on Au/Si at 80 °C; e, f) TiO$_2$ film deposited on Au/Si at 150 °C; g, h) TiO$_2$ film deposited on Au/Si at 200 °C. The conditions of them deposited via ALD are described in section 5.2.1.2.
The deposition of TiO$_2$ on Ag/Si however does show a change of morphology with temperature. After deposition at 80°C, the morphology is similar to the Ag/Si substrate. The roughness of Ag/Si substrate and the TiO$_2$/Ag/Si at 80 °C is 0.9 nm, RMS roughness is 1.2 nm. When the temperature increases to 150 °C, large grains appear while the roughness is 0.8 nm and the RMS roughness is 1.1 nm. The roughness of TiO$_2$/Ag/Si at 200 °C increases dramatically to 23 nm and the RMS roughness increases to 28 nm. This suggests that as the deposition temperature increases, the morphology of the substrate itself might have changed, the film appears hazy and white which suggests that the composition would have changed as well. Hence on Ag/Si substrate, a lower deposition temperature of 80 °C is required in order to grow higher uniform films.
Figure 5.11 AFM scan and 3D images of a, b) Ag/Si substrate; c, d) TiO$_2$ film deposited on Ag/Si at 80 °C; e, f) TiO$_2$ film deposited on Ag/Si at 150 °C; g, h) TiO$_2$ film deposited on Ag/Si at 200 °C. The conditions of them deposited via ALD are described in section 5.2.1.2.

XPS was used to analyse the composition of TiO$_2$/Au/Si and TiO$_2$/Ag/Si structures. The intensity of Au and Ag elements can also show if the TiO$_2$ films have coherent coverage on the substrate. Figure 5.12 shows the XPS spectra of Au 4f and Ti 2p in the TiO$_2$/Au/Si
samples. The peaks of Au 4f\textsubscript{5/2} and Au 4f\textsubscript{7/2} at 87.6 eV and 83.9 eV are consistent with Au metal. Ti 2p \textsubscript{3/2} and Ti 2p \textsubscript{1/2} peaks are located at 464.6 eV and 458.9 eV, respectively, but shift slightly to lower energy with increasing temperature. The two Ti peaks correspond to Ti\textsuperscript{4+}, which indicate the thin film is TiO\textsubscript{2}. The additional peak at 472 eV in the Ti 2p XPS spectra is known shake-up satellite peak from Ti 2p \textsuperscript{[238,239]}. From the spectra of film synthesized at 80 °C, Au 4f peaks show high intensity while the Ti 2p peaks show low intensity, which suggests that the TiO\textsubscript{2} film on Au layer is thin (<5 nm) or the film wasn’t deposited coherently on the surface. Conversely, the spectra of deposition at 150 °C shows weak Au 4f peaks and significant Ti 2p peaks which means there is a continuous TiO\textsubscript{2} film with no pinholes on the surface because the underlying Au layer is not exposed.

**Figure 5.12** XPS spectra of a) Au, b) Ti from TiO\textsubscript{2} film on Au/Si substrate generated at 80 °C, 150 °C and 200 °C. The conditions of them deposited via ALD are described in section 5.2.1.2.
Figure 5.13 XPS spectra of a) Ag, b) Ti from TiO$_2$ film on Ag/Si substrate generated at 80 °C, 150 °C and 200 °C. The conditions of them deposited via ALD are described in section 5.2.1.2.

In figure 5.13, the peaks of Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$ located 373.9 eV and 368.9 eV are attributed to Ag metal. 150 °C deposition shows weak Ag peaks indicating that underlying Ag layer is nearly not exposed, i.e. the film is thicker than 5 nm and pinhole free. The peak of Ti 2p$_{3/2}$ shows an energy shift from 464.8 eV to 464.4 eV and the Ti 2p$_{3/2}$ peak moves from 459.0 eV to 458.6 eV when the temperature increases. These peaks correspond to Ti$^{4+}$ in TiO$_2$. The energy shift of Ti$^{4+}$ peak in the TiO$_2$/Au/Si samples and the slight broadening in peak indicate a change in the sample condition so that TiO$_2$ film on Ag might be more disordered [240]. The XPS spectra indicate the TiO$_2$ layer is thinner
at 80 °C for 300 cycles and it shows increasing thickness from 80 °C to 150 °C. However, the film is thinner or has lower quality at 200 °C, AFM and spectral reflectance data suggest the film deposited at 200 °C is thicker than it should be and therefore lower film quality is more likely.

Figure 5.14 Picture of TiO₂ films on Au/Si (left) and Ag/Si (right). The area below arrows are covered with TiO₂. The conditions of them deposited via ALD are described in section 5.2.1.2.

Overall, considering the thickness data, AFM images, the surface roughness and XPS spectra, for TiO₂ deposited on Au/Si, 150 °C is a suitable temperature that synthesised the conformal film (figure 5.14). Films deposited on Ag at 150 °C and 200 °C show higher roughness and very different morphologies indicative of poor-quality film growth while reaction at 80 °C appears to produce a higher quality, although thinner, film (figure 5.13). More cycles are needed for films grow at 80 °C to reach 20 nm because the growth rate decreases.

5.2.3 Conclusions

TiO₂ thin films were deposited via atomic layer deposition on microscope glass slides using titanium isopropoxide and water as precursors. The properties and reaction mechanism of titanium isopropoxide were discussed. Precursor vapour pressure, dose/purge times, gas flow rate and deposition temperature were established. An ALD cycle of TiO₂ includes a 2.5 s TTIP dose, a 1 min Ar purge, a 2 s H₂O dose and a 3 min Ar purge with 70 sccm gas flow rate for each line. The precursor temperature was 25 °C, the deposition temperature was 200 °C.
The relationship between TiO$_2$ film thickness on glass, growth rate and reaction cycles were investigated and used as a reference for generating desired film thickness. The growth rate of TiO$_2$ deposition via this procedure was in the range of 0.5 – 0.7 Å/cycle. The surface structure of TiO$_2$ was analysed by SEM and AFM which showed the roughness change. The film was also examined by XRD to study the crystallinity of TiO$_2$. TiO$_2$ films were highly uniform, amorphous light brown thin films.

The TiO$_2$ films deposited on Au/Si and Ag/Si substrates were deposited under 80 °C, 150 °C and 200 °C for 300 reaction cycles to obtain 20 nm film. The films generated at higher temperature showed higher roughness. In consideration of roughness, surface morphology and film quality, 150 °C is more suitable for generating TiO$_2$ films on Au/Si and 80 °C is appropriate for Ag/Si.

XPS was also used to analyse the composition of TiO$_2$/Au/Si and TiO$_2$/Ag/Si structures. The energy shift of Ti$^{4+}$ spectra in the high-temperature (150 and 200 °C) deposition on Ag indicates that TiO$_2$ thin film on Ag has higher roughness and lower quality. Conversely, the spectra of deposition on Au at high temperatures shows weak Au 4f peaks and significant Ti 2p peaks which means there is a continuous, dense TiO$_2$ film with no pinholes on the surface.
5.3 ALD and CVD of Al$_2$O$_3$ films using different metal precursors

Different from TiO$_2$, Al$_2$O$_3$ thin is a dielectric material normally used as a protection layer. This section described the atomic layer deposition of aluminium oxide thin films. Depositions were carried out using aluminium isopropoxide (AIP) and aluminium tri-sec-butoxide (ATSB) as metal precursors respectively. The precursor properties and reaction mechanism are discussed. ALD reaction parameters were optimized to achieve self-limiting ALD growth; these include precursor dose time, purge time, precursor temperature, deposition temperature and gas flow rate. Thin film thickness, quality and conformity were analysed by various characterization techniques, XRD, SEM, AFM, XPS, spectral reflectance measurement and ellipsometry.

5.3.1 Aluminium precursors

5.3.1.1 [Al(OiPr)$_3$], AIP

![Figure 5.15](image)

*Figure 5.15 The structural formulas of [Al(OiPr)$_3$].*

Aluminium isopropoxide (AIP, [Al(OiPr)$_3$]) is a white solid chemical compound decomposed in water or over 250 °C. The structural formulas of AIP is shown in figure 5.15. AIP has similar structure with TTIP which made it also an CVD and ALD precursor [241]. As Al$_2$O$_3$ deposition had not previously been attempted on this reactor before, the substrate temperature, precursor temperature and gas flow rate were tested under CVD mode first before turning to ALD as it is easier to identify selected parameters for CVD. Bubbler (precursor) temperature depends on the vapour pressure of the precursor, aluminium isopropoxide. The vapour pressure of AIP at different temperature was
reported in the literature \[180\]. The relationship between vapour pressure and temperature can be described by equation 5.6

\[
\lg (P_{\text{Torr}}) = a - \frac{b}{T} \tag{5.6}
\]

Referring to the vapour pressure data in the literature, a function can be simulated as equation 6.1 and plotted in figure 5.7.

\[
\lg (P_{\text{Torr}}) = 11.88 - \frac{4610}{T} \tag{5.7}
\]

In the former experiment, TTIP precursor was kept at 25°C, which generated 0.133 Torr vapour pressure. Hence, the temperature (90 °C) which generated equivalent AIP vapour pressure was calculated and used as bubbler temperature. Bubbler temperatures below 90°C were also tested during the experiment but no films were observed on the glass substrate, therefore 90°C was considered the lowest bubbler temperature that could be used for AIP.

![Figure 5.16 Vapour pressure curve of AIP.](image)
The reaction mechanism when using AIP and water as ALD precursors may be expected as equation 5.8 [178,179],

\[
\begin{align*}
(1) & \quad x \cdot \text{OH} (s) + \text{Al(O}^\text{Pr})_3 (g) \rightarrow (\text{-O-})_x \text{Al(}^\text{O}^\text{Pr})_{3-x} (s) + x \cdot \text{iPrOH} (g) \\
(2) & \quad (\text{-O-})_x \text{Al(O}^\text{Pr})_{3-x} (s) + (3-x) \text{H}_2\text{O} (g) \rightarrow (\text{-O-})_x \text{Al(OH)}_{3-x} (s) + (3-x) \cdot \text{iPrOH} (g)
\end{align*}
\]

with \(x=1\) being the monodentate, \(x=2\), bidentate and \(x=3\), tridentate, respectively, depending on the number of alkoxide ligands.

A full ALD reaction contains two half reactions. In the first half reaction, AIP reacts with OH groups on the substrate surface to produce \((\text{-O-})_x \text{Al(O}^\text{Pr})_{3-x}\), where \(x\) is the number of OH surface sites react with AIP which also determines the geometrical configuration on the surface. The \((\text{-O-})_x \text{Al(O}^\text{Pr})_{3-x}\) group can react with H\(_2\)O to form \((\text{-O-})_x \text{Al(OH)}_{3-x}\) in the second half of the reaction, therefore, the surface layer is covered with OH groups again, allowing the first half reaction to take place again [179].

5.3.1.2 [Al(O\text{Bu})\text{$_3$}], ATSB

AIP was not an ideal precursor for our ALD system because it sometimes blocked the pipes. AIP is a solid at room temperature and if the temperature of the pipework falls below the sublimation temperature (> ~130 °C) it may condense in the pipework. It was also hard to unblock. On the other hand, aluminium tri-sec-butoxide [ATSB, Al(O\text{Bu})\text{$_3$}] is a high viscosity liquid and although in use it did form blockages occasionally, the frequency was lower, and it was easier to clean. The drawbacks of using ATSB are that it is more toxic, air sensitive and moisture sensitive compared to AIP [242]. Therefore, the suitability of ATSB was investigated as an Al precursor. At room temperature, ATSB is a non-pyrophoric liquid which contains no halogens atoms (Figure 5.17). ATSB has been previously reported once as a metal-organic chemical vapour deposition (MOCVD) precursor [243] and once as an ALD precursor [244].
First of all, the vapour pressure\textsuperscript{245,246} of ATSB at different temperature was calculated and plotted in figure 5.18. The function is simulated as equation 5.9

\[
\lg (P_{\text{Torr}}) = 10.16 - \frac{4177.25}{T} \tag{5.9}
\]

By reference to the previously used vapour pressure of TTIP, a bubbler temperature higher than 115 °C would generate enough vapour pressure for ATSB vapour to transfer to the reactor. After several attempts at 115 °C, 120 °C and 125 °C, the ATSB bubbler temperature was set to 120 °C.

The reaction mechanism when using ATSB and water as ALD precursors may be expected as equation 5.10
(1) \( x \cdot \text{OH} (s) + \text{Al(O}^\text{Bu})_3 (g) \rightarrow (-\text{O})_x \text{Al(O}^\text{Bu})_{3-x} (s) + x \cdot \text{BuOH (g)} \)

(2) \((-\text{O})_x \text{Al(O}^\text{Bu})_{3-x} (s) + (3-x) \text{H}_2\text{O (g)} \rightarrow (-\text{O})_x \text{Al(OH})_{3-x} (s) + (3-x) \cdot \text{BuOH (g)} \)

(5.10)

with \(x=1\) being the monodentate, \(x=2\), bidentate and \(x=3\), tridentate, respectively, depending on the number of alkoxide ligands.

A full ALD reaction contains two half reactions. In the first half reaction, ATSB reacts with OH groups on the substrate surface to produce \((-\text{O})_x \text{Al(O}^\text{Bu})_{3-x}\), where \(x\) is the number of OH surface sites react with ATSB which also determines the geometrical configuration on the surface. The \((-\text{O})_x \text{Al(O}^\text{Bu})_{3-x}\) group can react with \(\text{H}_2\text{O}\) to form \((-\text{O})_x \text{Al(OH})_{3-x}\) in the second half of the reaction, therefore, the surface layer is covered with OH groups again, allowing the first half reaction to take place again \([35]\).

### 5.3.2 Experimental

#### 5.3.2.1 ALD and CVD of \(\text{Al}_2\text{O}_3\) using AIP as metal precursor

Aluminium isopropoxide (AIP) and deionized water were added into the bubblers respectively as precursors. \(\text{Al}_2\text{O}_3\) films were attempted to be grown \(\text{via ALD}\) with 300 to 1000 deposition cycles. Each cycle consisted of a 20 s AIP pulse, a 1 min argon purge, then followed by a 2 s water vapour pulse and a 3 min argon purge. The gas flow rate through AIP bubbler and purge by-pass carrying AIP and argon was set to 140 sccm. The precursor bubbler temperature of AIP was 90°C, the temperature of water was 5°C. The substrate was heated to 275°C, 300°C, 350°C, 400°C for films deposition, respectively. To prevent the condensation in the pipelines, the pipelines were heated to 150°C.

For CVD mode, the outlet valve of the AIP bubbler was kept open for the entire deposition and no water co-reactant was used. The gas flow rate was set to 140 sccm. The substrate
was heated to 275°C, 300°C, 350°C or 400°C for film deposition. Each deposition took 24 hours. Deposition parameter details are shown in table 5.4.

<table>
<thead>
<tr>
<th>Deposition mode</th>
<th>Deposition recipe</th>
<th>Cycle (time)</th>
<th>Precursor temperature/°C</th>
<th>Substrate temperature/°C</th>
<th>Flow rate / sccm</th>
</tr>
</thead>
<tbody>
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<td>300 cycles</td>
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<td>70</td>
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<td>300 cycles</td>
<td>90</td>
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</table>

Table 5.4 Summary of the Al₂O₃ films deposition parameters for using AIP as metal precursor. Repeated works are not included.

5.3.2.2 ALD and CVD of Al₂O₃ using ATSB as metal precursor

Aluminium tri-sec-butoxide (ATSB) and deionized water were added into the bubblers respectively as precursors. Al₂O₃ films were attempted to be grown via ALD with 250 to 1000 deposition cycles. Each cycle consisted of an ATSB pulse (2 s, 2.5 s or 20 s), a 1 min argon purge, then followed by a 2 s water vapour pulse and an argon purge of at least 3 min. The gas flow rate through ATSB bubbler and purge by-pass carrying ATSB and
argon was set to 70, 120 or 150 sccm. The temperature of the ATSB bubbler was 120°C and the temperature of the water bubbler was 5°C. The substrate was heated to 175°C, 200°C, 250°C, 300°C, 350°C and 400°C for film deposition, respectively. To prevent precursor condensation in the pipelines, the pipelines were heated to 170°C.

For CVD mode, the outlet valve of the ATSB bubbler was kept open for the entire deposition and no water co-reactant was used. The gas flow rate was set to 150 sccm. The substrate was heated to 300°C, 350°C and 400°C for film deposition. Each deposition took 24 hours. A deposition mode between ALD and CVD, so called pulse CVD was also used for deposition inspection and optimization. A cycle in pulse CVD mode only contains one ATSB pulse (10 s, 20 s or 1 min) and one argon purge (1 min).

Glass microscope slide, quartz and silicon were used as substrates respectively for the comparative study of film growth situation and quality on different substrates. Deposition parameter details are shown in table 5.5.
### Deposition mode: CVD

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<th>Deposition recipe</th>
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<th>Substrate temperature/°C</th>
<th>Flow rate/sccm</th>
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### Deposition mode: Pulsed CVD

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<th>Substrate temperature/°C</th>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 5.5 Summary of the Al₂O₃ deposition parameters for using ATSB as metal precursor. Repeated works are not included.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Deposition recipe</th>
<th>Cycle</th>
<th>Substrate temperature/°C</th>
<th>Flow rate/ sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>20 s 1 min 2 s 3 min</td>
<td>500</td>
<td>200</td>
<td>120</td>
</tr>
<tr>
<td>Glass</td>
<td>20 s 3 min 2 s 5 min</td>
<td>250</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>2.5 s 1 min 2 s 5 min</td>
<td>500</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>2.5 s 2 min 2 s 5 min</td>
<td>500</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>2.5 s 3 min 2 s 5 min</td>
<td>250</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>2.5 s 3 min 2 s 5 min</td>
<td>250</td>
<td>200</td>
<td>120</td>
</tr>
<tr>
<td>Quartz</td>
<td>2.5 s 3 min 2 s 3 min</td>
<td>500</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>2 s 3 min 2 s 5 min</td>
<td>250</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>2 s 3 min 2 s 3 min</td>
<td>250</td>
<td>200</td>
<td></td>
</tr>
<tr>
<td>Silicon, FTO and Au/WO₃</td>
<td>2.5 s 3min 2 s 3 min</td>
<td>200</td>
<td>200</td>
<td>120</td>
</tr>
</tbody>
</table>

(Precursor temperature was 120 °C in all ALD process.)
5.3.3 Result and discussion

5.3.3.1 CVD and ALD of Al₂O₃ using AIP

The bubbler gas flow rate was varied between 100 sccm, 140 sccm and 200 sccm. At 100 sccm gas flow rate no film formation was observed, likely due to low precursor transport, however at 200 sccm the precursor blocked the pipes frequently, likely due to excessive precursor transport. Therefore, 140 sccm was selected for further experiments.

According to the literature [181], Al₂O₃ can be deposited via CVD in the temperature range of 200-700°C. Films are normally prepared between 275°C and 500°C, so 275°C, 300°C, 350°C and 400°C were set as deposition (substrate) temperature, respectively. The XPS spectra (figure 5.19) show the peak of Al 2p at 74.5 eV and the peak of O 1s at 531.3 eV at all deposition temperatures, which correspond to Al oxide [247,248].
The film thickness was examined by spectral reflectance measurement. The films synthesized under 275°C, 300°C, 350°C and 400°C show the thickness of 330, 600, 150 and 300 nm, respectively. The films displayed colour variance due to a thickness change from inlet to outlet. The coverage of the film on the 4 cm × 5 cm substrate could be observed from the colour changes with the films made at 275°C and 300°C having nearly full coverage while the films synthesized at higher temperature only covered half of the substrates. This is likely because all the precursor was depleted at the higher temperature.
Therefore, the optimized parameters were a substrate temperature of 275°C, a bubbler temperature of 90°C and a gas flow rate of 140 sccm. The top view and cross-sectional SEM image of as-synthesised Al₂O₃ film is shown in figure 5.20 demonstrating the less smooth surface and low film quality.

![SEM images of Al₂O₃ film](image)

**Figure 5.20** The SEM images of Al₂O₃ film generated at 300°C, a) cross-section view; b) top view. The deposition conditions are described in section 5.3.2.1.

After the optimization of CVD parameters, the dose time needed to be optimised to provide vapour transport under ALD process conditions. Several different conditions were tested but no films formed on the substrate (parameters displayed in table 5.4). It is certain that there is a suitable condition for using AIP as a metal precursor *via* ALD but as it blocks the pipelines quite often, a new metal precursor, aluminium tri-sec-butoxide (ATSB) was considered. Unlike AIP, which is a solid, ATSB is a (viscous) liquid and it was hoped this would prevent blockages forming at cold spots in the reactor.

### 5.3.3.2 CVD of Al₂O₃ using ATSB

A CVD process was used to find suitable gas flow rate and deposition temperature. Gas flow through Ar purge line and ATSB precursor line was set to 150 sccm.

Initial experiments focused on optimizing the precursor temperature, gas flow rate and deposition temperature for CVD deposition. After several attempts at 115 °C, 120 °C and
125 °C, the optimum ATSB bubbler temperature was found to be 120 °C. Meanwhile, increasing the precursor temperature further did not produce any significant increase in thickness at a deposition temperature of 350 °C (additional precursor not utilized in deposition). The composition of the films was analysed by XRD, Raman spectroscopy and XPS. The crystallisation temperature of \( \gamma \)-Al_2O_3 is at least 600 °C and 1000 °C is needed for it to transform to \( \alpha \)-Al_2O_3 \[249–251]\). As the deposition temperature here was much lower than the crystallization temperature of Al_2O_3, it is consistent that neither XRD patterns nor Raman spectra showed pronounced peaks (Figure 5.21 and 5.22). In this case, XPS is quite useful to detect the material composition. For a film deposited at 400 °C for 24 h with 120 °C ATSB precursor temperature and 150 sccm gas flow, the Al 2p spectrum (figure 5.23 a)) displayed an intense peak for the Al 2p ionisation at 73.6 eV which matches with the binding energy of Al\(^{3+}\) in Al_2O_3 \[252]\). The Si 2p peak is of very low intensity (Figure 5.23 b)), which indicates that no Si from the glass substrate is observed, thus the Al_2O_3 film covers the entire area of the analysis spot. These findings are consistent with the films deposited via CVD using ATSB as a single-source precursor being amorphous Al_2O_3.

**Figure 5.21** XRD pattern of Al_2O_3 film deposited via CVD. This example was made under condition: precursor temperature 120 °C; deposition temperature 350 °C; gas flow rate 150 sccm; deposition time 24 h. The deposition conditions are described in section 5.3.2.2.
Figure 5.22 Raman spectra of Al₂O₃ film deposited via CVD. This example was made under condition: precursor temperature 120 °C; deposition temperature 350 °C; gas flow rate 150 sccm; deposition time 24 h. The deposition conditions are described in section 5.3.2.2.

Figure 5.23 High resolution XPS spectra of a) Al 2p and b) Si 2p of Al₂O₃ film deposited on glass via CVD. The deposition conditions are described in section 5.3.2.2.

To observe the effect of substrate temperature, the CVD deposition temperatures were set to 300 °C, 350 °C and 400 °C (with a bubbler temperature of 125 °C). AFM scans (figure 5.24) show an increase in the roughness of film surface as deposition temperature increases; Rₐ (300 °C) = 3.5 nm, Rₐ (350 °C) = 3.8 nm and Rₐ (400 °C) = 18 nm, which can also be seen in SEM images (figure 5.24). Increasing the deposition temperature increases film roughness which is typically unfavourable for Al₂O₃ thin films. Though Al₂O₃ film is
transparent, the film deposited via CVD can be confirmed by birefringence because it’s thick (thickness ~ 600 nm) and uneven (figure 5.25).

![Figure 5.24](image-url)

**Figure 5.24** SEM images, AFM scans and 3D images of Al₂O₃ films deposited with 150 sccm Ar gas flow, precursor temperature at 125 °C and deposition temperature at a, b, c) 300 °C; d, e, f) 350 °C; g, h, i) 400 °C. The conditions of them deposited via CVD are described in section 5.3.2.2.

![Figure 5.25](image-url)

**Figure 5.25** Picture of Al₂O₃ film on glass substrate with birefringence. The parameters were deposition T: 350 °C, precursor T: 125 °C, gas flow rate: 150 sccm, CVD running for 24 h. The conditions of it deposited via CVD are described in section 5.3.2.2.
The thickness of Al₂O₃ films deposited via CVD are shown in table 5.6. The deposition film growth rate is not constant with increasing temperature, unlike previous research using AIP. According to a former study, a constant growth rate for Al₂O₃ from AIP was observed in CVD with increasing deposition temperature[^253].

<table>
<thead>
<tr>
<th>Precursor temperature/°C</th>
<th>Substrate temperature/°C</th>
<th>Flow rate/ cm³ min⁻¹</th>
<th>Thickness/ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>350</td>
<td></td>
<td>130</td>
</tr>
<tr>
<td>120</td>
<td>350</td>
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<td>350</td>
<td>380</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>670</td>
</tr>
</tbody>
</table>

Table 5.6 Summary of 24 h CVD of Al₂O₃ film thickness on glass. Repeated works are not included. The deposition conditions are described in section 5.3.2.2.

5.3.3.3 Pulsed CVD and ALD parameters optimization

After the optimization of CVD parameters, a pulsed CVD process was introduced to identify the minimum duration required for a metal precursor pulse, thereby preventing over-dosing, which requires longer purging to remove and hence increases the ALD cycle time. In order to obtain vapour transport (film growth), the pulse of ATSB was set to 20 s or 1 min, the deposition temperature was 350 °C and the precursor temperature was fixed at 120 °C with an Ar flow rate of 120 sccm. Some examples of Al₂O₃ film made by pulse CVD are shown in figure 5.26 and table 5.7. The 20 s recipe gave an acceptable even morphology (R_q~1.5 nm) and was used as the initial recipe for the ALD process.

[^253]: Reference number
Figure 5.26 SEM images, AFM scans and 3D images of Al₂O₃ films deposited via pulsed CVD. The conditions of them deposited via pulsed CVD are described in table 5.7.

<table>
<thead>
<tr>
<th>Figure 5.26</th>
<th>Deposition recipe</th>
<th>Cycle</th>
<th>Precursor temperature/°C</th>
<th>Substrate temperature/°C</th>
<th>Flow rate/sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, b, c</td>
<td>ATSB 10 s purge 1 min</td>
<td>2000</td>
<td>350</td>
<td>115</td>
<td>150</td>
</tr>
<tr>
<td>d, e, f</td>
<td>ATSB 1 min purge 1 min</td>
<td>2000</td>
<td>350</td>
<td>115</td>
<td>150</td>
</tr>
<tr>
<td>g, h, i</td>
<td>ATSB 20 s purge 1 min</td>
<td>1000</td>
<td>350</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>j, k, l</td>
<td>ATSB 20 s Purge 1 min</td>
<td>675</td>
<td>350</td>
<td>120</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 5.7 Summary of the Al₂O₃ deposition parameters of SEM images, AFM scans and 3d images in figure 5.26.
The thickness of Al₂O₃ films deposited via CVD was shown in table 5.8.

<table>
<thead>
<tr>
<th>Deposition recipe</th>
<th>Cycle</th>
<th>Precursor temperature/°C</th>
<th>Substrate temperature/°C</th>
<th>Flow rate/sccm</th>
<th>Thickness/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATSB 10 s purge 1 min</td>
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<tr>
<td>ATSB 1 min purge 1 min</td>
<td>2000</td>
<td>115</td>
<td>350</td>
<td>150</td>
<td>86</td>
</tr>
<tr>
<td>ATSB 1 min purge 1 min</td>
<td>1000</td>
<td>115</td>
<td>400</td>
<td></td>
<td>1160</td>
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<tr>
<td>ATSB 20 s purge 1 min</td>
<td>1000</td>
<td>120</td>
<td>400</td>
<td></td>
<td>81</td>
</tr>
<tr>
<td>ATSB 20 s Purge 1 min</td>
<td>1000</td>
<td>120</td>
<td>350</td>
<td>120</td>
<td>970</td>
</tr>
<tr>
<td>ATSB 20 s purge 1 min</td>
<td>675</td>
<td>350</td>
<td>350</td>
<td></td>
<td>410</td>
</tr>
</tbody>
</table>

Table 5.8 Summary of pulsed CVD of Al₂O₃ film thickness on glass. Repeated works are not included.

Comparing the AFM images of Al₂O₃ films deposited via continuous CVD (24 h), pulse CVD (1 min ATSB pulse, 1 min Ar purge, 1000 cycles) and pulsed CVD (20 s ATSB pulse, 1 min Ar purge, 1000 cycles). Figure 5.27 shows the surface roughness decrease from \( R_q \) (continuous deposition) = 10 nm to \( R_q \) (1 min pulse) = 2.5 nm and \( R_q \) (20 s pulse) = 2.3 nm. We concluded from these data that a 20 second pulse produced complete coverage and was therefore a suitable starting point for ATSB precursor dosing in an ALD process.
Figure 5.27 AFM scans and 3D images of Al₂O₃ films deposited at 350°C via a, b) continuous CVD; c, d) pulsed CVD (1 min ATSB pulse) and e, f) pulsed CVD (20 s ATSB pulse). The deposition conditions are described in section 5.3.2.2.

The deposition temperature used in ALD should be lower than that used in CVD to avoid uncontrolled CVD-like film growth, therefore the ALD deposition temperature was decreased in comparison to CVD in increments from 350 °C to 300 °C, 250 °C, 200 °C and 175 °C, whilst the other parameters were kept unchanged (20 s ATSB pulse, 1 min Ar purge, 2 s H₂O pulse and 3 min Ar purge with 120 sccm Ar gas flow deposited for 500 cycles). XPS spectra of this series of samples indicated that films deposited at 200 °C, 250 °C and 300 °C show similar binding energy intensity at approximately 74 eV. XPS spectra of this series of samples displays that at 175 °C, there is probably no film on the substrate since the intensity of Al 2p is almost zero in figure 5.28. The growth rate of
Al₂O₃ was between 8.2 – 11.3 Å/cycle in the deposition temperature range of 200 °C – 300 °C with a 20 s pulse time, thus 200 °C was selected in further experiments.

![High resolution XPS spectra of Al 2p under different ALD deposition temperature, 175 °C, 200°C, 250 °C, 300 °C and 350 °C. The deposition conditions are described in section 5.3.2.2.](image)

**Figure 5.28** High resolution XPS spectra of Al 2p under different ALD deposition temperature, 175 °C, 200°C, 250 °C, 300 °C and 350 °C. The deposition conditions are described in section 5.3.2.2.

All the thickness and growth rate of the Al₂O₃ films measured by ellipsometer are shown in table 5.9. The thickness and growth rate of the recipe used above (20 s ATSB pulse, 1 min Ar purge, 2 s H₂O pulse and 3 min Ar purge with 120 sccm Ar gas flow, 200 °C) were found to be much higher than previously reported values (1 Å/cycle) [253–261]. This indicates a combination of ALD and CVD-like growth. One likely explanation is that the dose time of ATSB was too long for the purge time used, therefore the ATSB dose time was reduced from 20 s to 2.5 s with the aim to avoid CVD-like growth. Also changing the ATSB purge time from 1 min to 3 min for a 2.5 s dose reduced the deposition rate, while more than 3 min for a 2.5 s dose time resulted in no change in the growth rate, therefore 3 min purge was considered optimum for a 2.5 s dose. Similarly, for a 2 s H₂O
dose, changing the purge time from 3 min to 5 min had no effect, indicating that a 3 min purge was sufficient to ensure all water was evacuated between cycles.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Deposition recipe</th>
<th>Cycle</th>
<th>Substrate temperature /°C</th>
<th>Thickness/nm</th>
<th>Growth rate/Å/cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>ATSB 20 s, Purge 1 min, H₂O 2 s, Purge 3 min</td>
<td>500</td>
<td>200</td>
<td>410</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>250</td>
<td>430</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>565</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>350</td>
<td>420</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>20 s, Purge 3 min, H₂O 2 s, Purge 5 min</td>
<td>250</td>
<td>200</td>
<td>310</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td>6 s, Purge 3 min, H₂O 2 s, Purge 3 min</td>
<td></td>
<td>200</td>
<td>260</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>2.5 s, Purge 3 min, H₂O 2 s, Purge 3 min</td>
<td></td>
<td>200</td>
<td>33</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>6 s, Purge 3 min, H₂O 2 s, Purge 5 min</td>
<td></td>
<td>200</td>
<td>260</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>6 s, Purge 3 min, H₂O 2 s, Purge 3 min</td>
<td></td>
<td>200</td>
<td>250</td>
<td>10.1</td>
</tr>
<tr>
<td>Glass</td>
<td>ATSB 2.5 s, Purge 3 min, H₂O 2 s, Purge 5 min</td>
<td>250</td>
<td>200</td>
<td>40</td>
<td>1.6</td>
</tr>
<tr>
<td>Silicon</td>
<td>ATSB 2.5 s, Purge 1 min, H₂O 2 s, Purge 3 min</td>
<td></td>
<td>200</td>
<td>25</td>
<td>1.2</td>
</tr>
<tr>
<td>Quartz</td>
<td>ATSB 2 s, Purge 3 min, H₂O 2 s, Purge 5 min</td>
<td></td>
<td>200</td>
<td>25</td>
<td>1.2</td>
</tr>
<tr>
<td>Silicon</td>
<td>ATSB 2 s, Purge 3 min, H₂O 2 s, Purge 5 min</td>
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<td>200</td>
<td>25</td>
<td>1.2</td>
</tr>
<tr>
<td>Quartz</td>
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<td></td>
<td>200</td>
<td>25</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Table 5.9** Summary of ALD of Al₂O₃ film thickness. Repeated works are not included.

With a 2.5 second dose time and 3 minute purge time, the thickness reduced to approx. 50 nm after 500 cycles, which gave growth rates in the range of 1 – 1.4 Å/cycle with successful deposition on silicon, quartz and glass substrates. The growth rate using ATSB as an ALD precursor is similar to that using TMA or AlCl₃ (0.8-2 Å/cycle) \(^{[144,261-263]}\). Thus, the ALD-like parameters were fixed at an ATSB bubbler temperature of 120 °C,
deposition temperature of 200 °C and gas flow rate of 120 sccm (a full cycle includes 2.5 s ATSB pulse, 3 min Ar purge, 2 s H₂O pulse and 3 min Ar purge). Figure 5.29 shows an approximately linear relationship between Al₂O₃ film thickness and number of reaction cycles.

![Graph showing the relationship between Al₂O₃ film thickness and number of ALD reaction cycles with film growth rate. The deposition conditions are described in Table 5.9.](image)

**Figure 5.29** The relationship between Al₂O₃ film thickness and number of ALD reaction cycles with film growth rate. The deposition conditions are described in Table 5.9.

The density of the Al₂O₃ component in the ellipsometric EMA model varied between 0.720 and 0.757 (Table 5.10 and Figure 5.30). The films deposited with short 2.5 s ATSB pulse times showed lower growth rates (1 – 1.4 Å/cycle) and higher densities than those grown with longer 20 s pulses. The RMS roughness of Al₂O₃ film on three substrates were R₉(silicon) = 1.5 nm, R₉(quartz) = 1.2 nm and R₉(glass) = 0.96 nm, suggesting an applicability of Al₂O₃ on a variety of substrates (Figure 5.31). The refractive index of the as synthesized Al₂O₃ films @632.8 nm shown in table are considered as ~1.56, lower than the reference n which is 1.77.
Figure 5.30 Refractive index of a) Al₂O₃ [48], and b) Al₂O₃/air (0.757/0.243) Effective Medium Approximation used for ellipsometric modelling of ALD film on glass, Figure 5.31e.

<table>
<thead>
<tr>
<th>Figure 5.31</th>
<th>Substrate</th>
<th>ATSB dose/s</th>
<th>Thickness/ nm</th>
<th>EMA concentration/ %</th>
<th>Refractive index @ 632.8nm</th>
<th>Fit quality R²</th>
<th>Growth rate/ Å/cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>a, b</td>
<td>silicon</td>
<td>2.5</td>
<td>29.8</td>
<td>74.5</td>
<td>1.56</td>
<td>0.997</td>
<td>1.2</td>
</tr>
<tr>
<td>c, d</td>
<td>quartz</td>
<td>2.5</td>
<td>37.7</td>
<td>74.2</td>
<td>1.56</td>
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<td>glass</td>
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<td>257.8</td>
<td>72.0</td>
<td>1.54</td>
<td>0.909</td>
<td>10.3</td>
</tr>
</tbody>
</table>

Table 5.10 Table of structural parameters from for ellipsometric model fitting between (1.25-5eV) for samples produced via ALD (250 cycles, ATSB pulse indicated, 3 min purge, 2 s H₂O pulse, 3 min purge).
Figure 5.31 AFM scans and 3D images of Al$_2$O$_3$ films after 250 ALD cycles, on a, b) silicon; c, d) quartz; e, f) glass. The deposition conditions are described in table 5.9.

5.3.3.4 Optical property: thickness and refractive index

Al$_2$O$_3$ film thickness and wavelength-dependent refractive index were simulated from ellipsometry measurement using Cauchy model $^{264}$. Refractive indexes at 632.8 nm for different film thicknesses are plotted in figure 5.32 if the Effective Medium Approximation is not used. The refractive index depends strongly on film thickness and shows a significant decrease when the thickness reaches 80 nm and probably stays constant when the thickness is more than 1 μm. As the refractive index does not vary greatly, the simulation model of ellipsometry can be considered reliable.
Atomic layer deposition of Al₂O₃ thin films were attempted using two aluminium precursors, aluminium isopropoxide (AIP) and aluminium tri-sec-butoxide (ATSB).

ALD of Al₂O₃ used AIP and water as precursors. The parameters of Al₂O₃ deposited using AIP via CVD and ALD have been investigated. Suitable precursor vapour pressure, gas flow rate and deposition temperature were identified. After optimization, AIP bubbler temperature was 90°C, the deposition temperature was 275°C and the gas flow rate was 140 sccm. XPS analysis showed aluminium oxide on the surface and SEM showed its uniform morphology. As an ALD precursor, AIP was unsuccessful due to the properties of the precursor and the design of the reactor, however it was effective as a CVD precursor.

The metal precursor was changed to ATSB due to the frequent blocking when using AIP. The parameters of Al₂O₃ thin films atomic layer deposition using aluminium tri-sec-butoxide as a new Al precursor and water for ALD were investigated. The process was first optimized in CVD mode to confirm desired precursor temperature and gas flow rate,
then in pulsed CVD mode to confirm the vapour dose. Finally, deposition temperature, dose time/purge time, deposition and gas flow rate were optimized. The best deposition conditions for ALD were as follows: ATSB bubbler temperature 120 °C; deposition temperature 200 °C; gas flow rate 120 sccm; ATSB pulse time 2.5 s; Ar purge time 3 min; H$_2$O pulse time 2 s; Ar purge time 3 min.

The composition and morphology of the as-synthesized films were analysed and followed by the comparison of film deposition under different conditions by ellipsometer, XPS, SEM and AFM. The film was confirmed to be Al$_2$O$_3$. A stable ALD process with a growth rate of 1 – 1.4 Å/cycle was observed by measuring the Al$_2$O$_3$ film thickness on different substrates using ellipsometry. Comparing the film morphology on silicon, quartz and glass, similar Al$_2$O$_3$ particle sizes (15 – 25 nm) with the root mean square roughness around 1 nm were observed. SEM, AFM and XPS data indicated that the obtained films were dense and continuous with a low concentration of impurities. The results also show uniformity, conformity and good control of thickness, strongly suggesting a potential of using ATSB as a new ALD precursor for Al$_2$O$_3$ thin films.

5.4 Deposition of ultrathin film layers via ALD with Metal/WO$_3$ heterojunctions

In former studies of ALD thin films including Al$_2$O$_3$ and other oxides [181,265,266], it has been mentioned that either ultrathin film of several nanometres or thin film with a thickness above 20 nm showed different degrees of current density enhancement during photoelectrochemical test. Therefore, we wanted to test the influence of TiO$_2$ and Al$_2$O$_3$ thin films deposited via ALD on the PEC performance of WO$_3$-based films.

5.4.1 Experimental

FTO glass and were cut into 2.5 cm × 2.5 cm pieces, cleaned by acetone, isopropanol, methanol and deionized water for 15 min, respectively, and dried in compressed air.
5.4.1.1 AACVD of WO\textsubscript{3} NNs, Au, Ag and Pt NPs

WO\textsubscript{3} NNs films were grown on FTO glass at 375 °C using 0.06 g W(CO)\textsubscript{6} in 10 ml acetone and 5 ml methanol as the precursor. The N\textsubscript{2} gas flow rate was 300 sccm. The as-synthesized film was annealed in air in a muffle furnace at 530 °C for 2 hours.

Au NPs were deposited on WO\textsubscript{3} NNs or TiO\textsubscript{2}/WO\textsubscript{3} at 300 °C using 0.5 mg or 0.1 mg (HAuCl\textsubscript{4}·3H\textsubscript{2}O in 15 ml methanol as the precursor. The N\textsubscript{2} gas flow rate was 300 sccm.

Ag NPs were deposited on WO\textsubscript{3} NNs or TiO\textsubscript{2}/WO\textsubscript{3} at 300 °C using 100 μL or 20 μL Ag-AMP in 15 ml methanol as the precursor. The N\textsubscript{2} gas flow rate was 300 sccm.

Pt NPs were deposited on WO\textsubscript{3} NNs or TiO\textsubscript{2}/WO\textsubscript{3} at 300 °C using 1.5 mg or 0.5 mg H\textsubscript{2}Cl\textsubscript{6}Pt·xH\textsubscript{2}O in 15 ml methanol as the precursor. The N\textsubscript{2} gas flow rate was 300 sccm.

5.4.1.2 ALD of TiO\textsubscript{2}

TiO\textsubscript{2} thin films were grown on FTO glass, Metal/WO\textsubscript{3}, and silicon using TTIP as the Ti precursor. Each cycle consisted of a 2 s TTIP dose, a 1 min argon purge, a 2 s water dose and a 3 min argon purge. The gas flow rate was set to 70 sccm. The precursor bubbler temperature of TTIP was 25 °C, the temperature of the water bubbler was 5 °C. The substrate was heated to 200 °C for film deposition. To prevent condensation in the pipework, the lines were heated to 130 °C.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Deposition recipe</th>
<th>Cycle</th>
<th>Substrate temperature/°C</th>
<th>Flow rate/sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon, FTO and Au/WO\textsubscript{3}</td>
<td>TTIP 2 s Purge 1 min H\textsubscript{2}O 2 s Purge 3 min</td>
<td>20</td>
<td>200</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.11 ALD of TiO\textsubscript{2} thin films using TTIP as metal precursor.
5.4.1.3 ALD of Al$_2$O$_3$

Al$_2$O$_3$ thin films were grown on FTO glass, Metal/WO$_3$, and silicon using ATSB as the Al precursor. Each cycle consisted of a 2.5 s ATSB dose, a 3 min argon purge, a 2 s water dose and a 3 min argon purge. The gas flow rate was set to 120 sccm. The precursor bubbler temperature of ATSB was 120 °C, the temperature of the water bubbler was 5 °C. The substrate was heated to 200 °C for film deposition. To prevent condensation in the pipework, the lines were heated to 170 °C.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Deposition recipe</th>
<th>Cycle</th>
<th>Substrate temperature/°C</th>
<th>Flow rate/ sccm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATSB Purge H$_2$O Purge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon, FTO and Au/WO$_3$</td>
<td>2.5 s 3min 2 s 3 min</td>
<td>20</td>
<td>200</td>
<td>120</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>100</td>
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<td></td>
</tr>
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<td>150</td>
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<td>300</td>
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Table 5.12 ALD of Al$_2$O$_3$ thin films using ATSB as metal precursor.

5.4.1.4 How to build the complex nanostructures

If we describe a sandwich structural material from top to bottom as A/B/C, then a WO$_3$ NN with Au NPs decoration and TiO$_2$ outer layer coating should be defined as TiO$_2$/Au/WO$_3$. Figure 5.33 describes the schematic procedure of building TiO$_2$/Au/WO$_3$, Al$_2$O$_3$/Au/WO$_3$, Au/TiO$_2$/WO$_3$ and Au/Al$_2$O$_3$/WO$_3$ via AACVD and ALD. First, WO$_3$ was deposited on FTO glass as the base. Then, Au NPs and TiO$_2$ thin film were deposited in that order to obtain TiO$_2$/Au/WO$_3$. By changing the order of Au NPs AACVD and TiO$_2$ ALD, Au/TiO$_2$/WO$_3$ was assembled. By changing TiO$_2$ ALD to Al$_2$O$_3$ ALD, Al$_2$O$_3$/Au/WO$_3$ and Au/Al$_2$O$_3$/WO$_3$ were produced.

By changing Au NPs deposition to Ag AACVD or Pt AACVD, the other two groups of complex nanostructures were obtained.
**Figure 5.33** Schematic procedure of building TiO$_2$/Au/WO$_3$, Al$_2$O$_3$/Au/WO$_3$, Au/TiO$_2$/WO$_3$ and Au/Al$_2$O$_3$/WO$_3$ via AACVD and ALD.

### 5.4.1.5 PEC test and sample preparation

All samples were cut into 0.8 cm × 2 cm pieces (film coverage 0.8 cm × 1.5 cm). The four edges of the films were coated with epoxy resin glue to prevent them from peeling and to prevent electrical leakage. They were dried until the glue hardened.

PEC tests were done in a three-electrode system in a cubic quartz cell connected to a potentiostat (Interface 1000, Gamry). The electrolyte was 0.1 M H$_2$SO$_4$, the counter electrode was a Pt mesh and the reference electrode was a Ag/AgCl electrode (CH111). The light source was a 75 W USHIO xenon lamp with a Newport AM 1.5 G filter. The light intensity was calibrated to one sun by a photodiode (CPC). Nernst equation was introduced to convert the as-measured working potential by Ag/AgCl electrode ($V_{\text{Ag/AgCl}}$) to reversible hydrogen electrode potential ($V_{\text{RHE}}$).

$$V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.0591pH + 0.1976$$

The linear sweep voltammetry (LSV) was scanned at a speed of 20 mV/s. The samples were measured for several scans for the reproducibility between measurements. The chronoamperometry stability tests were measured at 1 V (vs. RHE) constantly for 24 hours under one sun illumination.
5.4.2 Result and discussion


First, the ALD layer used in these complex nanostructures needs to be optimized. This was done when the Au precursor amount was 5 mg; TiO$_2$/Au/WO$_3$ and Au/TiO$_2$/WO$_3$ were built in these orders via AACVD deposition of WO$_3$, AACVD deposition of Au and ALD deposition of TiO$_2$. The WO$_3$ used was the standard WO$_3$ NNs (Chapter 3). However, different reaction cycles, 20, 50, 100, 150 and 300 cycles of TiO$_2$ were deposited via ALD. The colour of the TiO$_2$/Au/WO$_3$ appears greenish purple and the colour of Au/TiO$_2$/WO$_3$ appears purple (figure 5.34 and figure 5.35). With increasing number of ALD cycles, the sample colour becomes darker. As the number of ALD cycles is related to film thickness, the change of thin film thickness impacts the optical properties of the whole nanostructures.

**Figure 5.34** Photos of TiO$_2$/Au/WO$_3$ with 20, 50, 100, 150, 200 and 300 ALD cycles of TiO$_2$ (left to right). The deposition conditions are described in section 5.4.1.2.

**Figure 5.35** Photos of Au/TiO$_2$/WO$_3$ with 20, 50, 100, 150, 200 and 300 ALD cycles of TiO$_2$ (left to right). The deposition conditions are described in section 5.4.1.2.

Due to the complex structure, the thickness of the ALD layer was difficult to be measured using optical methods, therefore film thickness during deposition was recorded using a ‘witness’ planar substrate inserted in the reactor at the same time with the sample. The thicknesses of TiO$_2$ thin films related to ALD cycles were measured using ellipsometry.
and are shown in table 5.13. Growth rate as a function of number of cycles was plotted in figure 5.36. The thickness grows steadily with the reaction cycles with an ALD growth rate of 0.5 – 0.8 Å/cycle, as seen previously in Section 5.2.3.

<table>
<thead>
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<th>Cycle/ number</th>
<th>Thickness/ nm</th>
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<tbody>
<tr>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>50</td>
<td>3</td>
</tr>
<tr>
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<td>200</td>
<td>17</td>
</tr>
<tr>
<td>300</td>
<td>21</td>
</tr>
</tbody>
</table>

Table 5.13 Summary of the ALD cycles of TiO$_2$ thin film and their film thickness on Au/WO$_3$, WO$_3$ and silicon. The deposition conditions are described in section 5.4.1.2.

Figure 5.36 TiO$_2$ film growth rate (blue) and film thickness (red) with number of reaction cycles. The deposition conditions are described in section 5.4.1.2.

Due to the thickness and non-crystallinity of TiO$_2$ and Al$_2$O$_3$ thin films, no related peaks can be seen in XRD patterns, so only Au and WO$_3$ peaks can be distinguished which are at similar degrees and crystal phases (figure 5.37).
Figure 5.37 XRD pattern of 5 nm TiO$_2$/Au/WO$_3$ on FTO glass. The deposition conditions are described in section 5.4.1.2.

Figure 5.38 displays XPS spectra of TiO$_2$/Au/WO$_3$ with various TiO$_2$ thickness on FTO glass. The binding energies of Ti 2p$_{1/2}$, Ti 2p$_{3/2}$, Au 4f$_{5/2}$ and Au 4f$_{7/2}$ are still at the positions found for bare TiO$_2$ and Au NPs respectively. When the thickness of the TiO$_2$ thin film increases, the peak intensity of Ti 2p increases while the peak intensity of Au 4f drops. When the TiO$_2$ thin film is over 5 nm thick on the planar substrate (over the detection limit of XPS [267]), no Au 4f peak can be observed which shows the uniform and pinhole-free TiO$_2$ ALD film. The peak intensity of W 4f remains low. There is a peak shape change from W 4f doublet peaks to single peak with the increasing of TiO$_2$ thickness. The peaks at 38.2 eV and 36.3 eV are W 4f$_{5/2}$ and W 4f$_{7/2}$ peaks while TiO$_2$ ALD layer is thinner than 5 nm. When it is thicker than 5 nm only one peak at 37.6 eV is observed, which is Ti 3p peak [268]. This indicates that as the thickness of TiO$_2$ increases, W 4f peaks are no longer observable showing a whole coverage of ALD layer. The W 4f peaks of bare WO$_3$ are at 37.7 eV and 35.6 eV which are also lower than the binding energy of W 4f in TiO$_2$/Au/WO$_3$. It is due to the Schottky barrier interaction among each material, probably indicates the charge transfer from WO$_3$ to TiO$_2$. This is what we expected to see.
Figure 5.38 XPS spectra of a) Ti 2p; b) Au 4f and c) W 4f in TiO$_2$/Au/WO$_3$ nanostructures with various thickness of TiO$_2$ thin film. The deposition conditions are described in section 5.4.1.2.

SEM images of TiO$_2$/Au/WO$_3$ and Au/TiO$_2$/WO$_3$ nanostructures with 5 nm TiO$_2$ and 21 nm TiO$_2$ under low magnification are shown in figure 5.39. The nanostructures with thicker TiO$_2$ layers appear to have larger cross-sections. The nanostructures with TiO$_2$ layers on the top also look larger than the nanostructures with TiO$_2$ in the middle.
**Figure 5.39** SEM images of WO₃, Au/WO₃, TiO₂/WO₃, TiO₂/Au/WO₃ and Au/TiO₂/WO₃ nanostructures with two different TiO₂ thicknesses. The deposition conditions are described in section 5.4.1.2.

TEM images help confirm the thickness and uniformity of TiO₂ thin films. From figure 5.40 (a) and (b), 5 nm and 21 nm TiO₂ film in between of WO₃ NNs and Au NPs can be seen. From figure 5.40 (c) and (d), 5 nm and 21 nm TiO₂ film on top of Au NPs and WO₃ NNs can be seen. The thicknesses shown in TEM images match the measurement in table 5.14 by ellipsometer. High resolution TEM image in figure 5.41 display the amorphous TiO₂ layer, crystallized Au particle and formation of a thin interlayer between WO₃ and TiO₂.
Figure 5.40 TEM images of TiO$_2$/Au/WO$_3$ and Au/TiO$_2$/WO$_3$ nanostructures with two different TiO$_2$ thicknesses. The deposition conditions are described in section 5.4.1.2.

Figure 5.41 HRTEM image of 5 nm Au/TiO$_2$/WO$_3$ nanostructures. The deposition conditions are described in section 5.4.1.2.
Taking 5 nm TiO$_2$/Au/WO$_3$ as an example, electrical mapping and line scan were done by STEM (figure 5.42) to confirm the elements and distribution in the structure. A clear boundary of Ti, W, Au and O can be seen matching with the schematic we drawn in figure 5.33. The elements are uniformly distributed through TiO$_2$ layer, Au NPs and WO$_3$ NN. Line scan also confirms the thickness of TiO$_2$ is 5 nm.

Figure 5.42 Electrical mapping and line scan (top right) of 5 nm TiO$_2$/Au/WO$_3$ by STEM. The deposition conditions are described in section 5.4.1.2.
Al₂O₃/Au/WO₃ and Au/Al₂O₃/WO₃ were built in these orders using a fixed amount of 5 mg Au precursor via AACVD. WO₃ was the standard WO₃ NNS (Chapter 3). Different reaction cycles, 20, 50, 100, 150, and 300 cycles of Al₂O₃ were deposited via ALD. The colour of the Al₂O₃/Au/WO₃ appears purple. With increasing number of ALD cycles, the sample colour becomes darker. The colour of Au/Al₂O₃/WO₃ changed from purple to red with the ALD cycles increase (figure 5.43 and figure 5.44). As the number of ALD cycles relates to film thickness, the change of thin film thickness impacts the optical properties of the whole nanostructures.

**Figure 5.43** Photos of Al₂O₃/Au/WO₃ with 20, 50, 100, 150, 200 and 300 ALD cycles of Al₂O₃ (left to right). The deposition conditions are described in section 5.4.1.3.

**Figure 5.44** Photos of Au/Al₂O₃/WO₃ with 20, 50, 100, 150, 200 and 300 ALD cycles of Al₂O₃ (left to right). The deposition conditions are described in section 5.4.1.3.

The thicknesses of Al₂O₃ thin films related to ALD cycles were measured from the ‘witness’ planar substrate by ellipsometer and shown in table 5.14, and the growth rate as a function of number of cycles is plotted in figure 5.45. The thickness grows steadily with the reaction cycles with an ALD growth rate of 1.0 – 1.3 Å/cycle. There is a strong correlation between the film thickness and the number of ALD cycles.
<table>
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<th>Cycle/ number</th>
<th>Thickness/ nm</th>
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<tbody>
<tr>
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<tr>
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<td>7</td>
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<td>200</td>
<td>20</td>
</tr>
<tr>
<td>300</td>
<td>40</td>
</tr>
</tbody>
</table>

**Table 5.14** Summary of the ALD cycles of Al₂O₃ thin film and the film thickness on Au/WO₃, WO₃ and silicon. The deposition conditions are described in section 5.4.1.3.

**Figure 5.45** Al₂O₃ film growth rate (blue) and film thickness (red) with number of reaction cycles. The deposition conditions are described in section 5.4.1.3.

Figure 5.46 displays XPS spectra of Al₂O₃/Au/WO₃ with various Al₂O₃ thickness on FTO glass. The binding energies of Al 2p shift from 74.4 eV in bare Al₂O₃ to 74.0 eV in Al₂O₃/Au/WO₃. When the thickness of Al₂O₃ thin film increases, the peak intensity of Al 2p increases. The binding energies of Au 4f 5/2 and Au 4f 7/2 shift from 88.0 eV and 84.3 eV in bare Au NPs to 87.5 eV and 83.8 eV in Al₂O₃/Au/WO₃. The intensity of Au 4f peak decreases with the increase of the number of cycles, with very little Au 4f signal intensity remaining 5 nm Al₂O₃ and no Au signal detected after 15 nm which indicates the Al₂O₃ ALD film is less dense than TiO₂. The binding energies of W 4f remain the same of that in bare WO₃ at 37.7 eV and 35.6 eV. The peak intensity of W 4f drops while Al₂O₃ ALD
film thickness increases. The shift of Au 4f peaks indicates that the charge transfer occurs on Au NPs.

Figure 5.46 XPS spectra of a) Al 2p; b) Au 4f and c) W 4f in Al₂O₃/Au/WO₃ nanostructures with various thickness of Al₂O₃ thin films. The deposition conditions are described in section 5.4.1.3.

SEM images of Al₂O₃/Au/WO₃ and Au/Al₂O₃/WO₃ nanostructures with 7 nm Al₂O₃ and 40 nm Al₂O₃ under low magnification are shown in figure 5.47. The nanostructures with thicker Al₂O₃ layers seem slightly larger than that with thinner Al₂O₃ layers. The nanostructures with Al₂O₃ layers on the top also look larger than the nanostructures with Al₂O₃ in the middle.
Figure 5.47 SEM images of Al$_2$O$_3$/Au/WO$_3$ and Au/Al$_2$O$_3$/WO$_3$ nanostructures with two different Al$_2$O$_3$ thicknesses. The deposition conditions are described in section 5.4.1.3.

TEM images help confirm the thickness and uniformity of Al$_2$O$_3$ thin films. From figure 5.48 (a) and (b), 7 nm and 40 nm Al$_2$O$_3$ films in between of WO$_3$ NNs and Au NPs can be seen as 4 nm and 42 nm. From figure 5.48 (c) and (d), 7 nm and 40 nm Al$_2$O$_3$ films on top of Au NPs and WO$_3$ NNs can be seen. The thicknesses shown in TEM images match the measurement in table 5.15 by ellipsometer. For a given number of cycles, similar
thickness were achieved on both the planar substrate (measured using ellipsometry) and the complex nanostructures (measured by TEM). Due to the design of ALD reactor, the precursor flows horizontally. When structures like NNs stand vertically on the substrate, and the more ALD cycles are deposited, the film thickness at the front and back of the needle are more different (figure 5.48 (d)). This also happens with AACVD of Au NPs.

**Figure 5.48** TEM images of Al₂O₃/Au/WO₃ and Au/Al₂O₃/WO₃ nanostructures with two different Al₂O₃ thicknesses. The deposition conditions are described in section 5.4.1.3.

Figure 5.49 shows the UV/Vis absorption spectra of TiO₂/Au/WO₃, Au/TiO₂/WO₃, Al₂O₃/Au/WO₃ and Au/Al₂O₃/WO₃ on FTO glass with “5” nm ALD layers. Using WO₃
as a reference, SPR peak can be observed from all Au samples. TiO$_2$/Au/WO$_3$ has a plasmon peaks at 570 nm while the plasmon peaks for the others are at 540 nm.

![UV/Vis spectra of several nanostructures with 5 nm ALD layers.](image)

**Figure 5.49** UV/Vis spectra of several nanostructures with 5 nm ALD layers.

A group of Au samples were deposited via AACVD and ALD using 0.1 mg Au precursor and 0.5 mg Au precursor, details shown in figure 5.50. The thickness of Al$_2$O$_3$ and TiO$_2$ were set to be 2 nm. The colour of the 0.5 mg Au group follows the principle we mentioned above. The colour of the 0.1 mg Au group appears light pink on the yellow WO$_3$.

![Photos of WO$_3$, 0.5 mg Au/WO$_3$ and other complex structures (left), 0.1 mg Au/WO$_3$ and other complex structures (right).](image)

**Figure 5.50** Photos of WO$_3$, 0.5 mg Au/WO$_3$ and other complex structures (left), 0.1 mg Au/WO$_3$ and other complex structures (right).
Figure 5.51 XPS spectra of a) Au 4f; b) W 4f and c) Ti 2p of Au/WO₃ and other complex structures. XPS spectra of d) Au 4f; e) W 4f and f) Al 2p Au/WO₃ and other complex structures with 2 nm ALD layers.

Figure 5.51 displays XPS spectra of Au samples with TiO₂ (a, b and c) and with Al₂O₃ (d, e and f). For Au samples with TiO₂, the binding energy of Au 4f and W 4f are similar to
that of Au 4f and W 4f in Au/WO₃. The binding energies of Au 4f 5/2 and Au 4f 7/2 shift from 88.0 eV and 84.3 eV in bare Au NPs to 87.5 eV and 84.0 eV. The signal of Ti 2p are extremely low due to the low film thickness. 0.5 mg Au group show higher Au 4f intensity and lower W 4f intensity than 0.1 mg Au group, consistent with a greater amount of gold deposited on the surface of the WO₃.

For Au samples with Al₂O₃, the shift of Au 4f and Al 2p still exists. The binding energies of Al 2p shift from 74.4 eV in bare Al₂O₃ to 74.1 eV. The binding energies of Au 4f 5/2 and Au 4f 7/2 shift from 88.0 eV and 84.3 eV in bare Au NPs to 87.5 eV and 84.0 eV. 0.5 mg Au group also show higher Au 4f intensity and lower W 4f intensity than 0.1 mg Au group.

SEM images of TiO₂/0.5 mg Au/WO₃, 0.5 mg Au/TiO₂/WO₃ and Al₂O₃/0.1 mg Au/WO₃ nanostructures with 2 nm TiO₂ or Al₂O₃ are shown in figure 5.52. For 2 nm ALD layers, it is impossible to see any difference from SEM. Only the size and density difference or Au NPs (~10 nm level) can be distinguished.

![SEM images of TiO₂/Au/WO₃, Au/TiO₂/WO₃ and Al₂O₃/Au/WO₃ nanostructures.](image)

**Figure 5.52** SEM images of a) TiO₂/Au/WO₃; b) Au/TiO₂/WO₃ and c) Al₂O₃/Au/WO₃ nanostructures.

Finally, TEM images help confirm the thickness and uniformity of ALD layers. From figure 5.53 (a) Au/TiO₂/WO₃, small gap between Au NPs and WO₃ NN can be seen, which is believed to be TiO₂ thin layer. From figure 5.53 (b) Al₂O₃/Au/WO₃, 2 nm Al₂O₃ outside the Au/WO₃ can be distinguished.
Figure 5.53 TEM images of a) Au/TiO$_2$/WO$_3$ and b) Al$_2$O$_3$/Au/WO$_3$ nanostructures.

The atomic ratio of W, Au, O, Ti and Al of Au samples are calculated from EDS data. (table 5.15). Au% of 0.5 mg Au group is several times higher than Au% of 0.1 mg Au group. Due to the ultrathin film, Ti% appears zero, Al% is ~ 0.7%. There is also concern that whether detection by EDS is reliable when the wt% is lower than 0.1% [269].

<table>
<thead>
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Table 5.15 Atomic percentage of W, Au, O, Ti and Al of Au samples calculated from EDS data.
5.4.2.2 TiO$_2$/Ag/WO$_3$, Ag/TiO$_2$/WO$_3$, Al$_2$O$_3$/Ag/WO$_3$ and Ag/Al$_2$O$_3$/WO$_3$

A group of Ag samples were deposited via AACVD and ALD using 20 µL and 100 µL Ag precursor, details shown in figure 5.54. The thickness of Al$_2$O$_3$ and TiO$_2$ were set to be 2 nm. The colour of all the Ag samples appears yellow, different from the light yellow of WO$_3$. 100 µL Ag group’s colour is darker than 20 µL Ag group, consistent with greater deposition of Ag with increased precursor amount.

![Figure 5.54](image)

**Figure 5.54** Photos of WO$_3$, 100 µL Ag/WO$_3$ and other complex structures (left), 20 µL Ag/WO$_3$ and other complex structures (right).

Figure 5.55 (a), (b) and (c) show XPS spectra of Ag samples with TiO$_2$. The binding energies of Ag 3d \(3/2\) and Ag 3d \(5/2\) are 374.2 eV and 368.2 eV corresponding to Ag metal \[204\]. The W 4f peaks at 37.8 eV and 35.5 eV of W 4f \(5/2\) and W 4f \(7/2\) corresponding to WO$_3$, which shift 0.4 eV to higher binding energy. The intensity of Ti 2p are low due to the film thickness. Most samples in 100 µL Ag group show higher Ag 3d intensity than 20 µL Ag group, again consistent with greater deposition of Ag when more precursor is used.

Figure 5.55 (d), (e) and (f) show XPS spectra of Ag samples and with Al$_2$O$_3$. For Ag samples with Al$_2$O$_3$, the binding energies of Ag 3d \(3/2\) and Ag 3d \(5/2\) are 374.3 eV and 368.3 eV corresponding to Ag metal \[204\]. The W 4f peaks at 37.8 eV and 35.6 eV corresponding to W 4f \(5/2\) and W 4f \(7/2\) corresponding to WO$_3$. The intensity of Al 2p is barely observable, likely due to the low film thickness, but it is still can be seen at 74.2
eV corresponding to Al$_2$O$_3$. Most samples in 100 µL Ag group show higher Ag 3d intensity and lower W 4f intensity than 20 µL Ag group.

**Figure 5.55** XPS spectra of a) Ag 3d; b) W 4f and c) Ti 2p of Ag/WO$_3$ and other complex structures. XPS spectra of d) Ag 3d; e) W 4f and f) Al 2p Ag/WO$_3$ and other complex structures with 2 nm ALD layers.
Figure 5.56 shows the UV/Vis absorption spectra of all Ag samples on FTO glass with 2 nm ALD layers together. Using WO$_3$ as a reference, for 100 μL Ag/WO$_3$ and 100 μL Ag/TiO$_2$/WO$_3$, additional intensity at ~ 480 nm can be seen, which is associated with the Ag plasmon. No SPR peak can be observed from the rest of the Ag samples. It is probably because the impact of Ag NPs and ALD layers to the optical properties is too small to be observed.

![UV/Vis spectra of Ag samples](image)

**Figure 5.56** UV/Vis spectra of Ag samples.

SEM images of Al$_2$O$_3$/20 μL Ag/WO$_3$ and 20 μL Ag/Al$_2$O$_3$/WO$_3$ nanostructures with 2 nm Al$_2$O$_3$ are shown in figure 5.57. Only Ag NPs of 10 nm can be distinguished from SEM images. Figure 5.57 (a) and (b) show no obvious difference from the location of the Al$_2$O$_3$ layer. From TEM image of 20 μL Ag/Al$_2$O$_3$/WO$_3$ in figure 5.58, a small gap between Ag NPs and WO$_3$ NN can be seen, which is believed to be the Al$_2$O$_3$ thin layer.
Figure 5.57 SEM images of a) Al₂O₃/Ag/WO₃ and b) Ag/Al₂O₃/WO₃ nanostructures.

Figure 5.58 TEM images of Ag/Al₂O₃/WO₃ nanostructures.

The atomic percentage of W, Ag, O, Ti and Al of Ag samples are calculated from EDS data. (table 5.16). There is no obvious difference in Ag% of 20 μL Ag group and 100 μL Ag group. Due to the ultrathin film thickness and Ag NPs size, the atomic percentage of Ag, Ti and Al are all lower than 0.5%.
### EDS (at\%) Table 5.16 Atomic ratio of W, Ag, O, Ti and Al of Ag samples calculated from EDS data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>W</th>
<th>Ag</th>
<th>O</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 μL Ag/WO$_3$</td>
<td>26.0</td>
<td>0.3</td>
<td>73.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/100 μL Ag/WO$_3$</td>
<td>21.6</td>
<td>0.1</td>
<td>77.0</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>100 μL Ag/TiO$_2$/WO$_3$</td>
<td>21.8</td>
<td>0.2</td>
<td>77.8</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$/100 μL Ag/WO$_3$</td>
<td>26.4</td>
<td>0.1</td>
<td>73.4</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>100 μL Ag/Al$_2$O$_3$/WO$_3$</td>
<td>24.0</td>
<td>0.2</td>
<td>75.4</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>20 μL Ag/WO$_3$</td>
<td>23.3</td>
<td>0.1</td>
<td>76.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$/20 μL Ag/WO$_3$</td>
<td>29.7</td>
<td>0.1</td>
<td>69.9</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>20 μL Ag/TiO$_2$/WO$_3$</td>
<td>23.6</td>
<td>0.2</td>
<td>75.8</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$/20 μL Ag/WO$_3$</td>
<td>23.0</td>
<td>0.1</td>
<td>76.4</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>20 μL Ag/Al$_2$O$_3$/WO$_3$</td>
<td>21.2</td>
<td>0.1</td>
<td>78.3</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

5.4.2.3 TiO$_2$/Pt/WO$_3$, Pt/TiO$_2$/WO$_3$, Al$_2$O$_3$/Pt/WO$_3$ and Pt/Al$_2$O$_3$/WO$_3$

A group of Pt samples were deposited via AACVD and ALD using 0.5 mg Pt precursor and 1.5 mg Pt precursor, details shown in figure 5.59. The thickness of Al$_2$O$_3$ and TiO$_2$ were set to be 2 nm. The colour of the 1.5 mg Pt/WO$_3$, 0.5 mg Pt/WO$_3$ and those with TiO$_2$ and Al$_2$O$_3$ layers on the top appear brown. The colour of those with TiO$_2$ and Al$_2$O$_3$ layers in the middle appear blue.

![Figure 5.59](image.png)

**Figure 5.59** Photos of WO$_3$, 1.5 mg Pt/WO$_3$ and other complex structures (left), 0.5 mg Pt/WO$_3$ and other complex structures (right).
Figure 5.60 XPS spectra of a) Pt 4f, b) W 4f and c) Ti 2p of Pt/WO₃ and other complex structures. XPS spectra of d) Pt 4f, e) W /4f and f) Al 2s Pt/WO₃ and other complex structures with 2 nm ALD layers.

Figure 5.60 (a), (b) and (c) show XPS spectra of Pt samples with TiO₂. The binding energies of Pt 4f 5/2 and Pt 4f 7/2 shift from 74.5 eV and 71.4 eV in bare Pt NPs to 74.9 eV.
and 71.6 eV corresponding to Pt metal. The W 4f peaks at 38.2 eV and 36.0 eV corresponding to W 4f \( \frac{5}{2} \) and W 4f \( \frac{7}{2} \), which shift 0.8 eV to higher binding energy still corresponding to \( \text{WO}_3 \). Peak intensities seem unrelated to the amount of Pt precursor used, i.e. increasing the amount of Pt precursor did not appear to increase the amount of Pt deposited. Figure 5.60 (d), (e) and (f) show XPS spectra of Pt samples and with \( \text{Al}_2\text{O}_3 \). The Pt 4f and W 4f peaks are at position as that in bare \( \text{WO}_3 \) and Pt NPs. Because the binding energy of \( \text{Al} \) 2p overlaps with Pt 4f \( \frac{5}{2} \) at 74.2 eV, so \( \text{Al} \) 2s was observed at 118.1 eV instead \(^{[270]} \). Again, Pt peak intensities seem unrelated to the amount of Pt precursor.

Figure 5.61 shows the UV/Vis absorption spectra of all Pt samples on FTO glass with 2 nm ALD layers together. Using \( \text{WO}_3 \) as a reference, no SPR peaks can be seen from UV/Vis of the Pt samples but there is an increase in adsorption of Pt samples across the visible range comparing to \( \text{WO}_3 \).

![Figure 5.61 UV/Vis spectra of Pt samples.](image)
SEM images of TiO$_2$/1.5 mg Pt/WO$_3$, 1.5 mg Pt/TiO$_2$/WO$_3$ and Al$_2$O$_3$/1.5 mg Pt/WO$_3$ nanostructures with 2 nm TiO$_2$ or Al$_2$O$_3$ are shown in figure 5.6. The extra small Pt NPs of 4 nm are still recognizable on WO$_3$. From TEM images in figure 5.6, Al$_2$O$_3$/1.5 mg Pt/WO$_3$ and TiO$_2$/0.5 mg Pt/WO$_3$ show ultrathin Al$_2$O$_3$ ALD layers outside Pt/WO$_3$ which help confirm the thickness and uniformity of ALD layers.

**Figure 5.62** SEM images of a) TiO$_2$/Pt/WO$_3$; b) Pt/TiO$_2$/WO$_3$ and c) Al$_2$O$_3$/Pt/WO$_3$ nanostructures.

**Figure 5.63** TEM images of a) Al$_2$O$_3$/Pt/WO$_3$ and b) TiO$_2$/Pt/WO$_3$ nanostructures.

The atomic ratio of W, Pt, O, Ti and Al of Pt samples are calculated from EDS data. (Table 5.17). There is no obvious difference in Pt% of 1.5 mg Pt group and 0.5 mg Pt group. Because the electron configuration of W and Pt are too close, the Pt peaks and W peaks
in EDS are always overlapping. As W% is much higher than Pt%, the atomic ratio of Pt is more unreliable, probably undervalued.

<table>
<thead>
<tr>
<th>Sample</th>
<th>W</th>
<th>Pt</th>
<th>O</th>
<th>Ti</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 mg Pt/WO₃</td>
<td>24.5</td>
<td>0.5</td>
<td>75.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂/1.5 mg Pt/WO₃</td>
<td>20.2</td>
<td>0.2</td>
<td>79.4</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>1.5 mg Pt/TiO₂/WO₃</td>
<td>21.3</td>
<td>0.2</td>
<td>78.2</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃/1.5 mg Pt/WO₃</td>
<td>20.0</td>
<td>0.6</td>
<td>78.5</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>1.5 mg Pt/Al₂O₃/WO₃</td>
<td>23.2</td>
<td>0.5</td>
<td>75.0</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>0.5 mg Pt/WO₃</td>
<td>22.3</td>
<td>0.3</td>
<td>77.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂/0.5 mg Pt/WO₃</td>
<td>30.1</td>
<td>0.1</td>
<td>69.6</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>0.5 mg Pt/TiO₂/WO₃</td>
<td>26.1</td>
<td>0.1</td>
<td>73.8</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃/0.5 mg Pt/WO₃</td>
<td>23.4</td>
<td>0.2</td>
<td>74.3</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>0.5 mg Pt/Al₂O₃/WO₃</td>
<td>21.9</td>
<td>0.2</td>
<td>77.0</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.17 Atomic ratio of W, Pt, O, Ti and Al of Pt samples calculated from EDS data.

5.4.3 PEC test

5.4.3.1 Tests related to Au

The design of putting ALD layers on top of metal/WO₃ based on the hypothesis that the passivation layer can protect the base material and form a heterojunction between these two, which facilitates the charge separation and transportation and will enhance the PEC performance of this photoanode. The other design using ALD layer as a spacer layer between metal NPs and WO₃ would change the distance between them and therefore change the surface plasmon resonance.
Figure 5.64 I-V curve of Au samples with various thickness of ALD layers comparing to Au/WO$_3$.

TiO$_2$ thin film synthesized via ALD has been in agreement as a material for photocatalytic performance and gas sensing$^{[155,271]}$. Ideally, with TiO$_2$ layers up to a few tens nanometer, the photoelectrochemical performance of the samples should be enhanced. Figure 5.64 (a) and (c) show the linear sweep voltammetry measurement of 5 mg Au samples with various thickness of TiO$_2$ layers. According to literature, Akbari et al$^{[229]}$ reported a plain TiO$_2$-WO$_3$-Au heterojunction which had 3.5 nm ALD TiO$_2$ layers on top showing 2.2 times PEC enhancement of 11 mA at 1V comparing to WO$_3$-Au. 20 cycles TiO$_2$ layers (~2 nm) on WO$_3$-NS/CdS-NR arrays also enhanced the photocurrent density at 1 V (vs RHE) from 5.2 mA/cm$^2$ to 7.0 mA/cm$^2$ by 1.3 times comparing to WO$_3$-NS/CdS-NR arrays$^{[272]}$. No literature of TiO$_2$ as a spacer layer was reported. However, no photocurrent enhancement has been shown from our samples with TiO$_2$ layers. The samples with
thicker TiO$_2$ have lower photocurrent density, but the decay of photocurrent density does not follow the thickness increase of the ALD layer.

One usage of the conformal Al$_2$O$_3$ is as a barrier/corrosion resistant layer for electrochemistry/photoelectrochemistry. Al$_2$O$_3$ thin ALD layer of 0.1 to 2 nm was reported as a coating for Fe$_2$O$_3$ photoanode increasing the photocurrent by 3.5 times from 0.24 mA/cm$^2$ to 0.85 mA/cm$^2$ at 1.0 V (vs. RHE) under standard illumination conditions \cite{273}. With a 8.3 nm Al$_2$O$_3$ thin film on WO$_3$, the photocurrent is enhanced up to 3 times of WO$_3$ (2.4 mA/cm$^2$) at 0.97 V (vs. Ag/AgCl) under simulated AM 1.5G illumination (120 mW/cm$^2$) \cite{274}.

To evaluate the quality of the coating, the photoelectrochemical performance was tested (figure 5.64 (b) and (d)). The results demonstrate that increasing the Al$_2$O$_3$ film thickness beyond 100 deposition cycles (~ 10 nm) both on the top or in the middle of the nanostructures lead to a significant decrease in photocurrent density, as expected for high dielectric material. Consequently, both the XPS and PEC data indicate that even for a 100 cycles coating, the Al$_2$O$_3$ film was conformal and without pinholes on these high aspect ratio, porous nanostructures. It may be a good corrosion passivation layer which resist the generation and recombination of the electrons and holes, however, with worse PEC performance likely due to poor charge carrier transport across the layer.

As tested in Section 4.3.4, lower metal precursor amount provides better PEC performance. Subsequently lower Au concentrations, 0.1 mg and 0.5 mg Au precursor have been tried to prepare Au NPs. The thickness of ALD layers was set to 2 nm (50 cycles). This time, all Au samples show increase in photocurrent, especially the 0.1 mg Au group (figure 5.65 (a)). Table 5.18 Shows that the photocurrent density of bare WO$_3$ NNs film is 0.61 mA/cm$^2$ at 1.23 V (vs. RHE). 0.1 mg Au/WO$_3$ has the highest photocurrent density among all at 0.97 mA/cm$^2$ at 1.23 V (vs. RHE) which is 1.5 times of WO$_3$. Below this, 0.1 mg Au/TiO$_2$/WO$_3$ and TiO$_2$/0.1 mg Au/WO$_3$ have a photocurrent density at 0.91 mA/cm$^2$ at 1.23 V (vs. RHE). 0.1 mg Au/Al$_2$O$_3$/WO$_3$ has a photocurrent
density at 0.87 mA/cm$^2$ and Al$_2$O$_3$/0.1 mg Au/WO$_3$ have a photocurrent density at 0.86 mA/cm$^2$ at 1.23 V (vs. RHE). As mentioned in Section 4.3.4, in the literatures, the photocurrent enhancement rate of metal/WO$_3$ is 1.39 – 1.77 times of WO$_3$ \[95,226,227\]. The films reported with higher enhancement rate have lower photocurrent than this work. No samples with ALD coatings beat Au/WO$_3$ in 0.1 mg Au group, but the performance of all of them are greater than WO$_3$ NNs alone.

Figure 5.65 (b) measured the photocurrent density of 0.5 mg Au samples in 0.1 M H$_2$SO$_4$ which was also shown in table 5.18. The photocurrent density of 0.5 mg Au/WO$_3$ is 0.59 mA/cm$^2$ at 1.23 V (vs. RHE) showing no obvious change from that of WO$_3$ (0.61 mA/cm$^2$ at 1.23 V (vs. RHE)). Al$_2$O$_3$/0.5 mg Au/WO$_3$ has the highest photocurrent density at 0.87 mA/cm$^2$ at 1.23 V (vs. RHE) while 0.5 mg Au/Al$_2$O$_3$/WO$_3$ has a photocurrent density at 0.79 mA/cm$^2$ at 1.23 V (vs. RHE). 0.5 mg Au/TiO$_2$/WO$_3$ and TiO$_2$/0.5 mg Au/WO$_3$ have a photocurrent density at 0.72 mA/cm$^2$ at 1.23 V (vs. RHE). In this case samples with ALD layers show better PEC performance than 0.5 mg Au/WO$_3$. However, the total performances of 0.5 mg Au group are lower than that the 0.1 mg Au group. Together with previous measurement for 5 mg Au group, as the concentration of Au decreased, the photocurrent density increases. This is probably because of the over-deposition of Au NPs on WO$_3$ NNs which somehow reduce the effective area of WO$_3$ that absorbing light. Wu et al \[95\] also reported while the concentration of Au precursor for photodeposition on WO$_3$ increased from 0 to 240 μM, the PEC performance of Au/WO$_3$ first increases from 1.8 mA/cm$^2$ to 2.4 mA/cm$^2$ at 1.0 V (vs. SCE) for 8 μM precursor and decreases steadily to 1.5 mA/cm$^2$ when the precursor concentration added to 240 μM. By decreasing the amount and size of Au NPs, SPR effect would also enhance the photocurrent density.
Figure 5.65 I-V curve of Au samples with a) 0.1 mg and b) 0.5 mg Au precursor comparing to WO$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photocurrent density at 1.23 V (vs. RHE) / (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$ dark</td>
<td>0.03</td>
</tr>
<tr>
<td>WO$_3$ light</td>
<td>0.61</td>
</tr>
<tr>
<td>0.1 mg Au/WO$_3$</td>
<td>0.97</td>
</tr>
<tr>
<td>0.1 mg Au/TiO$_2$/WO$_3$</td>
<td>0.91</td>
</tr>
<tr>
<td>TiO$_2$/0.1 mg Au/WO$_3$</td>
<td>0.91</td>
</tr>
<tr>
<td>0.1 mg Au/Al$_2$O$_3$/WO$_3$</td>
<td>0.87</td>
</tr>
<tr>
<td>Al$_2$O$_3$/0.1 mg Au/WO$_3$</td>
<td>0.86</td>
</tr>
<tr>
<td>0.5 mg Au/WO$_3$</td>
<td>0.59</td>
</tr>
<tr>
<td>0.5 mg Au/TiO$_2$/WO$_3$</td>
<td>0.72</td>
</tr>
<tr>
<td>TiO$_2$/0.5 mg Au/WO$_3$</td>
<td>0.72</td>
</tr>
<tr>
<td>0.5 mg Au/Al$_2$O$_3$/WO$_3$</td>
<td>0.79</td>
</tr>
<tr>
<td>Al$_2$O$_3$/0.5 mg Au/WO$_3$</td>
<td>0.87</td>
</tr>
</tbody>
</table>

Table 5.18 Photocurrent density of samples shown in figure 5.56 at 1.23 V (vs. RHE).

To study the plasmonic effect of Au NPs, a 420 nm cut-off filter was used to shield the illumination whose wavelength is shorter than 420 nm. As the band gap of WO$_3$ NNs lies at $\sim$ 450 nm, cutting off the UV and near UV light will help isolate the enhancement provided by Au NPs whose peak absorption is at $\sim$ 560 nm. Taking 0.1 mg Au group as
an example in figure 5.66, the photocurrent density of bare WO₃ NNs film is 0.09 mA/cm² at 1.23 V (vs. RHE), i.e. in the absence of ultra-bandgap irradiation is near zero. Except 0.1 mg Au/Al₂O₃/WO₃, other samples have ~ 0.1 mA/cm² at 1.23 V (vs. RHE). Therefore, the main increasing of photocurrent under illumination is not coming from the plasmonic enhancement of Au NPs. Therefore, the reason is more likely to be that Au NPs help the further separation of electrons and holes.

![I-V curve of Au samples with 420 nm light cut-off filter using 0.1 mg Au precursor comparing to WO₃.](image)

**Figure 5.66** I-V curve of Au samples with 420 nm light cut-off filter using 0.1 mg Au precursor comparing to WO₃.

Using Au/TiO₂/WO₃ as an example, the diagram of the charge separation process is drawn in figure 5.67. When the film is under sufficient light illumination, electrons in the valence band (VB) are excited to the conduction band (CB) in both WO₃ and TiO₂, and holes are generated in valence band. Semiconductor/metal junctions are heterostructures that reduce the electron/hole recombination through the separation of the photoelectrons from the conduction band of the semiconductor to the surface of the metal NPs. The photogenerated electrons in the conduction band of TiO₂ can shift into Au NPs through the Schottky barrier because of its small work function and low overpotential of Au.
leaving the holes on the valence band of TiO$_2$. However, surface plasmon resonance helps electrons to transfer from Au NPs to TiO$_2$. Therefore, the photogenerated holes of WO$_3$ will transfer to the valence band of TiO$_2$ to oxidize water. The photogenerated electrons of TiO$_2$ transfer to the conduction band of WO$_3$ to reduce water. Au NPs help efficiently separate the electrons and holes and avoid the recombination of electrons and holes. This leads to the increasing of photoelectrochemical ability.

![Diagram of charge separation process of Au/TiO$_2$/WO$_3$.](image)

**Figure 5.67** Diagram of charge separation process of Au/TiO$_2$/WO$_3$.

### 5.4.3.2 Tests related to Pt

Pt samples have two concentration groups, 0.5 mg Pt group and 1.5 mg Pt group. The thickness of ALD layers deposited was set to 2 nm (50 cycles). In figure 5.68 (a) and table 5.19, the photocurrent density of bare WO$_3$ NNs film is 0.80 mA/cm$^2$ at 1.23 V (vs. RHE). 0.5 mg Pt/WO$_3$ has a photocurrent density at 0.86 mA/cm$^2$ at 1.23 V (vs. RHE). 0.5 mg Pt/TiO$_2$/WO$_3$ and TiO$_2$/0.5 mg Pt/WO$_3$ both have a photocurrent density at 0.76 mA/cm$^2$ at 1.23 V (vs. RHE), both lower than bare WO$_3$ NNs and Pt/WO$_3$. 0.5 mg Pt/Al$_2$O$_3$/WO$_3$ has the highest photocurrent density among all at 0.92 mA/cm$^2$ and Al$_2$O$_3$/0.5 mg Pt/WO$_3$ has the lowest photocurrent density at 0.47 mA/cm$^2$ at 1.23 V (vs. RHE). 0.5 mg Pt/WO$_3$ and those with TiO$_2$ ALD layers show low PEC performance curves before 1.2 V (vs.
RHE) which is not desirable for water splitting. Al₂O₃ ALD films give unexpected results which are hard to explain.

In figure 5.68 (b), the photocurrent density of bare WO₃ NNS film is 0.80 mA/cm² at 1.23 V (vs. RHE). 1.5 mg Pt/WO₃ has a photocurrent density of 0.55 mA/cm² at 1.23 V (vs. RHE), lower than that of WO₃ NNS. 1.5 mg Pt/TiO₂/WO₃ and TiO₂/1.5 mg Pt/WO₃ have photocurrent densities of 0.58 mA/cm² and 0.49 mA/cm² at 1.23 V (vs. RHE), similar to that of Pt/WO₃. 1.5 mg Pt/Al₂O₃/WO₃ and Al₂O₃/1.5 mg Pt/WO₃ have the photocurrent densities of 0.37 mA/cm² and 0.56 mA/cm² at 1.23 V (vs. RHE), similar to that with TiO₂ layers and Pt/WO₃ but lower than that of bare WO₃ NNS. The only Pt/WO₃ example from literature has a photocurrent enhancement rate of 2.63 times comparing to WO₃ [228]. The films reported with higher enhancement rate have lower photocurrent than this work. The photocurrent density increasing rate is slow at low voltage range. All samples in 1.5 mg Pt group have lower photocurrent densities than WO₃, which indicates the over-deposition of Pt NPs. In conclusion, Pt NPs deposited via AACVD, at least at these two concentrations, are not suitable for water splitting in our nanostructure. Typically, low loadings of metal NPs tend to be the optimal for achieving the highest potential of the electron trap process. When the metal NPs are overload, the electron traps are converted into charge carrier’s recombination sites, leading to the dramatic drop of the PEC performance. Naseri et al [96] reported photocurrent enhancement of Ag/WO₃ with 1 mol% and 2 mol% Ag but sharply decreased photocurrent for 5 – 20 mol% Ag. It confirmed that further increasing of the Ag mol% led to reduction of electron lifetime and photoelectrochemical reactions which is attributed to a high concentration of Ag⁺ ions on the surface which trap photogenerated electrons.
Figure 5.68 I-V curve of Pt samples with a) 0.5 mg and b) 1.5 mg Pt precursor comparing to WO₃.

Table 5.19 Photocurrent density of samples shown in figure 5.58 at 1.23 V (vs. RHE).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photocurrent density at 1.23 V (vs. RHE) (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₃ dark</td>
<td>0.03</td>
</tr>
<tr>
<td>WO₃ light</td>
<td>0.80</td>
</tr>
<tr>
<td>0.5 mg Pt/WO₃</td>
<td>0.86</td>
</tr>
<tr>
<td>0.5 mg Pt/TiO₂/WO₃</td>
<td>0.76</td>
</tr>
<tr>
<td>TiO₂/0.5 mg Pt/WO₃</td>
<td>0.76</td>
</tr>
<tr>
<td>0.5 mg Pt/Al₂O₃/WO₃</td>
<td>0.92</td>
</tr>
<tr>
<td>Al₂O₃/0.5 mg Pt/WO₃</td>
<td>0.47</td>
</tr>
<tr>
<td>1.5 mg Pt/WO₃</td>
<td>0.55</td>
</tr>
<tr>
<td>1.5 mg Pt/TiO₂/WO₃</td>
<td>0.58</td>
</tr>
<tr>
<td>TiO₂/1.5 mg Pt/WO₃</td>
<td>0.49</td>
</tr>
<tr>
<td>1.5 mg Pt/Al₂O₃/WO₃</td>
<td>0.37</td>
</tr>
<tr>
<td>Al₂O₃/1.5 mg Pt/WO₃</td>
<td>0.56</td>
</tr>
</tbody>
</table>

5.4.3.3 Tests related to Ag

Ag samples also have two concentration groups, 20 µL Ag group and 100 µL Ag group. The thickness of ALD layers deposited was set to 2 nm (50 cycles). In figure 5.69 (a) and Table 5.20, the photocurrent density of bare WO₃ NNs film is 0.61 mA/cm² at 1.23 V (vs.
20 μL Ag/WO$_3$ has a photocurrent density at 0.90 mA/cm$^2$ at 1.23 V (vs. RHE), an increase on bare WO$_3$ NNs. 20 μL Ag/TiO$_2$/WO$_3$ and TiO$_2$/20 μL Ag/WO$_3$ have photocurrent densities of 0.97 mA/cm$^2$ and 0.76 mA/cm$^2$ at 1.23 V (vs. RHE). 20 μL Ag/Al$_2$O$_3$/WO$_3$ and Al$_2$O$_3$/20 μL Ag/WO$_3$ have photocurrent densities of 0.64 mA/cm$^2$ and 0.95 mA/cm$^2$ at 1.23 V (vs. RHE). All 20 μL Ag samples have better PEC performance than bare WO$_3$. However, not all 20 μL Ag samples with ALD layers are better than 20 μL Ag/WO$_3$. There is no clear trend in terms of ALD layer on top or ALD layer in between.

In figure 5.69 (b), the photocurrent density of bare WO$_3$ NNs film is 0.61 mA/cm$^2$ at 1.23 V (vs. RHE). All 100 μL Ag samples have better PEC performance than bare WO$_3$. 100 μL Ag/WO$_3$ has a photocurrent density of 0.96 mA/cm$^2$ at 1.23 V (vs. RHE). From the literature, photocurrent enhancement rate for Ag/WO$_3$ is 1.44 – 3.67 [96,199,228] comparing to WO$_3$. 100 μL Ag/TiO$_2$/WO$_3$ and TiO$_2$/100 μL Ag/WO$_3$ have photocurrent densities of 0.96 mA/cm$^2$ and 0.82 mA/cm$^2$ at 1.23 V (vs. RHE). 100 μL Ag/Al$_2$O$_3$/WO$_3$ and Al$_2$O$_3$/100 μL Ag/WO$_3$ have the photocurrent densities of 0.94 mA/cm$^2$ and 0.67 mA/cm$^2$ at 1.23 V (vs. RHE). TiO$_2$ ALD layer in between the nanostructures seems to give better PEC performance than others. 100 μL Ag group shows higher photocurrent density than 20 μL Ag group. This indicates that Ag NPs concentration and size in Ag/WO$_3$ are in suitable range for SPR effect which enhancing water splitting ability.
Figure 5.69 I-V curve of Ag samples with a) 20 μL and b) 100 μL Ag precursor comparing to WO$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photocurrent density at 1.23 V (vs. RHE)/ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_3$ dark</td>
<td>0.03</td>
</tr>
<tr>
<td>WO$_3$ light</td>
<td>0.61</td>
</tr>
<tr>
<td>20 μL Ag/WO$_3$</td>
<td>0.90</td>
</tr>
<tr>
<td>20 μL Ag/TiO$_2$/WO$_3$</td>
<td>0.97</td>
</tr>
<tr>
<td>TiO$_2$/20 μL Ag/WO$_3$</td>
<td>0.76</td>
</tr>
<tr>
<td>20 μL Ag/Al$_2$O$_3$/WO$_3$</td>
<td>0.64</td>
</tr>
<tr>
<td>Al$_2$O$_3$/20 μL Ag/WO$_3$</td>
<td>0.95</td>
</tr>
<tr>
<td>100 μL Ag/WO$_3$</td>
<td>0.96</td>
</tr>
<tr>
<td>100 μL Ag/TiO$_2$/WO$_3$</td>
<td>0.96</td>
</tr>
<tr>
<td>TiO$_2$/100 μL Ag/WO$_3$</td>
<td>0.82</td>
</tr>
<tr>
<td>100 μL Ag/Al$_2$O$_3$/WO$_3$</td>
<td>0.94</td>
</tr>
<tr>
<td>Al$_2$O$_3$/100 μL Ag/WO$_3$</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 5.20 Photocurrent density of samples shown in figure 5.56 at 1.23 V (vs. RHE).

Using Ag/Al$_2$O$_3$/WO$_3$ as an example, the diagram of the charge separation process is drawn in figure 5.70. When the film is under sufficient light illumination, electrons in the valence band are excited to the conduction band in WO$_3$ and holes are generated in the valence band. As the thickness of Al$_2$O$_3$ ALD layer is very thin, it is not treated as a
dielectric material. It has been reported that coating Fe$_2$O$_3$ photoanode with a very thin layer (0.1 to 2 nm) of Al$_2$O$_3$ by ALD resulted in a significant decrease in the overpotential required to photo-oxidize water $^{[273]}$. The higher Fermi level of Ag than that of WO$_3$ results in the photogenerated electrons transferring from Ag NPs into the conduction band of WO$_3$ across the Schottky barrier in order to equalize the Fermi level and leave the holes in the valence band of WO$_3$. Ag NPs help efficiently separate the electrons and holes and avoid the recombination of electrons and holes, leading to increasing photoelectrochemical performance. Also because of the SPR effect of Ag NPs, which is expressed by the oscillation of the electrons in the conduction band of the electromagnetic excitation at a determined wavelength (by suitable NP distances) is provided $^{[276]}$.

**Figure 5.70** Diagram of charge separation process of Ag/Al$_2$O$_3$/WO$_3$.

As Ag samples have the best performance among all three metal NPs, chronoamperometry measurement of 20 μL Ag group and 100 μL Ag group were measured at 1 V (vs. RHE) to evaluate the stability of the photoanode during photoelectrochemical water splitting (figure 5.71 and figure 5.72) to ensure the performance enhancement was not related to oxidation of Ag metal. The photoactivity of WO$_3$ dropped rapidly in the first hour during light illumination with ~ 63% photocurrent retained. After 8 hours, only ~ 32% photoactivity of bare WO$_3$ remains, after 24 h, ~ 20%
remains. For 20 μL Ag/WO₃, ~ 73% photocurrent density is still remaining after 8 h illumination, and ~ 58% photocurrent density remains after 24 h. Other 20 μL Ag samples with ALD layers: 20 μL Ag/TiO₂/WO₃, 20 μL TiO₂/Ag/WO₃, 20 μL Ag/Al₂O₃/WO₃ and 20 μL Al₂O₃/Ag/WO₃ have approximately 54%, 54%, 51% and 31% photocurrent density at the end of test, all in excess of that found for WO₃ NNs alone. With 20 μL Ag NPs, the stabilities are much higher than bare WO₃, which indicates the long-term electrons/holes separation in the structure system. However, the ALD layers doesn’t show any further passivation function to prevent the photoanode from losing activity. This is in contrast with the literature[229] that ALD TiO₂ layers was found to prevent the photocurrent density of the base material without any decay for 1 h.

![Figure 5.71 I-T curve of Ag samples using 20 μL Ag precursor comparing to WO₃.](image)

For 100 μL Ag/WO₃, ~ 74% photocurrent density is still remaining after 8 h illumination, ~ 53% photocurrent density remains after 24 h compared to WO₃ (~ 20%). Other 100 μL Ag samples with ALD layers: 100 μL Ag/TiO₂/WO₃, 100 μL Ag/Al₂O₃/WO₃ and 100 μL
TiO₂/Ag/WO₃ have approximately 60%, 44% and 42% photocurrent density left, again all higher than bare WO₃ NNs. With 100 μL Ag NPs, the stabilities are also much higher than bare WO₃, which is similar to 20 μL group. 100 μL Ag/TiO₂/WO₃ has the most photocurrent density remaining among these samples.

The use of ALD layers in these complex nanostructures was not fully successful according to the previous discussion. The reason still needs to be investigated. It can be errors and uncertainty existing during deposition and measurement. Maybe the thickness, size or structure of each material need to be further optimized.

![Figure 5.72 I-T curve of Ag samples using 100 μL Ag precursor comparing to WO₃.](image-url)
5.5 Conclusions

WO₃ NNs film, Au, Ag and Pt NPs, TiO₂ thin film and Al₂O₃ thin film were deposited on FTO glass for water splitting via AACVD or ALD in specific order to build several complex nanostructures.

TiO₂/Au/WO₃, Al₂O₃/Au/WO₃, Au/TiO₂/WO₃ and Au/Al₂O₃/WO₃: Different cycles of ALD layers were deposited on Au samples. The thickness of the amorphous TiO₂ and Al₂O₃ thin film was monitored by ellipsometer. The growth rate of TiO₂ thin film is 0.5 – 0.8 Å/cycle. The growth rate of Al₂O₃ thin film is 1.0 – 1.3 Å/cycle. XPS spectra shows the uniform and pinhole free TiO₂ and Al₂O₃ films with no Au 4f signal when the films are thicker than 5 nm. SEM and TEM images confirm the film thickness of ALD layers and the whole morphology of these nanostructures. Electrical mapping and line scan of STEM were used to discuss the elements and distribution in one sample as an example. UV/Vis of Au samples show SPR peaks of Au NPs. These all confirm the successful construction of the complex nanostructures. The PEC measurements of all 5 mg Au samples give decreases of photocurrent density comparing to WO₃.

Au samples were successfully constructed with lower Au concentrations using 0.1 mg Au precursor and 0.5 mg Au precursor. The thickness of Al₂O₃ and TiO₂ were set to be 2 nm and confirmed by TEM. XPS spectra confirm the Al³⁺ and Ti⁴⁺ occurred in the nanostructures and show the peak shift of Au. SEM reaches the resolution limit when analysing the samples by only recognizing Au NPs. The atomic ratio of W, Au, O, Ti and Al of Au samples are calculated from EDS data which seems to be unreliable. 0.1 mg Au/WO₃ has the highest photocurrent density among all at 0.97 mA/cm² at 1.23 V (vs. RHE) which is 1.5 times of WO₃. 0.5 mg Au samples with ALD layers show better PEC performance than 0.5 mg Au/WO₃. But the photocurrent density of the 0.5 mg Au group is worse than the 0.1 mg Au group.
**TiO₂/Ag/WO₃, Al₂O₃/Ag/WO₃, Ag/TiO₂/WO₃ and Ag/Al₂O₃/WO₃:** Ag samples were successfully constructed with 20 μL and 100 μL Ag precursor and 2 nm ALD layer which was confirmed by TEM. XPS spectra confirm the Al³⁺ and Ti⁴⁺ occurred in the nanostructures. Binding energy peak intensity is related to Ag precursor amount. SEM gives the morphology of WO₃ NNs with 10 nm size Ag NPs. The atomic ratio of W, Ag, O, Ti and Al of Ag samples are calculated from EDS data with very low Ag%. 100 μL Ag/TiO₂/WO₃ has the highest photocurrent density of 0.96 mA/cm² at 1.23 V (vs. RHE). All 20 μL Ag samples have better PEC performance than bare WO₃. The current density of 100 μL group is even higher than 20 μL Ag group. Not all Ag samples with ALD layers are better than Ag/WO₃. The stability of the photoanodes were measured by chronoamperometry. Ag/WO₃ with and without ALD layers are all more stable than WO₃ film after 24 h. The use of ALD layers wasn’t fully successful, the parameters need to be further optimized.

**TiO₂/Pt/WO₃, Al₂O₃/Pt/WO₃, Pt/TiO₂/WO₃ and Pt/Al₂O₃/WO₃:** Pt samples were successfully constructed with 1.5 mg and 0.5 mg Pt precursor and 2 nm ALD layer which was confirmed by TEM. XPS spectra confirm the Al³⁺ and Ti⁴⁺ occurred in the nanostructures. SEM gives the morphology of WO₃ NNs with 4 nm size Pt NPs. The atomic ratio of W, Pt, O, Ti and Al of Pt samples are calculated from EDS data with undervalued low Pt%. Part of 0.5 mg Pt group and the whole 1.5 mg Pt group have lower photocurrent densities than WO₃, which indicates the over-deposition of Pt NPs.
Chapter 6. Conclusions and future work

6.1 Conclusions

This thesis used atomic layer deposition (ALD) and aerosol assisted chemical vapour deposition (AACVD) as the synthetical techniques to develop a series of materials for photoelectrochemical (PEC) purpose. In summary, 1. tungsten oxide (WO₃) nanoneedles, 2. gold (Au), silver (Ag) and platinum (Pt) nanoparticles, 3. titanium oxide (TiO₂) thin film and aluminium oxide (Al₂O₃) thin film were successfully synthesized and constructed to form 4. complex nanostructures. Their deposition parameters, properties and PEC performance were systematically studied.

WO₃ nanoneedles film was deposited via AACVD. The crystal structures of WO₃ are in monoclinic phase with a growth preference in [0 0 2] direction. The WO₃ NNs film is formed by a large number of 3 μm long WO₃ nanoneedles whose diameter changes from 150 nm (thick end) to 30 nm (thin tip). The band gap of WO₃ NNs calculated from UV/Vis spectra and Tauc plot is ~ 2.6 eV. WO₃ film morphologies caused by different precursors and solvents have been compared and morphology with higher surface area (NNs) produce higher photocurrent density. The reproducibility of WO₃ NNs film shows an average photocurrent density of ~ 0.68 mA/cm² at 1.23 V (vs. RHE) with a standard deviation of 0.1.

AACVD works relating to metal oxide and metal nanoparticles and their applications have been investigated. Till now, there is little research on using metal NPs decorated metal oxide deposited via AACVD for water splitting, especially metal/WO₃. Research was many done for gas sensing, transparent conducting oxide and photocatalysis. Some of these researches used capping agents to prevent the nanoparticles from aggregation. However, organic shells were more likely to remain on the nanoparticles which were confirmed by SEM. Most literature showed the decoration and dopant preparation using only one condition which makes it harder to know if it is the amount, size or coverage of
the materials is optimized. In our research, two steps AACVD reaction was performed to deposit WO$_3$ decorated evenly with Au, Ag and Pt NPs without the use of capping agent.

Au, Ag and Pt NPs were successfully deposited using HAuCl$_4$$\cdot$3H$_2$O, Ag-AMP and H$_2$ClPt$\cdot$xH$_2$O as the precursors dissolving in methanol deposited via AACVD on FTO glass and on WO$_3$ NNs film. Cubic phase pure Au, Ag and Pt were shown from separated characterisations. The calculation from XPS data indicates that lower deposition temperatures and lower metal precursor amounts provide higher metal to W ratio (at%). SPR peaks of Au, Ag and Pt NPs were investigated, respectively. The size, shape and density of the metal nanoparticles were studied regarding to the amount and deposition temperature of metal precursors. The size and density of Au NPs became smaller and lower, the shapes became more regular when the conditions were optimised. The size of Au, Ag and Pt NPs on WO$_3$ under the optimised conditions are $\sim$ 8 – 10 nm, $\sim$ 10 nm and $\sim$ 2 – 4 nm, respectively. The crystallized Pt NPs showed highly coverage and sometimes aggregation on WO$_3$ NNs. These as-deposited metal NPs show quite different morphologies and properties.

Linear sweep voltammetry was used to investigate the photoelectrochemical performance of Au/WO$_3$, Ag/WO$_3$ and Pt/WO$_3$. Bare Au NPs were confirmed not providing much photocurrent. For the Au NPs, it is found that while the amount of Au precursor increases (0.05 – 1.5 mg), the photocurrent density of Au/WO$_3$ first increases comparing to WO$_3$ and then decreases with higher precursor amount (1.7 – 5 mg). The photocurrent densities of Ag/WO$_3$ and Au/WO$_3$ under their optimized deposition conditions showed 1.5 times enhancement compared to WO$_3$ while Pt/WO$_3$ showed 1.33 times PEC enhancement.

TiO$_2$ thin films were deposited via atomic layer deposition on microscope glass slides using titanium isopropoxide (TTIP) and water as precursors. Precursor vapour pressure, dose/purge times, gas flow rate and deposition temperature were established. The relationship between TiO$_2$ film thickness on glass, growth rate and reaction cycles were investigated and used as a reference for generating desired film thickness. The growth
rate of TiO$_2$ deposition was in the range of 0.5 – 0.7 Å/cycle. The TiO$_2$ thin films were confirmed to be highly uniform, pinhole free and amorphous.

Atomic layer deposition of Al$_2$O$_3$ thin films were attempted using two aluminium precursors, aluminium isopropoxide (AIP) and aluminium tri-sec-butoxide (ATSB). The parameters of Al$_2$O$_3$ deposited using AIP via CVD and ALD have been investigated. Al$_2$O$_3$ was successfully deposited via ALD using ATSB as the metal precursor. The process was first optimized in CVD mode to confirm desired precursor temperature and gas flow rate, then in pulsed CVD mode to confirm the vapour dose and finally in ALD mode to optimize the deposition temperature, dose time/purge time, deposition and gas flow rate. The composition and morphology of the as-synthesized Al$_2$O$_3$ films under different conditions were analysed. A stable ALD process with a growth rate of 1 – 1.4 Å/cycle was observed by measuring the Al$_2$O$_3$ film thickness on different substrates using ellipsometry. By comparing the film morphology on silicon, quartz and glass, the similar Al$_2$O$_3$ particle size (15-25 nm) can be seen with the root mead square roughness around 1 nm. The obtained films were dense and continuous with a low concentration of impurities.

These WO$_3$ NNs film, Au, Ag and Pt NPs, TiO$_2$ thin film and Al$_2$O$_3$ thin film were constructed together on FTO glass in specific order for water splitting. WO$_3$ NNs was the base material on FTO surface. Au, Ag and Pt NPs were used as catalyst or surface plasmon resonance spot to enhance the PEC performance. TiO$_2$ and Al$_2$O$_3$ thin film were act as a protection layer outside or a spacer layer in between.

Different cycles of ALD layers were deposited on 5 mg Au samples to study the effect of layer thickness on PEC. The thickness of the amorphous TiO$_2$ and Al$_2$O$_3$ thin film was monitored by ellipsometer. PEC measurements of all 5 mg Au samples give decreases of photocurrent density comparing to WO$_3$. Au samples were successfully constructed with lower Au concentrations using 0.1 mg Au precursor and 0.5 mg Au precursor with the thickness of Al$_2$O$_3$ and TiO$_2$ set to be 2 nm. 0.1 mg Au/WO$_3$ has the highest photocurrent
density among all at 0.97 mA/cm² at 1.23 V (vs. RHE) which is 1.5 times of WO₃. 0.5 mg Au samples with ALD layers show better PEC performance than 0.5 mg Au/WO₃.

Pt samples were successfully constructed with 1.5 mg and 0.5 mg Pt precursor and 2 nm ALD layer. The atomic ratio of W, Pt, O, Ti and Al of Pt samples are calculated from EDS data with undervalued low Pt%. Part of 0.5 mg Pt group and the whole 1.5 mg Pt group have lower photocurrent densities than WO₃, which indicates the over-deposition of Pt NPs.

Ag samples were successfully constructed with 20 μL and 100 μL Ag precursor and 2 nm ALD layer. 100 μL Ag/TiO₂/WO₃ has the highest photocurrent density of 0.96 mA/cm² at 1.23 V (vs. RHE). All 20 μL Ag samples have better PEC performance than bare WO₃. The current density of 100 μL group is even higher than 20 μL Ag group. Not all Ag samples with ALD layers are better than Ag/WO₃. The stability of the photoanodes were measured by chronoamperometry. Ag/WO₃ with and without ALD layers are all more stable than WO₃ film after 24 h.

It was a new attempt to build these complex sandwich nanostructures and use them for water splitting. However, the performance of ALD layers in the structures wasn’t fully successful. The application mechanism remains unclear and the deposition parameters need to be further optimized.
6.2 Future work

Photocurrent density stability of the samples have not all been tested yet, which should be finished. The deposition temperature, precursor amount and gas flow rate of Ag NPs and Pt NPs were based on the optimization of Au NPs via AACVD and experience of the materials. More systematic optimization should be done to study the PEC performance of them. More PEC measurement can be done to further discuss their PEC properties.

The use of TiO$_2$ and Al$_2$O$_3$ thin films wasn’t fully successful. The relationship between ALD layers and metal NPs probably are unsuitable which need to be studied.

The fundamental mechanism of photocurrent enhancement in complex nanostructures is still unclear. The mechanism could be because of the SPR effect, more efficient light absorbing of the less shielded WO$_3$ or a Schottky barrier formed between the interface of metal NPs and WO$_3$. Monochromator equipped PEC instrument can be used to study the photocurrent density at specific wavelength. Transient absorption spectroscopy can be used to study the mechanism of separation and recombination of electrons and holes between each material.

The design of AACVD and ALD reactor may limit the deposition results. The gas flow in both reactors goes horizontally which causes film thickness and structure difference at the inlet side and outlet side. If the gas flows vertically from the top, a more orderly nanoarray or film will be deposited. This can be achieved by modifying the reactor.

The pipework of ALD have been changed from 1/8-inch to 1/4-inch diameter to reduce the chance of blockages. However, the heating method and the nature of solenoid valves leave some part of the pipes under temperature and still have the risk of blocking. The solenoid valves used on the ALD system have a switch on/off limit down to ~ 1.5 seconds which we also need to consider reducing the long reaction time. Otherwise, commercial
ALD can be tried to compare the different between the same TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} deposited from two systems.

The samples should also be tested in neutral electrolyte and basic electrolyte to investigate the use of metal NPs and ALD layers.

Other semiconductor materials such as ZnO, NiO thin films can also be used to replace TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} as the passivation layer or spacer layer.

Other methods such as sol-gel, electrical reduction and sputtering can be used to synthesis these materials. A combination of Au, Ag and Pt NPs is also an idea to test on the WO\textsubscript{3} NNs.

These complex nanostructures we design also have potentials in other aspect. Applications such as photodegradation, photocatalysis and gas sensing are interesting to be tested.
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Appendix

Comparison of different thickness measurement techniques

When the deposition method changed to ALD, the films become thinner and more uniform, which reduced the possibility of the appearance of birefringence. In addition, the standard refractive index (n) of Al$_2$O$_3$ at 587 nm is 1.77 while the refractive index of glass is 1.52 [277,278] which makes it difficult to distinguish the film and substrate from the substrate. Therefore, the accuracy of different thickness measurement and calculation methods need to be considered. In this report, we compared the thickness measured by spectral reflectance, ellipsometry and the Swanepoel method using UV/Vis data, along with the advantages and disadvantages of these three methods.

One sample was selected for these three measurements. The ALD parameters used for this sample were ATSB pulse 2.5 s, Ar purge 1 min, H$_2$O 2 s and Ar purge 5 min using 120 sccm Ar gas flow for 500 cycles. Deposition temperature was 200 °C, ATSB precursor temperature was 120 °C and H$_2$O precursor temperature was 5 °C.

![Figure A1 Spectral reflectance measurement and simulation of the film thickness of Al$_2$O$_3$ deposited at 200 °C for 500 cycles on glass.](image)
Spectral reflectance. From figure A1, the thickness obtained from spectral reflectance is 417.81 nm (goodness of fit is only 0.02166 but by eye it appears a reasonable fit).

Spectral reflectance is one of the most common optical measurement types which measures the amount of perpendicular incident light reflected from a thin film surface over a range of wavelengths [279]. The advantages of using spectral reflectance is that it is easy to use, only a recipe file with literature values and one measurement are needed then the software would do the simulation automatically. However, it is hard to tell if the simulation is correct or not as the goodness of fit parameter is unreliable. If the sample is not uniform or have larger porosity, spectral reflectance is not that suitable to do the measurement as it can’t realize accurate measurement for the porosity and roughness change. If the sample have multilayers of film with similar refractive index and thickness is not high enough to show a number of obvious oscillations (e.g. only part of one oscillation) in the graph, it is hard for the software to do the simulation especially for this Al₂O₃/glass sample, more than one result that match the measured reflectance might be shown. Later we changed the substrates to silicon and quartz which reduced this problem due to the change in refractive index of the substrate.
**Figure A2** Ellipsometry measurement and simulation of the film thickness of Al$_2$O$_3$ deposited at 200 °C for 500 cycles on glass. a) $\Psi$; b) $\Delta$.

Ellipsometry. The thickness obtained from ellipsometry is 442 nm ($R^2=0.7157$), the $\Psi$ and $\Delta$ (two parameters for polarization) fittings of 5 different incident angles are shown in figure A2. Refractive index ($n=1.5729$ @632.8 nm), extinction coefficient ($k=0.00000079$ @632.8 nm), dielectric constants ($\varepsilon_1$, $\varepsilon_2$) and correlation coefficients could be listed as well. Porosity can be measured by adding a void layer and doing simulation.

Ellipsometry is another common optical measurement method. If the film is too thin, too porous or too complicated to be measured by spectral reflectance, they can be measured by spectroscopic ellipsometry. The two different polarization and multiple incidence
angle measurements provide more information for simulation and the flexible parameters changes can provide more reliable results. The drawback is that the manual simulation might result in multiple outcomes if the models and parameters are not well fitted.

UV/Vis. Swanepoel method \cite{188} was first described by R. Swanepoel in 1983 using transmission spectrum from UV/Vis is to calculate the thickness of thin films. The calculations are listed in equation A1.

\begin{align}
\text{(1)} & \quad s = \frac{1}{T_s} + \left( \frac{1}{T_s} - 1 \right)^{\frac{1}{2}} \\
\text{(2)} & \quad N = 2s \frac{T_M - T_m}{T_MT_m} + \frac{s^2 + 1}{2} \\
\text{(3)} & \quad n = \left[ N^2 + (N^2 - s^2)^{\frac{1}{2}} \right]^{\frac{1}{2}} \\
\text{(4)} & \quad d = \frac{\lambda_1\lambda_2}{2(\lambda_1n_2 - \lambda_2n_1)} \quad (A1)
\end{align}

s, substrate index of refraction (1.51 in this case); \(T_s\), transmission through the substrate; n, film refractive index; \(T_M\), the maximum extremes of the interference fringes; \(T_m\), the minimum extremes of the interference fringes; \(\lambda_1\), \(\lambda_2\), two different wavelengths for adjacent maxima/minima; d, film thickness.
Figure A3 Transmittance of Al₂O₃ film deposited at 200 °C for 500 cycles on glass (red) and bare glass (black) measured by UV/Vis spectrophotometer.

<table>
<thead>
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<th>λ/ nm</th>
<th>T_M</th>
<th>T_m</th>
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<th>n</th>
<th>d</th>
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<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table A1 Simulated values for λ, T_M, T_m and calculation of N, n and d.

Therefore, from the measurement and calculation in figure A3 and table A1, this film thickness is 429 nm. For the thickness close to this value, the calculation is already difficult because of the high transmission of this sample. The fringes are hardly distinguished, however if the film becomes thinner, there will be less fringes in the wavelength range, and it becomes even harder to calculate.