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Plasmonic-Assisted Water–Gas Shift Reaction of Gold Particles on TiO\textsubscript{2}

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Abstract: The Localized Surface Plasmon (LSP) effect of 5 nm mean size Au particles deposited on TiO\textsubscript{2} P25 was investigated during the photo-thermal water gas shift reaction (WGSR). The effects of CO concentration, excitation light flux and energy, and molecular oxygen addition during the reaction were investigated. The photocatalytic WGSR rate under light excitation with wavelengths extending from 320 to 1100 nm was found to be higher than the thermal reaction alone at the same temperature (85\textdegree C). A H\textsubscript{2}/CO\textsubscript{2} ratio of near unity was found at high concentrations of CO. The addition of molecular oxygen during the reaction resulted in a slight decrease in molecular hydrogen production, while the rates of CO\textsubscript{2} formation and CO consumption changed by one order of magnitude. More importantly, it was found that the WGSR rates were still high under only visible light excitation (600–700 nm). The results prove that Au LSP alone triggers this chemical reaction without requiring the excitation of the semiconductor on which they are deposited.

Keywords: Au/TiO\textsubscript{2} P25; localized surface plasmon (LSP); photo-thermal water–gas shift reaction (WGSR); hydrogen production; preferential oxidation reaction (PROX)

1. Introduction

The water–gas shift reaction (WGSR) is one of the important industrial processes for adjusting the CO to H\textsubscript{2} ratio for methanol synthesis and for producing high-purity H\textsubscript{2} for ammonia synthesis. In the WGSR, CO(g) reacts with H\textsubscript{2}O(g), forming CO\textsubscript{2}(g) and H\textsubscript{2}(g).

\[
\text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g) \quad \Delta H = -41.1 \text{ kJ/mol}
\]

The WGSR is performed at low (190–250 \textdegree C) and high (400–500 \textdegree C) temperatures with Cu/ZnO and Fe\textsubscript{2}O\textsubscript{3}-based catalysts, respectively [1]. At high temperatures, the CO conversion is equilibrium-limited, and, at low temperatures, the reaction is kinetically limited.

In addition to iron- and copper-based catalysts, precious-metal (Au, Pt, and Pd)-containing catalysts have been investigated for WGSR at low temperatures [1–4]. Previous studies found a much higher WGSR activity of gold nanoparticles on reducible supports such as TiO\textsubscript{2} and CeO\textsubscript{2} than that on Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} [3,5]. Among these catalysts, Au/TiO\textsubscript{2} showed comparable WGSR activity to that of commercial Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts [2]. It has also been proposed that the WGSR on Au-based catalysts takes place at the interfacial sites [5,6]. The proposed active interfacial site on Au/TiO\textsubscript{2} is Au\textsuperscript{5−}...O\textsubscript{V}...Ti\textsuperscript{3+} (O\textsubscript{V}: oxygen vacancy), where electron-enriched Au\textsuperscript{5−} species enhance CO chemisorption, while O\textsubscript{V}...Ti\textsuperscript{3+} contributes to the dissociation of water [5].
Mainly, two reaction mechanisms, redox (also called regenerative) and associative, have been proposed for the WGSR [7]. In the redox mechanism, CO reacts with the lattice O of the catalyst, forming CO2 and creating vacant sites. Then, H2O dissociates, filling the vacant sites, whereas the two protons of water take the two electrons left upon the creation of the vacancy and thus make one hydrogen molecule. In the associative mechanism, intermediate species are formed from the reaction between CO and surface -OH species derived from the dissociation of water. The proposed intermediates in previous studies are formate species (HCOO(a)) [3,8], carbonate-like species, and carboxyl (HOCO) [9], which decompose, forming CO2 and H2. In some studies, formates and carbonate-like species have been reported to be spectators [10,11]. To our knowledge, the carboxyl species has not been observed experimentally on Au/TiO2.

The redox mechanism usually takes place at high temperatures, whereas the associative mechanism occurs at low temperatures. However, density functional theory (DFT) calculation results have indicated that it is difficult for carboxyl species to form during the WGSR on Au/TiO2 catalysts at low temperatures. It was also found that formates are too stable to release H2, and hence it was suggested that the redox mechanism is the primary reaction pathway at low temperatures [12]. Another DFT computation study on the WGSR mechanism over Au10, Au13, and Au20 clusters reported that the carboxyl mechanism occurred over Au10 and Au20 clusters, while the redox mechanism took place over the most active Au13 cluster [13]. Despite these theoretical studies, the associative mechanism is still widely accepted as the pathway of the WGSR at low temperatures.

On precious-metal/TiO2 catalysts such as Au/TiO2 [14], Pt/TiO2 [4,15], and Pd/TiO2 [16], not only thermal but also photo-assisted WGSRs have been studied. A photocatalytic WGS at low or ambient temperatures offers economical and environmental advantages. In particular, H2/CO2 would be generated at a desired ratio via a cleaner process using sunlight as an energy source. It has been proposed that the photo-assisted WGSR on M(Au, Pd, and Pt)/TiO2 occurs at the M/TiO2 interface [16], similar to the thermal WGSR [8]. However, the photocatalytic WGS over Pt/TiO2 and Pd/TiO2 occurs efficiently only at very low concentrations of CO. At high concentrations of CO, the rates of H2 and CO2 production decrease. There is a net negative effect on activity upon increasing the concentration of CO due to the strong adsorption of CO on Pt or Pd [15,16]. Au/TiO2 may function without a negative effect on the activity at higher CO concentrations due to the weak CO adsorption on Au particles.

Au/TiO2 catalysts have also been reported to show catalytic activity for CO oxidation at low temperatures [17]. Thermal CO oxidation on Au/TiO2 has been proposed to occur predominantly through a Au-assisted Mars–van Krevelen (MvK) mechanism for reaction temperatures of 80 °C and above [18]. In the MvK mechanism, first, CO molecules adsorb on Au particles and then abstract TiO2 lattice oxygen at the Au/TiO2 interface; finally, CO2 molecules desorb, forming oxygen vacancies and reduced Au/TiO22−.x. The next step in the Au-assisted MvK mechanism is the re-oxidation of the previously reduced catalyst [18]. Green et al. also proposed that CO oxidation on Au/TiO2 occurred on metal sites at the Au/TiO2 interface [19]. It has also been shown that O-O bond scission is activated by the formation of a CO-O2 complex at the Au/TiO2 interface [17,19]. Moreover, the performance of Au/TiO2 catalysts for CO oxidation improves in the presence of water [20]. A water-mediated reaction mechanism for room-temperature CO oxidation over Au/TiO2 catalysts has been proposed [21]. DFT calculations showed that proton transfer at the Au/TiO2 interface facilitates O2 activation and binding, leading to the formation of Au–OOH that readily reacts with adsorbed CO on Au, forming Au–COOH. Au–COOH decomposes and forms hydrogen and CO2.

Previous studies have also shown the preferential oxidation (PROX) of CO in the presence of H2 on Au/TiO2 [20,22–25]. The PROX reaction of CO on Au/TiO2 in the presence of light irradiation has also been reported previously [26–28]. The UV irradiation of Au/TiO2 promotes the preferential oxidation of CO in a H2-rich stream [27]. The chemisorption of CO on Au/TiO2 was enhanced by UV irradiation, but the chemisorption of H2 was sup-
pressed on both TiO$_2$ and Au surfaces. It has been reported that PROX reaction rates were increased by up to a factor of 3 when Au/TiO$_2$ was irradiated by visible or UV light [26]. Yoshida et al. reported that the PROX rates of CO on Au/TiO$_2$ under dark conditions increased in the presence of UV–visible light due to the effect of charge separation due to localized surface plasmon resonance (LSPR) and the promoted electron transfer to the adsorbed O$_2$ [26]. It has also been proposed that the photo-generated electrons from TiO$_2$ cause changes in the chemisorbed energy of CO, H$_2$, and O$_2$ on Au/TiO$_2$ in a manner that promotes the preferential oxidation of CO in a H$_2$-rich stream [27].

Localized surface plasmons resonance (LSPR) are oscillations of free electrons. These are confined to the surface of gold nanoparticles (among other materials). Upon resonance, the charge oscillations create an intense local electric field (EF) on the surfaces of these nanoparticles. These oscillations have been studied in order to enhance the photocatalytic activity of semiconductors such as TiO$_2$ [29–32]. The effect on enhancing the reaction rate was found to be generally weak. The mechanism by which plasmonic metal nanoparticles improve energy conversion can be seen as a photonic or electronic effect. Photonic enhancement occurs through far-field scattering or near-field enhancement, while an electronic effect occurs via increasing local generation of electron hole pairs through direct electron transfer or resonant energy transfer, directly exciting electron–hole pairs non-radiatively through the relaxation of the surface plasmon dipole.

Overall there are many studies on thermal WGSRs [5,10,33–36] and the PROX of CO [20,22,24,37,38] on Au/TiO$_2$, but only a few investigations have reported on photo-assisted WGSRs [14] and the PROX of CO [26,27], and further studies are required to acquire a fundamental understanding of these reactions. We have opted to study an unusually high loading of Au (8 wt.%) on TiO$_2$P25. We have previously studied a series of different Au wt.% on this support [39]; in these studies, Au particles were deposited via the deposition precipitation method [40]. This is particularly important in order to enhance their LSPR effect when compared to the semiconductor-alone (band gap) effect. In this study, we investigated the photo-assisted WGSR and the PROX of CO on 8 wt.% Au/TiO$_2$ at 85 °C.

2. Results and Discussion

We have previously studied a family of Au/TiO$_2$ P25 catalysts in some detail [39,41,42]. These studies included core and valence-level spectroscopy, XRD, photo-luminescence, UV-Vis absorbance, TEM, and EXAFS. Here, we give a brief description of the relevant information related to the present study. Figure 1 presents selected data replotted from ref. [39]. Figure 1A presents the UV-Vis of TiO$_2$ P25 without and with different gold loadings from 0.5 to 10 wt.%. TiO$_2$ P25 contains about 80–20 of anatase and rutile, with their band gaps being 3.2 (385 nm) and 3.0 (410 nm), respectively; here, only the edge is shown for simplicity. The absorbance due to gold plasmons (localized surface plasmon (LSP) of Au nanoparticles) starts at about 100 nm after the band gap of TiO$_2$. The LSP is centered at about 560 nm. Its intensity increases non-linearity with increasing Au coverage and becomes wider. A widening of the peak is seen at both energy sides (towards the IR and UV regions). It should be noted that the particles, even at 8–10 wt.%, are not touching each other; they are still dispersed on the surface. The TEM images in the insets show largely round particles from which an average size of 5.1 nm was extracted. Figure 1B shows XPS Au4f data of the same series. The binding energies at about 83.6 and 87.3 eV are for Au4f$_{7/2}$ and Au4f$_{5/2}$, respectively. Their peak areas increase linearly with increasing coverage and all have a small shift of about 0.2–0.4 eV to lower energy levels (when compared to bulk Au at 84.0 eV). The slight shift to lower energy might have been due to interfacial charge transfer or band bending and has not been corrected. The 8 wt.% corresponded to about 3 at.%. Recall that XPS presents the surface and near-surface atoms only and therefore the extracted number differs from that found for bulk. Figure 1C presents the valence band of the same series. It contains, in addition to the O2p structure in the 3–9 eV range (for pure TiO$_2$), the Au5d band when Au is present. The Fermi level was determined to be at the Au6s band binding energy position. This is more pronounced for the highly loaded
catalysts. The catalyst used in this study is therefore composed of Au particles (5.1 nm average size), largely in a metallic state (XPS Au4f, Au6d binding energy position), with 3 at. % and with a pronounced plasmon centered at about 560 nm and extending from 400 to 900 nm. The XRD patterns for the Au/P25 TiO2 photocatalysts [35,39] are dominated by peaks due to anatase and rutile phases (85/15 weight ratio). Broad and weak signals were seen at 2θ = 44.4°, 65.6°, and 77.6°, which were due to Au (200), Au (220), and Au (311) reflections, respectively. The Au particles were of a mean size of 5.1 nm, these are extracted from counting a large number of particles in different like those presented in Figure S1A.

In Figures S2–S8 in the Supporting Information, the fluxes and energies of the different light excitations used are given. In the following, we present the thermal and photo-thermal photocatalytic reactions of CO and H2O to CO2 and H2 over the 8 wt.% Au/TiO2 P25 catalyst. In order to do so, we changed the excitation energy in order to probe the effect of Au LSPR on the reaction rate. Similar results will be discussed in more detail in Section 2.3.

2.1. Photocatalytic Water–Gas Shift Reaction at ≈25 °C (Room Temperature)

First, we have investigated the photocatalytic WGSR at ≈25 °C. At this temperature, there was no contribution from thermal activity. The photons’ energy extended from 320 nm to 1100 nm, and the light fluxes in the UV (320–400 nm), visible (400–800 nm), and IR (800–1100 nm) regions were 8, 67, and 62 mW/cm². The rates of production of H2 and CO2 were found to be equal to 3.6 × 10⁻⁸ and 4.6 × 10⁻⁸ moles/min, respectively. Similar results will be discussed in more detail in Section 2.3.

2.2. Thermal Water–Gas Shift Reaction

To identify the effect of temperature, the thermal WGSR at 85, 150, 200, and 250 °C was performed in the absence of light irradiation. In all the experiments, water was used in excess (with a ratio of [H2O]/[CO] > 3), and [CO] was kept at 6.7 × 10⁻⁶ mol/mL. The H2 production rate was found to be about 4.9 × 10⁻⁷ mol/min at 85 °C, whereas
it was 40 times higher, ca. $2 \times 10^{-5}$ mol/min, at 250 °C. In these experiments, high concentrations of reactants were used so that the production rate would be less affected by changes in their concentration. Figure 2A,B show the production of H$_2$ and CO$_2$; CO consumption; and the Arrhenius plot for H$_2$ production from which an activation energy of 32.5 kJ/mol was extracted. The activation energy for industrial low-temperature and high-temperature water–gas shift reactions were reported to be 52 and 110 kJ/mol over CuZnO and Fe$_3$O$_4$–Cr$_2$O$_3$, respectively [43].

**Figure 2.** (A) CO consumption and H$_2$ and CO$_2$ production as a function of time at 150 °C during the WGSR reaction over 8 wt.% Au/TiO$_2$ P25. (B) Arrhenius plot for the hydrogen production rates of WGSR on the same catalyst. The rate constants are shown in Table 1. (C) H$_2$ and CO$_2$ formation and CO consumption during thermal WGSR at 85 °C.

In order to more accurately monitor the consumption of CO, the thermal WGSR was carried out with a lower initial concentration of CO, 5 mL of CO ($2.2 \times 10^{-4}$ moles/reactor volume or about $2 \times 10^{-6}$ mol/mL), and 20 μL of water at a temperature of 85 °C. The initial ratio of H$_2$O to CO in the gas phase was 3, and the results are presented in Figure 2C. The data show that the amounts of H$_2$ and CO$_2$ formed increased, whereas the amounts of CO decreased, with time. The rate of consumption of CO was $4.8 \times 10^{-7}$ mol/min, and the initial rates of production of H$_2$ and CO$_2$ were $2.4 \times 10^{-7}$ and $3.4 \times 10^{-7}$ mol/min, respectively. The rate of CO consumption was found to be 1.4 times higher than the rate of production of CO$_2$, indicating that a fraction of CO converted to form adsorbed species, which do not further react to form CO$_2$. In addition, a small fraction of CO converted to CH$_4$ as evidenced by the detection of a trace amount of this compound via gas chromatography. However, the methanation of CO generally requires reaction temperatures greater than 573 K [26]. The initial ratio of H$_2$ to CO$_2$ production was about 0.85, which was calculated after subtracting the CO$_2$ formed by CO oxidation with the residual O$_2$ ($\sim 6 \times 10^{-6}$ moles) present after purging the reactor. The observed H$_2$ to CO$_2$ ratio was lower than the expected value of 1.0, showing that H$_2$ is consumed by some side reactions, such as methanation to form CH$_4$, as discussed earlier, and reaction with residual O$_2$ to form H$_2$O. A ratio of H$_2$/CO$_2$ of less than 1.0 was reported by others for the WGSR on Au/TiO$_2$ [14] and Pt/TiO$_2$ [4]. The previously reported ratio of H$_2$ to CO$_2$ for a WGSR carried out on 1 wt.% Au/TiO$_2$ was 0.78, whereas it was in the range of 0.7–1.0 on Pt/TiO$_2$ with and without irradiation [4].

The thermal WGSR at 85 °C may take place via an associative mechanism described in the Introduction section. In the associative mechanism, first, intermediate species, such as formates, are formed at the Au/TiO$_2$ interface via the reaction between adsorbed
CO and surface OH groups, derived from the dissociation of H$_2$O on TiO$_2$, as reported previously [8]. Thus, the formed intermediate species react to form H$_2$ and CO$_2$. Adsorbed formate species on catalyst surfaces have been detected in many studies via infrared spectroscopy and have been proposed to be intermediates [3,8].

The formation and decomposition of formates on Au/TiO$_2$ can be seen in the following:

$$\text{CO (g) + H}_2\text{O (g) + O(s) }\rightarrow\text{CO(a) + OH(a) + OH(s)}$$ \hspace{1cm} (1)

The above reaction depicts the molecular and dissociative adsorption of CO and water, respectively.

Formate formation

$$\text{CO(a) + OH(a) }\rightarrow\text{HCOO(a)}$$ \hspace{1cm} (2)

Formate decomposition

$$\text{HCOO(a) }\rightarrow\text{CO}_2 + [\text{H(a)}]$$ \hspace{1cm} (3)

[ ] indicates that the species is a not stable intermediate

$$[\text{H(a)}] + \text{OH(s)} \rightarrow \text{H}_2\text{(g) + O(s)}$$ \hspace{1cm} (4)

Hydrogen production

Here, (g), (s), and (a) stand for gas, surface, and adsorbed, respectively.

Deviation from stoichiometry between CO$_2$ and H$_2$ occurred at 85 °C for both CO concentrations investigated. This was not found at higher temperatures (at 150, 200, and 250 °C the ratio was ≈1). This might be linked to the formation of hydrogen in the reaction (Equation (4)). The following sentences may explain the reason for this. Strictly, one hydrogen molecule originates from the reaction of a hydride (upon the dissociation of the C–H of a formate) and a proton (upon the dissociation of a molecule of water). In other words, this is a recombination reaction with two distinctly different species (one hydrogen with two electrons (a hydride) and a proton). It is notable that a hydride was not seen on Ti cations of TiO$_2$ (this is the reason the brackets on Equation (3) are put, so it is considered a transition-state intermediate). On the other hand, CO$_2$ formation results from the direct decomposition of a formate species (Equation (3)). It is possible that during the recombination (of H$^-$ (a) and H$^+$ (a)), the hydride loses one or two electrons to the lattice. When the temperature is increased, the species may have enough motion (thermal energy) to increase the reaction rate and prevent electron loss. These phenomena may explain the deviation of stoichiometry around a temperature of 85 °C.

Table 1. Hydrogen production rates at different temperatures during the WGSR over 8 wt.% Au/TiO$_2$ P25.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>T (K)</th>
<th>1/T(K)</th>
<th>Rate (H$_2$ moles/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>353</td>
<td>0.002832</td>
<td>4.87 × 10$^{-7}$</td>
</tr>
<tr>
<td>150</td>
<td>423</td>
<td>0.002363</td>
<td>8.69 × 10$^{-6}$</td>
</tr>
<tr>
<td>200</td>
<td>473</td>
<td>0.002113</td>
<td>9.00 × 10$^{-6}$</td>
</tr>
<tr>
<td>250</td>
<td>523</td>
<td>0.001911</td>
<td>1.97 × 10$^{-5}$</td>
</tr>
</tbody>
</table>

2.3. Photo-Assisted Water–Gas Shift Reaction at 85 °C: Effect of CO Concentration

Experiments were performed in the presence of light extending from the UV to IR regions (320–400; 400–750; 750–1100 nm). First, the effect of light intensity was studied while light energy was kept constant. This is shown in Figure 3A,B. The difference in the light flux between A and B was about two (for all light regions). The WGSR shows higher activity compared to the thermal reaction, at the same temperature, in both cases (two to three times higher). However, doubling the light intensity increased this activity by about 30%. We made no attempt to study the light intensity effect because our set up may
not be ideal for such an endeavor. The practical point to extract from this result is that slight variations in light flux reaching the catalyst from one experiment to the other (say, by 10%) would not dramatically affect the comparative study presented next. Again, as in the thermal reaction, the ratio of H₂ to CO₂ was less than the stoichiometric one and saturated faster than that of CO₂. Yet, increasing light intensity improved the ratio. At higher light intensity, the CO₂/H₂ ratio was closer to unity than that at low light intensity (about 0.9). Also, similar to the thermal WGSR, the rate of consumption of CO was 1.3 times higher than the rate of production of CO₂, indicating that a fraction of CO converted to form adsorbed species, which do not all further dissociate to form CO₂.

Figure 3. Effect of changing CO concentration on the H₂ to CO₂ ratio during the photo-thermal WGSR at 85 °C over 8 wt.% Au/TiO₂ P25. For all figures, the same light energy distribution was used. (A) CO₂ and H₂ production and CO consumption as a function of time with an initial CO concentration of ca. 2.5 × 10⁻⁶ mol. (B) The same reaction except for the fact that the light flux was decreased. (C) The same reaction as in B but with an increase in CO concentration to ca. 7.5 × 10⁻⁶ mol. (D) The same reaction as in B but with a further increase in CO concentration to ca. 7.5 × 10⁻⁵ mol.
To identify the effect of higher initial CO concentrations, a WGSR was carried out at higher CO concentration than that used in the experiments described above. In this experiment, the reactor was purged with CO instead of N₂ to decrease any possible outgassing from the wall of the reactor. Figure 3C presents the results for the WGSR under the same light energy and flux as those shown in Figure 3B. Figure 3C shows that the initial concentration of CO was three times that shown in Figure 3B, while that of water was the same. The initial rate of hydrogen doubled (2 × 10⁻⁶ mol/min) and became closer to that of CO₂ (2.4 × 10⁻⁶ mol/min). Figure 3D presents similar results but with an initial CO concentration of 5.8 × 10⁻³ mol, about 26 times that of Figure 3B (the CO to water ratio was near unity). Both CO₂ and H₂ production were virtually the same (with a ratio near unity), while the rate increased to 7 × 10⁻⁶ mol/min. To summarize the findings presented above, it appears that at a high concentration of CO (with negligible O₂ outgassing from the walls of the reactor) and when the ratio of CO/O₂ to H₂ is near unity or above, the ratio of CO₂ to H₂ is near unity, too (see also Table 2). It is most likely that experimental artefacts are behind the sub-stoichiometric ratios observed by others.

### Table 2. Effect of Changing CO concentration on the H₂/CO₂ ratio during the photo-thermal WGSR over 8 wt.% Au/TiO₂ P25.

<table>
<thead>
<tr>
<th>[CO]</th>
<th>[H₂O]</th>
<th>Ratio [H₂O]/[CO]</th>
<th>Initial ( r(H₂) ) mol/min</th>
<th>Initial ( r(CO₂) ) mol/min</th>
<th>Ratio [H₂]/[CO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00022</td>
<td>0.0011</td>
<td>5.0</td>
<td>1.2 × 10⁻⁶</td>
<td>1.5 × 10⁻⁶</td>
<td>0.8</td>
</tr>
<tr>
<td>0.00067</td>
<td>0.0011</td>
<td>1.6</td>
<td>2 × 10⁻⁶</td>
<td>2.4 × 10⁻⁶</td>
<td>0.9</td>
</tr>
<tr>
<td>0.0058</td>
<td>0.0055</td>
<td>≈1</td>
<td>7 × 10⁻⁶</td>
<td>6 × 10⁻⁶</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Cumulative analytical and experimental errors in rates and concentrations are about 10%.

Based on others’ results [14] and our own, one may describe the reaction as follows.

1. UV light excites the TiO₂ catalyst and generates electron hole pairs; then, photo-excited electrons transfer from the conduction band of TiO₂ to Au particles, which is in line with some of our more recent work on TiO₂ and ZnO [44–48], and a reduction of H₂O takes place on Au particles or at the Au/TiO₂ interface to produce H₂.

2. The photo-generated holes oxidize CO to form CO₂ on TiO₂ or at the Au/TiO₂ interface; interface; the oxygen atom, to make CO₂ originates from dissociated water in the form of surface hydroxyls. Although both thermal and photocatalytic WGSRs occurred since the experiment was performed at 85 °C under UV light irradiation, the former was much weaker.

### 2.4. Photo-Assisted Water–Gas Shift Reaction at 85 °C: Effect of O₂ Concentration

The effect of injecting O₂ during the reaction is presented in Figure 4. The objective here was to observe the effect of any potential contamination of O₂ on the reaction rates since both hydrogen and CO oxidation can take place under photon irradiation as well as at 85 °C in the presence of a Au/TiO₂ catalyst. The reaction was induced with a ratio CO to water equal to 1 and with the same photon energy and flux as those used in Figure 3B–D. Initially, only the thermal reaction was conducted at 85 °C (the first 30 min or so in the figure); then, light was turned on. The rates for H₂ and CO₂ production increased and are like those observed in Sections 2.2 and 2.3 (within experimental reproducibility). At about 200 min, 2 mL of O₂ was injected into the reactor. This resulted in a very fast increase in CO₂ production and a very fast consumption of CO. The consumption of CO was, however, higher than the production of CO₂. This indicates that only a fraction of surface species that consumed CO reacted to CO₂. This may point to the buildup of formate species and seems to indicate that their kinetics are too slow at the photon flux used. Also, the decay of the H₂ production rate was found to be mild, much less than the rise in CO₂. This is unlike Pd and Pt, as indicated in the Introduction section, where both are highly active for hydrogen oxidation. The results are in line with the preferential oxidation activity of Au particles observed thermally, shown here under the effect of photons. After a few minutes of reaction in the presence of O₂, the rates for both products started to rise again;
they were, however, weaker. The rate of hydrogen production decreased by half, and that of CO consumption was about four times slower. Table 3 presents the rates of the three compounds before, during, and after O₂ introduction. It is interesting to note that after O₂ injection and possibly its total consumption, the three rates became identical, indicating that the WGSR had become the sole reaction. This might be because the surface/gas reaction reached equilibrium at this point and because the fraction of available sites for reactions had become constant.

![Figure 4](image_url)

**Figure 4.** Effect of oxygen addition on the photo-thermal WGSR as a function of time over 8 wt.% Au/TiO₂ P25. (A) Hydrogen production. (B) CO₂ production. (C) CO consumption.

**Table 3.** Effect of O₂ addition (ca. 9 × 10⁻⁵ mol) on the reaction products and CO consumption during the photo-thermal WGSR over 8 wt.% Au/TiO₂ P25. The colours are used to highlight the three different regions during the reaction.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Molecules of H₂ (mol/min)</th>
<th>Molecules of CO (mol/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.75 × 10⁻⁸</td>
<td>0.5 × 10⁻⁸</td>
</tr>
<tr>
<td>10</td>
<td>1.2 × 10⁻⁸</td>
<td>1.1 × 10⁻⁸</td>
</tr>
<tr>
<td>20</td>
<td>1.3 × 10⁻⁸</td>
<td>1.2 × 10⁻⁸</td>
</tr>
<tr>
<td>30</td>
<td>1.4 × 10⁻⁸</td>
<td>1.3 × 10⁻⁸</td>
</tr>
<tr>
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It is worth presenting, in a few equations, the possible reactions that took place. There are two centers for reactions on the catalyst in the presence of light, namely, the semiconductor (TiO₂) and the metal (Au particles), including their interface. We will first address both separately for simplicity.

Upon light excitation, electrons are transferred from the valence band (VB) to the conduction band (CB) of TiO₂:

\[
h \nu \rightarrow e(CB) + h(VB) \quad (5)\]

In the presence of gas-phase O₂, the latter reacts with e(CB) and becomes O₂⁻, which may dissociate to O⁻ and an O atom.

\[
O_2(g) + e^- (CB) \rightarrow O_2^- \rightarrow O \text{ atom} + O^- \quad (6)\]

The oxygen atom reacts with CO, yielding CO₂, while the O⁻ may react with a proton of a surface OH group, yielding an OH radical (OH*). OH* are powerful oxidants. They then react with CO, yielding formats, and inject an electron into the VB.

\[
CO + O \text{ atom} \rightarrow CO_2(g) \quad (7) \]
\[
O^- + OH(s) \rightarrow OH^* + O(s) \quad (8) \]
\[
OH^* + CO(g) + h(VB) \rightarrow HOCO(a) \quad (9)\]
The sum of the above equations is Equation (10):

\[
2 \text{CO}(g) + \text{O}_2(g) + h\nu + \text{OH}(s) \rightarrow \text{CO}_2(g) + \text{HOCO}(a) + \text{O}(s) \tag{10}
\]

Equations (7) and (9) may explain why the rate of disappearance of CO is twice that of the appearance of \(\text{CO}_2\), since largely only one oxygen atom of molecular oxygen has reacted to give the \(\text{CO}_2\) while the other gave a formate species (if the latter do not have a major role in the reaction at this temperature and light flux). While the initial decrease of hydrogen is due to oxidation to water. The origin of the second decrease after all oxygen had been consumed (compare the photothermal lines before and after oxygen injection) is unclear. A plausible explanation is that \(\text{O}_2\) increases the concentration of formate species, and these have weak decomposition kinetics at the experimental conditions (Equation (9)), blocking some sites required for the regenerative mechanism to occur. This may indicate that, in reality, both mechanisms may occur and compete for the same sites.

The other route is that related to Au particles and their plasmonic effect (LSP). \(\text{O}_2\) can dissociate on Au particles, yet this occurs on those with sizes below 2 nm or so [49–51]. The Au particles of the catalyst used here have a mean particle size of 5 nm (about 3000 atoms); while defects on these and the possible presence of some much smaller particles (not identified by TEM) may still have activity for the dissociative adsorption of \(\text{O}_2\), their effect is neglected here. In particular, a recent time-dependent DFT computational study of Au particles with different sizes provided two important observations that might be relevant to this work [49]. First, it seems that under light excitation, particle size is not determinant, and second, \(\text{O}_2\) dissociates largely because of the presence of an electric field effect and not via charge transfer. Based on these results, there are two distinct ways in which \(\text{O}_2\) dissociation on \(\text{Au/ TiO}_2\) can occur either in the dark or under light excitation. 1. Dark dissociation seems to occur on small Au particles (<2 nm or so). 2. Light-induced dissociation can occur upon \(\text{TiO}_2\) excitation (UV) followed by charge transfer to Au particles and/or upon LSPR that directly excites Au particles (largely via an electric field effect).

2.5. Photo-Assisted Water–Gas Shift Reaction at 85 °C: Effect of Light Energy

Figure 5 presents the data for the WGSR under light excitation with different energies at 85 °C. These light excitation modes were (UV + visible + IR), (UV + visible), and visible. Figure 5A shows hydrogen production under (UV + visible + IR) and (visible + IR). The light flux was kept constant as well as all other parameters. The rates are virtually the same. Therefore, it is clear that light with a wavelength below 400 nm (about 3 eV) is not needed. Since anatase TiO\(_2\) absorbs light only below 400 nm, it is not directly implicated in the reaction. However, since P25 contains about 20% rutile TiO\(_2\), it may still participate in the reaction. Figure 5B presents hydrogen production under similar light excitations but upon removing the late fraction of visible light and all IR light. The rates of hydrogen production under (UV + visible) (up to 620 nm) and visible excitation are very similar. Yet, in this case, the rate has decreased by about 40%. It is thus clear that light with a wavelength above 620 nm still affects the reaction rate. Figure 5C presents the same reaction only under visible light between 500 and 700 nm. These wavelengths excite Au particles only. The rate of hydrogen production is about a third of that in Figure 5A. However, when normalized to the number of photons used, the rate is higher than that obtained when using UV light to excite TiO\(_2\) as well. Actually, when using light above 600 nm, the system still performs well. The straightforward conclusion is that a non-negligible fraction of the catalyst activity in this reaction is due to Au particles being directly excited by visible light, without requiring the use of UV light. Light with an energy level above 2 eV is not needed.
Based on the results found in this work, it appears that a Au/TiO$_2$ P25 catalyst composed of Au particles with an average size of 5 nm at a high enough surface density (3 at.% based on XPS, and about 10% per particle size based on TEM) and with a plasmon extending from 400 to 900 nm (centered at about 560 nm) presents activity for a WGSR under visible light without requiring the use of UV light to excite TiO$_2$. The main barrier for the reaction is that pertaining to electron transfer (initially from CO) leading to the formation of molecular hydrogen (from the protons of surface hydroxyls). Water dissociates readily on TiO$_2$ and does not require the presence of Au particles. CO may adsorb on both TiO$_2$ surfaces (where the adsorption energy is less than 0.5 eV, depending on the coverage) and on Au particles [52–54]). Upon visible light excitation, the LSPR of Au particles occurs. Energetically speaking, this is an electronic transition from 5d to 6s bands. Electrons at the 6s level have sufficient energy to reduce the protons of -OH group to atomic hydrogen while CO recombines with an adsorbed oxygen, with a net result of injecting electrons into the 5d energy level. This is presented in Scheme 1 and in Equations (11)–(15).

\[ \text{Au (LSPR) + visible light} \rightarrow \text{5d-6s transfer} \]  
\[ \text{H}_2\text{O} (a) + 2 e^- (6s) \rightarrow 2\text{H} + \text{O}^{2-} (s) \]  
\[ \text{O}^{2-} (a) + 2 h^+ (5d) \rightarrow \text{O} (a) \]  
\[ \text{O}(a) + \text{CO(a)} \rightarrow \text{CO}_2 (g) \quad \Delta H^\circ_f = -283 \text{ kJ/mol} \]  

Total

\[ \text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ_f = -41 \text{ kJ/mol} \]
The mean particle size is 5 nm. Visible light excitation of about 500–700 nm may enter into (XRD, Rigaku Co., Yokyo, Japan), UV–visible spectroscopy (Shimadzu, Kyoto, Japan), in the present study, the amount of matter was used in excess to avoid rate variations due to 

\[ \text{Ti}_3\text{d}, \text{(CB)} \] of \( \text{TiO}_2 \) react to the CB of \( \text{TiO}_2 \) in Au nanoparticle (5d to 6s excitation, represented by a black vertical arrow)) may be transferred to the CB of \( \text{TiO}_2 \). This would result in the reduction of \( \text{H}^+ \) (of an -OH group at the interface \( \text{Au}/\text{TiO}_2 \)) to a hydrogen atom (this process is repeated twice). At the valence band and adsorbed CO reacts with one O atom from the lattice to give \( \text{CO}_2 \) (the two electrons left regenerate the valence electrons); see Equations (11)–(13).

The 8 wt.% Au/TiO\(_2\) photocatalyst was characterized using transmission electron microscopy (TEM, JEOL Ltd., Tokyo, Japan), X-ray florescence (XRF, Bruker Corp., Billerica, MA, USA) spectroscopy, energy-dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD, Rigaku Co., Yokyo, Japan), UV–visible spectroscopy (Shimadzu, Kyoto, Japan),

\[ \text{Scheme 1. A schematic representation of plasmon enhanced WGS}. \]

Schematic representation of Au LSPR effect on WGS of a 8 wt.% Au/TiO\(_2\) P25 catalyst. Au mean particle size is 5 nm. Visible light excitation of about 500–700 nm may enter into resonance with the 5d–6s band excitation of the Au atoms in the particles. These leave holes in the 5d and transfer electrons to the 6s/Fermi level. At the interface, Au/TiO\(_2\) electrons may be transferred to protons of adsorbed water, while holes react with its oxygen anions. Note that CO oxidation is an exothermic reaction providing energy for the system. Therefore, the chemical input is provided by CO \([55]\) (see Equations (11)–(15)).

The photo-catalytic reaction rate is a function of light flux and exposed area, while catalytic reactions are directly a function of the amount of matter. Therefore, a direct comparison may not be made easily without a devoted study focusing on quantifying the needed parameters for comparison, and this was not the objective of the study. A typical rate for low-temperature-WGSR Au catalysts is about 0.5 mol/g(catal)/h \([56,57]\). In the present study, the amount of matter was used in excess to avoid rate variations due to light matter interaction from one measurement to the other, so only the volumetric rate is considered.

3. Experimental Section
3.1. Preparation and Characterization of 8 wt.% Au/ P25 TiO\(_2\)

The Au/P25 TiO\(_2\) photocatalyst was prepared as described previously \([39]\). Gold nanoparticles (8 wt.%) were deposited on Degussa P25 TiO\(_2\) via the deposition–precipitation-with-urea method described by Zanella et al. \([40]\), with some modifications. Briefly, HAuCl\(_4\)-3H\(_2\)O solution and urea were added to a glass Schott bottle and vigorously stirred. Degussa P25 TiO\(_2\) was then added, and the resulting suspension was thermostated at 80 °C in a dark room for 8 h. After 8 h, yellow Au(III)-impregnated TiO\(_2\) powder was collected via vacuum filtration, washed repeatedly with milli-Q water, and then air-dried at 70 °C overnight. The sample was then calcined at 300 °C for 2 h to thermally reduce the surface Au(III) species on TiO\(_2\) to metallic gold.

The 8 wt.% Au/TiO\(_2\) photocatalyst was characterized using transmission electron microscopy (TEM, JEOL Ltd., Tokyo, Japan), X-ray florescence (XRF, Bruker Corp., Billerica, MA, USA) spectroscopy, energy-dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD, Rigaku Co., Yokyo, Japan), UV–visible spectroscopy (Shimadzu, Kyoto, Japan),
photoluminescence (Horiba, Kyoto, Japan), and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Waltham, MA, USA), and results were reported in a previous publication [39]. The average Au particle size derived from TEM images was ~5.1 nm. The UV–visible absorbance spectrum for the 8 wt.% Au/TiO$_2$ shows an intense absorption below 400 nm due to the P25 TiO$_2$ support and a broad absorption feature ~560–570 nm for the localized surface plasmon resonance (LSPR) of Au nanoparticles supported on TiO$_2$.

3.2. Photoreaction Setup

Photoreactions were carried out in a 140 mL flat bottom glass reactor. A total of 250 mg of Au/TiO$_2$ catalysts was dispersed on the bottom of the glass reactor. We opted to use excess catalyst so that the photocatalytic rate (which is also dependent on the number of photons hitting the catalyst) would have negligible rate variations from one run to the next. Water was added through a micro syringe over the catalyst powder. The reactor was then purged with N$_2$ to remove O$_2$ present in the system. After purging, a small amount of O$_2$, $\approx -6 \times 10^{-6}$ moles (wall outgazing), was present in the reactor. CO was then added to the reactor using a syringe to obtain the desired CO/H$_2$O ratio. All the photo-assisted WGSRs except one were performed at 85 °C in order to keep water in a vapor form. A Xenon lamp, Max 303 from Asahi spectra (Tokyo, Japan), was used as the light source for photoreactions. In some experiments, a CoolLED pE-4000 LED light source (CoolLED, Hampshire, UK) was used and applied to the sample using fiber optics. The reactants and products were analyzed using Gas Chromatography (GC). Hydrogen was analyzed with a Hayesep Q packed column at 45 °C and a Thermal Conductivity Detector (TCD) by using N$_2$ as a carrier gas. Oxygen, CO, and CO$_2$ gases were analyzed with a molecular sieve 5A column at 80 °C and TCD detector, using He as a carrier gas. Fluxes for the different forms of light used are given in Supplementary Materials (Figures S2–S8). All work was conducted at the corporate research center of SABIC at KAUST.

4. Conclusions

A WGSR over 8 wt.% Au/TiO$_2$ P25 (3 at.% Au/TiO$_2$ P25) was investigated thermally and in photo-thermal conditions. The latter was studied under light with different energies and fluxes. This was applied to investigate the effect of the localized surface plasmon (LSP) of the 5 nm mean size Au particles deposited on TiO$_2$ for the reaction and to de-couple it from that of the semiconductor support. In addition, the effects of CO concentration and O$_2$ addition during the reaction were investigated. The photocatalytic WGSR rate under light excitation with wavelengths extending from 320 to 1100 nm was found to be higher than that of the thermal reaction alone at the same temperature (85 °C). The expected ratio H$_2$/CO$_2$ of near unity was found only at high concentrations of CO. The rate of H$_2$ production was much less affected by the addition of O$_2$ than that of CO$_2$ production, indicating that Au/TiO$_2$ performs well for both WGSR and PROX under photo-irradiation. Probably the most notable result observed is that Au particles of 5 nm in size and when present in a high density over the semiconductor oxide support (about 10% particle density) showed equal activity under visible light (600–700 nm) compared to when UV light was also present. Therefore, we concluded that Au LSPR alone triggers this chemical reaction, without requiring the excitation of the semiconductor on which the Au particles are deposited.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/catal13111444/s1. Figure S1: Transmission Electron Microscopy images of 8 wt.% Au/TiO$_2$ P25 with different magnifications; Figure S2: Light flux as a function of wavelengths from 320 to 1100 nm (25% light intensity), Figure S3: Light flux as a function of wavelengths from 320 to 1100 nm (40% light intensity), Figure S4: Light flux as a function of wavelengths from 400 to 1100 nm (25% light intensity), Figure S5: Light flux as a function of wavelengths from 320 to 620 nm (25% light intensity), Figure S6: Light flux as a function of wavelengths from 400 to 660 nm (25% light intensity), Figure S7: Light flux as a function of wavelengths from 610 to 700 nm (LED with band
pass filter at 80% intensity), Figure S8: Light flux as a function of wavelengths from 570 to 610 nm (band pass filter 40% light intensity).

**Author Contributions:** Conceptualization, H.I.; methodology, H.I. and A.K.W.; formal analysis, H.I. and A.K.W.; investigation, A.K.W.; writing—original draft preparation, A.K.W.; writing—review and editing, H.I. and K.M.; supervision, H.I. All authors have read and agreed to the published version of the manuscript.

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