Controllable proton and CO₂ photoreduction over Cu₂O with various morphologies

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Simultaneous photocatalytic reduction of water to H₂ and CO₂ to CO was observed over Cu₂O photocatalyst under both full arc and visible light irradiation (λ > 420 nm). It was found that the photocatalytic reduction preference shifts from H₂ (water splitting) to CO (CO₂ reduction) by controlling the exposed facets of Cu₂O. More interestingly, the low index facets of Cu₂O exhibit higher activity for CO₂ photoreduction than high index facets, which is different from the widely-reported in which the facets with high Miller indices would show higher photoactivity. Improved CO conversion yield could be further achieved by coupling the Cu₂O with RuOₓ to form a heterojunction which slows down fast charge recombination and relatively stabilises the Cu₂O photocatalyst. The RuOₓ amount was also optimised to maximise the junction’s photoactivity.

1. Introduction

Our world is facing complex and intertwined issues on pollution and energy. Rapid economic growth promotes insatiable demand for energy, causing spikes in energy prices coupled with depleting natural resources. At the same time, consumption of energy, fossil fuels in particular, contributes significantly to the increase of greenhouse gases such as CO₂. Many strategies were proposed, but a viable solution requires the utilisation of a renewable energy source and low (initial and running) costs. Photochemical reduction of CO₂ to fuels or value-added chemicals using inorganic semiconductor is an attractive solution for both rising demand for clean energy and the need for greenhouse gas reduction.

Cu₂O is a cheap, relatively abundant and intrinsically p-type semiconductor with a low bandgap of about 2–2.2 eV [12,13]. In theory, the narrow bandgap and appropriate positioning of the conduction and valence bands make Cu₂O an ideal photocatalyst for water splitting and CO₂ reduction.

It is acknowledged that Cu₂O has photo-stability issue that remains a challenge [11,16]. Several correlation studies between photocatalytic reduction activity (of water to H₂) on various Cu₂O exposed facets have been reported previously [22,23], indicating that unconventional Cu₂O shapes consisting mostly of high-index facets display significantly higher activities than conventional ones (cubes, etc.) with mainly low-index facets. We very recently found that Cu₂O is an appropriate candidate photocatalyst for CO₂ photoreduction driven by visible light [4]. It is very interesting to observe the influence of Cu₂O facets on CO₂ photoreduction and the correlation between different Cu₂O shapes and product selectivity between water and CO₂ photoreduction. In this paper, the morphology/exposed Cu₂O facets were tuned and the photocatalytic reactions were investigated in an aqueous suspensions system. Tuneable product selectivity was observed and discussed. Finally, heterojunction of RuOₓ/Cu₂O was optimised to improve Cu₂O photoactivity.

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2. Experimental

Two types of Cu$_2$O powders used in this study, cuboid and octahedral-shaped, were prepared using solvothermal method. Typical synthesis of cuboid-shaped Cu$_2$O involves the dissolution of Cu(NO$_3$)$_2$·2.5H$_2$O in a PTFE lined hydrothermal reactors containing ethanol-water mixture (64:36 volume ratio), and formic acid (1.3 M). Octahedral-shaped Cu$_2$O was synthesised by adding 0.65 M of NH$_4$OH. Deep red/purple precipitates obtained after 2 h reaction at 145°C were washed repeatedly (5–6 times) with copious amount of water (50 ml) and dried in an convection oven (70°C) overnight. Different Cu$_2$O-RuO$_x$ junctions were prepared by impregnation method using appropriate RuCl$_3$·xH$_2$O concentration in water followed by heat treatment then washed for a final time and let to dry at 70°C before finally heated at 200°C for 3 h.

Powder XRD was performed using Panalytical X’Pert powder diffraction system fitted with X’cellerator scanning linear detector in 0.0167° steps, at 10 s acquisition time per step. The incident X-ray is nickel filtered Cu radiation (CuK$_{a1}$: 1.540596 Å, CuK$_{a2}$: 1.544493 Å, CuK$_{a1}$/CuK$_{a2}$ ratio ca. 65/35).

Particle morphology was observed using JEOL-7400 high resolution field emission electron microscope operated at 3 kV accelerating voltage and 10 mA current 0° stage tilt on gold coated powders. TEM measurements were conducted using JEOL-2000-EX-MKII transmission electron microscope (200 kV). Ten points adsorption-desorption tests on the powder samples were performed on Micromeritics® TriStar 3000 with N$_2$ carrier gas to get an estimate of their surface area using BET calculation method.

CO$_2$ reduction reaction was carried out in photocatalyst suspension system using septa-sealed glass chambers fit with flat borosilicate top window (>90% transmittance for λ ≥ 350 nm). Prior to measurements, Cu$_2$O powders and glass chamber were treated at 200°C for 3 h in a convection oven and under 300 W Xe lamp light source for ca. 1 h to remove traces of organic contaminants. A typical photocatalytic experiment is conducted using 0.5 g of photocatalyst in 3 ml of CO$_2$ saturated deionised H$_2$O (Elga Centra). Excess (0.7 M) sodium sulphite was added in each run as hole scavenger while deionised H$_2$O was being purged with CO$_2$, to achieve close to neutral condition (pH ≈ 7.6) before introducing the Cu$_2$O photocatalyst. 150 W Xe lamp (Newport) was used as a light source. Various long pass filters (Comar Instruments) were applied to evaluate the visible light activity. The reaction products were monitored by periodical sampling of the gas phase from the glass chambers using a gas tight syringe to a gas chromatograph (Varian GC-450) fit with thermal conductivity detector (TCD) connected to molecular sieve column to detect H$_2$, CO$_2$, O$_2$ and N$_2$ and flame ionization detector (FID) connected to CP-SIL 5CB (Varian) capillary column to detect hydrocarbons. Argon was used as the GC carrier gas. A methaniser was installed to enable the FID to detect CO and CO$_2$ with 1000× higher sensitivity.

3. Results and discussions

Representative XRD data of both Cu$_2$O powders morphologies are shown in Fig. 1. While all peaks can be matched with the standard Cu$_2$O reference [7], octahedral-Cu$_2$O (Fig. 1a) displayed much sharper and more intense peaks compared to the cuboid-Cu$_2$O (Fig. 1b), suggesting much larger crystallite size. It was also noticed that the intensity ratio between the (111) and (002) reflexions for octahedral-Cu$_2$O was much higher at 3.3 vs. 2.9 for cuboid-Cu$_2$O. This indicates a pronounced {111} preferred orientation on octahedral-Cu$_2$O which are not seen on cuboid-Cu$_2$O.

Fig. 2 shows the different morphologies of as-grown Cu$_2$O. In line with the findings from XRD, it was observed that the octahedral-Cu$_2$O particles were larger than the cuboid-Cu$_2$O (Fig. 2a), in excess of 10 µm (Fig. 2c). Each octahedral displays eight uniform faces, which can be assigned to the Cu$_2$O {111} plane according to the preferred orientation found in the XRD

![Fig. 1](representative_XRD_data_of_octahedral-Cu2O_and_cuboid-Cu2O_aggregates_all_peaks_can_be_matched_with_standard_Cu2O_reference.png)
data. Cuboid-Cu₂O on the other hand, tends to form spherical aggregates of approx. 2 μm diameters (Fig. 2a). The BET surface area of the samples was measured, it is ca. 0.12 m² g⁻¹ for octahedral Cu₂O and 0.55 m² g⁻¹ for cuboid-Cu₂O.

It was also observed using TEM that the individual cuboid-shaped Cu₂O particles were defined as 50–100 nm particles with round edges and corners (Fig. 2b). Electron diffraction data (Fig. 2e) suggested that the six exposed faces of cuboid-Cu₂O could be assigned to the Cu₂O {002} plane, judged by the unusually bright {002} diffraction spot and much weaker {111} diffraction at the same time.

UV–Vis absorption spectra of both Cu₂O morphologies are shown in Fig. 3. While both Cu₂O morphology show similar band edge around 660 nm, although the cuboid-Cu₂O spectra were slightly blue-shifted, probably because of its smaller crystallite size. The estimated bandgaps of cuboid and octahedral-Cu₂O are approx. 1.87 and 1.83 eV respectively.

Despite having over four times lower surface area, octahedral-Cu₂O ([111] terminated) produces much more H₂ with
trace amounts of CO (Fig. 4a and b), indicating the surface are is not the dominating factor in the studies. Cuboid-Cu2O aggregates ([100] terminated) on the other hand display a peculiar preference towards CO2 reduction to CO in expense of reduced H2 production. As the same photocatalytic reaction conditions were applied on both Cu2O shapes, the photoreduction selectivity shift from H2 to CO can only be attributed to the exposed Cu2O facets taking into account the similar UV–Vis absorption of the two samples.

It has been shown previously that catalytic activity can be altered with varying catalyst shape and sizes [9]. The key argument is that the different catalyst shapes dictate the fraction of atom located on the edges, corners, or high-index facets [22]. These locations possess much greater density of unsaturated (slightly under-coordinated) steps, and imperfections like ledges, kinks compared to low indexed planes, which can serve as active sites for breaking chemical bonds [10–17,19]. In some other oxides like ZnO, higher catalytic activity could also rise from the different polarity of the exposed facets [20,21].

Reports on the use of Cu2O for photocatalytic water splitting have always been based on tetrapod-shaped Cu2O, which consists of mainly [111] exposed facets [5,6]. From the different photoreduction products observed in this study, it is proposed the Cu2O [111] facets, seen on the octahedral-Cu2O may be the dominant surface for proton reduction. The Cu2O [100] facets and the irregular edges observed in cuboid-Cu2O aggregates on the other hand is likely dominant for CO2 photoreduction sites. In other words, the low index facets exhibit higher activity for CO2 photoreduction than high index facets, which is different from the common rules mentioned in the introduction. The possible reason for this might be due to the adsorption of CO2 on different facets of Cu2O. More detailed studies are underway.

It was also noticed that the gas evolution rate profile of H2 and CO were different. H2 evolution rates for both Cu2O morphologies are more or less linear with time (Fig. 4b), while the CO evolution rate, especially in the spherical-shaped Cu2O, decreases after the first hour (Fig. 4a). It is possible that this is caused by differing stability of Cu2O [111] and [100] facets in presence of aqueous sulphate as reported previously [15]. Indeed the cuboid-Cu2O was more severely degraded after photocatalytic reactions than octahedral shaped particles (see Supporting Information Figs. S1 and S2), implying that the [111] facets seen on octahedral-shaped Cu2O are much more stable and indeed responsible for proton reduction reactions.

Rapid charge recombination is the key issue in photocatalytic reactions over many photocatalysts [18]. It has preliminarily been observed that a solid-state heterojunction based on CuO can efficiently separates holes from electrons, observed by time resolved spectroscopy [4]. Similar phenomenon was also observed on cobalt phosphate coated Fe3O4 photoelectrodes [1]. RuOx is a conductive metal oxide with large work function [2,3], which has been proven effective as oxidation catalyst for many substances including water [8,14,24]. Different loading amounts of RuOx were therefore investigated in detail herein on cuboid-shaped Cu2O aggregates to find out the optimum RuOx loading. The amounts of CO evolved for the first 30 min were plot in Fig. 5a. It is apparent that the photoreduction activity of the RuOx/cuboid-Cu2O ([100] dominated) junction generally increases with increasing RuOx amount up to 0.25%, due to the enhanced in situ charge separation effect. However as shown in the SEM micrograph of 0.25 wt% RuOx/Cu2O sample (Fig. 2d), the CuO2 surface is nearly fully covered by RuOx, above the amount the light screening effect by the RuOx particulates becomes dominant. The photocactivity decreases after this point onwards until 1.5 wt% of the RuOx loading. Furthermore, the stability of the cuboid-Cu2O ([100] dominated) is relatively enhanced by the surface coating of RuOx layer (see Supporting Information Figs. S1 and S3). It is also noted that the increase of CO production occurs at the expense of H2. The H2 production rate decreases from ca. 50 ppm g\(^{-1}\) h\(^{-1}\) for bare cuboid Cu2O to around 12 ppm g\(^{-1}\) h\(^{-1}\) for 0.25 wt% RuOx loaded cuboid Cu2O. This is likely because the low availability of suitable H2 evolution sites on the cuboid Cu2O surface is further blocked by the RuOx loading.

Cu2O is a narrow bandgap semiconductor. Its photocactivity was also investigated under visible light. The activities of bare and 0.25 wt% RuOx/cuboid-Cu2O were observed by filtering wavelengths below 420 nm using a long pass filter (Fig. 5b). The results clearly show that both bare Cu2O and RuOx/Cu2O junction exhibit visible driven activity for CO2

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**Fig. 4** – Averaged photocatalytic activity of various Cu2O particles or aggregates (a) CO yield, (b) H2 yield under full arc of 150 W Xe lamp. Test conditions: 0.5 g photocatalyst, 3 ml of CO2 saturated deionised H2O, 0.7 M Na2SO3 scavenger.
photoreduction, however the RuO\text{\textsubscript{x}}/Cu\text{\textsubscript{2}O} is much more active than bare Cu\text{\textsubscript{2}O} and able to sustain the CO evolution rate better after the first hour.

4. Conclusions

In summary, we highlighted that the photocatalytic reaction selectivity shifted in favour of CO\textsubscript{2} reduction by tuning the shape and exposed sites of Cu\text{\textsubscript{2}O} photocatalyst. Furthermore, different from the many reports in which the facets with high Miller indices show higher photoactivity, e.g. for water splitting, low index facets of Cu\text{\textsubscript{2}O} is beneficial for CO\textsubscript{2} photoreduction. It was also found that bulk Cu\text{\textsubscript{2}O} instability is a serious issue for photocatalytic CO\textsubscript{2} reduction than H\textsubscript{2} evolution, because the [111] exposed facet that prefers H\textsubscript{2} evolution reaction were found to be much more stable than the [100] in aqueous solution containing sulphates. As expected RuO\text{\textsubscript{x}} loading improves the CO evolution yield under both full arc and visible light irradiation, and the optimum loading for the cuboid-Cu\text{\textsubscript{2}O} aggregates were found at 0.25 wt%, above which the light blocking effect from RuO\text{\textsubscript{x}} dominates and reduce the overall photocatalytic activity.

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Appendix A. Supplementary data

Supporting information: FESEM micrograph of (S1) cuboid-Cu\text{\textsubscript{2}O}, (S2) Octahedral-Cu\text{\textsubscript{2}O} and (S3) heterojunction after 3 h reaction can be found online at http://dx.doi.org/10.1016/j.ijhydene.2013.03.128.

References


