Shape effects of cuprous oxide particles on stability in water and photocatalytic water splitting†

Yongwoo Kwon, Aloysius Soon, Haksoo Han and Hyunjoo Lee

Cuprous oxide (Cu₂O) has received much attention as a photocatalyst due to its direct band gap structure, small band gap energy, non-toxicity, and abundance. However, Cu₂O usually suffers from poor stability because the oxidation state of copper is easily changed. In this work, Cu₂O particles of three different shapes were prepared with distinct surface structures: cubes with (100) facets, octahedra with (111) facets, and rhombic dodecahedra with (110) facets. Their shape stability was estimated in deionized water with or without light irradiation. The Cu₂O(100) facets were selectively deformed under dark conditions, as expected from density functional theory calculations. The rhombic dodecahedra showed the most violent degradation under light irradiation, with many large thorns appearing on the surface. When water splitting was attempted using the shaped Cu₂O particles, the rhombic dodecahedra produced the most hydrogen, whereas the cubes produced none. Oxygen was not measured because the holes generated upon light absorption were used to oxidize the Cu₂O surface to CuO. A conformal TiIrOₓ overlayer was successfully formed on the rhombic dodecahedral Cu₂O particles, and the coated particles presented overall water splitting producing both hydrogen and oxygen. They also showed significantly improved stability over repeated water splitting reactions relative to bare Cu₂O particles or TiOₓ-coated Cu₂O particles.

Introduction

Cuprous oxide (Cu₂O) has been used as a catalyst or material for CO oxidation, CO₂ reduction, H₂ production, gas sensing, and batteries. It is an especially promising photocatalytic material because it has a direct band gap structure, a small band gap energy (2.0–2.2 eV), and a high absorption coefficient over the wavelength range of the solar spectrum. Additionally, it is non-toxic and highly abundant. The shape of the catalyst nanoparticles affects their activity, selectivity, and durability significantly. The shape of Cu₂O particles could be modulated. The surface crystalline structure (e.g., (100) facets vs. (111) facets) and the degree of branching could be controlled using electrochemical crystallization or colloidal methods. Their shape-dependent properties have been reported for photocatalytic methyl orange degradation.26 The band gap energy was also reported to be highly dependent on the size and shape of Cu₂O particles by theoretical simulations.23

Stability during the photocatalytic reaction is an important issue, but it is often neglected. Many photocatalysts suffer from poor stability under light irradiation. For example, CdS is one of the most widely studied photocatalysts for water splitting due to its small band gap energy and ideal band positions, but its stability is typically very poor because S is easily leached out upon photoreaction. When Cu₂O particles are used as catalysts in aqueous solutions, Cu₂O easily undergoes oxidation to CuO with degraded stability. Cu₂O is often studied as a promising candidate for water splitting because the positions of the conduction and valence bands are ideal for overall water splitting. However, its poor stability in aqueous solution prevents the actual application of Cu₂O for H₂ production. The energy potential for the oxidation of Cu₂O to CuO is also located above the valence band, making Cu₂O oxidation more favorable than water oxidation. The facile formation of CuO on Cu₂O surfaces degraded the photocatalytic activity of Cu₂O materials.

Cu₂O materials were deposited on electrodes, and used as a photocathode. They also suffered from poor stability, but the stability could be maintained by forming transparent and conducting overlayers such as ZnO:Al/TiO₂ formed by an atomic layer deposition method. A thin TiOₓ layer was also used to protect the organic conducting polymer while preventing the penetration of O₂ and H₂O. However, these overlayers were
applied for photoelectrochemical cells, in which electrons can pass through the protecting layer and holes can be dumped into the external circuit. When colloidal particle photocatalysts are used, both electrons and holes must be able to pass through the protecting overlayers.

In this work, we prepared colloidal Cu₂O particles of different shapes: cubes with (100) facets, octahedra with (111) facets, and rhombic dodecahedra with (110) facets. Their stability was tested in deionized water with or without light irradiation. The trend in stability over different shapes was confirmed by density functional theory (DFT) calculations. The Cu₂O particles were used as photocatalysts for overall water splitting, and the shape-dependence on the stability and H₂ production was investigated. The Cu₂O particles were coated with a TiIrOₓ overlay to enhance their stability and suppress photocorrosion. The TiIrOₓ film effectively consumed electrons and holes separately in a stable manner.

**Experimental**

**Materials**

Copper(ii) sulfate pentahydrate (CuSO₄·5H₂O, 98%), copper(ii) chloride dihydrate (CuCl₂·2H₂O, 98%), sodium hydroxide (NaOH, 97%), oleic acid (99%), iridium(III) chloride hydrate (IrCl₃·xH₂O, 99.9%), d- (+)-glucose (99%), l-ascorbic acid (99%), titanium butoxide (TBOT, 97%), and anhydrous ethanol (EtOH, 99.5%) were purchased from Sigma Aldrich. Deionized water (18.3 MΩ cm) was purified by Human Power II+ Scholar (Human Corporation).

**Synthesis of shape-controlled cuprous oxide**

Cu₂O cubes were synthesized by a previously reported method.¹¹ 1 mmol of CuCl₂·2H₂O was dissolved in 100 ml of H₂O. Next, 10 ml of 2 M NaOH solution was added to the solution under vigorous stirring. After 30 min, 10 ml of 6 M l-ascorbic acid was injected and stirred for additional 3 h. All processes were performed at 55 °C. Cu₂O octahedra and rhombic dodecahedra were synthesized by a previously reported method.¹² 1 mmol of CuSO₄·5H₂O was dissolved in 40 ml of H₂O. 3 ml or 6 ml of oleic acid dissolved in 20 ml of ethanol was added under vigorous stirring to obtain octahedra or rhombic dodecahedra, respectively. After the solution was heated to 100 °C, 10 ml of 0.8 M NaOH aqueous solution was injected, and the mixture was held at this temperature for 5 min. 3.42 g of d- (+)-glucose was dissolved in 30 ml of water and added to the above solution, which was then stirred for 3 h. The final solution was washed with isopropyl alcohol and ethanol and collected by centrifugation. The collected particles were dried at 50 °C for 3 h under vacuum. The stability in pure water was investigated by dispersing the Cu₂O particles in deionized water without purging in a ratio of 1 mg Cu₂O per 1 ml water under dark conditions for 3 weeks or with light irradiation with a 300 W Xe lamp for 9 h.

**Coating shape-controlled cuprous oxides with TiIrOₓ overlayers**

33 mg of Cu₂O particles were dispersed in 5.4 ml of anhydrous EtOH. 3.8 mg of IrCl₃·xH₂O was dissolved in 5 ml of anhydrous EtOH and 168 µl of water was added to the above solution. 45 µl of TBOT was added into 5 ml of cold anhydrous EtOH. Three solutions kept at 0 °C were mixed under vigorous stirring and kept at the same temperature for 1 h. The reddish precipitates were then washed with water and ethanol several times and dried in a vacuum oven at 50 °C. The powder was heated at 210 °C for 2 h under nitrogen.

**Hydrogen generation by water splitting**

The reactor consisted of a 100 ml round-bottom flask with a quartz plate window and a Teflon cover with two tubes connected to a gas chromatograph (GC) and an Ar cylinder. 100 mg of each sample was dispersed in 100 ml of pure water without sacrificial agents. After Ar purging for ~20 min (until no nitrogen peak was detected by GC), irradiation was applied for 24 h. The light source was a 300 W Xe lamp, and the distance from the light source to the reactor was 20 cm. A 1 cm thick water bath was located between the light source and the reactor. After the reaction, 25 ml of Ar was injected into the reactor, and the outlet products were analyzed by using a GC (Younglin GC 6000 series) equipped with a thermal conductivity detector.

**Characterization**

The morphology of the samples was investigated by field emission scanning electron microscopy (FE-SEM; JEOL6701, 5 kV) and transmission electron microscopy (TEM; JEOL2100). The X-ray powder diffraction (XRD) patterns of the prepared samples were measured on a Rigaku Miniflex diffractometer. An X-ray photoelectron spectrometer (XPS; K-alpha, Thermo U. K.) equipped with a monochromatic Al Kx X-ray source (12 kV, 3 mA) was used to measure the surface properties of the nanoparticles. Binding energies were calculated using the maximum intensity of the C 1s signal at 284.8 eV as a reference.

**Results and discussion**

Cu₂O particles of three shapes with well-defined surfaces were synthesized using the reported methods. The cubes exclusively feature (100) facets, the octahedra (111) facets, and the rhombic dodecahedra (110) facets. The SEM images of each type of particle are shown in Fig. 1(a)–(c). Fig. 1(d) shows the XPS Cu 2pₓ/₂ peak of the rhombic dodecahedral Cu₂O particles. Only the Cu(i) peak was observed, not the peak related to Cu(ii), indicating that the surface consists of only Cu₂O. From Fig. 1(d) and S1[a and d], all of the particle surfaces are Cu₂O, no other phase such as CuO was present. The Cu₂O crystalline structure was also confirmed by XRD (Fig. S2(a)†). The shaped Cu₂O particles were dispersed in deionized water under dark conditions to assess the stability of the particles in water. After 3 weeks, the surface of the Cu₂O particles was degraded, and the extent of surface degradation differed by the particle shape. The SEM images of each Cu₂O shape in water are shown in Fig. 2(a)–
In the case of cubic Cu$_2$O, the faces were deformed, with many bumps on the facet, while the edges and vertices showed no change. In the octahedral particles, the facets were stable, but all vertices were degraded, as shown by the circled areas in Fig. 2(b). In the rhombic dodecahedra, the facets were stable, but the vertices showed deformation. Here, interestingly, the vertices where four facets met were degraded as shown in circle A in Fig. 2(c), but the vertices where three facets met showed no degradation as shown in circle B. All these observations indicate that only (100) facets were degraded when Cu$_2$O particles were in contact with water. The XPS data in Fig. 2(d) and S1(b and e)† showed that the Cu$_2$O surfaces were oxidized after dispersion in water. Compared with XPS O 1s data in Fig. S3,† the oxidized Cu would have a form of Cu(OH)$_2$. The ratio of Cu(II) to Cu(I) was estimated by integrating the deconvoluted peaks. The ratio was 1.42 for cubes, 0.68 for octahedra, and 0.74 for rhombic dodecahedra. The cubes have the highest ratio of Cu(II) among different shapes, thus the surface of the cubic Cu$_2$O crystals was the most unstable in deionized water. However, the crystalline structure was still found to be Cu$_2$O in the XRD patterns (Fig. S2(b)†), and no other peaks were observed in any of the samples.

The relative thermodynamic stability of the Cu$_2$O surfaces has been analyzed using first principles density functional theory (DFT). The calculation details can be found in ref. 33 and 34. The surface energy was defined with respect to bulk stoichiometric Cu$_2$O. Any surface structure or surface composition that deviates from Cu : O = 2 : 1 will have a slope. Using the approach of DFT-based atomistic thermodynamics, both low and high Miller-index surfaces of Cu$_2$O were studied, and their surface free energies are plotted as a function of oxygen chemical potential in Fig. 3(a). Two low Miller-index Cu$_2$O surfaces, i.e., the Cu–O terminated Cu$_2$O(110) surface [Cu$_2$O(110):CuO] and the Cu$_2$O(111) surface with a surface Cu vacancy [Cu$_2$O(111)–CuCUS] show the lowest surface free energies, which means that they are the most thermodynamically stable within the considered range of oxygen chemical potential. In Cu$_2$O(110):CuO, the surface has both Cu and O in the same atomic level. The detailed atomic structures of the most stable form of each surface are shown in Fig. 3(b). The vertical dashed lines in Fig. 3(a) indicate the physical limits of the oxygen chemical potentials. If the oxygen chemical potential drops below the line, bulk Cu$_2$O will break down to form bulk Cu. Thus, the left area can be considered to be an oxygen-poor condition. The right line indicates the maximum value of the oxygen chemical potential, which is the thermodynamic ground state: dioxygen molecules. Thus, the right area is an...
oxygen-rich condition. From this thermodynamic analysis, it is clearly shown that both O- and Cu-terminated (100) surfaces of Cu$_2$O are relatively unstable under oxygen-containing conditions.

The stabilities of the shaped Cu$_2$O particles were also examined under light irradiation for 9 h. The Cu$_2$O particles were dispersed in deionized water and illuminated by a 300 W Xe lamp. All the shaped Cu$_2$O particles presented photocorrosion at the surface, but the degree of corrosion differed by the particle shape. Fig. 4 shows the SEM images of Cu$_2$O particles after irradiation. Many thorns were observed, especially at the edges. The density and the size of the thorns were the smallest for octahedra and largest for rhombic dodecahedra. This trend was also confirmed by XPS. The peak area ratio of Cu(II) to Cu(I) was 0.60 for the cubes, 0.50 for the octahedra, and 2.67 for the rhombic dodecahedra. The surface of the octahedra, which have the smallest ratio of Cu(II) by XPS, was degraded the least, and the surface of the rhombic dodecahedra, which have the highest ratio of Cu(II), was deformed the most. The formation of a CuO phase was also observed in the XRD pattern (Fig. S2(c)†). Clearly, the stability trend under light irradiation was different from that under dark conditions. The formation of electrons and holes upon light absorption affects the stability differently. Zheng et al. previously reported that Cu$_2$O(111) was more stable than the other surface structures and acted as a stable photocatalyst for methyl orange degradation under irradiation. From density of states calculations, they showed that the valence band of Cu$_2$O(100) and Cu$_2$O(110) extends to higher energies compared to Cu$_2$O(111), causing electrons to tend to move to the (111) surface from other surfaces.

Upon light absorption, Cu$_2$O can act as a water-splitting photocatalyst. Hydrogen production was measured for each sample after dispersing 0.1 g of the catalyst in 100 ml of water after Ar purging under light irradiation with a 300 W Xe lamp for 24 h. No sacrificial agent was used, and overall water splitting was expected, producing hydrogen and oxygen in a 2 : 1 ratio. When the Cu$_2$O particles of different shapes were used for photocatalytic water splitting, the H$_2$ production rates were obtained as shown in Fig. 5(a). No oxygen was detected because the holes that were supposed to oxidize water to produce oxygen were actually used to oxidize Cu$_2$O to CuO. The thorns shown in Fig. 4 are CuO oxidized by holes formed after light absorption. A strong shape dependence was observed for H$_2$ production. The Cu$_2$O cubes produced no hydrogen, and the Cu$_2$O rhombic dodecahedra generated the most hydrogen. Many thorns on the rhombic dodecahedra as shown in Fig. 4(c) indicate the high activity of this shape for photocatalytic reactions. Huang et al. also reported much better catalytic activity of rhombic dodecahedra than cubes for methyl orange degradation. However, when the water splitting was repeated for rhombic dodecahedra, the activity dropped significantly, and no H$_2$ was detected for the third run, as shown in Fig. 5(b). This degradation in photocatalytic activity is due to the photocorrosion of Cu$_2$O into CuO during water splitting. If the photocorrosion can be suppressed, stable H$_2$ production might be achieved.

Coating the Cu$_2$O particles would prevent direct contact between the Cu$_2$O surface and water. TiO$_2$ (x < 2) has been widely studied as a conducting and transparent overlayer and

![Fig. 4](image-url) SEM images of (a) cubic, (b) octahedral, and (c) rhombic dodecahedral Cu$_2$O dispersed in deionized water under light irradiation for 9 h. (d) XPS Cu 2p$_{3/2}$ peak for rhombic dodecahedral Cu$_2$O. Each sample was dispersed at a concentration of 1 mg sample per ml water. The deionized water was used without purging.

![Fig. 5](image-url) H$_2$ production from photocatalytic water splitting using (a) the Cu$_2$O particles of different shapes for 24 h of reaction and (b) the rhombic dodecahedral Cu$_2$O particles over repeated reaction. The deionized water was purged with Ar before each cycle.
has also been found to be effective in protecting Cu₂O electrode materials when used together with a ZnO layer. However, Cu₂O was deposited on the electrode in these works, and atomic layer deposition was used to form ultrathin and conformal TiOₓ overlayers. This method cannot be applied to powder-type Cu₂O particles. Instead, we used a sol–gel method to coat the Cu₂O particles and treated TiO₂ particles. Instead, we used a sol–gel method to coat the Cu₂O particles and treated TiO₂ particles. Anatase, TiO₂–coated samples at different temperatures. When the heating temperature was 240 °C, the CuO phase started to form as shown in Fig. S4(a).† When temperatures of 150, 180, and 210 °C were used to form the TiO₂ layer and the coated particles were exposed to light, 210 °C showed the least formation of CuO; thus, thermal treatment at 210 °C was chosen to preserve the CuO phase. It was confirmed that the formation of thorns was greatly reduced upon light irradiation for TiO₂–coated Cu₂O particles. However, the TiO₂ layer was not enough to guarantee stable water splitting. Although electrons can pass through the TiO₂ overlayer and generate H₂, holes would accumulate inside the particles, prohibiting further photocatalytic reactions. Therefore, IrO₂, an effective water oxidation catalyst, was also inserted into the overlayer. When Ir precursors were added into the sol solution, a TiIrOₓ–coated layer was successfully formed, as shown in Fig. 6. All the shapes could be coated conformably, and the coating layer has a thickness of ~20 nm. When the binding energy of Ti 2p peaks was observed as shown in Fig. 6(d), the TiO₂ layer on Cu₂O particles presented a lower binding energy than TiO₂ rutile or anatase, indicating an abundance of electrons on the TiO₂ layer. The addition of Ir produced little change in the electronic state of Ti. The SEM images in Fig. 6 rarely showed distinguishable separate particles in the overlayer although the rough layer in the TEM image (inset of Fig. 6(c)) may reflect the co-existence of the TiO₂ layer and IrO₂ particles. The XPS Ir 4f peaks in Fig. S3† presented Ir(IV) peaks only, indicating that most Ir existed as IrO₂ and that few Ir precursors remained.

The overall water splitting performance of the coated particles was tested as shown in Fig. 7. As expected, the TiO₂ layer did not enhance the stability; H₂ production stopped at the third run. For the TiIrOₓ layer, however, overall water splitting was obtained with a H₂ : O₂ ratio of 2.13 for the first run as shown in Fig. 7(b). Bare rhombic dodecahedral Cu₂O, TiO₂–coated particles, and TiIrOₓ–coated particles showed similar hydrogen production rates for the first run, implying that electron transfer at the bare Cu₂O surface differed little from that through the overlayers. IrO₂ at the overlayers facilitated hole transfer, preventing photocorrosion and thereby enabling water oxidation producing oxygen. Under dark conditions, there was no hydrogen production. To ensure further that the overall water splitting is not from ‘mechano-catalysis’, a round-bottom flask and an egg shaped stirring bar were used to minimize the contact area. When TiIrOₓ was synthesized without Cu₂O particles under otherwise the same synthesis conditions, hydrogen was not detected in the outlet under light irradiation. The stability was also checked by repeating the water splitting after collecting the coated particles and redispersing them in Ar-purged deionized water. The water splitting was observed to produce both hydrogen and oxygen, but the production rates decreased slightly. The ratio of hydrogen to oxygen increased from 2.13 for the first run to 2.20 for the second run and to 2.26 for the third run. The TiIrOₓ overlayer enabled both electron and hole transfer, suppressing photocorrosion and significantly

![Fig. 6](image_url)  
**Fig. 6** SEM images of TiIrOₓ–coated Cu₂O particles with (a) cubic, (b) octahedral, and (c) rhombic dodecahedral shapes. The inset in (c) shows a TEM image of TiIrOₓ coating on rhombic dodecahedral Cu₂O. (d) XPS Ti 2p peaks of TiO₂ anatase, TiO₂ rutile, TiO₂–coated Cu₂O, and TiIrOₓ–coated Cu₂O.

![Fig. 7](image_url)  
**Fig. 7** (a) Hydrogen production on TiO₂–coated rhombic dodecahedral Cu₂O particles and (b) hydrogen and oxygen production on TiIrOₓ–coated rhombic dodecahedral Cu₂O particles for repeated photocatalytic water splitting. The catalyst 0.1 g was dispersed in 100 ml of water under irradiation with a 300 W Xe lamp. The deionized water was purged with Ar before each cycle.
improving the stability. However, the coating might not completely prevent contact with water, allowing a small proportion of the holes to be used for surface oxidation with degraded hydrogen/oxygen production. When the coated particles were observed by SEM after the third cycle of photocatalytic water splitting, the shape and coating were mostly preserved in contrast to Fig. 4(c), and few thorns were observed (Fig. S6†).

Conclusions

Cu$_2$O particles of three different shapes [cubes, octahedra, and rhombic dodecahedra] were prepared with distinct surface structures ((100), (111), and (110) facets, respectively). Their shape stability was estimated in deionized water. The facets of the cubes, the vortexes of the octahedra, and certain vortexes of the rhombic dodecahedra were degraded, with rough surfaces. The Cu$_2$O(100) facets were selectively deformed when dispersed in deionized water, consistent with density functional theory results. When the shaped Cu$_2$O particles were exposed to light, a tendency of more violent deformation at the edges was observed. Upon light irradiation, the generated holes were used to oxidize Cu$_2$O to CuO; the smooth Cu$_2$O surface was deformed into a thorny CuO surface. When the overall water splitting was performed using Cu$_2$O particles as photocatalysts, a shape dependence was observed; no hydrogen was obtained for the cubes, whereas most hydrogen was produced by the rhombic dodecahedra. Oxygen was not produced because the holes were used to form CuO, and this was the reason that Cu$_2$O had poor stability. When the rhombic dodecahedral Cu$_2$O particles were coated with a conformal TiIrO$_x$ layer, overall water splitting producing both hydrogen and oxygen was observed. Bare Cu$_2$O particles or TiO$_2$-coated Cu$_2$O particles showed a sudden decrease in photocatalytic activity over repeated reactions due to severe photocorrosion. In contrast, TiIrO$_x$-coated Cu$_2$O particles presented significantly enhanced stability for the overall water splitting reaction.

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Notes and references

Supporting Information

Shape Effect of Cuprous Oxide Particles on Stability in Water and Photocatalytic Water Splitting

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Figure S1-S6;

![Figure S1](image)

**Figure S1.** XPS Cu 2p_{3/2} peaks of (a)\textendash (c) cubic and (d)\textendash (f) octahedral Cu\textsubscript{2}O. (a), (d) as-made Cu\textsubscript{2}O crystals; (b), (e) after three weeks in deionized water; (c), (f) after 9 hrs in photo-irradiation
Figure S2. XRD patterns of cubic, octahedral, and rhombic dodecahedral Cu₂O crystals; (a) as-made crystals; (b) after 3 weeks in deionized water; (c) after 9 hrs in light irradiation. (d) XRD patterns of TiIrOₓ-coated Cu₂O for each shape. ■ indicates the peaks of Cu₂O and ● indicates the peaks of CuO. The deionized water was used without purging.
Figure S3. XPS O1s peaks of (a)–(c) cubic (d)–(f) octahedral, and (g)–(i) rhombic dodecahedral Cu$_2$O. (a), (d), (g) as-made Cu$_2$O crystals; (b), (e), (h) after three weeks in deionized water; (c), (f), (i) after 9 hrs in photo-irradiation.
Figure S4. XRD patterns of (a) TiO$_x$-coated Cu$_2$O samples which were treated at different temperatures, and (b) after light irradiation for 9 hrs for TiO$_x$-coated Cu$_2$O samples treated at different temperatures. The deionized water was used without purging. ■ indicates the peaks of Cu$_2$O and ● indicates the peaks of CuO. The degree of phase deformation upon light irradiation was estimated by comparing the ratio of the peak intensity at 36.5° and 38.7° in (b).
Figure S5. XPS Ir 4f peaks for TiIrO$_x$ overlayers on rhombic dodecahedral Cu$_2$O particles
Figure S6. SEM image of TiIrOₓ-coated rhombic dodecahedral Cu₂O particles after the third run of photocatalytic water splitting