

# Cu<sub>2</sub>O as a photocatalyst for overall water splitting under visible light irradiation

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**Photocatalytic decomposition of water into H<sub>2</sub> and O<sub>2</sub> on Cu<sub>2</sub>O under visible light irradiation is investigated; the photocatalytic water splitting on Cu<sub>2</sub>O powder proceeds without any noticeable decrease in the activity for more than 1900 h.**

So far, many photocatalysts have been reported to decompose water into H<sub>2</sub> and O<sub>2</sub> under UV light irradiation.<sup>1–5</sup> From the view point of solar energy conversion, however, a photocatalyst which works under visible light irradiation (>400 nm) is indispensable, but such a photocatalyst has not yet been found. In this report, we introduce Cu<sub>2</sub>O, a well-known p-type semiconductor, which acts as a photocatalyst for overall water splitting under visible light irradiation (≤600 nm).

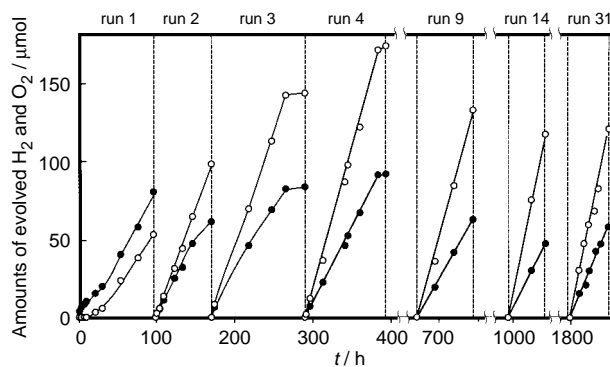
The solid state physics of Cu<sub>2</sub>O, which abundantly exists as cuprite in nature, has been extensively investigated for a long time since Cu<sub>2</sub>O is a simple metal oxide semiconductor with a small band gap energy. As shown in an energy correlation between the band gap model of Cu<sub>2</sub>O and the redox potentials of relevant electrode reactions in an aqueous solution at pH 7,<sup>6</sup> the conduction and valence band edges of Cu<sub>2</sub>O, which are separated by a band gap energy of 2.0–2.2 eV,<sup>7,8,9</sup> seem to be available for reduction and oxidation of water, respectively. Therefore, Cu<sub>2</sub>O is, in principle, capable of decomposing water into H<sub>2</sub> and O<sub>2</sub> under visible light excitation. However, as yet, such a photochemical reaction has not been accomplished on any Cu<sub>2</sub>O electrode since they undergo photodegradation in aqueous solution.<sup>9</sup> In fact, visible light irradiation (470 nm) of a cathode-polarized Cu<sub>2</sub>O single crystal electrode in aqueous solution resulted in reduction of Cu<sub>2</sub>O to metallic Cu.<sup>10</sup> For this reason, overall water splitting on Cu<sub>2</sub>O photocatalysts has not been investigated despite the band structure available for the reaction. In this study, we confirmed the photocatalytic overall water splitting on Cu<sub>2</sub>O powder under visible light irradiation.

Cu<sub>2</sub>O powder prepared by the hydrolysis of CuCl was used in this study. CuCl was hydrolyzed by adding 1 M aqueous Na<sub>3</sub>PO<sub>4</sub> (40 cm<sup>3</sup>) to a 5 M aqueous NaCl solution containing 0.04 mol of CuCl (400 cm<sup>3</sup>) with vigorous stirring under an Ar flow. A yellow precipitate was produced by the hydrolysis which was washed with distilled water (200 cm<sup>3</sup>) 5–7 times followed by decantation under vacuum and drying *in vacuo*. Cu<sub>2</sub>O powder was obtained by heating the yellow precipitate at 673 K for 24 h *in vacuo*, followed by boiling in water under an Ar atmosphere to remove unreacted CuCl from Cu<sub>2</sub>O. The particle size and surface area of Cu<sub>2</sub>O were estimated to be 0.3–0.5 μm and 6 m<sup>2</sup> g<sup>−1</sup>, respectively. Only the XRD pattern due to Cu<sub>2</sub>O was seen with no evidence for other diffraction patterns such as for CuO, metallic Cu or other impurities. The XP spectra of Cu 2p and the Cu LMM Auger spectra indicated that the surface of Cu<sub>2</sub>O was composed of Cu<sup>I</sup>.<sup>11,12</sup> The band gap energy of Cu<sub>2</sub>O was estimated at *ca.* 2.0 eV ( $\lambda$  *ca.* 620 nm) by UV–VIS spectroscopy.

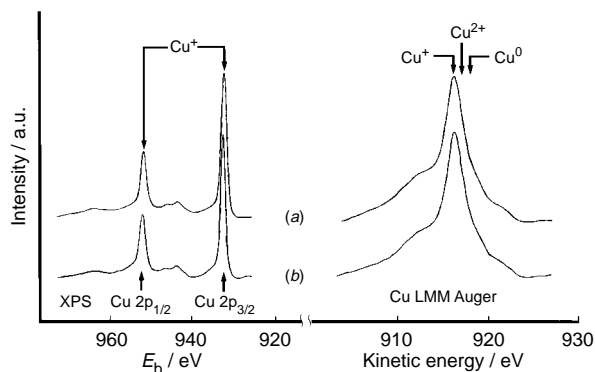
The photodecomposition of water was carried out in a Pyrex cell with 0.5 g of Cu<sub>2</sub>O and 200 cm<sup>3</sup> of distilled water, which

was vigorously magnetically stirred. The cell was irradiated at room temperature from one side with visible light ( $\lambda > 460$  nm) from a 300 W Xe lamp with a cut-off filter. A closed gas circulation and evacuation system (300 cm<sup>3</sup>) made of Pyrex glass was connected to the reaction cell, and evolved gases were directly transferred to a gas chromatograph to avoid any contamination from air.

Fig. 1 shows several typical time courses of H<sub>2</sub> and O<sub>2</sub> evolution from Cu<sub>2</sub>O under visible light irradiation (>460 nm). The reaction system was evacuated after each run. As shown in run 1, only O<sub>2</sub> evolved for 10 h after the beginning of the reaction, and then the evolution of H<sub>2</sub> was observed as the reaction proceeded. The rate of H<sub>2</sub> evolution increased gradually in the subsequent runs. The ratio of the amount of evolved H<sub>2</sub> to O<sub>2</sub> (H<sub>2</sub>/O<sub>2</sub>) was 0.8 in run 1 and increased to 1.8 in run 4. After run 4, the ratio was between 2.0 and 2.5. The reaction proceeds without any noticeable decrease in the activity for more than 30 runs as shown in Fig. 1. The total amounts of evolved H<sub>2</sub> and O<sub>2</sub> for 1900 h reached 3.8 and 1.9 mmol, respectively, and are comparable to the amount of Cu<sub>2</sub>O used (0.5 g, 3.5 mmol). Furthermore, there was no noticeable difference in pH of the suspension before reaction (pH 7.3) and after run 31 (pH 7.1). In order to elucidate the origin of the evolved O<sub>2</sub>, an experiment using H<sub>2</sub><sup>18</sup>O was carried out. In another small Pyrex cell (50 cm<sup>3</sup>), 0.1 g of Cu<sub>2</sub>O (after reaction for 400 h) suspended in a mixture of H<sub>2</sub><sup>16</sup>O (5 cm<sup>3</sup>) and H<sub>2</sub><sup>18</sup>O (1 cm<sup>3</sup>) was irradiated with visible light (>460 nm). H<sub>2</sub> and O<sub>2</sub> were stoichiometrically evolved after light irradiation and it was confirmed by mass spectral analysis that the ratio, <sup>16</sup>O<sub>2</sub>:<sup>16</sup>O<sup>18</sup>O:<sup>18</sup>O<sub>2</sub>, in the evolved O<sub>2</sub> species for 24 h was 254:94:13. The result indicates that the atomic ratio, <sup>16</sup>O:<sup>18</sup>O, in the total amount of evolved O<sub>2</sub> is 5.0 corresponding to that in the mixed water. As a result, the evolved O<sub>2</sub> is attributed to the water cleavage on Cu<sub>2</sub>O. The photoresponse on Cu<sub>2</sub>O was observed for visible light through a cut-off filter of 600 nm, while there was no photoresponse at  $\lambda > 650$  nm.



**Fig. 1** Time courses of H<sub>2</sub> (open circles) and O<sub>2</sub> (filled circles) evolution in Cu<sub>2</sub>O under visible light ( $\lambda \geq 460$  nm) irradiation. Catalyst: 0.5 g, H<sub>2</sub>O: 200 cm<sup>3</sup>. The reaction system was evacuated with light irradiation after each run. Time courses in runs 5–8, 10–13 and 15–30 are omitted.



**Fig. 2** X-Ray photoelectron spectra of Cu 2p and Cu LMM Auger spectra of  $\text{Cu}_2\text{O}$  before (a) and after (b) reaction for 400 h. The binding and kinetic energies were referenced to the Au  $4f_{7/2}$  level at 83.8 eV.

Fig. 2 shows the XP spectra of Cu 2p and Cu LMM Auger peaks of  $\text{Cu}_2\text{O}$  before and after reaction for 400 h. There was no noticeable difference in the XP spectra of  $\text{Cu}_2\text{O}$ , indicating that  $\text{Cu}_2\text{O}$  powder was neither reduced nor oxidized after photocatalytic reaction. These results are in total contrast to the observation on  $\text{Cu}_2\text{O}$  electrodes and strongly suggest that  $\text{Cu}_2\text{O}$  powder catalytically decomposes water into  $\text{H}_2$  and  $\text{O}_2$  under visible light irradiation. To the best of our knowledge, such a reaction on  $\text{Cu}_2\text{O}$  photocatalysts has not yet been reported. The reaction mechanism as well as the reason for the difference between the electrode and the powder systems are still not clear. Nevertheless it is inferred that the photocatalytic reaction on a  $\text{Cu}_2\text{O}$  particle in distilled water is clearly different from the photoelectrochemical reaction on polarized  $\text{Cu}_2\text{O}$  electrodes in an aqueous electrolyte. The quantum efficiency of the photocatalytic reaction was estimated at ca. 0.3% between 550 and 600 nm.

One of the characteristic features of the  $\text{Cu}_2\text{O}$  photocatalyst is the excess evolution of  $\text{O}_2$  above the stoichiometry at the early stage of the reaction (runs 1 and 2).  $\text{Cu}_2\text{O}$  is known to absorb a relatively large amount of oxygen in bulk as well as adsorbing oxygen as  $\text{O}^-$  or  $\text{O}_2^-$  on the surface.<sup>13,14</sup> The excess oxygen on the surface or in the bulk leads to p-type semiconducting behaviour and unique oxidation catalysis of  $\text{Cu}_2\text{O}$ . The release of these excess oxygen species from  $\text{Cu}_2\text{O}$  by visible light irradiation may cause the excess evolution of  $\text{O}_2$  above the stoichiometry at the early stage of the reaction. Another feature to be noted is the  $\text{O}_2$  pressure dependence of the reaction.

As shown in runs 3 and 4 of Fig. 1, the evolution rates of  $\text{H}_2$  and  $\text{O}_2$  became slow or stopped when the amount of evolved  $\text{O}_2$  exceeded ca. 80  $\mu\text{mol}$  which corresponded to 500 Pa of  $\text{O}_2$  in our system. In all runs after run 5,  $\text{H}_2$  and  $\text{O}_2$  evolved without any significant decrease in the activity so long as the evolved gas was evacuated before the pressure of  $\text{O}_2$  reached 500 Pa. These results suggest that  $\text{O}_2$  at more than a certain pressure (500 Pa) in the reaction system inhibits the overall water splitting on  $\text{Cu}_2\text{O}$ . Such an inhibition might be attributed to the photoadsorption of oxygen on the  $\text{Cu}_2\text{O}$  surface. p-Type semiconductors are known to photoadsorb  $\text{O}_2$  under light

irradiation when  $\text{O}_2$  in gas phase exceeds a certain pressure.<sup>15</sup> The photoadsorption largely depends on the  $\text{O}_2$  pressure as well as on the wavelength and intensity of incident light, temperature, etc. Although the dependence of photoadsorption on  $\text{O}_2$  pressure in a  $\text{Cu}_2\text{O}-\text{H}_2\text{O}-\text{O}_2/\text{H}_2$  system as in the present case has not yet been investigated, it is probable that preferential  $\text{O}_2$  photoadsorption inhibits the overall water splitting on the  $\text{Cu}_2\text{O}$  surface.

Although  $\text{Cu}_2\text{O}$  has been regarded as an unstable material for water decomposition under light irradiation from the results of photoelectrochemistry, the present study has revealed  $\text{Cu}_2\text{O}$  to be a photocatalyst able to decompose water into  $\text{H}_2$  and  $\text{O}_2$  under visible light irradiation. The reaction mechanism on  $\text{Cu}_2\text{O}$  is under investigation.

Recently, we have also found that  $\text{CuFeO}_2$  evolves  $\text{H}_2$  and  $\text{O}_2$  under visible light irradiation, and detailed results will be reported soon.  $\text{CuFeO}_2$  has a delafossite type layered structure where the iron oxide layers are connected to each other through linear  $-\text{O}-\text{Cu}^{\text{I}}-\text{O}-$  bonds.<sup>16-18</sup> The  $\text{Cu}_2\text{O}$  lattice consists of chains of linear bonds. This suggests that  $\text{Cu}^{\text{I}}$  containing materials with linear  $-\text{O}-\text{Cu}^{\text{I}}-\text{O}-$  bonds are available for the overall water splitting under visible light irradiation. Such  $\text{Cu}^{\text{I}}$  containing materials may become potential candidates for converting solar energy into  $\text{H}_2$  energy.

## Notes and References

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