Cu_2O as a photocatalyst for overall water splitting under visible light irradiation

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Photocatalytic decomposition of water into H_2 and O_2 on Cu_2O under visible light irradiation is investigated; the photocatalytic water splitting on Cu_2O 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_2 and O_2 under UV light irradiation.[1–5] 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_2O, a well-known p-type semiconductor, which acts as a photocatalyst for overall water splitting under visible light irradiation ($\leqslant 600$ nm).

The solid state physics of Cu_2O, which abundantly exists as cuprite in nature, has been extensively investigated for a long time since Cu_2O 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_2O and the redox potentials of relevant electrode reactions in an aqueous solution at pH 7,[6] the conduction and valence band edges of Cu_2O, which are separated by a band gap energy of 2.0–2.2 eV,[7,8,9] seem to be available for reduction and oxidation of water, respectively. Therefore, Cu_2O is, in principle, capable of decomposing water into H_2 and O_2 under visible light excitation. However, as yet, such a photochemical reaction has not been accomplished on any Cu_2O electrode since they undergo photodegradation in aqueous solution.[9] In fact, visible light irradiation (470 nm) of a cathode-polarized Cu_2O single crystal electrode in aqueous solution resulted in reduction of Cu_2O to metallic Cu.[10] For this reason, overall water splitting on Cu_2O 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_2O powder under visible light irradiation.

Cu_2O powder prepared by the hydrolysis of CuCl was used in this study. CuCl was hydrolyzed by adding 1 M aqueous Na_3PO_4 (40 cm^3) to a 5 M aqueous NaCl solution containing 0.04 mol of CuCl (400 cm^3) with vigorous stirring under an Ar flow. A yellow precipitate was produced by the hydrolysis which was washed with distilled water (200 cm^3) 5–7 times followed by decantation under vacuum and drying *in vacuo*. Cu_2O 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_2O. The particle size and surface area of Cu_2O were estimated to be 0.3–0.5 μm and 6 m^2 g^{-1}, respectively. Only the XRD pattern due to Cu_2O 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_2O was composed of Cu^{I}.[11,12] The band gap energy of Cu_2O was estimated at *ca.* 2.0 eV (λ *ca.* 620 nm) by UV–VIS spectroscopy.

The photodecomposition of water was carried out in a Pyrex cell with 0.5 g of Cu_2O and 200 cm^3 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^3) 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_2 and O_2 evolution from Cu_2O under visible light irradiation (>460 nm). The reaction system was evacuated after each run. As shown in run 1, only O_2 evolved for 10 h after the beginning of the reaction, and then the evolution of H_2 was observed as the reaction proceeded. The rate of H_2 evolution increased gradually in the subsequent runs. The ratio of the amount of evolved H_2 to O_2 (H_2/O_2) 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_2 and O_2 for 1900 h reached 3.8 and 1.9 mmol, respectively, and are comparable to the amount of Cu_2O 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_2, an experiment using $H_2{}^{18}O$ was carried out. In another small Pyrex cell (50 cm^3), 0.1 g of Cu_2O (after reaction for 400 h) suspended in a mixture of $H_2{}^{16}O$ (5 cm^3) and $H_2{}^{18}O$ (1 cm^3) was irradiated with visible light (>460 nm). H_2 and O_2 were stoichiometrically evolved after light irradiation and it was confirmed by mass spectral analysis that the ratio, ${}^{16}O_2 : {}^{16}O^{18}O : {}^{18}O_2$, in the evolved O_2 species for 24 h was 254 : 94 : 13. The result indicates that the atomic ratio, ${}^{16}O : {}^{18}O$, in the total amount of evolved O_2 is 5.0 corresponding to that in the mixed water. As a result, the evolved O_2 is attributed to the water cleavage on Cu_2O. The photoresponse on Cu_2O was observed for visible light through a cut-off filter of 600 nm, while there was no photoresponse at $\lambda > 650$ nm.

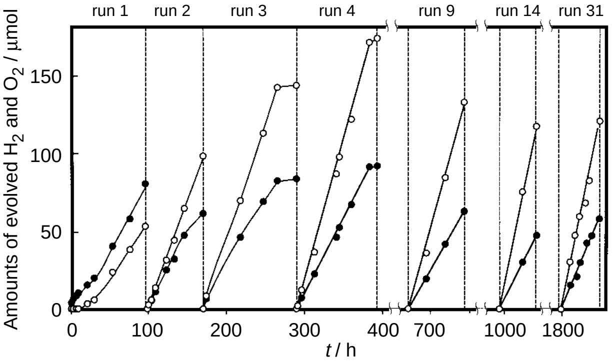

Fig. 1 Time courses of H_2 (open circles) and O_2 (filled circles) evolution in Cu_2O under visible light ($\lambda \geqslant 460$ nm) irradiation. Catalyst: 0.5 g, H_2O: 200 cm^3. The reaction system was evacuated with light irradiation after each run. Time courses in runs 5–8, 10–13 and 15–30 are omitted.

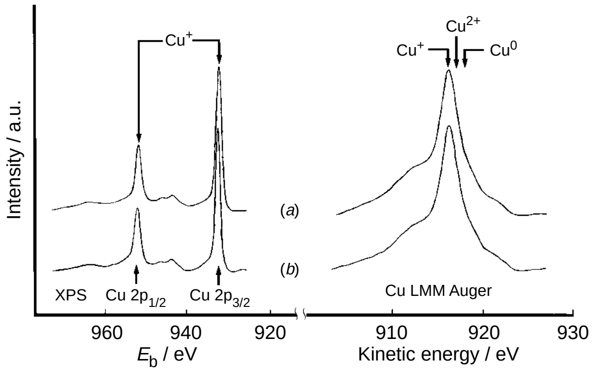

Fig. 2 X-Ray photoelectron spectra of Cu 2p and Cu LMM Auger spectra of Cu_2O before (*a*) and after (*b*) reaction for 400 h. The binding and kinetic energies were referenced to the Au $4f_{7/2}$ level at 83.8 eV.

Fig. 2 shows the XP spectra of Cu 2p and Cu LMM Auger peaks of Cu_2O before and after reaction for 400 h. There was no noticeable difference in the XP spectra of Cu_2O, indicating that Cu_2O powder was neither reduced nor oxidized after photocatalytic reaction. These results are in total contrast to the observation on Cu_2O electrodes and strongly suggest that Cu_2O powder catalytically decomposes water into H_2 and O_2 under visible light irradiation. To the best of our knowledge, such a reaction on Cu_2O 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 Cu_2O particle in distilled water is clearly different from the photoelectrochemical reaction on polarized Cu_2O 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 Cu_2O photocatalyst is the excess evolution of O_2 above the stoichiometry at the early stage of the reaction (runs 1 and 2). Cu_2O is known to absorb a relatively large amount of oxygen in bulk as well as adsorbing oxygen as O^- or O_2^- on the surface.[13,14] The excess oxygen on the surface or in the bulk leads to p-type semiconducting behaviour and unique oxidation catalysis of Cu_2O. The release of these excess oxygen species from Cu_2O by visible light irradiation may cause the excess evolution of O_2 above the stoichiometry at the early stage of the reaction. Another feature to be noted is the O_2 pressure dependence of the reaction.

As shown in runs 3 and 4 of Fig. 1, the evolution rates of H_2 and O_2 became slow or stopped when the amount of evolved O_2 exceeded *ca.* 80 μmol which corresponded to 500 Pa of O_2 in our system. In all runs after run 5, H_2 and O_2 evolved without any significant decrease in the activity so long as the evolved gas was evacuated before the pressure of O_2 reached 500 Pa. These results suggest that O_2 at more than a certain pressure (500 Pa) in the reaction system inhibits the overall water splitting on Cu_2O. Such an inhibition might be attributed to the photoadsorption of oxygen on the Cu_2O surface. p-Type semiconductors are known to photoadsorb O_2 under light irradiation when O_2 in gas phase exceeds a certain pressure.[15] The photoadsorption largely depends on the O_2 pressure as well as on the wavelength and intensity of incident light, temperature, *etc.* Although the dependence of photoadsorption on O_2 pressure in a Cu_2O–H_2O–O_2/H_2 system as in the present case has not yet been investigated, it is probable that preferential O_2 photoadsorption inhibits the overall water splitting on the Cu_2O surface.

Although Cu_2O has been regarded as an unstable material for water decomposition under light irradiation from the results of photoelectrochemistry, the present study has revealed Cu_2O to be a photocatalyst able to decompose water into H_2 and O_2 under visible light irradiation. The reaction mechanism on Cu_2O is under investigation.

Recently, we have also found that $CuFeO_2$ evolves H_2 and O_2 under visible light irradiation, and detailed results will be reported soon. $CuFeO_2$ has a delafossite type layered structure where the iron oxide layers are connected to each other through linear –O–Cu^I–O– bonds.[16–18] The Cu_2O lattice consists of chains of linear bonds. This suggests that Cu^I containing materials with linear –O–Cu^I–O– bonds are available for the overall water splitting under visible light irradiation. Such Cu^I containing materials may become potential candidates for converting solar energy into H_2 energy.

Notes and References

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