

Highly stable CuO incorporated TiO₂ catalyst for photocatalytic hydrogen production from H₂O

J. Bandara,^{*a} C. P. K. Udawatta^b and C. S. K. Rajapakse^a

^a Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka.

E-mail: jayasundera@yahoo.com; Fax: +94 81 2232131; Tel: +94 81 2232002

^b Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

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A CuO incorporated TiO₂ catalyst was found to be an active photocatalyst for the reduction of H₂O under sacrificial conditions. The catalytic activity originates from the photogeneration of excited electrons in the conduction bands of both TiO₂ and CuO resulting in a build-up of excess electrons in the conduction band of CuO. Consequently, the accumulation of excess electrons in CuO causes a negative shift in the Fermi level of CuO. The efficient interparticle charge transfer leads to a higher catalytic activity and the formation of highly reduced states of TiO₂/CuO, which are stable even under oxygen saturated condition. Negative shift in the Fermi level of CuO of the catalyst TiO₂/CuO gains the required overvoltage necessary for efficient water reduction reaction. The function of CuO is to help the charge separation and to act as a water reduction site. The amount of CuO and crystalline structure were found to be crucial for the catalytic activity and the optimum CuO loading was *ca.* ~5–10% (w/w).

A. Introduction

The construction of an artificial photosynthetic system that generates O₂ and H₂ by sunlight irradiation using an aqueous semiconductor suspension is of great interest and the subject of active research because H₂ is a clean energy source.^{1–7} The direct photosplitting of water to hydrogen and oxygen has been regarded as the most promising approach ever since Fujishima and Honda reported the photoelectrochemical water splitting at a TiO₂ electrode.¹ The direct photosplitting systems have received considerable attention and several efforts have been made to improve the catalytic activity. Recently Domen *et al.* reported the layered catalysts of K₄Nb₆O₁₇ and A₄Ta_{6-x}O₁₇ (A = K, Rb) for the stoichiometric formation of H₂ and O₂ from H₂O splitting.^{8–10} The higher catalytic activity of the layered perovskite structure was due to the layered structure which retards the electron–hole recombination leading to high photocatalytic activity. A new type of water splitting system mimicking the Z-scheme in photosynthesis and IO₃⁻/I⁻ shuttle redox mediator was reported by Abe *et al.*^{11–13} in which the quantum efficiency of the stoichiometric water splitting was *ca.* 0.1% at 420.7 nm. Some of these authors reported the direct water splitting using an oxide semiconductor photocatalyst of In_{1-x}Ni_xTaO₄ (x = 0–0.2), with a quantum yield of about 0.66%.¹⁴ However low quantum yield is the major concern of the direct water splitting systems and to date they do not guarantee practical H₂ generation.

The difficulty of the direct water splitting into H₂ and O₂ is the oxidation of H₂O to O₂, which involves high overvoltage.^{15–16} RuO₂ or IrO₂ have been introduced to decrease the oxygen overpotential and the kinetics of an effective RuO₂ oxygen electrocatalyst have been attributed to catalysis by the intervening RuO₄/RuO₂ redox couple.^{17–19} Attempts have been made to optimize the H₂O oxidation process by introducing electron acceptors such as Ce⁴⁺ and Fe³⁺ ions.²⁰ However, the direct water oxidation to O₂ is an undiminished challenge.

On the other hand, it has been demonstrated that the photoreduction of water to H₂ at the expense of consuming some sacrificial electron donors can be achieved with high efficiency.^{21–26} Since the oxidation of water by holes is a slower process than the reduction by electrons, hole scavengers are introduced to expedite the water oxidation. The sacrificial agents

react irreversibly with the photogenerated holes suppressing the recombination of photogenerated electrons and holes on the semiconductor surface leading to higher photocatalytic H₂O reduction to H₂. However, the problem of using sacrificial agents is the cost of the sacrificial compounds. If the sacrificial agents are sorts of industrial waste, the use of sacrificial agents is beneficial. In this report, H₂ production using a CuO coated TiO₂ catalyst and methanol as a model sacrificial agent has been investigated.

B. Experimental

The CuO incorporated TiO₂ catalyst was prepared by the following method. The desired amount of Degussa P25 TiO₂ powder was suspended in distilled water and various amounts of Cu(NO₃)₂ (0.1 M, Fluka analytical grade) were added. The suspension was then stirred for 1 h at room temperature followed by evaporation to dryness by drying at 5 °C min⁻¹. The dried sample was finally washed with distilled water several times to remove unbound copper. In this way, the TiO₂ surface was coated by copper through physical and chemical interactions. Finally the copper loaded TiO₂ sample was calcined at the desired temperature at a rate of 10 °C min⁻¹.

Photolysis experiments were carried out in a Photophysics reactor with 125 W medium pressure mercury lamp. A quantity of catalyst equivalent to 200 mg of (TiO₂/CuO) was suspended in the reaction mixture, which contained ~5% of methanol (v/v) in water. Experiments were conducted with and without UV filters and several other liquid filters. The blank experiments were conducted with the catalysts in the absence of light and without the catalysts in the presence of light. The XPS spectra of the samples were measured using a XPS spectrophotometer (Leybold EA200) with Mg K α radiation at 75 W. The background pressure during the data acquisition was kept below 10⁻¹⁰ bar.

The flat-band potentials of the oxides were determined from Mott–Schottky plots (*i.e.* a plot of C⁻² vs. V, where C was the capacitance and V was the potential across the space charge layer) and using photocurrent onset potential methods.^{27–28} For electrochemical measurements, thin films of nanocrystalline TiO₂, CuO and TiO₂/CuO were prepared by mixing TiO₂, CuO or TiO₂/CuO in an agate mortar and adding a few drops of

Carbowax and polyethylene glycol. The final slurry was applied on a clean conducting glass by the doctor blade method and sintered in air at 450 °C for 30 min. To measure the capacitance, oxide coated plates were immersed in a Na₂SO₄ solution and the capacitance was measured as a function of the potential across the space charge layer at frequencies of 500 Hz and 1 kHz. The onset potential was determined by measuring the photocurrent under applied voltage.²⁷ Using the flat-band values and the band gap energies of the oxides, conduction and valence band positions were calculated.²⁷⁻²⁸

Hydrogen was analyzed by gas chromatography (Shimadzu 2000) using a TCD detector, Ar as a carrier gas and molecular sieve as column material. UV-Vis absorption spectra were recorded using a Shimadzu UV-1601 spectrophotometer. The powder samples were characterized by X-ray diffraction analysis (XRD). The onset potential method was employed to determine the Fermi levels of the samples. Dissolved copper was analyzed by atomic absorption spectroscopy (Philips 800-2 AAS, sensitivity ~1 ppm). The sample was first digested with conc. HNO₃ and the filtrate was analyzed for copper. Diffuse reflectance spectra were measured with a Shimadzu 3000 UV-Vis spectrophotometer.

C. Results and discussion

Catalyst characterization

Fig. 1 shows the XRD patterns of the catalyst powders used. As shown in Fig. 1-a, the Degussa P25 TiO₂ contains both anatase and rutile forms. The XRD pattern of the copper oxide, which was prepared by heating Cu(NO₃)₂ at 400 °C, is also shown in Fig. 1-b. According to the diffraction peaks at $2\theta = 35.5$ (2.520)°, 38.5 (2.322)° and 49 (1.861)°, the structure of copper oxide corresponds to the CuO crystalline structure. In Fig. 1-b, the diffraction peaks due to Cu₂O were not observed and hence it can be concluded that heating Cu(NO₃)₂ in air would not produce the Cu₂O crystalline form.

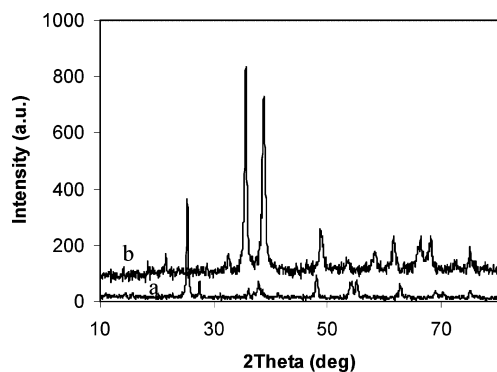


Fig. 1 XRD patterns of (a) P25 TiO₂, and (b) CuO prepared by heating Cu(NO₃)₂ at 400 °C.

Fig. 2A and 2B show the XRD patterns for 7% and 20% CuO coated TiO₂ respectively at different sintering temperatures. For 7% CuO loaded TiO₂, at 100 °C, weak signals due to amorphous CuO are noticeable. As the temperature increases, crystallinity begins at ~300 °C, and the crystalline peaks which appeared at $2\theta = 35.5$ (2.520)°, 38.5 (2.322)° and 49 (1.861)° correspond to the CuO crystalline structure. Therefore, from diffraction patterns it can be concluded that crystalline CuO on TiO₂ has been formed. Also it was noticed that other crystalline forms of copper oxide *i.e.* Cu₂O were not observed during the heat treatment of the copper oxide coated TiO₂ catalysts. The diffraction peaks of 7% CuO coated TiO₂ were weak, probably due to the formation of a thin CuO layer on TiO₂. Therefore, to confirm the crystalline nature of the copper oxide, we recorded the diffraction patterns of 20% Cu oxide loaded TiO₂ and these are shown in Fig. 2B. By comparing Fig. 2A and 2B, it can be

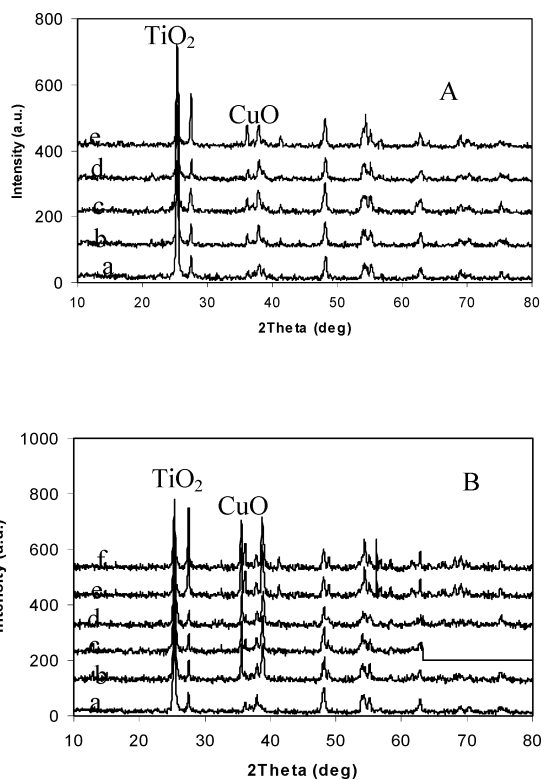


Fig. 2 (A) XRD patterns of TiO₂/CuO (7%) at the sintering temperatures: (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C. (B) XRD patterns of TiO₂/CuO (20%) at the sintering temperatures: (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C, (f) 600 °C.

concluded that the diffraction patterns of 20% CuO loaded TiO₂ catalyst were the same as those of 7% Cu loaded TiO₂ catalyst. This result confirms the crystalline form of copper oxide is CuO on the TiO₂ catalyst.

The diffuse reflectance spectra of TiO₂, CuO and CuO coated TiO₂ catalysts are shown in Fig. 3. The bare TiO₂ catalyst absorbs light mainly in the UV region while CuO absorbs mainly in the visible region. The CuO coated TiO₂ catalyst which was ash-yellow possesses absorption bands in the visible region whose intensity increases with the increase of the CuO content.

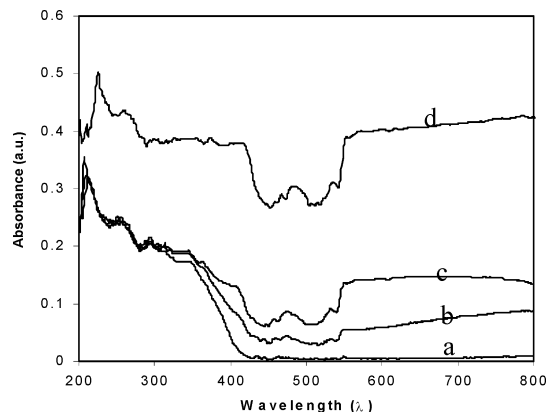


Fig. 3 Diffuse reflectance spectra of (a) TiO₂, (b) TiO₂/CuO (7%), (c) TiO₂/CuO (15%) and (d) CuO.

The XPS analyses of the samples TiO₂/CuO before and after irradiation (Fig. 4) show the appearance of spin-orbit split Cu2p_{1/2} and Cu2p_{3/2} with their shake-up satellites which indicates that Cu²⁺ species are formed on the titania film. The XPS peak intensity ratio of I_{Cu2p}/I_{Ti2p} is only 0.085 which is less than that of the threshold indicating highly dispersed CuO on the TiO₂ surface.

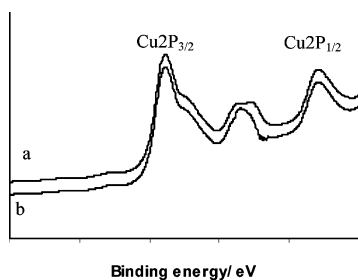


Fig. 4 Cu2p XPS spectra of samples: (a) TiO₂/CuO before irradiation and (b) TiO₂/CuO after irradiation.

Table 1 Calculated flat-band potential values of TiO₂, CuO and copper oxide loaded TiO₂ catalysts

Catalyst	Flat-band potential (vs. SCE)/eV
TiO ₂	-0.35
CuO	+0.12
TiO ₂ /CuO (3%)	-(0.30-0.33)
TiO ₂ /CuO (7%)	-(0.25-0.27)
TiO ₂ /CuO (10%)	-(0.22-0.25)
TiO ₂ /CuO (30%)	-(0.12-0.11)

The flat bands of TiO₂, CuO and CuO coated TiO₂ were measured using photocurrent onset potential and Mott-Schottky methods and the calculated conduction band (CB) and valence band (VB) positions are given in Table 1. The measured CB potentials of TiO₂ and CuO are -0.35 V and +0.12 V (vs. SCE) respectively and match well with the literature values. Coating of TiO₂ with 3% CuO, results in the formation of a CB at -0.30 V (vs. SCE) and the increase of the CuO content results in a slight movement of the Fermi potential in the anodic direction *i.e.* at 5% CuO coverage, the reported CB potential is -0.29 V and at 30% CuO coverage, the measured CB potential is -0.25 V.

Catalytic activity

Fig. 5 shows the H₂ evolution from an aqueous solution containing 5% methanol under UV light irradiation in the presence of CuO coated TiO₂ catalysts with the variation of the CuO content.

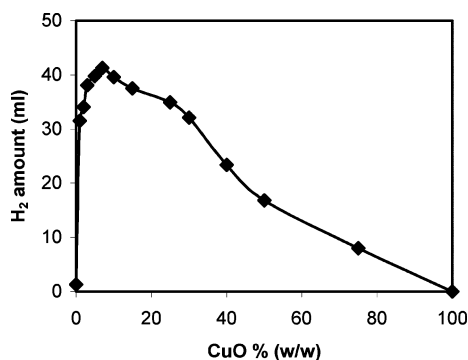


Fig. 5 Total hydrogen production amount for the catalyst TiO₂/CuO with the variation of the CuO content in the presence of UV light and methanol solution (95% H₂O, 5% methanol). The experiment was carried out for 2 h.

For bare TiO₂, the total amount of H₂ produced in 2 h is 1.25 ml (0.63 ml h⁻¹), while CuO alone did not give a measurable amount of H₂. At the optimum CuO loading, the H₂ production rate was found to be ~20 ml h⁻¹. Considering the CB potentials of CuO and TiO₂, the reason for not detecting H₂ with CuO could be understood. Further it was noticed that when UV cut-off filters (built in UV cut-off filter and NaNO₂ liquid cut-off filters) were used, no H₂ was generated. However, production of H₂ was noticed when a CuO cut-off filter (wavelength 500–

700 nm) was used. The H₂ production rate with the CuO cut-off filter is 9 ml h⁻¹ which is higher than the H₂ production rate for bare TiO₂, however it is less than the H₂ production rate when no filters were used. From the above results, one could conclude that the presence of both TiO₂ and CuO is essential for higher catalytic activity: TiO₂ plays an essential role for the reaction while CuO has a supportive role (*i.e.* catalytic) and the H₂ production reaction starts with the excitation of TiO₂ particles.

The H₂ yield is highly dependent on the sintering temperature of the catalyst. Shown in Fig. 6 is the H₂ yield for the catalyst TiO₂/CuO (7%) at different sintering temperatures. As prepared the TiO₂/CuO (7%) catalyst shows lower activity for H₂ production. However as the temperature increases, the H₂ production rate increases. The maximum H₂ production rate was observed at ~300–500 °C. Further increase of the sintering temperature, results in a decrease of the H₂ production rate. On the basis of the crystalline structure described in Fig. 2, the above results could be explained. The crystalline structure of CuO in as prepared TiO₂/CuO (7%) catalyst at 100 °C is amorphous. The crystallinity increases with the sintering temperature and at a temperature of ~300 °C, at which CuO is fully crystalline, the highest catalytic activity for H₂ production was observed. Therefore, it can be assumed that the crystalline nature of CuO is important for the H₂ production. As the sintering temperature is increased further, the surface area decreases and also the contact between the CuO–TiO₂ becomes weaker resulting in a decrease in the catalytic activity.

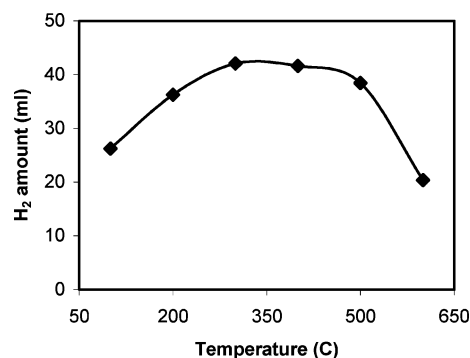


Fig. 6 Hydrogen production amount for 2 h UV irradiation of the catalyst TiO₂/CuO (7%) with the variation of the sintering temperature. The solution contained 95% H₂O and 5% methanol.

The stability of the TiO₂/CuO (7%) catalyst was studied by using the same catalyst for H₂ production several times. Fig. 7 shows the H₂ production rates with repeated use of the catalyst for H₂ production. As shown in Fig. 7, the catalytic activity decreases slightly after several experiments (curves a–e) but the original catalytic activity can be regained once the catalyst is again subjected to a heat treatment (curve f). The decrease in the catalytic activity with use could be due to accumulation of by-products on the catalyst surface which could easily be removed by the heat treatment without altering the surface properties. Copper was not detected in the reaction solution even after several hours of reaction and repeated use, which confirms that copper does not dissolve and leach into the reaction medium.

Mechanism

The results presented above clearly indicate that the TiO₂/CuO is a highly stable and active catalyst for the reduction of H₂O to H₂ under sacrificial conditions. No H₂ was observed when the reaction was carried out in absolute methanol indicating that the source of H₂ is H₂O. It was also noticed that there was total retardation of H₂ production when the excitation of TiO₂ was hindered. However, a comparable H₂ production rate was observed even when the excitation of CuO was prevented. The low H₂ production rate with the bare TiO₂ and the higher H₂

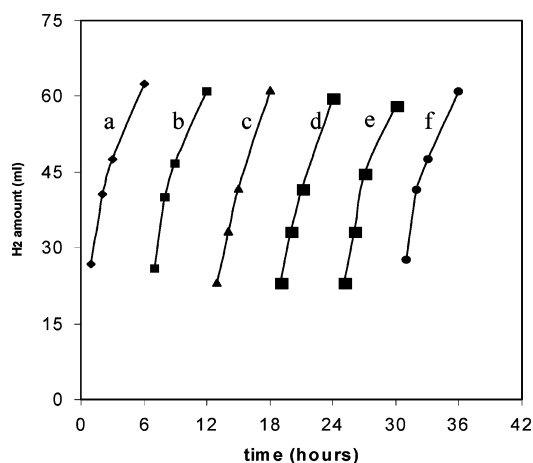


Fig. 7 Catalytic activity of TiO₂/CuO (7%) with repeated use of the catalyst (a) 1–6 h, (b) 7–12 h, (c) 13–18 h, (d) 19–24 h, (e) 25–30 h, (f) after cycle (e), the catalyst was sintered at 400 °C and the catalytic activity was checked for 1–6 h. Each time a fresh solution of 5% methanol was introduced.

production rate for TiO₂/CuO suggest that the coexistence of TiO₂ and CuO is necessary for higher catalytic activity. A metal coated TiO₂ photocatalyst (TiO₂-Pt) for the photoreduction of water where metal centers act as reducing centers by trapping excited electrons in the CB of TiO₂ has been reported.^{29–30} Considering the CB potentials of TiO₂ and CuO, one can argue that CuO may act similarly. However, XPS analyses showed that CuO was present as Cu²⁺ on the TiO₂ surface and metallic copper was not observed before or after irradiation of the TiO₂/CuO catalyst. This observation excludes the possibility of metal promoted photocatalytic hydrogen production from the water-methanol solution with the TiO₂/CuO catalyst. Considering the catalytic activity presented above, it can be assumed that the TiO₂ acts as the primary catalyst and CuO acts as a co-catalyst, helping charge separation as explained below. A recent research article by Slamet *et al.*,³¹ in which they reported the reduction of CO₂ using impregnated CuO on TiO₂ and assigned the higher catalytic activity of CuO to the redox cycle of Cu²⁺/Cu⁺, further supports the above observation.

An energy level diagram showing the positions of the bands of TiO₂ and CuO is presented in Fig. 8. Absorption of light greater than the band-gap energy of TiO₂ generates electrons and holes in the CB and VB respectively.

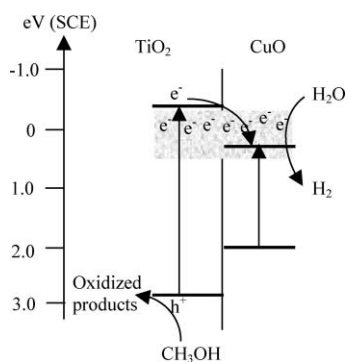


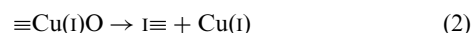
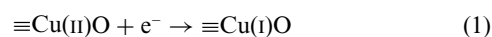
Fig. 8 Schematic diagram showing the energy band positions of TiO₂, CuO and the electron transfer direction.

The sacrificial electron donor consumes holes in the VB rapidly leaving electrons in the CB of TiO₂. The CB position of CuO below the CB of TiO₂ permits the transfer of electrons from the CB of TiO₂ to the CB of CuO. The catalyst turned to a purple-blue colour during irradiation. It has been reported that the purple colour is due to trapped electrons in TiO₂ which are

readily bleached on exposure to atmospheric oxygen because of the rapid transfer of trapped electrons to O₂ molecules. Additionally, the blue colour due to trapped electrons has not been observed when the reaction was carried out under O₂ saturated conditions. Surprisingly, the purple-blue colour developed in our system did not bleach instantly on exposure to air and the colour is quite stable for several hours in the atmosphere.

Also the H₂ production rates under Ar, O₂ and air saturated conditions are 23, 15 and 20 ml h⁻¹ respectively and the catalyst turned to a purple-blue colour during irradiation no matter what the reaction atmosphere was. This observation strongly suggests that the transfer of excited electrons from the CB to O₂ is competitive and, in the presence of CuO, the electrons in the CB of the TiO₂ particles are efficiently separated from the surface of TiO₂. One way of separating electrons from the CB of TiO₂ is to transfer the electrons to the CB of CuO. Since the CB of CuO is situated below the CB of TiO₂, the electrons in the CB of TiO₂ can rapidly transfer to the CB of CuO competing with the electron transfer to O₂. Once the electrons are transferred to CuO, the Fermi level of CuO is raised which results in a more negative CB potential of CuO. The negative shift of the CB potential was confirmed by the flat-band potential measurements obtained using the onset potential method and which are given in Table 1. The negative movement of the CB potential of CuO facilitates the interparticle electron transfer from CuO to trapped states of TiO₂ resulting in Fermi level equilibration and the appearance of a blue colour. Earlier it was shown that no H₂ was observed with the irradiation of CuO particles and the inability of CuO to reduce water was attributed to its inappropriate band energy position. However, in the composite catalyst, the measured band position is situated at -0.20–0.25 V (vs. SCE) favouring the water reduction. Therefore we believe that the purple colour developed during irradiation is due to reduced states of both TiO₂ and CuO and the rapid interparticle electron transfer increases the catalytic activity.

The TiO₂/CuO catalyst was found to be very stable with prolonged use and the stability of the catalyst could be understood on the basis of rapid electron transfer. In the TiO₂/CuO catalyst, CuO is the unstable catalyst compared to the stable TiO₂ catalyst because photodissolution of Cu²⁺ particles by accepting photogenerated electrons (as shown below) and leaching to the reaction solution³² may occur.



\equiv represents the oxide surface and $\text{I}\equiv$ represents the Cu(I) detached surface.

However, no copper ions were detected in our reaction solution even after many hours of irradiation and repeated use of the catalyst. (The copper detection limit is 1 ppm). This could be probably due to rapid interparticle electron transfer and efficient water reduction reaction which retard the photodissolution of CuO catalyst.

D. Conclusion

The TiO₂/CuO catalyst was found to be an active and stable photocatalyst for H₂ evolution from an aqueous solution under sacrificial conditions. The TiO₂ particles act as the primary catalyst and CuO acts as the co-catalyst. Bare CuO was found to be an inactive catalyst for water reduction and in the TiO₂/CuO catalyst, CuO acts as the water reduction site. Highly stable reduced states of TiO₂ and CuO were observed even under aerobic conditions, which was due to efficient interparticle charge transfer process. Higher catalytic activity and increasing stability of TiO₂/CuO also arise due to an efficient interparticle charge transfer process.

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