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# Multi-electron storage of photoenergy using $Cu_2O$ -TiO<sub>2</sub> thin film photocatalyst

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## Abstract

UV-vis irradiation of thin films of TiO<sub>2</sub> (ITO/TiO<sub>2</sub>) and Cu<sub>2</sub>O/TiO<sub>2</sub> (ITO/Cu<sub>2</sub>O/TiO<sub>2</sub>) coated on conducting glasses generate H<sub>2</sub> from H<sub>2</sub>O and once the illumination is ceased, the H<sub>2</sub> production was still noticeable under dark for ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> at a lesser production rate for up to 2 h. No such dark reactions were observed for ITO/TiO<sub>2</sub> or TiO<sub>2</sub>-coated copper metal foil (Cu/TiO<sub>2</sub>). It was noticed that the irradiation of ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> leads to formation of trapped electrons and this stored energy leads to generate H<sub>2</sub> from H<sub>2</sub>O in the dark.

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#### 1. Introduction

Photo-induced charge separation and electron transfer are the fundamental phenomena involved in the processes of light energy storage for photosynthesis in plants, xerography, photovoltaic energy conversion, etc [1]. For efficient harvesting of light energy, photo-induced charge separation is a process of central importance and it is necessary to have a well-stabilised charge-transfer products and stabilised charge-separated states. Charge separation is facilitated by carrier delocalisation and by spatial separation of electrons and holes [1-3]. Several methods have been attempted to achieve a spatial separation of electrons and holes: (a) combining of two semiconducting oxide materials (composites) SnO<sub>2</sub>/ZnO [4,5] and TiO<sub>2</sub>/WO<sub>3</sub> [6,7], (b) introduction of a thin insulating layer on semiconductor thin films [8,9], (c) supramolecular control over donor-acceptor complex [10,11], and (d) assembling dyads and triads [12,13], etc.

In an earlier report, we found that CuO-incorporated  $TiO_2$  catalyst was an active photocatalyst for the reduction of  $H_2O$  under sacrificial conditions [14]. The catalytic

activity originates from the photogeneration of excited electrons in the conduction bands (CB) of both TiO<sub>2</sub> and CuO resulting in an accumulation of excess electrons. The accumulation of electrons leads to formation of highly reduced states of TiO<sub>2</sub>/CuO, which are stable even under oxygen saturated condition. It has been demonstrated by Fujishima that the reductive energy generated at a  $TiO_2$ photocatalyst under UV light can be stored in WO<sub>3</sub> by coupling them together, and the stored energy can be used in dark [15-18]. The advantage of such a system is that energy storage photocatalyst can be operated even at dark conditions. In this investigation, we report the preparation of Cu<sub>2</sub>O/TiO<sub>2</sub> thin film on ITO conducting glass. Under UV-vis irradiation of these films, electrons are trapped in Cu<sub>2</sub>O/TiO<sub>2</sub> thin films and these trapped electrons are found to be stable even at oxygen saturated condition. These trapped electrons can be utilised later on, under dark conditions, to drive the chemical reactions such as watersplitting reaction.

# 2. Experimental

On ITO, Cu<sub>2</sub>O and TiO<sub>2</sub>, thin films were prepared as follows: 0.5 g of TiO<sub>2</sub> (P25 TiO<sub>2</sub>, Degussa) was mixed with 2.5 ml of CH<sub>3</sub>COOH and Triton followed by addition of

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25 ml of ethanol and the mixture was sonicated using ultrasonic horn for 10 min. On cleaned ITO glasses, a thin film of P25 TiO<sub>2</sub>, Degussa, was coated by spraying the above mixture and the film was sintered at 550 °C for 30 min in air. On the TiO<sub>2</sub>-coated ITO glass, Cu<sub>2</sub>O was electrodeposited potentiostatically at  $-200 \,\mathrm{mV}$  and  $60 \,^{\circ}\mathrm{C}$ using Ag/AgCl and Pt as reference and counter electrodes, respectively [19]. The electrolysis solution contained  $CuSO_4 \cdot 5H_2O$  (1.92 g), lactic acid (7.61 ml), and distilled water (22.4 ml) in which NaOH (4.8 g) was added. For light reaction, a piece of  $ITO/Cu_2O/TiO_2$  glass (1 × 1 cm) or  $ITO/TiO_2$  glass (1 × 1 cm) was placed in a 50 ml tube which contained 10 ml of 5% of methanol solution and sealed using a rubber septum. Irradiation was carried out at different atmospheric conditions at light intensity of 90 mW/cm<sup>2</sup> using Hanau Suntest setup. The gaseous products were analysed using gas chromatography with a thermal conductivity detector. The photovoltage  $(V_{oc})$  of the electrode (ITO/Cu<sub>2</sub>O/TiO<sub>2</sub>) was measured by using Keithly multimeter in the presence of an electrolyte of  $1.0 \times 10^{-3}$  M Na<sub>2</sub>SO<sub>4</sub> solution. X-ray diffraction (XRD) measurements were done on Shimadzu XD-7A.

# 3. Results and discussions

Fig. 1 shows the H<sub>2</sub> yield in the presence of 5% methanol under UV–vis irradiation of thin films of (a) ITO/TiO<sub>2</sub>, (b) ITO/Cu<sub>2</sub>O/TiO<sub>2</sub>, (c) Cu foil/TiO<sub>2</sub> and (d) ITO/Cu<sub>2</sub>O. For the results presented in Fig. 1, the irradiation was carried out exposing the oxide layer in Ar saturated condition. As shown in Fig. 1, curve (d), H<sub>2</sub> formation for ITO/Cu<sub>2</sub>O is not observed indicating that Cu<sub>2</sub>O alone is an inactive catalyst for H<sub>2</sub> production even though it has appropriate energy positions for water splitting. The fact that Cu<sub>2</sub>O is inactive for water splitting indicates that photogenerated charges are rapidly recombined in Cu<sub>2</sub>O particles. As expected, ITO/TiO<sub>2</sub>, Cu foil/TiO<sub>2</sub> and ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> films exhibit moderate H<sub>2</sub> yield. Somewhat higher H<sub>2</sub> yield for ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> film indicates that the presence of



Fig. 1. Change of  $H_2$  yield under 2 h of UV–vis irradiation and under dark of thin films: (a) ITO/TiO<sub>2</sub>, (b) ITO/Cu<sub>2</sub>O/TiO<sub>2</sub>, (c) Cu/TiO<sub>2</sub> and (d) ITO/Cu<sub>2</sub>O.



Fig. 2. Changes in  $H_2$  volume produced under dark after 2 h of initial UV-vis irradiation of thin films of ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> in (a) Ar-saturated, (b) Air-saturated, (c) O<sub>2</sub>-purged and (d) O<sub>2</sub>-pressurised conditions.

Cu<sub>2</sub>O enhances the photo-induced charge separation. The interesting point here is that once the illumination is ceased off after 2h of irradiation, the H<sub>2</sub> production was still noticeable under dark condition for ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> (curve b) film for up to 1.5–2h. For ITO/TiO<sub>2</sub> (curve (a)) and Cu foil/TiO<sub>2</sub> (curve (c)) films, total retardation of H<sub>2</sub> yield is observed once the illumination is ceased. The observed decrease in H<sub>2</sub> yield amount under dark condition for ITO/TiO<sub>2</sub> and Cu foil/TiO<sub>2</sub> in Fig. 1, is due to withdrawal of several gas samples.

In order to understand the  $H_2$  production of ITO/Cu<sub>2</sub>O/ TiO<sub>2</sub> film under dark condition, H<sub>2</sub> production was investigated with different atmospheric conditions. The H<sub>2</sub> production rates under dark condition for ITO/Cu<sub>2</sub>O/ TiO<sub>2</sub> film under different atmospheric conditions are shown in Fig. 2. For the results shown in Fig. 2, prior to dark H<sub>2</sub> production analysis, the film was initially irradiated for 2h and then illumination was discontinued and the H<sub>2</sub> was analysed under dark condition (H<sub>2</sub> production under dark condition only shown in Fig. 2). The H<sub>2</sub> production under dark is still evident under airsaturated condition (curve (b), Fig. 2), however, the  $H_2$ yield is less than under Ar-saturated condition (curve (a), Fig. 2). The production of  $H_2$  under dark condition in air when the illumination is ceased off is curious to be observed due to the short life-time of the photogenerated charge species under air or O2-saturated conditions due to rapid electron capture by O<sub>2</sub> molecules [20]. However, stable photo-induced electrons under Ar-saturated conditions have been reported [20]. For further confirmation of  $H_2$  production after illumination was discontinued, the  $H_2$ production was studied under different partial pressure of O<sub>2</sub> for ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> film in 5% methanol solution and the results are shown in Fig. 2, by curves (c) and (d). It is interesting to note the H<sub>2</sub> production under O<sub>2</sub>-purged condition ( $\sim$ 1 atm) during irradiation and followed by dark  $H_2$  production. However, when the  $O_2$  pressure was



Fig. 3. Schematic diagram showing the energy band positions of  $TiO_2$  and  $Cu_2O$  and the electron transfer directions.

increased further (approximately higher than  $1 \text{ atm}^1$ ), H<sub>2</sub> production under light decreases drastically and the H<sub>2</sub> production under dark is not observed at all.

We observed the following colour changes during above experiments. During irradiation of ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> film in 5% methanol in the presence of air, the  $TiO_2$  layer turned blue while Cu<sub>2</sub>O layer turned to dark black-purple colour. When the same experiment was carried out with different partial pressure of O2, appearance of blue colour was noticed even up to 1 atm but at high O<sub>2</sub> pressure (just above the atmospheric pressure), the blue colouration was not observed. When the reaction was carried out in H<sub>2</sub>O without sacrificial agent under Ar or air, H<sub>2</sub> formation was not observed in both cases. However, under Ar, the TiO<sub>2</sub> film turned blue and Cu<sub>2</sub>O layer turned purple-black while under air, the colour of Cu<sub>2</sub>O layer remains but a pale blue colour was noticed in TiO<sub>2</sub> layer. Also when ITO/Cu<sub>2</sub>O was irradiated in 5% Methanol solution or in H<sub>2</sub>O, the colour of the Cu<sub>2</sub>O film remains red.

By considering the above observations and the energy level diagrams of TiO<sub>2</sub> and Cu<sub>2</sub>O, the mechanism of the H<sub>2</sub> production of ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> and the formation of blue and purple-black colours in TiO<sub>2</sub> and Cu<sub>2</sub>O, respectively, under continuous light irradiation can be considered as follows. An energy level diagram showing the positions of the bands of TiO<sub>2</sub> and Cu<sub>2</sub>O is presented in Fig. 3. Absorption of light greater than the band-gap energies of TiO<sub>2</sub> and Cu<sub>2</sub>O generates electrons and holes in the CB and VB, respectively. Since the CB of TiO<sub>2</sub> is situated below the CB of Cu<sub>2</sub>O, electrons transfer from Cu<sub>2</sub>O to TiO<sub>2</sub> is thermodynamically permitted while holes transfer from VB of TiO<sub>2</sub> to Cu<sub>2</sub>O is permitted. For ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> film, earlier we noticed that during irradiation, no change in colour of Cu<sub>2</sub>O film was observed in the absence of a suitable sacrificial agent under air. However, under Ar without a sacrificial agent, we noticed the appearance in blue colour in TiO<sub>2</sub> and purple-black colour in Cu<sub>2</sub>O films. Therefore, one can argue that the blue and pink colour species are formed due to reductive process (by capturing electrons) and not by the oxidative process (by capturing holes), such as reaction (1). This argument is valid since in the presence of molecular O<sub>2</sub> (i.e. under air), the reductive process could not occur due to capture of excited electrons efficiently in the absence of a sacrificial agent.

$$Cu_2O + H_2O + 2h^+ \rightarrow 2CuO + 2H^+$$
(1)

The X-ray diffraction studies confirmed that the reaction (1) or the oxidative process does not take place during irradiation. The X-ray diffraction patterns of ITO/Cu<sub>2</sub>O/  $TiO_2$  films before (pattern (a)) and after (pattern (b)) irradiations are shown in Fig. 4. The peaks at  $2\theta$ ,  $25.51^{\circ}$ ,  $27.64^\circ$ ,  $38.03^\circ$ ,  $48.28^\circ$  and  $54.08^\circ$  are of TiO<sub>2</sub> while peaks at  $36.56^{\circ}$  (111),  $42.61^{\circ}$  (200) and  $51.68^{\circ}$  (211) are of Cu<sub>2</sub>O. In the after-irradiated sample, the diffraction patterns of CuO are absent while peaks due to Cu<sub>2</sub>O remains the same indicating the presence of a similar crystalline structure for Cu<sub>2</sub>O before and after irradiation. From these results, it can be concluded that although the holes transfer from the VB of TiO<sub>2</sub> to VB of Cu<sub>2</sub>O is thermodynamically allowed, the holes transfer did not take place. On the other hand, the appearance of blue colour in TiO2 and purple-black colour in Cu<sub>2</sub>O films under Ar saturated condition in H<sub>2</sub>O confirm that electron transfer takes place. The possible electrons transfer reactions are:

$$Cu_2O \xrightarrow{nv_1} Cu_2O(CB e^{-})$$
<sup>(2)</sup>

1

 $\Omega(CP)$ 

T:O

$$\operatorname{TiO}_2 \xrightarrow{nv_2} \operatorname{TiO}_2(\operatorname{CB} e^-)$$
 (3)

$$\operatorname{Cu}_2 \operatorname{O}(\operatorname{CD} \operatorname{C}) + \operatorname{HO}_2 \to \operatorname{Cu}_2 \operatorname{O} + \operatorname{HO}_2(\operatorname{CD} \operatorname{C})$$
(4)

 $T_{i}O_{i}(CP_{a}^{-})$ 

 $(\Lambda)$ 

$$Cu_2O(CB e^-) \rightarrow Cu_2O(trapped e^-)$$
 (5)



Fig. 4. XRD patterns of the thin films of  $ITO/Cu_2O/TiO_2$ : (a) before irradiation and (b) after UV-vis irradiation.

<sup>&</sup>lt;sup>1</sup>Since the experimental setup does not allow us to adjust the  $O_2$  pressure exactly, the pressure was adjusted controlling the gas outlet during purging of the experimental setup.

$$TiO_2(CB e^-) \rightarrow TiO_2(trapped e^-)$$
 (6)

Once the electron transfer takes place, the electrons in the CB or trapped electrons may participate for the hydrogen evolution reaction (7).

$$2e^{-}(TiO_2) + 2H_2O \rightarrow H_2 + 2OH^{-}$$
 (7)

The H<sub>2</sub> yield of reaction (7) for ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> films in H<sub>2</sub>O is negligible compared to the H<sub>2</sub> yield in the presence of a sacrificial agent indicating that an efficient hole transfer is necessary in order reaction (7) to take place.

The interesting point here is the continuation of  $H_2$ production with ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> films under sacrificial conditions through reaction (7) even under dark condition after the illumination was ceased off. As explained earlier, the appearance of blue colour on  $TiO_2$  and purple-black colour on Cu<sub>2</sub>O of ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> films impart the reductive process that takes place during irradiation. These reductive species could be trapped by electrons in both TiO<sub>2</sub> and Cu<sub>2</sub>O as it has been reported the presence of shallow and deep traps in semiconductors like TiO<sub>2</sub> [21,22] and insulators like MgO [23] in which the shallow traps are sensitive to the environmental condition while deep traps are less sensitive. The life-time of these trapped electrons from seconds to several microseconds has been reported [24]. Therefore, the mechanism of charge trapping and the follow-up dark reaction in ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> films is considered as follows; electrons excited by UV-vis light are trapped at electron trapping centres of both Cu<sub>2</sub>O and  $TiO_2$ . In the case of  $ITO/Cu_2O/TiO_2$ , the blue colour was found to be stable indicating that these electrons are trapped in deep traps. These deep-trapped electrons could release under dark and may eventually participate for the hydrogen evaluation reaction (7) in dark.

Electron trapping is further substantiated by the electron discharge study, which was shown in Fig. 5. The potential of ITO/Cu<sub>2</sub>O/TiO<sub>2</sub> electrode increased to  $\sim$ 600 mV during UV–vis irradiation in the presence of 0.01 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. After the illumination was turned off, the electrode potential droped to  $\sim$ 250 mV initially and then



Fig. 5. Change of potential of  $ITO/Cu_2O/TiO_2$  electrode under no light after 90 min of initial UV irradiation.

remained at  $\sim 300 \text{ mV}$  for several hours until it reaches to zero electrode potential which indicates that the ITO/ Cu<sub>2</sub>O/TiO<sub>2</sub> electrode was charged or the photogenerated electrons were trapped in Cu<sub>2</sub>O/TiO<sub>2</sub> films. Under these conditions, the extra electrons generated with sunlight, can be stored in trapped sites for later use. The energy storage system described here can be compared with the energy storage of TiO<sub>2</sub>–WO<sub>3</sub> photocatalytic system [16,17].

### 4. Conclusion

In conclusion, we investigated the generation of stable trapped electrons in  $ITO/Cu_2O/TiO_2$  films. The trapped electrons in  $TiO_2$  and  $Cu_2O$  films have extended life-time and these stored electrons can be utilised for follow-up dark reactions.

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