

## Photoelectrochemical production of H<sub>2</sub>: an example of a model system

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### Abstract

H<sub>2</sub> evolution was observed from a photoelectrochemical cell using an n-type Cu<sub>2</sub>O photoelectrode under visible light irradiation. Three-electrode configuration was used in the photoelectrochemical cell to observe H<sub>2</sub> evolution. AgCl/Ag calomel electrode and a platinum plate were used as the reference and counter electrodes, respectively. FeSO<sub>4</sub> (10<sup>-4</sup> M) and CuSO<sub>4</sub> (10<sup>-3</sup> M) solutions were used as the electrolytes. H<sub>2</sub> evolution was visible on the platinum electrode. The highest H<sub>2</sub> generation (8x10<sup>-2</sup> mol l<sup>-1</sup>/h) appears at the potential +0.5V vs NHE in the presence of CuSO<sub>4</sub> solution as the electrolyte. Degassing the system after each 4 hour cycle, the system is irradiated again. After each cycle, a decrease of the saturated value of evolved H<sub>2</sub> is observed. In case of FeSO<sub>4</sub> electrolyte, this decrease is due to the fact, that during the illumination, in addition to the H<sub>2</sub> evolution, a black amorphous product is formed gradually on the Pt electrode, thus decreasing the activity of the PEC cell acting the black amorphous product as a photocatalyst. When the biasing is more negative, band bending at semiconductor-electrolyte interface is small which reduces the concentration of the photogenerated charge carriers and thus decrease the H<sub>2</sub> evolution. When the bias is more positive than +0.5V vs NHE, the band position of CB becomes more positive compared to the H<sub>2</sub>/H<sup>+</sup> redox level that suppresses the H<sub>2</sub> evolution. V-I characteristics for the PEC were investigated. Typical V-I characteristic curves were observed under dark and illumination for a PEC with n-type semiconductor. When the applied potential is more negative than the onset potential, dark current increases rapidly. For the positive potentials (vs NHE) dark current is almost zero for some regions. Under irradiation, total current increases at positive applied potential. Onset potential occurs at +0.11V vs NHE.

### Introduction

Recently, particulate semiconductor systems have received much attention for the evolution of H<sub>2</sub> and O<sub>2</sub> from water for use as energy fuels<sup>1-8</sup>. Number of investigations were presented and found the yields obtained were very poor and could be detected only by using a polarographic detector or gas chromatography. A variety of semiconductor materials in the particulate or colloidal form are known to photo-reduce or photo-oxidize water under sacrificial conditions by absorbing UV light<sup>4-8</sup>. However there are few semiconductor materials which photo-reduce or photo-oxidize water under visible light with sacrificial agents, the yield of the gas evolution is in the micro moles range and evolution of gas is not visible.

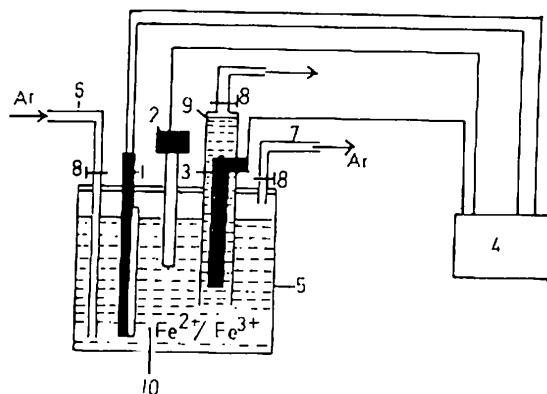
Cu<sub>2</sub>O (band gap = 2.0eV) is an attractive semiconductor material for low cost PEC devices<sup>10,11</sup>. Recently, Domen *et al.*<sup>12</sup> have demonstrated photocatalytic decomposition of water into H<sub>2</sub> and O<sub>2</sub> on p-Cu<sub>2</sub>O powder, without any noticeable decrease in the activity for more than 1900h, under visible light. However, the gas evolved was in micro-moles in this investigation. Further de Jongh *et al.*<sup>13</sup> demonstrated the splitting of water molecules into H<sub>2</sub> and O<sub>2</sub> with three electrode set-up in the presence of Na<sub>2</sub>SO<sub>4</sub> as the electrolyte using polycrystalline p-Cu<sub>2</sub>O photoelectrodes in a photoelectrochemical cell. The gas evolution was not detected with eyes from these systems since the yield was very small.

Recently, during the investigations of photoelectrochemical characteristics of n-type Cu<sub>2</sub>O<sup>10,11</sup> we have observed significant H<sub>2</sub> generation from n-Cu<sub>2</sub>O photoelectrodes in a photoelectrochemical cell under biasing conditions in the presence of CuSO<sub>4</sub> and FeSO<sub>4</sub> solutions as the electrolyte. H<sub>2</sub> generation can be observed on the platinum electrode with eyes under visible light irradiation. This paper presents a model system of H<sub>2</sub> generation using n-Cu<sub>2</sub>O thin films in the presence of CuSO<sub>4</sub> and FeSO<sub>4</sub> electrolytes.

### Experimental

A well cleaned copper plate (99% purity) is immersed into a (0.001M) CuSO<sub>4</sub> solution for two days<sup>10,11</sup>, or boiled in the CuSO<sub>4</sub> solution for 15min to obtain n-Cu<sub>2</sub>O on the copper substrate. X-ray diffractogram of boiled samples (Figure 1) confirmed that the obtained films on the copper substrate are entirely Cu<sub>2</sub>O<sup>10,11</sup>. Peaks corresponding to CuO or any other complexes were not significant in the diffractogram.

Scanning electron micrograph (SEM) picture of n-Cu<sub>2</sub>O prepared by boiling the copper substrate in a CuSO<sub>4</sub> solution shows hexagonal crystallites<sup>10,11</sup>.

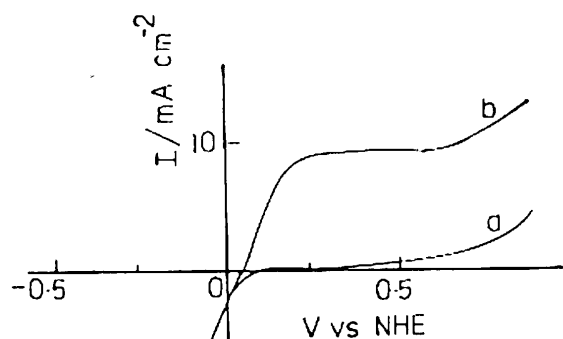


**Figure 1. Experimental set up used for the study of H<sub>2</sub> evolution**

- |                            |  |  |                 |
|----------------------------|--|--|-----------------|
| 1- Photoelectrode          | 2- Calomel electrode   | 3- Platinum counter electrode  | 4- Potentiostat |
| 5-Transparent perspex cell | 6- Inlet glass tube to flush Ar  | 7- Outlet glass tube to remove the dissolved H <sub>2</sub> and O <sub>2</sub> with flushed Ar |                 |
| 8- Gates                   | 9- Perspex cell to collect H <sub>2</sub> produced on the platinum counter electrode | 10- Electrolyte  |                 |

For PEC cell measurements, a potentiostat was used with three electrode configuration having Pt counter electrode and AgCl/Ag reference electrode as shown in Figure 1. Electrolyte level in the Perspex cell-9 was adjusted from gate-8 attached with the Perspex cell-9 before irradiation. Before irradiation, the cell was degassed by flushing Ar for 1 hr through inlet-6 and outlet-7 glass tubes opening the gates-8, reducing the dissolved H<sub>2</sub> and O<sub>2</sub> concentration in the electrolyte medium down to  $0.2 \times 10^{-6} \text{ mol l}^{-1}$ . After flushing with Ar, the entire cell was sealed to prevent the dissolution of H<sub>2</sub> and O<sub>2</sub> from the environment during the operation of the cell. A  $250 \text{ W cm}^{-2}$  tungstun filament lamp was used as the light source. During the illumination of the photoelectrochemical cell, the level of the electrolyte inside the perspex cell-9 goes down gradually due to the accumulation of H<sub>2</sub> produced on the Pt counter electrode. H<sub>2</sub> amount produced in the Perspex cell was separated by opening the gate-8 attached to the Perspex cell-9, after reaching the saturation. The entire system was degassed with Ar again and then illuminated. The amount of the produced H<sub>2</sub> gas was estimated from gas chromatography (Hitachi 263-50 gas chromatograph).  $10^{-3} \text{ M}$  CuSO<sub>4</sub> and FeSO<sub>4</sub> solutions were used as the electrolytes. Intensity measurements were done by using a Radiometer. Photocurrent spectra were measured with a monochromator. Double distilled water was used for the experiment. All the applied potentials measured with AgCl/Ag electrode were converted with respect to the natural hydrogen electrode (NHE).

## Results and Discussion



**V-I characteristics**

Figure 2. V-I characteristics of n-Cu<sub>2</sub>O a- dark and b- illuminated, in the presence of FeSO<sub>4</sub> ( $10^{-4} \text{ M}$ )

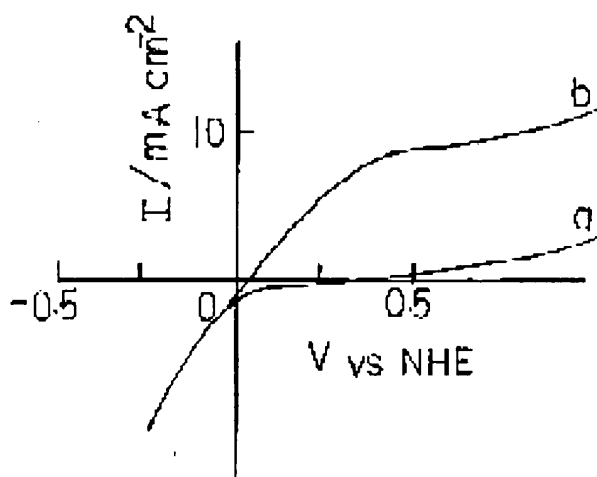


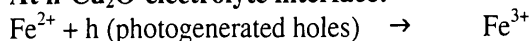
Figure 3. V-I characteristics of n-Cu<sub>2</sub>O a- dark and b- illuminated, in the presence of Cu SO<sub>4</sub> ( $10^{-4} \text{ M}$ )

V-I characteristics for the PEC in the presence of FeSO<sub>4</sub> and CuSO<sub>4</sub> solutions are shown in Figure 2 and Figure 3. Shapes of the curves show typical V-I characteristics under dark and illumination for a PEC with n-type semiconductor<sup>14</sup>. When the applied potential is more negative than the onset potential, dark current increases rapidly. For the positive potentials (vs NHE), dark current is almost zero for some regions. Under irradiation, total current increases at positive applied potentials (curve-b). Onset potential occurs at +0.11V vs NHE) is nearly equal to the flat band potential of n-Cu<sub>2</sub>O in the presence of FeSO<sub>4</sub> and CuSO<sub>4</sub> redox couples with respect to NHE.

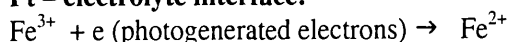
#### Photocurrent action spectra

Figures 4 and 5 show the photocurrent action spectra measured at various biasing conditions. Curve-a corresponds to the photocurrent action spectra measured at +0.5V vs NHE. To generate a photocurrent in the presence of FeSO<sub>4</sub> electrolyte, photogenerated holes must tunnel through the electrode-electrolyte interface to oxidize Fe<sup>2+</sup> ions and photogenerated electrons must reach the Pt counter-electrode through the internal circuit to reduce Fe<sup>3+</sup> ions, as given below:

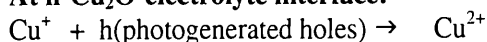
#### At n-Cu<sub>2</sub>O-electrolyte interface:



#### Pt – electrolyte interface:



#### At n-Cu<sub>2</sub>O-electrolyte interface:



#### Pt- electrolyte interface:

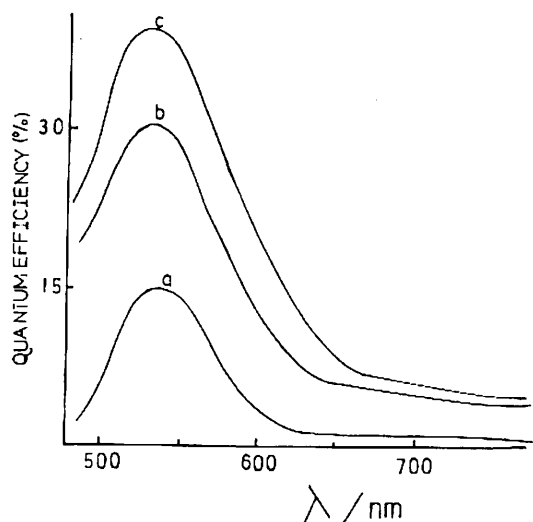
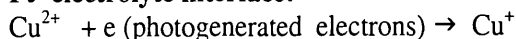


Figure 4. Photocurrent action spectra at different bias potentials a- +0.5V vs NHE, b- +0.55V vs NHE c- +0.6V vs NHE in the presence of FeSO<sub>4</sub> (10<sup>-4</sup> M)

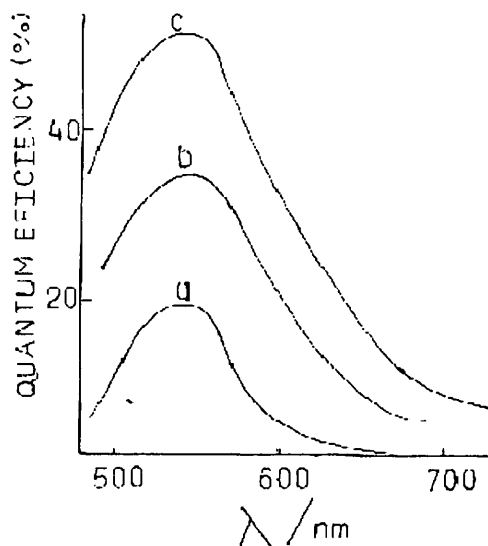


Figure 5. Photocurrent action spectra at different bias potentials a- +0.5V vs NHE, b- +0.55V vs NHE c- +0.6V vs NHE in the presence of CuSO<sub>4</sub> (10<sup>-3</sup> M)

When the biasing potential becomes more positive, photocurrent quantum efficiencies are enhanced in the photocurrent action spectra, as seen in the curves-b and c in the Figures 4 and 5 without changing the shape, indicating that the photocurrent enhancement is due to the increase of the photogenerated charge carriers and not due to any chemical reaction in the electrolyte medium. When the biased potentials are more positive than the onset potential, electric field in the space charge layer at n-Cu<sub>2</sub>O - electrolyte interface is increased, facilitating the separation of photogenerated charge carriers since both the CB and VB bend down.

Figure 6 shows the energy level positions of CB and VB of the semiconductor, redox levels of H<sup>+</sup> /H<sub>2</sub>, O<sub>2</sub>/H<sub>2</sub>O, Fe<sup>2+</sup> / Fe<sup>3+</sup> and Cu<sup>+</sup> / Cu<sup>2+</sup> measured with respect to NHE. Note that the redox levels (+0.65V vs NHE) of Fe<sup>2+</sup> / Fe<sup>3+</sup> and (+0.45V vs NHE) are located between CB (+0.11V vs NHE) and VB (+2.1V vs NHE). The location of the VB is more positive than the redox levels of Fe<sup>2+</sup> / Fe<sup>3+</sup> or Cu<sup>+</sup> / Cu<sup>2+</sup> making of possible to transfer photogenerated holes from the VB to Fe<sup>2+</sup> ions or Cu<sup>+</sup> ions efficiently<sup>16</sup>.

In case of  $\text{CuSO}_4$  electrolyte medium photocurrent generation can be presented as follows.

### $\text{H}_2$ evolution

Figure 7 shows the variation of  $\text{H}_2$  evolution with time at +0.5V vs NHE in the presence of  $\text{FeSO}_4$  and  $\text{CuSO}_4$  solutions. Degassing the system after each 4 hour cycle, the system is irradiated again. After each cycle, a noticeable decrease of the saturated value of evolved  $\text{H}_2$  is observed in case of the system in the presence of  $\text{FeSO}_4$ . This decrease due to the fact, that during the illumination, in addition to the  $\text{H}_2$  evolution, a black amorphous product is formed gradually on the Pt electrode, thus decreasing the activity of the PEC cell acting as a photo-catalyst<sup>13</sup>. In the presence of  $\text{CuSO}_4$  higher  $\text{H}_2$  yield was observed compared to that of the system in the presence of  $\text{FeSO}_4$ . After each cycle saturated value was not changed. We note that the most important factor to generate  $\text{H}_2$  from water in PECs is the favorable band positions<sup>13</sup>. CB band position of n- $\text{Cu}_2\text{O}$  (+0.11V vs NHE) and the  $\text{H}^+/\text{H}_2$  (0.0V vs NHE) redox level are very close to each other.

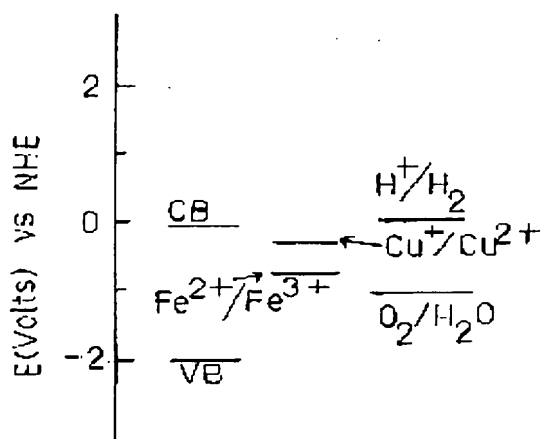


Figure 6. Estimated band positions of n- $\text{Cu}_2\text{O}$  and  $\text{H}^+/\text{H}_2$ ,  $\text{O}_2/\text{H}_2\text{O}$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Cu}^+/\text{Cu}^{2+}$  redox levels with respect to NHE.

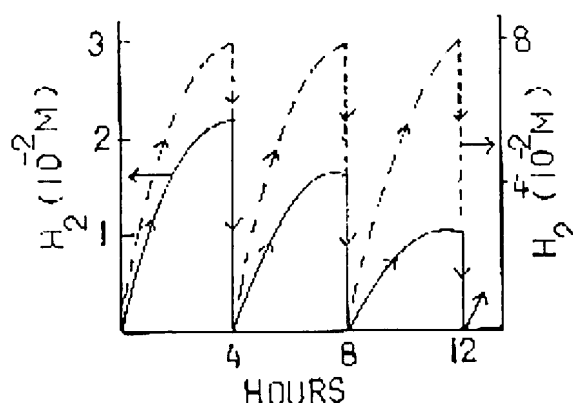


Figure 7. The variation of  $\text{H}_2$  produced with time measured by gas chromatography at +0.5V vs NHE in the presence of  $\text{FeSO}_4$  ( $10^{-4}$  M) and  $\text{CuSO}_4$  ( $10^{-3}$  M)

### Conclusions

n- $\text{Cu}_2\text{O}$  is a promising low cost material to generate  $\text{H}_2$  with visible light irradiation.  $\text{H}_2$  evolution rate is higher in the  $\text{CuSO}_4$  electrolyte medium compared to the system having  $\text{FeSO}_4$  electrolyte solution.

### Acknowledgements

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