Enhancement of Photoelectric Conversion Properties of α-Fe_2O_3/Cu_2O Bilayered Photoanode

Dipika Sharma, Sumant Upadhayy, Surbhi Choudhary, Vibha R. Satsangi, Rohit Shrivastav, and Sahab Dass

***Abstract*—Nanostructured thin films of pure Cu_2O, Fe_2O_3 and bilayered α-Fe_2O_3/Cu_2O were deposited on ITO glass substrates using simple Spray pyrolysis method. All samples were characterized using XRD, AFM and UV–Vis spectrometry. Photo electrochemical properties were also investigated in a three-electrode cell system. UV-Vis absorption spectrum for pure Cu_2O, Fe_2O_3 and bilayered Fe_2O_3/Cu_2O shows absorption in visible region. All nanostructured thin film samples were used as photoelectrode in the Photoelectrochemical cell for water splitting reaction. Our results exhibit that the photocurrent of the Fe_2O_3/ Cu_2O film 0.32 mAcm-2 was significantly higher than that of pure Fe_2O_3 (0.028 mAcm-2) under visible light illumination at 0.8 V/SCE.**

***Index Terms*—Photoelectrochemical, water splitting, bilayered, Cu_2O, Fe_2O_3, spray-pyrolysis.**

I. Introduction

The hydrogen production via solar energy is one of the direct approaches using a water splitting process without any complicated steps. However, the bottleneck of the technology development is the efficiency and stability of Photoelectrode used for the solar hydrogen energy conversion [1], [2]. Various methodological attempts have been carried out towards enhancing the efficiency of PEC water splitting including bilayer systems, doping [3], dye sensitization, metal ion loading, swift heavy ion irradiation[4] etc. Use of bilayered semiconductors system (as photoanode) is the recent modification technique attempted to improve the efficiency of PEC cell. Photoelectrochemical properties of Fe_2O_3 have been intensively studied during last few decades [5]-[8].

α-Fe_2O_3 has been of considerable interest in its use as a photoelectrode because of small band gap of about 2.1 eV, low cost, and good stability in aqueous solution, but the reported photocurrent quantum efficiency of *α*-Fe_2O_3 is relatively low. Also the recombination of electrons and holes on account of low mobilities of holes and trapping of electrons by oxygen-deficient iron sites were considered to be responsible for the low conductivities and poor photocurrent efficiencies of *α*-Fe_2O_3 [8]-[12]. In the present work, Fe_2O_3/Cu_2O bilayered thin film was synthesized using simple spray pyrolysis method. Photoelectrochemical results showed that the bilayered thin film had the strong absorption in visible range and lowers rapid recombination property of Fe_2O_3 limits its application as photoelectrode in PEC cell. Thus, developing this type of bilayered thin film, rather than single bandgap semiconductor devices, provides efficient charge carrier separation and more efficient matching of the solar spectra.

II. Experimental

All chemicals used in this study were of analytical grade; $Fe(NO_3)_3.9H_2O$ (99.9%, Aldrich), and $(CH_3COO)_2.H_2O$ (99.9%, Aldrich), Dextrose, isopropanol were used to prepare the precursor solution for Fe_2O_3 and Cu_2O respectively.

A. Preparation of Photoelectrode

1) Preparation of thin film Fe_2O_3

Nanostructured thin film of pure Fe_2O_3 was deposited on ITO conducting glass substrate using simple spray pyrolysis setup (laboratory built and designed). The spray precursor comprised of 0.15M Fe $(NO_3)_3.9H_2O$. Precursor solution was sprayed with air as carrier gas at a pressure of 2 kg cm^{-2} through a pneumatic nebulizer with a nozzle diameter of 0.1 mm onto ITO conducting glass substrate, kept on substrate heater at 350 ℃ temperature, The solution was sprayed for duration of 10 s with 3 min gap between each successive spray and films were sintered at 500 ^{0}C for 2 hours [13].

B. Preparation of Bilayered Fe_2O_3/Cu_2O Thin Film

TABLE I: Description for All the Thin Film Samples

	FilmThickness (nm)			
S. no.	**Cu_2O**	**Fe_2O_3**	**overall thickness**	**Acronym**
1	147	-	147	A
2	-	243	243	B
3	294	243	537	C

Bilayered Fe_2O_3/Cu_2O thin film was obtained by over layering the Cu_2O thin film onto predeposited Fe_2O_3 thin film using the same spray pyrolysis setup. For this spray precursor comprising of 0.04M Copper (II) acetate monohydrate $(Cu(CH_3COO)_2.H_2O$, 0.04M Dextrose dissolved in water to use as starting compounds. In addition 20 vol% of 2-propanol $((CH_3)_2$ CHOH) was added to the above described aqueous solution. Precursor solution was sprayed with air as carrier gas at a pressure of 2 kg cm^{-2} through a pneumatic nebulizer with a nozzle diameter of 0.1 mm onto (pre-deposited) Fe_2O_3 thin films, kept on substrate heater at 280 ℃ temperature,

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with nearly covering one-third surface of the substrate left for contact formation in previous step with aluminium foil [14]. Overall film thicknesses with other details of all samples prepared in this study have been summarized in Table I. All the films were converted into photoelectrodes using copper wire, silver paste and epoxy (Hysol, Singapore) for its use as photoelectrode in PEC cell. The effective area of the photoelectrode available for illumination was 1.0 cm^2.

III. Characterization

X-ray diffraction (XRD) patterns of pure α-Fe_2O_3, Cu_2O, and bilayered Fe_2O_3/Cu_2O thin film were measured in the range of ($20\text{-}60^0$) 2θ using a Bruker AXS, D8 advanced diffractometer employing Cu-Kα radiation (λ=1.5418A°). The morphology of the thin films was obtained using atomic force microscope.The optical properties of films were analyzed with a UV–visible spectrophotometer (Shimadzu, Japan, Model: UV-2450). The thickness of all samples thin films was measured by using alpha-step profilometer (tencor Alpha Step D-120).

A. Photoelectrochemical Measurements

Photoelectrochemical study was carried out in a three electrode quartz cell in which pure α-Fe_2O_3, Cu_2O, and bilayered Fe_2O_3/Cu_2O thin films were used as working electrode, saturated calomel (PAR, Model: K0077, USA) as a reference electrode (SCE), and platinum gauze as a counter electrode, all dipped in aqueous electrolyte of 0.1M NaOH. Current-voltage characteristics were recorded at a scan rate of 20 mV/s using scanning potentiostat (PAR, Model: VersaStat II, USA), under darkness and by illuminating the photoelectrode with visible light (150W Xenon Arc Lamp, Bentham, output intensity 150 mW/cm2), which was first passed through a water jacket to prevent IR radiation. The resistivity of all the samples were calculated from the slope of current-voltage characteristic curves under dark condition.

IV. Results and Discussion

A. X-ray Diffraction Analysis

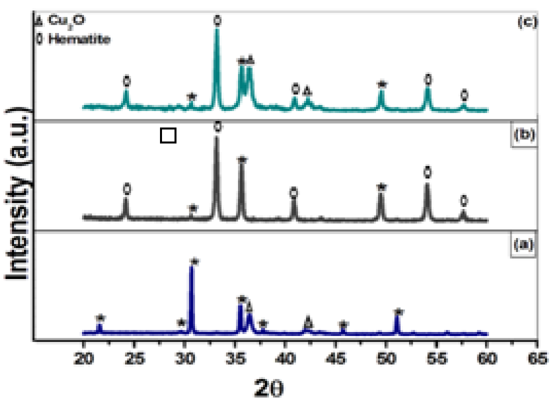

Fig. 1. X–ray diffraction pattern for (a) pure Cu_2O (b) pure Hematite and (c) Bilayered Fe_2O_3/Cu_2O thin film deposited on conducting glass substrate, ITO (In/SnO_2). Asterisks indicate the peaks corresponding to underlying ITO conducting glass substrate.

Fig. 1 shows the X-ray diffraction (XRD) patterns of pure Cu_2O, Fe_2O_3 and bilayered Fe_2O_3/Cu_2O thin films. The XRD pattern of bilayered thin film exhibited diffraction peaks at 2θ = 36.53, 42.43 which can be indexed to (110), (111) plane, respectively of the cubic cuprous oxide phase and peak at 2θ = 24.1, 33.3, 40.9, 54.0 and 57.8 °, which can be indexed to (012), (104), (113), (116) and (018) plane, respectively of the rhombohedral hematite phase. The absence of any unidentified peak in case of bilayered sample indicates that no mixed oxide has been formed.

B. Surface Morphology

Atomic force microscopy (AFM) images obtained for pure Fe_2O_3, and Fe_2O_3/Cu_2O bilayered thin films have been depicted in Fig. 2 along with the particle size distribution. Fe_2O_3 thin film as deposited on conducting glass substrate (Fig. 2a) showed the granular surface with average particle size of 25 nm. Surface morphology of bilayered sample, having 294 nm thick upper layer of Cu_2O (Fig. 2b), depicts the uniform deposition of Cu_2O over Fe_2O_3 with slightly larger grain size and porous surface morphology.

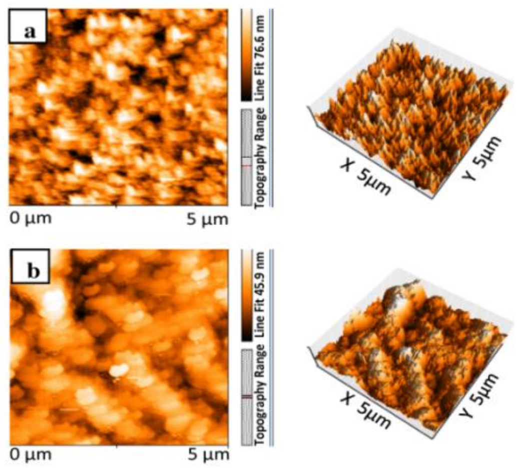

Fig. 2. AFM image with particle size distribution for (a) pure Fe_2O_3 and (b) Fe_2O_3/Cu_2O bilayered thin film samples.

C. UV-Visible Absorption Spectrum

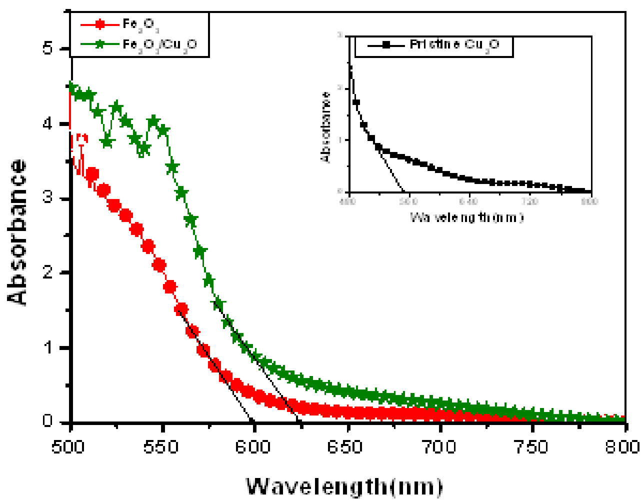

Fig. 3. UV-visible absorption spectra for (a) pure Cu_2O (b) pure Hematite and (c) Bilayered Fe_2O_3/Cu_2O thin film samples.

Fig. 3 shows the UV Visible absorption spectrum for all the samples. Pure Fe_2O_3, Cu_2O and Fe_2O_3/Cu_2O bilayered thin films show visible light absorption. The increase in the absorbance and red shift from 600 nm to 625 nm in absorption edge for Fe_2O_3/Cu_2O bilayered thin film may be attributed to the synergic effect of Cu_2O.

D. Photoelectrochemical Study

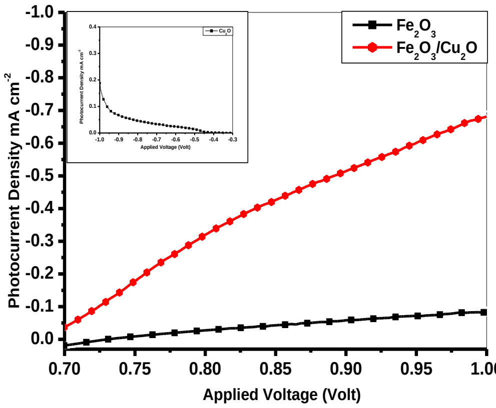

Fig. 4. Photocurrent density vs. applied potential curve for (a) pure Cu_2O (b) pure Hematite and (c) Bilayered Fe_2O_3/Cu_2O thin film samples under visible light illumination in 0.1M NaOH electrolytic solution using 150W visible light source of irradiation 150 mW cm-2 at the position of sample.

TABLE II: PHOTOCHEMICAL PERFORMANCE OF (A) PURE CU_2O (B) PURE HEMATITE AND (C) BILAYERED FE_2O_3/CU_2O PHOTOELECTRODE

Sample identification	Resistivity ($x10^4 \Omega$ cm)	Open –Circuit Photovoltage V_{oc}, (V/SCE)	Photocurrent Density at 0.8 V/SCE (mAcm^{-2})	ABPE Efficiency at 0.8 V/SCE
A	2.9	0.29	0.047	0.022
B	3.7	0.26	0.028	0.012
C	1.8	0.45	0.32	0.18

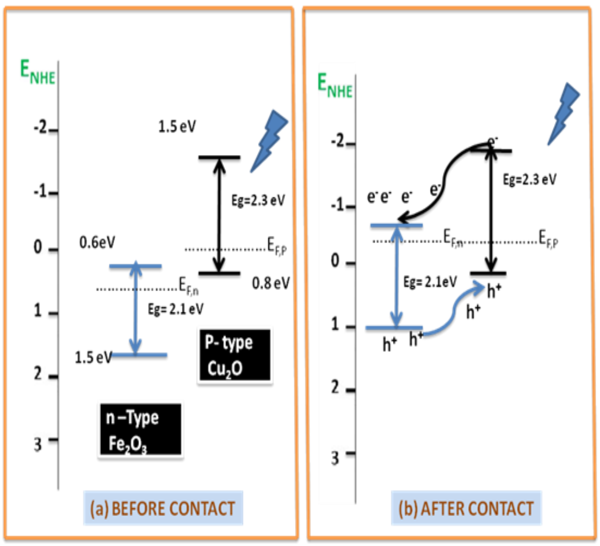

Fig. 5. Energy band diagram of Cu_2O and Fe_2O_3 before and after formation of p-n junction.

Current voltage characteristics Nanostructured thin films of pure Cu_2O, Fe_2O_3 and bilayered Fe_2O_3/Cu_2O were used as photoelectrode in PEC cell and current-voltage characteristics were recorded under darkness and illumination. The externally applied bias was varied from -1.0 V/SCE (cathodic bias) to +1.0 V/SCE (anodic bias). photocurrent for all the samples was calculated by subtracting dark current from current under illumination. Fig. 4 shows the photocurrent density versus applied potential curves for all thin films photoelectrodes. It is noted that photocurrent density increase for bilayered Fe_2O_3/Cu_2O with overall film thickness of 537 nm (for sample c). The observed value of the photocurrent density for sample c was 0.32mA/cm^2 at 0.80 V/SCE, which is approximately ten times higher than pristine Fe_2O_3 (Table II). Under illumination, the Fe_2O_3/Cu_2O photoelectrodes exhibit an n-type photocurrent which increases with an increase of the anodic bias. Maximum photocurrent density exhibited by bilayered Fe_2O_3/Cu_2O thin film sample may be attributed to many factors like formation of mixed oxides at the interface, improved absorption , coupled effect induced by the Cu_2O film and efficient separation of photogenerated charge carriers and their movement across the interface for photocurrent improvement (shown in Fig. 5). In order to explain the possible transfer mechanism of photogenerated charge carriers in bilayered Fe_2O_3/Cu_2O film, an energy band diagram of Fe_2O_3/Cu_2O has been proposed in Fig. 5. Similar energy band positioning and mechanisms showing electron-hole transfer across p-n junctions have also been reported earlier in case of $Bi_2O_3/BiVO_4$ [15]. Resistivity measurement indicated a reduction in the value of the resistivity for the sample c (Table II) which may be another reason for enhanced photoresponse.

E. Efficiency Calculation

The solar to hydrogen conversion efficiency by the water splitting reaction was calculated for all the samples with solar simulated light source at AM 1.5 conditions using the following equation [16].

η (%) = [(total power output - electrical power output)/light power input] $\times$100= [JP (E^0_{rev} - E_{app}) / I_0] $\times$100.

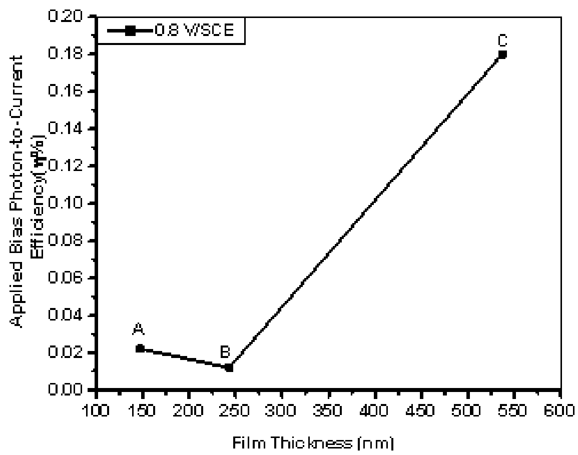

Fig. 6. Applied bias photon-to-current efficiency (ABPE) versus film thickness curve for (a) pure Cu_2O (b) pure Hematite and (c) Bilayered Fe_2O_3/Cu_2O thin films.

where the photocurrent density, Jp is in mA/cm^2, I_o is input intensity of light source, $E_{app} = E_{meas} - E_{oc}$, where E_{meas} is the electrode potential (V/SCE) of the working electrode at which the photocurrent was measured under illumination and Voc is the electrode potential (V/SCE) of the same working electrode at open circuit condition under same illumination (AM 1.5 solar simulator) and in the same electrolyte. The efficiency calculations were made for all the samples at 0.8 V/SCE and are given in Table II. Maximum conversion efficiency value of 0.18 % at 0.8 V/SCE was obtained for

Fe_2O_3/Cu_2O bilayered sample c as shown in Fig. 6. The higher efficiency obtained for bilayered photoelectrodes can be attributed to properly aligned band edges of Fe_2O_3 and Cu_2O as shown in Fig. 5 and in addition an external bias also helps in generation of more separated photogenerated charge carriers, thereby increasing the efficiency of these samples.

V. Conclusions

Bilayered Fe_2O_3/Cu_2O was successfully prepared by spray pyrolysis in order to study the synergistic behaviour of bilayered semiconductors on PEC performance. The photoelectrochemical performance of nanostructured Fe_2O_3/Cu_2O bilayered thin films has found to be superior to that of ITO/ Fe_2O_3. Maximum photocurrent density of 0.32mA/cm^2 at 0.8 V/SCE, was exhibited by Fe_2O_3/Cu_2O photoelectrode with applied bias photon-to-current efficiency of 0.18%. Combined effect of two major factors attributing to the improved photocurrent density: i) the electric field at the heterojunction that suppresses the recombination of photogenerated charge carriers, and ii) external applied bias favouring the transfer and separation of photogenerated charge carriers in Fe_2O_3/Cu_2O bilayered films. Enhancement in photocurrent density has also been attributed to proper band edge alignment of semiconductors, enhanced light absorption by both the semiconductors, and decrease in resistivity.

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References

[1] A. Fujishima, A. T. Rao, and D. T. Titanium, "Dioxide photocatalysis," *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 1, no. 1, pp. 1-21, 2000.

[2] T. Bak, J. Nowotny, M. Rekas, and C. C. Sorrell, "Photo-electrochemical hydrogen generation from water using solar energy- materials-related aspects," *Int. J. Hydrogen Energy*, vol. 27, no. 32, pp. 991-1022, 2002.

[3] S. Upadhyay, J. Shrivastava, A. S. S. Choudhary, V. Sharma, P. Kumar, N. Singh, V. R. Satsangi, R. t Shrivastav, U. V. Waghmare, and S. Dass, "Enhanced photoelectrochemical response of $BaTiO_3$ with fe doping experiments and first-principles analysis," *J. Phys. Chem. C*, vol. 115, pp. 24373–24380, 2011.

[4] A. Solanki, J. Shrivastava, S. Upadhyay, V. Sharma, P. Sharma, P. Kumar, P. Kumar, K. Gaskell, V. R Satsangi, R. Shrivastav, and S. Dass, "A case study of $SrTiO_3$ thin films irradiated by 120 Mev Ag9+ Ions," *Int. J. Hydrogen Energy*, vol. 36,pp. 5236-5245, 2011.

[5] T. H. Kim and K. H. Yoon, "Photoeffects in SnO_2 film electrodes deposited by spray pyrolysis," *J. Appl. Phys.*, vol. 70, pp. 2739-2743, 1991.

[6] K. Kobayashi, .F Mizuno, Y. Nakato, and H. Tsubomura, "Hydrogen evolution at a platinum-modified indium phosphide photoelectrode: improvement of current-voltage characteristics by hydrogen chloride etching," *J. Phys. Chem*., vol. 95, pp. 819-824, 1991.

[7] R. K. Quinn, R. D. Nasby, and R. J. Baughman, "Photoassisted electrolysis of water using single crystal α-Fe_2O_3 anodes," *Mater. Res. Bull*, vol. 11, pp. 1011-1017, 1976.

[8] K. L. Hardee and A. J. Bard, "Semiconductor electrodes- the application of chemically vapor deposited iron oxide films to photosensitized electrolysis," *J. Electrochem. Soc*. vol. 123, pp. 1024-1026, 1976.

[9] U. Bj ̈orkst ́en, J. Moser, and M. Gr ̈atzel, "Photoelectrochemical studies on nanocrystalline hematite films," *Chem. Mater.*, vol. 6, pp. 858-863, 1994

[10] S. U. M. Khan and J. Akikusa, "Photoelectrochemical splitting of water at nanocrystalline n-Fe_2O_3 thin-film electrodes," *J. Phys. Chem., B.*, vol. 103, no. 34, pp. 7184-7189, 1999.

[11] N. Beermann, L. Vayssieres, S. E. Lindquist, and A. Hagfeldt, "Photoelectrochemical studies of oriented nanorod thin films of hematite," *J. Electrochem. Soc*., vol. 147, pp. 2456-2461, 2000.

[12] A. Watanabe and H. Kozuka, "Array fabrication and photoelectrochemical properties of Sn-doped vertically oriented hematite nanorods for solar cells," *J. Phys. Chem., B.*, vol. 13, pp. 107-127, 2003.

[13] S. Kumari, C. Tripathi, A. P. Singh, D. Chauhan, R. Shrivastav, S. Dass, and V. R. Satsangi, "Characterization of Zn doped hematite thin films for photoelectrochemical splitting of water," *Current Science,* vol. 91, no. 8, pp. 1062-1064, 2006.

[14] T. Kosugi and S. Kaneko, "Novel Spray-Pyrolysis deposition of cuprous oxide thin films," vol. 81, no. 12, pp. 3117–3124, 1998.

[15] L. Chen, Q. Zhang, R. Huang, S. F. Yin, S.-L. Luo, and C. T. Au, "Porous peanut-like Bi_2O_3-$BiVO_4$ composites with heterojunctions: one-step synthesis and their photocatalytic properties," *Royal Society of Chemistry*, vol. 41, pp. 9513-9518, 2012.

[16] W. B. Ingler and S. U. M. Khan, "Photoresponse of spray pyrolytically synthesized magnesium-doped iron (III) oxide (p-Fe_2O_3) thin films under solar simulated light illumination," *Thin Solid Films,* vol. 461, pp. 301-308, 2004.

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