Synthesis and Characterization of Nanostructured Undoped/Doped CuO Films and their Application in Photoelectrochemical Water Splitting

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ABSTRACT

Metal oxide semiconductors are one of the most promising materials for photoelectrochemical production of hydrogen on account of a) easy availability, b) low cost, c) simple preparation methods and d) stability. The samples of undoped and (Cr/Fe) doped CuO were prepared using spray-pyrolysis technique. XRD analysis revealed the exclusive formation of CuO phase. Good adherence of films with substrate was confirmed by scotch tape method. The SEM analysis confirmed the granular surface of the film. Scherrer's calculation indicated the average grain size of the order of ~87 nm. Film samples were then converted into photoelectrodes by generating ohmic contact and photoelectrochemical behaviour was studied at pH 11 and 13 in NaOH. Enhanced photocurrent generation was observed in the sintered samples and also with the increase of electrolyte pH from 11 to 13, irrespective of nature and amount of dopant. However the variation in dopant concentration revealed a variable trend in the photocurrent generation.

Keywords: Photoelectrochemical properties, Cupric oxide, Spray-pyrolysis

1. INTRODUCTION

Versatile applications of metal oxides in technology development have infatuated the scientific community. Besides the advent of nanotechnology has given the new direction to tailor make the properties of materials for their potential high-tech applications due to high surface to volume ratio and enhanced surface effects. To overcome the problem of energy scarcity and global warming different ways of renewable energy production are being discovered. The pioneering work of Fujishima & Honda [1], followed by the development of efficient and cost effective semiconductor metal oxides for their application in the production of hydrogen by scientific community across the world.

In PEC cells, semiconductor photocatalysts are used as electrode to split water to produce H_2 – a valuable fuel, by utilizing vastly available sun light [2,3]. However, several oxides [3-13] have been investigated as privilege semiconductor materials, for this purpose, but on account of inappropriate band gaps and / or the instability of the semiconductor in the electrolyte has largely eluded the desired success so far. CuO on account of favorable bandgap (1.4 eV) absorbs throughout the visible region and is considered to be a material of choice as photoelectrode in PEC cell.

In the present work synthesis of nanostructured undoped/doped CuO films and their photoelectrochemcial behaviour has been investigated. The characterization of films by XRD and SEM has also been presented.

2. EXPERIMENTAL

2.1 Sample Preparation

Copper oxide films were deposited by spray-pyrolysis technique on conducting glass substrate (TCO). 0.1 M precursor solution was prepared by dissolving $Cu(NO_3)_2$ $2.5H_2O$ (99.99+%, Aldrich) and the calculated amount of dopant nitrate was added in double distilled water. The solution was sprayed onto heated (temperature $350^0C \pm 5^0C$) substrates of dimensions 4 cm. X 2.5 cm. Before spraying, nearly one-third length of the substrate was covered by an aluminium foil. Carrier gas used was compressed air with 3 Kg cm^{-2} pressure and spray rate was maintained at 4.4 ± 0.1 ml min^{-1}. The detailed experimental conditions and experimental set-up, used, are described elsewhere [6,14].

2.2 Characterization

The undoped/doped copper oxide films were characterized using glancing angle X-ray Diffraction Philips PW 3020 thin film diffractometer. The incident beam was slit collimated while the diffracted beam optics consisted of a thin film parallel plate Collimator and a flat graphite monochromator. Cu-Kα was used as the radiation source.

The average particle/grain size was calculated by Scherrer's equation (1).

$$B = 0.9\lambda / tCos\theta \quad (1)$$

Where B is FWHM (full width at half maximum) of the broadened diffraction line on the 2θ scale (radians) and t is average diameter of particle/grain size. The B is given, by equation (2)

$$B^2 = B_M^2 - B_S^2 \quad (2)$$

Here B_S the measured breadth, at half maximum intensity, of

the line from the standard while B_M is measured breadth of the diffraction line of sample.

In the present study surface morphology of films was performed for some arbitrarily chosen samples using JEOL JSM5800LV scanning electron microscope. The sputter coated samples with gold, were initially observed at low magnifications (a few 100 X) to get an overall picture of the features presented by the samples. Subsequently, the same features were observed under higher magnifications (up to 16000 X) to get the micro details of these features.

2.3 Photoelectrochemical Measurements

The film samples were converted into electrodes by making ohmic contact with copper wire using gallium-indium eutectic and silver paint. The exposed ohmic contact back side and edges were perfectly sealed with non-transparent and non-conducting epoxy resin, Hysol (Singapore).

The photoelectrochemical measurements involved monitoring current-voltage (I-V) characteristics, both under darkness (when the PEC cell was covered from outside using a thick black cloth cover) and under illumination (when the semiconductor electrode was illuminated using the light source) at different experimental conditions. The thin film electrode (working electrode, surface area of 1cm^2) was used in conjunction with platinum and saturated calomel electrodes (SCE), which were used as counter and reference electrodes, respectively. The potentiostat (Model ECDA-001, Con-Serv Enterprises) attached with PEC cell was used in this study. The light source for simulated solar radiation was a 250 W tungston-xenon lamp (Bentham) as light source. The electrolyte used was 1M NaOH (pH 13).

3 RESULTS AND DISCUSSION

The pyrolytic decomposition of copper nitrate formed its oxide. The films synthesized by this method were smooth, properly adhering with the substrate and were uniform. The film thickness of undped/doped film samples, determined by telestep was found of the order of 1.5 µm.

XRD analysis of film samples indicated the exclusive formation of CuO (Fig. 1). The formation of

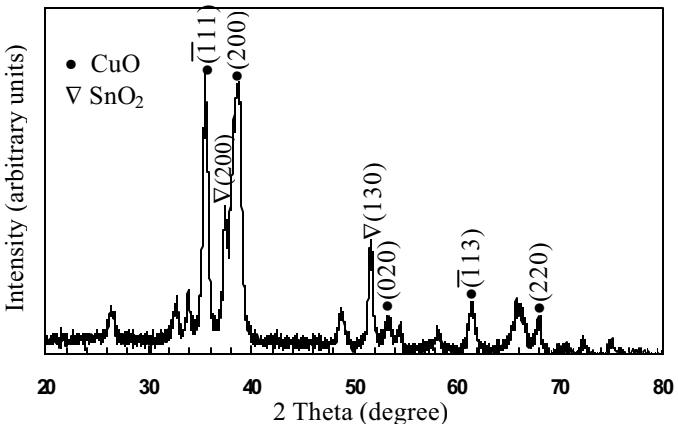

Fig.1 XRD pattern of undoped CuO film (unsintered)

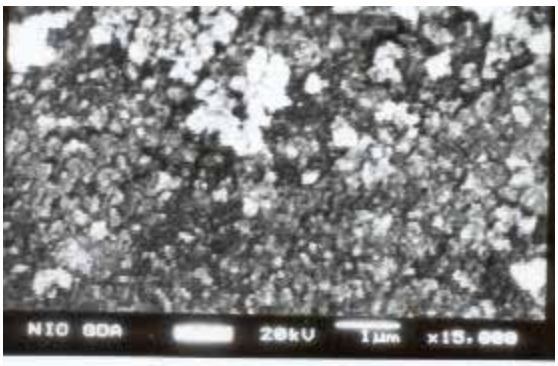

Fig. 2: Observed SEM image of CuO film (unsintered)

nanostructructred undoped/doped CuO films is clearly evident from Scherrer's calculation, which indicates the average particle/grain size of the order of 87 nm. SEM image also indicates the formation of crystalline structure. However, the average particle/grain size obtained from the SEM analysis is significantly higher then the values obtained from Scherrer's calculations. This disparity may be due the formation of particles/grains in cluster, which were infact observed by SEM analysis.

The current-voltage (I-V) characteristics of undoped CuO film electrodes before and after sintering are shown in Fig. 3(a & b). Similarly the I-V curves were obtained for other samples. The photocurrent density for all the samples is summarized in Table 1. It is evident that PEC response of doped samples was significantly higher, in most of the cases, than that of undoped samples, effect of variation in dopant concentration from 0.5% to 2% on the PEC response of the material has a varied trend. The sintered film electrodes showed enhanced photocurrent than the unsintered film electrodes. The effect may be understood in the light of the expected, and also observed through Scherrer's calculations, exhibiting clearly the increase in particles/grains size on sintering. With the increase in particles/grains size, the number of grain boundaries will decrease and this might be the reason for the observed higher photocurrent values upon sintering. The photocurrent density decreased with the increase in doping level in the case unsintered samples doped with Fe (at pH 11).

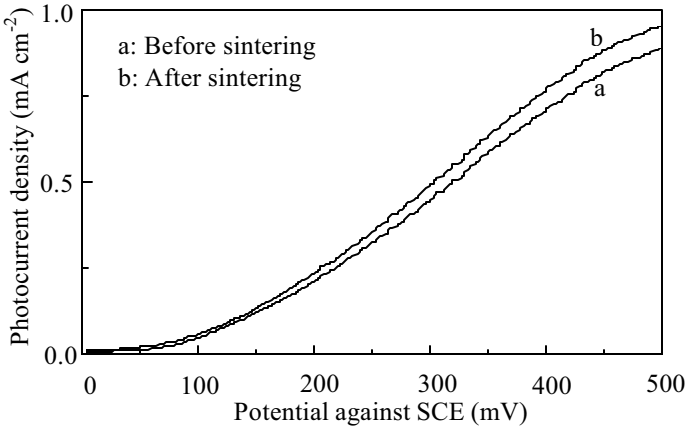

Fig. 3a Observed photocurrent density as a function of applied potential with CuO film (undoped) electrodes at pH-11

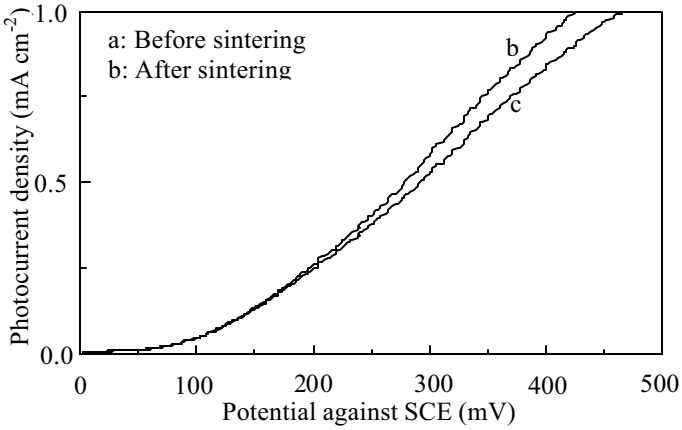

Fig. 3b Observed photocurrent density as a function of applied potential with CuO film (undoped) electrodes at pH-13

This can be explained by the increased electron concentration within quasi-neutral part of the electrode, where the probability of electron hole recombination increases. In case of unsintered Cr doped samples (at pH 11 and 13) and sintered samples doped with Cr (at pH 11) an increase in the photocurrent density with the increase in the doping concentration was seen. This might be due to the incorporation of the Cr in the CuO matrix, which increases the rate of charge transfer and hence the observed improvement in the electrochemical performance of the cell. Sintered samples doped with Cr (at pH 13) exhibit the increase in photocurrent density upto 1% doping, which decreases on increase. The decrease in photocurrent density at higher doping levels may be on account of greater rate of recombination, which is probably due to increased electron concentration within quasi-neutral part of the electrode. An unambiguous rise in photocurrent densities at higher pH may be attributed to the effect of increased ionic strength, which significantly reduces the internal resistance of the PEC cell.

4 CONCLUSION

This study reveals that nanostructured CuO film electrodes could be a potential candidate for PEC application. Better photocurrent generation was observed in the sintered samples and also with the increase in electrolyte pH from 11 to 13, irrespective of nature and amount of dopant. Thus sintering of samples and electrolytic pH also govern the PEC behaviour of material.

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Table 1

Sintering Condition	pH	Photocurrent density (μA cm^{-2})						
		Undoped	Cr-doped			Fe-doped		
			0.5%	1.0%	2.0%	0.5%	1.0%	2.0%
Before sintering	11	440	395	546	758	850	430	360
	13	485	385	818	1087	576	516	1474
After sintering	11	526	709	1788	964	1235	566	155
	13	578	1451	2029	1246	1561	1475	1721