



INSTITUTE OF PHYSICS - SRI LANKA

Research Article

Characterization of electrochemically prepared CuSCN films and their capabilities of application in dye sensitized photovoltaic cells

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Abstract

CuCNS was deposited on conducting glass substrates by cathodic electrochemical technique using rotating disc electrode. CuCNS films exhibited transparency over 85% for visible light. High transparency of these films suggests capability of utilization as an optical window in photovoltaic cells. Cathodic photocurrent was observed on sensitized CuCNS electrodes when in contact with an electrolyte. An enhancement in photocurrent was observed under back wall mode than front wall mode illumination on photocathode.

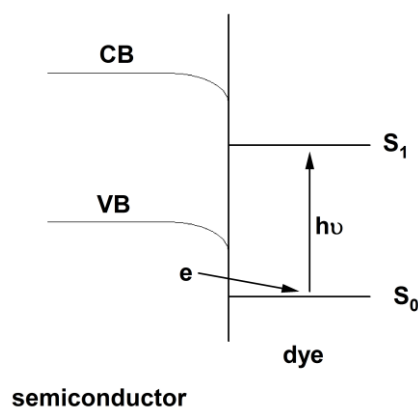
1. INTRODUCTION

Recently, tremendous interest has been focused on studies of p-type semiconductors. CuCNS, CuI, MgIn₂O₄, CuAl₂O₄ are most commonly used p-type semiconductors in simple electronic devices. Various techniques such as electrochemical [1, 2], solid-state reactions [3], pulse laser deposition [4, 5], solvent vaporization techniques [6, 7], sol-gel techniques [8] and solid-phase epitaxy [9] have been used to synthesis these materials. Deposition of p-type semiconductor thin film on various substrates implies wide range of applications in simple electronic devices. For example, thin films of CuCNS, CuI are with higher potential in using as a hole-conductor in solid-

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state solar cells [6, 7]. Sensitized CuCNS and CuI films are also with the capability of using in light harvesting electrodes in dye-sensitized photo-electrochemical cells [1, 2, 10]. Dye sensitization on semiconductor surfaces has attracted the attention of physicists and chemists for more than half a century. Subsequently dye sensitization of the semiconductor/electrolyte interface was investigated by many workers and it was established that anodic (cathodic) sensitization occurs when an excited dye molecule adsorbed at the semiconductor surface injects electrons (holes) into the conduction (valence) bands [11-14]. The type of sensitization depends on the band positions of the semiconductor and energy levels of the dye attached to the semiconductor surface. The cathodic sensitization process on CuCNS is well established and illustrated in Scheme 1.



Scheme 1 The mechanism of cathodic dye sensitization

Upon excitation an electron is transferred to upper excited singlet level (S_1) from the lower singlet level (S_0) of the dye molecule. As soon as an electron is transferred in to the singlet level of the dye molecule an equivalently hole is injected into the valence band. More recent studies have shown that not only the singlet but also the triplet excited states are effective in charge injection to the bands [15]. We have developed a simple technique to deposit micro-porous like wires structured thin CuCNS films via electrochemical method. Characteristics of electrochemically deposited CuCNS films are discussed. An attempt was used to utilize sensitized CuCNS films in solar cells. Cathodic photocurrent generation was observed on the sensitized electrodes.

2. EXPERIMENTAL

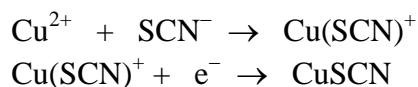
CuCNS was electrochemically deposited on fluorine doped tin oxide (FTO) electrodes by using rotating disc technique. Well cleaned FTO electrode was attached to a rotating disc electrode and placed horizontally at the electrolyte|air interface and was rotated at a constant rate of 300 rpm in a single compartment cylindrical cell. A Pt wire and a saturated Ag/AgCl electrode were used as the counter and the reference electrodes, for electrochemical deposition. Constant potential of + 0.15 V vs Ag/AgCl was applied on working electrode in $\text{Cu}(\text{ClO}_4)_2$ and LiSCN electrolyte. Unless especially mentioned an

aqueous solution of 2 mM $\text{Cu}(\text{ClO}_4)_2$ together with 1.5 mM LiSCN is used as the electrolyte. Electrochemical deposition was carried out at a constant temperature of 25 °C.

Photo-electrochemical properties of CuCNS electrodes sensitized with methyl violet 6B are also studied. Commercially available methyl violet chloride is converted to thiocyanate form due to high degree of stability of thiocyanate form in aqueous media, as is described elsewhere [10]. Methyl violet thiocyanate form was dissolved in ethanol and then diluted in water. Resulted dye solution was used as stock solution. CuCNS coated FTO electrodes were then kept immersed in a dye solution (10^{-5}M). The rate of dye adsorption was controlled by changing the duration of immersion. The amount of dye adsorbed on the film was determined by extraction of ethanol for spectroscopic estimation. A PEC was constructed by using a dye-sensitized CuCNS|FTO electrode as the photocathode and a platinum mesh as the counter electrode. The electrolyte used was KI containing I_2 ($\text{I}^- : \text{I}_3^- = 1:10^{-5}$). The photocathode was biased at + 0.1 V vs. SCE (standard calomel electrode) which to gave zero dark voltage for the cell. The photocurrent action spectra were recorded using a Nikon Monochromator Auto-Scanner As-C-101 after amplification in a lock-in system. The stability of the cell was monitored under illumination with a 60 W tungsten filament lamp. Photo-electrochemical measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 illustrates chronoampogram for deposition of CuSCN on FTO electrode. As is observed, Faradic current across the electrodes initially increases with time and reaches a saturation level. The physical parameters such as rotation speed and temperature of electrolytic bath are firmly maintained throughout the deposition, since they strongly influence on the saturation current. Gradual increment of thickness of the film is observed after reaching to the saturation. Deposition of CuSCN seems to be diffusion limited process and occurred via following intermediate reactions at aqueous atmosphere.



X-ray diffractogram of CuSCN coated FTO electrode is shown in Fig. 2. Characteristics peaks are identified due to CuSCN and the substrate (SnO_2). As is shown, CuSCN films exhibit high degree of crystallinity with the predominant orientation of (0,0,3) axis. Growth of thin films with a preferred orientation is a specific feature of thin films [16]. However peaks belonging to other lattice planes are also observed at higher angles. Size of the grains and thickness of CuSCN layer and can easily be controlled by changing concentration of reactance, deposition time and by changing the medium of the electrolyte.

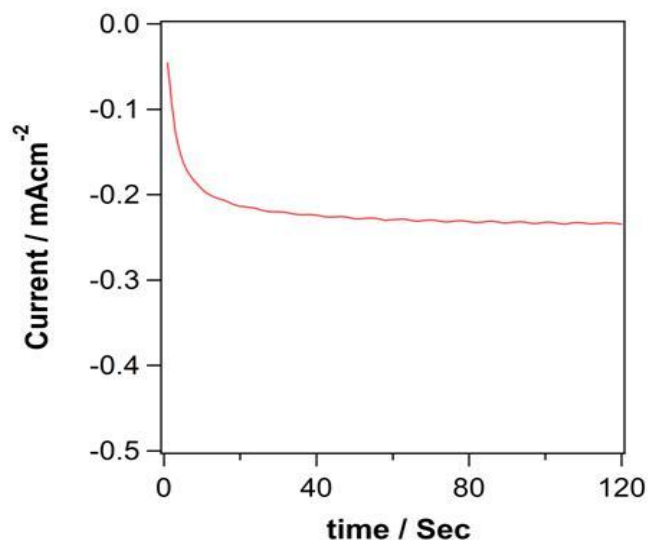


Fig. 1 Chronoamperogram for deposition of CuSCN on FTO electrode

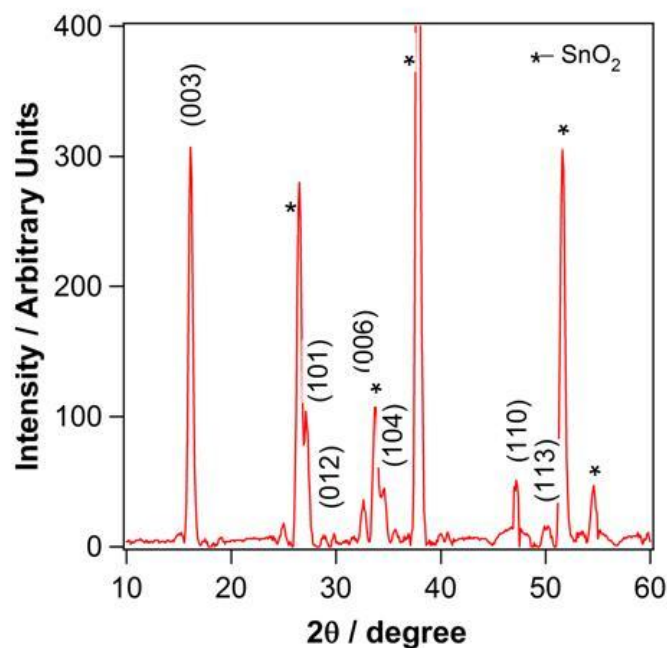


Fig. 2 X-ray diffractogram of a CuSCN film coated on FTO electrode

For example morphology of CuSCN films prepared by using different conditions are shown in Fig. 3. A well separated like wires structure is observed on FTO electrodes at the present experimental conditions (image a, Fig. 3). However, self aggregation of CuSCN grains is observed on FTO electrodes by increasing concentration of reactance or applied potential (images b & c, Fig. 3).

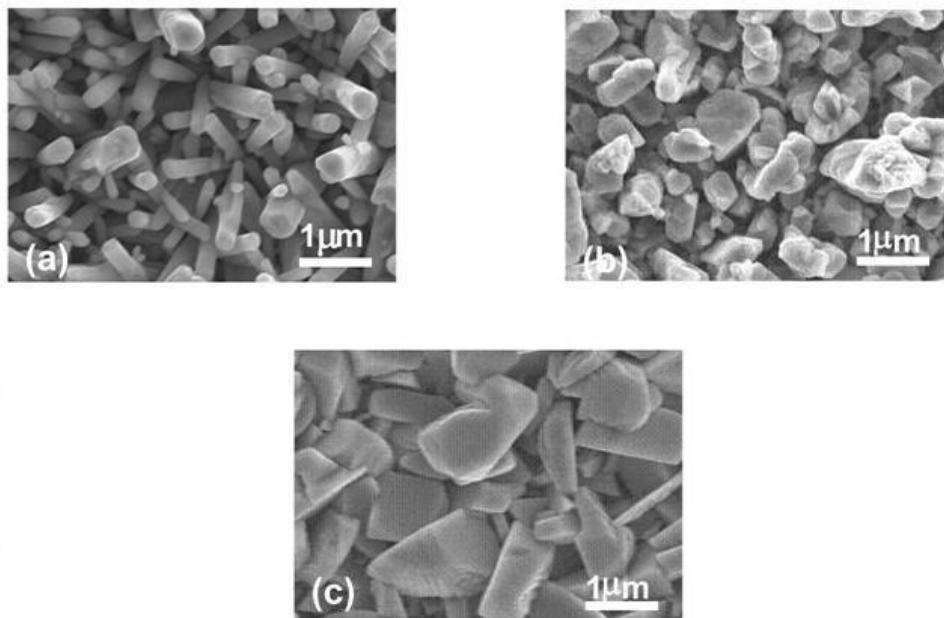


Fig. 3 Morphology of CuSCN films prepared by using different conditions, (a) electrolyte - 1.5 mM, LiSCN, 2 mM $\text{Cu}(\text{ClO}_4)_2$, biased potential 0.1V, (b) electrolyte - 5.0 mM LiSCN, 10 mM $\text{Cu}(\text{ClO}_4)_2$, biased potential 0.2V, (c) electrolyte - 5.0 mM LiSCN, 10 mM $\text{Cu}(\text{ClO}_4)_2$, biased potential 0.3V. Constant charge of 300 mC was passed in all cases.

CuSCN films exhibit average transparency over 85% for visible light (curve a, Fig.4). Higher transparency of these films suggests capability of utilization as optical window in photovoltaic cells or other electronic devices. The direct band gap energy of CuSCN is roughly evaluated as 3.4 eV from direct absorption measurements (not shown in the text) and well matches with previously reported value [17]. Absorption of UV and near visible portion by CuCNS film limits their application as light harvesting electrode in photovoltaic cells. Therefore, it is necessary to have a sensitizer on the films to extend the photo-response toward the visible region. Among tested sensitizers organic cationic dye methyl violet CNS^- form is readily absorbed on CuSCN films. Absorption spectrum of methyl violet (SCN^- form) is shown as curve b in the inset of Fig. 4. Action spectrum of methyl violet sensitized CuSCN electrode under front wall mode illumination (light comes through electrolyte) is also illustrate in the inset of Fig. 4 (curves c). The highest photocurrent generation is observed at 600 nm. The observed red shift between action spectrum that of compare to absorption spectrum of dye solution indicates strong chelation of dye molecules with CuCNS. We have studied stability of the cell by exciting electrodes by a constant wavelength of 600 nm. A higher stability and enhancement in photocurrent were observed under back wall mode illumination (light comes through the FTO) than that of front wall mode due to different charge transfer kinetics at $\text{CuSCN}|\text{FTO}$ and $\text{CuSCN}|\text{electrolyte}$ interfaces.

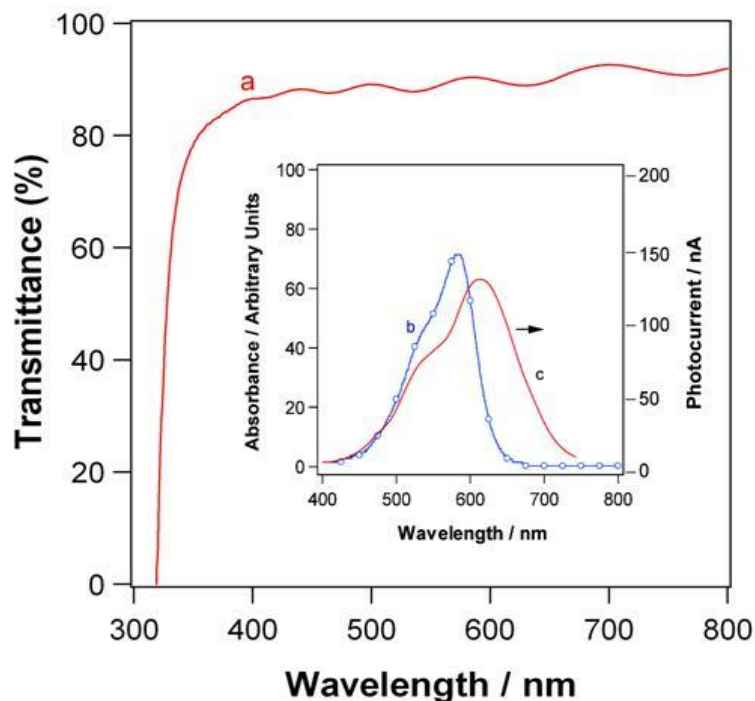


Fig. 4 (a) Transmittance of a CuSCN film, (b) absorption spectrum of cationic dye methyl violet (CNS^- form) in water (c) action spectrum of methyl violet sensitized CuSCN electrode under front wall illumination (light comes through electrolyte)

The variation of photocurrent (under back wall mode illumination) with the dye concentration is also studied by exciting the electrodes with the wavelength of 600 nm that has the highest light conversion efficiency (Fig. 5).

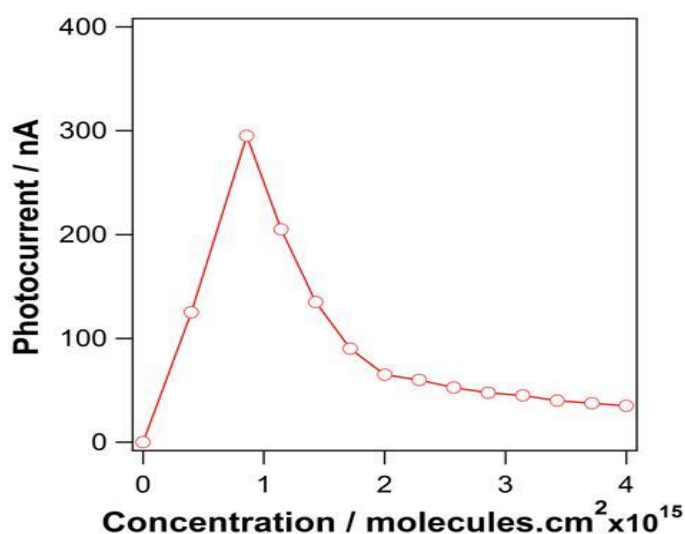


Fig. 5 The variation of photocurrent with dye amount of the electrode under back wall mode illumination (light comes through FTO)

The photocurrent of the cell initially increases with increasing of dye amount of the electrode and reaches maxima. Then gradually decrease with further increasing probably

may be due to loss of energy of excited dye molecules via quenching of dye molecules with each other. Quenching of dye molecules is identified as one of the main pathways of losing energy in dye sensitized systems [18]. Similar pattern of variation of photocurrent is observed with dye amount by illuminating poly-chromatic light. However, turning point of photocurrent slightly changes with the intensity of the light source.

4. CONCLUSION

CuCNS was deposited on conducting glass substrates by electrochemically. Higher transparency of these films suggests capabilities of utilization as a window material in photovoltaic cells. Cathodic photocurrent is observed on sensitized CuCNS electrodes when in contact with an electrolyte under illumination. Much higher sensitized photocurrent is observed under back wall mode than front wall mode.

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