Electrodeposited thin film SnO_2 photoelectrode for PEC applications

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1. ABSTRACT

Tin oxide (SnO_2) is a promising semiconductor material to develop photoelectrodes for photoelectrochemical (PEC) cells. Indeed, an effective PEC cell could be developed only if the photoelectrode is stable and free of corrosion in the selected electrolytic solution. In other words, the choice of an electrolyte for a PEC cell determines the stability of the photoelectrode in the PEC cell. In this study, we propose aqueous 0.1 M sodium nitrate ($NaNO_3$) as an effective electrolyte for the PEC cell where thin film SnO_2 is a photoelectrode. Current-voltage (I-V) measurements obtained by illuminated chopped ultra violate (UV) radiation established the electrodeposited thin films of SnO_2 are stable and free of corrosion/photocorrosion in our PEC cell. In addition, we report the dependence of the photoresponses of electrodeposited thin film SnO_2 in this PEC on the bath temperature and the deposition time.

2. INTRODUCTION

Generation of energy via PEC cells is simple, easy and cost-effective. Semiconductor photoelectrodes capable to convert photons into electron-hole pairs in PEC cells to generate electricity. Of course, it is challenging to choose proper photoelectrode material along with proper electrolyte in PEC cells. The quality and the structure of the photoelectrode determines the performance of the PEC cell.

Metal oxide semiconductors have become promising candidates for electrode materials in PEC systems because of their high stability under irradiated aqueous electrolytes. The first PEC was developed by Honda and Fujishima using TiO_2 electrode[1]. ZnO[2], Cu_2O[3], CuO[4], TiO_2[5], SnO_2[6] have widely been studied as effective photoelectrode materials in PEC cells. Stefik et al. have demonstrated porous niobium doped tin oxide electrodes with electrical conductivity of 37 S cm^{-1}[7]. Pan et al. have successfully developed 3-D hierarchical ternary $SnO_2/TiO_2/BiVO_4$ photoanode yielding photocurrent density of 5 mA cm^{-2} for PEC applications[8].

SnO_2 is an environmentally friendly, low-cost, n-type semiconductor with direct band gap of 3.6 eV at 300 K[9]. It has high transparency and chemical stability. Further, it is considered as an interesting material for a wide assembly of applications such as electrochemical cells[10], solar cells[11], gas sensors[12], and catalysts[13]. Thin film SnO_2 have been fabricated by a wide variety of deposition methods including spray pyrolysis[14], sol–gel processes[15], thermal plasma deposition[16], pulsed-laser deposition[17] and electrodeposition[18]. Among various physical and chemical approaches for the fabrication of SnO_2 films, electrodeposition method is eco-friendly, simple, low-cost and low-temperature method. It is a one step process suitable for large-

scale production and it could control the deposition of material on the substrate. Few literatures are available to explain the preparation of thin film SnO_2 by the electrodeposition method[18,19].

The study of undoped thin film SnO_2 in PEC cell is limited in literature. Selecting a suitable electrolyte that compatible with thin film SnO_2 photoelectrode in a PEC cell is challenging. It is very important that the electrolyte that we used in the PEC cell should exhibit the properties like corrosion free and stable medium to transfer carriers. Here we found that $NaNO_3$ is a good choice of electrolyte to study thin film SnO_2 electrodes in PEC cell. Further, tuning the deposition parameters of thin film SnO_2 electrodes were carried out by monitoring the deposition conditions such as temperature of the film deposition bath and deposition time.

3. MATERIALS AND METHODS

Thin film SnO_2 were potentiostatically electrodeposited in three-electrode electrochemical cell using a Hokuto Denko Potentiostat / Galvanostat HAB-151 instrument. The working electrode was a well-cleaned copper (Cu) substrate and the counter electrode was a platinum (Pt) foil. The reference electrode was a double junction Ag/AgCl electrode. The electrodeposition voltage is -0.45 V vs. Ag/AgCl. The film deposition bath consisted of 30 mM aqueous stannous chloride ($SnCl_2$ regent grade, 98%) and 150 mM nitric acid (HNO_3 regent grade, 69%). To oxidize the stannous ions (Sn^{2+}) in the bath to stannic ions (Sn^{4+}) oxygen gas was bubbled into the film deposition bath at room temperature for 1 hour. Then, a set of samples was deposited by varying the growth parameters such as temperature of the film deposition bath and the duration of the film deposition. Photoresponses and I-V measurements were obtained in a PEC cell consisted of 0.1 M aqueous $NaNO_3$. The Gamry G series potentiostat/galvanostat/ ZRA instrument was used for this purpose. The I-V characterization was conducted under illumination of chopped UV radiation.

4. RESULTS AND DISCUSSION

It is known that hydroxyl ion or O^- radicals should be present near the electrode surface to electrodeposit metal oxide thin films. In this study we used HNO_3 along with oxygen bubbling to oxidate the Sn ions. The half reaction on the cathode electrode surface is shown below[18]. (all potentials are versus the standard hydrogen electrode (SHE)):

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2\,OH^-, E^0 = 0.01\,V$$

Following this reaction, the hydroxyl anions and Sn^{4+} ions form SnO_2:

$$Sn^{4+} + 4OH^- \rightarrow SnO_2(s) + H_2O$$

In this study, thin film SnO_2 was successfully electrodeposited on Cu substrates. After washing the electrodeposited samples with the deionized water, no impurities were

observed on the electrode surface. The electrodeposited thin films SnO_2 were well-adhered to the Cu substrate.

The possible reduction–oxidation (redox) reaction steps along with their standard redox potential of $NaNO_3$ electrolyte as follows.

$$NaNO_3 + 2H^+ + 2e^- \rightarrow NaNO_2 + H_2O \qquad E^0 = 0.94\,V$$

$$NaNO_2 + H^+ + e^- \rightarrow NO + NaOH \qquad E^0 = 1.00\,V$$

$$2\,NO + 4H^+ + 4e^- \rightarrow N_2 + 2H_2O \qquad E^0 = 1.68\,V$$

The Figure 01 explains the charge transfer mechanism in a PEC cell. The requirement for an efficient thin film SnO_2 photoelectrode in the PEC is the energy separation between the conduction and valence band and the well-tailored redox processes at both electrodes. The difference in the electrochemical potential between the thin film SnO_2 electrode and the $NaNO_3$ electrolyte causes a charge transfer process at the solid/liquid interface, resulting in an electric current flowing through the junction until an electronic equilibrium is reached. It is found that when photons are absorbed with an energy larger than their bandgap, the photoelectrons are excited and migrate into the unoccupied conduction band and holes are left in the valence band. This generates the electron–hole pairs (exciton). When photoexcited charge carriers have a longer lifetime and larger diffusion distance, exciton will separate by the built-in electric field. The photoexcited electrons will swept toward the counter electrode through the back contact and an outside circuit, while the remaining holes will participate in the oxidation reaction. Thus, in a PEC cell, electron–hole pairs produced by incident photons will drive redox processes[20].

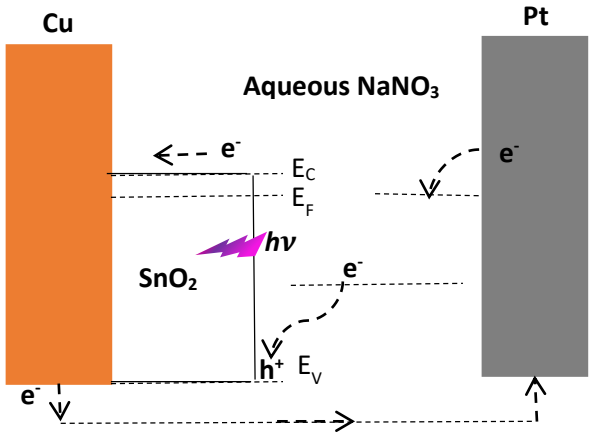


Figure 01: A schematic diagram of electron flow in a photoelectrochemical cell

The PEC response of Cu/SnO_2 electrode in electrolyte was recorded under UV light chopped illumination using linear sweep photovoltammogram. The Figure 02 represents three different I-V characteristic curves for electrodeposited thin film SnO_2 in 0.1 M aqueous $NaNO_3$ electrolyte. These curves were obtained for three different SnO_2 film deposition bath temperatures and for deposition time durations. The PEC response depicted in Figure 02 confirms that the electrodeposited thin film SnO_2 are photoactive

and stable in 0.1 M aqueous $NaNO_3$ electrolyte. It is also assuring that the SnO_2 photoelectrode was corrosion/photocorrosion free with the $NaNO_3$ electrolyte.

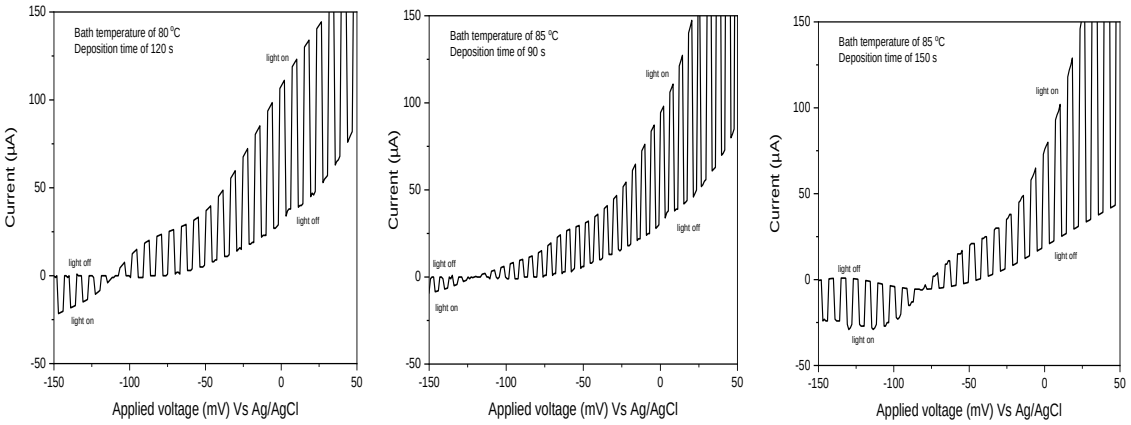


Figure 02: I-V characteristic curves for electrodeposited thin film SnO_2 in aqueous $NaNO_3$ electrolyte.

Figure 03 represents the dependance of bath temperature and film deposition time on the short-circuit current density (J_{SC}) and open-circuit voltage (V_{OC}) values of electrodeposited thin film SnO_2 in aqueous $NaNO_3$ electrolyte. It is clear from the Figure 03 (a), the highest J_{SC} and V_{OC} values resulted from the thin film SnO_2 electrodeposited on the bath temperature value of 85 ℃. For bath temperature above 85 ℃, it was difficult to maintain the concentration values due to high evaporation rate. And from the Figure 03 (b), it can be concluded that the best film deposition time is 120 s. Nevertheless, the thin film SnO_2 electrodeposited at bath temperature value of 85 ℃ for 120 s exhibited highest photoresponse and at this bath temperature value and film deposition duration visible bath evaporation was not observed.

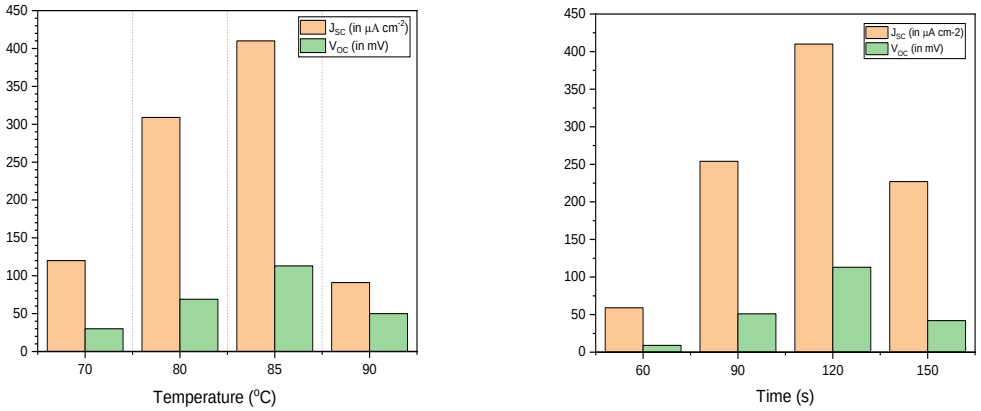
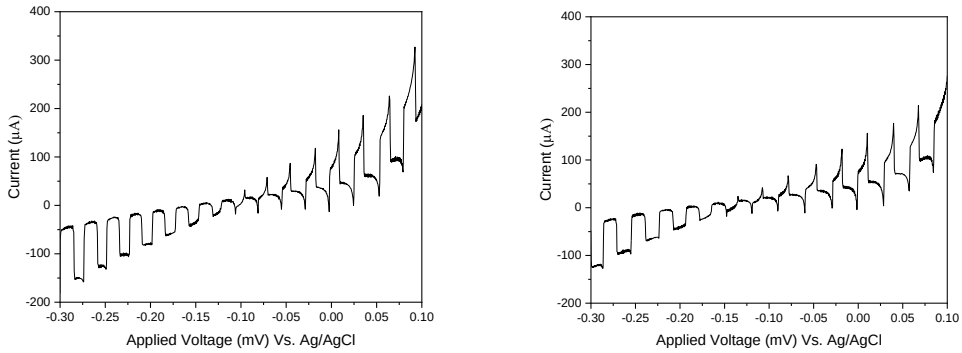


Figure 03: Dependance of (a) bath temperature and (b) film deposition time on the J_{SC} and V_{OC} values of electrodeposited thin film SnO_2 in aqueous $NaNO_3$ electrolyte.



(a) (b)

Figure 04: I-V curve for (a) before and (b) after immersing the SnO_2 electrode in $NaNO_3$ electrolyte for 1 hour with the illumination of light for 1 hour.

The Figure 04 represents the I-V curve for (a) before and (b) after immersing the SnO_2 electrode in $NaNO_3$ electrolyte for 1 hour with the illumination of light for 1 hour. According to the photoresponses of the I-V curve it is clear that no significant lossses in the photoresponse is observable. This indicates that the SnO_2 electrode in $NaNO_3$ electrolyte is corrosion/photocorrion free and stable.

5. Conclusion

In summary, the photoresponses of electrodeposited thin film SnO_2 was obtained in a PEC cell which was consisted of aqueous $NaNO_3$. It is observed that the Cu/SnO_2 photoelectrodes are corrosion/photocorrosion free in the $NaNO_3$ electrolyte and it is well stable in the PEC cell. In addition, high photoresponses are resulted from the thin film SnO_2 electrodeposited at the bath temperature of 85 ℃ and film deposition time of 120 s. The results obtained from this study is very useful in development of SnO_2 photoelectrodes for feasible applications of PEC cells.

6. Acknowledgement

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7. References

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