Electrodeposition of nano-structured ZnO/dye films for flexible dye-sensitized solar cells

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Realization of flexible dye-sensitized solar cells would be of a great value in extending new applications in our everyday life. The most serious problem to be solved for its realization is how to establish new techniques for preparing photoelectrodes at temperatures lower than *e.g.*,150ºC. Electrochemical techniques should be highlighted in view of their intrinsically heat treatment-free processing.

Through our systematic studies on the preparation of CdS films by the electrochemically induced chemical deposition (EICD) technique, we have found that atom-by-atom growth of CdS films takes place under optimized conditions to form homoepitaxially grown CdS films up to the thickness exceeding 1 µm.1) Another interesting finding is that some kinds of additives such as mercaptoethanol in the bath, which are strongly adsorbed on the surface of CdS, yields nano-particulate CdS films.2) Such a controllability encourages us to design nano-structured metal oxide semiconductor films for the application to the dye-sensitized solar cells by introducing some adsorptive organic dyes in the plating bath. A candidate material we have chosen for this purpose was ZnO, which have been known to be hopeful for a dye-sensitized photoelectrode and to be easily electrodeposited. The growth of ZnO has been found to take place *via* precipitation of Zn^{2+} by the electrochemical generation of hydroxyl ions, *e.g.*, reduction of nitrate ion or dissolved oxygen.3,4)

We have reported that crystalline ZnO thin films loaded with dyes are deposited from aqueous $Zn(NO_3)_2$ baths containing water soluble dyes such as tetrasulfonated metallophthalocyanines,5) tetrabromo-phenolblue 6) and eosinY. 7) In these processes dye molecules actively participate in the film growth, which is totally different from the conventional colloid-based photoelectrode preparation.

When dissolved oxygen was used as an electrochemical hydroxide ion generator in an aqueous $ZnCl_2$ solution containing eosinY, more stimulating results have been obtained. A remarkable feature in this system is that eosinY catalyzes the reduction of oxygen to accelerate the growth of ZnO film, which is in contrast to the case of $Zn(NO_3)_2$ bath, where the addition of eosinY slows down the growth rate of the hybrid film. Highly oriented crystalline hybrid thin films with two distinctive structures depending on the redox states of eosinY have been deposited. Polarizing at potentials more positive than that of eosinY reduction yields compact films consisting of ZnO crystals into which eosinY molecules are entrapped, which are apparently not suitable for dye-sensitized solar cells. When polarizing at potentials where eosinY is electrochemically reduced, on the other hand, thin films with very unique structures were obtained, which consist of highly oriented crystalline sponge-like ZnO crystals with internal nano-porous structure to which eosinY molecules are adsorbed. When polarizing at potentials where eosinY is electrochemically reduced, on the other hand, thin films with very unique structures were obtained, which consist of highly oriented crystalline sponge-like ZnO crystals with internal nano-porous structure to which eosinY molecules are adsorbed. The amount of eosinY loaded in a hybrid film amounts to $1.36x10^{-7}mol/cm^2$ for a film of 5.2µm thickness. It corresponds to the concentration of eosinY in the film as high as 0.36M, which is higher than that for the films obtained by conventional colloid-based method. These advantages can come from that films are built up with ordered structures at atomic and molecular levels with better controllability than the conventional method.

Thanks to such a favorable microstructure, this film behaves as an efficient dye-sensitized photoelectrode. The incident photon to current conversion efficiency (IPCE) of these films a in I^-/I_3^- redox-containing non-aqueous electrolyte mounts to values as high as 0.9. The films are highly crystallized and possess grain boundary-free structure, so that electron transport through the films is very fast and this in turn suppresses recombination of electrons. IMPS and IMVS measurements indicate that a fast diffusion and a long lifetime of electrons injected from photoexcited dyes into the conduction band of ZnO, which is also originated from the above-mentioned microstructure of the films.

It should be recalled that such favorable photoelectrochemical properties are obtained without any heat treatment, making these films very efficient photoelectrode for flexible dye-sensitized solar cells by using a conductive plastic substrate.

Detailed nano-structural characterization of the films obtained and the characteristics of dye-sensitized solar cells using these films are presented and disused in this paper.

References

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