Orientation Controlled Electrodeposition of Nanoporous ZnO/Dye Hybrid Thin Films for Solar Cell Applications

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We have established a new electrochemical synthetic route to the porous oxide semiconductor film as the photoelectrode in dye-sensitized solar cells [1-4]. Cathodic electrodeposition from aqueous mixed solution of zinc salt and water soluble dyes yields nanostructured hybrid thin films of crystalline ZnO and the added dye molecules in one step. The hybrid thin films exhibit high performances as dye-sensitized photoelectrodes. Since the process does not involve high temperature or aggressive chemicals, it is directly applicable to conductive plastic film substrates such as ITO coated PET, for the realization of high performance flexible dye-sensitized solar cells (DSSCs).

When eosinY is used as the dye, deeply red colored ZnO/eosinY hybrid thin film in a porous crystalline structure is obtained, namely, a film consisting with micrometer-sized large crystals of ZnO in which three-dimensionally interconnected nanopores are formed. The deposited ZnO grains are highly crystallized and oriented with their c-axis perpendicular with the substrate as seen in the comparison of the XRD patterns in Fig. 1. Almost perfect crystalline nature of this hybrid material despite of its high porosity has also been proven by the heteroepitaxial electrodeposition on GaN electrodes [5]. The loaded eosinY molecules exist in the pores as aggregates. They can be completely washed away by soaking the film in mild alkaline (dil. KOH). The resultant porous electrode can be reloaded with any dyes. A DSSC fabricated employing thus prepared photo electrode with re-adsorbed eosinY as the sensitizer achieved a conversion efficiency of 2.3% under AM 1.5 simulated sun light (100 mW cm^{-2}) [4]. The IMPS measurements have indicated fast electron transport for effective electron collection, owing to the absence of grain boundaries in this highly crystallized material.

When coumarin343 is used instead of eosinY for the film synthesis, a yellow colored ZnO/coumarin343 hybrid thin film was obtained. Interestingly, the crystallographic orientation of this film changes from that of ZnO/eosinY by 90º, namely, the c-axes are now aligned in parallel with the substrate as clearly seen in its XRD pattern which exhibits strong diffractions from (100) and (110) planes (Fig. 1). The loaded dye molecules could also be extracted from the film by the alkaline treatment. Since better electrical conduction is known along the a- and b-axes of ZnO than that along the c-axis, even higher performance can be anticipated for the use of ZnO/coumarin343 hybrid thin film as a photoelectrode in DSSCs.

Surface morphology as well as the internal nano-structure of the hybrid thin films was examined in high resolution FE-SEM images (Fig. 2). The vertical (ZnO/eosinY) and horizontal (ZnO/coumarin343) structures are clearly visualized.

References

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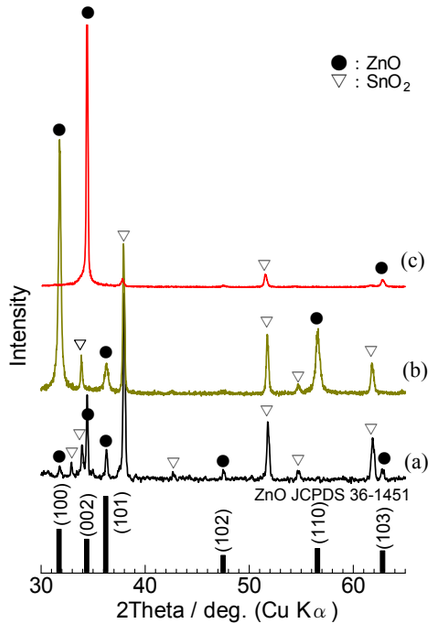

Fig. 1 XRD patterns of electrodeposited ZnO (a), ZnO/coumarin343 (b) and ZnO/eosinY (c) thin films in comparison with the powder diffraction standard of ZnO.

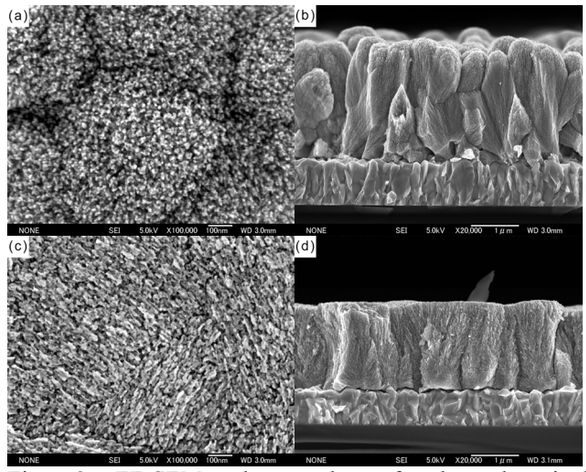

Fig. 2 FE-SEM photographs of electrodeposited ZnO/eosinY hybrid (vertical) thin film for its surface (a) and cross section (b), and ZnO/coumarin343 hybrid (horizontal) thin film for its surface (c) and cross section (d). All images were taken after dye extraction by KOH.