Fabrication and Characterizations of Nano-Structured ZnO/Eosin Y Hybrid Films by One-Step Electrodeposition

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Having a glance of the history of dye-sensitized solar cells (DSCs), it is noticed that development of new methods for the preparation of photoelectrodes has brought about a substantial improvement of DSCs. Recent achievements are mainly owing to the establishment of preparation of photoelectrode materials with extremely high surface area. Therefore, more efforts should be made to develop a new technique for getting nano-structured photoelectrodes. Recently, we have developed a novel and simple method to synthesize thin films of dye-modified ZnO by one-step cathodic electrodeposition from aqueous solution containing Zn^{2+} ion and water-soluble dye.[1)] The growth of ZnO takes place *via* precipitation of Zn^{2+} by the electrochemical generation of hydroxyl ions, *e.g.*, reduction of nitrate ion or dissolved oxygen. The mechanism of the hybrid film formation has been found not so simple, because loading of eosinY molecules into the film occurs not by passive inclusion but as a consequence of stable complex formation with Zn^{2+} upon their electrochemical reduction.[2)] As the material is grown from solution, namely, from the smallest constituents, their free interaction leads to a self-assembly of a three dimensionally ordered nano-hybrid structure, being totally different from the conventional colloid-based methods that inherently result in a formation of random structured films. The results so far obtained make us convince of the effectiveness of our technique. In the present paper, characterization of ZnO/eosin Y films obtained by this method will be demonstrated.

TEM photographs of the hybrid film deposited at -1.0 V (*vs.*SCE) interestingly suggests that the film has a nanoporous structure, constructed by nanometer sized crystallites of ZnO, each of which are interconnected to build a micrometer sized single crystal of ZnO. The nanopores are formed inside of large ZnO grains. As the hybrid material retains the ordered structure of ZnO crystal, it could be epitaxially grown on a GaN single crystal substrate. In addition, the loaded eosinY molecules sit on internal surfaces of the nanopores, thus enabling electrolyte to be accessible to them. This was confirmed by the fact that by dipping the films in a diluted KOH aqueous solution only dyes are desorbed and colorless ZnO films left. A schematic drawing of the microstructure as well as TEM photographs of the hybrid is displayed in Fig.1. Due to the formation of such favorable structure, higher amount of dye loading is achievable, compared to 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.

The electrodeposited ZnO/eosin Y thin film electrodes with deep red color actually exhibit efficient dye-sensitization. Incident photon to current conversion efficiency (IPCE) under the monochromatic light illumination of 520nm amounts to around 0.5 with the films after dried at 150℃. 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.

In conclusion, this technique has proven to be promising for getting efficient photoelectrodes of DSCs. Additionally, it should also be noted that ZnO/dye hybrid films with well-ordered structures are obtained without consuming any notable energy. This indicates a possibility of fabricating a flexible DSC using conductive plastic substrates, in turn contributing to a remarkable reduction in production cost.

References

1) For example, T.Yoshida and H.Minoura, *Adv. Mater.*, **12**, 1219 (2000).
2) K.Okabe *et al.*, *Trans. MRS-J.*, **26**, 523 (2001).

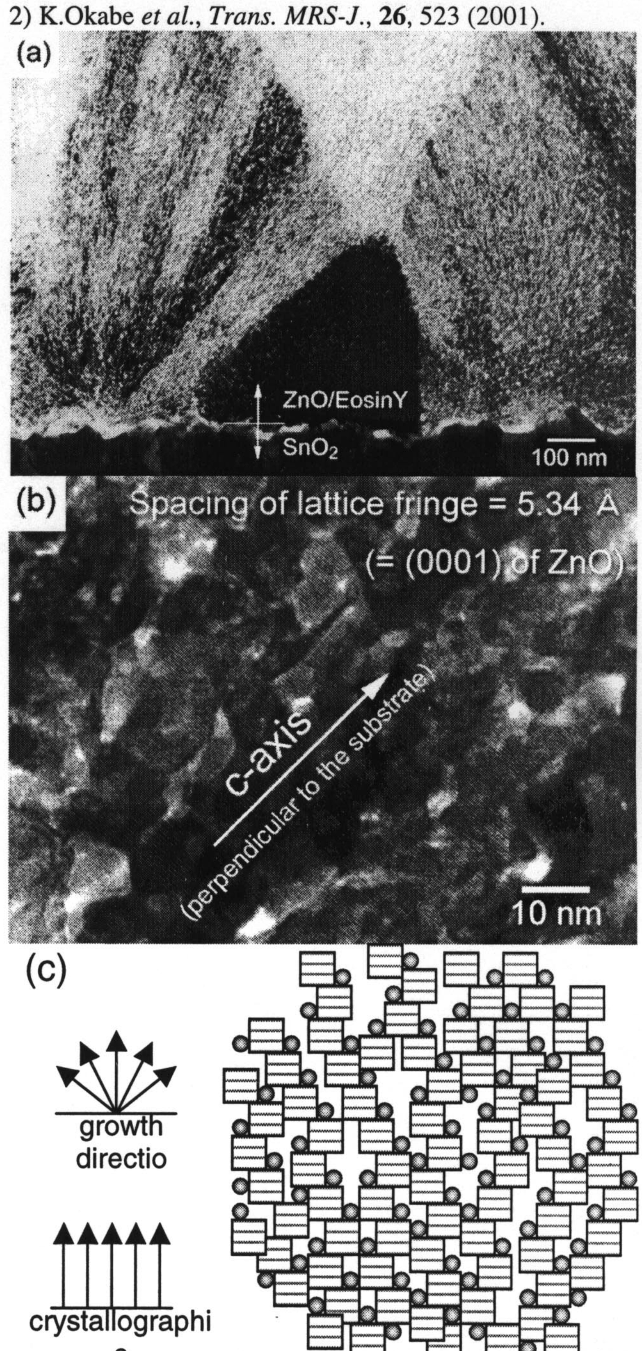

Fig.1 TEM photographs and microstructure model of ZnO/eosin Y film.