

Electrodeposition of Photoactive ZnO/Xanthene Dye Hybrid Thin Films

Kenji Okabe, Tsukasa Yoshida, Takashi Sugiura, and Hideki Minoura

Environmental and Renewable Energy Systems (ERES) Division, Graduate School of Engineering, Gifu University
Yanagido 1-1, Gifu 501-1193, JAPAN

Fax: 81-058-293-2587, e-mail: yoshida@apchem.gifu-u.ac.jp

One-step cathodic electrodeposition from aqueous solutions containing zinc nitrate and xanthene dyes such as fluorescein, eosinY, merbromine, phloxineB, erythrosinB and rose bengal resulted in a self-assembly of zinc oxide (ZnO)/dye hybrid thin films. The electrodeposited ZnO/dye hybrid thin film electrode in contact with an I/I_3^- redox electrolyte solution generated photoanodic current upon visible light illumination, indicating photosensitization of ZnO by the loaded dyes. The ZnO/phloxineB hybrid thin film exhibited especially high photoelectrochemical performance. Incident photon to current conversion efficiency (IPCE) of 42 % has been attained around the absorption maximum of phloxineB (550 nm) for the film deposited under optimum conditions, thus being superior than the ZnO/eosinY hybrid thin film (IPCE = ca. 21 %) previously reported by us. Electrochemical analysis for the redox reactions of phloxineB in the presence of Zn^{2+} evidenced complex formation between the reduced dye molecule and Zn^{2+} , which seems to play a key role in the self-assembly of the ZnO/dye hybrid structure.

Key words: zinc oxide, xanthene dyes, electrodeposition, self-assembly, photosensitization

1. INTRODUCTION

Dye sensitized solar cells (DSCs) have received considerable attention since O'Regan and Grätzel reported strikingly high conversion efficiencies approaching 10 % by using porous titanium dioxide thin film electrode modified by polypyridine ruthenium complexes [1]. The photoactive material, namely, the dye modified semiconductor, is usually prepared by a stepwise processing, that is, fabrication of porous semiconductor film by coating colloidal paste of semiconductor nano-particles on optically transparent conductive oxide (TCO) electrode and subsequent heat treatment at temperatures above 400 °C, then soaking the film in a dye solution for chemical adsorption of the sensitizers. The same method has been successfully applied to the other combinations of semiconductors and dyes. For example, a DSC employing porous ZnO thin films modified with merbromine attained a conversion efficiency of 2.5%. [2]. However, this method limits the TCO substrate to a heat resistant one. Development of a heat treatment free processing of the semiconductor/dye hybrid thin film therefore should enable use of plastic substrates for reduction of the device cost.

We have recently succeeded in one-step heat treatment free synthesis of ZnO/dye hybrid thin films by cathodic electrodeposition from aqueous mixed solutions containing zinc nitrate and water-soluble dyes [3-7]. Dye adsorption on the growing surface of ZnO caused crystal growth into specific directions to build up unique ZnO/dye hybrid structures, thus making this process to be categorized as electrochemical self-assembly [3,4]. The deposited films have been found to perform as sensitized photoelectrodes [5-7]. The hybrid thin film employing eosinY exhibited

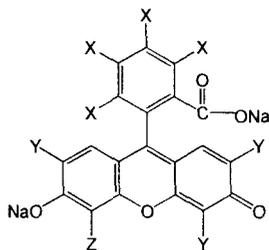
especially high activity, achieving an incident photon to current conversion efficiency (IPCE) of ca. 21 % [7].

In this study, we have attempted electrodeposition of ZnO/dye hybrid thin films using various kinds of xanthene dyes and examined their photoelectrochemical properties. The hybrid thin film deposited with phloxineB has been found to perform as remarkably active photoelectrode with the IPCE value exceeding 40 % for the film deposited under optimum conditions. We have also carried out structural analysis of the deposited thin film and electrochemical analysis of the redox reactions of the dye molecules in the presence of Zn^{2+} ion relevant to the electrochemical self-assembly of the ZnO/dye hybrid structures.

2. EXPERIMENTAL

The structure and some optical properties of the xanthene dyes used in this study are shown in Fig.1. Hereafter, the dyes are to be called as abbreviated in Fig. 1. All dyes were of commercially available purest grade and used as purchased. An indium tin oxide (ITO) coated glass used as a substrate was ultrasonically cleaned in 2-propanol, acetone, water and finally etched in 45 % nitric acid before use.

The electrodeposition of the hybrid thin films was carried out potentiostatically at $-0.9V$ vs. SCE and for 60min in a single compartment electrochemical cell equipped with a Zn wire counter electrode and an SCE reference electrode. Although a Pt wire was used as the counter electrode in our previous studies [3-7], the use of Zn wire has been found to improve the homogeneity of the deposited films because it prevents lowering of bath pH during the film deposition. Aqueous mixed solution of 0.1M $Zn(NO_3)_2$ and 30 μ M dye (pH = ca. 6) was used as deposition bath maintained at 70°C



| Dye | X | Y | Z | λ_{\max} (nm)* | ϵ ($M^{-1} \text{ cm}^{-1}$)* |
|-----|----|----|------|------------------------|--|
| FL | H | H | H | 401 | 63,600 |
| EY | H | Br | Br | 517 | 91,600 |
| MB | H | Br | HgOH | 507 | 65,900 |
| PB | Cl | Br | Br | 548 | 102,000 |
| EB | H | I | I | 525 | 87,200 |
| RB | Cl | I | I | 548 | 99,300 |

*; for aqueous solutions.

Fig. 1 Structures and optical properties of the xanthene dyes used in this study; fluorescein (FL), eosinY (EY), merbromine (MB), phloxineB (PB), erythrosinB (EB) and rose bengal (RB).

by a thermostat. For the deposition of ZnO/PB thin films, the potential was varied between -0.8 and -1.1 . The deposited films were rinsed by water, dried in air at room temperature and subjected to the further analyses without any heat treatment.

The film thickness was measured by using a contact stylus surface profilometer. A known area of the film was dissolved into a known volume of concentrated aqueous ammonia solution for measuring its optical absorbance at the absorption maxima of dyes to determine the amount of the loaded dye from Lambert-Beer's law. Surface morphologies of the films were observed by a TOPCON ABT-150FS scanning electron microscope (SEM). X-ray diffraction (XRD) pattern of the film was obtained by a Rigaku RAD-2R using Cu $K\alpha$ radiation.

Photoelectrocurrent measurements were performed on the electrodeposited ZnO/dye hybrid thin film electrodes in an acetonitrile/ethylene carbonate ($v/v=1:4$) mixture containing $0.5M$ KI and $0.03M$ I_2 , under visible light illumination by a $500W$ Xe lamp equipped with IR and $<420nm$ cutoff filters from the side of the ITO back contact. Light intensity was set to $20mW/cm^2$. A homemade Ag/Ag^+ reference electrode (Ag wire soaked in acetonitrile containing 0.01 mM $AgNO_3$) was used in these measurements. Its potential was $+0.41V$ vs. NHE (normal hydrogen electrode) as calibrated by measuring the potential of ferrocene/ferricenium ion redox couple. A Pt wire served as a counter electrode. Photocurrent action spectrum was measured at -0.1 V vs. Ag/Ag^+ using the same setup, but under monochromatic light illumination generated by using a Nikon G250 monochromator.

3. RESULTS AND DISCUSSION

We have first attempted to synthesize ZnO/dye hybrid thin films with various xanthene dyes using the bath composition and the deposition conditions which yielded the best ZnO/EY thin film in our previous report [7]. However, EB

and RB were found to form precipitates when they are added at the concentration of $55 \mu M$ to 0.1 M $Zn(NO_3)_2$, due probably to their high affinity to Zn^{2+} ion. We therefore reduced the dye concentration in the bath to $30 \mu M$, where homogeneous mixtures could be obtained for all dyes. Cathodic electrolysis in these mixtures at -0.9 V and for 60 min yielded translucent orange to red colored homogeneous thin films. The film thickness and the amount of the dyes loaded into the film are listed in Table 1. While film thickness does not vary so much for different dyes as reasonably expected from the similar amounts of the passed charge during the film deposition, the amount of the loaded dye significantly vary from dye to dye, suggesting their differences in the stability for the adsorption on ZnO.

The deposited ZnO/dye hybrid thin film electrodes were subjected to the photocurrent measurements. The maximum photocurrent values generated in contact with I^-/I_3^- redox electrolyte solutions upon white light illumination at 20 mW/cm^2 are also presented in Table 1. All of the thin film electrodes produced photoanodic current, indicating photosensitization by the loaded dye molecules. It can be noticed that the significance of photocurrent generation is not related to the amount of the loaded dyes, suggesting that the photon harvesting efficiency of the films is not limiting the photocurrent, because the molar extinction coefficients of these dyes are similar. Merbromine performs as a rather poor sensitizer for the electrodeposited hybrid thin film, although it was reported to work as an excellent sensitizer for the colloid processed ZnO electrode [2]. The photocurrent value obtained for the ZnO/EY film is surprisingly smaller than that attained for the film deposited from a bath containing $55 \mu M$ EY, which was previously reported [7]. Another important difference from our previous work is the material of the counter electrode. The use of Zn counter electrode was essential to obtain homogeneous thin films for all of the dyes used in this study. Because it maintains bath pH almost constant during the deposition, it facilitates the formation of ZnO which is often hindered in the presence of strongly adsorbing dye molecules [4]. Such subtle differences in the

Table 1 The passed charge, the film thickness, the amount of dye loaded into the film and the photocurrent values for the ZnO/dye hybrid thin films electrodeposited at -0.9 V and for 60 min from the baths containing 0.1 M $Zn(NO_3)_2$ and $30 \mu M$ dye.

| Dye | Passed charge (C/cm^2) | Film thickness (μm) | Dye loading per projected film area (10^{-9} mol/ cm^2) | Photocurrent density ^a ($\mu A/cm^2$) |
|-----------------|----------------------------|----------------------------|---|--|
| FL | 1.82 | 1.7 | 2.41 | 15.0 |
| EY | 2.14 | 1.8 | 60.3 | 10.6 |
| MB | 1.79 | 1.8 | 7.06 | 4.07 |
| PB | 2.10 | 2.6 | 12.4 | 67.5 |
| EB | 1.82 | 2.0 | 27.3 | 11.0 |
| RB | 1.62 | 2.3 | 14.3 | 12.2 |
| EY ^b | 2.70 | 1.7 | 48.0 | 140 |

^a; Measured at -0.1 V vs. Ag/Ag^+ and at the light intensity of 20 mW/cm^2 . ^b; Data from ref. 7.

deposition condition significantly change the photoelectrochemical properties of the hybrid thin films. Therefore, care must be taken to compare the present results. However, as long as the present deposition conditions are applied for the film synthesis, the ZnO/PB thin film has been found to perform as an exceptionally efficient photoelectrode. Further efforts have been concentrated in the optimization of the deposition conditions for the system employing PB and analyzed the ZnO/PB hybrid thin film in detail.

The electrodeposition of ZnO/PB hybrid thin films has been carried out at various potentials. The film thickness, the dye loading and the photocurrent values have been checked and their dependence on the deposition potentials is shown in Fig. 2. The film thickness and dye loading increase along with the negative shift of the deposition potential, then peak at -1.05 and -1.0 V, respectively. The photocurrent value is almost constant for the films deposited at the potentials down to -0.9 V and abruptly increases at more negative potentials. The maximum photocurrent of ca. $400 \mu\text{A}/\text{cm}^2$ was attained for the film deposited at -1.05 V. The photocurrent action spectrum measured for this ZnO/PB hybrid thin film electrode is compared with its absorption spectrum in Fig. 3. Photosensitization by the loaded PB molecules is evident from their close resemblance. The IPCE of 42 % was achieved around the absorption maximum of PB. The best ZnO/EY hybrid thin film electrode, which we reported earlier, achieved the maximum IPCE of 21 % in its as deposited state and it was improved to 47 % after mild heat

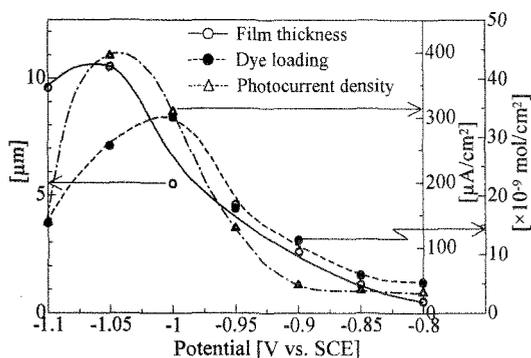


Fig. 2 Dependence of film thickness, dye loading and photocurrent density on the deposition potentials for the ZnO/PB hybrid thin films.

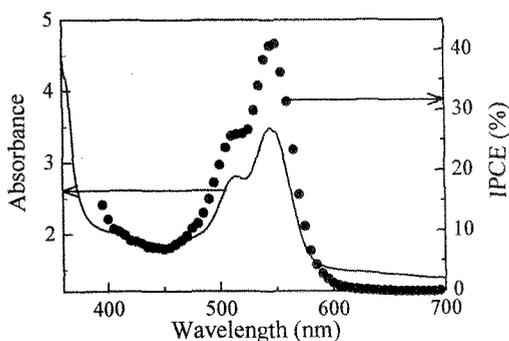
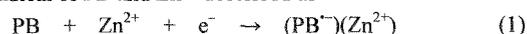


Fig. 3 Photocurrent action spectrum and UV-Vis absorption spectrum measured for the ZnO/PB hybrid thin film electrode deposited at -1.05 V.

treatment of the film at 150°C [7]. The present ZnO/PB hybrid thin film, without any heat treatment performs as good as the heat treated ZnO/EY hybrid thin film.

It should be noted that the ZnO/PB thin film right after the deposition at -1.05 V is colorless and regenerates the red color of PB after its exposure to air, while the films were red as deposited when the deposition was carried out at the potentials more positive than -0.9 V. The deposition of colorless thin films at negative potentials is due to the reduction of PB molecules. The redox reactions of PB in the presence of $\text{Zn}(\text{NO}_3)_2$ has been studied by means of cyclic voltammetry (CV) in order to elucidate the electrode reactions relevant to the formation of ZnO/PB hybrid thin films. Fig. 4 shows cyclic voltammograms measured in aqueous mixed solutions of PB, $\text{Zn}(\text{NO}_3)_2$ and KNO_3 , for which the concentration of PB is kept constant, while that of Zn^{2+} is varied. A couple of reversible redox peaks centered at ca. -0.92 V is seen for the solution without Zn^{2+} , corresponding to the reduction of PB. Upon increasing addition of Zn^{2+} to the solution, the cathodic peak for the reduction of PB shifts positively and the anodic peak of reoxidation diminishes. The cathodic peak potential is plotted vs. logarithmic strength of Zn^{2+} in the inset of Fig. 4. It is constant up to around $\log[\text{Zn}^{2+}] = -3$ and linearly shifts at higher Zn^{2+} strength toward positive potentials. The slope of the shifting part has been determined as ca. $63 \text{ mV}/\text{decade}$. The observed slope clearly indicates Zn^{2+} -coupled reduction of PB resulting in a complex formation between anion radical of PB and Zn^{2+} described as



The position of the borderline between the Zn^{2+} dependent and independent parts indicates the stability of the complex

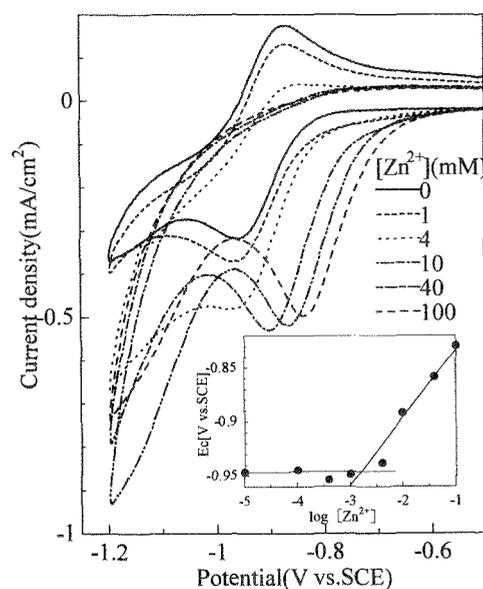
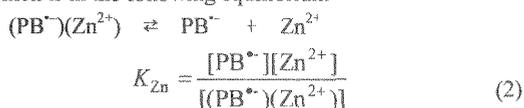


Fig. 4 Cyclic voltammograms measured at an ITO glass electrode in 0.5 mM PB aqueous solutions containing Zn^{2+} at various concentrations prepared by mixing 0.1 M $\text{Zn}(\text{NO}_3)_2$ and 0.2 M KNO_3 , saturated with Ar and maintained at 70°C . Scan rate = $500 \text{ mV}/\text{s}$. The inset shows cathodic peak potentials plotted vs. $\log[\text{Zn}^{2+}]$.

which is in the following equilibrium



The stability constant of $pK_{\text{Zn}} = 2.8$ for the complexation is determined from the strength of Zn^{2+} at the equilibrium point. The PB anion radical is greatly stabilized against reoxidation owing to the complex formation with Zn^{2+} . Such complex formation clearly explains the increase of the dye loading for the films deposited at the potentials more negative than ca. -0.85 V, the reduction potential of PB in its mixture with $\text{Zn}(\text{NO}_3)_2$ (Fig. 2). The dye loading under such circumstance is obviously not under control of the diffusion of PB molecules to the electrode surface, but is under control of the electrochemical complex formation. At more positive potentials, PB molecules are not reduced during the deposition and simply adsorbed on the electrodeposited ZnO surface.

The difference in the growth mechanism emerges in the difference of the film structure. Fig. 5 compares the SEM photographs of the ZnO/PB hybrid thin films deposited at -0.85 and -1.05 V. The film deposited without involving dye reduction (-0.85 V) has an irregular structure. Inclusion of hexagonal cylindrical particles is noticed. The pure ZnO thin film electrodeposited in the absence of dyes consist of only such hexagonal particles [4]. The XRD measurement of this ZnO/PB film revealed diffraction peaks assigned to ZnO

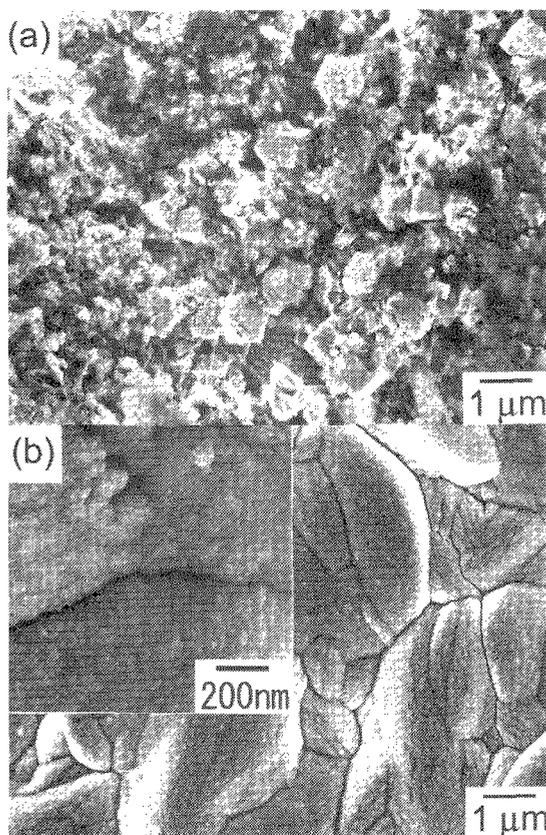


Fig. 5 SEM photographs of the ZnO/PB hybrid thin films electrodeposited at -0.85 V (a) and -1.05 V (b).

crystals, however, much smaller in intensity than those from the pure ZnO film deposited at the same potential and without PB. It is supposed that the passive adsorption of PB hinders the crystal growth, resulting in a formation of a film consisting of random structured mixtures of PB molecules with tiny crystals of ZnO or Zn hydroxide, together with some well-crystallized ZnO, which appear as the hexagonal particles. The film deposited involving PB reduction (-1.05 V), on the other hand, consists of densely packed particles with several μm in size. The XRD analysis of this film found sharp diffraction peaks of ZnO, indicating its high crystallinity. However, the high magnification image reveals porous surface of these particles as they are made as assemblies of much finer nano-particles. The high IPCE found for this ZnO/PB thin film proves that the electrolyte solution can penetrate through the film to be in contact with the loaded dye. The formation of the large particle "units" is a proof of coherent assembly of the nano-particles. It is likely that the reductive adsorption of PB molecules terminates the crystal growth so that PB stays on the surface of ZnO, but does not prevent the coherent growth of ZnO to create the unique ZnO/PB hybrid structure. The complexation between reduced PB molecule and Zn^{2+} therefore seems to play a key role in the electrochemical self-assembly of the photoactive ZnO/PB hybrid structure.

In conclusion, we have succeeded in heat treatment free one-step electrochemical synthesis of highly photoactive ZnO/dye hybrid thin films, which can open a way to realize fabrication of DSCs using plastic substrates. It has been found that dye molecules actively participate in the electrode process for the self-assembly of the hybrid structure. Further understanding of the complex electrochemical reactions between the organic molecules and inorganic ions should make it possible for us to optimize the deposition conditions for the improvement of the photoelectrochemical performance of the electrodeposited ZnO/dye hybrid thin films including the xanthene dyes else than PB.

ACKNOWLEDGMENT

The present work was partly defrayed by the Grant-in-Aid for Scientific Research on Priority-Area-Research "Electrochemistry of Ordered Interfaces" from the Ministry of Education, Science, Sports and Culture of Japan (09237105).

References

- [1] B. O'Regan and Grätzel, *Nature*, **363**, 737-40 (1991).
- [2] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara and H. Arakawa, *Solar Energy Materials & Solar Cells*, **64**, 115-34 (2000).
- [3] T. Yoshida and H. Minoura, *Adv. Mater.*, **12**, 1219-22 (2000).
- [4] T. Yoshida, M. Tochimoto, D. Schlettwein, D. Wöhrle, T. Sugiura and H. Minoura, *Chem. Mater.*, **11**, 2657-67 (1999).
- [5] T. Yoshida, J. Yoshimura, M. Matsui, T. Sugiura and H. Minoura, *Trans. MRS-J.*, **24**, 497-500 (1999).
- [6] D. Schlettwein, T. Oekermann, T. Yoshida, M. Tochimoto and H. Minoura, *J. Electroanal. Chem.*, **481**, 42-51 (2000).
- [7] T. Yoshida, K. Terada, D. Schlettwein, T. Oekermann, T. Sugiura and H. Minoura, *Adv. Mater.*, **12**, 1214-17 (2000).