

Electrochemical Growth of ZnO/eosinY Hybrid Thin Film

Daisuke Komatsu, Jingbo Zhang, Tsukasa Yoshida* and Hideki Minoura

Environmental and Energy Systems Division, Graduate School of Engineering, Gifu University,
Yanagido 1-1, Gifu 501-1193, Japan

Fax: 81-058-293-2593, *e-mail: yoshida@apchem.gifu-u.ac.jp

Electrochemical growth of ZnO/eosinY hybrid thin film was investigated. Two deposition potentials of -0.8 and -1.0 V vs. SCE were chosen to clarify the relationship between the redox state of eosinY and the structure of the products, because eosinY has its reduction potential at around -0.9 V. The hybrid thin film deposited at -0.8 V has a dense structure, while that at -1.0 V has a nanoporous structure. Almost steady current was observed during the potentiostatic electrodeposition. Deposition rates in film thickness, molar amount of ZnO and of eosinY were determined. Linear growth and constant composition were found regardless of the deposition potentials. The adsorption rate of eosinY at -1.0 V was about 10 times higher than that at -0.8 V. Because eosinY molecules can occupy as much as 38% of the total volume of the hybrid film deposited at -1.0 V, the film comes to possess an open porous structure after removal of the dyes by dipping the film in dilute KOH. On the other hand, eosinY molecules appear to be surrounded by ZnO due to the much lower loading efficiency at -0.8 V, so that the hybrid film is grown in a dense structure from which dyes cannot be fully removed by the KOH treatment.

Key words: Electrodeposition, ZnO, EosinY, Hybrid, Dye sensitized solar cells.

1. INTRODUCTION

Electrodeposition of ZnO thin film from aqueous zinc salt solution was reported independently by Izaki et al. [1, 2], and Peulon et al. [3-5], which are promoted by base generation upon electroreduction of nitrate ions and dissolved oxygen, respectively. When water-soluble dye is added into the deposition bath, self assembly of ZnO and dye molecules takes place to yield ZnO/dye hybrid films [6-9]. These hybrid thin films perform as efficient photoelectrodes for dye-sensitized solar cells (DSSCs). The same approach of materials synthesis has successfully been applied to preparation of hybrid thin films of ZnO and rare earth metal complexes, which exhibit photo luminescence in different colors [10].

The structure of ZnO/dye hybrid thin films is varied by the kind of dye added to the bath. When adding eosinY (EY) that is a kind of xanthene dyes (Fig. 1), three dimensionally interconnected nanopores are formed in ZnO crystal grains.

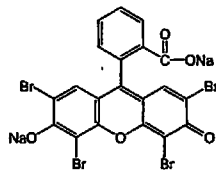


Fig. 1 Structure of EosinY

Such a structure is especially suited for DSSCs [11], because electrons injected from the photoexcited state of the dye do not have to travel across the grain boundaries. Because the process demands neither high temperature nor aggressive chemicals, the process is perfectly compatible with conductive plastic electrodes for realization of flexible solar cells. However, the

as-deposited hybrid thin films only showed moderate photoelectrochemical performance, because the loaded EY molecules form aggregates, so that not all of the loaded EY molecules act as sensitizers. This problem can be solved by desorption of the loaded EY by soaking the film into a weak alkaline solution of about pH 10.5. Various photosensitizer dyes can then be reabsorbed on the internal surface of the porous crystalline ZnO. In fact, DSSCs employing the photoelectrodes fabricated in this way showed good conversion efficiencies [12].

For further improvement of the performance of the solar cells employing the electrodeposited ZnO/dye hybrid thin films, detailed understanding of the growth mechanism is needed to enable precise control of the nanostructure optimized for the photosensitizer dye and electrolyte solution to be combined. The present study is dedicated to collect basic experimental data for the process of the hybrid film growth which are needed to discuss the growth mechanism.

It has previously been found that the structure of ZnO/EY hybrid film changes depending on the deposition potential [9]. Under certain negative potentials, EY can be electrochemically reduced during the film growth. Because reduced EY molecules form stable complexes with zinc ions, dye loading into the film can be enhanced [9]. On the other hand, hybrid thin films are also obtained at the potentials where EY molecules are in their oxidized state, because EY molecules have a property to be chemically adsorbed on ZnO. It is therefore useful to study the hybrid film growth with EY molecules of different redox states. Because reduction of EY occurs at around -0.9 V vs. SCE, the electrodeposition was performed at -0.8 and -1.0 V vs. SCE, the potentials representing the film growth with oxidized and reduced EY, respectively.

Electrodeposition was carried out for different periods and the films were analyzed to collect experimental data such as the film growth rate, faradic efficiency, chemical composition. The morphological difference of the films is also observed and discussed.

2. EXPERIMENTAL

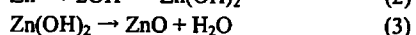
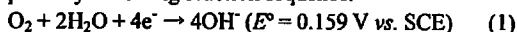
Fluorine doped SnO₂ (FTO) coated glass (10 Ω/□ Asahi glass) sheets were cleaned ultrasonically in acetone, 2-propanol, soap solution, and water. They were activated in 45 % HNO₃ for 2 min and finally rinsed with distilled water prior to the electrodeposition. An aqueous solution was prepared as deposition bath to contain 5 mM ZnCl₂ (Merck) and 0.1 M KCl (Merck) using Milli-Q pure water (18.2 MΩ). Disodium salt of EY (Kanto) was added into the deposition bath at 45 μM for preparing ZnO/EY hybrid film. A three-electrode single compartment cell was used. FTO glass was used as a working electrode by applying it to a Radiometer Analytical (ED1101 and CTV101) rotating electrode system. The rotation rate was set to 500 rpm. A Zn wire (99.9%) was used as a counter electrode. The potential was referred to a saturated calomel electrode (SCE). The cell was placed in a thermostat bath maintained at 70°C. Oxygen gas was bubbled at 100 ml min⁻¹ for 30 min prior to the actual electrolysis and the same gas flow was maintained during the deposition. The electrolysis was carried out for controlled periods between 5 and 60 min potentiostatically at -0.8 or -1.0 V (vs. SCE). A Hokuto Denko HSV-100 was used for the potential control and the current monitoring.

Film thickness was measured with a surface profilometer (SE-2300, Kosaka Lab. Ltd.). Amount of deposited ZnO was determined from the amount of precipitated Zn measured by inductively coupled plasma spectrometry (ICP) on the assumption that all of deposited zinc ions are precipitated in the form of ZnO. The dye concentration of 7N NH₄OH aqueous solution that dissolved ZnO/EY hybrid film was measured by spectrophotometer (U-3500, HITACHI), in order to calculate the amount of dye loaded into the film. Scanning electron microscopy (SEM) images were recorded using JEOL, JSM-6700F to study the surface and cross sectional morphology of the films.

3. RESULTS AND DISCUSSION

The chronoamperograms measured during the electrodeposition of ZnO and ZnO/EY hybrid film are shown in Fig. 2. Almost steady current was observed in all cases suggesting constant rates of the film growth. It is also noticed that the current is largely enhanced by addition of EY for given overpotentials.

It is considered that the electrodeposition of ZnO takes place by following reaction sequence.



The primary reaction is the reduction of O₂ to elevate the pH in the vicinity of the electrode followed by chemical reactions to precipitate ZnO on the electrode. The larger cathodic current with the higher overpotential indicates kinetic limitation of the O₂ reduction. The current enhancement in the presence of EY therefore indicates the increased rate of electron

transfer to O₂ due to the catalytic effect of EY. Contribution of electroreduction of EY molecules to the overall current for the electrolysis at -1.0 V is negligible as expected from its small concentration and diffusion coefficient [13]. Detailed analysis for the process of electrocatalysis has revealed different mechanisms for different redox states of EY molecules which are to be reported in a separate paper [14].

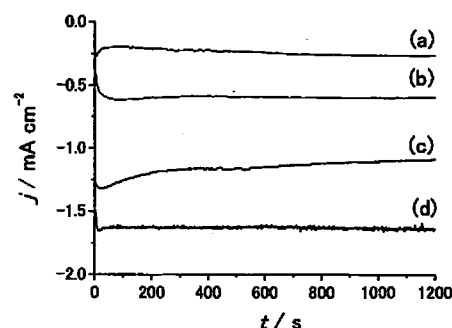


Fig. 2 Chronoamperograms measured during the potentiostatic electrodeposition of thin films under various conditions: ZnO from an aqueous solution of 5 μM ZnCl₂ and 0.1 M KCl saturated with O₂, at the potentials of (a) -0.8 and (b) -1.0 V, ZnO/EY from an aqueous solution of 5 mM ZnCl₂, 0.1 M KCl and 45 μM eosinY saturated with O₂ at the potentials of (c) -0.8 and (d) -1.0 V.

Film thickness, amount of deposited ZnO, and that of dye loaded into the film were found to proportionally increase to the extension of the deposition time (Fig. 3). Because current stays almost constant during the electrodeposition (Fig. 2), the linear increase of the molar amount of ZnO deposited on the electrode indicates constant Faradic efficiencies which presumably are determined by the efficiency of the chemical reaction (2). At the same time, the linear increase of dye loading indicates constant chemical composition of the hybrid films. Because the film thickness also increases linearly, the structure of the films with respect to their porosity also appears to be constant along their growth.

The average current during the electrolysis (j_{average}) were calculated from the chronoamperograms (Fig. 2). The deposition rates in film thickness (V_{film}), molar amount of ZnO and EY (ν_{ZnO} and ν_{EY}) are determined from the slopes of linear fittings in Fig. 3(a), (b) and (c), respectively. These values are listed in Table I. On assumption that the charge consumed for reduction of EY molecule does not contribute to the deposition of ZnO, Faradic efficiencies of 40.7, 81.8, 95.7 and 102% were calculated from the relationship between j_{average} and ν_{ZnO} for ZnO thin film deposited at -0.8 V, ZnO at -1.0 V, ZnO/EY hybrid at -0.8 V and ZnO/EY at -1.0 V, respectively. It can be understood that the faster rate of O₂ reduction leads to the higher Faradic efficiency. The higher the current is, the higher the level of supersaturation of ZnO should be in the neighborhood of the electrode, so that the most of the electrochemically generated OH⁻ ions are captured by Zn²⁺ ions. When the current is small, some part of OH⁻

ions dissipate by diffusing towards the bulk of the solution to reduce the Faradic efficiency for ZnO deposition. The values in the presence of EY are practically 100%. The last number actually exceeds 100% which can be due to the experimental error, but may also be caused by the reduction of EY because the 2 electron reduction of an EY molecule leads to a stable complex formation with 2 Zn^{2+} ions as written below [14],



This reaction not only contributes to the enhanced loading of EY into the film at -1.0 V but also to the increase of Zn^{2+} precipitation per consumed charge.

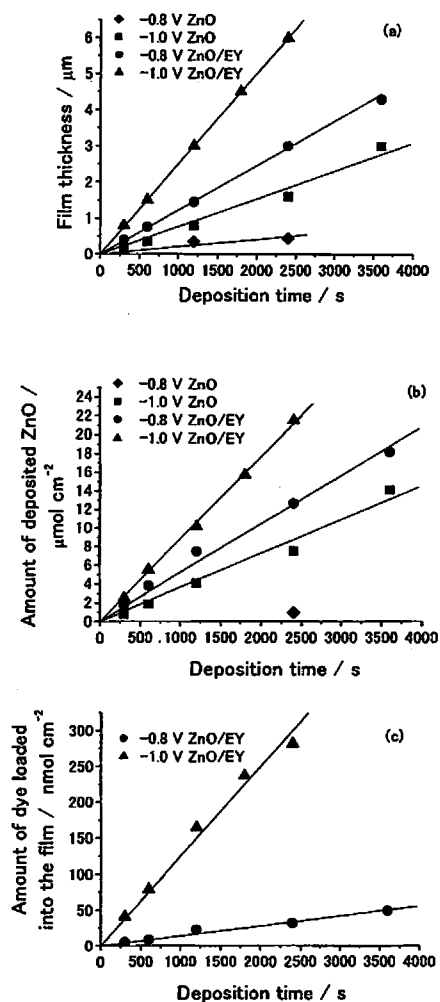


Fig.3 Thickness (a), molar amount of deposited ZnO (b), and molar amount of loaded dye (c) for electrodeposited ZnO and ZnO/EY hybrid films for different deposition time.

More information can be drawn from Fig. 3 and Table I. Comparison of the deposition rate in terms of their thickness to the total thickness of the film reveals the difference of the porosity of the films. The deposition rates of ZnO and EY can be expressed in thickness (V_{ZnO} and V_{EY}) by multiplying v_{ZnO} and v_{EY} with their formulae weight (FW_{ZnO} : 81.39 g mol^{-1} and FW_{EY} :

$691.86 \text{ g mol}^{-1}$) and dividing with their density (ρ_{ZnO} : 5.67 g cm^{-3} and ρ_{EY} : assumed as 1 g cm^{-3}).

$$V_{ZnO} = v_{ZnO} \times FW_{ZnO} / \rho_{ZnO} \quad (5)$$

$$V_{EY} = v_{EY} \times FW_{EY} / \rho_{EY} \quad (6)$$

V_{EY} of ZnO/EY hybrid film deposited at -1.0 V was found to be about 10 times larger than V_{EY} of -0.8 V because of the enhanced stability of dye attachment in its reduced form. By subtracting V_{ZnO} and V_{EY} from V_{film} , one can estimate the volume of void in the film, as also expressed in the growth rate in thickness (V_{void}) in Table I. From the values of V_{ZnO} , V_{EY} and V_{void} , one can estimate the ratio of volume occupancy of each component in the film, as expressed in ZnO : EY : Void ratios in Table I. For the as-deposited films, the ZnO/EY hybrid thin film deposited at -1.0 V appears to be the densest. EY molecules in this film occupies as much as 38% of the total volume of the film, while it is only 8% for the hybrid film at -0.8 V.

Before using the electrodeposited ZnO/EY hybrid thin films as photoelectrodes for solar cells, the loaded EY molecules have to be removed from the films by soaking them in dilute KOH solution [12]. While EY could be completely desorbed from the hybrid film deposited at -0.8 V, only 34% could be removed from that deposited at -1.0 V. It is likely that a major part of dye is loaded inside of ZnO grains, thus being inaccessible by KOH solution for the film deposited at -0.8 V, whereas dyes are deposited as totally separated from ZnO for that at -1.0 V. Removal of EY molecules from the film by the KOH treatment should create voids in the film. The ZnO : EY : Void ratios then changes as those shown in Table I after the KOH treatment. The void volume estimated for the as-deposited film should originate from the gap between the grains, while the large increment after the KOH treatment of the hybrid film deposited at -1.0 V represent that of the nanopores created by the removal of dyes.

The film structure observed by SEM is in clear accordance with the above mentioned discussion (Fig. 4). The film deposited without EY is made of hexagonal columnar particles with smooth surface typical of crystalline ZnO (Fig. 4a). These particles are supposedly monolithic and the void volume estimated for this film arises from the space in between them. The ZnO/EY hybrid film deposited at -0.8 V is composed of irregularly shaped deposits within which some sub structures are seen. Columnar growth and flat top of the deposits are apparent in the cross section image. The deposits appear to be dense. On the contrary, the hybrid film deposited at -1.0 V looks like an assembly of tiny particles of about 10 nm size from its surface view (Fig. 4c). Its cross section, however, shows that the deposits are actually made as bundles of interconnected nanowires. Round top of the deposit is also characteristic for this film. It has previously been elucidated that such bundles in fact possess single crystal structure of ZnO as a whole [9]. One can consider it is such a material that nanopores are formed in the interior of well-grown ZnO crystal of μm size. While some large voids are seen in between these porous crystals, the nano-sized pores formed within the nanowire bundles created after the removal of EY dyes should correspond to the increment of the void volume by the KOH treatment.

Table I Values relevant to the growth rate and volumetric composition of electrodeposited thin films.

	Deposition potential E V	j_{average} mA cm ⁻²	deposition rate in molar amount		faradic efficiency for ZnO %	deposition rate in thickness				volume ratio of as-deposited film ZnO : EY : Void	volume ratio after KOH treatment ZnO : EY : Void
			v_{ZnO} nmol cm ⁻² s ⁻¹	v_{EY} nmol cm ⁻² s ⁻¹		V_{film}	V_{ZnO}	V_{EY} **	V_{void}		
ZnO	-0.8	0.182	0.384 *	-	40.7	20.8	5.51	-	15.3	27 : 0 : 73	-
	-1.0	0.853	3.62	-	81.9	77.0	52.0	-	25.0	68 : 0 : 32	-
ZnO/EY	-0.8	1.05	5.20	0.0139	95.6	121	74.6	9.6	36.8	62 : 8 : 30	62 : 5 : 33
	-1.0	1.67	8.81	0.136	102	250	126	94.1	29.9	50 : 38 : 12	50 : 0 : 50

*: Calculated from the film thickness for 40 min deposition, assuming a liner growth.

** : Calculated by assuming the density of EY as 1 cm³ g⁻¹.

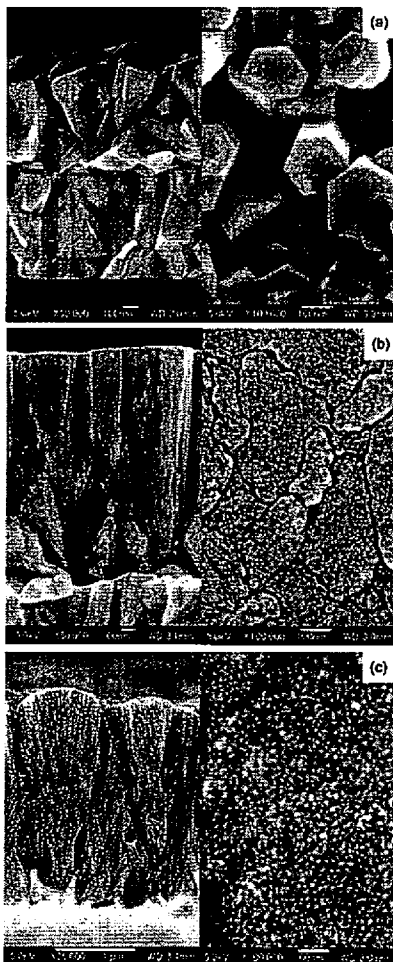


Fig. 4 SEM cross-sectional (left) and top views (right) of ZnO film deposited at -1.0 V (a) and ZnO/eosinY hybrid films deposited at (b) -0.8 V, (c) -1.0 V for 20 min from aqueous solutions of O₂ bubbled 5 mM ZnCl₂, 0.1 M KCl with 45 μM eosinY (b), (c), or without (a).

4. CONCLUSIONS

It has been shown that the electrochemical growth of ZnO/EY hybrid thin film under potentiostatic condition proceeds at a constant rate with respect to the thickness, molar amount of ZnO and EY, regardless of the deposition potential, thus the redox state of EY. These aspects make it simple to analyze the film growth, because Faradic efficiency, chemical composition and structure of the film are expected to be constant. When the analysis is completed, it should become possible to well predict the character of the product for given

conditions.

In the present examples, distinctively different features were found for the hybrid thin films deposited at -0.8 V and -1.0 V. While the addition of EY greatly enhances the rate of O₂ reduction, thus the rate of ZnO growth at both redox states, the rate of EY deposition was about 10 times larger when it is in its reduced state than in the oxidized state. Because the volume of EY molecules loaded into the ZnO/EY hybrid film deposited at -1.0 V occupies as much as 38 % of the total volume of the film, large empty space was created after its complete removal by the KOH treatment, while EY is loaded in a much smaller amount and could not be fully extracted for the film deposited at -0.8 V. Such differences of the film growth resulted in the differences of the internal structure of the films, i.e., that at -0.8 V is dense, while that at -1.0 V has a porous crystalline structure which is suitable for its application to dye-sensitized solar cell.

5. ACKNOWLEDGMENT

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