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Self-Assembly of ZnO / Tetrabromophenol Blue Mixed Thin Film by One-Step Electrodeposition and its Sensitized Photoelectrochemical Performance

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One-step electrodeposition in an aqueous mixture of zinc nitrate and tetrabromophenol blue (TB), a sulfonephthalein pH indicator dye, resulted in a formation of blue transparent thin film which is composed of zinc oxide particles modified with TB. Voltammetric analysis found reduction of TB upon its loading into the film. The morphology of the ZnO film was significantly altered by the addition of TB, suggesting its strong chemical interaction with the growing surface of ZnO. Color transition of TB by pH change was prohibited for the dye molecules incorporated into the film, due to stabilization of the blue form by the anchoring of sulfonic acid groups to the surface Zn^{2+} of ZnO. Fluorescence of TB molecules in the ZnO/TB film was quenched, indicating an efficient electron injection from the singlet excited state of TB to the conduction band of ZnO. As a consequence, the as-deposited ZnO/TB thin film electrode exhibited photo-anodic current by visible light irradiation. Photocurrent action spectrum and optical analysis of the film clearly indicated photosensitization of n-ZnO by the surface-attached TB molecules both in monomeric and H-aggregated forms. The maximum incident photon to current conversion efficiency of 5.3 % was attained by monochromatic light irradiation at 630 nm.

Key Words: electrodeposition, zinc oxide, pH indicator, dye, photosensitization

1. INTRODUCTION

Dye-modified semiconductor photoelectrode plays a decisive role in dye-sensitized solar cells. In almost all the previous studies, fabrication of such thin film electrodes has been made by stepwise processing, that is, preparation of porous semiconductor films by colloid coating and heat treatment, followed by adsorption of the dyes from their solutions [1-3]. Although the semiconductor / dye films prepared in such a manner do perform as sensitized photoelectrodes, several problems arose from the uncontrollability of the processing, such as incomplete dye adsorption, limited transport of the electrolyte and imperfect electrical contact among the colloid particles due to their inherent random agglomeration [4,5]. The need of the heat treatment also limits the choice of the conductive substrate to be of heat resistant materials. Development of an alternative method for the fabrication of the semiconductor / dye films is therefore necessary in order to actively control the dye loading, pore size distribution and the charge transport in the inorganic matrix.

We have recently reported self-assembled growth of nano-particulate porous ZnO thin films modified with sulfonated water-soluble zinc phthalocyanine (PC) by cathodic electrolysis in an aqueous mixture of $Zn(NO_3)_2$ and PC [6]. This technique was found to realize dye loading at a much higher concentration than that achieved by the conventional stepwise processing. Surface adsorption of the dye hindered crystal growth of ZnO, resulting in an automatic formation of a porous structured film. The as-deposited ZnO/PC film exhibited photoanodic current by visible light irradiation, clearly indicating photosensitization of ZnO by incorporated PC molecule [7].

In the present study, we have applied the same method to synthesize ZnO/dye films using a commercial water-soluble dye, tetrabromophenol blue (TB), which is a sulfonephthalein pH indicator. The color transition of the dye due to its structural change made us possible to learn about the binding mode of TB to the surface of ZnO. Sensitization ability of the incorporated dyes in the deposited ZnO/TB thin films has been studied by fluorescence and photoelectrochemical measurements.

2. EXPERIMENTAL

Sodium salt of TB was purchased from Aldrich and used as received. The color transition of TB from blue (neutral) to yellow (acidic) occurs at about pH 4 (Fig.1) [8]. All the other chemicals were of analytical reagent

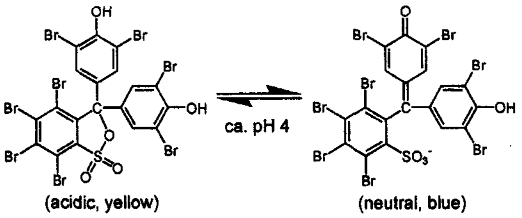

Fig.1 Color transition of tetrabromophenol blue (TB).

grade. Doubly distilled and ion-exchanged water was used throughout the experiments. An indium tin oxide (ITO) coated conductive glass (10 Ω / sq.) was used as the substrate.

Electrodeposition and cyclic voltammetry were performed in a single compartment cell equipped with three electrodes, the ITO working, a Pt foil counter and a saturated calomel reference (SCE). Thin films of ZnO were obtained by potentiostatic electrolysis at – 0.9 V vs. SCE for 60 min in a 0.1 M $Zn(NO_3)_2$ aqueous solution maintained at 70 °C. Base generation upon electroreduction of nitrate is supposed to promote the growth of ZnO, as reported by Izaki and Omi [9]. Deposition of dye-modified ZnO was achieved simply by adding TB at a concentration ca. 40 μM to the bath and carrying out electrolysis under the same conditions as above. Physical mixture of ZnO and TB was prepared for comparison by mixing dry powders of ZnO and TB.

X-ray diffraction (XRD) patterns of the deposited films were obtained by a Rigaku RAD-2R using CuKα radiation. Surface morphology of the films was observed by a Topcon ABT-150FS scanning electron microscope (SEM). Film thickness was determined by a Kosaka SE-2300 surface profilometer. The UV-VIS absorption spectra were measured in transmission or diffuse reflection on a Hitachi U-3500 or a U-4000 spectrophotometer. Fluorescence spectra were obtained by a Hitachi F-4500 fluorescence spectrophotometer.

Photoelectrochemical measurements were performed on the deposited ZnO/TB thin film electrodes in an acetonitrile/ethylene carbonate (v/v = 1/4) mixture containing 0.5 M KI. No attempts have been made to optimize the electrolyte composition. A self-made Ag/Ag^+ reference electrode (= +90 mV vs. SCE, as calibrated by measuring $E_{1/2}$ of ferrocene/ferricenium ion redox couple) was used in these measurements. A 500 W Xe lamp equipped with IR and <420 nm cut off filters was used as a light source. Photocurrent action spectrum was measured under monochromatic light illumination by using a Nikon G250 monochrometer. Light intensity was measured by an Eppley PTEI 901-414 thermopile.

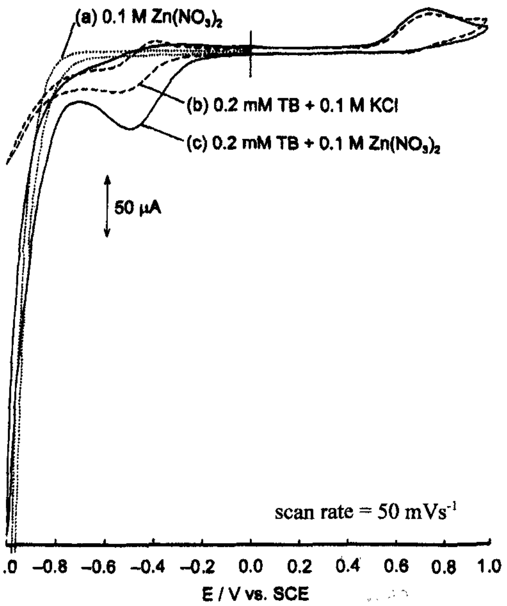

Fig.2 Cyclic voltammograms measured at an ITO glass electrode in aqueous solutions of 0.1 M $Zn(NO_3)_2$ (a), 0.2 mM TB+0.1 M KCl (b) and 0.2 mM TB+0.1 M $Zn(NO_3)_2$ (c) (pH 4.3, temperature = 70 °C, saturated with Ar).

3. RESULTS AND DISCUSSION

The electrochemical reactions in solutions were studied by cyclic voltammetry (CV) (Fig.2). In an aqueous solution of $Zn(NO_3)_2$, cathodic current sharply increases from around –0.7 V due to the irreversible reduction of NO_3^-. Thin film of crystalline ZnO is formed on the substrate along this cathodic reaction [6,7]. A reversible redox couple for the first reduction and an anodic peak for the quasi-irreversible first oxidation of TB are seen at $E_{1/2} = -460$ and $E_a = +730$ mV, respectively. When both TB and $Zn(NO_3)_2$ are present in the solution, the cathodic peak for the reduction of TB is significantly enhanced, while the corresponding anodic peak of re-oxidation disappears. It is also noticed that the cathodic current for the reduction of NO_3^- is somewhat attenuated in the presence of TB. When the potential scanning was reversed at –0.8 V, the re-oxidation of TB could be observed. Since no such enhancement of the reduction of TB was seen by the addition of KNO_3, it is likely that Zn^{2+} ion mediates electron transfer for the reduction of TB. The reduced TB is stabilized against re-oxidation upon formation of ZnO, probably because the nucleophilic reduced TB is chemically attached to the surface Zn^{2+} ion of n-ZnO.

When a potentiostatic electrolysis at –0.9 V was allowed in the TB + $Zn(NO_3)_2$ mixture for an extended period, a ZnO/TB mixed thin film was deposited on the ITO. A freshly prepared film was pale blue and it gradually became darker blue by exposing it to air. The CV measurements revealed reduction of TB upon its loading to ZnO. The observed color change is therefore attributed to the re-oxidation of TB by oxygen. The blue color of the film is a clear indication of the presence of TB in its neutral form. The incorporated TB molecules were not lost by dipping the film in water (Fig.3). The

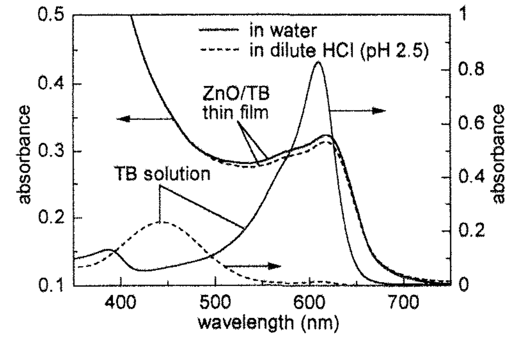

Fig.3 UV-VIS absorption spectra of ca. 13 μM aqueous solutions of TB and a ZnO/TB thin film dipped in water or dilute HCl.

film shows its absorption maximum at around 620 nm, which is red-shifted by ca. 10 nm from that of the blue solution, suggesting an electronic interaction between TB and ZnO. While the color of TB solution changes from blue to yellow by addition of HCl, the TB molecule in the ZnO/TB film is insensitive to the change of pH (Fig.3). The small decrease of the absorption peak at 620 nm may be attributed to a partial loss of TB from the film due to bond cleavage by acid. However, dipping of the film in acid up to 1 h did not lead to a further loss of TB. These findings support the irreversible binding of TB to ZnO through the sulfonic acid group.

SEM pictures of ZnO and ZnO/TB thin films are shown in Fig.4. Faceted growth of hexagonal cylindrical particles is seen for the ZnO film. High crystallinity of ZnO was confirmed by XRD (Fig.5). In contrast, the ZnO/TB film is made up with somewhat larger and flatter particles. Careful look of the picture reveals that these particles are assemblies of finer particles. Although XRD spectrum of the ZnO/TB film shows presence of ZnO as the only crystalline phase, the diffraction peaks are somewhat broadened as compared to those of the pure ZnO. The crystal size of ca. 30 nm was estimated from the full width at half maximum of the (002) diffraction peak. Such reduction of crystal size was seen also for the electrodeposited ZnO/PC thin film and was ascribed to the surface adsorption of the dye molecules to hinder the crystal growth of ZnO [6,7].

Fluorescence of TB solution, TB+ZnO mixed powder and the electrodeposited ZnO/TB thin film has been studied (Fig.6). While the solution and the powder of TB exhibit fluorescence with their maxima respectively at ca. 655 and 720 nm, that of TB in the ZnO/TB film is almost completely quenched. The quenching of fluorescence can be interpreted as due to an electron injection from the singlet excited state of TB to the conduction band of ZnO. It should be noted that

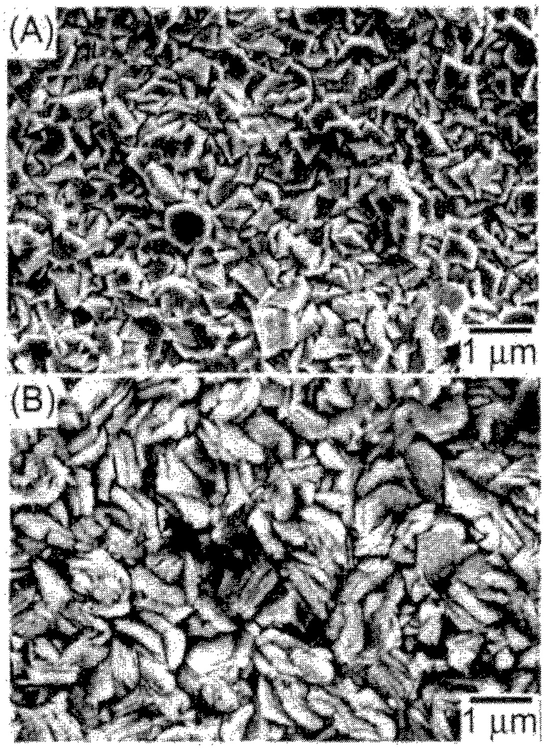

Fig.4 SEM photographs of electrodeposited thin films of pure ZnO (A) and ZnO/TB (B) (thickness = ca. 1 μm).

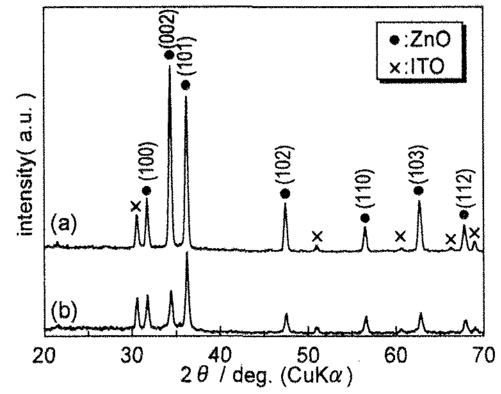

Fig.5 XRD spectra of ZnO (a) and ZnO/TB (b) thin films.

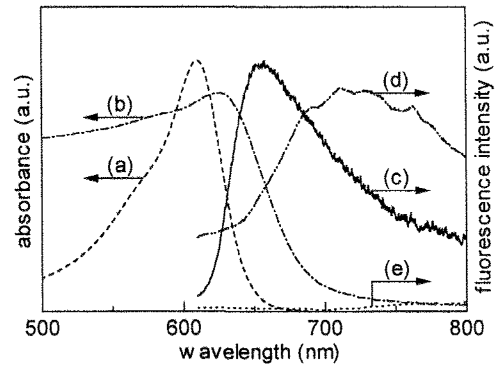

Fig.6 Absorption spectra of TB aqueous solution in transmission (a) and TB+ZnO powder in diffuse reflection (b). Emission spectra of TB solution (c), TB+ZnO powder (d) and electrodeposited ZnO/TB thin film (e). Excitation wavelengths were 600 nm for (c), 550 nm for (d) and (e).

fluorescence is not quenched when TB is simply in physical contact with ZnO. Efficient charge transfer should be achieved only when the dye molecules are chemically attached to the surface of semiconductor, as seen with the Ru complex anchored to TiO_2 [10].

Photoelectrochemical measurements were performed on the electrodeposited ZnO/TB thin film electrodes. Photoanodic current of ca. 40 $\mu A/cm^2$ was achieved at -0.1 V vs. Ag/Ag^+ upon visible light irradiation at 20 mW/cm^2 (Fig.7). Photocurrent action spectrum nicely tracks the absorption peak arising from the TB molecules in the ZnO/TB film (Fig.8a,b). The maximum incident photon to current conversion efficiency (IPCE) of 5.3 % was achieved at around 630 nm. It should be noticed that photocurrent is generated to a considerable extent in the wavelength region between 450 and 550 nm, where the light absorption of TB molecule in blue form becomes very small (Fig.8c). The solid TB powder has an absorption maximum at about 625 nm, but also possesses broad absorption in the shorter wavelength region (Fig.8d). The broadening of the absorption towards shorter wavelength indicates presence of H-aggregates, in which the chromophores of TB are aligned in a parallel arrangement. The absorption character of the ZnO/TB film in this wavelength region is in between those of the monomeric TB in solution and the solid TB, suggesting that a part of the TB molecules are stacked to form a two-dimentional H-aggregates on the surface of ZnO. Such regular arrangement of the dye molecules was also seen with the ZnO/PC film prepared by one-step electrodeposition [6,7]. The fact of significant importance is that the aggregated TB molecules can serve as sensitizers to achieve photocurrent generation in a relatively wide wavelength, in contrast to the ZnO/PC film, for which aggregated dyes exhibited much lower sensitizing ability than the monomeric one [7]. When preparation conditions are optimized, the present technique will open up a new way to synthesize highly efficient dye-modified ZnO thin films suitable for solar cell application.

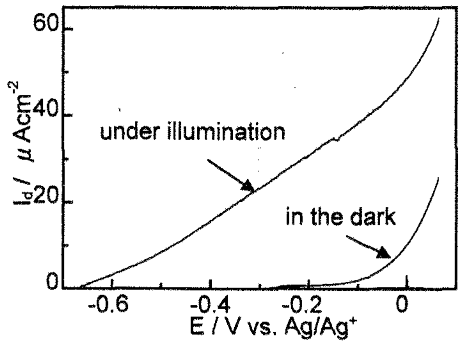

Fig.7 Potential-current characteristics of a ZnO/TB thin film electrode in acetonitrile / ethylene carbonate containing 0.5 M KI in the dark and under visible light (>420 nm) irradiation (light intensity = 20 mW/cm^2).

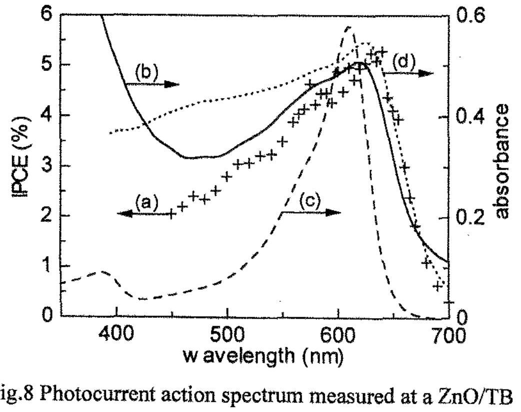

Fig.8 Photocurrent action spectrum measured at a ZnO/TB thin film electrode at –0.1 V vs. Ag/Ag^+ (a), in comparison with absorption spectra of the ZnO/TB film (b), an aqueous solution of TB (blue form) (c) and a TB + ZnO mixed powder (d).

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