Self Assembled Growth of Nano Particulate Porous ZnO Thin Film Modified by 2,9,16,23-Tetrasulfophthalocyanatozinc(II) by One-Step Electrodeposition

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(Received March 16, 1998; CL-980191)

A cathodic electrolysis in an aqueous mixture of $Zn(NO_3)_2$ and water soluble phthalocyanine, 2,9,16,23-tetrasulfophthalocyanatozinc(II) (TSPcZn), allows self organization of ZnO crystal growth and adsorption of the dye molecules. This process results in the formation of transparent and homogeneously blue thin film consisting of nano-particulate porous ZnO modified by TSPcZn.

Thin film processing of inorganic and organic compounds receives an increasing attention in recent years because the properties of the materials largely depend upon the fabrication techniques employed. It is also important to develop low cost and environmentally benign methods in order to realize wide applications of such materials. Methods employing chemical or electrochemical reactions in water bear the highest advantages in this respect. While such techniques have been successfully applied to inorganic compounds,[1-4] only limited methods have been available for the thin film processing of organic molecules.[5-13] Thin solid films of the pure material have been prepared by casting from solutions[5], vacuum evaporation[5] or molecular beam epitaxy.[6] They were also made into films together with other substances, such as those embedded in Langmuir-Blodgett films,[7] mixed or adsorbed into polymer membranes[8,9] or adsorbed on inorganic surfaces.[10-12] The use of the supports not only realizes the film formation but also often adds new properties, as recently shown in the studies of dye-sensitized solar cells, where the fast and efficient charge separation is achieved only by the dye molecules strongly bound to the inorganic semiconductor surface.[11-13]

In this study, we have developed a simple and versatile technique to deposit a thin film of inorganic semiconductors whose surface is modified by organic dye molecules. A thin film of nano-particulate porous ZnO modified by TSPcZn was obtained by a one-step electrodeposition in an aqueous mixture of $Zn(NO_3)_2$ and TSPcZn. Metallophthalocyanines (MPcs) are known to be excellent sensitizers owing to their high absorption coefficients in the visible region and high chemical stability. Saji has previously reported electrodeposition of phthalocyanine thin film in water which employs electro-oxidative disruption of micelles, although the resultant film was of random aggregates because the film growth took place in a cluster by cluster fashion.[14] The present work should provide a convenient way to obtain various kinds of inorganic / organic compound thin films with new properties.

Sodium salt of TSPcZn was synthesized according to the literature.[15] The electrodeposition of ZnO was carried out potentiostatically at -0.7 (vs. SCE) for 60 min in a 0.1 M $Zn(NO_3)_2$ aqueous solution maintained at 70 ℃.[1] An ITO (10 Ω / □) glass was used as the substrate. The deposition of ZnO/dye film was achieved simply by adding TSPcZn to the bath at ca. 35 μM. The products were characterized by XRD, UV-VIS absorption, SEM and TEM.

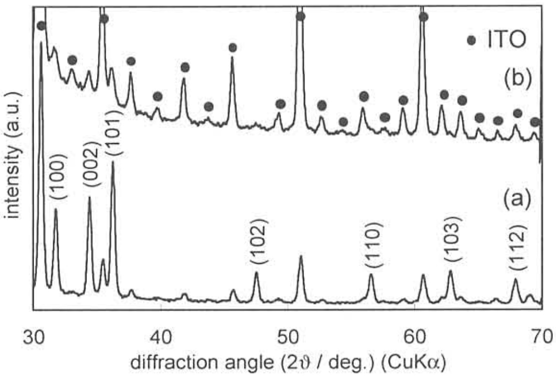

Figure 1. X-ray diffractograms of ZnO (a) and ZnO/TSPcZn (b) thin films electrodeposited at -0.7 V (vs. SCE) for 60 min in 0.1 M $Zn(NO_3)_2$ and 0.1 M $Zn(NO_3)_2$ + 35 μM TSPcZn aqueous solutions (70 ℃), respectively. The Miller indices for hexagonal ZnO are indicated in the figure.

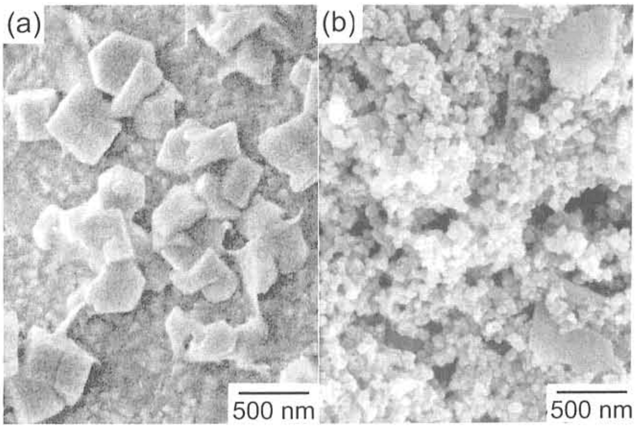

Figure 2. SEM photographs of the ZnO (a) and ZnO/TSPcZn (b) thin films same as those in Figure 1.

Base generation by electroreduction of nitrate has been frequently used in the electrodeposition of metal oxide thin films.[1,2] We have confirmed that nitrate is reduced to nitrite and partly to ammonia along the deposition of ZnO, as analyzed by HPLC. Such reduction of nitrate was not observed for a solution of KNO_3. Therefore, the overall reaction may be written as Eq.1.

$$Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^- \qquad (1)$$

The as-deposited ZnO is highly crystallized as indicated by the sharp XRD peaks assigned to wurtzite ZnO (Figure 1a). SEM observation of the deposits reveals faceted growth of hexagonal

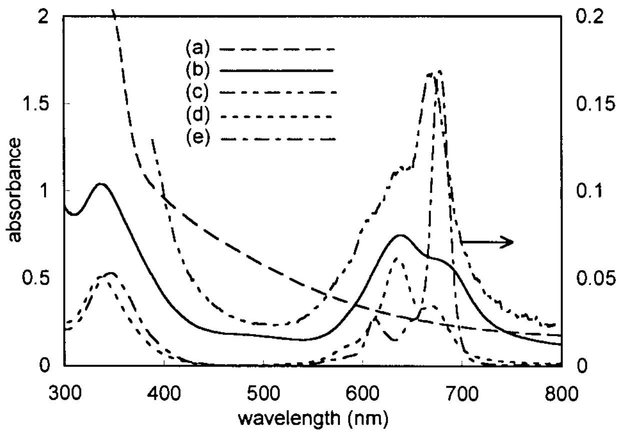

Figure 3. UV-VIS absorption spectra of ZnO (a), ZnO/TSPcZn (b) thin films same as those in Figure 1, physical mixture of TSPcZn and ZnO powders measured in diffuse reflection (c), aqueous solutions of TSPcZn corresponding to its aggregated form (d) and monomeric form (e). The monomer spectrum was measured in the presence of a detergent (cetyltrimethylammonium chloride).

cylindrical particles (Figure 2a). The film was translucent showing strong light scattering. Dye adsorption onto the electrodeposited ZnO has been attempted by dipping it into the solutions of TSPcZn. However, no change of the color of the film was observed, probably because the dye adsorption occurs only at a monolayer level and the surface area of this ZnO film is too small.

When TSPcZn was added to the bath, a blue transparent film was obtained (hereafter called ZnO/TSPcZn film). The XRD spectrum of this film indicates the presence of ZnO (Figure 1b). However, the broadening of the diffraction peaks suggests fining of the ZnO crystallites in the ZnO/TSPcZn film. The crystal size estimated was ca. 20 nm. The addition of TSPcZn to the bath was found to change the morphology of the film significantly (Figure 2). The ZnO/TSPcZn film is highly porous, consisting of fine particles with the diameter varying between 20 and 50 nm. Some thin plate-like crystals are also seen. TEM observation confirmed that both of these deposits were of ZnO. The ZnO/TSPcZn films were about twice thicker than the pure ZnO prepared under the same conditions. The remarkable change of the morphology can be reasoned as the hindrance of ZnO crystal growth by the adsorption of TSPcZn onto the growing surface of ZnO.

Intermolecular interactions in the solids as well as solutions of MPcs can be monitored by the optical absorption, especially in the Q-band regime. The absorption spectrum of the ZnO/TSPcZn film is compared with those of the electrodeposited ZnO film, TSPcZn solid mixed with ZnO powder, and aqueous solutions of TSPcZn (Figure 3). TSPcs are known to form dimers in water due to the hydrophobic intermolecular affinity.[16] The spectrum of monomeric TSPcZn in water can be seen only in the presence of cationic detergent.[15] A large blue shift of the Q-band absorption of the dimer (λ_{max} = 636 nm) as compared to the monomer (λ_{max} = 679 nm) is associated with the overlap of π-electronic clouds of the Pc system in the dimer.[16] It can be clearly seen that the spectrum of the ZnO / TSPcZn film closely resembles to that of the dimer, having its absorption maxima at 336 and 639 nms, although it seems that a certain fraction resides in the monomer form as indicated by the rise of the absorption around 680 nm. Co-existence of the aggregates and monomeric molecule was suggested also for tetracarboxyphthalocyanatozinc(II) (TCPcZn) adsorbed on TiO_2.[13] The light absorption by ZnO below ca. 400 nm should be partly responsible to the relatively high absorption in the Soret-band region. It should be also noticed that the spectrum is totally different from that of the physical mixture of TSPcZn solid with ZnO powder whose absorption in the Q-band looks dominated by the monomeric species, yet the peak is significantly broadened. It is evident that the dye molecules in the ZnO/TSPcZn film are assembled to cause a strong π-electronic interaction and different from the random aggregates. The absence of TSPcZn aggregates in the film was also evidenced by the no dissolution of the dye upon dipping the film in acetonitrile which is a good solvent of TSPcZn.

The ZnO/TSPcZn film of a known area was dissolved in a concentrated ammonia solution to determine the amount of the loaded dye. It exceeded a value of 5.8×10^{-8} mol/cm^2 for a film of 500 nm thick. It should be reasonable to expect that the TSPcZn molecules are adsorbed with their Pc ring perpendicular to the ZnO surface to maintain the stacking by the π-electronic system among the adsorbed molecules. An area of 0.35 nm^2 was estimated to be occupied by a single molecule of tetrasubstituted MPcs adsorbed in such an orientation.[10] From these values can be calculated the actual surface area for a unit geometrical area (roughness factor = R.F.) of the film. It resulted in a value of ca. 120 which closely matches the theoretical limit (R.F. = 110) predicted for a film made of densely packed spherical particles with a diameter of 20 nm. An R.F. of ca. 800 was reached for the fairly thick (> 10 μm) TiO_2 film processed by colloid coating, which has been used in the dye-sensitized solar cell[11]. The present method realizes a loading of the dye molecule to the semiconductor film at much higher concentration than that reached by the colloid processed film. In other words, a much thinner film can attain the same light harvesting efficiency when prepared by the present technique. The porous structure of the film is also favorable upon considering the application of the dye-modified film in photoelectrochemical cells because free transport of electrolyte through the film is an important prerequisite for a stable cell.[17] It should be emphasized that such dye loading at high concentration, formation of nano size crystallites and the porous structure were all realized in a self assembled manner. Studies on the photoelectrochemical property of the electrodeposited ZnO / TSPcZn films are in progress.

The present work is 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).

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