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Deposition of ZnO Particles by Photocatalytic Reaction

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Zinc oxide (ZnO) particles were deposited on a very thin titanium dioxide film by a photocatalytic reaction. The particles were formed in an aqueous solution of 0.10 mol dm^{-3} zinc nitrate at 343 K. The particles consisted of crystals with 0.20–1.0 µm-sized hexagonal columns. A photocurrent was observed in the electrodes containing such ZnO crystals during light irradiation.

Zinc oxide (ZnO) is an interesting material, and it has been used in various industries, for example, in a white pigment, cosmetics, or electrochemical devices. In recent years, ZnO was investigated as a varistor resistor and transparent electrode because it has semiconductor properties.[1,2] ZnO films are prepared by radio frequency magnetron sputtering and chemical vapor deposition. Among them, electrodeposition was invented by Izaki[3] and Lincot[4] in the 1990s and has been investigated as a low-temperature process. In the electrodeposition process, ZnO films are formed in an aqueous solution of zinc nitrate or zinc chloride.

We examined the preparation of ZnO films using a photochemical reaction instead of electrodeposition. Photochemical processes can be used to synthesize various materials because it does not require electrically conductive substrates. Izaki prepared ZnO films by a chemical reaction or a light-assisted chemical reaction of a solution containing zinc nitrate and dimethylamine–borane.[5,6] However, these methods require very strong reductants of the boranes and cause a small amount of boron to remain in the films. We tried to prepare ZnO films utilizing the photocatalytic function of titanium dioxide (TiO_2). In this study, we prepared ZnO particles on very thin TiO_2 films and observed a photocurrent in the electrodes containing such ZnO particles.

An aqueous solution of 0.10 mol dm^{-3} hydrated zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) was prepared with distilled water and sodium hydroxide in which the pH value was ca. 6. The glass substrates were coated with a very thin TiO_2 film by the sol–gel method. The TiO_2 films were prepared by dip-coating using a solution containing titanium tetraisopropoxide, ethanol, nitric acid, and distilled water and then heating at 773 K for 30 min. The film thickness was ca. 100 nm.

The substrates with the TiO_2 film were rinsed in 2-propanol and distilled water along with ultrasonication for 5 min. Furthermore, they were rinsed with 1.0% HCl and then immersed in a $SnCl_2$ solution as the sensitizer and $PdCl_2$ solution as the activator. Here Sn^{2+} was adsorbed on the substrate surface and then substituted with Pd because Sn^{2+} reduced Pd^{2+}. Consequently, Pd particles were formed on the surface as the nuclei for the ZnO crystal growth and as the promoter for the TiO_2 photocatalyst. The substrates were immersed in the zinc nitrate solution maintained at 343 K in the dark or during light irradiation using a high-pressure mercury lamp (SEN LIGHTS HB-100-A, 100 W) without stirring. The distance between the substrate and lamp was ca. 3 cm. After the irradiation for 2 or 4 h, the samples were washed with distilled water and then dried at room temperature.

Micromorphology of samples was examined using a scanning electron microscope (SEM, Hitachi S3000N), and elemental analysis was conducted by energy-dispersive X-ray spectroscopy (EDX, EDAX Falcon). The X-ray diffraction patterns were obtained using an X-ray diffractometer (XRD, Rigaku RINT2100). For examination of the photocatalytic properties, the substrates with a ITO film were coated with TiO_2 on which the ZnO particles were deposited by the method described above. The electrolyte solution consisting of acetonitrile/ethylenecarbonate (v/v = 1/4) containing 0.50 mol dm^{-3} KI and 0.030 mol dm^{-3} I_2 was allowed to soak into the space between the sample and the counter Pt electrode. The samples were irradiated with monochromatic light obtained from a fluorescence spectrophotometer (Shimadzu, F2000) with a Xe short arc lamp. During the light irradiation, the short circuit current was measured in the range from 350 to 400 nm by a digital multimeter (Agilent 34405A). The *I*–*V* curves of the electrodes were measured by a potentiostat (Hokuto Denko HA-151B) during the light irradiation using a Xe short arc lamp (350–1050 nm, 250 mW cm^{-2}). The samples without ZnO were used for the references.

The solutions became whitely turbid after the irradiation, indicating that the ZnO formation proceeded. Figure 1 shows the surface SEM images of the samples prepared by the 2-h and 4-h irradiations. The particles consisted of crystals with 0.20–1.0 µm-sized hexagonal columns. A greater number of crystals were found on the TiO_2 film of the sample prepared by the 4-h

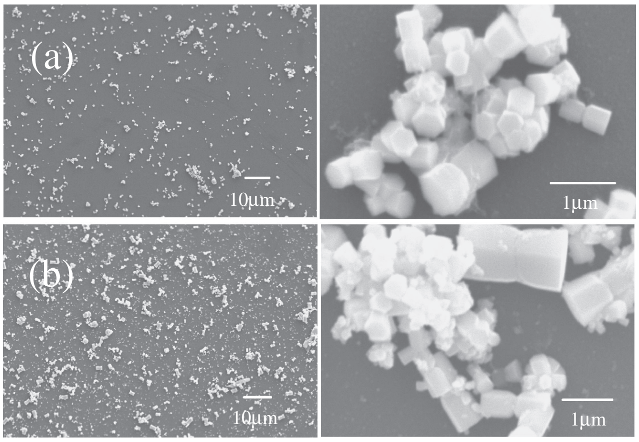

Figure 1. SEM images of the surface of the samples prepared by the (a) 2-h and (b) 4-h irradiations.

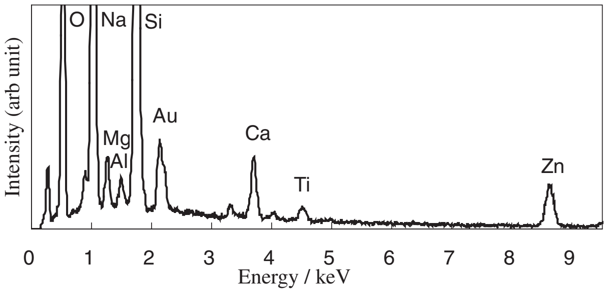

Figure 2. Energy-dispersive X-ray spectra of the surface of the sample prepared by the 4-h irradiation. The substrate contains Na, Mg, Al, Si, Au, and Ca.

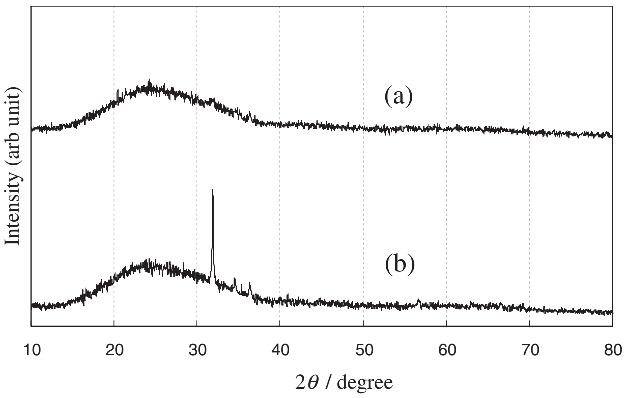

Figure 3. XRD patterns of the samples prepared by the (a) 2-h and (b) 4-h irradiations.

irradiation. No crystals were found on the glass substrate without the TiO_2 film. Figure 2 shows the energy-dispersive X-ray spectra of the surface of the sample prepared by the 4-h irradiation. Zinc and titanium were detected on the surface.

Figure 3 shows the XRD patterns of the samples prepared by the 2-h and 4-h irradiations. The sample prepared by the 2-h irradiation exhibited only a halo peak due to the substrate. The anatase TiO_2 cannot be detected due to the thinness of the layer. Sharp peaks were clearly observed at 31.8, 34.5, and 36.3° from the sample prepared by the 4-h irradiation, which were assigned to the $(10\bar{1}0)$, (0002), and $(10\bar{1}1)$ planes of wurtzite ZnO. The relative intensity of the $(10\bar{1}0)$ peak was the strongest of the three, reflecting that the plane perpendicular to the *c* axis was selectively dissolved by further light irradiation. This is presumed because the (0001) plane exhibits a high photocatalytic activity[7] and because the reactive surface of ZnO can be easily dissolved by light irradiation. These results indicate that the light irradiation caused the photocatalytic formation of ZnO on the TiO_2 film.

The formation process of the ZnO can be expressed as follows:[8]

$$TiO_2 + h\nu \rightarrow TiO_2 + e^- + h^+ \quad (1)$$

$$NO_3{}^- + H_2O + 2e^- \rightarrow NO_2{}^- + 2OH^- \quad (2)$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (4)$$

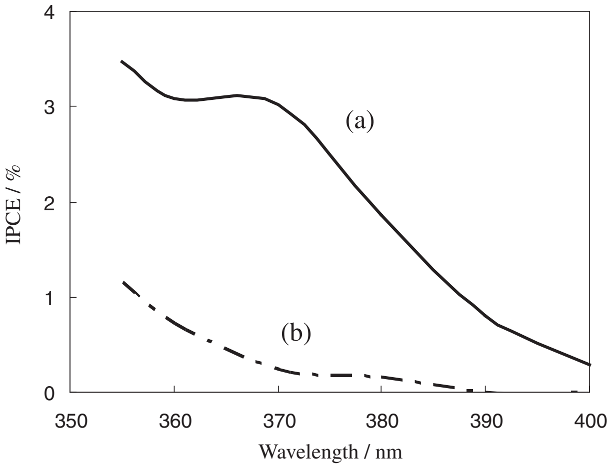

Figure 4. Photocurrect action spectra of the electrodes (a) with and (b) without the ZnO particles on the TiO_2-coated ITO substrates.

Upon irradiation of light at a wavelength shorter than ca. 390 nm, TiO_2 is excited and the charge separation of electrons and holes follows because the band gap of anatase TiO_2 is ca. 3.2 eV (eq 1). On the surface on the film, the nitrate ion in the solution is reduced to the nitrite ion, and water is transformed into hydroxide ions (eq 2). The pH value increases on the TiO_2 surface, which causes the $Zn(OH)_2$ formation on the film (eq 3). The $Zn(OH)_2$ was then dehydrated and transformed into ZnO (eq 4). Also, ZnO can be simultaneously dissolved in the water by light irradiation. A longer irradiation time induced the formation of a higher number of ZnO crystals. This suggests that the growth of ZnO is faster than the dissolution under this condition. ZnO was preferentially generated compared to $Zn(OH)_2$ at 343 K because ZnO is more stable than $Zn(OH)_2$ at such a high temperature.[4,9] It was reported that $Zn(OH)_2$ was dehydrated in an aqueous solution at a lower temperature.[10]

Figure 4 shows the photocurrent action spectra of the electrodes with and without the ZnO particles on the TiO_2-coated ITO substrates. The morphology of the electrode surface was slightly changed, and the ZnO particles were stable during the photoelectrochemical measurements. The short circuit current density of the electrode with the ZnO particle was much higher than those of the electrode with only the TiO_2 film. ZnO absorbs light at a wavelength shorter than ca. 380 nm because the band gap of ZnO is ca. 3.3 eV, which is close to that of anatase TiO_2. The incident photon-to-current efficiency (IPCE) values of the former and latter were 3.0 and 0.20% at 370 nm, respectively. The TiO_2 film exhibited a low photoelectric conversion efficiency due to its thinness. The ZnO crystal obviously functioned as a semiconductor and transferred the conduction band electrons to the ITO layer via the conduction band of the TiO_2 film. *I–V* curves of the electrodes are shown in Figure 5. The short circuit current density values for the electrodes with and without ZnO were 90 and $20\,\mu A\,cm^{-2}$, respectively. The energy conversion efficiencies for them were estimated to be 0.0050 and 0.0012%, respectively. Even though this value is very low for use in a solar cell, a further improvement is expected after an increase in the ZnO amount and dye sensitization.

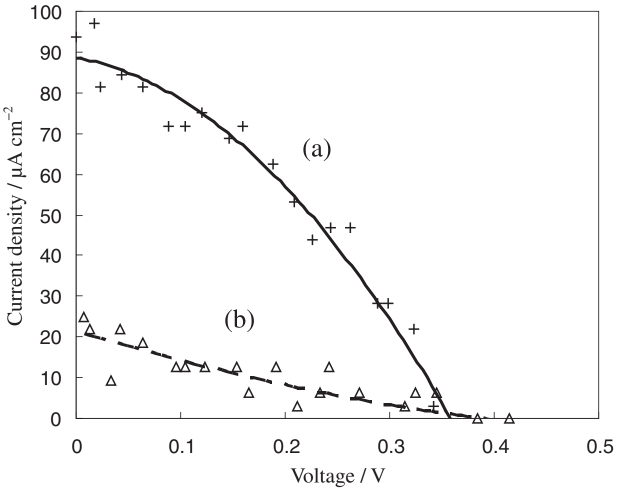

Figure 5. *I*–*V* curves of the electrodes (a) with and (b) without the ZnO particles on the TiO_2-coated ITO substrates observed during light irradiation.

In summary, we prepared ZnO particles on glass substrates coated with a very thin TiO_2 film in an aqueous solution of zinc nitrate at 343 K during light irradiation. The particles consisted of ZnO crystals with 0.20–1.0 μm-sized hexagonal columns. The light irradiation caused the photocatalytic formation of ZnO on the TiO_2 film. A photocurrent was observed in such ZnO electrodes, indicating that the ZnO crystal functioned as a semiconductor.

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