One-step Preparation and Photosensitivity of Size-quantized Cadmium Chalcogenide Nanoparticles Deposited on Porous Zinc Oxide Film Electrodes

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Size-quantized cadmium chalcogenide nanoparticles were effectively deposited on a porous zinc oxide particulate film electrode by a one-step hydrothermal method in which an increase in the concentration of 3-mercaptopropionic acid reduced the size of deposited nanoparticles. The photoelectrochemical properties of the resulting electrodes varied depending on the kind of metal chalcogenide nanoparticles deposited and their size.

Much interest has been shown in sensitization of a porous metal oxide semiconductor having a wide band gap with organic dyes[1,2] or narrow-band-gap semiconductor materials[3,4] for applications to visible-light-driven photocatalysts and solar cells.[1,2,5–9] Size-quantized semiconductor nanoparticles are promising sensitizers because their light-absorption properties and electronic energy structure can be adjusted depending on particle size.[10,11] Several methods for the deposition of semiconductor nanoparticles on porous metal oxide electrodes have been reported. For example, particles such as CdS and PbS particles have been deposited by successive ionic layer adsorption and reaction (SILAR) technique, and it has been shown that their size can be increased by increasing the number of deposition cycles.[3,12] Colloidal nanoparticles having well-defined diameters, such as CdSe and InP particles, have also been used for coating on a metal oxide particulate film surface.[13,14] These methods involve relatively complicated procedures consisting of two or more steps for particle preparation and deposition. Furthermore, it seems difficult to obtain a photofunctional electrode having a desired light-absorption property because nanoparticles have a strong tendency to coalesce with each other into larger particles, resulting in disappearance of the size quantization effect.

In this paper, we report a novel one-step strategy for the deposition of size-quantized semiconductor nanoparticles on porous zinc oxide (ZnO) particulate film electrodes. In this method, the size of deposited nanoparticles can be controlled by adjusting the amount of a surface modifier added. The photosensitivity of the prepared electrodes can be tuned in a wide visible light region.

Porous ZnO nanocrystallite films (thickness: ca. 7 μm) were prepared by spreading a viscous paste of nanocrystallites on a conducting glass support. The conducting glass with a fluorine-doped SnO_2 layer (FTO) has a sheet resistance of 10 Ω/□. The ZnO nanocrystallite paste was obtained by mixing a commercially available ZnO powder (NanoTeK, average diameter of 31 nm) (4.0 g) with acetylacetone (0.20 cm^3), Triton X-100 (0.20 cm^3) and Milli-Q water (8.8 cm^3). The ZnO paste was spread on an FTO and dried in air, followed by calcination at 723 K for 30 min. The thus-obtained ZnO film was immersed in 50 cm^3 of an aqueous solution (pH 5.0) containing 3-mercaptopropionic acid (MPA),[15] 1.0 mmol dm^{-3} cadmium chloride and 1.0 mmol dm^{-3} thiourea or selenourea in a Teflon-lined autoclave of 100 cm^3 in capacity, the concentration ratio of [MPA]/[Cd^{2+}] being varied from 0 to 1.0. The solution was heat-treated for 2 h in a hydrothermal condition (453 K), resulting in the deposition of cadmium sulfide (CdS) or cadmium selenide (CdSe) nanoparticles on the porous ZnO film electrode. After complete dissolution of the film in 1.0 mol dm^{-3} aqueous nitric acid solution, the content of Cd atoms in the CdS/ZnO film was determined by ICP analyses of the solution, when necessary. Photoelectrochemical measurements were performed in an aqueous solution (pH 13.5) containing Na_2S (0.35 mol dm^{-3}) and K_2SO_3 (0.25 mol dm^{-3}) with an Ag/AgCl (saturated KCl) reference electrode and a Pt wire counter electrode under filtered light from a xenon arc lamp (USHIO X300, 150 mW cm^{-2}, $\lambda > 350$ nm).

Photographs of the prepared electrodes are shown in Figure 1a. Depending both on the kind of nanoparticles deposited and on the ratio of [MPA]/[Cd^{2+}] used, the color of the electrode varied from red to light yellow. Figure 1b shows diffuse reflectance spectra of electrodes prepared with various ratios of [MPA]/[Cd^{2+}]. The CdS/ZnO film prepared without the addition of MPA ([MPA]/[Cd^{2+}] = 0) had an absorption

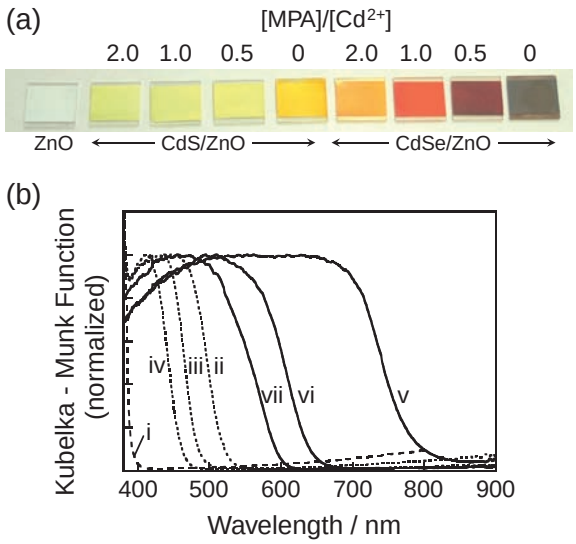

Figure 1. (a) Photographs of nanoparticle-deposited ZnO particulate film electrodes. (b) Diffuse reflectance spectra of ZnO (i), CdS/ZnO (ii–iv), and CdSe/ZnO (v–vii) electrodes. The ratios of [MPA]/[Cd^{2+}] used in the preparation were 0 (ii, v), 0.5 (iii, vi), and 1.0 (iv, vii).

onset around 550 nm, which agreed with that expected for bulk CdS. XRD analyses revealed that CdS particles deposited in the absence of MPA had a hexagonal crystal structure, and their size was estimated to ca. 10 nm by using Scherrer's equation. The spectra of CdS/ZnO were blue-shifted with an increase in [MPA]/[Cd^{2+}]. The particle sizes of CdS were estimated to 4.3 and 3.5 nm with cases of [MPA]/[Cd^{2+}] = 0.5 and 1.0, respectively, by fitting the energy gap (E_g) obtained from the wavelength of the absorption onset to the reported relation between E_g and particle diameter.[16] CdSe/ZnO films showed similar behavior: the absorption onset was blue-shifted with an increase in [MPA]/[Cd^{2+}]. The particle sizes of CdSe prepared with [MPA]/[Cd^{2+}] = 0.5 and 1.0 could be estimated from its energy gap in a similar way to be 7.5 and 5.9 nm, respectively.[17] On the other hand, the amount of Cd contained in the prepared films was almost constant at ca. 3 μmol cm^{-2} regardless of the kind of nanoparticles or the ratio of [MPA]/[Cd^{2+}] used in the preparation. These results suggested that strong adsorption of MPA on nanoparticles of CdS and CdSe could retard their crystal growth during the hydrothermal treatment, the degree being enhanced with an increase in [MPA]/[Cd^{2+}], but the amount of nanoparticle deposition on ZnO films was not affected by addition of the surface modification agent.

In the photoelectrochemical measurements, anodic photocurrents were observed at potentials more positive than ca. −0.9 V vs Ag/AgCl in the cases of both CdS/ZnO and CdSe/ZnO electrodes, regardless of the [MPA]/[Cd^{2+}] ratio, and their magnitude increased with anodic polarization of the electrode from the onset potential, indicating that the obtained electrodes behaved as n-type semiconductor electrodes. Since nanoparticles of CdS and CdSe were deposited on ZnO particulate films, these results indicated that the photogenerated electrons in the deposited nanoparticles were injected into the conduction band of ZnO porous electrodes, and then the onset potential of the anodic photocurrent was determined by the flat band potential of ZnO used as a substrate for nanoparticle loading. Figure 2 shows action spectra of anodic photocurrents of the prepared electrodes under potential application at 0 V vs Ag/AgCl. With an increase in [MPA]/[Cd^{2+}], that is, with a decrease in the size of nanoparticles deposited, action spectra of CdS/ZnO or CdSe/ZnO were blue-shifted. The threshold wavelength of each anodic photocurrent was slightly larger than that of diffuse reflectance spectra of the corresponding electrode, suggesting that nanoparticles deposited on ZnO electrodes coalesced with each other to form slightly larger particles in the conditions used for photoelectrochemical measurements. It should be noted that the prepared electrode showed a high conversion efficiency in the wavelength region of the strong photoabsorption assigned to nanoparticles deposited, where the incident photon-to-current efficiency (IPCE) reached about 80%, regardless of the ratio of [MPA]/[Cd^{2+}], except for the case of CdSe/ZnO prepared with [MPA]/[Cd^{2+}] = 0. These results suggested that the photosensitivity of nanoparticle-deposited ZnO porous electrodes could be tuned in a wide visible light region without losing light conversion efficiency, by selecting the kind of nanoparticles and their size.

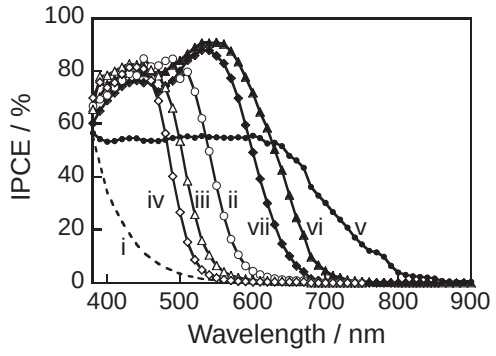

Figure 2. Photocurrent action spectra of ZnO (i), CdS/ZnO (ii–iv), and CdSe/ZnO (v–vii) electrodes. The ratios of [MPA]/[Cd^{2+}] used in the preparation were 0 (ii, v), 0.5 (iii, vi), and 1.0 (iv, vii).

In summary, we have demonstrated a one-step preparation of size-quantized cadmium chalcogenide nanoparticles onto a ZnO porous film electrode. The prepared electrode had photosensitivity depending on both the kind of nanoparticles and their size, and it worked as an n-type semiconductor electrode with high IPCE in the visible light region. These properties will be advantageous for the construction of efficient photovoltaic cells. Study along this line is currently in progress.

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