Immobilization of ZnS–AgInS$_2$ Solid Solution Nanoparticles on ZnO Rod Array Electrodes and Their Photoresponse with Visible Light Irradiation

Tetsuya Sasamura,[1] Ken-ichi Okazaki,[1] Ryuta Tsunoda,[1] Akihiko Kudo,[2] Susumu Kuwabata,[3,4] and Tsukasa Torimoto*[1,4]

[1]Department of Crystalline Materials Science, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603
[2]Department of Applied Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601
[3]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871
[4]Japan Science and Technology Agency, CREST, Kawaguchi, Saitama 332-0012

ZnS–AgInS$_2$ solid solution (ZAIS) nanoparticles having elements of low toxicity were immobilized on thin ZnO rod array films, and the resulting film worked as an n-type semiconductor electrode for which the photoresponse varied depending on the composition of particles immobilized.

The photosensitization of a wide band-gap semiconductor with organic dye[1,2] or narrow band-gap materials[3,4] has been an interesting research subject, because these can be utilized as solar cells[1,2] or photocatalysts.[5,6] In particular, semiconductor nanoparticles with narrow band-gap are promising material as visible light absorbers because their light absorbing properties and electronic energy structure can be controlled by their size.[7,8] So far, cadmium chalcogenide nanoparticles such as CdS[4,9–11] or CdSe[4,12] have been intensively investigated because they are direct band-gap semiconductors with a high absorption coefficient. However, these particles contain elements of high toxicity, such as Cd, Se, and Te, limiting the range of their use. On the other hand, chalcopyrite semiconductor nanoparticles of I–III–VI$_2$ groups are also attractive materials because they are direct band-gap semiconductors containing no highly toxic elements and their band gap energy is located at the red edge of the solar spectrum.[13] Various types of photovoltaic devices, such as thin film solar cells and nanoparticle-sensitized solar cells, have been developed by using colloidally synthesized nanoparticles of Cu-based I–III–VI$_2$ semiconductors of CuInS$_2$,[14] Cu(In$_x$Ga$_{1-x}$)Se$_2$,[14–16] and ZnS–CuInS$_2$[17] solid solutions. However, there has been little investigation of the photoelectrochemical properties of Ag-based particles of AgInS$_2$ and AgInSe$_2$ despite the fact that they are also promising materials for effective visible light absorbers.

Recently, we have successfully prepared nanoparticles of ZnS–AgInS$_2$ solid solution (ZAIS) that contain no highly toxic elements and have a tunable energy gap depending on the chemical composition of particles.[18] In this paper we report for the first time the immobilization of ZAIS nanoparticles on thin ZnO rod array film electrodes. The photochemical properties of the resulting electrode can be controlled by selecting the kind of ZAIS nanoparticles. ZnO nanorods were chosen as a support for nanoparticle loading because ZnO rods of a one-dimensional structure have less grain boundaries acting as electron trap sites than do porous films prepared by sintering spherical particles.[19]

ZnO rod arrays were deposited on fluorine-doped SnO$_2$ (FTO) in an aqueous solution containing hexamethylenetetramine and zinc nitrate with a slight modification of previously reported procedures.[20] A 0.10 mol dm^{-3} zinc acetate methanolic solution was spin-coated onto F-doped SnO$_2$ (FTO) glass

(2 × 4 cm^2; sheet resistance, 10 Ω/square) at 5000 rpm. After repetition of spin coating eight times, the substrate was heat-treated in air at 350 °C for 30 min. The thus-obtained substrate was immersed in an aqueous solution containing 25 mmol dm^{-3} zinc nitrate and 25 mmol dm^{-3} hexamethylenetetramine at 90 °C for 6 h to deposit ZnO rods. By repeating the deposition procedure of ZnO rods three times, ZnO rods were densely deposited on the FTO electrode, followed by calcination at 450 °C for 30 min to remove hexamethylenetetramine attached to the ZnO surface.

ZAIS nanoparticles were prepared by thermal decomposition of (AgIn)$_x$Zn$_{2(1-x)}$(S$_2$CNEt$_2$)$_4$ complex ($x = 1.0$ and 0.8) powder in amine solution at 180 °C using the same procedure as that reported in our previous paper[18] except for the use of octylamine in place of oleylamine. After removing large particles from the suspension by centrifugation, thin ZnO rod film electrodes (2 × 2 cm^2) were immersed in the thus-obtained ZAIS particle octylamine solution for 24 h. The resulting ZAIS-immobilized ZnO rod electrodes were washed with methanol several times and then heat-treated at 180 °C under vacuum. The resulting electrode was denoted in this study as ZAIS(x)/ZnO-rod, where x represents the chemical composition of the (AgIn)$_x$Zn$_{2(1-x)}$(S$_2$CNEt$_2$)$_4$ precursor complex, and the content of ZnS decreased with an increase in x as already reported.[18] Photoelectrochemical measurements of ZAIS(x)/ZnO-rod electrodes were performed in an aqueous solution (pH 13.5) containing Na$_2$S (0.35 mol dm^{-3}) and K$_2$SO$_3$ (0.25 mol dm^{-3}) as hole scavengers, using a 300-W Xe lamp (USHIO X300, $\lambda > 350$ nm). Electrodes of Pt wire and Ag/AgCl (sat. KCl) were used as counter and reference electrodes, respectively.

Figure 1a shows a typical cross-sectional SEM image of the ZAIS(1.0)/ZnO-rod electrode. The FTO surface was densely covered with ZnO rods with length of 3.7 µm and width of 180 nm, the long axis of each rod being nearly perpendicular to the surface of the FTO electrode. TEM measurements of the individual ZnO rods scratched off from the FTO surface (Figure 1b) revealed that ZAIS nanoparticles sparsely covered the surface of a ZnO nanorod. Since the surface of ZAIS was modified by the octylamine that had no functional groups available for the cross-linking between ZAIS particles and ZnO rods, the immobilization of ZAIS would be mainly attributed to the physical adsorption on the ZnO surface. The average size of ZAIS nanoparticles immobilized was determined to be 6.5 and 6.3 nm for $x = 1.0$ and 0.8, respectively. Since as-prepared ZAIS nanoparticles had averages size of 4.8 nm for $x = 1.0$ and 4.1 nm for $x = 0.8$, the heat treatment at 180 °C under vacuum slightly enlarged the size of ZAIS particles, probably due to the coalescence between nanoparticles on ZnO rod surface.
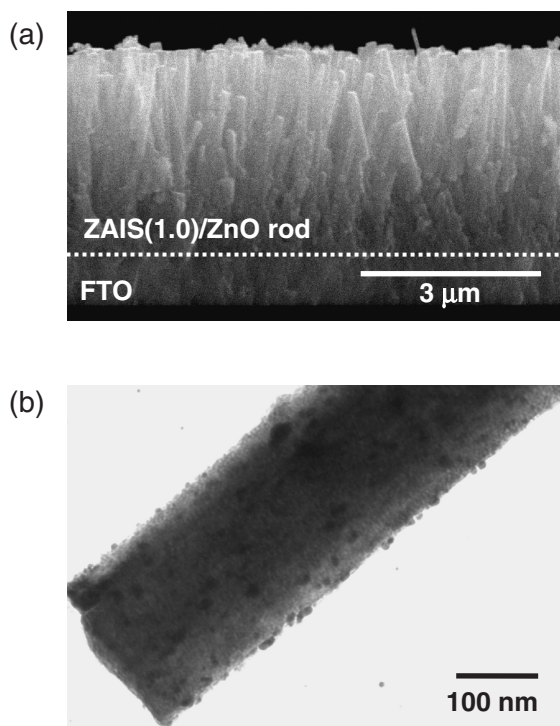
Figure 1. (a) A typical cross-sectional SEM image of ZAIS(1.0)/ZnO-rod electrode. (b) TEM image of a ZAIS(1.0) nanoparticle–immobilized ZnO rod scratched from FTO surface.
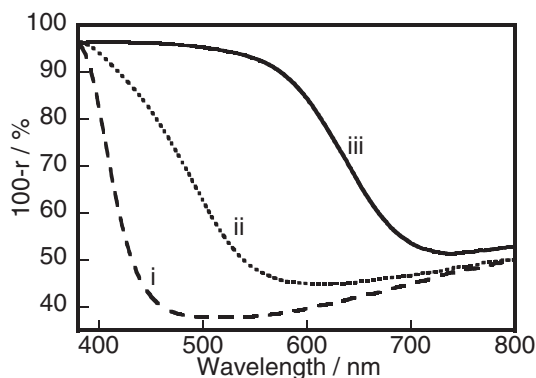

Figure 2. Diffuse reflectance spectra of ZnO-rod (i), ZAIS(0.8)/ZnO-rod (ii), and ZAIS(1.0)/ZnO-rod electrodes (iii).

The color of ZAIS(x)/ZnO-rod electrodes changed from yellow to dark red depending on the composition of ZAIS nanoparticles used. Figure 2 shows diffuse reflectance spectra of a ZnO nanorod array electrode not modified and modified with ZAIS particles. The immobilization of ZAIS particles on ZnO rods gave rise to a broad absorption band in the visible light region. Each absorption onset of the ZAIS(x)/ZnO rod agreed well with that of the corresponding ZAIS nanoparticles dissolved in octylamine, where the onset wavelength was blue-shifted with a decrease in x values in the precursors. Since the particle size of ZAIS particles immobilized on ZnO rods was almost the same regardless of x value, as mentioned above, it
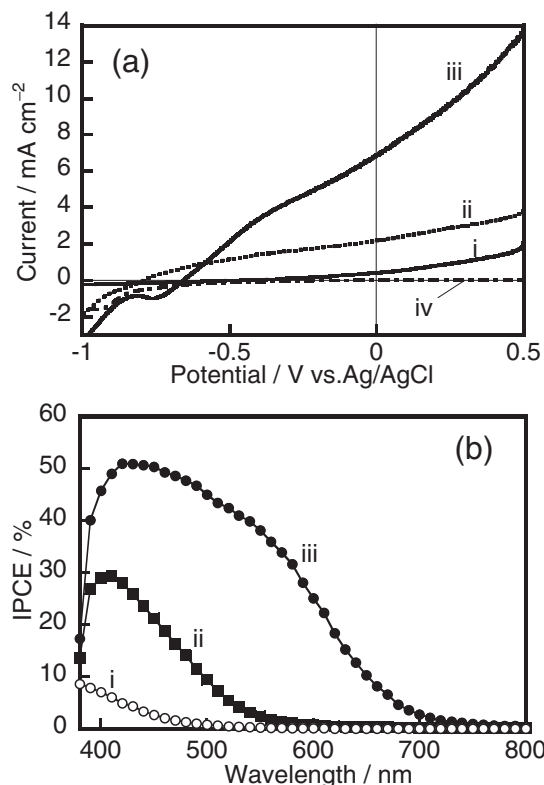

Figure 3. Current–potential curves (a), and action spectra of photocurrent measured at 0.5 V vs. Ag/AgCl (b) of ZnO-rod (i), ZAIS(0.8)/ZnO-rod (ii), and ZAIS(1.0)/ZnO-rod electrodes (iii, iv). The measurement was performed in an aqueous solution (pH 13.5) containing Na_2S (0.35 mol dm^{-3}) and K_2SO_3 (0.25 mol dm^{-3}) under irradiation (i, ii, iii) or in dark (iv).

could be assumed that the quantum size effect might hardly affect the difference in the absorption spectra between ZAIS particles prepared with $x = 0.8$ and 1.0. Therefore, the blue shift of the spectra in Figure 2 indicated that the energy gap of ZAIS particles was enlarged with an increase in the fraction of ZnS in the solid solution, as reported in our previous paper.[18]

It should be noted that the onset wavelength of ZnO nanorod electrode seems to be red-shifted from that of bulk ZnO (ca. 380 nm). This suggested that ZnO nanorods chemically grown at a low temperature (90 °C) had a large number of structural defects and thermal disorders that produced electronic states in the band gap, resulting in the enlargement of absorption band below the original optical gap (Urbach's tail[21–23]).

Figure 3a shows current–potential curves of ZAIS(x)/ZnO-rod electrodes. Almost no current flowed without irradiation in any electrodes at potentials more positive than -0.7 V vs. Ag/AgCl. Anodic photocurrents were observed in each case by irradiating light with wavelength longer than 350 nm, indicating that ZAIS(x)/ZnO-rod electrodes exhibited behavior similar to that of n-type semiconductor photoelectrodes in Na_2S/K_2SO_3 solution. The photocurrent intensity at potentials more positive than -0.6 V vs. Ag/AgCl was enhanced by loading of ZAIS nanoparticles prepared with a larger x value. The action spectra of the photocurrent were measured at 0.5 V vs. Ag/AgCl

(Figure 3b). The shape of the spectrum was in good agreement with that of the diffuse reflectance spectrum of each electrode. These results indicated that ZAIS particles immobilized on ZnO nanorods worked as a visible light photosensitizer and that photogenerated electrons in ZAIS nanoparticles were injected into the conduction band of ZnO rods. The photocurrent onset potential of ZAIS(0.8)/ZnO-rod in Figure 3a was ca. −0.8 V which was slightly more negative than that of ZAIS(1.0)/ZnO rod, ca. −0.7 V. It has been reported in our previous paper[18] that with increase in x value, the content of ZnS in ZAIS particles became large. The conduction band edge potential of bulk ZAIS was negatively shifted with an increase in the content of ZnS.[24] Therefore, the observed shift of onset potential indicated that a small fraction of electrons photogenerated in ZAIS particles was directly injected into FTO not through ZnO. It should be noted that IPCE values larger than 40% were obtained for ZAIS(1.0)/ ZnO-rod electrodes by monochromatic light irradiation in the wavelength range from 400 to 550 nm. These values were roughly comparable to those reported for metal oxide electrodes sensitized with conventional nanoparticles of CdS and CdSe, ca. 50–80%,[4] suggesting that Ag-based I–III–VI$_2$ semiconductor nanoparticles can be used for applications in light energy conversion systems. During the irradiation of monochromatic light at 500 nm, the photocurrent of ZAIS(1.0)/ZnO-rod electrodes gradually decreased and then became a half after 1 h irradiation. This suggested that the sacrificial electron donor of Na$_2$S/K$_2$SO$_3$ did not completely scavenge the photogenerated holes in ZAIS, a part of which could oxidatively decompose the particles themselves.

In conclusion, we have demonstrated facile immobilization of ZnS–AgInS$_2$ solid solution nanoparticles on thin ZnO nanorod array films. The immobilized nanoparticles worked effectively as a visible light photosensitizer. The photoelectro-chemical properties of ZAIS(x)/ZnO-rod electrodes could be controlled by varying the chemical composition of ZAIS particles immobilized. Being different from photoelectrodes containing conventional quantum dots, such as CdSe, CdTe, and PbS, the ZAIS(x)/ZnO-rod electrodes obtained in this study contain no highly toxic elements but exhibit relatively high IPCE in the visible light region. This property will offer advantages for application to practical thin film solar cells. Work in this direction is currently in progress.

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