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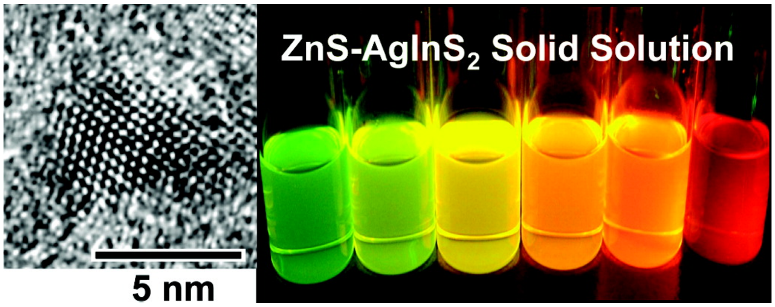

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Facile Synthesis of ZnS−AgInS$_2$ Solid Solution Nanoparticles for a Color-Adjustable Luminophore

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Luminescent semiconductor nanoparticles, such as CdSe and CdTe, have been intensively studied for applications such as biolabeling and design of novel optoelectronic devices[1−13] because their band gap emission is much more intense than those of bulk materials and the peak wavelength can be adjusted in the whole visible light region by controlling particle size. However, most luminescent nanoparticles contain highly toxic elements, such as Cd, Se, and Te, limiting the range of their uses.

For improvement of photocatalytic H_2 evolution with visible-light irradiation, we previously reported that the energy gap (E_g) of bulk particles (ca. 10 μm) of ZnS−AgInS$_2$ and ZnS−CuInS$_2$ solid solutions could be controlled in a wide range of visible light by changing the chemical composition.[14,15] The wavelength of the photoluminescence (PL) peak was blue-shifted with an increase in the fraction of ZnS, though PL of these bulk particles was observed only at a very low temperature of 80 K. By analogy to II−VI semiconductor nanoparticles, the PL intensity of these solid solution particles can be enhanced by decreasing the particle size to a nanometer region. However, there has been no investigation of the PL properties of I−III−VI$_2$ nanoparticles such as CuInS$_2$ and AgInS$_2$ and their solid solution particles other than a study on CuInS$_2$ nanoparticles by Castro et al.[16] and a study on ZnS−CuInS$_2$ solid solution particles by Maeda et al.,[17] in which PL was observed at ambient temperature with quantum yield of less than 5%. In this paper, we report a novel strategy to synthesize nanoparticles of ZnS−AgInS$_2$ solid solution (ZAIS) via a facile solution route. Their PL color at ambient temperature was adjustable by changing the fraction of ZnS in solid solution.

Solid solution nanoparticles of ZnS−AgInS$_2$ were prepared by thermal decomposition of a metal ion-diethyldithiocarbamate complex of $(AgIn)_xZn_{2(1-x)}(S_2CN(C_2H_5)_2)_4$. The precursor powder was prepared by mixing 50 cm^3 of a sodium diethyldithiocarbamate aqueous solution (0.050 mol dm^{-3}) with 50 cm^3 of an aqueous solution containing $AgNO_3$, $In(NO_3)_3$ and $Zn(NO_3)_2$ with a mole ratio of x:x:2(1 − x) (total concentration of metal ions: 0.025 mol dm^{-3}) followed by washing with water and methanol several times and drying. The results of elemental analyses were in good agreement with those theoretically expected from $(AgIn)_xZn_{2(1-x)}(S_2CN(C_2H_5)_2)_4$ within experimental error. Fifty mg of precursor powder was put into a test tube and heat-treated at 180 °C for 30 min in an N_2 atmosphere. Then oleylamine (3.0 cm^3) was added to the thus-obtained brown powder, followed by further heat treatment at 180 °C for 3 min in an N_2 atmosphere. The resulting suspension was subjected to centrifugation to remove large particles. ZAIS nanoparticles were separated from the supernatant by addition of methanol. The wet precipitates were washed with methanol several times and dissolved in chloroform for measurements.

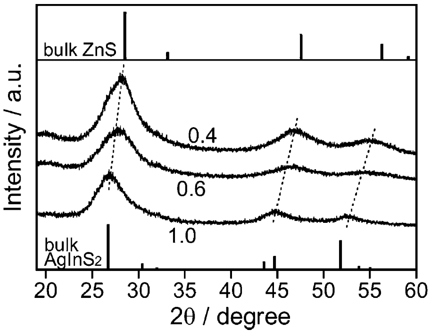

Figure 1. X-ray diffraction patterns of ZAIS nanoparticles prepared by pyrolysis of $(AgIn)_xZn_{2(1-x)}(S_2CN(C_2H_5)_2)_4$. The value of x is indicated in the figure. Reference patterns of bulk ZnS and AgInS$_2$ are also shown.

The crystal structures of the prepared particles were investigated by X-ray powder diffraction (XRD) with Cu Kα radiation. As shown in Figure 1, the particles prepared with $x = 1.0$ exhibited three broad peaks at $2\theta = 26.7$, 44.8, and 52.3°, which were assignable to diffractions of the (112), (204), and (312) planes, respectively, of tetragonal AgInS$_2$ crystal,[18] and the powder therefore did not contain the crystal phases, such as Ag_2S or In_2S_3 except for AgInS$_2$. Three broad peaks were also observed in the case of $x = 0.4$ and 0.6. Each peak was located between the corresponding peaks of bulk cubic ZnS[19] and tetragonal AgInS$_2$, being shifted to a higher angle with a decrease in x of $(AgIn)_xZn_{2(1-x)}(S_2CN(C_2H_5)_2)_4$ used as a precursor. These facts indicated that the obtained powders were not a mixture of ZnS and AgInS$_2$ but a ZnS−AgInS$_2$ solid solution in which the fraction of ZnS was enlarged with an increase in the content of Zn^{2+} in the precursors used, as reported for bulk materials.[14]

TEM observation (Figure S1) revealed that spherical nanoparticles had a clear lattice fringe with interplaner spacings of 0.33, 0.32 and 0.32 nm at $x = 1.0$, 0.6 and 0.4, respectively, which roughly agreed with those determined from diffraction peaks around 26−28° in the corresponding XRD patterns (Figure 1). The average sizes (standard deviations) were determined by TEM images to be 4.4 (0.79), 4.4 (0.85), and 4.1 nm (0.88 nm) at $x = 1.0$, 0.6 and 0.4, respectively, suggesting that change in the composition of the precursor used did not greatly influence the size and size distribution

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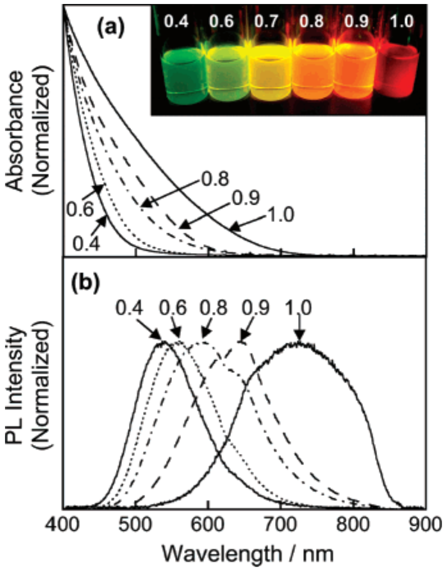

Figure 2. Absorption spectra (a) and photoluminescence spectra (b) of ZAIS nanoparticles. The value of x in $(AgIn)_xZn_{2(1-x)}(S_2CN(C_2H_5)_2)_4$ used as a precursor is indicated in the figure. The excitation wavelength in PL measurement was 350 nm. The inset in panel a shows photographs of UV-illuminated ZAIS nanoparticle solutions.

of the resulting nanoparticles. FTIR spectra of particles (Figure S2) showed the characteristic peaks assigned to oleylamine:[20] the bands at 3007 and 1583 cm^{-1} were due to the olefinic C−H stretching and the NH_2 deformation, respectively, indicating that oleylamine was adsorbed on the ZAIS surface to prevent coalescence between nanoparticles.

The absorption spectra of ZAIS particles (Figure 2a) were structureless, regardless of the kind of precursor used. Although the wavelength of absorption onset was not clearly identified, $AgInS_2$ nanoparticles (ZAIS prepared with $x = 1.0$) seemed to have an absorption onset around 700 nm (corresponding to E_g of 1.8 eV). Since the E_g of tetragonal bulk $AgInS_2$ has been reported to be 1.8 eV, most of the $AgInS_2$ nanoparticles possessed an energy gap similar to that of bulk material. On the other hand, the absorption onset was blue-shifted with a decrease in x. Since the particle size was almost same regardless of x value, as mentioned above, it could be assumed that the size quantization effect might hardly affect the difference in E_g between particles prepared. So this fact indicated that the E_g of ZAIS nanoparticles was enlarged with an increase in the fraction of ZnS in solid solution, as reported for the bulk materials.[14] It should be noted that the particles prepared with $x = 0$ were not dissolved in chloroform, probably because of the formation of large ZnS particles during the heat treatment of the corresponding precursor.

The nanometer-sized particles of ZAIS exhibited intense emission at room temperature (inset of Figure 2a), though PL of bulk materials was observed only at a very low temperature of 80 K as reported in our previous paper.[14] The peak wavelength of PL was blue-shifted from 720 to 540 nm with a decrease in the x value as shown in Figure 2b, similar to that in the case of the absorption spectra. This enabled us to obtain a desired emission color in the visible light region by control of the energy structure of ZAIS nanoparticles. PL excitation spectra of ZAIS particles (Figure S3) agreed well with the corresponding absorption spectra, indicating that PL originated from photoexcitation of the ZAIS particles. The optical properties of particles such as absorption and PL spectra were almost constant for at least 2 months when solutions were stored under N_2 atmosphere in the dark. It should be noted that the full-width at half-maximum intensity (fwhm) of the PL peak was considerably large (>100 nm) in each case, probably because of the radiative transitions in donor−acceptor levels and/or the emission from surface defects sites. This behavior is remarkably different from PL properties of some other semiconductor nanoparticles such as CdSe and CdTe, for which intense band gap luminescence was observed with fwhm of less than ca. 30 nm.[6] The quantum yield of PL fluctuated depending on the composition of precursors used, but the highest quantum yield of ca. 24% was obtained for ZAIS nanoparticles prepared with $x = 0.86$, which was much higher than the quantum yields reported for I−III−VI_2-based semiconductor nanoparticles, such as $CuInS_2$[16] and ZnS−$CuInS_2$ solid solution.[17]

In conclusion, we have successfully prepared highly luminescent ZnS−$AgInS_2$ solid solution nanoparticles containing no highly toxic elements. The resulting particles exhibited broad PL spectra but the emission color could be tuned from green to red, depending on their chemical composition. This property will offer advantages for use in visible and near-IR lighting. Furthermore, the tunability of electronic energy structure of solid solution nanoparticles will be useful to adjust the redox activity and the absorption property for applications, such as photocatalysts and quantum-dot solar cells. Work in this direction is currently in progress.

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Supporting Information Available: TEM images, FTIR spectra, and PLE spectra of ZAIS nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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