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Photoluminescence Enhancement of ZnS–AgInS$_2$ Solid Solution Nanoparticles Layer-by-layer-assembled in Inorganic Multilayer Thin Films

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Multilayer films of layered double hydroxide (LDH) nanosheets and semiconductor nanoparticles of ZnS–AgInS$_2$ solid solution (ZAIS) or CdS were prepared by a layer-by-layer deposition technique. The photoluminescence properties were remarkably dependent on the stacked structure of the films owing to the energy transfer from CdS to ZAIS nanoparticles.

The layer-by-layer deposition technique[1] has attracted much attention for the fabrication of multilayer films containing size-quantized nanoparticles of a metal[2,3] or semiconductor,[4–7] because nanoparticles can be immobilized on various substrates with negligible change in their shape and size. Furthermore, the physicochemical properties can be controlled by the stacked structures of the films.[5–7] For example, the photoluminescence (PL) intensity of CdTe nanoparticle layers with larger size was greatly enhanced when three monolayers with nanoparticles of different sizes were closely accumulated,[5] because electron–hole pairs photogenerated in nanoparticles having a larger energy gap (E_g) migrated to those with smaller E_g via the Förster resonance energy-transfer process.

Recently, we have successfully fabricated highly luminescent ZnS–AgInS$_2$ solid solution (ZAIS) nanoparticles in a solution.[8] The emission color was tunable from green to red, depending on the chemical composition. Since no highly toxic element is included, immobilization of the particles enables a wide variety of applications of these particles to solid devices, such as LEDs[9] and solar cells.[10,11] In this paper, we report, for the first time, the fabrication of layer-by-layer-assembled multilayer films of layered double hydroxide (LDH) nanosheets as a rigid spacer and semiconductor nanoparticles of ZAIS and CdS. The PL intensity of ZAIS particle layers is tunable through the control of the energy transfer from CdS nanoparticles having a larger E_g.

Oleylamine-modified ZAIS nanoparticles were fabricated by the same procedure as that reported previously,[8] except for using $(AgIn)_xZn_{2(1-x)}(S_2CN(C_2H_5)_2)_4$ with $x = 0.90$ as a precursor powder. The particles were surface-modified with sodium 2-mercaptoethane sulfonate (MES) by mixing as-prepared ZAIS nanoparticles suspended in 2-propanol (2.0 cm^3) with 0.50 mol dm^{-3} aqueous MES solution (2.0 cm^3) and stirring for 1 h. The resulting MES-modified ZAIS particles were isolated by centrifugation and dissolved in water. The average size (d_{av}) of ZAIS particles was 4.2 nm with a standard deviation (σ) of 0.98 nm. LDH nanosheets[12] or MES-modified CdS nanoparticles ($d_{av} = 5.0$ nm, $\sigma = 0.79$ nm)[13,14] were prepared using previously reported methods. Multilayer films of nanoparticles and LDH nanosheets were fabricated by the layer-by-layer deposition technique. A clean quartz plate pre-coated with polyethyleneimine and poly(sodium 4-styrene sulfonate) was dipped in a formamide dispersion of LDH nanosheets (0.50 g dm^{-3}) for 20 min. The thus-obtained substrate was immersed for 20 min in an aqueous solution containing MES-modified ZAIS nanoparticles (7.2×10^{17} particles dm^{-3}) (pH 6.8) or that containing MES-modified CdS particles (7.2×10^{17} particles dm^{-3}) (pH 4). These deposition procedures were repeated several times to prepare a desired thickness of hybrid multilayer films, and finally an LDH layer was accumulated as the uppermost layer on the films. The prepared film is denoted here as [LDH/nanoparticle]$_n$, where n is the accumulation number of a pair of LDH and nanoparticle layers. A hybrid film of [LDH/ZAIS]$_2$/[LDH/CdS]$_5$ was prepared by further accumulation of [LDH/ZAIS]$_2$ layers on [LDH/CdS]$_5$ film.

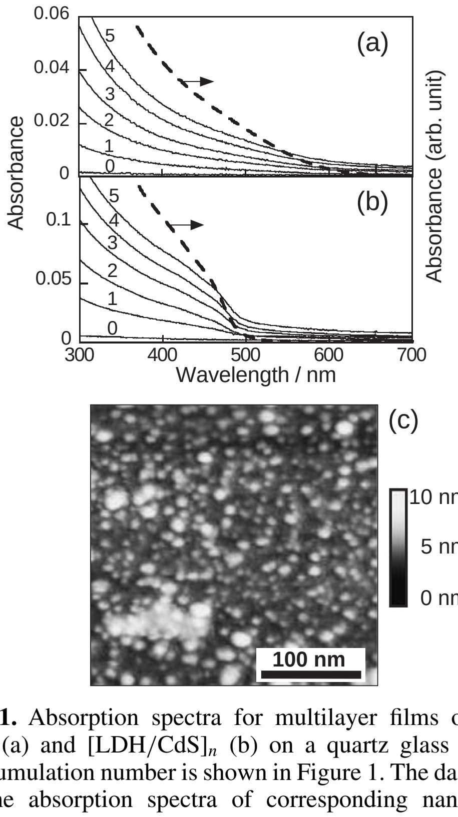

Figure 1. Absorption spectra for multilayer films of [LDH/ZAIS]$_n$ (a) and [LDH/CdS]$_n$ (b) on a quartz glass substrate. The accumulation number is shown in Figure 1. The dashed lines show the absorption spectra of corresponding nanoparticles dissolved in water. (c) AFM image of a ZAIS nanoparticle layer deposited on the first LDH layer. A mica sheet was used as a substrate.

The accumulation of LDH/nanoparticle multilayer films

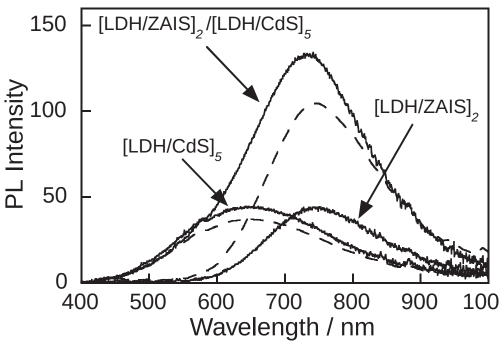

Figure 2. Photoluminescence spectra of layer-by-layer-assembled multilayer films. Broken lines are the result of deconvoluting the PL spectrum of the [LDH/ZAIS]$_2$/[LDH/CdS]$_5$ film with two profiles corresponding to those of [LDH/CdS]$_5$ and [LDH/ZAIS]$_2$ films.

was monitored by absorption spectra (Figure 1a), which were measured after each LDH deposition. The films of LDH/ZAIS exhibited broad spectra with absorption onset around 620 nm, in good agreement with those of MES-modified ZAIS nanoparticles dissolved in water. Furthermore, the absorbance of the film assigned to ZAIS particles linearly increased with an increase in the accumulation number. Similar behavior was observed in the case of the accumulation of CdS nanoparticles and LDH nanosheets (Figure 1b). These facts indicated that uniform deposition of nanoparticles occurred in each dipping cycle, regardless of the kind of nanoparticles used. This was supported by the AFM image of a ZAIS layer on the first LDH nanosheet layer (Figure 1c), where ZAIS nanoparticles were densely immobilized on LDH sheets.

Broad photoluminescence spectra were observed for both [LDH/ZAIS]$_2$ and [LDH/CdS]$_5$ films with peaks around 745 and 650 nm, respectively (Figure 2), which were attributed to the recombination of photogenerated carriers at the defect sites. Though the accumulation number was different, the PL peak intensity of the [LDH/ZAIS]$_2$ film was almost the same as that of the [LDH/CdS]$_5$ film. This can be explained by the fact that ZAIS nanoparticles dissolved in water exhibited strong PL with quantum yield of ca. 22%, which is much larger than that of CdS in water, ca. 0.84%.

The accumulation of [LDH/ZAIS]$_2$ layers on the [LDH/CdS]$_5$ film gave an absorption spectrum that was in good agreement with the sum of the absorption of individual [LDH/ZAIS]$_2$ and [LDH/CdS]$_5$ films, but the PL intensity of the thus-obtained hybrid film was considerably enhanced. The PL spectrum of the [LDH/ZAIS]$_2$/[LDH/CdS]$_5$ hybrid film was successfully reproduced by a combination of individual spectra of [LDH/CdS]$_5$ and [LDH/ZAIS]$_2$ films, as shown in Figure 2. The PL intensity of the former component became 0.84 times smaller than that of the original [LDH/CdS]$_5$ film, while a 2.4-fold enhancement was observed for the latter component in comparison with the [LDH/ZAIS]$_2$ film only. It has been reported that the close proximity of two nanoparticle monolayers with slightly different energy gaps enabled the migration of photogenerated electron–hole pairs from the particle layer having larger E_g to that of smaller E_g owing to energy transfer, resulting in remarkable enhancement of PL intensity of nanoparticles having smaller E_g.[5,6] Since the E_g of ZAIS particles (2.0 eV), which was estimated from their absorption onset, was smaller than that of CdS nanoparticle (2.5 eV), the PL enhancement observed in the hybrid film indicated that CdS and ZAIS particle layers acted as an energy donor and an acceptor, respectively, and electron–hole pairs in CdS nanoparticle layers were effectively transferred via the energy-transfer process to ZAIS layers, resulting in radiative recombination. From the PL quenching of CdS particles, the energy-transfer efficiency (Φ_{ET})[15] in the hybrid film was estimated to be 16%, which was smaller than that reported for the bilayers of CdTe nanoparticles of two different sizes (ca. 80%).[6] Since Φ_{ET} drastically decreases with an increase in the distance between donor and acceptor,[15] the fact suggested that the closest CdS and ZAIS layers mainly participated in the energy transfer while the other layers were too far apart to energetically interact.

In conclusion, we have successfully fabricated inorganic multilayer thin films by the alternate accumulation of semiconductor nanoparticles and LDH nanosheets. The PL properties of the films could be controlled by varying their stacked structures, where the energy transfer between nanoparticle layers was found to play an important role. This will enable the construction of effective light-harvesting systems in energy-conversion devices, such as quantum dot solar cells. Study along this line is in progress.

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