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Synthesis of TiO_2/CdS nanocomposite via TiO_2 coating on CdS nanoparticles by compartmentalized hydrolysis of Ti alkoxide

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Hydrolysis of Ti alkoxide in the presence of inverse micelles containing CdS nanoparticles in their hydrophilic interior results in formation of TiO_2/CdS nanocomposites in which the CdS nanoparticles are embedded in a TiO_2 matrix with a thickness of $\leq$10 nm at the surface of the particles. The primary hydroxyl groups introduced by 2-mercaptoethanol as a capping agent used for preparation of the CdS nanoparticles are considered to play an important role for successful adhesion and growth of the TiO_2 layer on the CdS surfaces. TEM observation strongly supports formation of semiconductor-in-semiconductor heteronanostructure by compartmentalized hydrolysis of Ti alkoxide within the inverse micelles in which the surface-capped CdS nanoparticles coexist. © *2001 Kluwer Academic Publishers*

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1. Introduction

Combinations of different semiconductors have widely been investigated in the field of nanostructured materials. In particular, a considerable interest has been focused on combinations of semiconductor nanoparticles, those including CdS-TiO_2 [1], CdS-ZnO [2], CdS-AgI [1], ZnO-ZnS [3], CdS-HgS [4], for example. However, surface coating or capping of semiconductor nanoparticles with another semiconductor has been mostly limited to combinations of the same family of materials such as binary chalcogenides or binary oxides, e.g., HgS-coated CdS [5], PbS-coated CdS [6], and TiO_2-coated SnO_2 [7]. There appears to be almost no report on the surface coating of an oxide semiconductor over another non-oxide semiconductor.

Sando *et al.* reported nanosized SiO_2 coating on the surfaces of Al_2O_3 submicron particles by utilizing hydrolysis of silicon alkoxide by water adsorbed on the particles [8]. Since they used inverse micelles in order to spatially confine the hydrolysis reaction, this approach would also enable us to restrict the reaction region to only close vicinity of surfaces of non-oxide particles. In this study, we have therefore attempted to encapsulate CdS nanoparticles in thin TiO_2 coating by employing inverse micelles, which also serving as a stabilizing agent of the nanoparticles in a hydrophobic solvent, as a compartmentalized reaction space for hydrolysis of titanium alkoxide. Such a semiconductor-in-semiconductor heteronanostructure would also be of a considerable interest in terms of semiconductor photocatalysis [9], size confinement effects [10], and optical properties of semiconductor nanoparticles [6].

2. Experimental

Surface TiO_2 coating on CdS nanoparticles was attempted by hydrolyzing titanium tetraisopropoxide ($Ti(OCH(CH_3)_2)_4$, $Ti(OPr)_4$) in a hydrophobic solvent in the presence of inverse micelles enclosing the CdS nanoparticles and adsorbed water on their surfaces.

The CdS nanoparticles were prepared from Na_2S and $Cd(ClO_4)_2$ by using 2-mercaptoethanol ($HSCH_2CH_2OH$) as a surface-capping agent. 250 ml of a 20 mM Na_2S aqueous solution was added under vigorous stirring to the same amount of a 20 mM $Cd(ClO_4)_2$ aqueous solution containing 1 ml of 2-mercaptoethanol. The resulting suspension was centrifuged, followed by washing with distilled water for several times in order to remove excess 2-mercaptoethanol and perchlorate. A white suspension thus obtained was stable in the dark for a few days without forming any precipitation.

The CdS nanoparticles thus obtained were re-dispersed in 300 ml of a 20 mM stearylamine solution in *n*-hexane, and $Ti(OPr)_4$ was added under N_2 atmosphere. The alkoxide was allowed to hydrolyze under stirring in the dark for two days. A suspension thus obtained was centrifuged and re-dispersed, twice in *n*-hexane and then twice in ethanol under N_2 atmosphere.

The morphology of the products was observed on a JEOL JEM-2000FX transmission electron microscope

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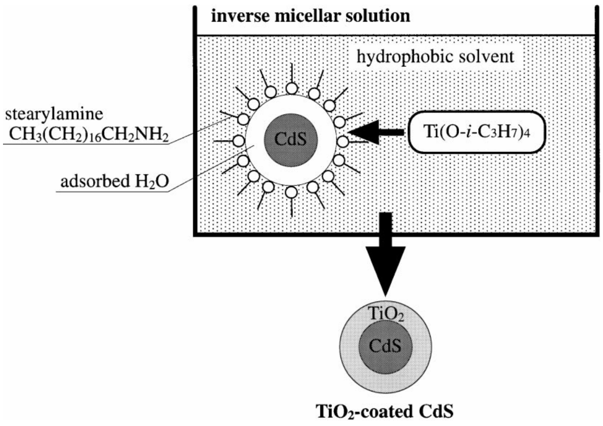

Figure 1 A schematic of TiO_2 coating on the CdS nanoparticles by compartmentalized hydrolysis of Ti alkoxide in an inverse micellar solution.

(TEM) equipped with an energy dispersive X-ray analyzer (EDX, Tracor Nothern TN-2000) at the HVEM Laboratory, Kyushu University, and on a JEOL JSM-T330A scanning electron microscope (SEM) with an EDX analyzer (JEOL JED-2000). Infrared absorption spectra were collected on a Shimazu FT-IR 8200D spectrometer. Transmission and diffuse-reflectance UV-VIS spectra were measured with a JASCO UVIDEC-660 spectrophotometer. Diffuse-reflectance UV-VIS spectra were converted by the Kubelka-Munk transform.

3. Results and discussion

Fig. 1 shows the concept of TiO_2 coating on CdS particles by compartmentalized hydrolysis of Ti alkoxide within the hydrophilic interior of inverse micelles. The surfactant molecules dissolved in a hydrophobic solvent will form inverse micelles by facing their hydrophilic head groups each other. In the presence of the CdS nanoparticles in the solution, the inverse micelles can accommodate the nanoparticles in their hydrophilic interior, and as a matter of fact, inverse micelles have been employed as a stabilizer of semiconductor nanoparticles in non-aqueous solutions [11]. Since a slight amount of water is considered to be adsorbed on the surfaces of the nanoparticles, $Ti(OPr)_4$ added into the solution will hydrolyze spontaneously within the hydrophilic interior of the inverse micelles, and may form a nanosized surface coating of TiO_2 covering the CdS nanoparticles.

As a preliminary experiment, TiO_2 coating on CdS was tried by using commercially purchased bulk CdS crystallites, in a manner similar to that for the SiO_2 coating on Al_2O_3 particles reported by Sando *et al.* An air saturated with water vapor at room temperature passed over the finely ground CdS crystallites in order to enrich the adsorbed water on the CdS surfaces. The CdS crystallites were then dispersed in a *n*-hexane solution of stearylamine, followed by addition and spontaneous hydrolysis of $Ti(OPr)_4$. Fig. 2 shows a SEM image and an EDX spectrum of the CdS crystallites after the TiO_2 coating procedure. The size of the CdS crystallites was $\sim 1\ \mu m$. The EDX spectrum shows distinct peaks attributed to Cd and S, and a strong peak from Ag is due to a silver paste used for mounting the sample for the SEM observation. However, there is no signal ascribed to Ti, which should appear around 4.5 keV in the spectrum. A detailed observation by TEM/EDX also failed to find TiO_2 on the surfaces of the CdS crystallites. Since SEM/EDX revealed that TiO_2 exists as independent particles being completely out of contact with the CdS crystallites, the failure of the TiO_2 coating on the CdS crystallites is probably due to weak contact to the CdS surfaces.

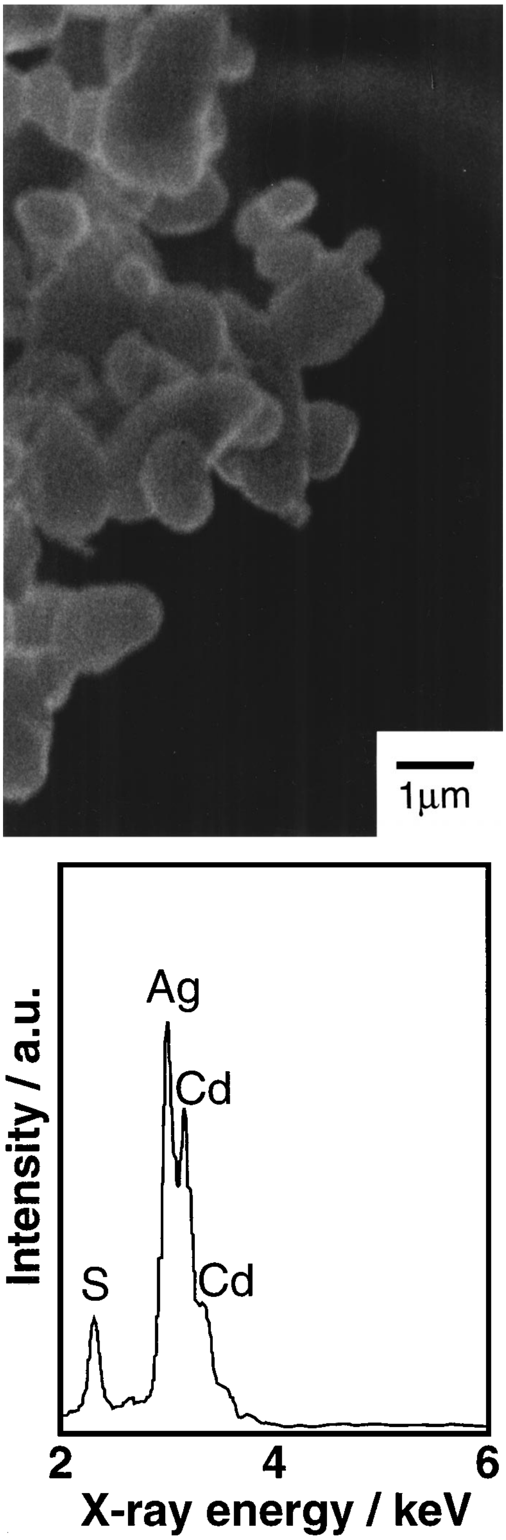

Figure 2 SEM image and EDX spectrum of bulk CdS crystallites after the TiO_2 coating procedure.

The poor adhesion of the TiO_2 coating to the CdS crystallites may be inevitable for oxide coating on

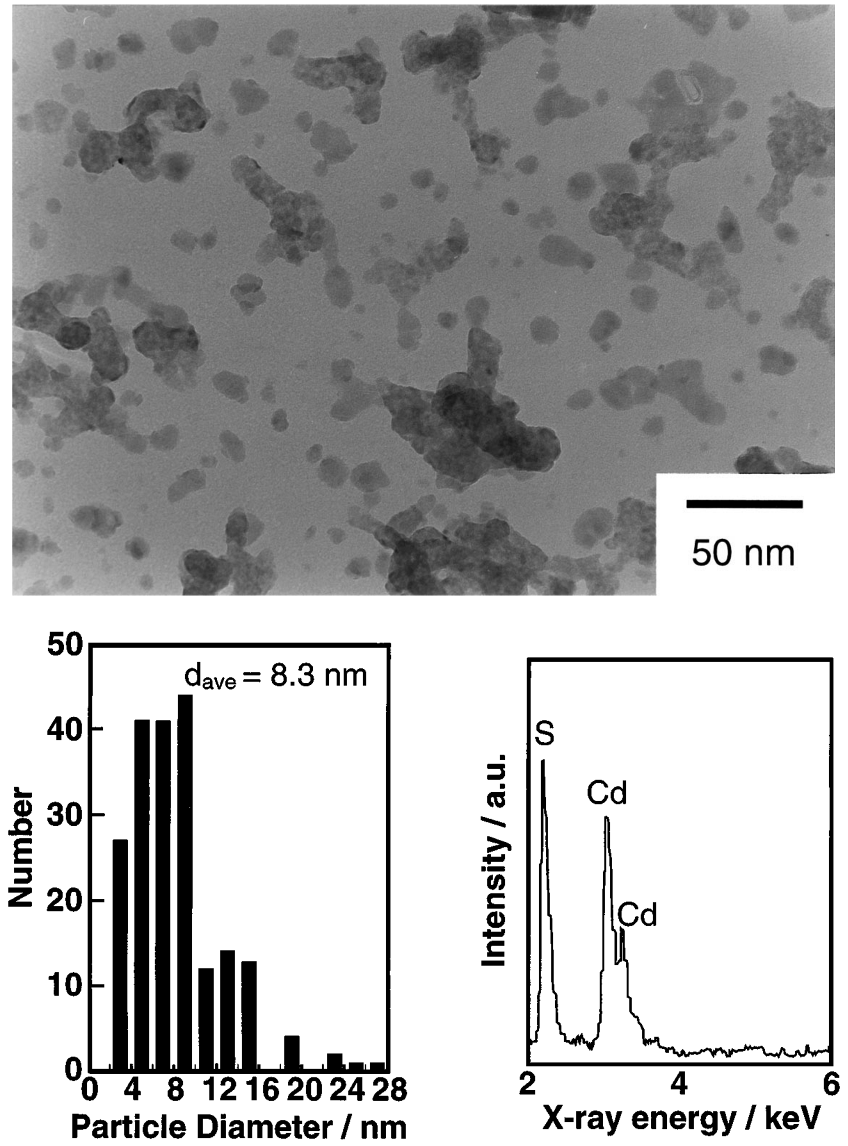

Figure 3 TEM image, size distribution, and EDX spectrum of CdS nanoparticles capped with 2-mercaptoethanol.

sulfide surfaces, because sulfide surfaces are usually much less abundant in the free hydroxyl groups compared to surface of oxides such as Al_2O_3. Nevertheless, the surface of sulfide nanoparticles can be modified by using surface-capping agents. We have employed 2-mercaptoethanol as a capping agent for preparation of CdS nanoparticles in order to provide the hydroxy groups as a reaction site for the Ti alkoxide.

Fig. 3 shows a TEM image, size distribution, and EDX spectrum of the CdS nanoparticles prepared in the presence of 2-mercaptoethanol. Whereas aggregates of $\sim$50 nm in size were found in the TEM image, the size distribution was determined as that of the primary particles. The nanoparticles were thereby revealed to have an average diameter of 8.3 nm, and the elemental composition was determined by the TEM/EDX analysis as Cd/S $\approx$1. Discrepancy in the relative peak intensity of Cd to S compared to Fig. 2 obtained by SEM/EDX analysis is mainly due to difference between the EDX analyzers in the sensitivity for lower energy X-ray.

An FT-IR spectrum of the CdS nanoparticles capped with 2-mercaptoethanol is shown in Fig. 4 in comparison with those of 2-mercaptoethanol and CdS

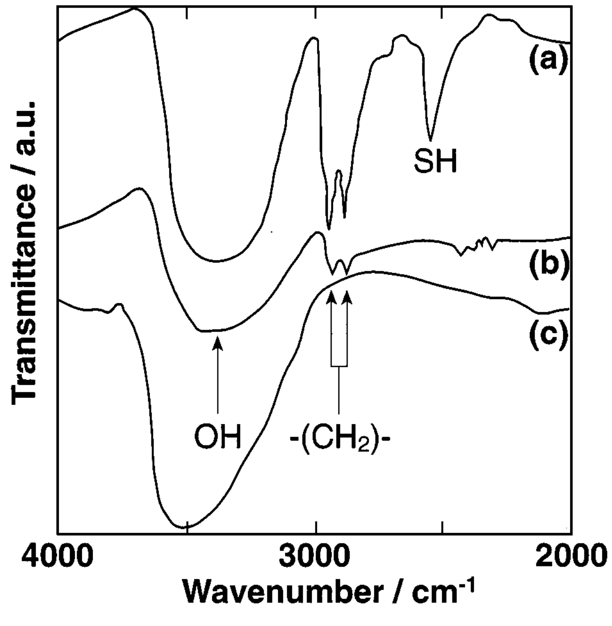

Figure 4 FT-IR spectra of (a) 2-mercaptoethanol, (b) CdS nanoparticles capped with 2-mercaptoethanol, and (c) CdS nanoparticles prepared without any capping agent.

nanoparticles prepared without the capping agent. A broad band around 3400 cm^{-1}, a strong doublet at 2873 and 2933 cm^{-1}, and a strong peak at 2555 cm^{-1} in the spectrum of 2-mercaptoethanol are assigned to the O-H stretching vibration, the symmetric and asymmetric stretching vibrations of the CH_2 groups, and the S-H stretching vibration, respectively. On the other hand, there was no peak in the same region between 2000 and 3000 cm^{-1} in the spectrum of the CdS nanoparticles prepared in the absence of 2-mercaptoethanol. Whereas the peaks due to the CH_2 groups of 2-mercaptoethanol was also observed for the CdS nanoparticles capped with 2-mercaptoethanol, the absorption of the S-H stretching vibration completely disappeared after the capping. This clearly excludes that intact 2-mercaptoethanol simply coexists with the CdS nanoparticles. Since the surface capping of sulfide particles by thiols is attributed to coordination of the deprotonated mercapto groups to the sulfide surfaces, these IR spectra strongly confirm the surface capping of the CdS nanoparticles by direct bonding of the deprotonated mercapto group of 2-mercaptoethanol, presumably to the Cd^{2+} site at the surface. These results also suggest that the primary hydroxyl groups at the other end of the capping thiol can serve as a surface hydrophilic moiety of the capped CdS nanoparticles, and H_2O might be adsorbed more readily on the modified sulfide surfaces.

The capped CdS nanoparticles prepared as above were washed with ethanol and *n*-hexane in order to remove excess H_2O, and then dispersed in a *n*-hexane solution of stearylamine under N_2 atmosphere, followed by addition of $Ti(OPr)_4$. Fig. 5 shows a TEM image and EDX spectra of the product thus obtained. The product was revealed to disagree with the conceptual sketch of the TiO_2-coated CdS nanoparticles in Fig. 1, being

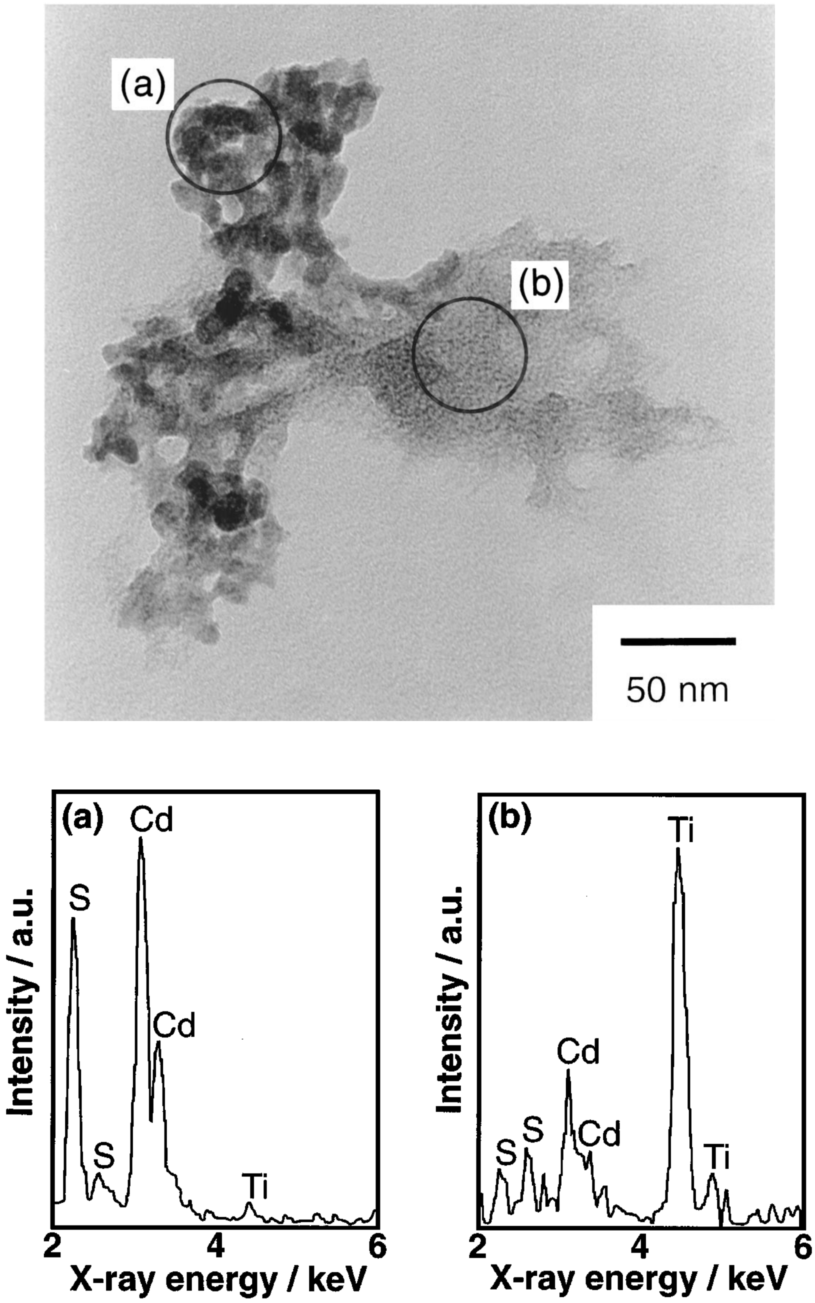

Figure 5 TEM image of TiO_2-coated CdS nanocomposite and EDX spectra of selected areas for (a) dark particles and (b) light gray region.

aggregates of the order of 100 nm in size. In Fig. 5, observed are many dark particles in the aggregate, and light gray regions surrounding and connecting the particles to form the whole body of the aggregate. As shown in the EDX spectra, these dark and light gray regions were determined to consist predominantly of CdS and TiO_2, respectively. The size of the CdS (dark) particles are of the order of 10 nm, being almost the same as the initial size before the TiO_2-coating procedure. Although the shape of the aggregates is highly irregular, the outline of the aggregates appears to consist mostly of the light gray region. Moreover, no clear image of the boundary between the dark particles and the light gray outer region was observed. These results would be understandable if the dark particles are embedded in a light gray matrix. It should also be noted that most of the objects are nanocomposites of CdS and TiO_2 phases, and neat TiO_2 phase without the CdS particles were hardly observed. Moreover, sole CdS particles apart from TiO_2 were completely unseen. These facts infer that every CdS particle was in contact with TiO_2 when the TiO_2 phase formed from hydrolysis of $Ti(OPr)_4$, and that the TiO_2 formation in the absence of the CdS particles scarcely occurred, unlike the result of the TiO_2 coating on the CdS crystallites. This strongly suggests formation of TiO_2 by compartmentalized hydrolysis within the inverse micelles, most of which have already contained the CdS nanoparticles in their hydrophilic interior.

The thickness of the TiO_2 phase where it coats the CdS nanoparticles was estimated as $\leq$10 nm from the TEM image. This thickness is comparable to or less than that of SiO_2 coating reported for the SiO_2-coated Al_2O_3 submicron particles [8]. The considerably smaller size of the CdS nanoparticles may have led not to coated individual nanoparticles but to nanocomposites embedded in the TiO_2 matrix. Although this structure appears to be rather dissimilar to the ideal core-shell structure illustrated in Fig. 1, it can be concluded that the semiconductor-in-semiconductor nanocomposite structure consisting of nanosized CdS particles covered with TiO_2 surface coating was established by utilizing compartmentalized hydrolysis of $Ti(OPr)_4$. It would therefore be expected that individual TiO_2-coated CdS nanoparticles may form, if more precise control of the hydrolysis reaction and growth of the TiO_2 phase would be possible to avoid aggregation.

Fig. 6 shows UV-VIS absorption spectra of the CdS nanoparticles and the TiO_2/CdS nanocomposite in comparison with that of bulk CdS. The absorption edge of the CdS nanoparticles observed around 400 nm indicates a significant blue shift of the bandgap energy compared to that of the bulk CdS, although the blue shift appears to be considerably larger than the value estimated from the quantum size effects [12] using the particle diameter determined from the TEM image shown in Fig. 3. It is therefore probable that those regarded as the primary particles on the TEM observation might be also aggregates of smaller nanoparticles. The absorption edge of the CdS nanoparticles almost unchanged even after the TiO_2-coating procedure. These results agree well to the intact size of the CdS nanoparticles in the TiO_2/CdS nanocomposite.

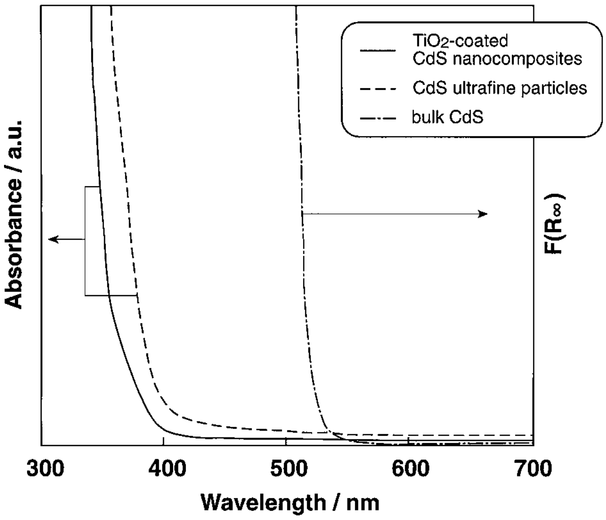

Figure 6 UV-VIS absorption spectra of bulk CdS, CdS nanoparticles, and TiO_2-coated CdS nanocomposites.

4. Conclusions

Although TiO_2 coating on CdS crystallites of ~1 μm failed, TiO_2-coated CdS nanoparticles successfully formed as nanocomposites via hydrolysis of $Ti(OPr)_4$ at the surfaces of the capped CdS nanoparticles stabilized in the inverse micellar solution. The hydroxyl groups of 2-mercaptoethanol as the surface capping agent of the CdS nanoparticles appear to play an important role for the successful TiO_2 coating on the surfaces of CdS. The typical structure of the nanocomposites consists of the CdS particles of ~10 nm in diameter and TiO_2 phase surrounding and connecting them with the thickness of $\leq$10 nm. A dominant population of the TiO_2/CdS nanocomposites and complete absence of the sole CdS particles without TiO_2 strongly support formation of TiO_2 within the hydrophilic interiors of the inverse micelles most of which have contained the CdS nanoparticles. Optimization of the nanocomposites would require further control of growth of the TiO_2 phase and prevention of particle aggregation. A strong quantum size effect observed for the increased band gap energy of the CdS nanoparticles remained intact even after formation of the semiconductor-in-semiconductor heterostructured nanocomposite.

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