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Composite nano-CdS–polyurethane transparent films

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Nano-CdS particles, as formed in reverse micelles, have been immobilized into polyurethane (PU), *via* surface-modification with 4-hydroxythiophenol or 2-mercaptoethanol, followed by polyaddition of ethylene glycol with toluenediyl 2,4-diisocyanate: the resulting composite, CdS–PU, obtained as powder, can be dissolved in organic solvents such as DMF and formed to make nano-CdS-containing transparent PU films, which show a quantum-size effect and are utilized for photocatalytic H_2 generation.

There has been much recent interest in the preparation and processing methods for semiconductor nanoparticles. We have recently developed two methods to immobilize nano-CdS particles formed in reverse micellar systems into polymers such as polyurea (PUA)[1] and polythiourethane (PTU).[2,3] In the latter case, a nano-CdS surface-modified with thiols, was immobilized in PTU *via* polyaddition of a dithiol with hexamethylene diisocyanate. PTU is, however, insoluble in most organic solvents, making it difficult to process. In the present study, a novel nano-CdS–polymer composite is developed using polyurethane (PU), which is processed easily to make optically transparent films. Yanagida *et al.*[4] reported the preparation of a poly(methyl methacrylate) (PMMA) transparent film incorporated with phenyl-capped CdS nanoparticles (Φ-CdS). In their method, however, Φ-CdS was merely dispersed in PMMA–pyridine solution prior to casting, without use of chemical bonding. The methods for preparation of nano-CdS–polymer composites *via* preparation of nanoparticles using reverse micellar systems may be advantageous to control the particle size and size distribution more precisely, compared with methods where nanoparticles are formed *in situ* in polymer matrices.[5–7] Fogg *et al.* reported a new method for preparing quantum dot–polymer composites.[8,9] They sequestered CdSe or ZnS-coated CdSe nanoclusters, separately prepared and surface modified by trioctylphosphine and trioctylphosphine oxide, into phosphine-functionalized block copolymers.

A reverse micellar system consisting of sodium bis(2-ethylhexyl) sulfosuccinate (AOT, 0.1 mol l^{-1}), water and isooctane (2,2,4-trimethylpentane) was used. CdS nanoparticles were prepared by the rapid addition of an AOT–isooctane micellar solution {100 ml, W_o (=$[H_2O]/[AOT]$)=4} containing $CdCl_2$ (1.2×10^{-3} mol l^{-1}) to another micellar solution of the same W_o value containing Na_2S (8.0×10^{-4} mol l^{-1}, 100 ml) with vigorous stirring using a magnetic stirrer at 298 K, in a glass vessel covered with aluminium foil. Following the addition of a 4-hydroxythiophenol (HTP)–propan-2-ol solution or a 2-mercaptoethanol (ME)–propan-2-ol solution (0.1 mol l^{-1}, 0.8 ml, 2 min after CdS formation) for the surface modification of the nano-CdS,[10] the particles were collected *via* centrifugation and dispersed in dry DMSO (15 ml), to which ethylene glycol (0.125 g) was added. This solution was poured dropwise into another DMSO solution (5 ml) containing toluenediyl 2,4-diisocyanate (0.7 g) in a flask at an oil bath temperature of 333–403 K for 2 h. The resulting DMSO solution was poured into water to give both white and slightly yellowish powders. The yellowish powder (CdS–PU) was separated as a precipitate by centrifugation, whereas the white powder (PU) remained dispersed.

The Cd content of the composite was determined to be 0.07–0.14 mol (kg CdS–PU)$^{-1}$. This was done by decomposing a weighed CdS–PU sample into concentrated H_2SO_4 and measuring the Cd concentration using an inductively coupled argon plasma atomic emission spectrometer. This value is lower than the corresponding values for CdS–PUA[1] and CdS–PTU,[2,3] by approximately one order of magnitude. The particle exposed fraction F (the ratio of the dissolved quantity of CdS obtained *via* contact with 6 mol l^{-1} HCl to that of the total quantity obtained *via* H_2SO_4 decomposition) was found to be almost unity. This is comparable to that for CdS–PUA,[1] and is greater than that for CdS–PTU.[2,3] Thus, almost all the CdS particles in CdS–PU are likely to be exposed to the external solution, and therefore CdS–PU is applicable for photocatalytic reactions.

Polyurethane can be dissolved in organic solvents such as DMSO, DMF and THF. A CdS–PU film was thus prepared easily by casting a DMF solution of the composite onto a glass sheet and an optically transparent film of *ca.* 15 μm thickness was obtained. The absorption spectra for the nano-CdS in the reverse micellar solution, following dispersion in DMSO, and in the PU film are shown in Fig. 1(a). Since CdS-free PU shows absorption at wavelengths <320 nm, this was subtracted from the observed absorption for CdS–PU. A red-shift of the absorption onset was observed during surface modification and dispersion of the nano-CdS in DMSO, indicating that the particle growth continues even after the addition of HTP. On the other hand, no appreciable red-shift was observed during polymerization and immobilization into PU. The value of the band gap E_g for immobilized CdS was determined to be 2.91 eV from the absorption onset, greater than the bulk value for CdS (2.5 eV[11]) owing to a quantum size effect. Thus, the diameter d_p for nano-CdS in CdS–PU was estimated to be 3.91 nm by use of the Brus equation.[12]

The effect of W_o of the reverse micellar solution for nano-CdS formation on the properties of CdS–PU composites was investigated. As seen from the absorption spectra in Fig. 1(b), the size of nano-CdS in CdS–PU becomes greater with increasing W_o. However, nano-CdS in CdS–PU still shows a quantum size effect; the values of E_g and d_p were 2.78 eV and 4.49 nm for $W_o=7$, and 2.71 eV and 5.00 nm for $W_o=10$, respectively. Thus, the particle size of nano-CdS in the CdS–PU transparent film, and also the absorption onset of the film, are easily controllable by changing the W_o value.

Although nano-CdS prepared in reverse micelles showed emission peaks at *ca.* 530 nm, this emission disappeared on adding HTP into the micellar solution. This result is similar to that reported by Premachandran *et al.*,[13] and indicates that the emission attributable to hole–electron recombinations at the surface traps is diminished by surface-capping by the HTP. On the other hand, the CdS–PU film showed fluorescence, as shown in Fig. 2. The emission peak at *ca.* 440 nm, attributable to recombination from the excitonic state in the particle

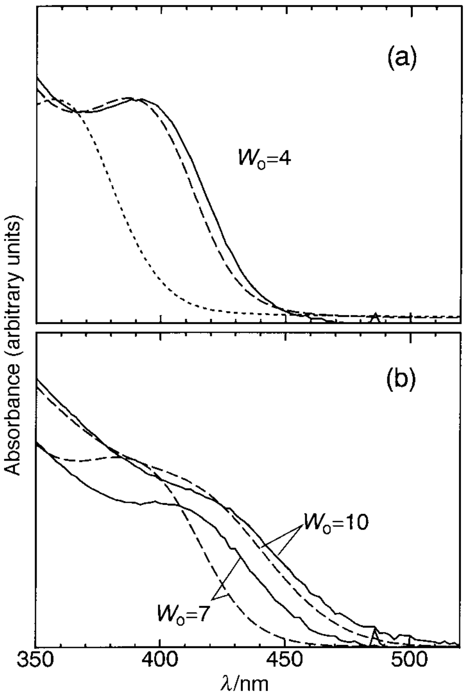

Fig. 1 Absorption spectra of nano-CdS prepared at (a) $W_0=4$ and (b) $W_0=7$ or 10. (·····) Nano-CdS in reverse micellar solution 1 min after formation; (–––) nano-CdS dispersed in DMSO, following surface-modification with 4-hydroxythiophenol; (—) nano-CdS in CdS–PU composite (absorption of PU was subtracted).

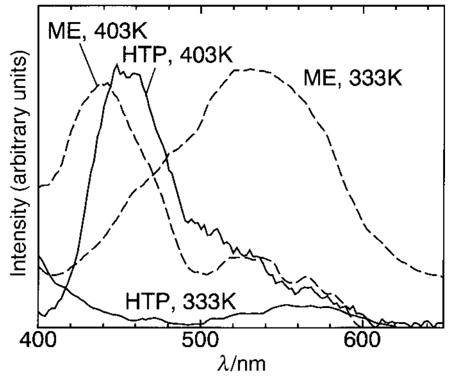

Fig. 2 Effect of thiols [4-hydroxythiophenol (HTP) or 2-mercaptoethanol (ME)] and polymerizing temperature (403 or 333 K) on fluorescence spectra of a CdS–PU film ($\lambda_{ex}=370$ nm).

interior, appeared after polymerization at 403 K. This 'activation' is likely to be caused by the heat treatment, since no emission peaks are observed following polymerization at the lower temperature of 333 K. Different fluorescent characteristics were observed by using an alternative thiol, 2-mercaptoethanol (ME), instead of HTP. An emission peak at *ca.* 530 nm was maintained, after surface-capping with ME and following polymerization at 333 K, whereas an emission peak at *ca.* 440 nm was seen when polymerization was carried out at 403 K. Thus, the fluorescent properties of CdS–PU composites can be altered, by choosing differing thiols and changing polymerization conditions. A similar thermal treatment for the CdS–PU transparent film is also viable. When the CdS–PU film prepared using ME at a polymerization temperature of 333 K was heated at 373 K, the emission at 530 nm decreased and the emission at 440 nm increased.

Photocatalytic generation of H_2 was carried out, according to the procedure employed in previous work,[1] using a 10 vol% propan-2-ol aqueous solution and photoirradiation using a 2 kW xenon lamp. Irradiation light with wavelengths <300 nm and light in the IR range was cut off by the Pyrex glass of the tube and by a water filter. Approximately 6 mg of the CdS–PU powder was dispersed in the solution (20 ml) by ultrasonication with sodium hexametaphosphate (0.01 g). The quantities of H_2 formed in the gas phase in the tube, measured by gas chromatography, are shown in Fig. 3. The CdS–PU prepared using ME generates a greater quantity of H_2, probably *via* the reduction of water with propan-2-ol as the sacrificial agent. The difference in the fluorescent properties is unlikely to affect the photocatalytic property in the present study, since the emission at 530 nm decreases and the emission at 440 nm increases during the initial stage (0–3 h) of photoirradiation using a 2 kW xenon lamp. Thus, the lower photocatalytic activity for CdS–PU prepared using HTP is mainly attributable to steric hindrance and surface hydrophobicity caused by surface modification by HTP molecules. No appreciable red-shift of the absorption onset for nano-CdS in CdS–PU was observed during the photoirradiation. This indicates that the nano-CdS particles in PU are much more stable than those immobilized in PUA.[1]

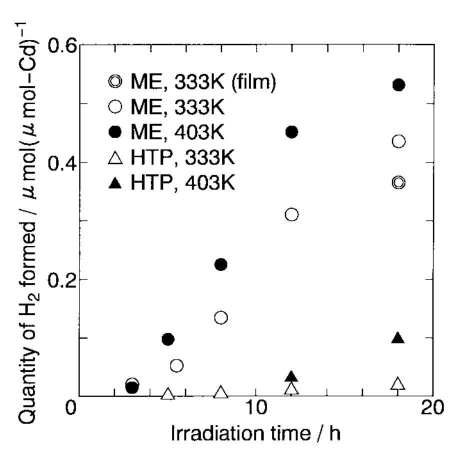

Fig. 3 Quantities of H_2 formed from a 10 vol% propan-2-ol aqueous solution by photoirradiation of dispersed CdS–PU powders or a CdS–PU film prepared inside a glass tube. Effect of thiols [4-hydroxythiophenol (HTP) or 2-mercaptoethanol (ME)] and polymerizing temperature (403 or 333 K).

The photocatalytic property of the CdS–PU film was also investigated. In this experiment, the film was prepared inside the glass tube, and then 20 ml of a 10 vol% propan-2-ol aqueous solution was introduced into the tube and was photoirradiated for 18 h. As shown in Fig. 3, the quantity of H_2 formed is slightly lower than that obtained for the powder, although the film contains the same quantity of CdS–PU (*ca.* 6 mg). Because the film is of *ca.* 15 μm thickness, a certain amount of nano-CdS buried in the PU film can not participate in the photocatalytic reaction. The CdS–PU film has, however, better transparency, which can be advantageous for optical utilization.

The present study thus describes a novel composite of nano-CdS and polyurethane, and resulting optical properties. This composite is advantageous for processing, *i.e.*, a transparent film can be made *via* dissolving the composite in an appropriate organic solvent and casting, and can thus be utilized for optical devices, as well as for photocatalysts in the powder form.

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