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Preparation of nano-CdS–polyurethane composites *via in situ* polymerization in reverse micellar systems

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Nano-CdS particles, formed in reverse micelles containing ethylene glycol, have been immobilized in polyurethane, *via* an *in situ* polymerization of ethylene glycol with hexamethylene diisocyanate: the resulting composite can be utilized as a photocatalyst and processed to make a transparent film.

There has been much recent interest in the preparation and processing of nanoparticles formed from various materials, including metals, metal sulfides, and oxides, based on reverse micellar systems. In previous papers, the thiol-mediated immobilization of nano-CdS particles, both in polythiourethane (PTU)[1,2] and polyurethane (PU),[3] have been investigated. The nano-CdS particles, when formed in reverse micelles, are recovered into toluene or DMSO, utilizing a surface modification with thiol molecules, and the dispersed particles are then immobilized in PTU or PU *via* the polyaddition of dithiol or ethylene glycol with diisocyanate. The resulting composites are then utilizable as photocatalysts for the generation of H_2, from propan-2-ol aqueous solution. These methods, however, require rather complicated procedures. In addition, binding of the thiol molecules inevitably affects the surface structure of the sulfide particles and thus passivates the surface sulfur vacancies.

An effective method of overcoming the above problems is to use an *in situ* formation of polymer supports for the nano-CdS particles in the reverse micellar system. The CdS and CdS–ZnS nanoparticles are immobilized in polyurea (PUA), by the simple addition of diisocyanate to the reverse micellar solution, *via* polymerization of the diisocyanate with the water in the micelles.[4,5] An *in situ* method of formation of polyurethane (PU) in the reverse micellar system has therefore been investigated, in order to develop a simpler method for the immobilization of the nanoparticles, formed in the micelles, into useful and processable polymer, PU. A reverse micellar system containing ethylene glycol, in place of water, has therefore been utilized for the preparation of nano-CdS and for reaction with added diisocyanate to give *in situ* formation of PU. Absorption spectrophotometry has been used to characterize the resulting CdS–PU composite and the composite has also been utilized as a photocatalyst.

The reverse micellar solution was prepared by dissolving $CdCl_2$-containing ethylene glycol in 0.1 $mol\ l^{-1}$ sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/isooctane (2,2,4-trimethylpentane) solution, where the symbol W_e is used to denote the molar ratio of ethylene glycol to AOT (= [ethylene glycol]/[AOT]). The nano-CdS particles were prepared in a glass vessel by introducing H_2S gas (0.1 $mmol\ l^{-1}$) into the reverse micellar solution (100 ml) containing 0.1 $mmol\ l^{-1}$ $CdCl_2$ and stirring for 1 h at 298 K. The manganese salt of naphthenic acid (*ca.* 27 mg) was then added to the micellar solution as a catalyst for the polymerization,[6] followed by the addition of hexamethylene diisocyanate (HDI) to a concentration of 0.01 $mol\ l^{-1}$. After stirring for 20 h, the formed polymer was collected by centrifugation, washed with *n*-hexane and diethyl ether and then dried *in vacuo* overnight.

Formation of the polymer was negligible in the absence of the naphthenic acid manganese salt. The polymer particles thus obtained coagulated irregularly and with sizes smaller than 1 mm. The IR absorption spectra for the polymer showed characteristic peaks, which are attributable to the urethane bond, at 1270 cm^{-1} (C–N, C–O), 1540 and 3330 cm^{-1} (N–H), and 1690 cm^{-1} (C=O). When the reverse micelles contain a water molecule, formation of polyurea occurs *via* the addition of HDI[4,5] and the resulting polymer is insoluble in DMSO. In the present case of ethylene glycol micelles, PU is formed, and the resulting PU is soluble in DMSO.

Nano-CdS particles were prepared as successfully in the ethylene glycol micelles, as in ordinary water reverse micelles,[7–9] and were successfully immobilized in PU prepared *in situ*. The absorption spectra for the CdS nanoparticles were recorded using a diode-array UV–visible spectrophotometer (Hewlett-Packard 8452A), as shown in Fig. 1. The results show that the absorption onset wavelength for the nano-CdS is controllable by means of changing the W_e value and that the onset wavelength is shifted towards the shorter wavelength region, as compared with that for bulk CdS materials (*ca.* 500 nm), owing to a quantum size effect. The diameter of the nano-CdS particles (d_p) was estimated using the absorption onset, according to the Brus equation[10] as shown in a previous paper.[9] In this way, the estimated size for the immobilized nano-CdS particles was determined to be *ca.* 4 nm at $W_e = 0.3$ and *ca.* 5 nm at $W_e = 0.5$. The Cd content of the CdS–PU composite was determined, following dissolution of a weighed CdS–PU powder in concentrated H_2SO_4 solution, by using an

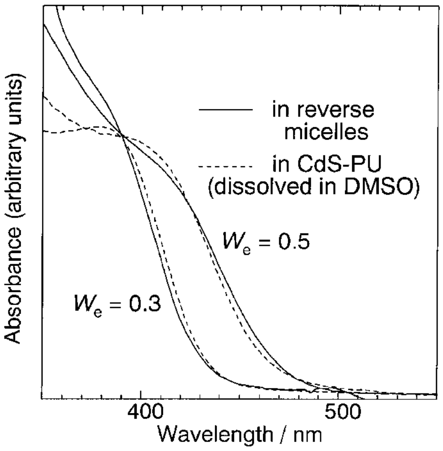

Fig. 1 Absorption spectra for nano-CdS in reverse micellar solution (solid lines, $W_e = 0.3$ or 0.5) and in CdS–PU (dotted lines, after dissolving in DMSO). Stirring time: 20 h.

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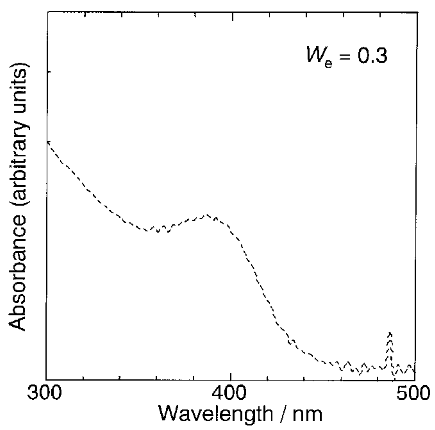

Fig. 2 Absorption spectrum for nano-CdS in CdS–PU film formed on a glass sheet.

inductively coupled argon plasma emission spectrometer (ICP-AES, Nippon Jarrell-Ash ICAP-575 Mark II). The Cd content was determined to be *ca.* 0.05 mmol Cd $(\text{g-CdS–PU})^{-1}$ at both $W_e = 0.3$ and 0.5. This value is lower than that obtained for CdS–PU, prepared using water reverse micelles and surface modification using thiol molecules.[3] This probably occurs owing to the lower CdS concentration of the micellar solution employed in the present study.

The photocatalytic generation of H_2 was carried out according to the procedure described in previous works.[3,4] Approximately 20 mg sample of CdS–PU composite was dispersed in 25 ml of a 10 vol% propan-2-ol aqueous solution, using ultrasonication. In this procedure, the propan-2-ol was employed as a sacrificial electron donor for the positive hole, photogenerated in nano-CdS. A 20 ml aliquot of this mixture was purged in a test tube with argon for 1 h, sealed with a septum, and then photoirradiated with a 2 kW xenon lamp (Ushio UXL-2003D-O) for 20 h. Irradiation light with wavelengths $\lambda < 300$ nm and wavelengths in the IR range were cut off respectively by means of the Pyrex glass tubing and by the water filter. When wavelengths greater only than 400 nm were required, the water filter was replaced by 10 wt% $NaNO_2$ aqueous solution. The quantity of H_2 formed in the gas phase of the tube was measured by gas chromatography (Shimadzu GC-14B), as described previously.[9] For wavelengths of $\lambda > 400$ nm, 0.70 mol H_2 $(\text{mol-Cd})^{-1}$ was generated, whereas for irradiation $\lambda > 300$ nm 1.30 mol H_2 $(\text{mol-Cd})^{-1}$ was produced. These values are superior to those obtained with CdS–PU prepared *via* surface modification with thiol molecules and where 0.53 mol H_2 $(\text{mol-Cd})^{-1}$ was generated during an 18 h irradiation at $\lambda > 300$ nm.[3] The present *in situ* polymerization method is thus effective in better realizing the photocatalytic properties of nano-CdS, since this method requires no surface modification of the CdS with thiol molecules which passivates the surface sulfur vacancies and thus substantially changes the particle surface characteristics.

A CdS–PU film was prepared, by casting a DMSO solution (0.5 ml) of CdS–PU (*ca.* 50 mg) onto a glass sheet, with drying *in vacuo* at 313 K. Since PU does not absorb visible light, an optically transparent film of *ca.* 20 µm thickness was thus obtained. The absorption spectrum for the nano-CdS in the resulting CdS–PU film is shown in Fig. 2. In this case, no red shift of the absorption onset wavelength is observed, as compared to that for the CdS–PU in DMSO (Fig. 1); thus indicating that both the particle size and the quantum size effect of the CdS nanoparticles are retained.

The present study thus describes a novel methodology for the preparation of composite nano-CdS and polyurethane. This composite is advantageous both for photocatalytic reactions and for processing, *i.e.*, a transparent film can be made by dissolving the composite in DMSO, followed by casting, and the material can thus be utilized for optical devices.

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