Immobilization of semiconductor nanoparticles formed in reverse micelles into polyurea *via in situ* polymerization of diisocyanates

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Nanoparticles of CdS, ZnS, TiO_2 or AgI, formed in reverse micelles, have been immobilized into polyurea *via in situ* polymerization of hexamethylene diisocyanate; the CdS– or ZnS–polyurea composites obtained were utilized as photocatalysts.

There has been much recent interest in the preparation and processing methods for nanoparticles formed from various materials, including metals,[1,2] metal selenides,[3] sulfides[1,3–8] and oxides,[9] using reverse micellar systems. One of the most powerful methods for recovering the metal sulfide particles is that of particle surface modification using thiols.[3,6–8] The binding of the thiols, however, passivates the surface sulfur vacancies of the sulfide particles, and may substantially change the particle surface characteristics. Moreover, thiol modification cannot be applied to metal oxides; some of which are no less important than sulfides as catalysts and photocatalysts. The present study describes a novel immobilization method for nanoparticles formed in reverse micelles into polymer particles synthesized *in situ*. Addition of a diisocyanate, which reacts with water to form polyurea,[10] to the reverse micellar solution leads to the formation of polyurea fine particles. This polymerization in the presence of nanoparticles formed *in situ* brings about the encapsulation of the nanoparticles into the formed polyurea particles.

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 for the nanoparticle preparation. CdS or ZnS nanoparticles were prepared by the rapid addition of an AOT–isooctane micellar solution {100 ml, W_0 (= $[H_2O]/[AOT]$) = 6} containing $Cd(NO_3)_2$ or $Zn(NO_3)_2$ to another micellar solution (100 ml, W_0 = 6) containing Na_2S and stirring vigorously with a magnetic stirrer at 298 K. A glass vessel covered with aluminium film and a final composition of $[S^{2-}] = [Cd^{2+}]$ or $[Zn^{2+}] = 6.0 \times 10^{-4}$ mol l^{-1} was used. Hexamethylene diisocyanate [HDI, 0.385 ml (0.0024 mol)] was added rapidly to the nanoparticle-containing reverse micellar solution 2 min after nanoparticle formation.

The broken lines in Fig. 1 represent the absorption spectra for (*a*) CdS and (*b*) ZnS nanoparticles, 1 min after their formation in the reverse micellar systems. The absorption spectra after the HDI addition gradually increased owing to the turbidity of the polyurea (PUA) formation in the solutions. After stirring for 18 h for CdS (19.5 h for ZnS) the nanoparticles were collected together with the formed polymer powder by centrifugation. The precipitate was washed with *n*-hexane and diethyl ether and dried *in vacuo* overnight. The CdS or ZnS nanoparticle–polyurea composites are denoted CdS–PUA or ZnS–PUA, and were yellow and white, respectively, reflecting the colour of the corresponding metal sulfide particles.

Polymerization in a water–acetone homogeneous system produced irregularly shaped PUA particles of *ca.* 1 µm in diameter. Fig. 2(a) shows an FE-SEM image for metal sulfide-free PUA particles formed in the reverse micellar system and in which the PUA has led to a rather ordered morphology consisting of twisted rods. Polymerization in the presence of CdS nanoparticles, however, produced fused rod-like aggregates [Fig. 2(b)]. The presence of nanoparticles or NO_3^- may also influence polymer morphology. The PUA particles showed IR absorption peaks (1260, 1570, 1650 and 3300 cm^{-1}) attributable to urea bonds. Elemental analysis for the CdS-free PUA gave: C, 58.5; H, 10.5; N, 17.5 (calc. C, 59.1; H, 9.92; N 19.7%). The polyurea and PUA composites were slightly soluble in *m*-cresol but insoluble in most organic solvents.

The solid lines in Fig. 1 represent the absorption spectra for CdS (*c*) and ZnS (*d*) nanoparticles in PUA composites (measurement was by diffuse reflectance, owing to the turbid disperison of PUA composites in the photoreaction solution, as described below). The red shifts of the absorption onset compared with spectra (*a*) and (*b*) of Fig. 1 are due to particle growth following HDI addition. The values of the band gap for immobilized CdS and ZnS, as calculated in a previous report[5] were 2.75 and 3.92 eV, respectively, which are larger than the bulk values for CdS (2.5 eV[11]) and ZnS (3.7 eV[11]) owing to the quantum size effect.[12] The diameter of the immobilized CdS and ZnS nanoparticles was estimated using the above obtained values and the Brus' equation,[12] as also in the previous report,[5] to be 4.70 and 4.37 nm, respectively.

The metal content of the PUA composites (total analysis) was determined[8] by decomposing a given quantity of a PUA composite in concentrated H_2SO_4 and measuring the eluted metal ions, using an inductively coupled argon plasma atomic emission spectrophotometer. Since the PUA was not decomposed in HCl (6 mol l^{-1}), only the exposed sulfide particles from the PUA composite were dissolved in the acid and this was also measured. The ratio of the partial dissolved quantity, obtained *via* contact with 6 mol l^{-1} HCl, to that of the total quantity obtained *via* H_2SO_4 decomposition is denoted as particle exposed fraction *F*.[8] Table 1 lists the total metal content and the particle exposed fraction for CdS–PUA and ZnS–PUA.

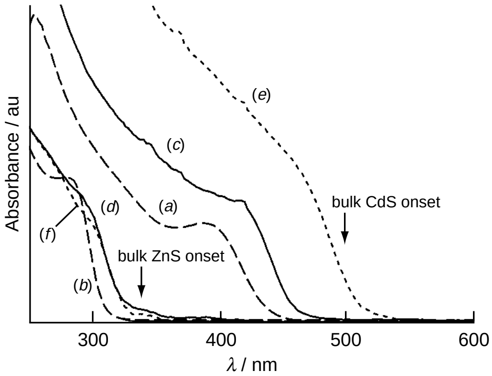

Fig. 1 Broken lines: absorption spectra of metal sulfide nanoparticles in reverse micellar systems 1 min after formation [(*a*) CdS; (*b*) ZnS]. (*c*)–(*f*): absorption spectra of metal sulfide nanoparticles immobilized in PUA composites [(*c*) and (*e*) CdS; (*d*) and (*f*) ZnS] before [solid lines, (*c*) and (*d*)] and after [dotted lines, (*e*) and (*f*)] photoirradiation for 18 h (diffuse reflectance spectra, scattering was subtracted).

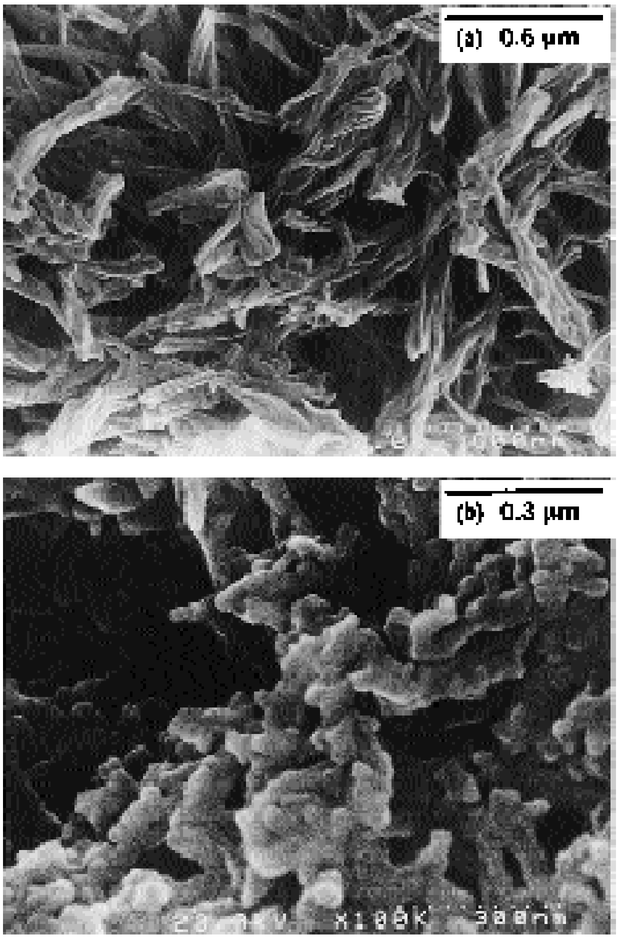

Fig. 2 SEM images for (a) metal sulfide-free PUA particles and (b) CdS–PUA prepared in a reverse micellar system

Table 1 Metal content and particle exposed fraction *F* of CdS–PUA and ZnS–PUA composites and results of photocatalytic H_2 generation

			H_2 formed (18 h irradiation)	
PUA composite	Total Cd or Zn content/ µmol (mg PUA composite)$^{-1}$	*F*	µmol (mg PUA composite)$^{-1}$	µmol (µmol exposed Cd or Zn)$^{-1}$
CdS–PUA	1.71	0.969	2.63	1.59
ZnS–PUA	1.56	0.866	8.56	6.34
CdS–PUA	1.71	0.969	0.0077	0.0047[a]
CdS-free PUA	—	—	0	—

[a] No propan-2-ol present.

The values of *F* obtained for both approach unity, thus indicating almost all sulfide nanoparticles are more or less exposed to the external solution.

Photocatalytic generation of hydrogen on the CdS–PUA or ZnS–PUA composites in a 10 vol% propan-2-ol aqueous solution was demonstrated. Such experiments, *ca.* 4 mg of PUA composite was dispersed in 25 ml of a 10 vol% propan-2-ol aqueous solution by ultrasonication with sodium hexametaphosphate (0.0125 g). 20 ml of this mixture was purged with argon for 1 h, sealed with a septum and photo-irradiated with a 2 kW xenon lamp. Irradiation light with wavelength < 300 nm and light in the IR range was cut off by the Pyrex glass of the tube and by the water filter, respectively. The quantity of H_2 formed in the gas phase in the tube was measured by gas chromatography.

The quantities of H_2 formed during the photo-irradiation of CdS–PUA or ZnS–PUA are also listed in Table 1. The H_2 generation with the PUA composites, probably *via* the reduction of water with propan-2-ol as the sacrificial agent, is very prominent as compared with the results of control experiments. ZnS–PUA is superior to CdS–PUA under the present experimental conditions, owing to the greater reducing ability of the conduction band electrons in ZnS than in CdS.

The dotted lines in Fig. 1 show the absorption spectra (diffuse reflectance spectra) for CdS–PUA (*e*) and ZnS–PUA (*f*) after photo-irradiation. The absorption onset for CdS–PUA shifts towards a longer wavelength and appears to reach that of bulk CdS, thus indicating photo-induced CdS growth *via* the fusion of CdS particles adjacent to each other in the PUA composites. The band gap for the CdS particles, after photo-irradiation, was calculated to be 2.5 eV, the same as that for bulk CdS. On the other hand, a relatively small red shift is seen for ZnS–PUA, with the band gap for the ZnS particles in ZnS–PUA after the photo-irradiation being calculated as 3.86 eV, which is larger than the bulk value of 3.7 eV.

The HDI polymerization method was also applied to nanoparticles of TiO_2 and AgI. These nanoparticles were prepared in AOT–isoocatane systems as described previously.[9,13] The nanoparticles of TiO_2 or AgI were also easily recovered from the micellar system *via in situ* polymerization of HDI and centrifugation, although the method for measuring the particle exposed fraction could not be employed in these cases.

The present study thus describes a novel immobilization method for semiconductor nanoparticles formed in reverse micelles into polyurea *via in situ* polymerization of hexamethylene diisocyanate. This may prove to be a universal method applicable to nanoparticles of any material formed in reverse micellar systems, since the surface properties of the target nanoparticles can be chosen freely. The effect of micellar conditions on PUA morphology and the photocatalytic properties of metal sulfide–PUA materials is worthy of further study.

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