

# Size-Selective Incorporation of CdS Nanoparticles into Mesoporous Silica

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CdS nanoparticles, prepared in reverse micellar systems, were incorporated into thiol-modified MCM-41 (FM41) mesoporous material, of differing pore sizes, designated as large (L-FM41), middle (M-FM41), and small (S-FM41). A particle-sieving effect of the FM41 was observed, in that the incorporation of the CdS nanoparticles was decreased by increased size of particle, and by a decreasing pore size of the FM41. The resulting CdS–FM41 composite showed photocatalytic activity for H<sub>2</sub> generation from water.

## Introduction

There has been much recent interest in the utilization of the pores of mesoporous silica, such as MCM-41, as catalytic reaction fields. Metal oxide catalysts, such as Fe<sub>2</sub>O<sub>3</sub><sup>1</sup> and TiO<sub>2</sub>,<sup>2–4</sup> are prepared mostly via the adsorption or impregnation of the metallic precursor, or by the chemical modification of mesopores, followed by thermal oxidation. Xu and Langford have reported on the preparation of TiO<sub>2</sub>-incorporated MCM-41 photocatalyst by adding MCM-41 into TiO<sub>2</sub> sol.<sup>5</sup> However, the size-selectivity of the mesopores for the nanoparticles was not described. The present study concerns a “particle-sieving effect” of mesoporous silica. In this, CdS nanoparticles, prepared in reverse micellar systems, are incorporated selectively according to size into thiol-modified MCM-41.

## Experimental Section

MCM-41 was prepared via a procedure similar to that reported by Cheng et al.<sup>6</sup> The pore size of the MCM-41 was controlled by changing the reaction time (1–2 day) at 343–438 K and aging time<sup>7</sup> (0–7 day) at 423 K, as shown in Table 1. The functionalization of the MCM-41 with surface thiol groups was carried out using tris(methoxy)mercaptopropylsilane, as reported by Feng et al.<sup>8</sup> for the synthesis of 75% functionalized monolayers on mesoporous support (FMMS) samples. The resulting thiol-modified MCM-41 powders, denoted hereafter as L-, M-, and S-FM41, representing large, medium, and small pore sizes, respectively, were approximately 17 μm in size. The *d*<sub>100</sub> values and pore size of these FM41 samples were determined by XRD (Philips, PW-3050) and N<sub>2</sub> adsorption (Bel Japan Inc., Belsorp28SP) analyses, respectively.

CdS nanoparticles were prepared in a reverse micellar system consisting of sodium bis(2-ethylhexyl)sulfosuccinate (AOT, 0.1 mol/L), water, and isooctane (2,2,4-trimethylpentane). An AOT–isooctane reverse micellar solution of the required water content, *W*<sub>0</sub> = [H<sub>2</sub>O]/[AOT], containing 0.2 mmol/L Cd(NO<sub>3</sub>)<sub>2</sub> was added rapidly to another micellar solution of the same *W*<sub>0</sub>

containing 0.1 mmol/L Na<sub>2</sub>S and stirred vigorously by magnetic stirrer at 298 K in a glass vessel. Two minutes following the formation of the CdS nanoparticles, 0.04 g of FM41 was added to 20 mL of the reverse micellar solution, stirred for 12 h, and separated by centrifugation. The percentage incorporation of the CdS nanoparticles was determined by subtracting the absorbance of CdS in the supernatant from that in the feed micellar solution.

## Results and Discussion

The absorption spectra for CdS nanoparticles in reverse micellar solution are shown in Figure 1. Although the CdS particles grow in the micelles during the 12-h stirring procedure, they still show a quantum size effect, as shown by the blue-shift of the absorption onset compared with that for bulk CdS (500 nm). The addition of L-MCM-41 suppresses the growth of CdS slightly, probably because of the decrease in the value of *W*<sub>0</sub>, caused by adsorption of water into the mesopores. In the case of the addition of L-FM41, the absorption corresponding to the CdS nanoparticles disappears, indicating that the CdS nanoparticles are incorporated via chemical bonding between the thiol groups on the FM41 and excess Cd<sup>2+</sup> ions on the CdS nanoparticles. Diffuse reflectance spectra of the resulting FM41, measured following the incorporation of CdS nanoparticles, separation, and redispersion in water, show the characteristic absorption of size-quantized CdS, as shown in Figure 2. The incorporation of the CdS, prepared at *W*<sub>0</sub> = 3, was confirmed by EDX analysis after burying L-FM41 in an epoxy resin and slicing this with a rotary microtome, since the signal corresponding to Cd was obtained from the cross section of the impregnated L-FM41 contacted with CdS nanoparticles, but not from an empty L-FM41.

As shown in Figure 3, the percentage incorporation is affected remarkably by the *W*<sub>0</sub> value of reverse micellar solution. The percentage incorporation decreases progressively with increasing *W*<sub>0</sub> for L-FM41, while for M-FM41 incorporation hardly occurs at *W*<sub>0</sub> > 3, even though M-FM41 has greater quantity of surface thiol groups than L-FM41 (Table 1). Thus, this is attributable to a “particle-sieving effect” for the FM41, since smaller CdS particles are formed in the reverse micellar system of lower *W*<sub>0</sub>.<sup>9,10</sup> Estimated diameters for the CdS particles after 12-h stirring, calculated using Brus’ equation<sup>11</sup> from the absorption onsets, are 3.04 (*W*<sub>0</sub> = 2), 3.29 (*W*<sub>0</sub> = 3), 3.58 (*W*<sub>0</sub> = 4), and

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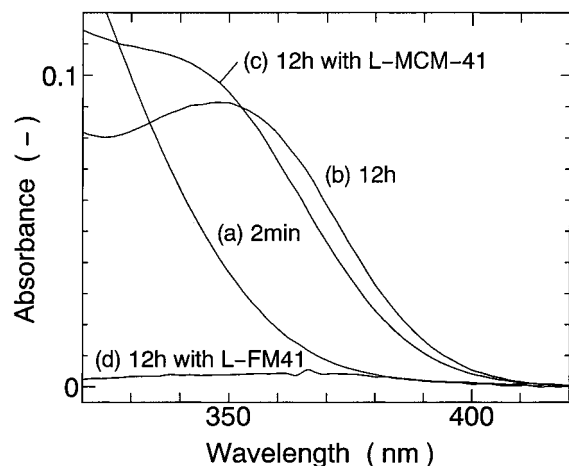
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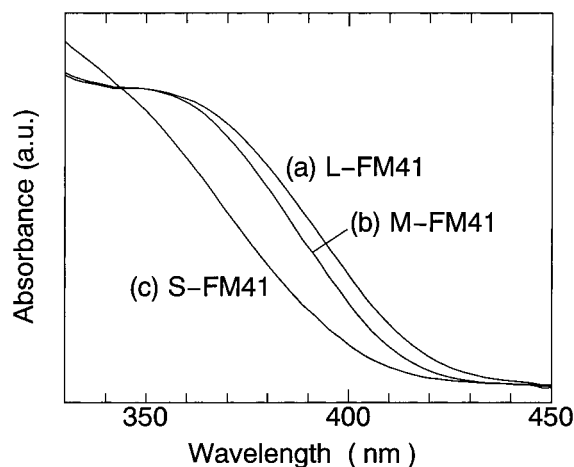
**TABLE 1: Preparation Conditions and Resultant Properties of the Large (L-), Medium (M-), and Small (S-) Pore Size Thiol-Mediated MCM-41 (FM41) Powders<sup>a</sup>**

	reaction time (day)	reaction temp. (K)	aging time (day)	$d_{100}$ (nm)	pore size (nm)	quantity of -SH (mol/g-FM41)	H <sub>2</sub> formed ( $\mu\text{mol}/\mu\text{mol CdS}$ )	
							with 2-propanol	without 2-propanol
L-FM41	2	438	7	5.67	3.8	0.30	1.43	1.23
M-FM41	2	423	0	4.62	3.6	0.36	1.03	0.71
S-FM41	1	343	0	3.87	2.0	0.73	0.23	0.09

<sup>a</sup> The CdS nanoparticles were prepared at  $W_0 = 2$ .  $d_{100}$  values were determined by XRD analysis, pore sizes were determined by N<sub>2</sub> adsorption analysis, and the quantity of thiol group was determined by iodometric titration. The quantities of H<sub>2</sub> formed were those generated by 48 h of photo irradiation in water with and without 15 vol % 2-propanol.

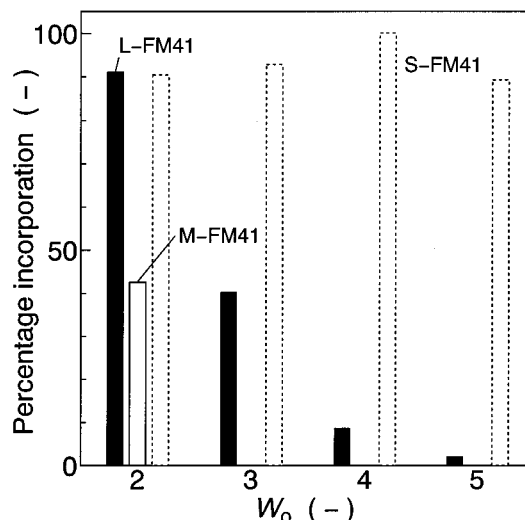


**Figure 1.** Absorption spectra for CdS nanoparticles in reverse micellar solution ( $W_0 = 2$ ): (a) 2 min after formation, (b) following 12 h of stirring without mesoporous silica, (c) following 12 h of stirring with L-MCM-41, and (d) following 12 h of stirring with L-FM41.



**Figure 2.** Diffuse reflectance spectra of CdS nanoparticles prepared at  $W_0 = 2$  and incorporated in (a) L-FM41, (b) M-FM41, and (c) S-FM41, measured after dispersion in water.

3.73 ( $W_0 = 5$ ) nm, respectively. Smaller CdS particles are incorporated more easily into the mesopores of the FM41. The incorporation is also more obvious for the case of L-FM41 having the larger pores (3.8 nm in diameter). The diffuse reflectance spectra (a) and (b) in Figure 2 show that an additional red-shift in the absorption onset, compared with spectrum (b) in Figure 1, is observed for CdS in L- and M-FM41 and especially for L-FM41. The particle sizes estimated from the absorption onset are 3.30 and 3.20 nm for impregnated L- and M-FM41, respectively; which values are slightly smaller than the corresponding pore sizes. Therefore, CdS nanoparticles incorporated in the L- and M-FM41s are likely to grow slightly and to retain the quantum size effect.



**Figure 3.** Percentage incorporation of CdS nanoparticles prepared in reverse micellar systems at various  $W_0$  values for L-, M-, and S-FM41.

Referring again to Figure 3, however, for the case of S-FM41, more than 90% of the CdS particles, irrespective of  $W_0$  value, are incorporated, although the size of the CdS particles prepared at  $W_0 = 2-5$  is greater than the pore size (2.0 nm). This is explained by XRD analysis and N<sub>2</sub> adsorption measurement which showed that S-FM41 had a lower crystallinity and macropores of 20–40 nm in diameter. Thus, CdS nanoparticles are probably incorporated in the macropores, rather than in the mesopores. This explanation seems to be consistent with the suppression of the growth of CdS particles incorporated in S-FM41, as compared with the cases of L- and M-FM41 and shown in Figure 2. The relatively rapid and sparse incorporation of CdS nanoparticles into S-FM41 may suppress the particle growth.

The photocatalytic generation of H<sub>2</sub> on CdS–FM41 in water, with or without 15 vol % 2-propanol, is demonstrated, under similar conditions to those of a previous study for CdS– and ZnS–polyurea composites,<sup>12</sup> except for hexametaphosphate which was not used in the present case. The quantities of H<sub>2</sub> formed during photoirradiation are listed in Table 1. The highest photocatalytic property is obtained with the highest pore size of the FM41. This pore-size dependency is consistent with previous reports concerning photocatalytic CO<sub>2</sub> reduction on TiO<sub>2</sub>–MCM-41 and MCM-48,<sup>4</sup> and the photoionization of porphyrins in MCM-41.<sup>13</sup> It is noteworthy that H<sub>2</sub> generation also occurs in the absence of 2-propanol, which acts as hole scavenger, without appreciable O<sub>2</sub> generation.

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