

Preparation of Novel Silica–Cadmium Sulfide Composite Nanoparticles Having Adjustable Void Space by Size-Selective Photoetching

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Surface coating of nanoparticles with various materials to form core–shell morphologies results in the formation of materials that can be used for development of catalysts and optoelectronic devices.^{1–8} The core–shell structures have also been used as precursors to prepare hollow structures by the complete removal of core materials through chemical etching or combustion,^{1b,c,4b,9,10} and partial elimination of the core has enabled preparation of novel nanostructures inside the shell.^{11,12} However, precise control of the interior structure is very difficult.

We have recently reported the size-selective photoetching technique as a means for preparing monodisperse CdS nanoparticles in the size quantization regime by which the particle size is simply determined by the wavelength of monochromatic light and can be controlled within the range of 3.5–1.7 nm by changing the wavelength of irradiation light within the range of 488–365 nm.¹³ This technique is also applicable to core-size control even after core–shell structures have been constructed, but this has not been attempted. Here, we report the advantage of the size-selective photoetching technique for precise modification of core size after preparation of CdS core and silica shell structures. The resulting particles have an adjustable void space inside the silica shell that depends on the CdS core size.

CdS nanoparticles in inverse micelles were prepared by a method similar to previously reported methods.^{7b,14} A 1.3 cm³ portion of 1.0 mol dm⁻³ aqueous Cd(ClO₄)₂ solution or that of 1.0 mol dm⁻³ aqueous Na₂S solution was added separately to 200 cm³ of heptane solution containing 14 g of sodium di(2-ethylhexyl) sulfosuccinate and 5.7 cm³ of water. After each of the solutions had been stirred for 1 h, they were mixed together, resulting in the formation of CdS nanoparticles in the inverse micelles. An additional 0.26 cm³ portion of 1.0 mol dm⁻³ aqueous Cd(ClO₄)₂ solution was added to the solution, and the solution was stirred for another 1 h, and then the solvent was removed by the vacuum evaporation. After dissolution of the resulting solid in 400 cm³ toluene, 1.1 mmol of 3-mercaptopropyltrimethoxysilane (MPTS) was added to modify the CdS surface, and then the solution was stirred for several hours. Hydrolysis of the trimethoxysilyl group was performed by dropwise addition of 400 cm³ of water to the refluxed solution of MPTS-modified CdS solution, resulting in the precipitation of silica-coated CdS nanoparticles. The obtained CdS core–silica shell nanoparticles were washed with methanol several times and vacuum-dried and then were subjected to size-selective photoetching by using monochromatic light with wavelengths of 514, 488, 458, and 436 nm.^{13a} Eighty milligrams of the obtained powder particles was suspended in a 50 cm³ oxygen-saturated aqueous solution containing

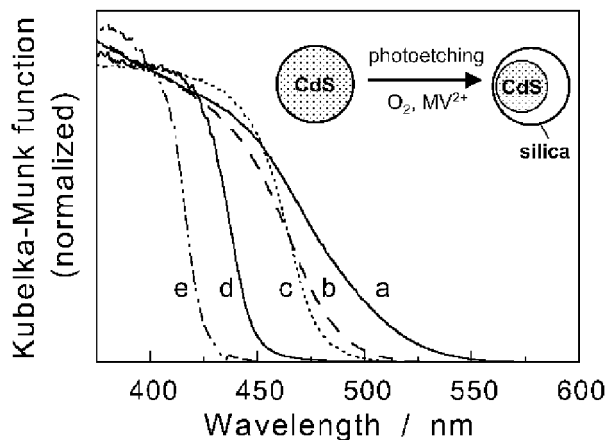


Figure 1. Diffuse reflectance spectra of silica-coated CdS nanoparticles prepared by irradiation with various wavelengths: original core–shell particles (a) and nanoparticles prepared by irradiation at (b) 514, (c) 488, (d) 458, and (e) 436 nm. Spectra were normalized at 400 nm. (Inset) Schematic illustration of photoetching of a silica-coated CdS nanoparticle.

50 $\mu\text{mol dm}^{-3}$ methyl viologen (MV^{2+}) that acts as an electron relay from CdS nanoparticles to oxygen molecules^{13d} and was irradiated with monochromatic light at various wavelengths.

FT-IR analyses of original particles revealed that an absorption band assigned to S–H vibration at 2560 cm^{-1} observed for MPTS was absent, but broad absorption bands due to Si–O–Si vibrations (ca. 1120, 1040, and 900 cm^{-1})¹⁵ were developed, suggesting that modification of Cd²⁺ sites of CdS surface with MPTS was achieved by Cd–SR bond formation and the hydrolysis of the trimethoxysilyl group of MPTS formed Si–O–Si networks that composed the shell structure. Figure 1 shows diffuse reflectance spectra of silica-coated CdS nanoparticles before and after irradiation of monochromatic light. Diffuse reflectance spectra of the original nanoparticles exhibited an absorption onset around 550 nm, indicating that most of CdS particles incorporated in the silica shells possessed an energy gap similar to that of the bulk material. With monochromatic light irradiation, the diffuse reflectance spectra of the resulting nanoparticles were blue-shifted. The absorption onset of each spectrum agreed well with the wavelength of irradiation light used, suggesting that the photocorrosion of CdS nanoparticles proceeded until the nanoparticles could not absorb the light due to an increase in the energy gap along with a decrease in the particle size (i.e., the size quantization effect). These results indicated that size-selective photoetching of silica-coated CdS nanoparticles can be successfully performed and that the size of the resulting CdS nanoparticles is adjustable by varying the wavelength of the monochromatic light, as already reported for CdS particles without a silica shell in our previous reports.¹³ When the monochromatic light at 458 nm was

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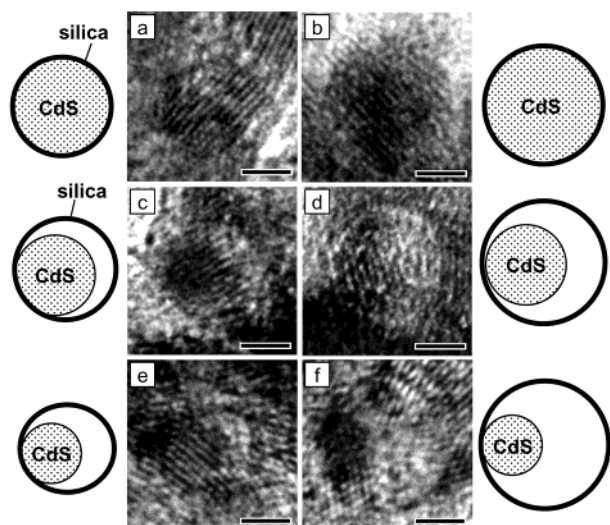


Figure 2. TEM images of typical silica-coated CdS nanoparticles. Original nanoparticles (a, b), and those prepared by irradiation at 514 (c, d) and 458 nm (e, f). Schematic illustration of the structure of each nanoparticle is also shown beside the corresponding TEM image. The bars in the pictures represent a length of 2 nm.

irradiated to CdS nanoparticles modified with 2-mercaptoethanesulfonate or 2-mercaptoethanol that had no cross-linking between the modifiers, the complete photocorrosion of CdS occurred without exhibiting any blue-shift of absorption onset, that is, the photoetched CdS nanoparticles were unstable and coalesced with each other to form larger particles that were subjected to further photocorrosion. Considering these facts, the results shown in Figure 1 suggest that the silica shell surrounding a photoetched CdS nanoparticle prevents the coalescence between nanoparticles.

Figure 2 shows typical high-resolution TEM images of silica-coated CdS nanoparticles. The CdS nanoparticles observed were almost spherical and had clear lattice fringes with interplanar spacing of 0.33 nm assigned to the (111) planes of the CdS cubic crystal structure. The results of electron diffraction analyses revealed that CdS nanoparticles had a cubic crystal structure. The original CdS nanoparticles seemed to be in close contact with the amorphous silica shell, leaving almost no clearance (Figure 2a,b), although some of the shell was difficult to identify due to poor contrast at the boundaries between the CdS surface and the silica shell. On the other hand, it was clear that the monochromatic light irradiation caused a decrease in the size of the CdS core particles but the shell structure seemed to be unchanged irrespective of the wavelength of irradiated light, resulting in a void space formation between the photoetched core particle and the shell (Figure 2c–f). Elemental analyses with energy-dispersive X-ray spectrometry performed at the same time as the TEM observation (electron probe diameter, ca. 1 nm) revealed that the atom ratios of Cd/Si and S/Si of the core part of a TEM image were 0.82 and 1.9, respectively, reflecting the chemical composition of both the core and the shell through which an electron probe was transmitted. By subtracting S/Si ratio of MPTS (1.0) from that experimentally obtained, the S/Si ratio originating only from the core was estimated, and then Cd/S ratio of the core could be calculated to 0.91, indicating almost stoichiometric composition of CdS. In contrast, smaller Cd/Si and S/Si ratios of 0.17 and 1.4, respectively, were observed for the shell and its inner vicinity. The fact suggested that the shell was porous and the large fraction of Cd²⁺ and SO₄²⁻ released by the CdS photocorrosion could escape from the inside of the shell.

The size distributions of CdS nanoparticle cores before and after irradiation were determined by TEM measurements (more than 100

particles) (see Supporting Information). The original CdS core had an average diameter (d_{av}) of 5.0 nm with standard deviation (σ) of 0.79 nm. The irradiation caused disappearance of the large CdS particles found in the original nanoparticles and induced the formation of smaller CdS nanoparticles with a decrease in the wavelength of irradiated light, where the irradiation at 514 and 458 nm produced the CdS nanoparticle with d_{av} (σ) of 3.7 (0.33) and 2.8 nm (0.21 nm), respectively. On the other hand, d_{av} (σ) of silica shell estimated after irradiation at 514 and 458 nm were 5.1 (0.62) and 5.2 nm (0.81 nm), respectively, being similar to or even a little larger than that of the original CdS nanoparticle used as a core. The differences between the average size of the photoetched CdS nanoparticles and that of their silica shells were calculated to be ca. 1.4 and 2.4 nm with the irradiation at 514 and 458 nm, respectively, and might correspond to an average void space available in the shells. These results indicated that the size-selective photoetching technique could adjust the void space formed in the core–shell structure by choosing the wavelength of irradiation light. The regulation of void space will be useful for the purpose of applications, such as catalytic reaction sites and fabrication of metal–semiconductor nanojunctions. Work in this direction is currently in progress.

Supporting Information Available: The size distributions of CdS nanoparticle cores before and after irradiation and those of the silica shell (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Wang, W.; Asher, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 12528. (b) Chang, S. Y.; Liu, L.; Asher, S. A. *J. Am. Chem. Soc.* **1994**, *116*, 6739. (c) Chang, S. Y.; Liu, L.; Asher, S. A. *J. Am. Chem. Soc.* **1994**, *116*, 6745.
- (2) (a) Hara, M.; Lean, J. T.; Mallouk, T. E. *Chem. Mater.* **2001**, *13*, 4668. (b) Keller, S. W.; Johnson, S. A.; Brigham, E. S.; Yonemoto, E. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1995**, *117*, 12879.
- (3) (a) Mulvaney, P.; Liz-Marzan, L. M.; Giersig, M.; Ung, T. *J. Mater. Chem.* **2000**, *10*, 1259. (b) Ung, T.; Liz-Marzan, L. M.; Mulvaney, P. *J. Phys. Chem. B* **2001**, *105*, 3441. (c) Liz-Marzan, L. M.; Giersig, M.; Mulvaney, P. *Langmuir* **1996**, *12*, 4329.
- (4) (a) Caruso, F. *Adv. Mater.* **2001**, *13*, 11. (b) Caruso, R. A.; Susha, A.; Caruso, F. *Chem. Mater.* **2001**, *13*, 400.
- (5) Mews, A.; Eychmueller, A.; Giersig, M.; Schooss, D.; Weller, H. *J. Phys. Chem.* **1994**, *98*, 934.
- (6) (a) Kamat, P. V.; Shanghavi, B. *J. Phys. Chem. B* **1997**, *101*, 7675. (b) Bedja, I.; Kamat, P. V. *J. Phys. Chem.* **1995**, *99*, 9182.
- (7) (a) Dabbousi, B. O.; Rodriguez-Viejo, J.; Mikulec, F. V.; Heine, J. R.; Mattoussi, H.; Ober, R.; Jensen, K. F.; Bawendi, M. G. *J. Phys. Chem. B* **1997**, *101*, 9463. (b) Kortan, A. R.; Hull, R.; Opila, R. L.; Bawendi, M. G.; Steigerwald, M. L.; Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1990**, *112*, 1327.
- (8) Gerion, D.; Pinaud, F.; Williams, S. C.; Parak, W. J.; Zanchet, D.; Weiss, S.; Alivisatos, A. P. *J. Phys. Chem. B* **2001**, *105*, 8861.
- (9) (a) Marinakos, S. M.; Anderson, M. F.; Ryan, J. A.; Martin, L. D.; Feldheim, D. L. *J. Phys. Chem. B* **2001**, *105*, 8872. (b) Marinakos, S. M.; Novak, J. P.; Brousseau, L. C.; House, A. B.; Edeki, E. M.; Feldhaus, J. C.; Feldheim, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 8518.
- (10) (a) Dick, K.; Dhanasekaran, T.; Zhang, Z. Y.; Meisel, D. *J. Am. Chem. Soc.* **2002**, *124*, 2312. (b) Makarova, O. V.; Ostafin, A. E.; Miyoshi, H.; Norris, J. R.; Meisel, D. *J. Phys. Chem. B* **1999**, *103*, 9080.
- (11) (a) Rodriguez-Gonzalez, B.; Salgueirino-Maceira, V.; Garcia-Santamaria, F.; Liz-Marzan, L. M. *Nano Lett.* **2002**, *2*, 471. (b) Giersig, M.; Ung, T.; Liz-Marzan, L. M.; Mulvaney, P. *Adv. Mater.* **1997**, *9*, 570.
- (12) (a) Sun, Y. G.; Mayers, B. T.; Xia, Y. N. *Nano Lett.* **2002**, *2*, 481. (b) Yin, Y.; Lu, Y.; Gates, B.; Xia, Y. *Chem. Mater.* **2001**, *13*, 1146.
- (13) (a) Torimoto, T.; Kontani, H.; Shibutani, Y.; Kuwabata, S.; Sakata, T.; Mori, H.; Yoneyama, H. *J. Phys. Chem. B* **2001**, *105*, 6838. (b) Miyake, M.; Torimoto, T.; Sakata, T.; Mori, H.; Yoneyama, H. *Langmuir* **1999**, *15*, 1503. (c) Torimoto, T.; Nishiyama, H.; Sakata, T.; Mori, H.; Yoneyama, H. *J. Electrochem. Soc.* **1998**, *145*, 1964. (d) Matsumoto, H.; Sakata, T.; Mori, H.; Yoneyama, H. *J. Phys. Chem.* **1996**, *100*, 13781.
- (14) Torimoto, T.; Maeda, K.; Maenaka, J.; Yoneyama, H. *J. Phys. Chem.* **1994**, *98*, 13658.
- (15) (a) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley & Sons: New York, 1980. (b) Buining, P. A.; Humbel, B. M.; Philipse, A. P.; Verkleij, A. J.; *Langmuir* **1997**, *13*, 3921.

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