Abs. 1577, 206th Meeting, © 2004 The Electrochemical Society, Inc.

Preparation of Silica-coated Cadmium Sulfide Nanoparticles Having Anisotropic Shapes and Their Photochemical Properties

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The structural control of size-quantized semiconductor nanoparticles has been intensively studied in recent years, because their physicochemical properties are greatly dependent on the shape and size of particles. Recently, we reported(1,2) that the size-selective photoetching technique enabled to modify the core-shell structure of spherical silica (SiO_2)-coated cadmium sulfide (CdS) (SiO_2/CdS) nanocomposites; the size of CdS core particles could be adjusted from 3.7 to 2.8 nm by changing the wavelength of monochromatic light used in the size selective photoetching from 514 to 458 nm, respectively, while the shape and size of SiO_2 shell were unchanged. Here we report the preparation of core-shell structure using CdS nanoparticles having an anisotropic shape (rod shape). The obtained particles were subjected to the size selective photoetching to modify the structure of CdS nanorod core.

CdS nanorods were prepared following reported procedures.(3) The surface of CdS nanorods was modified by 3-mercaptopropyltrimethoxysilane, followed by the hydrolysis of trimethoxysilyl groups to form SiO_2 shell structure (SiO_2/CdS). The obtained particles were suspended in an oxygen-saturated aqueous solution and then subjected to the size selective photoetching by using laser light of wavelength at 488 and 458 nm.

TEM observation revealed that CdS nanorods had an average width of 3.4 nm with an aspect ratio of ca. 9. CdS nanorod as prepared had an absorption onset at 500 nm, which was the same as that obtained after SiO_2 coating. This fact indicated that the shape and size of CdS rod were not changed significantly by the surface modification procedures. Figure 1 shows the diffuse reflectance spectra of SiO_2/CdS prepared by irradiation at various wavelengths. With the monochromatic light irradiation, the absorption onset was gradually blue-shifted and finally agreed well with the wavelength of irradiation light. It has been reported that the energy gap of semiconductor nanorods increases with a decrease in the width rather than length of the nanorod due to the size quantization effect.(4) Therefore, the results in Fig. 1 suggested that thick CdS nanorods were photoetched to thinner ones as shown in Scheme 1, until the irradiated photons were not absorbed by the photoetched nanoparticles owing to an increase in the energy gap. Furthermore, since the photoetched particles were stable and did not coalesce with each other, SiO_2 shells surrounding CdS nanorods maintained their structure after the photoetching.

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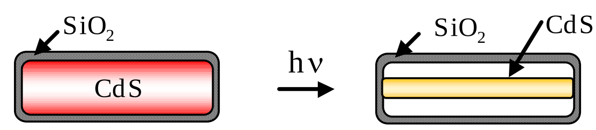

Scheme 1. Schematic illustration of size-selective photoetching of SiO_2/CdS.

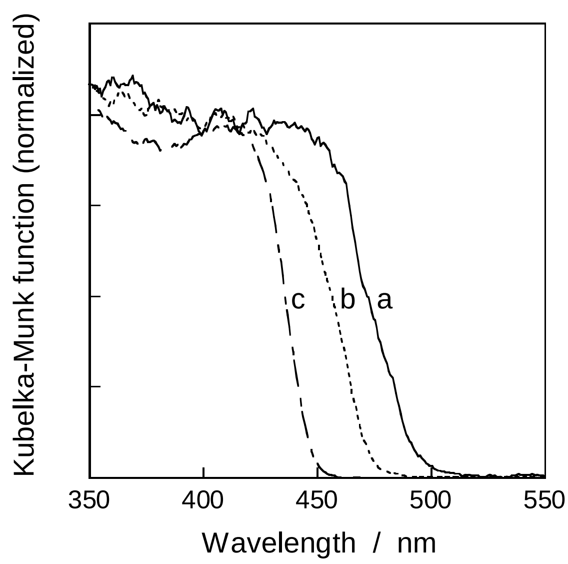

Fig. 1. Diffuse reflectance spectra of SiO_2/CdS prepared by irradiation at various wavelengths: (a) original particles and nanoparticles prepared by irradiation at (b) 488 and (c) 458 nm.