

## Novel fabrication of silica nanotube by selective photoetching of CdS nanorod template

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### Abstract

CdS/silica core–shell nanorod was prepared by silica coating over the CdS nanorod template of which the surface was initially capped by (3-mercaptopropyl)trimethoxysilane. The silica nanotube with both ends closed was fabricated from the core–shell nanorod by selective photoetching of the core CdS nanorod template with controlled photon energy in the oxygen-saturated aqueous solution including methyl viologen.

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### 1. Introduction

One-dimensional (1D) nanotube is one of the most attractive target materials in the nanoscience due to its novel structural, optical, and electrical properties. Until now, a variety of nanotubes have been developed with the various functional components of metals, semiconductors, insulators, and organics [1–5]. Among them, silica nanotube has recently attracted special attentions in the fields of nanoscience and technology [6,7]: Since the silica nanomaterials can easily be modified with functional molecular systems, they can potentially be utilized as basic platform to build up more complex hybrid nanocomposites. Especially, hollow silica nanotube is of unique nanosystem that can afford encapsulation of optically active molecules inside of its tubular nanospace. In the tubular nanospace, it was previously reported that excited state properties of encapsulated molecules were dramatically modified [8,9], which consequently endow this hybrid nanotubular system with a potential to utilize as linear/non-linear optical nanomaterials.

To date, the reported silica nanotubes have been fabricated with the typical templating method by utilizing the nanotemplates of porous alumina [6,10,11] and nanorod or nanowire [12–14]. Such templating method has the advantages of fine tunability of both the diameter and length of the resulting silica nanotube. In the templating

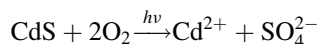
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methods, the silica nanotubes are obtained after the template removal. So far, the template removal process has mostly been done with the conventional chemical methods.

In this study, for the preparation of the silica nanotube, a photon-induced etching process, so-called photoetching, was utilized to remove the inside nanotemplate from the outer silica nanotube with the controlled photon energy. The great advantage of utilizing the photon is the control ability of the etching energy compared with the conventional chemical process. Such control ability of the etching energy can provide the efficient selectivity in the species to be removed and, furthermore, the quantitative degree of the removal amount of a particular component.

Previously, it was reported that some of inorganic semiconductors were dissolved in aqueous solution with the light irradiated [15–17]. Among the photodissociable semiconductors, the CdS has frequently been studied due to its well-known physical and chemical properties. The overall photoetching reaction for the CdS can be expressed as follows [16–18]:



where the  $h\nu$  is the photon energy which is higher than the band-gap energy of the CdS. In the photoetching process, it is known that the photogenerated hole works as a critical factor in the etching of the CdS and the electron–hole recombination generally reduces the quantum efficiency of the photochemical etching [16]. Therefore, for efficient photochemical etching, the photoexcited electron should be excluded from the CdS host by using an electron scavenger such as methyl viologen ( $\text{MV}^{2+}$ ), which leaves the active hole within the CdS [16,17].

In this study, we fabricated the silica nanotube with both ends closed from the CdS nanorod template which was removed with the controlled photon energy. Initially, CdS/silica core–shell nanorod was prepared by silica coating over the CdS nanorod template. The silica nanotube with both ends closed was fabricated from the core–shell nanorod by selective photoetching of the core CdS nanorod template in the oxygen-saturated aqueous solution.

## 2. Experimental

The CdS nanorod template was prepared by hydrothermal reaction at 120 °C from the lyotropic mixture consisted of the triblock copolymer (Pluronic P123,  $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) and the cadmium and sulfur precursors dissolved in ethylenediamine [19]. For the preparation of the CdS nanorod template, 1.5 g of Pluronic P123 (Aldrich) and 0.080 g of cadmium nitrate tetrahydrate (Kanto Chemical, Japan) were added into 32 ml of anhydrous ethylenediamine (Kanto Chemical, Japan). After the solution was stirred for 8 h, 0.016 g of elementary sulfur (Samchun Pure Chemical, South Korea) was added into the ethylenediamine solution, and the final mixture was reacted in Teflon-lined autoclave at 120 °C for 12 h. This hydrothermal reaction produced the bright yellow precipitate (CdS nanorod) in the reaction vessel.

For the CdS/silica core–shell nanorod, 10 mg of the CdS nanorod template which was dispersed in 10 ml of methanol was treated with 0.014 ml of (3-mercaptopropyl)trimethoxysilane (MPTMS; Aldrich) for 2 h. Subsequently, 0.020 ml of aqueous sodium silicate solution (15 wt.%; Aldrich) was added into the above mixture solution and vigorously stirred for 30 min. This solution was stored at room temperature for 12 h and the resulting precipitate was repetitively washed with methanol and dried in an oven at 60 °C.

The prepared CdS/silica core–shell nanorod (3.0 mg) was dispersed in 10 ml of oxygen-saturated aqueous solution including methyl viologen ( $5 \times 10^{-3}$  mmol; Aldrich). For the photoetching of the core CdS component within the CdS/silica core–shell nanorod, a Q-switched Nd:YAG laser (B.M. Industries; pulse width of 5 ns) at a frequency of 10 Hz with a light intensity of 15 mW/cm<sup>2</sup> was utilized as a light source. As the monochromatic light (355 nm; third harmonic generation from an Nd:YAG laser) was irradiated, the characteristic yellow color of the aqueous solution containing the CdS/silica core–shell nanorod was gradually disappeared for the radiation period of 5 h.

For the morphology study of the resulting nanostructures, field-emission scanning electron microscope (FE-SEM) images were obtained on a microscope (JEOL, JEM-6700F) operated at 15 kV. Transmission electron microscope (TEM) images and energy dispersive X-ray (EDX) spectra were obtained with a microscope (Philips, CM-20) that was operated at 200 kV with the sample deposited on a carbon coated copper grid. X-ray diffraction (XRD) data were obtained on a diffractometer (Mac Science, M03XHF<sup>22</sup>) with Cu K $\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ) radiation. Absorption spectra were measured with a UV–vis spectrophotometer (Shimadzu, UV-160A). For the powder samples, diffuse reflectance spectra were recorded on a UV–vis spectrophotometer (Jasco, V-550) equipped with an integrating sphere (Jasco, ISV-469). Photoluminescence (PL) spectra were obtained by using a fluorescence spectrometer (Hitachi, F-4500).

### 3. Results and discussion

Fig. 1 shows FE-SEM and TEM images of the CdS nanorod template and the CdS/silica core-shell nanorod which are shown to be rod-shape with a width of 8–15 nm and a length of 300–500 nm. The EDX analysis clearly presents the constituent elements of cadmium and sulfur. From the XRD analysis, it is proved that the diffraction pattern for the CdS nanorod template is well correlated with that for the wurzite crystal structure (JCDPS card no. 41-1049) of CdS. For the CdS/silica core-shell nanorod, the rod-shaped morphology and the characteristic wurzite structure is still conserved. Furthermore, two elements of silicon and oxide were additionally detected from the EDX analysis (Fig. 1(f)), which indicate that the CdS nanorod template is coated with silica.

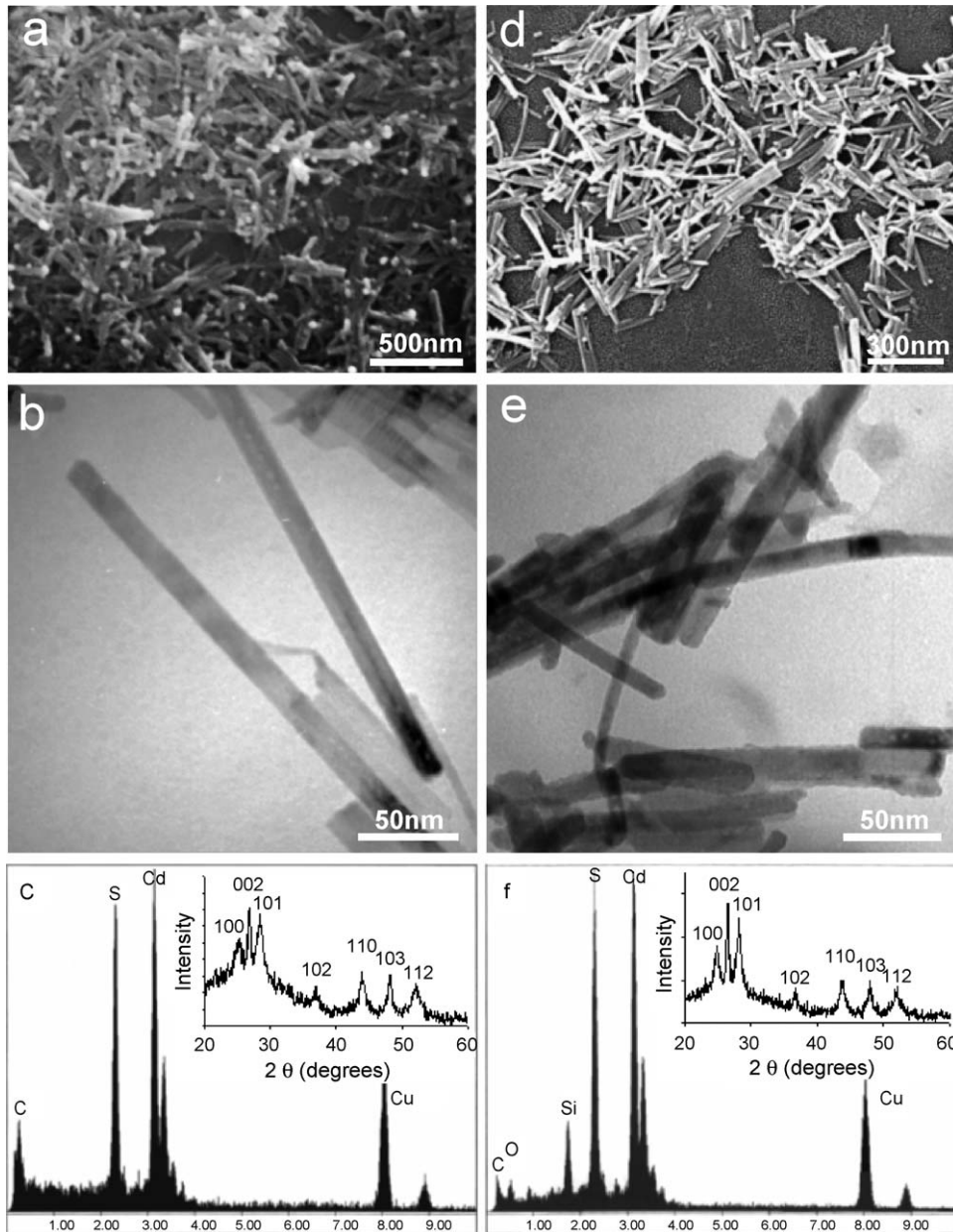


Fig. 1. FE-SEM (a) and TEM (b) images and the corresponding EDX spectrum (c) of the CdS nanorod template and FE-SEM (d) and TEM (e) images and the corresponding EDX spectrum (f) of the CdS/silica core-shell nanorod. The detected carbon and copper elements from the EDX spectra are due to the utilized carbon-coated copper grid. Inset is the XRD patterns of the corresponding nanorods.

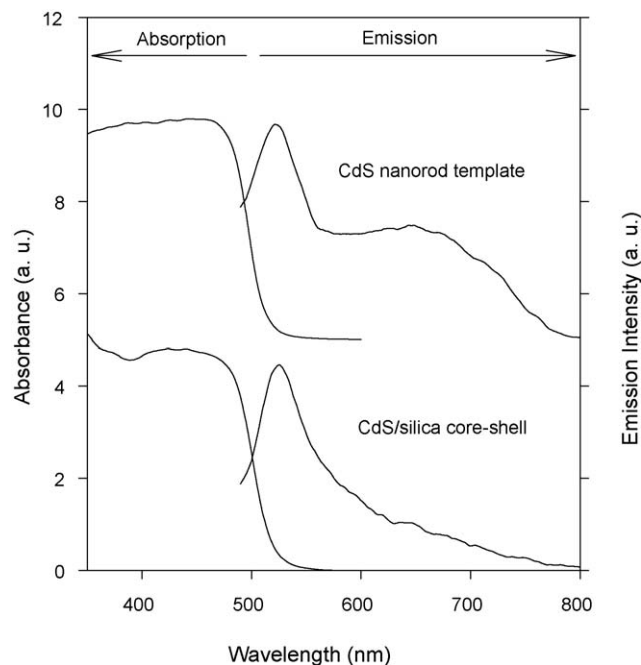


Fig. 2. Absorption and emission spectra of the CdS nanorod template and the CdS/silica core-shell nanorod at room temperature. The absorption spectra were obtained by applying the Kubelka–Munk function to the measured diffuse reflectance spectra. Excitation wavelength for the emission spectra is 430 nm.

Fig. 2 presents the absorption and emission spectra of both the CdS nanorod template and the CdS/silica core-shell nanorod at room temperature. The CdS nanorod template shows the absorption edge at  $\sim 510$  nm, which is blue-shifted from the bulk band-gap absorption ( $\sim 520$  nm) at room temperature [20]. This slight blue-shift is due to the weak quantum confinement effect in the CdS nanorod with a diameter of 8–15 nm ( $R_{\text{CdS}} \approx 2a_{\text{B}}$ ;  $a_{\text{B}}$  is the Bohr radius of 2.9 nm for CdS), as indicated in the previous literature [21]. The emission of the CdS nanorod template presents two distinct emission bands at 525 and 670 nm; the former is located around the absorption edge, which originates from the direct exciton recombination and/or shallowly-trapped exciton recombination, and the latter that is largely Stokes-shifted from the absorption spectrum is expected to be due to the deep trapped exciton recombination in the surface defect sites [22,23]. For the CdS/silica core-shell nanorod, the absorption and emission spectra are similarly preserved with those of the CdS nanorod template except for the largely suppressed Stokes-shifted emission centred at  $\sim 670$  nm. This emission change implies that the number of the surface emissive defect sites is largely reduced after surface capping with the MPTMS and the subsequent silica shell coating.

This efficient surface capping could be accomplished by the following process; in the initial step, the reactive thiol-group of the MPTMS was well introduced into the surface defect site on the CdS nanorod template due to the strong binding tendency of the thiol-group with the surface sulfur vacancy [24–26], which resulted in ethoxysilane terminated CdS nanorod. In the following step, the ethoxysilane terminated CdS nanorod was further condensed with the added silicate species. After the consecutive inorganic polymerization reaction [27], the silica shell was observed to be efficiently formed on the CdS nanorod template.

In order to fabricate the silica nanotube from the core-shell nanorod, the photoetching process was utilized to remove only the core CdS nanorod template. For the CdS/silica core-shell nanorod, the absorption spectrum shows the characteristic band-to-band absorption before the photoetching (Fig. 3). During the photoetching reaction with the monochromatic light ( $\lambda = 355$  nm) for 5 h, the absorption spectra of the oxygen-saturated aqueous solution containing the CdS/silica core-shell nanorod show that the absorption optical density gradually decreases, which is well correlated with the experimental observation of the gradual bleaching of the yellow color during the photoetching. This absorption spectral change possibly indicates that the core CdS nanorod template within the CdS/silica core-shell nanorod is dissolved out to be the ionic species, like a typical photochemical etching reaction of the CdS in solution [15,17].

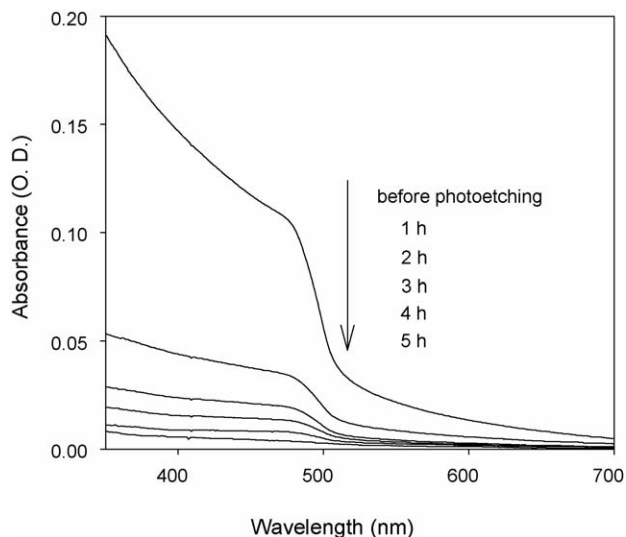


Fig. 3. Absorption spectra of the CdS/silica core-shell nanorod measured during the photoetching reaction in the oxygen-saturated aqueous solution containing  $MV^{2+}$  under light ( $\lambda = 355$  nm) irradiation for 5 h.

In particular, since the silica shell has a wide band-gap energy which is more than at least 6 eV, the silica shell does not absorb the irradiated monochromatic light of 355 nm (3.5 eV). Therefore, only the core CdS nanorod template is selectively excited and dissolved by the monochromatic light, resulting the empty silica shell. Fig. 4 is FE-SEM and TEM images of the empty silica shell resulted after photoetching of the CdS/silica core-shell nanorod. The FE-SEM image of the empty silica shell presents the preserved nanorod shape and, in particular, it is noticeable that the TEM image shows the hollow structure with the closed ends. It implies that the irradiated monochromatic light selectively removes only the core CdS nanorod template, even with coated silica layer on the nanorod surface.

Previously, Liz-Marzán and co-workers reported CdS/silica core-shell nanoparticles in order to enhance the stability of core CdS nanoparticles against oxidative photodegradation [28,29]. They observed that the core CdS nanoparticles that were coated with thick silica shell were quite stable over an extended period of several weeks under irradiation. Meanwhile, they also mentioned that thin silica coating layer did not completely protect core CdS nanoparticles against photodegradation because intrinsic nanopores existing at the silica coating layer admitted oxygen diffusion.

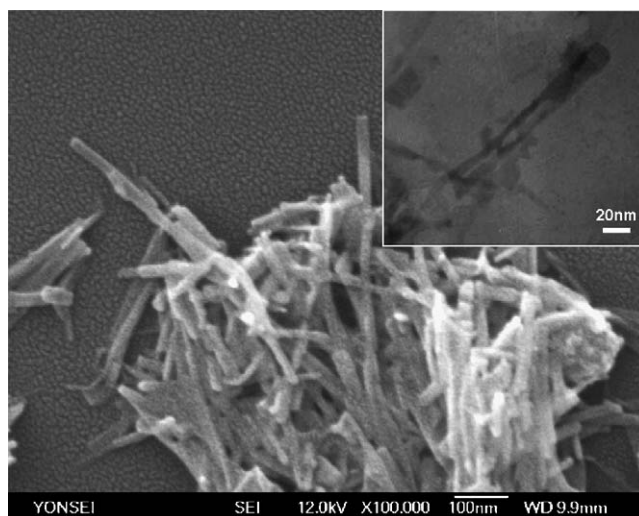


Fig. 4. FE-SEM image of the silica nanotube with both ends closed. Inset is TEM image of the corresponding silica nanotube with the closed ends.



In this study, in order to coat CdS nanorod with thin silica layer, we have used a reduced amount of the precursor (i.e. sodium silicate) by at least three times compared with that used by Liz-Marzán et al. Therefore, it is expected that the resulting thinner silica layer possibly has more nanopores, which can be a factor for efficient photoetching of the core CdS. However, the more important factor for the efficient photoetching is attributed to the addition of the catalyst (methyl viologen) in the solution. It was experimentally observed that our photoetching reaction was quite slow without the catalyst: based on the disappearance of the characteristic color (yellow) of CdS during the photoetching process, it was considered that the photoetching of the core CdS nanorod did not occur, significantly even in 1 day without the catalyst. However, with the catalyst, the color disappearance, which indicated the photoetching of the CdS was complete after a reaction time of 5 h. It was previously reported that the catalyst of methyl viologen greatly enhanced the photoetching reaction rate up to three orders of magnitude [30–32]. Therefore, it is suggested that the observed efficient photoetching of the core CdS nanorod, even with coated silica layer, is mainly caused by the catalyst in the oxygen-saturated solution with some contribution from the thin layer of silica.

The electron microscope images of the resulting silica nanotubes are often shown as the aggregated clumps (Fig. 4), although well-dispersed silica nanotubes are more desirable for further applications. Generally, silica particles tend to be aggregated each other due to van der Waals interaction [33]. Therefore, particle dispersion against agglomeration can be accomplished by reducing van der Waals interparticle interaction, which can simply be realized by adding a proper amount of inorganic salt to the aqueous solution of colloidal silica particles [34]. Such stable dispersion is achieved due to the balanced competition between attractive van der Waals force among colloidal silica particles and repulsive force among charged species of the inorganic salts.

#### 4. Conclusion

In summary, we present a new methodology for the fabrication of tubular nanomaterial by utilizing photon energy. The CdS/silica core–shell nanorod was prepared by the polymerization of silica on the surface of the CdS nanorod template. The selective removal of the CdS core within the CdS/silica core–shell nanorod was successfully accomplished by the photoetching process with controlled photon energy, which resulted in the formation of the silica nanotube with both ends closed. In our further study, it is expected that the remained propylthiol groups coated inside of silica nanotube can hopefully work as linkage block to optically active molecules.

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