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An Easy Approach to Fabrication of Silica Nanofibers/Nanotubes via Wrapping Sacrificial $Cd(OH)_2$ Nanostrands

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An easy approach to synthesis of silica nanofibers and nanotubes via wrapping sacrificial $Cd(OH)_2$ nanostrands was developed, and a plausible formation mechanism was proposed.

In recent years, much attention has been paid to one-dimensional (1D) nanomaterials because of their peculiar physicochemical properties.[1,2] A variety of fabrication methods have been developed. Among them, template synthesis is a frequently used wet chemical process. So far, templates used include porous alumina membrane,[3] surfactants,[4] cholesterol assemblies,[5] and gold nanorods.[6] These templates, however, are difficult to regenerate by simple means after removal. Very recently, Ichinose et al. prepared $Cd(OH)_2$ nanostrands by simply adjusting the pH value of Cd^{2+} solution.[7] In our preliminary experiments, we noticed that these nanostrands could be readily dissolved by lowering the solution pH value. This unique feature of $Cd(OH)_2$ nanostrands would allow them to be a convenient, sacrificial, and reproducible template. The current communication shows that it is in fact the case by syntheses of silica nanofibers and nanotubes.

$Cd(OH)_2$ nanostrands were synthesized according to the literature.[7] In a typical procedure, a given amount of aqueous NaOH (1.6%) was quickly added with stirring into 50 mL of aqueous $CdCl_2$ (2.0 mM), and the pH value of the resulting mixture was measured to be ca. 8.2. After the mixture was stirred for additional 5 min, aqueous NaOH (1.6%) was slowly dropped into the mixture until its pH value increased to 9.0. As a result, a white suspension was obtained. After it was stirred for another 10 min, a drop of the suspension (Suspension A) was transferred onto a carbon-coated copper grid, dried in vacuum overnight and observed on a JEOL JEM-200CX transmission electron microscope (TEM).

Figure 1a shows a TEM image of $Cd(OH)_2$ nanostrands. The $Cd(OH)_2$ nanostrands interlaced with each other and formed a network morphology. The width of the nanostrands could be roughly estimated to fall within 4 nm. It was also found that the nanostrands would become less stable and tend to aggregate with aging. For example, thicker $Cd(OH)_2$ nanostrands (4–10 nm in width) were observed after stirring Suspension A for additional 20 min. If the as-prepared suspension was aged for over 120 h, flocculent $Cd(OH)_2$ precipitates were formed.

Wrapping[8] of $Cd(OH)_2$ nanostrands were carried out by slow hydrolysis of tetraethoxysilane (TEOS) on their surfaces. To allow slow hydrolysis of TEOS, the pH value of the suspension was maintained between 8.2–9.0 for 48 h after 750 µL of TEOS was added into Suspension A. Finally, a suspension (Suspension B) was obtained. The product in Suspension B was observed by TEM. As shown in Figure 1b, composite nanostrands of a sheath–core structure were obtained. They had uniform width (ca. 13 nm) and interlaced with each other as $Cd(OH)_2$ nanostrands (Figure 1a). The darker core of composite nanostrand is $Cd(OH)_2$ nanostrand. Its width was estimated to be ca. 3 nm, in agreement with that observed in Figure 1a. The lighter part is SiO_2 sheath that wraps the $Cd(OH)_2$ core tightly. The silica sheath had a rough outer surface and a thickness of ca. 5 nm. Interestingly, a trifurcate morphology of the nanostrands was also noticed, as highlighted by a circle in Figure 1b.

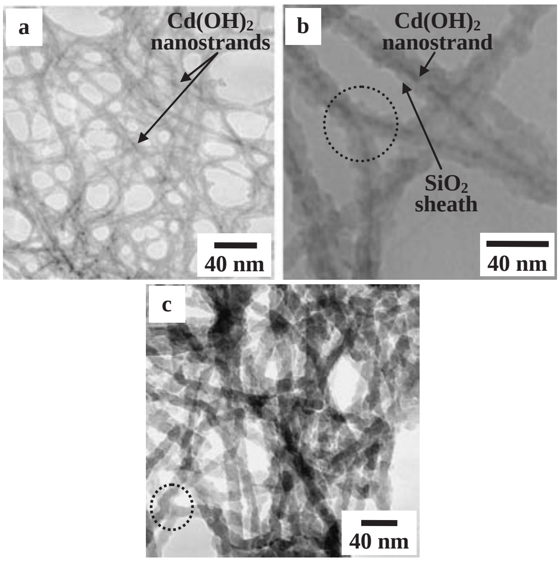
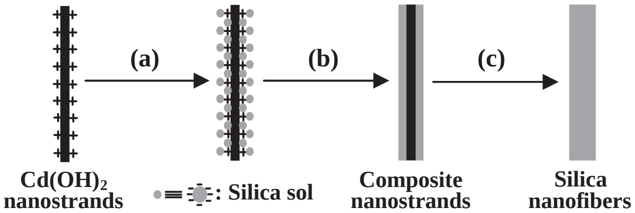


Figure 1. TEM images of (a) $Cd(OH)_2$ nanostrands in Suspension A, (b) sheath(SiO_2)–core($Cd(OH)_2$) composite nanostrands in Suspension B, and (c) silica nanowires in Suspension C.

Generally, $Cd(OH)_2$ can dissolve completely at pH ≈ 4. In the case of the above sheath–core nanostructure, H^+ ions must penetrate the silica sheath and react with the $Cd(OH)_2$ core. So the pH value of Suspension B was adjusted to ca. 2 with aqueous HCl (5%) to assure removal of the $Cd(OH)_2$ core. With the increase of the Cd^{2+} concentration difference inside and outside the silica sheath, Cd^{2+} ions would diffuse through the SiO_2 layer and eventually enter solution. Lowering the Cd^{2+} concentration outside the SiO_2 layer should facilitate this process. Thioglycolic acid (TGA) is known as a strong ligand to Cd^{2+} ions[9] and was thus added to Suspension B to lower the concentration of free Cd^{2+} ions before decreasing pH value. After the mixed suspension was continuously stirred at pH ≈ 2 for 24 h, Suspension C was obtained.

A large number of nanofibers rather than nanotubes were found by TEM in Suspension C (Figure 1c). The nanofibers are interweaved with each other as the template $Cd(OH)_2$ nanostrands. The nanofibers are uniform in width (ca. 15 nm) that is



Scheme 1. Schematic illustration of formation of silica nanofibers. (a) Electrostatic assembly of silica sol on the surface of $Cd(OH)_2$ nanostrand, (b) growth of silica layer, (c) removal of $Cd(OH)_2$ template and formation of silica nanofibers.

slightly larger than that of the sheath–core composite nanostrand (ca. 13 nm). The uniform contrast of each nanofiber indicates that the $Cd(OH)_2$ nanostrand had been completely removed. As shown in Figure 1c, trifurcate morphology as highlighted by a circle was also observed.

It is important to confirm the composition of the obtained nanofibers. They were coated with gold by a Hitachi E-1010 Ion Sputter, and their composition was estimated by a Hitachi S-4300 field emission scanning electron microscope (FE-SEM) equipped with energy dispersive spectroscopy (EDS). In the EDS spectrum, the narrow peaks at ca. 0.275, 0.517, and 1.751 keV, and the wide one at ca. 2.150 keV were assigned to C, O, Si, and Au elements, respectively. The C element originated from ultrathin carbon film coated on copper grid. The Au element had been introduced during the sputtering process. No peaks were found over 2.300 keV. As the peaks assigned to Cd element are known to appear at ca. 2.800, 2.912, 3.122, and 3.311 keV, the EDS results indicated that $Cd(OH)_2$ nanostrands had been completely removed, and the nanofibers only consist of Si and O elements.

$Cd(OH)_2$ nanostrands are positively charged in a proper pH range.[10] After TEOS was added into Suspension A, it was slowly hydrolyzed to produce negatively charged silica sol. The silica sol was assembled onto the surface of $Cd(OH)_2$ nanostrand by electrostatic attraction (Scheme 1 step (a)). The silica layer became thicker by further hydrolysis of TEOS, as described in step (b). Thus, sheath–core composite nanostrands were formed, as observed in Figure 1b. When the pH value was lowered to ca. 2, the $Cd(OH)_2$ nanostrands were dissolved. Simultaneous hydrolysis of TEOS both on the outer and inner surfaces of the silica layer led to the increase of the nanofiber width from 13 to 15 nm and to the fill of the channel left by removing the $Cd(OH)_2$ nanostrand (step (c)), respectively. Thus, silica nanofibers were eventually formed.

From the above mechanism, it should be possible to obtain silica nanotubes by carefully controlling hydrolysis or by removing TEOS before dissolution of $Cd(OH)_2$ nanostrands. They are in fact the cases. Under otherwise identical conditions, silica nanorods and nanotubes (left and right insets, respectively, in Figure 2a) were produced by using a smaller amount of TEOS (250 µL). The wall thickness of silica nanotube is nearly 6 nm, and is slightly larger than that (5 nm) of silica sheath in the composite nanostrand. The inner diameter of the silica nanotube is close to 2 nm and is slightly smaller than the width (3 nm) of the $Cd(OH)_2$ core in the composite nanostrand. Clearly, the silica sheath grew less quickly on its inner and outer surfaces during the removal of the $Cd(OH)_2$ core at lower TEOS concentrations, resulting formation of silica nanotubes. In order to completely eliminate the growth of the silica sheath in the dissolution of the $Cd(OH)_2$ core, the composite nanostrands were isolated from Suspension B. Nanotubes obtained by dissolving the cores are shown in Figure 2b. Their inner diameter is ca. 3 nm, which agrees well with the width of $Cd(OH)_2$ nanostrand.

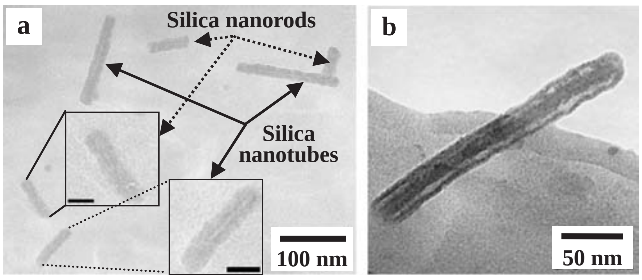


Figure 2. TEM images of silica nanorods and nanotubes obtained by using $V_{TEOS} = 250\,\mu L$ (a), and by separation of composite nanostrands before dissolving the template. The scale bars of two insets in (a) are 20 nm.

In summary, an easy approach to fabrication of silica nanofibers and nanotubes by wrapping and subsequent removal of sacrificial $Cd(OH)_2$ nanostrands was developed. It can be accomplished by simply adjusting the pH value of solution. Clearly, the current approach is not limited to fabrication of silica nanofibers and nanotubes. Nanofibers and nanotubes of other metal oxides would be obtainable by using varied precursors. Such efforts are currently being carried out in our laboratory.

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