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Colloids Seeded Deposition: Growth of Titania Nanotubes in Solution

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Recently, considerable attention has been focused on one-dimensional (1D) nanostructured materials due to their unique properties and potential applications in very many aspects;[1−5] among them, the nanotubes have attracted research interests since the discovery of carbon nanotubes by Iijima in 1991.[6] A number of methods have been demonstrated for generating nanotubes from most kinds of materials,[7−10] and it has also been recognized that solid materials from layered precursors can be prepared as nanotubes by carefully controlled experimental conditions, based on a "rolling-up" mechanism, such as graphite carbon, BN, vanadium oxide, WS_2, $NiCl_2$, TiO_2, and several metals.[11−16] Kasuga et al.[17] and Peng et al.[18] have reported the preparation of titanate nanotubes by treating the titania precursor in 10 M NaOH solution via the rolling-up mechanism.

Although the VLS (vapor−liquid−solid) method, analogous to nanowire growth,[19] has been used to prepare nanotubes in gas phase,[20] a similar process in solution phases has been seldom reported. Prof. Xia's group has demonstrated the synthesis of Te nanotubes by directly nucleating and growing from aqueous orthotelluric acid solution.[21] Liu et al. have also reported the synthesis of 1D nanostructures by controlling heterogeneous nucleation and growth in solution.[22−24] Very recently, our group has found the titania nanotubes can be produced in solution under ambient and mild conditions by means of "colloids seeded deposition" process, in which nano ceria particles were used as catalysts and poly titanium oxo ions as growth resources. The process, similar to the "VLS" method or "salt−gel" process,[25] produces titania nanotubes in good shape and controllable length.

At first, the ∼50 nm CeO_2 nanoparticles were fabricated by a hydrothermal treatment of a mixture of $Ce(SO_4)_2$ and ammonium solutions. The crystalline and highly homogeneous ceria nanoparticles were obtained and used as the seeds in the followed growth process of titania nanotubes. Then 20 mL of a 0.1 $mol \cdot dm^{-1}$ $Ti(SO_4)_2$ solution was added, in ∼2 h, into 100 mL of $\sim 5.8 \times 10^{13}$ ∼50 nm ceria nanoparticles containing aqueous solution at 303 K. The titanium sulfate hydrolyzed to sol gradually at that temperature, reflected by the change in pH value of the solution. The resulting dispersion was allowed to age at the temperature of 290−300 K for several days. A part of the solid deposits was taken out for TEM observation at different times of the reaction. With the increase of the reaction time, the quantities of nanotubes and their lengths, as observed by TEM, gradually increased.

Figure 1 depicts a TEM photograph of the titania nanotubes with the ceria seeds at the prolonged reaction time. The nanotube diameters matched the sizes of ceria nanoparticles, and the walls of the nanotubes are about 10 nm. At one end of the nanotubes, dark condensed ceria nanoparticles can be seen. All the nanoparticles appear to have a thin capping shell in the thickness of ∼10 nm, similar to the thickness of the nanotube walls. The nanotubes are almost closed at the both ends.

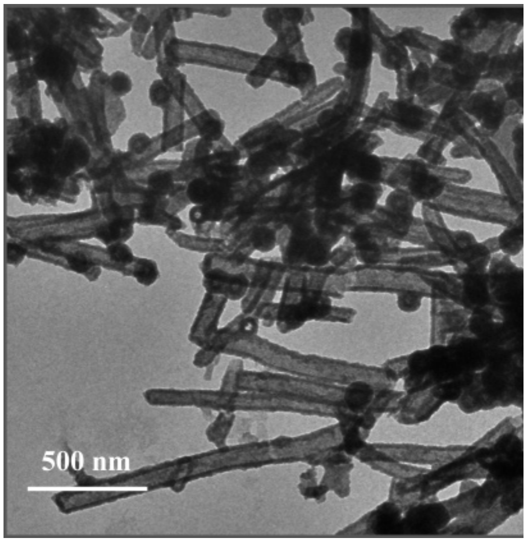

Figure 1. TEM image of the titania nanotubes grown by ceria nanoparticle-catalyzed deposition of titania sol, which formed by hydrolysis of $Ti(SO_4)_2$.

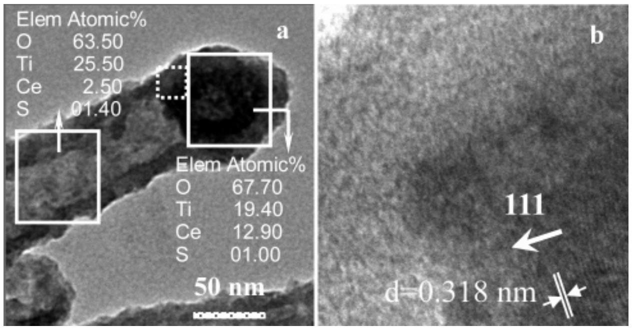

Figure 2. (a) EDXS results at different regions of one titania nanotube. (b) HRTEM observation at the interface of titania/ceria at the site indicated by the dashed square in (a).

To provide further insight into the nanostructures of the product, the compositions of the product were determined by energy-dispersive X-ray spectroscopy (EDXS) performed at the different locality of an individual nanotube, as shown in Figure 2a. The results clearly indicate the nanotube is titania, for the middle part of the nanotube contains basically titanium and oxygen, while its head part contains titanium and cerium. Obviously, the head of the nanotube is the core/shell structure of ceria coated by titania. Sulfur was also detected due to the adsorption of SO_4^{2-}.

The ceria nanoparticles used as catalysts are single crystalline, although their external shape is not so cubic (Supporting Information). HRTEM observation provided insight about the relation between the growth direction of the titania nanotubes and the crystalline direction of ceria nanoparticles. Figure 2b shows the core/shell structure of ceria/titania, and the titania shell is amorphous

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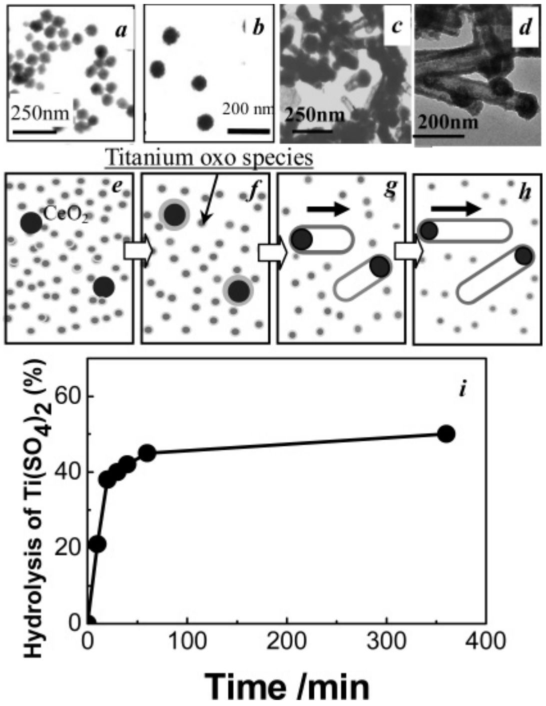

Figure 3. Schematic diagrams of the process for the titania nanotubes growth. (a) TEM image of the ceria nanoparticles. (b) TEM image of titania-coated ceria nanoparticles at ∼2 h reaction. (c) Short titania nanotubes at ∼24 h reaction. (d) Elongated titania nanotubes at prolonged reaction time. (e−h) Model showing of the process for colloid-catalyzed deposition. (i) Percentage of hydrolyzed Ti(SO$_4$)$_2$ versus time at 303 K, detected by the change in pH value of the solution.

but the head core is crystalline. The crystalline strips are visible from the figure and recognized as ceria ⟨111⟩ planes with intervals of 0.318 nm. Basically, the titania nanotube grows along the direction of ceria ⟨111⟩. The XRD profile of as-prepared nanotubes shows only crystalline ceria diffraction peaks (Supporting Information).

For a complete view of the formation process of the nanotubes and their growth mechanism, a time-dependent morphology evolution study was conducted from several hours to several days at ∼290 K. Corresponding TEM images are shown as the Figure 3. The ceria nanoparticles (Figure 3a) developed into titania-coated ceria (Figure 3b) in ∼2 h. Short tubes with ceria nanoparticles at one end (Figure 3c) emerged in ∼24 h, and the elongated nanotubes with ceria seeds (Figure 3d) appeared at prolonged time of reaction.

The formation mechanism of the present nanotubes is intriguing, and a possible mechanism is proposed and shown in Figure 3e−h. The status of the titanium species in the solution should be some type of titanium oxo ion aggregates, due to the hydrolysis of Ti(SO$_4$)$_2$, as detected by the change in pH of the mixed solution (Figure 3i). It is well known that the neonatal titania adsorbed SO$_4^{2-}$ strongly, forming so-called solid superacid.[26] The strongly adsorbed SO$_4^{2-}$ ions cause the titania clusters to become negatively charged and stabilize the titania sols, but at the conditions employed (pH = 1.6−2.1), the ceria nanoparticles are positively charged, for their point-of-zero charge is about 8.1.[27] Through electrostatic interactions, the titania clusters deposit onto the surface of CeO$_2$ nanoparticles as the capping layer. For the limited electrostatic attraction, the capping layer must be very thin and undergo structural change and lose some charges, facilitating the continuous deposition of titania. The external surfaces of one ceria nanoparticle with different structure appear to differentiate the interaction between the ceria and titania capping layer because of the different ceria/titania interfacial energy. The total effect is the directional growth of titania nanotubes, similar to the seeded growth of 1D materials[28] or an anisotropic salt−gel process.[25] During the deposition, the incoming titanium oxo species prefer to deposit at the specific side of the ceria/titania interface with higher interfacial energy and to condense to titanium oxide. The condensed titania then scramble along the ceria surface to the specific low energy sides and are pushed away from the ceria by the subsequent deposition of titanium oxo species and form the closed nanotubes.

In summary, the formation of titania nanotubes through CeO$_2$ colloids seeded deposition process in solution has been demonstrated. The interactions among colloidal particles play important roles for the solution VLS-type growth of nanotubes. The observation has significance for understanding solution nucleation and for developing new methods for nanomaterials preparation via the disclosed colloids seeded deposition mechanism.

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Supporting Information Available: Properties of the ceria nanoparticles used as catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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