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BRIEF COMMUNICATION

Synthesis of zirconium dioxide nanotubes, nanowires, and nanocables by concentration dependent solution deposition

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Abstract Nanowires and nanotubes of ZrO_2 were successfully synthesized in this study by concentration dependent solution deposition (CDSD) using $Zr[O(CH_2)_3CH_3]_4$ as the precursor and anodic aluminum oxide (AAO) as the substrate. Here, we synthesized one-dimensional zirconium dioxide with a simple and efficient method by sucking the precursor solution though the AAO channels. In these experiments, the key factor in the formation of nanowires and nanotubes is the concentration of the precursor, $Zr[O(CH_2)_3CH_3]_4$ butanol solution. Concentrated $Zr[O(CH_2)_3CH_3]_4$ solutions cause the formation of solid one-dimensional materials, whereas dilute precursor solutions form hollow nanotubes. The dimensions of the nanomaterials synthesized correspond to the scope of the AAO template are 200–450 nm in diameter and about 60 μm in length. Furthermore, the cable structures of these nanomaterials, wire-in-tube and tube-in-tube, were synthesized by alternately operating the processes. We are reporting an uncomplicated, fast and versatile method applicable to a wide range of materials, taking advantage of the sol–gel process to prepare a vast variety of nanocomposite full of potential applications, especially cable nanomaterials.

Keywords AAO · Condensation · Hydrolysis · Sol–Gel Process · Zirconium(IV) *n*-butoxide · Nanotubes · Nanowires · Nanocables · Colloids

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Introduction

One-dimensional materials have drawn much attention in recent years in the optical, photoelectric, physics and semiconductor fields owing to their unique properties. Several synthesizing processes have been developed, including both physical and chemical methods. However, chemical methods have attracted the most interest. Wang et al. employed thermal evaporation (Pan et al. 2001) to make nanobelts of various compositions (such as ZnO, SnO_2, In_2O_3, CdO) and morphologies (such as rings, loops, tadpoles, and diskettes) (Hughes and wang 2004; Gao and wang 2002; Dai et al. 2002). Other processes have been used, including sol–gel (Shen et al. 2004), template-assisted (Bao et al. 2002), surfactant-assisted (Woo et al. 2003) and chemical vapor deposition (CVD) (Duan and Lieber 2000). Among those mentioned, the template-assisted

method is generally thought of as a popular and simple process, because it can be used to form nanomaterials of uniform-size. Also, templates are versatile and applicable to most materials, so researchers have investigated numerous shapes of templates, including spherical (polystyrene, silica and Se) (Itoh et al. 2004; Jeong and Xia 2005), tubular anodic aluminum oxide (AAO) (Bao et al. 2001) and layered (block copolymers) (Kim et al. 2004) ones. In this methods, precursor reagents are introduced into channels or vacancies among closely-packed spheres or cylinders, where they react by electrochemical (Mu et al. 2004) or oxidation-reduction reactions (Kijima et al. 2003) to yield materials with various morphologies. Final products are obtained when the templates are removed by appropriate methods, for example using HF or NaOH etching for AAO (Bao et al. 2002), thermal treatment (Mayers et al. 2003) for polystyrene, Se and copolymer. Aside from the vigorous evolution in single nanowires and nanotubes, many researchers have made efforts to produce more complex nanowire devices (Goldberger et al. 2006; Schmidt et al. 2006). Yang and co-workers developed a Si vertically integrated nanowire field effect transistor (Si VINFETs) which can overcome lithographic problems in the horizontal method and increase transistor density.

Although a number of one-dimensional materials have been reported, only a few have described the synthesis of zirconia nanomaterials. Kim and coworkers reported that ZrO_2 nanotubes prepared by atomic layer deposition (Qu et al. 2004). Palmese utilized polyester track-etched (PETE) membranes as polymer templates to synthesize ZrO_2 nanotubes (Chen et al. 2007). Besides, Shinkai and coworkers used a self-assembly technique to synthesize double layers metal oxides including ZrO_2 (Jung et al. 2005). The very expensive equipment and very complicated process was used to preparing the one-dimensional ZrO_2. However, zirconia provides a new option as structural materials since it has excellent mechanical characteristics, such as its high level of hardness and chemical stability. Moreover, zirconia is an excellent insulator containing a wide band gap of 5.0 eV. In the age of competitive downscaling, it is a good candidate to avoid tunneling of current between individual devices.

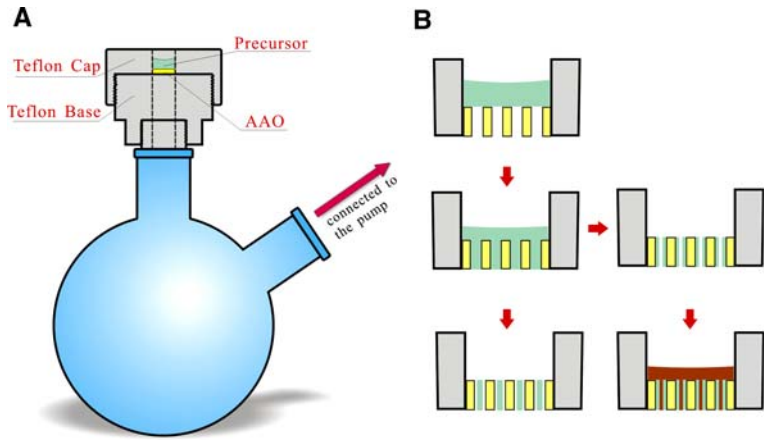
This work reports a straightforward and effective concentration dependent solution deposition (CDSD), taking only a few seconds for fabricating zirconium dioxide nanomaterials using $Zr[O(CH_2)_3CH_3]_4$ as the precursor and AAO as the substrate. This method also has the potential to produce various one-dimensional nanocomposite by selecting suitable precursors and reaction conditions.

Experimental

Scheme 1 shows the setup of the experiment with two parts-holder and flask. The holder made from Teflon can be taken apart as three components for cleaning. The general operating procedure is to connect the holder and the pumping system to the flask, with a valve between the pump and the flask to control the gas flow. Firstly, the AAO disc (Cat. No. 6809-7023, Whatman, with non-uniform pore diameters in the range 200–450 nm) was placed on the center of the holder. A few drops of $Zr[O(CH_2)_3CH_3]_4$ (Aldrich) precursor ethanol (Aldrich, 99.5%) solution of either 0.87 M, 1.07 M, 1.30 M, 1.69 M, 1.84 M or 2.10 M were then dripped onto the AAO disc. As the valve was turned on, the precursor solution was sucked into the AAO channels in a few seconds (generally 5–10 s). After the AAO discs had dried naturally, they were annealed at 450 °C for 1.5 h (heating rate 5 °C/min). Then, they were immersed in 5 M NaOH at room temperature for 15–20 min to remove the AAO. After they have been washed with deionized (D.I.) water and dried at room temperature, one-dimensional ZrO_2 arrays were acquired.

The cable structures were obtained by alternating the CDSD processes. Between two consecutive operating steps, the surface of the AAO disc was roughly grinded to remove the oxide deposit on top of the AAO surface.

For characterization, X-ray diffraction patterns were obtained using a Bruker D8 (Cu–K_α, $\lambda = 1.54187$ Å) and SEM observations were acquired using a JEOL-6500 scanning electron microscope operating at 15 kV. TEM images were captured with a JEOL-2010 electron microscope and the percentage of nanowire in Fig. 2 was obtained by calculation of over 150 nanowires and nanotubes at each concentration under TEM characterization.



Scheme 1 (**a**) The experiment setup in this work. The Teflon holder holds an AAO substrate and a two-necked Pyrex flask were used. During the experiment, an AAO disc is placed on the center of the holder channel and the bottom of the holder is connected to one neck of the flask. The other neck is connected to a pumping system. (**b**) The flow chart of the process. Initially, the precursor solution of desired concentration was dropped on to the AAO disc with a micropipette, which was then sucked into the AAO channels when the valve between the flask and the pump was turned on. When the precursor solution was concentrated, nanowires were obtained, as shown in the bottom-left picture. Various concentrations of the precursor solution in the pumping step yielded nanotubes or core-shell structures; right column presents the flow chart

Results and discussion

Figure 1 presents scanning electron microscopic (SEM) images of zirconia nanowires and nanotubes synthesized with different concentrations 2.10 M and 0.87 M, respectively. The diameter of each tube matches that of the AAO channels and the diameter of the nanowires is slightly less than that of the nanotubes. Figure 1a shows a large bundle of wire-like materials with lengths of about 60 μm, the same as the thickness of the AAO disc, obtained from the more concentrated precursor solution. Figure 1b shows a magnified image of the nanowires: their terminals clearly present their solid internal structure. Figure 1c and d display another one-dimensional material, produced by the dilute precursor solution, the broken part of which shows that the material is hollow and therefore concrete evidence of their tubular morphology.

The microstructure of both wires and tubes was tetragonal ZrO_2 following thermal treatment at 450 °C, as shown in the X-ray diffraction patterns (Fig. 2). The diffraction peaks which were observed at $2\theta = 30.3$, 35, 50.5 and 60.1 are assigned to (101), (110), (112) and (211) reflections of the ZrO_2 tetragonal phase in the JCPDF card (PDF number 79–1770), respectively.

Figure 3 shows the transition electron microscopy (TEM) images of the one-dimensional zirconia attained from various precursor solutions. Figure 3a presents a nanotube with a 15 nm-thick wall and an outer diameter of around 400 nm, synthesized using a precursor solution of 0.87 M. As the concentration of precursor solution increased, the thickness of the wall of the nanotube increased while the outer diameter declined. (Figure 3b–d) When the concentration reached 2.10 M, nanowires formed instead of nanotubes (Fig. 3f). Consistent with the SEM observations, nanowires and nanotubes synthesized with higher concentrations shrank during sintering (Fig. 3 c–f). Under some extreme conditions, for example when the concentration was 0.87 M, intact nanotubes could not be obtained because cracks appeared after the AAO was etched by NaOH, causing the nanotubes to collapse. Additionally, nanowires and nanotubes coexisted with the moderate concentration of precursor solutions (Fig. 3b–e). The relationship between the percentage of nanowires and precursor concentration is shown in the inset of Fig. 2. The quantity of nanowires increases with the increase of precursor concentration. However, the products synthesized with the extreme concentrations 0.87 M and 2.10 M were nanotubes and nanowires only, respectively.

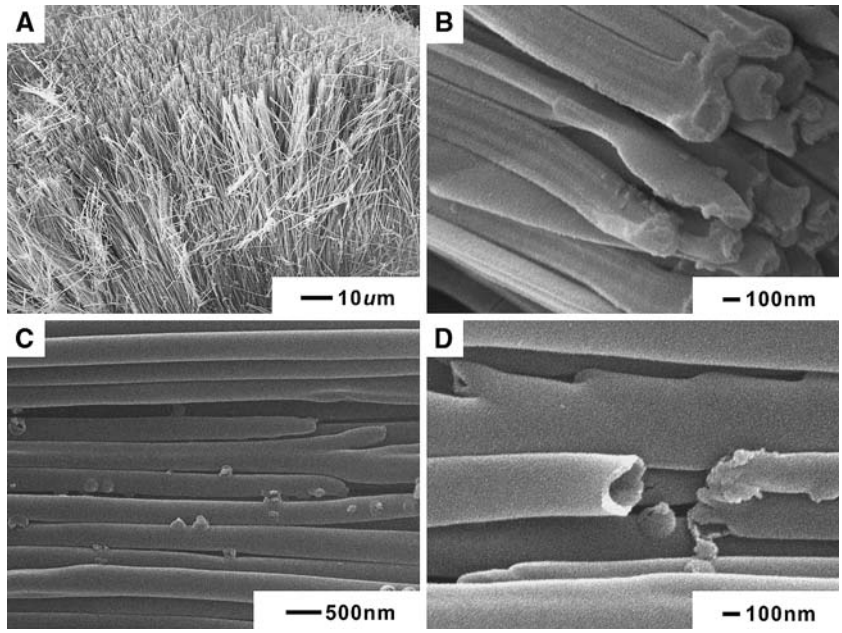


Fig. 1 SEM images of nanowires and nanotubes obtained with different precursor concentrations. (**a**) A bundle of nanowires formed at 2.10 M. The length of the nanowires is about 60 μm. (**b**) The enlarged image of ends of the nanowires. (**c**) A bundle of nanotubes synthesized at 0.87 M. (**d**) The end of a nanotube shows a hollow structure inside

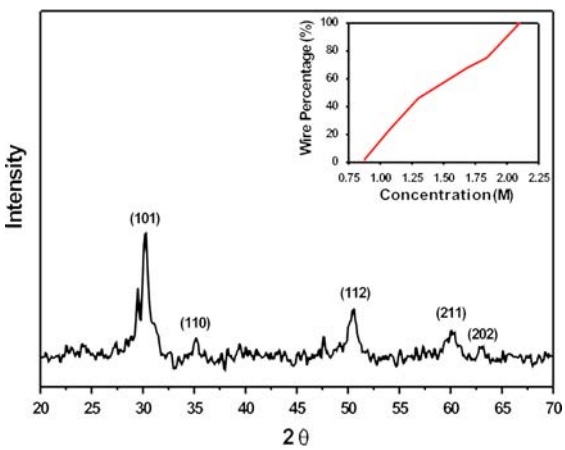


Fig. 2 X-ray diffraction pattern of zirconium dioxide products. The peaks indicate that the product is in the tetragonal phase. The inset reveals that the nanowire percentage in the products increases when the precursor concentration increases

The crystalline nature of one-dimensional ZrO_2 also depends on the concentration of the precursor solution. The insets in Fig 3a–f display the EDs of one-dimensional ZrO_2 obtained from various precursor solutions (0.87–2.10 M). For instance, the blurry ring-shaped ED patterns in the insets of Fig. 3a–e reveal poor crystalline nature, whereas the inset in Fig. 3f exhibits a distinct spot ED indicating single crystalline nature. However, the spot ED pattern was obtained using a smaller aperture, marked by the circle in Fig. 3f. The nanowire is not a single crystal but an agglomeration of crystalline grains. The consistency between ED and X-ray patterns gives another evidence of tetragonal phase. The (101) plane was observed, labeled in Fig. 3a–e, and has the highest intensity in tetragonal phase; (101) and (110) planes of the single crystal are pointed out by arrows in Fig. 3f. Another special characteristic revealed by the TEM images is that the surface of products synthesized using $Zr[O(CH_2)_3CH_3]_4$ is much smoother than those synthesized by pyrolysis (Qu et al. 2004).

Based on above observations, the concentration dominates the morphologies and crystallization of ZrO_2. Nanowires are the major products when the concentration is high, but when the concentration is low mostly nanotubes are produced. The degree of crystallization increases with the concentration.

As we know, in the ceramic process of powder metallurgy the crystallinity of bulk material will improve by compacting the powder as densely as possible into a disc using a hydraulic press before thermal treatment. In the experiments herein, nano-spherical clusters were compressed tightly inside the AAO channels as the precursor was being sucked through. The squeezing among the clusters is significant at high concentration precursor solutions, yielding denser coatings and higher crystallinity.

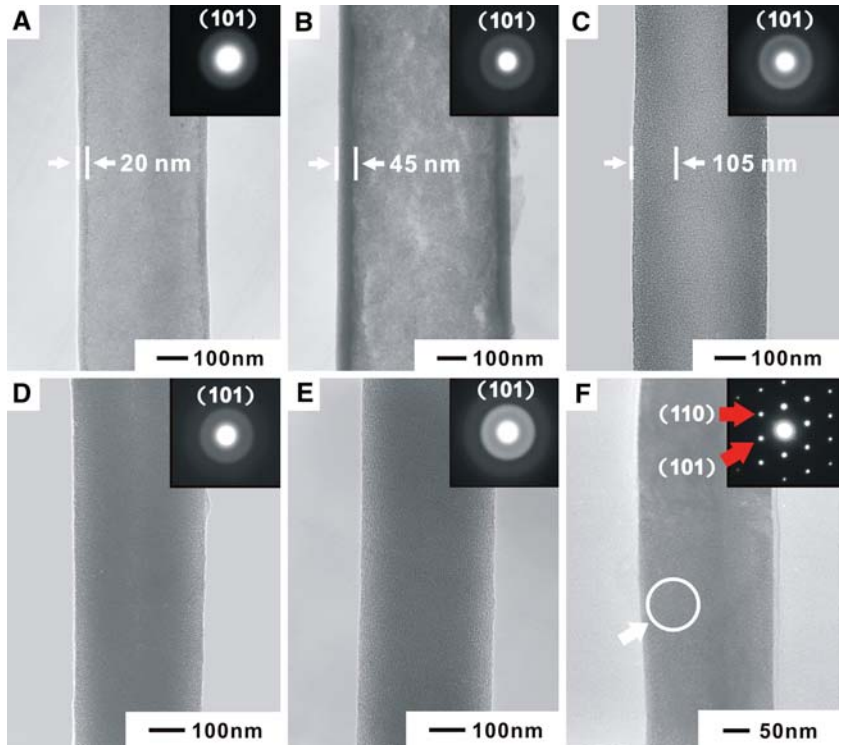


Fig. 3 TEM images and the corresponding ED (inset) of nanowires and nanotubes synthesized with various precursor concentrations. (**a**) 0.87 M, (**b**) 1.07 M, (**c**) 1.30 M, (**d**) 1.69 M, (**e**) 1.84 M and (**f**) 2.10 M

The CDSD which occurs in the AAO channels is the typical sol–gel process, hydrolysis and condensation.

$$\text{Hydrolysis } Zr{-}OR + H_2O \rightarrow Zr{-}OH + ROH \quad (R = n{-}\text{butyl group})$$

$$\text{Condensation } Zr{-}OH + Zr{-}OX \rightarrow Zr{-}O{-}Zr + XOH$$

Figure 4 depicts the reaction scheme. Zirconium n-butoxide was hydrolyzed instantaneously by water vapors in air when the precursor was sucked through the AAO channels (Fig. 4b) and condensation proceeded inside accompanied by the evaporation of the solvent (Fig. 4c). As the solvent evaporated, the nano-spherical particles that were formed by hydrolysis and condensation aggregated into nanotubes or nanowires.

This study proposes that the formation of various morphologies of one-dimensional ZrO_2 is related to the competitive attraction between the inner walls of the AAO channels and the clusters, as well as among the clusters themselves. A more concentrated $Zr[O(CH_2)_3CH_3]_4$ solution generated excess clusters in the condensation step which increased the strength of inter-cluster attraction above that between the wall and the clusters, so they cohered into nanowires as the solvent evaporated. However, dilute $Zr[O(CH_2)_3CH_3]_4$ solution generated few clusters, providing insufficient force to compete with the attraction from the wall, so the clusters attached to the wall to form nanotubes.

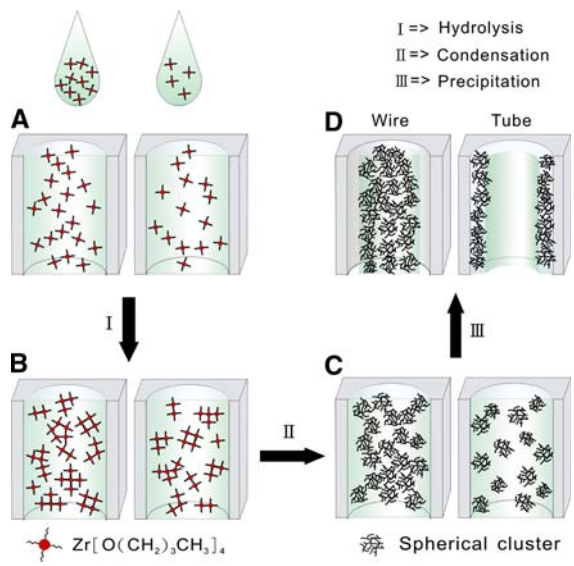


Fig. 4 Schematic diagrams of the formation of nanotubes and nanowires prepared by using different precursor concentrations

The CDSD process reported herein is not only used to produce common one-dimensional ZrO_2 but also complex materials. One-dimensional ZrO_2 with a cable structure was synthesized by alternating the processes. Figure 5a shows a wire-in-tube structure formed by using different concentrations of $Zr[O(CH_2)_3CH_3]_4$ solution, 0.87 M followed by 2.10 M. Most of the nanowires reside at the center of the nanotubes while some of them are attached to the wall of the tubes. However, if the $Zr[O(CH_2)_3CH_3]_4$ solution of 1.69 M is used instead of the 2.10 M, both the tube-in-tube and the wire-in-tube structure of ZrO_2 could be observed (In the Fig. 5b, only the tube-in-tube structure is shown.). Furthermore, when an even lower concentration, 1.30 M, was used, the morphology varied even within the same tube. Figure 5c–e show a particular case of a nanotube with a junction structure. Below the junction (Fig. 5e) a nanowire stands freely at the center, but above the junction (Fig. 5c) the wire split to become part of the tube. Based on this property, the walls of the tube may be thickened by repeating the CDSD process using a dilute precursor solution such as 1.30 M.

In conclusion, nanotubes and nanowires of ZrO_2 were successfully synthesized by CDSD, using $Zr[O(CH_2)_3CH_3]_4$ as the precursor and AAO as the template. In these experiments, the concentrated $Zr[O(CH_2)_3CH_3]_4$ solution caused the formation of solid one-dimensional materials, whereas dilute

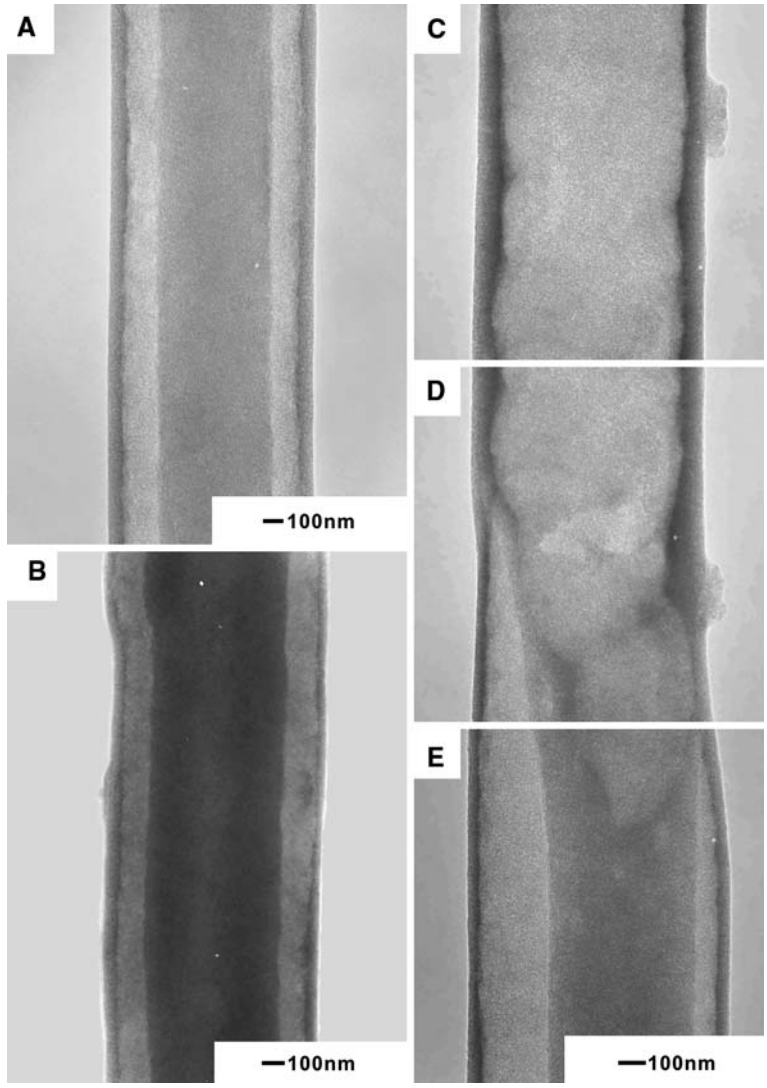


Fig. 5 TEM images of cable structure synthesized by duplicating the synthetic process. (**a**) The wire-in-tube structure whose outer tube and inner wire were synthesized by using 0.87 M and 2.10 M, respectively. (**b**) The tube-in-tube structure was synthesized by using 0.87 M and 1.69 M. (**c**–**e**) The junction structure was synthesized with 0.87 M and 1.30 M

precursor solution yielded hollow nanotubes. The length of the nanowires and the nanotubes is about 60 μm and their diameter ranges from 200 nm to 450 nm, corresponding to the dimension of the AAO template. Additionally, the cable structures of these nanomaterials, wire-in-tube and tube-in-tube, were synthesized by alternating the processes. This simple and efficient method also has potential to be used to produce various one-dimensional nanocomposite by selecting suitable precursors and reaction conditions.

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