J|A|C|S
ARTICLES
Published on Web 08/10/2006

Water-Dissolvable Sodium Sulfate Nanowires as a Versatile Template for the Fabrication of Polyelectrolyte- and Metal-Based Nanotubes

Ying-Chih Pu,† Jih Ru Hwu,‡ Wu-Chou Su,§ Dar-Bin Shieh,|| Yonhua Tzeng,⊥ and Chen-Sheng Yeh*,†

Contribution from the Department of Chemistry and Center for Micro/Nano Technology Research, National Cheng Kung University, Tainan 701, Taiwan, Department of Chemistry, National Tsing Hwa University, Hsinchu 300, Taiwan, Department of Internal Medicine, National Cheng Kung University, Tainan 701, Taiwan, Institute of Oral Medicine and Department of Stomatology, National Cheng Kung University, Tainan 701, Taiwan, and Department of Electrical Engineering and Center for Micro/Nano Technology Research, National Cheng Kung University, Tainan 701, Taiwan

Received May 9, 2006; E-mail: csyeh@mail.ncku.edu.tw

Abstract: This study presents the synthesis of water-dissolvable sodium sulfate nanowires, where Na_2SO_4 nanowires were produced by an easy reflux process in an organic solvent, *N*,*N*-dimethylformamide (DMF) and formed from the coexistence of $AgNO_3$, $SnCl_2$, dodecylsodium sulfate (SDS), and cetyltrimethylammonium bromide (CTAB). Na_2SO_4 nanowires were derived from SDS, and the morphology control of the Na_2SO_4 nanowires was established by the cooperative effects of Sn and NO_3^-, while CTAB served as the template and led to homogeneous nanowires with a smooth surface. Since the as-synthesized sodium sulfate nanowires are readily dissolved in water, these nanowires can be treated as soft templates for the fabrication of nanotubes by removing the Na_2SO_4 core. This process is therefore significantly better than other reported methodologies to remove the templates under harsh condition. We have demonstrated the preparation of biocompatible polyelectrolyte (PE) nanotubes using a layer-by-layer (LbL) method on the Na_2SO_4 nanowires and the formation of Au nanotubes by the self-assembly of Au nanoparticles. In both nanotube synthesis processes, PEI (polyethylenimine), PAA (poly(acrylic acid)), and Au nanoparticles served as the building blocks on the Na_2SO_4 templates, which were then rinsed with water to remove the core templates. This unique water-dissolvable template is anticipated to bring about versatile and flexible downstream applications.

Introduction

Tubular nanostructured materials have drawn a lot of scientific attention because of their diverse applications in drug delivery, catalysis, optics, electronic, and magnetic devices.[1] A number of approaches have been demonstrated in preparing various nanotubes made of metals, metal oxides, semiconductors, and conductive polymers.[2] Template-based synthesis is the most widely used method, and an effective way for generating hollow structures. Following this style of synthesis, different compositions can be prepared using chemical vapor deposition or simple stepwise adsorption.[3] Templates including porous membranes, metal nanorods and nanowires, carbon nanotubes, and organic substrates have been successfully employed to create tubular structures. However, most of the template-based methods require the use of a base or acid medium or high temperature to remove the templates.[4] Considering safety and environmental hazards, such processes greatly increase the cost and risk of large-scale manufacture. In this regard, we have developed a new type of water-dissolvable inorganic Na_2SO_4 nanowire, which greatly enhances the template-based synthesis of nanotubular materials. With regard to inorganic nanowires and nanofibers such as sulfates, carbonates, and chromates, considerable fabrication strategies have been restricted in utilizing reverse micelles, microemulsion, and polymer-mediated techniques.[5−7] Herein,

---

† Department of Chemistry and Center for Micro/Nano Technology Research, National Cheng Kung University.

‡ Department of Chemistry, National Tsing Hwa University.

§ Department of Internal Medicine, National Cheng Kung University.

|| Institute of Oral Medicine and Department of Stomatology, National Cheng Kung University.

⊥ Department of Electrical Engineering and Center for Micro/Nano Technology Research, National Cheng Kung University.

(1) (a) Mitchell, D. T.; Lee, S. B.; Trofin, L.; Li, N.; Nevanen, T. K.; Söderlund, H.; Martin, C. R. *J. Am. Chem. Soc.* **2002**, *124*, 11864−11865. (b) Liu, Z.; Zhang, D.; Han, S.; Li, C.; Lei, B.; Lu, W.; Fang, J.; Zhou, C. *J. Am. Chem. Soc.* **2005**, *127*, 6−7.

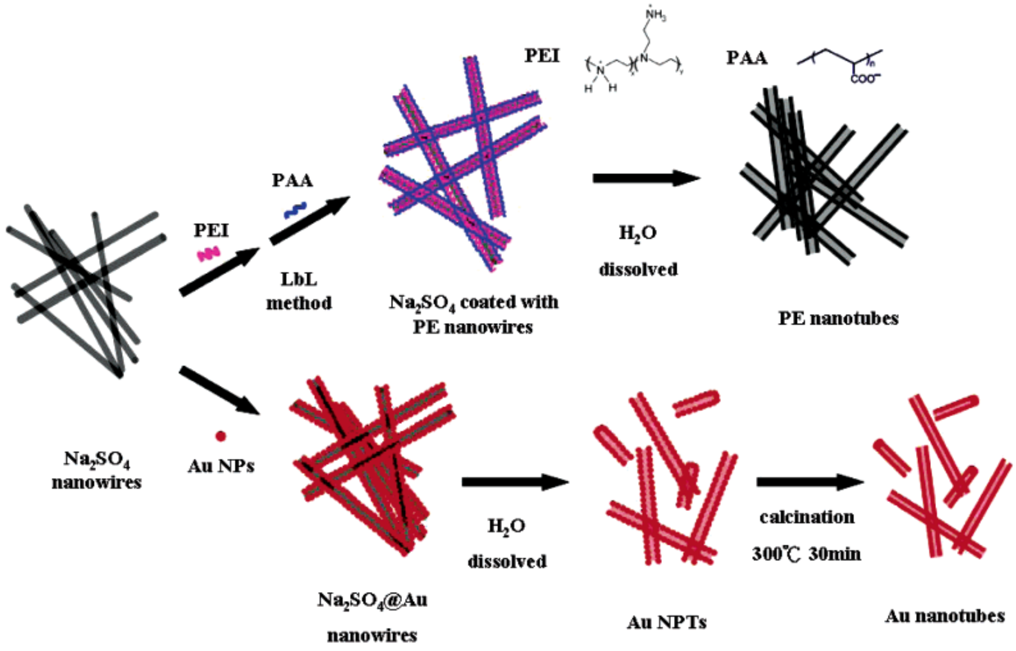
(2) (a) Jeong, J. S.; Lee, J. Y.; Cho, J. H.; Suh, H. J.; Lee, C. J. *Chem. Mater.* **2005**, *17*, 2752−2756. (b) Martin, C. R. *Science* **1994**, *266*, 1961−1966.

(3) (a) Goldberger, J.; He, R.; Zhang, Y.; Lee, S.; Yan, H.; Choi, H. J.; Yang, P. *Nature* **2003**, *422*, 599−602. (b) Liang, Z.; Susha, A. S.; Yu, A.; Caruso, F. *Adv Mater*. **2003**, *15*, 1849−1853.

(4) (a) Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Schilling, J.; Choi, J.; Gösele, U. *Science* **2002**, *296*, 1997. (b) Obare, S. O.; Jana, N. R.; Murphy, C. J. *Nano Lett*. **2001**, *1*, 601−603. (c) Mayya, K. S.; Gittins, D. I.; Dibaj, A. M.; Caruso, F. *Nano Lett*. **2001**, *1*, 727−730. (d) Sun, Z.; Yuan, H.; Liu, Z.; Han, B.; Zhang, X. *Adv. Mater*. **2005**, *17*, 2993−2997.

10.1021/ja063221z CCC: $33.50 © 2006 American Chemical Society

Scheme 1. Nanotubes Synthesis Processes Using Water-Dissolvable Na_2SO_4 Nanowire Templates[a]



[a] PE nanotubes can be fabricated either by LbL deposition or interlayer crosslinking. The Au NPTs and Au Nanotubes are produced by surface adsorption of Au nanoparticles and the subsequent calcination, respectively.

an easy reflux process in an organic solvent is presented to form Na_2SO_4 nanowires.

In this work, we also demonstrate the layer-by-layer (LbL) templating of Na_2SO_4 nanowires to synthesize polyelectrolyte (PE) nanotubes, as well as the utilization of metal nanoparticles as the building blocks for self-assembling metal nanoparticle tubes (NPTs). The resulting NPTs could then be further calcined to form metal nanotubes. The metal NPTs have been reported as a new class of template synthesis of metal nanotubes.[8] As shown in Scheme 1, we have utilized the LbL method to assemble a positively charged polyethylenimine (PEI) layer followed by a negatively charged poly(acrylic acid) (PAA) layer in a sequential way on the Na_2SO_4 nanowire surface to form Na_2SO_4 covered by PE nanowires. Alternatively, a strategy involving interlayer cross-linking via 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) conjugation was introduced to prepare Na_2SO_4 coated with PE nanowires as well. After water rinsing, the core nanowire templates are dissolved to obtain the PE *nanotubes*. Another application shown in Scheme 1 is derived from the surface deposition of gold nanoparticles on the Na_2SO_4 nanowire surface to form Na_2SO_4@Au nanowires and the subsequent dissolution process to yield Au NPTs. The as-synthesized Au NPTs were able to transform into Au nanotubes after calcination for 30 min at 300 °C.

Experimental Section

Preparation of Na_2SO_4 Nanowires. Na_2SO_4 nanowires were prepared by the reflux of 0.02 M dodecylsodium sulfate (SDS, $CH_3(CH_2)_{11}OSO_3Na$), 1 mM $AgNO_3$, 4 mM $SnCl_2{\cdot}2H_2O$, and 2 mM cetyltrimethylammonium bromide (CTAB) in 5 mL of *N*,*N*-dimethylformamide (DMF) at 160 °C for 60 min until the limpid solution turned a milky-white color. The sample was removed from the hot plate and cooled to room temperature. We then collected the white precipitates by centrifugation (10,000 rpm, 5 min) and further washed them with 2-propanol several times. The derived Na_2SO_4 nanowires were stored in 2-propanal until use.

Preparation of PE_{12}, PE_{10}, and PE_{11} Nanotubes with Internally Embedded DNA (DNA-in-PE). The numbers in PE_{12}, PE_{10}, and PE_{11} denote the number of polymer layers. One milliliter of the prepared Na_2SO_4 nanowire solution was mixed with 100 μL of PEI (1 mM in 2-propanol, MW: 25,000) and stirred for 2 h. PEI formed the innermost layer of the nanotube coated on the nanowire template. The Na_2SO_4@PEI was collected by centrifugation (12,000 rpm, 5 min), followed by a double washing with 2-propanol to remove residual PEI. The Na_2SO_4@PEI was then redispersed in 1 mL of 2-propanol, added with 100 μL PAA (10 mM in 2-propanol, MW: 2000), and stirred for 2 h. The Na_2SO_4@PEI/PAA was thus obtained after centrifugation (12,000 rpm, 5 min) and washing with 2-propanol. The number of layers can be controlled by alternatively coating with PEI and PAA. The final PE nanotubes were then obtained by simply dissolving Na_2SO_4 coated with PE nanowires in water. The multilayer wall can be strengthened by interlayer chemical cross-linking using 2 μL of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC, 1 M in H_2O) per mL of the nanowires. To prepare the PE_{11} nanotubes with internally embedded DNA, the prepared Na_2SO_4@PEI nanowires were mixed with 10 μL of DNA−FITC (FITC-5′-ATGATCTTGATCTTCATGGA-3′ 100 μM in H_2O) and stirred for 2 h. The resulting Na_2SO_4@PEI/DNA nanowires were redispersed in 2-propanol after being washed twice. The final product of Na_2SO_4@PE_{11} with internally embedded DNA nanowires could be obtained following the layer-by-layer coating process as mentioned above, and a subsequent dissolving in water resulted in PE nanotubes containing DNA. A confocal fluorescence microscopy image of PE_{11} with internally embedded DNA nanotubes was recorded on a Leica TCS MP II system equipped with a 100× oil immersion objective and operating in fluorescence mode. The DNA-based PE nanotube solution was placed on a glass cover slip, and the image of the DNA-based PE nanotubes was captured immediately.

---

(5) (a) Li, M.; Mann, S. *Langmuir* **2000**, *16*, 7088−7094. (b) Qi, L.; Cölfen, H.; Antonietti, M.; Li, M.; Hopwood, J. D.; Ashley, A. J.; Mann, S. *Chem. Eur. J.* **2001**, *7*, 3526−3532.

(6) Yu, S. H.; Antonietti, M.; Cölfen, H.; Hartmann, J. *Nano. Lett.* **2003**, *3*, 379−382.

(7) Oaki, Y.; Imai, H. *Langmuir* **2005**, *21*, 863−869.

(8) (a) Lahav, M.; Sehayek, T.; Vaskevich, A.; Rubinstein, I. *Angew. Chem., Int. Ed.* **2003**, *42*, 5576−5579. (b) Sehayek, T.; Lahav, M.; Popovitz-Biro, R.; Vaskevich, A.; Rubinstein, I. *Chem. Mater.* **2005**, *17*, 3743−3748.

Preparation of Au NTPs. The synthesis of Au nanoparticles was carried out in toluene, following a previous report by Schiffrin and co-workers.[9] Briefly, an aqueous solution of $HAuCl_4$ (0.75 mL of 30 mM) was mixed with tetraoctylammonium bromide in toluene (2 mL of 50 mM). The mixed solution was vigorously stirred until all Au^{3+} ions were transferred into the toluene, followed by the slow addition of $NaBH_4$ (0.625 mL of 0.4 M). After further stirring for 20 min, the organic phase was separated from the flask, and 100 μL of an Au nanoparticle solution was directly added into 1 mL of the as-synthesized Na_2SO_4 nanowires solution. The mixture was incubated for 10 minutes after sonication for seconds. The Au NPTs were then collected by centrifugation (13,000 rpm, 10 min) and then washed several times in H_2O. Subsequently, Au nanotubes could be fabricated after calcination of the Au NPTs at 300 °C for 30 min.

Field emission scanning electron microscopy (Hitachi S4200) and transmission electron microscopy (JEOL JSM-1200EX and PHILIPS CM-200 TWIN) were performed for morphological characterization. The X-ray diffraction (XRD) was analyzed in a Shimadz XD-D1 diffractometer using Cu Kα radiation ($\lambda = 1.54056$ Å) at 30 kV and 30 mA.

Results and Discussion

The sodium sulfate nanowires can be obtained by a simple reflux of the solution containing SDS, $AgNO_3$, $SnCl_2{\cdot}2H_2O$, CTAB, and DMF. Upon heating to 160 °C for 1 h under vigorous stirring, the color of the solution changed from colorless to milky white, leading to the formation of white precipitates. The white precipitates were washed with 2-propanol several times and were collected using centrifugation. High-resolution scanning electron microscopy (HR-SEM) observation of the white precipitates is illustrated in Figure 1a. These white precipitates were found to be one-dimensional nanowires with diameters of 71 ± 16 nm and lengths up to $4-7$ μm. The TEM image (inset of Figure 1a) shows a solid core for these nanowires. The X-ray diffraction (XRD) pattern indicates the formation of crystalline Na_2SO_4 as shown in Figure 1b. The as-synthesized nanowires are highly water soluble.

The formation of sodium sulfate nanowires is intriguing. We have schematically studied the nanowires formation. First, the synthesis process was modified by the addition of SDS (0.02 M) to DMF only, without the presence of $AgNO_3$, $SnCl_2{\cdot}2H_2O$, and CTAB for reaction. The milky-white solution and the final product of white precipitates could also be obtained. (Figure 2,a and b) However, irregular rodlike and platelike structures as evidenced by the SEM image were observed. The energy dispersive X-ray spectrometer (EDS) indicates the presence of Na, S, and O elements in the products derived (see Supporting Information). This suggests that Na_2SO_4 nanomaterial can be readily formed in a mixture of SDS and DMF solution in the absence of $AgNO_3$, $SnCl_2{\cdot}2H_2O$, and CTAB, although nonuniform rodlike and platelike structures are synthesized. Additionally, if the dried DMF was used to react with SDS and the reflux was performed in argon, no precipitate was observed (Figure 2c). Apparently, the presence of H_2O is important for the Na_2SO_4 formation, and the reaction takes place as follows:

$$2\,CH_3(CH_2)_{11}OSO_3^- + 2\,Na^+ + 2\,H_2O \rightarrow Na_2SO_4 + 2\,CH_3(CH_2)_{11}OH + H_2SO_4$$

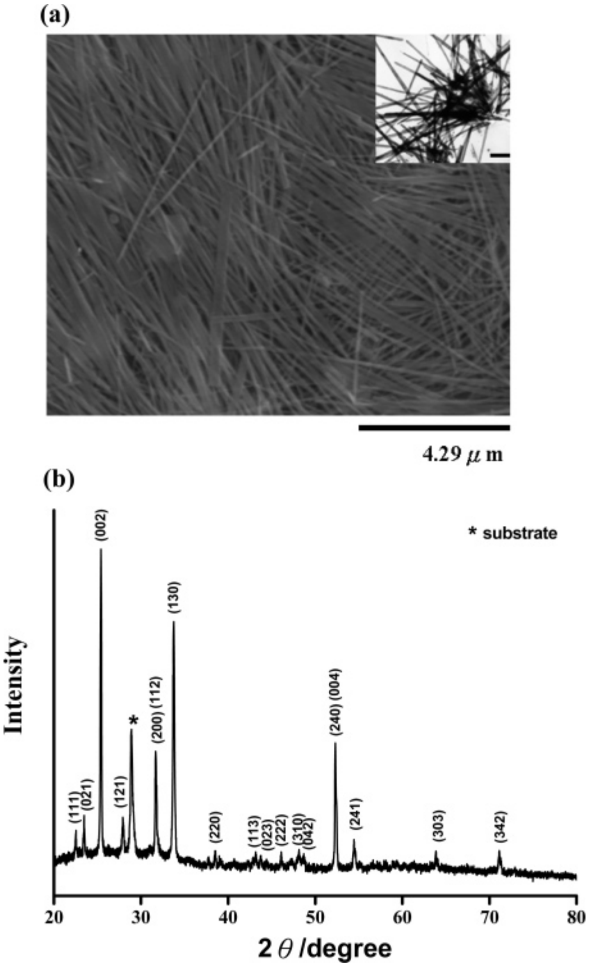


Figure 1. (a) SEM image of the Na_2SO_4 nanowires. (Inset) TEM image of the corresponding nanowires (scale bar = 500 nm). (b) XRD pattern of the Na_2SO_4 nanowires.

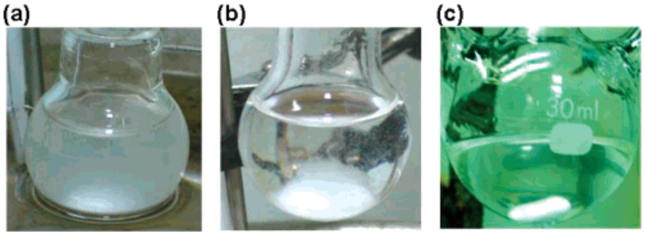


Figure 2. (a) Milky-white color was observed after adding only SDS (0.02 M) to 5 mL of DMF, after a reaction time of 1 h. (b) White precipitates corresponding to (a) were obtained after stirring was stopped. (c) No precipitation was observed by the addition of SDS (0.02 M) in the dried DMF for a reaction in an argon atmosphere.

Gas chromatography measurements have confirmed a $CH_3(CH_2)_{11}$-OH component in the resulting solution.

FTIR characterization of as-synthesized Na_2SO_4 nanowires (Figure 1a) shows evidence of DMF adsorption by the observation of the C═O signal (Supporting Information). In addition, the asymmetric and symmetric deformation modes pertaining to CH_3-N^+ of the CTAB headgroup appear at ~1466 and ~1357 cm^{-1} (Supporting Information), respectively, which are consistent with the signals of two bands at ~1490 and ~1390 cm^{-1}.[10,11] This indicates the positively charged CTAB adsorbed

---

(9) Fink, J.; Kiely, C. J.; Bethell, D.; Schiffrin, D. J. *Chem. Mater.* **1998**, *10*, 922−926.

(10) Li, H.; Tripp, C. P. *Langmuir* **2002**, *18*, 9441−9446.

(11) Huang, C.-C.; Yeh, C.-S.; Ho, C.-J. *J. Phys. Chem. B* **2004**, *108*, 4940−4945.

electrostatically via the headgroup $^+N(CH_3)_3(C_{16}H_{33})$ on the Na_2SO_4 surface as well. Interestingly, the ξ-potential measurements of the Na_2SO_4 nanowires (Figure 1a) give a −45 mV negative surface charge of the nanowires. This suggests that the surface of the nanowires is not fully covered, but is partially covered by both DMF and CTAB molecules. It is worth mentioning that the addition of less CTAB (2 mM) as compared with SDS (0.02 M) introduced in the reaction not only allows the functionality of CTAB to properly serve as a template and results in homogeneous nanowires with a smooth surface but also avoids the complete passivation of CTAB on the Na_2SO_4 negative surface, which provides the adsorption sites for the further LbL approach to fabricate polyelectrolyte and self-assembly of Au nanoparticles to yield Au nanotubes.

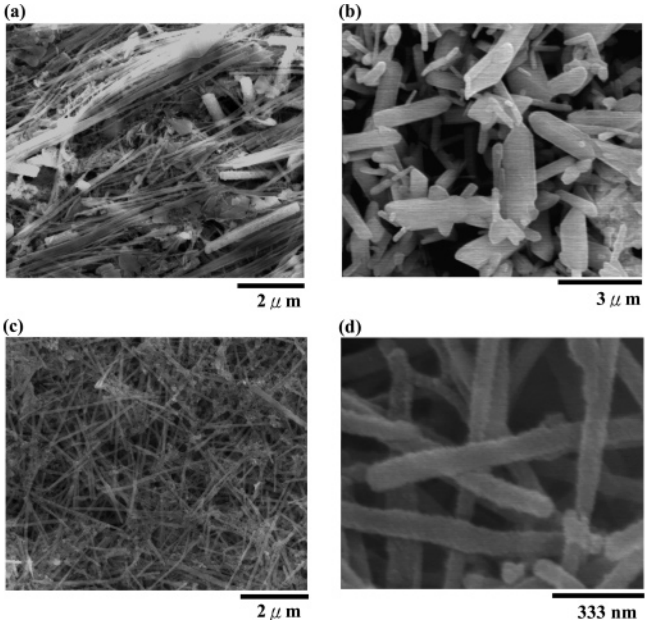


Figure 3. SEM images of the resulting precipitates from different experimental conditions: (a) in the mixture containing $SnCl_2{\cdot}2H_2O$, SDS, and CTAB; (b) in the mixture containing $AgNO_3$, SDS, and CTAB; (c) in the mixture containing $NaNO_3$, $SnCl_2{\cdot}2H_2O$, SDS, and CTAB; (d) in the mixture containing $AgNO_3$, $SnCl_2{\cdot}2H_2O$, and SDS.

We have shown that Na_2SO_4 materials can be simply synthesized from the solution mixture containing *only* SDS and DMF. Notably, it has been known that the addition of foreign species in the solution-phase approach facilitates the growth of anisotropic structures. For example, the introduction of Ag^+ by adding $AgNO_3$ has been found to assist in the growth of gold nanorods and Pt nanocrystals with shapes varying from cubes to octahedrals.[12,13] It was found that the Ag^+ ions have acted as a shape-control agent during the reaction. In this synthesis, $SnCl_2{\cdot}2H_2O$ and $AgNO_3$ were added to form the high yield of nanowires as seen in Figure 1a. The mechanisms by which both $SnCl_2$ and $AgNO_3$ assist in the growth of Na_2SO_4 nanowires are not understood yet. However, addition of $SnCl_2$ was found to particularly enhance nanowires formation. A control experiment was performed by addition of $SnCl_2{\cdot}2H_2O$ in the mixture of SDS, CTAB, and DMF (without $AgNO_3$). Following the same reaction time (1 h), significant wire-like shapes were generated, accompanied by particle-like products (Figure 3a). However, only irregular particles were observed when $AgNO_3$ was reacted with a mixture containing SDS, CTAB, and DMF (Figure 3b). For both products obtained in Figures 1a and 3a, EDX measurements identified the presence of the Sn signal. It is possible that tin deposits, e.g. Sn^{2+} adsorption, at the specific surface on Na_2SO_4, followed by a reduction of Sn^{2+} to Sn, and inhibits its growth, leading to preferential growth along one direction. There were no detectable Cl (from $SnCl_2$) and Br (from CTAB) signals in the EDX detection limit. Although the introduction of $SnCl_2$ significantly enhances one-dimensional growth as seen in Figure 3a, additional foreign $AgNO_3$ additive is needed to achieve the exclusive nanowires with high uniformity as shown in Figure 1a. Interestingly, we have observed that the presence of the NO_3^- anion appears to be critical, instead of silver, for generating high uniform nanowires. Separate experiments were conducted to understand the fate of the NO_3^- anions for nanowire formation. Since AgCl was immediately precipitated when $AgNO_3$ was added to the mixture containing $SnCl_2{\cdot}2H_2O$, SDS, CTAB, and DMF, AgCl precipitate was removed first by centrifugation, leaving the supernatant for reaction. In the synthesis of Na_2SO_4 nanowires, it should be noted that 1 mM of $AgNO_3$ and 4 mM of $SnCl_2$. $\cdot 2H_2O$ were used for reaction. The complete consumption of Ag^+ is expected to occur by the reaction of Cl^-, leading to the supernatant containing no Ag^+ in it. Following this operation, the reaction of the supernatant resulted in the same product (Figure 1a) with a high yield and uniform nanowires. The other parallel experiment was also performed by replacing $AgNO_3$ with $NaNO_3$. In this trial, significant nanowires with reasonable uniformity were formed, as well as spherical-like particles (Figure 3c). Perhaps the excessive sodium from $NaNO_3$ might have resulted in the spherical byproduct. Although exclusive nanowires are not achieved using $NaNO_3$, it is shown that the preparation of Na_2SO_4 nanowires can be applicable to the appropriate metal nitrates, e.g. $AgNO_3$, $NaNO_3$, and NO_3^- have a crucial role in forming such nanowire structures. Clearly, the morphology control of the Na_2SO_4 nanowires is established by the cooperative effects of Sn and NO_3^-. Finally, Figure 3d shows the Na_2SO_4 nanowires with a rough surface, where the wire-like structures were obtained from the mixture containing $AgNO_3$, $SnCl_2{\cdot}2H_2O$, and SDS in the absence of CTAB, thus indicating that CTAB serves as a template to form nanowires exhibiting a smoother surface. We have carried out the thermal stability measurements of the resulting Na_2SO_4 nanowires by a calcination process. Nanowires retained their shape without apparent collapse after calcination at 500 °C for 60 min. However, Na_2SO_4 nanowires began to melt and fused together if the temperature was further increased up to 600 °C (Supporting Information).

An important objective achieved in this study was to utilize the water dissolvable Na_2SO_4 nanowires as a versatile template to prepare polyelectrolyte (PE) and metal-based nanotubes by different tactics. Polyelectrolyte materials have a variety of biomedical applications. For example, polyelectrolyte fibrous structures can be used to serve as scaffolds for tissue engineering.[14] The Na_2SO_4 nanowires feature a surface of negative phase (−45 mV), and thus are ideal to build up tubular structures

---

(12) (a) Jana, N. R.; Gearheart, L.; Murphy, C. J. *Adv. Mater.* **2001**, *13*, 1389. (b) Orendorff, C. J.; Murphy, C. J. *J. Phys. Chem. B* **2006**, *110*, 3990−3994.

(13) Song, H.; Kim, F.; Connor, S.; Somorjai, G. A.; Yang, P. *J. Phys. Chem. B* **2005**, *109*, 188−193.

(14) Wan, A. C. A.; Tai, B. C. U.; Leck, K.-J.; Ying, J. Y. *Adv. Mater.* **2006**, *18*, 641.

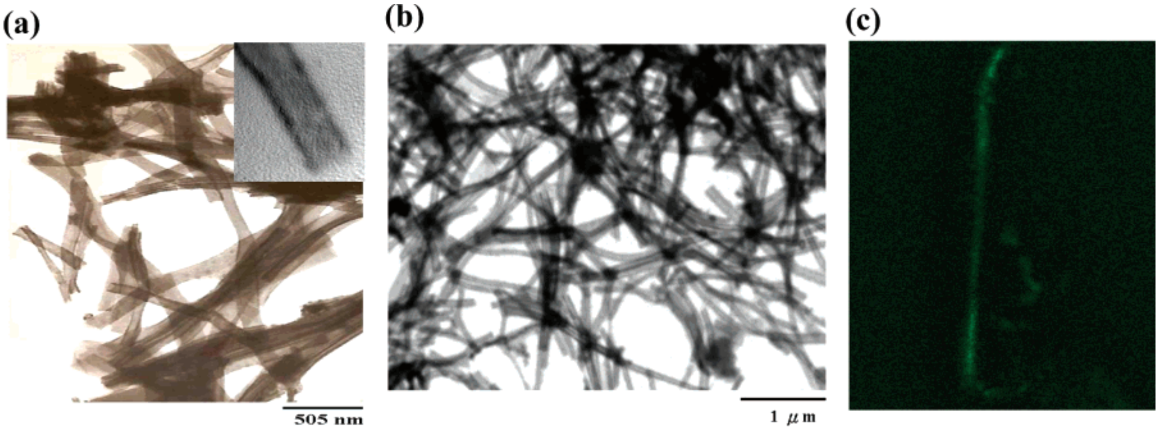


Figure 4. TEM images of (a) PE_{12} nanotubes. (Inset) Magnified view, scale bar = 20 nm). (b) PE_{10} nanotubes with interlayer amide bond chemical cross-link. (c) The confocal fluorescence microscopy image of the PE_{11} nanotube with internally embedded DNA−FITC (FITC-5′-ATGATCTTGATCT-TCATGGA-3′) tagged with fluorescent dye.

derived by the LbL method. The LbL templating of Na_2SO_4 nanowires to prepare PE nanotubes was carried out utilizing polyethylenimine (PEI) and poly(acrylic acid) (PAA) as building blocks by a sequential deposition on the Na_2SO_4 nanowire surface. The PEI provides a positively charged layer while the PAA forms the wrapping around negatively charged layer over the first coating of the PEI layer by layer. PEI/PAA mutilayers were thus sequentially coated on the Na_2SO_4 nanowires. After repetitive water rinsing, PE_{12} (12 is the number of layers) was derived. As shown in the TEM image of Figure 4a, the PE_{12} formed tubelike nanostructures. These polyelectrolyte nanotubes exhibited high flexibility and readily entangled together. Additional TEM images taken from different views are also provided for the purpose of giving a more comprehensive understanding for the morphology of these polyelectrolyte nanotubes (Supporting Information). The inset of Figure 4a shows the open-ended structure of these PE_{12} nanotubes. Since the formation of PE nanotubes relies on the interaction between oppositely charged polymers, nanotubes can only be obtained reproducibly when the number of the coated layers is greater than 12 via the LbL strategy. FTIR analysis of as-synthesized PE_{12} nanotubes was conducted and provided the evidence of formation of polyelectrolyte nanotubes. Since the outmost layer of the PE_{12} nanotubes was coated with PAA, the FTIR spectrum of pure PAA polymer was determined as well (Supporting Information). Alternatively, we are able to cross-link the polymer layers with each other by covalent bonds when the number of the coated layers is below 12. After coating PE_{10} layers on Na_2SO_4 nanowires surface, we simply added 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) to form amide bonds between the $-NH_2$ of PEI and $-COOH$ of PAA under an incubation time of 2 h. Upon removal of the Na_2SO_4 nanowires by water, the PE_{10} nanotubes (Figure 4b) exhibited a more rigid structure due to the covalent bond formation. We further demonstrated that the LbL-derived nanotubes could carry DNA by adsorption of DNA−FITC (FITC-5′-ATGATCT-TGATCTTCATGGA-3′) over the PEI in PE nanotubes. We replaced the *second* layer PAA of the PE nanotubes by DNA−FITC in the synthesis process. Figure 4c shows the confocal fluorescence microscopy image of the derived DNA-harbored PE_{11} nanotubes.

Metal nanoparticle tubes (NPTs) have been categorized as a new class of template-synthesized nanomaterials.[8a] We have also successfully fabricated Au NPTs and Au nanotubes using the templates of Na_2SO_4 nanowires. The deposition of Au nanoparticles on the surface of Na_2SO_4 nanowires followed by dissolving the nanowires in water resulted in the formation of Au NPTs in less than 10 min at room temperature. Gold nanoparticles were synthesized in toluene using a two-phase system that has been reported by Schiffrin and co-workers.[9] The derived Au nanoparticles in toluene have the particle size of 4.3 ± 1.2 nm and exhibit a positively charged surface in the presence of quaternary ammonium. These Au nanoparticles were added into the as-synthesized Na_2SO_4 nanowires in 2-propanol solution, followed by an incubation of 10 minutes until the ruby-red solution of Au nanoparticles turned into the final deep-purple color. Subsequently, precipitates were observed and collected by centrifugation. The Na_2SO_4 nanowire templates were then removed by washing in water several times. The TEM images of the resulting Au NPTs are shown in panels a and b of Figure 5. The positive surface charge of the Au nanoparticles adsorbed on the Na_2SO_4 nanowires accompanied with coalescence to form tubular structures, while the excess Au nanoparticles were self-aggregated as indicated by the arrows. The inset of Figure 5b presents the ED (electron diffraction) pattern of a single Au NPT showing four rings, (111), (200), (220), and (311) from center to outside, which were identified as Au. The Au NPTs can be further calcined to 300 °C (5 °C/min) for 30 min. This temperature is sufficient for the melting of the nanoparticles on the surface of the Au NPTs. Figure 5c displays the resulting Au nanotubes, where the aggregates of Au nanoparticles also melted and formed particles with relatively larger diameters, as indicated by the arrows. To separate Au nanoparticles from Au NPTs or Au nanotubes, a simple centrifugation process (500 rpm, 1 min) was operated twice and removed 50% of particles. A higher centrifugation rate did not apparently improve efficiency to exclude particles since the resulting nanotubes in length can be readily longer than 1 μm. Size exclusion was also performed by filtration using filter papers with pore sizes ∼1 μm and could achieve an efficacy of about 60−70% in separation (Supporting Information). A more efficient separation method needs to be developed and is currently underway.

Conclusions

We have successfully synthesized sodium sulfate nanowires by a simple solution approach. The as-synthesized Na_2SO_4

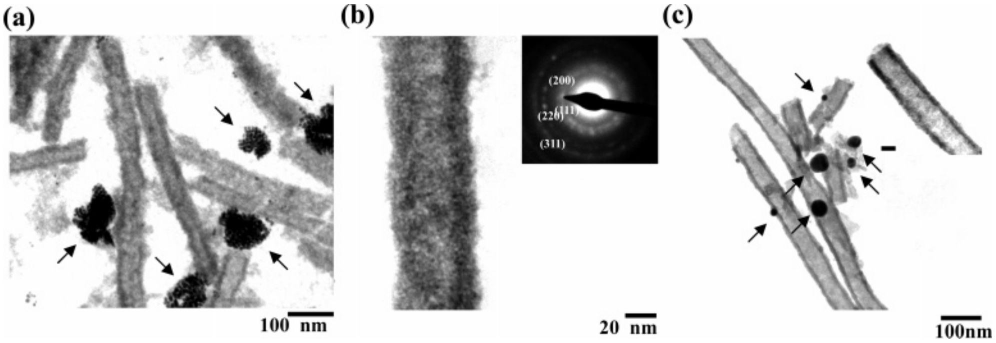


Figure 5. (a) TEM image of the Au NPTs and Au nanoparticle aggregates (arrows). (b) TEM image with high magnification of a single Au NPT. (Inset) ED pattern of the corresponding nanotubes). (c) Au nanotubes derived from the calcination of the Au NPTs at 300 °C for 30 min accompanied by large Au nanoparticles as indicated by the arrows. (Inset) High magnification of a single nanotube (scale bar = 20 nm).

nanowires can be readily dissolved in water. We also demonstrated that the Na_2SO_4 nanowires served as a water-removable template for the fabrication of PE and Au nanotubes using the LbL method and particle self-assembly, respectively. This versatile new nanotube-synthesis protocol based on water-dissolvable Na_2SO_4 nanowires holds great potential for innovative composite materials and biomedical applications such as artificial genes or tissue engineering.

Acknowledgment. We thank the National Science Council of Taiwan for financially supporting this work.

Supporting Information Available: TEM and SEM images and the analysis of EDX and FTIR spectra for the relevant Na_2SO_4 nanomaterials, TEM images and FTIR characterization for PE_{12} nanotubes, and TEM view for Au NPTs. This material is available free of charge via the Internet at http://pubs.acs.org.

JA063221Z