

Large-Scale Synthesis of Uniform Nanotubes of a Nickel Complex by a Solution Chemical Route

Lin Guo,^{*,†} Chenmin Liu,[†] Rongming Wang,[‡] Huibin Xu,^{*,†} Ziyu Wu,[§] and Shihe Yang^{*,||}

School of Materials Science and Engineering, Beijing University of Aeronautics and Astronautics, 100083, China, Electron Microscopy Laboratory and State Key Laboratory for Mesoscopic Physics, School of Physics, Peking University, Beijing 100871, China, Beijing Synchrotron Radiation Facility, Chinese Academy of Sciences, 100039, China, and Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

Received November 2, 2003; E-mail: guolin@buaa.edu.cn; chsyang@ust.hk

In the past few years, tubular nanostructures have aroused considerable interest due to their exceptional properties and potential applications in catalysis, composite materials, and optoelectronics.^{1–4} The discovery of carbon nanotubes (CNT) in 1991 has sprawled the belief that other layered materials may also roll up into tubes just as the graphite sheets do.⁵ This is reasonable because the layered structures tend to bend to eliminate dangling bonds by the intralayer linkage. As a result, the syntheses of many inorganic tubular structures such as MoS₂, WS₂, BN, and V₂O₅ nanotubes have been achieved.^{6–11} However, these nanotube synthesis methods require either extreme conditions such as high temperatures or preformed templates. Therefore, it remains a challenge to find simple and mild routes to synthesize tubular nanostructures of inorganic materials. Recently, relatively mild conditions of chemical precipitation were adopted for the synthesis of nanotube-like structures of NiS,¹² Cu(OH)₂,¹³ and titanate.¹⁴ Here, we demonstrate a simple solution-phase approach for the synthesis of novel nanotubes of a nickel complex [Ni(NH₃)₆]Cl₂. [Ni(NH₂NH₂)₂]Cl₂ is found to be the precursor, which is decomposed to form the nanotubes. The nanotubes are very stable in ambience after surface modification using PVP, a very important feat for future applications.

The layer-rolled [Ni(NH₃)₆]Cl₂ nanotubes were obtained by the reduction of NiCl₂·6H₂O with hydrazine monohydrate in the presence of poly(vinylpyrrolidone) (PVP, *M_w* 40 000) (see S-1 in Supporting Information). First, a solution was prepared by dissolving NiCl₂·6H₂O and PVP in ethylene glycol (EG). This was followed by a dropwise addition of hydrazine monohydrate at room temperature with simultaneous vigorous agitation. Second, the homogeneous mixture was heated to the boiling point of EG for refluxing (~197 °C). After the mixture was refluxed for 5 h, a light violet precipitate was obtained, which was separated by centrifugation and washed with absolute ethanol. The composition of the as-prepared product was determined by XRD (Figure 1). The diffraction peaks, except those marked with stars and diamonds arising respectively from the undecomposed [Ni(N₂H₄)₂]Cl₂ (JCPDS No. 28-0695) and nested nickel particles (JCPDS No. 04-0850), conform to the {111} facet group, including (111), (222), (333), and (444), of the fcc structure of [Ni(NH₃)₆]Cl₂ (JCPDS 76-1842). The disappearance of the diffraction peaks of (220), (311), (400), (422), etc., when compared to the standard powder XRD pattern, indicates the rolling of the (111) crystal plane.

The low-magnification TEM (Figure 2a) images show that the product was formed in a rodlike morphology with a remarkably uniform shape and size. The Ni complex nanotubes have diameters

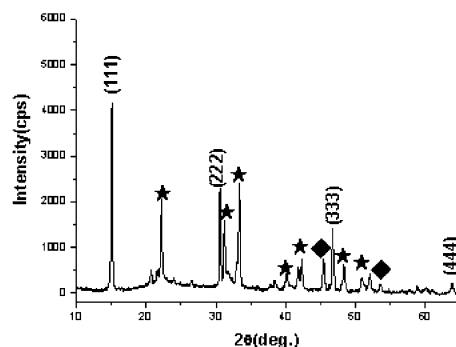


Figure 1. XRD pattern of as-synthesized Ni complex nanotubes.

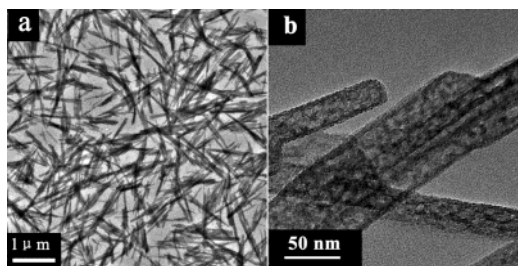


Figure 2. (a) TEM image of the as-prepared Ni complex nanotubes at a low magnification. (b) TEM image of the same samples as in (a) but with a higher magnification.

ranging from 20 to 40 nm and lengths of ~2 μm. More importantly, the nanotube yield is rather high and the purity is outstanding as is evident from the images. The TEM image at a higher magnification (Figure 2b) reveals the tubular structure of the product with a strong contrast between the dark edges and the pale center. However, close inspection of Figure 2b reveals that the center of the nanotube is not completely hollow. Instead, the nanotubes are often filled with amorphous substances, which are decomposed rapidly under the electron beam, leaving behind a few particles nested in the tubes.

Further information on the tubular structure was acquired using the HRTEM technique. Figure 3a and 3b shows HRTEM images of a tube from the portions of the stem and the head, respectively. The corresponding fast Fourier transformation (FFT) pattern is given in the inset of Figure 3b. It can be seen that the nanotube has closed but amorphous tips and the thickness of the nanotube wall is about 3–5 nm. The spacing between the rolling layers in the perpendicular direction to the tube axis is 0.584 nm, which is almost the same as the *d*₁₁₁ spacing of [Ni(NH₃)₆]Cl₂. This is in excellent agreement with the XRD result presented above. Moreover, the HRTEM images show clearly that the upper portion of the tube has one more layer than the lower portion; there are, respectively, 5 and 4

[†] Beijing University of Aeronautics and Astronautics.

[‡] Peking University.

[§] Chinese Academy of Sciences.

^{||} The Hong Kong University of Science and Technology.

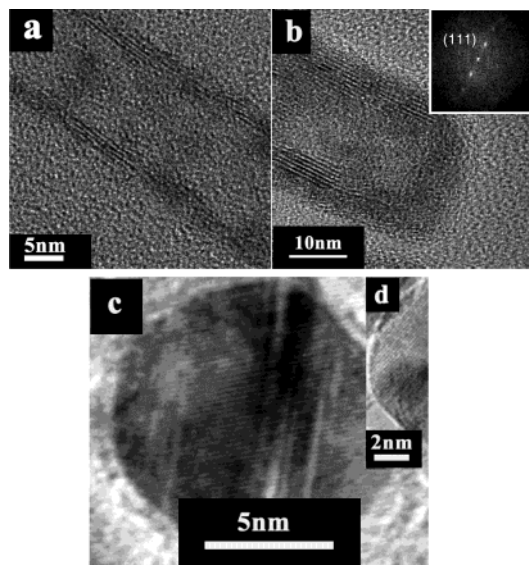


Figure 3. (a) Lattice-resolved HRTEM image taken at the stem of a single nanotube. (b) Lattice-resolved HRTEM image taken at the head of a single nanotube. The inset shows the corresponding fast Fourier transformation (FFT) pattern from the digitalized 1024×1024 HRTEM image. (c) and (d): Lattice-resolved HRTEM images of nested Ni nanoparticles, which are obtained from the decomposition of the amorphous substances in the nanotube.

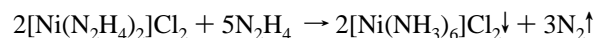
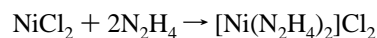
layers in Figure 3a and 8 and 7 layers in Figure 3b. This strongly supports that the nanotubes are formed by the rolling mechanism. More specifically, the closest-packed (111) sheets of the fcc Ni complex are continuously rolled into nanotubes. More evidence for the formation of the $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ nanotubes can be found in the Supporting Information (S-2).

Recalling that there are some amorphous substances left inside the nanotube, which are decomposed rapidly into nested particles under the electron beam, Figure 3c shows the HRTEM image of a remnant nanocrystal nested in a nanotube with an interplane spacing of 0.203 nm. Another interplane spacing of 0.180 nm has also been found (Figure 3d). These interplane spacings match well the corresponding literature values of (111) and (200) planes of a pure nickel crystal (fcc), respectively (JCPDS No. 04-0850). As mentioned above, the existence of the fcc Ni phase is also manifest in the XRD pattern in Figure 1.

In the nanotube synthesis, after the hydrazine monohydrate was added to the reaction system, the solution turned turbid and sky-blue, indicating the formation of a stable complex between Ni^{2+} and N_2H_4 .¹⁵ This complex is $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$, as identified by the XRD analysis. We believe that the nanotubes are produced from the decomposition of the complex $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$. Note that the decomposition is slow according to our XRD investigation (see S-5 in Supporting Information). Such a slow decomposition may be essential for the nanotube formation. The amorphous materials observed are then from the remnants of $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$, which is very sensitive to the electron beam illumination and rapidly decomposed to fine Ni particles as shown in Figures 2 and 3.

The reactions that account for the growth of the $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ nanotubes are essentially composed of complexation, reduction, and decomposition. In the beginning, Ni^{2+} reacts with hydrazine to form a sky-blue complex, $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$, which is very stable in ambience.¹⁵ When the temperature is raised to the boiling point of ethylene glycol, the $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ complex begins to decompose accompanied by the color change from sky-blue to orange and the brisk bubbling in the solution. Finally, light violet precipitates are formed, which have been testified to be $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ nanotubes.

The posited reactions are as follows:



Yet how are the layer-rolled nanotubes formed during the decomposition of $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$? It seems that the presence of hydrated H_2O in $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ plays an important role simply from the experimental results (see S-3 in Supporting Information). Conceivably, the decomposition product $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ may self-organize into a layer structure induced by the presence of a small amount of water as proposed by Jiang et al.¹² Here, the water molecules help to passivate the surfaces of the $[\text{Ni}(\text{NH}_3)_6]^{2+}$ layers by forming the $\text{NH} \cdots \text{OH}_2$ hydrogen bonds. Such a layer-structured precursor tends to bend under stress and roll into a tubular form accompanied by the elimination of water. During the rolling process, some undecomposed $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ may be nested in the nanotubes. This explains why the decomposition of $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ is very slow. Further studies on the mechanistic details are in progress.

In summary, a novel tubular nanostructure of $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ has been synthesized by a simple wet chemical method. The $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ nanotubes are 30–40 nm in diameter and $\sim 2 \mu\text{m}$ in length. The walls of the nanotubes are about 3–5 nm thick. All of our data indicate that the nanotubes are assembled by rolling the (111) sheets of the Ni complexes. The advantages of our method for synthesizing the Ni complex nanotubes lie in its simplicity, high yield, and mild reaction conditions. Therefore, it offers an attractive and convenient path to large-scale production. In ongoing experiments, we hope to effectively control the amount of encapsulated materials in the nanotubes, extend our method to the synthesis of nanotubes of other transition metal complexes, and investigate the properties of the new nanotube materials.

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Note Added after ASAP: In the version published on the Web 3/20/2004, the reference to Figure 3d in the first paragraph on this page is incorrect. The final Web version published 3/26/2004 and the print version are correct.

Supporting Information Available: Experimental details; additional spectroscopic data; data on the effects of hydrated water and PVP; data on the decomposition of $[\text{Ni}(\text{N}_2\text{H}_4)_2]\text{Cl}_2$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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