

Fabrication of Ru and Ru-Based Functionalized Nanotubes

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The chemical preparation of nanoscale Ru and Ru-based materials is of fundamental importance in areas such as advanced material synthesis,¹ energy storage and conversion,² and heterogeneous catalysis.³ Despite the extensive efforts of research for Ru nanoparticles to date, there has been no report on the preparation of Ru nanotubes. Meanwhile, the template synthesis⁴ has been successfully used to prepare various nanotubes and nanofibrils made of carbon,⁵ metal,⁶ semiconductor,⁷ polymer,⁸ and other materials.⁹ In this approach, the template membrane serves as a scaffold for other materials to be assembled with a morphology similar (or complementary) to that of the template pore. Because Ru and Ru-based nanoparticles have shown potentials as catalysts in fuel cells based on Nafion membranes,¹⁰ and, furthermore, hollow nanostructures of noble metals such as Au, Pd, and Pt exhibit properties completely different from those of their bulk form,^{11–13} Ru-based functionalized nanotubes should be of great interest. Here, we describe the synthesis of Ru and Ru–Pt nanotubes via a template method, the preparation of Ru–Pt-core/Nafion-sheath composite nanotubes by a dip-and-dry process, and the catalytic activity of the composite nanotubes for the electrochemical oxidation of methanol.

A pressure-filter-template technique that overcomes the problem of pore blocking by applying external pressure¹⁴ was utilized to prepare Ru and Ru–Pt nanotubes (Figure S1). In brief, to synthesize Ru nanotubes, Ru(NH₃)₆Cl₃ (99.9 wt %, Johnson & Matthey) solution (0.1 M) was squeezed through an aluminum oxide template (Φ10 mm with a mean inner pore diameter of 0.05 μm and a height of 60 μm, supplied by Whatman International Ltd). This aluminum oxide template was first sandwiched by commercial Millipore filters (Millipore Co.), and then further reinforced by placing Pt meshes on both the top and the bottom sides of the sandwich, and finally it settled in a vertical cylindrical stainless steel tube. A heated hydrogen–argon atmosphere (5% H₂ + 95% Ar) was introduced into the tube with a flow rate of 8 mL/min, while the furnace was held at 180 °C for 1 h, with alternation of the squeezing and washing (by distilled water) steps. After being cooled to room temperature, the aluminum oxide membrane was dissolved by 2 M NaOH solution. The remaining black solid was collected, washed several times with absolute ethanol and distilled water, and finally dried at 80 °C for 1 h under reduced pressure.

The phase purity of the as-synthesized sample was characterized by X-ray diffraction (XRD) (Rigaku D/Max-2500 diffractometer with Cu Kα radiation, λ = 0.15405 nm). Figure 1a shows a typical XRD pattern of the product, which can be readily indexed to a pure hexagonal phase of Ru [space group: *P63/mmc* (194)] with lattice constants *a* = 0.27061 nm and *c* = 0.42823 nm. This is in good agreement with the standard values for the bulk hexagonal Ru (ICDD-JCPDS card No. 06-0663). The morphologies of the product were examined by scanning electron microscopy (SEM) (Philips 505 microscope). Figure 1b shows a characteristic SEM image of the as-synthesized sample, which indicates that a large quantity of nanotube-bundle filaments with good uniformity were obtained. These Ru nanotubes bundles are approximately 60 μm

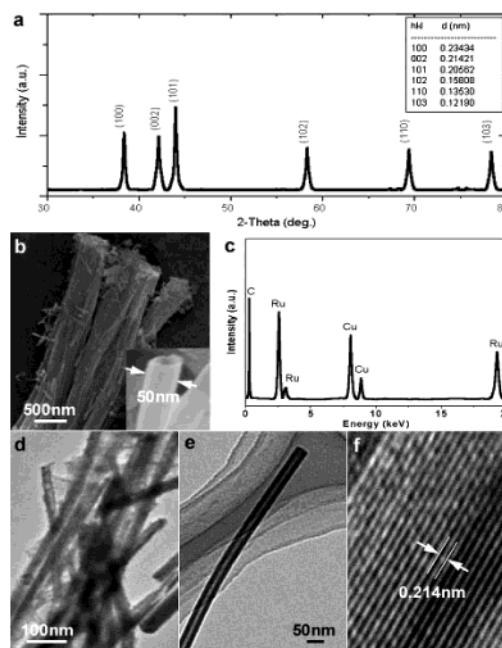


Figure 1. (a) XRD, (b) SEM, (c) EDXS, (d,e) TEM, and (f) HRTEM of the tube-edge analysis of Ru nanotubes that were synthesized by the pressure-filter-template method.

in length, similar to the height of the template used. A significant proportion (>95%) of the sample exhibits a tubular (inset of Figure 1b) rather than a nanoparticle structure. The compositions of the nanotubes were determined by energy-dispersive X-ray spectroscopy (EDXS) (Oxford 6650 Instrument), as shown in Figure 1c, where the C and Cu fluorescence is due to diffuse scattering from the supporting substrate. This indicates that the nanotubes contain only Ru.

Transmission electron microscopy (TEM) (Philips Tecnai F20 microscope with 200 kV operating voltage) provides further insight into the morphology and microstructure of the as-synthesized Ru nanotubes (Figure 1d–f). A low magnification TEM image of the nanotubes is shown in Figure 1d. The outer diameter of the nanotubes is about 50 nm, while the inner diameter is around 20–40 nm. The thin nanotube wall (~5 nm) is strong enough to support the tube to extend and keep straight, because of the superior elasticity of the bonding between metal atoms. As shown in Figure 1e, the hollow interior nanotube is clearly visible. A high-resolution TEM (HRTEM) image of the edge of a single Ru nanotube with the tube axis perpendicular to the *c*-direction is shown in Figure 1f, which indicates its highly crystalline structure and the uniformity in wall thickness. Layer fringes are visible along the tube walls, and a layer separation of approximately 0.214 nm was observed. This value corresponds to the separation between (002) planes in bulk Ru.

The present template technique can be easily extended to prepare Ru-based nanotubes, such as Ru–Pt composite nanotubes (Figure

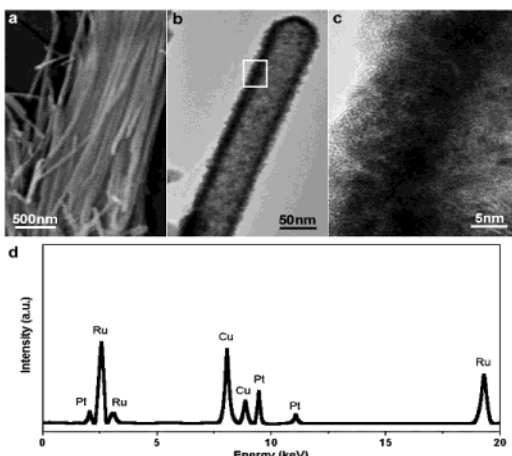


Figure 2. (a) SEM, (b) TEM, and (c) HRTEM of a magnified area marked in (b), and (d) EDXS analysis of the as-synthesized Ru–Pt nanotubes. The strong singlets for Cu in the EDXS spectrum came from the copper grid on which Ru–Pt nanotubes were supported for TEM measurement.

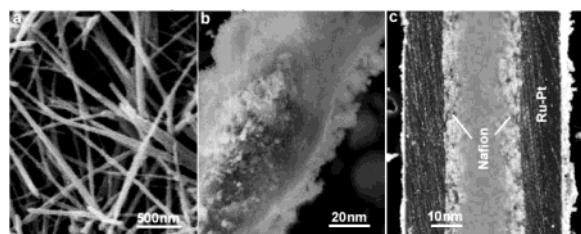


Figure 3. SEM images of Ru–Pt/Nafion composite nanotubes at (a) low magnification, (b) high magnification, (c) and cross-section analysis.

2). When a solution of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (0.06 M) and K_2PtCl_6 (0.02 M) was used, the crystalline morphologies of the formed nanostructures were somewhat different from those of Ru nanotubes. As compared to the Ru nanotubes obtained from using $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, the tubules formed from $\text{Ru}(\text{NH}_3)_6\text{Cl}_3 + \text{K}_2\text{PtCl}_6$ may have multiple nanoparticles to block the template pores. However, the formation of blocks inside the pores could be avoided by using a low concentration of the mixture precursor (<0.1 M). Close inspection shows the grain sizes of the tube walls range in diameters from 2 to 5 nm with a number of defects (Figure 2b,c), confirming the growth mechanism of “nanoparticle nanotubes”.¹⁵ The copresence of Ru and Pt was verified by EDXS as shown in Figure 2d. Quantitative analysis of the yield reveals a composition of 74.6 atom % Ru and 25.4 atom % Pt in the irradiated nanotubes. These data were consistent with those expected on the basis of the stoichiometric ratio between the complex precursors, that is, 0.06 M $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ with 0.02 M K_2PtCl_6 , which led to an average Ru content of 75 atom %.

We also have prepared Ru–Pt-core/Nafion-sheath coaxial nanotubes by repeatedly dipping the as-synthesized Ru–Pt nanotubes into a 5% Nafion solution and allowing the solvent to dry between dipping. After five dip-and-dry cycles, it can be seen that the Nafion microencapsulated well on both the outside and the inner surfaces of the Ru–Pt nanotubes (Figure 3). The thickness of Nafion is approximately 2–8 nm on top of each surface of the Ru–Pt nanotubes. It can be clearly seen that the Nafion is tightly bound to the Ru–Pt nanotubes.

One advantage of the as-prepared Ru–Pt-core/Nafion-sheath composite nanotubes is their high catalytic activity for methanol oxidation at 25 °C (Figure S2). It was shown that this nanocomposite exhibited the onset of methanol oxidation at about 0.19 V versus Ag/AgCl and a large methanol oxidation peak at around 0.5 V (versus Ag/AgCl). The potential of this methanol oxidation

peak was much lower as compared to that on Pt–Ru alloy¹⁶ and Pt–Ru nanoparticles.¹⁷ In addition, no peak was observed on the reverse scanning process, indicating that the Nafion coating well protects the Pt oxidation. This catalytic enhancement is critically needed to achieve enhanced performance in direct methanol fuel cells (DMFC).

In summary, Ru and Ru–Pt nanotubes were prepared using a pressure-filter-template technique. In addition, Ru–Pt-core/Nafion-sheath composite nanotubes were fabricated by a dip-and-dry process. Interestingly, the direct methanol oxidation is observed with such composite nanotubes, showing high catalytic activity at 25 °C. Further work on the application properties of such nanostructures as catalysts is underway.

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Supporting Information Available: Methods and schematic illustration for the preparation of Ru and Ru–Pt nanotubes, electrochemical measurements for methanol oxidation on Ru–Pt-core/Nafion-sheath composite nanotubes, and the cyclic voltammogram (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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