

Preparation of Platinum and Palladium Nanotubes Using MPTMS-Functionalized Silica Spheroids as Templates

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Abstract: Platinum and palladium nanotubes were prepared by the adsorption of metal nanoparticles onto functionalized silica templates. The silanizing agent 3-mercaptopropyl trimethoxysilane was reacted with the surface of the silica templates to present thiol-terminal groups. Dissolution of the silica template using 10 M HF solution enabled the formation of self-organized metallic platinum and palladium nanotubes. When the temperature of the metal reduction process was increased from 4 to 80 °C, this method was more effective than the metal reduction conducted at room temperature. The platinum and palladium nanotubes were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS).

Keywords: platinum nanotube, palladium nanotube, silica template, coating, metal reduction

Introduction

The development of new materials has increased in recent years and it is expected to be even more prominent in the future. Since the initial discovery of carbon nanotubes (CNT) in 1991 [1], a number of one-dimensional (1-D) controlled nanotube materials have attracted a great deal of attention. These nanotube materials possess unique physical and chemical properties, which can be utilized in technological applications such as electronics [2], chemical sensing [3], and electron field emission [4].

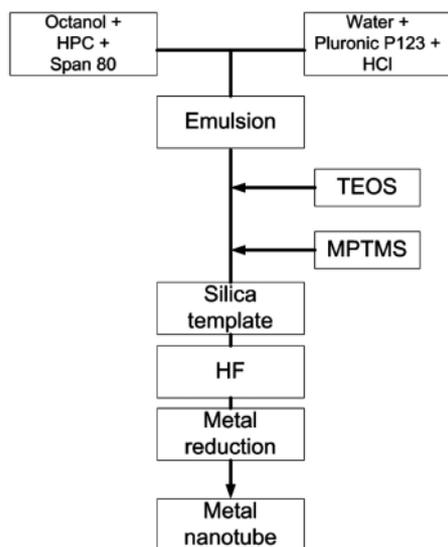
Nowadays, much effort has been exerted toward the preparation of non-carbon nanotubes because of their wide range of industrial and biological applications, e.g., as promising candidates for elementary units of electronic devices, drug delivery system (DDS), catalysis, and separation [5]. In particular, research into new classes of nanotubes including metal oxides [6] and elemental metals (Ag [7], Au [8], Pt [9], Pd [10]) has progressed greatly; such metal nanotubes (MNT) often exhibit properties that are substantially different from those of general particles. Structurally controlled MNTs have

been synthesized through template-based processes using self-assembled surfactants [11], alumina membranes [12], and metal templates [13]. Nanostructures with hollow interiors were commonly prepared by coating a thin layer of the desired materials onto the surfaces of templates, followed by selective removal of the templates through wet chemical etching or calcination.

Sol-gel chemistry is commonly used for the preparation of inorganic materials such as glasses and ceramics. In general, most silica materials are prepared by sol-gel processes. Stöber firstly performed it to synthesize monodisperse silica particles in 1968 [14]. This process is based on the hydrolysis of tetraethoxysilane (TEOS) in alcoholic media under catalysis of ammonia. In addition, emulsion-gel technology can be used to obtain micro-sized silica particles [15]. This method employs the Stöber method in emulsions to extend the particle size as micro-sized and to change the silica properties using other surfactants or polymers.

Herein, we report a novel versatile approach toward the fabrication of platinum and palladium nanoshells on silica templates that had been functionalized with terminal thiol groups. Some MNTs are partly bent or broken as a result of dissolution and drying, due to the limitation of weak mechanical strength, when the MNTs are made us-

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Scheme 1. Experimental procedure for the preparation of metal (Pt and Pd) nanotubes.

ing soft templates or membranes. However, in our approach, the MNTs exhibit increased strength. The silica surface was modified easily using a sulfur-based organic layer to coat the metal nanoparticles. This method is useful to attach noble metals on the surfaces of the templates and to produce noble metal nanotubes. Metal layers of platinum or palladium were coated directly on the silica templates by increasing the temperature stepwise and then the silica template was treated in HF solution to remove silica materials. To analyze the characteristics of metal nanotubes, we used FE-SEM, TEM, and XPS techniques.

Experimental

Preparation of Functionalized Silica Micro-Spheroid

All commercial chemicals were used without further purification. To increase the stability of the emulsion and prevent irregular growth of the silica particles, hydroxypropyl cellulose (HPC, Sigma-Aldrich) polymer was used in the oil phase. HPC was dissolved in 1-octanol at 80 °C. This solution was cooled to 40 °C and then 3 wt% of sorbitan monooleate (Span 80, Sigma-Aldrich) was mixed. 10 wt% P123 (Sigma-Aldrich) was dissolved in deionized water containing HCl (Duksan Pure Chemical) and then it was added in the oil phase to form an emulsion. The P123 was used to control the shape of the silica particles and to disperse the water droplets in the oil phase. The weight ratio of the water phase to the oil phase in the emulsion was kept at 1:9. After the W/O emulsion was formed, tetraethyl orthosilicate (TEOS) of $R_w = 10$ (R_w = molar ratio of water to TEOS) was added to a previously prepared W/O emulsion. After 1 h,

3-mercaptopropyl trimethoxysilane (MPTMS, Sigma-Aldrich) as an activating agent of the surfaces was added to the emulsion. TEOS and MPTMS molecules were reacted with water droplets for 12 h. The reaction temperature was maintained at 40 °C. The final products were washed repeatedly with ethanol and kept at room temperature for 24 h.

Preparation of Platinum or Palladium Metal Nanotubes

First of all, the surface of the silica templates was treated with the thiol-terminated silanizing agent MPTMS. Next, 1 g of functionalized silica particles was dispersed in 300 g of water. This solution was cooled to 4 °C. Subsequently, 0.1 g of H_2PtCl_6 or $Pd(NO_3)_2$ and 6 g of NH_4OH were injected into the solution while stirring moderately. After 10 min, 10 mL of an ice-cold aqueous solution containing 0.132 g of sodium borohydride ($NaBH_4$) was added to the silica-solution and maintained for 2 h. Metal reduction of platinum or palladium was initiated by sodium borohydride in the ammonia aqueous solution. To generate small metal particles, the metal reduction was conducted at 4 °C. By increasing the temperature from 4 to 80 °C step by step, numerous metal nanoparticles were eventually formed and they are aggregated together on the template surface layer. To obtain an MNT, the silica templates were etched out using 10 M HF solution.

Characterization

The particle morphologies were determined by field emission scanning electron microscopy (FE-SEM) using a JEOL JSM-6700F system operated at a 5.0-kV accelerating voltage. For transmission electron microscopy (TEM) studies, a small drop was taken from a suspension of ethanol and placed on a copper TEM grid pre-coated with amorphous carbon. The resulting sample was examined with a JEOL JEM-2000EXII instrument operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed with an electron spectroscopy for chemical analysis (ESCA, Omicron EA125, Philadelphia, PA) system using a Mg $K\alpha$ source at 1253.6 eV. The X-ray powder supply was operated at 200 W (20 mA \times 10 kV). The pressure in the analysis chamber during scans was kept below 2×10^{-10} mmHg.

Results and Discussion

Metal nanotubes consisting of platinum and palladium were successfully synthesized using silica templates functionalized with thiol groups. These functionalized silica templates were made in W/O emulsions including Pluronic P123 copolymer. An emulsion is a very fine dispersion of one liquid in another solution that is immisci-

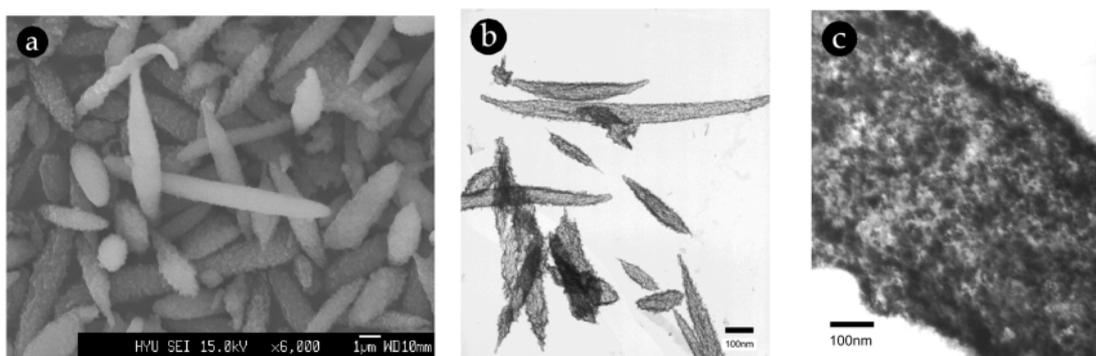


Figure 1. FE-SEM and TEM images; (a) SEM image of Pt-coated silica materials. (b) TEM image of Pt nanotubes prepared by treating $\text{SiO}_2@\text{Pt}$ samples in (a) with 10 M HF. Scale bar is equal to 1 μm . (c) Magnification of the TEM image in (b). Scale bar is equal to 100 nm.

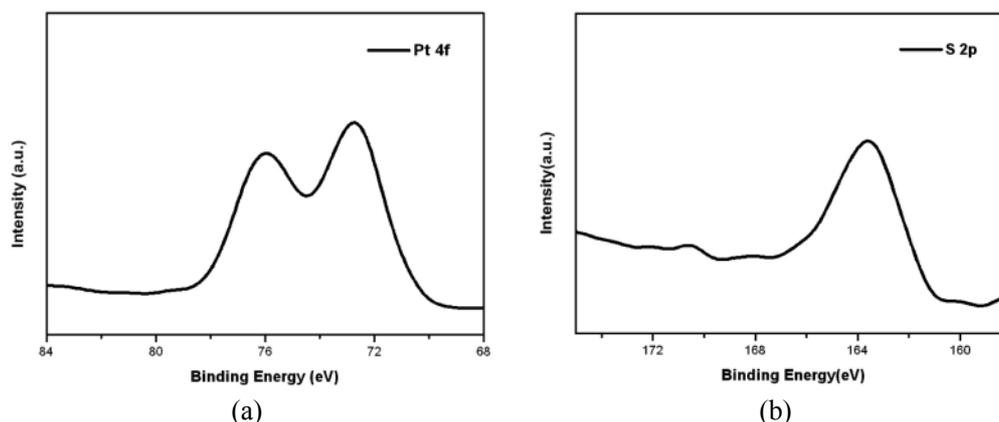


Figure 2. XP spectra acquired from (a) a Pt sample after chemical reduction adsorbed on (b) the thiol groups.

ble. Because TEOS molecules were hydrolyzed by contact with water molecules at the W/O interface, they penetrate into the water phase of the W/O emulsion through the oil phase and interfacial surfactant layer. As the hydrolysis proceeds, the SiOH-based molecules become more water-soluble because of the presence of polar silanol groups. In addition, the condensation takes place at the W/O interface and within the aqueous droplets that serve as micro-reactors.

Many groups have employed the triblock copolymer Pluronic P123 to synthesize mesoporous silica materials such as SBA-15 under strongly acidic conditions [16]. We used Pluronic P123 not as a template but as a controller of the shape of silica particles to obtain spheroidal-type silica particles. Generally, silica particles prepared in a W/O emulsion have spherical shape. However, when the poly(ethylene oxides)-*b*-poly(propylene oxides)-*b*-poly(ethylene oxides) (PEO-PPO-PEO) triblock copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123) was added in the W/O emulsion under acidic conditions, water droplets arrange regularly and link among about three to five droplets. Consequently this phenomenon affects the shape of the silica particles [17].

The thiol terminal groups act as a chemical protocol between silica templates and metal nanoparticles for the coalescence of the metal particles. Under these conditions, metal salts exist in stable positively charged states and they can be easily deposited on the negatively charged silica templates having thiol groups on their surfaces. Metal reduction was started at 4 °C (low temperature) to produce small metal particles. By increasing the temperature from 4 to 80 °C, many metal nanoparticles were formed and mutually aggregated on the surfaces of the templates coated by a metal layer. Through a change of the reaction temperature, the size of the metal nanoparticles in the outside was larger than that inside the metal nanoparticles. The amount of metal nanoparticles coated on the templates could be increased by increasing the temperature stepwise. As a result, the surfaces of the silica micro-spheroids were covered with metal particles as seeds, which provide nucleation sites for the growth of new metal layers. In addition, the size of the metal nanoparticles in the outer region was larger than that in the inner because the sizes of metal particles tend to increase with increasing temperature.

A field emission scanning electron microscopy (FE-

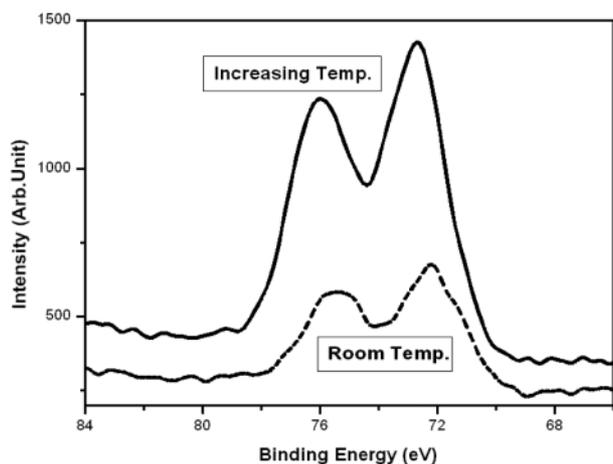


Figure 3. XP spectra acquired from a Pt sample reduced through (a) stepwise increasing the temperature and (b) maintaining room temperature.

SEM) image (Figure 1a) shows the general morphology. The product is a uniform sharp-ended $\text{SiO}_2\text{@Pt}$ micro-spheroid. The spheroid silica coated by platinum had an average length over $5\ \mu\text{m}$ with a diameter of ca. $0.5\ \mu\text{m}$. The bare silica surface was rough, which helped many metal nanoparticles to attach on the silica surface. Figure 1b shows the transmission electron microscopy (TEM) image of the products treated using 10 M HF solution. Silica was released by the dissolution of the template using 10 M HF solution from the metal composite to provide self-organized platinum nanotubes. The TEM image of the MNT (Figure 1b) represents the metal layer on the surface. In this case, the center portion of each material is lighter than its edge, indicating the formation of a shell-type nanostructure. Figure 1c displays the platinum nanoparticles on the shell of a sample, which further confirms the formation of the MNT. The thickness of the shell is 100 nm and the diameter of the central core of the nanotubes is ca. 600 nm. The size of the metal nanoparticles is ca. 10 nm.

X-ray photoelectron spectroscopy (XPS) was used to identify the presence of a platinum shell attached to the sulfur groups of the silica surfaces. The sample appears in terms of Pt 4f and S 2p XPS spectra (Figure 2). Figure 2a is a XPS spectrum of the sample; the Pt 4f has two different peaks. The Pt 4f peaks represent binding energies of 73 and 76 eV, with a spin-energy separation of 3 eV [18]. But, the small difference of 2 eV to higher binding energies would show any binding-energy shift with respect to bulk platinum. Figure 2b shows a symmetric peak at 163.5 eV; it corresponds to S 2p treated with MPTMS on the surface of the silica template. The S 2p binding energy was less than 164 eV, which is in good agreement with sulfur-metal chemical bonding [19].

The adsorption mechanism of platinum metal on the silica template is dependent on the reduction temperature. In Figure 3 (XPS data), different reduction temperatures affect the degree of metal coating. It is obvious that the variations of signal intensity are predominantly due to the difference in the interaction strength of the platinum nanoparticles. The interaction strengths between the metal particles and the thiol-terminated surfaces changed depending upon the reduction temperature during the preparation of the metal nanoparticles. The XPS intensity of the platinum nanoparticles prepared by increasing the temperature stepwise was larger than that of the particles formed at room temperature. It is likely that more metal was attached on the silica surfaces when the reduction was conducted by increasing the temperature. We found that the reduction temperature influenced the thickness of the metal layer and the formation of the hollow interior nanostructure. As a result, the reduction method involving increasing the temperature from 4 to $80\ ^\circ\text{C}$ was more effective for preparing MNTs than was reduction of the metal at room temperature.

Figure 4a reveals an FE-SEM image of powders that comprised the palladium-coated spheroidal micro-silica. The length of micro-spheroid $\text{SiO}_2\text{@Pd}$ materials was in

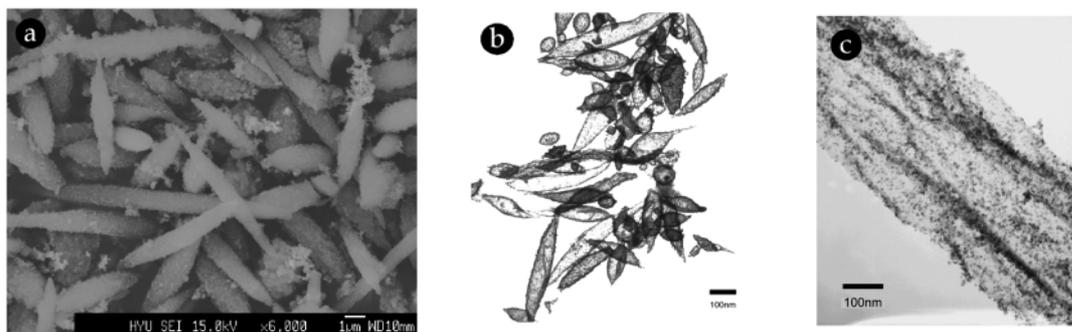


Figure 4. FE-SEM and TEM images; (a) SEM image of Pd-coated silica materials. (b) TEM image of Pd nanotubes prepared by treating the $\text{SiO}_2\text{@Pd}$ samples in (a) with 10 M HF. Scale bar is equal to $1\ \mu\text{m}$. (c) Magnification of the TEM image in (b). Scale bar is equal to 100 nm.

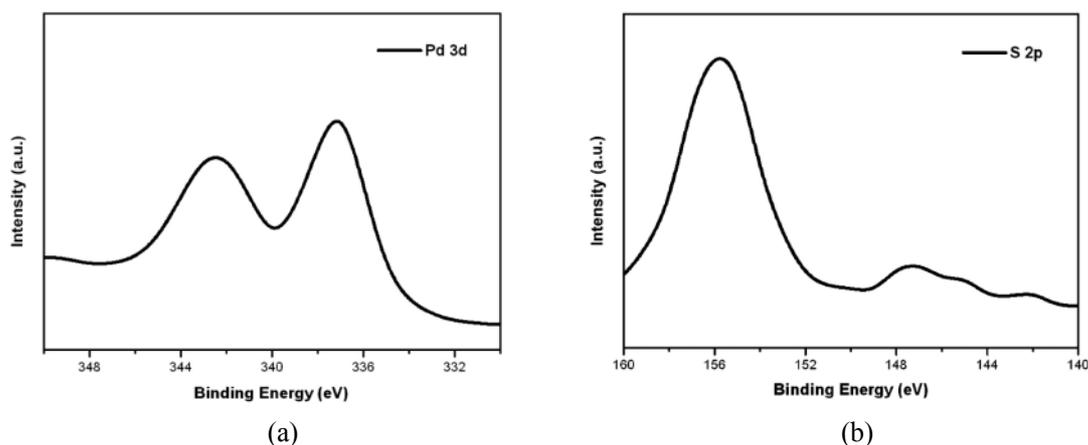


Figure 5. XPS spectra acquired from (a) the Pd sample after chemical reduction adsorbed on (b) the thiol groups.

range of several micrometers and the width was ca. 1 μm . This $\text{SiO}_2@\text{Pd}$ micro-spheroid has a sharp-ended morphology and tough wall surfaces. A TEM micrograph of the $\text{SiO}_2@\text{Pd}$ sample is shown in Figure 4b. It is noted that the morphology of these palladium MNT shells is similar to that of the platinum nanoshells. From the TEM image (Figure 4b), we observe pale regions in the central parts, in contrast to the dark edges, which confirms the hollow structure of the palladium MNT. Figure 4c is a magnified view of a Pd nanotube from Figure 4b. The size of the palladium nanoparticles (Figure 4c) is similar to that of the platinum nanoparticles (Figure 1c). In addition, the thickness of the platinum coated layer is larger than that of the palladium layer. This result indicates that platinum is a more suitable source than palladium in the fabrication of metal nanotubes.

To analyze the chemical states of the Pd and S atoms, XPS studies were performed (Figure 5). The Pd 3d peaks were centered at 337 and 342 eV, with a spin-energy separation of 5 eV [20]. This result proves that the MNT consisted mostly of palladium. Figure 5b focuses on the XPS region for sulfur. This one used metal particles cleaved on the silica surface well. The peak for S 2p was found at ca. 156 eV.

Conclusions

Platinum and palladium metal nanotubes can be prepared by using silica templates. The surfaces of the silica templates presented thiol groups, which helped to make the MNTs easily. Reduction of metals (platinum and palladium) was performed using an increasing temperature. It was not possible to synthesize gold metal nanotubes because of the weak interaction between the thiol terminal groups and the gold nanoparticles. When the $\text{SiO}_2@\text{Au}$ composite materials were etched with HF solution, the silica templates were destroyed and the gold

nanoparticles remained in the HF solution. Fabrication of other metal nanotubes and the development of their applications are under investigation in our laboratory.

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