Fabrication of Pd and Pt Nanotubes and Their Catalytic Study on p-Nitrophenol Reduction

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Abstract. Pd and Pt nanotubes were fabricated using self-assembled DC₈,₉ PC lipid tubules under mild conditions at room temperature. Scan electron microscope (SEM) show the hollow and open-ended structures of prepared Pd and Pt nanotubes. The Pd and Pt nanotubes demonstrate both high catalytic activity toward p-nitrophenol reduction and excellent stability. This work has indicated the application potentials of lipid tubules in fabricating hollow metal nanomaterials.

1. Introduction

p-Nitrophenol is one of the most intractable pollutant, while its reduction product is of great commercial importance as an intermediate in pharmaceutical manufacture.[1, 2] Compared with conventional routes, it is relatively simple and clean to use sodium borohydride as reducing agent in aqueous medium under mild conditions. However, the absence of suitable catalysts makes the reaction hard to happen.[3, 4] Therefore, the study about efficient catalysts for direct hydrogenation of p-aminophenol becomes more significant.

One-dimensional (1D) nanostructures have attracted special attention due to their distinctive geometries, novel physical and chemical properties.[17, 18] Until now, all kinds of synthesis strategies of 1D nanostructures have been reported in the literatures, e.g. applying electrochemical techniques,[20] chemical vapor deposition process,[21, 22] as well as vapor-liquid-solid (VLD) growth,[23] hydrothermal/solvothermal,[24, 25] and template-directed method.[26, 27] Compared with other methods, template-directed strategy has many superiority, such as easy operation, large scale output and controllable physical dimension.

Platinum-group alloy metals as catalysts often exhibit unique catalytic properties exceeding monometallic in activity and/or selectivity due to electronic effect,[8, 9] and geometry factor and co-catalyzed methanism.[10, 11] The formation of heteroatomic bonds changes the electronic environment resulting in modification of electronic configuration.[8] Chemical bonds, forming between catalyst surface and the reactants, helps to break intramolecular bonds and form new ones during catalysis, thus the bonding ability can affect the catalytic property of catalyst.[12]

Herein, hollow and open-ended Pd and Pt nanotubes with self-assembly 1, 2-bis(10,12-tricosadiynoyl)-sn-glycero-3-phosphocholine (DC₈,₉ PC) lipid tubules as templates were fabricated
successfully. These hollow Pd and Pt nanotubes show excellent catalytic activity toward hydrogenation.

2. Experimental section

2.1. Materials

Hexachloroplatinic acid (H₂PtCl₆·6H₂O) , Palladium chloride (Shenyang Jinke reagent) , Formic acid (HCOOH) , Sodium borohydride (Sinopharm Chemical Reagent Co., Ltd) , 1,2-bis(10,12-tricosadiynoyl)-sn-glycero-3-phosphocholine (DC₈₉PC) powders , Polycarbonate membranes (Avanti Polar Lipids) , and Ethanol(Tianjin Reagents) , were used in the experiment. Millipore Milli-Q water with a resistivity of 18.2 MΩ cm was used as solvents in all experiments.

2.2. Fabrication of Pd nanotubes

There are 3 steps for fabricating Pd nanotubes, e.g., synthesis of metal tube templates, metal seed growth, and metal plating and then template removed.

(1) Synthesis of lipid nanotubule templates. 0.3 mg DC₈₉PC was dissolved in 210 μl C₂H₅OH, followed by adding 90 μl H₂O.

(2) Pd seed growth. 300 μl H₂PdCl₄ (56 mM) was added into the vial for allowing PdCl₄²⁻ adsorb to template surfaces in 5 hours. Then solution was centrifuged and replaced by 300 μl 0.67 M ascorbic acid to reduce Pd²⁺ into Pd nanoparticles. The above-mentioned procedures were repeated for several times.

(3) Preparation of Pd nanotubes. The seeded templates were diluted with 300 μl of 0.67 M ascorbic acid, and then 300 μl of 56 mM H₂PdCl₄ was added within 3 minutes. Then the template of tubules , were removed by ethanol.

2.3. Fabrication of hollow Pt nanotubes

Pt nanotubes fabrication was conducted at room temperature. 0.003g hexachloroplatinic acid (H₂PtCl₆·6H₂O) and 1 ml reduce agent, i.e., HCOOH were added into vial containing lipid tubule templates at the same time . Then vial was stable without disturb for 24 h at room temperature.

2.4. Catalytic reactions

50 mg NaBH₄ was dissolved in 50 ml deionized water firstly. Then 1 ml nitrophenol (1 mM) and 4 ml NaB₄H₄ solution were mixed in 6 ml deionized water. After a while, 3 ml solution was taken and put into the vial, followed by adding 1 mg hollow Pd or Pt nanotubes for catalytic reaction. In recycling experiment, the catalysts were centrifuged (8000, 15 min). The supernatant was removed while the catalysts were reused. For comparison of catalytic performance, 1 mg hollow Pd or Pt nanotubes were employed in the catalytic test.

2.5. Characterization

The morphology, composition, and elemental distribution of alloy nanotubes were characterized by Scanning electron microscope (SEM) and X-ray energy dispersive spectra (EDS) using Quanta 200 FEG scanning electron microscopy. X-ray diffraction (XRD) was used in the reflection mode (Cu K radiation) on a D/Max-RB diffractometer. The d-spacing value was calculated by using Bragg’s law. A Cary 5000 Scan UV-Vis spectrophotometer was used to collect UV-Vis spectra.

3. Results and discussion

For Pd plating, H₂PdCl₄ is added into Pd seeded nanotubule solution. When there were emerging black sediment at vial bottom, it means Pd nanotubes were formed successfully following removing the templates by ethanol. The morphology of Pd nanotubes was characterized using SEM and was shown in the Fig. 1a. The diameter of typical Pd nanotubes were approximate 600 nm and the diameter of lipid tubule was 500 nm. And the structure with open-ended of Pd nanotubes was seen clearly and the surface was very rough surfaces due to abundant Pd nanoparticles. The XRD pattern of
Pd nanotubes gives three strong diffraction peaks at Bragg angles of 40.15°, 46.68° and 68.11° (Figure 1b), corresponding to the (1 1 1), (2 0 0) and (2 2 0) reflections respectively and stemming from the facets of palladium crystal, e.g., representative face-centered-cubic lattice structures.[5]

Adopting HCOOH as reducing agent for Pt plating is helpful for the accurate control of nanostructure morphology, while there is no need for centrifugation or stir in the reaction process. As shown in Figure 1(c), the diameter of hollow Pt nanotube is typically approximate 500 nm. Pt nanotubes have smooth surfaces as well as uniform dimension. From Figure 1(d), there are four strong diffraction peaks at the Bragg angles corresponding to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) reflections. These diffraction peaks derive from the facets of platinum crystal and also reveal representative face-centered-cubic (fcc) lattice structures of Pt nanotubes.

Figure 1. Pd nanotubes (a) Scanning electron microscope image and (b) XRD pattern. Pt nanotubes (c) SEM image and (d) XRD pattern.

Hollow Pd and Pt nanotubes are employed for the catalytic reduction of \( p \)-nitrophenol through NaBH₄. Without catalyst, NaBH₄ is not able to reduce \( p \)-nitrophenol even for one weak. With the presence of Pd or Pt nanotubes, the color of solution turned from yellow to transparent and it turned black sediment at the bottom of vial. The precipitation was separated by centrifugation leaving colorless supernatant, i.e., complete conversion. UV-Vis spectra collected at different points in time (Figure 2a, b) show that the absorption of \( p \)-nitrophenol at 400 nm decreases while the peak of \( p \)-aminophenol at 300 nm increases concomitantly within 6 min or 5 min with Pd and Pt nanotubes as catalysts, respectively.[6, 7] There is no peaks at 388 or 302 nm suggesting that no 4-benzoquinone monoxime or 4-nitrosophenol producing.[8] The UV-Vis spectra also exhibit an isosbestic point (313 nm) between two absorption bands, and indicate that only two principal species, \( p \)-nitrophenol and \( p \)-aminophenol, influence the reaction kinetics. In addition, since the concentration of NaBH₄ greatly exceeds those of \( p \)-nitrophenol and nanotubes, the reduction rates are assumed to solely depend on the concentration of \( p \)-nitrophenol.[9] Therefore, pseudo-first-order kinetics could be applied for the evaluation for rate constants. The ratio of \( C_t \) and \( C_o \), which represent \( p \)-nitrophenol concentrations at time \( t \) and 0 respectively, is measured from the relative intensity of respective absorbance, \( A_t/A_o \). The linear relationships between \( \ln(C_t/C_o) \) and time are observed for both catalysts, implying that the reactions follow first-order kinetics. The rate constants are estimated from diffusion-coupled first order reaction kinetics using the slopes of straight lines in Figure 2c. The rate constants vary from 0.00402 to -0.0075. Moreover, the catalytic activities of Pd and Pt nanotubes keeps almost constant in 11 cycles with a slight decline of ca. 5~8% (Figure 2d), implying their excellent chemical stability.
Catalytic activity of alloy nanotubes was investigated in acetone hydrogenation. 10 mg alloy nanotubes were mixed with 0.5 mL of NaBH₄ aqueous solution (0.1 mM) and 3 mL of H₂O containing 10 μL acetone at room temperature. Ultraviolet visible spectroscopy (UV-Vis) was used to monitor the catalyzing reaction. The hydrogenation reaction was evaluated for 35 min. To verify the product from the hydrogenation of acetone, a gas chromatography analysis was performed. HP-INNOWax fused silica capillary column was used to filter analyte. The efficiency was calculated using the relation (Eq.(1))

\[
\text{Yield} \% = \frac{C_A - C_B}{C_A} \times 100\% \quad (1)
\]

Where \(C_A\) and \(C_B\) are the initial and final concentration of acetones, respectively.

![Figure 2.](image)

**Figure 2.** (a) UV-Vis adsorption spectra of p-nitrophenol solution with Pd nanotubes as catalysts. (b) UV-Vis adsorption spectra of p-nitrophenol solution with Pt nanotubes as catalysts. (c) Kinetic curve of p-nitrophenol catalyzed by hollow Pd and Pt nanotubes. (d) Cycling stability of hollow Pd and Pt nanotubes.

### 4. Conclusion

In this study, we demonstrate a novel method to prepare hollow Pt and Pd nanotubes with open ends by shear-induced lipid tubules templating. The hollow Pd and Pt nanotubes show good catalytic activities toward hydrogenation of p-nitrophenol into p-aminophenol. This work herein manifests that lipid tubules was useful for fabricating 1D nanostructures, and also exhibit application potentials for fabricating nanomaterials of other metals. Due to the heterogeneous property of hydrogenation of p-nitrophenol and operating at room temperature, the metal nanotubes could be as a potential alternative for eco-friendly and economic large-scale isopropanol production.

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