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Organic molecules modified palladium nanowires arrays prepared by high temperature liquid phase reduction*

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This paper reports high temperature liquid phase synthesis of Pd nanowires using chemically modified porous anodic aluminium oxide as template. In this synthesis process, oleic acid is used to modify the inner wall of the pores and Pd^{2+} complex with oleylamine is filled into the channel of the template. The complex is then reduced to give oleylamine-capped Pd nanowires. This paper suggests that oleic acid can improve the environment of inner wall of the pores, leading to the formation of uniform Pd nanowires. The synthetic process can be extended to make other types of nanowires.

Keywords: palladium nanowires, anodic aluminium oxide template, oleylamine-capped
PACC: 6146, 8120

1. Introduction

One-dimensional nanostructure materials including nanowires and nanotubes are of fundamental and technological importance.[1−5] They can be used as model systems for testing and understanding the fundamental concepts about the dimension and size effects on physical properties. On the other hand, they have potential applications in nanodevices. In recent decades, much effort has been devoted to fabricate one-dimensional nanostructured materials. Among these, template synthesis is one of the efficient ways in controlling the shape and dimensions of the material. Porous alumina membranes possessing uniform and straight cylindrical holes with controlled aspect ratio have been extensively used as templates for preparing uniformly sized one-dimensional nanostructure materials using various methods, such as electrochemistry,[6−12] sol-gel,[13−17] immersion technique,[18−20] chemical vapour deposition (CVD),[21,22] molecular beam epitaxy.[23] However, it is also found that the precursors used in the synthesis can not completely fill the pore of the template and uniform length nanowires are difficult to obtain. Furthermore, most of the metal nanowires have been synthesized by electrochemical deposition method. There are very few reports on producing metal nanowires using solution phase chemistry. Herein, we report a simple method to prepare single crystal Pd nanowires in organic solution using high temperature reduction method. We found that oleic acid and oleylamine could act as both lubricant for metal precursor to enter the core and surfactant for final stabilization of the nanowires. This leads to the formation of uniform nanowires.

2. Experimental Section

Materials: palladium acetylaceonate, oleic acid (>90%), oleylamine (>70%), phenyl ether (>98%) and 1, 2-dodecanol, were purchased from ACROS. All the reagents were used as received materials without further purification. Anodic aluminium oxide (AAO) template was purchased from Walfman Com., with average diameter of hole about 200 nm. AAO template was washed using ethanol and dried at vacuum atmosphere.

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2.1. Synthesis of Pd nanowires

A piece of AAO template was added into the mixture containing 0.5mmol of $Pd(acac)_2$ and 8ml phenyl ether in a three-neck flask at argon atmosphere. The mixture solution was heated to 100°C, 2.0mol 1, 2-dodecanol, 1.5mmol oleic acid and 1.5mmol oleylamine were added into mixture solution. Then this solution was heated to 200°C for 15min under argon atmosphere and to reflux at 260°C for 30min. The colour of solution was gradually changed from brown-red to black, indicating the reduction of the Pd^{2+} salt to Pd metal. When the reaction finished the solution was cooled to room temperature. The AAO template was taken from solution and washed with ethanol three times. The colour of AAO template showed slight black.

2.2. Characterization of Pd nanowires

The crystalline structure of Pd nanowires was measured by using Rigaku D/MAX 2400 x-ray diffractometer with Cu-K_α radiation (λ=0.15408 nm). In order to eliminate effect of AAO template, the Pd nanowires / AAO template was stuck on silica wafer, then immerged in 2.0 M NaOH solution for 5min to dissolve a portion of Al_2O_3. After the silica wafer was taken out from the solution, it was washed by deionized water three times and dried at argon atmosphere. A field-emission type scanning electron microscope (FE-SEM, XL30 S-FEG, FEI Corp.) was used to observe the morphologies of Pd nanowire arrays. The surface of sample was sputter-coated with gold in order to improve conductivity of the sample before FE-SEM measurement. The composition of the sample was measured from energy dispersive x-ray analysis (EDXA, FE-SEM, XL30 S-FEG, FEI Corp.). Transmission electron microscope (TEM, Tecnai-20, PHILIPS) and high-resolution transmission electron microscope (HRTEM, Tecnai F20, FEI Corp.) were used to provide low-resolution and high-resolution images of Pd nanowires, respectively. The sample for TEM was obtained by dissolving Pd nanowires / AAO template in 3 ml of 2 M NaOH solution for 30min, followed by adding 5 ml ethanol into this solution. The composition analysis of Pd nanowires was carried out on the ESCA LAB5 x-ray photoelectron spectrometer (XPS) with monochromated Mg x-ray at 10kV. The preparation of XPS samples: Pd nanowires / AAO template is adhibited on the Si wafer using conducting glue. The AAO templates were dissolved in 2M NaOH solutions for 15min and washed several times with deionized water. The Si wafer containing Pd nanowires was blown by using argon gas at room temperature.

3. Results and discussion

3.1. Morphologies of Pd nanowires

Figure 1 shows the FE-SEM images of Pd nanowires prepared by 1, 2-dodecandiol reduction of $Pd(acac)_2$ at 260°C in the AAO templates. It can be clearly seen from Fig.1 that Pd nanowires grown in AAO membranes show uniform size and a parallel arrangement. The diameters of Pd nanowires ranged from 150 to 200 nm when grown in AAO membranes with pore of 200 nm, which is less than the pore size of the template used. This could be explained by the aggregation when Pd^{2+} ions were reduced to Pd metal. Figures 1(a) and 1(b) show FE-SEM images of large area Pd nanowires after AAO templates were removed partly and completely. It could be seen that these nanowires are continuous, high oriented and dense. Inset images in Figs.1(a) and 1(b) show that all nanowires grow through the template from one side to the other, and the length of nanowires was about 8 μm. It supported that the high ordered nanowires were obtained and orientation of nanowires was toward to the same direction. Figure 1(c) is a cross-sectional FE-SEM image of Pd nanowires array after the template has been eroded in 2 M NaOH solution for 15min. It showed that the surface of Pd nanowires was smooth and cylindrical nanowires grown from the hexagonal cell of the AAO template. Some interesting phenomena are observed in this work. It is shown in Fig.1(d) that some Y-branched structures of Pd nanowires are formed. The reason for the formation of Y-branched structure may be attributed to irregular pore structure in the AAO template. This again indicated that the Pd nanowires could grow along and adhering to the inner wall of the template channels.

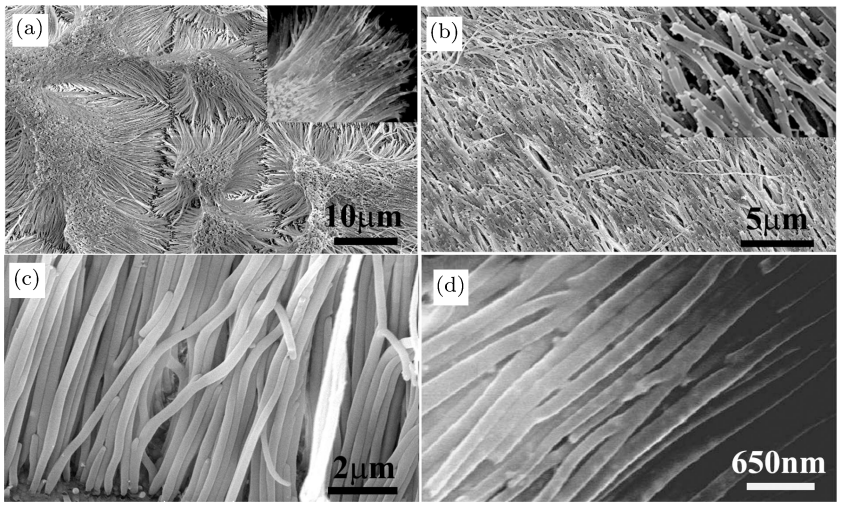

Fig.1. FE-SEM images of Pd nanowires prepared by high temperature liquid phase method. (a), large area image (inset is local magnified image); (b), top image (inset is local magnified image); (c), cross-sectional image; (d), image from cross-section area.

Figure 2 shows the TEM images of Pd nanowires. The as-prepared Pd nanowires were uniformly distributed and their average diameter distributed from 150 nm to 200 nm. It was consistent with results of SEM. The Pd nanowires show relatively straight morphologies and smooth surfaces. In the Fig.2(a), it could be seen that some of Pd nanowires crossed and overlapped with each other. Figure 2(b) showed an isolated Pd nanowire after completely dissolving the alumina. The selected-area electron diffraction pattern taken from a single Pd nanowire is shown in the inset on the upper left in Fig.2(b). It could be indexed as single-crystal Pd [110] and the nanowires grew along [110] direction. HRTEM image of Pd nanowires shown in Fig.2(c) reveals that the nanowire is single crystal.

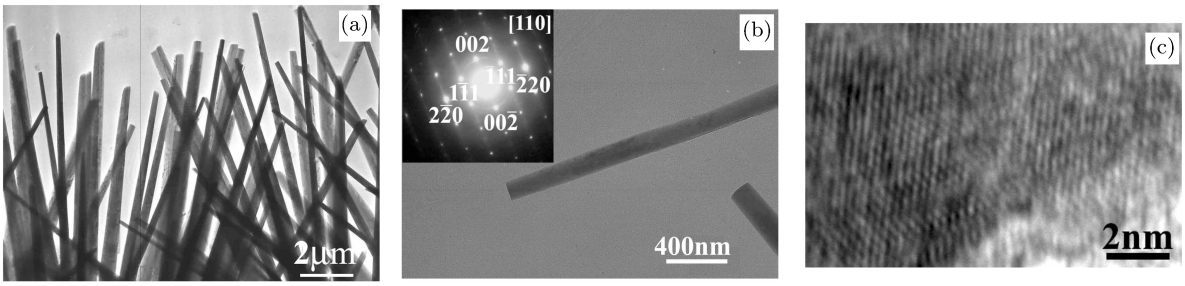

Fig.2. TEM image of Pd nanowires prepared by high temperature liquid phase method: (a), large area image; (b), isolated Pd nanowire (inset image is SAED image); (c), HRTEM image of Pd nanowire.

3.2. EDX and EELS analysis

The energy dispersive x-ray (EDX) spectrum of Pd nanowires arrays is shown in Fig.3. The EDX analysis carried out on top of Pd nanowires arrays is shown in Fig.3(a) and the peaks of element Pd are observed. In Fig.3(a), we could find peak of element C and O. The peaks of element C and O can be ascribed to the oleic acid and oleylamine capped on the surface of Pd nanowires. Another element Au is also found in the spectrum due to the Au layer sputtered to improve the conductibility of sample. In order to further confirm components of Pd nanowires, electron energy loss spectrum (EELS) is used to analyse Pd nanowires. The result is shown in Fig.3(b) and the strong Pd $M_{4,5}$, Pd M_3 edge are observed at about 336 eV and 531 eV, respectively, corresponding to the standard value of element Pd shown in inset image. We could also see peaks of N–K edge and O–K edge, indicating that oleylamine molecule has been capped

on the surface of Pd nanowires. Peaks of N–K edge and O–K edge partially overlap with peaks Pd $M_{4,5}$ edge and Pd M_3 edge because their edge values were very close.

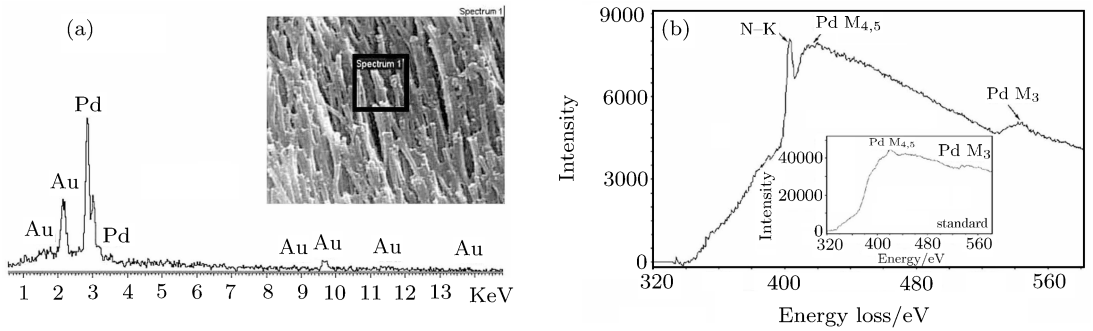

Fig.3. EDX and EELS spectra of Pd nanowires prepared by high temperature liquid phase method: (a), EDX image of Pd nanowires on the top region; (b) EELS spectrum of Pd nanowires (inset image in Fig.2(b) is standard EELS spectrum of Pd nanowires).

3.3. XRD analysis

Figure 4 shows XRD of Pd nanowires. The major reflection peaks of a fcc bulk Pd are observed. Two main diffraction peaks with 2θ values of 39.9° and 47.1° were obtained, corresponding to (111) and (200) planes of crystalline Pd, respectively.

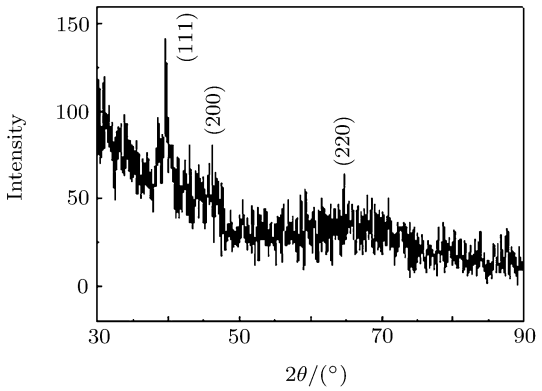

Fig.4. XRD spectrum of Pd nanowires prepared by high temperature liquid phase method.

3.4. XPS analysis

In order to investigate the composition of nanowires, XPS measurement is used to monitor surface of nanowires. Figure 5 shows XPS spectra of Pd nanowires containing a proportion of AAO template. From full XPS spectra, it can be clearly seen that the element Pd, N, O, C, and Al exist in sample. The appearance of element Al and O peaks was derived from AAO template. The peaks of N and C indicated that oleic and oleylamine molecule has been capped on the surface of Pd nanowires, which is in accordance with the result of EDX and EELS analyses. The two peaks at 335.1 eV and 340.3 eV corresponds to the binding energy of metallic Pd $3d_{5/2}$ and Pd $3d_{3/2}$, indicating that the nanowires are comprised of metallic Pd.

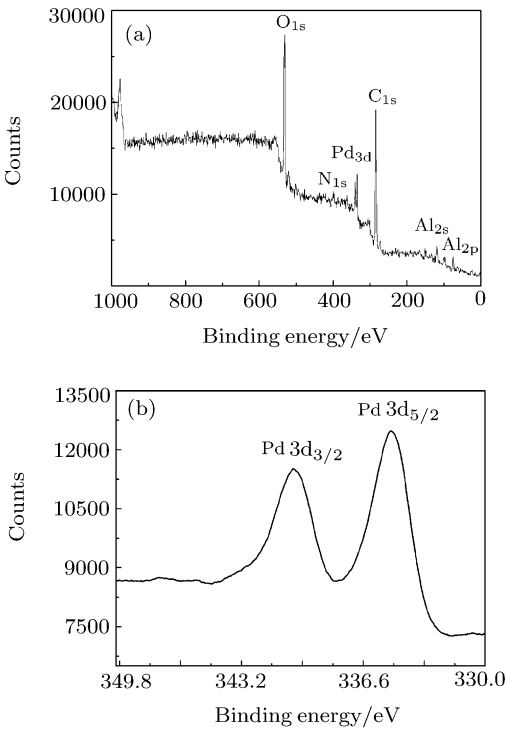

Fig.5. XPS spectra of Pd nanowires prepared by high temperature liquid phase method: (a), full spectrum; (b), XPS spectrum of Pd.

3.5. Mechanism of ordered nanowires growth

In general, direct filling can be used to grow nanoscale one-dimensional materials, but there are some potential limitations to this technique. The main drawback is that capillary force will prevent solution from entering pore and adsorbing to the inner template walls, and the incompletion of filling in AAO template may lead to either formation of short nanorods or nonuniform nanowires.[7] So the surface modification of the inner wall of pore is essential for the preparation of nanowires. Due to charge of inward-wall of AAO template pore is positive charge,[24] negative charge surfactants, such as oleic acid can be used to modify surface of inner walls by electrostatic and chemical band.[25] The hydrophobic group of surfactant can form hydrophobic environment in the channel of pore for negative charge hydrophilic group (COO^-) of surfactant can be combined with positive charged wall of pore by electrostatic attraction. A possible formation mechanism of Pd nanowires is proposed here (shown in Fig.6). (i) After the AAO template is immersed in organic solution, oleic acid modified the inner wall of pore by electrostatic attraction because the pore wall charge of AAO template is positively charged. On the other hand, capillary action can promote oleic acid to fill in the pore. In this process, hydrophobic environment is formed in pore of template and nonpolar molecule can enter into channel of pore. (ii) At the same time, Pd^{2+} ions could form complex with oleylamine (OA) by coordinating action in the solution.[26] The Pd^{2+}–OA complex can easily fill into modified pore of template due to the fact that surface of Pd^{2+}ions is surrounded by OA molecules. However, the repulsion of Pd–OA complex from the wall will confine them near the centre of pore because Pd–OA complex is positively charged.[27] (iii) When reaction temperature heated up to 200°C, Pd^{2+} ions are reduced into metal Pd^0 nuclei by polyol. Then the nuclei of Pd gradually grow near the pore centre as reaction time increases. High crystalline oleylamine-capped Pd nanowires are obtained after reaction temperature is kept at 260°C for 30min.

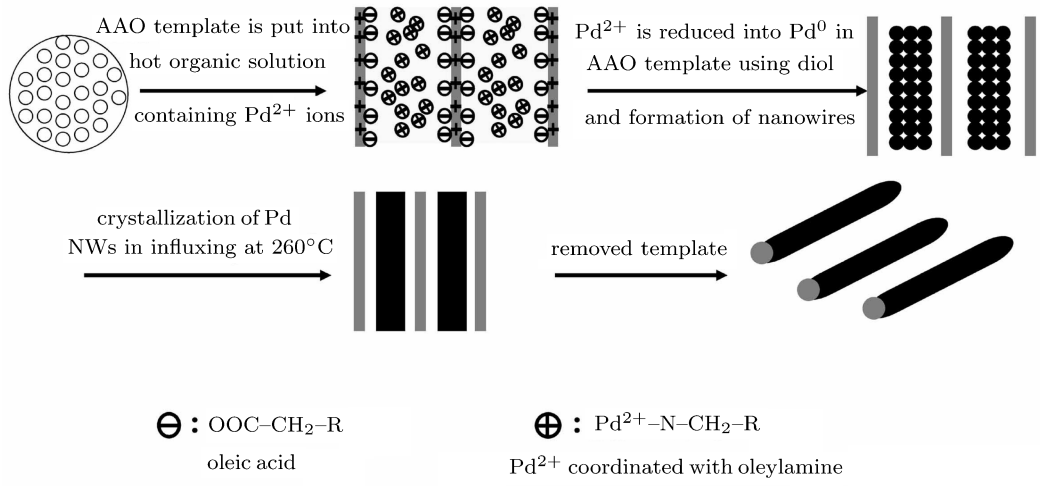

Fig.6. Schematic diagram to illustrate ordered Pd nanowires growth.

4. Conclusions

The single-crystalline Pd nanowire arrays have been prepared in porous AAO by using a simple high temperature liquid phase reduction method. In this method, the inner wall of pore are modified by using oleic acid and the Pd^{2+} complex with OA is filled into channel of template due to hydrophobic environment in pore. The complex is reduced to form Pd high ordered nanowires. Organic molecules can modify the properties of inward wall of pore and Pd nanowire arrays of uniform size are obtained. This simple method can be extended to other metal systems.

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