

Single-crystal Pt nanorods with tunable lengths fabricated by a simple glycol-assisted vacuum impregnation method†

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Received 6th January 2009, Accepted 15th January 2009

First published as an Advance Article on the web 6th February 2009

DOI: 10.1039/b900262f

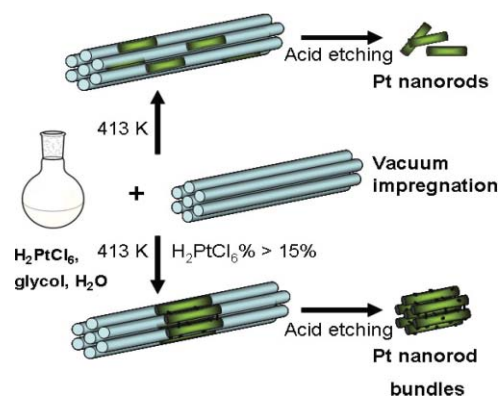
Single-crystal platinum nanorods with high aspect ratios and tunable length were fabricated on a large scale by a glycol-assisted one-step vacuum impregnation method, using mesoporous inorganic silica SBA-15 as the host.

Nanostructured materials exhibit novel properties that largely differ from those of the bulk solids. This is due to the quantum confinement effect from the changes in the density and effective band gap of the electronic energy levels as well as their high ratio of surface-to-bulk atoms.¹ Among the noble metals, platinum plays important roles in many applications in catalysis, electronics and photonics, owing to its unique physical and chemical properties.^{2–4} Therefore, the design and synthesis of size or shape controlled Pt nanostructures have been intensely studied over the years.

Beside soft template approaches,⁵ protocols coupling porous materials with electrochemical deposition, chemical vapour deposition, thermal hydrogen reduction, photo-reduction and chemical reduction have been studied.^{6–19} Anodic aluminum oxide (AAO) is one of the most widely used templates for the generation of well defined metal structures, but it is not suitable for the fabrication of nanorods/nanowires smaller than 20 nm due to an intrinsic limitation in AAO itself.⁶ For the preparation of platinum nanostructures with a smaller diameter, mesoporous silicas have been considered a good template, which was attributed to their high BET surface areas, and uniform and tunable pore sizes. Different Pt nanostructures synthesized using mesoporous silicas such as MCM-41, SBA-15, FSM-16, MCM-48 and HMM-1 *etc.* as templates have been reported in recent years.^{7–19} However, normally polycrystalline Pt nanowires or nanowire networks have resulted from using these templates, thus the fabrication of individual single-crystal Pt nanorods confined inside the mesoporous silica remains a challenge. Lee *et al.* developed a strategy to prepare single-crystal Pt nanowires using electrochemical deposition, but with this method, it is critical to have the channels of the silica run vertically on the substrate surface and interconnections between nanowires in the template pore structure cannot be completely avoided.²⁰ In this paper, a simple (one-pot) method to fabricate individual single-crystal Pt nanorods with high aspect ratios is reported. No hydrogen treatment at high temperature was needed to obtain metallic Pt nanostructures. The individual nanorods that resulted were evenly distributed inside

the mesoporous silica matrix and had lengths tunable from 20–100 nm. With proper modification, interconnected Pt nanorod bundles composed of 3–7 Pt nanorods could be obtained. The nanorod bundles have an average length of 100 nm and width of 50 nm.

Scheme 1 shows the schematic procedure for the fabrication of the single-crystal Pt nanorods and nanorod bundles. The template-free mesoporous silica (in this case SBA-15) was dehydrated at 383 K for about 4 h under vacuum.



Scheme 1 Pt nanorods and nanorod bundles prepared by a vacuum impregnation method.

After cooling to room temperature, it was immersed into a mixture of glycol, water and H₂PtCl₆·6H₂O and was transferred very quickly into an oven at 413 K for 30 min. The obtained materials were washed, filtrated and dried at 373 K to get Pt nanostructures encapsulated inside the silica matrix. The silica host was removed by HF etching, and unsupported Pt nanorods or nanorod bundles were collected. Experimental details are available in the ESI.†

Fig. 1A is a TEM image of the Pt-SBA-15. The loading of Pt was 4 wt%. It can be seen that the channels of SBA-15 were filled with many individual Pt nanorods while there were almost no Pt nanoparticles inside the channels nor large aggregated Pt nanoparticles on the external surface. The Pt nanorods have a uniform diameter of 6–7 nm, which is equal to or a little smaller than the pore size of SBA-15 (7 nm) (ESI, Fig. S1).† The as-synthesized Pt nanorods were not connected to each other and were oriented parallel to the channels of the SBA-15 (Fig. 1B). The nanorods have a narrow length distribution, which is shown in Fig. 1B, inset. This shows that the present improved vacuum impregnation method has a better control over the nucleation and crystallization of Pt crystallites, which leads to the formation of uniform length Pt nanorods.

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† Electronic supplementary information (ESI) available: Details of sample preparation and characterization. See DOI: 10.1039/b900262f

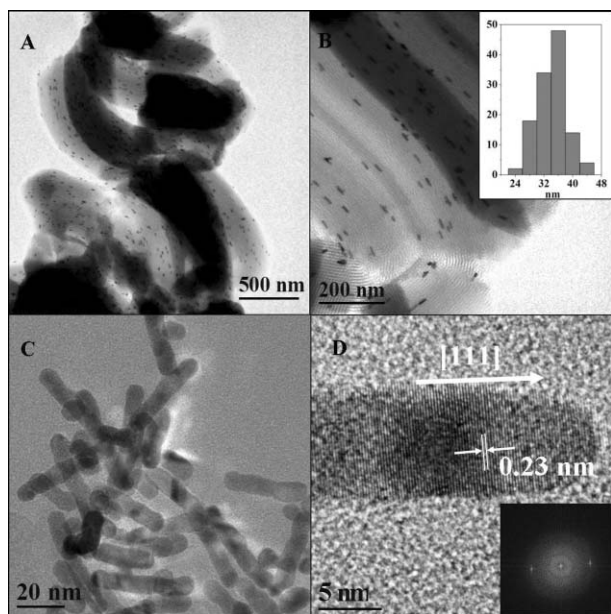


Fig. 1 (A) and (B) TEM images of Pt-SBA-15 (4 wt%), inset of (B) is the particle length distribution of the nanorods. (C) TEM image of individual Pt nanorods after removing silica matrix. (D) HRTEM image of single Pt nanorods (the insert shows the corresponding fast Fourier transform image).

After the growth of the Pt nanorods, a type IV isotherm with a H1 hysteresis loop was also obtained in a BET measurement, which is similar to that of the parent SBA-15 (Fig. 2A). This means that the parent mesoporous structure was maintained after growth of the Pt nanorods, while the BET surface (S_{BET}) and the

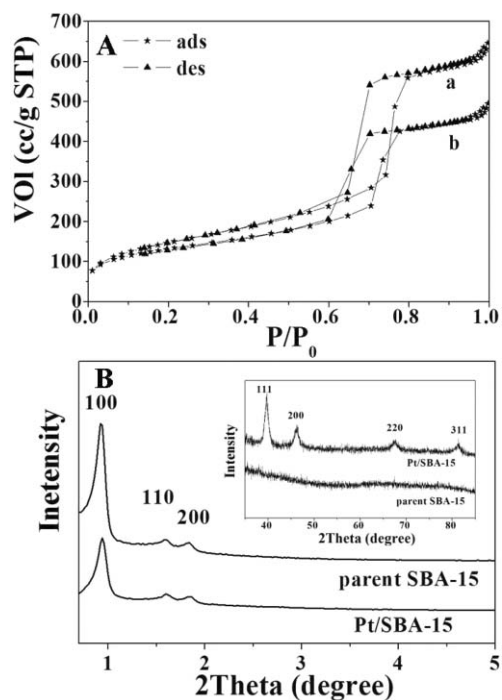


Fig. 2 (A) Nitrogen adsorption isotherm of (a) parent SBA-15 and (b) Pt-SBA-15 (4 wt%). (B) Small-angle XRD pattern of parent SBA-15 and Pt-SBA-15 (4 wt%); inset is their wide-angle XRD patterns.

total pore volume (V_t) of Pt-SBA-15 (4 wt%) decreased from 711 to 583 $\text{m}^2 \text{g}^{-1}$ and from 0.92 to 0.73 $\text{cm}^3 \text{g}^{-1}$, respectively (ESI, Table S1).[†] Fig. 2B shows the XRD patterns of the parent SBA-15 and that with grown Pt nanorods. In the low angle region, it can be observed that the mesoporous structure of SBA-15 was well preserved after the incorporation of Pt nanorods. The decrease of the peak intensity is another indication of the encapsulation of Pt nanorods inside the channels.⁷ Four peaks at 39.8, 46.2, 67.4 and 81.2° corresponding to the [111], [200], [220] and [311] diffraction of Pt, respectively, were observed in the high angle region (Fig. 2B inset), which indicated that the Pt nanorods synthesized have a face centered cubic (fcc) structure, similar to Pt bulk solid.

The silica host can be removed by a 5% HF-ethanol solution to give unsupported Pt nanorods (Fig. 1C). It can be seen from Fig. 1C that all the individual Pt nanorods have a uniform diameter of 6–7 nm and average length of 30–40 nm. From the high magnification image (Fig. 1D) of the selected nanorod, one can see that the Pt nanorods are single crystalline in nature. The nanorod grew along the [111] direction with a lattice spacing of the [111] planes of 0.23 nm, which is in good agreement with that of bulk Pt crystal and XRD results. The fast Fourier transform (FFT) of the atomic lattice fringing, in the inset in Fig. 1D, further demonstrates the crystallinity of the Pt nanorods. If SBA-15 zeolites with different pore sizes were used as the template with the same procedure, individual single-crystal Pt nanorods with different diameters can be obtained (details not shown here). This confirmed that the glycol-assisted one-step vacuum impregnation method is an efficient and effective method to prepare individual single-crystal Pt nanorods.

Interestingly, when the amount of Pt precursor in the H_2PtCl_6 -glycol-water solution was changed, it was possible to prepare individual Pt nanorods with different lengths. Fig. 3A and C, displays the TEM images of the Pt nanorods grown in the SBA-15 matrix with different Pt weight loadings (2 and 8%). Clearly, when the Pt loading was 2%, very short Pt nanorods in the SBA-15 channels were obtained. The diameter of these nanorods was the same, *i.e.* around 6–7 nm, but the length of them had changed to be 15–25 nm. Fig. 3A inset shows that a quite narrow length distribution was obtained for the Pt nanorods hosted inside the SBA-15 channels (2 wt%). The corresponding HRTEM image demonstrated that these short Pt nanorods were single crystals, showing the effectiveness of the present glycol-assisted one-step vacuum impregnation method. With further increases in the concentration of Pt (8 wt%), Pt nanorods with average lengths of 60 nm were obtained (Fig. 3C). Again, these nanorods had a fairly narrow length distribution (Fig. 3C inset), and were single crystals (Fig. 3D and E). After acid etching to remove the silica host by HF-ethanol solution, the morphology and size of the nanorods were well maintained, and resulted in pure individual Pt nanorods (ESI, Fig. S2).[†] Significantly, when the loading of the Pt precursor was higher than 15%, very evenly distributed Pt nanorod bundles were obtained that have an average length of 100 nm and average diameter of 50 nm (Fig 3F). From a close look at these bundles, it was seen that they were 3–7 interconnected Pt nanorod networks. Each nanorod was around 100 nm in length and, again, 6–7 nm in diameter. It has been reported that there are many mesopores in the wall of the hexagonal channel of SBA-15, and the Pt nanorods were actually connected to each other by small bridges.¹⁸ After removing the silica host by acid

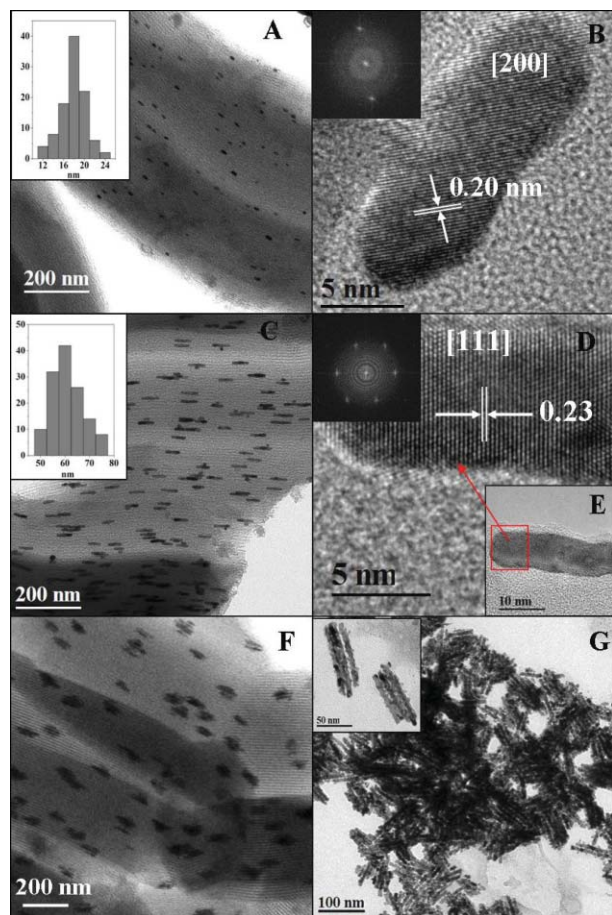


Fig. 3 TEM images of Pt nanorods/SBA-15 with different lengths: (A) 15–25 nm, (C) 50–80 nm, insets are the length distribution. (B) and (D) HRTEM images of the unsupported Pt nanorods with different lengths after the silica host removed by HF etching; insets are the fast Fourier transform of the images. (E) TEM image of a selected Pt nanorod for HRTEM analysis. (F) TEM image of Pt nanorod bundles incorporated in the SBA-15 matrix. (G) TEM image of the unsupported Pt nanorod bundles with the silica host removed by HF etching; the inset shows two Pt nanorod bundles.

etching, very uniform pure Pt nanorods bundles were obtained (Fig. 3G). Although the preparation of Pt nanorod networks have been reported before,^{13–16} the current result is distinguished by their uniform size and very even distribution inside the silica host. Interestingly, it was observed that in all the bundles, each nanorod was in the single crystalline state, *i.e.*, each nanorod and even the small bridges were grown along the same crystal direction (ESI, Fig. S3).[†] The driving force for the aggregation of the Pt nanorods under a higher Pt precursor concentration is still not clear, but it is believed that the local concentration of the Pt precursor and

the lower nucleation rate may contribute to the formation of these nanorod bundles.

In conclusion, a simple glycol-assisted one-step vacuum impregnation method has been developed to prepare individual single-crystal Pt nanorods in the channels of a mesoporous silica host. The length of the Pt nanorods was tunable from 20–100 nm by simply changing the concentration of Pt in the mixture solution (H_2PtCl_6 –glycol–water). It was also possible to prepare uniform Pt nanorod bundles. Each bundle was composed of 3–7 Pt nanorods. This method provides a facile approach to prepare individual single-crystal metal nanorods that can be used in various fields, *e.g.* as nanosensors, catalysts and in fuel cell applications.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20773121) and Chinese Academy of Science (KJCX2.YW.H16). D. M. thanks the Chinese Academy of Science for financial support through the Bairen project.

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