Ultralong Pt-on-Pd bimetallic nanowires with nanoporous surface: nanodendritic structure for enhanced electrocatalytic activity[†]

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We for the first time report a facile, wet-chemical strategy for the high-yield ($\sim 100\%$) synthesis of ultralong Pt-on-Pd bimetallic nanowires (NWs) with the cores being Pd NWs and the shells being made of dendritic Pt, which exhibit high surface area and enhanced electrocatalytic activity towards methanol oxidation reaction.

One-dimensional metal nanostructures such as nanowires (NWs), nanotubes and nanobelts have received considerable interest on account of their various potential applications deriving from their unique optical, electronic and catalytic properties.^{1–7} In particular, Pt and Pd NWs have been more extensively investigated because of their important technological applications, including as catalysts in many chemical reactions, as gas sensors, and as electrode materials in fuel cells.⁶ To date, various chemical protocols have been developed for preparing Pt and Pd NWs.4-7 Prominent examples include the synthesis of single-crystal Pt NWs by a polyol process,⁴ a phase-transfer method for Pt and Pd NWs,⁵ making Pt NWs from electrospinning⁶ and wet-chemical approach to the preparation of Pt and Pd NWs.⁷ Despite these successful demonstrations, all of these studies have been limited to NWs with smooth surfaces, which are disadvantageous for supplying high catalytic activity from the viewpoint of design of nanocatalysis. Therefore, developing an effective approach to the synthesis of catalysts with high surface areas for better catalytic performance and utilization efficiency is highly desirable and technologically important.

Hybridization (such as designing core/shell nanostructure) provides an effective strategy for enhancing the functionality of materials. Particularly, effectively controlling the morphology of the exterior metal (*e.g.* Pt) can provide a great opportunity to improve its surface area and increase its activity on a mass or specific basis.⁸ Recently, three areas have attracted particular attentions in the development of Pt-based nanoelectrocatalysts with controllable morphology. (1) 3D dendritic nanoparticles (NPs) have shown the good potential for reducing the Pt consumption, providing high surface area, and facilitating enhanced performance in catalytic applications.⁸ For instance, Yamauchi *et al.*^{8a} reported dendritic NPs could be synthesized in high yield *via* a block copolymer mediated reduction process. The as-prepared dendritic NPs gave a surface area of 56 m² g⁻¹, which is the highest for unsupported Pt materials. (2) It has

been shown that the performance of catalysts for fuel-cell reactions could also be improved by changing the morphology of Pt from NPs to multi-dimensional nanostructures such as NWs, whose large side surface could provide additional catalytic active facets.^{4c-e,7c} The typical example was from Dodelet's work,^{7c} which demonstrated that Pt NWs/C nanocomposites show enhanced catalytic activity for the oxygen reduction reaction compared with a state-of-the-art Pt/C catalyst made of Pt NPs. (3) Moreover, the increase in the interconnectivity of Pt NPs can also lead to significantly enhanced electrocatalytic activities of Pt nanoelectrocatalysts.⁹ However, with respect to the above designed procedures and materials reported, high-yield production of binary metal NWs with a nanoporous surface (dendritic structure) is far from being trivial despite the fact that the binary complex nanoarchitectures will be very promising for the development of highly active, cost-effective nanocatalysts. In this communication, we for the first time report a facile, wet-chemical strategy for the high-yield ($\sim 100\%$) synthesis of ultralong Pd-Pt bimetallic NWs with the cores being Pd NWs and the shells being made of dendritic Pt. Specifically, many small singlecrystal Pt nanobranches interweave with each other and thus form many nanopores on the surface of Pd NWs, which exhibit a high surface area (90.7 $\text{m}^2 \text{g}^{-1}$) and enhanced electrocatalytic activity towards methanol oxidation reaction.

The whole preparation strategy for constructing the Pt-on-Pd bimetallic NWs with nanodendritic morphology (PBNNM) is shown in Scheme 1. First, a large-scale and reproducible hydrothermal route was employed for preparing well-defined Te NWs according to ref. 7*d* with a slight modification (for detailed process see ESI†). Second, the as-prepared small-size Te NWs were used as both reducing agent and sacrificial template for obtaining Pd NWs in aqueous solution at room temperature in less than 5 min, which is different from Yu's process^{7*d*} (reaction time: 13 h, temperature: 50 °C, solvent: ethylene glycol). Third, the as-obtained Pd NWs were used as seeds to direct the dendritic growth of Pt upon the reduction of K₂PtCl₄ by ascorbic acid (AA) in aqueous solution.

The morphologies of the resulting products were investigated by scanning electron microscopy (SEM) and



Scheme 1 Procedure to design Pt-on-Pd bimetallic NWs with dendritic morphology.

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Fig. 1 TEM images of Te NWs (A, B) and Pd NWs (C, D).



Fig. 2 TEM (A–B, D–E), HAADF-STEM (C) and HRTEM (F) images of PBNNM. FFT pattern (G) of the HRTEM image shown in Fig. 2F (circled part).

transmission electron microscopy (TEM). Fig. 1A and B show the typical TEM images of the as-prepared Te NWs. From the magnified image (Fig. 1B), it is observed that these Te NWs have the diameter of about 11 nm.

Fig. 1C and D show the TEM images of Pd NWs derived from the Te NWs. A great number of Pd NWs with diameter (Fig. 1D) similar to that of pristine Te NWs are obtained. When the Pd precursor was added into the Te NW solution, the solution color immediately changes from blue-black to black (the color of Pd NWs), indicating that the redox reaction between Te NWs with the Pd precursor is a fast process. Fig. 2A–E show the typical TEM (A–B, D–E) and high-angle annular dark-field scanning TEM (HAADF-STEM, C) images of PBNNM at different magnifications. From the magnified image (Fig. 2D), it is observed that the as-obtained bimetallic NWs show a much rougher surface than the Pd NWs, indicating Pt has grown onto the surface of Pd NWs (Pd and Pt have a lattice mismatch of only 0.77%).^{8b} Particularly, many Pt nanobranches had grown from a Pd NW core, coalesced together and interconnected, forming dendritic tendrils with nanoporous structures (Fig. 2E and Fig. S1, ESI⁺). Further, the SEM image of PBNNM (Fig. S2, ESI[†]) suggests the as-prepared PBNNM with lengths $>10 \ \mu m$ possess high purity. In order to further reveal the detailed structure of PBNNM, the HRTEM image of one part from a typical NW is shown in Fig. S3, ESI[†] which clearly shows overgrowth of Pt branches at multiple sites on the Pd NW. An HRTEM image of an individual Pt nanobranch (Fig. 2F) shows its single crystalline structure with highly ordered, continuous fringe patterns. The measured interplanar spacing for the lattice fringes is 0.23 nm, which corresponds to the (111) lattice



Fig. 3 HAADF-STEM-EDS mapping images (A–C) of PBNNM. The cross-sectional compositional line profiles of individual PBNNM. (D) Pd-L; (E) Pt-M.

plane of face centered-cubic (fcc) Pt while the fast Fourier transform (FFT) pattern (Fig. 2G) of the HRTEM image (Fig. 2F, circled part) further indicates that the Pt nanobranch is a single crystal. In addition, elemental mapping of Pd and Pt (Fig. 3A–C) and the line profiles of the corresponding compositions (Fig. 3D and E) on individual PBNNM reveal the core–shell nanostructure of the bimetallic materials, consisting of the Pd as a core and a complete shell of Pt.

The formation of PBNNM was further characterized by X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray (EDX) spectroscopy and N₂ adsorption-desorption. The XPS pattern (Fig. S4A, ESI[†]) of the resulting Pd NWs shows significant Pd 3d signals corresponding to the binding energy of Pd (low Te XPS signals, data not shown), suggesting that Te NWs have reacted with the Pd precursor through galvanic reaction. Fig. S4B, C (ESI[†]) shows XPS patterns of the PBNNM. Strong Pt4f signals corresponding to the binding energy of Pt (Fig. S4B, ESI[†]) and Pd 3d signals corresponding to the binding energy of Pd (Fig. S4C, ESI[†]) are observed, indicating that Pd/Pt hybrid NWs have been readily obtained. The EDX spectrum (Fig. S5, ESI[†]) of PBNNM shows the peaks corresponding to Pt, Pd and Si (from Si substrate), further confirming that bimetallic Pd/Pt hybrid NWs are obtained. The N₂ adsorption-desorption isotherm (A) and corresponding pore-size distribution (B) of the PBNNM are shown in Fig. S6 (ESI[†]), which gave a distribution of pore sizes with a size range of 1.8-2.0 nm [in accordance with the result from TEM (1.6-2.4 nm)].

Interestingly, the density of Pt nanobranches on Pd NWs could be controlled *via* simply changing the molar ratio of Pd NWs to Pt precursor. For instance, Pt-on-Pd bimetallic NWs with fewer Pt branches could be obtained when 1 mL of Pt precursor was added into the mixture instead of 2 mL (Fig. S7A, B, ESI†). Continuously decreasing the amount of Pt precursor to 0.5 mL, the density of Pt nanobranches could further decrease (Fig. S7C, D, ESI†).

Inspired by their attractive dendritic structure and special property (good solubility in water, Fig. S8, ESI†), the PBNNM were tested as nanoelectrocatalysts for studying their catalytic activity. By using hydrogen adsorption–desorption methods in conjunction with cyclic voltammetry (CV), the electrochemical surface area (ECSA) of PBNNM and *E*-TEK Pt/C catalyst (20 wt%) were measured (see Fig. S9, ESI†). It is found that the ECSA value of PBNNM (90.7 m² g⁻¹) is higher than those of *E*-TEK catalyst (53.5 m² g⁻¹) and recent state-of-art nanomaterials such as Pd–Pt bimetallic nanodendrite



Fig. 4 (A) CVs (A) of *E*-TEK catalyst (trace a) and PBNNM (trace b) modified GC electrodes at a scan rate of 50 mV s⁻¹. (B) Transient current of *E*-TEK catalyst (trace a) and PBNNM (trace b) for methanol electrooxidation at 0.50 V in 0.5 M H₂SO₄–0.5 M CH₃OH aqueous solution. (C) Potential-dependent steady-state current (recorded at 120 s) of methanol electrooxidation on the *E*-TEK catalyst (trace a) and PBNNM (trace b). The loading amounts of Pt are 55.5 and 70.7 µg cm⁻² for PBNNM and *E*-TEK catalyst, respectively.

(57.1 m² g⁻¹),^{8b} carbon nanotube (CNT)/ionic liquid/Pt NPs hybrids (71.4 m² g⁻¹),^{10a} CNT/Pt hybrids (44 m² g⁻¹),^{10b} mesoporous Pt with giant mesocages (74 m² g⁻¹),^{10c} and dendritic Pt NPs (56 m² g⁻¹),^{8a} etc., most likely a result of the particular structure of the bimetallic Pd–Pt NWs. Furthermore, the surface roughness factors (50.3) on bimetallic Pd–Pt NWs modified glassy carbon (GC, 3 mm) electrode is higher than that of *E*-TEK catalyst (29.7) (indexed to the same amount of Pt). Therefore, for the present PBNNM, the combination of their high surface area and surface roughness with the complex nanoarchitectures is advantageous for catalytic applications.

Methanol was selected as a model molecule for studying the electrocatalytic performance of PBNNM. Fig. 4A shows the CVs of *E*-TEK catalyst (trace a) and PBNNM (trace b) modified GC electrodes in 0.5 M H₂SO₄ solution containing 0.5 M methanol. Relative to the commercial *E*-TEK catalyst, a significant enhancement of the peak current and a negative shift of the onset potential of methanol oxidation can be observed on PBNNM. It should be noted that the mass activity of PBNNM is also higher than those of recent state-of-art Pt-based nanomaterials such as carbon nanofibers or CNTs supported Pt NPs,¹¹ CNTs/ionic liquid/Pt NPs hybrids,^{10a} CNT/Pt composite catalysts,¹² polyaniline/Pt NPs hybrids,¹³ and graphene/Pt NPs hybrid,¹⁴ *etc.* (indexing to 0.5 M methanol).

Chronoamperometry, a useful method for the evaluation of the electrocatalysts in fuel cells,¹⁵ was employed to further investigate the electrochemical performance of PBNNM, and a typical result is shown in Fig. 4B. We also investigated several potentials and the dependence between the steady-state current and the potential is plotted in Fig. 4C. These results suggest that the PBNNM exhibit better performance for methanol electrooxidation than the *E*-TEK catalyst for all applied potentials.

The higher activity in electrochemical performance observed here can probably be attributed to three major factors. (i) Bimetallic NWs with dendritic and nanoporous structure could provide high ECSA and surface roughness, thus leading to high electrocatalytic activity. (ii) The multi-dimensional nanostructures with abundant interconnected nanobranches could provide facile pathways for electron transfer by reducing the interface resistance between nanobranches.⁹ In general, for *E*-TEK electrocatalysts with low Pt NPs interconnectivity, the Pt NPs exist as isolated particles, which are likely to impose a high impedance for electron transfer from NP to NP. (iii) The increased interconnectivity of Pt NPs could also lead to the significant increase in the grain boundaries between Pt NPs, thus generating discontinuities in the crystal planes of interconnected Pt NPs and providing a large number of defect sites.^{86,9}

In summary, we have developed a facile wet-chemical procedure to synthesize ultralong Pt-on-Pd bimetallic NWs with nanoporous surface using thin Pd NWs as a support. Many small single crystalline Pt nanobranches interweave with each other and thus form many nanoporous structures, which exhibit an enlarged ECSA and enhanced electrocatalytic performance. The new hybrid nanostructure is scientifically interesting and may also find use as catalysts beyond fuel cell applications.

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