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Hollow PtPd Nanorods with Mesoporous Shells as an Efficient Electrocatalyst for Methanol Oxidation Reaction

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Abstract: Tailoring the morphology and composition of Pt-based electrocatalysts is of significant importance for the development of highly efficient direct methanol fuel cells. Herein, we present a dual-templating method to design hollow PtPd nanorods with mesoporous shells (mPtPd HNRs), in which F127 micelles favor the formation of mesoporous structure and SiO₂ nanorods serve as hard template to create cavity. The well-developed mesopore, hollow structure, and bimetallic composition of the mPtPd HNRs offers sufficient active sites and facilitated channels for methanol electro-oxidation, leading to enhanced activity and stability. Our present strategy allows the reliable preparation of mesoporous hollow Pt-based electrocatalysts with desired composition and morphology for catalysis applications.

Introduction

Direct methanol fuel cells (DMFCs) as sustainable energy conversion devices have received intensive attention in powering portable electronic systems due to their high energy density, low operation temperature, and easy storage and transportation of methanol.^[1] The development of high-performance electrocatalysts for methanol oxidation reaction (MOR) is crucial to fulfill the commercial applications of DMFCs. Until now, Pt is considered as the most efficient electrocatalyst for the MOR due to its outstanding catalytic activity.^[2] However, the high cost and poor stability of Pt heavily limit the large-scale commercialization of DMFCs. There is an urgent need to develop alternative Pt-based catalysts to enhance their catalytic performance and utilization efficiency of Pt.

To this end, abundant efforts have been devoted to fine control of the composition and morphology of Pt-based catalysts. Alloying Pt with other metals can generate strain and electronic effects, which is considered as an attractive strategy to improve catalytic activity and stability.^[3] Among investigated metals, Pd is regarded as one of most promising candidates because Pd possesses excellent stability toward the MOR. Meanwhile, the similar electronic configuration and lattice constant between Pt and Pd favors the formation of single-crystallinity PtPd alloys with particular functionalities.^[4] Therefore, various PtPd

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bimetallic nanocrystals have been explored to promote the electrocatalytic performance for the MOR.

Given that the catalytic performance of catalysts is highly related to their morphology, the shape-controlled synthesis of efficient catalysts has been widely developed for various electrocatalytic applications.^[5] Among investigated candidates, hollow nanomaterials with low density can provide high interior surfaces and large pore space to adsorb and interact with reactants.^[6] In generally, the hard-templating approach using silica is an effective method for preparing hollow materials due to the facile control of template morphology and cavity size.^[7] However, most hollow nanostructures lack porous structures on the surface. Porous structures not only provide sufficient active sites and facilitated channels for catalytic reactions, but also effectively mitigate dissolution, Ostwald ripening, and aggregation of catalysts.^[8] Therefore, engineering hollow nanocrystals with porous shells, which allow the effective utilization of internal and external surfaces of catalysts, is expected to an attractive strategy for further improvement of catalytic performance.

Herein, hollow PtPd nanorods with mesoporous shells (mPtPd HNRs) have been synthesized through a dualtemplating approach and investigated the catalytic performance for the MOR. During the synthesis process, F127 micelles direct the formation of mesopores on the surface and SiO₂ NRs act as sacrificial templates to generate hollow structures. Owing to well-developed mesopore, hollow structure, and bimetallic composition, the obtained mPtPd HNRs show excellent MOR activity and HNRs stability. The mPtPd achieve large а electrochemically active surface area of 92.7 m² g⁻¹, high mass activity of 0.71 A $\text{mg}_{\text{Pt}}^{-1}$ and high specific activity of 1.5 mA cm⁻², which are superior to the values of the counterpart catalyst and commercial Pt/C.

Results and Discussion

The mPtPd HNRs with uniform size are synthesized *via* a dual-templating approach, in which tri-block copolymer F127 and SiO₂ NRs act as soft template and hard template, respectively (Scheme 1). In our strategy, the combination of the self-assembly of surfactant micelles and moderate chemical reduction of metal species is critical to generate mesoporous structures. Scanning electron microscopy (SEM) image clearly shows that the obtained silica has uniform nanorod morphology in a high yield, which possesses the length of ca. 200 nm and the diameter of ca. 100 nm (Figure S1). The SiO₂ NRs are served as the hard

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Scheme 1. Schematic illustration of the formation of the mPtPd HNRs.

template to grow PtPd shells using ascorbic acid (AA) as reductant. As shown in Figure S2, the uniform PtPd mesoporous structures are gradually formed on the surfaces of the SiO₂ NRs (SiO₂@mPtPd NRs). After HF etching, mesoporous PtPd shells are still maintained without any changes (Figure 1a and Figure S3). The welldefined mesoporous structures possess uniform pore size of around 14.5 nm (Figure S4a). The small angle X-ray scattering (SAXS) profile also confirms the presence of mesepores, as illustrated by the broad peak in the q range of 0.4 and 0.5 nm⁻¹ (Figure S5). The hollow structure is illustrated by a strong contrast in a transmission electron microscope (TEM) image (Figure 1b), and the shell thickness of the hollow structure is measured to approximately 25 nm (Figure S4b). High-resolution TEM (HRTEM) image (Figure 1c) displays clear lattice fringes on the edge of the mPtPd HNRs, which reveals a d-spacing distance of 0.225 nm (Figure 1d), corresponding to the (111) facet of face-centered cubic (fcc) metallic structure. The dspacing distance of the mPtPd HNRs is smaller than that of pure Pt (0.227 nm), revealing the formation of bimetallic structure.



Figure 1. SEM (a) and TEM (b) images of the mPtPd HNRs. (c) HRTEM image of the mPtPd HNRs and (d) corresponding Fourier filtered lattice fringe image of the square area in (c).

In order to explore element component in the products, we perform energy-dispersive X-ray (EDX) spectroscopy. A highangle annular dark field scanning TEM (HAADF-STEM) image of

one mesoporous hollow PtPd nanorod and its corresponding EDX line-scanning profiles and elemental mapping images confirm the hollow structure and the uniform distribution of Pt and Pd elements in the shell of the nanorod (Figure 2). The atomic ratio of Pt/Pd is calculated to around 74/26 by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), similar to the initial ratio of the metal precursors. The crystal structure of the mPtPd HNRs is characterized by X-ray diffraction (XRD). The XRD pattern of the mPtPd HNRs exhibits four diffraction peaks at 39.9°, 46.5°, 67.8°, and 81.7°, which are indexed to the (111), (200), (220), and (311) facets of the fcc metallic structure, respectively (Figure 3). Interestingly, their diffraction peaks have a slight shift to higher angle compared with those of pure Pt (JCPDS card No: 04-0802), indicating decreased lattice constant due to the incorporation of smaller Pd atoms into Pt atoms. The above results demonstrate the successful synthesis of bimetallic hollow PtPd nanorods.



Figure 2. (a) HAADF-STEM image and compositional line profiles and (b-d) EDX elemental mapping images of one hollow PtPd nanorod.

The formation process of the mPtPd HNRs is investigated by some control experiments. In the absence of HCl, abundant small mesoporous spheres except few mesoporous nanorods are obtained (Figure S6a) because the reduction rate of AA is too fast to grow mesoporous structures on the silica surface. When HCl is increased to 0.1 mL, the reducing capability of AA is greatly decreased, resulting in very slow reduction kinetics, making the difficulty in the formation of mesoporous structures (Figure S6b). The results indicate the significant effect of HCI on the morphology of products by tailoring nucleation and crystal growth of metals. In addition, hollow Pt nanorods with poor mesoporous structures (mPt HNRs) are formed when K₂PtCl₄ solution is used as the only precursor (Figure S7a). Without the Pt precursor, abundant Pd nanoparticles are agglomerated on the surface without porous structures (Figure S7b). The use of F127 is vital for the formation of well-developed mesopores. In

the absence of F127 under the typical synthetic process, the products exhibit solid surface without porous structures (Figure S8). With increasing reduction time, well-defined mesoporous structures could be gradually developed, resulting in robust mesoporous nanorods (Figure S9). The synthesis of the uniform mPtPd HNRs is dependent on the balance between nucleation and crystal growth by precise control of the reduction kinetics of various metal precursors with the assistance of micelles.



Figure 3. XRD pattern of the mPtPd HNRs.

According to above results, a possible formation mechanism would be inferred. In the present synthetic strategy, the concentration of F127 (ca. 0.9 wt%) exceeds the critical micelle concentration, resulting in the formation of spherical micelles.^[9] The metal precursors are easily coordinated with water to form metal-aqua complexes that can combine with hydrophilic ethylene oxide groups in F127,^[10] leading to sufficient coverage of metal species on the micelle surface. After addition of AA, Pt and Pd species are reduced to PtPd seeds covering on the silica surface owing to strong affinity between its amino groups and PtPd seeds. As the crystal growth proceeds, surfactant molecules are gradually self-assembled into an ordered array at the solid-liquid interface. After the removal of the micelles and silica, well-developed mesoporous shells and hollow structure are formed.

Given the mesoporous hollow structure and bimetallic compositions, the mPtPd HNRs are considered as effective MOR electrocatalysts for investigating their catalytic activity, compared with the counterpart mPt HNRs and commercial Pt/C. All potentials are converted to reversible hydrogen electrode (RHE) for electrochemical measurements. The typical cyclic voltammograms (CVs) are conducted in N₂-saturated H₂SO₄ (0.5 M) at the scan rate of 50 mV s⁻¹ (Figure S10), which can be employed to calculate the electrochemically active surface area (ECSA) by integrating the charge passing the electrode during hydrogen adsorption/desorption process after double-layer correction. The ECSA of the mPtPd HNRs is calculated to be 92.7 m² g⁻¹, superior to that of the Pt HNRs (44.2 m² g⁻¹),

commercial Pt/C (65.0 m² g⁻¹), and recently reported Pt-based electrocatalysts such as Pt hierarchical nanowire arrays (60 m² g⁻¹),^[11] PtRuTe mesoporous nanotubes (50.2 m² g⁻¹),^[12] and AgAu@Pt nanoframes (24.6 m² g⁻¹).^[3a] The results reveal that the mPtPd HNRs can provide sufficient active sites to react with species, which is of great significance for the electrocatalytic applications.

The MOR performance of samples is measured by CVs in N2saturated 1.0 M CH₃OH + 0.5 M H₂SO₄ solution. The current densities normalized to the mass loading of Pt and ECSA stand for mass activity and specific activity, respectively (Figure 4a and 4b). The CVs exhibit two-peak profiles, in which forward peaks are assigned to the methanol oxidation and backward peaks correspond to the oxidation of generated intermediates during the MOR process. It is noted that the mPtPd HNRs possess higher current density than that of the mPt HNRs and commercial Pt/C, indicative of their enhanced activity for the electro-oxidation of methanol due to the unique structure. The specific activity (1.50 mA cm⁻²) of the mPtPd HNRs is 1.1 and 2.8 times that of the mPt HNRs (1.32 mA cm⁻²) and Pt/C (0.54 $mA cm^{-2}$), respectively, indicating the high intrinsic activity of the mPtPd HNRs (Figure 4c). Moreover, the mPtPd HNRs possess a high mass activity of 0.71 A mg_{Pt}⁻¹, superior to the mPt HNRs $(0.58 \text{ A mg}_{Pt}^{-1})$ and commercial Pt/C $(0.21 \text{ A mg}_{Pt}^{-1})$, respectively. They are superior to recently reported Pt-based electrocatalysts under the same conditions (Table S1), such as Pd nanohollows/Pt nanorods nanocomposites (0.50 A mgpt⁻¹),^[13] PtPdTe nanowire (0.59 A mgpt⁻¹),^[14] and Au-Pt nanodendrites $(0.45 \text{ A mg}_{pt}^{-1})$.^[15] The superb mass activity reveals that the mPtPd HNRs can effectively reduce the Pt usage while still maintaining high activity. As shown in linear sweep voltammetry (LSV) curves (Figure 4d), the onset potential of the mPtPd HNRs is smaller than that of the mPt HNRs and commercial Pt/C, suggesting that it is more favorable to catalyze the MOR on the mPtPd HNRs.



Figure 4. (a) Mass-normalized and (b) ECSA-normalized CVs in 1.0 M CH₃OH + 0.5 M H₂SO₄. (c) Comparisons of mass activity and specific activity for different catalysts. (d) LSV curves of different catalysts.

The MOR kinetics of the catalysts is studied by CVs under different scan rates. As shown in Figure 5a, we can

see that the current density increases and the peak potential has a positive shift with the increase of the scan rate (v). Furthermore, a linear relationship is observed between the forward peak current density (j_m) and $v^{1/2}$, suggesting the diffusion-controlled process for the MOR.^[5g] The slope of the mPtPd HNRs (0.04) is higher than that of the mPt HNRs (0.025) and the Pt/C (0.0085), confirming more favorable kinetics of methanol oxidation on the mPtPd HNRs (inset of Figure 5a, Figure S11 and Figure S12). The electrocatalytic stability of the MOR is a critical factor for practical applications, which is evaluated by accelerated durability tests. After measurements at the potential range of 0.22 and 1.22 V in 1.0 M CH₃OH + 0.5 M H₂SO₄ solution, the current densities of all the catalysts have degradation with the increase of CV cycles (Figure 5b and Figure S13). We can see from the Figure 5c that the mPtPd HNRs maintain 66% of the initial mass activity, which is much higher than the mPt HNRs (35%) and commercial Pt/C (32%). Furthermore, chronoamperometric measurements are further performed to estimate the stability of catalysts (Figure 5d). After tests at 0.92 V for 5000 s, the mPtPd HNRs retain a higher current density with slower decay than the mPt HNRs and commercial Pt/C, indicating the excellent stability of the mPtPd HNRs for the MOR.



Figure 5. (a) CVs of the mPtPd HNRs at different scan rates and corresponding fitted plot of the j_m vs. the $v^{1/2}$. (b) Mass activities of samples before and after 1000 cycles, and (c) corresponding mass activity changes under different cycles. (d) Chronoamperometric curves of samples at 0.92 V.

The excellent electrocatalytic MOR performance of the mPtPd HNRs can be explained by their well-defined mesoporous hollow structure and bimetallic component (Figure 6). The alloy structure of Pt and Pd can tailor their electronic structures and generate synergistic effect derived from the Pt-Pd interaction, thus modifying the *d*-band center of Pt and weakening the electronic interaction between Pt atoms and adsorbates, which favors enhanced intrinsic MOR activity. On the other hand, the mesoporous

hollow structure in the mPtPd HNRs not only facilitates diffusion of guest species due to the uniform mesopores in the shells as well as the large hollow interiors, but also improves the effective utilization of active surfaces from both the interior and exterior surfaces of the mesoporous shells, making them superior electrocatalytic activity. Moreover, the mesoporous hollow structure greatly suppresses the dissolution, Ostwald ripening, and aggregation of catalysts, leading to excellent catalytic stability.





Conclusions

In summary, we have successfully developed a reliable approach to prepare the mPtPd HNRs using F127 and SiO₂ NRs as soft template and hard template, respectively. Due to the well-developed mesoporous structure, large hollow cavity, and synergistic effect on the mPtPd HNRs, they display excellent electrocatalytic activity and stability toward MOR. This synthetic approach is a universal strategy, which can be extended to prepare many other Pt-based alloys with well-developed mesoporous structure by choosing appropriate precursors. Moreover, by tuning morphology of templates, more complicated mesoporous hollow structures with versatile functions will be obtained in the future.

Experimental Section

Materials and Chemicals

Potassium tetrachloroplatinate (K₂PtCl₄), sodium tetrachloropalladate (Na₂PdCl₄), Pluronic F127 (poly (ethylene oxide)₁₀₀–poly (propylene oxide)₆₅–poly (ethylene oxide)₁₀₀) and 3-aminopropyltrimethoxysilane (APTMS) were purchased from Sigma-Aldrich. Tetraethyl orthosilicate (TEOS, \geq 99.8%), hexadecyltrimethyl-ammonium bromide (CTAB, \geq 99.8%), ascorbic acid (AA), hydrochloric acid (HCl, 36.0–38.0%), aqueous ammonia (28 wt%), isopropanol, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of SiO₂ NRs

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The SiO₂ NRs were synthesized based on the previous report with minor modification.^[16] Typically, F127 (1.26 g), CTAB (100 mL, 40 mM) and ammonia solution (120 mL, 2.5 wt%) were mixed under stirring at room temperature, followed by adding TEOS (4.8 mL). After the solution was stirred at room temperature for 6 h, the products were collected by centrifugation and washed three times with ethanol and water, and they were further immersed in HCl at 90 °C for 20 h to remove the surfactant. Finally, the SiO₂ NRs were washed with ethanol and dried in a vacuum oven for 24 h. For modification of amino groups on silica surface, the obtained SiO₂ NRs (50 mg) were mixed with isopropanol (10 mL) and APTMS (200 μ L), and the solution was heated at 80 °C for 12 h under reflux. After that, the modified SiO₂ NRs were thoroughly washed with ethanol and dried at 60 °C.

Synthesis of the mPtPd HNRs

In brief, K₂PtCl₄ (3 mL, 20 mM), Na₂PdCl₄ (1 mL, 20 mM), HCl (50 μ L, 6 M) and modified SiO₂ NRs (3 mg) were mixed, followed by adding F127 (40 mg) under sonication. Then, AA (4 mL, 0.1 M) was rapidly added to the above solution, reacting for 4 h at room temperature. After the reaction was finished, the products were collected by centrifugation and washing with water several times, which were treated with HF (10 wt%) for 12 h to remove SiO₂ templates. Finally, the mPtPd HNRs were obtained after centrifugation, washing and drying.

Materials Characterization

The morphology of the synthesized samples was measured by SEM (JCM-7000). TEM images and element mapping were carried out by a JEM-2100F apparatus equipping with an EDX spectroscopy. XRD was recorded on an X-ray diffractometer (Shimadzu, XRD-6000) with Cu K α radiation. SAXS experiment was conducted with a Rigaku D-Max 2550 X instrument using Cu K α as radiation The chemical composition of mPtPd HNRs was analyzed by ICP-AES (Thermo Elemental IRIS Intrepid).

Electrochemical Measurements

Electrochemical measurements were conducted on a CHI 842D electrochemical workstation in a three-electrode system with Ag/AgCI (3 M KCl) electrode, Pt wire, and modified glassy carbon electrode (GCD, 3 mm in diameter) as reference electrode, counter electrode, and working electrode, respectively. The working electrode was prepared as follows. In brief, obtained catalyst (2 mg) was dispersed in water (1 mL) to form the ink under ultrasonication for 30 min, and then the ink (5 μ L) was dropped on the surface of the clean GCD and dried in oven. Subsequently, Nafion solution (5 $\mu\text{L},$ 0.05%) was further coated on the surface and dried in an oven. The ECSA of electrocatalysts was determined from CVs measured in a N_2 -saturated H_2SO_4 (0.5 M) at a scan rate of 50 mV s⁻¹. The ECSA of the catalysts can be estimated by the equation (ECSA = $Q/m \times 210$), where Q is the charge collected in the underpotentially deposited hydrogen adsorption/desorption region after double-layer correction, m is the mass loading of Pt on the electrode, and 210 $\mu C \ cm^{-2}$ stands for the monolayer adsorption of hydrogen on Pt surface. For MOR measurements, CVs and LSV curves were measured in a mixed solution containing CH_3OH (1.0 M) and H_2SO_4 (0.5 M) at a scan rate of 50 mV s⁻¹. Chronoamperometry measurements were conducted at the potential of 0.92 V.

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Keywords: PtPd nanorod • hollow structure • mesoporous shell • electrocatalyst • methanol oxidation reaction

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