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PtPdAg Hollow Nanodendrites: Template-free Synthesis and High Electrocatalytic Activity for Methanol Oxidation Reaction

Tao Zhang,^{a,b} Yiqiang Sun,^a Xuejiao Li,^{a,b} Xinyang Li,^a Dilong Liu,^a Guangqiang Liu,^a
Cuncheng Li,^c Hong Jin Fan^{d,*} and Yue Li^{a,*}

^a Key Laboratory of Materials Physics and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China.

^b School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, 230026, China.

^c School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, Shandong, P. R. China

^d School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore

*Corresponding author. E-mail: fanhj@ntu.edu.sg, yueli@issp.ac.cn

Abstract

To boost the electrocatalytic activity of metal nanoparticles, it is important to rationally design the composition and surface atomic structure, and develop efficient synthesis protocols. Herein, we deploy a facile one-pot self-templated method for preparing PtPdAg hollow nanodendrites (HNDs). These HNDs possess rich atomic steps and grain boundaries, leading to evidently higher catalytic activity in methanol electrooxidation reaction than commercial Pt black and solid nanoparticles with smooth surfaces. From control experiments and density-function-theory (DFT) calculations, it is proven that the trimetallic HND has a stronger electronic coupling as compared with the PtPd and PtAg NPs. As a result, the PtPdAg HNDs show high anti-poison capability and catalytic activity for MOR. Our study provides a new strategy for controllable synthesis of hollow alloy nanocatalysts with high-efficiency.

KEYWORDS: Hollow nanoparticles, galvanic replacement reaction, atomic steps, electrocatalyst, methanol oxidation reaction

1. Introduction

Proton exchange membrane fuel cells (PEMFCs), as a potential clean energy to replace nonrenewable fossil fuels, can not only reduce the associated environmental crisis, but also lessen the burden of ever-increasing demand for energy resources.¹⁻⁶ Remarkably, methanol, as a green energy source, holds numerous superiority including low price, high theoretical energy density, good portability and low toxicity.⁷⁻⁸ Thus, direct methanol fuel cell (DMFC) derived from PEMFCs has been considered as an ideal candidate for energy conversion.⁹⁻¹³ The state-of-the-art commercial nanocatalyst for methanol oxidation reaction (MOR) is platinum (Pt). One of prominent problems of Pt catalyst is that the CO-like carbonaceous intermediates generated from the methanol oxidation have poisoning effect on the electrocatalytic performance of Pt, which decreases the activity and operation durability.¹⁴⁻¹⁵ In addition, the low abundance, high cost, and high methanol crossover hinder the large scale utilization of Pt catalyst.¹⁶⁻¹⁸

There are several ways to mitigate the issue of Pt-based electrocatalysts. First, alloying Pt with other metals to form various nanostructures is considered as an effective strategy to promote the catalytic performance. The added species can weaken the affinity of Pt to the poisonous species by modifying its electronic structure.¹⁹⁻²¹ For example, spongy AuAgPt alloy nanospheres,⁶ atomic layer Pt/Pt₃Ga,²² PdRuPt nanowire networks,¹⁷ Au/PtCu nanowires,²³ PtPdAg/C and PtPdAg tri-metal alloy nanostructures show enhanced electrocatalytic activity.²⁴⁻²⁵ In addition, a hollow and dendritic nanostructure has unique advantages over solid and smooth ones for electrocatalysis, including abundant active sites, high mass utilization and fast mass transfer.²⁶⁻²⁹ Finally, the grain boundaries can act as effective active sites and participate in the catalytic reactions, resulting in effectively higher activity per mass.³⁰⁻³² Despite these progress, most of these beneficial features are presented separately in different catalysts. There has been no attempt to achieve nanocatalysts with all the above features (hollow interior, dendritic branches, grain boundaries and atomic steps) integrated in one system. Part of the reasons is the challenge in synthesis. Herein, we intend to develop a synthesis protocol that allows us to realize Pt-based ternary metal alloys, in which all the aforementioned desirable features are integrated in a controllable way.

In this work, we report a direct facile synthesis strategy towards PtPdAg hollow nanodendrites (HNDs). This ternary alloy can be used as the highly effective catalyst towards the electrocatalytic oxidation of methanol. We firstly conduct detailed characterization of the nanostructures, and understand the growth mechanism. Then we demonstrate that such three-dimensional (3D) PtPdAg HNDs have higher anti-poison capability and are more energetically favorable compared with the binary alloys of PtPd and PtAg for MOR. The high performance could be attributed to more favorable electronic coupling effect in the trimetal composition, and the hollow dendritic structures with increased active surface areas. Importantly, we identified numerous grain boundaries and atomic steps along the surfaces of the HNDs, which is believed to offer additional active sites. As a result of these advantageous features, the obtained 3D PtPdAg HNDs deliver significantly enhanced MOR catalytic activity (4.5 times higher than the commercial Pt black). In addition, the surface composition and nanostructures are well preserved during long-term operation which accounts for their stable catalytic activity. This work develops an attractive one-pot strategy to rationally synthesize 3D hollow Pt-based alloy catalysts that can potentially deliver high performance in a wide range of electrochemical reactions.

2. Results and Discussion

2.1. Characterization of PtPdAg HNDs

The crystal structure of the as-synthesized PtPdAg HNDs was firstly characterized using PXRD (Fig. 1a). A set of diffraction peaks can be ascribed to the face centered cubic (fcc) crystal structure. Note that each peak lies in between those of pure Pt (or Pd) and of pure Ag, and no peak splitting can be observed. This indicates that the Pt, Pd, and Ag co-exist in the particle in an alloy state rather than individual phases. Based on the high angle annular dark field scanning TEM (HAADF-STEM) and TEM images in Fig. 1b and 1c, the PtPdAg HNDs have a uniform size of 18 ± 1.6 nm and a high production yield. The obvious TEM contrast indicates a hollow structure. A magnified view of a typical PtPdAg HND (Fig. 1d) shows that the particle has a dendritic shell. Based on the HRTEM lattice images, it is found the (111) lattice constant (0.23 nm) is smaller than that of (111) plane for fcc Ag (0.236 nm), while larger than that of (111) plane for fcc Pt (0.226 nm) and Pd (0.225 nm). This coincides with a

tri-metal alloy phase of the PtPdAg particle. In addition, a closer view of the lattice images reveals grain boundaries and atomic steps around the shell surface (Fig. 1e). The line scanning profiles and EDS elemental mapping images explicitly manifest uniform distributions of all the three components within the PtPdAg alloy particle (Fig. 1f and g). The molar ratio of Pt, Pd, and Ag was calculated by ICP-MS (Table S1), from which we can estimate the atomic percentage of Pt, Pd, and Ag to be about 34.5 %, 34.0 %, and 31.5 %, respectively.

Fig. 1. Structural and compositional characterizations of PtPdAg HNDs. (a) Powder XRD pattern; (b) HAADF-STEM and (c) TEM images; (d) high-resolution TEM image of an individual PtPdAg HND; (e) enlarged HRTEM image of the selected area in 1d. **The dashed lines indicate representative grain boundaries and the arrows indicate surface atomic steps;** (f) EDS line profile of a single PtPdAg HND; (g) STEM image and corresponding EDS elemental mappings. The insets in (b) is the histogram of the particle size distribution.

The surface composition and valence states of PtPdAg HNDs were measured by XPS. Fig. S1b-S2d presents the deconvolution of the Pt 4f, Pd 3d, and Ag 3d spectrum energy region of the PtPdAg HNDs. These deconvoluted Pt, Pd, and Ag peaks suggest that the metallic Pt, Pd, and Ag are predominant species in the alloy, which play a key role in promoting electrocatalysis.^{1, 6} The oxide species (Pt^{2+} , Pd^{2+} , and Ag^+) are probably due to the surface partial oxidation upon exposure to air during the sample handling.³³⁻³⁶ For comparison, we also synthesized PtPd, PtAg, and PdAg bimetallic NPs using the similar procedure without introducing the respective third metal salt into the initial precursors (Fig. S2 and Fig. S7a). The corresponding XPS signals from Pt and Pd in PtPd, PtAg, and PdAg NPs are presented in Fig. 2. The Pt 4f_{7/2} binding energies of PtPdAg HNDs show an obvious positive shift compared to PtPd and PtAg NPs (Fig. 2a). However, the dominant peaks of metallic Pd of PtPdAg HNDs moved from higher to lower binding energies (Fig. 2b). The observed shifts in the binding energies indicate electron transfer from Pt to Pd and Ag, which may enhance their anti-poison capability and activity.^{24, 37} Furthermore, compared with the three bimetal alloy NPs, the relative content of Pt and Pd oxides in the PtPdAg HNDs is significantly decreased, implying the well oxidation resistance of PtPdAg HNDs.³⁸

Fig. 2. Comparison of XPS spectra between PtPdAg HNDs, PtPd NPs, and PtAg NPs. (a) Pt 4f and (b) Pd 3d spectra.

2.2. The formation mechanism of PtPdAg HNDs

Fig. 3. Evolution of the hollow dendrites. HAADF-STEM images (a, b) and the corresponding EDS line scanning (c) of the PtPdAg products synthesized with various time. From left to right: 0.5 h, 2 h, 3 h, and 4 h. (d) Schematic diagram of the corresponding products shown in (a)–(d).

In order to understand the formation mechanism of PtPdAg HNDs, control experiments were conducted by changing the reaction time (Fig. 3). It is observed that uniform solid nanodendrites are produced when the reaction was terminated at 0.5 h. Their EDS line scanning profile shows that the solid nanodendrites have a core-shell structure that is composed of a PdAg-rich core and a Pt-rich shell. The EDS result shows that the atomic ratio of Pt/Pd/Ag is about 20.1/38/41.9 (Fig. S3). When the reaction time was extended to 2 h, the

obtained nanodendrites start to exhibit a hollow structure. The relative contents of Pd and Ag at the center synchronously decrease, while that of Pt, Pd, and Ag located in border generally increased (atomic ratio of Pt/Pd/Ag: 28.5/36.2/35.3), forming a quasi-volcano like overlap (Fig. 3b). As the reaction continues, the inner hole of the products was enlarged at a reaction time of 3 h, which was verified by HAADF-STEM images and EDS line scanning profile (Fig. 3c). The atomic ratio of Pt/Pd/Ag was changed to 31/35.9/33.1, as illustrated by the EDS spectrum (Fig. S3). When the reaction time reached 4 h, the PtPdAg HNDs with a Pt/Pd/Ag atomic ratio of about 35.1/33.4/31.5 were obtained. Their EDS line scanning profile demonstrated an overlapped distribution of Pt, Pd, and Ag elements, forming a clearer volcano-like overlap. This further confirms the alloy feature of PtPdAg HNDs. If the reaction time was further prolonged to 10 h, the morphology and composition of final product do not changed and are similar to the PtPdAg HNDs achieved at 4 h. This indicate the typical reaction completes with a short period of about 4 h (Fig. S4).

On the basis of above morphology and composition evolution process, a possible hollowing mechanism is presented (also schematically illustrated in Fig. 3d). The core-shell structured solid nanodendrites composed of PdAg-rich core and Pt-rich surface are first formed. This is because Pd precursors have a relative faster reduction rate, even though the standard reduction potential of Pt species ($[\text{PtCl}_4]^{2-}/\text{Pt}$: 0.755 V vs standard hydrogen electrode (SHE)) is more positive than of Pd species ($[\text{PdCl}_4]^{2-}/\text{Pd}$: 0.591 V vs. SHE).³⁹⁻⁴⁰ Furthermore, the previous study showed that when the ascorbic acid is present, the oxidative corrosion of Ag^+ (Ag^+/Ag : 0.8 V vs. SHE) during galvanic replacement reaction can be minimized, leading to coreduction of Pd and Ag to form PdAg alloy.⁴¹⁻⁴² Therefore, in our reaction system, the coreduction of Pd and Ag ions by ascorbic acid primarily occurs at the initial stage and results in PdAg-rich nanodendrites with a small content of Pt. Then, the solid nanodendrites as sacrificial template are oxidized during the galvanic replacement reaction with Pt(II) precursor, which removes Ag from the interior. As a result, the solid nanodendrites grow into hollow ones, similar to the hollowing process due to galvanic replacement reactions of other bi-metal systems.⁴¹⁻⁴³ It is remarkable that the inner hole gradually enlarges with increasing the reaction time, till the formation of the final PtPdAg HNDs after 4 h.

2.3. The Influence Factors for Forming PtPdAg HNDs

It is found that the reaction temperature has a drastic influence to the morphology of the resulting products (Fig. S5). In this experiment, 30 °C was identified to be the optimal temperature to obtain PtPdAg HNDs. When the reaction temperature is set as 20 °C, PtPdAg HNDs still have the 3D hollow dendritic feature, but the inner hole suffered from a contraction in size, as displayed in Fig. S5a. This phenomenon could be comprehended by the kinetics controlled galvanic replacement reaction. A lower reaction temperature will decrease the reaction rate and the kinetics of growing inner holes is also lowered. When the reaction temperature was up to 40 °C, the size of inner holes in products also became smaller because higher temperature increased the reaction rate (Fig. S5c). During the initial nucleation, a part of Pt precursor was also reduced into Pt atoms with the reduction of Pd and Ag ions, forming solid PtPdAg nanodendrites. The residual Pt precursor could not give rise to bigger inner holes in solid PtPdAg nanodendrites. If the reaction temperature further increased to 50 °C, the inner holes of products almost disappeared by the rapid coreduction of Pt, Pd, and Ag precursors (Fig. S5d).

Furthermore, we also explored the influence of AgNO₃ on the product structure. As illustrated in Fig. S6a, when the AgNO₃ was absent and other parameters were unchanged, the solid PtPd nanodendrites were obtained. In spite of varying the molar ratio of Pt/Pd from 1/3, 1/1 to 3/1, the hollow structure still could not be obtained (Fig. S7). However, when the concentration of AgNO₃ was kept to 5 mM, only changing the Pt/Pd molar ratio from 1:3, 1:1 to 3:1, the final product produced hollow dendritic structures (Fig. S8). This indicated that AgNO₃ played an essential role in constructing the hollow structure in this system. If we further tuned the concentration of AgNO₃ from 0.25 to 1.5 mM, the inner holes of final products gradually became smaller due to the relatively reduction of Pt precursor in galvanic replacement reaction (Fig. S6b-6d). These experiments certified that the formation of PtPdAg HNDs derived from the precise control on several synthetic parameters.

2.4. Electrooxidation Catalytic Performance

Fig. 4. MOR performance of the catalysts. CV curves from different catalysts tested (a) in 0.1 M HClO₄ and (b) in 0.1 M HClO₄ + 0.2 M CH₃OH solution at a sweep rate of 50 mV s⁻¹. (c) Mass and (d) specific activities obtained from (b). Specific currents (e) tested at 0.9 V vs. RHE. (f) Durability tests. The molar ratio of Pt/Pd for PtPdAg HNDs, PtPdAg HNDs-1, and PtPdAg HNDs-2 is 1:1, 3:1, and 1:3, respectively.

The PtPdAg HNDs with different atomic ratios were evaluated as electrocatalysts toward MOR, and benchmarked against the commercial Pt black catalyst. Fig. 4a shows the cyclic voltammetry (CV) curves of PtPdAg HNDs with different atomic ratios and commercial Pt

black that were measured in N₂-saturated 0.1 M HClO₄ solution with a sweep rate of 50 mV s⁻¹. Based on the integration of charge generated during the hydrogen adsorption/desorption process, the as-prepared catalysts exhibit high electrochemically active surface area (ECSA), with 42.04 m² g⁻¹ for PtPdAg HNDs, 32.95 m² g⁻¹ for PtPdAg HNDs-1, and 36.71 m² g⁻¹ for PtPdAg HNDs-2, all being larger than that of commercial Pt black (19.34 m² g⁻¹). Figure 4b shows the MOR CV curves of the catalysts. The intense anodic peak during the positive scan is a characteristic feature of the electrooxidation of freshly adsorbed methanol. The relatively narrow anodic peak during the opposite scan is usually ascribed to the further oxidation of carbonaceous intermediates. Our results indicated that the PtPdAg HNDs have a more negative onset potential in comparison with the PtPdAg HNDs-1, PtPdAg HNDs-2, and commercial Pt black catalysts, reflecting enhanced kinetics of MOR.

The ratio between forward and reverse current densities (I_f/I_b) can serve as a reference to evaluate the carbonaceous intermediates tolerance of Pt-based electrocatalysts toward MOR.⁴⁴ It is noted that the 3D PtPdAg HNDs exhibit the highest I_f/I_b ratio (1.56) among all the investigated electrocatalysts (1.49 for PtPdAg HNDs-1, 1.48 for PtPdAg HNDs-2, and 1.24 for commercial Pt black), demonstrating their better tolerance toward carbonaceous intermediates poisoning. Carbon monoxide (CO) stripping test was also conducted to better understand the stability. Figure S9 shows the CO stripping voltammograms of the four samples: Compared to other three electrocatalysts, the anodic wave of PtPdAg HNDs shows a more negative peak, implying higher CO oxidation activity. This may explain the stability of PtPdAg HNDs.

The mass and specific activities were obtained by normalizing with forward currents densities with respect to the mass loading of Pt and ECSAs, respectively. The mass activity of PtPdAg HNDs is 1.58 A mg_{Pt}⁻¹, which is 1.34, 2.19 and 4.5 times higher than that of PtPdAg HNDs-1 (1.18 A mg_{Pt}⁻¹), PtPdAg HNDs-2 (0.72 A mg_{Pt}⁻¹), and commercial Pt black (0.35 A mg_{Pt}⁻¹), as indicated in Fig. 4c. Moreover, PtPdAg HNDs exhibit a high specific activity of 3.75 mA cm⁻², which is 3 times higher than that of commercial Pt black (1.25 mA cm⁻²) (Fig. 4d). As summarized in Table S2, this value is comparable or even superior to those of recently reported Pt-based catalysts.

Control experiments were conducted in order to give insights into the structure advantages of PtPdAg HNDs on catalytic ability. Firstly, solid PtPdAg nanodendrites with the same Pt/Pd/Ag ratio were obtained at 50 °C (Fig. S5d). The mass activity of the solid PtPdAg nanodendrites is 0.96 A mg_{Pt}⁻¹, compared to 1.58 A mg_{Pt}⁻¹ of PtPdAg HNDs (Fig. S10). Furthermore, we also prepared PtPdAg HNDs without atomic steps by annealing the as-obtained PtPdAg HNDs at 200°C in 10 % H₂+ 90 % N₂ for 1 h (Fig. S11a-11c). It is found that these PtPdAg HNDs are less active for MOR than the samples with presence of atomic steps, which verifies the significant role of active atomic steps (which are defects) in the catalytic performance.

Fig. 5. Characterization of PtPdAg HNDs after durability test. TEM images in (a, b) showing the existence of hollow and dendritic structures. (c-e) Comparison of XPS spectra of the PtPdAg HNDs before and after the MOR reaction. CV curves tested in two solutions (f) 0.1 M HClO₄ and (g) 0.1 M HClO₄ + 0.2 M CH₃OH solution after the catalysts were exposed to ambient laboratory condition for 30 days.

Apart from catalytic activity, we also tested the durability of catalysts, which is another key parameter for practical applications. The durability test of the PtPdAg HNDs, PtPdAg HNDs-1, PtPdAg HNDs-2, and commercial Pt black toward MOR were conducted by chronoamperometric measurements at a given potential (0.9 V vs. RHE). As indicated in Fig. 4e, the current density of electrocatalysts decreased quickly at initial stage and then reached a stable state. The initial decay of current density was mainly due to the blockage and poisoning of active sites by adsorbed carbonaceous products.^{29, 35, 44-45} After 10000 s electrocatalysis, the PtPdAg HNDs maintained a specific current of 206 mA mg⁻¹, which was highest among all control samples including the commercial Pt black (Fig. 4e). We also compare to recently reported Pt-based catalysts and find that our PtPdAg HNDs also displayed better current retention (Table S3). Moreover, even after 5000 cycles, the PtPdAg HNDs still maintained 58.1 % of their initial mass activity, while the PtPdAg HNDs-1, PtPdAg HNDs-2, and Pt black kept 35.4%, 26.3%, and 21.1%, respectively (Fig. 4f and S12). Notably, compared with Pt black, the structure of individual PtPdAg HNDs is better retained after the durability tests (compare Fig. 5 and S13). In Fig. 5c-e, the XPS spectra of Pt 4f, Pd 3d, and Ag 3d of the PtPdAg HNDs after the stability test are almost identical to that of the initial sample, manifesting that no obvious composition change had occurred. In another test, we drop cast the PtPdAg HNDs onto the glassy carbon electrode followed by coating with a thin Nafion layer. The electrode was then left at ambient laboratory condition for 30 days. It is found that the MOR catalytic activity and ECSA show no obvious change (Fig. 5f and g). To conclude, all above electrochemical tests and morphology characterization prove that our PtPdAg HNDs exhibit outstanding performance for MOR.

2.5. DFT Calculations

Fig. 6. DFT computation of MOR reactions. Ball-and-stick models of optimized structures of intermediates (Pt, dark blue; Pd, blue; Ag, brown; C, black; O, red; H, white) on the PtAg (111), PtPd (111), and PtPdAg (111) surfaces, and the corresponding calculated reaction pathways. All the elementary steps involve the dissociation of a ($H^+ + e^-$) pair.

Density functional theory (DFT) computation was conducted to explore and compare the reaction mechanisms of MOR on PtAg(111), PtPd(111), and PtPdAg (111) surfaces. Figure S14 shows the reaction network. The computational hydrogen electrode (CHE) model was used to calculate the Gibbs free energies of each electrochemical step.⁴⁶⁻⁴⁷ The MOR on PtAg(111), PtPd(111), and PtPdAg(111) undergoes a CO pathway, in which the CH_3OH exhibits a successive dehydrogenation process ($CH_3OH \rightarrow CH_2OH^* \rightarrow CHOH^* \rightarrow COH^* \rightarrow CO^*$) leading to the formation of CO^* (Tables S4-S6). The newly-formed CO^* further interacts with surface hydroxyl (OH^*) groups to produce CO_2 . All intermediates in reaction process possess the same structure on the three types of surfaces, which agrees well with previous report.⁴⁸ According to the Gibbs free energy profiles, the PtPdAg(111) exhibits higher MOR catalytic activity than the PtAg(111)

and PtPd(111) surfaces (Fig. 6). The highly stable COH* and CO* on PtAg(111) and PtPd(111) surfaces generate a deeper “thermodynamic sink” than that on PtPdAg(111) surfaces, resulting in disadvantageous conversion from CO* to CO₂. This phenomenon can give rise to the decline of catalytic performance by CO poisoning. This also indicates PtPdAg HNDs possess better CO tolerance. From the reaction coordinate, the step 5 (CO*→CO*+HO*) on three types of surfaces is the rate-limiting step. Compared with PtAg(111) and PtPd(111) surfaces, this limiting step on the PtPdAg(111) surface has the lowest energy barrier and thus thermodynamically more favorable. The calculation result conveys that the PtPdAg tri-metal alloy exhibit better intrinsic catalytic activity than binary ones, which corroborates the experiment result (Figure S15).

3. Conclusion

We have developed a straightforward and potent strategy for the rational synthesis of high-quality trimetallic alloy PtPdAg HNDs as effective electrocatalysts for MOR. The PtPdAg HNDs with a small diameter of 18.0±1.6 nm exhibit unique hollow and dendritic nanostructure, and their surfaces have rich atomic steps and grain boundaries. These important structural features and the electronic coupling of Pt, Pd, and Ag in the alloy account for the superior electrocatalytic activity and durability for MOR. DFT calculations indicate that such a unique metal alloy possesses a high anti-poison capability and is energetically favorable for MOR. Specifically, the mass and specific activities of PtPdAg HNDs is 1.58 A mg_{Pt}⁻¹ and 3.75 mA cm⁻², respectively, which are 4.5 and 3 times higher than that of commercial Pt black. Moreover, the chronoamperometric (10000 s) and cycling (5000 cycles) measurements prove the superior durability performance. Hence, the one-step synthetic method could be a potential strategy to synthesis the other metal with the hollow nanostructures and the tuneable composition, which are highly demanded for the electrocatalysts.

4. Experimental Section

4.1. Materials

Potassium tetrachloroplatinate (K_2PtCl_4 , 98.0%), sodium tetrachloropalladate (Na_2PdCl_4 , 98.0%), and commercial Pt black were acquired from Sigma-Aldrich. Hexadecyltrimethylammonium chloride (CTAC, 99%), silver nitrate (AgNO_3 , $\geq 99.8\%$), and ascorbic acid (AA, 99.0%) were purchased from Sinopharm Chemical Reagent Corporation. All chemicals were used without further purification. Deionized water was produced by Milli-Q water purification machine.

4.2. Synthesis of PtPdAg hollow nanodendrites

Typically, 20 μL of 0.1 M K_2PtCl_4 , 20 μL of 0.1 M Na_2PdCl_4 , and 20 μL of 0.1 M AgNO_3 aqueous solutions were sequentially added to an 1.5 mL deionized water under continuous stirring. The formed mixture was named Solution A. Then, 400 μL of 0.2 M CTAC and 64 μL of 0.25 M AA aqueous solution was introduced into 2 mL deionized water in a glass vial (Solution B). Subsequently, the as-prepared solution A was continuously injected into solution B under magnetic stirring through syringe pump within 5 min. The obtained mixed solution in a glass vial was put in an oil bath under continuous stirring at 30 $^\circ\text{C}$ for 4 h. After reaction, the product was washed through centrifugation using deionized water. The obtained PtPdAg HNDs were redispersed in deionized water for further use. Trimetal alloy products with various atomic ratios were realized by changing the amount of K_2PtCl_4 and Na_2PdCl_4 in the initial precursor solution while keeping other parameters the same. When the molar ratio of K_2PtCl_4 to Na_2PdCl_4 was 3:1 and 1:3, the products were named as PtPdAg HNDs-1 and PtPdAg HNDs-2, respectively.

4.3. Characterizations

XRD measurements were operated by Philips X'pert Pro X-ray diffractometer (Cu $\text{K}\alpha$ radiation, $\lambda=0.15419$ nm), in which the scanning angle was from 30 to 90 degrees. The reaction solution was injected into glass vial by syringe pump (Suzhou Wenhao Chip Technology Co., Ltd.) The morphology information of the as-synthesized PtPdAg HNDs were investigated by transmission electron microscopy (TEM), high-resolution TEM (HRTEM), energy dispersive X-ray spectroscopy (EDS) on Tecnai G2 F20 transmission electron microscope. Inductively coupled plasma mass spectrometry (ICP-MS) (ICAP Qc, Thermofisher) was conducted to evaluate the Pt mass of the electrocatalysts. X-ray

photoelectron spectroscopy (XPS) were performed by an ESCALABMK II X-ray photoelectron spectrometer.

4.4. Electrochemical Measurements

The electrochemical tests were conducted using a CHI 760E electrochemical workstation with standard three electrode system at room temperature. Pt wire and Ag/AgCl electrode served as the auxiliary and reference electrode, respectively. The glassy carbon electrode (GCE) with a diameter of 5 mm was used as the working electrode (WE). Prior to the catalyst loading, the WE was polished with alumina slurry and washed thoroughly with deionized water to obtain a clean surface. The as-prepared PtPdAg HNDs aqueous suspension was sonicated to form a uniform catalyst ink. Subsequently, a certain amount of catalyst ink was applied onto a GCE and dried at 40 °C for 20 min, where the Pt loading was 5 µg. Before the electrochemical tests, the electrode was covered with 5 µL of Nafion layer and dried at 40 °C. Cyclic voltammetry (CV) and methanol oxidation reaction (MOR) curves were recorded in N₂-saturated 0.1 M HClO₄ and 0.1 M HClO₄ + 0.2 M CH₃OH solution with a scan rate of 50 mV s⁻¹. For comparison, the commercial Pt black as the reference catalysts was also measured under the same condition.

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Conflicts of interest

The authors declare no conflicts of interests.

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