



Template-engaged synthesis of hollow porous platinum–palladium alloy nanospheres for efficient methanol electro-oxidation



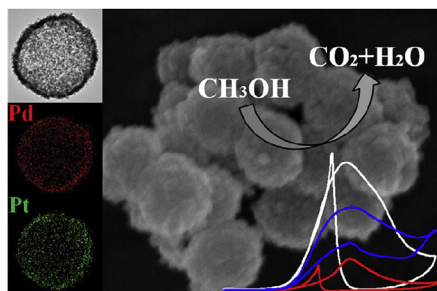
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HIGHLIGHTS

- Facile template-engaged synthesis of Pt–Pd HPNSs via layer-by-layer assembly.
- Unique compositional and structural features of hollow porous Pt–Pd catalyst.
- Markedly enhanced electrocatalytic performances toward methanol oxidation reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Hollow porous structures of Pt–Pd bimetallic alloy possess unique compositional and structural superiorities for catalytic and electrocatalytic applications, and are thus anticipated to manifest novel properties and/or enhanced performance compared with their monometallic counterparts. Herein, a general electrostatic-attraction-directed layer-by-layer assembly approach has been developed for the construction of a novel type of hollow porous Pt–Pd alloy nanospheres (Pt–Pd HPNSs) using SiO₂ nanospheres as templates. Moreover, the Pt–Pd HPNSs with controllable shell thickness are prepared and their comparative electrocatalytic performances toward methanol oxidation reaction (MOR) are investigated. It's found that optimized Pt–Pd HPNSs manifests markedly enhanced catalytic activity and durability in comparison with both commercial Pt black and Pd black catalysts.

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1. Introduction

Direct methanol fuel cells (DMFCs) are promising energy conversion devices, which can directly convert chemical fuels to

electricity with high efficiency. Methanol oxidation reaction (MOR) is the main reaction occurring in the anode of a DMFC. It is well known that noble metals, especially Pt-based and Pd-based nanostructures, are considered as the most efficient catalysts for the electro-oxidation of methanol [1–8]. Specifically, Pt-based and Pd-based alloy nanostructures are able to manifest desirable catalytic performance owing to the presence of ligand effect, geometric effect, and ensemble effect in the noble-metal alloy electrocatalysts [9–14]. Among them, Pt–Pd bimetallic alloy has proven its

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superiority over single-component components due to their synergistic effects on catalytic applications [12–14]. For example, the strain and electronic coupling in Pt–Pd alloy catalysts lead to the shifts of the d-band centers and thus the modification of their electronic properties and catalytic performances. Therefore, various Pt–Pd alloy catalysts have demonstrated novel properties and/or enhanced performance in a rich variety of reactions including nitrobenzene hydrogenation [15], ammonia borane dehydrogenation [16], oxygen reduction [17], methanol [18–22], and formic acid [23,24] oxidation compared with their monometallic counterparts.

In addition to compositional feature, the structural characteristic also plays a critical role in the performances of the noble-metal catalysts. Various noble-metal nanostructures have been designed to realize enhanced catalytic performance owing to their high surface area and fast charge-transport pathways [6–8]. Among them, hollow porous structures possess additional advantages [25–29]. Concretely, the hollow porous structures with ample edges and corners can provide abundant active sites, which is beneficial for the improved reaction kinetics and catalytic activity. Moreover, hollow porous structures are less vulnerable to Ostwald ripening, dissolution, and aggregation, leading to enhanced structural stability and catalytic durability. Therefore, the hollow porous structures of Pt–Pd alloy catalysts are anticipated to manifest desirable performances by virtue of their unique compositional and structural characteristics.

As inspired by this, a novel type of hollow porous structure of Pt–Pd bimetallic alloy, *i.e.* hollow porous Pt–Pd alloy nanospheres (Pt–Pd HPNSs) with controllable shell thickness, has been designed and constructed through a template-engaged layer-by-layer assembly approach using SiO₂ nanospheres as templates. When utilized as a potential catalyst for methanol oxidation reaction (MOR), the optimized Pt–Pd HPNSs manifests markedly enhanced catalytic activity and durability in comparison with both commercial Pt black and Pd black catalysts.

2. Experimental

2.1. Reagents and chemicals

Poly (allylamine hydrochloride) (PAH, $M_w = 150,000$ Da) was supplied from *Nitto Boseki Co. Ltd.* (Tokyo, Japan). Poly (sodium 4-styrenesulfonate) (PSS, $M_w = 700,000$ Da) was purchased from *Alfa Aesar Co. Ltd.* Potassium tetrachloropalladate(II) (K_2PdCl_4), potassium hexachloroplatinum(II) (K_2PtCl_4), and sodium borohydride ($NaBH_4$) were purchased from *Sinopharm Chemical Reagent Co. Ltd.* (Shanghai, China). Commercial Pt black and Pd black were purchased from *Johnson Matthey Corporation*. All the reagents were of analytical reagent grade and used without further purification.

2.2. Synthesis of the Pt–Pd HPNSs

First, SiO₂ spherical templates with a diameter of *ca.* 200 nm were synthesized through a modified Stöber method [30]. Then, SiO₂@Pt–Pd nanospheres were prepared through an electrostatic-attraction-directed layer-by-layer assembly approach [31]. Typically, SiO₂ templates were modified with PAH and PSS in sequence, yielding positively charged PAH/PSS/PAH modified SiO₂ nanospheres [31,32]. Subsequently, 30 mg PAH/PSS/PAH modified SiO₂ nanospheres were dispersed in 40 mL distilled water, and then 19.1 mg (0.046 mmol) K_2PtCl_4 and 15 mg (0.046 mmol) K_2PdCl_4 were added. After sonication for 10 min, a 10 mL aqueous solution containing 0.25 mmol $NaBH_4$ was added dropwise into the above-mentioned solution, and the mixture was further mechanically stirred for 1 h at room temperature. The resulting solid product was

washed with distilled water and ethanol, resulting in the SiO₂@Pt–Pd nanospheres. Finally, the Pt–Pd HPNSs were obtained by dissolving the SiO₂ templates with a 2 M NaOH aqueous solution.

2.3. Electrochemical measurement

All electrochemical experiments were measured with a CHI 660C electrochemical analyzer and a conventional three electrode electrochemical cell at 30 ± 1 °C. A saturated calomel electrode (SCE) was used as the reference electrode, whereas a platinum wire was used as the auxiliary electrode. The working electrodes were prepared as follows: an evenly distributed suspension of catalyst was prepared by sonicating the mixture of 10 mg catalyst, *i.e.* Pt–Pd HPNSs, and 5 mL distilled water for 30 min, and 6 μ L of the resulting suspension was loaded on the surface of a glassy carbon electrode (3 mm in diameter, 0.07 cm²). After drying, 3 μ L Nafion solution (5 wt %) was covered on the modified electrode surface, resulting in the working electrode. Cyclic voltammetry tests were performed in N₂-saturated 0.1 M KOH solution with or without 0.5 M CH₃OH at a scan rate of 50 mV s⁻¹, whereas chronoamperometry curves were obtained in N₂-saturated 0.5 M CH₃OH + 0.1 M KOH mixture solution for 3000 s at -0.4 V (vs. SCE).

2.4. Characterization

The morphology, structure, and composition of the products were characterized by X-ray powder diffraction (XRD, Rigaku D/max-RC), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010F, 200 kV), and scanning electron microscopy (SEM, JEOL JSM-7600F) equipped with an energy-dispersive X-ray spectrometer (EDX). The composition of the catalysts was determined by using inductively coupled plasma atomic emission spectrum (ICP-AES) techniques. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo VG Scientific ESCALAB 250 spectrometer with an Al K α radiator. The vacuum in the analysis chamber was maintained at about 10⁻⁹ mbar and the binding energy was calibrated by means of the C 1s peak energy of 284.6 eV. Nitrogen adsorption/desorption tests were performed using a Micromeritics ASAP 2050 instrument at 77 K, and the surface area and pore diameter of the sample were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

3. Results and discussion

The morphology of the products at different stages was first investigated by TEM. SiO₂ nanospheres (inset in Fig. 1A) are chosen as sacrificial templates owing to their hydrophilia, size controllability, and ease of preparation. After the layer-by-layer assembly process, a rough coating layer composed of numerous Pt–Pd nanocrystals is uniformly deposited on the surface of SiO₂ nanospheres (Fig. 1A). No isolated nanocrystal could be observed in the sample except for the surface of SiO₂ templates owing to the strong electrostatic attraction between charged species during the synthetic process. Furthermore, the Pt–Pd HPNSs can be obtained by etching the SiO₂ spherical core in core–shelled SiO₂@Pt–Pd nanospheres, and reveals typical hollow spherical morphology with high mechanical stability and structural integrity (Fig. 1B). Additionally, the Pt:Pd atomic ratio is determined to be 51.8:48.2 by EDX analysis (Fig. 1C). ICP-AES measurement also shows the exact Pt:Pd atomic ratio is 51.5:48.5 in the product, in good matchup with the molar ratio of K_2PtCl_4 and K_2PdCl_4 reactants (50:50).

Fig. 1D reveals the XRD patterns of the samples in different stages of evolution. As can be seen, the broad diffraction peak

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