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# Simple one-pot synthesis of platinum-palladium nanoflowers with enhanced catalytic activity and methanol-tolerance for oxygen reduction in acid media

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## ABSTRACT

In this work, bimetallic alloyed platinum-palladium (PtPd) nanoflowers are fabricated by one-pot solvothermal co-reduction of Pt (II) acetylacetonate and Pd (II) acetylacetonate in oleylamine system. The as-prepared nanostructures show the enhanced electrocatalytic activity for oxygen reduction reaction (ORR), dominated by a four-electron pathway based on the Koutecky-Levich plots, mainly owing to the inhibition of the formation of Pt–$OH_{ad}$ via the downshift of d-band center for Pt. Meanwhile, PtPd nanoflowers display good methanol tolerance and improved stability for ORR. The chronoamperometry test reveals that the current of PtPd nanoflowers remains 45.9% of its original value within 6000 s, much higher than those of commercial Pt (36.7%) and Pd (32.2%) black catalysts. Therefore, PtPd nanoflowers with unique interconnected structures can be used as a promising cathode catalyst in direct methanol fuel cells.

## 1. Introduction

Direct methanol fuel cells (DMFCs) have attracted increasing attention because of their high energy density, environmental friendliness, ambient-temperature operating and fast start-up [1,2], in which Pt nanomaterials are widely used as catalysts. However, there are several severe drawbacks that block the commercial applications such as the sky-rocketing price, scarcity of Pt [3], and sluggish oxygen reduction reaction (ORR) kinetics on Pt surface [4]. Moreover, Pt catalysts are not selective to ORR, because methanol can diffuse from anode to cathode through polymer electrolyte membrane (PEM) [5].

Alloying a second metal M (M = Pd, Fe, Co, Ni, etc.) with Pt is one of the effective strategies to solve these issues [6–9]. Among them, PtPd nanostructures are good candidates to integrate advantages of Pt and Pd together towards ORR with good methanol tolerance, because Pd is active for ORR [7] and inactive for methanol oxidation reaction (MOR) in acid media [10]. Moreover, the two metals display better chemical stability than others, which are vulnerable to leach out under acid conditions [3].

It is known that the catalytic performance of a catalyst strongly depends on its morphology, size, composition, and structure [11]. Particularly, the morphology control can tailor the catalytic properties, because the catalyst surface is enclosed by specific crystal facets based on their shapes [12,13]. Now, a variety of PtPd nanostructures have been prepared, including cages [14], wires [15], cubes [16], octahedral [17], tetrahedral [18], and porous structure [19]. The catalytic reaction can be greatly facilitated by porous PtPd branches because of more active sites available by their enlarged specific surface areas, abundant edges, junctions, and narrow gaps [20]. Despite various porous PtPd nanoparticles have been synthesized, many of the methods need to prepare seeds in advance [3,21–23]. Thus, it is necessary to develop a one-pot strategy for preparation of porous PtPd nanoparticles.

In this work, bimetallic alloyed PtPd nanoflowers were prepared by a simple one-pot solvothermal route via co-reduction of Pt (II) acetylacetonate ($Pt(acac)_2$) and Pd (II) acetylacetonate ($Pd(acac)_2$) in oleylamine (OAm) system. The catalytic performance and methanol-tolerance of PtPd naonoflowers were examined in some detail, using ORR as a model system evaluated under half cell conditions.

## 2. Experimental section

### 2.1. Chemicals

Platinum(II) acetylacetonate ($Pt(acac)_2$), palladium(II) acetylacetonate ($Pd(acac)_2$), OAm, 1-dodecyl-3-methylimidazolium, and

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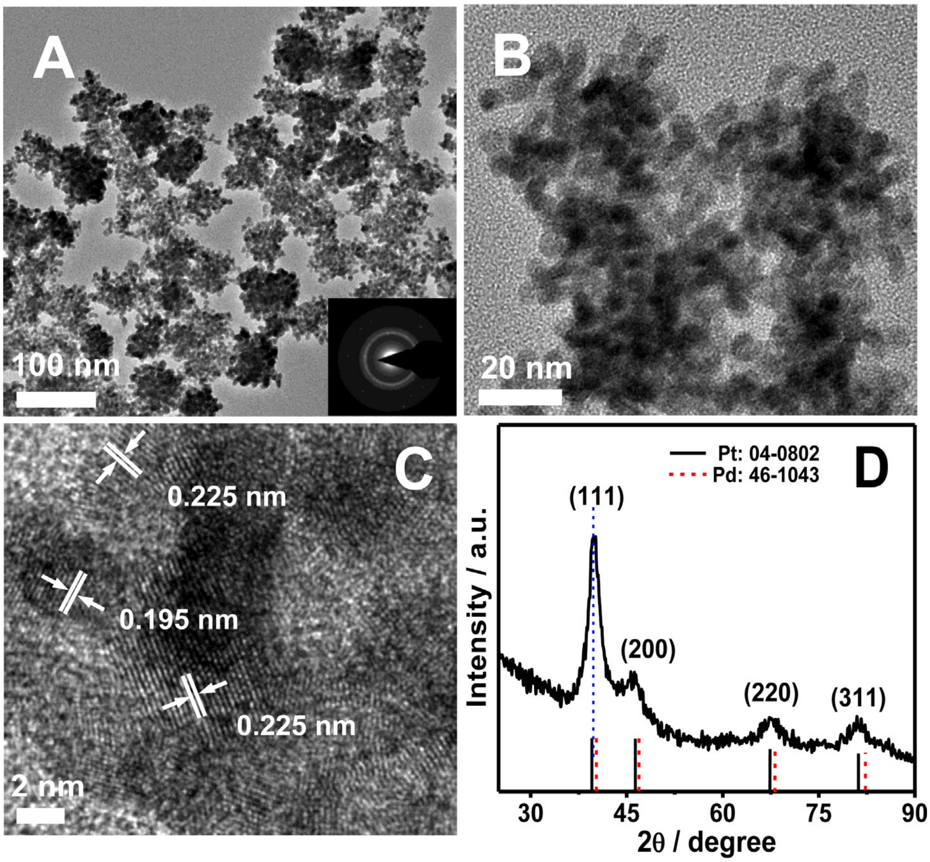

**Fig. 1.** (A, B) TEM images, (C) HRTEM image, and (D) XRD pattern of PtPd nanoflowers and the standard patterns of bulk Pt and Pd. Inset shows the SAED pattern of PtPd nanoflowers.

commercial Pt and Pd black were purchased from Aladdin chemistry Co., Ltd. Other chemicals were of analytical grade and used without further purification. All aqueous solutions were prepared with twice-distilled water.

### 2.2. Synthesis of PtPd nanoflowers

Typically, 0.1 g of 1-dodecyl-3-methylimidazolium was put into 20 mL of OAm under gentle agitation, followed by ultrasonication for 30 min to obtain a homogeneous solution. Then, 0.020 g of Pt(acac)$_2$ and 0.016 g of Pd(acac)$_2$ were put into the mixed solution under stirring. After ultrasonication for 1 h, the mixture was transferred into a Teflon-lined stainless autoclave, heated at 170 °C for 24 h, and then cooled to room temperature in air. The final product was collected by centrifugation, washed thoroughly with ethanol, and dried in a vacuum oven.

### 2.3. Characterization

The structure and composition of the samples were examined by a JEM-2010 high resolution transmission electron microscope (HR-TEM) coupled with an energy-dispersive X-ray spectrometer (EDS, Dxford-1NCA) at an acceleration voltage of 200 kV. The scanning transmission electron microscopy (STEM) imaging and elemental mappings were acquired on a scanning transmission electron microscope with high-angle annular dark-field (HAADF). The surface oxidation states were determined by a K-Alpha XPS spectrometer (ThermoFisher, E. Grinstead, UK) with an Al Kα X-ray radiation (1486.6 eV) for excitation. The crystal structure was checked by X-ray diffraction (XRD, Rigaku Dmax-2000 diffractometer) with the Cu Kα radiation.

### 2.4. Electrochemical measurements

All electrochemical measurements were conducted on a CHI832b electrochemical workstation (CH Instruments, Chenhua Co., Shanghai, China) at room temperature. A standard three-electrode system was employed for all the electrochemical measurements, which consists of a Pt mesh as counter electrode, a Ag/AgCl electrode as reference electrode, and a bare/modified glassy carbon electrode (GCE, 3 mm in diameter), or glassy carbon rotating disk electrode (GCRDE, 4 mm in diameter) as working electrode. All the potentials were referred to the Ag/AgCl electrode (Ag/AgCl in a solution saturated with KCl). In addition, rotating disk electrode tests were performed on a Gamry's Rotating Disk Electrode (RDE710).

For typical preparation of PtPd nanoflowers modified electrodes, 1 mg of the sample was put into 1 mL of water and ultrasonicated for 60 min to obtain a homogeneous suspension (1 mg mL$^{-1}$). Next, 6 and 10 μL of the suspensions were casted on the GCE and GCRDE, respectively. After drying in air, 3 and 5 μL of Nafion (0.05 wt%) were covered on the electrode surfaces and allowed to dry again naturally. For comparison, commercial Pt and Pd black catalysts modified electrodes were prepared under the similar conditions. The metal loading is 0.085 and 0.080 mg cm$^{-2}$ for the three catalysts modified GCE and GCRDE electrodes, respectively.

The cyclic voltammograms (CVs) of these catalysts modified electrodes were recorded in N$_2$-saturated 0.5 M H$_2$SO$_4$ at the scan rate of 50 mV s$^{-1}$. The electrochemically active surface area (EASA) of a catalyst was calculated from integrated hydrogen desorption region based on the following equation [24]:

$$EASA = \frac{Q}{m \times C} \quad (1)$$