



## Short communication

## Highly monodispersed ternary hollow PtPdAu alloy nanocatalysts with enhanced activity toward methanol oxidation

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## ABSTRACT

Highly monodispersed hollow PtPdAu nanoalloys (HNAs) are synthesized through two-step successive reduction (PtPdAu HNAs-1) and one-pot co-reduction method (PtPdAu HNAs-2) using PEO<sub>19</sub>-PPO<sub>69</sub>-PEO<sub>19</sub> (P123) as both reductant and stabilizer. Subsequent X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and HRTEM revealed that both two kinds catalysts have a hollow alloy structure and the average particle size reached 10.4 and 9.6 nm, respectively. This work demonstrates that the addition of Au can effectively improve the electrocatalytic performance of Pt-based catalysts. By compared with PtPdAu HNAs-1 and commercial Pt/C, PtPdAu HNAs-2 exhibited superior performance toward methanol oxidation reaction (MOR), including a more negative onset potential of ~0.2 V, higher mass peak current density of 263.5 mA mg<sub>Pt</sub><sup>-1</sup> and long-term durability.

## 1. Introduction

Platinum (Pt) is widely recognized as an ideal catalyst for direct methanol fuel cells (DMFC), because of its superior methanol oxidation reaction (MOR) activity, but its high price, poor long-term durability and low anti-CO poisoning capacity limit its further application. Previous studies have demonstrated that the introduction of another metal element is a viable approach, bimetallic catalyst such as noble metal catalyst (e.g. PtPd [1], PtAu [2], PtAg [3], PtRh [4], PtRu [5]), noble-transition metal catalyst (e.g. PtFe [6], PtCo [7], PtCu [8], PtNi [9], PtSn [10]), and the preparation of alloy structure catalyst is considered as an effective strategy [11,12] which will not damage its intrinsic activity, but can also effectively improve long-term durability of Pt-based catalysts. As previous works stated, pure Au is inactive for methanol oxidation in acid medium [13,14], and is not conducive to the removal of CO<sub>ad</sub> on Pt surface. It seems that Au has little benefit to the MOR long-term durability of Pt-based catalysts. However, Eichhorn and coworkers [15] demonstrated that PtAu bimetallic NPs could significantly enhance the CO poisoning tolerance in acid medium. The improved anti-CO poisoning capacity could be attributed to the oxidation of CO on Au-Pt interface, and then resume their initial catalytic activity. Moreover, Zhang and coworkers reported that Au clusters on the surface of Pt catalysts can effectively suppress the dissolution and oxidation of Pt atoms, thereby improving the oxygen reduction reaction

(ORR) durability [16]. Compared with the bimetallic catalyst, trimetallic catalyst reported relatively little, much less trimetallic hollow catalyst [17]. Li and co-workers confirmed that Pt-on-Pd bilayer of initial designed Au@PdPt would finally evolve into stable PtPdAu alloy during long-term potential cycling, resulting in an enhancement of Pt mass ORR activity and nearly perfect activity maintenance [18].

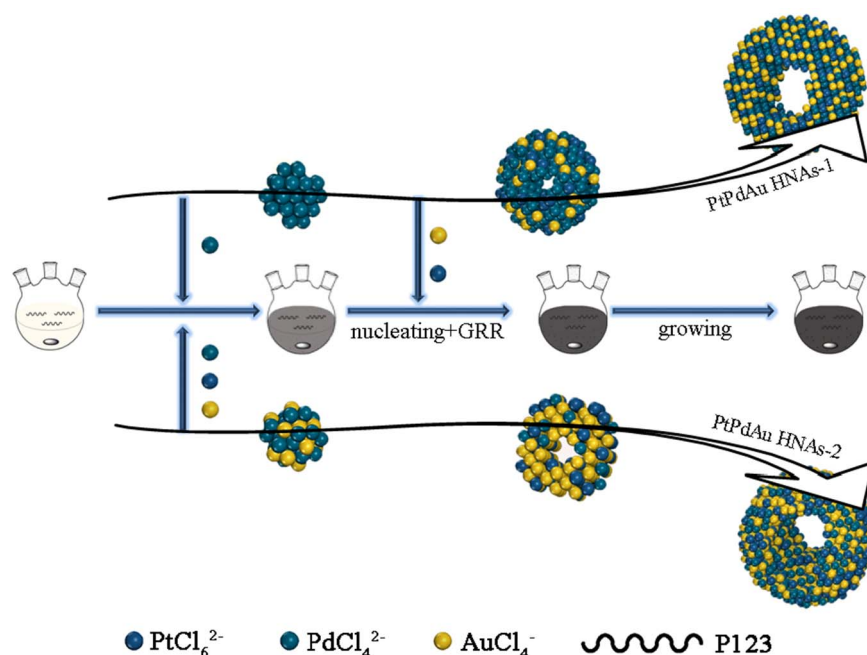
Here, highly monodispersed ternary PtPdAu hollow nanoalloys (HNAs) were synthesized by a facile, economical synthesis method (Scheme 1). The electrocatalytic performance of as-prepared PtPdAu HNAs were investigated in acid system and compared with commercial Pt/C (20%, Johnson Matthey) catalyst.

## 2. Materials and methods

## 2.1. Materials

Potassium tetrachloropalladate (K<sub>2</sub>PdCl<sub>4</sub>, 99.99%), potassium hexachloroplatinate (K<sub>2</sub>PtCl<sub>6</sub>, 99.99%) and poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (PEO<sub>19</sub>-PPO<sub>69</sub>-PEO<sub>19</sub>, P123) were purchased from Sigma-Aldrich Co. Chloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O, 99%) were purchased from Alfa Aesar Co. Commercial Pt/C (20%Pt, JM) catalyst was obtained from Johnson-Matthey Co. 5% (w/w) Nafion solution was from Du Pont Company (USA). All the chemicals were used as received without further purification. Water

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Scheme 1. Schematic of two facile synthesis methods of PtPdAu HNAs.

used in the experiment was supplied by a water purifier Nanopure water system (18.3 M $\Omega$  cm).

## 2.2. Synthesis of PtPdAu catalysts

PtPdAu HNAs-1 were prepared by a galvanic replacement reaction (GRR) at 30 °C. In short, 1.2 g P123 was dissolved in 50 mL of water with ultrasonication and stirring by glass bar. Then, 10 mL 0.03 mM potassium chloropalladate (K<sub>2</sub>PdCl<sub>4</sub>) was added dropwise and magnetically stirred at 30 °C for 30 min. After that, 20 mL 0.03 mM potassium chloroplatinate (K<sub>2</sub>PtCl<sub>6</sub>) and chloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O) were slowly added dropwise and the reaction was continued until the mixture was completely precipitated. The product was then washed and centrifuged 3 times with distilled water and ethanol to remove the residual P123 and redispersed in ethanol for further study.

We also used one-pot co-reduction reaction (CRR) to prepare PtPdAu HNAs-2 at 30 °C. In brief, all three precursor (11.92 mg K<sub>2</sub>PdCl<sub>4</sub> + 14.58 mg K<sub>2</sub>PtCl<sub>6</sub> + 11.84 mg HAuCl<sub>4</sub>·3H<sub>2</sub>O) were mixed in 30 mL water and dropped into 50 mL P123 solution (24 mg mL<sup>-1</sup>).

## 2.3. Material characterizations

Transmission electron microscope (TEM) and High-resolution transmission electron microscopy (HRTEM, FEI Tecnai-F30 at 300 kV) equipped with Energy Dispersive Spectroscopy (EDS) were used to characterize the morphology and component analysis. Rigaku (Ultima IV) powder X-ray diffractometer with Cu K $\alpha$  X-ray source ( $\lambda = 1.5405 \text{ \AA}$ ) was employed for obtaining X-ray diffraction (XRD) patterns. X-ray photoelectron spectroscopy (XPS) spectrum was obtained from a PHI Quantum 2000 XPS system (Physical Electronics, Inc.) using Al K $\alpha$  radiation. High-angle annular dark-field scanning TEM (HAADF-STEM) and element analysis mapping images were carried out on a JEM-2010 (HR) microscope at 200 kV.

## 2.4. Electrochemical measurements

A standard three-electrode system, platinum flakelet for the counter electrode, saturated calomel electrode as the reference electrode, glass carbon electrode (GCE,  $\Phi = 5 \text{ mm}$ ) for the working electrode, was used

for the electrochemical measurements performing on Autolab electrochemical work station (PGSTAT12) at room temperature. The electrochemical surface area (ECSA) of each catalyst was obtained via CO-stripping measures, using the equation  $ECSA = Q_{CO}/(C \times m_{Pt})$ , where C represents the oxidation charge of monolayer CO and its value was assumed to be 0.42 mC cm<sup>-2</sup>.

## 3. Results and discussion

XRD patterns in Fig. 1 were performed to investigate the crystalline structure of PtPdAu HNAs with scanning angle ranging from 20° to 90°. The diffraction peaks reveal a typical face-centered cubic (fcc) crystal structure. In detail, the diffraction peaks located at 38.82°, 45.06°, 65.93°, 78.81° could be assigned to the (111), (200), (220) and (311) facets, which can be regarded as a typical fcc lattice. Comparing with the Pt and Pd standard card, it's obvious that the diffraction peaks of PtPdAu HNAs-1 and PtPdAu HNAs-2 are located between Au and Pd,

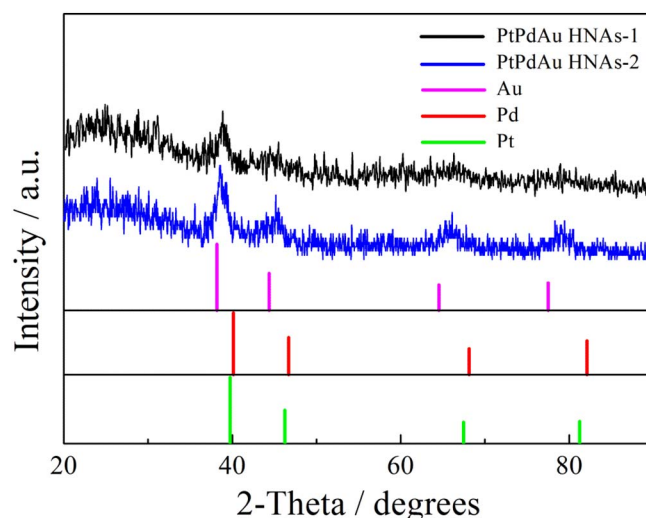


Fig. 1. XRD patterns of PtPdAu HNAs-1, PtPdAu HNAs-2 and standard pure Pt (PDF#65-2868), Pd (PDF#46-1043); Au (PDF#04-0784).

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