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# Single-step aqueous synthesis of AuPt alloy nanodendrites with superior electrocatalytic activity for oxygen reduction and hydrogen evolution reaction

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## ABSTRACT

Herein, well-dispersed porous AuPt alloy nanodendrites (AuPt NDs) were facilely synthesized by a single-step seedless approach by using 5-aminouracil-6-carboxylic acid (AUCA) as the capping agent and weak stabilizer. The architectures showed large electrochemically active surface area ( $29.67 \text{ m}^2 \text{ g}^{-1}$ ), and enhanced catalytic performances for oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) both in acid and alkaline media. Specifically, the mass activity and specific activity of the as-made catalyst were  $31.55 \text{ mA mg}^{-1}$  and  $2.65 \text{ mA cm}^{-2}$  ( $0.1 \text{ M HClO}_4$ ),  $29.49 \text{ mA mg}^{-1}$  and  $2.5 \text{ mA cm}^{-2}$  ( $0.1 \text{ M KOH}$ ) for ORR, respectively, along with a notably low Tafel slope of  $34 \text{ mV dec}^{-1}$  ( $0.5 \text{ M H}_2\text{SO}_4$ ) and  $55 \text{ mV dec}^{-1}$  ( $0.1 \text{ M KOH}$ ) towards HER. This synthetic approach can be explored to fabricate other catalysts with improved catalytic performances in fuel cells and renewable energy.

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## Introduction

As well known, Pt-based nanocatalysts are essential for hydrogen evolution reaction (HER) and oxygen reduction reaction (ORR) in renewable energy and fuel cells [1–3]. However, the high cost of Pt and the sluggish ORR kinetics on Pt surface [4] have limited their wide applications [5,6], albeit

with the slight small hydrogen absorption energy and minimum overpotential [7].

Alloying Pt with another metal ( $M = \text{Pd, Ni, Fe, Au, etc.}$ ) is practical to solve these problems [8]. Researchers have constructed many Pt-based bimetallic nanocatalysts to improve the catalytic performances [9–12]. Dominguez-Crespo's group synthesized PtNi nanoparticles with enhanced catalytic activity for hydrogen evolution reaction (HER) [13]. Choi et al. synthesized urchin-like PtNi alloy nanocrystals by a

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controlled one-pot method for oxygen reduction reaction (ORR) [14]. Raof and coworkers fabricated CuPt bimetallic nanoparticles by the galvanic replacement of Cu nanoparticles with Pt for HER [15].

Among Pt-based bimetallic nanocatalysts, AuPt nanocrystals have drawn significant attention because of the unique function of Au [16]. According to the previous literature, the incorporation of Au into Pt catalysts can profoundly enhance the catalytic activity and stability [17,18]. Also, Au can effectively stabilize Pt catalysts, because Au can modify the electronic structure of Pt and reduce the respective d-band center [19,20].

Moreover, the morphologies of nanocatalysts have influence on the catalytic activity [21]. Recently, three-dimensional (3D) dendrite-like nanomaterials are widely investigated because of their large surface areas, providing more active sites available for reactants during ORR [22,23]. Hence, it is important to synthesize porous nanocrystals for the enhanced catalytic behaviors [24]. Wang's group synthesized porous dendritic NiPt nanoparticles for ORR [25]. Li and coworkers constructed Au nanodendrites on graphene oxide nanosheets for ORR [26]. Kim et al. fabricated size-controlled Pt dendrites for ORR [27]. It is interesting and challenging for simple preparation of dendrite-like nanocrystals for ORR and HER under mild conditions.

5-Aminouracil-6-carboxylic acid (AUCA, as described in Fig. S1, Supporting Information, SI) is commonly used to inhibit the metabolic process of the cardioprotective drug dexrazoxane [28]. Herein, with the assistance of AUCA, we facilely synthesized uniform bimetallic AuPt alloy nanodendrites (AuPt NDs) by a single-step seedless aqueous approach. The catalytic properties of AuPt NDs were tested by using ORR and HER as two model systems.

## Experimental

### Preparation of AuPt NDs

For the preparation of AuPt NDs, 0.648 mL of  $\text{H}_2\text{PtCl}_6$  (38.62 mM), 1.029 mL of  $\text{HAuCl}_4$  (24.3 mM) and 0.0428 g of AUCA (dissolved by 0.5 mL of 1 M NaOH solution) were put into 5 mL of polyvinylpyrrolidone (PVP) with the concentration of 0.5 wt% under stirring at room temperature. The mixture was diluted to 10 mL. Afterwards, 100  $\mu\text{L}$  of hydrazine hydrate solution (16.5 M) was dropwise put into the system and reacted for 10 min. The resulting solution was centrifuged and the precipitates were obtained by completely washing several times to remove the excess PVP. Finally, the product was dried in vacuum at 60 °C for further characterization.

For comparison,  $\text{Au}_1\text{Pt}_3$  and  $\text{Au}_3\text{Pt}_1$  nanocrystals, and Pt nanospheres (NSs) were prepared by changing the ratios of  $\text{HAuCl}_4$  and  $\text{H}_2\text{PtCl}_6$  while the other experiments were kept unchanged.

### Electrochemical experiments

All the electrochemical measurements were conducted on a conventional three-electrode system [29]. For preparation of AuPt NDs modified electrode, 1 mg of AuPt NDs was firstly put

into 1 mL of water by ultrasonication (1 mg  $\text{mL}^{-1}$ ) to form a homogeneous suspension. Next, 6  $\mu\text{L}$  of the suspension and 4  $\mu\text{L}$  of Nafion solution (0.05 wt%) was orderly dropped on the clean glassy carbon electrode (GCE) and then dried in air. For comparison,  $\text{Au}_1\text{Pt}_3$ ,  $\text{Au}_3\text{Pt}_1$ , Pt NSs, Pt black and Pt/C (20 wt%) catalysts modified electrodes were prepared using the same method.

More details of the experimental sections were provided in Supporting Information (SI).

## Results and discussion

### Physical characterization

The morphology and size of the as-obtained AuPt NDs were examined by transmission electron microscopy (TEM) images (Fig. 1A–C). As displayed in Fig. 1A and B, the low-magnification TEM images reveal that the product contains many uniformly well-dispersed dendrites with the mean size of 35.45 nm. Each nanodendrite is consisted of many smaller grains, showing the interconnected porous nanostructures. High-resolution TEM (HRTEM, Fig. 1C) image reveals the well-defined fringes with the d-spacing distances of 0.226 (a), 0.225 (b), and 0.224 nm (c). These values are smaller than that of the face-centered cubic (fcc) Au (0.235 nm), but are very close to that of Pt (0.226 nm) [30], indicating the formation of AuPt alloy [31]. Furthermore, the selected-area electron diffraction (SAED) pattern of one nanodendrite implies their polycrystalline nature (Fig. 1D).

The high-angle annular dark-field scanning TEM (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDS) mapping, and EDS line scanning profiles manifest the elemental distribution of AuPt NDs (Fig. 2) [32]. As shown in Fig. 2A–D, Au and Pt are evenly distributed among the whole nanodendrite, which reflects the formation of AuPt alloy [33]. The EDS line scanning profiles (Fig. 2E) show the coexistence of Pt and Au elements, proving their homogeneous distribution of AuPt NDs. According to the EDS analysis, the atomic ratio of Au to Pt is estimated to be 0.79. Additionally, C and Cu elements are also found in the product, which are originated from the copper grid (Fig. 2F).

Fig. 3 shows the TEM images of  $\text{Au}_1\text{Pt}_3$ ,  $\text{Au}_3\text{Pt}_1$  and Pt nanocrystals synthesized by regulating the molar ratios of  $\text{HAuCl}_4$  and  $\text{H}_2\text{PtCl}_6$ . It clearly indicates that the nanocrystals are aggregated together (Fig. 3A and C) and sphere-like Pt nanocrystals are obtained with the relative smooth surface and the size of about 109.2 nm (Fig. 3E and F). These reveal the important role of Au in the process to form the nanodendrites. The as-prepared AuPt NDs may have improved electrochemical activity owing to their porous dendrite-like nanocrystals [34].

X-ray diffraction (XRD, Fig. 4) spectra were provided to inspect the crystal structure of AuPt NDs. Apparently, the representative diffraction peaks of AuPt NDs are matched perfectly with those of the fcc structures ( $2\theta = 39.15^\circ$ ,  $45.51^\circ$ ,  $66.75^\circ$ , and  $79.75^\circ$ , corresponding to the (111), (200), (220), and (311) planes, respectively). Furthermore, the above-mentioned peaks locate between monometallic Au and Pt [35]. It is worthy to note that the intensity ratio of the (111) planes relative to the (200), (220) and (311) planes are about 3.10, 4.57, and 5.54,

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