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# Simple wet-chemical strategy for large-scaled synthesis of snowflake-like PdAu alloy nanostructures as effective electrocatalysts of ethanol and ethylene glycol oxidation

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## ABSTRACT

In this work, snowflake-like bimetallic PdAu alloy nanostructures with tunable composition and size were large-scaled synthesized at room temperature via a facile wet-chemical strategy. Their morphology and size depend on the composition and concentration of poly(1-vinyl-3-ethylimidazolium bromide) (PVEIB) as the stabilizing agent and structure director. The as-prepared architectures exhibit excellent electrocatalytic activity and stability towards ethanol and ethylene glycol oxidation in alkaline media. And snowflake-like Pd<sub>1</sub>Au<sub>3</sub> nanostructures display the best catalytic performance. This is due to the unique snowflake-like structures, alloy nature, and tunable composition and size, along with effectively avoiding the support corrosion usually occurred on commercial catalysts.

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## Introduction

Direct alcohol fuel cells (DAFCs) are a kind of potential power sources to solve the energy and environmental problems, owing to their low emission, high efficiency, and easy operation [1–4]. Among different types of alcohols for DAFCs,

ethanol and ethylene glycol have attracted significant attention for their high energy density and low toxicity, as well as the easy production from biomass and industry [5–9]. Besides, the alkaline operating media can accelerate the oxidation kinetics of alcohols and reduce the risk of corrosion of materials for high durability [10–12]. However, the poor catalytic performances of anode catalysts for ethanol and ethylene glycol

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oxidation hinder their large-scaled applications in DAFs [6]. Therefore, it is urgent to prepare novel catalysts with high catalytic activity for ethanol oxidation reaction (EOR) and ethylene glycol oxidation reaction (EGOR) [13,14].

Pt- and Pd-based nanocatalysts are commonly regarded as the most effective catalysts toward ethanol and ethylene glycol oxidation in alkaline electrolyte [5,15]. Particularly, Pd-based ones are the promising alternative candidates in comparison with Pt, due to their relatively high abundance and low cost [12,16–18]. Nevertheless, there are some disadvantages still confined their commercial applications in hand-held fuel cells, such as the comparatively poor durability and low catalytic activity [16]. Also, the efficient utilization of Pd in the above catalysts is critical for their practical applications [19,20].

Among Pd-based nanocatalysts, PdAu bimetallic nanocatalysts have received significant attention because of their superior catalytic activity in the industrial synthesis of vinyl acetate, low-temperature CO oxidation, direct H<sub>2</sub>O<sub>2</sub> synthesis from H<sub>2</sub> and O<sub>2</sub>, hydrodechlorination of Cl-containing pollutants in underground water, hydrosulfurization of S-containing organics, hydrogenation of hydrocarbons, and acetylene trimerization [21], as well as DAFs [22,23].

Lately, it is found that the catalytic property of PdAu bimetallic nanocatalysts strongly depends on the size, morphology and composition [12]. And remarkable catalytic performances toward alcohols oxidation and higher utilization of Pd can be achieved by facily adjusting these parameters [24]. For instance, Hong et al. synthesized PdAu nanowire networks with tunable compositions, showing the improved catalytic performance toward EOR and the highest utilization of Pd obtained in the case of Pd<sub>1</sub>Au<sub>1</sub> [12]. In another example, Park's group prepared flower-like Au@Pd nanostructures with better catalytic property for methanol oxidation when compared with truncated octahedral Au@Pd nanostructures [25].

Herein, we report a facile synthesis of well-defined PdAu nanosnowflakes (NSFs) with tunable composition and size only with the assistance of poly(1-vinyl-3-ethylimidazolium bromide) (PVEIB, Fig. S1, Supporting Information, SI). The catalytic performances of PdAu NSFs were evaluated by EOR and EGOR as model systems.

## Experimental

### Preparation of PdAu NSFs

For typical preparation of Pd<sub>1</sub>Au<sub>3</sub> NSFs, 1.24 mL of HAuCl<sub>4</sub> (24.3 mM), 0.1 mL of H<sub>2</sub>PdCl<sub>4</sub> (100 mM), and 2 mL of PVEIB (1%, w/v) were successively put into 5.67 mL of water under stirring, followed by dropwise adding 1 mL of the freshly-prepared ascorbic acid (AA, 0.1 M). The reaction was continued for 0.5 h under stirring and kept static for 23 h. The final product was collected by centrifugation and thoroughly washing with water.

In controlled experiments, Au, Pd<sub>1</sub>Au<sub>1</sub>, Pd<sub>3</sub>Au<sub>1</sub> and Pd nanocrystals were synthesized in a similar way via the changes of the molar ratios (HAuCl<sub>4</sub> against H<sub>2</sub>PdCl<sub>4</sub>) from 1:0,

1:1, 1:3, to 0:1, respectively, while the total concentrations of the precursors were kept constant.

### Construction of PdAu NSFs modified electrodes

For preparation of Pd<sub>1</sub>Au<sub>3</sub> NSFs modified electrode, 6 μL of Pd<sub>1</sub>Au<sub>3</sub> NSFs suspension (1 mg mL<sup>-1</sup>) was casted on the surface of a bare glassy carbon electrode (GCE, 3 mm in diameter), followed by coating with 4 μL of Nafion (0.05%) to form another layer to tight the deposit. Meanwhile, Pd<sub>1</sub>Au<sub>1</sub> NSFs, Au nanocrystals, and commercial Pd black catalysts modified electrodes were constructed in a similar way for comparison.

More specific information of Chemicals, Characterization and Electrochemical experiments were provided in Supporting Information (SI).

## Results and discussion

### Characterization

Fig. 1A and B exhibits the low- and medium-magnification transmission electron microscopy (TEM) images, displaying numerous snowflake-like nanocrystals with well dispersion for the typical product. The average particle size is about 400 nm. High-resolution TEM (HR-TEM) images show the well-resolved lattice fringes of the product (Fig. 1C and D), revealing their polycrystalline nature. The inter-planar spacing distance is estimated to be 0.23 nm from the marked tips, which corresponds to the (111) crystal planes of the face-centered cubic (fcc) PdAu alloy [26], demonstrating their preferential growth along the [111] directions [27]. Meanwhile, the selected area electron diffraction (SAED) pattern (inset in Fig. 1B) manifests their polycrystalline nature again. It is known that the defect sites frequently emerge along the branches and also at the joints where the branches change the growth directions [28]. The corners and edges in the snowflakes (blue arrows in Fig. 1C and D) would produce abundant defect sites [28], which are expected to provide more active sites available and improve the catalytic activity [28,29].

Fig. 2A–D shows the high-angle annular dark-field-scanning transmission electron microscopy-energy dispersive spectroscopy (HAADF-STEM-EDS) elemental mapping images of the product. Obviously, Au and Pd elements homogeneously distribute in the whole architectures, further reflecting the formation of PdAu alloy (Fig. 2A–C). However, Pd is rich in the surface and the surface segregation is occurred from the PdAu overlap image (Fig. 2D), which is in disagreement with the formation of PdAu alloy. The extensive exposure of Pd atoms on the surface result from the image drift due to the long-time sampling process of EDS-mapping, which also causes the anamorphose of the snowflake-like structures (Fig. S2, SI), as supported by the previous work [30]. The alloy structures were further confirmed by the cross-sectional line scanning profiles from the same HAADF-STEM image (Fig. 2E), which reveal the bimetallic alloy structures with uniform distribution of Pd and Au atoms. Besides, the EDS spectrum displays that the atomic ratio of Pd to Au (Pd/Au) is 25.96:74.03 in the product (Fig. 2F), reflecting the formation of Pd<sub>1</sub>Au<sub>3</sub> NSFs. This value is consistent with the original ratio of the

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