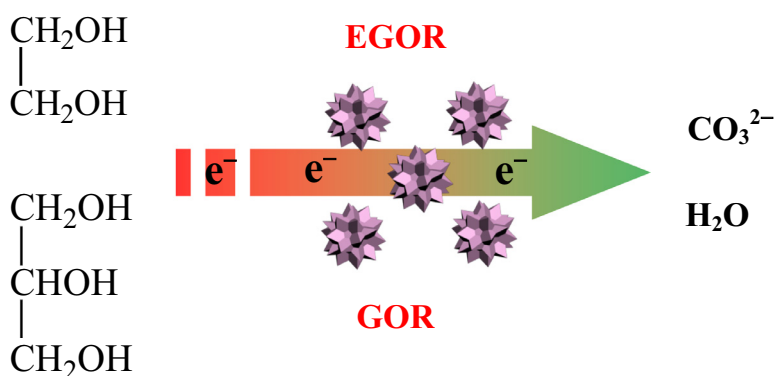


Regular Article

Facile synthesis of bimetallic gold-palladium nanocrystals as effective and durable advanced catalysts for improved electrocatalytic performances of ethylene glycol and glycerol oxidation

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GRAPHICAL ABSTRACT



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ABSTRACT

In this work, well-defined bimetallic AuPd alloyed nanocrystals (AuPd NCs) were facilely synthesized by a straightforward and controllable one-step wet-chemical strategy, using a biomolecule (*L*-hydroxyproline, *L*-Hyp) as the green stabilizer and the structure-directing agent. Their morphology, size, composition, crystal structures and growth mechanism were investigated by a series of techniques. The synthesized architectures exhibited enlarged electrochemically active surface area (ECSA), improved catalytic activity, enhanced durability and stability towards ethylene glycol oxidation reaction (EGOR) and glycerol oxidation reaction (GOR) in alkaline electrolytes in comparison with commercial Pd black catalyst.

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1. Introduction

Today, the over-usage of fossil fuels and the great energy demand induce serious environmental crisis and energy shortages

[1]. Thus, it is urgent to search environmentally-friendly and sustainable energy candidates. Direct alcohol fuel cells (DAFCs) are promising and efficient alternative energy sources owing to their high energy-conversion efficiency, low emission, easy operation, storage and transportation [2].

Among different types of alcohol fuel cells, ethylene glycol (EG) and glycerol as promising fuel substitutes have attracted

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significant interest for their high energy density, low toxicity and superior reactivity [3]. However, the poor catalytic properties of the anode catalysts for EG and glycerol oxidation heavily hinder their large-scaled commercialization when compared with those of methanol and ethanol in DAFCs [4,5]. Hence, the development of highly efficient catalyst is urgent for ethylene glycol oxidation reaction (EGOR) and glycerol oxidation reaction (GOR) [6,7].

In general, Pt catalysts have the highest efficiency and wide applications in EGOR and GOR [8,9]. However, the scarcity and high cost of Pt are seriously limited its commercial applications in practice [10]. Besides, Pt and Pt-based nanocatalysts are easily poisoned by the poisoning CO-like intermediates, which hinder their large-scaled production and commercial applications [11]. Alternatively, Pt-free catalysts especially Pd counterparts are extensively investigated, thanks to their low cost, comparable catalytic features and relatively high abundance [12]. To this end, plenty of Pd-based nanocatalysts with the highly enhanced catalytic activity and durability are prepared recently [6]. Note that alloying Pd with another metal is feasible to improve the catalytic performance and reduce the Pd loading by virtue of the rich diversity and remarkable synergistic effects of the compositions [13].

Impressively, Au exhibits particularly promising electrochemical features in both resistance to deactivation and catalytic activity in comparison with Pt- and Pd- catalysts [14,15]. Moreover, Au is miscible with Pd in the bimetallic systems, which promotes the formation of AuPd alloys [16]. In combination with the low-potential CO oxidation and superior catalytic properties in alcohol and polyol oxidation [4,16], there are many bimetallic PdAu alloyed nanocatalysts are designed and constructed lately [17]. For example, Medlin et al. developed a simple and efficient way for preparation of Au, Pd, and Au-Pd nanoparticles (NPs) for selective oxidation of EG and 1,2-propanediol [18]. In another example, Inoue's group prepared AuPd NPs-loaded carbon black catalyst with remarkably catalytic performance for glycerol oxidation [19].

It is well known that capping agents play the important roles in the synthesis of metal nanomaterials with scalable sizes and shapes [20]. *L*-Hydroxyproline (*L*-Hyp, Fig. S1, Supporting Information, SI) is produced from the hydroxylation of proline by enzyme prolyl hydroxylase [21], which contains carboxyl, hydroxyl and amine groups with strong chelating ability to the metal precursors [22]. Furthermore, the introduction of *L*-Hyp causes the hydrogen-bonding and electrostatic interactions with the precursors, which have great influence on the final morphology of nanomaterials [23]. Herein, by employing *L*-Hyp as the stabilizer and structure-directing agent, well-defined alloyed AuPd nanocrystals (AuPd NCs) were prepared by a facile one-step reduction strategy. Their catalytic characters and durable abilities were investigated by using EGOR and GOR as the two model systems.

2. Experimental

2.1. Chemicals

Chloroauric acid (HAuCl₄), palladium chloride (PdCl₂), *L*-Hyp, ascorbic acid (AA), and commercial Pd black were all purchased from Shanghai Aladdin Chemistry Co. Ltd (China). For preparation of the stock H₂PdCl₄ solution (100 mM), 1.77 g of PdCl₂ was dissolved with 0.4 mL of the concentrated HCl solution (37%), followed by diluting with water to 100 mL.

2.2. Preparation of AuPd NCs

Typically, 617 μ L of HAuCl₄ (2 mM) and 150 μ L of H₂PdCl₄ (100 mM) solutions were sequentially added to the *L*-Hyp solution

(25 mM) under stirring in a water bath at 25 °C. Then, 1.00 mL of the freshly-prepared AA (100 mM) was dropwise put into the mixture. The solution color changed from yellow green to purplish red, and eventually became purple black. After continuously reacting for 30 min, the reaction mixture remained static for two hours. Finally, the resulting product was collected by centrifugation, washed thoroughly with water and ethanol, and dried at 60 °C in a vacuum for further characterization.

For comparison, the other AuPd NPs were also prepared by adjusting the *L*-Hyp concentrations in controlled experiments, while the other experimental conditions were kept constant.

2.3. Physical characterization

The morphology of the samples was investigated by transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) measurements on a JEM-2010F transmission electron microscope operating at an accelerating voltage of 200 kV. The elemental mappings were acquired on the scanning transmission electron microscope with a high-angle annular dark-field (HAADF-STEM) detector operated at 30 kV (HITACHI S-5500). The chemical composition was examined by energy dispersive spectroscopy (EDS) with Vantage Digital Acquisition Engine (Thermo Noran, USA). The crystal structures were investigated by a Philips PW3040/60 diffractometer with Cu K α radiation ($\lambda = 0.15405$ nm). The chemical surface properties were checked by the X-ray photoelectron spectroscopy (XPS) measurements at the K-Alpha XPS spectrometer with Al K α X-ray radiation (1486.6 eV).

2.4. Construction of AuPd NCs modified electrodes

For the electrochemical experiments, AuPd NCs modified glassy carbon electrode (GCE, $\phi = 3$ mm) was firstly constructed. Typically, 3 mg of the AuPd NCs was dropped into water (3.00 mL) and ultrasonicated for 30 min to obtain a homogeneous suspension. Afterwards, 6 μ L of the suspension was dispersed onto the electrode surface and dried naturally, accompanied by coating with another layer of Nafion (4 μ L, 0.05 wt%) and dried at room temperature. Similarly, Pd black catalyst modified electrode was constructed by the similar way.

2.5. Electrochemical experiments

All of the electrochemical measurements were performed by using a CHI 660D electrochemical workstation with a standard three-electrode system at room temperature, containing a saturated calomel electrode (SCE) as the reference electrode, a platinum wire as the counter electrode, and a bare or modified GCE as the working electrode.

The cyclic voltammetry (CV) curves of the AuPd NCs catalyst were recorded in 0.5 M H₂SO₄ to estimate the electrochemically active surface area (ECSA), using commercial Pd black as the referenced catalyst. The reduction peak of the Pd oxide is employed to calculate the respective ECSA, assuming that the charges (C) are 420 μ C cm⁻¹ for the desorption of surface oxygen monolayer on the AuPd NCs catalyst. The ECSA is calculated as Q/C based on the reduction peak area of the Pd oxide, in which Q represents the quantity of electricity.

The electrocatalytic activity and stability of AuPd NCs and Pd black catalysts were investigated by CV and chronoamperometry in 0.5 M KOH containing 0.5 M EG or glycerol. The associated stability test was performed at the potential of -0.2 V accordingly.

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