



Facile synthesis of platinum–gold alloyed string-bead nanochain networks with the assistance of allantoin and their enhanced electrocatalytic performance for oxygen reduction and methanol oxidation reactions



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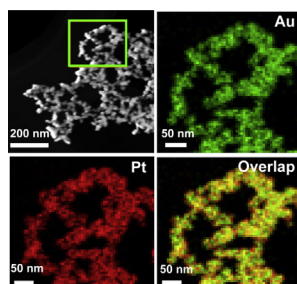
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HIGHLIGHTS

- Bimetallic Pt–Au alloyed string-bead nanochain networks are prepared by a simple one-pot wet-chemical method.
- Allantoin is used as a structure-directing agent, without using any template, surfactant or seed.
- The as-prepared Pt–Au nanocrystals display the improved catalytic activity for ORR and MOR.
- The Pt–Au nanocrystals show high resistance to poisoning CO-like intermediates.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a facile one-pot wet-chemical method is developed for preparation of bimetallic platinum–gold (Pt–Au) alloyed string-bead nanochain networks, using allantoin as a structure-directing agent, without any template, surfactant, or seed. The characterization experiments are mainly performed by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) spectroscopy. The as-prepared Pt–Au nanocrystals show enhanced electrocatalytic performance toward oxygen reduction reaction (ORR) mainly predominated by a four-electron pathway, and display improved catalytic activity and high stability for methanol oxidation reaction (MOR) over commercial Pt black and Pt–Ru black.

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1. Introduction

Noble-metal nanomaterials have attracted much interest in electrochemistry and biochemistry for their inspiring optical, electronic, plasmatic, chemical, and catalytic properties, as well as their broad applications [1,2]. Nevertheless, noble-metal catalysts

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such as Pt are usually suffer from slow kinetics in fuel cells for methanol oxidation reaction (MOR) at the anode and oxygen reduction reaction (ORR) at the cathode [3,4]. Therefore, it is still a challenge to explore novel metal catalysts in fundamental studies, with the goal of optimizing electrocatalytic performance and minimizing the usage of noble metals.

As well known, the catalytic activity and tolerance for Pt catalysts is severely poisoned by carbon monoxide (CO)-like intermediates generated in fuel cells [5], which can efficiently overcome by introducing a second metal to modify the electronic structure of Pt [1]. This strategy is the most practical approach to minimize the required quantities of Pt and enhance the electrocatalytic performance of Pt-based bimetallic catalysts [6]. Pt–Pd nanodendrites showed the enhanced catalytic activity for oxygen reduction reaction (ORR), compared with commercial Pt black [7]. Pt–Cu core–shell nanoparticles displayed enlarged electrochemical surface area and enhanced electrocatalytic properties for ORR than those of commercial Pt-black [8]. Pt–Ag bimetallic nanoislands exhibited enhanced catalytic activity and superior stability in comparison with commercial Pt black [9].

Meanwhile, the size and shape of a catalyst are closely associated with its physical and chemical properties, which are essential for potential and practical applications of a catalyst [10,11]. Therefore, a variety of strategies have been developed for synthesis of Pt-based bimetallic nanostructures with different morphologies [12], including core/shell structures [13], dendrites [14], spheres [15], cubes [16] and hollow particles [17]. Despite the above good demonstration, it is still highly desirable and technologically important for fabrication of Pt-based catalysts with novel morphology and property.

Metallic nanochains, as a highly intriguing class of advanced materials, have the advantages of stability, enlarged surface area, and enhanced electrocatalytic activity towards oxygen reduction reaction (ORR) [18]. Combining the intrinsic advantages of Pt-based catalysts, metallic nanochains have been verified the enhanced performances over monometallic solid counterparts [19–21].

In this report, a facile one-pot wet-chemical strategy was designed for synthesis of bimetallic Pt–Au alloyed string-bead nanochain networks in the presence of allantoin as a structure-directing agent. The electrocatalytic properties of the as-prepared nanocrystals were investigated, using ORR and MOR as bench model systems.

2. Experimental

2.1. Chemical materials

Hydrazine, allantoin, chlorauric acid (HAuCl_4), chloroplatinic acid (H_2PtCl_6), commercial Pt–Ru black (Pt 50%, Ru% atomic wt%) and Pt black were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. All the other chemicals were analytical grade and used without further purification. All aqueous solutions were prepared with twice-distilled water throughout the whole experiments.

2.2. Synthesis of Pt–Au string-bead nanochain networks

For typical preparation of Pt–Au string-bead nanochain networks, 15.8 mg of allantoin was put into 10 mL water and stirred in an ice-water bath to obtain a homogeneous suspension. Next, 100 μL of HAuCl_4 (0.243 mM) and 63 μL of H_2PtCl_6 (38.62 mM) were injected into the aqueous suspension under vigorous stirring, followed by the quick addition of 100 μL hydrazine (80%) under stirring. The solution color changed from faint yellow to dark, and continually reacted for 30 min. Finally, the precipitate was collected

by centrifugation, completely washed with ethanol and water to remove the adsorbed allantoin, and dried at 60 °C in a vacuum.

Control experiments were performed by varying the concentrations of allantoin, while the other conditions were remained unchanged.

2.3. Characterization

The morphology and chemical compositions of the samples were determined by JEM-2100F high-resolution transmission electron microscopy (HR-TEM) coupled with an energy-dispersive X-ray spectrometer (EDS, Oxford-1NCA) at an acceleration voltage of 200 kV. High angle annular dark-field scanning TEM (HAADF-STEM) image and elemental mapping images were examined on a scanning transmission electron microscope (STEM). The oxidation states were examined on a K-Alpha X-ray photoelectron spectroscopy (XPS, ThermoFisher, E. Grinstead, UK) with an Al $K\alpha$ X-ray radiation (1486.6 eV) for excitation. The crystal structures were characterized by powder X-ray diffraction (XRD) pattern (Rigaku Dmax-2000 diffractometer) using Cu $K\alpha$ radiation.

2.4. Electrochemical measurements

The electrochemical measurements were conducted on CHI832b electrochemical workstation (CH Instruments, Chenhua Co. Shanghai, China), using a conventional three electrode system. A platinum wire was used as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a glassy carbon electrode (GCE, 3.0 mm diameter) or a glassy carbon rotating disk electrode (Model 616, RDE, 4 mm diameter) as the working electrode.

For typical preparation of Pt–Au string-bead nanochain networks modified electrode, 2 mg of the sample was put into 2 mL water and dispersed homogeneously by ultrasonication for 30 min. Next, 6 and 15 μL of the suspension were casted onto the GCE and RDE, respectively. Subsequently, 3 and 8 μL of Nafion (0.05 wt%) were deposited onto the electrode surfaces, followed by drying in air.

Cyclic voltammetric (CV) curves were recorded at a scan rate of 50 mV s^{-1} in 0.5 M H_2SO_4 at room temperature. The measured currents were converted to a current density by normalization to the geometric surface area of the modified electrode. The electrochemically active surface area (ECSA) was calculated by measuring the areas of H-desorption between 0.05 and 0.35 V (vs. RHE) after the deduction of the double-layer region, on the basis of the following equation (1) [22,23]:

$$\text{ECSA} = \frac{Q}{m \times 210} \quad (1)$$

where m represents the loading amount of Pt in the electrode (mg); Q is the charge for H-desorption (μC); and 210 is the charge required to oxidize a monolayer of H_2 on clean Pt ($\mu\text{C cm}^{-2}$).

The electrocatalytic activity and stability of Pt–Au string-bead nanochain networks modified electrodes were investigated by cyclic voltammetry and chronoamperometry in 0.5 M KOH + 1 M methanol at a scan rate of 50 mV s^{-1} , while the ORR polarization curves were recorded on the Pt–Au string-bead nanochain networks modified RDE in O_2 -saturated 0.5 M KOH with a sweep rate of 5 mV s^{-1} at different rotation rates ranging from 100 to 2500 rpm. The Koutecky–Levich plots were analyzed at different potentials (from 0.003 to -0.603 V vs. RHE). The corresponding slopes were used to calculate the number of transferred electrons (n) according to the Koutecky–Levich equation [24]:

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