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Epitaxial growth of zigzag PtAu alloy surface on Au nano-pentagrams with enhanced Pt utilization and electrocatalytic performance toward ethanol oxidation reaction

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ABSTRACT

Improving Pt utilization is of fundamental importance for many significant processes in energy conversion, which is strongly dependent on the surface structure of used catalysts. Based on the traditional Pt-on-Au system which has been proved to be an ideal nanostructure for improving the catalytic activity and stability of Pt, and the recent follow-up studies on this system, we introduce here a new strategy for fabricating Pt surface with high-index facets over the Pt-on-Au system. To achieve this goal, we elaborately designed and fabricated a unique zigzag PtAu alloy nanosurface on Au nano-pentagrams (PtAu/Au NPs) through epitaxial growth of Pt along the high-index facets on the pre-synthesized Au nano-pentagrams. Owing to the surface electronic interaction between Au and Pt and the exposed high-index facets from the unique morphology of zigzag PtAu alloy nanosurface, the as-prepared PtAu/Au NPs exhibited excellent electrocatalytic performance toward ethanol oxidation reaction (EOR) in alkaline condition. The specific activity (8.3 mA cm^{-2}) and mass activity (4.4 A mg^{-1}) obtained from PtAu/Au NPs are about 5.2 and 5.5 times, respectively, higher than those from commercial Pt/C for EOR.

1. Introduction

Many important processes in energy conversation are strongly dependent on the catalysts to enhance the related reaction rates [1]. Pt has been widely used as catalyst for both anodic and cathodic reactions in fuel cells due to its excellent catalytic activity. However, the high price and rare reserve on earth has severely hampered the wide usage of Pt for commercial fuel cells. In order to maximize the Pt utilization, and then lower the cost of Pt-based catalysts, intensive research has been paid to enhance the catalytic activity of Pt by designing innovative surface nanostructures. Previous studies have showed that Pt-on-Au system (loading Pt nanoparticles on the surface of Au) is a type of promising nanostructure which can greatly improve the catalytic activity of Pt, especially for electrochemical reactions [2–4]. Experimental and density functional theory (DFT) studies showed that the nature of the enhancement in Pt activity comes from the electronic interaction between Au and Pt [2,5]. Namely, Au can modify the d-band center of Pt entities, as the d-band center energy determines the adsorption enthalpy of the substrate on Pt. In order to further improve the activity of Pt in the Pt-on-Au system, recently, much effort has been devoted to tuning the surface morphology of Au and developing new surfactant-free synthetic methods [6,7].

Based on the traditional Pt-on-Au system and the recently follow-up studies on this system, herein, a thin Pt layer with high-index facets is fabricated on the surface of Au nanocrystals. Owing to the plentiful steps, edges, and kinks on the high-index facets, the high-index faceted nanocrystals usually exhibit enhanced catalytic activities [8,9]. It should be noted that to retain the unstable high-index facets, organic surfactants often have to be involved in the synthesis of high-index faceted nanocrystals, which may severely

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block the active sites on the surface [10]. Meanwhile, it is hard to decrease the size of metal nanocrystals with high-index facets to below 5 nm. Actually, the inner components are not fully utilized since only the atoms on surface or sub-surface are useful for the catalysis [2,8,11]. Therefore, depositing thin layer of catalytically active Pt on other substrates is an effective strategy to reduce the loading of Pt and lower the cost of a catalyst with Pt surface.

To successfully introduce Pt surface with high-index facets in Pt-on-Au system and circumvent the large crystal size and surfactant problems, in this work, a surfactant-free method was developed to induce the epitaxial growth of Pt surface along the high-index facets on the pre-synthesized Au nano-pentagrams. What's more, we are surprised to find that the deposited Pt entities on Au surface are alloyed with Au, which may be caused by the surface segregation process, namely atomic diffusion of Au atoms and reduced Pt atoms on the surface. As a result, a unique zigzag PtAu alloy nanosurface with about 2–3 nm thickness and adequate high-index facets was elaborately fabricated on the surface of Au nano-pentagrams (PtAu/Au NPs) through a surfactant-free method. To demonstrate the effectiveness of our strategy in maximization of the Pt utilization, electrochemical ethanol oxidation reaction (EOR), which is full of great application prospect as well as huge challenges for its slow kinetics in polymer electrolyte membrane fuel cells (PEMFCs), was selected as a model catalytic reaction. The systematic electrochemical studies showed that the as-prepared unique PtAu/Au NS exhibited excellent catalytic performance toward EOR in alkaline condition with the specific activity of 8.3 mA cm^{-2} and mass activity of 4.4 A mg^{-1}, which are about 5.2 and 5.5 times higher than commercial Pt/C, respectively.

2. Experimental

2.1. Chemicals

Cloroplatinic acid (H_2PtCl_6, Beijing Chemical Works), chloroauric acid ($HAuCl_4$, Beijing Chemical Works), cupric chloride dehydrate ($CuCl_2{\cdot}2H_2O$, Beijing Chemical Works), sodium hydroxide (NaOH, Beijing Chemical Works), hexadecylamine (HDA), glucose ($C_6H_{12}O_6{\cdot}H_2O$, Beijing Chemical Works) and absolute ethanol (C_2H_5OH, Beijing Chemical Works). Commercial Pt/C (20 wt%) and perfluorosulfonic acid–PTFE copolymer (Nafion, 5% w/w solution) were purchased from Alfa Aesar. Water was obtained from a water purification system (18.25 MΩ cm). All reagents are analytical grade and used without further purification.

2.2. Synthesis of Au nano-pentagrams (Au NPs)

The Au nano-pentagrams were prepared according to the previous reports [12,13]. Typically, 45 mg HDA was completely dissolved in 4 mL H_2O with the assistance of ultrasonication. Then 0.3 mL 0.1 M $HAuCl_4$ and 0.3 mL 0.1 M $CuCl_2$ were mixed with the HDA aqueous solution in a three-necked flask. The mixed solution was then heated at 100 °C under strong stirring in an oil bath. Three minutes later, 0.3 mL 1.0 M fresh glucose aqueous solution was rapidly injected into the flask. After 30 min, the temperature was increased to 150 °C. The color of the solution changed to purple-brown in about 15 min, suggesting the formation of Au NPs. The obtained Au NPs were washed thoroughly with water and ethanol and then dispersed in ethanol for the synthesis of PtAu/Au NPs.

2.3. Synthesis of PtAu/Au nano-pentagrams (PtAu/Au NPs)

The PtAu/Au NPs were synthesized through a facile, green and surfactant-free method. Typically, 50 μL 0.1 M H_2PtCl_6 (5 μmol) was mixed with the above Au NPs in 15 mL ethanol and then refluxed at 80 °C with strong stirring for about 2 h. Afterwards, 80 μmol NaOH was added into the ethanol solution to ensure the complete deposition of Pt. The obtained PtAu/Au NPs were washed with water and ethanol, and dried at 60 °C in vacuum overnight.

2.4. Characterizations

X-ray diffraction (XRD) measurements were carried out on a Rigaku Dmax 2500 Powder Diffractometer with Cu-Kα radiation (λ = 0.15406 nm). The working voltage and current are 40 kV and 20 mA, respectively. X-ray photoelectron spectroscopy (XPS) measurements were operated on a VG Thermo ESCALAB 250 spectrometer at 120 W. The resulted spectrum was calibrated by the C1s line. Scanning electron microscopy (SEM) images were captured on a Hitachi S4800 with a working accelerating voltage of 15 kV. High-resolution transmission electron microscopy (HRTEM) was carried out on a FEI Tecnai G2 F20 TEM equipped with energy-dispersive X-ray spectroscopy (EDS) at 200 kV. The composition and contents of the as-prepared samples were examined with inductively coupled plasma-atomic emission spectrometry (ICP-AES, X Series 2, Thermo Scientific USA). All electrochemical tests were measured on a CHI 660D electrochemical workstation.

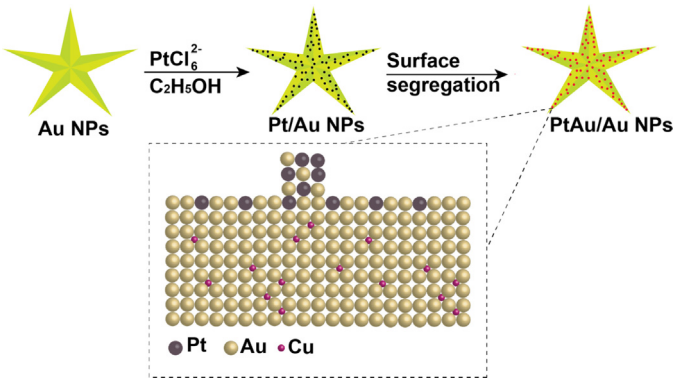
2.5. Electrochemical measurements

All electrochemical experiments were carried out at room temperature by a standard three-electrode system. Before the electrochemical tests, catalyst ink was firstly prepared by mixing the as-prepared sample with water, isopropanol and 5% Nafion solution (v:v:v = 4:1:0.05). The resulted concentration of catalyst inks was 2 mg mL^{-1} for both of the as-prepared PtAu/Au NPs and commercial Pt/C. To ensure the uniform dispersion of catalyst inks, they were treated by ultrasonication at least half an hour. Then 2.5 μL of the catalyst ink was deposited on the pre-polished glassy carbon (GC) electrode with a diameter of 3 mm, which serves as the working electrode. A saturated calomel electrode (SCE) was used as the reference electrode. Counter electrode is a platinum wire with a diameter of 0.5 mm and length of 4 cm. The EOR experiments were carried out in 1.0 M KOH solution under the protection of high-pure N_2.

3. Results and discussion

3.1. Synthesis and characterization of materials

In the present study, the PtAu/Au NPs were prepared with the pre-synthesized Au NPs as template by using H_2PtCl_6 as Pt-



Scheme 1. The hypothetical formation mechanism of PtAu/Au nano-pentagrams.