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Synthesis of highly active and dual-functional electrocatalysts for methanol oxidation and oxygen reduction reactions

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ABSTRACT

The promising Pt-based ternary catalyst is crucial for polymer electrolyte membrane fuel cells (PEMFCs) due to improving catalytic activity and durability for both methanol oxidation reaction and oxygen reduction reaction. In this work, a facile strategy is used for the synthesis ternary RuMPt (M = Fe, Co, Ni, and Cu) nanodendrities catalysts. The ternary RuMPt alloys exhibit enhanced specific and mass activity, positive half-wave potential, and long-term stability, compared with binary Pt-based alloy and the commercial Pt/C catalyst, which is attributed to the high electron density and upshifting of the d-band center for Pt atoms, and synergistic catalytic effects among Pt, M, and Ru atoms by introducing a transition metal. Impressively, the ternary RuCoPt catalyst exhibits superior mass activity (801.59 mA mg^{-1}) and positive half-wave potential (0.857 V *vs.* RHE) towards MOR and ORR, respectively. Thus, the RuMPt nanocomposite is a very promising material to be used as dual electrocatalyst in the application of PEMFCs.

1. Introduction

In the last few decades, the increasingly deteriorating environmental problems and the demands for low-cost, renewable energy have raised a great deal of interests in terms of the alternative energy conversion and storage devices as clean and sustainable energy sources [1]. Polymer electrolyte membrane fuel cells (PEMFCs), is getting more attention due to their high energy density, high theoretical efficiency, convenient operation, and friendly environmental characteristics [2–4]. Therefore, designing a suitable electrocatalyst to catalyze the methanol oxidation reaction (MOR) at the anode and the oxygen reduction reaction (ORR) at the cathode, which are the most crucial processes in PEMFCs should be a priority for achieving highly efficiency [5]. It is well known that Pt-based alloys have been considered as excellent electrocatalysts, but practical applications were limited due to their scarcity, high cost and low catalytic efficiency. Therefore, to maximize the efficiency of Pt and reduce the cost, great efforts have been made to fabricate binary Pt-based alloys by alloying of Pt with a second kind of metal to produce highly active catalysts with less Pt loading [6]. So far, PtRu have attracted great attentions owing to their high catalytic activity and stability for MOR and ORR resulting from their surface catalytic synergistic effects [7–9]. Nevertheless, optimization of their compositions, morphologies or facets still deserves to be discussed in order to further increase the catalytic performance and stability [10–13].

Nowadays, alloying with transitional metals (Fe, Ni, Cu, and Co) to form ternary alloys catalysts is an elegant and effective method. Recent studies have demonstrated that Pt-based ternary alloys exhibit excellent electrochemical activity [14]. For instance, Li et al. have successfully prepared PtNiCo ternary alloys electrocatalysts by a three-step process based on electrodeposition technique and showed an efficient ORR activity [15]. Truncated octahedral Pt-Ni-Ir ternary nanoparticles were synthesized by Wang et al. through a facile method, and the mass and specific activities of the catalyst are nearly 4.8 and 6.0 times higher than that of the commercial Pt/C catalyst [16]. Yoo et al. have accomplished morphology-controlled synthesis of ternary Pt-Pd-Cu alloy nanoparticles, particularly for efficient electrocatalytic towards ORR [17]. The catalysts mentioned above only apply to either MOR or ORR, and the synthesis methods of these ternary alloys are so cumbersome that they are not suitable for practical applications. Therefore, a simple synthesis procedure for well-controlled dual-functional Pt-based electrocatalysts with high catalytic performance remains highly challenging.

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Herein, a facile method was used to synthesize ternary RuMPt (M = Fe, Co, Ni, and Cu) nanodendrities (NDs) catalysts, which are not only suitable for MOR but also for ORR. The as-prepared ternary RuMPt NDs exhibit enhanced specific and mass activity, positive half-wave potential, and long-term stability, compared with binary Pt-based alloy and the commercial Pt/C catalyst. The high electron density and upshifting of the d-band center for Pt atoms, and enhanced synergistic catalytic effects among Pt, M, and Ru atoms, which led to weaken the binding strength between OH*/CO* intermediate species and Pt atoms, and consequently increase surface active sites and enhance the electrocatalytic activities contribute to the high electro-catalytic performance of the electrocatalysts. The present work highlights a novel strategy for enhancing the catalytic activity of trimetallic Pt-based alloys through the introduction of transition metals. We anticipate that this effective and facile preparation procedure has more general applicability to highly active and hierarchical nanocatalysts, and should lead to improvements in environmental protection and energy production.

2. Experimental section

2.1. Chemicals

Nickel (II) chloride hexahydrate ($NiCl_2 \cdot 6H_2O$), Chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), Iron chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), Copper (II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) were purchased from Sinopharm Chemical Reagent Co. Ltd. Sodium malonate dibasic monohydrate ($Na_2C_3H_2O_4 \cdot H_2O \geq 98\%$ non-aqueous titration) was received from Aldrich. Poly (vinylpyrrolidone) (PVP; Mw ~ 24,000, Sigma-Aldrich), Platinum (II) acetylacetonate ($Pt(acac)_2$ 97%), Oleylamine (OAm), 1-Octadecene (ODE > 90.0%), Ruodium Chloride Hydrate ($RuCl_3 \cdot xH_2O$), Sulfuric acid (H_2SO_4, 98%), perchloric acid ($HClO_4$, 70–72%), Methanol (CH_3OH), Nafion® perfluorinated resin solution, were purchased from Shanghai Aladdin Chemical Reagent Company (Shanghai, China).

2.2. Preparation of catalysts

2.2.1. Synthesis of Ru nanoparticles

The Ru nanoparticles precursor was prepared by a solvothermal method. 25 mg of $RuCl_3 \cdot xH_2O$, 140 mg of $Na_2C_3H_2O_4 \cdot H_2O$, and 100 mg of PVP were added into 10 mL of deionized water and stirred in a 25 mL glass vial. Then, 0.4 mL of HCHO was quickly dropped into the mixed solution and continued to add deionized water until reaching 15 mL. The above mixture was transferred into a Teflon-lined stainless steel autoclave and sealed, which was further heated to 160 °C for 8 h and then cooled to room temperature. The products were collected by centrifugation at 9000 rpm for 5 min and washed thoroughly with deionized water and ethanol several times, then re-dispersed in 10 mL of deionized water.

2.2.2. Synthesis of binary RuPt and ternary RuMPt NDs

60 mg of $Pt(acac)_2$, a certain amount of $MCl_a \cdot bH_2O$ (M = Fe, Co, Ni, and Cu), 4 mL of 1-octanol and 5 mL ODE were mixed with 10 mL of OAm in a 25 mL round-bottom, the mole ratio of Pt/M was kept at 3:1. The solution was heated to 80 °C in an oil bath with vigorous mechanical stirring. Then 600 uL of prepared Ru NPs precursor solution was rapidly injected into above solution with vigorous mechanical stirring. And the solution was transferred into a 25 mL Teflon-lined stainless steel autoclave, which was further heated to 200 °C for 8 h before it cooled to room temperature. The products were collected by centrifugation at 10,000 rpm for 5 min, washed thoroughly with deionized water and ethanol several times, and dried under a vacuum for 12 h at 60 °C. The same reaction without adding $MCl_a \cdot bH_2O$ or $RuCl_3 \cdot XH_2O$ produced binary RuPt and PtM NPs.

2.3. Characterization

Powder X-ray diffraction (XRD) measurements were carried out on a PuXi XD3 diffractometer (Cu Kα radiation, $\lambda = 0.15406$ nm). Transmission electron microscopy (TEM) characterization was performed on a JEM-2010 system and a HITACHI 800 operated at acceleration voltages of 120 kV and 200 kV, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed in a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh-vacuum (UHV) chambers. The actual Pt content in the catalyst was estimated with a VARIAN VISTA-MPX ICP-Mass spectroscope (MS, USA). A Zennium electrochemical workstation (Zahner, Germany) was used to record the electrochemical impedance spectroscopy.

2.4. Preparation of catalyst-modified GCE and RDE

Before modification, a glassy carbon electrode (GCE) (3.0 mm in diameter) or a glassy-carbon rotating disk electrode (RDE) (3.0 mm in diameter) was polished with 0.05 mm a-Al_2O_3 powder, and then ultrasonically rinsed with ethanol and ultrapure water, and dried in N_2 at room temperature. To prepare a catalyst-coated working electrode, the catalyst was dispersed in a mixture of solvents containing water, ethanol and Nafion® (5%) (v/v/v = 15/5/1), and formed a 10 mg mL^{-1} suspension. Then, 2 μL of catalyst ink was cast on a newly polished GCE/RDE and dried under ambient condition. The commercial Pt/C catalyst (20%) was used for the contrast experiment.

2.5. Electrochemical measurements

2.5.1. MOR

Voltammetric measurements were carried out with a CHI 750D electrochemical workstation. Ag/AgCl and Pt wire were used as the reference and counter electrode, respectively. The electrodes were immersed in the nitrogen-saturated 0.5 M H_2SO_4 solution (25 °C), and the potential was scanned from −0.2 to 1.0 V at a scan rate of 100 mV s^{-1}. The scan was repeated several times in order to obtain a stable cyclic voltammogram (CV). The CVs were used to estimate the electrochemically active surface area (ECSA) of the catalyst by calculating the hydrogen under potential desorption (H_{upd}) area of the catalyst. The ECSA of the catalyst was calculated by the following equation:

$$ECSA = \frac{Q}{C \times m} \tag{1}$$

where Q is the charge passed during the hydrogen adsorption/desorption from the electrode surface after the double layer correction, m represents the amount of Pt on the electrode surface (mg), and C (210 μC/cm^2) is the charge needed to oxidize a monolayer of H_2 on the Pt catalyst, respectively. CVs for MOR were conducted in 0.5 M H_2SO_4 + 1.0 M methanol from 0 to 1.0 V at a scan rate of 50 mV s^{-1}. The amperometric current density-time (i–t) curves were measured at a fixed potential for 3600 s in 0.5 M H_2SO_4 + 1.0 M CH_3OH. For each catalyst, the mass and specific activities are given as kinetic current densities (j) normalized with reference to the ESCA and loading amount of metal, respectively. All experiments were conducted at room temperature.

2.5.2. ORR

Voltammetric measurements were carried out with a CHI 760E electrochemical workstation. The glassy-carbon rotating disk electrode (RDE) (3.0 mm in diameter) was used as working electrode.