



Surface tuning of carbon supported chemically ordered nanoparticles for promoting their catalysis toward the oxygen reduction reaction



Yezheng Cai, Peng Gao, Fanghui Wang, Hong Zhu*

State Key Laboratory of Chemical Resource Engineering, Institute of Modern Catalysis, Department of Organic Chemistry, Beijing Engineering Center for Hierarchical Catalysts, School of Science, Beijing University of Chemical Technology, Beijing 100029, China

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ABSTRACT

The surface microstructure plays a key role in affecting the catalytic performances of platinum (Pt) base nanomaterials used for the oxygen reduction reaction (ORR) catalysts in fuel cell. In this work, carbon supported chemically ordered PtFe nanoparticles (PtFe/C) with small average particle size (~ 5 nm) were effectively synthesized *via* a microwave-assisted polyol reduction process and followed by heat treatment. Then, the PtFe/C catalyst was surface doped with small amounts of transition metal Au and Cr. The structural characteristics of the as-synthesized catalysts were characterized by X-ray diffraction, transmission electron microscopy, inductively coupled plasma-atomic emission spectroscopy, X-ray photoelectron spectrometer, and energy dispersive spectrometer in association with high-angle annular dark field scanning transmission electron microscopy; the electrochemical performances were tested by cyclic voltammetry and linear sweep voltammetry using a rotating disk electrode. The mass activities of the as-synthesized catalysts toward the ORR increased in the order of PtFe/C ($314 \text{ mA mg}^{-1} \text{ Pt}$) < Au-PtFe/C ($414 \text{ mA mg}^{-1} \text{ Pt}$) < Cr-PtFe/C ($487 \text{ mA mg}^{-1} \text{ Pt}$); all the as-synthesized catalysts showed higher mass activity than that ($158 \text{ mA mg}^{-1} \text{ Pt}$) of JM Pt/C catalyst. Moreover, Au-PtFe/C and Cr-PtFe/C catalysts showed higher stability than JM Pt/C catalyst. The superior catalytic performances of these doped catalysts were attributed to the chemically ordered structure and the modified surface electric properties.

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1. Introduction

Platinum (Pt) nanomaterials are commonly used as highly efficient catalysts for catalyzing the cathodic oxygen reduction reaction (ORR) of proton electrolyte membrane fuel cells [1]. However, the scarcity and the high cost of Pt resources limit the widespread use of Pt catalysts. Therefore, lots of efforts have been devoted to develop high active catalyst with low Pt-loading. Alloying Pt with 3d-transition metal M (M = Cr, Fe, Co, Ni, and Cu) has been proven to be an effective measure to reduce the amount of Pt and to simultaneously increase the catalytic activities of the Pt-based alloy catalysts [2,3]. However, the crystal structure of these catalysts is usually chemically disordered; the relative active 3d-transition metals are easily dissolved from these catalysts under the harsh environment of fuel cell, which will lead to structural damage and significantly decreased activity [4,5]. Intermetallic or chemically ordered alloy, which shows outstanding catalytic

activity and stability for the ORR, plays an increasingly important role in the fuel cell catalysts [6–9].

So far, some binary and ternary chemically ordered nanoparticles have been developed and were found to be excellently active and stable catalysts for catalyzing the ORR [9–15]. Their excellent ORR catalytic performances were commonly attributed to the uniquely electronic properties and ordered structure [11–14,16,17]. Note that the formation of chemically ordered structure generally need high temperature heat treatment. The heat treatment will lead to the particle growth or aggregation that limits the increase of catalytic activity [8,17]. In order to obtain highly active chemical ordered catalysts, some efforts focused on decreasing the particle size (< 10 nm) of these catalysts so as to increase the catalytically active sites [17–19]; the other efforts dedicated to develop multimetallic chemically ordered catalysts such as supported PtFeCo, PtFeCu, and PtFeNi intermetallic NPs [7,9,14,20]. Another feasible approach is to tune the surface electronic structure of Pt-base NPs for effectively increasing catalytic activity [20]. However, there are few reports on tuning the catalytic performance of the chemically ordered Pt-based catalysts through surface modification, which has been confirmed

* Corresponding author.

E-mail address: zhuho128@126.com (H. Zhu).

to be an effective strategy for increasing the catalytic activity [21,22]. The physical and chemical properties of Pt-base catalysts can be effectively tuned by introducing a suitable transition metal on the NP surface, which is also defined as surface doping [23–26].

Though the chemically ordered Pt base catalysts have been demonstrated both superior catalytic activity and stability toward the ORR, there are few reports on the surface doping of these catalysts for further increasing the catalytic activity. The surface microstructure of ordered catalyst is expected to be controlled by doping special element. In order to effectively increase the catalytic activity, the synthesis of ordered catalyst with small particle size is also expected. In this work, carbon supported chemically ordered PtFe NPs (PtFe/C) were firstly synthesized *via* a microwave-assisted polyol reduction process and followed by heat treatment at high temperature; ordered PtFe NPs with an average particle size of ~ 5 nm were obtained in this step. Secondly, the PtFe/C catalyst was doped by introducing gold (Au) and chromium (Cr) on the surface of PtFe NP. The microstructure characteristics and electrochemical properties of the as-synthesized catalysts were measured by X-ray diffraction, transmission electron microscopy, inductively coupled plasma-atomic emission spectroscopy, X-ray photoelectron spectroscopy, energy dispersive spectrometer in association with high-angle annular dark field scanning transmission electron microscopy, cyclic voltammetry, and linear sweep voltammetry. The results showed that surface Au and Cr doping can effectively improve the catalytic ability of ordered PtFe/C catalyst; the obtained Au-PtFe/C and Cr-PtFe/C showed higher catalytic stability for the ORR when compared to JM Pt/C catalyst. This work demonstrated a feasible strategy to synthesize surface doped ordered catalysts with high catalytic performances toward the ORR.

2. Experimental section

2.1. Chemicals and Materials

Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), chromium chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$), chloroauric acid sodium ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$), borohydride (NaBH_4), potassium hydroxide (KOH), and ethylene glycol (EG) were purchased from the Beijing Chemical Factory of China and were used as received without any purification. The purity of all used chemicals is analytical grade. 5 wt% Nafion solution was

obtained from Dupont. EC-300J carbon black was purchased from Beijing Chemical Reagent Center and functionalized by nitric acid.

2.2. Synthesis of chemically ordered PtFe/C catalyst

In order to obtain highly dispersed and small particle size NPs, carbon supported PtFe NPs were synthesized using a microwave-assisted polyol reduction process as described in our previous work [27]. In a typical synthesis of carbon supported PtFe NPs with a metal loading of 20 wt%, 40 ml of EG and 80 mg of carbon support were added into a flask and were well mixed with ultrasound for 30 min. Next, 2.06 ml of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}/\text{EG}$ (20 mg ml^{-1}) solution and 1.34 ml of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{EG}$ (24 mg ml^{-1}) solution were added into the above mixed solution by dropwise under magnetic stirring. The pH of the mixed solution system was then tuned to 9 by adding 1 M KOH/EG solution. After magnetic stirring for 30 minutes at room temperature, the system was heated to 190°C by a microwave reactor (Apex, China). The reaction was continued for 15 min and the system was then cooled down to room temperature. The obtained carbon supported PtFe NPs were centrifuged, washed, and filtered with ethanol and water. These carbon supported PtFe NPs were dried at 80°C for 10 h and reserved for later use. The obtained PtFe NPs were chemically disordered in structure.

To turn the structure of the above carbon supported PtFe NPs from chemically disordered into chemically ordered, they were annealed at 700°C for 1 h under nitrogen atmosphere; the heating rate was of 8°C per minute. The final carbon supported chemically ordered PtFe NPs was noted as PtFe/C catalyst.

2.3. Surface doping of ordered PtFe/C catalyst

The obtained chemically ordered PtFe/C catalyst was doped by Au and Cr; the Au and Cr doped PtFe/C catalysts were noted as Au-PtFe/C and Cr-PtFe/C, respectively. The Au-PtFe/C was synthesized through a spontaneous displacement reaction. First, the PtFe/C was ultrasonically dispersed in deionized water to form a uniform PtFe/C catalyst dispersion having a concentration of 1 mg ml^{-1} . Second, $25 \mu\text{l}$ of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ aqueous (20 mg ml^{-1}) solution was added to 20 ml of catalyst dispersion under stirring. After continued stirring for 3 h at room temperature, the obtained carbon sample was centrifuged, washed, filtered with ethanol and water, and dried at 80°C for 10 h. The Cr-PtFe/C was synthesized through a NaBH_4 reduction method. First, $25 \mu\text{l}$ of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous (20 mg ml^{-1}) was added to 20 ml of PtFe/C catalyst dispersion (1 mg ml^{-1}) under stirring. Second, 5 ml of NaBH_4 solution (2 M) was added to the dispersion to reduce the precursor. After continued stirring for 3 h at room temperature, the obtained carbon sample was centrifuged, washed, filtered with ethanol and water, and dried at 80°C for 10 h.

2.4. Characterizations

The crystal structures of the as-synthesized catalysts were characterized by X-ray diffraction (XRD) on a Shimadzu XD-3A diffractometer (Japan) with Cu K α radiation at $\lambda = 1.54 \text{ \AA}$ and at a rate of 4°min^{-1} . The morphologies were characterized by transmission electron microscopy (TEM) (JEOL TEM 2010 microscope). The compositions of the catalysts were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) system (Agilent Technologies, USA). The electronic characteristics of the catalysts were tested using an X-ray photoelectron spectrometer (XPS, LAB250 ESCA System, Thermo Fisher, USA) with an Al K α radiation source. The elemental distributions of the catalysts were examined using energy dispersive spectrometer (EDS) in association with high-angle annular dark field scanning

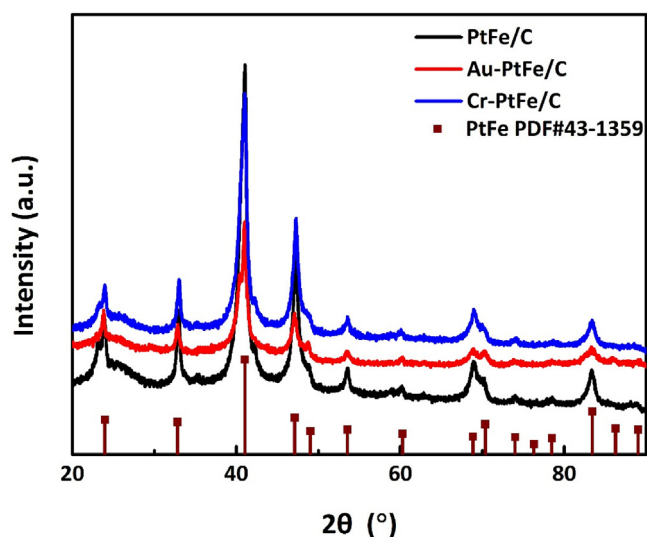


Fig. 1. XRD patterns of PtFe/C, Au-PtFe/C, and Cr-PtFe/C catalysts.

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