Journal of Catalysis 362 (2018) 85–93

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

One-step solid state synthesis of PtCo nanocubes/graphene nanocomposites as advanced oxygen reduction reaction electrocatalysts

Chunyong He [a,b,*], Shengkai Zhang [a,b], Juzhou Tao [a,b,*], Pei Kang Shen [c]

[a] Dongguan Neutron Science Center, Dongguan 523803, China
[b] Institute of High Energy Physics, Chinese Academy of Sciences (CAS), Beijing 100049, China
[c] Collaborative Innovation Center of Sustainable Energy Materials, Guangxi University, Nanning, Guangxi 530004, China

ARTICLE INFO

Article history:
Received 6 November 2017
Revised 17 March 2018
Accepted 21 March 2018

Keywords:
PtCo nanocubes
Graphene
Core–shell structure
Solid state synthesis
Oxygen reduction reaction

ABSTRACT

Here, we report the synthesis of PtCo nanocubes with core–shell structure on graphene surface by a novel solid state method. Since no organic agent and surfactant was used during the synthesis process, the PtCo nanocubes surface is definite clean. The mean grain size of PtCo nanocubes is just about 5 nm, and PtCo nanocubes possess core-shell structure with PtCo core and a thin Pt-rich shell (about 3–5 atomic layers) on the surface. Compared with commercial Pt/C catalyst, the PtCo nanocubes exhibit an 8.4 times mass activity enhancement toward oxygen reduction reaction (ORR). Besides, the PtCo nanocubes show extreme high electrochemical durability.

1. Introduction

Recent rapid advance in fuel cell vehicles calls for immediate R&D of oxygen reduction reaction (ORR) catalysts beyond the DOE 2020 target [1]. The challenge is reduce the costs and improve the performance at the same time. Even though a large number of catalysts with high performance have been produced [2–7], a catalyst meeting the performance criteria of high activity, high stability and reasonable cost, which is prerequisite for its large-scale commercialization in, is yet to be realized [8,9]. One effective program is the fabrication of Pt-based bi- and tri-metallic alloys with early-transition metals, such as Sc or Y [10,11], or later-transition metals, such as Fe [12,13], Co [12], Ni [2,14,15], Cu [16], W [17]. Dealloying of Pt-based bi- and tri-metallic alloys is another approach to achieve high activity, which is accessible through preferential chemical or electrochemical leaching of a non-noble alloy component (Cu, Ni, and so on) in acid or during electrode potential cycling [18–22]. Pt monolayer (ML) or few-layer catalysts with bi- and tri-metallic alloy cores also exhibited enhanced activity and durability compared with Pt nanoparticles [4,23]. The ORR activities of these nanostructured Pt-based catalysts were improved by inducing a slight contraction in the Pt bonds that downshifts the electronic Pt valence d-band center, which lead to the decrease of the reactivity of Pt [2,24]. Among them, Pt-Co alloys in particular have attracted considerable interests because of their relatively high ORR activity [12,24] as well as stability in acidic environments [25].

Substantial research efforts have proved that the ORR activity and stability of Pt-based catalysts depend on the chemical composition, microstructure and morphology. Therefore, it is necessary to maximize the activity of Pt-based catalysts by engineering their morphologies [5]. On that account, the controlled synthesis of noble metal nanocrystals with uniform and well-defined shape has been intensively studied with the aim of tailoring their catalytic, optical, electronic, or magnetic properties for devices, sensing, therapy and catalysis applications [26–29]. Some successful attempts have been reported so far, including FePt and CoPt alloy nanowires (NWs) [12], Pt and PtPd Nanotubes (NTs) [30], Pt–Ni octahedra [5], and Pt_3Fe nanocubes [31]. These Pt-based nanocrystals are prepared via wet-chemical method that employ special organic solvents and surfactants (capping agents) for shape control, which need to be removed since they would absorbed on the catalyst surface and impede the ORR. However, the conventional thermal treatment cannot be readily applied for that purpose as the temperature range needed is often too high to preserve the catalyst morphologies [36]. It is also difficult to remove them completely by UV-ozone [32], plasma [33], potential cycling [34], and chemical treatment [35]. Thus it remains a great

---

* Corresponding authors at: Dongguan Neutron Science Center, Dongguan 523803, China.

E-mail addresses: hechunyong@ihep.ac.cn (C. He), taoj@ihep.ac.cn (J. Tao).

https://doi.org/10.1016/j.jcat.2018.03.025

challenge to synthesize clean Pt-based bimetallic catalysts with controllable morphology without catalytic active sites being partly blocked by the residual organics.

Keeping these important issues in mind, we developed a one-step solid state synthesis method for PtCo core–shell nanocubes/-graphene nanocomposites. This method is organic solvent and surfactant free and produces clean PtCo nancubes. This solid-state method is compare favorable to the wet-chemical method. Both the ORR activity and durability are notably enhanced, making them the latest candidates for the next generation electrocatalysts in PEMFCs.

2. Experimental section

2.1. Synthesis of graphite oxide

Graphite oxide was prepared by the oxidation of natural graphite powder (325 mesh, XFNANO Material Technologic Co. Ltd., Nanjing, China) according to modified Hummers method. Typically, graphite powder (2.0 g) was added to concentrated H_2SO_4 (46 mL) under stirring in an ice bath and the mixture was stirred for 15 min. Under vigorous agitation, $KMnO_4$ (10.0 g) and $NaNO_3$ (5.0 g) was added slowly to keep the suspension temperature lower than 20 °C. Successively, the reaction system was transferred into an oil bath at 40 °C and vigorously stirred for about 35 mins. Afterwards, 50 mL deionized water was added to the mixture slowly and keep the temperature of the suspension at 95 °C. After 30 min, 200 mL deionized water and 10 mL 30% H_2O_2 were added to end the reaction, the suspension color transformed from dark brown to yellow. The mixture was filtered and washed with 1:10 HCl aqueous solution (250 mL) to remove metal ions.

2.2. Synthesis of PtCo core–shell nanocubes/graphene nanocomposites

The PtCo core–shell nanocubes/graphene nanocomposites (PtCo/G) were prepared via a one-step solid state synthesis method. 0.16 g graphite oxide was dissolved in 200 mL DI water, after 2 h of ultrasonic agitation, the suspension was transformed to graphene oxide (GO), sodium cobaltinitrite ($Na_3Co(NO_2)_6$-$\cdot 0.5H_20$, 141 mg) and chloroplatinic acid (H_2PtCl_6, 3.6 mL, 18.5 mgPt ml^{-1}) were put into the GO suspension and increased the temperature to 80 °C until the suspension ink was dried. The GO exchange and absorb $Co(NO_2)_6^{3-}$ and $PtCl_6^{2-}$ ions though the carboxyl and hydroxyl groups at ion-lever, which gives rise to high dispersion and restrains the size growth of PtCo nanocubes. Finally, the precursors were treated in the tube furnace under the CO atmosphere from 400 °C to 600 °C for 2 h.

2.3. Synthesis of conventional cubic PtCo nanocrystals on graphene

The conventional cubic PtCo nanocrystals on graphene (PtCo/G-C) nanocomposition was synthesized by wet-chemical method. Sodium cobaltinitrite ($Na_3Co(NO_2)_6\cdot 0.5H_20$, 141 mg), Platinum(II) acetylacetonate ($Pt(acac)_2$, 3.6 mL, 18.5 mgPt ml^{-1}) and 0.16 g graphite oxide were mixed together with 100 mL benzyl alcohol in a glass pressure vessel. After 2 h of ultrasonic agitation, the resulting mixture was charged with CO to 1 bar and then heated in oil bath which was preheated to 180 °C for 3 h with vigorous stirring. The resulting products were collected by centrifugation, and washed several times with ethanol.

2.4. Characterizations

The X-ray diffraction (XRD) analyses were performed on a D/Max-III (Rigaku Co., Japan) using Cu Kα radiation, operating at 30 kV and 30 mA. The 2θ angular regions between 10° and 80° were explored at a scan rate of 6° min^{-1}. The Raman spectroscopic measurements were carried out on a Raman spectrometer (Renishaw Corp., UK) using a He/Ne laser with a wave length of 514.5 nm. The high-resolution transmission electron microscope (HRTEM) and High-angle annular dark-field scanning transmission electron microscopy- energy dispersive spectroscopy HADDF-STEM-EDS elements mapping studies were performed on a Tecnai G2 F30 (FEI) operating at 300 kV. TEM samples were prepared by drop-drying the samples from their diluted aqueous suspensions onto carbon coated on Lacey support film copper grids. The Pt and Co loadings of the PtCo nanocubes catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRIS(HR)).

2.5. XAFS experiment and data analyses

X-ray absorption fine structure (XAFS) measurements at Pt–L_3 edge in transmission mode were performed at BL14W1 beamline in Shanghai Synchrotron Radiation Facility (SSRF), China. The electron beam energy was 3.5 GeV and the stored current was 240 mA (top-up). A 38-pole wiggler with the maximum magnetic field of 1.2 T inserted in the straight section of the storage ring was used. A fixed-exit double-crystal Si(1 1 1) monochromator was used. A 32-element Ge solid-state detector was used to collect the transmission signal, and the energy was calibrated by using Pt foil at the third ionization chamber. The photon flux at the sample position was 7.2×10^{11} photons per second.

2.6. Electrochemical measurements

A bipotentiostat (Pine Instrument Company, USA) with rotating ring/disk electrode (RRDE) was used to perform the electrochemical measurements in a thermostat-controlled standard three-electrode cell at room temperature with a reversible hydrogen electrode (RHE) as the reference electrode, a platinum foil ($1.0 \times 1.0\ cm^{-2}$) as the counter electrode, and a rotating ring/disk electrode with a glassy carbon disk (area: 0.2475 cm^{-2}) as working electrode. A mixed solution of 5.0 mg catalysts, 0.5 mL ethanol and 0.5 mL Nafion solution (0.05 wt%, DuPont, USA) was ultrasonicated for an hour to form a well-dispersed ink. A certain amount of the ink was transferred onto the glass carbon electrode surface. After dried under infrared lamp for 5 min, a catalyst thin film was obtained.

To calculate the electrochemical active surface area (ECSA) of the catalysts, cyclic voltammetry was conducted from +0.05 V to +1.2 V at a scan rate of 50 mV s^{-1} in 0.1 M $HClO_4$ solution. ECSA values were calculated by integrating the area under the curve for the hydrogen adsorption/desorption region for the reverse sweep in the cyclic voltammetry and using a conversion factor of 210 μC cm^2, as shown in the following equation:

$$ECSA(\mathrm{m}^2\mathrm{g}_{\mathrm{Pt}}^{-1}) = \frac{Q_{H-absorption}[\mu\mathrm{Ccm}^{-2}]}{210[\mu\mathrm{Ccm}_{\mathrm{Pt}}^{-2}] \times Pt_{loading}[\mathrm{mgcm}^{-2}]} \times 10^{-1} \qquad (1)$$

The oxygen reduction reaction (ORR) experiments were carried out in oxygen-saturated 0.1 mol L^{-1} $HClO_4$ solution at 25 °C in a thermostatic water bath. The potential range was controlled between 0.05 and 1.1 V (vs. RHE) with a scan rate of 5 mV s^{-1}, the rotating rate is 1600 rpm. The mass activities (depicted as kinetic current densities normalized to the loading Pt mass) and specific activities (depicted as kinetic current densities normalized to ECSA) of catalysts calculated from the experimental data using the well-known mass transport correction for rotating disk electrode:

$$i_k = \frac{i_d \times i}{(i_d - i)} \qquad (2)$$