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One-step synthesis of cobalt, nitrogen-codoped carbon as nonprecious bifunctional electrocatalyst for oxygen reduction and evolution reactions

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Abstract It is highly desired for the development of efficient bifunctional electrocatalyst for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in renewable energy technologies. In this work, cobalt, nitrogen-codoped carbon was prepared by a facile one-step method and demonstrated to exhibit good electrocatalytic performance for ORR and OER via a complete four-electron process. Besides, the catalyst prepared at 900 °C also displayed excellent stability for both ORR and OER. Furthermore, the origin of catalytic activity was also explored, which was attributed to the synergistic effects of metallic Co and quaternary N.

Keywords Carbon quantum dots · Bifunctional catalyst · Electrochemical performance

1 Introduction

The conversions between O_2 and H_2O are the key points in renewable energy technologies such as metal–air batteries, fuel cells, and water splitting [1–4]. Up to now, platinum (Pt)-based materials are considered as the best catalysts for oxygen reduction reaction (ORR), while ruthenium (Ru) and iridium (Ir) oxides are the best catalysts for oxygen evolution reaction (OER). However, the wide applications of these materials are hindered largely by their high cost, poor durability, and scarcity [5, 6]. Therefore, the development of highly efficient and low-cost catalyst with good stability to replace conventional precious metals is highly desirable and remains to be a great challenge.

In past decades, various transition metal materials, especially cobalt (Co)-based electrocatalysts, have been demonstrated to show excellent catalytic activity in replacing precious metals for ORR or OER. For example, Dong's group [7] synthesized cobalt and nitrogen-cofunctionalized graphene (Co/N-GN), which showed extraordinary electrocatalytic performance with high onset potential, superior methanol tolerance, and excellent stability toward ORR in alkaline solution. Recently, a hybrid catalyst of Co_3O_4 nanocrystals embedded on N-doped mesoporous graphene (Co_3O_4/N-MG) was prepared and demonstrated to exhibit prominent catalytic activity for the four-electron ORR with positive onset potential (0.93 V vs reverse hydrogen electrode (RHE)) and high current density [8]. Besides, various highly efficient OER catalysts based on Co have also been reported [9–11]. However, there are few reports on metallic Co(0) nanoparticles (Co NPs) as bifunctional catalyst reported mainly due to their easily agglomerating behavior, poor chemical and thermal stabilities [5].

In this field, carbon-based nanostructure (carbon quantum dots, graphene, and carbon nanotube) also has received numerous attracts due to their abundant photo-physical/chemical properties [12–16], as well as their catalytic applications in new energy field [17, 18]. Notably, N-doped

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carbon materials are demonstrated to be promising electrocatalysts in terms of high efficiency, long-term stability, and excellent selectivity [19, 20]. In addition, the above-mentioned Co NPs may be stabilized by carbon and/or N-doped carbon nanostructures [7]. And then, the corporation of Co NPs to N-doped carbon materials should be an ideal strategy to fabricate excellent electrocatalyst for ORR and OER.

Herein, the metallic Co, N-codoped carbon (Co/N-C) structure was obtained by a facile one-step pyrolysis method from dikaryon phthalocyanine cobalt sulfonate (PDS). Due to the synergistic effects of metallic Co and quaternary N, the Co/N-C prepared at 900 °C (Co/N-C-900) exhibited efficient catalytic activity as catalyst for both ORR and OER process in 0.1 mol/L KOH solution. Moreover, both ORR and OER processes revealed a complete four-electron path. The Co/N-C-900 was demonstrated to be a promising material as bifunctional electrocatalyst for ORR and OER processes.

2 Experimental

2.1 Materials

PDS was purchased from Shanghai Dibo Chemical Technology Co., and KOH was purchased from Sinopharm Chemical Reagent limited corporation. All chemicals were used as received without further purification.

2.2 Synthesis of Co/N-C

Typically, pristine PDS was transferred into a quartz tube furnace for pyrolysis under N_2 atmosphere. The temperature of furnace was raised from room temperature to a certain value (300, 500, 700, 900, and 1,000 °C) at a heating rate of 5 °C/min and constant pressure of 1.5 Torr (1 Torr = 133.332 Pa) for 2 h. Finally, the furnace was slowly cooled to room temperature by natural convection to obtain a serious of samples (black powder).

2.3 Characterization

Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) images were recorded on a FEI/Philips Tecnai F20 TEM. TEM samples were prepared by dropping the solution of as-synthesized samples on carbon-coated Cu grids followed by drying in air. Scanning electron microscope (SEM) images were recorded on Philips XL30. SEM samples were prepared by drying a dispersion of samples on a piece of Si wafer. Raman spectra were obtained by using an HR 800 Raman spectroscopy with a synapse CCD detector and a confocal Olympus microscope. X-ray powder diffraction (XRD) patterns were obtained on X-ray diffractometer (Empyrean, Holand Panalytical) with Cu Kα radiation ($\lambda = 0.154178$ nm). X-ray photoelectron spectroscopy (XPS) was collected on KRATOS Axis ultra-DLD XPS with a monochromatized Mg Kα X-ray ($hv = 1{,}283.3$ eV).

2.4 Electrochemical measurements

ORR and OER measurements were all taken in a standard three-electrode cell. The detailed data were recorded using a computer-controlled CHI 920C workstation (CH Instruments). For the preparation of working electrode, 8 μL aqueous sample (5 mg/mL) and 5 μL nafion solution (0.1 wt%) were deposited onto a prepolished glassy carbon electrode and then left to dry in air. Platinum wire and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. The electrolyte which was used for all the electrochemical measurements was 0.1 mol/L KOH solution.

Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) were performed to investigate the reaction mechanisms of ORR and OER, respectively. To determine the hydrogen peroxide yields during OER process, 0.65 V versus SCE was applied on the ring to oxidize the hydrogen peroxide.

3 Results and discussion

3.1 Characterizations

In this work, PDS was utilized as the only raw material and the structure of pristine PDS is shown in Fig. S1 (online). The catalyst prepared at 900 °C was denoted as Co/N-C-900 for brevity. SEM and TEM were used to characterize the structure of Co/N-C-900. Figure S2a, b (online) shows the typical SEM images of Co/N-C-900 with different magnifications, in which Co NPs are attached to the surface of bulks uniformly with size in the range of 80–100 nm. Figure 1a is the TEM image of Co/N-C-900, showing layered structure with many Co NPs embedded in carbon, which is consistent with the SEM results. In Fig. 1b (HRTEM image of Co/N-C-900), many smaller metallic Co NPs (~5 nm) are observed with lattice space of 0.20 nm, which are consistent with that of (111) plane of cubic Co [21, 22]. Besides, the lattice space of 0.33 nm (Fig. 1b) is attributed to (002) plane of carbon, indicating the formation of graphitized nanocarbon [23, 24]. It is noted that the crystalline metallic Co and tiny graphite fragments are considered to be highly conductive to