Non-noble bimetallic alloy encased in nitrogen-doped nanotubes as a highly active and durable electrocatalyst for oxygen reduction reaction

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A B S T R A C T

Exploring highly active, cost-effective and durable oxygen reduction reaction (ORR) electrocatalysts as substitutes for the rare platinum-based catalysts is of great significance in energy conversion and storage devices, such as alkaline fuel cells, metal-air batteries, etc. Herein, we fabricated a new type ORR electrocatalyst of Ni–Co nanocrystal alloy encapsulated in N-doped carbon nanotubes (NCNTs) through a facile, scalable route utilizing nickel acetate and cobalt chloride as metallic Ni and Co precursors, thiourea as a nitrogen and carbon source, respectively, under a Ni/Co atomic ratio of 3:7 at 700 °C. The obtained nanocomposite catalyst NiCo@NCNT-700 exhibited an outstanding ORR activity close to that of the state-of-the-art Pt/C catalyst and superior operational durability under alkaline conditions, which could be attributed to the co-contributions among the uniformly distributed Ni–Co alloy nanoparticles, graphitic NCNTs and the formation of Co–N species. This work provides a new insight for the rational design and development of efficient non-noble metal electrocatalysts by integrating electrochemically active units into the nanocomposite for challenging electrochemical energy-related technologies.

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1. Introduction

Oxygen reduction reaction (ORR) is an important electrochemical process for energy-related devices associated with efficient energy conversion and storage, such as fuel cells, metal-air batteries and certain electrolysers (for example, chlor-alkali ones) [1,2]. The sluggish ORR kinetics and performance deterioration at the cathode has been being one of the greatest challenges against these electrochemical energy storage and conversion systems [3]. Therefore, it is urgent to develop highly active and durable electrocatalysts to ensure the high performance during the ORR processes. The commercial Pt/C-based composites are still the commonly used ORR catalysts exhibiting relatively high activity, while its large-scale application is greatly hampered by the quick activity reduction, rarity and the consequent high cost of the noble metal [4]. Hence, searching for high-active, cost-effective and stable precious metal-free ORR electrocatalysts has attracted tremendous

attentions [5–8].

Recently, the metal-based catalysts, especially from the 3d transition metals, have been extensively demonstrated to be highly active to ORR and other catalytic reactions [8–11]. Among them, nickel and cobalt, which are abundant and environment-friendly, have been widely explored to show great potentials in the applications in energy conversion and storage devices [12,13]. Furthermore, bimetallic-based catalysts including bimetallic alloy, such as FeCo, NiCo, FeNi, are increasingly becoming promising substitutes for the electrochemical noble metal catalysts [10,14–16]. Very surprisingly, however, no reports of bimetallic alloy catalysts for ORR can be found to date. Apart from the metal-based catalysts, the N-incorporated carbon nanotubes (CNTs) have been found to facilitate the formation of defects in regularly arranged carbon atoms, leading to the enhancement of ORR activity in alkaline medium [17,18]. According to the previous report, the encapsulated metal-related particles were favorable in activating the outer graphitic layers, contributing to the enhancement of active site density toward ORR [19]. Considering the current status of ORR catalyst exploration, a nanocomposite between Ni–Co bimetallic alloy nanoparticles and N-doped carbon nanotubes was

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proposed to desirably provide more catalytically active sites to accelerate the ORR kinetics and improve the long-term operational stability.

Herein, we report the fabrication of N-doped carbon nanotube-supported Ni–Co bimetallic alloy nanoparticles via a facile pyrolysis method using metal salts (nickel acetate and cobalt chloride) as metal precursors, and thiourea as carbon and nitrogen sources. The catalyst, labelled as NiCo@NCNT-700, exhibits highly catalytic activity and excellent operational durability for ORR in basic medium. A control experiment of metal-etching was examined, which indicate that the metal-related species have played a key role in the contribution to the ORR activity. The co-contributions from the Ni–Co alloyed particles, N-doped CNTs and the formation of Co–N are proposed to account for the high ORR activity comparable to commercial Pt/C.

2. Experimental section

2.1. Preparation of NiCo@NCNT electrocatalysts

The NiCo@NCNTs samples were prepared following a reported procedure with several modifications [11]. Briefly, The nickel acetate tetrahydrate (Ni(CH$_3$COO)$_2$·4H$_2$O) and cobalt(II) chloride hexahydrate (CoCl$_2$·4H$_2$O) were dissolved in 10 ml of ethanol with varying metal molar ratios (0:10, 3:7, 5:5, 8:2, 10:0), keeping a total molar content of 1 mmol. Then, 2 g of thiourea was introduced into the solution, followed by sonication treatment for 5 min. Next, the mixture was subjected to water bath under stirring at 80 °C until the ethanol was completely evaporated. The resulting dried mixture was thoroughly ground into a homogeneous fine powder and subsequently placed at the center of corundum tube furnace. Then the temperature was ramped from 25 °C to 450 °C at a rate of 1 °C/min under Ar atmosphere and maintained at 450 °C for 2 h. After that, the samples was heated to 700 °C within 1 h and kept at 700 °C for 2 h. Finally, NiCo@NCNTs were collected after cooled to ambient temperature under Ar flow. As a control, a part of the collected NiCo@NCNT-700 was dispersed in 3 M HCl aqueous solution and stirred for 12 h at 80 °C. Then the etched sample was collected through centrifugation, rinsed with deionized water and lyophilized. Thus as-prepared Ni–Co alloyed particles encapsulated by graphitic carbon nanotubes (denoted as NiCo@NCNT-X, X refers to pyrolysis temperature) were obtained.

2.2. Materials characterizations

The powder X-ray diffraction (PXRD) was performed on a Rigaku D/Max-2550 V X-ray diffractometer with a Cu K$_\alpha$ radiation target (40 KV, 40 mA). Scanning electron microscope (SEM) imaging was carried out using a Hitachi-S4800 scanning electron microscope (10 kV). Transmission electron microscopy (TEM), energy-dispersive X-ray (EDX) mapping was conducted using a JEOL-2100F high resolution transmission electron microscope (200 kV). X-ray photoelectron spectroscopy (XPS) signals were measured on a VG Micro MK II instrument using monochromatic Mg Kα X-rays (150 W, 1253.6 eV), and the C 1s electron peak (BE = 285 eV) was used as internal reference to perform spectrum calibration. Raman spectra were recorded on a DXR Raman Microscope (Thermal Scientific, USA) with a 532 nm excitation length. The nitrogen adsorption-desorption measurements were carried out using Micromeritics Tristar 3000 at 77 K, and the specific surface area and pore size distribution were obtained by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. A CHI 760E electrochemical workstation (CH Instruments) was used to measure the electrocatalytic properties of the samples.

2.3. Electrochemical measurements

The electrochemical measurements were carried out in a standard three-electrode glass cell filled with 0.1 M KOH solution on a CH Instruments 760E electrochemical workstation. A glassy carbon electrode (GCE) coated with catalysts, a Pt foil and an Ag/AgCl electrode were employed as the working electrode, counter electrode and reference electrode, respectively. To prepare catalyst ink for ORR test, 6 mg of catalyst and 50 μL of 5% Nafion solution (DuPont) were dispersed in 950 μL of deionized water and absolute ethanol solution (v: v = 1:1). Then the mixture was sonicated for at least 30 min to form a homogeneous ink. An aliquot of 2.5 μL of the catalyst ink was pipetted onto a glassy carbon electrode, giving a catalyst loading of 0.212 mg cm^{-2}. A commercial Pt/Vulcan XC-72 sample (20 wt % Pt on Vulcan carbon black) was measured for comparison with the same loading amount as the prepared catalysts. All potentials were calibrated relative to the reversible hydrogen electrode (RHE) scale according to the Nernst equation (E$_{RHE}$ = E$_{Ag/AgCl}$ + 0.059 × pH + 0.198 V), where E$_{Ag/AgCl}$ is the external potential measured against the Ag/AgCl reference electrode. For all the measurements, high-purity N$_2$/O$_2$ gas was bubbled into the solution for 30 min before the electrochemical measurements and throughout the whole testing process. Prior to linear sweep voltammetry (LSV) measurements, the electrodes were scanned at 50 mV s^{-1} until reproducible cyclic voltammograms (CVs) were achieved. The LSV measurements were performed in an O$_2$-saturated KOH solution with a scan rate of 5 mV s^{-1} at a rotating speed of 1600 rpm. Likewise, the LSV curves were also measured in an O$_2$-saturated HClO$_4$ solution with the same rotating speed and scan rate. The electrochemical impedance spectroscopy measurements were conducted in a frequency range of 0.01 Hz−100 kHz with an amplitude of 5 mV at a fixed voltage of 0.82 V vs. RHE. The polarization plots collected at various rotating speeds were employed to analyze the kinetics for the catalysts. The kinetics parameters including electron transfer number (n) and kinetic current density (j_k) could be calculated by the Koutecky-Levich equations shown as follows [8].

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l} = \frac{1}{B\omega^{\frac{1}{2}}} + \frac{1}{j_k} \qquad (1)$$

$$B = 0.2nFC_0D_{O_2}^{2/3}\nu^{-1/6} \qquad (2)$$

$$j_k = nFkC_0 \qquad (3)$$

where j is the measured current density, j_k and j_l are the kinetic and diffusion limiting current densities, ω is the rotating rate of electrode (rpm). n is the overall number of electrons transferred in oxygen reduction, F is Faraday constant (96 485 C mol^{-1}), C$_0$ is the bulk concentration of O$_2$ (1.2 × 10^{-3} mol L^{-1}), and υ is the kinetic viscosity of electrolyte (0.01 cm^2 s^{-1}). D$_{O_2}$ is the diffusion coefficient of O$_2$ in 0.1 M KOH (1.9 × 10^{-5} cm s^{-1}), k is the electron transfer rate constant. B is determined from the slope of the Koutecky-Levich plots (j^{-1} vs $\omega^{-1/2}$). The constant 0.2 is adopted when the rotating speed is expressed in rpm.

3. Results and discussion

3.1. Characterization of the as-prepared catalysts

Among the prepared samples of various molar ratios between Ni and Co, the sample NiCo@NCNT-700 (Ni:Co = 3:7) shows a pure alloy phase (Fig. S1a), and its XRD pattern displays three distinctive peaks (44.38°, 51.68°, 76.12°) located in between those of Co (PDF-#