



The use of cheap polyaniline and melamine co-modified carbon nanotubes as active and stable catalysts for oxygen reduction reaction in alkaline medium



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ABSTRACT

In this work, an active and stable electrocatalyst for alkaline electrolyte oxygen reduction reaction was prepared by using single-wall carbon nanotubes with high specific surface area as the carbon source, and polyaniline and melamine as dual nitrogen sources via high-temperature pyrolysis process. Electrochemical experiments suggest that the metallic cobalt in the precursor can facilitate the oxygen reduction reaction to be carried out with an efficient 4-electron transfer pathway. Besides, the prepared catalyst has exhibited superior tolerance against methanol crossover effect and outstanding stability compared with commercial Pt-based catalysts in alkaline medium.

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1. Introduction

The low-temperature fuel cells (LTFCs) are focused on solving energy shortage and environmental contamination because of their excellent feature such as favorable eco-environment and high energy density [1]. Noble-metal Pt or its alloys have been widely applied at the cathode side of LTFCs, and are considered as the effective catalysts for cathodic oxygen reduction reaction (ORR) [2]. However, their large-scale commercial applications are hindered by high cost and scarcity [3,4]. As well, due to anode methanol penetration in direct methanol alkaline fuel cells (DMAFCs), oxygen reduction and methanol oxidation simultaneously occur at the surface of metal-Pt, which has led to produce a “mixed potential”, decrease the cell performance and poison the cathodic Pt catalysts [5]. Therefore, it is one of the hottest topics in fuel cell fields to explore cheap catalysts with high ORR activity, long-term stability, and methanol-tolerance performance alternatives to the Pt-based catalysts. In recent years, both non-precious metal catalysts (NPMCs) and heteroatom-doped metal-free catalysts (HDMCs) become good choices to replace commercial Pt-based catalysts.

Since Jasinski [6] found in 1964 that cobalt phthalocyanine (CoPc) has electrocatalytic activity towards the ORR in alkaline environment, many researchers have observed that the use of metal macrocyclic complexes with transition metal/nitrogen structures (TM-N_x) (TM = Co, Fe, etc., and normally $x = 2$ or 4), in particular cobalt/iron phthalocyanine and porphyrin and their derivatives, etc., can function as the cathode electrocatalysts (labeled as TM/N/C) for ORR in acidic or alkaline environments [7–11]. It has been proved that the heat-treatment at high temperatures can enhance the ORR catalytic activity and durability of TM/N/C catalysts [12,13], but the intrinsic TM-N_x macrocyclic structures have been destroyed [14]. For this reason, several reports abandon the transition metal macrocyclic complexes which are prepared complicatedly and costly, and expand the nitrogen source to synthesize the catalysts for ORR. Maruyama et al. [15] prepared the cathode catalysts with high ORR electrocatalytic activity and specific surface area (1005 m²/g) by means of hemoglobin carbonization. Liao et al. [16] synthesized a cathode catalyst by loading hemin onto the surface of carbon black, following by heat-treatment process at high temperatures. Additionally, some nitrogen-containing macromolecules [17] and small molecules [18,19] as specific nitrogen sources were also exploited to produce ORR electrocatalysts.

We have recently formed a series of active ORR catalysts with outstanding long-term stability, and excellent methanol-tolerant performance through the co-pyrolysis of blood protein from

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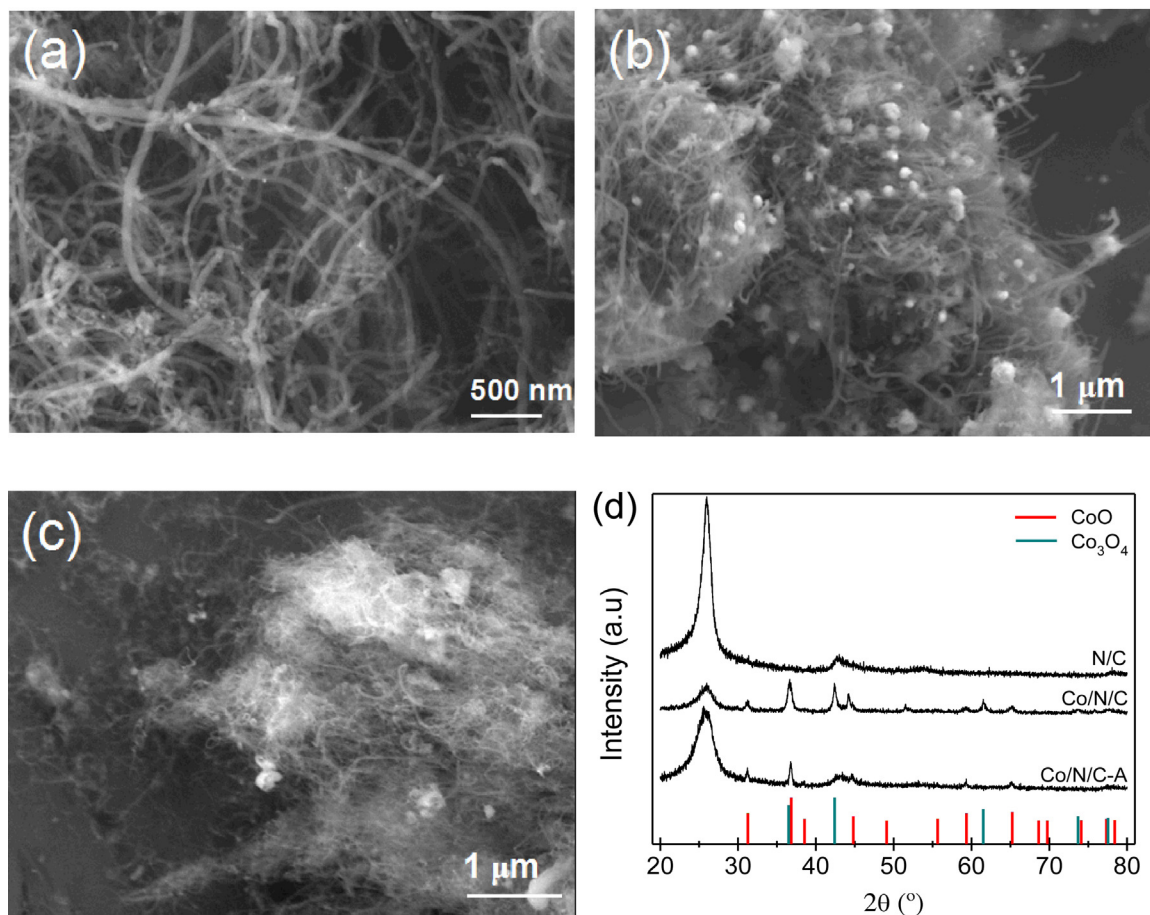


Fig. 1. The SEM images (a–c) and XRD pattern (d) of N/C, Co/N/C, and Co/N/C-A.

animals and carbon nanoparticles [20–22], and then explore their electrocatalytically active center structures by conducting rigorous design of experiments [23]. In this study, here we have chosen polyaniline (PANI) and melamine (ME) as dual nitrogen (N) sources, single-wall carbon nanotubes (CNTs) as the carbon source, and metallic cobalt as the transition-metal source to fabricate Co/N/C catalysts *via* high-temperature pyrolysis process. The ORR activity, stability and methanol-tolerant property of as-prepared catalysts have been carefully checked. Also, we have studied the influence of the metallic cobalt in the precursor on the ORR catalytic activity and ORR mechanism for the catalysts prepared in this work.

2. Experimental

2.1. Chemicals

Commercial Pt/C catalyst (40 wt.% Pt) was purchased from Johnson Matthey (UK). CNTs was supplied from Beijing DK nanotechnology Co. Ltd. Other chemicals were obtained from Chongqing Chemical Reagent Co., China.

2.2. Preparation method

The nitrogen source, including melamine and polyaniline (mass ratio of 1:1), was mixed with CNTs (mass ratio of 2:1) by ball-milling. The obtained sample was pyrolyzed in flowing N_2 at $800^\circ C$ for 2 h to form N-doped CNTs, which is hereafter called N/C. 0.1 g $CoCl_2 \cdot 6H_2O$ was mixed with 0.3 g the above mixture of dual nitrogen sources and CNTs, and then the same annealing process

was carried out at $800^\circ C$ for 2 h to get the Co/N/C sample. To remove excess metal species, Co/N/C was immersed in 5 mol l^{-1} HCl solution for 24 h at room-temperature. The sample obtained after acid-leaching is hereafter named Co/N/C-A. Other catalysts were obtained by the pyrolysis of relevant substance by using the same annealing process at high temperatures.

2.3. Characterization

The surface morphology was observed by a scanning electron microscope (JSM-7800F, Japan). X-ray diffraction (XRD) analysis was carried out by using an X-ray diffractometer by Shimadzu XRD-6000 (Japan) with Cu $K\alpha_1$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 4° min^{-1} . X-ray photoelectron spectroscopy (XPS) analysis was

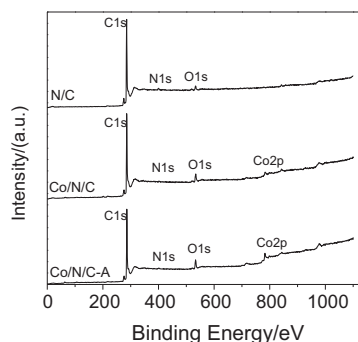


Fig. 2. The full-scanning XPS spectra of N/C, Co/N/C, and Co/N/C-A.

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