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Nitrogen-doped amorphous carbon with effective electrocatalytic activity toward oxygen reduction reaction

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ABSTRACT

Highly efficient metal-free catalysts to improve the performance of oxygen reduction reactions (ORR) have attracted significant attention. Here, nitrogen-doped amorphous carbon (NDAC) were synthesized with a one-step method that pyrolyzed dopamine in a N_2 atmosphere at 700 °C, 800 °C, and 900 °C (NDAC-700, NDAC-800, and NDAC-900, respectively). The NDAC-700 demonstrates good catalytic activity with terrific positive onset potential (0.96 V VS RHE), which is close to Pt-C (1.0 V) (20%) toward ORR. Moreover, versus commercial Pt/C (20%) catalyst, it has better long-term operational stability and tolerance to methanol for ORR in alkaline solution. This exciting result increases the possibility of large-scale application of metal-free nanomaterials in fuel cells.

1. Introduction

Fossil fuels are becoming increasingly scarce, and fuel cells are an efficient and clean power generation technology [1–4]. The oxygen reduction reaction (ORR) is very important due to its wide application in fuel cells [5–7] and other applications in biodegradable reactions [8]. In recent years, many researchers have studied the process of ORR and have put forward efficient methods to improve the performance of ORR [9–13]. The ORR occurs by four-electron transfer via two different mechanisms. First, there is a two-electron process in which oxygen becomes hydrogen peroxide before becoming water after gaining another two electrons [14–16].

Highly efficient catalysts fall into two categories—precious doped metal material and unprecious metal or metal-free material [17–23]. For instance, Zhong [11] presented a new approach to synthesize a novel hybrid composed of Pt@Au nanorods (NRs) uniformly dispersed via the pyridynecyclo addition of graphene (Pt@Au-PyNG). This material serves as a high-performance catalyst for ORR. Sanchez-Padilla [24] reported that the rapidly synthesized M@Pt (M = Pd, Fe_3O_4, or Ru) core-shell nanostructures also have a highly effective performance for ORR in acidic media. They have a better tolerance for the Pd(UT)@Pt cathode in the presence of ethanol than other core-shell materials and Pt-alone. In addition, the use of non-precious metals such as Fe or carbon- or nitrogen–doped carbon can enhance the catalytic activity in the ORR [23–25].

However, precious metals are scarce and not cost effective. Therefore, many researchers have sought unprecious metal or metal-free materials as a substitute for precious catalyst. This would improve ORR by decreasing over-potential as well as increasing current density. Deng et al. synthetized cobalt-carbon-nitrogen thin films in vacuum and found a loss of cobalt and nitrogen from the surface region inducing the activity decreasing for oxygen reduction, indicating N element doping in carbon material play a key role in superior catalyst. [17] In addition, Gong et al. produced vertically-aligned nitrogen-containing carbon nanotubes (VA-NCNTs) that act as a metal-free electrode with a much better electrocatalytic activity, long-term operational stability, and tolerance to crossover effects than platinum for oxygen reduction in alkaline fuel cells [18]. Liu synthesized nitrogen-doped graphene nanoribbon (N-GNR) nanomaterials with different nitrogen contents. These were easily prepared via high temperature pyrolysis of grapheme nanoribbon (GNR)/polyaniline (PANI) composites and had excellent catalytic activity toward ORR in an alkaline electrolyte. They had large kinetic-limiting current density and long-term stability as well as a good four-electron pathway for the formation of water [26]. Liang reported a simple method to prepare three-dimensionally ordered macroporous g-C_3N_4/C with outstanding ORR performance for fuel

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cells [27]. This novel catalyst catalyzes ORR and is comparable to commercial Pt/C in both reaction current density and onset potential. Furthermore, the macroporous g-C_3N_4/C showed much better fuel crossover resistance and long-term durability than commercial Pt/C in alkaline medium. Although many investigators have prepared different kinds of materials such as graphite, graphene hybrid or carbon nanotubes to enhance the activity toward ORR [26,28–32], people rarely notice that amorphous carbon also has large eletrocatalytic activity for ORR.

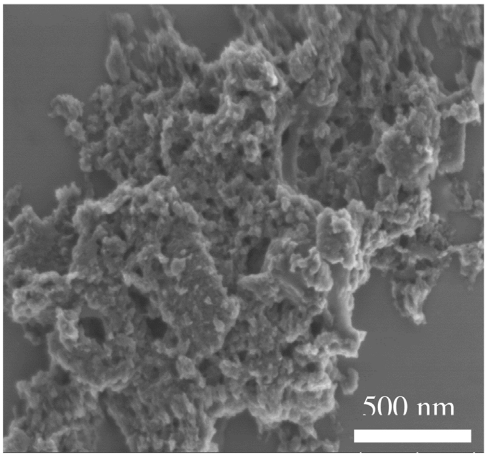
Here, we synthesized nitrogen-doped amorphous carbon (NDAC) by pyrolyzing dopamine in a N_2 atmosphere at 700 °C, 800 °C, and 900 °C. The NDAC-700 material had the best performance in ORR. Not only does it have better eletrocatalytic activity for ORR, but it also is easier to prepare. The onset potential of ORR occurred on the NDAC-700 electrode at 0.96 V. This is similar to the Pt-C catalyst. The current density of NDAC-700 is bigger than Pt-C (vs RHE) in 0.1 M KOH solution. We also investigated electron transfer with RDE, and n is 3.5, which indicates that the 4-electron ORR transfer is improved. Furthermore, the NDAC-700 material is stable and has better tolerance to methanol than commercial Pt/C (20%) catalysts in alkaline media.

2. Experimental

2.1. Apparatus and sample characterization

Electrochemical measurements were performed with a computer-controlled electrochemical analyzer (CHI600E, Chenhua, China) in a two-compartment electrochemical cell with a bare or modified GCE (3 mm in diameter) and RDE (PINE) (5 mm in diameter)working electrode, a platinum wire counter electrode, and an Ag/AgCl (KCl-saturated) reference electrode. All of the electrochemistry experiments were performed at room temperature.

SEM (Scanning Electron Microscopy) images were obtained by a Hitachi S-2600N scanning electron microscope. FT-IR (Fourier Transform Infrared Spectroscopy) spectra were measured on a Bruker Vector 22 FTIR spectrometer in the frequency range of 4000–500 cm^{-1}. XPS (X-ray Photoelectron Spectroscopy) measurements were carried out on a VG Micro-tech ESCA 2000 using a monochromic15Al X-ray source. Elemental analysis data were from Flash EA 1112.



Element	Wt%	At%
C K	93.54	94.96
N K	01.13	00.98
O K	05.33	04.06

Fig. 2. SEM images (Top) and the EDX analysis data of NDAC-700 (Bottom).

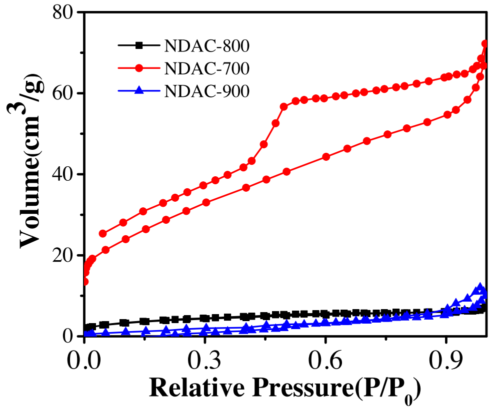


Fig. 3. Nitrogen adsorption/desorption isotherms of NDAC-700, NDAC-800 and NDAC-900, respectively.

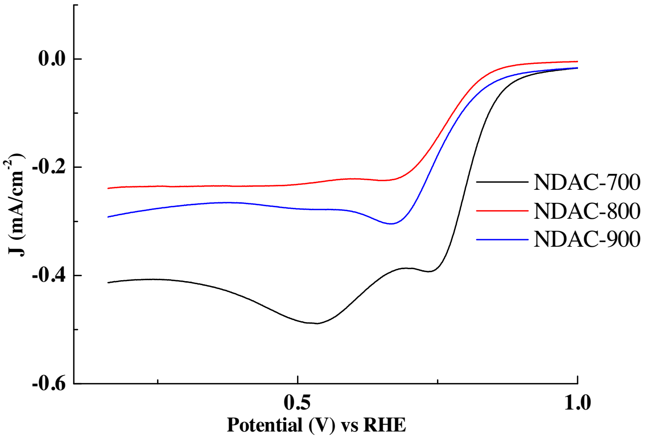


Fig. 1. LSV curve for oxygen reduction in O_2-saturated 0.1 M KOH at the NDAC-700, NDAC-800, NDAC-900 material with the scan rate 10 mv s^{-1}.

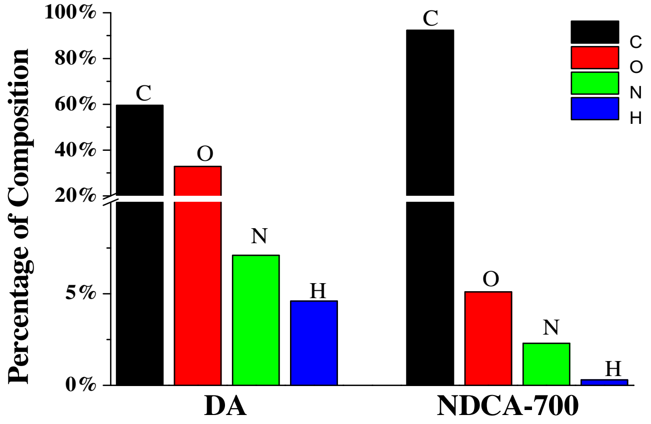


Fig. 4. Elemental analysis data of carbon, oxygen, nitrogen and hydrogen of DA and NDAC-700.