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Uniform nitrogen and sulfur co-doped carbon nanospheres as catalysts for the oxygen reduction reaction

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ABSTRACT

Uniform nitrogen and sulfur co-doped carbon nanospheres with an average diameter of approximately 200 nm were prepared using sulfur and polyacrylonitrile as precursors. The materials were characterized using scanning electron microscopy, transmission electron microscopy, elemental analysis, and X-ray photoelectron spectroscopy. The characterization results suggest the as-prepared materials had uniform, porous, nanospherical morphologies and high surface areas. For the typical sample containing 9.5% sulfur, the surface area is up to 653 $m^2 g^{-1}$. The catalysts exhibited enhanced catalytic activity, outstanding long-term stability, and excellent methanol tolerance in an alkaline medium. Significantly, the sulfur addition was found to be vital in improving materials' catalytic performance through preventing aggregation of the nanospheres, constructing porous structures, increasing the surface area, and participating in the formation of active sites.

1. Introduction

Due to their high energy efficiency and low emission, proton exchange membrane fuel cells (PEMFCs) are recognized as promising power sources for mobile and stationary applications. However, their practical application is still hindered by their high cost due to the use of platinum as the catalysts in both anodes and cathodes. Furthermore, the oxygen reduction reaction (ORR) at the cathode requires much higher Pt loading due to its sluggish kinetic process. Thus, developing non-precious catalysts to replace platinum-based catalysts in the cathode has become one of the hottest topics in fuel cell fields. During the past few years, many alternative catalysts have been proposed [1–15]. Among these catalysts, doped carbons attract significant attention due to their good catalytic performance [2,3,16,17] and low cost. Although great progresses have been made in recent years, major breakthroughs are still needed to make these carbon-based catalysts feasible in PEMFCs.

Recently, several groups reported that carbon materials' ORR performance can be significantly improved when sulfur was introduced [7–10,18–25]. Qiao et al. confirmed the synergistic effect of S and N in enhancing ORR performance by employing density functional theory (DFT) calculations [19]. Fiechter's group found that sulfur doping could induce a porous structure which would result in high surface areas and enhanced ORR performance [26]. Meanwhile, some other research groups are working on the improvement of catalysts' performance by adjusting their structures and morphologies [5,27,28]. Inspired by these efforts, we recognized that a multi-element co-doped carbon with special structures and morphologies might exhibit exceptional ORR performance.

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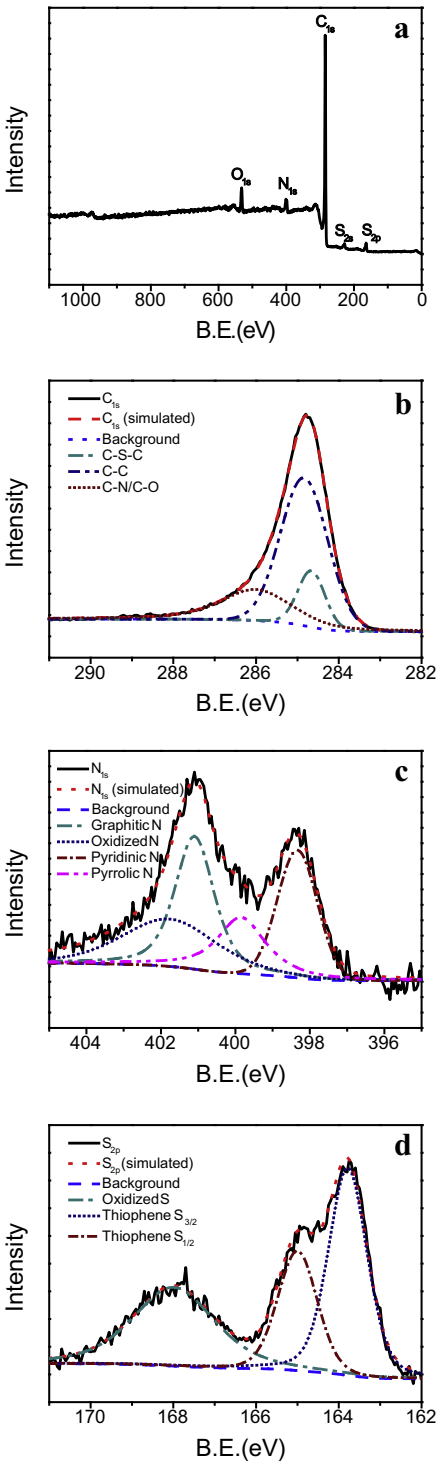

Fig. 1 – XPS spectra of PAC/5S: (a) survey spectrum; (b) high-resolution C_{1s} spectrum; (c) high-resolution N_{1s} spectrum and (d) high-resolution S_{2p} spectrum. (A color version of this figure can be viewed online.)

In this work, we developed a facile strategy to prepare S and N co-doped carbon catalysts with uniform, porous nanospherical morphologies by using element sulfur and polyacrylonitrile nanospheres as precursors. As expected, the catalysts exhibits enhanced ORR performance, outstanding long-term stability and excellent methanol tolerance in an alkaline medium. It is also discovered that sulfur played a very important role in improving the catalysts' ORR performance.

2. Experimental

2.1. Reagents

Acrylonitrile (AN, analytical grade), sublimed sulfur (analytical grade), ammonium persulfate (APS, analytical grade), and dimethylformamide (DMF, analytical grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nafion (5 wt.%) was purchased from DuPont Corp. (USA). Commercial 20 wt.% Pt/C electrocatalyst was purchased from Johnson Matthey (UK). Acrylonitrile was distilled before use. Other chemicals were used as received without any further purification.

2.2. Preparation of polyacrylonitrile nanospheres

Polyacrylonitrile nanospheres were prepared via a soapless emulsion polymerization similar to a procedure previously reported [29]. The main steps are as follows. First, 30 mL AN and 250 mL deionized (DI) water were charged into a flask and stirred intensively in an oil bath. After purging with N_2 for 30 min, the system temperature was increased to 60 °C, and then 30 mL of a solution containing 30 mg APS was injected. The polymerization was continued for 6 h in N_2 flow, followed by (i) filtrating, (ii) washing with DI water, and (iii) drying at 80 °C overnight. The as-synthesized precursor was denoted as PANS.

2.3. Preparation of the catalysts

1 g PANS and varying amounts of sulfur were thoroughly mixed and milled in a mortar with ethanol. After drying in air naturally, the mixtures were pyrolyzed at 900 °C for 1 h in a tubular furnace protected by high-purity Ar gas. Three final samples, with sulfur contents of 4.25, 6.71, and 9.52 wt.% (obtained from EA results), were obtained and denoted as PAC/S, PAC/3S, and PAC/5S, respectively. For comparison, the sample without any sulfur was also prepared through the same procedure and denoted as PAC.

2.4. Evaluation of the catalysts

Electrochemical measurements were conducted on an electrochemical workstation (Ivium, Netherlands) coupled with a rotating disk electrode (RDE) system (Pine Research

Table 1 – Doping level of N and S for PAC/5S, calculated from XPS results.

N species [at.%]				S species [at.%]	
Oxidized-N	Graphitic-N	Pyrrolic-N	Pyridinic-N	Oxidized-S	Thiophene-S
25.3	31.6	18.0	25.1	35.3	64.7