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One-step nanocasting synthesis of sulfur and nitrogen co-doped ordered mesoporous carbons as efficient electrocatalysts for oxygen reduction

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ABSTRACT

Ordered mesoporous carbon co-doped with sulfur and nitrogen (SN–OMC) is synthesized via one-step nanocasting route. Diphenylthiocarbazone is used as a single precursor for carbon, sulfur and nitrogen in the preparation of SN–OMCs. These catalysts are subjected to the physicochemical characterization and electrochemical evaluation toward the oxygen reduction reaction (ORR) in an alkaline electrolyte. SN–OMC obtained at 900 °C exhibits a high electrocatalytic activity for ORR and the impressive durability and methanol-tolerance. The synergistic effect of nitrogen and sulfur in mesoporous carbon walls may contribute to high oxygen electroreduction performance of SN–OMC.

1. Introduction

Oxygen reduction reaction (ORR) is the key reaction in fuel cells and metal–air batteries [1]. Recently, non-precious metal-based [2] and metal-free carbon materials [3] have been extensively investigated as the potential alternatives of expensive Pt/C. Non-metal heteroatom could introduce the defect sites into carbon framework. Owing to the uneven charge distribution, these sites might be used as the active sties for ORR. Heteroatom-doped carbon is also stable in long-time operation because heteroatoms often covalently bond within carbon framework. Metal-free carbon materials have been considered to be the effective candidates and reported in a large body of literature. Single-doped carbons (N, P, S, B, F, I) [4,5] and co-doped carbons (S/N, B/N, P/N) [6,7] have demonstrated high electrocatalytic activities for ORR. Carbon materials co-doped by sulfur and nitrogen were reported to be efficient catalysts for ORR. For the preparation of S, N co-doped carbon, two or three raw materials as the precursors of carbon, sulfur and nitrogen were often used in the present synthesis process [8–10]. It may bring into many difficulties in controlling he distribution of S and N species on carbon frameworks. The inexpensive diphenylthiocarbazone as the single precursor could facilitate the distribution of active species and improve the reproduction of active catalysts.

Here, we reported a facile nanocasting synthesis of nitrogen and sulfur dual-doped OMC (SN–OMC). Diphenylthiocarbazone was used as the sources of carbon, sulfur, and nitrogen. SN–OMC-900 has demonstrated the efficient ORR electrocatalytic activity in an alkaline medium, with long-term stability and an impressive methanol tolerance.

2. Experimental

SBA-15 silica was prepared using the synthesis procedures reported in literature [11]. Dried SBA-15 (1 g) and diphenylthiocarbazone (1 g) were added into carbon tetrachloride (15 mL) and stirred for 12 h at 25 °C in a fume hood. After the solvent was evaporated, the obtained residues were heated to the predetermined temperatures (800–1000 °C) for 4 h under high purity nitrogen, with a heating rate of 2 °C min^{-1}. The products were finally obtained after stirring in 80 ml 5 wt% HF solution for 12 h to remove the silica templates, which were designated as SN–OMC-n (n=800, 900 and 1000, n was the heat-treatment temperature). Diphenylthiocarbazone, used as the single precursor of carbon, sulfur and nitrogen, avoided the complicated filling process of different precursors, making the experiment easy to repeat.

Powder X-ray diffraction patterns (XRD) were recorded on a D/MAX 2550 VB/PC diffractometer with CuKα radiation. Transmission electron microscopy (TEM) images were obtained on a JEM-

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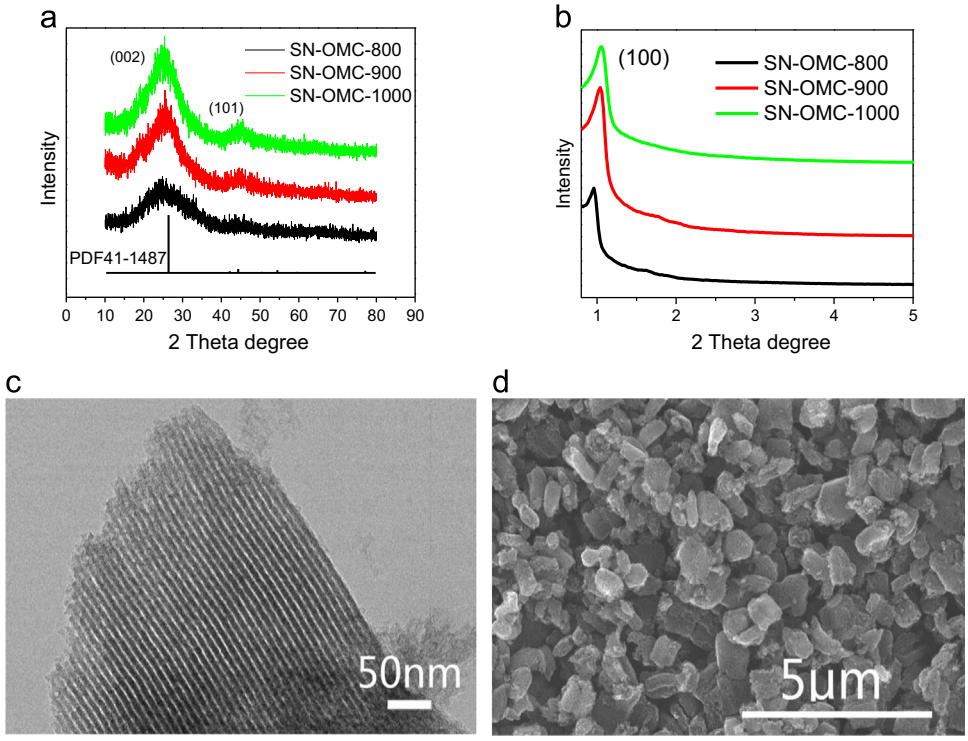

Fig. 1. (a) High-angle XRD patterns of SN–OMC-n; (b) low-angle XRD patterns of SN–OMC-n; (c) TEM image of SN–OMC-900; and (d) SEM image for the SN–OMC-900.

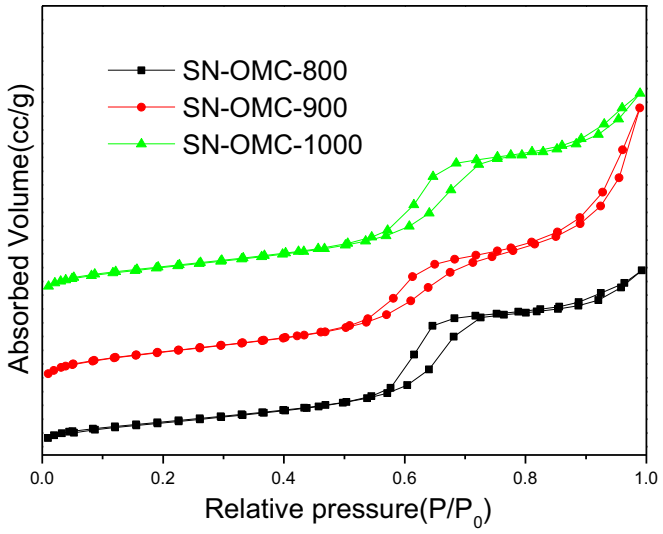

Fig. 2. The N_2 adsorption–desorption isotherms of SN–OMC-n.

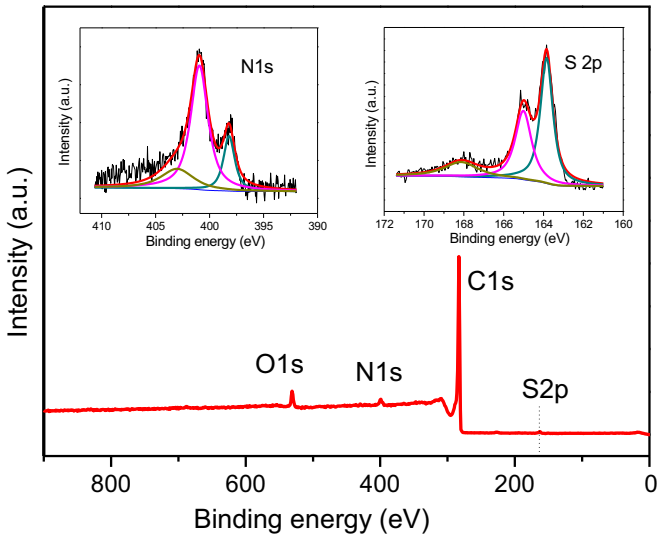

Fig. 3. Full XPS spectrum for SN–OMC-900. (Inset images: the high-resolution XPS spectrum of N 1s and S 2p).

2010 transmission electron microscope. N_2 adsorption/desorption measurements were carried out on a Micromeritics Tristar 3000 analyzer. The X-ray photoelectron spectra measurements (XPS) were performed on the instrument of Thermo ESCALAB 250 using Al Kα radiation (1486.6 eV), and C 1s (284.6 eV) was utilized as a reference to correct the binding energy. A ST-4800 (Hitachi) scanning electron microscope (SEM) was used to determine the morphology.

Electrochemical experiments were carried out on CHI 660E electrochemical workstation with a standard three-electrode cell. A Pt wire electrode and an Ag/AgCl, KCl (3 M) electrode were used as the counter electrode and reference electrode, respectively. The work electrodes were prepared as follows: a catalyst ink was prepared and coated on glassy carbon electrode, which leaded to a catalyst loading of 0.1 mg cm^{-2} for all working electrodes. For comparison, Pt/C electrode (JM, 20 wt%) with the catalyst loading of 30 μg cm^{-2} was used. All of the potentials (vs Ag/AgCl) have been converted to vs. reversible hydrogen electrode (RHE) potentials [12] (Fig. S1).

3. Results and discussion

XRD, TEM and SEM measurements were conducted to analyze the structures and morphologies of SN–OMC materials. Two broad XRD peaks (Fig. 1a) at $2\theta=26°$ and 44° in high-angle XRD profiles of three SN–OMC materials matched well with the interlayer (002) and (101) diffractions of graphitic-2H (PDF41-1487), which suggested the formation of a graphitic phase in pore walls. As the