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Article

Self-assembled three-dimensional carbon networks with accessorial Lewis base sites and variational electron characteristics as efficient oxygen reduction reaction catalysts for alkaline metal-air batteries

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ABSTRACT

Heteroatom-doped carbon has been demonstrated to be one of the most promising non-noble metal catalysts with high catalytic activity and stability through the modification of the electronic and geometric structures. In this study, we develop a novel solvent method to prepare interconnected N, S co-doped three-dimensional (3D) carbon networks with tunable nanopores derived from an associated complex based on melamine and sodium dodecylbenzene sulfonate (SDBS). After the introduction of silica templates and calcination, the catalyst exhibits 3D networks with interconnected 50-nm pores and partial graphitization. With the increase of the number of Lewis base sites caused by the N doping and change of the carbon charge and spin densities caused by the S doping, the designed N, S co-doped catalyst exhibits a similar electrochemical activity to that of the commercial 20-wt% Pt/C as an oxygen reduction reaction catalyst. In addition, in an aluminum-air battery, the proposed catalyst even outperforms the commercial 5-wt% Pt/C catalyst. Both interconnected porous structures and synergistic effects of N and S contribute to the superior catalytic performance. This study paves the way for the synthesis of various other N-doped and co-doped carbon materials as efficient catalysts in electrochemical energy applications.

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1. Introduction

With the rapid development of electric vehicles, high capacity and quick charging ability are required. Metal-air battery is one of the most promising energy storage devices for practical applications [1,2]. However, the sluggish kinetics of the oxygen reduction reaction (ORR) in the cathode impedes the process of electrochemical energy conversion, leading to a high overpotential. Studies on cathode modification mainly focused on catalysts. Although Pt-based catalysts are the most active catalysts [3], their high price and low abundance hinder practical appli-

cations. Therefore, studies on non-noble metal catalysts attract significant attention [4,5].

Carbon-based materials have been revealed as alternative ORR catalysts, which can lower production costs and increase the voltage and energy densities of the metal-air battery [6,7]. The ORR occurs in the gas-solid-liquid three-phase interface, which requires a stable skeleton and porous structure. Furthermore, nanocarbon has promising catalytic activity and stability; the catalytic properties could be further enhanced by introducing heteroatoms, including N, S, and B, through modification of the electronic and geometric structures [8–12]. Both

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theoretical calculations and experimental results revealed that the excellent catalytic activity of NC materials towards ORR originated from the substitution of C atoms with N atoms in the sp^2 lattice of the carbon matrix, which can undermine the electroneutrality of adjacent C atoms and create positively charged sites conducive to O_2 adsorption or splitting. In contrast to the N atom's action mode, which changes the C electronic structure owing to its more-positive electronegativity than that of C, S possesses a similar electronegativity to that of C ($\delta_C = 2.55$, $\delta_N = 3.04$, and $\delta_S = 2.58$), which could contribute to the increase of the electron spin and further provide active sites for the catalysis of the oxygen reduction. Synergistic effects of heteroatom co-doping contribute to enhance electrocatalytic performances. Chen et al. [13] fabricated N, S co-doped carbon spheres with thiourea as a doping source, phenolic resin as a basement, and F127 as templates, which exhibited a good catalytic activity. Zhang et al. [14] synthesized N and S co-doped graphene where the matrix material was graphene sheets and N, S sources were a precursor combined by polydopamine (PDA) film and cysteine. However, the irritant sulfurous gas (H_2S) could be easily produced in the decomposition process of short chain chalcogenides.

Melamine is one of the most common materials used to synthesize N-doped carbon owing to its abundant N content. A common approach to utilize melamine is through a polymerization reaction. Zhang et al. [15] developed porous N, P co-doped graphitic carbon by preparing melamine-phytic-acid supermolecule with melamine and phytic acid gathered in a solution of graphene oxide. Liao et al. [16] produced N-doped graphene with α -hydroxy acids as carbon source and melamine as nitrogen source. During the processes, the acids can react with melamine to form organic salts to enhance the connection between the carbon and nitrogen sources. In fact, melamine is a type of cross-linking agent, which could generate melamine cation (MA^+) in the solution, which makes it a potential ingredient for an N-based co-doped material. In a solvent environment, anionic surfactant could also ionize an anion group linking with MA^+ . Sodium dodecylbenzene sulfonate (SDBS) is widely used as an anionic surfactant; the anion group with sulphur reacting with MA^+ could realize the N, S co-doping.

In this study, we present a unique solvent approach to synthesize N, S co-doped three-dimensional (3D) carbon networks based on melamine as an efficient catalyst for ORR and aqueous metal-air battery. The designed 3D carbon networks maintain the pores of regulable silica templates as well as N, S co-doped homogeneous networks with cross-linking agents as precursors. With various superior characteristics in the composition, synergistic N and S co-doping, and 3D structures, the prepared catalysts reveal an enhanced electroactivity benchmarking with a commercial Pt/C catalyst under the same testing electrolytes. The prepared catalyst has comparable properties with those of the commercial Pt/C catalyst in terms of both electrocatalytic activities including the onset and half-wave potentials and battery performances in terms of discharge voltages and energy densities.

2. Experimental

2.1. Material synthesis

All of the reagents were of analytical purity and used without further purification. In a typical synthesis, 3 g melamine was dissolved in a hydrochloric acid solution; 1 g SDBS was dissolved in 20 mL of deionized water with an addition of 1 g nanosilica (~50 nm) after the complete dissolution of SDBS. The above two solutions were then mixed under continuous stirring for 12 h. The mixture was evaporated at 90 °C to obtain the white residue. The white products were paved in a ceramic boat and then heated to 800 °C for 2 h in a tube furnace with a heating rate of 5 °C/min under Ar atmosphere. The final product was denoted as pH-pNSC. In order to better investigate the reaction process, a contrast sample with melamine dissolved in deionized water without silica was synthesized and denoted as NSC; the remaining steps were the same. In order to better show the tunable nanopores, a contrast sample without silica was synthesized and denoted as pH-NSC; the remaining steps were the same.

2.2. Characterization of the materials

A field-emission scanning electron microscopy (FESEM, FEI Quanta-200) and a scanning transmission electron microscopy (STEM, MIRA3 TESCAN) were taken to run morphology tests. N_2 adsorption/desorption curve were taken with a Quantachrome instrument (Quabrorb SI-3MP) at -196 °C. Expressions for chemical states of the carbon, nitrogen and sulfur in the material were performed by X-ray photoelectron spectroscopy (XPS, ESCA LAB 250Xi).

2.3. Electrochemical measurements

Eight milligrams of catalysts were dispersed in a solution of 2 mL ethanol mixed with 8 μ L of a 5-wt% Nafion solution to obtain the test ink. The ORR activity was evaluated by employing an electrochemical workstation (Solartron 1470E) and rotating disk electrode (RDE) technique on a Pine modulated speed rotator (PINE AFMSRCE 3406). The measurement was performed with a three-electrode system in a 0.1 mol/L KOH aqueous solution saturated with O_2 at room temperature. The working electrode was fabricated by dropping 5 μ L catalyst ink on a freshly polished glassy carbon, while the counter and reference electrodes were platinum and Ag/AgCl electrodes, respectively. The ORR activity was detected at a scanning potential range of 0.2 to -1.0 V by linear sweep voltammetry (LSV) at a speed of 5 mV/s. The durability of pH-pNSC and 20 wt% Pt/C was tested at -0.30 V after 10,000 s in a 0.1 mol/L KOH solution (0.1 mol/L). Further investigations on an aluminum-air battery were performed by fabricating an air electrode using the prepared catalyst; details of the method are presented in Ref. [17] and Supporting Information S2.

3. Results and discussion

The synthetic route for pH-pNSC is shown in Fig. 1. Melamine generates a cation in the solution A (Reaction (1)), and

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