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Facile preparation of three-dimensional $Co_{1-x}S$/sulfur and nitrogen-codoped graphene/carbon foam for highly efficient oxygen reduction reaction

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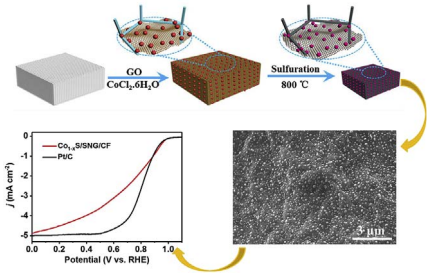
HIGHLIGHTS

- The experimental design is extremely ingenious.
- The melamine foam is used as a template and green nitrogen precursor.
- The electrocatalyst shows excellent ORR activity and stability.
- The electrocatalyst might be alternative to the Pt/C catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

Because of the urgent need for renewable resources, oxygen reduction reaction (ORR) has been widely studied. Finding efficient and low cost non-precious metal catalyst is increasingly critical. In this study, melamine foam is used as template to obtain porous sulfur and nitrogen-codoped graphene/carbon foam with uniformly distributed cobalt sulfide nanoparticles ($Co_{1-x}S$/SNG/CF) which is prepared by a simple infiltration-drying-sulfuration method. It is noteworthy that melamine foam not only works as a three-dimensional support skeleton, but also provides a nitrogen source without any environmental pollution. Such $Co_{1-x}S$/SNG/CF catalyst shows excellent oxygen reduction catalytic performance with an onset potential of only 0.99 V, which is the same as that of Pt/C catalyst (E_{onset} = 0.99 V). Furthermore, the stability and methanol tolerance of $Co_{1-x}S$/SNG/CF are more outstanding than those of Pt/C catalyst. Our work manifests a facile method to prepare S and N-codoped 3D graphene network decorated with $Co_{1-x}S$ nanoparticles, which may be utilized as potential alternative to the expensive Pt/C catalysts toward ORR.

1. Introduction

On account of the shortage of oil resource and the increasing attention on the environmental protection, exploring sustainable and environmentally friendly pollution-free energy is of critical significance [1]. The key to solve the problem of energy shortage and globalized environmental pollution is developing highly efficient fuel cells and metal-air batteries. Oxygen reduction reaction (ORR) plays an important role in determining the performance of these energy conversion devices [2–5]. At present, development of stable and efficient non-precious-metal catalysts for ORR is of crucial importance to reduce the cost and optimize the performance of fuel cells [6]. Platinum (Pt) based

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catalysts usually have ultrahigh ORR electrocatalytic performance, but their high cost, low stability, and poor tolerance to methanol seriously hinder their commercialization in fuel cells area. Hence, the development ORR catalysts with low cost, high activity, and superb stability will facilitate their commercialization [7].

Three-dimensional porous graphene materials are desired alternatives to Pt catalyst due to their outstanding physical and chemical properties, such as high specific surface area, excellent electrical conductivity, good stability and environmental friendliness [8–11]. At present, the doping effect of heteroatoms like N, S, P, B and O have been widely considered to enhance the oxygen reduction properties of the graphene-related materials [12–14]. These doping heteroatoms can alter the charge and spin density of carbon atoms and act as catalytic centers for adsorbing oxygen molecules [15–20]. On account of the conjugation between the nitrogen atom's lone-pair electrons and the carbon lattice's π system, the density of active sites on the nitrogen-doped materials will be increased. As a result, the catalytic activity for ORR will be significantly enhanced [16,21,22]. At the same time, the sulfur atom is often applied to co-dope carbon material because it can facilitate the induction of polarization of adjacent carbon and nitrogen atoms [23,24]. In the oxygen reduction reaction, non-noble metal is relatively easy to replace the platinum catalyst in alkaline solutions [25]. Recently, the carbon materials containing transition metal (Fe, Co, Ni) sulfide have shown superb ORR catalytic activity comparable with the commercial Pt/C catalyst in alkaline solutions [21,26,27]. It is worth mentioning that the higher catalytic activity and stability should result from the synergistic effect between transition metal sulfides and heteroatom-codoped carbon materials which could supply more active sites [24,28]. However, in the process of nitrogen doping (chemical vapor deposition or arc discharge), strict experimental condition, special instruments, and toxic precursors (ammonium, pyridine, pyrrole, ammonium fluoride, and so on) are usually required.

Herein, a novel and simple green synthetic route was firstly reported to synthesize three-dimensional porous nitrogen-doped graphene/carbon foams with $Co_{1-x}S$ nanoparticles ($Co_{1-x}S$/SNG/CF) using melamine foams (MF) as skeleton. In the synthesis process, the MF was used not only as a three-dimensional support for graphene networks, but also as a green nitrogen source. During the subsequent sulfuration process, the generation of $Co_{1-x}S$, reduction of graphene oxide, codoping of sulfur and nitrogen into the graphene sheets, and carbonization of MF were realized simultaneously. The high levels of graphite N and pyridine N are essential for high efficient ORR, and the presence of sulfur components further promotes the catalytic activity. In addition, $Co_{1-x}S$/SNG/CF owns the following advantages for the oxygen reduction reaction: (I) It has large specific surface area and microporous structure, which can enhance charge storage and ion transport. (II) The 3D porous structure of MF could effectively prevent graphene sheets from restacking, supplying more exposed active sites for ORR. (III) Co-existence of carbonized foam skeletons and conductive graphene results in high conductivity and rapid electron transfer. As a result, compared to commercial Pt/C catalysts, the resulting composite should have high catalytic activity, better stability, and higher resistance to methanol.

2. Experimental section

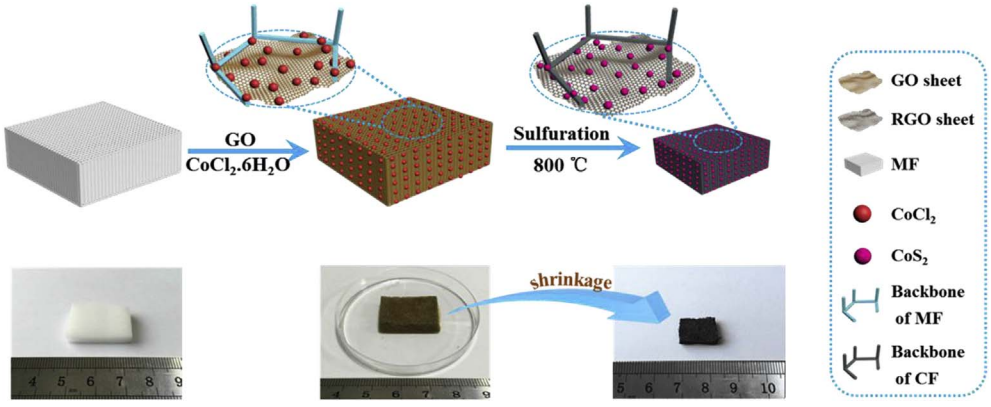
2.1. Reagents

All chemicals were used without any purification. Natural graphite powders with an average diameter of 300 mm were purchased from Qingdao Fujin Graphite Co., Ltd. Sulfuric acid (98%, AR) Potassium permanganate (AR) and hydrogen peroxide (30%, AR) were obtained from Shanghai Jinlu Chemical Co., Ltd. Ethanol (AR) was supplied by Tianjin Fuyu Fine Chemical Co., Ltd. Cobalt (II) chloride hexahydrate (AR) and sublimed sulfur (AR) were purchased from Sinopharm Chemical Reagent Co. The melamine foam was obtained from Ltd. Chuanhua Co., Ltd (Sichuan Province, China). Distilled water was made by the Flom ultrapure water system.

2.2. Synthesis of electrocatalysts

Graphene oxide (GO) was synthesized using a modified Hummers method [29]. The MF was cut into small pieces (20 × 20 × 5 mm) and then sonicated for 30 min in deionized water and absolute ethanol, respectively. For synthesis of $Co_{1-x}S$/SNG/CF, 20 mL of GO (2 mg mL^{-1}) with 73 mg cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$) was sonicated for 0.5 h to obtain a homogeneous and stable suspension. A piece of MF was completely immersed in the mixed suspension and the MF was repeatedly squeezed and then immersed in the mixed suspension to fully absorb the solution for 5 times. After that, the composite was completely dried in an oven at 60 °C for 6 h. The dried sample and 2.5 g of sublimed sulfur were placed respectively in two porcelain boats, the porcelain boat containing sublimed sulfur was in the upstream of the tube furnace. Whereafter, the sample was heat treated at 800 °C for 1 h at a heating rate of 5 °C min^{-1} in an argon atmosphere and then naturally cooled to room temperature. After the heat treatment, the sample has significant color changes from brown to black and shrinkage. For comparison, the pure $Co_{1-x}S$ nanoparticles were synthesized using the same method in the absence of GO and MF. The pure nitrogen-doped graphene/carbon foam (SNG/CF) was also synthesized under the same condition in the absence of $CoCl_2{\cdot}6H_2O$ and sublimed sulfur.

The schematic illustration for the preparation of $Co_{1-x}S$/SNG/CF by a simple immersion/squeeze process followed by the sulfuration in the presence of sublimed sulfur is shown in Scheme 1. Firstly, the commercially purchased MF was immersed in the mixture of cobalt (II) chloride hexahydrate and GO to allow the mixture to be fully adsorbed into the MF. The MF was then squeezed, re-immersed in the mixture of cobalt (II) chloride hexahydrate. This process was repeated for 5 times



Scheme 1. Schematic diagram showing the stepwise preparation of $Co_{1-x}S$/SNG/CF.