



Effective sulfur-doping in carbon by high-temperature molten salt bath and its electrocatalysis for oxygen reduction reaction

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ABSTRACT

A facile high-temperature molten salt bath method was developed to effectively dope sulfur into carbon. Molten potassium sulfide acts as a high-concentration sulfur source and provides an immersion bath, thus favoring sulfur doping. Resultant sulfur-doped carbon shows an exceptionally high sulfur content of 1.50 at.%, manifesting its favorable effect on catalysing the oxygen reduction reaction.

1. Introduction

Heteroatom-doped carbon has attracted intensive attention for a variety of applications in very recent years [1–7]. As a promising metal-free electrocatalyst, nitrogen-doped carbon has been well developed, which shows decent activity to the oxygen reduction reaction (ORR) [8], oxygen evolution reaction (OER) [9], and hydrogen evolution reaction (HER) [10]. A huge body of papers have been published on nanostructured doped carbon; however, no substantial advance has been achieved in the intrinsic activity. Particularly, nitrogen-doped carbon shows an inferior activity to the ORR in acid media [11]. Such a bottleneck is proposed to originate from the inherent protonation of the nitrogen dopant in strong acid, which hinders the electron transfer to oxygen molecules [11].

Sulfur has a much lower basicity than nitrogen and, therefore, its protonation is not that serious when doped in carbon. More importantly, sulfur has two electron pairs and is supposed to be highly effective in tuning the electronic structure [1,12–15]. In the literature, sulfur-doping is achieved by either pyrolysis of a sulfur-containing precursor or post-treatment in a sulfur-containing gas. For example, Pumera et al. [16] synthesized sulfur-doped graphene by a thermal exfoliation of graphite oxide (GO) in the presence of H₂S, SO₂, or CS₂ gas. Chen et al. [17] synthesized S-doped graphene/carbon nanotube composites by using phenyl disulfide as a sulfur source at 900 °C.

Very recently, sulfur-containing salt was used as a sulfur source to synthesize the sulfur-doped carbon in a solid–liquid phase [12,18,19]. Wang et al. [12] used Li₂SO₄ as a sulfur source to synthesize S-doped reduced GO in a molten salt, in which the S content is 0.37 at.%. Sulfur

in an oxidized form is widely used as it is chemically active to etch carbon and thus doped into the sp² framework. However, it is noted that sulfate is a very strong oxidant at high temperatures, which is highly reactive and even explosive in contact with carbon. That is the reason that in the above work an inert salt bath is essential to dilute the reactants and lower the risk of explosion. A reductant sulfur source (like Na₂S, FeS) can avoid the above issue, which has been rarely investigated in open report. Besides its safety nature in chemistry, other advantages include: i) the salt acts as both a sulfur source and reductant salt bath, avoiding the usage of redundant ‘inert’ salts and thus increasing the ‘sulfur’ concentration; ii) carbon source is flexible as no rigorous oxidant is involved; iii) the content of S can be well controlled, which relies on the oxygen-groups of carbon and temperature. In this work, we synthesized sulfur-doped carbon in a molten K₂S salt bath, and confirmed the positive effect of sulfur-doping in enhancing the electrocatalytic activity of the ORR.

2. Material and methods

2.1. Material preparation

2.1.1. Pre-oxidation of Vulcan XC72

The semi-graphitic carbon black Vulcan XC72 was pretreated as follows. Carbon powders were heated in HCl aqueous solution ($V_{\text{HCl}}/V_{\text{H}_2\text{O}} = 1:5$) at 120 °C for 10 h, boiled in 5.0 M HNO₃ solution at 120 °C for 10 h, and finally dried under vacuum at 150 °C for 8 h. The obtained powders are denoted as XC72.

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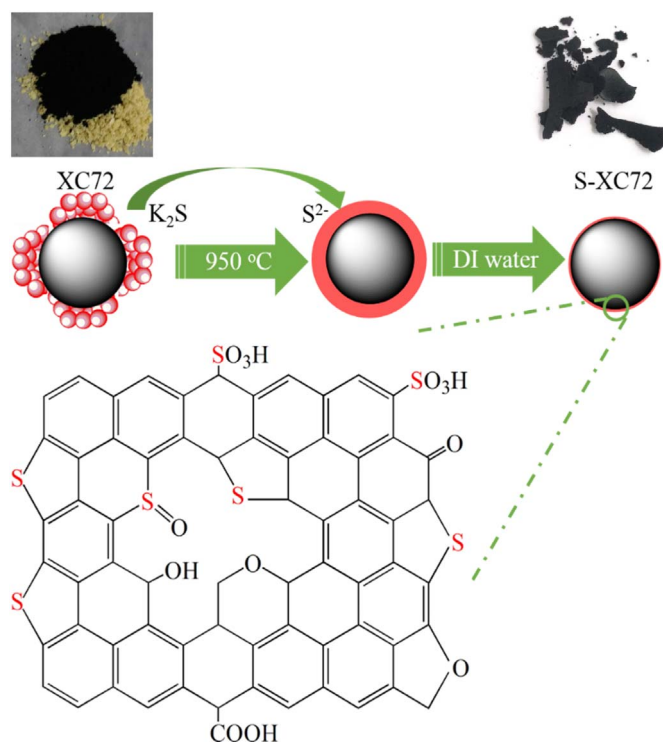


Fig. 1. Schematic illustration of the preparation of sulfur-doped Vulcan XC72.

2.1.2. Synthesis of sulfur-doped Vulcan XC72

A simple and efficient method was developed to synthesize sulfur-doped Vulcan XC72, denoted as S-XC72. First, 300 mg XC72 and 1375 mg potassium sulfide (K_2S) were ground uniformly. Second, the mixtures were annealed at three high temperatures (viz. 950 °C, 1100 °C, and 1200 °C) in Ar (99.999%) for 60 min. Finally, the obtained powders were washed to neutral pH and then dried under vacuum, which are denoted as S-XC72-950, S-XC72-1100, and S-XC72-1200, respectively.

For comparison, XC72 was treated at 950 °C without adding K_2S by the same procedure as a reference sample, which is denoted as XC72-950.

2.2. Physical characterization

Field-emission scanning electron microscopy (FE-SEM) images and energy dispersive spectroscopy (EDS) were performed on a Nova Nano SEM 200 scanning electron microscope (FEI, Inc.). Raman spectra were collected on a Labram-010 microscopic confocal Raman spectrometer with a 633 nm laser excitation. X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5600, US) measurement was carried out with a multi-technique system using an Al monochromatic X-ray at a power of 350 W. The pore structure of samples was probed by nitrogen adsorption/desorption isotherms at 77 K (Micromeritics ASAP 2020, US). Before measurement, the samples were out-gassed at 200 °C for 12 h.

2.3. Electrochemical characterization

The working electrode was prepared in a typical way [20,21]. 10.0 mg sample was dispersed in 1.0 mL Nafion/ethanol (0.84 wt%

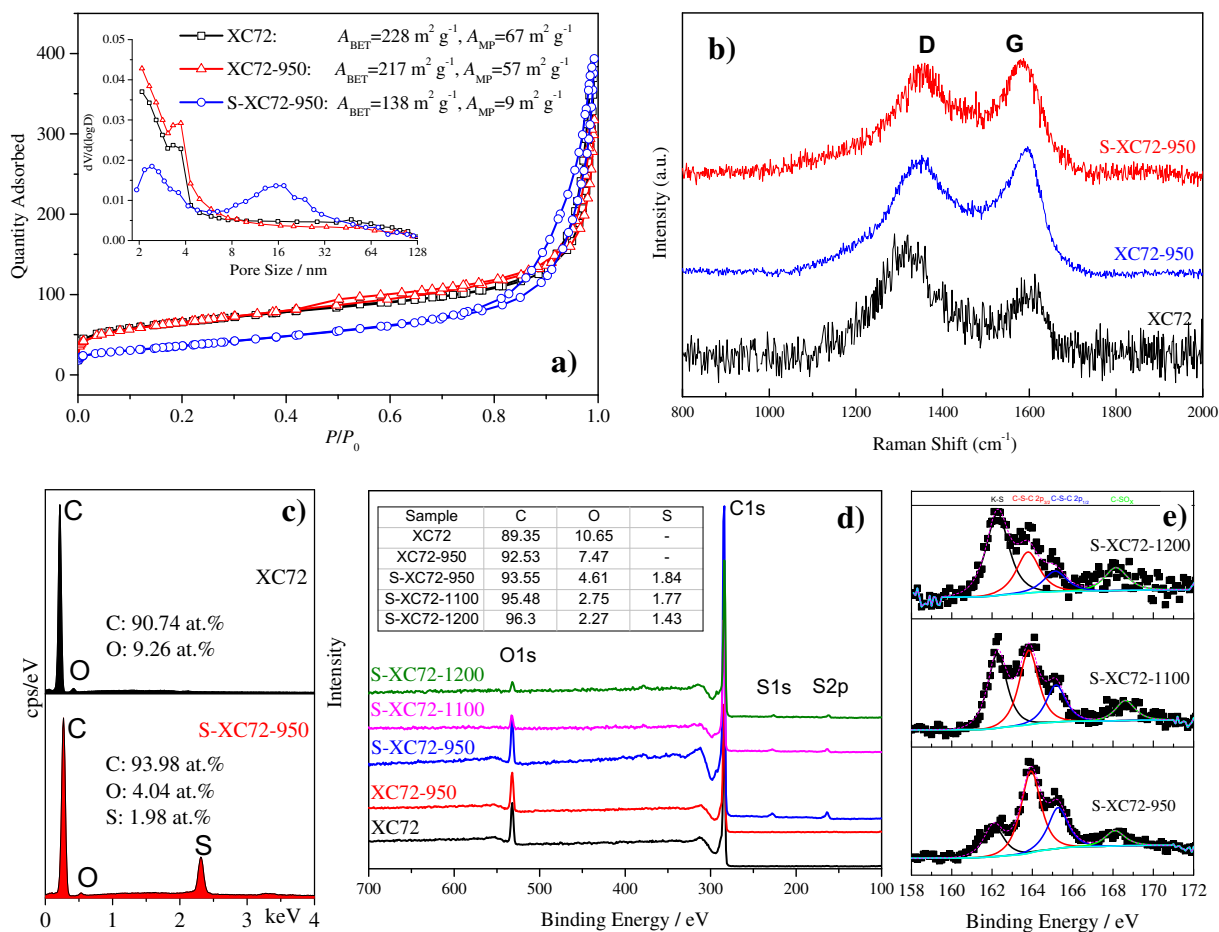


Fig. 2. a) Nitrogen adsorption-desorption isotherms; b) Raman spectra; c) EDS results; d) XPS survey spectra; e) high-resolution S2p peak and the peak fitting results.

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