



One-pot synthesis of nitrogen and sulfur co-doped onion-like mesoporous carbon vesicle as an efficient metal-free catalyst for oxygen reduction reaction in alkaline solution



Ce Han, Xiangjie Bo^{*}, Yufan Zhang, Mian Li, Liping Guo^{*}

Faculty of Chemistry, Northeast Normal University, Changchun 130024, PR China

HIGHLIGHTS

- High ORR catalytic activity at N and S co-doped mesoporous carbon vesicle.
- N and S co-doping and surface area are key factors in ORR activity.
- Good durability and methanol tolerance of N and S co-doped mesoporous carbon vesicle.

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ABSTRACT

Nitrogen and sulfur co-doped onion-like mesoporous carbon vesicle (NS-MCV) with multilayer lamellar structure is synthesized as a metal-free catalyst through a convenient and economical procedure. The synthesized materials are systematically characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectra, nitrogen adsorption–desorption, and X-ray photoelectron spectroscopy (XPS). The characterization results demonstrate that N and S atoms can be successfully doped into the framework of MCV with little impact on the morphology and structure. The NS-MCV manifests a remarkably high electrocatalytic activity as a metal-free electrocatalyst for the oxygen reduction reaction (ORR) with mainly a four-electron transfer pathway. Moreover, in contrast to the commercially available Pt/C catalyst, the NS-MCV shows much better long-term stability and tolerance toward methanol crossover in an alkaline medium. Such excellent performances can be mainly attributed to the synergistic effect arising from the addition of N and S heteroatom, optimized S content and high surface area. The NS-MCV with a simple synthesis method may further exploited as potentially efficient and inexpensive metal-free ORR catalyst materials.

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1. Introduction

Fuel cells have attracted broad attention due to their low operation temperature, environmentally-friendly nature, high energy density, high energy efficiency and long life. The sluggish kinetics of the cathodic oxygen reduction reaction (ORR) is one of the most crucial factors in limiting the performance of fuel cells [1]. Among the developing catalyst materials, platinum (Pt)-based catalysts are widely used as electrocatalysts for ORR owing to their relatively low over-potential and high current density [2]. Nevertheless, Pt and Pt-

based materials still suffer from several severe problems, including anode crossover, poor stability in the electrochemical environments and their limited natural reserves [3,4]. To overcome these barriers and alleviate the cost of Pt catalysts, some innovative alternative materials have been obtained to increase the activity and decrease the cost, such as non-precious metal, their alloys or oxides [5–10]. In addition, replacement of Pt with heteroatom-doped nanostructured carbon materials is a desirable way to alleviate the high cost of Pt-based catalysts and facilitate the commercialization of fuel cells. Enormous efforts have been devoted to the doping of heteroatoms into carbon materials to modify the chemical and physical properties of catalysts. The recently progress of heteroatoms-doped carbon-based catalysts for ORR has been well summarized in reviews [11,12]. Furthermore, both experimental researches and quantum calculations have

^{*} Corresponding authors. Tel./fax: +86 0431 85099762.

E-mail addresses: baoxj133@nenu.edu.cn (X. Bo), guolp078@nenu.edu.cn (L. Guo).

confirmed that the doping of heteroatoms into the carbon framework makes a great contribution to the enhancement of activity in ORR. The widely used heteroatoms are nitrogen, which has the strong electronic affinity and substantially high positive charge density on the adjacent C atoms resulting in very favorable adsorption of oxygen molecule [13]. Beside the nitrogen, other elements, such as S, P, B, Cl, I, Se, have been doped into carbon materials as a metal-free electrocatalyst for ORR with improved performance compared to undoped carbon [14–19]. Due to a synergistic effect arising from nitrogen and non-nitrogen element co-doping, the co-doped carbon materials showed a superb ORR performance than the carbon materials doped solely with one kind of heteroatoms. The different heteroatoms doped in the carbon framework make the catalysts non-electron-neutral and consequently favors the molecular adsorption of oxygen and its reduction [20–22]. The result of density functional theory (DFT) calculations indicates synergistic reaction of N and non-nitrogen element plays a key role in the improvement of ORR performance [23]. Among these co-doped carbon materials, N and S co-doped carbons showed excellent catalytic behavior as metal-free electrocatalysts for ORR, even comparable to the commercial Pt–C catalyst [23–26]. The common-used nanostructured carbon materials are graphene and carbon nanotubes. However, graphene sheets tend to form irreversible agglomerates or even restack to form graphite through π – π stacking. The irreversible agglomeration leads to the partial overlapping of the graphene sheets and lowers the surface area of GR. Many active sites are secluded in the stacking graphene sheets, which is not favorable for ORR. The carbon nanotubes easily packed in the bundle, which blocks the diffusion path of carbon nanotubes and sets a high resistance for the diffusion of reactant molecules. From the viewpoint of the published literature [26–28], the large surface area of porous carbon materials becomes another factor that affect the density of the catalytically active sites, which is closely related to the catalytic activity. The porous structure provides a favorable path for mass transport, while the high surface area and a large number of pores facilitates the exposure of active sites for catalysis. The novel work reported by Qiao indicates that porous N and S co-doped graphene exhibited high activity for ORR [23]. So, it is anticipated that co-doped carbon materials with high surface area and porous structure can show a high activity for ORR.

Since its discovery, ordered mesoporous carbon (OMC) becomes a very popular candidate as catalyst support and sensor [29,30]. The OMC exhibits many desirable characteristics, including ordered porous structure, high surface area, and narrow pore size distribution, which are greatly favorable for catalysis. N-doped OMC has been used as metal-free catalysts for ORR with good stability and selectivity [31–33]. As a new mesoporous carbon material, onion-like mesoporous carbon vesicle (MCV) with multi-layer lamellar structure was synthesized by a simple aqueous emulsion co-assembly approach under a hydrothermal treatment, which have uniform distribution of pore size, large pore volume and big specific surface-area [34]. However, to our knowledge, the application of MCV for ORR has been hardly reported. Considering the structural features of MCV and the advantages of dual heteroatom doping above mentioned, it is believed that the novel heteroatom co-doped MCV with multilayer lamellar structure may be a high-performance metal-free ORR electrocatalyst to replace Pt/C. Although N and S co-doped mesoporous carbon template from ordered mesoporous silica (SBA-15) has been reported as metal-free ORR catalysts [28,35], the difference of our methodology is synthesis of onion-like MCV using a one-step synthesis without the use of hard template. Compared with the hard-template route, our synthesis method avoids the preparation of mesoporous silica.

Herein, we have developed a one-step synthesis of N and S dual-doped MCV (NS-MCV) by using cyanamide and benzyldisulfide as precursors. The introduction of N and S into the carbon material can modify the electron distribution of MCV and provide favorable oxygen chemisorption on the material surface. The large surface area and a large number of mesopores of NS-MCV supply a high density of active surface sites for ORR. It is also discovered that the content of S plays an important role in improving the ORR performance of catalysts. As a metal-free catalyst, NS-MCV exhibit much better long-term durability and methanol tolerance than the commercial Pt/C in alkaline medium. The excellent electrocatalytic performance of the NS-MCV can be mainly attributed to the synergistic effect arising from the addition of N and S heteroatom, the optimized S content and the high surface area, as illustrated in Scheme 1.

2. Experimental

2.1. Reagents and apparatus

Pluronic F127 (non-ionic triblock copolymer, PEO₁₀₆PPO₇₀-PEO₁₀₆) and Nafion (5 wt%) were purchased from Sigma–Aldrich. 20 wt% Pt/C commercial electrocatalysts were purchased from Johnson Matthey. Cyanamide and benzyldisulfide were purchased from Aladdin Industrial Inc. All other chemicals were purchased and used without any further purification.

The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 spectrometer (Thermo Electron Corp.) with Al K α radiation (1486.6 eV) as the excitation source. The morphology characterizations were performed via scanning electron microscopy (SEM) (XL-30 ESEM, Philips Company). The samples were cast on indium tin oxide glass for SEM measurement. Transmission electron microscopy (TEM) images recorded on a JEM-2100F transmission electron microscope (JEOL, Japan) operating at 200 kV. The specific surface areas of the samples are analyzed with a surface area analyzer (ASAP 2020, Micromeritics, USA) using physical adsorption/desorption of N₂ at the liquid-N₂ temperature. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface area. The pore size distribution plot was derived from the adsorption branch by using the Barrett–Joyner–Halenda (BJH) model. Raman spectroscopy patterns were obtained using a confocal microprobe Raman system (HR800, Jobin Yvon).

Cyclic voltammetry (CV) experiments were performed with a CHI660C Electrochemical Analyzer (CH Instruments, China). Rotating disk electrode (RDE) voltammetry experiments were performed using a PARSTAT 2273 Electrochemistry Workstation. Rotating ring-disk electrode (RRDE) voltammetry experiments were performed using a speed control unit-Princeton Applied Research Model 636 Electrode Rotator and a PINE RRDE with GC disk and Pt ring. A modified glassy carbon (GC, 3.0 mm in diameter, 0.07065 cm² in geometric surface area for the examination for CV, 5.0 mm in diameter, 0.19625 cm² in geometric surface area for the examination for RDE, 5.61 mm in diameter, 0.24706 cm² in geometric surface area for the examination for RRDE.), an Ag/AgCl electrode (in saturated KCl solution) and a platinum electrode served as working, reference and counter electrodes, respectively.

2.2. Materials preparation

The resol precursor of onion-like MCV was prepared according to the method reported by Zhao et al. [34]. NS-MCV with similar N concentration and different S concentration were obtained by keeping the mass of cyanamide and adjusting the addition of benzyldisulfide. In a typical procedure, 0.5 g precursor, 0.5 g

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