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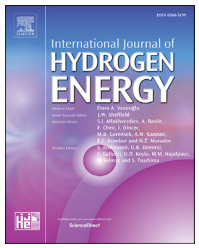

Metal-free mesoporous carbon with higher contents of active N and S codoping by template method for superior ORR efficiency to Pt/C

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ARTICLE INFO

Article history:
Received 17 October 2017
Received in revised form
26 December 2017
Accepted 3 January 2018
Available online 1 February 2018

Keywords:
S, N doped carbon
Mesoporous structure
Oxygen reduction reaction
Electrocatalyst
Electrochemical stability

ABSTRACT

Carbon materials with more exposed N or S atoms result in higher activity for oxygen reduction reaction. In this paper, mesoporous carbon based materials with 5.3 at% of N and 7.1 at% of S are synthesized (defined as porous-S-N-C). The solid core mesoporous shell silica as template results in mesoporous structure of the porous-S-N-C which favors mass transfer and higher doping (both increase by ~20%) and exposing of active N and S atoms. The electrochemical characterization results show that the mesoporous structure and the S modification favor much to the N-C based catalysts in catalyzing ORR. Typically, the porous-S-N-C has a 3.99 electron transfer number at 0.4 V, and higher ORR efficiency, much better CO tolerance, much better methanol tolerance and much higher electrochemical stability than commercial Pt/C. This novel method of improving the contents of doped and exposed N and S atoms is imagined to be applied to preparation of other high-content-heteroatom doped materials.

Introduction

Fuel cells have drawn intensive attention due to their high efficiency of energy conversion and environmental friendliness [1]. The cathodic oxygen reduction reaction (ORR) is one of the key processes in fuel cells. The sluggish kinetics of ORR has remained a key challenge which results in high overpotential and need to be solved [2].

Platinum (Pt) catalysts have been widely studied in catalyzing ORR. The high price of Pt metal forces researchers to make fully use of Pt metal by developing cheap catalyst supports or promoters [3,4]. These materials include porous carbon [5], graphite [6], graphene [7], oxide [8], carbide [9–11], nitride [12,13], alloys [14–16] and so on. Palladium (Pd) is cheaper than Pt. The Pd-based electrocatalysts have good ORR performance in alkaline media [17,18], yet their ORR activity in acidic media is lower than the Pt-based electrocatalysts. Fortunately, by loading Pd nanoparticles on bimetallic carbides, the Pd based catalysts show much increased ORR activity in acidic media and show superior activity to Pt/C [19].

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https://doi.org/10.1016/j.ijhydene.2018.01.013
0360-3199/

However, the metal particles fall off easily from the supporting materials after long-time operation, resulting in decrease of activity. Moreover, the cost of noble metal based fuel cell catalyst need to be further reduced to meet commercialization. Recently, non-metallic- and trace-cheap-metallic heteroatom-doped carbon materials drew extensive attention due to their competitive activity, excellent stability and low cost [20–27]. Among these materials, N-doped materials have been studied most [28–31]. Nitrogen atoms have several states in carbon matrix. The state of N that is most active still remains disputable [32–37]. Yet the higher content and higher exposure degree of the doped N are generally considered to result in higher activity [38]. In addition, the codope of two or more heteroatoms has more advantages than one heteroatom-doped carbon materials due to synergistic effect [38–44]. Therein, S and N-coped carbon is one of the most important codoped carbon materials. Experimental and theoretical data indicate that S, N-codoped carbon materials have improved ORR activity comparable to Pt/C [45–50]. There are many methods to prepare S, N-codoped carbon. However, the contents of heteroatom-doped atoms, especially for the S content, are still low (S < 6 at%, N < 4 at%) [38,45–50]. Much of the S and N atoms are discharged as waste gases such as H_2S and NH_3 in the carbonization process, which restrict their activity and pollute the environment. Moreover, the structure of catalysts should be further improved to expose more active sites. Therefore, to improve the use ratio of S and N atoms in the original materials and obtain high contents of exposed S and N in carbon matrix is of great significance.

Herein, dopamine hydrochloride and 2-mercaptoethanol are used as N and S sources; solid core mesoporous shell silica spheres (SCMSSs) are used as templates to form mesoporous structure as well as increase the exposure degree of S and N in carbon matrix. As a result, a 5.3 at% of N and a 7.1 at% of S are obtained in the synthesized porous-S-N-C catalyst by Raman analysis, both are 20% higher than template-free S-N-C catalyst. Therefore, the porous-S-N-C catalyst shows much higher ORR activity than the template-free S-N-C and also much higher than the S-free porous-N-C. This kind of porous-S-N-C is even superior to the commercial Pt/C, indicating potential economic value.

Experimental

SCMSSs were used as templates to synthesize hollow core mesoporous shell materials. The SCMSS templates with a core diameter of 230 nm and a shell diameter of 50 nm were synthesized according to literature [51].

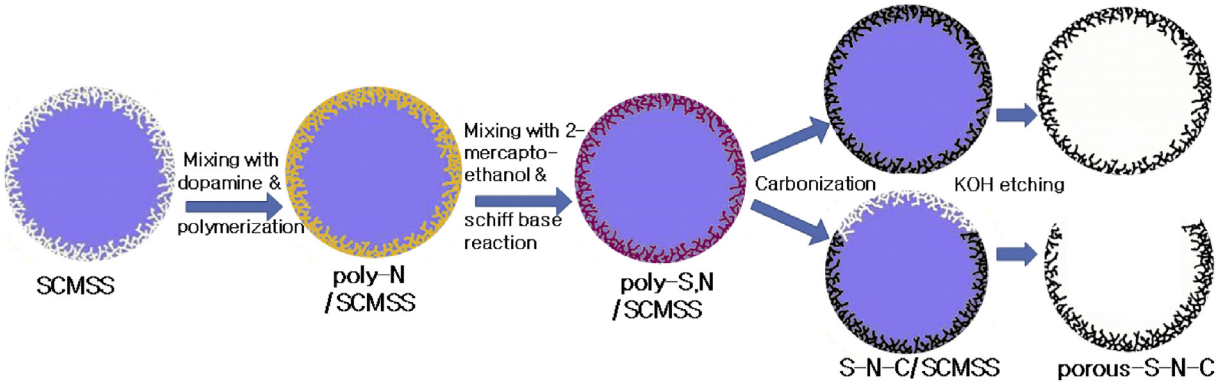
Preparation of porous-S-N-C

Typically, 1.0 g SCMSS, 0.5 g dopamine hydrochloride (Sigma-Aldrich) and 100 ml deionized water were mixed uniformly under 30 min of sonication. Then 50 mL PBS buffer (0.5 mol L^{-1}, pH = 8.0) was dumped into the mixture with stirring and kept stirring for 24 h at room temperature. Afterwards, 0.5 g 2-mercaptoethanol (Sigma-Aldrich) was added into the mixture and kept stirring for 12 h. The mixture was then filtrated and washed for 5 times with deionized water. The collected solid was dried at 90 °C in atmosphere and heated at 800 °C for 3 h with a heating rate of 5 °C/min. After cooled down to room temperature, the solid was immersed in 100 mL 1.0 mol L^{-1} KOH solution with stirring at 70 °C for 24 h. The porous-S-N-C was finally obtained after filtration, washing and drying.

Scheme 1 depicts the formation process of the porous-S-N-C. The first step is to mix the SCMSS and dopamine to produce poly-dopamine in holes of the SCMSS (defined as poly-N/SCMSS). The second step is to mix the poly-N/SCMSS and 2-mercaptoethanol to produce poly-(2-mercaptoethanol, dopamine)/SCMSS (defined as poly-S,N/SCMSS) through Schiff base reaction. The third step is to carbonize the poly-S,N/SCMSS and form S-N-C/SCMSS. Some melted poly-S,N may flow down through the open holes of the SCMSS in this step [52]. The last step is to remove the SCMSS template by KOH etching and form the porous-S-C-N with hollow sphere or hemisphere structures.

Preparation of porous-N-C

The preparation process of porous-N-C is similar to that of the porous-S-N-C (Section Preparation of porous-S-N-C), the



Scheme 1 – Formation process of the porous-S-N-C. Poly-N means poly-dopamine; poly-S,N means composite of poly-N and 2-mercaptoethanol.