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Regular Article

Interface self-assembly preparation of multi-element doped carbon nanobowls with high electrocatalysis activity for oxygen reduction reaction

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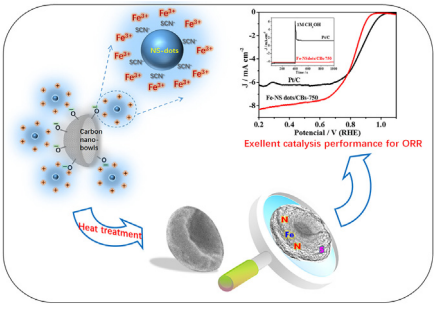
GRAPHICAL ABSTRACT

Fe, N and S codoped carbon nanobowls exhibit excellent electrocatalytic activity, long-term stability and methanol-tolerance for the oxygen reduction reaction in alkaline media.



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ABSTRACT

Developing an efficient, stable and low cost oxygen reduction reaction electrocatalyst is desirable for fuel cells and metal-air batteries. Here, we have successfully prepared multi-element doped carbon nanobowls by simply mixing the porous carbon nanobowls and sulfur doped graphitic carbon nitride quantum dots in $FeCl_3$ solution and subsequent high temperature treatment processes. Compared with the commercial Pt/C electrocatalyst, the multi-element doped carbon nanobowls display a comparable half-wave potential of 0.82 V, much larger limiting diffusion current density (0.4–0.8 V), better methanol-tolerance and higher long-term stability for the oxygen reduction reaction in alkaline media. The robust three-dimensional porous structure of carbon nanobowls and multiple active centers derived from Fe, N, S and O co-doping are responsible for the excellent performance. This work suggests that such multi-element doped carbon nanobowls can be a promising alternative for Pt-based catalysts in fuel cells.

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1. Introduction

Oxygen reduction reaction (ORR) plays an important role in the energy conversion efficiency for the fuel cells and metal-air batteries [1]. Due to the sluggish kinetics of the ORR, platinum (Pt) is commonly used as the ORR electrocatalyst because of its high activity [2]. However, the high cost, and poor stability and low methanol resistance of Pt have extremely restricted its commercial application, and the development of non-noble metal electrocatalyst becomes a trend and necessity. To date, various carbon materials doped with nonmetallic elements (such as N, S, O, etc.) [3–5] and transition metallic elements (such as Fe, Co and Ni) [6] have shown excellent electrocatalytic activity for the ORR. Especially, iron-nitrogen-carbon (Fe-N/C) nanomaterials are considered as the most promising non-precious metal electrocatalysts to replace Pt-based electrocatalyst because of high activity and stability for the ORR in both alkaline and acidic medium [7–11].

It is generally accepted that the nitrogen-coordinated iron species of Fe-Nx (x = 2–4), as well as the non-metallic atoms (N, S, etc.) doped in the carbon framework, are the active sites for the ORR [12,13]. Thus, to further improve the electrocatalytic activity of Fe–N/C, more active sites are introduced into the Fe–N/C nanomaterials through additional doping of S or P heteroatoms [14,15]. In addition, constructing three-dimensional porous structures in Fe–N/C nanomaterials is also effective in the improvement of catalytic activity, due to the strong diffusion effect of ORR-relevant molecules in the pores on the reaction rate [16,17]. Consequently, various heteroatoms ternary-doped porous carbon materials have been prepared, such as Fe/N/S co-doped honeycomb carbon [18], Fe/N/S co-doped carbon with graphene-like structure [19], and Fe/N/S co-doped hollow carbon nanorods [20]. These nanomaterials have shown superior electrocatalytic activity for the ORR compared to Pt/C elecrtocatalyst. However, most of such nanomaterials are fabricated by pyrolyzing the mixtures of N, S or P-containing compounds and iron salts, which makes it difficult to well control the Fe–Nx active sites and effectively avoid the formation of inactive species such as iron oxide nanoparticles.

Graphitic carbon nitride possesses high nitrogen content (57.1 at%) but low electrical conductivity, resulting in an unsatisfactory electrocatalytic activity for the ORR, even it was integrated with conductive supports or doped with heteroatoms to modulate its electrical conductivity [21–24]. However, by means of its thermal decomposition into N doped carbon-based fragments beyond 700 °C [25], it can be used as sacrificial template and nitrogen sources to prepare ORR electrocatalyst, and the resultant nanomaterials show relatively high activity [26]. In this method, to obtain the uniformly mixed precursor, the bulk graphitic carbon nitride was generally pre-exfoliated to nanosheets, which is a process of time-consuming and low efficiency. Compared with the bulks and nanosheets, the quantum dots of graphitic carbon nitride have larger specific surface area, more edge effects and abundant superficial functional groups (–NH or –NH_2), which favour to the assembly with other materials by hydrogen bonds, Van der Waals forces and so on [27]. Besides, preparation of heteroatoms doped graphitic carbon nitride quantum dots, such as S-doped graphitic carbon nitride quantum dots (NS-dots), is very facile [28]. Therefore, NS-dots should be a suitable precursor to prepare N, S, Fe co-doped carbon-based electrocatalyst for the ORR.

In this work, we proposed to take full advantage of the high surface area and abundant pore structure of the carbon nanobowls (CBs) [29], and the high N and S doping level of NS-dots to develop a ORR electrocatalyst with high activity, where, the CBs was as the provider of porous structure but also supporter to avoid the aggregation of NS-dots and thus highly expose the active sites. A one-step preparation method was explored to combine CBs and NS-dots together and simultaneously introduce Fe^{3+} into the hybrids, by simply mixing NS-dots and CBs in $FeCl_3$ solution and a subsequent heat treatment at N_2 atmospheres. Compared with the commercial 20 wt% Pt/C, the prepared sample shows excellent ORR activity, featuring comparable half-wave potential ($E_{1/2}$) of 0.82 V, larger current density, much better cyclic stability and higher methanol tolerance in alkaline media.

2. Experimental

2.1. Reagents and chemicals

Citric acid (CA, 99 wt%), thiourea (CN_2H_4S, 99 wt%), iron trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 99 wt%), ethanol (C_2H_5OH, 99 wt%) were supplied by Aladdin Reagent Co. Ltd. Commercial 20 wt% Pt/C elelctrocatalyst was supplied by E-TEK, Inc.

2.2. Preparation of NS-dots and CBs

NS-dots were prepared according to the literature with minor modification [28]. In a typical synthesis, 0.21 g of citric acid and 0.23 g thiourea were grinded in a mortar for 10 min, and then was heated in a stainless steel autoclave at 200 °C for 2 h. The product was dissolved with 40 mL water, and further purified with a 0.22 μm filter membrane to discard non-fluorescent deposit. The filtrate was collected for characterization and later use. The prepared NS-dots have similar morphology, structure and optical properties (Fig. S1) to that reported by literature [28].

2.3. Preparation of Fe-NS dots/CBs-750

In a typical preparation process, 14.48 mg $FeCl_3{\cdot}6H_2O$ was dissolved in the collected filtrate containing NS-dots and stirred for 30 min, and then 50 mg CBs were added [29]. The mixture was treated with ultrasonic wave for 2 h and subsequently centrifugalized. The collected solids were washed with water and ethanol, respectively, followed by air-drying at 80 °C for 24 h. The dried powders were heated in a tubular furnace at 750 °C for 2 h under a N_2 flow with a heating rate of 2 °C min^{-1}. After cooling to room temperature, the obtained sample was named as Fe-NS dots/CBs-750. For comparison, a series of controlled experiments were prepared with the same process, that is, the Fe-free sample of NS-dots/CBs-750, and the samples of NS-dots-750 and Fe-NS dots-750 without CBs, respectively.

2.4. Electrochemical measurements

Electrochemical experiments were carried out in a standard three-electrode system with computer-controlled CHI 760E electrochemical workstation equipped with rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) apparatus (Pine Company) at room temperature. A saturated calomel electrode and a carbon rod acted as reference electrode and counter electrode, respectively. The working electrode was prepared by dropping 15 μL of the elelctrocatalyst ink on the polished glassy carbon disk electrode and then dried at room temperature. The elelctrocatalyst ink was obtained by mixing 10 mg of electrocatalyst and 5 mL of water/Nafion solution, and sonicating the mixture for 60 min. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) conducted on RDE system. LSV tests were conducted in 0.1 M KOH solution through varying the rotation speed varied from 500 to 2500 rpm with a scan rate of 10 mV s^{-1}. The electron transfer number was calculated from the slope of the Koutecky-Levich (K-L) plots. The H_2O_2 yield and the electron transfer number during ORR were access with RRDE system at a scan rate of 10 mV/s and a rotation speed of 1600 rpm and calculated with the equations of

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