



# One-step synthesis of shell/core structural boron and nitrogen co-doped graphitic carbon/nanodiamond as efficient electrocatalyst for the oxygen reduction reaction in alkaline media



Xiaoxu Liu<sup>a,b</sup>, Yanhui Wang<sup>a</sup>, Liang Dong<sup>a</sup>, Xi Chen<sup>a</sup>, Guoxiang Xin<sup>a</sup>, Yan Zhang<sup>a</sup>, Jianbing Zang<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Metastable Materials Science and Technology, College of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, PR China

<sup>b</sup> Department of Physics, Hebei Normal University of Science and Technology, Qinhuangdao 066004, PR China

## ARTICLE INFO

### Article history:

Received 1 December 2015

Received in revised form 23 January 2016

Accepted 1 February 2016

Available online 16 February 2016

### Keywords:

shell-core structure

boron and nitrogen co-doped graphitic carbon

nanodiamond

oxygen reduction reaction

## ABSTRACT

Shell/core structural boron and nitrogen co-doped graphitic carbon/nanodiamond (BN-C/ND) non-noble metal catalyst has been synthesized by a simple one-step heat-treatment of the mixture with nanodiamond, melamine, boric acid and FeCl<sub>3</sub>. In the process of the surface graphitization of nanodiamond with catalysis by FeCl<sub>3</sub>, B and N atoms from the decomposition of boric acid and melamine were directly introduced into the graphite lattice to form B, N co-doped graphitic carbon shell, while the core still retained the diamond structure. Electrochemical measurements of the BN-C/ND catalyst show much higher electrocatalytic activities towards oxygen reduction reaction (ORR) in alkaline medium than its analogues doped with B or N alone (B-C/ND or N-C/ND). The high catalytic activity of BN-C/ND is attributed to the synergetic effect caused by co-doping of C/ND with B and N. Meanwhile, the BN-C/ND exhibits an excellent electrochemical stability due to the special shell/core structure. There is almost no alteration occurred in the cyclic voltammetry measurements for BN-C/ND before and after 5000 cycles. All experimental results prove that the BN-C/ND may be exploited as a potentially efficient and inexpensive non-noble metal cathode catalyst for ORR to substitute Pt-based catalysts in fuel cells.

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## 1. Introduction

The cathodic oxygen reduction reaction (ORR) which is a crucial process in fuel cells, is catalyzed normally on cathodes by platinum (Pt)-based catalysts. Although Pt-based catalysts perform well in ORR of fuels to generate energy, the limited natural reserves and high cost, combined with the issues of instability and deactivation by anode methanol penetration and CO deactivation, have hindered their large-scale applications [1,2]. Thus, non-precious metal catalysts and metal-free catalysts have been proposed as alternatives to Pt catalysts for large-scale applications in the fuel cells [3–5].

Recently, there have been extensive studies regarding metal-free catalysts for ORR. Among them, the carbon materials engineered by doping heteroatoms, for instance nitrogen (N), boron (B), sulphur (S) and phosphorus (P), have attracted intense

attention because the introduction of heteroatoms to carbon materials can tailor their electron-donor properties and consequently enhance their catalytic activities [6–10]. In particular, it has been found that the co-doping of carbon materials with two heteroatoms can effectively create more catalytically active sites than single-doped counterparts. For example, Xue et al. synthesized three-dimensional B,N co-doped graphene foam by chemical vapor deposition method, which had a much higher onset potential of  $-0.16$  V (vs. SCE) in ORR than the B or N single-doped counterparts resulting from synergistic coupling effects between B and N [11]. Similarly, Zhong et al. reported a B,N co-doped core-shell carbon nanoparticles catalyst that showed an enhanced ORR kinetics by comparison to the N doped analogue, which was very similar to Pt/C catalyst [12]. In this respect, the co-doping with two or more selected heteroatoms to carbon materials is a feasible main trends in order to improve the properties of carbon materials for desired catalytic applications.

Most reported B and N doped carbon materials mainly include carbon nanotube (CNT), graphene and porous carbon etc [13–15]. Compared with the original carbon materials, their ORR catalytic

\* Corresponding author. Tel.: +86 335 8387679.  
E-mail address: [diamondzjb@163.com](mailto:diamondzjb@163.com) (J. Zang).

activities have been improved significantly. However, as  $sp^2$ -bonded carbon materials, their oxidation resistance and structural stability are still poor. As  $sp^3$ -bonded carbon materials, nanodiamond (ND) attracts increasing attention because it has excellent chemical stability. Liu et al. synthesized boron and nitrogen codoped nanodiamond (BND) on a Si rod array substrate by microwave plasma enhanced chemical vapor deposition [16]. The resultant BND exhibits high ORR activity and excellent stability. In order to obtain high catalytic activity and avoid the corrosion in typical cathode conditions, we designed and fabricated a novel shell/core structural carbon material using the ND produced by a high pressure and high temperature method, which are inexpensive and mass-produced. The surface of ND was graphitized to  $sp^2$ -bonded carbon layer which could be easy to be doped and simultaneously improved the conductivity of ND, while the core still retained the diamond structure. In the process of the graphitization, B and N atoms were synchronously introduced into the graphite lattice to form shell/core structural boron and nitrogen co-doped graphitic carbon/nanodiamond (BN-C/ND).

To synthesize the BN-C/ND catalyst, a facile one-step heat-treatment of ND with ferric chloride ( $FeCl_3$ ), boric acid and melamine has been used. During the heat-treatment processes, the surfaces of ND would be graphitized to  $sp^2$ -bonded carbon layer [17], into which the heteroatoms of B and N coming from the pyrolysis of boric acid and melamine were synchronously co-doped. We used  $FeCl_3$  as catalyst to reduce the graphitization temperature of ND, which was good for B and N doping. The restructuring of C–C bond in the process of graphitization makes

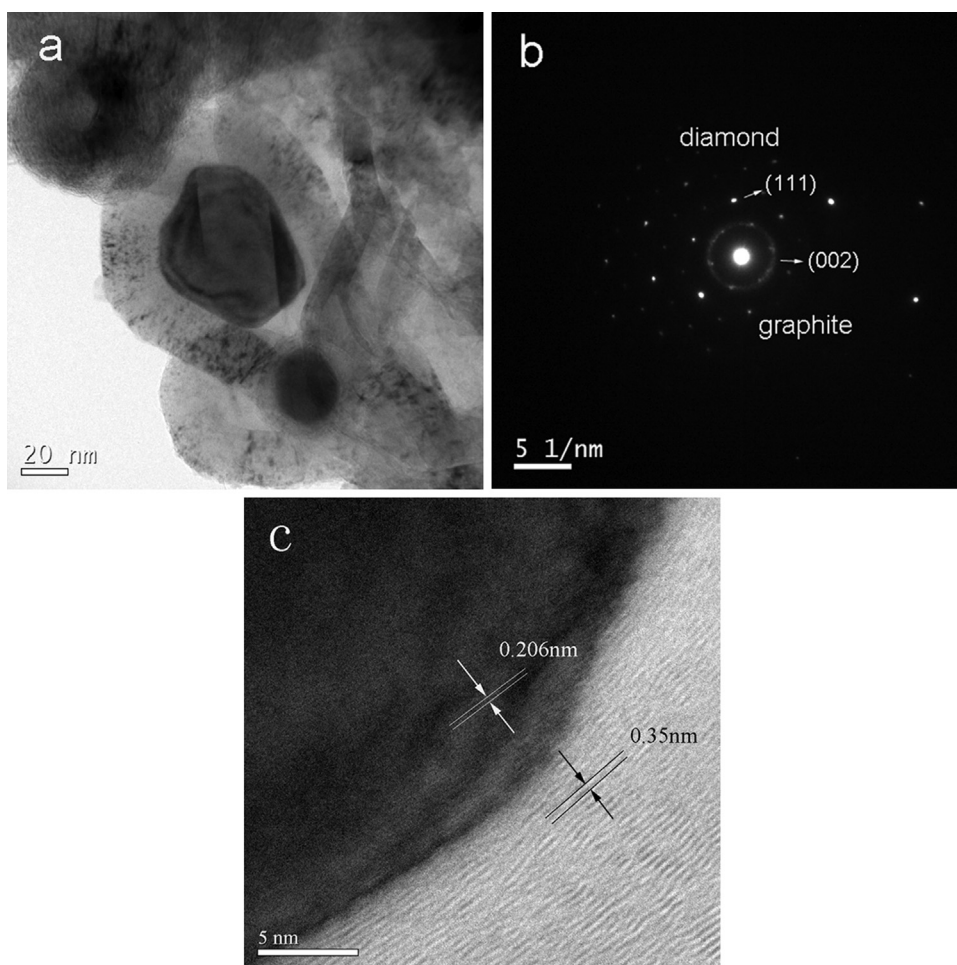
it easy to introduce heteroatoms into the graphite lattice, and then the B and N co-doped carbon material with high catalytic activity can be obtained. Otherwise, the retained diamond core with a high morphological stability under oxidising conditions provides a stiff support for the graphitic carbon shell, which could avoid electrode collapse due to the oxidization of graphite sheets. It was presented in our previous report that the C/ND prepared by vacuum annealing exhibited a high oxidation resistance when used as supports for electrocatalysts of fuel cell [18,19]. The possible synergetic effects on the ORR activities have been investigated, which coming from the co-doping with B and N in BN-C/ND, compared with the B or N single-doped shell/core structural nanodiamond (B-C/ND, N-C/ND).

## 2. Experimental

### 2.1. Preparation of B-C/ND, N-C/ND and BN-C/ND by heat-treatment

The preparation process is as follows: To prepare BN-C/ND, ND (0.3 g),  $FeCl_3$  (0.1 g), boric acid (1 g) and melamine (1 g) were fully mixed in DI-water by sonicate. Then the mixture was stoving in  $80^\circ C$  and ground to a powder. The mixture powder was heat-treated at  $1000^\circ C$  for 3 h under a nitrogen atmosphere. Then, the calcined product was washed by HCl (3 M) and deionized water to remove Fe. After drying in a vacuum at  $60^\circ C$ , the BN-C/ND product was obtained.

By contrast, N-C/ND was performed by mixing with ND (0.3 g),  $FeCl_3$  (0.1 g) and melamine (1 g) in the same manner as mentioned



**Fig. 1.** (a) TEM image of BN-C/ND. (b) The corresponding SAED pattern. (c) HRTEM image of BN-C/ND.

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