Nanosheet-Structured Boron Carbon Nitride Spheres as Stable Electrocatalyst Support for Oxygen Reduction Reaction

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Abstract: A novel nanosheet-structured boron carbon nitride spheres (BCNSs) have been prepared for application as electrocatalyst support of oxygen reduction reaction (ORR) for the first time. The BCNSs were prepared by a catalyzed thermal evaporation method from solid B powders. The BCNSs are hollow with the diameter in the range of 450-500 nm and composed of many radially oriented ultrathin nanosheets with a mean thickness of 8.6 nm. Due to immobilization in the spheres the constituting BCN nanosheets are free of agglomeration, capable of preserving high surface area during application. Small Pt nanoparticles with diameters of 2-8 nm were deposited onto the BCNSs by ethylene glycol reduction method. The Pt/BCNSs catalyst shows excellent electrocatalytic performance for ORR with the onset potential at 0.10 V and current retention of 85.4 % after 20 000s, which is superior to the commercial 20 % Pt/C catalyst. The improved electrocatalytic performance of the Pt/BCNSs arises from the unique structure and high chemical stability of the BCNSs support and the possible synergistic effect between Pt and the support. The present work indicates that the BCNSs are excellent electrocatalyst support for ORR, which can be further improved by optimizing the composition and structure.

Key words: Boron carbon nitride, nanosheets, spheres, oxygen reduction reaction.

1. Introduction

Fuel cell is regarded as one of the most promising energy conversion devices due to its high energy conversion efficiency [1], low emission [2], and high energy density [3]. The cathode electrocatalysts for oxygen reduction reaction (ORR) play a key role in the running of the fuel cells [4], [5]. Platinum (Pt) is conventionally used as the electrocatalysts [6]-[8]. Generally, the Pt catalysts are used by dispersing on various supports, which is necessary for obtaining excellent electrocatalytic performance [9], [10]. Carbon black has been widely used as the electrocatalyst support due to the high specific surface area (SSA) and good electrical conductivity [11]. However, the carbon black in the form of particles suffers from the problems of agglomeration and electrochemical corrosion, resulting in the performance decrease of the catalysts [12], [13]. Recently, many research groups have studied alternative non-carbonaceous supports of electrocatalysts such as carbides [14], nitrides [15], and transition metal oxides [16], [17]. Although these materials appear promising for making high efficient electrocatalytic systems of ORR, some obstacle issues

such as small specific surface area or poor electrical conductivity still degrade the performance of the supported catalysts [18]-[20]. Therefore, it is necessary to develop novel electrocatalyst supports and thus maximize the performance of the electrocatalysts.

Hexagonal boron nitride (BN) with the graphite-like structure has been used as the catalyst supports for chemical engineering, which shows excellent performance due to the high chemical and thermal stability [21]-[23]. However, the poor electrical conductivity of BN constitutes a big obstacle for its application as electrocatalyst support for ORR. Boron carbon nitride (BCN) formed by introducing carbon atoms into the BN structure possesses much improved electrical conductivity comparing with BN and much improved chemical and thermal stability comparing with carbon [24], [25], which endows BCN the superiority for application as the electrocatalyst support. Recent reports indicate that the BCN materials possess electrocatalytic activity for ORR [26]-[28]. However, to the best of our knowledge, the application of the BCN materials as electrocatalyst support to immobilize Pt nanoparticles for ORR has not been reported yet so far.

Appropriate nanostructure with high effective surface area and abundant active adsorption sites is required for the catalyst supports to generate excellent catalytic performance. Different nanostructures such as nanowires [29] and graphene [30], [31] have been used to support Pt catalyst for fuel cell application. As a typical two-dimensional (2D) nanomaterial, BCN nanosheets may be a good candidate of Pt catalyst support due to its higher surface area and abundant edge sites with high activity [24]. However, the 2D nanosheets generally show a strong tendency to agglomerate [32], which leads to great loss of the effective surface area and thus the catalytic performance. Recently, by a catalyzed thermal evaporation process we prepared nanosheet-structured BN spheres [32], in which the BN nanosheets are radially oriented with the sheet edges oriented on the surface. For this architecture, the BN nanosheets are fixed and the problem of agglomeration is thus avoided. Due to full exposure of the nanosheet surface and presence of highly active edge sites on the sphere surface, the nanosheet-structured BN spheres exhibit excellent adsorption performance for many molecules and ions. It is expected that the nanosheet-structured BCN spheres (BCNSs) with similar structure may be good Pt supports for ORR. However, the BCNSs with radially grown nanosheets have not been prepared yet.

In this paper, we prepared BCNSs by a simple catalyzed thermal evaporation approach and investigated their application as Pt catalyst support for ORR. The BCNSs are composed of radially grown ultrathin BCN nanosheets with the sheet edges oriented on the surface [32]. Due to the superior structure of no agglomeration and radially orientation of the nanosheets and high chemical stability of the BCN material, the Pt/BCNSs catalyst shows excellent electrocatalytic performance for ORR with onset potential as high as 0.10 V and stability up to 85.4 % current retention after 20 000 s.

2. Experimental

The BCNSs were prepared by a catalyzed thermal evaporation method from solid B powders. A Mixture of CoFe_2O_4 and CoO with a molar ratio of 1:1 was used as the catalyst to assist evaporation of the B powders. CH_4 and NH_3 were used as C and N sources, respectively. The growth of the BCNSs was carried out in a conventional tube furnace. In a typical process B powders and $\text{CoFe}_2\text{O}_4/\text{CoO}$ mixture catalyst were mixed and put on the bottom of a crucible, which was then placed at the center of a tube furnace. The mass ratios of the B powders and the mixture catalyst were controlled at 1:4. Subsequently, the reactor temperature was increased to 1300 °C in N_2 at a flow rate of 100 sccm. Then NH_3 and CH_4 were introduced into the reactor with the flow rates of 120 sccm and 10 sccm, respectively. The growth time is 1 h. After cooling to room temperature a large amount of gray product could be obtained on the crucible walls. The detailed growth process has also been described in a previous report [32].

The Pt/BCNSs electrocatalysts were prepared using the ethylene glycol (EG) reduction method [33].

Firstly, 10 mg BCNSs was put in 10 mL EG with ultrasonic stirring for 30 min to obtain a liquid suspension. Then, 0.2 mL H_2PtCl_6 solution in EG (7.5 mg mL^{-1}) was added into the above suspension dropwise with magnetic stirring for 4h. The pH value of the suspension was adjusted to above 13 by NaOH (2.5 M in EG solution). This mixture was refluxed at 140 °C for 3 h to ensure the sufficient reduction of the Pt species. The whole preparation process was protected by an argon flow. Finally, the Pt/BCNSs catalyst with a nominal Pt weight loading of 15 % was obtained after thorough washing with ethanol and drying in vacuum at room temperature.

The structures of the obtained samples were characterized by scanning electron microscopy (SEM, HITACHI S-4700), transmission electron microscopy (TEM, JEM-2100), and X-ray diffraction (XRD, Rigaku D/Max 2500Pc). The composition and bonding state of the samples was detected by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250).

The electrochemical performance of the Pt/BCNSs catalyst was tested by an electrochemical workstation (CHI 660C, Shanghai Chenhua Instrument Co., Ltd. China) in 0.1 M KOH solution. Cyclic voltammogram (CV) and rotating-disk electrode (RDE) polarization curves were measured in a conventional three-electrode electrochemical cell with a platinum wire (CHI 115) as counter electrode and an Ag/AgCl (3 M KCl solution) (CHI 111) electrode as reference electrode. A glassy carbon (GC) disk (4 mm in diameter, Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd) coated with the Pt/BCNSs catalysts was used as working electrode. Before measurements, the GC disk was washed with distilled water and dried in vacuum. The catalyst suspension was prepared by dispersing 1 mg Pt/BCNSs powders in Nafion solution (1 mL, 0.5 vol % in ethanol) with sonication for 1 h. Then 10 μL Pt/BCNSs suspension was dropped onto the GC disk, giving a Pt loading about 1.5 μg . The RDE polarization curves were measured in the potential range from 0.2 to -0.8 V vs Ag/AgCl (3 M KCl solution) at a scan rate of 10 mV s^{-1} and rotation rates from 400 to 2500 rpm. The CV curves were measured in the same potential range. The current-time (i-t) curves were measured at constant potential of -0.4 V for 20 000s at a fixed rotation rate of 1600 rpm.

3. Results and Discussion

Fig. 1 shows the SEM images of the BCNSs. It is observed that the BCNSs are spherical and composed of radially oriented nanosheets. The diameters of the BCNSs are in the range of 400-500 nm and the thickness of the constituting nanosheets is measured to be less than 10 nm. It is obvious that this structure can effectively avoid agglomeration of the nanosheets and the spheres.

Fig. 1. Magnetization as a function of applied field.

Fig. 2 shows the TEM images of the BCNSs (panels a-c) and Pt/BCNSs catalyst (panels d-f). It is noticed that the BCNSs are hollow and composed of many ultrathin nanosheets, which are radially oriented with the sheet edges exposed on the surface (Fig. 2a and b). These nanosheets are fixed in the BCNS structure and separate from each other, eliminating the problem of agglomeration. The diameter of the spheres is about

450-500 nm. The constituting nanosheets exhibit a tapered morphology with a mean thickness of 8.6 nm (Fig. 2a, b). The high resolution TEM (HRTEM) image shown in Fig. 2c clearly reveals straight and parallel lattice fringes in the nanosheets, suggesting the high crystallinity of the BCNSs. The average spacing between adjacent fringes is about 0.33 nm, corresponding to (002) crystal planes of the graphitic BCN [34]. It is considered that the unique structure of the BCNSs is superior for supporting the Pt particles. For example, the BCN nanosheets interconnect and form macropores in the BCNSs. The Pt particles supported on the pore walls can be fully exposed towards the electrolyte. Additionally, the Pt particles supported on the BCNSs subject to less loss during operation because they can still keep contact with the support at a different position even if they separate from the original position on the support. Fig. 2d-f show the TEM images of the Pt/BCNSs catalyst. It is clearly observed that the Pt nanoparticles have successfully been anchored uniformly on the nanosheets of the BCNSs with no agglomeration. The size of the Pt nanoparticles is measured to be in the range of 2-8 nm. This unique BCNSs support, small Pt particle size, and well dispersion of the Pt nanoparticles will lead to high utilization efficiency of the Pt catalyst and excellent electrocatalytic properties.

Fig. 2. TEM image of BCNSs (a-c) and Pt/BCNSs catalyst (d-f).

XRD patterns of the BCNSs and Pt/BCNSs are shown in Fig. 3. The pattern of the BCNSs sample exhibits two strong diffraction peaks at 26.6° and 42.0° , and two weak peaks at 54.8° and 76.4° , corresponding to the diffractions of (002), (100), (004), and (110) planes of graphitic BCN, respectively [35]. The sharpness of the main peaks indicates that the BCNSs are relatively well crystallized. The Pt/BCNSs catalyst displays several additional diffraction peaks at 39.72° , 46.20° , 67.52° , 81.52° , and 86.14° , which can be ascribed to the diffraction planes of (111), (200), (220), (311), and (222) planes of cubic Pt, respectively (JCPDS, No. 04-0802) [36], [37]. The XRD results suggest that the Pt species were reduced to the metallic state through the EG reduction method.

XPS spectra were measured to determine the chemical composition and bonding states of the BCNSs and Pt/BCNSs samples, as shown in Fig. 4. It can be seen that the BCNSs contain B, C, and N elements while additional Pt and O elements are present in the Pt/BCNSs sample. The O component should mainly originate from PtOx species and the unavoidable adsorption of O₂ on the surface. As shown in Figure 4c, the blue lines correspond to the Pt-O bond. Figure 4b shows the B 1s, C 1s, and N 1s spectra of the BCNSs. The B 1s peak can be deconvoluted into two peaks at 190.2 and 191.3 eV, arising from the B-C and B-N bond,

respectively [38]. The relatively higher intensity of the B-C peak indicates that more B atoms bond with C in the network. The three deconvoluted peaks in the C 1s spectrum at 284.4, 284.7, and 285.1 eV could be assigned to C-B, C-C, and C-N, respectively [39]. As can be seen in Figure 4b, the percentage of C-B is higher than that of C-N. N 1s spectrum could be deconvoluted into two separated peaks at 397.8 and 398.4, corresponding to the N-B bond and N-C bond, respectively [40]. The XPS spectra reveal that the BCNSs contain C-C, B-C, B-N, and C-N bonds, suggesting that the three atoms are atomically bonded, forming a ternary compound. The atomic percentages of B, C, and N calculated from the XPS spectra are 15.3, 63.3, 21.4 at.%, respectively. No additional impurities are present in the samples. Figure 4c shows the Pt spectrum of the Pt/BCNSs. Pt 4f peak can be convoluted into two pairs of doublets. The peaks at 71.6 and 75.0 eV (green) can be attributed to Pt 4f_{7/2} and 4f_{5/2} of metallic Pt(0), respectively, and the peaks at 72.75 and 75.35 eV (blue) correspond to Pt(II) [41]. The presence of oxidized Pt species may be attributed to the oxidation of surface Pt in air.

Fig. 3. XRD patterns of BCNSs (a) and Pt/BCNSs catalyst (b).

Fig. 4. (a) XPS spectra of BCNSs and Pt/BCNSs catalyst. (b) B 1s, N 1s, and C 1s spectra of BCNSs, in which the blue line corresponds to B-C bond, green line corresponds to B-N bond, dark yellow line corresponds to C-N bond, and magenta line corresponds to C-C bond. (c) Pt 4f spectrum of the Pt/BCNSs.

The electrocatalytic performance of the Pt/BCNSs catalysts was investigated by measuring the CV and RDE curves in O₂-saturated 0.1 M KOH solution. For comparison, the BCNSs and commercial 20 % Pt/C (E-TEK) were also investigated under the same conditions. As shown in Figure 5a, all the CV curves exhibit obvious oxygen reduction peaks, which locate at -0.35, -0.08, and -0.13 V for BCNSs, Pt/BCNSs, and Pt/C catalysts, respectively. This result indicates that the BCNSs support itself is catalytically active for the ORR. The Pt/BCNSs catalysts exhibit much better electrocatalytic activity for the ORR than the support. Comparing with the Pt/C catalyst the Pt/BCNSs catalyst displays a more positive peak potential, indicating

considerable improvement of the catalytic activity for the ORR. The RDE curves were measured to further compare the ORR activity of Pt/BCNSs with that of BCNSs and commercial 20 % Pt/C (E-TEK). The RDE curves (Fig. 5b) show a similar changing trend to the CV curves in electrocatalytic activity for the different samples. The onset potentials for BCNSs, Pt/BCNSs, and Pt/C catalysts are -0.12, 0.10, and 0.05 V with the corresponding current densities to be 1.08, 4.46, and 5.28 mA cm⁻² at -0.40 V, respectively. Obviously, the Pt/BCNSs catalyst exhibits more positive onset potential, even better than the Pt/C catalyst. This may arise from the synergistic effect mainly between the BCNSs support and Pt.

Fig. 5. (a) CV curves of the different samples. (b) RDE curves of the different samples. (c) RDE curves of Pt/BCNSs at different rotation speeds. (d) K-L plots calculated from the RDE curves in panel c. (Electrolyte: O₂-saturated 0.1 M KOH solution, scan rate: 10 mV s⁻¹).

To further probe into the ORR performance of the Pt/BCNSs catalysts, the RDE curves were tested at different rotation speeds (400 to 2500 rpm). In order to investigate the kinetic process the RDE polarization curves were analyzed using the Koutecky–Levich (K–L) equation described below [42].

$$\frac{1}{J} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6} \quad (2)$$

$$J_K = nFkC_{O_2} \quad (3)$$

The meaning of the symbols in the equations are as follows: J -measured current density, J_K -kinetic limiting current density, ω -angular velocity of the disk, n -overall number of electrons transferred per oxygen molecule during ORR, D_{O_2} -diffusion coefficient of O₂ molecules in the electrolyte solutions, F -Faraday constant, C_{O_2} -bulk concentration of O₂ molecules in the electrolyte solutions, ν -kinematic

viscosity of the electrolyte solutions, k -electron transfer rate constant. C_{O_2} , D_{O_2} , and ν for O_2 -saturated 0.1M KOH solution are $1.2 \times 10^{-6} \text{ mol cm}^{-3}$, $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and $0.01 \text{ cm}^2 \text{ s}^{-1}$, respectively [42]. Fig. 5c and d give the RDE curves of the Pt/BCNSs electrode and the corresponding K - L plots, respectively, in which the ORR current densities increased with increasing the rotation speed. In the investigated potential range (0.30-0.45 V), the K - L plots show good linearity and parallelism, indicating that the ORR process over the Pt/BCNSs electrocatalysts follows first-order kinetics with respect to the concentration of oxygen [43]. Calculated from the K - L plots, the average electron number transferred per oxygen molecule is 4.0. This four-electron transfer process and high kinetic current density confirm the high ORR activity of the Pt/BCNSs electrocatalysts.

The stability of the Pt/BCNSs and commercial 20 % Pt/C catalyst was evaluated in alkaline media (Fig. 6). After reaction for 20000 s, 85.4 % of the initial current is maintained for the Pt/BCNSs catalyst while the current retention of the commercial Pt/C catalyst is 76.5 %. The improved durability of the Pt/BCNSs catalyst is possibly attributed to the excellent corrosion resistance of the BCNSs and less loss as stated above.

Fig. 6. Current-time (i - t) curves of the Pt/BCNSs and commercial 20 % Pt/C (E-TEK) catalyst tested at -0.40 V in O_2 -saturated 0.1 M KOH solution.

4. Conclusion

In summary, we have successfully prepared nanosheet-structured BCN spheres (BCNSs) from B powders through a facile catalyzed thermal evaporation approach. The BCNSs are composed of many ultrathin nanosheets, which grow with radial orientation with the sheet edges exposed on the sphere surface. The BCNSs possess excellent performance for application as supports of electrocatalysts for ORR. The prepared Pt/BCNSs catalyst exhibits improved electrocatalytic performance including more positive ORR potential and higher operation stability than the 20 % Pt/C catalyst. The unique structure of the BCNSs support and the possible synergistic effect between Pt and the support are responsible for the improvement of the electrocatalytic performance.

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