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Nitrogen-boron Dipolar-doped Nanocarbon as a High-efficiency Electrocatalyst for Oxygen Reduction Reaction

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ABSTRACT

Nitrogen-boron dipolar-doped commercial multi-walled carbon nanotubes (MWCNTs) were prepared and demonstrated as a high-efficiency and low-cost electrocatalyst for oxygen reduction reaction (ORR). The resulting nitrogen-boron dipolar-doped MWCNTs (N, B-CNTs) exhibit a doubled peak current density and a small negative shift in onset potential in ORR compared with the commercial Pt/C catalyst. The doped nitrogen and boron form n- and p-type active centers in the N, B-CNT, respectively, which can weaken the O—O stretching and extend the O—O bond length in oxygen reduction reaction. First-principles calculations reveal that the O_3H^- and O_3H_2 transitional states of oxygen are formed on the doped nitrogen and boron, which promotes the four-electron reaction in ORR.

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1. Introduction

High cost of traditional anode and cathode catalysts in fuel cells, e.g., precious metals and alloys such as Pt, Pd-based alloys, is an obstacle for their wide application [1–8]. To reduce the cost of fuel cells, many non-precious metal catalysts, especially catalysts for oxygen reduction reaction (ORR) in anode, have been widely investigated [9–11]. This includes transition metal-based carbides, nitrides, and oxides [11–22]. In addition to transition metal-based catalysts, carbon-based nanomaterials, as represented by carbon nanotubes (CNTs) and graphene, have attracted great attention due to their unique structures and versatile characteristics [23–25].

The catalytic activity of pristine CNTs in ORR is relatively weak, but its catalytic performance could be promoted by doped elements such as nitrogen, sulfur, transitional elements, etc. [26–33]. For instance, nitrogen-doped vertically-aligned CNTs were reported to have outstanding catalytic activity, good long-term stability and tolerance to the methanol crossover effect than platinum for ORR in alkaline fuel cells [34]. In one review article on

boron- and nitrogen-doped CNTs, Panchakarla et al. discussed that the doping method could be an efficient route to enhance the catalytic activity of CNTs [35]. Compared with nitrogen doping, the boron doping was usually performed with a chemical vapor deposition (CVD) method using borane as the boron source [36]. However, the toxicity of borane and the low efficiency of the CVD method have made the large-scale production of boron-doped CNT a great challenge. In addition, since the catalytic performance was determined by the state of doped elements in the catalyst [37], developing a facile method to controllably dope nitrogen and boron into nanocarbons is highly needed.

Here, we report a facile and low-cost method to prepare dipolar-doped nitrogen and boron MWCNTs with surprisingly high catalyst performance for ORR. The peak current density of oxygen reduction for the nitrogen and boron dipolar-doped CNTs (N, B-CNTs) is more than twice higher than that of the commercial Pt/C, and the onset potential of the N, B-CNT is only 50 mV lower than that of Pt/C, indicating an outstanding performance of the N, B-CNTs. Density functional theory (DFT) calculations show that the dipolar-doped nitrogen and boron promote the four-electron reaction in ORR, thus enhance the catalytic activity of the catalyst in ORR. We believe this method could be applied to other nanocarbon materials, e.g., graphene, or their hybrids to prepare high-performance and low-cost electrocatalysts.

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2. Experimental Details

2.1. Materials synthesis

The preparation of boron-doped CNTs (B-CNT), nitrogen-doped CNTs (N-CNT), and N, B-CNT are illustrated in Fig. 1. The CNTs were provided by Nano Technology Ltd. and labelled as pristine CNTs and adopted without any treatment. In a typical experiment, 300 mg of pristine CNTs were treated for 30 min in 8 M nitric acid at 40 °C with sonication. The treated CNTs were dried at 333 K and –0.08 MPa (vacuum) for 12 hours, and then heated up to 800 °C under ammonia atmosphere to obtain N-CNTs. To prepare B-CNT and N, B-CNT, 50 mg H_3BO_3 were added to the CNT solution with nitric acid and dried. The obtained mixture was divided into two portions and heated to 800 °C for two hours under hydrogen and ammonia atmosphere, respectively. The heat-treated samples were washed with 1.0 M NaOH and DI water to remove the residue H_3BO_3 and boron oxide. Then B-CNTs and N, B-CNTs were obtained.

2.2. Structure Characterization

The morphology of the as-prepared samples and the selected area electron diffraction (SAED) patterns were obtained using a Hitachi (H 9000 NAR) transmission electron microscope (TEM) and a Hitachi (S-4800) scanning electron microscope (SEM) equipped with an energy-dispersive spectroscopy analyzer. Powder X-ray diffraction (XRD) was performed on a Scintag XDS 2000. X-ray powder diffractometer with monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The data were collected between scattering angles (2θ) of 10° and 85°. X-ray photoelectron spectroscopy (XPS) was conducted using an HP 5950A ESCA spectrometer with an Mg $\text{K}\alpha$ source. N_2 adsorption–desorption measurements were carried out at 77 K using a Quantachrome Autosorb gas-sorption system to determine the specific surface area of pristine CNT, N-CNT, and N, B-CNT.

2.3. Electrochemical measurements

The electrochemical tests were carried out in 1 M KOH solution at room temperature using a CHI 760E electrochemical workstation (CHI Inc., USA). The three-electrode cell consists of an Ag/AgCl electrode as the reference electrode, a graphite electrode as the counter-electrode, and a glassy carbon electrode with catalysts as the working electrode. To prepare the working electrode, 3.0 mg prepared catalyst was mixed with 50 μl Nafion solution (5.0% Nafion in ethanol) and 450 μl DI water. The mixture was sonicated for 30 min to obtain a black ink. Then, 5.0 μl ink was taken and

dropped onto a glassy carbon electrode with a diameter of 3 mm and fully dried. Before the electrochemical tests, the working electrode was kept in an Ar-saturated electrolyte by cycling the potential from 0.2 to –0.8 V at a scan rate of 0.1 V/s until reproducible results appeared. Thereafter, the electrolyte was saturated with oxygen and cyclic voltammogram tests for ORR were carried out and recorded from 0.2 to –0.8 V at sweeping rates of 0.1, 0.05, 0.02, 0.01, and 0.005 V/s. Linear-sweep voltammograms (LSV) tests were conducted from 0 to –0.4 V at a sweeping rate of 0.005 V/s. The Tafel and current(i)-time(t) tests were also conducted at the same sweeping rate. The rotate disc and rotate ring disc electrocatalysis tests were conducted from 0.0 to –0.4 V (vs. Ag/AgCl) by an RDE-3A electrode.

3. Results and discussions

3.1. N, B-CNT structure

The successful synthesis of N, B-CNT was confirmed by TEM images and XPS spectra. Fig. 2a and b shows the TEM and high-resolution TEM (HRTEM) images of the pristine CNTs. It is clearly observed that the surface of pristine CNT is quite smooth [38–40]. In comparison, Fig. 2c reveals that the surface of N, B-CNT is much rougher than that of pristine CNTs, which is likely attributed to the doped nitrogen and boron. The HRTEM images of N, B-CNT (Fig. 2d) shows a stair-like structure, likely originating from the oxidation of CNTs in nitric acid with sonication. The SAED patterns of CNT and N, B-CNT are shown in the insets of Fig. 2a and c, respectively, which are consistent with MWCNT structures. Fig. S1a–b and c–d in Supplementary Information show the TEM and HRTEM images of N-CNT and B-CNT, respectively. Similar structures were also observed. For each layer of CNTs, the carbon atoms are normally in sp^2 electron hybridization, which promotes the formation of a perfect hexagonal carbon ring structure and eventually forms a smooth carbon layer. The doped boron and nitrogen in the hexagonal structure granulate the surface of CNTs, leading to a rougher surface. Calculations on the structure of nitrogen-doped CNT also indicated that nitrogen-doping could granulate the surface of CNT [34,41]. Fig. S1f in Supplementary Information shows the XRD patterns of pristine CNT and N, B-CNT. The XRD patterns of N, B-CNT was indexed from the Joint Committee on Powder Diffraction Standards (JCPDS) (#35-1292), which indicates that the N, B-CNT has a hexagonal structure with a nominated $(\text{NB})_{0.26}\text{C}_{0.74}$ composition.

The XPS survey spectra of pristine CNT, N-CNT, B-CNT, and N, B-CNT are shown in Fig. 2e. The XPS survey spectra clearly demonstrate the successful doping of N or/and B in CNTs. Fig. 2f–h shows the high-resolution XPS spectra of C1s, N1s, and B1s of N, B-CNT, which further confirm the successful doping of nitrogen and boron. The discrepancy between the observed C1s signal and the slight shifting of perfect sp^2 hybridized graphitic carbon were attributed to the disordered graphitic network [42]. The N–B and N–C bond in the N1s spectra (Fig. 2g) and B–N and B–C bonds in the B1s spectra (Fig. 2h) are in a good accordance with the XPS spectra of C1s. The UV–vis absorption spectra, Raman spectra, and Fourier Transform infrared spectroscopy (FT-IR) results are provided in Supplementary Information Fig. S3. These results also confirm the successful doping of nitrogen and/or boron in CNTs. The specific surface areas of the samples tested by the Brunauer–Emmett–Teller (BET) method are provided in Supplementary Information Fig. S3. The specific surface areas of pristine CNT, N-CNT and N, B-CNT are 268 m^2/g , 281 m^2/g , and 324 m^2/g , respectively. The increased specific surface areas are likely attributed to the doped nitrogen- and boron-induced granulation of CNTs.

Fig. 1. Preparation process for N-CNT, B-CNT, and N, B-CNT.

Fig. 2. TEM and HRTEM images of (a), (b) pristine CNTs and (c), (d) N, B-CNTs. The inset in (a) and (c) are the SAED patterns of pristine CNTs and N, B-CNTs. (e) XPS spectra of pristine CNT, B-CNT, N-CNT, and N, B-CNT. (f)–(h) High-resolution XPS spectra of C 1s, N 1s, and B 1s in N, B-CNT.

3.2. Electrocatalytic performance study

The cyclic voltammetry (CV) tests in Fig. 3a–e show that no oxygen reduction peaks were detected in the argon-saturated 1 M KOH solution for all samples, and on the contrary, the oxygen-reduction peaks were clearly observed in the oxygen-saturated 1 M KOH solution. Based on the CV tests, the onset potential and peak current density of ORR for each catalyst are obtained and shown in Fig. 3f. The pristine CNT shows the smallest current density and the

lowest onset potential among all the catalysts. The catalytic activity of pristine CNT is usually attributed to the structure defects and the open tips of CNTs. Interestingly, the catalytic activity of pristine CNTs are greatly enhanced by the doped nitrogen or/and boron. The ORR peak current intensities of nitrogen- or/and boron-doped CNTs were higher than that of pristine CNTs and even higher than that of Pt/C catalysts. Specifically, the peak current density of N, B-CNT is more than two times higher than that of the Pt/C catalyst.

Fig. 3. Cyclic voltammetry (CV) tests of oxygen-reduction in argon- and oxygen-saturated 1 M KOH solution with (a) pristine CNT, (b) N-CNT, (c) B-CNT, (d) N, B-CNT, and (e) Pt/C catalysts at a sweeping rate of 5 mV/s, respectively. (f) Onset potential (E) and peak current intensity (I) of pristine CNT, N-CNT, B-CNT, N, B-CNT, and Pt/C catalysts. (g) Tafel slope, (h) linear scanning voltammetry (LSV), and (j) Current (i)–time (t) chronoamperometric results of pristine CNT, N-CNT, B-CNT, and N, B-CNT, respectively.

The onset potential is another critical parameter in evaluating the ORR catalytic activity. As shown in Fig. 3f, the Pt/C catalyst has the smallest onset potential close to -0.02 V (vs. Ag/AgCl), indicating the high catalytic activity of Pt/C in ORR. However, the N, B-CNT also shows a relatively good onset potential, which is only 50 mV lower than that of the Pt/C catalyst. Compared with pristine CNT, N-CNT, and B-CNT, the onset potential of N, B-CNT is better, which is attributed to co-doped nitrogen and boron [43–46].

The plotted polarization curves shown in Fig. 3g are known as “Tafel plots” and are derived from the Tafel equations shown below:

$$\eta = b \cdot \lg \frac{i}{i_0}, \text{ where } b = \frac{2.3RT}{(1 - \alpha)nF} \quad (1)$$

where η refers to the electrode polarization potential, b is tafel slope, i is the experimentally obtained electrode current, i_0 is the exchange current density, α is electron transfer constant, R is gas constant 8.314 J/(mol·K), T is test temperature in K, F is Faraday constant (96,485 C/mol), and n is the electron transfer number. Based on calculations and CV results, the Tafel slopes, charge transfer coefficients, electron exchange current densities, onset potential, and half-wave potentials of the samples are obtained and shown in Table 1. It is found that the onset potential (E_0), half-wave potential ($E_{1/2}$), and peak current intensities increase in the order of pristine CNT, N-CNT, B-CNT, and N, B-CNT. The exchange current density (i_0) also increased in the same order, except for N-CNT. The exchange current density of N, B-CNT is the largest among the catalysts. The enhanced current density is closely related to the doped elements in CNTs. In N, B-CNT, The doped boron presented a positive electron active center and the doped nitrogen presents a negative electron center [47]. The electronic structure of the surface carbon layer was tailored by the doped nitrogen and boron, which improved the catalytic performance of the CNTs [48]. On the other hand, the dipolar-doped nitrogen and boron lead to more defects in N, B-CNT, which served as active sites for oxygen adsorption and reduction. In addition, the nitrogen-doped graphitic layer possesses a faster charge-transfer rate at the electrode/electrolyte interface, which is favourable to the electron transfer of ORR [49–51]. Supplementary Information Fig. S4 shows the CVs of the samples at different sweeping rates and the correlation of the peak current density and the square root of sweeping rate. It is clearly observed that, for each catalyst, the peak current density linearly increases with the increase of sweeping rate, which means that the oxygen reduction is controlled by the diffusion of oxygen on the electrode surface.

Fig. 3h shows the LSV results of ORR, in which the onset potential shifts to positive direction and current density increases in the order of pristine CNT, N-CNT, B-CNT, and N, B-CNT. Fig. 3j shows the current(i)-time(t) chronoamperometric tests of the catalysts. The i - t performances of N, B-CNT is the best among the samples after 3500 seconds test and is much better than that of the Pt/C catalyst, which indicates that nitrogen- and boron-doping may also help enhance the long-term stability of the catalyst. The Pt/C catalyst with a loading of 20% Pt was obtained from Umicore Ltd. (Germany).

Table 1
Electrocatalytic activity and kinetic parameters of the catalysts for ORR.

Catalyst	E_0 (V)	$E_{1/2}$ (V)	i_p (mA/cm ²)	b (mV/dec)	α	i_0 (mA/cm ²)
Pristine CNT	−0.189	−0.222	0.46	62.71	0.552	4.59×10^{-9}
N-CNT	−0.135	−0.168	0.84	43.64	0.368	2.15×10^{-9}
B-CNT	−0.124	−0.154	1.11	49.12	0.491	9.61×10^{-9}
N, B-CNT	−0.070	−0.131	1.35	55.87	0.584	6.26×10^{-8}
Pt/C	−0.020	−0.082	0.65	–	–	–

Fig. 4 shows the rotating-disk electrode (RDE) voltammogram tests and corresponding Koutecky-Levich plots of the catalysts at different potentials. The oxygen-reduction current density increased with increasing rotating speed, which originated from the enhanced oxygen diffusion on the electrode surface [52]. Based on the RDE tests, the electron transfer number (n) of ORR can be calculated according to Koutecky-Levich theory [53]:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_D} = \frac{1}{I_k} + \frac{1}{B\omega^{1/2}} \quad (2)$$

where I is the experimentally obtained current, I_k refers to the mass-transport-free kinetic current, I_D refers to the measured diffusion-limited current and ω is the electrode rotating speed. To calculate the electron transfer number, following equations are used along with Eq. (2):

$$B = 0.62nF(D_0)^{2/3}v^{-1/6}C_0 \quad (3)$$

$$I_k = nFkC_0 \quad (4)$$

where F is the Faraday constant (96485 C/mol), D_0 is the diffusion coefficient of O_2 in 1 M KOH (1.9×10^{-5} cm²/s), v is the kinetic viscosity (0.01 cm²/s), and C_0 is the bulk concentration of O_2 (1.2×10^{-6} mol/cm³). The constant 0.62 is adopted when the rotation speed ω is expressed in rad/s. Fig. 4b, d, f, and h shows the calculated electron transfer number of each catalyst at different potentials. The calculated electron transfer number of the catalysts distributed between two and four, which indicates the reduction of O_2 with the catalysts is a mixed process of two electron and four electron reactions. For general comparison, the electron transfer numbers of N, B-CNT are larger than other catalysts and more close to four, indicating the synergistic effect of dipolar-doped nitrogen and boron in N, B-CNT enhanced the four-electron oxygen-reduction reaction. Similar phenomenon was also reported in nitrogen- and boron-doped graphene catalyst, in which the electron transfer number was believed to be influenced by the doped elements [54]. The electron transfer numbers were also calculated with rotate ring disc electrode (RRDE) tests, as shown in Supplementary Information Fig. S5. The calculated results are in good accordance with the RDE results.

3.3. First-principles calculations

The effects of doped boron and nitrogen on ORR catalytic performance of CNT were calculated by B3LYP hybrid density functional theory (DFT, DMol3). The details of the calculations are provided in Supplementary Information. The calculated Mulliken charge distribution for the N, B-CNT and schematic representations of possible reaction patterns on the surface of N, B-CNT are displayed in Fig. 5A.

The modeling results indicate that boron and carbon atoms that adjacent to the nitrogen atom have a stronger positive charge density to counterbalance the strong electronegativity of nitrogen atom compared with that of pristine CNT and B-CNT structures [55–57]. The doped nitrogen in CNT can exist in both p-type and n-type states in the form of pyrrolic, pyridinic, and graphitic [58,59]. The pyrrolic nitrogen was sp³ hybridized, and pyridinic and graphitic nitrogen were sp² hybridized. The doped nitrogen enhanced the oxygen reduction activity, which was proved by both theoretical calculations and experimental tests [19,44,60]. DFT calculation, alongside local N-configuration mappings during plasma treatment, reveals that the origin of the improved capacitance was a certain N-configuration at basal planes [43,61]. Electrochemical characterizations clearly demonstrated excellent electrocatalytic activity of N-RGO for oxygen reduction in

Fig. 4. Rotating-disk electrode (RDE) voltammogram tests and corresponding Koutecky-Levich plot (I^{-1} v.s. $\omega^{-0.5}$) at different potentials of (a, b) pristine CNT, (c, d) N-CNT, (e, f) B-CNT, and (g, h) N, B-CNT.

alkaline electrolytes via a four-electron pathway. The total content of graphitic and pyridinic nitrogen atoms plays a key role in enhancing the electrocatalytic activity for ORR. The nitrogen-induced strong positive ionicity of boron and carbon atoms enhances the chemisorptions of O_2 and OH^- . The O_2 has more favorite priority to be adsorbed on the boron atom than OH^- and H_2O while the OH^- adsorbs at the end of O_2 to have an O_3H^-

configuration. This chemisorption will transit to a more stable state while the two OH^- are adsorbed on the adjacent carbon atoms of nitrogen atom and an O_2H^- on the boron atom in the water. The curve illustrates the activation energy changes in the process of oxygen reduction. Based on the calculation, the obtained oxygen reduction course may include the following reactions:

Fig. 5. (left) The calculated Mulliken charge distribution for the N, B-CNT. The blue ball is the doped nitrogen atom, the pink ball represents the doped boron atom, and the grey balls are carbon atoms. (right) Schematic representations of possible reaction patterns on the surface of N, B-CNT.

Reaction (5) first happened as shown in Fig. 5B (a) and (b), where oxygen molecular first absorbed on N, B-CNT. Reactions (7) and (8) are corresponding to Fig. 5B (c). Reaction (9) is corresponding to Fig. 5B (d), where the H_2O_2 are absorbed on the surface of N, B-CNT and eventually transit to two OH^- . The active energy changes with the change of oxygen transitional state. B-CNT showed higher oxygen reduction performance compared with N-doped carbon-nanotube. Quantum chemical calculations on boron-doped graphene proved that the doped boron weakened O—O stretching and extended the O—O bond length, which eventually enhanced the oxygen reduction catalytic characteristics [62,63]. The doped-boron atoms also introduced holes to the graphene, changing the electronic structure of the planer sheet and resulting in local positive charge centers. The positive charged areas on the flat surface attracted pyridine to form strong chemical bonds at the interface and promoted the adsorption of OOH^- on itself, facilitating oxygen reduction reaction.

4. Conclusions

The catalytic performance of pristine CNT, N-CNT, B-CNT, and N, B-CNT in oxygen reduction reaction was investigated. The N, B-CNT catalyst exhibited the highest activity and stability for ORR in alkaline solutions. The dipolar-doped nitrogen and boron form n-type and p-type active centers, which promote the four-electron transfer oxygen reduction reaction. This facile method used to prepare nitrogen and boron co-doped CNTs represents a general approach to synthesize high-efficiency and durable electrocatalysts for a wide range of electrochemical reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2016.10.201>.

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