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Synergetic effect of pyrrolic-N and doped boron in mesoporous carbon for electrocatalytic ozone production[†]

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The exploration of highly efficient and inexpensive electrochemical ozone production (EOP) electrocatalysts for various in situ industrial applications is a recent hot topic in the catalysis field. In this work, B, N co-doped mesoporous carbon materials were designed and their EOP performance was predicted via density functional theory (DFT). In accordance with the theoretical predictions, a multifunctional site, pyrrolic-N, B co-doped defective mesoporous carbon (D-BNC) material with a high content of pyrrolic N, which exhibits excellent EOP electrocatalytic activity, was successfully synthesized. The high activity of D-BNC can be attributed to the synergetic effect played by pyrrolic-N, B, its neighboring C elements, and the defects. Furthermore, the five-membered cyclic structure formed between B and the neighboring C atoms which connects to O₃ reduces the activation energy (0.41 eV) of the compound and promotes EOP. This work offers a new reference for the development of inexpensive metal free carbon-based electrocatalysts for EOP.

Introduction

Due to its strong oxidizing nature, O_3 is often used for *in situ* applications, such as deodorization, decolorization and sterilization.¹⁻⁴ While high ozone concentrations can be efficiently and easily produced *via* electrolysis by using a polymer electrolyte membrane (PEM), the electric discharge (corona) method requires a complex system design based on high-voltage power supply, gas feeds, and a mixing process.⁵⁻⁹ Currently, electrocatalysts including but not limited to β -PbO₂,¹⁰ Pt,^{11,12} Ni–Sb/SnO₂,^{11,12} and boron-doped diamond (BDD)^{13,14} have been employed for electrochemical ozone production

(EOP) by making use of their natural molecular oxygen adsorption mechanism.¹⁵ However, two main factors limit the use of PEM systems in commercial applications:¹⁶ (1) several electrocatalysts, such as β -PbO₂ and Sb, are harmful to human health and their use should be limited; (2) the high cost of Pt-and BDD-based anodes jeopardizes their large-scale commercialization and industrial application.^{11,17–21}

Diversified carbon-based non-metallic electrocatalysts show potential in displacing noble metals in energy conversion and storage processes. For this reason, several investigations focused on their optimization.^{22–25} However, rarely these studies tackle metal-free carbon-based materials to improve the EOP process.^{26–28} The O₂ and O₃ formation reactions and standard electrode potentials in a direct water electrolysis process can be expressed as follows:^{7,17,29}

Anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-, E^0 = 1.23 V$$
 (1)

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^-, E^0 = 1.51 V$$
 (2)

Cathode:

$$2H^+ + 2e^- \rightarrow H_2, E^0 = 0 V$$
 (3)

Since the potential E^0 for the oxidation of water to O_2 is 1.23 V (eqn (1)) and O_3 needs a voltage higher than 1.51 V to be produced (eqn (2)), O_2 is inevitably produced simultaneously with O_3 when the voltage is >1.51 V. This is known as the preferential oxygen evolution reaction (OER) since it is thermodynamically favored.^{17,30–32} Furthermore, EOP is a sixelectron reaction and involves the adsorption of a series of intermediates onto the catalyst surface, such as OH*, H*, O*, O_2^* , and O_3^* , and these intermediates at different adsorption sites need to react with each other to produce O_3 .³³ Therefore, it is vital to design a new local multifunctional site electrocatalyst. In addition, high-efficiency EOP electrocatalysis generally exhibits three key characteristics: (1) it fosters the adsorption of H₂O and its deprotonation into OH and O; (2) it facilitates the

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strong chemisorption of the O_2 molecule to guarantee its reaction with other adsorbed O^{*} atoms; and (3) it desorbs the O_3 species to improve the catalyst performance. The localization of multiple active centers can be effectively achieved by designing a catalyst which presents such features.

In this work, the adsorption of H_2O^* , O_2^* , and O_3^* , which plays a pivotal role in the EOP process, was calculated for a series of carbon-based materials to define the characteristics of an ideal EOP catalyst. Among the investigated samples, the pyrrolic-N and B co-doped defective mesoporous carbon (D-BNC) structure exhibits efficient H_2O dissociation adsorption, strong O_2 adsorption, and weak O3 adsorption. Based on these findings, a low-cost metal-free mesoporous carbon material with a high concentration of pyrrolic-N and B (D-BNC) was successfully prepared and analyzed. The theoretical and experimental results reveal that D-BNC can serve as a high-performance electrocatalyst in the EOP process. The theoretical calculations further show that the origin of such enhanced EOP activity of D-BNC can be attributed to the synergetic effect of pyrrolic-N and B. Pyrrolic-N promotes the decomposition of H₂O and OH into the O intermediates. B and the neighboring C atoms provide the active sites for both O₂ and O₃ adsorption. The stable five-membered cyclic structure reduces the reaction barrier for O₃ formation and avoids its decomposition. In addition, the porous morphology of D-BNC offers a higher number of more accessible active sites and improves the rapid mass transfer of O₃.

Results and discussion

BNC models with and without defects (D) were screened as shown in in Fig. 1a (C, BN, BC, NC, BNC, D-C, D-BC, D-NC, D-BNC-1 and D-BNC-2). Following criterion (1), the adsorption energy for H₂O adsorption for each structure was computed (Fig. 1b). The results show that H₂O dissociates both in the D-BNC-1 ($E_{ads} = -2.00 \text{ eV}$) and D-BNC-2 ($E_{ads} = -1.93 \text{ eV}$) structures due to the synergetic effect of B, N co-doping and the defects. In the case of the other catalysts, only a physical adsorption is observed. Following criterion (2), the D-BNC-1 species was further investigated since it exhibits a relatively strong adsorption for the O₂ species ($E_{ads} = -1.85$ eV) when compared to D-BNC-2 ($E_{ads} = -1.23$ eV). More importantly, following criterion (3), the O₃ adsorption is relatively weak for D-BNC-1 and D-BNC-2. Therefore, the D-BNC structure with a unique electronic structure is predicted as a suitable metalfree carbon based electrocatalyst for EOP, which satisfies all three screening criteria. Since the heteroatoms (e.g. N and B) are doped in a graphitic structure, more active sites with different electronic and structural properties are generated on their neighboring carbon atoms. The carbon elements in the surroundings of B carry negative charges due to the strong electronegativity of C when compared to the B atom (Fig. S1[†]). Such a neighboring carbon is a vital active site for the adsorption of the O and O2 intermediates. Moreover, the defective carbon atoms may play a crucial role in the electrocatalytic reaction due to their abundant unsaturated carbon sites. The co-doped atoms and the unsaturated carbon atoms provide



Fig. 1 Screening procedure of a series of heteroatom doped carbon models. (a) Density functional theory (DFT) calculations of the geometric structure of heteroatom-doped carbon materials. C: carbon; BC: B atom doped with carbon; NC: N atom doped with carbon; BNC: B and N atoms co-doped with carbon; D-C: carbon defect; D-BC: B atom doped with a carbon defect; D-NC: N atom doped with a carbon defect; D-BNC-1: B and N (pyrrolic N) atoms co-doped with a carbon defect; D-BNC-2 (pyridinic N): B and N atoms co-doped defective carbon; (b) adsorption energies of the H₂O, O₂, and O₃ species onto different catalysts. The color code is as follows: C brown, N blue, B green and H pink.

a series of potential active sites that make D-BNC a potentially metal-free EOP electrocatalyst.

Encouraged by these results, we prepared a D-BNC sample via a facile two-step synthetic strategy and used it in the EOP. Its B and N content was systematically controlled by adjusting the B and N precursor proportion. Fig. 2a illustrates the preparation process of D-BNC by varying the ratio of two different B and N precursors. This procedure allows one to systematically investigate the effects of the concentration of the doped functional groups on the EOP performance. Briefly, a homogeneous mixture of boric acid and urea was used as the boron and nitrogen source. Resol was employed as a carbon precursor and F127 was employed as a pore-directing agent. The samples were obtained via a two-step polymerization and pyrolysis procedure (for further details, refer to the Experimental procedure in the ESI[†]). The elemental content of the different catalysts is listed in Table S1[†] and it was obtained via elemental analysis (EA) and ICP-MS. The morphology of the samples was investigated by transmission electron microscopy (TEM). Fig. 2b and c display the TEM images of the D-BNC sample and the successful introduction of the nanosized pores into the catalyst structure can be observed. The porous morphology can be attributed to the effects of the thermal decomposition of the precursors. The energy dispersive X-ray (EDX) mapping of C, N, B, and O



Fig. 2 Preparation and characterization of D-BNC. (a) Schematic illustration of the D-BNC preparation process and EOP reaction of the D-BNC sample. (b–d) D-BNC TEM images and its corresponding EDX elemental mapping of B, C, N, and O. (e) Nitrogen adsorption and desorption isotherms of the D-BNC and BNC samples. (f, g) High-resolution XPS of B 1s and N 1s of D-BNC.

(Fig. 2d) shows that heteroatoms originate from boric acid and urea (B and N) overlap, confirming their homogeneous distribution in the carbon skeleton.

The TEM observations reveal that D-C, D-BC, and D-NC maintain a porous morphology (Fig. S4a-c[†]). In contrast, no visible holes can be observed in the BNC sample (Fig. S4d[†]). The TEM images of other different catalysts (Fig. S5[†]) show no effect on the porous morphology after being treated in an Ar atmosphere, while the pyrolysis temperature and time change the porous morphology of D-BNC obviously. The results of the TEM images indicate that the resol and F127 contribute to the formation of the mesoporous structure of the catalysts. The porosity and the surface area of D-BNC were investigated via the Brunauer-Emmett-Teller (BET) method. The typical adsorption-desorption isotherm curves of the samples are reported in Fig. 2e. The D-BNC sample possesses a larger surface area (378.7 $m^2 g^{-1}$) than BNC (257.8 $m^2 g^{-1}$). The pore size distribution of D-BNC is contained in the 20-40 nm range, and this result satisfactorily matches the HRTEM values (Fig. S6[†]). These results demonstrate that the D-BNC porous structure can be adjusted by changing the precursors and carbonization conditions and that a B, N co-doped mesoporous carbon material has been successfully prepared. Such a dense pore morphology introduces additional defect active sites into the catalyst structure and leads to a fast charge and mass transport during the EOP process, improving its performance.

The elemental composition of the samples was verified *via* the peak deconvolution of their X-ray photoelectron spectroscopy (XPS) results. Fig. S7† shows the spectra of the different samples. The spectrum of D-BNC exhibits two pronounced B 1s and N 1s features, indicating the incorporation of B, N into the carbon matrix *via* thermal annealing in the presence of boric acid and urea. The analysis shows that the high-resolution spectra of the B 1s peak (Fig. 2f) of the D-BNC sample can be deconvoluted into three peaks corresponding to B-C (190.0 eV), B-N (191.5 eV), and B-O (192.5 eV).34-37 No B-N feature can be observed in the D-BC sample (Fig. S8[†]), indicating that B-N peak formation is affected by the preparation method of the specimen. The N 1s peak of D-BNC (Fig. 2g) can be fitted with three peaks, which correspond to pyridinic N (399.0 eV), pyrrolic N (400.4 eV), and quaternary N (401.9 eV).³⁸⁻⁴¹ The concentration of pyrrolic N (71%) in D-BNC is particularly higher when compared to pyridinic N and quaternary N, whereas the intensity of the N 1s peak shows that the pyrrolic N concentration reaches a much lower level in D-NC and BNC (Fig. S9 and S10[†]). When B doping occurs onto the carbon surface, B interacts with two C atoms to form two B-C bonds, leaving an empty sp³ orbital and a half occupied sp³ orbital. Therefore, the incorporated B atom exhibits a strong binding strength with a H₂O and O₂ molecule. According to the Bader charge analysis, the B atom has a positive charge, and the pyrrolic N and pyridinic N elements have negative ones of -0.93 |e| and -1.22 |e|, respectively. For this reason, the N atom can easily be captured by the H atom of a water molecule, fostering the H₂O decomposition into OH and H in the first step of the EOP reaction.

The chemical composition of different catalysts (Fig. S11[†]) was revealed by X-ray diffraction (XRD). A broad diffraction peak, which corresponds to the (002) diffraction of graphitic carbon, was observed.^{40,42} The structure of the electrocatalysts was further characterized by Raman spectroscopy (Fig. S12[†]). The spectra exhibit two peaks, which are located at 1590 and 1340 cm^{-1} , corresponding to the G band of the sp² graphite carbon and to the D band of sp³-disordered carbon atoms, respectively. The D-BNC sample exhibits the most pronounced $I_{\rm D}/I_{\rm G} = 1.00$ and this implies that its defect concentration is the highest and that these structural defects affect the electrocatalytic EOP activity.43 The results show that B, N co-doped carbon samples with a mesoporous structure were successfully obtained. Moreover, the B and N dopants vary the electronic structure of the carbon lattice, influencing their EOP performance.

To evaluate the EOP activity of the electrocatalysts, a series of linear sweep voltammetry (LSV) measurements was conducted in a saturated K₂SO₄ aqueous solution by using a typical threeelectrode configuration at room temperature. To perform a systematic study, the D-BNC elements, B : N dopant ratio, and pyrolysis temperature were varied. Fig. S13[†] shows that the optimum B: N molar ratio is 1.5: 1.0 and that the optimal temperature is 900 °C. The polarization curves confirm that the EOP process for the D-BNC sample is rather efficient: an onset potential of 2.54 V versus the reversible hydrogen electrode (RHE) (iR corrected) can be obtained for a current density of 10 mA cm⁻². The electrocatalytic EOP activity of D-BC, D-NC, D-C, BNC, commercial BN, and β -PbO₂ was also determined under the same conditions to obtain a comparative measurement. Fig. 3b shows that the volcanic curve confirms that the overpotential of D-BNC for a current density of 10 mA cm⁻² is higher than for the other electrocatalysts in general and for the widely



Fig. 3 Electrochemical ozone production activity evaluation. (a) EOP polarization curves for different catalysts in a saturated K_2SO_4 aqueous solution. The curves were obtained by setting a potential scan rate of 5 mV s⁻¹. (b) EOP potential of all catalysts obtained from (a) for a current density of 10 mA cm⁻². (c) Dissolved ozone concentrations of β -PbO₂ and D-BNC when different potentials are applied. (d) Dissolved ozone concentrations at 3.0 V vs. RHE for different catalysts. (e) Gaseous ozone concentrations at 25 mA cm⁻² for different catalysts. (f) DMPO-'OH ESR measurement for the D-BNC sample.

used β -PbO₂. In addition, the Tafel slope results were analyzed to further understand the electrocatalytic kinetics of the specimens (Fig. S14†). The curves clearly exhibit two linear segments, which suggest that two anodic processes take place.^{44,45} The lowcurrent-density region is dominated by the OER process. In this region, the large Tafel slope value of the D-BNC results in a slower OER catalytic kinetics. At the higher current densities, the value of the Tafel slope is determined by the synchronous OER and EOP processes. Moreover, the D-BNC specimen exhibits a larger Tafel slope in this region, which implies that much more efficient EOP electrocatalytic kinetics than that in the β -PbO₂ case takes place.²⁷

In order to have a more reliable estimate of the EOP performance, both qualitative and quantitative tests to obtain the concentration of dissolved O_3 and gaseous O_3 were conducted. A rapid detection reagent was employed to detect the dissolved O_3 . The results are shown in Fig. S15:† the color depth represents the concentration of dissolved O_3 – the deeper the color is, the higher is the concentration of dissolved O_3 . Moreover, the performance of an electrocatalyst carrier carbon fiber (CF) was investigated. The results show that the CF substrate contributes only partially to the intrinsic EOP activity and that D-BNC plays the major role in the determination of the EOP

performance. In addition, indigo disulphonate spectrophotometry (IDS) was used to quantitatively analyze the concentration of dissolved O_3 at different voltages (Fig. 3c, d, S16 and S17†): D-BNC produces the highest concentration of dissolved O_3 (3.5 mg L⁻¹) for 3.0 V vs. RHE.

Furthermore, the gaseous O₃ released from the cell was also detected with an ozone monitor. Fig. 3e shows that initially the concentration of gaseous O3 in the D-BNC sample is lower than in the β -PbO₂ case. After 10 minutes, the concentration in D-BNC is higher than that in the β -PbO₂ sample. A moistened starch potassium iodide paper was suspended above the working electrode in the anode to provide a qualitative comparison of the concentration of gaseous O3 for the D-BNC and β -PbO₂ samples (Fig. S18[†]).²⁷ In the case of the β -PbO₂ electrode, the gaseous O_3 was detectable until 37.5 mA cm⁻². Excitingly, the gaseous O3 concentration was found to be enhanced by using the D-BNC electrode, which visually confirmed the generation of gaseous O_3 at 25 mA cm⁻². By combining this observation with the detection of dissolved and gaseous O₃, we confirm that D-BNC exhibits an excellent performance for the EOP process. Although the faradaic efficiency (FE) value (1.7%) measured for the D-BNC sample is rather lower than that of the other metal based electrocatalysts (Table S2[†]), future investigations are planned to improve it. Moreover, the stability of the EOP process for D-BNC was tested by using a current density of 20 mA cm^{-2} (Fig. S19[†]). After 100 hours, almost no degradation can be observed for the D-BNC catalyst, confirming that this compound has high electrocatalytic EOP durability in a neutral solution. In addition, the TEM images, XRD and XPS of D-BNC after the stability evaluation (Fig. S20–S22[†]) show that the catalyst is almost unchanged, further demonstrating the outstanding stability of this material. Such results pave the way for the use of D-BNC as a metal free, safe, and low cost EOP electrocatalyst.

The measurement of the electrochemical double-laver capacitance (C_{dl}) was carried out to estimate the relative electrochemically active surface area (ECSA). The cyclic voltammetry (CV) curves presented in Fig. S23 and S24[†] were obtained by using different scan rates in the 0.61-0.81 V vs. RHE potential range. The normalized exchange current density $(J_{0,normalized})$ was calculated as shown in Table S3:† the J_{0.normalized} value for D-BNC is similar to the one of other electrocatalysts and this further indicates that the high EOP performance of this material is generated by the intrinsic activity induced by the defects and B, N co-doping.⁴⁶ A series of electrochemical impedance spectroscopy (EIS) measurements was carried out in the frequency range of 0.1-100 kHz. The Nyquist plots show the impedance for the different catalysts (Fig. S25⁺). Moreover, D-BNC exhibits a remarkably low charge transfer resistance when compared to the other compounds: this supports the hypothesis that B, N co-doping reduces the charge transfer resistance, induces high electrical conductivity, and fosters quicker EOP kinetics.47,48 The electron paramagnetic resonance (EPR) resonance signal of D-BNC exhibits a g-value of 2.0036 (Fig. S26[†]), demonstrating the presence of vacancies.⁴⁹ Moreover, such a signal of D-BNC is stronger than that of the BNC and D-C samples, which implies the presence of a larger

concentration of vacancies in D-BNC and it indicates that the defects may contribute in improving the EOP performance of the material.

To further investigate the EOP mechanism, a series of electron spin resonance (ESR) measurements was performed by using 5,5-dimethyl-1-pyrroline (DMPO) as the spin-trapping agent. Fig. 3f shows well-defined quartet lines at 15 min with a peak height ratio of 1:2:2:1, which can be assigned to the typical spin adduct of DMPO-'OH.^{27,50} No signal can be detected at 0 min, revealing that 'OH is generated during the EOP process. The ESR peaks of D-BNC are similar to the β -PbO₂ ones (Fig. S27†) and this confirms that D-BNC follows a common O₃ evolution pathway.²⁷ The EOP electrocatalytic performance of D-BNC-1 was then assessed *via* the CI-NEB method calculation. Fig. 4a shows that O₃ formation consists of four reaction steps:

$$H_2O \rightarrow OH + H^+ + e^- \tag{R1}$$

$$OH \rightarrow O + H^+ + e^-$$
 (R2)

$$2O \to O_2(abs) \to O_2 \tag{R3}$$

 $O_2 + O \rightarrow O_3(abs) \rightarrow O_3$ (R4)

The main purpose of the first two steps is to decompose H_2O^* and OH^* and to form O^* intermediates. The DFT calculations indicate that the H_2O molecule can dissociate automatically into OH^* and H^* and that OH^* can deprotonate

Fig. 4 EOP mechanism of the D-BNC-1 electrocatalyst. (a) Schematic of the EOP mechanism of the D-BNC electrocatalyst. (b) Energy profile for O_3 formation: formation of an O intermediate upon OH deprotonation; the O_2 molecule is adsorbed from two adsorbed oxygen atoms and the transformation of O_2^* and O^* into O_3 occurs. (c) Optimized structures of O^* , O_2^* , and O_3^* adsorbed onto D-BNC-1. (d) Charge density differences (CDDs) between O^* , O_2^* , O_3 , and D-BNC-1 with an isovalue of 0.005 e Å⁻³. (e) Plots of the electronic localized function (ELF) of O_3 onto D-BNC. The red regions indicate a high local electron distribution, the green regions represent an electronic -gas-like pair probability, and the blue regions show a high electronic delocalized distribution in the 0.0–1.0 b range.

forming O* and H* with a reaction barrier of 0.36 eV (Fig. 4b). Due to the low value of the reaction barrier, these two steps can occur almost spontaneously, whereas the formation of O2 and O₃ is challenging. The distances between the B active center and a pyrrolic-N atom on the D-BNC-1 surface are only 3.54 Å based on the DFT calculation. Thus, two O* intermediates, which are located at the top site of the B atom and on a bridge site of the C and pyrrolic-N atoms, have sufficient potential to form an adsorbed O_2^* molecule – if their geometric structure is taken into consideration. As shown in Fig. S28a,† an O* atom, which is positioned on a B element, exhibits a negative charge of 1.20 |e| that is higher than that of the O^* at the bridge site (0.57 |e|). Hence, the bridge O* shows a strong disposition move toward the top O* atom and to form an adsorbed O2 molecule since the reaction barrier is only 0.38 eV. Moreover, the O₂ molecule adsorbed onto D-BNC-1 has an adsorption energy of -1.85 eV due to strong electron transfer which occurs between O_2^* and D-BNC-1 (Fig. 4c–e). If the O_2^* molecule remains on the D-BNC-1 surface long enough, the formation of O_3 can occur in the next step of the reaction.

During the last step of O₃ formation, B and its neighboring C atoms provide an adsorption site for O₂^{*} and O^{*}, respectively: the multifunctional sites of the D-BNC-1 catalyst play a key role in the O2 and O3 formation process. As shown in the Fig. S28b,† the O_2^* molecule is adsorbed onto the B site in a single-site configuration and it is only 2.70 Å away from the adsorbed O*. On the other hand, the electronic-gas-like pair which is formed between O2* and O* almost overlaps based on the ELF analysis. These results indicated that O_2^* and O^* have potential to form an O₃ molecule. Since 1.33 |e| transfer from D-BNC-1 to O^* , the adsorbed O_2^* molecules are closer to O^* and can form an O₃ molecule with a five-membered cyclic configuration. The initial O–O bond length of 1.36 Å for an adsorbed O_2^* molecule elongates to 1.60 Å in the case of the O_3 molecule. Due to the orbital symmetry match between the non-localized π electron cloud of O3 and D-BNC-1 via the five-membered cyclic structure, O₃, the central B atom, and its neighboring C element form a special five-membered cyclic configuration (Fig. S29[†]) with an adsorption energy of -1.15 eV, which is higher than that of the single-site configuration (-0.86 eV). The large adsorption strength, charge transfer, and the increase in the stability of O₃ may play a central role in the EOP process of D-BNC-1. The reaction barrier for O₃ formation is 0.41 eV, which is identical to the one of PbO₂ and lower than that of NiSb/SnO₂ (0.76 eV).⁵¹ Such a low reaction barrier strongly supports the analysis presented in this manuscript. Moreover, according to the results, the high performance of the EOP process of D-BNC-1 can be attributed to its local multifunctional sites. In addition, the heteroatoms and defects play different roles during the different EOP stages and the high content of defects defines the electron configuration with higher charge densities for water decomposition and favors the mass transfer process.

Conclusions

In summary, this study presents a facile and efficient strategy to prepare a metal free D-BNC material by using theoretical



guidelines. The mesoporous D-BNC compound exhibits excellent electrocatalytic performance toward EOP when compared to singly doped carbon materials and commercial β -PbO₂. Both the qualitative and quantitative tests to evaluate the concentration of dissolved O₃ and gaseous O₃ produced from D-BNC support the theoretical data. The outstanding EOP performance originates from the presence of local multifunctional sites including pyrrolic-N, boron, neighboring C, and the defects in the D-BNC structure. Moreover, the five-membered cyclic structure between O₃ and D-BNC-1 exhibits high structural stability, which offers significant advantages in terms of O₃ synthesis. The current work provides new insights into the design and synthesis of a metal free heteroatom-doped carbon for EOP.

Conflicts of interest

The authors declare no competing financial interests.

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References

- 1 K. Ikehata, N. Jodeiri Naghashkar and M. Gamal El-Din, Ozone: Sci. Eng., 2006, 28, 353-414.
- 2 B. L. Loeb, Ozone: Sci. Eng., 2018, 40, 3-20.
- 3 R. Pandiselvam, S. Sunoj, M. R. Manikantan, A. Kothakota and K. B. Hebbar, *Ozone: Sci. Eng.*, 2016, **39**, 115–126.
- 4 R. G. Rice, Ozone: Sci. Eng., 1996, 18, 477-515.
- 5 K. Onda, T. Ohba, H. Kusunoki, S. Takezawa, D. Sunakawa and T. Araki, *J. Electrochem. Soc.*, 2005, **152**, D177–D183.
- 6 S. Han, J. Kim, K. C. Singh and R. S. Chaudhaty, *Indian J. Chem.*, 2004, 1599–1614.
- 7 F. Okada and K. Nay, Intech, 2012, 12, 243-272.
- 8 N. Kishimoto, T. Nakagawa, M. Asano, M. Abe, M. Yamada and Y. Ono, *Water Res.*, 2008, **42**, 379–385.
- 9 Y. Cui, Y. Wang, B. Wang, H. Zhou, K.-Y. Chan and X.-Y. Li, *J. Electrochem. Soc.*, 2009, **156**, E75–E80.
- 10 R. Amadelli, L. Samiolo, A. D. Battisti and A. B. Velichenko, *J. Electrochem. Soc.*, 2011, **158**, P87–P92.
- 11 P. A. Christensen, T. Yonar and K. Zakaria, *Ozone: Sci. Eng.*, 2013, 35, 149–167.
- 12 A. R. Rahmani, G. Azarian and D. Nematollahi, *J. Electroanal. Chem.*, 2018, **824**, 216–225.
- 13 K. Arihara, C. Terashima and A. Fujishima, *Electrochem. Solid-State Lett.*, 2006, **9**, D17–D20.
- 14 J. Choi, C. Kim, J. Kim, S. Kim, Y. Tak, C. Lee and J. Yoon, *Desalin. Water Treat.*, 2015, 57, 10152–10158.
- 15 P. Tatapudi, J. Electrochem. Soc., 1993, 141, 1174–1178.
- 16 Y.-H. Wang, S. Cheng and K.-Y. Chan, *Green Chem.*, 2006, 8, 568.

- 17 Y. Nishiki, N. Kitaori and K. Nakamuro, *Ozone: Sci. Eng.*, 2011, 33, 114–120.
- 18 P. A. Christensen and A. Imkum, *Ozone: Sci. Eng.*, 2011, 33, 389–395.
- 19 A. Kraft, M. Stadelmann, M. Wunsche and M. Blaschke, *Electrochem. Commun.*, 2006, **8**, 883–886.
- 20 P. A. Christensen, K. Zakaria and T. P. Curtis, *Ozone: Sci. Eng.*, 2012, 34, 49–56.
- 21 Y.-H. Wang, S. Cheng, K.-Y. Chan and X. Y. Li, *J. Electrochem. Soc.*, 2005, **152**, D197–D200.
- 22 Y. Fang and X. Wang, *Angew. Chem., Int. Ed.*, 2017, **56**, 15506–15518.
- 23 Y. Ding, X. Huang, X. Yi, Y. Qiao, X. Sun, A. Zheng and D. S. Su, Angew. Chem., Int. Ed., 2018, 57, 13800–13804.
- 24 S. Zhao, D. W. Wang, R. Amal and L. Dai, *Adv. Mater.*, 2019, 31, 1801526.
- 25 R. Paul, L. Zhu, H. Chen, J. Qu and L. Dai, *Adv. Mater.*, 2019, **31**, 1806403.
- 26 P. A. Christensen, W. F. Lin, H. Christensen, A. Imkum, J. M. Jin, G. Li and C. M. Dyson, *Ozone: Sci. Eng.*, 2009, 31, 287–293.
- 27 C. Zhang, Y. F. Xu, P. Lu, X. H. Zhang, F. F. Xu and J. L. Shi, *J. Am. Chem. Soc.*, 2017, **139**, 16620–16629.
- 28 L. M. Da Silva, L. A. De Faria and J. F. C. Boodts, *Electrochim. Acta*, 2003, **48**, 699–709.
- 29 M. I. Awad, M. M. Saleh and T. Ohsaka, J. Electrochem. Soc., 2006, 153, D207–D212.
- 30 X. Wang, A. Vasileff, Y. Jiao, Y. Zheng and S. Z. Qiao, Adv. Mater., 2019, 31, 1803625.
- 31 K. Gao, B. Wang, L. Tao, B. V. Cunning, Z. Zhang, S. Wang, R. S. Ruoff and L. Qu, *Adv. Mater.*, 2019, **31**, 1805121.
- 32 L. Tao, Y. Wang, Y. Zou, N. Zhang, Y. Zhang, Y. Wu, Y. Wang,
 R. Chen and S. Wang, *Adv. Energy Mater.*, 2019, 1901227.
- 33 G. Gibson, A. Morgan, P. Hu and W.-F. Lin, *Chem. Phys. Lett.*, 2016, 654, 46–51.
- 34 X. Yu, P. Han, Z. Wei, L. Huang, Z. Gu, S. Peng, J. Ma and G. Zheng, *Joule*, 2018, 2, 1610–1622.
- 35 F. Sun, Z. Qu, J. Gao, H. B. Wu, F. Liu, R. Han, L. Wang,
 T. Pei, G. Zhao and Y. Lu, *Adv. Funct. Mater.*, 2018, 28, 1804190.
- 36 S. Chen, Z. Chen, S. Siahrostami, D. Higgins, D. Nordlund, D. Sokaras, T. R. Kim, Y. Liu, X. Yan, E. Nilsson, R. Sinclair, J. K. Norskov, T. F. Jaramillo and Z. Bao, *J. Am. Chem. Soc.*, 2018, **140**, 7851–7859.
- 37 H. Tabassum, W. Guo, W. Meng, A. Mahmood, R. Zhao,
 Q. Wang and R. Zou, *Adv. Energy Mater.*, 2017, 7, 1601671.
- 38 Y. Zheng, Y. Jiao, L. Ge, M. Jaroniec and S. Z. Qiao, Angew. Chem., Int. Ed., 2013, 52, 3110–3116.
- 39 L. Qin, L. Wang, X. Yang, R. Ding, Z. Zheng, X. Chen and B. Lv, J. Catal., 2018, 359, 242–250.
- 40 M. Wang, Y. Yang, Z. Yang, L. Gu, Q. Chen and Y. Yu, *Adv. Sci.*, 2017, 4, 1600468.
- 41 T. Sun, J. Wang, C. Qiu, X. Ling, B. Tian, W. Chen and C. Su, *Adv. Sci.*, 2018, **5**, 1800036.
- 42 C. Huang, C. Chen, M. Zhang, L. Lin, X. Ye, S. Lin, M. Antonietti and X. Wang, *Nat. Commun.*, 2015, **6**, 7698.

- 43 S. Wang, L. Zhang, Z. Xia, A. Roy, D. W. Chang, J.-B. Baek and L. Dai, *Angew. Chem., Int. Ed.*, 2012, **51**, 4209–4212.
- 44 R. Amadelli, A. Maldotti, A. Molinari, F. I. Danilov and A. B. Velichenko, *J. Electroanal. Chem.*, 2002, **534**, 1–12.
- 45 M. H. P. Santana, L. A. De Faria and J. F. C. Boodts, *Electrochim. Acta*, 2004, **49**, 1925–1935.
- 46 X. Zhong, Y. Sun, X. Chen, G. Zhuang, X. Li and J.-G. Wang, *Adv. Funct. Mater.*, 2016, **26**, 5778–5786.
- 47 H. Tabassum, R. Zou, A. Mahmood, Z. Liang, Q. Wang,
 H. Zhang, S. Gao, C. Qu, W. Guo and S. Guo, *Adv. Mater.*,
 2018, 30, 1705441.
- 48 X. Cheng, D. Li, F. Liu, R. Xu and Y. Yu, *Small Methods*, 2018, 3, 1800170.
- 49 Z. Yang, B. Chen, W. Chen, Y. Qu, F. Zhou, C. Zhao, Q. Xu, Q. Zhang, X. Duan and Y. Wu, *Nat. Commun.*, 2019, **10**, 3734.
- 50 Z. Guo, Y. Xie, J. Xiao, Z. J. Zhao, Y. Wang, Z. Xu, Y. Zhang, L. Yin, H. Cao and J. Gong, *J. Am. Chem. Soc.*, 2019, 141, 12005–12010.
- 51 G. Gibson, Z. Wang, C. Hardacre and W.-F. Lin, *Phys. Chem. Chem. Phys.*, 2017, **19**, 3800–3806.