Oxygenated boron-doped carbon via polymer dehalogenation as an electrocatalyst for high-efficiency O₂ reduction to H₂O₂

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ABSTRACT The direct electrochemical synthesis of H₂O₂ from O₂ is currently the most promising alternative to energy-intensive industrial anthraquinone oxidation/reduction methods. However, its widespread use is hampered by the lack of efficient low-cost electrocatalysts. In the current study, oxygenated boron-doped carbon (O-BC) materials were realized via a green synthetic strategy involving polymer dehalogenation and employed as electrode materials for the electrochemical synthesis of H₂O₂ via a 2e[−] oxygen reduction. The catalytic activity of the O-BC materials was optimized through systematic variation of the boron source (H₃BO₃) dosage and annealing temperature. Electrochemical measurements revealed that the optimal sample (O-BC-2-650) exhibited a selectivity of 98% for the 2e[−] oxygen reduction to H₂O₂ and an average H₂O₂ production rate of 412.8 mmol g_{cat}^{−1} h^{−1} in an H-type alkaline electrolyzer. Density functional theory simulations indicated that the functionalization of active B sites with one oxygen atom provides the lowest Gibbs free energy change (ΔG) of 0.03 eV for the hydrogenation of *O₂, while functionalization with zero or two O atoms results in much larger ΔG values (0.08 and 0.10 eV, respectively). Thus, this work details a new type of green, low-cost, and metal-free electrocatalyst for H₂O₂ production.

Keywords: doped carbon material, oxygenated dopant, boron, oxygen reduction reaction, hydrogen peroxide

INTRODUCTION

H₂O₂ is an eco-friendly oxidant that produces clean water as the main byproduct and is used extensively in the fields of chemistry and environmental remediation [1–3]. The industrial synthesis of H₂O₂ is heavily dependent on anthraquinone oxidation/reduction methods, which involve complex procedures, high energy consumption, and the generation of organic byproducts [4–6]. Accordingly, alternative H₂O₂-synthesis methods are desired. One promising alternative is the two-electron electrochemical oxygen reduction reaction (2e[−] ORR), which enables straightforward, eco-friendly, low-cost H₂O₂ production [7–10]. The most advanced 2e[−] ORR electrocatalysts are currently noble-metal-based, for instance, Pt/Pd/Au-based alloys [11–14], which provide yield rates of 0.06 to 546 mmol g_{cat}^{−1} h^{−1}. How-

ever, their high cost limits their large-scale industrial application. Therefore, the development of low-cost and efficient 2e[−] ORR catalysts is a key challenge.

In recent years, numerous metal-free heteroatom-doped carbonaceous materials with good 2e[−] ORR selectivities have been demonstrated as potential catalysts for this process [15–19]. For instance, Kim *et al.* [20] reported that graphene oxide annealed at 600°C exhibits excellent H₂O₂ selectivity (~100%), high stability (99% activity loss at >15 h), and very low overpotential (<10 mV). Furthermore, Li *et al.* [21] synthesized nitrogen-rich few-layer graphene and demonstrated experimentally that its pyridine-N content is positively correlated to H₂O₂ yield. Excellent selectivity of over 95% was obtained for the conversion of O₂ to H₂O₂ via the 2e[−] ORR.

It is well established that the activity and selectivity of the ORR at active carbon sites can be adjusted by introducing heteroatoms to their neighboring sites. Specific doping configurations including pyridinic N [16,18,22–25], O [15,26,27], and F [28] have been reported to be effective for promoting the 2e[−] ORR pathway at their corresponding carbon sites. In addition to the above-mentioned heteroatom dopants, boron has a lower electronegativity (2.04) than that of carbon (2.55). Thus, a B site is positively charged when situated adjacently to a C site, facilitating the chemisorption of O₂ molecules and promoting the ORR at B instead of nearby C sites [29–31]. Nevertheless, the use of self-initiative heteroatom dopants like B to promote the 2e[−] ORR remains relatively under researched.

In the present study, a simple, cost-effective, and nontoxic method to access oxygenated B-doped carbon material (O-BC) for promoting the 2e[−] ORR was developed. The B doping was realized under mild synthesis conditions by coupling boric acid with dehalogenated polymeric carbon at room temperature via ball milling. Furthermore, the byproducts of this process (H₂O and KCl) are nontoxic and environmentally friendly. The catalytic activity of O-BC for the 2e[−] ORR was optimized by systematic variation of the H₃BO₃ dosage and annealing temperature. The optimal sample (O-BC-2-650) exhibits a rich hierarchically porous structure and a high B content (up to 5.3 at%), and it provides excellent 2e[−] ORR performance, i.e., a 2e[−] selectivity of over 98%, outstanding long-term stability (>10 h), and an average H₂O₂ yield rate exceeding 400 mmol g_{cat}^{−1} h^{−1} (in an H-type electrolyzer). Density func-

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tional theory (DFT) calculations indicate that the B atom in the BC_2O structure is the preferred active site for the 2e^- ORR, and this is attributed to its optimized OOH^* binding.

EXPERIMENTAL SECTION

Materials and reagents

Boric acid (H_3BO_3 , 99.5%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Polyvinylidenechloride (PVDC) was purchased from Solvay (American company). Hydrochloric acid (HCl), potassium hydroxide (KOH), and carbon black were purchased from Beijing Chemical Works. Absolute ethanol was purchased from Tianjin Kemeiou Chemical Reagent Co., Ltd. Nafion solution (5 wt%) was purchased from DuPont China. All chemical reagents can be used without further purification. All water used in the experiment was purified using the Millipore system.

Preparation of oxygenated boron-doped carbon (O-BC)

Typically, PVDC (1.00 g), H_3BO_3 (1.14 g), KOH (2.00 g), and 20.0 mL of absolute ethanol were added into the zirconia (ZrO_2) ball mill jar, and then the mixture was ball-milled at 150 r min^{-1} for 4 h to obtain a yellow-brown slurry. It was dried in a vacuum oven at 90°C for 12 h, then washed with deionized water and dried to obtain a yellow powder, labeled as RT-O-BC-2. The unwashed RT-O-BC-2 samples were annealed at 550, 600, 650, or 700°C under Ar for 2 h, and then washed once with 5 wt% HCl and twice with deionized water, and dried in a vacuum oven at 60°C to obtain a series of O-BC, named as O-BC-2-550, O-BC-2-600, O-BC-2-650, and O-BC-2-700, depending on their annealing temperature. To explore the effect of the amount of B doping on the electrocatalytic properties of O-BC, a series of O-BC were obtained by regulating the amount of H_3BO_3 . O-C-650, O-BC-0.5-650, O-BC-1-650, and O-BC-3-650 were synthesized using H_3BO_3 dosages of 0, 0.287, 0.572, and 1.72 g, respectively, and other steps were the same as those for the synthesis of O-BC-2-650.

Characterizations

The morphology of the samples was observed using a scanning electron microscope (SEM, JSM-7401F) and a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2100, accelerating voltage = 20 kV). Powder X-ray diffraction (XRD) was recorded using a Shimadzu XRD-6000 (Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$, 40 kV) in the 2θ range of 5° – 90° . X-ray photoelectron spectra (XPS) were obtained with a Thermo ESCALAB 250Xi spectrometer. Raman spectra were examined at 532 nm on a LabRAM ARAMIS Raman spectrometer (HORIBA Jobin Yvon). The N_2 adsorption-desorption isotherms were measured using Micromeritics ASAP 2460. The pore size distribution was determined using the non-local DFT (NLDFT) method and the Brunauer-Emmett-Teller (BET) surface area was calculated by the BET equation.

Measurements of oxygen reduction to H_2O_2 on rotating ring-disk electrode

The electrochemical properties were firstly measured using a CHI 760E electrochemical workstation (Shanghai, Chenhua) with a three-electrode system in an O_2 -saturated 0.1 mol L^{-1} KOH electrolyte. The catalyst ink was prepared with 5.0 mg of samples, 1.0 mg of carbon black, $30.0 \mu\text{L}$ of Nafion (5 wt%), and

$470.0 \mu\text{L}$ of ethanol. Then, $10.0 \mu\text{L}$ of catalyst ink was drop-casted on a rotating ring-disk electrode (RRDE, PINE brand) with a mass loading of 0.201 mg cm^{-2} . The saturated calomel electrode (SCE) and platinum wire were used as the reference and counter electrodes, respectively, and RRDE loaded with dried catalyst as the working electrode. Cyclic voltammetry (CV) curves of the samples were tested at 10 mV s^{-1} over a potential range of 0–1 V (vs. reversible hydrogen electrode (RHE)). Linear sweep voltammetry (LSV) curves of the samples were obtained at 5 mV s^{-1} with the electrode rotating at 1600 r min^{-1} . All the potentials were calibrated to an RHE according to the Nernst equation (Equation (1)) [32]:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.098\text{pH} + 0.241, \quad (1)$$

where E_{RHE} is the potential relative to RHE, and E_{SCE} is the measured potential relative to the SCE reference electrode. The transfer electron number (n) and the H_2O_2 yield were determined by the following equations [33–36]:

$$n = 4 \frac{I_d}{\left(\frac{I_r}{N}\right) + I_d}, \quad (2)$$

$$\text{H}_2\text{O}_2 \text{ \%} = 200 \frac{I_r}{\left(\frac{I_r}{N}\right) + I_d}, \quad (3)$$

where I_d is the disk current, and I_r is the ring current. The current collection efficiency N for the Pt ring electrode is 0.37.

Measurements of H_2O_2 production in H-cell electrolyzer

The measurement of H_2O_2 productions was carried out in a homemade two-chamber H-type electrolyzer [21,37]. Selemion AHO membrane (CSO, Selemion, Japan) was used as the separator. The electrolyte solution for both anode and cathode was 145 mL of 0.1 mol L^{-1} KOH. The H_2O_2 production was tested by the chronoamperometry method with 85% manual iR compensation at 0.5 V . After removing 2.0 mL of electrolyte from the cathode chamber of the H-type electrolyzer, the peroxide test solution ($\text{Ce}(\text{SO}_4)_2$) was quickly added to the above 2.0 mL of electrolyte [26]. The resulting mixture was filled into a standard $70\text{-}\mu\text{L}$ cuvette for ultraviolet-visible (UV-vis) absorption spectroscopy measurement. The standard concentration-absorbance curves were calibrated using standard hydrogen peroxide solutions including 0.05, 0.1, 0.3, 0.5, and 1.0 mmol L^{-1} H_2O_2 . H_2O_2 concentrations were subsequently determined from the calibration curves.

Computational methods

Spin-unconstrained DFT calculations using the projector-enhanced plane wave method and the Generalized Gradient Approximation of Perdew-Burke-Ernzerhof (GGA-PBE) function were performed in the Vienna *Ab initio* Simulation Package (VASP) code. Plane-wave cut-off energy of 420 eV was used, which is 1.6 times higher than the cut-off energy value suggested in POTCAR. The convergence standards for energy and force were set at $3 \times 10^{-5} \text{ eV}$ and $0.05 \text{ eV \AA}^{-1}$, respectively. The boron-doped carbon structure was simulated as lamellar. A vacuum region of about $20 \text{ \AA}$ was used to decouple the periodic replicas. To simulate the doped boron in the basal plane, supercells with a transverse dimension of 8×8 were used, and the Brillouin zone was sampled with a $(2 \times 2 \times 1)$ Monkhorst-Pack of K points. The selectivity of H_2O_2 was controlled by the binding energy of

OOH^* on the catalyst surface, which is the only intermediate for the electro-power generation of H_2O_2 via the $2e^-$ ORR pathway. The catalytic activity of the materials was determined by the binding energy of the active site of the catalyst to OOH^* . Herein, the free energy (G) of a species was calculated via $\Delta G = \Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T\Delta S$, where ΔE_{DFT} , ΔE_{ZPE} , T and ΔS are the basis state energy, the zero-point energy, the temperature (298.15 K), and the entropy, respectively [26,38]. The computational hydrogen electrode (CHE) model was used to identify the free energy level in the free energy curve and the theoretical overpotential (η^t) for the $2e^-$ ORR was derived using the equation $\eta^t = |\Delta G_{\text{OOH}^*}/e - 4.22 \text{ V}|$ [38]. As the activity descriptor ΔG_{OOH^*} was established without considering the solvation effect, the solvation effect was not included when determining the value of ΔG_{OOH^*} , which governs the comparison of a resonance.

RESULTS AND DISCUSSION

Characterization of O-BC

The O-BC materials were comparatively synthesized following the polymer dehalogenation strategy previously established by our group [39–42]. As shown in Fig. 1a, the carbon source

PVDC undergoes dehalogenation in the presence of KOH, removing Cl and H functional groups to generate the clean byproducts KCl and H_2O [40]. The dehalogenated carbon sites exhibit very high reactivity, coupling with H_3BO_3 to form C–B or C–O–B bonding, leading to the formation of O-BC. To verify the successful B doping of the carbon skeleton at room temperature, the obtained precursor of O-BC, i.e., RT-O-BC-2, was thoroughly washed with deionized water to remove any impurities. Then, its structure, morphology, and composition were determined. Fig. S1a–c show that RT-O-BC-2 presents an irregular shape and structure. The energy-dispersive spectrometry (EDS) element mapping images shown in Fig. S1d–f confirm the abundant and uniform presence of B and O atoms in the carbon substrate. For comparison, the precursor of B-free oxygenated carbon, termed RT-O-C, was synthesized to verify that PVDC can undergo dehalogenation and carbonization at room temperature.

The Raman spectra of PVDC, RT-O-C, and RT-O-BC-2 are shown in Fig. S2. RT-O-C and RT-O-BC-2 present two strong peaks at 1126 and 1508 cm^{-1} , which can be attributed to the $\nu(\text{C}-\text{C})$ and graphitic carbon signals, respectively, while the two weak peaks at 2231 and 2621 cm^{-1} correspond to the $\nu(\text{C}\equiv\text{C})$

Figure 1 (a) The schematic diagram of the synthesis of B-doped carbon via polymer dehalogenation strategy. (b) SEM image of O-BC-2-650, (c) HR-TEM image of O-BC-2-650, (d) the dark-field HR-TEM image and element mapping images of carbon, oxygen, and boron, in O-BC-2-650. (e) XRD patterns of RT-O-C, RT-O-BC-2, O-C-650, and O-BC-2-650. BET measurements of O-C-650 and O-BC-2-650: (f) N_2 adsorption-desorption isotherms and (g) pore distribution curves. SSA: specific surface area.

and two-dimensional (2D) signals, respectively. Compared with the spectrum of PVDC, the lack of $\nu(\text{C}-\text{Cl}_2)$ bands at 636 and 693 cm^{-1} in the spectra of RT-O-BC-2 and RT-O-C indicates that PVDC can be defunctionalized of Cl-containing groups at room temperature. In addition, the XRD patterns of RT-O-C and RT-O-BC-2 present only the (002) and (101) signals of graphitic carbon at approximately 23° and 43° (Fig. 1e), respectively, indicating their amorphous states.

XPS was used to characterize the chemical states and bonding configurations of the main dopants (B and O). The XPS survey spectrum for RT-O-BC-2 shown in Fig. S3a indicates the co-presence of B, C, O, and some K, specifically 73.4 at% C, 20.4 at% O, 4.7 at% B, and 1.5 at% K (from KCl), confirming the obtainment of highly carbonized boron-doped carbon at room temperature. The high-resolution C 1s spectrum (Fig. S3b) of RT-O-BC-2 shows four main peaks for C-B (~283.8 eV), C=C/C-C (~284.6 eV), C-B-O/C-O (~285.4 eV), and C=O (~286.5 eV), respectively [43]. The O 1s spectrum (Fig. S3c) of RT-O-BC-2 can be deconvoluted into three peaks corresponding to C=O (~531.5 eV), C-OH/C-O-B (~532.4 eV), and O-C=O (~533.5 eV), respectively [29]. It is worth noting that the B 1s spectrum (Fig. S3d) of RT-O-BC-2 features three peaks attributed to BC_3 (~189.8 eV), O- BC_2 (~191.9 eV), and C- BO_2 (~192.6 eV), which reaffirms the incorporation of B atoms into the carbon substrate [29].

The unwashed RT-O-BC-2 and RT-O-C were subjected to inert annealing to improve their electrical conductivities and electrochemical activities. In particular, the retained KOH can activate the O-BC for the generation of more porous structures. The morphology and structure of O-BC-2-650 were observed

using electron microscopy. Fig. 1b, c and Fig. S4 show the SEM and HRTEM images of O-BC-2-650, which evidence a 3D interconnected porous structure and an amorphous state with short-range graphitization. The EDS mapping images of O-BC-2-650 (Fig. 1d) indicate the uniform distribution of B and O in the carbon matrix, which demonstrates that B has been successfully introduced. The structural features of O-BC-2-650 were confirmed by XRD analysis and pore-size distribution curves. The XRD patterns of O-BC-2-650 in Fig. 1e present only two broad diffraction peaks at 23° and 43° that can be indexed to the (002) and (101) diffractions of graphite. Porosity information for O-BC-2-650 and O-C-650 was obtained using N_2 adsorption-desorption isotherms. The isotherms of the samples in Fig. 1f combine type-I and type-IV isotherms, indicating the co-presence of abundant micropores and mesopores [44,45]. Based on the BET equation, the specific surface areas of O-C-650 and O-BC-650-2 are 679.7 and 314.7 $\text{m}^2 \text{g}^{-1}$, respectively. The pore size distribution curves indicate that O-BC-2-650 and O-C-650 contain abundant micropores and mesopores along with some macropores.

XPS further reveals the doping extents of O-BC-2-650 and O-C-650. As shown in Fig. 2a, the atomic percentage of B in O-BC-2-650 is 5.3 at%, which is higher than those of the majority of reported boron-doped carbon materials. Further resolving the C 1s spectra of O-BC-2-650 and O-C-650 reveals five-component peaks centered at 283.8, 284.6, 285.4, 286.8, and 288.8 eV, corresponding to C-B, C=C/C-C, C-B-O/C-O, C=O, and O-C=O bonds, respectively (Fig. 2b) [46,47]. The O 1s spectra of O-BC-2-650 and O-C-650 in Fig. 2c are deconvoluted into four peaks: C=O (~531.3 eV), C-OH/C-O-B (~532.6 eV), O-C=O

Figure 2 XPS characterizations of O-C-650 and O-BC-2-650: (a) XPS survey and element content, (b) C 1s spectra, (c) O 1s spectra, and (d) B 1s spectra.

(~533.5 eV), and COOH (~534.3 eV). Summarily, the contents of C and O as well as their forms are essentially the same in O-BC-2-650 and O-C-650. The B 1s spectrum of O-BC-2-650 can be deconvoluted to three peaks assigned to BC_3 (~190.3 eV), O-BC_2 (~192.2 eV), and C-BO_2 (~192.9 eV) (Fig. 2d) [47]. Notably, the percentage of O-BC_2 in O-BC-2-650 is 23.8%, which is higher than that in RT-O-BC-2 (19.8%). The homogeneous distribution of boron-oxygen-carbon structures can also enhance the wettability and durability of a carbon surface and improve the electrochemical activity of a carbon substrate [29].

The doping quantity and conformation of the B component in O-BC were regulated by varying the amount of B source used. As shown in Fig. S5, O-C-650, O-BC-0.5-65, and O-BC-1-650 have typical sheet-like structures, while O-BC-3-650 has a porous structure similar to that of O-BC-2-650. The Raman spectra and XRD patterns of the samples are shown in Fig. S6, revealing the amorphous state of all the synthetic carbon materials. To investigate the effect of annealing temperature on the electrochemical properties of O-BC, unwashed RT-O-BC-2 was subjected to annealing at 550, 600, or 700°C to prepare control samples. The as-obtained products were labeled O-BC-2- x , where x is the annealing temperature. Their morphologies were preliminarily analyzed by SEM. As shown in Fig. S7, all the samples have a 3D amorphous morphology with abundant pores, similar to that of O-BC-2-650. The Raman spectra in Fig. S8a show that the I_D/I_G value increases with temperature, indicating an increase in the degree of defective carbon in the

samples annealed at higher temperatures [10]. Fig. S8b shows the XRD patterns of all the samples, reaffirming their amorphous states and the absence of any other crystalline contaminants.

H_2O_2 selectivity of O-BC

To evaluate the $2e^-$ ORR performances of the O-BC samples, a three-electrode system equipped with an RRDE and O_2 -saturated 0.1 mol L^{-1} KOH electrolyte was employed. The effect of boric acid usage on ORR performance was first investigated. Fig. 3a and Fig. S9 show the disk and ring currents, which represent the oxygen reduction and H_2O_2 oxidation currents, respectively, for O-BC annealed at 650°C

Fig. 3d shows that the H_2O_2 yields for the samples decrease in the order of O-BC-2-650 > O-BC-1-650 > O-BC-0.5-650 > O-BC-3-650 > O-C-650, indicating that B doping is beneficial to $2e^-$ ORR selectivity. Furthermore, the electrochemically active surface area (ECSA) of the O-BC samples was determined. As shown in Fig. S10, the ECSA of O-BC-2-650 is the highest at 55.5 mF cm^{-2} , followed by those of O-BC-1-650 (52.6 mF cm^{-2}), O-BC-3-650 (45.9 mF cm^{-2}), O-BC-0.5-650 (38.0 mF cm^{-2}), and O-C-650 (23.3 mF cm^{-2}). Electrochemical impedance spectroscopy was further applied to assess the electrochemical behaviors at the material interfaces of the samples [18,50]. As shown in Fig. S11, O-BC-1-650 and O-BC-2-650 exhibit lower charge-transfer resistances (R_{ct}) in the high-frequency region, indicating their superior electron-transfer kinetics. However, $2e^-$ ORR

Figure 3 Oxygen reduction performance of O-C-650, O-BC-0.5-650, O-BC-1-650, O-BC-2-650, and O-BC-3-650 in O_2 -saturated 0.1 mol L^{-1} KOH solution: (a) LSV curves of disk currents with a scan rate of 5 mV s^{-1} , (b) the number of transferred electrons as a function of the potential, (c) calculated H_2O_2 selectivity from RRDE tests, and (d) H_2O_2 selectivity and electron transfer number comparison at 0.55 V, showing the relationship between both activity and selectivity and B content.

performance begins to decay at a B source loading higher than that for O-BC-2-650, which is likely due to a decrease in electrical conductivity with higher B doping.

The effect of annealing temperature on the catalytic performance of O-BC was also investigated. As shown in Fig. 4a–c and Fig. S12, the $2e^-$ ORR catalytic activity of the O-BC materials increases with annealing temperature from 550 to 650°C, with O-BC-2-650 exhibiting the highest H_2O_2 selectivity; when the temperature exceeds 650°C (i.e., O-BC-2-700), the $4e^-$ ORR pathway is promoted. The excellent H_2O_2 selectivity of O-BC-2-650 can be attributed to its abundance of doped boron sites and

porous structure [19,31]. The electrochemical stability of O-BC-2-650 was investigated by the steady-state polarization method. In addition, chronoamperometry was used to further evaluate the H_2O_2 production of O-BC-2-650 in an H-type electrolyzer. As shown in Fig. 4d, the average H_2O_2 production rate for O-BC-2-650 is $412.8 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$, and this rate is maintained in a consecutive 3-h long-term measurement with a Faradic efficiency of 74%. The $2e^-$ ORR performance of BC-2-650 is comparable or even superior to those of the most advanced carbon-based catalysts recently reported (for alkaline electrolytes) [51–55], as summarized in Fig. S13. As shown in Fig. 4e,

Figure 4 Oxygen reduction performance of O-BC-2-550, O-BC-2-600, O-BC-2-650, and O-BC-2-700 in O_2 -saturated 0.1 mol L^{-1} KOH solution: (a) LSV curves of disk and ring currents with a scan rate of 5 mV s^{-1} , (b) calculated H_2O_2 selectivity from RRDE tests, (c) H_2O_2 selectivity and electron transfer number comparison at 0.55 V , indicating that activity and selectivity are related to the annealing temperature, (d) the H_2O_2 production in H-cell, and (e) the stability measurement of O-BC-2-650 at 0.55 V (RHE).

O-BC-2-650 achieves steady disk and ring currents narrowly distributed at -3 and 1 mA cm^{-2} at 0.55 V (vs. RHE) during 10 h of continuous electrolysis, respectively, while its H_2O_2 selectivity remains above 97% , demonstrating its excellent durability for long-term use.

DFT calculations

To identify the sites in O-BC responsible for its 2e^- ORR catalysis, DFT calculations were performed to investigate the effect of B-containing functional species. A 2D graphene sheet was taken as a model system, and different B-containing functional groups, including BC_3 , BCO_2 , and B_2CO were introduced based on the XPS results illustrated in Fig. 2d. A 2e^- ORR activity of a catalyst is generally governed by the binding strength of its active site to the specific ORR intermediate OOH^* . The reaction equations are as follow [26]:

Accordingly, we calculated the differences in the adsorption energies for OOH^* on the surfaces of different types of B-containing functional species. The corresponding ΔG_{OOH^*} values for the different B-containing sites are shown in a volcano plot (Fig. 5c). The limiting potential (U_L) is the lowest point at which the free energy drops for all reaction steps. As shown in Fig. 5a, 13 models have been proposed, of which seven possible site models represent BC_3 , three site models represent BCO_2 , and three site models represent BCO . The majority of sites weakly bind OOH^* , making step (1) the rate-determining step (RDS). For site No. 1, which binds OOH^* more strongly, step (2)

becomes the RDS (Fig. 5b). For optimal 2e^- ORR catalysis, the intermediate OOH^* should be bound in a thermodynamically neutral way, typically with a $U_L = 0$ [38,56]. Fig. 5c shows that the B site for a BC_2O structure is closest to the peak of the volcano and can thus be considered a representative 2e^- ORR-active site, typically with an overpotential of 0.028 V . Therefore, we conclude that introducing B–O motifs to a carbon-matrix-based electrocatalyst can significantly boost its 2e^- ORR selectivity.

CONCLUSIONS

In summary, we demonstrated an inexpensive, simple, and green method for the preparation of O-BC materials and their application as catalysts for the electrochemical synthesis of H_2O_2 via the 2e^- ORR. The compositions and morphological structures of the O-BC materials were systematically regulated by altering the quantity of the B source used and the annealing temperature, allowing us to identify the optimal synthesis parameters. The resulting optimal sample (O-BC-2-650) exhibited a high B doping ($5.3 \text{ at}\%$) and a pore hierarchy comprising abundant micropores, mesopores, and some macropores. Remarkably, this material exhibited a H_2O_2 selectivity of over 98% , excellent long-term stability in a three-electrode system, an average H_2O_2 yield rate of $412.8 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$, and a Faradic efficiency of 74% in an H-type electrolyzer. According to these experiments and DFT analysis, the insertion of B–O species into a carbon matrix significantly enhances its catalytic performance for the electrochemical synthesis of H_2O_2 via the 2e^- ORR, and the B atoms in BC_2O structures behave as the most active sites. Thus, our work provides a new perspective for the design and applications of

Figure 5 DFT results of the 2e^- ORR activities on O-BC-2-650. (a) Different boron-doped types were examined. The carbon atoms or boron atoms denoted by a red circle are the active sites under investigation, (b) ΔG_{HOO^*} for 2e^- ORR to H_2O_2 at the equilibrium potential of $U_{\text{O}_2/\text{H}_2\text{O}_2} = 0.70 \text{ V}$ and the corresponding free-energy profiles, and (c) the calculated catalytic activity volcanoes for the production of H_2O_2 via 2e^- ORR, with the limiting potential plotted as a function of ΔG_{OOH^*} .

metal-free oxygenated heteroatom-doped carbon catalysts.

Received 1 September 2021; accepted 3 November 2021;

published online 5 January 2022

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Acknowledgements This work was financially supported by the National Natural Science Foundation of China (22071137), and the Program for Tsingtao Al-ion Power and Energy-storage Battery Research Team in the University (17-2-1-1-zhc).

Author contributions Chang Y designed the experiments and synthesized the materials; Li J performed the ORR experiments and data analyses; Ma J conducted the theoretical calculations. Liu Y and Xing R contributed to the data analyses and discussion. Zhang G and Wang Y conceived the project. Zhang G, Wang Y, and Chang Y co-wrote the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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通过聚合物脱卤策略合成氧化硼掺杂碳及其高效 O_2 还原制 H_2O_2

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摘要 O_2 通过电化学法直接合成 H_2O_2 是目前最有可能替代工业上高耗能的蒽醌氧化/还原法的合成方法,但其一直受限于难以开发出高效且低成本的电催化剂。在此,我们通过聚合物脱卤的绿色策略合成了氧化硼掺杂碳(O-BC)材料,将其用作 2e^- 氧还原反应(ORR)的电极材料,采用电化学的方法制备 H_2O_2 。通过实验调控硼源(H_3BO_3)的用量和退火温度,优化了O-BC材料的催化活性。电化学测试表明:最佳的O-BC-2-650样品表现出高达98%的 H_2O_2 选择性;在H型碱性电解槽中 H_2O_2 平均产率为 $412.8 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ 。密度泛函理论计算模拟表明:与一个氧原子相连的硼原子是最佳的活性位点,在吸附 O_2 的氢化过程中获得最低的吉布斯自由能差(ΔG)0.03 eV;而没有与氧原子相连或者与两个氧原子相连的B原子则具有较大的 ΔG (分别为0.08和0.10 eV)。这项工作详细报道了一种用于生产 H_2O_2 的新型绿色低碳成本的无金属电催化剂的调控合成方法。