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Boron and phosphorous-doped graphene as a metal-free electrocatalyst for the oxygen reduction reaction in alkaline medium[†]

Gayoung Jo, Jakkid Sanetuntikul and Sangaraju Shanmugam*

An efficient solid-state pyrolysis route is presented to prepare boron- and phosphorous-doped graphene without using a template, solvent, or catalyst. By controlling the pyrolysis temperature, selective doping of phosphorous or boron was achieved. Phosphorous-doped graphene (PDG) and boron-doped graphene (BDG) samples are obtained when pyrolysing the precursor at 700 °C and at 900 °C, respectively under autogenic pressure. PDG and BDG electrodes show a considerable oxygen reduction activity by a direct four-electron pathway in alkaline medium. Further, these catalysts show improved durability under continuous oxygen reduction, resistance to methanol oxidation and CO-tolerance than the commercial catalyst. The results suggest that by tuning the reaction temperature, selective doping of either boron or phosphorous in graphene was achieved and the doped graphene samples were used as non-precious and metal-free catalysts for oxygen reduction.

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1. Introduction

Fuel cell electrodes account for 33% of the whole cost of fuel cells1 because of the use of precious platinum in both electrodes. Therefore, the development of non-precious catalysts has received tremendous importance in recent years to reduce the overall cost of the fuel cell electrode components.² An alkaline polymer electrolyte membrane fuel cell (APEFC) is a counterpart of a PEMFC that uses an anionic exchange membrane. It allows the use of non-precious catalysts owing to its faster ORR kinetics and better stability of the electrode materials under alkaline conditions.³ For these reasons, we focus on the development of non-precious catalysts for the ORR in alkaline medium. Recently, heteroatom-doped carbon nanostructures have received enormous attention as nonprecious metal electrode materials for oxygen reduction.4-9 Doping the heteroatom into a carbon network can be mainly conducted by; (1) intercalation and (2) substitution.¹⁰ Particularly, substitutional doping of a heteroatom into carbon is able to modify the electronic properties of the carbon network, and accordingly tune the electrocatalytic activities.

Generally, three methods have been mainly reported to substitute heteroatoms into the carbon network: (1) arc-discharge method,¹¹⁻¹³ (2) laser-ablation method,^{14,15} and (3) chemical vapor deposition (CVD).^{16,17} These techniques require

high energy consumption, expensive hardware and multistep processes, which cause a costly manufacturing process. On the other hand, solid-state pyrolysis^{7,9,18} is a cost-effective and facile single-step synthetic approach to fabricate heteroatom-doped carbon. The synthetic approach has been considered as a green process since the approach does not need templates, solvents, or catalysts. In addition, this process can be easily scaled up.

Boron doping into a carbon network makes the host carbon array have p-type conductivity and act as an electron acceptor due to the strong electron withdrawing capability at the hexagonal site.19-21 The strong electron withdrawing capability of doped-boron induces adsorption of O2 molecules on the doped boron sites. Yang and coworkers7 also illustrated that O2 adsorption is favourable on the boron dopant rather than the adjacent carbon atoms because of the more positively charged boron atom compared with the carbon atom^{22,23} due to the lower electronegativity of boron (2.0) than that of the carbon atom (2.5). O₂ adsorption is an important step for further steps of the oxygen reduction.24 Whereas, phosphorous-doping creates more positive charge than the parent carbon atom.4 This indicates that O₂ adsorption is favourable on the phosphorous atom in phosphorous-doped carbon, which has the same tendency as a doped boron atom in the carbon network. This tendency is due to the lower electronegativity of phosphorous (2.1) than that of carbon (2.5) even though the electron configuration and number of valence electrons of phosphorous is the same as for the nitrogen atom.

Even though nitrogen-doped carbons have been widely investigated as oxygen reduction catalysts,^{6,7,18} only a few reports emphasized using phosphorous or boron-doped carbon as non-

Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu, 711-873, Republic of Korea. E-mail: sangarajus@dgist.ac. kr; Fax: +82 53 785 6409

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precious catalysts for the ORR in alkaline medium. Herein, we describe a versatile and efficient synthetic route to dope heteroatoms selectively using a single precursor. This method is facile, solvent-, catalyst-, and template-free and it is easy to handle, and thus might even be scalable. The prepared boron-doped graphene (BDG) or phosphorous-doped graphene (PDG) is used as a metal-free electrocatalyst for the oxygen reduction reaction in alkaline electrolyte. These electrodes exhibited an efficient four-electron transfer process with high selectivity compared with a commercial Pt/C catalyst.

2. Experimental

2.1 Preparation of BPG precursor

The graphene (N002-PDR, Angstrom materials) dispersion and tetraphenylphosphonium tetraphenylborate (TPP-TPB, Aldrich) solution were prepared separately with sonication of the contents for 30 min. The graphene dispersion consists of 100 mg of graphene and 10 mL of ethanol, and the TPP-TPB solution consists of 200 mg of TPP-TPB and 10 mL of ethanol. The TPP-TPB (precursor) solution was slowly added into the graphene dispersion with magnetic stirring and heating at a temperature of 60 °C. Once the addition of the TPP-TPB solution was finished, the temperature was kept for 6 h with continuous stirring. After 6 h, ethanol was removed by centrifugal separation, and the residue dried at 60 °C under vacuum. Afterwards, B and P precursor impregnated graphene (BPG) was obtained, which was used as a precursor for the preparation of phosphorous-doped and boron-doped graphene as described in Section 2.2.

2.2 Preparation of phosphorous-doped and boron-doped graphene

For a typical synthesis, 0.035 g of the BPG precursor was enclosed in a Swagelok union cell; subsequently it was thermally decomposed at a temperature of 700 °C and 900 °C for a period of 3 h in a tubular furnace under autogenic atmosphere without any gas flow. The cell was cooled automatically under ambient conditions. BPG precursor calcined at 700 °C and 900 °C was named as PDG and BDG, respectively. The kind of heteroatom that was doped into the graphene was determined by elemental composition analysis using XPS and ICP-MS. For purification, as-prepared PDG and BDG were treated with 10 mL of concentrated HCl (\sim 37%) for 24 h to remove any oxide on the surface of the as-prepared samples. Acid treated samples were washed by using copious distilled water and ethanol, and dried overnight in a vacuum oven at 60 °C. All supernatant such as used HCl, distilled water, and ethanol were removed by using centrifugal separation at a rotation speed of 10 000 rpm for 10 min.

2.3 Physico-chemical characterization

Electron microscope studies were conducted to confirm the morphology and *d*-spacing (interlayer distance) using FE-TEM (Hitachi, HF-3300). Samples for the TEM studies were prepared by dropping an ultrasonically dispersed solution of

black powdered catalysts and isopropyl alcohol (IPA) on a substrate. As the substrate, a copper (Cu) grid coated with amorphous carbon film was used for TEM measurements. TEM experiments were performed at an acceleration voltage of 300 kV. The crystallinity of the products was studied using powder XRD (Panalytical, Empyrean) using Cu K-alpha radiation at a generator voltage of 40 kV and a tube current of 30 mA. To examine the nature of the carbon with a ratio of structural defects to graphitic array, Raman spectroscopy was performed using a high resolution dispersive Raman microscope (Horiba Jobin Yvon, LabRAM HR UV/Vis/NIR). Elemental analysis was performed using XPS (Thermo Fisher Scientific, ESCALAB250 XPS system, Theta Probe XPS system) using a monochromated Al K-alpha source at 15 kV and 150 W. Binding energy values at the x-axis were calibrated by using C1s from a carbon value taken as 284.6 eV. The amount of P and B in PDG and BDG catalysts was also analyzed using inductively coupled plasmaatomic emission spectroscopy (ICP-MS, Thermo Scientific, ICAP Q).

2.4 Electrochemical characterization

The ORR electrocatalytic performance of the PDG and BDG catalysts was studied using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) with a 3-electrode system using a bipotentiostat (Bio-Logic, VSP). For the 3-electrode system, a saturated calomel electrode (SCE, Hg/HgCl), a spiral platinum wire, and a glassy carbon electrode (GCE, $\emptyset = 3 \text{ mm}$) were used as a reference, counter, and working electrode, respectively. The voltammograms were recorded in a N2- and O2-saturated 0.1 M KOH aqueous solution at a scan rate of 10 mV s⁻¹. The N₂- and O₂-saturated electrolytes were prepared by bubbling N₂ and O₂ gas respectively for 30 min at a flow rate of 80 sccm. For the working electrode, bare glassy carbon stuck on Teflon was used. On the bare glassy carbon electrode (GCE), catalyst ink was dropped on the surface, and dried at 50 °C in a forced convection oven; afterwards, Nafion® 5 wt% solution (Aldrich) was dropped on top of the dried catalyst ink. Nafion® was used as a binder to hold the catalyst to the GCE. All the electrochemical experiments (CVs and LSVs) were continued until a stable voltammogram was obtained. Potential values were converted from saturated calomel electrode (SCE) to reversible hydrogen electrode (RHE), and the current was normalized to the geometric area of the electrode. For comparison, 10 wt% loaded platinum on carbon black, Vulcan XC-72 (E-TEK), was used as a reference catalyst.

2.5 Catalyst ink preparation

The catalyst ink was prepared with 1 mg of black powdered PDG and BDG, and 100 μ L of aqueous solution (distilled water: 75 μ L, Nafion® 5 wt% solution: 20 μ L, IPA: 5 μ L). The ink was vigorously sonicated for 30 min using a sonicator. For CV, the working electrode was prepared by dropping 10 μ L of catalyst ink onto the surface of the glassy carbon electrode at first, and then 5 μ L of Nafion® 5 wt% solution (Aldrich) was dropped onto the same area. The ink coated GCE was dried at room temperature. For LSV, 5 μ L of catalyst ink was dropped firstly, and then

 $2~\mu L$ of Nafion® 5 wt% solution (Aldrich) was dropped onto the GCE.

2.6 Selectivity test: methanol oxidation and CO poisoning tolerance test

The LSV technique was used with the RDE technique and 3electrode system for both methanol oxidation tolerance and CO poisoning effect tests. Methanol oxidation tolerance and CO poisoning tests were conducted at a potential window of 0.2 V to -0.8 V at a scan rate of 10 mV s⁻¹ with an electrode rotation speed of 1600 rpm. O2-saturated 0.1 M KOH was used as electrolyte. The experiments were conducted under two different environments. The first LSV was obtained in O2-saturated electrolyte. Afterwards, the second LSV was obtained in 2 mL of 2 M methanol added O₂-saturated electrolyte. To ensure the sufficient mixing of methanol in electrolyte, the experiment started 10 min after the addition of methanol. O₂ bubbling was kept at a flow rate of 20 sccm during the experiments. CO poisoning effect tests were performed under three different environments. The first LSV was obtained in O2-saturated 0.1 M KOH electrolyte. The second LSV was obtained in both CO- and O2-saturated electrolyte. To consider the decreased partial pressure effect of O₂ gas in electrolyte due to addition of CO gas, the third LSV was obtained in both N2- and O2-saturated electrolyte. During the experiments, all gases bubbling (O2, CO, and N_2) were kept at a flow rate of 20 sccm.

2.7 Durability test

A durability test under continuous oxygen reduction was conducted using a chronoamperometric technique using the RDE technique at a fixed potential of -0.26 V *vs.* SCE for 43 200 s (12 h) with an electrode rotation speed of 1600 rpm. A 3-electrode system was used with the same reference, counter, and working electrode as the previous electrochemical study. For the electrolyte, O₂-saturated 0.1 M KOH aqueous solution was prepared by O₂-bubbling at a flow rate of 80 sccm for 30 min. During the experiments, O₂ gas bubbling was maintained at 20 sccm. The data was recorded every 100 μ A and 5 s.

3. Results and discussion

Morphological studies using TEM revealed the thin sheet-like structures with random wrinkles of PDG and BDG (Fig. 1a and c), which is the same morphology as pristine graphene (Fig. S1, ESI[†]). High resolution TEM images show the presence of lattice fringes, which correspond to the C(002) interlayer plane of carbon (Fig. 1b and d).

The interlayer distances obtained from the XRD results are 0.366, 0.353 and 0.369 nm for PDG, BDG and pristine graphene, respectively (Fig. 2). From the XRD data, the interlayer distances of the PDG and BDG samples were found to be smaller than that of pristine graphene. This change is due to the heat treatment effect under high temperature (700 °C and 900 °C). Takai *et al.*²⁴ and Endo *et al.*²⁵ reported that high temperature treatment decreases the interlayer spacing. In fact, the interlayer distance of BDG (0.353 nm) is smaller than that of PDG (0.366 nm) owing



Fig. 1 Low resolution TEM images of (a) PDG and (c) BDG. High resolution TEM images of (b) PDG and (d) BDG with lattice fringes.

to the higher temperature treatment. Other evidence of the higher interlayer distance of PDG is the bigger covalent radius of phosphorous (110 pm) in PDG than the boron (88 pm) doped in BDG.

The Raman spectra shown in Fig. 3a exhibit the presence of two strong peaks at 1341 cm⁻¹ and 1584 cm⁻¹ for PDG, and 1343 cm⁻¹ and 1578 cm⁻¹ for BDG. The bands observed at around 1341 cm⁻¹ and 1584 cm⁻¹ correspond to the D and G bands of carbon, respectively. The I_D/I_G ratio for PDG and BDG is 1.03 and 1.36, respectively, which indicates that BDG has more defects in its composition than PDG. The I_D/I_G ratio is 0.97 for the pristine graphene sample. This observed difference in ratio can be attributed to the higher doping of heteroatom content in BDG than PDG. Generally, phosphorous^{4,26} or boron^{8,21,27-31} doping forms defect sites in the parent carbon network due to the larger covalent radius of phosphorous and boron than carbon. The greater number of defect

Fig. 2 XRD patterns of PDG, BDG, and pristine graphene.

sites in BDG can contribute to providing more reaction sites for the oxygen reduction. This contribution can be proof of the higher ORR performance of BDG over PDG, which will be discussed further.

The wide survey XPS spectra show the presence of C, O, P, or B in PDG and BDG (Fig. 3b). Importantly, the sample prepared at 700 °C exhibits only phosphorous (0.18 at.%) and no boron was observed, whereas the sample prepared at 900 °C possesses only boron with a doping of 0.82 at.%, and surprisingly no phosphorous was observed (Table S1, ESI[†]). Further, the B & P content present in the two catalysts was determined by ICP-MS analysis. The B & P content was found to be 0.02 and 0.21% for PDG and 0.91 and 0.04% for the BDG sample, respectively. With an increase in the temperature of 200 °C, that is from 700 to 900 °C, the doping of only boron in graphene was observed, suggesting that at 900 °C phosphorous doping did not occur, which may be due to the easy sublimation of elemental phosphorous compared with boron. Moreover, the higher doping concentration of B in the BDG sample, indicates the easier doping of boron, due to the similar covalent radius of boron to the carbon atom, rather than the doping of phosphorous into the carbon network. We observed that P and B doping levels decreased with increasing the temperature from 700 to 900 °C, which indicates that the heteroatom-doping level is non-linearly dependent on the heating temperature.

To confirm the chemical bonding between B or P and carbon (B–C or P–C), high resolution XPS spectra are shown in Fig. 3c and d. In PDG, the phosphorus 2p (P2p) peak is observed at a binding energy of 132.1 eV, which is positively shifted compared to the binding energy of the pure P2p peak (129.7 eV). Similarly, in BDG, the boron 1s peak, observed at 189.8 eV, is found to be positively shifted compared to the binding energy of the pure B1s peak (187 eV). These shifts of binding energy are ascribed to incorporated P or B in the graphene. After deconvolution of the high resolution P2p

Fig. 3 (a) Raman spectra of PDG, BDG and pristine graphene, (b) wide survey XPS spectra, and high resolution XPS spectra of (c) P2p of PDG, and (d) B1s of BDG.

spectrum, the P2p spectra for PDG are separated into two components, as shown in Fig. 3c. For PDG, the highest binding energy at 133.7 eV is assigned to P–C bonding. The peak at 132.0 eV is due to P–O bonding. The B1s peak of the BDG catalyst is deconvoluted into four components as shown in Fig. 3d. The peak with the highest binding energy at 192.5 eV is derived from BCO₂. The peak observed at 190.7 eV is owing to BC₂O. The peaks centered at 188.7 eV and 186.7 eV correspond to BC₃ and B₄C, respectively. The surface analysis observed by XPS, combined with ICP-MS elemental analysis strongly suggest the possibility of selective doping depending on the pyrolysis temperature, and easy tuning of the types of heteroatom doped into carbon materials without any consideration regarding precursor and other synthetic conditions.

The electrocatalytic activity was evaluated by using cyclic voltammetry and linear sweep voltammetry. In Fig. 4, the CV of untreated pristine graphene shows an unclear cathodic peak at 0.65 V vs. RHE with a peak current of 0.9 mA cm⁻². On the other hand, PDG and BDG exhibit a well-defined oxygen reduction cathodic peak at 0.66 V and 0.71 V vs. RHE with a peak current of 1.08 mA cm⁻² and 1.12 mA cm⁻², respectively. The observed current density value is about 1.1 times higher than that of the pristine graphene. In addition, the current density difference between the background and reduction curve at 0.7 V vs. RHE was compared among the prepared samples and the pristine graphene. The value of pristine graphene is found to be 0.47 mA cm^{-2} . However, the values of PDG and BDG are determined to be 0.67 mA $\rm cm^{-2}$ and 1.1 mA cm⁻², and these are 1.4 to 2.4 times higher than that of the graphene, respectively. The above results indicate that heteroatom doping enhances the oxygen reduction current due to electronically modifying the pristine graphene by incorporating heteroatoms into the graphene array. The most positive onset potential of the three samples is observed at 0.83 V vs. RHE for the BDG sample. This value of BDG is 40 mV more positive than that of the untreated graphene.

This observation indicates that BDG enhances the oxygen reduction kinetics of the graphene better than PDG. In turn, this finding indicates that boron doping in graphene results in faster kinetics of the ORR with a high current density. The evidence for this difference of the contribution between PDG and BDG will be introduced in a latter section of the paper with hydrodynamic LSVs using the RDE technique.

Fig. 5a and b depict LSVs and the insets show the corresponding Koutecky–Levich (K–L) plots of PDG and BDG. In the LSVs, the current density increases with an increase of the electrode rotation speed from 400 rpm to 2500 rpm, which follows the Levich equation. At lower rotations, the LSVs show a peak around 0.67 V, which is due to the oxygen reduction and the reactant is depleted in the inner region and pores of the catalyst layer. This peak disappears at higher electrode rotations (>1600 rpm). The corresponding K–L plots show great linearity and good parallelism. The linearity and parallelism of the plots indicate first-order kinetics and constant electron transfer over a wide potential range.³² In particular, all K–L plots of both prepared samples are found to have

Fig. 4 Cyclic voltammograms of PDG, BDG, and pristine graphene. The dotted line is for N₂-saturated 0.1 M KOH and the solid line is for O_2 -saturated 0.1 M KOH.

similar slopes to ideal K–L plots when electron transfer is four, which suggests that both prepared samples follow a four-electron pathway for oxygen reduction. ORR performance was enhanced by increasing the pyrolysis temperature from 700 $^{\circ}$ C to 900 $^{\circ}$ C.

Fig. 5c compares the ORR activities of PDG, BDG and pristine graphene catalysts at the electrode rotation speed of 1600 rpm. The calculated n values of PDG and BDG are 3.98 and 3.94 respectively, while the values for pristine graphene are 2.1 to 2.7, as reported by Sheng et al.28 These results suggest that heteroatom (B or P) doping into the graphene has the possibility of inducing single-step four-electron transferred oxygen reduction like Pt-based catalysts. The onset potentials of PDG, BDG, and graphene are found to be 0.80, 0.83, and 0.79 V respectively, which are similar to the values observed in CVs. The BDG catalyst showed a 30 mV positive shift of the onset potential compared with PDG (Table S1, ESI[†]). The half-wave $(E_{1/2})$ potentials of PDG, BDG and pristine graphene were found to be 0.68, 0.72, and 0.55 V, respectively. The $E_{1/2}$ of BDG catalyst is 40 mV more positive than the PDG catalyst and 170 mV higher than the pristine graphene catalyst (Fig. 5c). In comparing PDG and BDG catalysts, BDG shows higher oxygen reduction performance

Fig. 5 Hydrodynamic linear sweep voltammograms (LSVs) of the ORR on (a) PDG, and (b) BDG in 0.1 M KOH at 10 mV s⁻¹ at various electrode rotation speeds. Insets: corresponding K–L plots. (c) LSVs of the ORR on PDG, BDG, and Pt/C in 0.1 M KOH at 10 mV s⁻¹ at 1600 rpm.

than PDG. This difference is ascribed to differences of defect concentration related to sp³ disordered carbon between the two samples owing to different doping levels (Table S1, ESI†). The doping concentrations of PDG and BDG are different although the synthetic precursor that possesses simultaneously P and B with the same atomic concentration was used for pyrolysis. The higher doping concentration of BDG results from much easier doping of boron, due to the similar covalent radius of the boron and carbon atoms, rather than the doping of phosphorous into the carbon network. As mentioned previously, the difference in doping level induced more defect sites in samples that can act as harsh reaction sites. Namely, the presence of more reaction sites for the ORR in BDG contributed to the higher electrocatalytic activity in the ORR.

Fig. 6a, c and e, depict the selectivity studies of PDG, BDG, and commercial Pt/C catalysts for the ORR in the presence methanol fuel. The solid line was obtained in O_2 -saturated electrolyte, and the dotted line was obtained in methanol added

O2-saturated electrolyte. The solid and the dotted lines in LSVs of PDG and BDG closely overlap; however, the dotted line in the LSV of Pt/C is not matched significantly and forms a gap with the solid line. This gap observed in LSVs of Pt/C corresponds to the oxygen reduction current decay due to simultaneous methanol oxidation, and strongly suggests the outstanding methanol tolerance of PDG and BDG. The results of the CO poisoning effect test on the oxygen reduction are illustrated in Fig. 6b, d and f for PDG, BDG, and Pt/C, respectively. The solid line was attained in O2-saturated electrolyte, and the dotted blue line was obtained in both CO- and O₂-saturated electrolyte. To consider a decrease in O2 partial pressure owing to the addition of CO gases, the dotted red line was obtained in both N2- and O2-saturated electrolyte. For PDG and BDG catalysts, the dotted blue line and the dotted red line are closely matched. On the other hand, the blue line and the red line in the LSVs of Pt/C show a critical disparity. This disparity suggests that the oxygen reduction on the commercial Pt/C electrode can be affected by CO poisoning while PDG and BDG show strong resistance against CO poisoning.

The electrochemical ORR stability of the metal-free heteroatom-doped graphene catalysts was evaluated using a chronoamperometric technique for a period of 12 h. Fig. 7 indicates that the relative current decay of the Pt/C electrode to 64.8%. On the contrary, the PDG and BDG catalysts exhibit better durability than the Pt/C catalyst. The relative current decay of the PDG and BDG catalysts was found to be 87% and 89%, respectively, suggesting that both the PDG and BDG

Fig. 6 LSVs with addition of 2 M methanol on (a) PDG, (c) BDG, and (e) Pt/C. LSVs with addition of CO (blue line) and N₂ gases (red line) at the same flow rate as O_2 gas on (b) PDG, (d) BDG, and (f) Pt/C in O_2 -saturated 0.1 M KOH solution at 1600 rpm.

Fig. 7 Chronoamperometric response of PDG, BDG, and Pt/C at -0.26 V vs. SCE in O₂-saturated 0.1 M KOH solution for durability testing during 12 h.

catalysts exhibit long-term stability in the ORR in alkaline medium.

4. Conclusion

A facile solid-state pyrolysis route was introduced to fabricate heteroatom-doped graphene as a non-precious catalyst for oxygen reduction. The elemental analysis reveals a selective doping of either phosphorous or boron by tuning of the pyrolysis temperature. The BDG catalyst exhibited improved oxygen reduction activity compared to the PDG catalyst in an alkaline medium and the enhanced electrocatalytic activity of the BDG electrode was derived from the greater number of defect sites on the catalyst than on the PDG catalyst due to the difference in doping level. The durability of the PDG and BDG electrodes was much better than that of Pt/C. In addition, the tolerance of methanol oxidation and CO poisoning of PDG and BDG was outstanding compared with the commercial Pt/C. These results strongly suggest that heteroatom doping and a pyrolysis synthetic route can be used as a rational approach for nonprecious and metal-free catalysts for oxygen reduction and various catalytic applications.

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