Role of phosphorus in nitrogen, phosphorus dual-doped ordered mesoporous carbon electrocatalyst for oxygen reduction reaction in alkaline media

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A R T I C L E   I N F O

Article history:
Received 31 August 2017
Received in revised form 7 November 2017
Accepted 29 November 2017
Available online 19 December 2017

Keywords:
Oxygen reduction reaction
Nitrogen
Phosphorus
Carbon materials
Heteroatom doping

A B S T R A C T

In this paper, we have investigated the role of phosphorus (P) in nitrogen (N) and phosphorus dual-doped carbon electrocatalyst for oxygen reduction reaction (ORR) in alkaline media with three samples prepared by varying the doping orders of N and P. Results show that the resultant N-POMC (first doped with P, then N) exhibits an outstanding activity for ORR in alkaline media. The mechanism leading to the improved activity is found to be associated with the orientation effect of the first doped P on the later doped N, by increasing the ratio of graphitic-N significantly. Furthermore, a portion of the first doped P can act as the doping sites and be replaced by the later doped N, called ‘self-sacrifice’ mode, which is confirmed by both experiments and density functional theory (DFT) calculations. However, this orientation effect cannot be observed in the other two dual-doped samples. In addition, experimental and DFT calculation also prove that the amount of graphitic-N is important in improving the activity for ORR. The doping strategy reported in this work is applicable to various co-doping systems in exploring the synergy effect of different dopants and improving activity for ORR.

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Introduction

Recent studies have shown that nitrogen (N)-doped carbon nanomaterials (such as ordered mesoporous carbons, carbon nanotubes, graphene, etc.) could be an efficient and metal-free alternative to platinum (Pt) for oxygen reduction reaction (ORR), which enables a significant cost reduction while maintaining high efficiency with economic viability for applications in fuel cells and other energy devices [1–7]. When introducing N into a carbon framework, defects would be produced in the nearby sites due to the differences in bond length and atomic size. In addition, the difference in electronegativity could induce uneven charge distribution on the N atom and the neighboring C atoms. This uneven charge distribution in turn changes the adsorption mode of oxygen on the surface of catalyst, facilitating the breakage of the O–O bond [6,8]. Therefore, the amount and the chemical state of the doped N in carbons bear a significant influence on the ORR performance [4,5]. It was reported that the doped N functionalities presented in carbon are in the forms of pyridinic-N, pyrrolic-N, graphitic-N, and pyridinic-N–O. [9–14].

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https://doi.org/10.1016/j.ijhydene.2017.11.165
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Experimental studies suggested that either pyridinic-N $[9,10]$ or graphitic-N $[11,12]$ could be the active sites for ORR.

To dope with a secondary heteroatom on the N-doped carbon materials, such as B and P, has been proved to be an effective approach to further enhance the activity towards ORR $[15–26]$. In particular, N, P dual-doped carbon illustrates a much better activity than that of the single N-doped carbon $[16,19,20,24,27]$, indicating that synergy effect might exist in the dual-doped carbons, which is due to the bond between N and P. In some other previous investigations $[26]$, N and P are isolate located from each other in the co-doped carbon, therefore the improvement of activity for ORR might be just the combination of single N-doped and P-doped, other than the synergy effect. Thus, up till now, whether synergy effect is formed in N, P dual-doped carbon and how it influences the ORR performance is still unclear.

Here we report a combined experimental and theoretical approach to uncover the role of P in N, P dual-doped carbon electrocatalyst for ORR in alkaline media. Ordered mesoporous carbon (OMC) was chosen as the substrate material for its unique textural structure, large specific surface area and tailored pore size with narrow distribution $[28,29]$. The N, P dual-doped OMCs were prepared in a strategy by varying in doping orders of N and P, as indicated in Fig. 1. Our results demonstrate that the OMC doped with P first, and then with N has exhibited the highest ORR performance, due to the orientation effect of the first doped P on later doped N by significantly increasing the ratio of graphitic-N, which is confirmed by both experiments and DFT calculations.

**Experimental**

**Preparation of the samples**

Ordered mesoporous carbon (OMC) was prepared using a soluble resol solution and SBA-15 as the carbon source and the template agent, respectively. The resol solution and SBA-15 were synthesized according to the previous literature $[30,31]$, and OMC was prepared by a nano-casting method, according to the literature $[32]$.

Triphenylphosphine (TPP) and dicyandiamide (DCDA) were used as P and N precursors, and a post-treatment method was adopted to prepare the dual-doped OMC samples by changing the doping orders of N and P. For the first sample (N and P doping simultaneous), 0.2 g of TPP and 0.2 g of DCDA were stirred and dissolved in 20 g of ethanol to form a solution, before 0.1 g of OMC was added. The mixture was further stirred at room temperature to evaporate ethanol. The obtained TPP/DCDA/OMC composite was dried at 60 °C for 24 h and then heated at 800 °C for 3 h at an argon atmosphere with a flow rate of 50 mL min$^{-1}$, which the resultant sample was denoted as N, P-OMC. In the second doping mode (first doped with N, then P), the OMC was first mixed with DCDA, and pyrolyzed at 800 °C, denoted as NOMC; After that, the doping process was conducted again with NOMC and TPP, and the resultant was denoted as P-NOMC. The third doping mode (first doped with P, then N) is different from the second mode in that the doping order is just the opposite, and the result samples were denoted as POMC and N-POMC.

**Characterization**

Nitrogen sorption isotherms were measured with a Beckman Coulter SA3100 Surface Area Analyzer. The BET and BJH methods were utilized to calculate the specific surface area ($S_{BET}$) and the pore size distribution (PSD). Transmission electron microscopy (TEM) experiments were conducted on a TEM 2010F (JEOL) to observe the microscopic features of the as-prepared OMC samples before and after doping. The samples for TEM measurements were suspended in ethanol and dropped onto a holey carbon film supported on a Cu grid. X-ray photoelectron spectroscopy (XPS) analyses were carried out with a Kratos Axis Ultra DLD multi-technique surface analysis system. Raman spectrum tests were carried out on a MicroRaman System.
Electrochemical measurements

Electrochemical measurements were performed at room temperature with an Autolab instrument. A three-electrode system was used, in which a Pt mesh was used as the counter electrode and an Ag/AgCl with saturated KCI solution as the reference electrode. The potential (vs Ag/AgCl) was calibrated with respect to a reversible hydrogen electrode (see Supplementary Information for details). The working electrode was made as follows: 5 mg of catalyst was dispersed in 2 mL of ethanol and ultrasonicated for 20 min, then 25 µL of 5% Nafion solution was added and ultrasonicated for another 20 min. 20 µL of the above-prepared catalyst ink was injected onto a polished glassy carbon electrode by several times with a micro-syringe and dried at ambient conditions, and the catalyst loading was about 0.255 mg cm⁻².

Cyclic voltammetry (CV) measurements were conducted in 0.1 M KOH aqueous solution. Linear sweep voltammetry (LSV) measurements with rotating disk electrode (RDE) for oxygen reduction reaction (ORR) were performed with 10 mV s⁻¹ of scan rate in oxygen-saturated 0.1 M KOH aqueous solution at rotation speed varying from 400 to 2500 rpm. The number of electrons (n) involved in the ORR can be deduced from the Koutecky-Levich (K-L) equation:

\[ J = J_L + J_K = \frac{BnFC}{C_0} \left( \frac{1}{v} \right)^{1/6} \]

where \( J \), \( J_L \), and \( J_K \) are the measured-, diffusion limiting- and kinetic current density, \( n \) is the angular velocity of the disk, \( C_0 \) is the Faraday constant (96485 C mol⁻¹), \( D_0 \) is the diffusion coefficient of dissolved oxygen in the 0.1 M KOH (1.2*10⁻³ cm² s⁻¹), \( D_0 \) is the concentration of dissolved oxygen in the 0.1 M KOH (1.2*10⁻³ mol L⁻¹), \( D_0 \) is the diffusion coefficient of dissolved oxygen in the 0.1 M KOH (1.2*10⁻³ cm² s⁻¹), and \( v \) is the kinematic viscosity of the 0.1 M KOH (0.01 cm² s⁻¹) [33]. According to Equations (1) and (2), \( n \) can be obtained from the slope of the K-L plot.

Results and discussion

Characterization

The structure and morphologies of the as-prepared carbons were characterized by TEM images. It clearly shows that large domains of ordered hexagonal arrays were shaped for the pristine OMC (Fig. 2a), which still remained after the doping with N and P for the other three samples (Fig. 2b–d). Nitrogen sorption isotherms were conducted to characterize the specific surface areas. For all the as-prepared samples, the isotherms of the combination of type I and type IV with a hysteresis loop indicates the formation of a mesoporous structure and a lot of micropores in the carbon framework (Fig. 3a). The pristine OMC has the largest specific surface area (1090 m² g⁻¹) and pore volume (0.95 mL g⁻¹). After doping with N and P, the specific surface areas for the three dual-doped samples decreased and exhibited similar values (800 m² g⁻¹) (Table 1). Pore size distribution curves (Fig. 3b) show that the dominant pore sizes are about 4 nm for all the samples. The degree of graphitization was examined from Raman spectra by calculating the ratio of ID/IG, and results show that the values of ID/IG are 0.83 (N, P-OMC), 0.91 (P-NOMC), and 0.87 (N-POMC), larger than that of the pristine OMC (0.69) (Fig. 4), indicating the decline of the degree of graphitization, which could be attributed to the introduction of defects, due to the doping process of N and P.

XPS was used to check the amounts of doped N and P. It is noted that the N, P-OMC and the P-NOMC have the very similar total amounts of N and P (4.08 at.% and 4.1 at.%, respectively), while the N-POMC has the least total amount of N and P (3.74 at.%) of the three dual-doped samples, even less than the single-doped NOMC (3.8 at.%), which can be seen from Table 2.

High resolution of P2p reveals the existence of both P−O bonds (133.8 eV) and P−C bonds (132.7 eV), and the ratios of the two bonding were quite similar for all the samples (Fig. 5). In high resolution of N1s spectrum, the ratios of N species in the N, P-OMC and P-NOMC were similar to those of the single-doped NOMC (Fig. 6). While the ratio of the graphic-N in the N-POMC increased dramatically to 51.9%, much larger than that in the N, P-OMC and P-NOMC (27.6% and 25.1% each), which is in the same level of the NOMC (24.5%) (Fig. 6, Table S2). As we know, the amounts of N, P, and C precursors used in the three samples were the same. However, the amounts of N and P and their species in their final samples were different, indicating the different doping processes had exerted various influences. For the N, P-OMC (doped simultaneously) and the P-NOMC (first doped with N, then P), the amounts of the dopants and the ratios of the doped species are very similar. However, for the N-POMC (first doped with P, then N), the amount of the total dopants is a little less than that of the above two samples. Furthermore, the ratios of N species varied much in that the amount of graphic-N increased significantly, implying the first doped P had an orientation effect on the later doped N.

Electrochemical measurements

CV experiments were performed to investigate the electrocatalytic activity of the three as-prepared samples for ORR in oxygen-free and oxygen-saturated 0.1 M KOH solution at a scan rate of 100 mV s⁻¹. The corresponding voltammograms can be obtained in Fig. 7a–c. In oxygen-free condition, all the OMCs exhibited a typical behavior of a capacitor. In the oxygen-saturated condition, a characteristic cathodic peak could be observed for all the samples, confirming that all the dual-doped samples have the electrocatalytic activities for ORR. Among them, N-POMC has the most positive peak potential (0.72 V), compared with those of the N, P-OMC (0.70 V), and P-NOMC (0.70 V), as well as the largest peak current density, implying the highest activity for ORR.

LSV were conducted to further understand the ORR performance of the as-prepared samples, which was performed in an oxygen-saturated 0.1 M KOH solution at a rotation speed of 1600 rpm and a scan rate of 10 mV s⁻¹. As shown in Fig. 8a, the POMC shows the lowest ORR performance with a two-step ORR process at the onset potentials of 0.71 V and 0.29 V, which is attributed to the reduction of O₂ to HO₂⁻ and HO₂⁻ to OH⁻, respectively. The NOMC is observed with an
onset potential of 0.8 V. The dual-doped carbons show higher activities for ORR with more positive onset potentials. The N, P-OMC and the P-NOMC show a very similar onset potential of 0.84 V. The N-POMC shows the best activity with the most positive onset potential of 0.88 V, which is still far behind that of the commercial Pt/C (0.95 V). The Tafel slopes were calculated to be about 66 mV dec$^{-1}$ for the Pt/C, 85 mV dec$^{-1}$ for the N-POMC, 90 mV dec$^{-1}$ for the P-NOMC, 89 mV dec$^{-1}$

Fig. 2 — TEM images of (a) OMC, (b) N, P-OMC, (c) P-NOMC (d) and N-POMC.

Fig. 3 — (a) Nitrogen sorption isotherms and (b) pore size distribution for the as-prepared samples.

Table 1 — Physicochemical property of the as-prepared samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{total}$ (mL g$^{-1}$)</th>
<th>$S_{micro}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{micro}$ (mL g$^{-1}$)</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMC</td>
<td>1090</td>
<td>0.9463</td>
<td>439.1</td>
<td>0.1994</td>
<td>0.69</td>
</tr>
<tr>
<td>N, P-OMC</td>
<td>774.3</td>
<td>0.5948</td>
<td>168.3</td>
<td>0.0768</td>
<td>0.83</td>
</tr>
<tr>
<td>P-NOMC</td>
<td>801.1</td>
<td>0.6044</td>
<td>145.4</td>
<td>0.0639</td>
<td>0.91</td>
</tr>
<tr>
<td>N-POMC</td>
<td>797.8</td>
<td>0.7245</td>
<td>115.2</td>
<td>0.0509</td>
<td>0.87</td>
</tr>
</tbody>
</table>
for the N, P-OMC, 104 mV dec\(^{-1}\) for the NOMC, and 112 mV dec\(^{-1}\) for the POMC (Fig. 8b). It is noted the Tafel slope of the N-POMC is the lowest among all the as-prepared doped catalysts, further confirming the high catalytic activity for ORR.

The transferred electron number (n) was calculated from the RDE measurements (Figs. S1a, c and e) and K-L plots (Figs. S1b, d and f) was plotted, which the potential range is chosen according to the previous literature [34,35]. All the samples demonstrate a same trend: n increases with the increasing of the overpotential. The values of n were lower than 4, implying the combination of 4-electron pathway and 2-electron pathway for ORR. For N-POMC, the value of n is always higher than that of the N, P-OMC and the P-NOMC, indicating 4-electron pathway for ORR plays more important role for the N-POMC than the other samples, marking the high activity for ORR.

It is understood that the samples of N, P-OMC and P-NOMC have similar activities for ORR, due to their similar amounts of the dopants. In addition, the above two samples show much better activities for ORR than POMC and NOMC, because their higher amounts total dopants, confirming the amounts of dopants is important to influence the ORR performance. However, the N-POMC illustrates the best activity among the as-prepared samples with less amounts of the dopants, which is even less than the single-doped NOMC, indicating another reason more than the amount of the dopants should be responsible for the high activity for ORR. XPS results show the main difference of the as-prepared samples is the enhancement of the ratio of graphitic-N in the N-POMC, compared with others.

### DFT calculation

To fully understand the orientation effect of the first doped P, density functional theory (DFT) calculations were used to illustrate how the later doped N was influenced (detailed [Fig. 4](#fig4) Raman spectra of the as-prepared samples.

<p>| Amounts of dopants in the as-prepared samples from XPS. |
|-----------------|------|------|---------|--------|</p>
<table>
<thead>
<tr>
<th>N (at. %)</th>
<th>P (at. %)</th>
<th>O (at. %)</th>
<th>Total of N + P (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N, P-OMC</td>
<td>3.58</td>
<td>0.50</td>
<td>3.79</td>
</tr>
<tr>
<td>NOMC</td>
<td>3.80</td>
<td>0.49</td>
<td>3.54</td>
</tr>
<tr>
<td>P-NOMC</td>
<td>3.61</td>
<td>0.65</td>
<td>3.42</td>
</tr>
<tr>
<td>POMC</td>
<td>3.36</td>
<td>0.38</td>
<td>3.46</td>
</tr>
</tbody>
</table>

Fig. 4 — Raman spectra of the as-prepared samples.

**Table 2**

Fig. 5 — High resolution of P2p spectrum of (a) POMC (b) N, P-OMC (c) P-NOMC and (d) N-POMC. P-C (132.7 eV, P1) and P-O (133.8 eV, P2).
information can be found in SI). When P was introduced to carbon framework, it may either bond with carbon outside the carbon surface (outside mode) or doped into the carbon surface which makes distortion of the 2D carbon framework [17] (inside mode). For the outside mode (Fig. 9a), the bonded P could decrease the energy needed for the formation ($E_f$) of graphitic-N on its next-nearby sites (0.14 eV) compared with that on pristine carbon (0.40 eV) (Table S2), leading to the increase of the graphitic-N. For the inside mode (Fig. 9b), the value of $E_f$ for graphitic-N on the next-nearby sites (0.32 eV) of the doped P, is also smaller than that needed on pristine carbon (0.40 eV). Surprisingly, we also found that the adsorption energy ($E_{ads}$) of N on the doped P site (5.68 eV) is much higher than on pristine carbon (3.68 eV) which makes the structure shown in Fig. 9c could be formed easily (Table S3). More interestingly, when N adsorbed on the doped P sites, new N–C bonds were formed and the former P–C bonds were elongated and weakened significantly, which indicates that the formed graphitic-P sites would be replaced by graphitic-N. This mechanism has never reported before. With the so called ‘self-sacrifice’ mode, the results of XPS could be perfectly explained that why the content of P decreased significantly after N doping. The Bader charge analysis results (Fig. S2) were also listed in Tables S2 and S3. In all the cases, P

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**Fig. 6** – High resolution of N1s spectrum of (a) NOMC (b) N, P-OMC (c) P-NOMC and (d) N-POMC. Pyridinic-N (398.2 eV, N1), pyrrolic-N (399.5 eV, N2), graphitic-N (401.2 eV, N3) and pyridinic-N+–O– (403.0 eV, N4).

**Fig. 7** – CV curves for the (a) N, P-OMC (b) P-NOMC and (c) N-POMC in nitrogen- and oxygen-saturated 0.1 M KOH solution.
bears positive charges while N bears negative charges, which are consistent with their electronegativities. For the other two dual doped P-NOMC and N, P-OMC, the orientation effect of P would not be revealed.

To further reveal the role of graphitic-N towards ORR, oxygen adsorption on the carbon surface was also calculated by DFT method. It is found that the adsorption energy of oxygen molecule on the graphitic-N neighboring carbon is 0.25 eV, higher than on pure carbon (0.16 eV) (Table S4), making it possible that the oxygen adsorption changes from Pauling mode (Fig. 10a) to Yeager mode (Fig. 10b) [6]. The Bader charge analysis (Fig. S3) and the charge transfer analysis on oxygen molecule (Fig. 54) confirm that the two oxygen atoms were negative charged, when adsorbed in Yeager mode on the graphitic-N neighboring carbon, leading to the bond length of oxygen elongated from 1.21 Å to 1.25 Å. The elongation of O=O bond would inevitably facilitate its break, resulting in the promotion of 4-electron pathway for ORR and better activity [15,36–38]. Therefore, the more amount of the graphitic-N in the doped samples, the more ratio of 4-electron pathway for ORR happens, leading to higher value of n, which is consistent with the experimental results.

Fig. 8 — (a) LSV curves and (b) Tafel plots for the as-prepared samples, compared with the commercial Pt/C in oxygen-saturated 0.1 M KOH solution at a scan speed of 10 mV s⁻¹ and a rotation speed of 1600 rpm.

Fig. 9 — Schematic illustrations of orientation effect of the first doped P on the later doped N. (a) Outside mode (b) inside mode and (c) self-sacrifice mode.

Fig. 10 — Schematic illustrations of adsorption of oxygen on (a) pure carbon and (b) graphitic-N doped carbon.
Conclusion

In summary, doping order of N and P has a great influence on the amount and species of N, when preparing N, P dual-doped carbon. Electrochemical measurement shows the OMC first doped with P, and then with N exhibits superior activity for ORR, due to the orientation effect of the first doped P on the later doped N by increasing the ratio of graphitic-N significantly. Furthermore, a portion of the first doped P can act as the doping sites and be replaced by the later doped N, called ‘self-sacrifice’ mode and confirmed by experiments and DFT calculations. However, this orientation effect of P cannot be observed in other samples. Furthermore, our experimental and DFT calculation prove that the amount of graphitic-N is important in determining the activity for ORR. Therefore, it is recommended that the doping strategy developed in this work may be widely applicable to various systems in studying the synergy effect of different dopants and enhancing the activity for ORR.

Acknowledgement

The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. HKUST9/CRF/11G).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijhydene.2017.11.165.

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