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

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ABSTRACT

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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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.

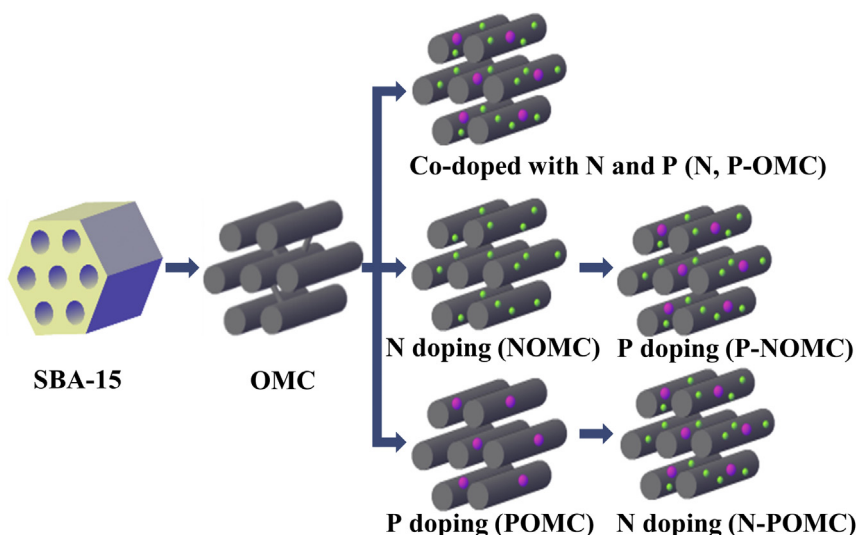


Fig. 1 – Schematic illustration of the preparation of the N, P dual-doped OMCs.

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