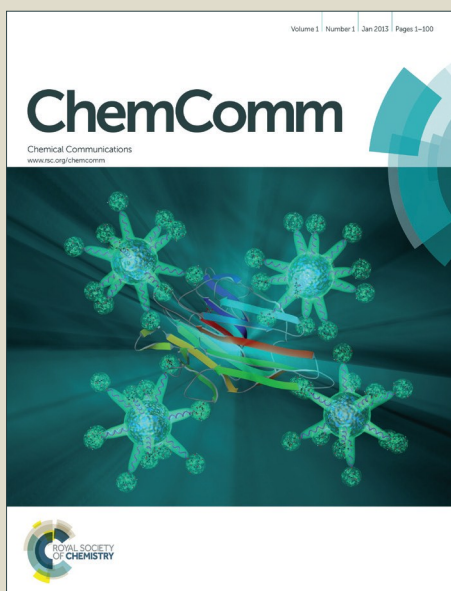


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Biochemistry-inspired direct synthesis of nitrogen and phosphorus dual-doped microporous carbon spheres for enhanced electrocatalysis†

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Polydopamine-derived N,P-codoped microporous carbon spheres are rationally synthesized through the self-polymerization of dopamine induced by the phosphonic species, showing efficient performance towards electrocatalytic oxygen reduction and hydrogen evolution reactions, due to the well-developed porosity and doping effect.

Weakening the high dependence of modern society on conventional fossil fuels represents a worldwide target of high priority, which has initialized a variety of advanced technologies for sustainable energy conversion and storage, such as metal-air batteries, fuel cells, and water electrolysis.¹ The key fact of these technologies and devices lies in a series of electrochemical processes, for instance, oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). Noticeably, Pt exhibits considerable electrocatalytic activity along with low overpotential and fast reaction kinetics towards both ORR and HER, though the low abundance as well as unfavorable price prohibit the application potential. In spite of tremendous endeavor to develop cost-effective alternatives to substitute noble Pt, transition-metal-based materials have been well spotted due to the various crystalline phases and the corresponding fantastic electron properties;² however, the deterioration susceptibility and low electrical conductivity greatly prevent the practical utilization. A new category beyond metals has been recognized as a promising candidate for Pt so as to broaden the selection range of catalytic systems.³

Featuring adjustable molecular structures, metal-free carbonaceous materials have been investigated for designated catalysis ranging from organics synthesis to electrochemistry.⁴

Further introduction of porosity into carbons can efficiently improve reaction processes owing to optimized mass transport and well-exposed active sites, among which micropores associated with a large surface area are essential for large energy conversion and storage.⁵ Although hard-templating and physical/chemical activation methods are capable of enhancing the microporosity,⁶ the constraints of typical synthesis are complication and involvement of toxic reagents. On the other side, the intentional engineering of pristine carbons through chemical doping in the carbonaceous backbone, such as N, P, B, and S, is a promising route to tailor the electronic characteristics and thus the apparent electrochemical activities.⁷ Particularly, the codoping of two different heteroatoms, e.g., N and P, into the carbon backbones can induce synergistic effect between the two elements, accordingly resulting in much enhanced electrocatalytic activity.⁷ However, the establishment of effective, yet controllable methodologies for the rational synthesis of heteroatom-doped microporous carbons in a manner of low costs and natural friendliness remains challenging.

Dopamine, a kind of biomolecules that contains amine and catechol functional groups, can easily self-polymerize under alkaline conditions to generate polydopamine (PDA), which can ideally perform as a carbon precursor to prepare N-doped carbons upon carbonization.⁸ Indeed, the codoping of two elements within the carbonaceous framework can remarkably boost the electrocatalytic performance, due to the synergistic effect between the heteroatoms by inducing large asymmetrical spin and charge density relative to single doping.⁹ Nonetheless, there is still scarce study focused on heteroatoms-codoped carbons depending on dopamine polymerization chemistry towards electrochemistry to the best of our knowledge. Herein, taking advantage of the strong and versatile self-polymerization capability of dopamine, we demonstrate our attempts to prepare N,P-codoped microporous carbon spheres (NP-MCS) in the presence of soft templates, wherein organophosphonic species serve as both P source and pH buffer. The resultant molecular peculiarity and

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Fig. 1 Schematic synthesis process of N,P-codoped microporous carbon spheres.

textual property of NP-MCS ensure excellent activity and durability for uses as electrocatalysts in ORR and HER.

Note that the organophosphonic moieties, as herein presented as sodium salt hydroxyethylidene diphosphonic acid (HEDPS), can be reversely protonized or alkalinized (Fig. S1), signifying the capability for pH buffering. Correspondingly, the addition of dopamine monomers into the basic HEDPS solution can mildly initialize the polymerization reaction; the amine functional groups in dopamine facilitate the easy incorporation of organophosphonic linkages because of the acid-base interaction with phosphoric sites (Fig. 1). As illustrated in the Fourier transform infrared (FT-IR) spectrum (Fig. S2), the characteristic spectral peaks of functional groups including N–H and C–N bands can be identified in the pristine polydopamine, while the typical amine bands weaken, accompanied with the appearance of weak phosphate vibrations in the HEDPS-incorporated polydopamine, suggesting the intimate linking from both components. The strong interactions between polymerized species and block

copolymers can favor the introduction of templates with high molecular weight. Further calcination under the protection of nitrogen is capable of carbonization and introduction of heteroatoms into the carbon backbones.

Scanning electron microscopic (SEM) image (Fig. 2a) displays that the NP-MCS material obtained exhibits the structural integrity and spherical morphology with diameter of 300–400 nm, consistent with the observation from transmission electron microscopic (TEM) analysis (Fig. 2b). Further magnification reveals the smooth surface of the carbon sphere (Fig. 2c), while high-resolution TEM (HR-TEM) graph in Fig. 2d shows that NP-MCS possesses micropore channels, but with no detectable mesopores or macropores. Energy-dispersive X-ray (EDX) mapping confirms that N and P elements are effectively introduced and homogeneously distributed throughout the carbon sphere matrix at the nanoscale (Fig. S3).

X-ray photoelectron spectroscopy (XPS) measurements were performed to identify the stoichiometry and chemical state. As depicted in Fig. 3a, the C 1s fine spectra for NP-MCS can be deconvoluted into four components, *i.e.*, 284.6 eV (π - π^* hybridized graphitic C), 285.9 eV (N- sp^2 C), 286.8 eV (C=O), and 288.7 eV (O–C=O).³ Fitting of N 1s spectra indicates the existence of pyridinic N, quaternary N, and pyridinic-N-oxide, attributable to binding energies of 397.8, 400.1, and 403.4 eV, respectively (Fig. 3b).^{3,9} For the P 2p region spectra, the main contribution is situated at the dominant contribution located at 133.7 eV can be assigned to phosphate-like structures bound to carbon lattices, as well as a shoulder at 131.8 eV corresponding to P–C bond (Fig. 3c).⁷ These functional groups as detected by XPS are indicative of carbons that contain N and P heteroatoms chemically bonded in the carbonaceous network.

Indeed, chemical doping can result in the variation of electronic structures, as evidenced by Raman spectroscopy. Fig. 3d demonstrates two sharp peaks in the Raman spectrum at low frequency of 1360 cm^{-1} (D band) and 1585 cm^{-1} (G band), ascribed to the imperfections in sp^2 carbon structures and the E_{2g} vibrational mode of graphitic carbon atoms, respectively, whereas the wide 2D band located around 2700 cm^{-1} in the high frequency is associated with graphitic carbons.³ The graphitic property is further illustrated by the X-ray diffractive (XRD), which shows one broad peak at $2\theta = 24.2^\circ$ and the other weak diffraction around $2\theta = 41^\circ$ (Fig. S4), characteristics of graphitic carbon materials with a low degree of graphitization. Moreover, the downshift of the G band in comparison with pristine carbons provides additional evidence for the defective structures resulted from the doping effect.¹⁰ By calculating the ratio of intensities of D band and G band (I_D/I_G), the relative degree of disorder/order can be determined. The increased I_D/I_G value of NP-MCS (1.53) relative to that of the N-doped counterpart (1.43), prepared in the absence of phosphonic reagent (marked as N-MCS, Fig. S5 and S6), can be related to the additional P modification.

N_2 adsorption-desorption isotherms were collected to evaluate the textual properties of the synthesized carbons. The adsorption isotherm for NP-MCS is of typical H1 together with

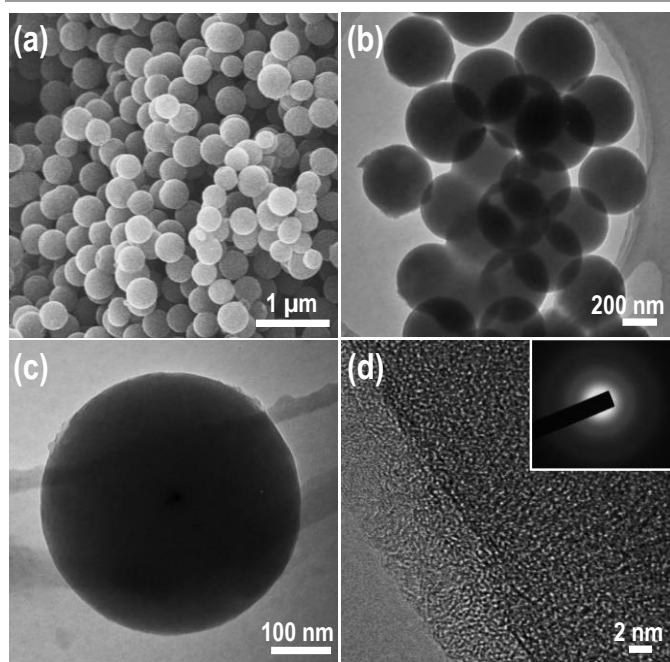


Fig. 2 SEM (a) and TEM (b–d) images of NP-MCS. Inset of (d) shows the selected area electron diffraction (SAED) pattern.

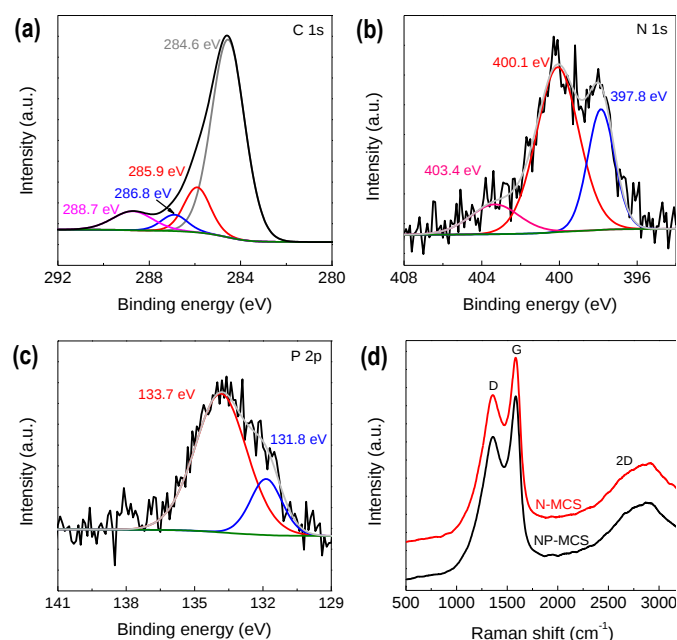


Fig. 3 (a-c) High-resolution XPS spectra of C 1s, N 1s, and P 2p in NP-MCS. (d) Raman spectra of N-MCS and NP-MCS.

significant adsorption below relative pressure (P/P_0) < 0.1 (**Fig. S7**), due to the capillary filling of micropores. There are almost no hysteresis loops in the medium P/P_0 range, revealing the absence of mesoporosity of the resulting carbons. Accordingly, the pore size distribution curve shows a maximum around 1.3 nm. The N_2 condensation close to atmospheric pressure in the adsorption branch means the presence of cavities between the spheres. Of note is that NP-MCS possesses a higher Brunauer–Emmett–Teller (BET) specific surface area of $634 \text{ m}^2 \text{ g}^{-1}$ than that of N-MCS ($542 \text{ m}^2 \text{ g}^{-1}$), indicating that introducing P heteroatoms into the carbonaceous framework can efficiently improve the textural properties.¹¹ Although soft templates are employed in the typical synthesis, mesostructures cannot be reasonably achieved. It should be noted that PDA can robustly adhere on a diversity of matrix,¹² as herein on supermolecular copolymers (**Fig. 1**). Further polymerization reaction can significantly disturb the general self-assembly behavior of block copolymers that is driven by relatively weak intermolecular interaction, leading to the unfolding of copolymer supermolecules and thus inducing the embedding of block chains into the polydopamine. The removal of the template molecules upon calcination can result in the generation of microporosity, as the block chains of triblock copolymer are able to make some disfigurement in the pore wall of the final products.¹³ In comparison with NP-MCS, the much lower specific surface area of the carbonaceous material prepared in the absence of F127 further confirms the positive role of template molecules in improving the resultant porosity (**Fig. S8**).

Introducing heteroatoms into the porous carbon frameworks is believed to play a crucial role in elevating the electrocatalytic activity. Cyclic voltammograms (CVs) are first carried out in 0.1 M KOH solution saturated with O_2 to evaluate the electrochemical ORR performance (**Fig. 4a**). Well-

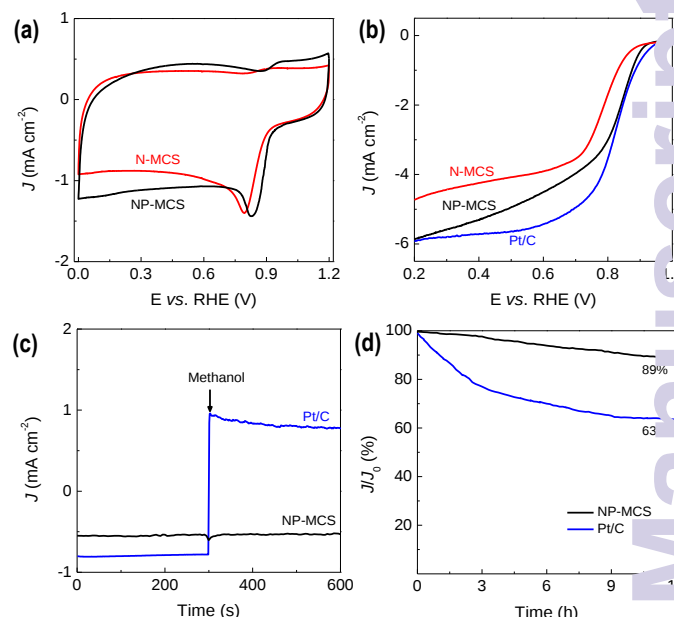


Fig. 4 (a) CV curves of NP-MCS in O_2 -saturated 0.1 M KOH solutions at a scan rate: 20 mV s^{-1} . (b) LSV curves of N-MCS, NP-MCS and Pt/C in O_2 -saturated 0.1 M KOH. (Scan rate: 5 mV s^{-1} , rotating speed: 1600 rpm). (c) The chronoamperometric response curve of NP-MCS and Pt/C after the instant addition of methanol. (d) The chronoamperometric responses of NP-MCS and Pt/C at 0.8 V.

resolved cathodic oxygen reduction peaks appear in the both cases of NP-MCS and N-MCS, whereas NP-MCS exhibits larger CV area and more positive peak potential, implying that the incorporation of P dopant is effective to enlarge the electrocatalytically active surface area by generating additional active sites and facilitate the ORR process. In the linear sweep voltammograms (LSVs) recorded on rotating disk electrode (RDE) (**Fig. 4b**), the dual-doped NP-MCS sample outperforms the singly doped N-MCS catalyst in terms of reaction current density, half-wave potential, and onset potential, coinciding well with the CV results and thereby revealing the enhanced synergistic effect of N and P codoping. Notably, the onset potential and limiting current density for NP-MCS approach the commercial Pt/C reference. A series of more detailed measurements of the RDE systems at different rotation speeds from 900 to 2500 rpm were conducted to illustrate the electrochemical oxygen reduction kinetics (**Fig. S9** and **S10**). The current density increases with the raise of rotating rate because of the shortened diffusion distance at high speed and electron transfer number (n) can be determined according to Koutecky–Levich (K–L) equation (**Fig. S9** and **S10**). From the linear relationship of K–L plots, the n value in one ORR process is determined to be 3.82 for NP-MCS, close to that of Pt/C (3.87), indicating the pseudo-four-electron-dominated oxygen reduction pathway.

High catalytic selectivity against fuel oxidation during cathodic reactions is of great importance in developing low-temperature fuel cells. For Pt/C, the cathodic current shifts to the anodic current immediately after the addition of methanol (**Fig. 4c**), which is accompanied with one new peak observed (**Fig. S11**), attributed to methanol oxidation–reduction, i.e., a poisoning of the noble catalyst. In sharp contrast, no activity

specific to methanol is happened to NP-MCS (Fig. 4c and S12), suggesting the excellent tolerance ability to methanol crossover effect. Moreover, chronoamperometric response test show that NP-MCS retains 89% of the initial current after 12 h continuous operation at 0.8 V, whereas Pt/C loses nearly 37% of its initial current (Fig. 4d). The strong long-term durability of the carbon-based catalyst can be ascribed to the stable chemical bonding of N and P in the carbonaceous backbone.

Additionally, the electrocatalytic activities of the carbonaceous materials towards HER were examined in acidic medium (0.5 M H₂SO₄). From the polarization curves and Tafel plots (Fig. S13), NP-MCS shows certain superiority over N-MCS in both onset potential (148 vs 183 mV) and Tafel slope (108 vs 126 mV dec⁻¹). The dual-doped NP-MCS material requires an overpotential of 270 mV to realize a HER current density of 10 mA cm⁻², lower than N,P-codoped or singly doped carbons.^{9a} It should be noteworthy that the HER activity of NP-MCS can even rival some classical metallic catalysts, for instance, nanostructured molybdenum carbide, nickel-molybdenum nitride nanosheets, and hierarchical molybdenum disulfide microboxes.¹⁴ In addition, both NP-MCS and N-MCS present Tafel slopes in the region of 90–130 mV dec⁻¹, manifesting that an initial proton adsorption (Volmer step: H⁺ + e⁻ → H*) is the rate-controlling step of the whole HER process. The chemical doping of N and P heteroatoms endows the resultant carbons with enhanced capability to adsorb hydrogen that therefore can accelerate the most sluggish step (H* adsorption) during the whole hydrogen evolution process.^{9a} Remarkably, the stable current output over 12 h of continuous operation suggests the pronounced stability of NP-MCS for HER in acid electrolyte (Fig. S14).

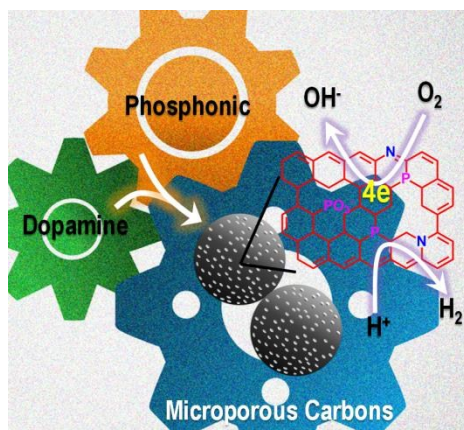
To conclude, we have disclosed an efficient strategy to prepare microporous N and P dual-doped carbon spheres, wherein the self-polymerization effect upon the stimulation of organophosphonic moieties permits the successful introduction of dopant atom. The remarkable features of abundant porosity, chemical doping and carbonaceous framework render the microporous carbons a promising candidate for electrochemical ORR and HER with enhanced catalytic activity and long-term stability. The synthetic method described in this study towards porous carbon spheres holds the potential to exploiting alternative metal-free multifunctional electrocatalysts for renewable and sustainable energy conversion and storage applications.

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TOC Content



N,P-doped microporous carbon spheres based on the self-polymerization peculiarity of dopamine show enhanced electrocatalytic performance in ORR and HER.