Constrained-volume assembly of organometal confined in polymer to fabricate multi-heteroatom doped carbon for oxygen reduction reaction

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ABSTRACT The design and preparation of non-precious metal and carbon-based nanocomposites are critical to the development of efficient catalysts for technologies ranging from water splitting to fuel cell. Here, we present a constrained-volume self-assembly process for the one-step continuous precipitation-induced formation of soft colloidal particles, in which hydrophobic organoferrous compound, $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$, is encapsulated within poly(styrene-co-acrylonitrile) nanoparticles (NPs). The protective and confining polymer matrix ensures uniform carbonization and dispersion of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ within a carbon matrix after a pyrolysis process. The obtained carbon NPs are successfully co-doped with Fe, P and N with a relatively high surface area of $\sim 380 \text{ m}^2 \text{ g}^{-1}$. The Fe-P-N-doped carbon catalyst exhibits high catalytic performance and stability toward oxygen reduction reaction in both alkaline and acidic electrolytes *via* a favorable four-electron pathway. Meanwhile, the catalytic capability of Fe-P-N-doped carbon can be tailored by the tunable nanostructures.

Keywords: heteroatom doping, carbon, constrained-volume, self-assembly, electrocatalyst

INTRODUCTION

Owing to the high power density and energy-conversion efficiency, fuel cells have been regarded as one of the most promising and available energy conversion technologies with nearly no environmental contamination [1,2]. Currently, Pt based nanomaterials are considered to be the most efficient electrocatalyst for cathodic oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs) [3,4]. Nevertheless, high cost, limited

supply, and low stability of Pt catalyst still greatly hamper their commercialization. Alternatively, a great number of efforts have been made to the design and synthesis of heteroatom doped carbon as an efficient catalyst [5–11]. For example, N-doped carbon materials exhibit good performance towards ORR as O_2 species are easily reduced on the positively charged C neighboring N atoms [12–14]. Moreover, more active sites with varied charge density were introduced when a small amount of transition metal (e.g., Fe, Ni, or Co) and N were co-doped in carbon matrix. Therefore, co-doping of metal and non-metal elements would be beneficial to various electrochemical processes [15–18].

Polyacrylonitrile (PAN) is a widely used polymer precursor for carbon with inherent N dopant [19]. However, strong dipole–dipole interaction between the highly polar nitrile groups endows PAN low solubility and limits most of PAN structures to a fibrous morphology [20]. One strategy to improve the solubility and the ability in microphase-separated nanostructures is to incorporate soft polymer block into PAN backbone. A series of PAN-based copolymers, such as poly(acrylonitrile-*b*-butyl acrylate), were prepared and expanded the possibility of copolymer self-assembly. At the same time, the derived carbon materials present varied morphologies and structures [21–23]. On the other hand, the general preparation of PAN-derived carbon/metal nanocomposites involves multiple steps: i) PAN carbonization into carbon nanofiber (CNF); ii) functionalization of CNF; iii) subsequent dispersion of metal nanoparticles (NPs) [24]. An *in-situ* encapsulation method would avoid the tedious steps of post-modification as well as facilitate the uniform

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dispersion of metallic NPs within the framework of CNFs. For example, Huang and coworkers [25] have directly electrospun a mixture of PAN and Pd(acetate)₂, followed by carbonization. The obtained Pd/CNF composites exhibited good performance towards the reduction of H₂O₂ and the oxidation of nicotinamide adenine dinucleotide (NADH).

The rational design and processing of multi-doped carbon derived from PAN-based polymers and metal precursors remains a challenge in the production of efficient nanocomposites for catalytic ORR. Here, we report a novel polymer processing technique, constrain-volume self-assembly, for co-precipitation of poly(styrene-co-acrylonitrile) (PS-*c*-PAN) (see Fig. S1a in Supplementary information) with a hydrophobic organoferrous compound, (Ph₃P)₂Fe(CO)₃ (Fig. S1b). By confining a rapid self-assembly to small volume, we are able to overcome the different speeded phase-separation and produce hydrophobic organometallic species confined within a polymer assembly with a high efficiency. Pyrolysis of the PS-*c*-PAN NPs entrapped (Ph₃P)₂Fe(CO)₃ results in carbon nanomaterials with co-doping of Fe, P and N with a relatively high surface area. We demonstrate that the obtained Fe-P-N-doped carbon catalysts show an enhanced electrocatalytic activity and durability for ORR with tailoring capability.

EXPERIMENTAL SECTION

Materials synthesis

All the reagents were analytical grade. (Ph₃P)₂Fe(CO)₃ was prepared according to the previously reported method [26]. (Ph₃P)₂Fe(CO)₃@PS-*c*-PAN NPs were prepared *via* flash nanoprecipitation (FNP) using an impinging jet mixer. In detail, Stream 1 contained 3 mg PS-*c*-PAN and 5 mg (Ph₃P)₂Fe(CO)₃ dissolved in 2 mL of THF, while Stream 2 contained 2 mL of water. The two input streams were expelled from both syringes with the same rate (~37 mL s⁻¹), causing two streams to merge and drop into a beaker filled with 20 mL H₂O. (Ph₃P)₂Fe(CO)₃@PS-*c*-PAN NPs were collected by centrifugation and then dried at 60°C. Then the dried NPs were placed in a tube furnace and stabilized at 280°C for 1 h in air with heating rate of 5°C min⁻¹ and carbonized at 800°C for 2 h under N₂ flow with a heating rate of 5°C min⁻¹. This as-prepared Fe-P-N-doped carbon was designated as FNP-5. FNP-3 and FNP-1 were prepared using the same procedure except varying the amount of 3 or 1 mg (Ph₃P)₂Fe(CO)₃ dissolved in 2 mL of THF for Stream 1, respectively. Pure PS-*c*-PAN NPs were prepared using the

same FNP procedure except that only PS-*c*-PAN polymer in Stream 1. A control experiment was carried out by slow addition of H₂O (2 mL) into THF (2 mL) mixture of 3 mg PS-*c*-PAN and 5 mg (Ph₃P)₂Fe(CO)₃.

Characterization

X-ray diffraction (XRD) patterns were recorded on a D/MAX 2550 powder diffractometer (D/max 2550V, Rigaku, Tokyo, Japan), using Cu K α radiation. Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were conducted on a JEM-2100 F electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. Nitrogen adsorption-desorption isotherms were performed with a Quadachrome adsorption instrument (Autosorb-iQ3; Quantachrome, America) at 77 K. The specific surface area was calculated by using the adsorption data *via* the Brunauer-Emmett-Teller (BET) method. The pore size distribution and the total pore volume were derived from the related adsorption branch by using the Barrett-Joyner-Halenda (BJH) model. X-ray photoelectron spectroscopic (XPS) analysis was performed on a ESCALAB 250Xi operated at 120 W.

Electrochemical characterization

The electrochemical activities of Fe-P-N-doped carbon for ORR were measured at room temperature by using a CHI-760E electrochemical analyzer with a three-electrode cell system. A glassy carbon disk electrode (5 mm in diameter, Pine Instrument Co., USA) coated with Fe-P-N-doped carbon was employed as working electrode, while a Ag/AgCl (saturated KCl) and Pt electrode were used as reference and counter electrode in the measurement, respectively. For preparation of the working electrode, the catalyst inks were prepared by dispersing 10 mg Fe-P-N-doped carbon or commercial Pt/C-JM catalyst (Johnson Matthey, 20 wt% Pt) in a mixture of 1.25 mL ethanol and 0.03 mL Nafion (5%), and the desired amount of such catalyst inks as deposited onto the polished glassy carbon electrode and dried at room temperature before measurement.

Cyclic voltammetry (CV) and rotating ring disk electrode (RRDE) techniques for ORR were carried out in O₂-saturated 0.1 mol L⁻¹ KOH solution or 0.1 mol L⁻¹ HClO₄ solution. The loadings of Fe-P-N-doped carbon on the working electrode were 0.36 and 0.60 mg cm⁻² in O₂-saturated 0.1 mol L⁻¹ KOH and 0.1 mol L⁻¹ HClO₄, respectively. The loadings of Pt/C (20 wt.%) catalysts on the working electrode were 0.10 mg cm⁻² in both electrolytes. For all the CVs, linear sweep voltammetry (LSV), and chronoamperometric measurements, the scan rate was

10 mV s⁻¹. All potentials in this study were reported with respect to the reversible hydrogen electrode (RHE).

Hydrogen peroxide yields and the electron transfer number (n) were calculated using the equations below:

$$n = \frac{4I_D}{I_D + I_R/N}, \quad (1)$$

$$\% \text{HO}_2^- = 200 \times \frac{I_R/N}{I_D + I_R/N}, \quad (2)$$

where I_D , I_R and N are the disk current, ring current and the ring collection efficiency, respectively. In this measurement, $N=0.37$.

RESULTS AND DISCUSSION

Synthesis, structure, and composition of materials

Constrained-volume self-assembly is a continuous process exploiting an impinging jet mixer to bring about the precipitation of polymers under turbulent conditions [27–29]. The process is different from the slow time scale of solvent exchange and thermodynamic equilibrium of polymer assembly in conventional solution self-assembly. The polymer solution confined within a small volume would rapidly mix with the non-solvent in millisecond time-scale to induce self-assembly of polymers into kinetically frozen NPs [30,31]. As a result, the rapid mixing of polymers with active ingredients would avoid the diffusion-limited formation of polymer micelles and precipitates of ingredients. Thus, instead of individually separated ensembles, a composite structure is co-assembled in which small aggregate of active ingredients are entrapped within a polymer shell [32]. Using this technique, also termed FNP, Prud'homme and coworkers [33–36] have successfully incorporated hydrophobic drugs, fluorophores and inorganic NPs within block copolymer ensembles. In addition, Priestley and coworkers [37–39] have exploited FNP to process a series of polymer NPs ranging from homogeneous latex to patchy colloids.

Fig. 1 illustrated the schematic process of one-step constrained-volume self-assembly, in which polymer and metal precursors assembled into organometal@polymer colloids in a controllable manner by confining the volume and time scale of mixing. In detail, a confined impinging jet (CIJ) mixer was used to achieve a rapid mixing within a confined space. The interior structure of CIJ mixer is T-shape mixer (Fig. S2), where syringe pumps are employed to drive two opposing liquid streams at high velocity and collide in the mixing chamber [40,41]. A syringe containing PS-*c*-PAN and (Ph₃P)₂Fe(CO)₃ dissolved in THF was placed at the inlet of stream 1, and a syringe con-

Figure 1 Schematic illustration of constrained-volume self-assembled (Ph₃P)₂Fe(CO)₃@PS-*c*-PAN NPs and conversion into Fe-P-N-doped carbon materials.

Figure 2 TEM images of (a) pure PS-*c*-PAN NPs; (b) (Ph₃P)₂Fe(CO)₃@PS-*c*-PAN NPs. (c) STEM and elemental mapping of (Ph₃P)₂Fe(CO)₃@PS-*c*-PAN NPs.

taining H₂O was placed at the inlet of stream 2. Subsequently, fluid was expelled manually from both syringes at the same rate (~1 mL s⁻¹), causing the two streams to merge and then be diluted into a water reservoir. The water reservoir quenched the precipitated NPs and a stable colloid solution was formed. After steps of purification, stabilization and further carbonization, Fe-P-N-doped carbon composites were obtained.

The TEM image in Fig. 2a shows that the pure PS-*c*-PAN NPs through FNP are spherical in shape with the average diameter of ~140 nm. Simultaneous feeding of both PS-*c*-PAN and (Ph₃P)₂Fe(CO)₃ leads to an increase of NP size to ~175 nm (Fig. 2b), which comes from the expanded volume after (Ph₃P)₂Fe(CO)₃ encapsulation. No other precipitates or side-products are observed, indicating high encapsulation efficiency. Scanning transmission electron microscopy (STEM) with elemental

Figure 3 TEM images of (a) FNP-5, (b) FNP-3 and (c) FNP-1; (d) corresponding HRTEM images of FNP-5.

mapping results revealed a homogeneous distribution of P and Fe elements within a PS-c-PAN NP (Fig. 2c).

A control experiment was carried out by slow addition of H_2O into a THF mixture of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ and PS-c-PAN. The obtained NPs (Fig. S3a) possess irregular morphologies while clusters of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ are visible and dispersed on the surface of polymer, which results from the different precipitation kinetics of the two compounds during a slow self-assembly process. Hence, the formation of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3/\text{PS-c-PAN}$ NPs through FNP can be envisioned as follows: solvent exchange in confined-volume is faster than the aggregation process of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ while at the same time, rapid mixing balances the timescale of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ nucleation and growth with the timescale of polymer self-assembly, ensuring the formation of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3/\text{PS-c-PAN}$ NPs.

Carbonization at high temperature leads to the con-

version of PS-c-PAN encapsulated $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ NPs into Fe-P-N-doped carbon. FNP-5, FNP-3 and FNP-1 are denoted as a series of Fe-P-N-doped carbon obtained from different organoferrous feed amounts of 5, 3 and 1 mg in stream 1, respectively, while pure carbon NPs (denoted as FNP-0, TEM image shown in Fig. S3b) were also prepared by pyrolyzing pure PS-c-PAN NPs through FNP (see experimental details in SI). TEM image of FNP-5 in Fig. 3a shows that Fe-based NPs with average size of ~ 40 nm were uniformly dispersed inside a carbon matrix. Element mapping in Fig. S4 indicates that Fe, N and P elements were uniformly distributed within carbon matrix. An HRTEM image (Fig. 3d) displays clear lattice fringes with interplanar spacing of 0.20 and 0.34 nm, consistent with the (031) basal planes of crystalline Fe_3C or (110) planes of cubic Fe and the (002) plane of graphitic C, respectively [42]. The XRD results confirm the existence of Fe_3C (JCPDS No. 85-1317) and graphitized carbon, as shown in Fig. S5a.

The confinement effect of PS-c-PAN shell makes the $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ well protected during carbonization and results in a uniform distribution of carbonized products among the carbon matrix. The results demonstrate the successful encapsulation of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ inside PS-c-PAN NPs during FNP. The effect of processing parameters on the preparation was studied by decreasing the feeding amount of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ in stream 1. As shown in Fig. 3b, c, FNP-3 and FNP-1 from lower $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ feed concentrations retain a good dispersion of Fe-based NPs while the size decreases to 15 and 5 nm, respectively. Meanwhile, a sparser distribution of Fe_3C NPs within the carbon support is observed when lowering the $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ feed concentration in stream 1, indicating the ability to tune the metal NPs arrangement by changing process conditions.

Raman spectra in Fig. 4a exhibit two obvious peaks

Figure 4 (a) Raman spectra of FNP-5 (black line) and FNP-0 (red line); (b) N_2 sorption isotherm and pore size distribution (inset) of FNP-5.

Figure 5 Deconvoluted high resolution XPS of FNP-5: (a) Fe 2p, (b) N 1s and (c) P 2p; (d) a simplified model of Fe-P-N doped carbon (green ball: N; blue ball: P; red ball: Fe; black ball: C).

around 1,330 and 1,580 cm^{-1} , corresponding to D and G band for carbon [43]. Fe and P doping lead to a smaller I_D/I_G value of FNP-5 compared with that of FNP-0, suggesting a higher graphitization degree after co-doping [44]. N_2 sorption isotherms of FNP-5 in Fig. 4b show a type IV isotherm and a H_4 -type hysteresis loop with a relatively high surface area of $\sim 380 \text{ m}^2 \text{ g}^{-1}$ and a pore size of $\sim 4 \text{ nm}$, revealing the mesoporous structure derived from the degradation of PS during carbonization. XPS spectra of FNP-5 in Fig. S5b confirm the co-existence of Fe (1.3 at%), P (3.9 at%) and N (6.1 at%) in the carbon matrix. The peaks of Fe 2p spectrum (Fig. 5b) at 706.9, 710.4, 712.7, 724.6 and 729.9 eV are corresponding to metallic Fe, $\text{Fe}^{2+} 2p_{3/2}$, $\text{Fe}^{3+} 2p_{3/2}$, $\text{Fe}^{2+} 2p_{1/2}$ and $\text{Fe}^{3+} 2p_{1/2}$, indicating the binding state between iron and nitrogen, phosphorus or carbon [45,46]. In addition, the existence of metallic Fe can boost the activity of Fe-N_x and plays an important role in enhancing the ORR activity of the catalysts [47]. In the high-resolution N 1s spectrum (Fig. 5b), the four deconvoluted peaks near 398.4, 399.9, 401.1 and 404.3 eV are attributed to pyridinic-, pyrrolic-, graphitic-N, and pyridine N-O, respectively [48,49]. The deconvoluted P 2p spectrum (Fig. 5c) reveals two peaks at 133.1 and 134.1 eV, assigned to isolated P-C and surface

P-O species, respectively. The successful doping of P and Fe is believed to arise from $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ while N from PS-c-PAN. Moreover, the entrapment of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ in PS-c-PAN guarantees a synergetic effect for carbonization into Fe-N-P-doped carbon: i) uniformly encapsulation of organometallic precursor in PS-c-PAN results in the well-dispersed dopants (e.g., Fe, N, P) within carbon matrix; ii) pyrolyzing active ingredients within a confined space bestows a high doping efficiency; iii) sufficient reaction between each element occurring in a nano-confinement leads to the formation of active metal Fe NPs, Fe_3C , Fe-P, Fe-N, and N-P in the doped carbon materials (as shown in a molecular model of Fig. 5d) for electrochemical applications.

Electrocatalytic performance of catalysts

Electrocatalytic performances of FNP-5, FNP-3, FNP-1 and commercial Pt/C for ORR were investigated and compared in both O_2 -saturated 0.1 mol L^{-1} KOH and 0.1 mol L^{-1} HClO_4 electrolyte solution. ORR peak E_p (Fig. 6a) and half-wave potential $E_{1/2}$ (Fig. 6b) are observed for FNP-1 ($E_p=0.80 \text{ V}$; $E_{1/2}=0.78 \text{ V}$), FNP-3 ($E_p=0.83 \text{ V}$; $E_{1/2}=0.81 \text{ V}$) and FNP-5 ($E_p=0.85 \text{ V}$; $E_{1/2}=0.83 \text{ V}$) in 0.1 mol L^{-1} KOH. It is noted that the half-wave potential

Figure 6 CV curves of the prepared Fe-P-N-doped carbon in O₂-saturated (a) 0.1 mol L⁻¹ KOH and (d) 0.1 mol L⁻¹ HClO₄. RRDE polarization curves for Fe-P-N-doped carbon and commercial Pt/C at 1,600 rpm in O₂-saturated (b) 0.1 mol L⁻¹ KOH and (e) 0.1 mol L⁻¹ HClO₄. Calculated peroxide yields and the electron transfer number based on the corresponding RRDE polarization curves in O₂-saturated (c) 0.1 mol L⁻¹ KOH and (f) 0.1 mol L⁻¹ HClO₄.

of FNP-5 is close to that of commercial 20 wt% Pt/C ($E_{1/2}$ =0.85 V). In Fig. 6c, H₂O₂ yields for FNP-1, FNP-3, FNP-5 and Pt/C are 4%, 2%, 1.5% and 1.5%, and the corresponding electron transfer number are 3.92, 3.96, 3.97 and 3.97, respectively. When tested in 0.1 mol L⁻¹ HClO₄, FNP-5, FNP-3 and FNP-1 show ORR peak at 0.65, 0.63 and 0.60 V (see Fig. 6d), and a half-wave potential at 0.63, 0.61, and 0.58 V (Fig. 6e). H₂O₂ yields in HClO₄ for FNP-1, FNP-3, FNP-5 and Pt/C are 6.7%, 3.4%, 1.9% and 2.3%, and the corresponding electron transfer numbers are 3.86, 3.93, 3.96 and 3.95, respectively (Fig. 6f). While further increasing the feeding amount of organoferrous to 7 mg, Fe-based NPs in FNP-7 with average size of ~100 nm dispersed inside a carbon matrix could be observed in Fig. S6a. FNP-7 shows comparable ORR activity to FNP-5 (Fig. S6b–d), indicating that the density of accessible active sites reached a maximum value in both FNP-5 and FNP-7.

It is worth noting that FNP-5 shows the lowest H₂O₂ yield and a nearly 4 electron process either in alkaline or acidic medium, indicating it possesses a similar ORR kinetics to commercial Pt/C. On the other hand, the series of FNP catalysts reported herein demonstrate excellent catalytic performance compared to the reported Fe-P-C, Fe-N-C and P-N-C catalysts [50–52]. The outstanding performance is mainly attributed to the unique composition and structure of the nanocomposites through constrained-volume self-assembly. Firstly, the organo-

metal and polymer precursors contain a diversity of active elements, leading to a variety of energetic centers such as Fe–C, Fe–P, Fe–N, N–P and N–C for electrochemical process [47,50,51]. At the same time, the polymer coating leads to the uniform distribution of Fe-based NPs within the carbon matrix and a strong interaction between them. The voids due to the volatilization of PS blocks make the active sites more accessible. All these advantages make FNP-5 an efficient ORR catalyst that is comparable to the recently reported doped carbon catalysts [43,48,53]. Another unique feature of our materials is the catalytic tunability when co-feeding different concentrations of organometallic compound, resulting in the controllable amount of metal, size distribution and particle dispersion in doped-carbon catalysts.

Methanol crossover property and durability of FNP-5 were also investigated. No notable changes for the half-wave potential and current density were observed in the presence of 2 wt% methanol in both alkaline and acidic medium (Fig. S7a, d). By contrast, a significant half-wave potential decrease of the commercial Pt/C was observed after the injection of methanol (Fig. S7b, e). The comparison clearly demonstrates a better tolerance to methanol crossover for FNP-5. The durability of the FNP-5 for ORR was also evaluated (Fig. S7c, f). The current density of FNP-5 shows a low decay (about 4% in 0.1 mol L⁻¹ KOH and 15% in 0.1 mol L⁻¹ HClO₄) after running for 20,000 s. In contrast, the current on Pt/C

suffered a 25% loss in 0.1 mol L⁻¹ KOH and 33% loss in 0.1 mol L⁻¹ HClO₄ after running for 10,000 s, respectively. It is apparent that FNP-5 exhibits an excellent stability compared to the commercial Pt/C. The better catalytic stability of FNP-5 is related to the lower H₂O₂ yields of ORR over FNP-5 (Fig. 6c, f). However, owing to the easy-poisoning property of nanosized Pt metal and the ex-foliation of Pt metal from carbon supports [54], the commercial Pt/C catalyst suffers more loss of current density than FNP-5.

Another advantage of FNP is its characteristics of continuous-flow, making the whole process controllable and scalable. As shown in video S1, a CIJ mixer and a high-precision programmable syringe pump were used to scale up the synthesis process. Stream 1 containing THF solution of PS-c-PAN and (Ph₃P)₂Fe(CO)₃ and stream 2 containing H₂O were admitted into the CIJ mixer at a flow rate controlled through the syringe pump with ~4 mg s⁻¹ production ability for (Ph₃P)₂Fe(CO)₃@PS-c-PAN NPs. The low energy and continuous process enables large scale production. For example, the reported production capability could reach 3.5 kg day⁻¹ using continuous-flow setup and commercial production of β -carotene nanoparticles were produced at 1,400 kg day⁻¹ using CIJ technology [37].

CONCLUSIONS

In summary, we report a constrained-volume precipitation technique for the preparation of organometal-polymer assembly. Spherical nanocomposites composed of (Ph₃P)₂Fe(CO)₃-confined PS-c-PAN NPs were converted into well-dispersed Fe-P-N-doped carbon with a high porosity. Controlling over distribution of dopants and nanostructure has been achieved by simply changing the processing parameters. The obtained multiple heteroatom-doped carbon catalysts provide a favorable structure for ORR and exhibit excellent electrocatalytic activity and stability. Tunable nanostructure and composition of Fe-P-N-doped carbon lead to tailored catalytic ORR capability. Another significant advantage of our process is that the inherent continuous-flow feature makes particle production scalable. Therefore, the constrained-volume self-assembly is a promising approach in the rational design and preparation of a variety of nanocomposites for fuel cells, supercapacitors and metal-air batteries.

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Supplementary information Experimental details are available in the online version of the paper.

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聚合物限域金属有机化合物自组装构筑高效多孔多元掺杂碳基氧还原催化剂

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摘要 非贵金属碳纳米复合材料的设计和制备对于开发电解水及其燃料电池等技术的高效催化剂至关重要。本文提出了一种连续沉淀诱导形成胶体颗粒的限域自组装方法, 其中疏水性金属有机化合物($(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$)被包裹在聚(苯乙烯-共聚-丙烯腈)纳米颗粒中。具有限域作用的聚合物能够确保 $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ 在高温热解过程中均匀碳化并分散在碳基质中, 成功制备出Fe、P和N共掺杂的碳纳米颗粒, 其比表面积高达 $380 \text{ m}^2 \text{ g}^{-1}$ 。Fe-P-N掺杂的碳催化剂在酸性和碱性电解质中均表现出4电子的氧还原过程, 以及高的电催化活性和电化学稳定性。同时, 通过简单调节制备参数易于获得可调控催化活性的Fe-P-N掺杂碳基氧还原催化剂。