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Sp² C-Dominant N-Doped Carbon Sub-micrometer Spheres with a Tunable Size: A Versatile Platform for Highly Efficient **Oxygen-Reduction Catalysts**

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Carbon sub-micrometer spheres (carbon SMSs) are of great practical interest, not only because they are extraordinary building blocks for multifunctional hybrid materials, but also because these carbon SMSs can be used in a broad range of applications, for instance, for drug delivery or as catalysts or nanodevices.^[1–10] The success of these applications strongly depends on the availability of high-quality carbon SMSs with controllable sizes. In particular, controlling the monodispersity and maintaining a size smaller than 200 nm are essential in biomedicine.^[11]

Until now, the carbonization of phenol/formaldehyde resin (PFR) SMSs has been accepted as the most effective method for preparing carbon SMSs, due to several advantages of PFR including facile preparation, high thermal stability and easy conversion to carbon materials.^[1-10] Despite recent progress, we believe there is still considerable room for improvement in the synthesis and properties of the carbon precursor as well as the as-prepared carbon SMSs. Firstly, it would be desirable to use nontoxic carbon resources instead of the strongly carcinogenic phenol/formaldehyde; this would reduce harm both to humans and environment. Secondly, maximizing the reduction in sp³ C occurring in traditional carbon materials, such as PFR-based carbon SMSs, would be highly beneficial for enhancing the material's electroconductivity. Thirdly, the presence of nitrogen heteroatoms in carbon nanomaterials can strongly enhance the materials' electrochemical performance. However, a lack of nitrogen heteroatoms in PFR results in an absence of electroactive nitrogen in the final carbon SMSs. Thus, it is challenging but desirable to explore new polymer analogues that feature low toxicity, excellent thermal stability, high monodispersity, and the presence of heteroatom within a framework to prepare carbon SMSs for practical applications.

With this point of view, we present for the first time a simple yet versatile strategy for the large-scale manufacture

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of monodisperse and size-controlled carbon SMSs, using biomolecule dopamine as the carbon resource. In contrast with phenol/formaldehyde, dopamine is nontoxic, widespread, and a sustainable resource. It contains carbon and nitrogen atoms and is well-known for its chelating capability with many types of metal ions. It can self-polymerize and spontaneously deposit polydopamine films on virtually any surface in a Tris buffer.^[12–18] Based on this property, hollow carbon spheres have been prepared by immersing the silica template in a dopamine Tris-buffer solution, followed by carbonization and HF etching of the template.^[16] However, this approach requires a multistep synthesis procedure and also uses highly toxic HF. Herein, dopamine can be directly polymerized into monodisperse submicrometer spheres without using any template, in a mixture containing water, ethanol, and ammonia at room temperature. The resulting polydopamine SMSs exhibit excellent thermal stability and can successfully convert to carbon SMSs without deterioration of their structure and morphology. Their size can be easily controlled over a wide range, even below 200 nm, which is a primary challenge in preparing uniform carbon spheres. Specifically, the as-prepared carbon SMSs contain much less sp³ C than RFR-based carbon SMSs; thus, they exhibit enhanced electroconductivity. Lastly, this strategy enables the in situ introduction of high-level electroactive nitrogen into the carbon matrix, due to the presence of nitrogen in dopamine. This makes the carbon SMSs highly suitable as a nonprecious metal catalyst for oxygen reduction reaction.

Indeed, this facile strategy can also provide an important platform for many practical applications. First, polydopamine SMSs inherit catechol and N-H groups from their starting material, which facilitates the loading of many types of transition metal ions. This enables yields of metal-carbon hybrid materials with specific properties. To demonstrate their versatility, we fabricate nanocatalysts composed of Fe@Fe3C in carbon SMSs, and this hybrid materials show comparable oxygen reduction reaction catalytic activity to the commercial 20 wt% Pt/C, but with higher stability, better catalytic selectivity and potential applications in energy conversion and storage technologies that typically proceed in acidic media. Furthermore, porous carbon SMSs with an extremely large surface area (2006 m² g⁻¹) can also be obtained based on the as-prepared carbon SMSs. These features make this strategy highly promising for many practical applications, such as in catalyst, drug delivery, water treatment, gas absorption, and supercapacitors.

Our strategy for the preparation of carbon SMSs is schematically illustrated in Figure 1a. Polydopamine (PDA) SMSs as a carbon precursor were prepared through polymerization of dopamine in a mixture containing water, ethanol, and ammonia

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Figure 1. a) Schematic illustration of the synthesis of PDA SMSs. b) Typical TEM image of PDA SMSs with an average diameter of 380 nm. c–h) SEM images of PDA SMSs with different diameters prepared at different ratios of ammonia to dopamine.

at room temperature. Typical transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images showed that the resultant PDA SMSs were uniformly spherical in shape. Their size could be easily controlled in the range from 120 to 780 nm by tuning the ratio of ammonia to dopamine (Figure 1b-h, Supporting Information, Figure S1). This control over the size of PDA SMSs is of great importance in practical applications, particularly in the field of biomedicine. Use in drug delivery requires the nanoparticles smaller than 200 nm in order to avoid rapid recognition and clearance by the phagocyte. The Fourier transform infrared (FTIR) spectrum of PDA SMSs showed the characteristic spectral peaks of several functional groups, such as N-H, -OH, C-O, and C-N (Supporting Information, Figure S2a). The presence of these functional groups endowed PDA SMSs with an active surface for absorbing metal ions, and could also introduce nitrogen heteroatoms in the final carbon SMSs.

The thermal stability of carbon precursors determines their successful conversion to carbon materials. Thermogravimetric analysis (TGA) was performed to examine the thermal stability of PDA SMSs (Supporting Information, Figure S3). Encouragingly, PDA SMSs exhibited excellent thermal stability; even at 1000 °C, 54.19% of the residues still remained. Such a high thermal stability suggests that PDA SMSs are excellent carbon precursors that yield carbon SMSs. As expected, after carbonization, the resultant carbon materials appeared to preserve the structural integrity, monodispersity, and spherical morphology with a slightly decreased size (Supporting Information, Figure S4). To verify the successful conversion of the carbon precursor to carbon, we compared the 13 C NMR spectra of the

carbon precursor before and after carbonization (Supporting Information, Figure S5). The peak centered at approximately 150 ppm was assigned to diphenolic phenoxy C.[19,20] After carbonization, this peak disappeared, which indicated the removal of most of the oxygen. Complementary to the ¹³C-NMR data, electron energy-loss spectroscopy (EELS) mapping and energy-dispersive X-ray analysis (EDAX) provided further evidences for this result (Figure 2a,b and Supporting Information, Figure S6). Interestingly, the peak at 30-45 ppm corresponding to the aliphatic signals also nearly disappeared, suggesting there is little sp³ C in the final carbon matrix. In contrast, traditional PFR SMSs retained a much higher amount of sp³ C after carbonization. To better understand the mechanism underlying the formation of the carbon SMSs, we next employed X-ray photoelectron spectroscopy (XPS) analysis to investigate changes in the C component of carbon SMSs obtained at different temperatures, and we observed a remarkable reduction of sp3 C with increasing temperature (Supporting Information, Figure S7, Table S2). This significant reduction of sp³ C was mainly attributed to the PDA, which possessed C that was entirely located within

its rings; this was unlike PRF which had part of the C outside the rings (Supporting Information, Figure S8a). The C within the rings could convert into sp² C more easily than the C outside the rings during carbonization. As a result of the significant reduction of sp³ C, combined with high-level N-doping, a substantial improvement in their electroconductivity relative to PFR-based carbon SMSs was achieved (Supporting Information, Figure S9). Using electrochemical impedance spectroscopy analysis, PDA-based carbon SMSs showed a much smaller semicircle, as well as a lower intercept of the semicircle with the real axis (5.84 Ω) in the high frequency region of the Nyquist plot compared to PFR-based carbon SMSs (6.16 Ω). This implied that PDA-based carbon SMSs had superior electron transfer ability. The higher electroconductivity of PDA-based carbon SMSs was believed to play a crucial role for enhancing their electrochemical performance.

The oxygen reduction reaction (ORR) is important in many energy conversion and storage technologies such as fuel cells. The ORR is sluggish in nature and typically requires the use of expensive Pt-based catalysts. Metal-free N-doped carbon materials have been accepted as a potential substitute for Pt as they reduce the cost of ORR catalysts thereby promoting the commercialization of fuel-cell technology.^[21–26] For instance, N-doped graphitic carbon,^[21b] N-CNT,^[22,26] and ammonia-treated mesoporous carbon^[23,24] have been investigated as catalysts or catalyst supports for the ORR. Despite their high catalytic activity, these materials generally require chemical pretreatment with HNO₃, NH₃, or HCN to introduce the nitrogen; however, this pretreatment may result in poor control over the chemical homogeneity and reproducibility, long preparation times, and sometimes the





Figure 2. a,b) EELS mapping analysis of PDA SMSs and PDA-based carbon SMSs, respectively. c) N 1s XPS spectrum of PDA-based carbon SMSs. d) Schematic illustration of chemical structure of PDA-based carbon SMSs. e) CV plots of PDA- and PFR-based carbon SMSs in N₂- and O₂-saturated 0.1 $\,$ KOH. f) Polarization curves of PDA- and PFR-based carbon SMSs at 1600 rpm in O₂-saturated 0.1 $\,$ KOH.

deterioration of the materials' structure. In contrast, carbonization of PDA SMSs by our proposed method could produce in situ nitrogen-rich carbon SMSs without the need for additional treatments. To assess the ORR catalytic activity of PDAbased carbon SMSs, both this material and traditional PFRbased carbon SMSs were tested using cyclic voltammetry and a rotating disk electrode (RDE). As shown in Figure 2e,f, PDAbased carbon SMSs exhibited a cathodic ORR peak at -0.218 V and an onset potential at -0.1 V; these were more positive than those of PFR-based carbon SMSs, suggesting enhanced ORR catalytic activity. Remarkably, the enhanced catalytic activity also made it one of the most active metal-free N-doped carbon ORR catalysts (Supporting Information, Table S1). We reasoned that N doping in PDA-based carbon SMSs mainly contributed to an enhancement in ORR catalytic activity compared to N-free PFR-based carbon SMSs. It has been demonstrated that graphitic N could greatly increase the



limiting current density, and pyridinic N could improve the onset potential, while other N species such as pyrrolic N or N–O had little effect on the electrochemical performance of carbon materials.^[27] Thus, we proceeded to examine the N component in PDA-based carbon SMSs using XPS analysis, and only electroactive pyridinic N and graphitic N were detected in PDA-based carbon SMSs (Figure 2c). We also investigated the effect of carbonization temperature on the catalytic activity, and we observed that carbon SMSs obtained at 800 °C showed the highest activity (Supporting Information, Figure S10a). This result further confirmed the above conclusion, since carbon SMSs obtained at 800 °C had the optimal N composition. The elevation in temperature resulted in a reduction of electroactive N, while high-level pyrrolic N was presented in carbon SMSs with carbonization temperature below 800 °C (Supporting Information, Figure S7, Table S2).

Another substantial benefit to this strategy is that PDA SMSs inherit functional groups from their starting material, such as catechol and N-H groups. Thus, they can effectively absorb transitional metal ions, which enables the further introduction of transitional metal-based electroactive substances into the N-doped carbon matrix. As a proof of concept, we synthesized monodisperse Fe@ Fe₃C-loaded N-doped carbon (Fe@Fe₃C/C-N) spheres and evaluated their use as ORR catalysts. TEM image demonstrated that Fe@Fe₃C/C-N preserved the spherical morphology with both micropores and mesopores (Figure 3a,d). The generation of the pores was attributed to the formation of Fe₃C and the graphitization of amorphous carbon catalyzed by Fe metal. This was confirmed by high-resolution TEM imaging and X-ray diffraction (XRD) analysis (Figure 3b,c). Their

ORR catalytic activity was then investigated in O2-saturated 0.1 M KOH. Relative to metal-free PDA-based carbon SMSs, the ORR catalytic activity of Fe@Fe₃C/C-N was greatly enhanced. A more positive cathodic ORR peak (-0.138 V vs. -0.218 V) and onset potential (0 V vs. -0.1 V) were observed (Figure 3e,f). The half-wave potential was about -0.1 V, similar to that of the commercial 20 wt% Pt/C, and the catalytic current was even higher relative to the commercial 20 wt% Pt/C at a voltage below -0.4 V. We hypothesized that the introduction of iron in carbon SMSs formed new active sites, which led to the further enhancement of ORR catalytic activity. To confirm this hypothesis, we performed RDE measurements to check the ORR activity of Fe@Fe₃C/C-N in 0.1 M KOH containing 0.01 M KCN (Supporting Information, Figure S10b). CN⁻ ions are capable of coordinating strongly to iron and poisoning the iron-centered catalytic sites.^[28] In the presence of CN⁻, Fe@Fe₃C/C-N exhibited a significant loss of ORR catalytic activity. The onset

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Figure 3. a,b) TEM (a) and high-resolution TEM (b) images of Fe@Fe₃C/C–N. c,d) XRD pattern (c) and nitrogen adsorption and desorption isotherms (d) of Fe@Fe₃C/C–N. The inset in (d) shows the pore-size distribution. e) CV plots of Fe@Fe₃C/C–N and the commercial 20 wt% Pt/C in N₂- and O₂-saturated 0.1 \bowtie KOH. f) Polarization curves of Fe@Fe₃C/C–N and the commercial 20 wt% Pt/C at 1600 rpm in O₂-saturated 0.1 \bowtie KOH.

potential decreased by more than 0.1 V, and was coupled with a decrease in the diffusion-limiting current. This indicated the crucial role of iron in improving the catalytic activity of Fe@ $Fe_3C/C-N$. Interestingly however, when the Fe@Fe_3C was loaded on N-free PFR-based carbon SMSs, the resulting Fe@ Fe_3C/C was found to be much less active than $Fe@Fe_3C/C-N$ (Supporting Information, Figure S11), clearly clarifying that nitrogen species were also important to the high ORR catalytic activity observed in the Fe@Fe_3C/C-N.

To shed light on the kinetics of electrochemical catalytic ORR on both $Fe@Fe_3C/C-N$ and PDA-based carbon SMSs, Koutecky–Levich (K–L) plots derived from RDE measurements were obtained at different potentials (Supporting Information, Figure S12). Good linear relationships between the inverse current density and the inverse square root of the rotational speed were observed, regardless of the potential setting. This clearly suggested first-order reaction kinetics with respect to the oxygen concentration and a similar electron transfer number (*n*) for ORR at different potentials on the two electrodes.

Calculated from the slope of the K–L plots (see Supporting Information for the detailed calculation), the *n* values for the two electrodes all approached 4. This value indicated ideal four-electron reaction pathways for the direct reduction of O_2 to OH^- instead of HO_2^- on the two electrodes, similar to ORR catalyzed by the commercial Pt/C. This

the direct reduction of O_2 to OH^- instead of HO_2^- on the two electrodes, similar to ORR catalyzed by the commercial Pt/C. This result was visually verified by rotating ringdisk electrode (RRDE) measurements (Supporting Information, Figure S13), in which both Fe@Fe₃C/C–N and PDA-based carbon SMSs yielded little H₂O₂ during the ORR process. In contrast, 30–60% of H₂O₂ was detected for PFR-based carbon SMSs, suggesting a dominant two-electron reaction pathway.

For applications as effective ORR catalysts for fuel cells, there should be a high catalytic selectivity for ORR against fuel oxidation, particularly for use in methanol fuel cells. This is because methanol can cross over the membrane from anode to cathode, seriously compromising the whole cell performance.^[25a] We therefore evaluated the tolerance of both PDA-based carbon SMSs and Fe@Fe3C/C-N to methanol in comparison with the commercial Pt/C (Supporting Information, Figure S14a-c). Upon addition of methanol, we observed a drastic decrease in the ORR catalytic activity of Pt/C. Conversely, neither PDA-based carbon SMSs nor Fe@Fe₃C/C-N exhibited an obvious fading of activity, which revealed their extraordinary selectivity for oxygen to evade the crossover effects of methanol.

Another major concern with fuel cell applications is the durability of the catalysts. PDAbased carbon SMSs and Fe@Fe₃C/C–N were analyzed for durability using chronoampero-

metric measurements (Supporting Information, Figure S14d). Both displayed excellent catalytic stability with less than 10% activity loss over 10000 s of continuous operation, whereas Pt/C suffered more than 30% activity decay over this time period.

In addition, Fe@Fe₃C/C–N was found to be an effective ORR catalyst in acidic media as well. The catalytic activity was much higher compared with that of Fe@Fe₃C/C, PDA-, PFR-based carbon SMSs, and some carbon materials reported elsewhere (Figure 4).^[29] Moreover, they also possessed low H₂O₂ yield, superior catalytic selectivity and stability to the commercial 20 wt% Pt/C (Supporting Information, Figure S15). These features make Fe@Fe₃C/C–N very attractive as an ORR catalyst for many important energy conversion and storage technologies that typically proceed in acidic media, such as proton-exchange membrane fuel cells.

Finally, the presented strategy can provide an important platform for other critical applications besides ORR. Firstly, PDA SMSs could act as a general building block for fabricating other metal-carbon hybrid materials besides $Fe@Fe_3C/C-N$,



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Figure 4. a) CV plots and b) polarization curves of 20 wt% Pt/C, Fe@ Fe_3C/C–N, Fe@Fe_3C/C, PDA- and PFR-based carbon SMSs in O_2-saturated 0.5 $\rm M$ H_2SO_4.

such as Ni- and Co-C spheres (Supporting Information, Figure S17,S18). Fe@Fe₃C/C–N is highly promising for drug delivery and water treatment due to its strong ferromagnetism (Supporting Information, Figure S16), large surface area, and porous structure, while Ni- and Co-C spheres may be used for protein separation and catalysis. Secondly, after activation by KOH, PDA-based carbon SMSs become highly porous, with a majority of micropores derived from etching by KOH. Their Brunauer–Emmett–Teller (BET) surface area reached 2006 m² g⁻¹ (Supporting Information, Figure S19). Along with high-level oxygen and nitrogen heteroatoms (Supporting Information, Table S3), these properties may allow the carbon SMSs to be used as potential electrode materials for supercapacitors.^[30]

In summary, we have developed a simple and versatile method for preparing monodisperse and size-controlled carbon SMSs. In this approach, dopamine was selected as the carbon resource due to its biocompatibility and self-polymerization capability at alkaline conditions. The as-prepared polymer SMSs had excellent thermal stability and could directly convert to

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monodisperse N-rich carbon SMSs without any change in morphology. In contrast with traditional RFR-based carbon SMSs, the present carbon SMSs contained high-level electroactive N and much less sp³ C, leading to higher electroconductivity and thus higher ORR catalytic activity. Moreover, metal-carbon hybrid materials and porous carbon could also be prepared. This feasible strategy presents new opportunities for tailoring the structure, composition, and size of carbon SMSs for applications in supercapacitors, catalysts, energy conversion, storage, and as adsorbents for drug delivery and water-treatment processes.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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