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MOF-Templated Assembly Approach for Fe₃C Nanoparticles Encapsulated in Bamboo-Like N-Doped CNTs: Highly Efficient Oxygen Reduction under both Acidic and Basic Conditions

Arshad Aijaz, Justus Masa, Christoph Rösler, Hendrik Antoni, Roland A. Fischer, Wolfgang Schuhmann,* and Martin Muhler*

Abstract: Developing high-performance non-precious metal catalysts (NPMCs) for the oxygen reduction reaction (ORR) is of critical importance for sustainable energy conversion. We report a novel NPMC consisting of iron carbide (Fe₃C) nanoparticles encapsulated in N-doped bamboo-like carbon nanotubes (b-NCNTs), synthesized by a new metal-organic framework (MOF)-templated assembly approach. The electrocatalyst exhibits excellent ORR activity in 0.1 M KOH (0.89 V at -1 mA cm⁻²) and in 0.5 M H₂SO₄ (0.73 V at -1 mA cm⁻²) with a hydrogen peroxide yield of below 1% in both electrolytes. Due to encapsulation of the Fe₃C nanoparticles inside porous b-NCNTs, the reported NPMC retains its high ORR activity after ~70 h in both alkaline and acidic media.

The oxygen reduction reaction (ORR) is a key process in fuel cells and metal-air batteries.^[1] The state-of-the-art catalysts for this sluggish cathodic reaction are based on platinum and its alloys.^[2] However, the limited availability of platinum, high cost, and insufficient durability preclude its long-term wide scale use. In recent years, non-precious metal catalysts (NPMCs), especially metal-nitrogen-carbon (M-N-C, M = Co, Fe, Mn), have drawn much attention owing to their low cost and high catalytic ORR activity.^[3,4] They are very promising catalysts in harsh ORR conditions but need further improvement in terms of synthetic approach and durability. Very few NPMCs have been found to have sufficient ORR activity and stability in the more challenging acidic media.^[5,6] Therefore, platinum is still the most used ORR catalyst.

The use of metal-organic frameworks (MOF) as self-sacrificial templates for porous carbon was first reported in 2008 by Xu et al.,^[7d] resulting in an enormous upsurge of interest in MOF-

derived nanostructured materials for energy storage and conversion applications.^[7] MOF-derived NPMCs often exhibit large surface area and hierarchical porous structures, which are essential for high ORR performance.^[8] Recently, NPMCs based on iron carbide (Fe₃C), encapsulated in carbon nanostructures, have been reported to be very active towards the ORR.^[3,5] For example, Yu and co-workers synthesized Fe₃C nanoparticles encapsulated in porous Fe-N-doped carbon fibers exhibiting high ORR activity.^[5a] Jia and Guo et al. found that bamboo-like carbon nanotube (CNT)/Fe₃C composites had excellent ORR activity in both alkaline and acidic media.^[5b] Li and coworkers demonstrated very efficient ORR electrocatalysis using hollow spheres of Fe₃C nanoparticles encased in graphitic layers.^[5c] Encapsulating metal nanoparticles inside carbon structures provides a unique synergistic effect that also activates the adjacent atoms surrounding the nanoparticle, and the outer surface carbon atoms for the ORR.^[9] In addition, encapsulation provides resistance against corrosion of the metal nanoparticles especially in acidic electrolytes, which is a necessary prerequisite to ensure long-term performance.^[10] Very few studies have reported the synthesis of Fe₃C-based catalysts from MOF precursors, probably because of two reasons. First, carbonization of Fe-MOF mostly leads to a mixed phase product, for example, Fe₃C, iron oxide or metallic iron,^[11] which complicates unambiguous identification of the true active sites for the ORR. Second, the prepared catalysts do not have well-defined nanostructures.^[12] Hence, new synthesis strategies are needed to explore the potential of MOF-derived nanostructured Fe-electrocatalysts. Herein, we report a new MOF-template-assembly strategy for synthesis of a new NPMC based on Fe₃C nanoparticles encapsulated in porous bamboo-like N-doped carbon nanotubes. The as-synthesized catalyst possesses the desired features for efficient ORR including intrinsic active sites (Fe₃C@carbon or Fe-N_x/C or N-doped carbon), high surface area, nanoporous structure, as well as a highly graphitic bamboo-like carbon framework. As a result, the electrocatalyst showed excellent ORR activity and stability in both alkaline and acidic media.

In a typical synthesis, 1.0 g of ZIF-8 (pre-activated at 200 °C under vacuum) and 1.0 g of pyrrole were thoroughly mixed, followed by drop-wise addition of 6.0 mL of an aqueous solution of FeCl₃·6H₂O (0.1 M) over a period of ~3 h. This led to polymerization of pyrrole residing inside and outside of the ZIF-8 pores, and coordination of pyrrole nitrogen to Fe³⁺. ZIF-8 was deliberately chosen as this N-containing Zn-MOF is known for its high thermal/chemical stability and large surface area with 1.2 nm cavity size. The resulting homogeneous mixture was left to dry overnight at room temperature. The obtained powder was pyrolyzed at a rate of 5 °C/min to 800 °C in a N₂ atmosphere and kept at this temperature for 2 h. The resulting catalyst is denoted as Fe₃C/b-NCNT, where b-NCNT refers to bamboo-like nitrogen-doped carbon nanotube.

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The powder X-ray diffraction (PXRD) pattern of $\text{Fe}_3\text{C}/\text{b-NCNT}$ displayed a strong peak at $\sim 26.5^\circ$ assigned to the (002) reflection of graphitic carbon, in agreement with the structure of multi-walled CNTs (Figure 1a). The other peaks in Figure 1a located at $37.8, 43.1, 43.1, 43.9, 44.9, 46.0, 48.7$ and 49.3° correspond to the Fe_3C phase. No diffraction pattern corresponding to zinc was observed due to formation of amorphous zinc metal followed by its vaporization,^[8g] although residual 2.8 wt% zinc was found by inductively coupled plasma mass spectrometry (ICP-MS) analysis. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis of $\text{Fe}_3\text{C}/\text{b-NCNT}$ revealed typical features of b-NCNTs with a diameter of 50–100 nm (Figures 1b, 1c, and S1–S2). Small Fe_3C nanoparticles, visible as black dots in Figure 1c, were distributed mainly within b-NCNTs. High-angle annular dark-field scanning TEM (HAADF-STEM) further identified the encapsulated black particles in b-NCNTs as iron carbide with a lattice distance of 0.21 nm, corresponding to the (211) crystal planes of Fe_3C (Figure 1d). Selected area electron diffraction (SAED) patterns also demonstrated the presence of crystalline Fe_3C (Figure S3). Careful evaluation of the HAADF-STEM images revealed the porous and hollow nature of the b-NCNTs (Figure 1e). We further investigated the elemental distribution in $\text{Fe}_3\text{C}/\text{b-NCNT}$ using HAADF-STEM and energy-dispersive X-ray spectroscopy (EDS) techniques, which indicated the presence of C, N, and Fe (Figures 1f–1h). Notably, except for the nanoparticle regions, all elements were homogeneously distributed in the $\text{Fe}_3\text{C}/\text{b-NCNT}$ sample. High uniformity of the Fe species in the b-NCNT matrix was observed at the atomic level, and the Fe and N intensities coincided to a significant degree with each other, suggesting that there are probably Fe species stabilized by N coordination, so-called Fe-N_x sites, which are commonly assumed to be active sites for the ORR.^[5a] In the nanoparticle region, the strong Fe signals and weak C signals were observed simultaneously, which possibly indicate the iron carbide phase. Indeed, PXRD measurement confirmed that the nanoparticles in $\text{Fe}_3\text{C}/\text{b-NCNT}$ are pure Fe_3C .

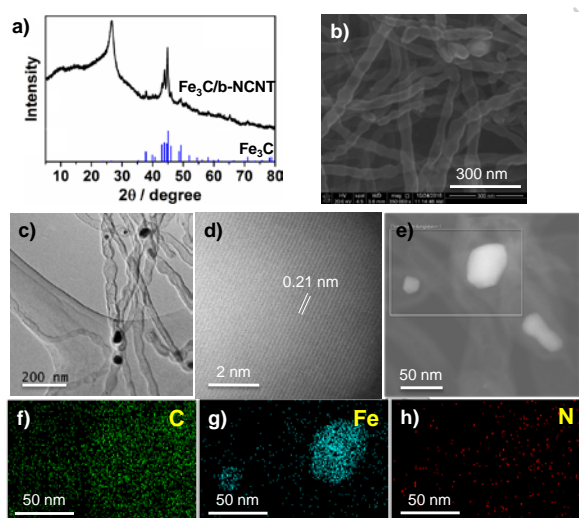


Figure 1. a) PXRD pattern, b) SEM image, and c) TEM image of $\text{Fe}_3\text{C}/\text{b-NCNT}$. d) High-resolution HAADF-STEM image of a single Fe_3C nanoparticle

in $\text{Fe}_3\text{C}/\text{b-NCNT}$. e) HAADF-STEM image of $\text{Fe}_3\text{C}/\text{b-NCNT}$, and its (f–h) EDS elemental mappings.

The porous nature of $\text{Fe}_3\text{C}/\text{b-NCNT}$ was further assessed by N_2 sorption analysis. Figure 2a shows typical adsorption-desorption isotherms for samples with both micro- and mesopores. The Brunauer-Emmett-Teller (BET) surface area and pore volume were $185 \text{ m}^2/\text{g}$ and $0.35 \text{ cm}^3/\text{g}$, respectively, with a pore size distribution mainly centered at 3.7 nm (Figure S4). The elemental composition and graphitic nature of $\text{Fe}_3\text{C}/\text{b-NCNT}$ were evaluated by ICP-MS analysis and Raman spectroscopy respectively. The amount of Fe and N in $\text{Fe}_3\text{C}/\text{b-NCNT}$ was 7.1 and 8.6 wt%, respectively. The D (1360 cm^{-1}) and G (1590 cm^{-1}) bands in the Raman spectrum provide information on the defect density and crystallinity of sp^2 carbon. $\text{Fe}_3\text{C}/\text{b-NCNT}$ showed a I_D/I_G value of 1.09 indicating a high degree of graphitization in agreement with the PXRD results (Figure 2b). The porous and graphitic nature of $\text{Fe}_3\text{C}/\text{b-NCNT}$ is favorable for rapid diffusion and enhanced electrical conductivity, respectively.

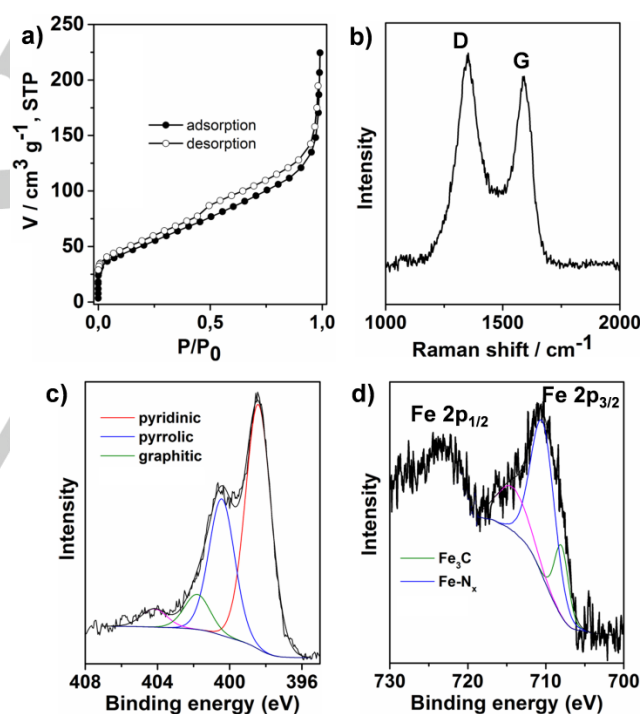


Figure 2. a) N_2 sorption isotherms, b) Raman spectrum, c) N 1s XPS spectrum, and d) Fe 2p XPS spectrum for $\text{Fe}_3\text{C}/\text{b-NCNT}$.

High-resolution X-ray photoelectron spectroscopy (XPS) measurements were conducted to elucidate the surface properties of $\text{Fe}_3\text{C}/\text{b-NCNT}$. The deconvoluted N 1s spectrum showed 4 peaks, assigned to pyridinic N (398.5 eV), pyrrolic N (400.4 eV), graphitic N (401.7 eV), and oxidized N (404.2 eV) (Figure 2c). The peak at a binding energy of 398.5 eV also includes some contribution from N bound to iron (N-Fe), because there is only a small difference between the binding energies of pyridinic N and N-Fe.^[5a] The amount of pyridinic N

was determined to be about 59%. The Fe 2p_{3/2} and Fe 2p_{1/2} signals were centered at 710.7 eV and 723.4 eV, respectively (Figure 2d). Deconvolution of the Fe 2p_{3/2} region suggests the presence of Fe₃C (or metallic Fe) (707.8 eV).^[3b] The main peak at 710.7 eV strongly supports the EDS elemental analysis that Fe is present as N-coordinated Fe in the Fe₃C/b-NCNT sample.^[3b,13] It has to be noted that the peak at 710.7 eV assigned to Fe-N_x in Fe₃C/b-NCNT shows a 0.7 eV higher binding energy as compared to the standard values (~710 eV).^[3b,13] This shift suggests a lower electron density on the Fe atoms, which could originate from the interaction of Fe-N_x and Fe₃C nanoparticles.^[3b] Recent reports have demonstrated that a high proportion of pyridinic N can increase the spin density and the density of π states of the carbon atoms near the Fermi level, thus enhancing O₂ reduction.^[14] Therefore, a high amount of pyridinic N together with highly dispersed Fe-N_x active sites in Fe₃C/b-NCNT is expected to enhance the intrinsic ORR activity.

The structure of Fe₃C/b-NCNT can therefore be described as crystalline Fe₃C nanoparticles being entirely encapsulated in highly graphitic N- and Fe-N_x-doped porous bamboo-like carbon nanotubes. Previous studies showed that despite the encapsulated Fe₃C nanoparticles are shielded from direct contact with electrolytes, they are able to activate surrounding graphitic carbon toward the ORR,^[5c,9] most likely through electronic interaction. Therefore, the unique confinement of Fe₃C nanoparticles within graphitic porous b-NCNTs is believed to efficiently improve the ORR electrocatalysis. Additionally, synergistic interaction between the two species Fe-N_x and Fe₃C can further enhance the ORR activity. To the best of our knowledge, this is a rare report of homogeneous bamboo-like CNTs based on a MOF as precursor.

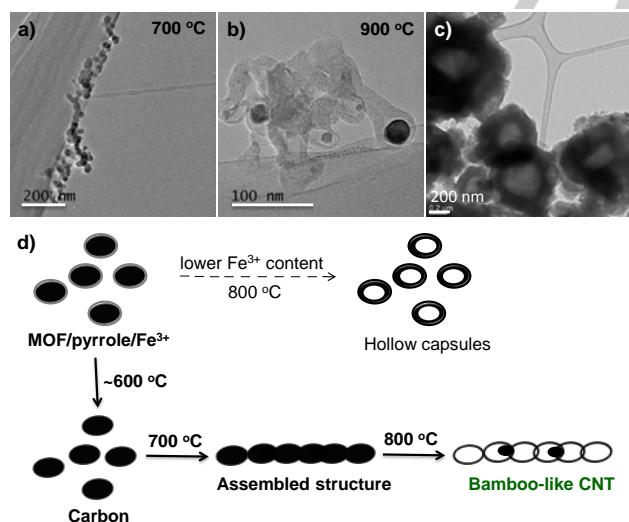


Figure 3. TEM images of samples synthesized a) at 800 °C, b) at 900 °C, and c) at 800 °C using a lower Fe³⁺ content. d) Schematic representation of Fe₃C/b-NCNT formation.

A possible mechanism of the formation of Fe₃C/b-NCNT is suggested in Figure 3. The final carbonization temperature to form hollow b-NCNTs is critical. At 600 °C, the ZIF-8 structure collapses to generate carbon only. At 700 °C, a one-dimensional

carbon structure is formed. TEM images confirm that the assembled carbon structure was not hollow in nature, and carbon particles were mostly connected in a one-dimensional chain (Figure 3a). Increasing the temperature to 800 °C led to homogeneous Fe₃C/b-NCNT (Figure 1b), whereas a higher carbonization temperature (900 °C) only produced collapsed Fe₃C/b-NCNT nanostructures (Figure 3b). The sample prepared without using ZIF-8 did not produce any CNTs (Figure S5). The mechanism of formation of porous hollow b-NCNTs at 800 °C was further investigated by adjusting the iron content, because iron is known to catalyze CNT formation.^[15] As shown in Figure 3c, hollow carbon capsules were generated at 800 °C when a lower amount of Fe³⁺ was used (2 mL of 0.1 M FeCl₃·6H₂O). These findings suggest that the composite of polypyrrole with ZIF-8 synergistically produced the hollow structure at 800 °C, requiring a sufficient amount of iron to catalyze homogeneous growth of the b-NCNTs. Such coupling/conversion of hollow structures into b-NCNTs has been observed recently.^{5b} Therefore, we conclude that pyrolysis protocol, polypyrrole/ZIF-8 composite, effective release (vaporization) of the zinc by-product and the adjusted iron content are all together responsible for the formation of the novel Fe₃C/b-NCNT catalyst.

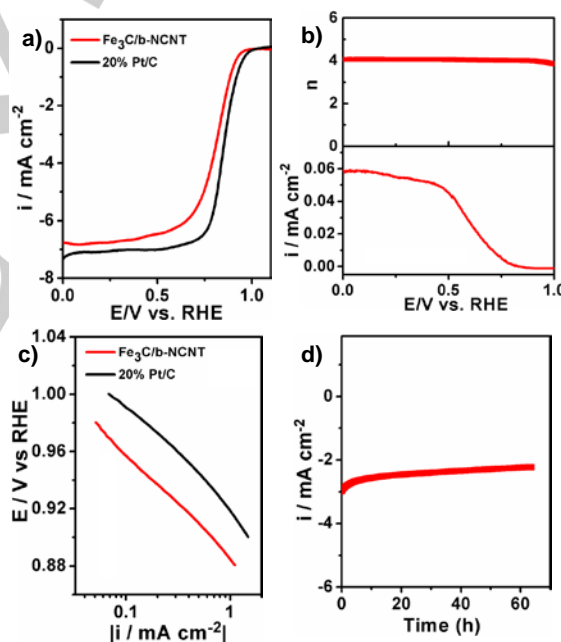


Figure 4. a) Voltammograms of Fe₃C/b-NCNT and 20 wt % Pt/C. b) Rotating ring-disk voltammogram showing the hydrogen peroxide ring current and the electron transfer number (*n*) of a Fe₃C/b-NCNT modified electrode. c) Tafel plots of Fe₃C/b-NCNT and 20 wt % Pt/C modified electrodes. d) Chronoamperometric ORR stability measurement of Fe₃C/b-NCNT at 0.78 V vs. RHE. All measurements were obtained in O₂-saturated 0.1 M KOH solution at a rotation speed of 1600 rpm, except the chronoamperometric stability measurement which was performed at 900 rpm. The catalyst loading was 0.42 mg cm⁻² for Fe₃C/b-NCNT and 0.21 mg cm⁻² (42 μg_(Pt) cm⁻²) for Pt/C. The scan rate was 5 mV s⁻¹.

The ORR activity of Fe₃C/b-NCNT was assessed in both alkaline and acidic electrolytes using rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) techniques. To

perform these tests, 0.42 mg cm^{-2} of $\text{Fe}_3\text{C/b-NCNT}$ was loaded on the surface of a glassy carbon electrode. As shown in Figure 4a, $\text{Fe}_3\text{C/b-NCNT}$ displayed impressive ORR activity in 0.1 M KOH with 0.96 V onset potential, and 0.83 V at a current density of -3 mA cm^{-2} . This performance is very close to that of commercially available state-of-art $20\% \text{ Pt/C}$ catalyst (Pt-ETEK) with a potential of 0.86 V at a current density of -3 mA cm^{-2} . These data are comparable to the previous activity benchmarks of Fe_3C -based ORR electrocatalysts.^[3,5] Moreover, extremely low H_2O_2 oxidation currents were detected at the ring in the RRDE measurements corresponding to less than 1% H_2O_2 yield at all potentials (Figure 4b), which is much lower as compared to previously reported benchmark Fe_3C -based NPMC.^[5b] The number of electrons transferred per O_2 molecule (n) during the ORR was calculated to be close to 4, suggesting a predominantly four electron oxygen reduction pathway to produce water as the main product (Figure 4b). Tafel plots of the kinetic currents corrected for the background and mass transport effects yielded a Tafel slope of 71.2 mV/dec for $\text{Fe}_3\text{C/b-NCNT}$ at low overpotentials, close to 62.9 mV/dec for $20\% \text{ Pt/C}$ catalyst (Figure 4c). These Tafel slopes do not vary significantly from low to high overpotentials suggesting that the mechanism of oxygen reduction at $\text{Fe}_3\text{C/b-NCNT}$ in 0.1 M KOH follows a similar mechanism as at Pt/C . Therefore, corresponding to the known ORR processes on Pt/C the transfer of the first electron is most probably the rate-determining step of the ORR on $\text{Fe}_3\text{C/b-NCNT}$.^[5c] Chronoamperometric stability evaluation (at 0.78 V vs RHE) showed no significant loss in ORR activity after $\sim 70 \text{ h}$ of continuous measurement indicating that $\text{Fe}_3\text{C/b-NCNT}$ is able to sustain a stable ORR performance over a long period of time (Figure 4d).

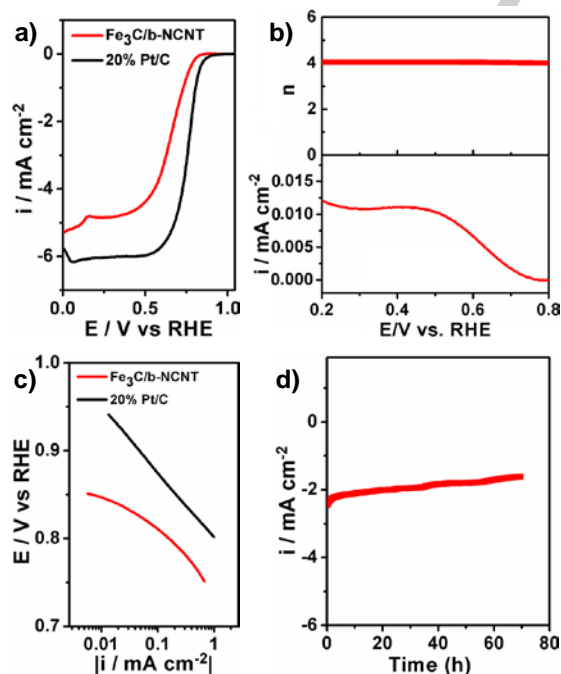


Figure 5. a) Voltammograms of $\text{Fe}_3\text{C/b-NCNT}$ and $20 \text{ wt } \%$ Pt/C . b) Hydrogen peroxide ring current and electron transfer number (n) of $\text{Fe}_3\text{C/b-NCNT}$. c) Tafel plots of $\text{Fe}_3\text{C/b-NCNT}$ and $20 \text{ wt } \%$ Pt/C . d) Chronoamperometric ORR stability measurement of $\text{Fe}_3\text{C/b-NCNT}$ at 0.61 V vs. RHE. All measurements were obtained in O_2 -saturated $0.5 \text{ M H}_2\text{SO}_4$ solution at a rotation speed of

1600 rpm except chronoamperometric stability measurement which was performed at 900 rpm . The catalyst loading was 0.42 mg cm^{-2} for $\text{Fe}_3\text{C/b-NCNT}$ and 0.21 mg cm^{-2} ($42 \mu\text{g(Pt)} \text{ cm}^{-2}$) for Pt/C . The scan rate was 5 mV s^{-1} .

Furthermore, we evaluated the ORR performance of $\text{Fe}_3\text{C/b-NCNT}$ in $0.5 \text{ M H}_2\text{SO}_4$ (Figure 5). The ORR polarization curve of $\text{Fe}_3\text{C/b-NCNT}$ exhibited a potential of 0.63 V at a current density of -3 mA cm^{-2} . In contrast, the potential at -3 mA cm^{-2} obtained with $20\% \text{ Pt/C}$ was 0.75 V (Figure 5a). The H_2O_2 yield during ORR on $\text{Fe}_3\text{C/b-NCNT}$ in $0.5 \text{ M H}_2\text{SO}_4$ was below 1% over the entire investigated potential range (Figure 5b), which is lower than in 0.1 M KOH . The very low H_2O_2 yield indicates that this catalyst reduces O_2 nearly exclusively to H_2O via the 4-electron transfer process. Kinetic currents derived from the curves in Figure 5a generated Tafel plots of $\text{Fe}_3\text{C/b-NCNT}$ and $20\% \text{ Pt/C}$ are shown in Figure 5c. Although the hydrogen peroxide generation curves are similar in both 0.1 M KOH and $0.5 \text{ M H}_2\text{SO}_4$, the Tafel slope of the ORR on $\text{Fe}_3\text{C/b-NCNT}$ in $0.5 \text{ M H}_2\text{SO}_4$ varied significantly from 27 mV/dec in the lower overpotential region to 83 mV/dec at higher overpotentials. This indicates that the mechanism of the ORR on $\text{Fe}_3\text{C/b-NCNT}$ in acidic electrolyte varied significantly with potential in this narrow potential range. Moreover, the mechanism of the ORR on $\text{Fe}_3\text{C/b-NCNT}$ is different in both electrolytes. Chronoamperometric stability studies performed at a potential of 0.61 V vs RHE, showed minimal loss in the ORR current after $\sim 70 \text{ h}$ of continuous polarization (Figure 5d). The novel $\text{Fe}_3\text{C/b-NCNT}$ catalyst thus exhibits promising durability even in the more challenging acidic electrolytes.

Based on the structural and compositional characterization of $\text{Fe}_3\text{C/b-NCNT}$, we conclude that five important aspects are responsible for its excellent ORR activity and stability: 1) High content of N ($8.6 \text{ wt } \%$) enhances hydrophilicity, thus strengthening the electrode-electrolyte interaction. 2) High percentage of pyridinic N (59%) promotes O_2 adsorption owing to the reduced local work function of carbon.^[9c] 3) Unique bamboo-like CNTs offer a higher number of edges, thus introducing a higher number of ORR active sites. 4) High content of N-doping in b-NCNTs as a prerequisite for the formation of active Fe-N_x sites. 5) Encapsulated metal NPs can lead to unique host-guest electronic interactions which make the outer surface of the carbon layer more active in the ORR.^[9]

In summary, we developed a novel NPMC-based ORR electrocatalyst consisting of Fe_3C nanoparticles encapsulated in porous bamboo-like N-doped CNTs, synthesized by a new MOF-templated assembly approach. The excellent electrocatalytic activity, negligible hydrogen peroxide formation, and long-term stability in both acidic and basic media render $\text{Fe}_3\text{C/b-NCNT}$ a promising low-cost, highly efficient ORR catalyst. This work provides a new protocol to construct pure-phase Fe_3C hybrids from MOF, and opens new avenues for further development of active and durable ORR catalysts.

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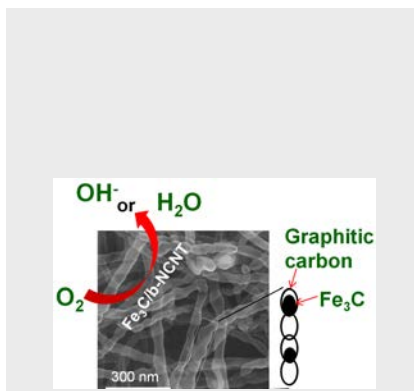
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Keywords: metal-organic frameworks • nanostructured materials • heterogeneous catalysts • iron carbide • oxygen reduction reaction

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COMMUNICATION

Fe₃C nanoparticles encapsulated homogeneously in N-doped bamboo-like carbon nanotubes are fabricated from a pyrrole-loaded MOF using a well-controlled pyrolytic approach. The obtained catalyst shows high activity and stability towards the oxygen reduction reaction in both acidic and basic electrolytes.



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MOF-Templated Assembly Approach for Fe₃C Nanoparticles Encapsulated in Bamboo-Like N-doped CNTs: Highly Efficient Oxygen Reduction under both Acidic and Basic Conditions