A Nitrogen-doped Ordered Mesoporous Carbon/Graphene Framework as Bifunctional Electrocatalyst for Oxygen Reduction and Evolution Reactions

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Abstract

Highly ordered N-doped mesoporous carbon/graphene frameworks (N-MCF/N-MGF) were prepared using superlattice of self-assembled Fe_3O_4 nanoparticles as template. The prepared N-MCF catalyst shows enhanced oxygen reduction reaction (ORR) activity compared with commercial Pt/C catalyst. The N-MGF catalyst demonstrates lower oxygen evolution reaction (OER) overpotential (324 mV at 10 mA cm^{-2}) than most of the previously reported carbon based materials, non-noble metal oxides and their hybrids, and comparable with noble metal oxides (ruthenium/iridium oxide, RuO_2 and IrO_2) catalysts. The prepared N-MGF catalysts also exhibit negligible mass transfer resistance, good durability and bifunctionality in ORR and OER. The significantly improved electrocatalytic performance results from their large surface area, ordered pores, excellent internal diffusion property, and superior intrinsic conductivity. The materials show great potential for various applications in energy conversion and storage, including fuel cells, electrolyzers and metal-air batteries.

Keywords: Graphene, Mesoporous Structure, Non-noble Metal Catalyst, Oxygen Reduction Reaction, Oxygen Evolution Reaction, Electrocatalyst.

1. Introduction

The past decades have witnessed increasing research efforts on developing electrocatalysts of high efficiency, low cost and environmental benignity for the utilization and implementation of renewable energy techniques such as fuel cells, metal-air batteries, and water splitting [1-9]. One

important research topic in the field is electrochemical redox between H_2O and O_2 for the design of regenerative electrochemical energy storage and conversion system, which involves oxygen reduction reaction (ORR) during discharging process and oxygen evolution reaction (OER) upon charging process [10-18]. However, both ORR and OER have sluggish reaction kinetics and thus require development of good catalyst, which have been long standing challenges and greatly hinder applications of those regenerative energy techniques [19, 20]. In particular, large amounts of noble metal Pt would be required to improve the reaction rate and confront the prevailing catalyst degradation in ORR [21-23]. Noble metal oxides (ruthenium/iridium oxide, RuO_2 and IrO_2) catalysts are also needed in OER to overcome the large overpotential [24-28]. Thus, it is of great importance to develop a bifunctional electrocatalyst which is active in both ORR and OER and can reduce the usage of noble metals. In recent years good research progresses have been made in developing noble metal-free catalysts, among which carbon-based materials received most attention for their manifested promising properties when their chemical structures were finely engineered [29-31]. Nonetheless, most current catalysts are not bifunctional, typically exhibiting good property in one reaction but having low activity in the other. Moreover, agglomeration of carbon-based nanomaterials, for instance self-restacking of graphene nanosheets and heavy entanglement of carbon nanotubes, often occurs and causes remarkable decrease in their active surface areas [32, 33]. The agglomeration would also cause diffusion issue due to decreased accessibility for the reacting species, because they need to transport through unordered microchannels between carbon particles to reach the active sites [34]. Thus, it is highly desirable to develop new carbon-based catalyst with excellent property in both OER and ORR. Herein, this work reports the design of highly ordered mesoporous carbon framework (MCF)/mesoporous graphene framework (MGF) structures and their N-doped deviates, with

prominent OER and ORR electrocatalytic properties. The remarkable catalytic performance of these catalysts could be attributed to their large surface area, ordered porosity, good conductivity, and surface-functionalized active sites.

2. Results and discussion

As illustrated in **Scheme1**, the ordered catalytic structures were prepared by simple and direct carbonization of superlattice of self-assembled Fe_3O_4 nanoparticles with size of 16.4 ± 2.2 nm (Figure S1), in which Fe_3O_4 served as both template and catalyst and oleic acid molecules capping on Fe_3O_4 surface acted as carbon source [35].

Figure 1A shows transmission electron microscopy (TEM) image of the as-prepared mesoporous carbon framework (MCF) and high-resolution TEM (HRTEM) of the carbon wall layers. The pores of the MCF were of similar size as the diameter of Fe_3O_4 nanoparticles (Figure S1), confirming the templated growth of carbon layers. These carbon wall layers showed a low crystallinity, evidenced by no clear lattice (Figure S2). The amorphous MCF was graphitized at elevated temperature, which led to the formation of mesoporous graphene framework (MGF) (Figure 1B). Careful TEM characterizations indicated the ordered mesoporous structure of MCF was substantially maintained during its transformation to MGF. Meanwhile, the crystallinity of the carbon wall layers was largely improved, with clear lattice fringes of graphene being observed for the MGF. Most carbon wall layers contained around 5 graphene layers, which constructed the ordered mesoporous graphene framework (Figure S3). BET measurements of the mesoporous structures showed the type-IV isotherms (Figure S4) with an average pore size of 18.7 nm and carbon layer thickness of about 2 nm.

The long-range ordered structures of MCF and MGF were also manifested in Figure S5-6 and characterized with small angle X-ray scattering (SAXS), which showed a series of well-resolved scattering peaks assignable to the highly ordered *fcc* structure. Shift in the diffraction peaks of MGF compared to that of MCF was observed, with the shift in the SAXS pattern being associated with a shrinkage of internal carbon structures and the shift in the XRD pattern being attributed to a decreased lattice interlayer spacing during graphitization (Figure S7). The Raman spectra of MCF and MGF showed clear D (1351 cm^{-1}), G (1607 cm^{-1}) and 2D (2721 cm^{-1}) peaks in which the intensity of D peaks are related to the amount of defects such as in-plane substitution heteroatoms, vacancies, or grain boundaries/edges, and positions and intensity ratio of 2D and G peaks described the compressive strain and/or doping effect [36, 37].

N-doped MCF and MGF were prepared by thermally treating the precursor materials under ammonia atmosphere or in ammonium hydroxide solution. Interestingly, the best-performed N-MCF catalyst was obtained using the ammonia atmosphere treatment and the best N-MGF catalyst was obtained using the ammonium hydroxide treatment. **Figure 2** shows the structures and compositions of N-doped MGF (treated by ammonium hydroxide at $210\text{ }^{\circ}\text{C}$, N-MGF) and MCF (treated by NH_3 annealing at $750\text{ }^{\circ}\text{C}$, N-MCF). Both N-MGF and N-MCF show negligible change on morphology after the nitration process, indicating strong stiffness of the frameworks (Figure 2A-B). Compared to the pristine MGF and MCF, the Raman peaks of the N-MGF and N-MCF exhibited a higher ID/IG ratio, suggesting a higher amount of nitration-induced defects (Figure 2C-D). The peak around 1060 cm^{-1} was related to the asymmetric vibration of C-O-C band [38]. The X-ray photoelectron spectroscopy (XPS) spectra of the nitrated samples showed significant N signals (Figure 2E-F), confirming nitrogen has been successfully introduced into the matrix of MGF and MCF. Fe and O signals were also detected, which were related to

unleached iron oxide residues. The results were consistent with the energy-dispersive X-ray spectroscopy (EDX) elemental mapping analyses and atomic absorption (AA) measurements, which showed presence of both Fe and N elements and their uniform distribution through the samples (Figure S8-S10). Quantitative analyses determined surface composition of the N-MCF as C 1s 84.2%, N 1s 9.8%, O 1s 4.8%, Fe 2p 1.2% and the N-MGF as C 1s 88.1%, N 1s 1.9%, O 1s 9.2%, and Fe 2p 0.8%. The N content in the N-MCF was 4 times more than that in the N-MGF, indicating more efficient and concentrated doping. A higher O content of the N-MGF than that of the N-MCF could be associated with oxygen incorporation as carbonyl groups or rings in oleic acid derivatives at high annealing temperatures (500-1000 °C) [39]. Deconvolution of the high-resolution N 1s spectra of the N-doped samples showed distinct N-containing functional groups coexisted, identified by their different bonding states in the carbon matrix (Figure 2G-H). The peaks located at 398.1 eV, 399.8 eV, 401.5 eV, and 403.9 eV can be attributed to pyridinic N (Pyr-N), pyrrolic N (Pyo-N), graphitic N (Gra-N), and N oxides (Oxi-N) respectively [7, 32]. Their relative atomic ratios were determined to be 36.5% : 29.8% : 18.3% : 15.4% for the N-MGF and 44.5% : 33.7% : 14.7% : 7.1% for the N-MCF, respectively. The different distributions of N-containing groups in the N-MGF and N-MCF were originated from the different crystallinity between the MGF and MCF precursors and suggested distinct surface properties. The several N configurations were described in Schematic 1, where Pyr-N refers to sp^2 -bonded N atoms at the edges of graphene planes (C-N=C) with one p -electron donation to the aromatic π system, Pyo-N atom refers to the N in a five membered heterocyclic pyrrole rings with two p -electrons donation to the π system, Gra-N atoms are the incorporated N atoms that substitute carbon atoms within the graphene plane, and Oxi-N atoms refer to the N atoms bonded with two carbon atoms and one dangling oxygen atom [32].

The ORR properties of both N-doped and pristine MCF and MGF, as well as state-of-the-art Pt/C for comparison purpose, were investigated in 0.1 M KOH electrolyte. The MGF and MCF exhibited small current density and an obvious plateau at 0.3~0.5V, indicating low activity of the two catalysts and mixed ORR pathways (**Figure 3A** and Figure S11). The N-MCF and N-MGF showed significant improvements in the ORR activity comparing to their pristine counterparts, suggesting N doping plays a critical role in promoting the reaction kinetics. Figure 3B provided more quantitative comparisons for these catalysts by measuring the current densities at 0.80 V and 0.85 V vs. RHE. The MGF and MCF delivered negligible current responses under both potentials. The ORR activity of the N-MGF was around 3 times that of the MGF at the same potentials. The N-MCF appeared to be the most active among the four samples, with high current densities of 3.53 and 1.26 mA cm⁻² at those two potentials. More interestingly, the N-MCF exhibited a 47 mV positive shift in the half-wave potential and higher current densities compared with the Pt/C (2.24 and 0.74 mA cm⁻²), suggesting its superior ORR activity. The measured Tafel slopes followed the order of MGF $\approx$ MCF > N-MGF > N-MCF (Figure 3C), which was consistent with their exhibited ORR activities. The Tafel slope of the N-MCF was close to that of Pt/C (42 vs. 38 mV/dec), suggesting a favorable reaction kinetics. Electrochemical impedance spectroscopy (EIS) measurements showed greatly reduced charge transfer resistances for the N-MGF and the N-MCF comparing to the pristine ones, confirming the promoted ORR kinetics [13]. The Nyquist plot of N-MCF largely overlapped with Pt/C, which further explained the prominent catalytic performance of the N-MCF. The measured ORR activity using the N-MCF was comparable or even higher compared with most recently reported non-noble metal catalysts, suggesting an excellent catalytic property of the N-MCF originated from its unique structure. [40-44] The excellent ORR activity of the N-MCF could be attributed to a high content of N-

doped active sites and the Fe residuals, evidenced by the high-resolution XPS (Figure 2G-H). Previous density functional theory (DFT) studies have suggested that the ORR properties on graphene can be significantly altered with N doping, among which pyridinic N was found to be more energy favorable to promote the reaction kinetics comparing to other typed N dopants [45, 46]. Besides, some metal dopants were found with a promotive effect on ORR catalysis of the carbon-based materials.[47-49]

The OER properties of the catalysts were also evaluated in 0.1 M KOH electrolyte. The commercial Pt/C showed low OER activity in the tested potential range (**Figure 4A**). In comparison, the MCF and the MGF showed significantly higher current density and were thus more active. Remarkably, the N-MGF and the N-MCF showed even more dramatic enhancement in the OER activity (Figure S12). In particularly, the overpotential required for current density of 10 mA cm^{-2} was determined to be 402 mV using the N-MGF treated by ammonium hydroxide, which is comparable with many nickel (Ni), cobalt (Co), iron (Fe), and manganese (Mn)-based OER electrocatalysts (Table S1) [50, 51]. The area normalized OER current density of the N-MGF was more than 56 times of that of the Pt/C (0.18 mA cm^{-2}) and about 12 times of that of the MGF. The N-MGF also exhibited higher OER activity compared to most reported compared to N-doped graphene/carbon nanotube and their composites (Table S1) [18, 52]. The N-MGF showed a Tafel slope of 67 mV/dec, which was significantly lower than those of other catalysts and agreed with its higher OER activity (Figure 4C). The higher OER activity of the N-MGF could be attributed to its lower interfacial charge transfer resistance comparing to the other catalysts, which were determined from EIS recorded at $E = 1.632 \text{ V}$ and followed the order of $\text{N-MGF} < \text{N-MCF} < \text{MGF} < \text{MCF} \ll \text{Pt/C}$.

The MCF/MGF-based catalysts, benefiting from the unique ordered mesoporous framework structure, showed big advantages in terms of eliminating internal diffusion issue. The ammonium hydroxide treated N-MGF, a less active ORR catalyst but able to outperform the Pt/C by simply increasing the catalyst loading, was tested to demonstrate the excellent internal diffusion property of the framework structure. As shown in **Figure 5A-D**, the internal diffusion effects of both the N-MGF and the Pt/C on the ORR activity were examined in parallel by exploring the relationship between mass-normalized current density and catalyst loading. For the N-MGF, the determined mass current densities went through a horizontal line and were close to the theoretical values expected for the catalyst without any internal diffusion. The data indicated that there was negligible internal diffusion issue with the N-MGF even when the catalyst loading increased by 10 times. For the Pt/C, the dependency of mass current densities over the catalyst loading showed an obvious deviation from the theoretical expectation. There were dramatic decreases in the measured mass current density with increasing Pt/C loading, confirming a big internal diffusion resistance. The excellent internal diffusion using the N-MGF was believed to be associated with their highly ordered mesoporous structures, which enabled faster mass transfer of reacting species in the pores comparing to that in the random pores between Pt/C nanoparticles.

The good durability and bifunctionality of the N-MGF catalyst were further demonstrated by testing the OER, ORR, and ORR-OER sequence properties (Figure 5E-H). The durability of the catalyst in OER was evaluated using both chronoamperometry and potential cycling measurements. It retained as high as 87.8% and 94.4% of its initial OER activity after a 4,000 seconds and 1,000 cycles, suggesting a good OER durability of the N-MGF catalyst. The good OER durability property of the N-MGF was attributed to its excellent structural stability, which

showed little structural change during the test (Figure S13). The N-MGF also exhibited good durability in ORR, with only 6.1% activity loss after 4000 sweeping cycles. The results suggested the N-MGF structure is a durable catalyst for both OER and ORR. The bifunctionality of the N-MGF was demonstrated by running LSV in a broadened potential window for both ORR and OER. With a 100 μg loading, the N-MGF showed further decreases in the onset overpotential and increases in the current density compared to the N-MGF with a 10 μg loading. The overpotential at 10 mA cm^{-2} was measured to be 324 mV, which was comparable with the OER benchmarking catalysts such as noble metal/metal oxide Ru, Ir and IrO_2 , but with a much lower cost (Table S1) [50-53].

3. Conclusion

In conclusion, this work demonstrated the synthesis of highly ordered MCF/MGF structures and their N-doped derivatives, which possessed large surface area, high porosity, excellent internal diffusion property, and superior intrinsic conductivity and exhibited promising catalytic properties in both ORR and OER. As a bifunctional catalyst, the N-doped MGF exhibited overpotential as low as 324 mV for harvesting 10 mA cm^{-2} OER current density, which was lower than most of previously reported carbon-based materials and were comparable with the benchmarking noble metal oxide catalysts. The catalyst was also durable under both OER and ORR conditions. These results presented a low-cost bifunctional ORR/OER electrocatalyst with high activity and good durability as well as their negligible internal diffusion resistance, which could be potentially utilized and implemented in renewable energy techniques such as metal-air batteries, fuel cells, and water splitting devices.

4. Materials and methods

4.1. Materials

Oleic acid (OA, 90%), oleylamine (OAm, 70%), 1-octadecene (ODE, 90%), ammonium hydroxide (NH_4OH , 28%), and potassium hydroxide (KOH) were purchased from Aldrich. Anhydrous ethanol (EtOH , 95.3%) was purchased from Fisher Scientific. Commercial Pt/C (HP 20 wt.% Pt, Lot #591278) was purchased from fuel cell store. Ammonia (NH_3 , 99.999%) and nitrogen (N_2 , 99.999%) gases were obtained from Praxair.

4.2. Synthesis of MCF and MGF

The MCF and MGF were prepared by a recently reported strategy using Fe_3O_4 nanocrystals superlattices as template. The 16 nm, OA-stabilized Fe_3O_4 NCs were synthesized according to the previous report [35]. By slowly drying the colloidal solution of Fe_3O_4 NCs under ambient conditions, the Fe_3O_4 NC superlattices were obtained. To carbonize the surface-coating OA ligands, the superlattices were annealed in argon (Ar) at 500 °C for 2 h. Then HCl was used to remove the Fe_3O_4 NCs, thus yielding the ordered structure MCFs. MGFs were obtained by further heat treatment of MCFs in Ar at 1200 °C for 1 h, which graphitized the amorphous MCFs without structural collapse.

4.3. Synthesis of N-MCF/MGF-210

30 mg MCF/MGF was added into 30 ml ammonia aqueous solution (Conc. 16.7 w.t.%) and sonicated for 30 min. Then, the mixture was transferred into autoclave and heated up to 210 °C in 20 min and maintained at 210 °C for another 18 hours. After being cooled down to room temperature, the mixture was washed by DI-water till the pH of supernatant reaching 7-7.5 and dried in oven.

4.4. Synthesis of N-MCF/MGF-750

20 mg MCF/MGF was annealed in NH_3 under 750 °C for 1.5 hr and the products were cooled down in NH_3 prior to any characterization.

4.5. Structure and Morphology Characterizations

TEM, HRTEM, STEM, XPS, SXAS, Raman, BET. Transmission electron microscopy (TEM) characterizations of the prepared samples were conducted with a JEOL JEM-1230 microscope operated at 120 KV. High-resolution TEM (HRTEM) images were taken using a FEI Tecnai G2 F20 microscope operated at 200 KV. X-ray photoelectron spectroscopy (XPS) was accomplished using a PHI VersaProbe II Scanning XPS Microprobe with Al-K α line excitation source. Prior to the XPS measurement, the sample was left under UHV for 12 hr for degassing. The Raman spectroscopy study on N-doped MCF/MGF was carried out using a DXR Smart Raman spectrometer (Thermo Fisher Scientific) with a 532 nm laser source, and spectra of MCF and MGF were collected on an XploRA Raman spectrometer (HORIBA JobinYvon) also with a 532 nm laser source. SAXS patterns were recorded by a Nanostar U small-angle X-ray scattering system using Cu K α radiation. Nitrogen adsorption–desorption isotherms were measured by a Micrometer ASAP 3000 instrument after degassing at 200 °C for 10h. EDS analysis and elemental mapping were conducted with an Oxford X-Max 80T detector. X-ray diffraction (XRD) patterns of the samples were collected on a PANalytical X'pert PRO X-ray diffractometer. Compositional analyses were carried on an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Varian VISTA-MPX).

4.6. Electrode Preparation

All electrochemical measurements were performed under identical conditions with the same catalyst mass loading except for commercial Pt/C (20w.t.%). 4 mg of the synthesized catalysts were first ultrasonically dispersed in the mixture of 4 mL of isopropanol and 20 μ L of Nafion® solution (5.0 wt. % .) 10 μ L of the catalyst dispersion (1.0 mg/mL) were then transferred onto the glassy carbon rotating disk electrode (RDE, 0.196 cm² , Pine Research Instrumentation, USA) via a rotating casting approach [21-23]. For commercial Pt/C, the electrode was prepared as same as above except the composition of dispersion solution, in which the volume ratio of DI water: isopropanol: Nafion is 60:40:0.5. Electrodes with various catalyst loadings were prepared by continuous casting and drying for multiple times. The resulting electrode served as a working electrode.

4.7. Electrochemical Characterization

The data were recorded using a CHI 760 D bipotentiostat (CHI instruments, Inc., USA). Ag/AgCl electrode and a platinum wire were used as the reference electrode and counter electrode, respectively. The current density was normalized by a geometrical surface area (GEO, 0.196 cm²). The measured potentials vs. Ag/AgCl were converted to scale referred to reversible hydrogen electrode (RHE) after a careful calibration in H₂ saturated electrolyte. During the electrochemical measurements of oxygen reduction reaction, O₂ was kept bubbling into the electrolyte (0.1 M KOH), and N₂ for oxygen evolution reaction. Linear sweep voltammograms (LSVs) were carried out using a RDE (1600 rpm), not-corrected by iR-compensation. The scan rate of LSVs was 10 mV/s for ORR and 5 mV/s for OER. Electrochemical impedance spectroscopy was measured in O₂/N₂-saturated 0.1 M KOH at 0.8 V for ORR and 1.632 V for OER. The frequency is from 0.03 to 10⁵ Hz with potential amplitude of 5 mV. Koutecky-Levich (K-L) equations were applied to determine the ORR kinetic current densities at 0.8V for various

catalysts. Chronoamperometry technique was used to determine the stability of prepared catalysts to OER at current density = 10 mA cm⁻² and potential cycling was measured between 1.2 and 1.75 V in N₂-saturated 0.1 M KOH with scan rate of 5 mV/s.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/XXX>.

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Scheme 1. Schematic illustration of preparation of Fe₃O₄ nanocrystal superlattice derived highly ordered mesoporous carbon/graphene framework (MCF/MGF) and their nitrogen-doped structures N-MGF/N-MCF, with corresponding configurations of N-containing functional groups.

Figure 1. Morphological characterization and structural analysis of MCF and MGF structures: TEM image of (A) MCF and (B) MGF (Insets: colored Z-contrast HRTEM images of carbon wall layers), and their (C) SAXS patterns and (D) Raman spectra. Scale bars in A, B: 20 nm, and in insets: 2 nm.

Figure 2. Morphological characterization and structural analysis of N-doped MGF and MCF structures: (A-B) TEM, (C-D) Raman spectra, (E-F) XPS, and (G-H) high-resolution N 1s XPS spectra. Scale bars in A, B: 50 nm.

Figure 3. The oxygen reduction reaction using MGF, MCF, N-MGF, N-MCF, and commercial Pt/C catalysts in 0.1 M KOH electrolyte: (A) LSV plots, (B) bar chart of current density at E = 0.80 and 0.85 V, (C) Tafel plots, and (D) Nyquist plots at E = 0.80 V. N-MGF was treated by ammonium hydroxide at 210 °C and N-MCF was treated by NH₃ annealing at 750 °C

Figure 4. The oxygen evolution reaction on MGF, MCF, N-MGF, N-MCF, and commercial Pt/C in 0.1 M KOH electrolyte: (A) LSV plots, (B) bar chart of current density at E =1.632 V, (C) Tafel plots, and (D) Nyquist plots of selected electrodes at E =1.632 V. N-MGF/MCF were treated by ammonium hydroxide at 210 °C

Figure 5. Comparisons on the diffusion and stability properties of N-MGF and commercial Pt/C in 0.1 M KOH electrolyte. (A-D) ORR current response-loading relationship for N-MGF and Pt/C, (E) OER chronoamperometric test on N-MGF for 4000 s, (F) OER long-term stability test

on N-MGF for 1000 repeating cycles, (G) ORR stability test on N-MGF after 4000 sweeping cycles, (H) ORR and OER profiles for N-MGF in potential range 0-1.6 V.

Viate

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