**3D Nitrogen–Doped Graphene Aerogel–Supported Fe3O4 Nanoparticles as Efficient Electrocatalysts for the Oxygen Reduction Reaction**

<table>
<thead>
<tr>
<th>Journal:</th>
<th><em>Journal of the American Chemical Society</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID:</td>
<td>ja-2012-030565.R1</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Communication</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>22-May-2012</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Wu, Zhong-Shuai; Max-Planck-Institut für Polymerforschung, Synthetic Chemistry Yang, Shubin; Max-Planck-Institut für Polymerforschung, Sun, Yi; Max-Planck-Institut für Polymerforschung, Parvez, Khaled; Max Planck Institute for Polymer Research, Feng, Xinliang; Max-Planck Institute for Polymer Research, Synthetic Chemistry Mullen, Klaus; Max-Planck-Institute for Polymer Research,</td>
</tr>
</tbody>
</table>
ABSTRACT: Three-dimensional nitrogen-doped graphene aerogel–supported \( \text{Fe}_3\text{O}_4 \) nanoparticles (\( \text{Fe}_3\text{O}_4/\text{N–GAs} \)) as efficient cathode catalysts for the oxygen reduction reaction (ORR) is reported. The graphene hybrids exhibit an interconnected macroporous framework of graphene sheets with uniform dispersion of \( \text{Fe}_3\text{O}_4 \) nanoparticles. In studying the carbon support effects on the \( \text{Fe}_3\text{O}_4 \) nanoparticles for ORR, we find that \( \text{Fe}_3\text{O}_4/\text{N–GAs} \) shows more positive onset potential, higher cathodic density, lower \( \text{H}_2\text{O}_2 \) yield and higher electron transfer number for ORR in alkaline medium than \( \text{Fe}_3\text{O}_4 \)-supported on N-doped carbon black or on N-doped graphene sheets, highlighting the importance of 3D macropores and high specific surface area of graphene aerogel support for improving the ORR performance. Furthermore, \( \text{Fe}_3\text{O}_4/\text{N–GAs} \) shows better durability than the commercial Pt/C catalyst.

Catalysts for the oxygen reduction reaction (ORR) are key components of fuel cells.\(^1\) \( \text{Pt} \) and its alloys remain the most efficient ORR catalysts, but the high cost and scarcity of \( \text{Pt} \) hamper further development of fuel cell technologies based on these materials. In this respect, a broad range of alternative catalysts based on non–precious metals (\( \text{Fe, Co, etc} \))\(^2\) or oxides (\( \text{Fe}_3\text{O}_4, \text{Fe}_2\text{O}_3, \text{Co}_3\text{O}_4, \text{Ir}_2\text{O}_3 \))\(^3\), as well as nitrogen-coordinated metal on carbon,\(^4\) and metal-free doped carbon materials\(^5\) have been actively pursued. Metal or metal oxide catalysts frequently suffer from dissolution, sintering and agglomeration during the fuel cell operation which can result in catalyst degradation.\(^6\) To overcome this obstacle, nanostructured catalyst supports such as carbon (active carbon, porous carbon, carbon nanotube and graphene), metal, carbide, mesoporous silica and conducting polymers have been developed to maximize the electro–active surface area of catalysts and improve their catalytic activity and durability.\(^6\) Among these, graphene, a two–dimensional single–layer sheet of hexagonal carbon, has emerged as a new generation catalyst support due to its excellent electrical conductivity, high surface area, good chemical and environmental stability, and strong adhesion to catalyst particles. Despite the tremendous progress of graphene–based catalysts for ORR,\(^3,4,6\) there has been no report of the controllable assembly of non–precious metal oxide nanoparticles (NPs) supported on a three–dimensional (3D) graphene network as ORR catalysts. Such systems are attractive targets as they allow the unique features of graphene sheets, such as rich macroporosity and multi–dimensional electron transport partway to be utilized.

In this communication, we demonstrate a novel class of monolithic \( \text{Fe}_3\text{O}_4 \) NPs supported on 3D nitrogen–doped graphene aerogels (\( \text{Fe}_3\text{O}_4/\text{N–GAs} \)). The graphene hybrids show an interconnected macroporous framework of graphene sheets with uniform deposition of \( \text{Fe}_3\text{O}_4 \) NPs. In studying the carbon support effects on the \( \text{Fe}_3\text{O}_4 \) NP ORR catalyst, we find that \( \text{Fe}_3\text{O}_4/\text{N–GAs} \) exhibits a more positive onset potential, a higher cathodic density, a lower \( \text{H}_2\text{O}_2 \) yield and a higher electron transfer number for ORR in alkaline condition than \( \text{Fe}_3\text{O}_4 \)-supported on N-doped carbon black (\( \text{Fe}_3\text{O}_4/\text{N–CB} \)) or on N-doped graphene sheets (\( \text{Fe}_3\text{O}_4/\text{N–GSs} \)). Additionally, \( \text{Fe}_3\text{O}_4/\text{N–GAs} \) shows better durability than the commercial Pt/C catalyst.

Figure 1. Fabrication process for a 3D \( \text{Fe}_3\text{O}_4/\text{N–GAs} \) catalyst. (a) A stable suspension of GO, iron ions and polypyrrole (PPy) are dispersed in water in a vial. (b) \( \text{Fe}^- \)– and PPy–supported graphene hybrid hydrogel prepared by hydrothermal self-assembly and floated on water in a vial, and its ideal assembled model. (c) A monolithic hybrid aerogel of \( \text{Fe}_3\text{O}_4/\text{N–GAs} \) obtained after freeze–drying and thermal treatment.
graphene–based hydrogel at 180 °C for 12 h (Figure 1b). In this way, Fe₃O₄ NPs could nucleate and grow on the graphene surface while simultaneously incorporating nitrogen species into the graphene lattice. The as–prepared hydrogel was then directly dehydrated via a freeze–drying process to maintain the 3D monolithic architecture and then heated at 600 °C for 3 h under nitrogen (Figure 1c). The final product from this process was a black monolithic hybrid aerogel comprised of N–doped graphene networks and Fe₃O₄ NPs (see below).

Figure 2. Structure and morphology of Fe₃O₄/N–GAs catalysts. (a) XRD pattern and, (b–d) Typical SEM images of Fe₃O₄/N–GAs reveal the 3D macroporous structure and uniform distribution of Fe₃O₄ nanoparticles in the graphene aerogel. Red rings indicate that Fe₃O₄ NPs are encapsulated in thin graphene layers. (e) Representative TEM and (f) HRTEM images of Fe₃O₄/N–GAs reveal a wrapped structure of Fe₃O₄ NP by graphene layers.

The structure and morphology of as–prepared Fe₃O₄/N–GAs were investigated by means of X–ray diffraction (XRD), scanning (SEM) and transmission (TEM) electron microscopy. The XRD pattern confirms the formation of Fe₃O₄ (JCPDS No. 65–3107) in the hybrids (Figure 2a). Remarkably, no apparent diffraction peak can be identified in the range of 20~30°, indicating that Fe₃O₄ NPs have been efficiently deposited on the graphene surface suppressing the stacking of graphene layers. SEM images reveal an interconnected 3D porous graphene framework with continuous macropores in the micrometer size range (Figure 2b and c). Apart from the decoration of Fe₃O₄ NPs on both sides of graphene sheets (Figure 2c), it is noteworthy that a significant portion (30% based on statistical analysis of SEM images) of NPs are encapsulated within graphene layers (Figure 2d), suggesting an efficient assembly between NPs and graphene sheets. Such a geometric confinement of metal oxide NPs within graphene layers has been reported to enhance their interface contact and to suppress the dissolution and agglomeration of NPs, and in this way to promote the electrochemical activity and stability of hybrids. TEM characterization further validates the uniform distribution of Fe₃O₄ NPs with a size of 20–80 nm on graphene (Figure 2e). The high–resolution TEM (HRTEM) image reveals that a typical Fe₃O₄ NP with a well–crystalline texture is entirely encapsulated by graphene sheets (<6 layers, Figure 2f).

Figure 3. Elemental mapping images and XPS of Fe₃O₄/N–GAs. (a) Typical scanning transmission electron microscopy (STEM) image, (b) STEM image taken from the square region in (a) and corresponding elemental mapping images of (c) iron, (d) carbon, (e) nitrogen, and (f) oxygen in (b). (g, h) High–resolution (g) Fe 2p XPS and (h) N 1s XPS of Fe₃O₄/N–GAs.

Elemental mapping analysis of Fe₃O₄/N–GAs suggests the presence of Fe, C, N and O components in the hybrids (Figure 3a). It is notable that the nitrogen content is much higher in the region of Fe₃O₄ NPs than in graphene layers (Figure 3e), indicating that Fe–N–C active sites have been established at the Fe₃O₄ NP interface. X–ray photoelectron spectroscopy (XPS, Figure 3g) shows two peaks at 725 and 711 eV, assignable to Fe 2p½ and Fe 2p½ for Fe₃O₄, respectively. Further, 3.5 wt% nitrogen can be estimated to be present in these hybrids based on XPS analysis. The high–resolution scan of N 1s indicates the presence of two forms of
nitrogen, namely, pyrrolic N (401.2 eV) and pyridinic N (398.1 eV, Figure 3b), both of which have proven to be the catalytically active sites for oxygen reduction.

To gain insight into the ORR of Fe₃O₄ NPs supported on the 3D macroporous N–GAs, we first examined the electrocatalytic properties of Fe₃O₄/N–GAs using cyclic voltammetry in nitrogen– and oxygen–saturated 0.1 M KOH aqueous electrolyte solution at a scan rate of 100 mV s⁻¹ (Figure 4a). For comparison, we also prepared Fe₃O₄ NPs loaded on other carbon supports such as N–doped graphene sheets (Fe₃O₄/N–GSs) and carbon black (Fe₃O₄/N–CB) via the same procedure (Supporting Information, Figure S5–S8). In the case of an argon–saturated solution, CV curves within the potential range of −1.2~+0.2 V present similar features for all three samples. A small redox response could be observed at −0.5~−0.7 V, attributable to the pseudocapacitive behavior of nitrogen-doped carbons (Figure 4a, Figure S6). In contrast, when the electrolyte was saturated with oxygen, three electrodes showed a substantial reduction process. Apparently, Fe₃O₄/N–GAs exhibited a pronounced electrocatalytic activity for ORR associated with a more positive ORR onset potential (−0.19 V) and higher cathodic current density (−2.56 mA cm⁻²) (Figure 4a) than in the case of Fe₃O₄/N–GSs (−0.26 V, −1.46 mA cm⁻², Figure S6a) and Fe₃O₄/N–CB (−0.24 V, −1.99 mA cm⁻², Figure S6b). Subsequently, rotating disk electrode (RDE) was performed to examine the reaction kinetics for Fe₃O₄/N–GAs, Fe₃O₄/N–GSs and Fe₃O₄/N–CB electrodes in O₂–saturated 0.1 M KOH electrolyte at a scan rate of 10 mV s⁻¹ (Figure 4b, Figure S6). Two–step reaction pathways could be observed for Fe₃O₄/N–GSs (from −0.26 to −0.62 V and from −0.62 to −1.2 V, Figure S6c) and Fe₃O₄/N–CB (from −0.24 V to −0.60 V and from −0.60 to −1.2 V, Figure S6d), suggesting the key role of a two–electron transfer to produce hydrogen peroxide anions (HO₂⁻) as intermediates in alkaline medium. In contrast, the linear sweep voltammetry (LSV) curves of Fe₃O₄/N–GAs presents a direct four–electron transfer pathway from −0.19 to −1.2 V for producing hydroxide (OH⁻) (Figure 4b).

We further employed a rotating ring–disk electrode (RRDE) technique to quantify the ORR electron transfer pathway, in which the amount of H₂O₂ generated at the disk electrode could be accurately determined. Figure 5a shows the disk and ring currents for Fe₃O₄/N–GAs, Fe₃O₄/N–GSs, and Fe₃O₄/N–CB, respectively. All three electrodes generated ring currents at the onset potential for ORR. Notably, both Fe₃O₄/N–GSs and Fe₃O₄/N–CB exhibit much higher ring currents than that of Fe₃O₄/N–GAs (Inset in Figure 5a). Specifically, the measured H₂O₂ yield for Fe₃O₄/N–GAs is 11% at the potential of −0.4 V, while that for Fe₃O₄/N–GSs is 45%, and for Fe₃O₄/N–CB is 38%, respectively (Figure 5b). Figure 5c reveals that the electron transfer number strongly varies with the measured potential. Based on the ring and disk current, the electron transfer number is 3.09~3.80 for Fe₃O₄/N–GSs and 3.24~3.80 for Fe₃O₄/N–CB in a potential range from −0.20 to −1.2 V. In sharp contrast, the n value of Fe₃O₄/N–GAs electrode lies between 3.72 to 3.95 over the whole potential range, emphasizing that the Fe₃O₄/N–GAs ORR proceeds mainly via a four–electron mechanism. Taking into account the similar elemental compositions of the three samples, the enhanced ORR activity of Fe₃O₄/N–GAs can be attributed to the effect of macropores on the diffusion rate of the electrolyte and to the exposed active sites, which are closely related to its high BET surface area (Figure S2) relative to that of Fe₃O₄/N–GSs (Figure S7) and Fe₃O₄/N–CB (Figure S8).

Figure 5. (a) RRDE test of ORR on Fe₃O₄/N–GAs, Fe₃O₄/N–GSs, Fe₃O₄/N–CB in oxygen–saturated 0.1 M KOH electrolyte at a rotation rate of 1600 rpm. Inset is the ring current as a function of the electrode potential. (b) Percentage of peroxide and (c) the electron transfer number (n) of Fe₃O₄/N–GAs, Fe₃O₄/N–GSs, and Fe₃O₄/N–CB against the electrode potential. (d) Percentage of peroxide and electron transfer number as a function of Fe₃O₂ loading at −0.4 V, measured by RRDE in an O₂–saturated 0.1 M KOH electrolyte.

The durability of Fe₃O₄/N–GAs with respect to commercial Pt/C was assessed through chronoamperometric measurements at −0.4 V in O₂ saturated aqueous solution of 0.1 M KOH at a rotation rate of 1600 rpm. As revealed in Figure S9, the current–time (i–t) chronoamperometric response for Fe₃O₄/N–GAs exhibited a very slow attenuation with a high current retention (79.3%) after 20000 s. In contrast, a commercial Pt–C electrode showed a much faster current decrease with ~61.0% retention. The better durability of Fe₃O₄/N–GAs can be ascribed to the unique confined structure of Fe₃O₄ NPs within graphene layers (Figure 2b–f), which can enhance their
interfacial contact, suppress the dissolution/agglomeration of NPs, and facilitate the transport of electrolyte ions. The influence of Fe$_3$O$_4$NP loading on the catalytic activity of Fe$_3$O$_4$/N-NGs was also examined by RRDE. Figure 5d demonstrates that with increasing Fe$_3$O$_4$ loading from about 4.1 to 46.2 wt% in Fe$_3$O$_4$/N-NGs, the yield of HO$_2^-$ decreases and the overall electron transfer number increases from 2.9 to 3.8. However, a high Fe$_3$O$_4$ loading of 63.3 wt% in these hybrid results in an increase of HO$_2^-$production. This can be explained by (i) the decrease of the electrical conductivity of the Fe$_3$O$_4$/N-NGs electrode upon increasing the Fe$_3$O$_4$ loading, and (ii) the onset of non–bonded interactions with N–NGs for the excessive Fe$_3$O$_4$ NPs.

Furthermore, we found that 3D N-NGs is also a universal carbon support, which is superior to other carbon supports of GSs and CB, for loading non-precious metal electrocatalysts. For example, Fe NPs were also successfully incorporated into N-NGs, which show remarkable ORR performance in acidic medium (Figure S10–S14, and Table S1).

In summary, we have successfully fabricated 3D monolithic Fe$_3$O$_4$/N-NGs hybrids via a combined hydrothermal self–assembly, freeze–drying and thermal treatment process. Due to the 3D macroporous structure and high surface area, the resulting Fe$_3$O$_4$/N-NGs show excellent electrocatalytic activity for ORR in alkaline electrolytes, including higher current density, lower ring current, lower H$_2$O$_2$ yield, higher electron transfer number (~4), and better durability, which makes Fe$_3$O$_4$/N-NGs a potentially non–precious metal cathode catalyst for fuel cells. We believe that our present synthetic strategy can be further extended to develop other 3D metal or metal oxide/graphene–based monolithic materials for various applications, such as sensors, batteries, and supercapacitors.

### SUPPORTING INFORMATION

Full synthesis and characterization details, AFM image of graphene oxide, nitrogen cryosorption isotherm and pore distribution, TGA and XPS of Fe$_3$O$_4$/N-NGs, SEM images, CV, LSV curves, nitrogen cryosorption isotherm and pore distribution of Fe$_3$O$_4$/N-GSs and Fe$_3$O$_4$/N-CB, durability of Fe$_3$O$_4$/N-NGs and Pt/C in alkaline solution. XRD, SEM, TEM, EDX and RRDE curves of Fe/N-NGs, Fe/N-GSs and Fe/N-CB, durability of Fe/N-NGs and Pt/C in acidic solution. This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

Corresponding Author
feng@mpip–mainz.mpg.de; muellen@mpip–mainz.mpg.de

### ACKNOWLEDGMENT

Financial support by the Max Plank Society through the program ENERCHEM, DFG Priority Program SPP 1355, DFG MU 334/32–1, DFG Priority Program SPP 1459, and ESF Project GOSPEL (Ref Nr: 9–EuroGRAPHENE–FP–001), EU Project GENIUS, BMBF LiLBZ Project, and ERC grant on NANOGRAH.