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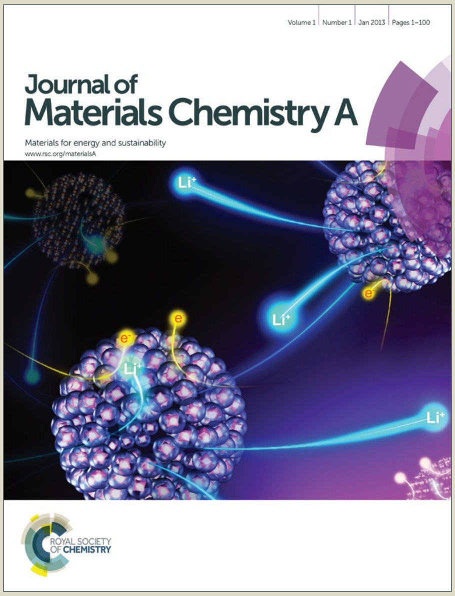

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Nanocarbon-intercalated and Fe-N-codoped graphene as a highly active noble-metal-free bifunctional electrocatalyst for oxygen reduction and evolution†

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We report a rationally designed electrocatalyst with high activities for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) based on a nanocarbon-intercalated graphene (CIG) material doped with nitrogen (N) and iron (Fe) (Fe-N-CIG). This easily made novel 3D Fe-N-CIG catalyst exhibits a surprisingly high ORR and OER activity and stability, making it a new noble-metal-free bifunctional catalyst for future applications in regenerative energy conversion systems.

Energy crisis has roused tremendous and continuous research interests in finding sustainable energy conversion systems with high efficiency and low cost.[1-3] Catalysts towards electrochemical oxygen reduction and evolution reactions play a central role in renewable energy related technologies.[4,5] Usually, oxygen reduction reaction (ORR) with a reasonably low overpotential on the cathode side is a vital issue for fuel cells.[6,7] On the other hand, oxygen evolution reaction (OER) on an anode lies at the heart of electrochemical water splitting and metal-air batteries.[8-10] Currently, Pt and its alloys are the most active catalysts for ORR,[11-14] while ruthenium and iridium oxides are the best OER catalysts.[15,16] However, a widespread use of these catalysts will accelerate the consumption of the rarest elements on earth, and thus hinder their industrialization. As a result, intensive research has been focused on reducing the use of noble metals in ORR and OER catalysts but still maintaining similar or even higher activities. Some other efforts intend to improve catalyst stability and increase catalyst utilization. Among these pursuits, one important trend is to develop noble-metal-free materials for ORR and OER applications, including earth abundant metal-based or metal-free catalysts.[9,10,17-20] However, finding a noble-metal-free electrocatalyst possessing high activities for both ORR and OER is very challenging, which has been rarely reported.[4,21,22] Such a dual-function catalyst is of great significance for rechargeable metal-air batteries or unitized regenerative fuel cells (URFCs) capable of working as a fuel cell to form water and in reverse as a water electrolyzer producing H_2 and O_2 to refeed the fuel cell.[4,20]

In response to the urgent demand for reduced use of noble metals in both ORR and OER catalysts, nitrogen-doped carbon materials have shown great promises due to their high catalytic activity, zero consumption of noble metals, and environmental friendliness.[17-20] In particular, N-doped graphene (N-G) has drawn special attentions recently, largely due to its high surface area, excellent thermal and electrical conductivities, and superior mechanical and chemical stabilities,[21-24] which make N-G attractive as a high performance ORR or OER catalyst.[10,25-28] However, the existence of strong π-π stacking interactions between graphene nanosheets (GNS) often results in irreversible agglomerates of graphene layers,[23,29] causing a loss of their unique 2D structure. This effect significantly reduces the surface area and limits the permeation of electrolyte between graphene layers. As a result, catalytically active sites generated upon N-doping would be largely compromised, forming a serious barrier for graphene-based materials as active electrocatalysts.

In the present work, we report on a conductive nanocarbon-intercalated nitrogen-doped graphene material containing trace amount of iron (Fe-N-CIG) as a high performance ORR and OER dual-functional catalyst (**Fig. 1**). The existence of interplanar carbon nanospheres (CNS) in the graphene-based structures provides abundant electrolyte channels which are expected to facilitate the diffusion of reactive species to catalytically active sites. In addition, the carbon nanospheres can serve as “shortcuts” for interplanar electron transports, and thus guarantee a good conductivity of the materials. The resulting Fe-N-CIG catalyst exhibits higher ORR activity and enhanced stability in an alkaline medium, in comparison with a commercial Pt/C catalyst (Johnson Matthey Corp., 20 wt. % Pt on Vulcan XC-72). In the meantime, the Fe-N-CIG shows an excellent OER activity with an onset potential at least 100 mV lower than that of iridium oxide (IrO_2), a well-known precious metal-based catalyst for electrochemical water oxidation.

As shown in **Fig. 1**, the Fe-N-CIG catalyst was synthesized by a simple two-step process. In the first step, urea, ferric ammonium

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sulfate, and CNS (Vulcan XC-72, Cabot Co., washed by 1 M H_2SO_4 before use) were added to an aqueous solution of graphene oxide (GO). The mixture was thoroughly dispersed under the assistance of ultrasonication, and then dried by rotary evaporation and subsequent lyophilization. In the second step, the lyophilized solid was subjected to a thermal treatment at 900 ºC in an argon flow. This resulted in an N and Fe co-doped and thermally reduced GO material with a nanocarbon-intercalated three dimensional (3D) structure (Fe-N-CIG) (see Supporting Information (SI) for details).

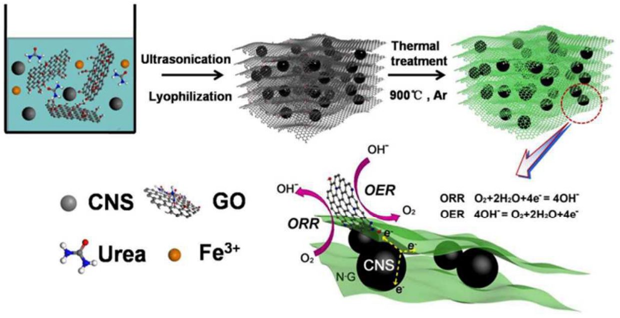

Fig.1 Schematic illustration of a synthetic process for Fe-N-CIG which shows enhanced catalytic activities for both ORR and OER.

The special architecture of the nanosphere/nanosheet composite was confirmed by scanning electron microscopy (SEM) (**Fig. 2a, b**) and transmission electron microscopy (TEM) (**Fig. 2c**). The SEM and TEM data showed that the Vulcan XC-72 carbon nanospheres were nicely sandwiched between the N-doped graphene nanosheets (GNS). In contrast, the N-doped graphene material containing trace amount of iron in the absence of CNS (Fe-N-G, a control sample) showed a closely restacked multilayer GNS structure with crumpled morphologies (**Fig. S1**). X-ray photoelectron spectroscopy (XPS) revealed an existence of 7.39 at. % nitrogen in the Fe-N-CIG, which was greater than the Fe-N-G sample (3.21 at.%, **Fig. S2, S3**). This probably meant that the intercalated Fe-N-CIG structure could facilitate the N doping reactions. The high resolution XPS N1s spectrum could be deconvoluted into three sub-peaks which disclosed the presence of pyridinic (398.6 eV), pyrrolic (400.2 eV), and quaternary nitrogen (401.3 eV) species in the Fe-N-CIG structure (**Fig. 2d**).[30] The Fe-N-CIG showed a higher ratio of pyridinic N (42.6%) than that of N-CIG without Fe doping (21.1%, **Fig. S4**). The high resolution XPS Fe 2p signals (**Fig. 2e**) with two peaks at 724 eV and 711 eV and no obvious satellite peak at around 719 eV were assignable to Fe $2p_{1/2}$ and Fe $2p_{3/2}$ of Fe_3O_4.[25, 32] By a careful checking of the TEM images (**Fig. S5**), scattered nanoparticles showing a clear lattice fringe with an inter-plane spacing of 0.298 nm were found, in good agreement with the (220) crystal face of Fe_3O_4[31]. Inductively coupled plasma mass spectroscopic (ICP-MS) analysis showed a relatively low iron content of ~1.51 wt. % in the Fe-N-CIG sample (**Fig. S3**). N_2 adsorption-desorption isotherm and the accordingly calculated pore size distribution of the as-prepared Fe-N-CIG were given in **Fig. 2f**. These data revealed a type IV isotherm with a H_3 hysteresis loop,[33] indicating the presence of predominant mesopores and slit shaped pores. After the intercalation of CNS, Fe-N-CIG showed a significantly increased BET specific surface area (457 m^2 g^{-1}) compared to Fe-N-G (202 m^2 g^{-1}, **Fig. S6**) for which no CNS intercalation was present.

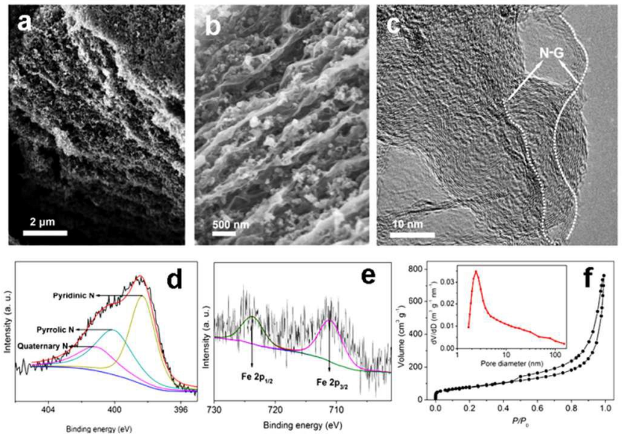

Fig. 2 Characterizations of Fe-N-CIG hybrid materials. (a, b) SEM cross-sectional views under different magnifications of the Fe-N-CIG hybrid deposited on a silicon substrate from its aqueous suspension. (c) High magnification TEM image of the Fe-N-CIG hybrid. Dotted lines indicate the edges of two N-doped graphene (N-G) layers. (d, e) High-resolution XPS N 1s (d) and Fe 2p (e) spectra of Fe-N-CIG. (f) The nitrogen adsorption/desorption isotherm along with a pore size distribution (inset) of the Fe-N-CIG catalyst.

Electrochemical measurements on both static and rotating disk electrodes (RDE) were employed to characterize the ORR kinetics of different catalysts. **Fig. 3a** showed cyclic voltammograms (CVs) on static glassy carbon electrodes (GCEs) loaded with Fe-N-G, Fe-N-CIG, and commercial Pt/C (20 wt. %), respectively, in an unstirred N_2 or O_2 saturated 0.1 M KOH aqueous solution. A potential scan rate of 10 mV s^{-1} in the range of 0.05-1.25 V versus reversible hydrogen electrode (RHE) was employed for all CV tests. The CV curve of the Fe-N-CIG loaded electrode exhibited a much higher ORR peak than those of the Fe-N-G and commercial Pt/C catalysts. In **Fig**. **3b**, well-defined steady state diffusion-limiting currents following mixed kinetic-diffusion regions were observed on the linear sweep voltammetric (LSV) curves of the Fe-N-CIG coated RDE under various rotation speeds from 400 to 1600 rpm. The linearity of the Koutecky-Levich plots based on the RDE data and the near parallelism of the fitting lines suggested first-order reaction kinetics towards dissolved oxygen. The slopes of the Koutecky-Levich plots at different potentials gave an averaged electron transfer number of 4.0 for the Fe-N-CIG catalyst (inset of **Fig. 3b**), which was larger than that of Fe-N-G (n=3.95) (**Fig. S7)**. The excellent ORR performance of the Fe-N-CIG was also evidenced from its Tafel slope of 79 mV/decade in 0.1 M KOH at low overpotentials, similar to commercial Pt/C (78 mV/decade) (**Fig. 3c**). Rotating ring-disk electrode (RRDE, with a Pt ring electrode) voltammetry was further used to monitor the formation of peroxide (HO_2^-) by-products during the ORR at the catalyst-loaded disk electrode (**Fig. 3d**). The measured HO_2^- yields were below 7.0% and 4.0% for Fe-N-G and Fe-N-CIG, respectively, through the potential range of 0.4-0.80 V, giving corresponding electron transfer (ET) numbers of ~3.95 and ~3.98 (**Fig. 3e**). The ET numbers obtained from the RRDE experiments coincided well with those from the Koutecky-Levich plots, suggesting that the ORRs on the Fe-N-CIG and Fe-N-G catalysts were governed by 4e pathways. The high ORR activity of the Fe-N-CIG was also inferred from its half-wave potential (~0.84 V) of the RDE voltammogram (**Fig. 3d**), which was even more positive than that of Pt/C catalyst (~0.82 V). In addition, Fe-N-CIG had a higher limiting current than Fe-N-G (**Fig. 3d**) under the same catalyst loading, implying that the intercalated architecture of Fe-N-CIG could offer more active sites for ORR. Moreover, the steady-state voltammetric ORR curves on Fe-N-CIG, iron and nitrogen codoped carbon nanopheres (Fe-N-CNS), Nitrogen-doped graphene (N-G), naoncarbon-intercalated nitrogen-doped graphene (N-CIG), and Fe-N-G loaded rotating disk electrodes (RDE) at 1,600 rpm were compared in **Fig. S8**. On the other hand, the Fe-N-CIG also exhibited a superior electrochemical stability under a constant polarizing potential of 0.7 V in 0.1 M KOH, with a very small current decay (4%) over 1000 s of continuous running (**Fig. 3f**). In contrast, the Pt/C catalyst exhibited a 12% decrease of its activity under the same condition, which would prohibit its long-term use.

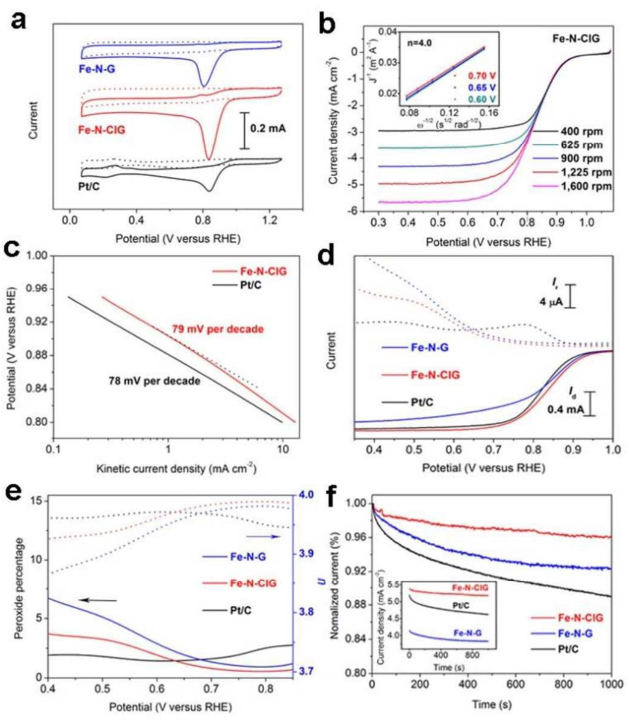

Fig. 3 Electrochemical ORR tests of as-obtained materials. (a) CV curves of the Fe-N-G (~0.23 mg cm^{-2} loading), Fe-N-CIG (~0.23 mg cm^{-2}) and Pt/C (20 wt. % Pt on Vulcan XC-72, ~0.1 mg cm^{-2}) catalysts in N_2-saturated (dotted lines) and O_2-saturated (solid lines) 0.1 M KOH solutions, respectively. (b) Rotating disk electrode (RDE) voltammograms of Fe-N-CIG in O_2-saturated 0.1 M KOH at different rotation speeds. The inset in (b) shows corresponding Koutecky-Levich plots at different potentials. (c) Tafel plots of the Fe-N-CIG and Pt/C catalysts. (d) Rotating ring-disk electrode (RRDE) voltammograms recorded for Fe-N-G, Fe-N-CIG, and Pt/C catalysts in O_2-saturated 0.1 M KOH at 1600 rpm. Solid and dotted curves correspond to the disk and ring currents, respectively. (e) Peroxide yields (solid lines) and corresponding electron transfer numbers (n) (dotted lines) of the Fe-N-G, Fe-N-CIG and Pt/C catalysts as a function of applied potential, derived from the RRDE data in (d). (f) Chronoamperometric responses of Fe-N-G, Fe-N-CIG and Pt/C loaded RDEs kept at 0.7 V versus RHE in O_2-saturated 0.1 M KOH electrolytes at 1600 rpm, showing an improved stability for the Fe-N-CIG catalyst. Inset shows the chronoamperometric data before normalization.

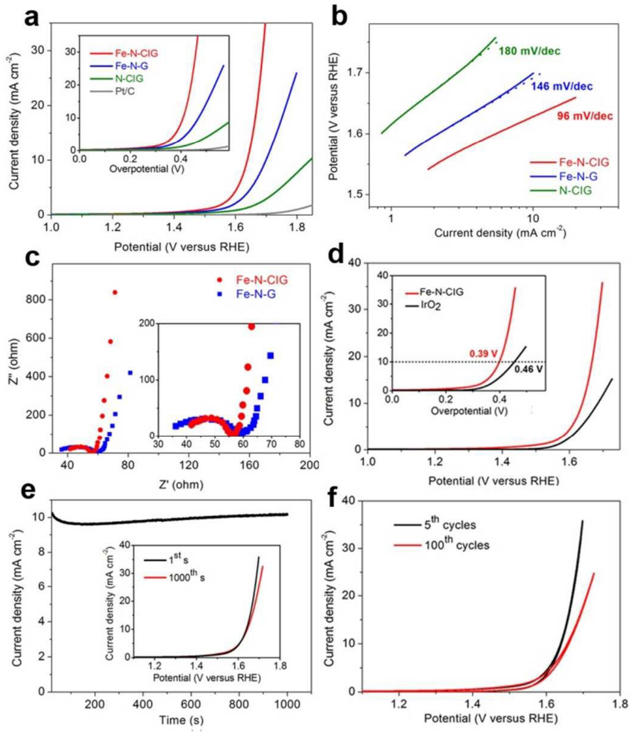

Fig. 4 Electrochemical OER and impedance tests of as-obtained materials. (a) *iR*-corrected OER voltammograms of Fe-N-G, Fe-N-CIG, N-CIG, and Pt/C loaded glassy carbon RDEs at 1600 rpm. (b) Tafel plots based on the OER data in (a). (c) Nyquist plots of electrochemical impedance spectra (EIS) for Fe-N-G and Fe-N-CIG; Inset shows magnified semicircle domains of the EIS curves. (d) A comparison of iR-corrected OER voltammograms between Fe-N-CIG and commercial IrO_2 catalysts on glassy carbon RDEs at 1600 rpm. (e) Chronoamperometric response of Fe-N-CIG continuously recorded for 1000 s; Inset shows *iR*-corrected OER voltammograms after 1 and 1000 s polarizations. (f) *iR*-corrected OER cyclic voltammograms corresponding to the 5th and 100th CV cycles. The insets in (a) and (d) are replotted current density curves versus overpotential. See Fig. S9 for details of the *iR* correction.

In addition to the ORR tests, we evaluated the Fe-N-CIG and Fe-N-G catalysts for their oxygen evolution reaction (OER) activities in 0.1 M KOH. The Fe-N-CIG loaded RDE (0.38 mg cm^{-2}) produced higher OER current and more negative onset potential than Fe-N-G, N-CIG and Pt/C (**Fig. 4a**). In the meantime, the Fe-N-CIG exhibited a lower Tafel slope (96 mV/dec) compared to that of both Fe-N-G (146 mV/dec) and N-CIG (180 mV/dec) (**Fig. 4b**). The electron transfer properties of the Fe-N-CIG and Fe-N-G electrodes were further characterized by electrochemical impedance spectroscopy (EIS). As shown in **Fig. 4c**, the Fe-N-CIG had a smaller semicircle part in the EIS Nyquist plot than that of Fe-N-G, indicating a lower electron-transfer resistance at the catalyst-electrolyte interface.[34,35] Furthermore, we compared Fe-N-CIG with commercially available IrO_2 (Sigma, ∼0.2 mg cm^{-2} loading) for their OER activities in 0.1 M KOH at room temperature (**Fig. 4d**). The onset potential of Fe-N-CIG was estimated to be ~1.4 V, corresponding to a negligible overpotential of ~170 mV (at least 100 mV lower than that of iridium oxide). Moreover, we compared the overpotentials for different catalysts at a current density of 10.0 mA cm^{-2} (inset of **Fig. 4d**), which indicated an obviously lower potential for Fe-N-CIG (0.39 mV) than IrO_2 (0.46 mV). Importantly, the Fe-N-CIG exhibited excellent durability with insignificant performance loss under a constant polarizing at 1.67 V (where the current density was about 10 mA cm^{-2}) (**Fig. 4e**) or after 100 cycles of consecutive CV scans (**Fig. 4f**). This might be attributed to the unique 3D structure and the high mechanical stability of the carbon nanosphere intercalated graphene materials. The above results clearly demonstrated that the noble-metal-free Fe-N-CIG hybrid was an excellent bifunctional catalyst for both oxygen reduction and evolution reactions.

Theoretical and experimental works[22, 36, 37] have pointed out that N doping can promote both ORR and OER, and Fe-N$_x$ interactions can mimic an Fe-porphyrin coordination for ORR.[38,39] As well, oxide forms of first row transition metals including Fe are catalysts for OER.[40] In consistence with our XPS analysis, several groups have found that transition metals can facilitate the incorporation of active N-containing functionalities into graphitic carbon at high temperature and increase catalytic activities[10,41]. Moreover, the Fe-N-CIG showed a higher ratio of pyridinic N than that of N-CIG. It has been reported that pyridinic N at a graphitic edge is critical for electrocatalysis.[42,43] Therefore, the significantly enhanced ORR and OER activities of Fe-N-CIG could be attributed to three major reasons (**Fig. 1**). Firstly, the existence of interplanar carbon nanospheres results in a large spacing between two graphene nanosheets, which avoids a serious re-stacking (induced by π electron interactions) of graphene layers and facilitates the N doping reaction. Secondly, the increased distance between N-doped graphene planes makes the catalytically active sites (N, Fe_3O_4, and possibly FeN$_x$) on the graphene surface easily accessible to ORR and OER related species. Thirdly, the high conductivity of the carbon nanospheres bridging adjacent graphene planes guaranteed an efficient electron transport between different graphene layers.

Conclusions

In summary, surprisingly high ORR and OER activities were simultaneously achieved when conductive nanocarbons were intercalated into nitrogen-doped graphene nanosheets containing trace amount of iron (Fe-N-CIG). The Fe-N-CIG exhibited an improved ORR activity and a superior stability in an alkaline solution, in comparison with noble Pt catalysts. In addition to ORR, the Fe-N-CIG also showed an excellent activity towards water oxidation (OER), with an onset potential at least 100 mV lower than that of commercial iridium oxide catalyst. This enables a potential application of the easily fabricated Fe-N-CIG as a dual-functional electrocatalyst for oxygen electrochemistry towards unitized regenerative fuel cells (URFCs) and rechargeable metal-air batteries, which is important for a variety of energy technologies and applications. The nanocarbon intercalation strategy we developed should be adaptable to other two dimensional nanomaterials towards improved performance. Our work opens up a new avenue for the development of energy-conversion-oriented catalytic materials based on earth-abundant elements.

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