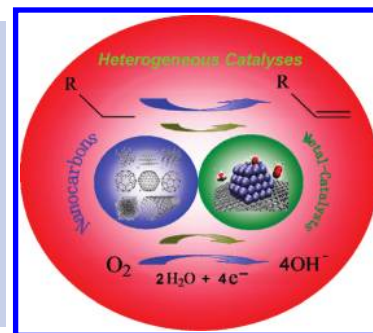


Metal-Free Carbon Nanomaterials Become More Active than Metal Catalysts and Last Longer

Dingshan Yu, Enoch Nagelli, Feng Du, and Liming Dai*

Department of Chemical Engineering, Case Western Reserve University, Cleveland, Ohio 44106

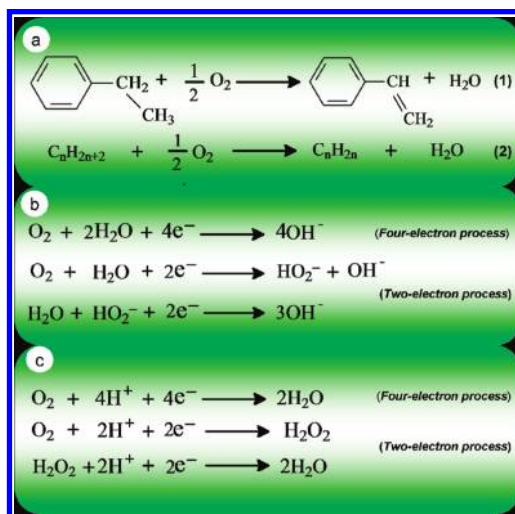
ABSTRACT Many reactions involve metals, especially noble metals or metal oxides as catalysts. Although metal-based catalysts have been playing a major role in various industrial processes, they still suffer from multiple competitive disadvantages, including their high cost, susceptibility to gas poisoning, and detrimental effects on the environment. Owing to their wide availability, environmental acceptability, corrosion resistance, and unique surface properties, certain carbon nanomaterials have recently been demonstrated to be promising metal-free alternatives for low-cost catalytic processes. This perspective highlights recent progresses in the development of carbon-based metal-free catalysts.



Generally speaking, a working catalyst must possess surface active sites necessary for adsorption of the reactants, bond-breaking and bond-formation, and desorption of the products. Additionally, an excellent structural stability is also essential to ensure that the catalytic activity is effective and efficient over a long period. Metals and metal oxides are undoubtedly the most widely used catalysts in many industrialized catalytic processes. Pt, Au, and Ru are a few examples of the noble metal catalysts used in fuel cells to accelerate the oxygen reduction reaction (ORR) at the cathode,^{1–4} while many hydrogenation and dehydrogenation reactions involve metal oxides as catalysts.^{5,6} However, these metal-based catalysts often suffer from multiple competitive disadvantages, including their high cost, low selectivity, poor durability, and detrimental environmental effects caused by catalyst residues and/or undesirable side-products.⁷ Therefore, it is highly desirable to develop inexpensive, metal-free catalysts of high performance.

Owing to their wide availability, environmental acceptability, corrosion resistance, and unique surface properties, carbon nanomaterials are ideal candidates for metal-free catalysts. While activated carbon and glassy carbon (GC) have been long used as catalysts for certain chemical and electrochemical processes,^{8,9} the recent availability of carbon nanomaterials of various peculiar molecular structures and optoelectronic properties, including fullerenes, carbon nanotubes (CNTs), nanodiamonds, and graphene sheets, offer new opportunities for the development of advanced carbon-based catalysts with much improved catalytic performance.^{7,10–12} The introduction of surface heteroatoms (e.g., nitrogen) into these carbon nanomaterials could further cause electron modulation to provide desirable electronic structures for many catalytic processes of practical significance.⁷ Consequently, considerable effort has recently been directed toward the development of metal-free carbon nanomaterials for various catalytic processes, involving either

Scheme 1. ODH of (1) Ethylbenzene and (2) Alkanes (a) and ORR in Alkaline (b) and Acidic (c) Media



oxidation or reduction reactions.^{7,13} This perspective highlights recent progresses in the development of carbon-based metal-free catalysts with an emphasis on the use of CNTs for oxidative dehydrogenation (ODH) of aromatic hydrocarbons and alkanes as well as ORRs, particularly in alkaline medium (Scheme 1).

Metal-Free Carbon Catalysts for ODH of Aromatic Hydrocarbons and Alkanes. Conventional heterogeneous catalysts often contain many active sites with a low free energy for chemisorptions, which also act as a matrix for a relatively small

Received Date: April 26, 2010

Accepted Date: June 23, 2010

Published on Web Date: July 01, 2010

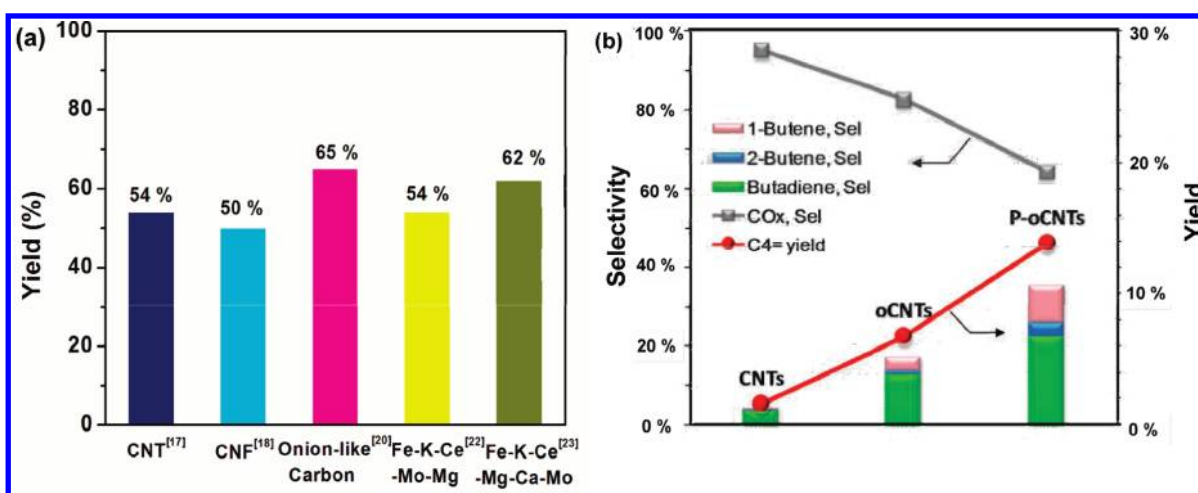


Figure 1. (a) Comparison of styrene yield from dehydrogenation reactions catalyzed by nanocarbons and metal catalysts (adapted from refs 17, 18, 20, 22, and 23). (b) Performance of various MWCNTs for ODH of butane under oxygen-rich conditions: 0.18 g, 0.67% butane, O_2 /butane = 2, 15 mL min⁻¹, 400 °C (adapted from ref 26).

number of high-energy reactive sites for converting the adsorbed molecules into products via bond rearrangements.¹⁴ For nanostructured carbon materials (e.g., CNTs, graphene sheets), the weak adsorption sites are normally associated with their basal planes consisting of the hexagonal arrangement of carbon atoms, while the high energy sites appear at the edges often saturated with hydrogen heteroatoms. The edge hydrogen atoms can be replaced by other heteroatoms, for example, oxygen and/or nitrogen atoms, to provide strong chemical reactivities for redox or acid–base reactions. Along with its use as a support for pure and heterogeneous metal catalysis,¹⁵ carbon has also been demonstrated to show interesting catalytic activities toward, for example, the ODH of saturated hydrocarbons.^{16–21} In particular, a variety of nanostructured carbons, such as CNTs,¹⁷ carbon nanofibers (CNFs),^{18,19} carbon onions,²⁰ and nanodiamonds,²¹ have been found to efficiently catalyze the ODH reaction of ethylbenzene to styrene (Scheme 1a). As an important monomer for polystyrene and its derivatives, styrene has normally been produced by the direct dehydrogenation of ethylbenzene in the temperature range 560–650 °C using iron oxide catalysts of a low energy efficiency.⁷ Compared with the traditional metal oxide catalyst,^{22,23} certain nanocarbons were demonstrated to exhibit a comparable, or even better, catalytic performance and long-term stability for the ODH reaction (Figure 1a) within the optimal temperature range of 350–550 °C.^{17,18,20,24} The large surface area of nanostructured carbons, with and without functionalization, can provide numerous active sites, and hence the excellent catalytic activity, while the graphitic structure can tightly hold the active moieties for an excellent thermal stability even under an oxidative atmosphere. Although the presence of oxygen-containing surface functional groups on the nanocarbon catalysts has been shown to be responsible for the catalytic ODH of ethylbenzene,^{24,25} the exact mechanism for the dissociative adsorption of gas-phase oxygen

molecules on carbon is still unknown and requires further study.

Compared with the traditional metal oxide catalyst, certain nanocarbons were demonstrated to exhibit a comparable, or even better, catalytic performance and long-term stability for the ODH reaction.

On the other hand, the activation of alkanes to alkenes has attracted considerable interest during the past decades. Despite considerable effort devoted to this important energy-related research field, the existing alkane activation process still suffers from the limited selectivity for alkene. Recently, Zhang et al.²⁶ have demonstrated that simple oxidation of multiwalled CNTs (MWCNTs) by HNO_3 increased the alkene yield from 1.6% to 6.7% (Figure 1b). Subsequent passivation of MWCNT defects with phosphorus oxide further increased the alkene yield up to 13.8% with a comparable selectivity to the widely used V–Mg–O catalytic system.²⁶ Similar catalytic activity enhancement was also observed with both the phosphorus- and boron-modified MWCNTs (P- and B-MWCNTs, respectively) for the ODH of propane to propene.^{27,28} In this case, however, the propene selectivity for either P-MWCNTs or B-MWCNTs is still lower than that of metal oxide catalysts due to the relatively long product retention time caused by strong interactions of propene molecules with the carbon catalyst surface. In addition, Meyer et al.,²⁹ found that the selective adsorption of nitro-substituted aromatics onto oxidized CNTs, fullerene, and even graphite could accelerate the rate of hydrolysis of 4-nitrophenyl acetate

on carbon surfaces. MWCNTs have recently been shown to also catalyze the ODH of dihydroanthracene to anthracene under mild reaction conditions,⁵⁰ while ordered mesoporous carbons (OMCs) were reported to act as promising catalysts for hydrogen production via methane decomposition.⁵¹ However, further study on the reaction kinetics and mechanisms is still needed.

Metal-Free N-Doped Carbon Catalysts for ORR. N-doping of CNTs has been studied for some years with attempts to modulate the nanotube electronic and other properties by introducing nitrogen heteroatoms into the nanotube structure.^{32,33} N-doped carbon nanostructures can be prepared either by in situ doping during the nanocarbon synthesis or through post-treatment (i.e., postdoping) of preformed carbon nanostructures with nitrogen-containing precursors (e.g., NH₃).^{34–38} Postdoping of carbon nanomaterials often leads to surface functionalization only without altering their bulk properties.^{35–38} In contrast, the in situ doping can incorporate nitrogen atoms into the entire carbon nanomaterials homogeneously. Examples for N-doped carbon nanomaterials from in situ doping include the high surface area porous carbons with a high nitrogen content prepared by cyclotrimerization reactions of carbonitriles under isothermal conditions,³⁹ and N-doped CNTs or CNFs synthesized by arc-discharge, laser ablation, or chemical vapor deposition (CVD)^{40–43} in the presence of appropriate nitrogen-containing precursors. Carbon nanomaterials of ordered structures^{44–46} can facilitate electron conduction and mass transport. Ordered N-doped CNTs or CNFs have been developed by substrate-assisted growth,^{47–51} with and without template, for various catalytic applications,^{52,53} including their use as metal-free catalysts for ORR at the cathode in fuel cells.^{48,54}

Instead of burning fuel to create heat, fuel cells convert chemical energy directly into electricity.⁵⁵ By pumping, for example, hydrogen gas onto the anode, hydrogen is split into its constituent electrons and protons. While the protons diffuse through the cell toward the cathode, the electrons flow out of the anode to provide electrical power. Electrons and protons both end up at the cathode to combine with oxygen to form water. While the very facile H₂ oxidation kinetics greatly reduces the amount of platinum catalyst at the anode, the slow ORR on the platinum cathode, either through a four-electron process or a less efficient two-step two-electron pathway (Scheme 1b,c),⁵⁵ is a key step to limit the energy conversion efficiency of a fuel cell. Although platinum nanoparticles have long been regarded as the best catalyst for the ORR, the Pt-based electrode suffers from its susceptibility to time-dependent drift and CO deactivation.⁵⁵ Furthermore, the high cost of the platinum catalysts, together with its limited reserves in nature, has been shown to be the major “showstopper” to mass market fuel cells for commercial applications. This is why the large-scale practical application of fuel cells has not been realized, although alkaline fuel cells with platinum as an ORR electrocatalyst were developed for the Apollo lunar mission in the 1960s.⁵⁶ The large-scale practical application of fuel cells will be difficult to realize if the expensive platinum-based electrocatalysts for ORR cannot be replaced by other efficient, low cost, and stable electrodes.

Recent intensive research efforts in reducing/replacing expensive platinum-based electrode in fuel cells have led to the development of some new ORR electrocatalysts from certain Pt-based alloys,⁵⁷ transition metal chalcogenides,⁵⁸ carbon-nano-

tube-supported metal particles,^{59–61} enzymatic electrocatalytic systems,⁶² and even conducting poly(3,4-ethylenedioxythiophene) (PEDOT)-coated membranes.⁶³ Apart from their use as the noble-metal-catalyst supports,^{64,65} aligned CNTs formed by high-temperature treatment of certain metal heterocycle molecules (e.g., ferrocene/NH₃) have been recently demonstrated to show some ORR electrocatalytic activities.⁶⁰ The observed electrocatalytic activity was attributed to the presence of FeN₂-C and/or FeN₄-C active sites in the nanotube structure.⁶⁰ In addition to the use of N-doped carbon nanomaterials as the catalyst support,⁶⁶ N-doped CNF electrodes, prepared by a floating catalyst CVD of a gas mixture containing ferrocene and either xylene or pyridine, have been demonstrated to show electrocatalytic activities for ORR via a two-step two-electron pathway.⁶⁷ The N-doped CNFs showed an over 100-fold increase in catalytic activity for H₂O₂ decomposition in both neutral and alkaline conditions,⁶⁸ albeit still less electroactive than the platinum catalyst. Noble-metal-free ORR active catalysts with significantly improved ORR performance compared to the N-doped CNFs have also been prepared via high-temperature pyrolysis of either acetonitrile over alumina and metal-doped alumina^{66,69,70} or Co-Fe-N chelate complex.^{71,72} The observed ORR activities were attributed to the presence of the Fe-N₄/N₂ active sites bound to carbon support and/or the exposed edge plane defects coupled with nitrogen doping to influence the adsorption of reactive intermediates.⁶⁷ Although N-doping has greatly improved ORR activity, these noble-metal-free catalysts still exhibited poorer, or at the best comparable, ORR performance with respect to Pt catalysts.

Along with the recent intensive research efforts in reducing or replacing Pt-based electrode in fuel cells, Gong et al.⁷³ recently found that vertically aligned nitrogen-containing CNTs (VA-NCNTs, Figure 2) could act as extremely effective metal-free ORR electrocatalysts. The metal-free VA-NCNTs were shown to catalyze a four-electron ORR process (Scheme 1b) free from CO “poisoning” with a much higher electrocatalytic activity and better long-term operation stability than that of commercially available Pt-based electrodes in alkaline electrolytes (Figure 2).⁷³ The high surface area, good electrical and mechanical properties, and superb thermal stability of aligned CNTs provide additional benefits for the nanotube electrode to be used in fuel cells under both ambient and harsh conditions (e.g., for high-temperature use).

The metal-free VA-NCNTs were shown to catalyze a four-electron ORR process free from CO “poisoning” with a much higher electrocatalytic activity and better long-term operation stability than that of commercially available Pt-based electrodes in alkaline electrolytes.

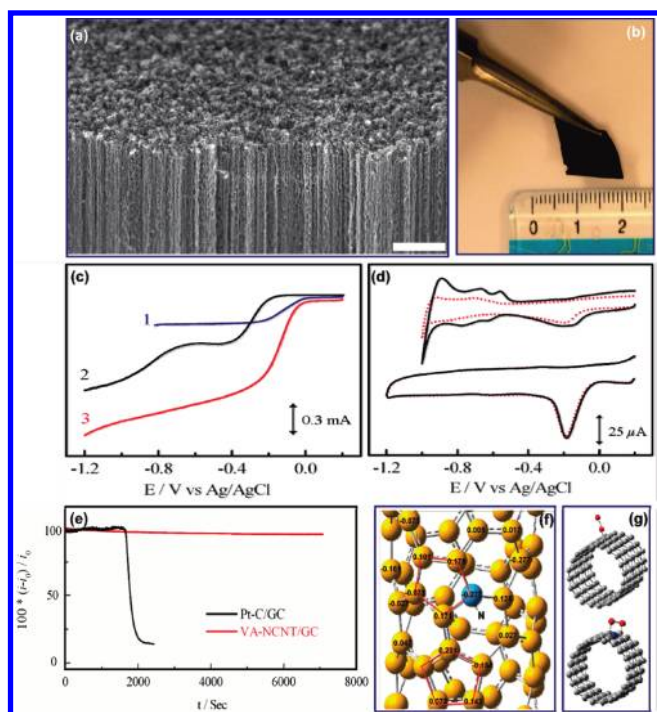


Figure 2. (a) SEM image of the as-synthesized VA-NCNTs on a quartz substrate (scale bars, $2 \mu\text{m}$). (b) Digital photograph of the VA-NCNT array after having been transferred onto a polystyrene-nonaligned CNT conductive nanocomposite film. (c) Rotating ring-disk electrode (RRDE) voltammograms for oxygen reduction in air saturated 0.1 M KOH at the Pt-C (curve 1), VA-CCNT (curve 2), and VA-NCNT (curve 3) electrodes. (d) Cyclic voltammograms (CVs) for the ORR at the Pt-C (top) and VA-NCNT (bottom) electrodes before (solid curves) and after (dotted curves) a continuous potentiodynamic sweep for about 100 000 cycles in air-saturated 0.1 M KOH at room temperature ($25 \pm 1^\circ \text{C}$). Scan rates: 100 mV s^{-1} . (e) The CO-poison effect on the $i-t$ chronoamperometric response for the Pt-C (black curve) and VA-NCNT (red line) electrodes. 55 mL/min CO gas was first added into the 550 mL/min O_2 flow, and then the mixture gas of $\sim 9\%$ CO (v/v) was introduced into the electrochemical cell at about 1700 s. (f) Calculated charge density distribution for the NCNTs. (g) Schematic representations of possible adsorption modes of an oxygen molecule at the CCNTs (top) and NCNTs (bottom) (adapted from ref 73).

On the basis of the experimental observations and quantum mechanics calculations by B3LYP hybrid density functional theory, Gong et al.⁷³ attributed the improved catalytic performance to the electron-accepting ability of the nitrogen atoms, which creates net positive charge on adjacent carbon atoms in the nanotube carbon plane of VA-NCNTs (Figure 2f) to readily attract electrons from the anode for facilitating the ORR. The nitrogen-induced charge delocalization could also change the chemisorption mode of O_2 from the usual end-on adsorption (Pauling model) at the nitrogen-free CNT (CCNT) surface (top, Figure 2g) to a side-on adsorption (Yeager model) onto the NCNT electrodes (bottom, Figure 2g). The N-induced charge-transfer from adjacent carbon atoms could lower the ORR potential, while the parallel diatomic adsorption could effectively weaken the O–O bonding, facilitating ORR at the VA-NCNT electrodes.⁷³ Uncovering this new ORR mechanism in the nitrogen-doped CNT electrodes is significant as the same principle could be applied to the development of various other metal-free efficient ORR

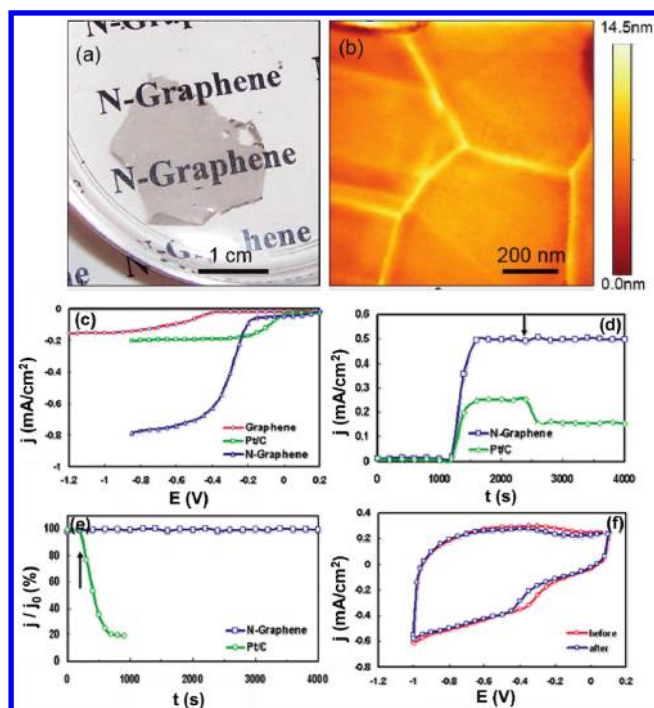


Figure 3. (a) A digital photo image of a transparent N-graphene film floating on water after removal of the nickel layer by dissolving in an aqueous acid solution. (b) Atomic force microscopy (AFM) image of the N-graphene film; (c) RRDE voltammograms for the ORR in air-saturated 0.1 M KOH at the C-graphene electrode (red line), Pt-C electrode (green line), and N-graphene electrode (blue line). Electrode rotating rate: 1000 rpm . Scan rate: 0.01 V/s . (d) Current density (j) vs time (t) chronoamperometric responses obtained at the Pt-C (circle line) and N-graphene (square line) electrodes at 0.4 V in air-saturated 0.1 M KOH . The arrow indicates the addition of 2% (w/w) methanol into the air-saturated electrochemical cell. (e) j vs t chronoamperometric response of Pt-C (circle line) and N-graphene (square line) electrodes to CO. The arrow indicates the addition of 10% (v/v) CO into air saturated 0.1 M KOH at 0.4 V ; j_0 defines the initial current. (f) Cyclic voltammograms of the N-graphene electrode in air-saturated 0.1 M KOH before (circle line) and after (square line) a continuous potentiodynamic sweep for 200 000 cycles at room temperature. Scan rate: 0.1 V/s (adapted from ref 78).

catalysts for fuel cell applications. Recent research activities carried out in many laboratories, including our own, have not only confirmed the above findings but also further proved that the important role of nitrogen-doping has a large impact on the design/development of new catalytic materials for fuel cell applications and even beyond fuel cells.^{74–82}

As a building block for CNTs, graphene is an attractive candidate for potential uses in many areas where the CNTs have been exploited. Superior to CNTs, the one-atom-thick graphene sheets with a two-dimensional (2D) planar geometry should further facilitate electron transport, and hence the more effective electrode materials. Indeed, N-doped graphene (N-graphene) films (Figure 3) produced by CVD in the presence of ammonia have recently been demonstrated to show a superb ORR performance similar to that of VA-NCNTs with the same nitrogen content in alkaline medium (Figure 3).⁷⁸ The ease with which graphene materials and their N-doped derivatives can be produced by various low-cost large-scale methods, including CVD,⁸³ chemical reduction of graphite oxide,⁸⁴ exfoliation of

graphite,⁸⁵ microwave plasma reaction,⁸⁶ and atmospheric pressure graphitization of silicon carbide,⁸⁷ suggests considerable room for cost-effective preparation of metal-free efficient graphene-based catalysts for oxygen reduction.

More recently, Ozaki et al.⁸¹ reported ORR activity in 0.5 M H₂SO₄ from the shell-like nanocarbons produced by carbonization of furan resin in the presence of acetylacetonates and metal phthalocyanines. These authors found that the high ORR activity did not result from metal species on the surface, which had been removed by acid washing.

As the CVD processes for producing the VA-NCNTs and N-graphene films used in the aforementioned work involve metal catalysts (e.g., Fe, Ni),^{73,78} considerable care has been taken during the electrode preparation to completely remove the catalyst residue. In particular, the VA-NCNT electrode was purified by electrochemical oxidation in a phosphate-buffered solution (pH 6.8) at a potential of 1.7 V (vs Ag/AgCl) for 300 s at room temperature (25 °C), followed by potential sweeping from 0.0 to 1.4 V in 0.5 M H₂SO₄ until a stable voltammogram free from any Fe redox signal was obtained. X-ray photoelectron spectroscopic (XPS) measurements on the electrochemically purified VA-NCNTs confirmed the removal of residual iron catalyst particles.⁷³ In view of the detection limitation intrinsically associated with the electrochemical and XPS measurements, however, possible effects of metal contaminants on the observed superb ORR performance could still be a matter of controversy unless nitrogen-doped carbon materials with excellent ORR electrocatalytic activities can be produced by a metal-free preparation procedure. In this regard, it is important to note that Liu et al.⁷⁷ reported an ORR electrocatalytic performance better than platinum for nitrogen-doped ordered mesoporous graphitic arrays (NOMGAs) prepared by a metal-free nanocasting technology using a nitrogen-containing aromatic dyestuff, *N,N'*-bis(2,6-diisopropylphenyl)-3,4,9,10-perylene-tetracarboxylic diimide (PDI) as the carbon precursor (Figure 4a). Owing to the metal-free preparation procedure, the reported electrocatalytic activity can be attributed exclusively to the incorporation of nitrogen in PDI-NOMGAs (Figure 4).⁷⁷ Metal-free N-doped MWCNTs or OMCs have also been produced through carbonization of an MWCNT-supported polyaniline (PANI) coating⁷⁹ or via NH₃ activation.⁸⁰ These metal-free N-doped nanocarbons have also been demonstrated to exhibit high ORR activities even in acidic electrolytes.

As discussed above, most recent studies on the N-doped carbon nanostructures focused on the ORR reaction in alkaline electrolytes, although fuel cells that operate with acidic electrolytes, particularly the polymer electrolyte fuel cell (PEMFC), could have a more significant economic impact. Recently, Kundu et al.⁷⁶ found that NCNTs prepared by pyrolysis of acetonitrile could show a considerably higher and more stable ORR activity in 0.5 M H₂SO₄ compared with their undoped counterparts. They pointed out that the incorporation of nitrogen functional groups within the carbon structure improved the oxidative stability of the NCNTs under ORR conditions even in the acidic medium. More recently, Wang et al.⁸⁰ demonstrated that nitrogen-doped OMCs via NH₃ activation can also act as alternative metal-free catalysts with a high ORR activity and better stability than Pt-based electrocatalysts in 0.05 M H₂SO₄. However, the catalytic

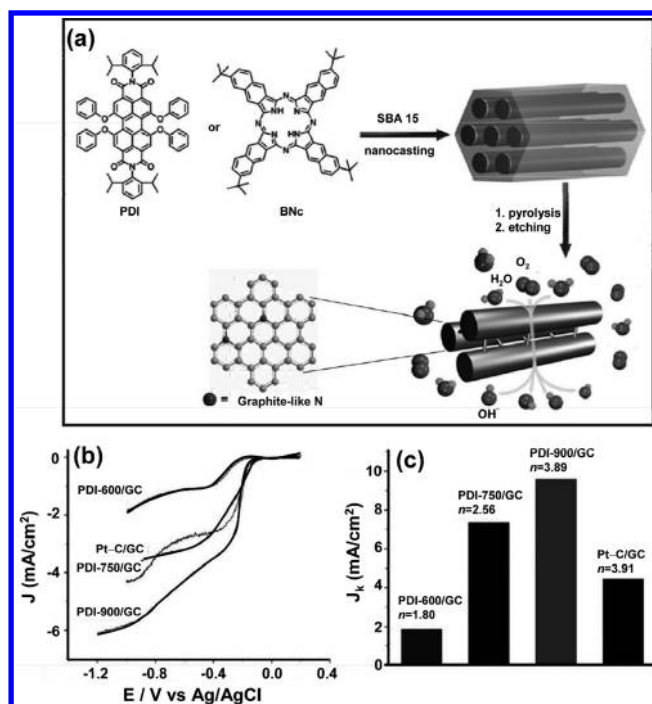


Figure 4. Preparation of NOMGAs as metal-free catalysts for the ORR. (b) RDE voltammograms of the series of PDI-NOMGAs and Pt-C supported on GC electrodes at a rotation rate of 1600 rpm. (c) Electrochemical activity given as the kinetic-limiting current density (J_k) at 0.35 V for the PDI-NOMGAs supported on GC electrodes in comparison with that of a commercial Pt-C electrode (adapted from ref 77).

performance of these reported N-doped carbon nanomaterials in acidic medium still needs to be further improved to meet the requirement for practical applications.

Since nitrogen plays an essential role in the active sites for the nanocarbon ORR catalysts and at least three different forms (i.e., pyrrolic, pyridinic, and graphitic) of the surface nitrogen atoms have been observed, it is important to understand the influence of the nitrogen content and its chemical nature on the ORR performance. Using ethylenediamine (EDA-NCNT) and pyridine as different precursors, Chen et al.⁷⁵ produced NCNTs with varying nitrogen contents through a single-step CVD process. These authors found that NCNTs with higher nitrogen content and more defects exhibited better ORR performance in acidic electrolytes.⁷⁵ On the other hand, Kundu et al.⁷⁶ prepared NCNTs via pyrolysis of acetonitrile over cobalt catalysts at different temperatures. The NCNTs prepared at 550 °C was found to possess a higher amount of pyridinic groups and a higher ORR electrocatalytic activity than its counterpart prepared at 750 °C. However, recent studies suggest that more graphitic nitrogen atoms rather than the pyridinic ones are important for the ORR.^{77,88} Therefore, the exact catalytic role for each of the nitrogen forms in nanocarbon ORR catalysts is still a matter of controversy.^{75–78} In addition, it is a challenge to determine the exact locations of nitrogen atoms in the nanocarbon structures, chemical nature of the catalytic sites, and electrochemical kinetics of the N-doped nanocarbon electrodes. A combined experimental and theoretical approach would be essential. Computer simulation and calculation have proved to be a

powerful technique in searching novel electrocatalysts and studying the basic science behind the electrocatalysis. Thus, theoretical calculations should be employed in studying the N-doped nanocarbon catalysts.

In summary, metals and metal oxides have been widely used as catalysts in various industrial processes. To address multiple competitive disadvantages associated with metal-based catalysts, such as the high cost, susceptibility to gas poisoning, and detrimental effects on the environment, recent research has demonstrated that certain nanostructured carbon materials could be used to replace metal-based catalysts for high-performance and low-cost catalytic processes. The performance of the metal-free carbon-based catalysts can be further optimized by doping/functionalizing with appropriate heteroatoms (e.g., N, O, P). Certain nanocarbons (e.g., CNTs with and without activation by HNO_3 or phosphorus oxide) have already been demonstrated to exhibit a comparable or even better catalytic performance than metal oxides (e.g., iron oxide, V-Mg-O) for the ODH of ethylbenzene (propane) to styrene (propene). More recently, N-doping of carbon nanomaterials (e.g., nanotube, graphene, graphite) have been shown to be a promising approach to the development of metal-free, carbon-based catalysts with even a much higher electrocatalytic activity and better long-term operation stability than that of commercially available platinum-based electrodes for oxygen reduction in fuel cells. These recent progresses proved to have a large impact on not only the commercialization of the fuel cell technology but also many other catalytic processes beyond fuel cells, and their repercussions are continuing. However, further study on the catalytic mechanism and kinetics is still needed in order to design and develop carbon-based catalysts with a desirable activity and durability, and the performance evaluation of these nanocarbon catalysts in actual fuel cells should be performed. For industrial applications, it is also essential to develop simple and cost-efficient methods for the large-scale production of carbon nanomaterials with a well-defined structure and surface chemistry.

AUTHOR INFORMATION

Corresponding Author:

*To whom correspondence should be addressed. E-mail: liming.dai@case.edu. Tel: 216-368-4151. Fax: 216-368-3016.

Biographies

Dingshan Yu is a postdoctoral research fellow in the Dai laboratory at Case Western Reserve University. His research interest centers on the development of novel carbon-based nanomaterials for multifunctional applications, including optoelectronic and electrochemistry applications.

Enoch Nagelli is a doctoral student in the Dai laboratory at Case Western Reserve University. His research interest includes the development and functionalization of nanomaterials for electrochemical applications.

Feng Du is a PhD student in the Dai laboratories at the University of Dayton and at Case Western Reserve University. His research interest covers the growth of carbon nanotubes, electrospinning, nanotube membranes, and dry adhesives.

Liming Dai is the Kent Hale Smith Professor in the Case School of Engineering, Case Western Reserve University. Before joining the

Case Western Reserve University, he was the Wright Brothers Institute Endowed Chair Professor of Nanomaterials at the University of Dayton. He obtained a bachelor's degree in chemical engineering from Zhejiang University in 1983 and a doctorate in chemistry from the Australian National University in 1990. His present research focuses on the synthesis and functionalization of polymers and carbon nanomaterials for energy-/biorelated applications. Webpages: http://www.case.edu/cse/eche/faculty_Dai.html; <http://academic.udayton.edu/limingdai>.

ACKNOWLEDGMENT The authors acknowledge the support from NSF (CMMI-1000768) and AFOSR (FA9550-09-1-0331).

REFERENCES

- (1) Winter, M.; Brodd, R. J. What Are Batteries, Fuel Cells, and Supercapacitors? *Chem. Rev.* **2004**, *104*, 4245–4270.
- (2) Yu, X.; Ye, S. Recent Advances in Activity and Durability Enhancement of Pt/C Catalytic Cathode in PEMFC Part II: Degradation Mechanism and Durability Enhancement of Carbon Supported Platinum Catalyst. *J. Power Sources* **2007**, *172*, 145–154.
- (3) Chen, Z. W.; Waje, M.; Li, W. Z.; Yan, Y. S. Supportless Pt and PtPd Nanotubes as Electrocatalysts for Oxygen-Reduction Reactions. *Angew. Chem., Int. Ed.* **2007**, *119*, 4138–4141.
- (4) Lim, B.; Jiang, M.; Camargo, P. H. C.; Cho, E. C.; Tao, J.; Lu, X.; Zhu, Y.; Xia, Y. Pd–Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction. *Science* **2009**, *324*, 1302–1305.
- (5) Botella, P.; García-González, E.; Dejoz, A.; López Nieto, J. M.; Vázquez, M. I.; González-Calbet, J. J. *Catal.* **2004**, *225*, 428–438.
- (6) Ait-Lachgar-Ben Abdelouahad, K.; Roulet, M.; Brun, M.; Burrows, A.; Kiely, C. J.; Volta, J. C.; Abon, M. Surface Alteration of $(\text{VO})_2\text{P}_2\text{O}_7$ by $\alpha\text{-Sb}_2\text{O}_4$ as a Route to Control the *n*-Butane Selective Oxidation. *Appl. Catal. A: Gen.* **2001**, *210*, 121–136.
- (7) Su, D. S.; Zhang, J.; Frank, B.; Thomas, A.; Wang, X.; Paraknowitsch, J.; Schlogl, R. Metal-Free Heterogeneous Catalysis for Sustainable Chemistry. *ChemSusChem* **2010**, *3*, 169–180.
- (8) Muñoz, J.; Marbán, G.; Fuertes, A. B. Low Temperature Selective Catalytic Reduction of NO over Modified Activated Carbon Fibres. *Appl. Catal. B: Environ.* **2000**, *27*, 27–36.
- (9) Sarapuu, A.; Vaika, K.; Schiffrin, D. J.; Tammeveski, K. Electrochemical Reduction of Oxygen on Anthraquinone-Modified Glassy Carbon Electrodes in Alkaline Solution. *J. Electroanal. Chem.* **2003**, *541*, 23–29.
- (10) Dai, L., Ed. *Carbon Nanotechnology: Recent Developments in Chemistry, Physics, Materials Science and Device Applications*; Elsevier: Amsterdam, 2006.
- (11) Wu, J.; Pisula, W.; Müllen, K. Graphenes as Potential Material for Electronics. *Chem. Rev.* **2007**, *107*, 718–747.
- (12) Allen, M. J.; Tung, V. C.; Kaner, R. B. Honeycomb Carbon: A Review of Graphene. *Chem. Rev.* **2010**, *110*, 132–145.
- (13) Schreiner, P. R. Metal-free Organocatalysis through Explicit Hydrogen Bonding Interactions. *Chem. Soc. Rev.* **2003**, *32*, 289–296.
- (14) Hellman, A.; Baerends, E. J.; Biczysko, M.; Bligaard, T.; Christensen, C. H.; Clary, D. C.; Dahl, S.; Harreveld, R. V.; Honkala, K.; Jonsson, H.; et al. Predicting Catalysis: Understanding Ammonia Synthesis from First-Principles Calculations. *J. Phys. Chem. B* **2006**, *110*, 17719–17735.

- (15) Radovic, L. R.; Rodriguez-Reinso, F. Carbon Materials in Catalysis. *Chemistry and Physics of Carbon: A Series of Advances*; Marcel Dekker, Inc.: New York, 1997.
- (16) Schraut, A.; Emig, G.; Sockel, H.-G. Composition and Structure of Active Coke in the Oxydehydrogenation of Ethylbenzene. *Appl. Catal.* **1987**, *29*, 311–326.
- (17) Su, D. S.; Maksimova, N.; Delgado, J. J.; Keller, N.; Mestl, G.; Ledoux, M. J.; Schlögl, R. Nanocarbons in Selective Oxidative Dehydrogenation Reaction. *Catal. Today* **2005**, *102–103*, 110–114.
- (18) Zhao, T. J.; Sun, W. Z.; Gu, X. Y.; Rønning, M.; Chen, D.; Dai, Y. C.; Yuan, W. K.; Holmen, A. Rational Design of the Carbon Nanofiber Catalysts for Oxidative Dehydrogenation of Ethylbenzene. *Appl. Catal. A: Gen.* **2007**, *323*, 135–146.
- (19) Mestl, G.; Maksimova, N. I.; Keller, N.; Roddatis, V. V.; Schlögl, R. Carbon Nanofilaments in Heterogeneous Catalysis: An Industrial Application for New Carbon Materials? *Angew. Chem., Int. Ed.* **2001**, *40*, 2066–2068.
- (20) Keller, N.; Maksimova, N. I.; Roddatis, V. V.; Schur, M.; Mestl, G.; Butenko, Y. V.; Kuznetsov, V. L.; Schlögl, R. The Catalytic Use of Onion-like Carbon Materials for Styrene Synthesis by Oxidative Dehydrogenation of Ethylbenzene. *Angew. Chem., Int. Ed.* **2002**, *41*, 1885–1888.
- (21) Su, D. S.; Maksimova, N. I.; Mestl, G.; Kuznetsov, V. L.; Schlögl, R.; Keller, N. Oxidative Dehydrogenation of Ethylbenzene to Styrene over Ultra-dispersed Diamond and Onion-like Carbon. *Carbon* **2007**, *45*, 2145–2151.
- (22) Addiego, W. P.; Liu, W.; Boger, T. Iron Oxide-Based Honeycomb Catalysts for the Dehydrogenation of Ethylbenzene to Styrene. *Catal. Today* **2001**, *69*, 25–31.
- (23) Rubini, C.; Cavalli, L.; Conca, E. Catalysts for Dehydrogenating Ethylbenzene to Styrene. U. S. Patent 6184174, 2001.
- (24) Zhang, J.; Su, D. S.; Zhang, A.; Wang, D.; Schlögl, R.; Hérbert, C. Nanocarbon as Robust Catalyst: Mechanistic Insight into Carbon-Mediated Catalysis. *Angew. Chem., Int. Ed.* **2007**, *46*, 7319–7323.
- (25) Pereira, M. F. R.; Órfão, J. J. M.; Figueiredo, J. L. Oxidative Dehydrogenation of Ethylbenzene on Activated Carbon Catalysts. *Appl. Catal. A: Gen.* **2001**, *218*, 307–318.
- (26) Zhang, J.; Liu, X.; Blume, R.; Zhang, A.; Schlögl, R.; Su, D. S. Surface-Modified Carbon Nanotubes Catalyze Oxidative Dehydrogenation of *n*-Butane. *Science* **2008**, *322*, 73–77.
- (27) Sui, Z.; Zhou, J.; Dai, Y.; Yuan, W. Oxidative Dehydrogenation of Propane over Catalysts Based on Carbon Nanofibers. *Catal. Today* **2005**, *106*, 90–94.
- (28) Frank, B.; Zhang, J.; Blume, R.; Schlögl, R.; Su, D. S. Heteroatoms Increase the Selectivity in Oxidative Dehydrogenation Reactions in Nanocarbons. *Angew. Chem., Int. Ed.* **2009**, *48*, 6913–6917.
- (29) Meyer, A. G.; Dai, L. M.; Chen, Q.; Easton, C. J.; Xia, L. Selective Adsorption of Nitro-substituted Aromatics and Accelerated Hydrolysis of 4-Nitrophenyl Acetate on Carbon Surfaces. *New J. Chem.* **2001**, *25*, 887–889.
- (30) Bégin, D.; Ulrich, G.; Amadou, J.; Su, D. S.; Pham-Huu, C.; Ziesel, R. Oxidative Dehydrogenation of 9,10-Dihydroanthracene Using Multi-Walled Carbon Nanotubes. *J. Mol. Catal. A: Chem.* **2009**, *302*, 119–123.
- (31) Serrano, D. P.; Botas, J. A.; Pizarro, P.; Guil-López, R.; Gómez, G. Ordered Mesoporous Carbons as Highly Active Catalysts for Hydrogen Production by CH₄ Decomposition. *Chem. Commun.* **2008**, 6585–6587.
- (32) Ewels, C. P.; Glerup, M. J. Nitrogen Doping in Carbon Nanotubes. *J. Nanosci. Nanotechnol.* **2005**, *5*, 1345–1363.
- (33) Shao, Y.; Sui, J.; Yin, G.; Gao, Y. Nitrogen-Doped Carbon Nanostructures and Their Composites as Catalytic Materials for Proton Exchange Membrane Fuel Cells. *Appl. Catal. B: Environ.* **2008**, *79*, 89–99.
- (34) Wang, E. G. A New Development in Covalently Bonded Carbon Nitride and Related Materials. *Adv. Mater.* **1999**, *11*, 1129–1133.
- (35) Jiang, L.; Gao, L. Modified Carbon Nanotubes: An Effective Way to Selective Attachment of Gold Nanoparticles. *Carbon* **2003**, *41*, 2923–2929.
- (36) Roy, S. C.; Harding, A. W.; Russell, A. E.; Thomas, K. M. Spectroelectrochemical Study of the Role Played by Carbon Functionality in Fuel Cell Electrodes. *J. Electrochem. Soc.* **1997**, *144*, 2323–2328.
- (37) Sidik, R. A.; Anderson, A. B.; Subramanian, N. P.; Kumaraguru, S. P.; Popov, B. N. O₂ Reduction on Graphite and Nitrogen-Doped Graphite: Experiment and Theory. *J. Phys. Chem. B* **2006**, *110*, 1787–1793.
- (38) Titirici, M.; Thomas, A.; Antonietti, M. Aminated Hydrophilic Ordered Mesoporous Carbons. *J. Mater. Chem.* **2007**, *17*, 3412–3418.
- (39) Lee, J. S.; Wang, X.; Luo, H.; Baker, G. A.; Dai, S. Facile Ionothermal Synthesis of Microporous and Mesoporous Carbons from Task Specific Ionic Liquids. *J. Am. Chem. Soc.* **2009**, *131*, 4596–4597.
- (40) Glerup, M.; Steinmetz, J.; Samaille, D.; Stéphan, O.; Enouz, S.; Loiseau, A.; Roth, S.; Bernier, P. Synthesis of N-Doped SWNT Using the Arc-Discharge Procedure. *Chem. Phys. Lett.* **2004**, *387*, 193–197.
- (41) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F. Isolation of the Heterofullerene C₅₉N as its Dimer (C₅₉N)₂. *Science* **1995**, *269*, 1554–1556.
- (42) Qu, L.; Du, F.; Dai, L. Preferential Syntheses of Semiconducting Vertically Aligned Single-Walled Carbon Nanotubes for Direct Use in FETs. *Nano Lett.* **2008**, *8*, 2682–2687.
- (43) Terrones, M.; Terrones, H.; Grobert, N.; Hsu, W. K.; Zhu, Y. Q.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M.; Kohler-Redlich, P.; Rühle, M.; et al. Efficient Route to Large Arrays of CN_x Nanofibers by Pyrolysis of Ferrocene/Melamine Mixtures. *Appl. Phys. Lett.* **1999**, *75*, 3932–3934.
- (44) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. Carbon Nanotubule Membranes for Electrochemical Energy Storage and Production. *Nature* **1998**, *393*, 346–349.
- (45) Parthasarathy, R. V.; Phani, K. L. N.; Martin, C. R. Template Synthesis of Graphitic Nanotubules. *Adv. Mater.* **1995**, *7*, 896–897.
- (46) Vinu, A.; Ariga, K.; Mori, T.; Nakanishi, T.; Hishita, S.; Golberg, D.; Bando, Y. Preparation and Characterization of Well-Ordered Hexagonal Mesoporous Carbon Nitride. *Adv. Mater.* **2005**, *17*, 1648–1652.
- (47) Trasobares, S.; Stéphan, O.; Colliex, C.; Hsu, W. K.; Kroto, H. W.; Walton, D. R. M. Compartmentalized CN_x Nanotubes: Chemistry, Morphology, and Growth. *J. Chem. Phys.* **2002**, *116*, 8966–8972.
- (48) Kudashov, A. G.; Okotrub, A. V.; Bulusheva, L. G.; Asanov, I. P.; Shubin, Y. V.; Yudanov, N. F.; Yudanov, L. I.; Danilovich, V. S.; Abrosimov, O. G. Influence of Ni–Co Catalyst Composition on Nitrogen Content in Carbon Nanotubes. *J. Phys. Chem. B* **2004**, *104*, 9048–9053.
- (49) Hou, P.; Orikasa, H.; Yamazaki, T.; Matsuoka, K.; Tomita, A.; Setoyama, N.; Fukushima, Y.; Kyotani, T. Synthesis of Nitrogen-Containing Microporous Carbon with a Highly Ordered Structure and Effect of Nitrogen Doping on H₂O Adsorption. *Chem. Mater.* **2005**, *17*, 5187–5193.
- (50) Maiyalagan, T.; Viswanathan, B. Template Synthesis and Characterization of Well-Aligned Nitrogen Containing Carbon Nanotubes. *Mater. Chem. Phys.* **2005**, *93*, 291–295.

- (51) Jang, J.; Oh, J. H. A Facile Synthesis of Polypyrrole Nanotubes Using a Template-Mediated Vapor Deposition Polymerization and the Conversion to Carbon Nanotubes. *Chem. Commun.* **2004**, *7*, 882–885.
- (52) Maiyalagan, T.; Viswanathan, B.; Varadaraju, U. V. Nitrogen Containing Carbon Nanotubes as Supports for Pt - Alternate Anodes for Fuel Cell Applications. *Electrochem. Commun.* **2005**, *7*, 905–912.
- (53) Wang, C.; Waje, M.; Wang, X.; Tang, J. M.; Haddon, R. C.; Yan, Y. Proton Exchange Membrane Fuel Cells with Carbon Nanotube Based Electrodes. *Nano Lett.* **2004**, *4*, 345–348.
- (54) Shao, Y.; Sui, J.; Yin, G.; Gao, Y. Nitrogen-Doped Carbon Nanostructures and Their Composites as Catalytic Materials for Proton Exchange Membrane Fuel Cell. *Appl. Catal. B: Environ.* **2008**, *79*, 89–99.
- (55) Basu, S. *Recent Trends in Fuel Cell Science and Technology*; Anamaya Publishers: New Delhi, 2007.
- (56) Fuel cells. <http://americanhistory.si.edu/fuelcells/alk/alk3.htm> (accessed June 28, 2010).
- (57) Zhang, J.; Sasaki, K.; Sutter, E.; Adzic, R. R. Stabilization of Platinum Oxygen-Reduction Electrocatalysts Using Gold Clusters. *Science* **2007**, *315*, 220–222.
- (58) Gong, K.; Yu, P.; Su, L.; Xiong, S.; Mao, L. Polymer-Assisted Synthesis of Manganese Dioxide/Carbon Nanotube Nanocomposite with Excellent Electrocatalytic Activity toward Reduction of Oxygen. *J. Phys. Chem. C* **2007**, *111*, 1882–1887.
- (59) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. Carbon Nanotubule for Electrochemical Energy Storage and Production. *Nature* **1998**, *393*, 346–349.
- (60) Yang, J.; Liu, D.; Kariuki, N. N.; Chen, L. X. Aligned Carbon Nanotubes with Built-In FeN₄ Active Sites for Electrocatalytic Reduction of Oxygen. *Chem. Commun.* **2008**, *3*, 329–331.
- (61) Kongkanand, A.; Kuwabata, S.; Girishkumar, G.; Kamat, P. Single-Wall Carbon Nanotubes Supported Platinum Nanoparticles with Improved Electrocatalytic Activity for Oxygen Reduction Reaction. *Langmuir* **2006**, *22*, 2392–2396.
- (62) Collman, J. P.; Devaraj, N. K.; Decreau, R. A.; Yang, Y.; Yan, Y.; Ebina, W.; Eberspacher, T. A.; Childsey, C. E. A Cytochrome c Oxidase Model Catalyzes Oxygen to Water Reduction Under Rate-Limiting Electron Flux. *Science* **2007**, *315*, 1565–1568.
- (63) Winther-Jensen, B.; Winther-Jensen, O.; Forsyth, M.; MacFarlane, D. R. High Rates of Oxygen Reduction over a Vapor Phase-Polymerized PEDOT Electrode. *Science* **2008**, *321*, 671–674.
- (64) Che, G.; Lakshmi, B. B.; Fisher, E. R.; Martin, C. R. Carbon Nanotube for Electrochemical Energy Storage and Production. *Nature* **1998**, *393*, 346–349.
- (65) Kongkanand, A.; Kuwabata, S.; Girishkumar, G.; Kamat, P. Single-Wall Carbon Nanotubes Supported Platinum Nanoparticles with Improved Electrocatalytic Activity for Oxygen Reduction Reaction. *Langmuir* **2006**, *22*, 2392–2396.
- (66) Matter, P. H.; Wang, E.; Arias, M.; Biddinger, E. J.; Ozkan, U. S. Oxygen Reduction Reaction Catalysts Prepared from Acetonitrile Pyrolysis Over Alumina-Supported Metal Particles. *J. Phys. Chem. B* **2006**, *110*, 18374–18384.
- (67) Maldonado, K.; Stevenson, K. J. Direct Preparation of Carbon Nanofiber Electrodes via Pyrolysis of Iron(II) Phthalocyanine: Electrocatalytic Aspects for Oxygen Reduction. *J. Phys. Chem. B* **2004**, *108*, 11375–11383.
- (68) Maldonado, S.; Stevenson, K. J. Influence of Nitrogen Doping on Oxygen Reduction Electrocatalysis at Carbon Nanofiber Electrodes. *J. Phys. Chem. B* **2005**, *109*, 4707–4716.
- (69) Matter, P. H.; Ozkan, U. S. Non-metal Catalysts for Dioxygen Reduction in an Acidic Electrolyte. *Catal. Lett.* **2006**, *109*, 115–123.
- (70) Matter, P. H.; Wang, E.; Arias, M.; Biddinger, E. J.; Ozkan, U. S. Oxygen Reduction Reaction Activity and Surface Properties of Nanostructured Nitrogen-Containing Carbon. *J. Mol. Catal. A: Chem.* **2007**, *264*, 73–81.
- (71) Nallathambi, V.; Lee, J.; Kumaraguru, S. P.; Wu, G.; Popov, B. N. Development of High Performance Carbon Composite Catalyst for Oxygen Reduction Reaction in PEM Proton Exchange Membrane Fuel Cells. *J. Power Sources* **2008**, *183*, 34–42.
- (72) Nallathambi, V.; Wu, G.; Subramanian, P.; Kumaraguru, S. P.; Lee, J.; Popov, B. Highly Active Carbon Composite Electrocatalysts for PEM Fuel Cells. *ECS Trans.* **2007**, *11*, 241–247.
- (73) Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Nitrogen-Doped Carbon Nanotube Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Science* **2009**, *323*, 760–764.
- (74) Tang, Y.; Allen, B. L.; Kauffman, D. R.; Star, A. Electrocatalytic Activity of Nitrogen-Doped Carbon Nanotube Cups. *J. Am. Chem. Soc.* **2009**, *131*, 13200–13201.
- (75) Chen, Z.; Higgins, D.; Tao, H.; Hsu, R. S.; Chen, Z. Highly Active Nitrogen-Doped Carbon Nanotubes for Oxygen Reduction Reaction in Fuel Cell Applications. *J. Phys. Chem. C* **2009**, *113*, 21008–21013.
- (76) Kundu, S.; Nagaiah, T. C.; Xia, W.; Wang, Y.; Van Dommele, S.; Bitter, J. H.; Santa, M.; Grundmeier, G.; Bron, M.; Schuhmann, W. M.; et al. Electrocatalytic Activity and Stability of Nitrogen-Containing Carbon Nanotubes in the Oxygen Reduction Reaction. *J. Phys. Chem. C* **2009**, *113*, 14302–14310.
- (77) Liu, R.; Wu, D.; Feng, X.; Müllen, K. Nitrogen-Doped Ordered Mesoporous Graphitic Arrays with High Electrocatalytic Activity for Oxygen Reduction. *Angew. Chem., Int. Ed.* **2010**, *49*, 2565–2569.
- (78) Qu, L.; Liu, Y.; Baek, J.; Dai, L. Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalyst for Oxygen Reduction in Fuel Cell. *ACS Nano* **2010**, *4*, 1321–1326.
- (79) Jin, C.; Nagaiah, T. C.; Xia, W.; Spliethoff, B.; Wang, S.; Bron, M.; Schuhmann, W.; Muhler, M. Metal-Free and Electrocatalytically Active Nitrogen-Doped Carbon Nanotubes Synthesized by Coating with Polyaniline. *Nanoscale* [Online early access]. DOI: 10.1039/b9nr00405j.
- (80) Wang, X.; Lee, J. S.; Zhu, Q.; Liu, J.; Wang, Y.; Dai, S. Ammonia-Treated Ordered Mesoporous Carbons as Catalytic Materials for Oxygen Reduction Reaction. *Chem. Mater.* **2010**, *22*, 2178–2180.
- (81) Ozaki, J.; Tanifuji, S.; Furuichi, A.; Yabutsuka, K. Enhancement of Oxygen Reduction Activity of Nanoshell Carbons by Introducing Nitrogen Atoms from Metal Phthalocyanines. *Electrochim. Acta* **2010**, *55*, 1864–1871.
- (82) Numerous refereed papers cited our *Science* paper (i.e., ref 73) just within about 1 year after its publication; see, for example, ISI Web of Knowledge.
- (83) Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R. D.; Velamakanni, A.; Jung, I.; Tutuc, E.; et al. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science* **2009**, *324*, 1312–1314.
- (84) Yu, D.; Dai, L. Self-Assembled Graphene/Carbon Nanotube Hybrid Films for Supercapacitors. *J. Phys. Chem. Lett.* **2010**, *1*, 467–470.
- (85) Li, X.; Zhang, G.; Bai, X.; Sun, X.; Wang, X.; Wang, E.; Dai, H. Highly Conducting Graphene Sheets and Langmuir–Blodgett Films. *Nat. Nanotechnol.* **2008**, *3*, 538–542.

- (86) Dato, A.; Radmilovic, V.; Lee, Z.; Phillips, J.; Frenklach, M. Substrate-Free Gas-Phase Synthesis of Graphene Sheets. *Nano Lett.* **2008**, *8*, 2012–2016.
- (87) Emtsev, K. V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G. L.; Ley, L.; McChesney, J. L.; Ohta, T.; Reshanov, S. A.; Röhrl, J. et al. Towards Wafer-Size Graphene Layers by Atmospheric Pressure Graphitization of Silicon Carbide. *Nat. Mater.* **2009**, *8*, 203–207.
- (88) Niwa, H.; Horiba, K.; Harada, Y.; Oshima, M.; Ikeda, T.; Terakura, K.; Ozaki, J.; Miyata, S. X-ray Absorption Analysis of Nitrogen Contribution to Oxygen Reduction Reaction in Carbon Alloy Cathode Catalysts for Polymer Electrolyte Fuel Cells. *J. Power Sources* **2009**, *187*, 93–97.