

**“Metal-free and Oxygen-free Graphene as Oxygen Reduction Catalysts
for Highly Efficient Fuel Cells”**

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Abstract

Oxygen reduction reaction (ORR) is important in fuel cells. Although platinum nanoparticles can catalyze the ORR in an efficient way, 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. Following our earlier work on metal-free, nitrogen-doped carbon nanotubes (Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. *Science* **2009**, 323, 760) and nitrogen-doped graphene sheets (Qu, L.; Liu, Y.; Baek, J.-B.; Dai, L. *ACS Nano* **2010**, 4, 1321) as highly efficient ORR, we have developed in this project new metal-free and oxygen-free graphene materials by either edge-functionalization or ball milling as efficient electrocatalysts for ORR in fuel cells and other applications, including dye-sensitized solar cells (DSSCs).

Introduction

Instead of burning fuel to create heat, fuel cells convert chemical energy directly into electricity. By pumping, for example, hydrogen gas onto one electrode (the anode), hydrogen is split into its constituent electrons and protons. While the protons diffuse through the cell toward a second electrode (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 oxygen reduction reaction (ORR) on the platinum cathode is a key step to limit the energy conversion efficiency of a fuel cell. The oxygen reduction reaction (ORR) can proceed either

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14. ABSTRACT Oxygen reduction reaction (ORR) is important in fuel cells. Although platinum nanoparticles can catalyse the ORR in an efficient way, 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. Following our earlier work on metal-free, nitrogen-doped carbon nanotubes (Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. Science 2009, 323, 760) and nitrogen-doped graphene sheets (Qu, L.; Liu, Y.; Baek, J.-B.; Dai, L. ACS Nano 2010, 4, 1321) as highly efficient ORR, we have developed in this project new metal-free and oxygen-free graphene materials by either edge-functionalization or ball milling as efficient electrocatalysts for ORR in fuel cells and other applications, including dye-sensitized solar cells (DSSCs).					
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through a four-electron process to directly combine oxygen with electrons and protons into water as the end produce or a less efficient two-step, two-electron pathway involving the formation of hydrogen peroxide ions as an intermediate. The four-electron process usually is more efficient than two-electron one. 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 (Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. *Science* **2009**, 323, 760). Besides, 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, though alkaline fuel cells with platinum as an ORR electrocatalyst were developed for the Apollo lunar mission in the 1960s.

Along with recent intensive research efforts in reducing or replacing Pt-based electrode in fuel cells, we have found that vertically aligned nitrogen-containing carbon nanotubes (VA-NCNTs) produced by pyrolysis of iron(II) phthalocyanine (a metal heterocyclic molecule containing nitrogen) (Huang, S.; Dai, L.; Mau, A.W.H. *J. Phys. Chem. B* **1999**, 103, 4223.), in either the presence or absence of additional NH₃ vapor (Panchakarla, L.S.; Govindaraj, A.; Rao, C.N.R. *ACS Nano* **2007**, 1, 494.), could act as extremely effective metal-free ORR electrocatalysts (Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. *Science* **2009**, 323, 760). The metal-free VA-NCNTs were shown to catalyze a four-electron ORR process free from CO "poisoning" with a much higher electrocatalytic activity, smaller crossover effect, and better long-term operation stability than that of commercially available or similar platinum-based electrodes (C2-20, 20% platinum on Vulcan XC-72R; E-TEK) in alkaline electrolytes (Gong, K.; Du, F.; Xia, Z.; Durstock, M.; Dai, L. *Science* **2009**, 323, 760.). Subsequent research carried out in our team members' laboratories (CWRU and UNIST) has also clearly shown that N-doped graphene sheets also exhibited high electrocatalytic activities toward ORR. However, possible effects of oxygen-containing surface groups on the ORR have not been investigated for either the metal-free N-NCNTs or N-Graphene, which inevitably contain oxygen-rich groups (*e.g.* carbonyl, hydroxyl, epoxy) from the synthesis/post-synthesis processes. In this project, various metal-free and oxygen-free N-doped graphene sheets have been prepared through a newly-discovered edge functionalization method to directly exfoliate graphite into graphene sheets by "direct" covalent attachment of organic molecular wedges to the edges of pristine graphite, instead of graphite oxide (GO), followed by subsequent N-doping under appropriate conditions. High quality metal-free and oxygen-free graphene sheets doped with various heteroatoms have also been prepared by ball milling. As originally proposed, the major goal of this project is to develop the transformational N-doping technology further for a dramatically cheaper, longer-lasting way to commercialize fuel cells with carbon-based metal-free ORR catalysts to compete with current market technologies, including gasoline internal combustion engines.

As a result of full or partial funding of the AFOSR (FA2386-10-1-4071), we have published 35 peer refereed journal papers during the past three years or so, including 1 *PNAS* (**2012**, 109, 5588-5593); 1 *Scientific Reports* (**2013**, 3, 1810); 1 *Acct. Chem. Res.* (**2013**, 46, 31-42); 3 *JACS* (**2013**, 135, 1386. **2011**, 133, 5182. **2010**, 132, 15127), 4 *Angew. Chem. Int. Ed.* (**2012**, 51, 12124. **2012**, 124, 4209. **2011**, 50, 6575); and 7 *ACS Nano* (**2012**, 6, 5259. **2012**, 6, 6345. **2012**, 6, 1715. **2011**, 5, 6202. **2011**, 5, 4974. **2010**, 4, 5633. **2010**, 3, 1321); plus 2 book chapters. Below, I briefly describe the important ones.

Experiment

Materials Characterization: The morphology of the electrode materials were examined by scanning electron microscopy (SEM). X-ray photoelectron spectroscopic (XPS) measurements were performed on a VG Microtech ESCA 2000 using a monochromic Al X-ray source (97.9 W, 93.9 eV). The thermogravimetric analysis was carried out by a TA instrument with a heating rate of 10 °C in N₂. The Raman spectra were collected on a Raman spectrometer (Renishaw) using 514-nm laser. Thermal stability was performed by TGA under nitrogen atmosphere.

Electrochemical Characterization: The catalyst suspensions in ethanol (1 mg/ml) were prepared by introducing a predetermined amount of appropriate electrode materials in the pure solvent (ethanol) under sonication (Power: 75 W). For the electrode preparation, 10 µl of the catalyst suspension was dropped onto the surface of a pre-polished glassy carbon electrode (GCE, MTI Cooperation), followed by dropping 5 µl Nafion solution in isopropanol (0.5 wt%) as a binder. Electrochemical measurements were performed using a computer-controlled potentiostat (CHI 760C, CH Instrument, USA) with a typical three-electrode cell. A platinum wire was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. The activity of the electrocatalysts was evaluated by the cyclic voltammetry and linear sweep voltammetry techniques on rotating ring-disk electrode (RRDE). All the experiments were conducted at room temperature (25±1 °C).

The detailed kinetic analysis was conducted according to Koutecky-Levich plots:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}} \quad (1)$$

where, j_k is the kinetic current and B is Levich slope which is given by:

$$B = 0.2nF(D_{O_2})^{2/3}\nu^{-1/6}C_{O_2} \quad (2)$$

Here n is the number of electrons transferred in the reduction of one O₂ molecule, F is the Faraday constant ($F = 96485$ C/mol), D_{O_2} is the diffusion coefficient of O₂ ($D_{O_2} = 1.9 \times 10^{-5}$ cm² s⁻¹), ν is the kinematics viscosity for KOH ($\nu = 0.01$ cm² s⁻¹) and C_{O_2} is concentration of O₂ in the solution ($C_{O_2} = 1.2 \times 10^{-6}$ mol cm⁻³). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

DFT Calculation: The electrocatalytic activity of the electrode materials was also studied theoretically via B3LYP hybrid density function theory (DFT) through Gaussian 03 (Revision E.01; Gaussian, Inc., Wallingford, CT, 2004). The details of the calculation can be found elsewhere (Zhang, L.; Xia, Z. *J. Phys. Chem. C* **2011**, *115*, 11170).

Results and Discussion

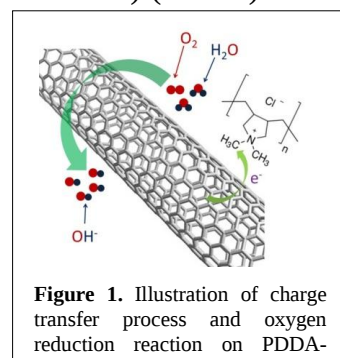
- 1) “Highly-Efficient Metal-Free Growth of Nitrogen-Doped Single-Walled Carbon Nanotubes on Plasma-Etched Substrates for Oxygen Reduction” (Yu, D.; Zhang, Q.; Dai, L. *J. Am. Chem. Soc.* **2010**, *132*, 15127)

As originally proposed, we have developed new concepts for manufacturing high-performance catalysts for the oxygen reduction reaction (ORR) in fuel cells. At CWRU, we have for the first time developed a simple plasma-etching technology to effectively generate metal-free particle

catalysts for efficient metal-free growth of undoped and/or nitrogen-doped single-walled carbon nanotubes (NCNTs). Compared with undoped CNTs, the newly-produced metal-free NCNTs were demonstrated to show a relatively good electrocatalytic activity and long-term stability towards ORR in acidic medium. Owing to the metal-free growth, the observed electrocatalytic activity towards ORR for the newly-produced NCNTs could be attributed exclusively to the incorporation of nitrogen in the CNT structure.

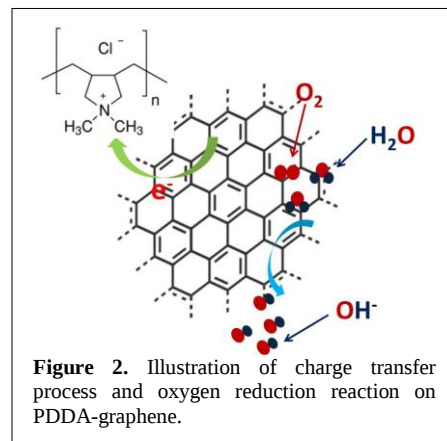
2) “Polyelectrolyte Functionalized Carbon Nanotubes as Efficient Metal-free Electrocatalysts for Oxygen Reduction” (Wang, S.; Yu, D.; Dai, L. *J. Am. Chem. Soc.* **2011**, 133, 5182)

We have also functionalized/adsorbed poly(diallyldimethylammonium chloride) (PDDA) with a strong electron-withdrawing ability onto nitrogen-free pure CNTs to create net positive charge for carbon atoms in the nanotube carbon plane via intermolecular charge transfer (Figure 1), and found that the resultant PDDA functionalized/adsorbed nitrogen-free CNTs, either in an aligned or nonaligned form, to act as metal-free catalysts toward ORR in fuel cells with similar performance as Pt catalysts. Thus, the adsorption-induced *intermolecular charge-transfer* should provide a general approach to various carbon-based efficient metal-free ORR catalysts for oxygen reduction in fuel cells, and even new catalytic materials for applications beyond fuel cells.



3) “Polyelectrolyte-functionalized Graphene as Metal-free Electrocatalysts for Oxygen Reduction” (Wang, S.; Yu, D.; Dai, L.; Chang, D. W.; Baek, J.-B. *ACS Nano* **2011**, 5, 6202)

In a somewhat related but independent study, we have also used poly(diallyldimethylammonium chloride), PDDA, as an electron acceptor for functionalizing graphene to impart electrocatalytic activity for oxygen reduction reaction (ORR) in fuel cells. Raman and X-ray photoelectron spectroscopic (XPS) measurements indicate the occurrence of charge transfer from graphene to PDDA (Figure 2). The positively-charged graphene via intermolecular charge transfer with PDDA was demonstrated to show remarkable electrocatalytic activity toward ORR with a better fuel selectivity, more tolerance to CO poisoning, and higher long-term stability than that of commercially available Pt/C electrode. Comparing with carbon nanotubes, the ease with which graphene materials can be produced by various low-cost large-scale methods, including the chemical vapor deposition, chemical reduction of graphite oxide, exfoliation of graphite, suggests considerable room for cost-effective preparation of metal-free efficient graphene-based catalysts for oxygen reduction. Furthermore, this work clearly indicates that the important role of intermolecular charge-transfer to ORR demonstrated with N-free carbon nanotubes and N-free graphene can be applied to other carbon materials for the development of various efficient metal-free ORR catalysts.



- 4) “BCN Graphene as Efficient Metal-free Electrocatalyst for Oxygen Reduction Reaction” (Wang, S.; Zhang, L.; Xia, Z.; Roy, A.; Chang, D.W.; Baek, J.B.; Dai, L. *Angew. Chem. Int. Ed.* **2012**, 51, 4209)

In the present work, we developed a facile approach to metal-free BCN graphene of tunable B/N co-doping levels (Figure 3) as efficient ORR electrocatalysts simply by thermal annealing GO in the presence of boric acid and ammonia. The resultant metal-free BCN-graphene samples were demonstrated to show ORR electrocatalytic activities even better than the commercial Pt/C electrocatalyst (C2-20, 20% platinum on Vulcan XC-72R; E-TEK). In a good consistence with the experimental observation, the First-Principle Calculations revealed a doping-level dependent energy bandgap, spin density and charge density. BCN-graphene with a modest N- and B-doping level was demonstrated to show the best ORR electrocatalytic activity, fuel selectivity and long-term durability, along with an excellent thermal stability and porosity. The thermal annealing graphene oxide in the presence of boric acid under ammonia can thus provide simple, but efficient and versatile, approaches to low-cost mass production of BCN graphene as efficient metal-free ORR electrocatalysts for fuel cell and many other applications (*e.g.*, metal-air batteries).

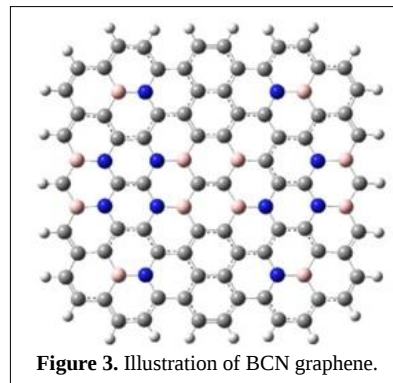


Figure 3. Illustration of BCN graphene.

- 5) “Edge-carboxylated Graphene Nanosheets via Ball Milling” (Jeon, I.-Y.; Shin, Y.-R.; Sohn, G.-J.; Choi, H.-J.; Bae, S.-Y.; Mahmood, J.; Jung, S.-M.; Seo, J.-M.; Kima, M.-J.; Chang, D. W.; Dai, L.; Baek, J.-B. *PNAS* **2012**, 109, 5588)

Low-cost, high-yield production of graphene nanosheets (GNs) is essential for practical applications. We have achieved high yield of edge-selectively carboxylated graphite (ECG) by a simple ball milling of pristine graphite in the presence of dry ice (Figure 4). The resultant ECG is highly dispersible in various solvents to self-exfoliate into single- and few-layer (≤ 5 layers) GNs. These stable ECG (or GN) dispersions have been used for solution processing, coupled with thermal decarboxylation, to produce large-area GN films for many potential applications, ranging from electronic materials to electrochemical catalysts for oxygen reduction reaction in fuel cells. The electrical conductivity of a thermally decarboxylated ECG film was found to be as high as 1214 S/cm, which is superior to its GO counterparts. Ball milling can thus provide simple, but efficient and versatile, and eco-friendly (CO_2 -capturing) approaches to low-cost mass production of high-quality GNs for applications where GOs have been exploited and beyond.

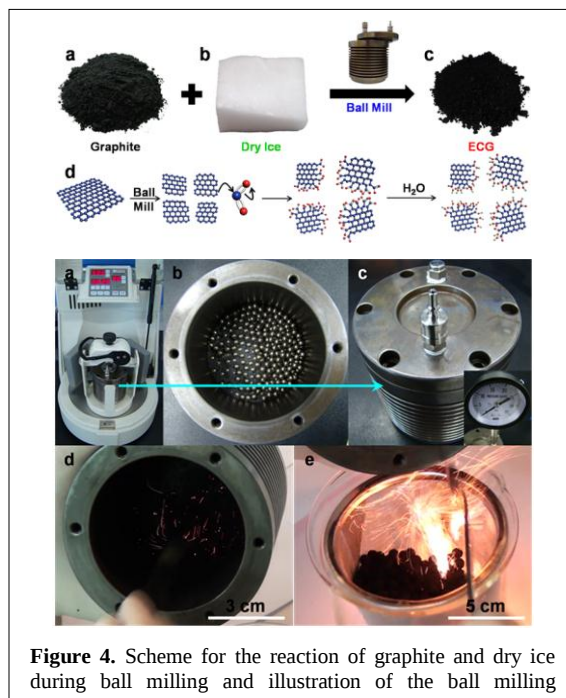
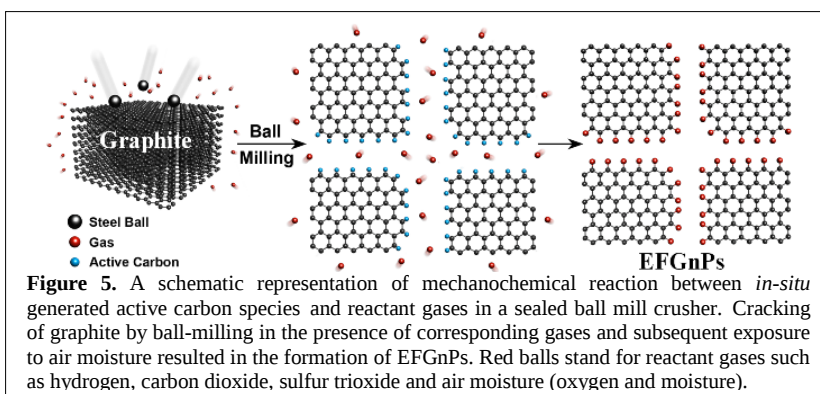


Figure 4. Scheme for the reaction of graphite and dry ice during ball milling and illustration of the ball milling

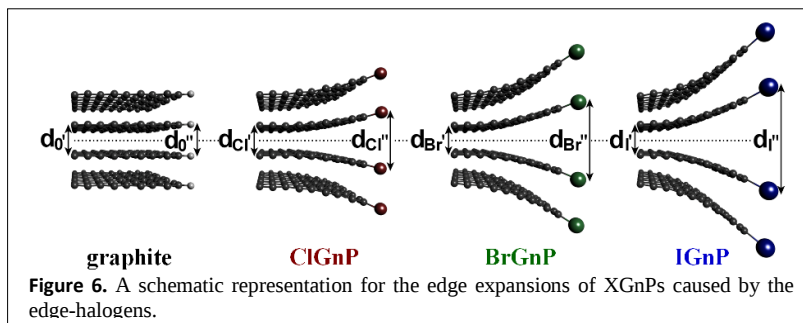
- 6) “Large-scale Production of Edge-selectively Functionalized Graphene Nanoplatelets via Ball-milling and Their Use as Metal-free Electrocatalysts for Oxygen Reduction Reaction” (Jeon, I.-Y.; Choi, H.-J.; Dai, L.; Baek, J.-B. *JACS* **2013**, 135, 1386).

Edge-selectively functionalized graphene nanoplatlets (EFGnPs) with different functional groups were efficiently prepared simply by dry ball-milling graphite in the presence of hydrogen, carbon dioxide, sulfur trioxide, or carbon dioxide/sulfur trioxide mixture (Figure 5). Upon exposure to air moisture, the resultant hydrogen-(HGnP), carboxylic acid-(CGnP), sulfonic acid-(SGnP), and carboxylic acid/sulfonic acid-(CSGnP) functionalized GnPs readily dispersed into various polar solvents, including neutral water. The resultant EFGnPs were then used as electrocatalysts for oxygen reduction reaction (ORR) in an alkaline electrolyte. It was found that the edge polar nature of the newly-prepared EFGnPs without heteroatom doping into their basal plane played an important role in regulating the ORR efficiency with the electrocatalytic activity in the order of SGnP > CSGnP > CGnP > HGnP > pristine graphite. More importantly, the sulfur-containing SGnP and CSGnP were demonstrated to show superior ORR performance to commercially available platinum-based electrocatalyst (Pt/C).



- 7) “Facile, Scalable Production of Edge-halogenated Graphene Nanoplatelets as Efficient Metal-free Electrocatalysts for The Oxygen Reduction Reaction” (Jeon, I.-Y.; Choi, H.-J.; Choi, M.; Seo, J.-M.; Jung, S.-M.; Kim, M.J.; Zhang, S.; Zhang, L.; Xia, Z.; Dai, L.; Park, N.; Baek, J.-B. *Scientific Reports* **2013**, *3*, 1810).

A series of edge-selectively halogenated (X = Cl, Br, I) graphene nanoplatelets (XGnPs = ClGnP, BrGnP, IGnP) were prepared simply by ball-milling graphite in the presence of Cl_2 , Br_2 and I_2 , respectively. High BET surface areas of 471, 579 and 662 m^2/g for ClGnP, BrGnP and IGnP, respectively, have been observed, indicating a significant extent of delamination during the ball-milling and subsequent workup processes. The newly-developed XGnPs can be dispersed well in various solvents, and hence are solution processable.

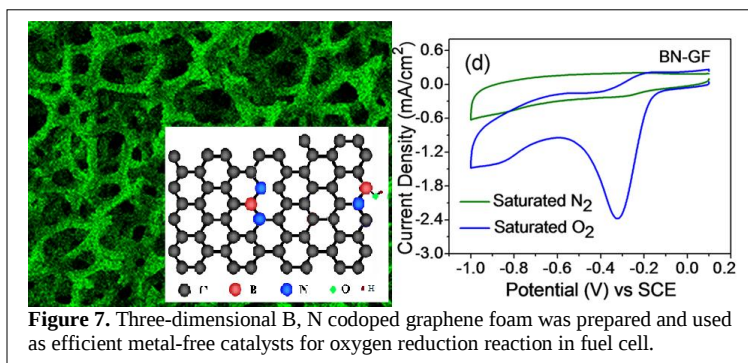


Furthermore, XGnPs showed remarkable electrocatalytic activities toward oxygen reduction reaction (ORR) with a high selectivity, good tolerance to methanol crossover/CO poisoning effects, and excellent long-term cycle stability. First-principle density-functional calculations

revealed that specific types of halogenated graphene edges provided decent adsorption sites for oxygen molecules. The tendency of the calculated adsorption strength and the charge transfer is in good correlation with the experimental observations.

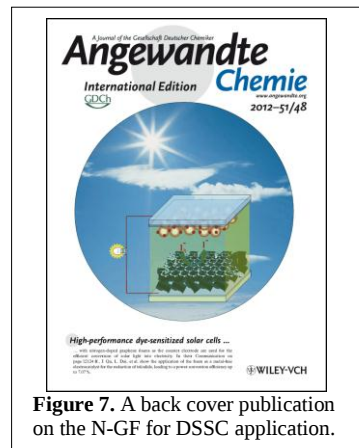
8) “Three-dimensional B, N-doped Graphene Foam as Aetal-free Catalysts for Oxygen Reduction Reaction” (Xue, Y.; Yu, D.; Dai, L.; Wang, R.; Li, D.; Roy, A.; Lu, F.; Chen, H.; Liu, Y.; Qu, J. *Phys. Chem. Chem. Phys.* **2013**, DOI: 10.1039/C3CP51942B)

Using a modified chemical vapor deposition (CVD) method, we have prepared a class of new graphene foams (GFs) doped with nitrogen, boron or both. Nitrogen-doped graphene foams (N-GFs) with a nitrogen doping level of 3.1 atom% were prepared by CVD of CH₄ in the presence of NH₃ while boron-doped graphene foams (B-GFs) with a boron doping level of 2.1 atom% were produced by using toluene and triethyl borate as carbon and boron source. On the other hand, graphene foams co-doped with nitrogen (4.5 atom%) and boron (3 atom%) (BN-GFs) were prepared by CVD using melamine diborate as the precursor (Figure 7). In all cases, scanning electron microscope (SEM) images revealed well-defined foam-like microstructures, while electrochemical measurements showed much higher electrocatalytic activities toward oxygen reduction reaction for the doped graphene foams than their undoped counterparts.



9) “Nitrogen-Doped Graphene Foams as Metal-free Counter Electrodes in High-Performance DSSCs” (Xue, Y.; Liu, J.; Chen, H.; Wang, R.; Li, D.; Qu, J.; Dai, L. *Angew. Chem. Int. Ed.* **2012**, 51, 4209)

Owing to its low cost, easy fabrication, and high energy conversion efficiency, dye sensitized solar cells (DSSCs) have attracted much attention since Oregan and Grätzel’s seminal report in 1991. A typical DSSC device consists of a dye-adsorbed TiO₂ photoanode, counter electrode, and iodide electrolyte. The counter (cathode) electrode plays a key role in regulating the DSSC device performance by catalyzing the reduction of the iodide-triiodide redox species used as a mediator to regenerate the sensitizer after electron injection. Because of its excellent electrocatalytic activity for the iodine reduction, high conductivity and good chemical stability, platinum has been widely used as a counter electrode in DSSCs. However, the high cost of Pt and its limited reserves in nature have been a major concern for the energy community. Recently, much effort has been made to reduce or replace Pt-based electrode in DSSCs. In particular, carbon black, carbon nanoparticles, carbon nanotubes, and graphene nanosheets have been studied as the counter electrode in DSSCs. However, their electrical conductivities and



reduction catalytic activities still cannot match up to those of platinum. In the present study, we have, for the first time, prepared the N-doped 3D graphene foam (N-GF) and demonstrated its use as the metal-free electrocatalyst for triiodide reduction to replace the Pt cathode in DSSCs, leading to a power conversion efficiency up to 7.07%. This value of efficiency is among the highest efficiencies reported for DSSCs with carbon-based metal-free counter electrodes, comparable to that of a DSSC with a Pt counter electrode constructed under the same condition. Our results indicate that further electrode/device optimization will lead to DSSCs based on the N-GF counter electrode even outperforming their counterparts with a Pt counter electrode. This work indicates that N-doped graphene, in particular, and N-doped carbon nanomaterials, in general, can be used as effective metal-free counter electrodes to replace Pt in high-performance DSSCs.

10) Other Significant Results

Our research has been highlighted by numerous (hundreds) scientific, business, and popular press, including *SinceDaily*, *UPI*, and *Reuters* (See, for example: <http://jbbaek.unist.ac.kr/index.sko>; <http://case.edu/cse/eche/daigroup/index.html>).

List of Publications and Significant Collaborations that resulted from your AOARD supported project (from UNIST and/or CWRU)

a) Papers Published in Peer-reviewed Journals

1. Chang, D. W.; Lee, E. K.; Park, E. Y.; Yu, H.; Choi, H.-J.; Son, G.-J. Shin, D.; Park, N.; Oh, J. H.; Dai, L.; Baek, J.-B. "Nitrogen-doped graphene nanoplatelets from simple wet-chemical reactions and their use as n-type field-effect transistors" *Journal of the American Chemical Society* **2013**, *135*, 8981-8988.
2. Jeon, I.-Y.; Choi, H.-J.; Zhang, S.; Zhang, L.; Xia, Z.; Dai, L.; Baek, J.-B. "Facile, scalable production of edge-halogenated graphene nanoplatelets as efficient metal-free electrocatalysts for the oxygen reduction reaction" *Scientific Reports* **2013**, *3*, 1810-**Highlighted in Science Daily, Cover Story in Ulsan Jeil Daily, Graphene Times.com and more than Fourty Global News Hits.**
3. Jeon, I.-Y.; Choi, H.-J.; Dai, L.; Baek, J.-B. "Large-scale production of edge-selectively functionalized graphene nanoplatelets via ball-milling and their use as metal-free electrocatalysts for oxygen reduction reaction" *Journal of the American Chemical Society* **2013**, *135*, 1386-1393-**Highlighted in Science Daily, Chosun Daily, Dong-A Daily, Graphene Times.com and more than Twenty Global News Hits.**
4. Dai, L. "Functionalization of graphene for efficient energy conversion and storage" *Acc. Chem. Res.* **2013**, *46*, 31-42.
5. Xue, Y.; Yu, D.; Dai, L.; Wang, R.; Li, D.; Roy, A.; Lu, F.; Chen, H.; Liu, Y.; Qu, J. "Three-dimensional B, N-doped graphene foam as metal-free catalysts for oxygen reduction reaction" *Phys. Chem. Chem. Phys.* **2013**, DOI: 10.1039/C3CP51942B.
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c) Interactions with Air Force Research Laboratory Scientists

Our existing collaborations with Air Force Research Laboratory scientists, including Mike Durstock and Ajit Roy, have been greatly enhanced by the strong interactions with them that resulted from this work.

DD882: As a separate document, please complete and sign the inventions disclosure form.

No invention disclosure.