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(54) Title: GRAPHENE - Co/CoO NANOPARTICLE COMPOSITE, MANUFACTURE, AND USE IN AN ELECTROCHEMICAL CELL

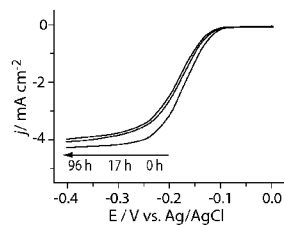


Fig. 4A

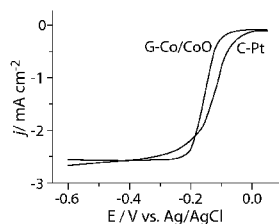


Fig. 4B

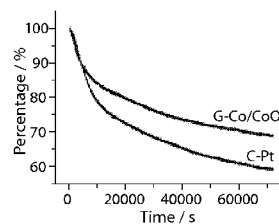


Fig. 4C

(57) Abstract: The synthesis and self-assembly of core/shell Co/CoO nanoparticles (NPs) onto the surface of graphene (G) as a catalyst for electrocatalytic reduction of oxygen in alkaline media. The Co NPs are first synthesized and then oxidized in a controlled environment to add a Cobalt oxide shell, forming core/shell Co/CoO NPs with shell thickness tunable from 1-3 nm. Compared to G, and to carbon supported Co/CoO (C-Co/CoO) NPs, the G-Co/CoO NPs show enhanced catalytic activity in O<sub>2</sub>-saturated 0.1 M KOH solution. Fabrication of monodisperse ten nm particles with a 1 nm thick oxide shell on graphene exhibited activity comparable to, and stability better than, a commercial C-Pt NP catalyst. The nanoparticle composite is thus a promising candidate for high performance inexpensive fuel cells and batteries using an oxygen reduction reaction in alkaline solutions.



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**Graphene - Co/CoO Nanoparticle Composite, Manufacture,  
and Use in an Electrochemical Cell**

Field of the Invention

5           This invention relates to nanoparticle (NP) materials for electrocatalytic reduction of oxygen, to the use of the materials in an electrochemical cell, battery or the like, and to methods of making the NP materials.

Background of the Invention

10           The oxygen reduction reaction of O<sub>2</sub> (ORR) at or near ambient temperatures is an important cathodic reaction in the operation of polymer membrane electrolyte fuel cells (PEMFCs) and metal-air batteries MABs). Y. Bing, H. Liu, L. Zhang, D. Ghosh, J. Zhang, *Chem. Soc. Rev.* 2010, 39, 2184-2202. Platinum (Pt) has generally been considered the best metal for catalyzing ORR. However, platinum is costly, and in corrosive PEMFC and MAB reaction conditions, Pt-based catalysts tend to have very limited durability. See, for example, 15 Z. Peng, H. Yang, *J. Am. Chem. Soc.* 2009, 131, 7542-7543; M.-H. Shao, K. Sasaki, R. R. Adzic, *J. Am. Chem. Soc.* 2006, 128, 3526-3527; V. R. Stamenkovic, B. Fowler, B. S. Mun, G. J. Wang, P. N. Ross, C. A. Lucas, N. M. Markovic, *Science* 2007, 315, 493-497; S. Guo, E. Wang, *Nano Today* 2011, 6, 240-264; and G. Wu, K. L. More, C. M. Johnston, P. Zelenay, *Science* 2011, 332, 443-447. In searching for more robust and practical catalysts with 20 comparable or even better catalytic performance than Pt, early transition metals supported on graphene (G) have been considered. G is typically a single-layer, two-dimensional honeycomb-type carbon sheet that has large surface area, excellent conductivity and good chemical stability. S. Guo, S. Dong, *Chem. Soc. Rev.* 2011, 40, 2644-2672; S. Guo, S. Dong, E. Wang, *ACS Nano* 2010, 4, 547-555; and S. Guo, D. Wen, S. Dong, E. Wang, *ACS Nano* 25 2010, 4, 3959-3968.

          Graphene has been explored either as a non-metal catalyst through molecular engineering (see Y. Li, Y. Zhao, H. Cheng, Y. Hu, G. Shi, L. Dai, L. Qu, *J. Am. Chem. Soc.* 2012, 134, 15-18; L. Qu, Y. Liu, J.-B. Baek, L. Dai, *ACS Nano* 2010, 4, 1321-1326; Z.-H. Sheng, L. Shao, J.-J. Chen, W.-J. Bao, F.-B. Wang, X.-H. Xia, *ACS Nano* 2011, 5, 4350- 30 4358; Z. Yao, H. Nie, Z. Yang, X. Zhou, Z. Liu, S. Huang, *Chem. Commun.* 2012, 48, 1027-1029; and Y. Li, W. Zhou, H. Wang, L. Xie, Y. Liang, F. Wei, J.-C. Idrobo, S. J. Pennycook, H. Dai, *Nat. Nanotech.* 2012, 7, 394-400). Graphene has also been explored as a unique support for metal catalysts. See Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nat. Mater.* 2011, 10, 780-786; Z.-S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K.

Müllen, *J. Am. Chem. Soc.* 2012, 134, 9082-9085; H. Wang, Y. Liang, Y. Li, H. Dai, *Angew. Chem. Int. Ed.* 2011, 50, 10969-10972; and Y. Liang, H. Wang, J. Zhou, Y. Li, J. Wang, T. Z. Regier, H. Dai, *J. Am. Chem. Soc.* 2012, 134, 3517-3523.

Studies on G-metal interactions have reported that, depending on G-metal spacing and Fermi level difference between G and the metal, a charge transfer across the G-metal interface may arise. S. Guo, S. Sun, *J. Am. Chem. Soc.* 2012, 134, 2492-2495. Without being bound by any particular theory, it is believed that charge transfer contributes to the enhanced catalysis displayed by certain NPs when supported on a G surface, as demonstrated variously in the catalysts of G-Co<sub>3</sub>O<sub>4</sub> (Y. Li, W. Zhou, H. Wang, L. Xie, Y. Liang, F. Wei, J.-C. Idrobo, S. J. Pennycook, H. Dai, *Nat. Nanotech.* 2012, 7, 394-400); of G-Fe<sub>3</sub>O<sub>4</sub>, (Z.S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K. Müllen, *J. Am. Chem. Soc.* 2012, 134, 9082-9085); of G-Co<sub>x</sub>S<sub>1-x</sub> (H. Wang, Y. Liang, Y. Li, H. Dai, *Angew. Chem. Int. Ed.* 2011, 50, 10969-10972); and of G-MnCo<sub>2</sub>O<sub>4</sub> (Y. Liang, H. Wang, J. Zhou, Y. Li, J. Wang, T. Z. Regier, H. Dai, *J. Am. Chem. Soc.* 2012, 134, 3517-3523, for ORR in alkaline media (G-Co<sub>3</sub>O<sub>4</sub>, G-Fe<sub>3</sub>O<sub>4</sub>, and G-MnCo<sub>2</sub>O<sub>4</sub>), or in acid media (G-Co<sub>x</sub>S<sub>1-x</sub>).

In these described G-metal oxide catalyst systems, metal oxide NPs were deposited directly onto G *via in-situ* chemical deposition processes. However, despite the fact that the depositions led to tight G-NP contact, NPs prepared from these methods generally lacked a desired degree of control over size and morphology, making it difficult to tune the G-NP interaction to enhance catalytic performance.

#### Summary of the Invention

Applicants have now achieved synthesis and self-assembly of core/shell Co/CoO NPs onto the surface of graphene (G) to form an effective catalyst for electrocatalytic reduction of oxygen in alkaline media. The Co NPs are first synthesized and then partially oxidized in a controlled environment to form a monodisperse distribution of Co/CoO NPs having a core/shell structure, with CoO shell thickness tuneable from about 1 to about 3 nm. The NPs are then deposited on graphene to form the G-CoCoO composite. Compared to G, and compared to carbon-supported Co/CoO NPs (C-Co/CoO NPs), the G-Co/CoO NPs show much enhanced catalytic activity for oxygen reduction reaction in O<sub>2</sub>-saturated 0.1 M KOH solution. G acts as the support, and varying the core/shell dimensions of the Co/CoO NPs tunes electrocatalysis for efficient oxygen reduction reaction. The G-Co/CoO NPs having a 1 nm thick CoO shell showed the greatest activity. The G-Co/CoO NPs thus produced were found to have activity comparable to, and stability better than, the commercially available C-Pt catalyst (HP 20% Platinum on Vulcan XC-72; 20% loading, diameter of 2.5-3.5 nm,

available from Fuel Cell Store, Phoenix, Arizona, SKU 591278). The G-Co/CoO NPs thus offer a lower-cost alternative to use of a Pt catalyst for oxygen reduction reactions in alkaline solutions.

To make the G-Co/CoO NPs, applicants developed a self-assembly process to deposit  
5 monodisperse Co/CoO NPs on a G surface. The resulting G-Co/CoO catalytic material is a high-performance electrocatalyst for ORR in 0.1 M KOH solution, reducing O<sub>2</sub> to OH<sup>-</sup> in a reaction predominately following a four -electron process. Without being bound by any particular theory it is believed that high catalytic performance results from a combination of the graphene-NP interaction, and from the controlled and improved dimensional tuning of the  
10 respective metal and metal oxide portions of the nanoparticles. As tested, an optimized G-Co/CoO NP catalyst with 8 nm diameter Co core and 1 nm thick CoO shell outperformed the commercial Pt NP catalyst supported on carbon (C-Pt) in ORR current density near the diffusion-limit current region, and also provided better stability.

An embodiment of the invention includes a carbon-supported metal/metal oxide NP  
15 composite, wherein the metal/metal oxide NPs have a structure tuned for enhanced catalysis of O<sub>2</sub> reduction.

In an embodiment of the invention, the carbon is graphene and the graphene - supported metal/metal oxide NPs comprise monodisperse Co/CoO NPs which are affixed to the graphene, having particle size and an oxide layer thickness for enhanced catalysis of O<sub>2</sub>  
20 reduction.

An embodiment of the invention includes graphene-supported surface-oxidized cobalt nanoparticles forming a composite G-NP catalyst that is stable in basic media and catalyzes reduction of O<sub>2</sub> to OH<sup>-</sup> in a basic medium predominantly via a direct four-electron process.

An embodiment of the method for forming an oxygen reducing composite catalyst  
25 comprising metal/metal oxide on graphene, comprises the steps of (i) combining a dispersion of as-prepared substantially monodisperse cobalt NPs in an alkane fluid, and a DMF solution containing graphene at room temperature; (ii) sonicating the combined solutions; (iii) precipitating the product; (iv) dispersing the product in butylamine and stirring at ambient temperature; (v) separating the resulting metal NP on graphene catalyst by centrifuging; and  
30 (vi) forming an oxide on the NPs in air at a designated temperature and a time period to form a graphene Co/CoO NP composite having high ORR activity and stability in alkaline media.

An embodiment of the method of using the graphene-Co/CoO composite catalyst of this invention includes positioning the composite catalyst to reduce oxygen in an electrochemical cell containing O<sub>2</sub> in an alkaline solution for producing electric charge.

In another embodiment of the invention the metal/metal oxide NPs employ two metals, and are  $\text{MnFe}_2\text{O}_3$  NPs; these may be supported on Ketjen carbon, carbon nanotubes, or graphene surfaces.

#### Brief Description of the Drawings

5 Fig. 1 shows TEM images of Co NPs (Fig. 1A), Co/CoO core/shell NPs (Fig. 1B), Co/CoO NPs treated for 17 h (Fig. 1C) and 96 h (Fig. 1D) in air, and the Co/CoO core/shell NPs deposited on G surface (Fig. 1E).

Fig. 2 shows a room temperature hysteresis loops of Co NPs (trace A), Co/CoO core/shell NPs (trace B), Co/CoO core/shell NPs heated at 70 °C in the air for 17 h (trace C) and 96 h (trace D), and hollow CoO NPs (trace E).

Fig. 3 Panels A, B: show cyclic voltammograms (CVs) (Panel A) and ORR polarization curves (Panel B) of G (i), C-Co/CoO (ii), and G-Co/CoO (iii) - modified glassy carbon (GC) electrodes. Panel A: scan rate: 50 mV/s; Panel B: scan rate: 10 mV/s and rotation rate: 1600 rpm. Panels C, E: ORR polarization curves of the G-Co/CoO (Panel C) and C-Co/CoO (Panel E) at different rotation rates. Panels D, F: K-L plots of ORR from the G-Co/CoO (Panel D) and C-Co/CoO (Panel F). The measurements were performed in  $\text{O}_2$ -saturated 0.1 M KOH solution.

Fig. 4 shows ORR polarization curves of G-Co/CoO NPs heated at 70 °C in air for 0 h, 17 h and 96 h (Fig. 4A); ORR polarization curves of the G-Co/CoO NPs and commercial C-Pt catalyst (Fig. 4B) using a scan rate of 10 mV/s in A and B, and rotation rates of 1600 rpm in A and 400 rpm in B; and chronoamperometric responses for ORR on G-Co/CoO NPs and commercial C-Pt at -0.3 V. Rotation rate: 200 rpm (Fig. 4C). The measurements were performed in  $\text{O}_2$ -saturated 0.1 M KOH solution.

Fig. 5 shows a TEM image of Co/CoO core/shell NPs stored under air for 5 days.

25 Fig. 6 shows a TEM image of Co/CoO core/shell NPs stored under air for 9 days.

Fig. 7 shows TEM images (Fig. 7A) and high-resolution TEM (HRTEM) images (Fig. 7B) of hollow CoO NPs. The spacing of the adjacent fringes is 0.246 nm, corresponding to the {111} interplanar distance of face centered cubic (fcc) CoO.

Fig. 8 shows XRD patterns of Co NPs and hollow CoO NPs. Note that the thin CoO coating on the Co NPs cannot be detected under the current XRD analysis condition.

Fig. 9 shows ORR polarization curves of C-Co/CoO NPs.

Fig. 10 shows EDX spectra of Co/CoO NPs after washing in ethanol (Fig. 10 Panel A) and in butylamine (Fig. 10 Panel BB).

Fig. 11 Panel A shows ORR polarization curves at various rotation rates and Fig 11

Panel B shows K-L plots on G-Co/CoO NPs, treated at 70 °C in air for 17 h. The measurements were performed in O<sub>2</sub>-saturated 0.1 M KOH solution.

Fig. 12 Panel A shows ORR polarization curves at various rotation rates, and Fig. 12 Panel B shows K-L plots on G-Co/CoO NPs, treated at 70 °C in air for 96 h (measurements  
5 were performed in O<sub>2</sub>-saturated 0.1 M KOH solution).

Fig. 13 shows chronoamperometric responses of the G-Co/CoO NPs and C-Co/CoO NPs in O<sub>2</sub>-saturated 0.1 M KOH solution at -0.3 V (electrode rotation rate: 200 rpm).

#### Detailed Description of the Invention

This disclosure will be better understood with reference to the description below of  
10 the manufacture and characterization of certain NP-based catalysts for Oxygen Reduction Reaction (ORR), and discussion of related technology. A principal property of the invention is the achievement of high catalytic performance. Operating characteristics are compared to a benchmark of certain conventional platinum-based catalytic NPs commercially available for O<sub>2</sub>-reducing applications, such as in the construction of electrochemical fuel cells. A relevant  
15 measure of catalytic performance of conventional platinum-based NP oxygen reduction electrocatalysts has sometimes been phrased in terms of platinum mass activity, in milliamperes/microgram of Pt at 0.90 V. That definition, based on the amount of platinum used, is a cost-sensitive measure motivated by the high cost of platinum; it ranks metal-substituted platinum NPs better if the inclusion of the other non-Pt metals doesn't reduce the catalytic  
20 activity. However more generally, and in the description below, the term high catalytic performance shall mean, activity comparable to that of the reported benchmark Pt-based NP catalysts or an accepted numerical performance measure. High catalytic performance can also be understood as high activity as measured by conventional measures of catalytic oxygen-reducing activity.

25 Similarly, the term stability shall refer to relative constancy, or lack of degradation, of electrocatalytic characteristics of the material over a protracted operating interval in a reported environment, which is, for example, the basic medium of a oxygen-reducing fuel cell. A test interval of suitable duration for detecting such changes may be about fifteen or twenty hours, and the percentage change in relevant characteristics is advantageous compared  
30 to that of the commercial platinum-based NP catalysts. The properties of high catalytic activity and stability thus indicate that the subject materials are suitable for constructing a battery or electrochemical cell having excellent efficiency and stable performance under a stated operating environment and suitable duty cycles.

As defined in greater particularity below, certain preferred metal/metal oxide NP composites are formed of metal/oxide NPs on a conductive support, wherein the NPs have a particular NP structure, and/or have substantially uniform size and are of a particular diameter and thus are “tuned” to achieve high catalytic performance or stability. The  
5 conductive support may be a graphene support. The dimensional and conductive characteristics of the graphene support are believed to contribute to enhanced stability and/or catalytic activity. The diameter of individual particles and the relative core and oxide shell dimensions of Co/CoO NPs can be imaged with TEM, and one may also monitor NP size or size distribution of the bulk product of a reaction process, e.g., to adjust the parameters such  
10 as time, temperature and medium concentrations in various NP fabrication process steps; for example, relevant measurements may be performed employing dynamic light scattering and signal processing transformations with an analysis instrument intended for measurement of particle size and other particle characteristics, such as SZ-100 Nanoparticle Analyzer sold by Horiba Scientific.

15 The preferred Co/CoO NPs of this invention for deposition on a graphene support are monodisperse, i.e., formed with a narrow size distribution of  $\pm 10\%$ , with an oxide shell of thickness between 1 and 3 nm. In one embodiment the metallic cobalt core of these particles has a diameter of about 8 nm, surrounded by a cobalt oxide shell having a thickness of about 1 nm.

#### 20 EXAMPLES and MEASUREMENT of CATALYST CHARACTERISTICS

Graphene production: In one embodiment, G was produced by heating graphene oxide (GO) dimethyl formamide (DMF) solution at 150 °C for 6 h. In a specific embodiment, a mixture containing 100 mL of DMF dispersion of GO (1 mg/mL) and 4 mL ammonium hydroxide (25% wt.) was heated and the solution was refluxed for 6 h and cooled down to  
25 room temperature to convert GO to G, as described in S. Guo, S. Sun, *J. Am. Chem. Soc.* 2012, 134, 2492-2495.

Production of Cobalt NPs: Co NPs were synthesized by thermal decomposition of Dicobalt octocarbonyl  $\text{Co}_2(\text{CO})_8$  in solution in 1,2,3,4-tetrahydronaphthalene in the presence  
of  
30 oleic acid and dioctylamine as described in S. Peng, J. Xie, S. Sun, *J. Solid State Chem.* 2008, 181, 1560-1564.

In one embodiment, 10 nm Co NPs were synthesized as follows:

(i) A mixture containing 0.35 mL of oleic acid (OA), 0.5 mL of dioctylamine (DOA) and 18 mL of 1,2,3,4-tetrahydrophthalene was heated at 110 °C for 0.5 h under nitrogen protection and then cooled down to room temperature.

(ii) 0.54 g of  $\text{Co}_2(\text{CO})_8$  was quickly added into the above solution and the mixture was re-heated to 100 °C for 30 min, followed by rapidly heating to 208 °C for 30 min at the heating rate of 15 °C/min under nitrogen protection.

(iii) After being cooled to about room temperature ( $\approx 20$  °C), the obtained Co NPs were precipitated by adding 60 mL of ethanol.

(iv) The product was separated by centrifugation at 9000 rpm for 10 min. The Co NPs were dispersed in hexane before use.

In these embodiments, materials were as follows: Dicobalt octacarbonyl ( $\text{Co}_2(\text{CO})_8$ , stabilized with 1-10% hexane), 1-octadecene ODE (90%), oleylamine (OAm, >70%), dimethylformamide (DMF, 99.9%), trimethylamine N-oxide ( $\text{Me}_3\text{NO}$ , 98%), butylamine (99%), dioctylamine (DOA, 98%), 1,2,3,4-tetrahydronaphthalene (99%), oleic acid (OA, technical grade, 90%), hexane (98.5%), ethanol (100%) and Nafion (5% in a mixture of lower aliphatic alcohols and water), all purchased from Aldrich. The C-Pt (20% mass loading, 2.5-3.5 nm Pt NPs catalyst was obtained from Fuel Cell Store.

Materials were prepared and a range of catalytic NP preparations made as follows for experimental characterization. Synthesis of G-Co/CoO and C-Co/CoO: 60 mg of Co NPs (synthesized as described above) dispersed in 60 mL of hexane was added into 60 mL of DMF solution of G (1 mg/mL) under sonication and the mixture was further sonicated for 1 h. Similarly, 60 mg of Co NPs was also deposited on 60 mg of Ketjen carbon via sonication to make C-Co/CoO NPs as described in V. Mazumder, S. Sun, *J. Am. Chem. Soc.* 2009, 131, 4588-4589; and S. Guo, S. Zhang, X. Sun, S. Sun, *J. Am. Chem. Soc.* 2011, 133, 15354-15357. After 120 mL of ethanol was added, the precipitate was separated from the solvents by centrifuging for 10 min at 9500 rpm. The as-obtained NP catalyst was dispersed in 60 mL butylamine through sonication, and further stirred for 3 days at ambient temperature. Wu et al. *J. Am Chem Soc.* 2010, *supra*. After 60 mL of ethanol was further added into the above butylamine solution, the catalyst was centrifuged at 9000 rpm for 10 min. After that, the catalyst was further dried and divided into several parts. Two parts of catalysts were heated at 70 °C in air for 17 h and 96 h in order to get G-Co/CoO core/shell NPs with different shell thickness.

Catalyst Preparation and Deposition on the Working Electrode: The NP catalyst was re-dispersed in a mixture of solvents containing water, isopropanol and Nafion (5%) (v/v/v = 4/1/0.025) to form a 2 mg/mL suspension. The GC working electrode was first polished with 1.0 and 0.05  $\mu\text{m}$  alumina powder, rinsed with deionized water, and sonicated first in ethanol  
5 and then in double-distilled water. 10  $\mu\text{L}$  of the catalyst ink was cast on the electrode and dried at ambient condition. CVs of different catalysts were carried out in a 0.1 M KOH solution at a scan rate of 50 mV/s. The RDE measurements of different catalysts were conducted in  $\text{O}_2$ -saturated 0.1 M KOH solution at the scan rate of 10 mV/s and different rotation rates.

10 TEM images were acquired on a Philips CM 20 EM microscope operating at 200 kV. X-ray diffraction (XRD) characterization was carried out on a Bruker AXS D8-Advanced diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). HRTEM image was obtained on a JEOL 2010 with an accelerating voltage of 200 kV. The electrochemical measurements were performed on a potentiostat (Autolab 302) with Ag/AgCl (vs. 4 M KCl) as a reference  
15 electrode and Pt wire as a counter electrode.

The Co-based NPs and G-Co/CoO NPs were characterized by transmission electron microscopy (TEM). Fig. 1A shows the typical TEM images of the as-prepared Co NPs. They are monodisperse 10 nm NPs with a narrow size distribution at  $\pm 0.7 \text{ nm}$ . When exposed to air at ambient condition, the top surface layers of Co were oxidized, forming Co/CoO  
20 core/shell NPs. TEM analysis revealed that this CoO shell reached  $\sim 1 \text{ nm}$  thick (Fig. 1B and Fig. 5) and had no more thickness increase in 9 days of continuous air exposure (Fig. 6). While not being bound by any particular theory, it is believed that this indicates that CoO shell was able to protect Co from further oxidation in air at room temperature. However, at higher temperatures, Co in the Co/CoO NPs was further oxidized when the NPs were heated  
25 at 70  $^\circ\text{C}$  in air. Fig. 1C and Fig. 1D show the TEM images of the Co/CoO NPs heated at 70  $^\circ\text{C}$  for 17 and 96 hours, respectively. After 17 hours heating in air, the CoO layer grew to about 3 nm, while 96 hours of heating led to higher-degree oxidation of Co, resulting in a NP mixture of Co/CoO and hollow CoO NPs.

When Co NPs were oxidized by excess of trimethylamine N-oxide ( $\text{Me}_3\text{NO}$ ) at  
30 230  $^\circ\text{C}$ , hollow CoO NPs were obtained, as shown in Fig. 7. Here the hollow CoO NPs are formed via the nanoscale Kirkendall effect, which causes faster Co diffusion outward than oxygen diffusion inward in the structure. See, S. Peng, S. Sun, *Angew. Chem. Int. Ed.* 2007, 46, 4155-4158; Y. Yin, R. M. Rioux, C. K. Erdonmez, S. Hughes, G. A. Somorjai, A. P. Alivisatos, *Science* 2004, 304, 711-714.

The Cobalt-based NPs were assembled onto Graphene G by mixing the hexane dispersion of the NPs with DMF solution of G under sonication as explained further below. Fig. 1E shows a TEM image of the Co/CoO NPs assembled on G. Similarly, the Co/CoO NPs were also deposited on Ketjen carbon (C) (C-Co/CoO). These C-Co/CoO NPs were used  
5 as a control to compare with G-Co/CoO NPs in the ORR studies.

X-ray diffraction (XRD) analyses indicate that the as-synthesized Co NPs have a multi-twinned face-centered cubic (fcc) structure with the (111) peak appearing at 44.3 °C (Fig. 8). This is similar to what has been reported for Co NPs obtained from thermal decomposition of  $\text{Co}_2(\text{CO})_8$ . Peng et al. 2008, supra. After Co NPs were transformed into  
10 hollow CoO NPs, new diffraction peaks at 36.7, 42.7 and 62.1 °C, which belong to (111), (200) and (220) diffractions of the fcc CoO, were observed (Fig. 8).

The Co/CoO NPs show typical Co and CoO dimension-dependent magnetization behaviour, as shown in the room temperature hysteresis loops of a series of Co/CoO NPs measured by vibrating sample magnetometer (VSM) (Fig. 2). The as-synthesized Co NPs  
15 show a superparamagnetic hysteresis loop with saturation moment of 70.4 emu/g NPs (Fig. 2A). When Co NPs were exposed to air for 5 days, forming 8 nm/1 nm Co/CoO NPs, their moment was reduced to 40.4 emu/g NPs (Fig. 2B). Once further heated at 70 °C in air for 17 h and 96 h, the resultant Co/CoO NPs had their saturation moment reduced from 40.4 emu/g NPs to 24.2 and 16.2 emu/g NPs (Fig. 2C&D). When the Co NPs were completely oxidized,  
20 the hollow CoO NPs were paramagnetic (Fig. 2E). Without being bound by any specific theory it is believed that the moment reduction and magnetic property change was caused by the higher degree of Co oxidation in the Co/CoO structure.

The as-synthesized G-Co/CoO NPs and C-Co/CoO NPs were treated with butylamine, as described below, to remove the original long-chain surfactant. See J. Wu, J. Zhang, Z.  
25 Peng, S. Yang, F. T. Wagner, H. Yang, *J. Am. Chem. Soc.* 2010, 132, 4984-4985. This room-temperature treatment was useful to produce active Co/CoO catalysts.

Fig. 9 shows ORR polarization curves observed for the C-Co/CoO NPs from different treatments. After being washed with butylamine, the C-Co/CoO NPs exhibited more positive half-wave potential for ORR than those washed with ethanol under the same condition.  
30 Furthermore, energy dispersive X-ray (EDX) analysis on the Co/CoO NPs showed the reduced C/Co ratio after the butylamine treatment (Fig. 10). These indicate that butylamine washing was effective to remove oleate/DOA.

Fig. 3A shows the typical cyclic voltammograms (CVs) of oxygen reduction on the G, C-Co/CoO and G-Co/CoO modified glassy carbon (GC) electrodes in  $\text{O}_2$ -saturated 0.1 M

KOH solution with each catalyst having a mass loading of 20  $\mu\text{g}$ . On the G modified GC electrode, only a weak peak is seen at -0.360 V (vs Ag/AgCl) (Fig. 3A-i). When the C-Co/CoO is present on the electrode, the peak becomes stronger and appears at -0.276 V (Fig. 3A-ii). Compared to the G and the C-Co/CoO NPs, the G-Co/CoO NPs show a much stronger cathodic peak with the peak potential at -0.198 V (Fig. 3A-iii). These measurements are believed to indicate that  $\text{O}_2$  is reduced more easily with lower overpotentials on G-Co/CoO NPs than on G and C-Co/CoO NPs.

Rotating-disk electrode (RDE) measurements were employed to better define ORR activity and kinetics of G, C-Co/CoO NPs and G-Co/CoO NPs in the  $\text{O}_2$ -saturated 0.1 M KOH solution. Fig. 3B shows the ORR polarization curves obtained at a rotation rate of 1600 rpm. The curve from G has a slow current increase and no current plateau (Fig. 3B-i), indicating that the ORR process on G is mainly a two-electron reduction of  $\text{O}_2$  to  $\text{OOH}^-$ . See, Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith, M. Jaroniec, G. Q. Lu, S. Z. Qiao, *J. Am. Chem. Soc.* 2011, 133, 20116-20119.

In contrast, ORR polarization curves from both C-Co/CoO and G-Co/CoO NPs have a sharp increase and reach quickly to the saturation (Fig. 3B-ii-iii). The G-Co/CoO NPs show a more positive half-wave potential (-0.176 V) for ORR than the C-Co/CoO NPs (-0.290 V), indicating that G as a support has indeed a significant enhancement in Co/CoO catalysis for ORR. RDE measurements also show that the limiting current density increases with increasing rotation rate (Fig. 3C). Fig. 3D is the corresponding Koutecky-Levich (K-L) plots that demonstrate the inverse current density ( $j^{-1}$ ) as a function of the inverse of the square root of the rotation speed ( $\omega^{-1/2}$ ) at different potential values. The number of electrons involved per  $\text{O}_2$  in the ORR on G-Co/CoO NPs were determined by the Koutechy-Levich equation:

$$1/j = 1/j_k + 1/B\omega^{1/2} \quad (1)$$

where  $j_k$  is the kinetic current and  $\omega$  is the electrode rotating rate.  $B$  is determined from the slope of the K-L plots based on the Levich equation:

$$B = 0.2nF(D_{\text{O}_2})^{2/3}v^{-1/6}C_{\text{O}_2} \quad (2)$$

where  $n$  represents the number of electrons gained per  $\text{O}_2$ ,  $F$  is the Faraday constant ( $F = 96485 \text{ C mol}^{-1}$ ),  $D_{\text{O}_2}$  is the diffusion coefficient of  $\text{O}_2$  in 0.1 M KOH ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),  $v$  is the kinetic viscosity ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ), and  $C_{\text{O}_2}$  is the bulk concentration of  $\text{O}_2$  ( $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ ). See S. Wang, D. Yu, L. Dai, *J. Am. Chem. Soc.* 2011, 133, 5182-5185; S. Wang, D. Yu, L. Dai, D. W. Chang, J.-B. Baek, *ACS Nano* 2011, 5, 6202-6209; S. Wang, E. Iyyamperumal, A. Roy, Y. Xue, D. Yu, L. Dai, *Angew. Chem. Int. Ed.* 2011, 50, 11756-11760; and K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, *Science* 2009, 323, 760-764.

Fig. 3D shows three linear K-L plots at different potentials, suggesting the first-order reaction kinetics toward the concentration of  $O_2$  on G-Co/CoO NPs from -0.3 V to -0.7 V.  $n$  in eq. 2 can be calculated to be between 4.08-4.15, indicating that the ORR from -0.3 V to -0.7 V is dominated by a four electron (4e) process and  $O_2$  is reduced to  $OH^-$ . Similarly, the ORR kinetics on the C-Co/CoO NPs can be analyzed, as shown in Fig. 3E. The corresponding K-L plots (Fig. 3F) give  $n = 3.9$  at -0.5 V, revealing that the C-Co/CoO NPs still favour a 4e oxygen reduction process. Furthermore, compared to those from the C-Co/CoO NPs (Fig. 3E), the ORR polarization curves from the G-Co/CoO NPs (Fig. 3C) have steeper slopes in the kinetic region, further confirming that the G-Co/CoO NPs are more favourable for oxygen reduction than the C-Co/CoO NPs.

Considering that the Co core in Co/CoO NPs may have important role in enhancing the activity of ORR, we further studied the ORR activities of the G-Co/CoO NPs with different CoO thickness under the same condition, as shown in Fig. 4A. With the CoO coating increased from 1 to 3 nm, the G-Co/CoO NPs exhibited negative polarization shifts, indicating that the thin CoO shell facilitates the oxygen reduction. We should note that although the G-Co/CoO NPs with thick CoO shell have lower half-wave potential for ORR, they can still catalyze the ORR via a 4e process, as shown in Fig. 11 and Fig. 12.

The ORR activity of the G-Co/CoO NPs was compared with the commercial C-Pt catalyst in  $O_2$ -saturated 0.1 M KOH solution. As shown in Fig. 4B, the half-wave potential difference between the G-Co/CoO and the C-Pt is 25 mV under the same condition. However, the G-Co/Co NPs have a steeper polarization curve and a higher current density than the C-Pt catalyst from -0.185 V to -0.6 V, indicating that the G-Co/CoO and C-Pt have the comparative ORR activity. The durability of the G-Co/CoO NPs and the C-Pt was also evaluated via a chronoamperometric method at -0.3 V (Fig. 4C). The current densities from both G-Co/CoO and C-Pt decrease with time at the same pace initially. But the G-Co/CoO shows a slower decrease than the C-Pt after 20 h stability test, demonstrating a longer-term stability of the G-Co/CoO compared to the C-Pt/ catalyst. Similar study indicates that the G-Co/CoO is also more stable than the C-Co/CoO (Fig. 13). These measurements prove that G can activate and stabilize Co/CoO NPs more efficiently for ORR, and the present G-Co/CoO NPs are a promising alternative to the C-Pt catalyst in KOH.

In summary, the G-Co/CoO NPs were synthesized by self-assembly of Co NPs onto the surface of G. The Co NPs tend to form a layer (~1 nm) of natural CoO once they are exposed to ambient environment. This CoO layer prevents deep oxidation of the Co NPs unless they are heated at an elevated temperature (70 °C). With this controlled oxidation, we

have obtained a series of G-Co/CoO NPs with tuneable Co size and CoO thickness. Co in Co/CoO can be completely oxidized by the excess of  $\text{Me}_3\text{NO}$ , forming hollow CoO NPs. Compared to CoO and C-Co/CoO NPs, the G-Co/CoO NPs show much enhanced catalytic activity for ORR in  $\text{O}_2$ -saturated 0.1 M KOH solution and their activity is CoO thickness-  
5 dependent with 1 nm CoO shell coated G-Co/CoO showing the maximum activity. The work demonstrates the importance of Co/CoO dimension and of G as a support in tuning electrocatalysis for efficient ORR. The optimized G-Co/CoO NPs have comparable activity to, and better stability than, the commercial C-Pt NPs and are thus a promising alternative to C-Pt catalyst for ORR in alkaline solutions, for devices operating by reducing  $\text{O}_2$ .

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What is claimed is:

1. A nanoparticle composite oxygen-reducing (ORR) catalyst comprising Co/CoO nanoparticles on a graphene support.
2. The nanoparticle composite catalyst of Claim 1, wherein the Co/CoO nanoparticles are about 10nm in diameter and have a CoO shell.
3. The nanoparticle composite catalyst of Claim 2 wherein the CoO shell is about 1 nm thick.
4. The nanoparticle composite catalyst of Claim 1 wherein the nanoparticles are monodisperse and are effectively supported on a graphene monolayer.
5. The nanoparticle composite catalyst of according to claim 1, wherein the catalyst has an activity for the oxygen reduction reaction comparable to or better than a commercial C-Pt NP catalyst.
6. The nanoparticle composite catalyst of according to claim 1 or 5, wherein the catalyst has high activity for the oxygen reduction reaction and has stability comparable to or better than a commercial carbon-platinum nanoparticle Pt catalyst, or such that after 17 h of testing at a potential of -0.3 V vs. Ag/AgCl (4 M KCl), the catalyst performs greater than 60% of its original capacity under representative operating conditions.
7. The nanoparticle composite catalyst according to claim 6, wherein the catalyst reduces oxygen predominantly via direct four-electron reduction of O<sub>2</sub> to OH<sup>-</sup>.
8. A method of forming an ORR composite catalyst comprising metal/metal oxide NPs on graphene, the method comprising the steps of
  - (i) combining a hexane dispersion of as-prepared Co NPs and a DMF solution containing graphene at room temperature;
  - (ii) sonicating the combined solutions at room temperature;
  - (iii) precipitating the product;
  - (iv) dispersing the product in butylamine and stirring at ambient temperature;

- (v) precipitating the metal NP on graphene catalyst by centrifuging; and
- (vi) forming an oxide on the NPs in air at a designated temperature and a time period to form a graphene Co/CoO NP composite.

- 5        9. The method of claim 8, wherein the Co NPs are monodisperse particles.
10. The method of claim 8, wherein the monodisperse NPs have a diameter under 15 nanometers, and the oxide forms a shell under about 3 nm thick, and preferably about 1 nm thick.
- 10       11. The method according to claim 8, wherein graphene-Co/CoO composite catalyst has Co/CoO NPs supported on the surface of graphene in the form of monolayer.
12. The method according to claim 9, wherein reducing oxygen is predominantly due to
- 15       direct four-electron reduction of O<sub>2</sub> to OH<sup>-</sup>.
13. A method of using graphene-Co/CoO composite catalyst for promoting the oxygen reduction reaction, the method comprising positioning the composite catalyst to reduce oxygen in an electrochemical cell containing O<sub>2</sub> in potassium hydroxide
- 20       (KOH).
14. The method according to claim 13, wherein the KOH is approximately 0.1 molar (M) concentration.

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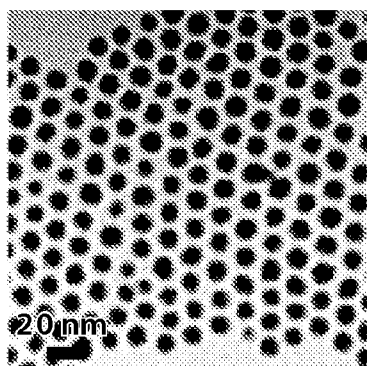


Fig. 1A

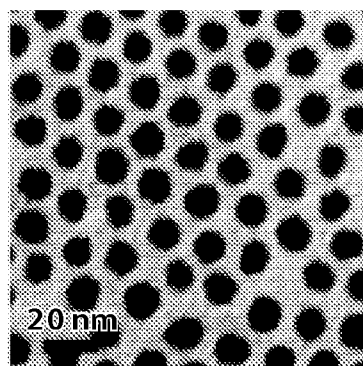


Fig. 1B

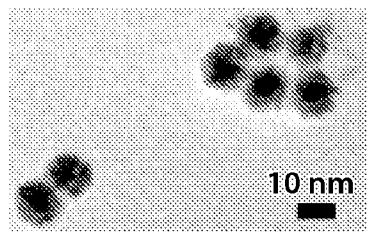


Fig. 1C

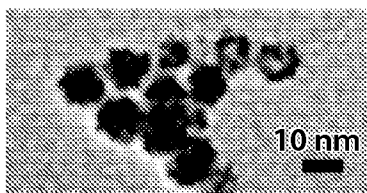


Fig. 1D

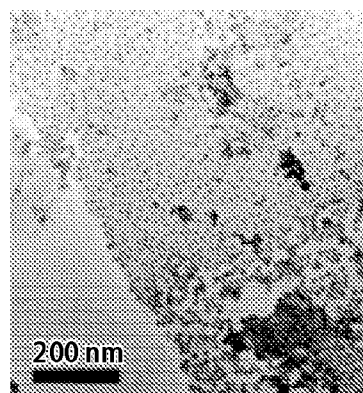


Fig. 1E

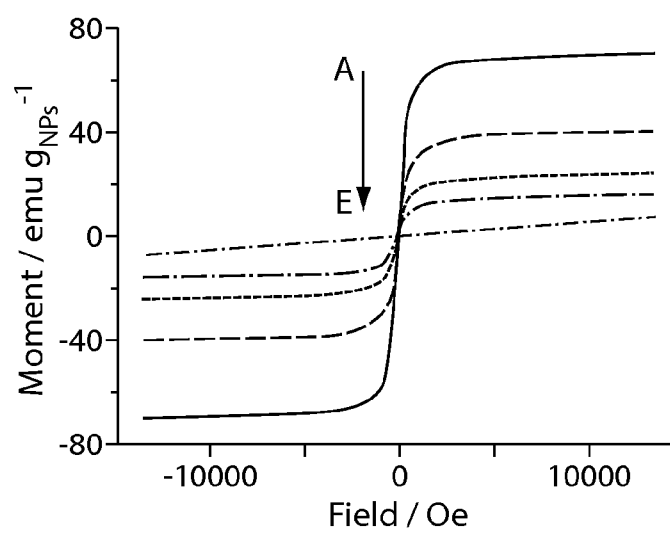


Fig. 2

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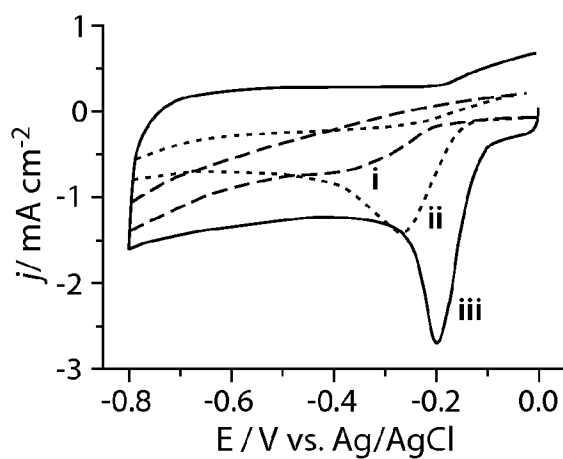


Fig. 3A

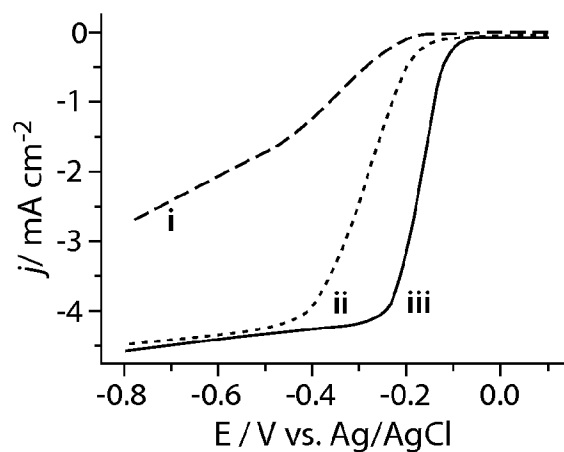


Fig. 3B

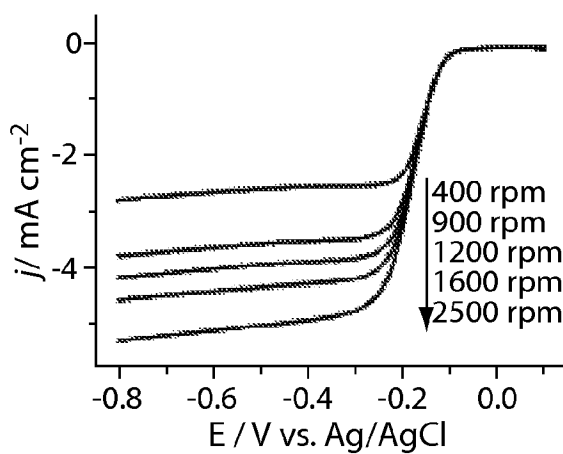


Fig. 3C

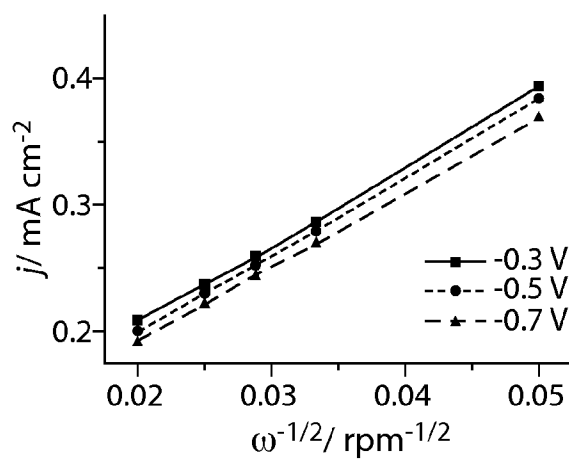


Fig. 3D

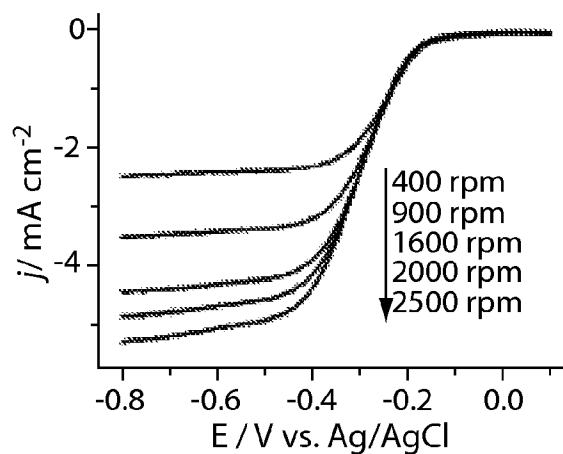


Fig. 3E

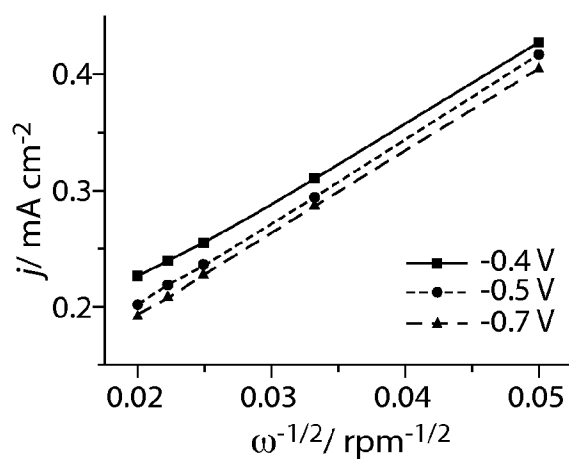


Fig. 3F

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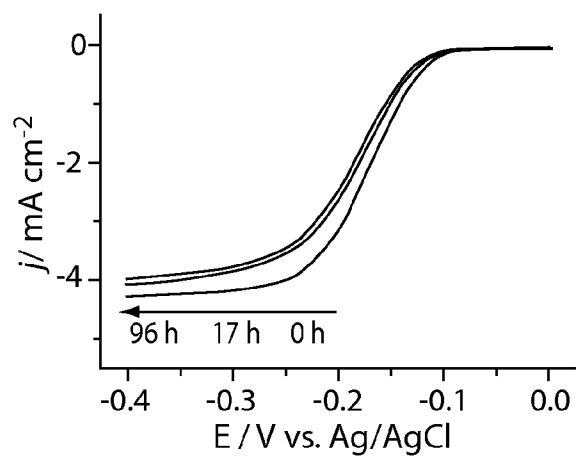


Fig. 4A

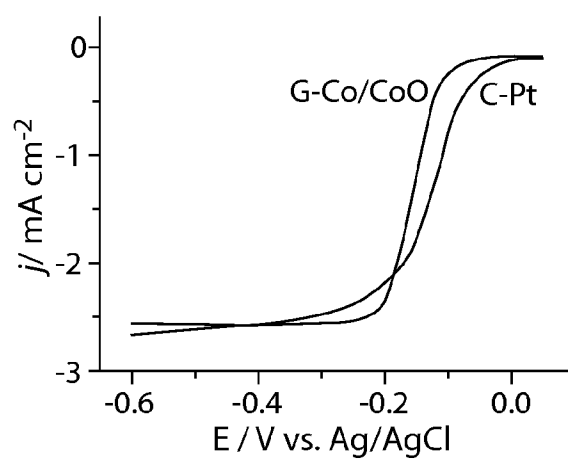


Fig. 4B

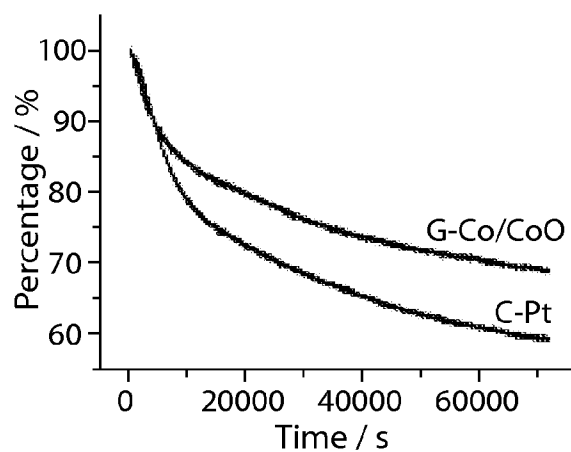


Fig. 4C

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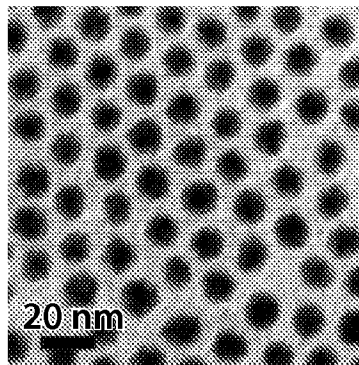


Fig. 5

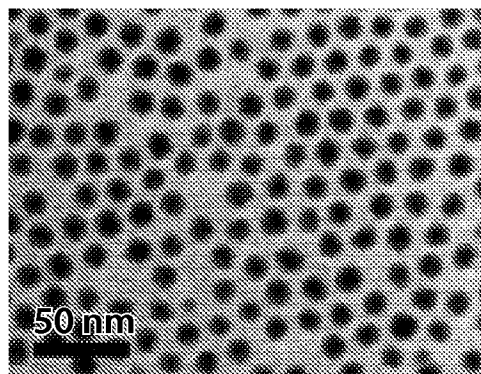


Fig. 6

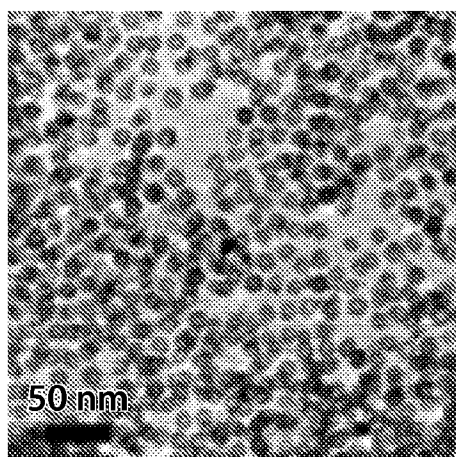


Fig. 7A

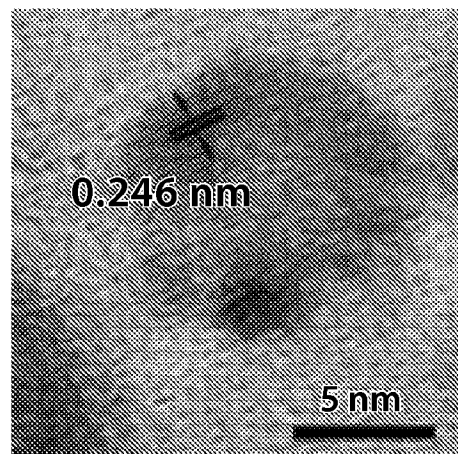


Fig. 7B

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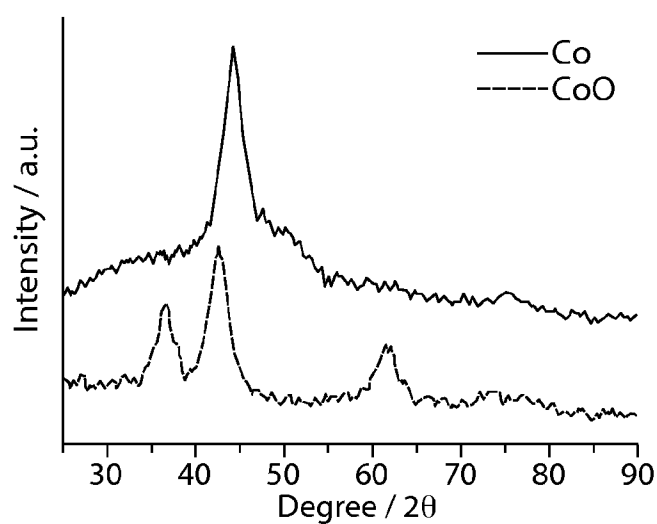


Fig. 8

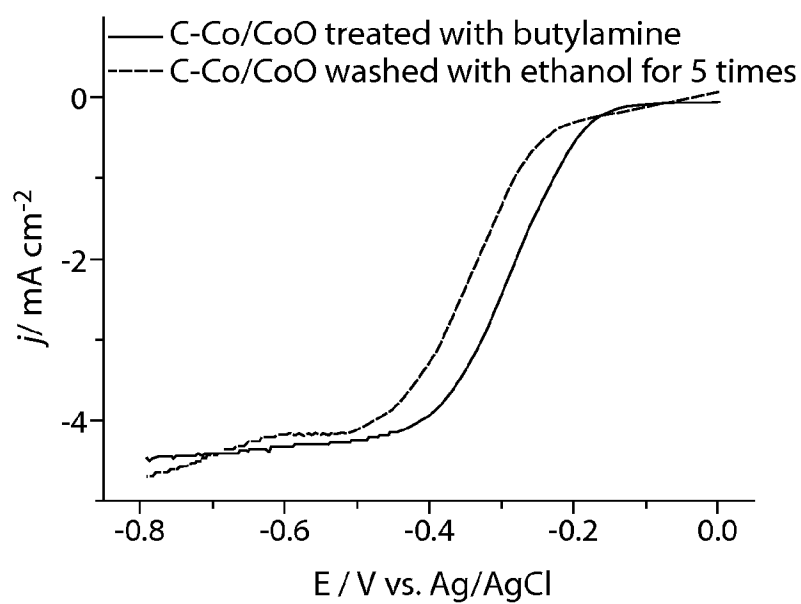


Fig. 9

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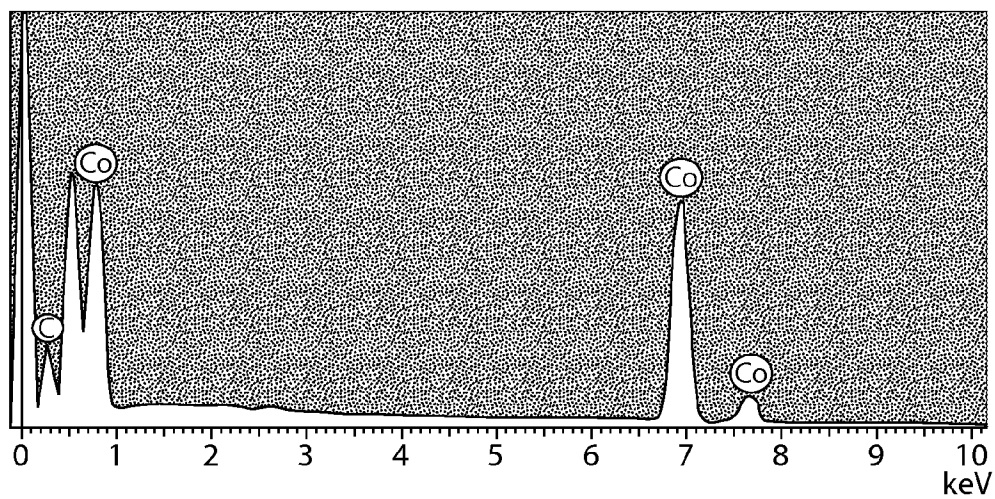


Fig. 10A

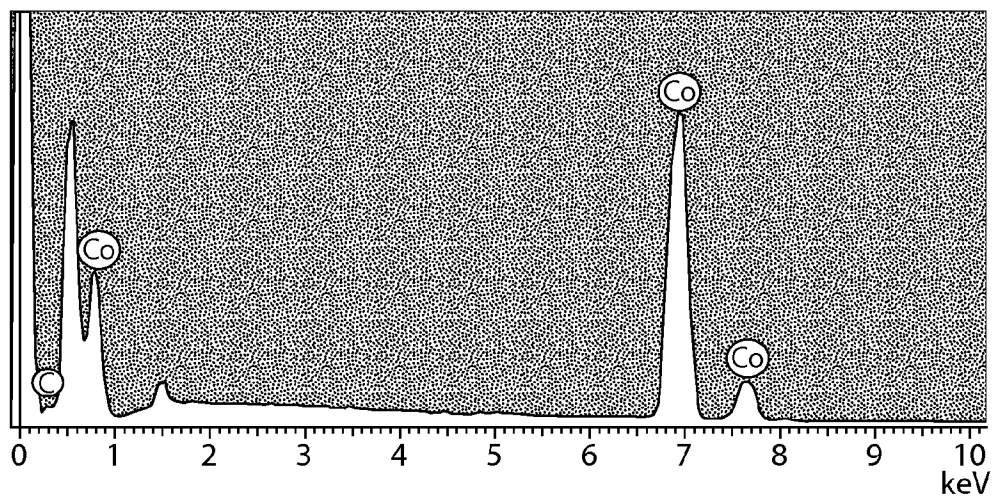


Fig. 10B

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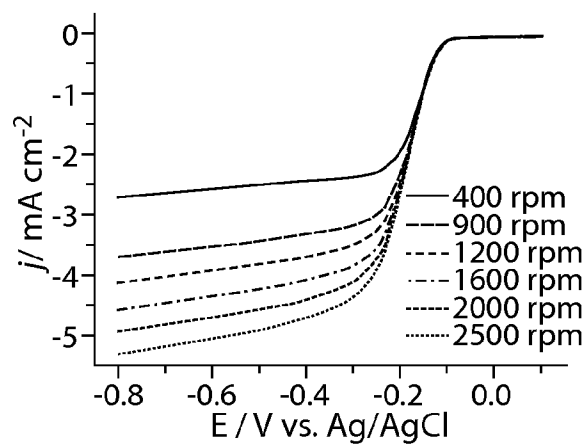


Fig. 11A

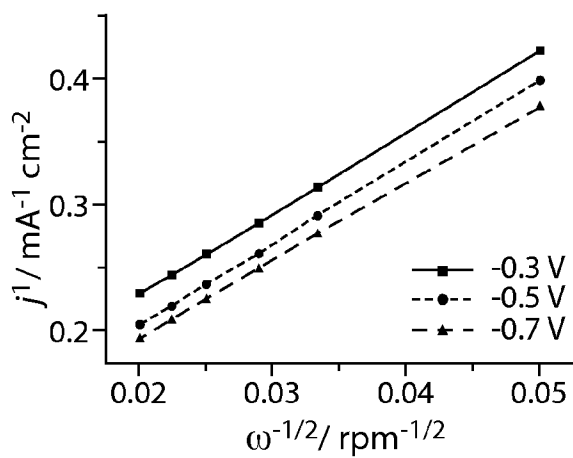


Fig. 11B

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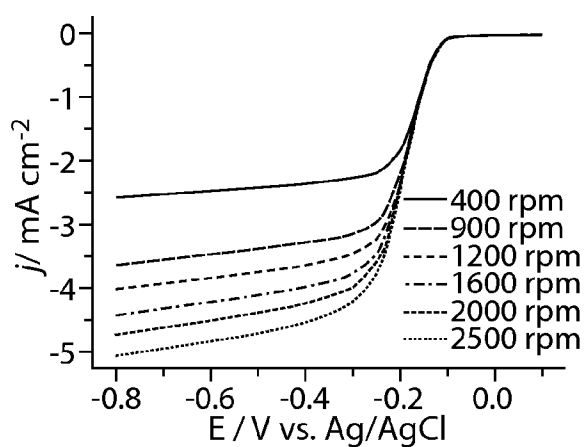


Fig. 12A

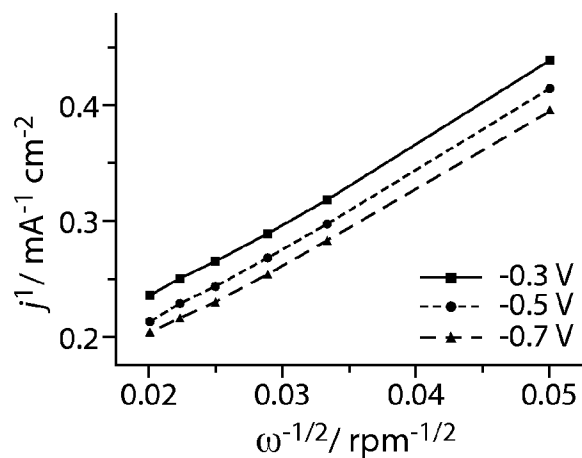


Fig. 12B

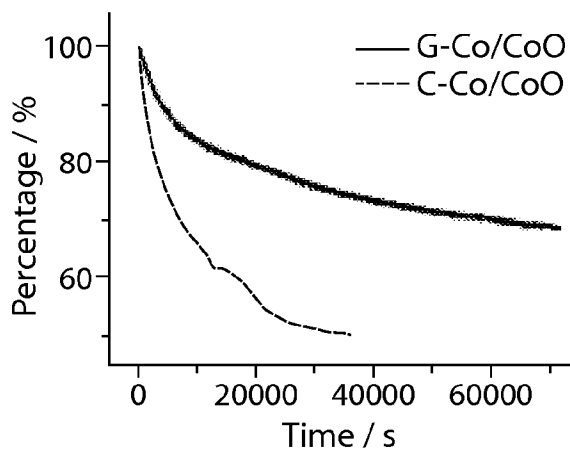


Fig. 13

**A. CLASSIFICATION OF SUBJECT MATTER****C01B 31/02(2006.01)i, H01M 10/05(2010.01)i, B82B 1/00(2006.01)i, B82B 3/00(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C01B 31/02; H01M 10/05; B82B 1/00; B82B 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) &amp; Keywords:oxygen reducing reaction, ORR, cobalt, cobalt oxide, Co/CoO, nanoparticle, graphene, catalyst, electrochemical cell

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                       | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | LIANG, YONGYE et al., 'Co3O4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction', Nature Materials, 2011, Vol. 10, pages 780-786. (Published online 07 August 2011)<br>See abstract.                                       | 1-14                  |
| A         | FEYGENSON, M. et al., 'Low-energy magnetic excitations in Co/CoO core/shell nanoparticles', Physical Review B, 2011, Vol. 83, 174414(10 pages). (Published online 05 May 2011)<br>See abstract.                                                          | 1-14                  |
| A         | SHI, PENGHUI et al., 'Supported cobalt oxide on graphene oxide: Highly efficient catalysts for the removal of Orange II from water', Journal of Hazardous Materials, 2012, Vol. 229-230, pages 331-339. (Published online 15 June 2012)<br>See abstract. | 1-14                  |
| A         | LIANG, YONGYE et al., 'Oxygen Reduction Electrocatalyst Based on Strongly Coupled Cobalt Oxide Nanocrystals and Carbon Nanotubes', J. Am. Chem. Soc., 2012, Vol. 134, pages 5849-15857 (Published online 08 September 2012)<br>See abstract.             | 1-14                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

17 December 2013 (17.12.2013)

Date of mailing of the international search report

**17 December 2013 (17.12.2013)**

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2013/062818**Patent document  
cited in search reportPublication  
datePatent family  
member(s)Publication  
date

None