Co₃O₄ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction

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Catalysts for oxygen reduction and evolution reactions are at the heart of key renewable-energy technologies including fuel cells and water splitting. Despite tremendous efforts, developing oxygen electrode catalysts with high activity at low cost remains a great challenge. Here, we report a hybrid material consisting of Co₃O₄ nanocrystals grown on reduced graphene oxide as a high-performance bi-functional catalyst for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Although Co₃O₄ or graphene oxide alone has little catalytic activity, their hybrid exhibits an unexpected, surprisingly high ORR activity that is further enhanced by nitrogen doping of graphene. The Co₃O₄/N-doped graphene hybrid exhibits similar catalytic activity but superior stability to Pt in alkaline solutions. The same hybrid is also highly active for OER, making it a high-performance non-precious metal-based bi-catalyst for both ORR and OER. The unusual catalytic activity arises from synergetic chemical coupling effects between Co₃O₄ and graphene.

Increasing energy demands have stimulated intense research on alternative energy conversion and storage systems with high efficiency, low cost and environmental benignity1,2. Catalysts for oxygen reduction and evolution reactions are at the heart of key renewable-energy technologies including fuel cells3,4 and water splitting. Despite tremendous efforts, developing oxygen electrode catalysts with high activity at low cost remains a great challenge. The current bottleneck of fuel cells lies in the sluggish ORR on the cathode side1. Pt or its alloys are the best known ORR catalysts. Owing to the high cost of Pt and declining activity, alternative catalysts based on non-precious metals5–7 and metal-free materials8–10 have been actively pursued. On the other hand, the reverse reaction of ORR, OER or water oxidation plays an important role in energy storage such as solar fuel synthesis11,12. Ruthenium and iridium oxides in acidic conditions and first row spinel and perovskite metal oxides in basic conditions have been used to catalyse OER with moderate over-potentials (about 300–400 mV; ref. 13).

It is highly challenging but desirable to develop efficient bi-functional catalysts for both ORR and OER, particularly for unitized regenerative fuel cells, a promising energy storage system that works as a fuel cell and in reverse as a water electrolyzer producing H₂ and O₂ to feed the fuel cell14,15.

Here, we show that Co₃O₄ nanoparticles, a material with little ORR activity by itself, when grown on reduced mildly oxidized graphene oxide (rmGO) exhibits surprisingly high performance in both ORR and OER in alkaline solutions. The hybrid exhibits comparable ORR catalytic activity to a commercial carbon-supported Pt catalyst (20 wt% Pt on Vulcan XC-72, Pt/C) and superior stability, thus leading to a new bi-functional catalyst for ORR and OER.

Co₃O₄/graphene hybrid was synthesized in solution16–20 by a general two-step method. In the first step, Co₃O₄ nanoparticles were grown on mildly oxidized GO sheets (mGO) freely suspended in solution by hydrolysis and oxidation of cobalt acetate (Co(OAc)₂) at 80 °C (see Supplementary Information for details of the synthesis). Controlled nucleation of Co₃O₄ on mGO sheets was achieved by reducing the hydrolysis rate of Co(OAc)₂ by adjusting the ethanol/H₂O ratio and reaction temperature. Subsequent hydrothermal reaction at 150 °C led to crystallization of Co₃O₄ and reduction of mGO (signalled by a shift in the optical absorbance peak of graphene oxide (GO); refs 21,22) to form the Co₃O₄/rmGO hybrid. We also added NH₃·OH in our synthesis steps to mediate hydrolysis of Co⁴⁺ and its oxidation23, and obtained an N-doped hybrid material denoted as Co₃O₄/N-rmGO (see Supplementary Information). The amount of Co₃O₄ in our hybrids was ∼70 wt% (~20 at% of Co), as revealed by thermal-gravimetric measurements.

Growth of Co₃O₄ nanocrystals on rmGO sheets was confirmed by scanning electron microscopy (SEM) for both Co₃O₄/N-rmGO (Fig. 1a) and Co₃O₄/rmGO (Supplementary Fig. S1a). Transmission electron microscopy (TEM) revealed smaller particles in Co₃O₄/N-rmGO (~4–8 nm in size, Fig. 1b) than Co₃O₄/rmGO (~12–25 nm in size, Supplementary Fig. S1b), attributed to NH₃ coordination with cobalt cations in reducing Co₃O₄ particle size21,24 and enhanced particle nucleation on N-doped rmGO (N-rmGO).

High resolution TEM showed the crystalline spinel structure of Co₃O₄ nanocrystals (Fig. 1c and Supplementary Fig. S1c), consistent with X-ray diffraction (XRD) data (Fig. 1d and Supplementary Fig. S1d). X-ray photoelectron spectroscopy (XPS) revealed 4 at% nitrogen in Co₃O₄/N-rmGO (Fig. 1e), but not in the Co₃O₄/rmGO sample made without NH₃·OH (Supplementary Fig. S2a). In a control experiment, we verified that N-dopants were on reduced GO sheets (not in Co₃O₄ nanocrystals, see Supplementary Fig. S2b) by hydrothermal reactions between functional groups on mGO and NH₃·OH in the solution25. High resolution XPS spectra of the N peak revealed pyridinic and pyrrolic nitrogen species in Co₃O₄/N-rmGO (Fig. 1e inset) and in N-rmGO (Supplementary Fig. S2c).

To assess their ORR catalytic activity, our materials were first loaded (with the same mass loading) onto glassy carbon electrodes
for cyclic voltammetry (CV) in O₂ versus Ar-saturated 0.1 M KOH (see Supplementary Information for experimental details). Free Co₃O₄ nanocrystals (size ∼4–8 nm, similar to those grown on GO) or rmGO alone exhibited very poor ORR activity (Supplementary Fig. S3). Remarkably, the Co₃O₄/rmGO hybrid showed a much more positive ORR onset potential (∼0.88 V relative to the reversible hydrogen electrode (RHE), see Supplementary Information for RHE calibration) and higher cathodic currents (Fig. 2a against Supplementary Fig. S3), suggesting synergistic ORR catalytic activity of Co₃O₄ and rmGO in the hybrid.

We used rotating-disk electrode (RDE) measurements to reveal the ORR kinetics of our Co₃O₄/rmGO hybrid in 0.1 M KOH (Fig. 2b). The linearity of the Koutecky–Levich plots and near parallelism of the fitting lines suggests first-order reaction kinetics toward the concentration of dissolved oxygen and similar electron transfer numbers for ORR at different potentials²⁶ (Fig. 2b...
Figure 2 | Co$_3$O$_4$/graphene hybrid as oxygen reduction catalysts. a, CV curves of Co$_3$O$_4$/rmGO hybrid, Co$_3$O$_4$/N-rmGO hybrid and Pt/C on glassy carbon electrodes in O$_2$-saturated (solid line) or Ar-saturated 0.1 M KOH (dash line). Catalyst loading was 0.17 mg cm$^{-2}$ for all samples. b, Rotating-disk voltamograms of Co$_3$O$_4$/rmGO hybrid (loading ~0.1 mg cm$^{-2}$) and Co$_3$O$_4$/N-rmGO hybrid (loading ~0.1 mg cm$^{-2}$) in O$_2$-saturated 0.1 M KOH with a sweep rate of 5 mV s$^{-1}$ at the different rotation rates indicated. The insets in b and c show corresponding Koutecky–Levich plots ($J^{-1}$ versus $\omega^{-0.5}$) at different potentials. d, Tafel plots of Co$_3$O$_4$/rmGO and Co$_3$O$_4$/N-rmGO hybrids derived by the mass-transport correction of corresponding RDE data (see Supplementary Information).

The performance of our hybrid catalyst was greatly enhanced with Co$_3$O$_4$/N-rmGO, made by adding NH$_4$OH during synthesis to afford N-doping in rmGO. The CV curve of Co$_3$O$_4$/N-rmGO hybrid exhibited a more positive ORR peak potential and higher peak current (Fig. 2a) than Co$_3$O$_4$/rmGO. RDE measurement revealed an electron transfer number of ~4.0 at 0.60–0.75 V (Fig. 2c). The half-wave potential at 1,600 r.p.m. was 0.83 V (Fig. 2c), similar to that of Pt/C (0.86 V; Supplementary Fig. S4a) and more positive than that of Co$_3$O$_4$/rmGO (0.79 V; Fig. 2b). Importantly, N-doped graphene (N-rmGO) alone, without Co$_3$O$_4$, exhibited low ORR activity (Supplementary Fig. S3) with an electron transfer number of ~2.7 at 0.50–0.65 V, suggesting a dominant 2e$^-$ reduction process (Supplementary Fig. S5). Excellent ORR activity of the Co$_3$O$_4$/N-rmGO hybrid catalyst was also gleaned from the much smaller Tafel slope of 42 mV/decade at low over-potentials (Fig. 2d) than that measured with Co$_3$O$_4$/rmGO hybrid (54 mV/decade) in 0.1 M KOH.

To verify the ORR catalytic pathways of the hybrid materials, we performed rotating ring-disk electrode (RRDE) measurements to monitor the formation of peroxide species (HO$_2^-$) during the ORR process (Fig. 3a). The measured HO$_2^-$ yields are below ~12% and ~6% for Co$_3$O$_4$/rmGO and Co$_3$O$_4$/N-rmGO, respectively, over the potential range of 0.45–0.80 V, giving an electron transfer number of ~3.9 (Fig. 3b). This is consistent with the result obtained from the Koutecky–Levich plots based on RDE measurements, suggesting the ORR catalysed by our hybrids is mainly by 4e$^-$ reduction.

We loaded our catalyst materials onto Teflon-treated carbon fibre paper (CFP) (~0.24 mg cm$^{-2}$ for all samples) to measure their steady-state iR-compensated (i, cell current; R, nuisance resistor) polarization curves (Fig. 4). The Teflon-treated porous CFP is highly hydrophobic, providing a three-phase contact point for oxygen, electrolyte and catalyst (known as the gas diffusion layer) useful in actual fuel cells to minimize the gas diffusion limitation. In 0.1 M KOH at 0.7 V versus RHE (a typical half-cell cathodic potential in an operating fuel cell), our Co$_3$O$_4$/rmGO and Co$_3$O$_4$/N-rmGO hybrids afforded an ORR current density of ~12.3 mA cm$^{-2}$ and ~52.6 mA cm$^{-2}$ respectively (Fig. 4a), approaching that of the Pt/C catalyst (~68.0 mA cm$^{-2}$). The oxygen reduction currents of our hybrid catalysts were 1–3 orders of magnitude higher than Co$_3$O$_4$ (0.012 mA cm$^{-2}$), rmGO (0.19 mA cm$^{-2}$) or N-rmGO alone (3.5 mA cm$^{-2}$; Supplementary Fig. S6), further suggesting synergetic coupling effects between two catalytically non-active components in our hybrid for ORR catalysis. In 1 M and 6 M KOH electrolytes, our Co$_3$O$_4$/N-rmGO ORR catalyst matched the performance of freshly loaded Pt/C catalyst in current density (Fig. 4b,c), accompanied by a positive shift in the ORR onset potential from 0.1 M KOH. The Tafel slope of kinetic current was down to ~37 mV/decade for Co$_3$O$_4$/N-rmGO in 1 M KOH (Supplementary Fig. S7), among the smallest Tafel slopes afforded by ORR catalysts. Importantly, our hybrid exhibits superior durability to Pt/C catalyst in 0.1–6 M KOH, with little.
Assessment of peroxide percentage in ORR catalysed by hybrid catalysts. a, Rotating ring-disk electrode voltammograms recorded with Co$_3$O$_4$/N-rmGO hybrid (loading ~0.1 mg cm$^{-2}$) and Co$_3$O$_4$/N-rmGO hybrid (loading ~0.1 mg cm$^{-2}$) in O$_2$-saturated 0.1 M KOH at 1,600 r.p.m. Disk current ($i_d$) (solid line) is shown on the lower half and ring current ($i_r$) (dotted line) is shown on the upper half of the graph. The disk potential was scanned at 5 mV s$^{-1}$ and the ring potential was constant at 1.5 V versus RHE. b, Percentage of peroxide (solid line) and the electron transfer number (n) (dotted line) of Co$_3$O$_4$/rmGO and Co$_3$O$_4$/N-rmGO hybrids at various potentials, based on the corresponding RRDE data in a.

...decay in ORR activity over 10,000–25,000 s of continuous operation (Fig. 4d–f). In contrast, the Pt/C catalyst exhibited 20%–48% decrease in activity in 0.1–6 M KOH (Fig. 4d–f), giving lower long-term ORR currents than the stable currents sustained by the Co$_3$O$_4$/N-rmGO hybrid catalyst.

We further compared the Co$_3$O$_4$/N-rmGO hybrid catalyst with other catalysts (Supplementary Fig. S8). Although the Pt/C ~ 50% (50 wt% Pt on Vulcan XC-72), a state-of-the-art Pt catalyst, showed slightly higher activity (Supplementary Fig. S8a), it suffered a significant 30% decrease in current density over 10,000 s of continuous operation in 1 M KOH (Supplementary Fig. S8b). A commercial Pd/C catalyst (10% Pd on activated carbon) showed lower activity than Co$_3$O$_4$/N-rmGO hybrid and obvious decay in activity over time (by ~20% in 10,000 s). Non-precious metal-N/C catalysts have shown excellent ORR activity in acidic and in base conditions. For comparison, we prepared a high quality Fe-N/C catalyst following refs 6,30 (see Supplementary Fig. S9 for RDE data). Notwithstanding a more positive onset potential, the Fe-N/C catalyst showed slightly lower activity than our Co$_3$O$_4$/N-rmGO hybrid at around 0.7 V. Furthermore, the Fe-N/C catalyst exhibited ~10% decreases in current density over 10,000 s continuous operation, suggesting lower stability/durability than the Co$_3$O$_4$/N-rmGO hybrid. Activity instability of metal-N/C catalysts in acidic electrolyte is also well known and has been a limiting factor to the practical use of this material. Pt catalyst is known to gradually degrade over time because of surface oxides and particle dissolution and aggregation, especially in the alkaline electrolytes used for alkaline fuel cells (Fig. 4f). Long-term stabilities of other ORR catalysts, such as Ag in alkaline solutions, are improved over Pt, but still suffer from deactivation and are below the targets for applications. As the lack of catalyst durability has been one of the major challenges for alkaline fuel cells, the excellent stability of our Co$_3$O$_4$/N-rmGO hybrid makes it promising for ORR and other important catalytic reactions in alkaline solutions.

We performed X-ray absorption near edge structure (XANES) measurements to glean the interactions between Co$_3$O$_4$ and GO in our hybrids (Fig. 1f). Compared to N-rmGO, Co$_3$O$_4$/N-rmGO hybrid showed a clear increase of carbon K-edge peak intensity at ~288 eV, corresponding to carbon atoms in graphene attached to oxygen or other species. This suggested the possible formation of interfacial Co–O–C and Co–N–C bonds in the Co$_3$O$_4$/N-rmGO hybrid. In the oxygen K-edge XANES, an obvious decrease in unoccupied O 2p–Co 3d hybridized state (~532 eV; ref. 38) was observed (Fig. 1f inset), accompanied by an increase in the Co L-edge XANES (mapping of the unoccupied Co 3d projected state, see Supplementary Fig. S10) peak in the hybrids compared to pure Co$_3$O$_4$ nanocrystal, suggesting a higher electron density at the O site and a lower electron density at the Co site, and consequently a higher ionic Co–O bonding in the hybrid. Bond formation between Co$_3$O$_4$ and N-rmGO (as suggested by C K-edge XANES and changes in the chemical bonding environment for C, O and Co atoms in the hybrid material) are probably responsible for the synergistic ORR catalytic activity.

N-doping of GO could afford stronger coupling between Co and graphene in Co$_3$O$_4$/N-rmGO than in Co$_3$O$_4$/rmGO. N-groups on reduced GO serve as favourable nucleation and anchor sites for Co$_3$O$_4$ nanocrystals owing to coordination with Co cations. This is consistent with a smaller Co$_3$O$_4$ nanocrystal size (higher degree of nucleation) on N-rmGO than on rmGO. Electronic effects of N-doping of graphene could also play a role in ORR. Note that Metal-N species is believed to be ORR-active sites in Fe- or Co-N/C catalysts prepared at much higher temperatures (600–1,000 °C) with much lower metal loadings (<1–2 at% of metal; ref. 7). Our hybrid catalysts exhibit higher stability and differ in low temperature solution-phase synthesis and the Co in our hybrid is in the form of oxides (see XPS in Supplementary Fig. S2d) with a high Co loading of ~20 at%. Lowering the Co loading to 3–10 at% in our Co$_3$O$_4$/N-rmGO catalyst led to systematic reduction in ORR activity (Supplementary Fig. S11), suggesting that the active reaction sites in our hybrid materials could be Co oxo species at the interface with graphene.

The mechanism of ORR with our hybrid catalyst remains unclear. The Tafel slope of kinetic current down to ~37 mV/decade for Co$_3$O$_4$/N-rmGO in 1 M KOH is among the lowest for spinel oxide ORR catalysts and close to 2.303 (RT/3F) V/decade ($R$, universal gas constant; $F$, Faraday constant), suggesting protonation of O$_2^−$ on the active sites of catalyst as the rate limiting step. A dual-site mechanism has been proposed for cobalt-polypryrole/C ORR catalyst, in which oxygen is reduced to peroxide at Co–N–C sites and further reduced to OH$^−$ at Co$_3$O$_4$/Co sites. A similar mechanism may be at work in our hybrid system. However, we note that Co$_3$O$_4$/rmGO without any N species has very similar ORR onset potential to Co$_3$O$_4$/N-rmGO, suggesting that the active sites may not directly involve N species in the hybrids but are enhanced by N doping of mGO. It is also found that physical mixtures of Co$_3$O$_4$ with rmGO or N-rmGO afforded much lower ORR activities than the corresponding hybrid material (Supplementary Fig. S12), suggesting synergistic coupling between Co$_3$O$_4$ and graphene is indispensable to the high ORR activity of the hybrid.

We also used the same method to prepare Co$_3$O$_4$ hybrids with other forms of carbon and compared their ORR performances.
Figure 4 | ORR performance and stability of catalysts. a–c, Oxygen reduction polarization curves of Co$_3$O$_4$/rmGO, Co$_3$O$_4$/N-rmGO and a high quality commercial Pt/C catalyst (catalyst loading ∼0.24 mg cm$^{-2}$ for all samples) dispersed on CFP in O$_2$-saturated (a) 0.1 M KOH, (b) 1 M KOH and (c) 6 M KOH electrolytes respectively. d–f, Chronoamperometric responses (percentage of current retained versus operation time) of Co$_3$O$_4$/N-rmGO hybrid and Pt/C on carbon fibre paper electrodes kept at 0.70 V versus RHE in O$_2$-saturated (d) 0.1 M KOH, (e) 1 M KOH and (f) 6 M KOH electrolytes respectively. The Co$_3$O$_4$/N-rmGO hybrid showed comparable ORR catalytic activity to Pt/C and superior stability in alkaline solutions.

( Supplementary Fig. S13). The result indicated that high conductivity, high surface area, and suitable functional groups on carbon materials are important for the high activity of hybrid materials.

Lastly, we extended the potential of our hybrid electrode to 1.70 V versus RHE to the water oxidation regime and evaluated electrocatalytic oxygen evolution reaction (OER). In 0.1 M KOH, the same sample used for ORR containing Co$_3$O$_4$/N-rmGO loaded on CFP (at 0.24 mg cm$^{-2}$) afforded higher OER currents than either free Co$_3$O$_4$ nanocrystals or Pt/C (Fig. 5a). Furthermore, we loaded our Co$_3$O$_4$/N-rmGO catalyst onto Ni foam at ∼1 mg cm$^{-2}$ and evaluated OER performance in 1 M KOH at room temperature (Fig. 5b). Our catalyst afforded a current density of 10 mA cm$^{-2}$ at a small overpotential of ∼0.31 V (Fig. 5b) and a small Tafel slope down to 67 mV/decade (Fig. 4c), comparable to the performance of the best reported Co$_3$O$_4$ nanoparticle OER catalyst at the same loading$^{42}$. N-doping of graphene did not affect OER activity, as Co$_3$O$_4$/rmGO hybrid showed only slightly lower OER activity than Co$_3$O$_4$/N-rmGO (Fig. 5b). Stability tests on glassy carbon electrodes showed that both Co$_3$O$_4$/N-rmGO and Co$_3$O$_4$/rmGO hybrids are inherently stable during OER cycling (Supplementary Fig. S14). These results make our hybrid material a powerful bi-functional catalyst for both oxygen reduction and water oxidation. Previously, manganese oxide was shown to be a bi-functional catalyst for ORR and OER (ref. 15). Our Co$_3$O$_4$/N-rmGO catalyst outperforms manganese oxide with smaller over-potentials for both ORR and OER, presenting the highest performance non-precious metal-based bi-functional catalyst.
In summary, although Co₃O₄ or graphene oxide alone have little catalytic activity for ORR, their hybrid materials exhibit unexpected, surprisingly high ORR activities in alkaline solutions, comparable to fresh commercial Pt/C catalyst but far exceeding Pt/C in stability and durability. This presents a highly promising third generation synchrotron source. (SGM) beamline (1.2.1.) operated at the Advanced Light Source (ALS). (SGM) beamline (1.2.1.) operated at the Advanced Light Source (ALS). (SGM) beamline (1.2.1.) operated at the Advanced Light Source (ALS).

Methods
Materials synthesis. GO was made by a modified Hummers method, in which a six times lower concentration of KMnO₄ was used than that for Hummers’ GO. In the first step of Co₃O₄/rmGO hybrid synthesis, Co(OAc)₃ aqueous solution was added into GO/ethanol dispersion at room temperature. The reaction was stirred for 10 h at 80 °C. In the second step, the reaction mixture from the first step was transferred to an autoclave for hydrothermal reaction at 150 °C for 3 h. To synthesize Co₃O₄/N-rmGO, NH₄OH was added after Co(OAc)₃ addition in the first step. See Supporting Information for detailed experimental procedures.

Electrochemical measurements. A saturated calomel electrode was used as the reference electrode in all measurements and was calibrated with respect to a reversible hydrogen electrode (see Supporting Information for details). Cyclic voltammetry was conducted in a three-electrode electrochemical cell using a graphite rod as the counter electrode. 12 µg of sample was loaded on the glassy carbon working electrode (3 mm in diameter). In the rotating disk electrode and rotating ring-disk electrode measurements, the working electrode was prepared by loading 20 µg of sample on a glassy carbon electrode of 5 mm in diameter (0.1 mg cm⁻²). For the measurement on carbon fibre paper, the working electrode was prepared by loading 0.24 mg of sample on 1 cm² carbon fibre paper from its ethanol dispersion with Nafion (10% to sample). All the data from carbon fibre paper were iR-compensated. The scan rate was 5 mV s⁻¹ for all electrochemical measurements.

Characterizations. Scanning electron microscopy was carried out on an FEI XL30 Sirion scanning electron microscope. Transmission electron microscopy was carried out on an FEI Tecnai G2 F20 transmission electron microscope. X-ray diffraction (XRD) was carried out on a PANalytical X’Pert instrument. XPS was carried out on an SSi S-3 Probe XPS Spectrometer. The XANES at the Co K-edge, O K-edge and Co L-edge were obtained on the spherical grating monochromator (SGM) beamline (E/ΔE ~ 5.000) at the Canadian Light Source (CLS), the 2.9 GeV third generation synchrotron source.

Received 21 December 2010; accepted 30 June 2011; published online 7 August 2011

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Figure 5 | Co₃O₄/graphene hybrid bi-functional catalyst for ORR and water oxidation (OER). a, Oxygen electrode activities within the ORR and OER potential window of Co₃O₄/N-rmGO hybrid. Co₃O₄ nanocrystal and Pt/C catalysts (catalyst loading ~0.24 mg cm⁻² for all samples) dispersed on carbon fibre paper in O₂-saturated 0.1 M KOH. Co₃O₄/N-rmGO hybrid showed excellent catalytic activities for both ORR and OER. Free Co₃O₄ showed little ORR activity whereas Pt/C showed little OER activity. b, Oxygen evolution currents of Co₃O₄/N-rmGO hybrid, Co₃O₄/rmGO hybrid and Co₃O₄ nanocrystal loaded onto Ni foam (to reach a high catalyst loading of ~1 mg cm⁻²) measured in 1 M KOH. c, Tafel plots of OER currents in b.
