Co$_3$O$_4$ nanoparticles anchored on nitrogen-doped reduced graphene oxide as a multifunctional catalyst for H$_2$O$_2$ reduction, oxygen reduction and evolution reaction

Tingting Zhang, Chuansheng He, Fengzhan Sun, Yongqi Ding, Manchao Wang, Lin Peng, Jiahui Wang & Yuqing Lin

This study describes a facile and effective route to synthesize hybrid material consisting of Co$_3$O$_4$ nanoparticles anchored on nitrogen-doped reduced graphene oxide (Co$_3$O$_4$/N-rGO) as a high-performance tri-functional catalyst for oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and H$_2$O$_2$ sensing. Electrocatalytic activity of Co$_3$O$_4$/N-rGO to hydrogen peroxide reduction was tested by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry. Under a reduction potential at $-0.6$ V to H$_2$O$_2$, this constructing H$_2$O$_2$ sensor exhibits a linear response ranging from 0.2 to 17.5 mM with a detection limit to be 0.1 mM. Although Co$_3$O$_4$/rGO or nitrogen-doped reduced graphene oxide (N-rGO) alone has little catalytic activity, the Co$_3$O$_4$/N-rGO exhibits high ORR activity. The Co$_3$O$_4$/N-rGO hybrid demonstrates satisfied catalytic activity with ORR peak potential to be $-0.26$ V (vs. Ag/AgCl) and the number of electron transfer number is 3.4, but superior stability to Pt/C in alkaline solutions. The same hybrid is also highly active for OER with the onset potential, current density and Tafel slope to be better than Pt/C. The unusual catalytic activity of Co$_3$O$_4$/N-rGO for hydrogen peroxide reduction, ORR and OER may be ascribed to synergetic chemical coupling effects between Co$_3$O$_4$, nitrogen and graphene.

With the transition from traditional fossil fuels to clean and sustainable energy, lots of attentions have been paid on storage systems with environmental benignity, high efficiency and alternative energy conversion. Fuel cells have been considered as the most efficient and clean energy conversion device because fuels react with oxygen via mild electrochemical processes without combustion and the overall fuel-conversion efficiency is not limited by the Carnot cycle laws. Designing bifunctional catalysts with good oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) activities would be highly beneficial to the development of metal-air batteries. However, developing catalysts for ORR and OER with high activity at low cost remain great challenges. Platinum-based materials are known to be the most active electrocatalysts for the ORR and the OER. However, the limited reserves of Pt, high cost, the activity deterioration with time and poor durability severely hinder the large-scale applications of Pt in ORR and OER.

On the other hand, the determination of hydrogen peroxide (H$_2$O$_2$) has aroused more and more interests of researchers as its significance in the fields of applications in industry as well as biological reactions. Therefore, a rapid, accurate and reliable method to detect H$_2$O$_2$ is of highly demanded. Among various techniques for H$_2$O$_2$ detection, electrochemical H$_2$O$_2$ electrocatalysts are promising due to their high sensitivity, low cost, good selectivity, easy for automation and operational simplicity. Catalysts for hydrogen peroxide reduction, oxygen reduction and oxygen evolution reactions are vital in biological assay and renewable-energy technologies including fuel cells and water splitting.

Recently, transition metal oxides including magnanimous oxide, cobalt oxide, iron oxide and nickel oxide as promising materials have received considerable attention due to their low cost, high abundance and perfect

Department of Chemistry, Capital Normal University, Beijing, 100048, China. Correspondence and requests for materials should be addressed to Y.L. (email: linyuqing@cnu.edu.cn)
catalytic activity for the ORR, OER and immobilizing enzymes for further applications in fabrication of hydrogen peroxide biosensor. Among them, Co₃O₄ with spinel crystal structure is beneficial to electron transportation between Co²⁺ and Co³⁺ ions, which has been extensively considered as an efficient electrocatalyst for OER and ORR. Previous studies reported that the efficiency of cobalt oxide as an OER catalyst could be ascribed to the increasing population of Co⁴⁺ centers at the oxide surface during electrochemical oxidation. More interesting, Co₃O₄, which exhibits catalase-like activity for the decomposition of H₂O₂, can be applied to the detection of H₂O₂ in aqueous medium. However, these Co₃O₄-based catalysts usually suffer from the poor electrical conductivity, short active site density and the dissolution or agglomeration during electrochemical processes. Co₃O₄ itself is a material with a little ORR, OER and H₂O₂ sensing activity and further studies exhibit that synergy between the carbon materials and Co₃O₄ can give a huge promotion of the electrocatalytic activity. Therefore, lots of researches have used conductive carbon nanomaterials such as carbon nanotubes (CNTs), carbon foam and graphene etc. To improve the conductivity of Co₃O₄ based hybrid catalysts as well as obtain uniformly dispersed Co₃O₄ nanoparticles and thus to improve the electrocatalyst activity.

Graphene, a two-dimensional layer framework of sp²-hybridized carbon with outstanding chemical and physical properties, has attracted a lot of attention in the last years. Graphene could be an attractive support for metal oxides to form a new class of nanocomposites for ORR due to their notable electronic conductivity and high surface area. Dai’s group reported a hybrid material consisting of Co₃O₄ nanocrystals grown on reduced graphene oxide as a high-performance bi-functional catalyst for the ORR and OER. Wang etc. synthesized a novel multifunctional nanohybrid by chemically coupling ultrafine metal oxide nanoparticles to reduced graphene oxide (rGO) as an effective catalyst for oxygen reduction reaction. Anchoring Co₃O₄ nanocrystals on carbon-based supports could significantly improve their electrocatalytic activity contributed by the small crystalline size and conductive support. What’s more, chemical doping with hetero atoms is an efficacious method to regulate electronic properties and surface chemistry of assembled graphene by the modulation of the carbon-carbon bonds. It has been also reported that nitrogen-doped graphene can promote the electrochemical reduction of H₂O₂. As previous study, the introduction of the Co–N₄ complex onto the graphene basal plane facilitates the activation of O₂ dissociation and the desorption of H₂O during the ORR. Nitrogen-graphene can produce the synergistic support effect because the reactive intermediates such as hydrogen peroxide are known to decomposed by nitrogen doped carbon nanostructures. However, so far, few researches have reported catalyst which has three functions for H₂O₂ reduction, ORR and OER.

We report herein the synthesis of Co₃O₄ nanoparticles anchored on nitrogen-doped reduced graphene oxide (Co₃O₄/N-rGO) through a simple and scalable method as tri-functional catalysts for H₂O₂ reduction, ORR and the OER, as shown in Fig. 1. Co₃O₄ anchored uniformly into laminar nitrogen-doped reduced graphene oxide was confirmed by scanning electron microscopy (SEM). Co₃O₄/N-rGO possesses a good electrocatalytic activity toward H₂O₂ reduction by enhancing the current response and decreasing H₂O₂ reduction over potential. The electrochemical results demonstrate that the Co₃O₄/N-rGO can exhibit higher activity for both the ORR and the OER and better durability than a commercial carbon-supported Pt catalyst. The strong coupling between Co₃O₄, nitrogen and reduced graphene oxide (rGO) is found to play an important role in the high electrocatalytic activities of the Co₃O₄/N-rGO. This synthesis route can be easily adopted for large-scale manufacturing due to its process simplicity and the accessibility of precursor materials.
Results and Discussion
Characterization. Figure 2A and B illustrated field emission scanning electron microscopy (FE-SEM) images of Co₃O₄/N-rGO. We can clearly see from SEM images in Fig. 2B that Co₃O₄ nanoparticles are uniformly anchored on the rGO substrate with an approximate average diameter of 150 nm. This may be attributed that Co²⁺ ion was coordinated with negatively charged oxygen-containing functional groups on N-rGO sheets. During the hydrothermal process, Co²⁺ was oxidized into Co³⁺ by oxygen-containing groups, and crystallized to form Co₃O₄ nanoparticles anchored into N-rGO sheets. However, Fig. 2C demonstrate Co₃O₄/rGO does not exhibit such a uniform morphology distribution of Co₃O₄. In addition, we only found that a typical corrugated structure in Fig. 2D, suggesting there is no Co₃O₄ particles nucleate on N-rGO surface. The oxygen-containing functional groups of rGO were beneficial for the nucleation and anchoring of nanocrystals on the sheets to achieve covalent attachments, which help to shape the uniform formation of Co₃O₄. In addition, these uniform structures of Co₃O₄ particles anchored into N-rGO can also be ascribed to NH₃ together with oxygen-containing functional group coordinating with cobalt cations and thus reducing Co₃O₄ particles size and enhancing particles nucleation on N-rGO. XRD was performed to investigate the phase structure of Co₃O₄/N-rGO. As shown in Fig. 3A, the diffraction peaks of the pristine Co₃O₄ was consistent with the standard Co₃O₄ (JCPDS card: 42-1467). The major diffraction peaks of Co₃O₄/N-rGO were well in agreement with those of Co₃O₄ except for the broad (002) peak at approximately 25°, which can be ascribed to disordered stacked graphitic sheets. This manifest that the original GO has been reduced to rGO during the hydrothermal process, again confirming we have successfully incorporated Co₃O₄ into rGO. BET experiments was conducted to obtain specific surface area of as-prepared samples and the isotherms exhibit typical IV isotherms where the recorded BET surface area of Co₃O₄/N-rGO, N-rGO and Co₃O₄ are 103.9 m²/g, 139.7 m²/g, and 62.8 m²/g, respectively. These results indicate the change of N-rGO structure after doping with Co₃O₄.

Raman spectroscopy was carried out to extend the study for the carbon structures in Co₃O₄/N-rGO, N-rGO and Co₃O₄/GO hybrid which are shown in Fig. 3B, where the peaks of Raman spectrum of Co₃O₄ anchored on the N-rGO and Co₃O₄/GO hybrid at 193, 470 and 680 cm⁻¹, can be attributed to the Eg, F₂g and A₁g modes of Co₃O₄. It is noted that there are two remarkable peaks around 1339 and 1591 cm⁻¹ refer to the D-band (arising from the edge or defect sites of carbon) and G band (representing the sp² carbon) of the graphene domain, respectively.
X-ray photoelectron spectroscopic (XPS) measurements were performed to determine the surface element constitution in Co₃O₄/N-rGO. The sharp peaks in Fig. 3C are corresponded to the characteristic peaks of C₁s, O₁s, N₁s, and Co₂p, indicating the existence of carbon, oxygen, nitrogen and cobalt elements in the prepared sample. The XPS spectrum for Co₂p shown in Fig. 3D reveals two major peaks with binding energies at 780.1 and 795 eV, corresponding to Co₂p₃/2 and Co₂p₁/2, respectively, with a spin energy separation of 15 eV, which is attributed to the Co²⁺ oxidation state, indicating that a portion of Co³⁺ is reduced to Co²⁺ with generating oxygen vacancies. These results again confirmed that Co₃O₄ nanoparticles have been anchored on N-rGO, Co²⁺ and Co³⁺ in the crystal structure of Co₃O₄ are being considered to be playing a vital role in improving catalytic performance of oxygen reduction reaction and oxygen evolution reaction. Furthermore, the main beautiful structure of Co₃O₄ is the peculiar cation distribution in the face centered cubic (FCC) crystal where the Co²⁺ ions reside on the 1/8th of the tetrahedral A sites while the Co³⁺ ions occupy 1/2 of the octahedral B sites, endow the system viable for electrocatalytic applications. The high-resolution N₁s XPS spectrum of Co₃O₄/N-rGO was used primarily to determine the bonding configurations of N atoms in the composite, as seen in Fig. 3E. The peak deconvolution suggests four components were centered at about 398, 400, 401, and 403 eV, corresponding to pyridinic N, pyrrolic N, quaternary N, and oxidized N, respectively. N atom have the lone electron pairs which can hybridize with sp² carbon atoms to celebrate oxygen reduction reaction. The performance of ORR depends on the bonding configuration of N atoms in carbon materials. It has been reported that the onset potential of a nitrogen-doped
Catalyst has strong relation with pyridinic form nitrogen, but little effect by pyrrolic nitrogen and oxidized type nitrogen.

**Electrocatalytic activity of Co$_3$O$_4$/N-rGO for H$_2$O$_2$ reduction.** Though enzyme based electrochemical sensors have been widely developed to sensing H$_2$O$_2$ due to the advantages of high sensitivity and good selectivity, these sensors often suffer from unstable response due to the intrinsic nature of enzymes. Therefore, it is necessary to develop a simple non-enzymatic strategy for sensing H$_2$O$_2$ with high sensitivity. To date, electrocatalysts for design H$_2$O$_2$ sensors with high sensitivity, good selectivity and easy regulation properties hold leading position among various sensors. It has been proved that functional nano-structured transition-metal oxides exhibit good electrocatalytic activity toward the H$_2$O$_2$ reduction, which provides valuable strategy for the nonenzymatic determination of H$_2$O$_2$. Among various kinds of transition metal oxides, Co$_3$O$_4$ shows attracting electronic and electrocatalytic properties. Particularly, its normal spinel crystal structure is favorable for electron transportation between Co$^{2+}$ and Co$^{3+}$ ions and Co$_3$O$_4$ possess catalase-like activity, which is benefit to sensing H$_2$O$_2$. Therefore, Co$_3$O$_4$ have been extensively explored as the sensing materials for developing enzyme-free H$_2$O$_2$ sensors. However, Co$_3$O$_4$-based catalysts usually suffer from the poor electrical conductivity, low active site density and the dissolution or agglomeration during electrochemical processes.

In our study, Co$_3$O$_4$ nanoparticles were incorporated into nitrogen doped graphene, leading to improved conductivity, enhanced catalytic activity and stability of the metal oxide nanocatalyst, and thus a better catalytic effect to H$_2$O$_2$ reduction due to the synergistic effect. To investigate the electrocatalytic characteristics to H$_2$O$_2$ reduction of Co$_3$O$_4$/N-rGO, voltammetric measurements were performed using the Co$_3$O$_4$/N-rGO, Co$_3$O$_4$/rGO and N-rGO modified GC electrodes in the presence of 5 mM H$_2$O$_2$ at a scan rate of 0.05 V s$^{-1}$. Figure 4A exhibit that a distinct catalytic current peak at $-0.40$ V could be ascribed for Co$_3$O$_4$/N-rGO modified GC electrode. Figure 4B reveals the CVs of Co$_3$O$_4$/N-rGO modified GC in the presence of different concentration of H$_2$O$_2$ (from the top: 0, 0.5, 1, 2 and 5 mM). It demonstrates that the reduction current gradually increases with the increase of H$_2$O$_2$ concentration, which manifest the Co$_3$O$_4$/N-rGO material have improved electrocatalytic activity to H$_2$O$_2$ and pave a route for quantitive analysis.

It is a significant way for amperometric technique to test the sensing property of Co$_3$O$_4$/N-rGO modified GC electrode. We studied the effect of the applied potential in order to improve the Co$_3$O$_4$/N-rGO modified GC electrode performance towards non-enzymatic H$_2$O$_2$ sensing. We investigated applied potential on the amperometric response on the Co$_3$O$_4$/N-rGO modified GC electrode towards sequential addition of 0.5 mM H$_2$O$_2$ by varying the potential between $-0.6$ V and $-0.3$ V. As shown in Fig. 5A and B, amperometric response of the Co$_3$O$_4$/N-rGO modified GC electrode has the optimal sensitivity, the applied potential at $-0.6$ V was selected. Figure 5A shows a typical current-time plot of the Co$_3$O$_4$/N-rGO modified GC electrode on successive addition of H$_2$O$_2$ at an applied potential of $-0.6$ V. Catalytic currents showed linear response to H$_2$O$_2$ from 0.5 mM to 17.5 mM ($R^2 = 0.994$) with a detection limit (S/N = 3) to be 0.1 mM, which are comparable to or even better than those of the other metal-free or enzyme based H$_2$O$_2$ biosensors. To investigate the selectivity for H$_2$O$_2$ sensing, the amperometric responses of ascorbic acid (AA), dopamine (DA), uric acid (UA) and glucose (Glu) are investigated on the Co$_3$O$_4$/N-rGO modified GC electrode. As shown in Fig. 5D, when the Co$_3$O$_4$/N-rGO-modified GC electrode was polarized at $-0.6$ V, the addition of 0.2 mM AA, 0.02 mM DA, 0.2 mM UA and 5 mM Glu did not produce an observable current response while the addition of H$_2$O$_2$ induced obvious reduction currents reponse, indicating that the measurements of H$_2$O$_2$ are essentially interference-free from other relevant electroactive species. Therefore, the as-prepared the Co$_3$O$_4$/N-rGO modified GC electrode is a good
candidate for the fabrication of stable and specific amperometric sensor for the nonenzymatic detection of H$_2$O$_2$.

The excellent performance of H$_2$O$_2$ sensor can be ascribed to the well distributed and high loading amount of Co$_3$O$_4$ nanoparticles.

**The performance of oxygen reduction reaction.** To evaluate the ORR catalytic activity of Co$_3$O$_4$/N-rGO, N-rGO and Co$_3$O$_4$/rGO, CV measurements were performed in both O$_2$ and N$_2$-saturated 0.1 M KOH solution. As shown in Fig. 6A, CV of N-rGO and Co$_3$O$_4$/rGO in the O$_2$-saturated electrolyte shows a reduction peak at $-0.34$ V and $-0.33$ V respectively, suggesting their electrochemical catalytic activity for ORR. As for Co$_3$O$_4$/N-rGO composite modified electrode, a reduction peak at ca. $-0.26$ V is observed, which is more positive than those of N-rGO and Co$_3$O$_4$/rGO while it also has a highest current density, suggesting a great improvement of catalytic activity, which is better than tri-functional carbon materials in previous study$^{32}$. Previous have reported that the electrocatalytic activity of Co$_3$O$_4$ was mainly affected by structure$^{46}$. Co$_3$O$_4$ particles have a spinel structure and the direct Co-Co interactions across shared octahedral edges of its spinel framework can enhance the electronic conductivity which is beneficial to the ORR catalytic activity. On the other hand, the N-graphene also exhibited a much better electrocatalytic activity, long-term operation stability for oxygen reduction reaction$^{22}$. Therefore, such an excellent electrocatalytic activity of the Co$_3$O$_4$/N-rGO toward ORR can be ascribed to the synergetic chemical coupling effects of Co$_3$O$_4$ and N-graphene$^{18,49,50}$.

To investigate the oxygen reduction mechanism of Co$_3$O$_4$/N-rGO modified GC electrodes, the ORR was studied by RRDE technique via measurement of the yield of the generated intermediate H$_2$O$_2$. The RRDE technique was applied to quantitatively determine the n value toward ORR and the H$_2$O$_2$ generation rate by setting the potential of the ring electrode at 0.4 V.

The electron transfer number n of ORR and HO$_2^-$ intermediate production percentage (HO$_2^-$ %) were determined as

$$n = \frac{4 \times I_d}{I_d + I_r/N}$$
where $I_d$ is the disk current, $I_r$ is the ring current, and $N$ is the current collection efficiency of the Pt ring, which was determined to be $0.4^{11,46}$. From the Fig. 6B, it was calculated $H_2O_2\%$ value for the $Co_3O_4/N-rGO$ during ORR process is about $63.5$–$32.2\%$ at potentials ranging from $-0.3$ to $-0.8$ $V$. The calculated $n$ value for the $Co_3O_4/N-rGO$ is about $2.9$ to $3.4$ from $-0.3$ to $-0.8$ $V$. These results reveal that the electrocatalytic process of $Co_3O_4/N-rGO$ is an improved four-electron pathway and a two-electron transfer pathway occurred simultaneously for ORR.

Methanol poisoning and stability are key issues challenging the cathode materials in current fuel cell techniques$^{51}$. The effect of methanol poisoning and stability on the $Co_3O_4/N-rGO$ was investigated in Fig. 7A and B by current-time ($i$-$t$) chronoamperometry. As shown in Fig. 7A, when methanol was injected, a significant decrease (90.7\%) in current was observed for the Pt/C electrode, whereas only a slight decrease (13.3\%) was observed for the $Co_3O_4/N-rGO$, suggesting poor tolerance of Pt/C to methanol compared with the $Co_3O_4/N-rGO$ material. Figure 7 Bshows that the amperometric response of ORR on the $Co_3O_4/N-rGO$ which exhibits a very slow attenuation of relative current, after 2000 s i.e. a current loss of approximately 31.37\%. In contrast, the Pt/C reveals degraded stability with a current loss (39.58\%) after 2000 s, indicating the $Co_3O_4/N-rGO$ has a better stability than Pt/C.

**The catalytic property of oxygen evolution reaction.** Previous studies have reported $Co_3O_4$ particles deposited on stable supporting and conducting substrates can be used as effective electrode materials for both
the oxygen reduction (ORR) and evolution (OER) reactions via decreasing overpotential in fuel cells and water electrolyzers.\textsuperscript{17,52} The good catalytic performance of OER can be ascribed to the small crystalline size and the mixed valences Co\(^{2+}\) and Co\(^{3+}\) of Co\(_3\)O\(_4\) as well as with conductive support substrates. Sun and his groups synthesize Co\(_3\)O\(_4\) nanorod–multiwalled carbon nanotube hybrid with a onset potential of about 0.47 V vs. Ag/AgCl and Tafel slope of 65 mV/dec. In our work, a rotational disk electrode (RDE) tests were also carried out in alkaline solution to further evaluate the OER catalytic activity of the Co\(_3\)O\(_4\)/N-rGO. Figure 8A showed the typical linear sweep voltammograms using the RDE at an electrode rotating speed of 1600 rpm and a potential scanning rate of 5 mV s\(^{-1}\). From the OER region, the Co\(_3\)O\(_4\)/N-rGO afforded a sharp onset potential at 1.54 V, which is worse than that of RuO\(_2\) at 1.49 V and better than Pt/C. The OER overpotential at current density of 10 mA cm\(^{-2}\) is close to that of RuO\(_2\), indicating the Co\(_3\)O\(_4\)/N-rGO has a good OER property. The Tafel slope is usually used to study the catalytic mechanism of electrocatalysis for OER. In Fig. 8B, The Tafel slope comparison showed that Co\(_3\)O\(_4\)/N-rGO has Tafel slope of 204 mV/dec which is much smaller than those for Pt/C (308 mV/dec) and is bigger than RuO\(_2\) (63 mV/dec), suggesting Co\(_3\)O\(_4\)/N-rGO has an improved performance of OER.

Conclusions

In summary, this study describes a facile and effective route to synthesize hybrid material consisting of Co\(_3\)O\(_4\) nanoparticles anchored on nitrogen-doped reduced graphene oxide (Co\(_3\)O\(_4\)/N-rGO) as a high-performance tri-functional catalyst for ORR, OER and H\(_2\)O\(_2\) sensing. Owing to the synergetic chemical coupling effects between Co\(_3\)O\(_4\) and graphene, the Co\(_3\)O\(_4\)/N-rGO exhibited excellent electrocatalytic activity with a direct reduction to H\(_2\)O\(_2\) at –0.6 V and sensing ability towards H\(_2\)O\(_2\). Although Co\(_3\)O\(_4\)/rGO or N-rGO alone has little catalytic activity, the Co\(_3\)O\(_4\)/N-rGO exhibits high ORR activity with ORR peak potential to be –0.26 V (vs. Ag/AgCl) and the number of electron transfer number is 3.4, excellent tolerance to methanol crossover and exceptionally good stability to Pt/C (20%) in alkaline solutions. Catalytic studies of Co\(_3\)O\(_4\)/N-rGO for OER display a better onset potential, overpotential under the current density of 10 mA cm\(^{-2}\) and a smaller Tafel slope with Pt/C (20%). Due to the ease of synthesis and electrode fabrication, the method developed by this study could be used for large-scale synthesis of non-precious metal-based trifunctional metal catalyst for hydrogen peroxide reduction, ORR and OER.

Experimental

Chemicals and materials. Nafion perfluorinated resin solution (5 wt% in a mixture of lower aliphatic alcohols and water) and commercial platinum/carbon (Pt/C) 20 wt% (Pt loading: 20 wt%, Pt on carbon black) were obtained from Sigma-Aldrich. All other chemicals (analytical grade) were purchased from Beijing Chemical Reagent Company (Beijing, China) and used without further purification. Ultra-pure water was obtained with a Milli-Q plus water purification system (Milli-pore Co. Ltd., USA).

Materials characterization. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-2600 N scanning electron microscope. Elemental analysis data were obtained through Flash EA 1112. The X-ray photoelectron spectra (XPS) spectra were obtained using a VG Micro-tech ESCA 2000 using a monochromatic 15 Al X-ray source. For rotating ring–disk electrode (RRDE) measurements, a bipotentiostat (CHI 832, Shanghai Chenhua Instrument Co. Ltd.) and a rotating ring–disk electrode with a rotating GC disk electrode and a platinum ring electrode (ALS RRDE-2) were used. The collection efficiency of the ring–disk electrode was evaluated with the Fe(CN)\(_6^{3-}/4^-\) redox couple and was calculated to be 0.4. Electrochemical measurements were performed with a computer-controlled Electrochemical analyzer (CHI600E, Chenhua, China) in a two-compartment electrochemical cell with as-prepared material modified on a glassy carbon electrode (3 mm in diameter) as working electrode, a platinum wire as counter electrode, and a Ag/AgCl (3 M KCl) electrode as reference electrode. All electrochemical experiments were performed at room temperature.

Figure 8. (A) The OER polarization curves of Co\(_3\)O\(_4\)/N-rGO catalyst and commercial Pt/C (20%) at a sweep rate of 5 mV s\(^{-1}\) using RDE with a rotation speed of 1600 rpm and (B) corresponding Tafel plots.
Preparation of Co$_3$O$_4$/N-rGO, N-rGO and Co$_3$O$_4$/rGO materials. 16.5 mg oxidized graphene oxide (GO) were redispersed in 50 mL anhydrous ethanol to form GO anhydrous ethanol suspension with concentration to be 0.33 mg/mL. The first step to prepare Co$_3$O$_4$/N-rGO was performed by adding 3.6 mL of 0.2 M Co(AC)$_2$ aqueous solution to 72 mL of GO anhydrous ethanol suspension, followed by the addition of 1.8 mL of NH$_4$OH (30% solution) and 2.1 mL of water, consequently. The reaction was kept at 80 °C with stirring for 10 h. After that, the reaction mixture from the first step was transferred to a 100 mL autoclave for hydrothermal reaction at 180 °C for 12 h. Co$_3$O$_4$/GO hybrid was made by the same steps without adding NH$_4$OH (30% solution) in the first step. N-rGO hybrid was also made by the same steps just as making Co$_3$O$_4$/N-rGO preparation without adding Co(AC)$_2$ aqueous solution.

The fabrication of as-prepared materials modified electrodes.

A rotating ring-disk electrode (RRDE) with a rotating glassy carbon (GC) disk electrode (4 mm diameter) and a platinum ring electrode (ALS RRDE-2), and a GC electrode with a diameter of 3 mm working electrode were used as working electrode in this study. Prior to the surface modification, the electrode were polished with 1.0, 0.3, and 0.05 μm alumina slurries, and finally rinsed with Milli-Q water under an ultrasonic bath for 1 min. A Co$_3$O$_4$/N-rGO modified GC electrode was prepared by casting the 4 μL of 2 mg/mL Co$_3$O$_4$/N-rGO suspension on the disk electrode surface and drying in air to evaporate the solvent. Similarly, 4 μL of 2 mg/mL N-rGO solution and 4 μL of 2 mg/mL Co$_3$O$_4$/GO suspension were dropped on GC electrodes, respectively and dried in air to evaporate the solvent for control experiment. Finally, 5 μL nafion (0.5%) solution (diluted 10 times with deionized water) was covered onto electrode surface and dried to form modified working electrode.

All of the electrochemistry experiments were performed at room temperature. The Co$_3$O$_4$/N-rGO modified GC electrode was pretreated by electrochemical oxidation in a phosphate buffered solution (pH = 6.8) at a potential of 1.7 V (vs. Ag/AgCl) for 300 s at room temperature, followed by potential sweeping from 0.0 V to 1.4 V in 0.5 M H$_2$SO$_4$ until a stable voltammogram was achieved, the purpose of electrochemical oxidation in phosphate buffered solution was to increase more oxygen containing functional group in carbon materials to increase the active site in oxygen reduction reaction. Some Co$_3$O$_4$ nanoparticles may dissolve in H$_2$SO$_4$ thus leaves on the surface and dried to form modified working electrode.

References

1. Jiang, H. et al. Iron Carbide Nanoparticles Encapsulated in Mesoporous Fe-N-Doped Graphene-Like Carbon Hybrids as Efficient Bifunctional Oxygen Electro catalysts. ACS Appl Mater Interfaces 7, 21511–21520 (2015).
2. Nishio, K. et al. Oxygen reduction and evolution reactions of air electrodes using a perovskite oxide as an electrocatalyst. Journal of Power Sources 278, 645–651 (2015).
3. Devoille, A. M. & Love, J. B. Double-pillared cobalt Pacman complexes: synthesis, structures and oxygen reduction catalysis. Dalton Trans 41, 65–72 (2012).
4. Kong, A. et al. From cage-in-cage MOF to N-doped and Co-nanoparticle-embedded carbon for oxygen reduction reaction. Dalton Trans 44, 6748–6754 (2015).
5. Daems, N., Sheng, X., Vankelecom, I. F. J. & Pescarmona, P. X. Metal-free doped carbon materials as electrocatalysts for the oxygen reduction reaction. Journal of Materials Chemistry A 2, 4085–4110 (2014).
6. Wang, Y. et al. One-step replication and enhanced catalytic activity for cathodic oxygen reduction of the mesostructured Co$_3$O$_4$/carbon composites. Dalton Trans 43, 4163–4168 (2014).
7. Wang, Y.-J., Wilkinson, D. P. & Zhang, J. Synthesis of conductive rutile-phased Nb0.06Ti0.94O2 and its supported Pt electrocatalysts (Pt/Nb0.06Ti0.94O2) for the oxygenreduction reaction. Dalton Trans 41, 1187–1194 (2012).
8. Chen, L. et al. One-step synthesis of sulfur doped graphene foam for oxygen reduction reactions. Dalton Trans 43, 3420–3423 (2014).
9. Wang, K., Liu, Q., Wu, X. Y., Guan, Q. M. & Li, H. N. Graphene enhanced electrochemiluminescence of CdS nanocrystal for H$_2$O$_2$ sensing. Talanta 82, 372–376 (2010).
10. Jia, L., Liu, J. & Wang, H. Preparation of poly(diallyldimethylammonium chloride)-functionalized graphene and its applications for H$_2$O$_2$ and glucose sensing. Electrochimica Acta 111, 411–418 (2013).
11. Wu, Q., Sheng, Q. & Zheng, J. Nonenzymatic amperometric sensing of hydrogen peroxide using a glassy carbon electrode modified with a sandwich-structured nanocomposite consisting of silver nanoparticles, Co$_3$O$_4$, and reduced graphene oxide. Microchimica Acta 183, 1943–1951 (2016).
12. Lin, Y., Li, L., Hu, L., Liu, K. & Xu, Y. Multifunctional poly(dopamine)-assisted synthesis of silver nano particles/carbon nanotubes nanocomposite: Toward electrochemical sensing of hydrogen peroxide with enhanced sensitivity. Sensors and Actuators B: Chemical 202, 527–533 (2014).
13. Li, X. et al. MOF derived Co$_3$O$_4$ nanoparticles embedded in N-doped mesoporous carbon layer/MWCNT hybrids: extraordinary bifunctional electrocatalysts for OER and ORR. J. Mater. Chem. A 3, 17392–17402 (2015).
14. Zhu, J. et al. Significantly enhanced oxygen reduction reaction performance of N-doped carbon by heterogeneous sulfur incorporation: synergistic effect between the two dopants in metal-free catalysts. J. Mater. Chem. A 4, 7422–7429 (2016).
15. Liu, H.-W. et al. Triplane passivation improved hot-carrier instability by zirconium-doping in hafnium oxide in a nanoscale n-metal-oxide semiconductor-field effect transistors with high-k/metal gate. Applied Physics Letters 108, 173504 (2016).
16. Aijaz, A. et al. Co@Co$_3$O$_4$ Encapsulated in Carbon Nanotube-Grafted Nitrogen-Doped Carbon Polyhedra as an Advanced Bifunctional Oxygen Electrode. Angew Chem Int Ed Engl 55, 4087–4091 (2016).
17. Xu, L. et al. Plasma-Engraved Co$_3$O$_4$ Nanosheets with Oxygen Vacancies and High Surface Area for the Oxygen Evolution Reaction. Angew Chem Int Ed Engl 55, 5277–5281 (2016).
18. Liu, S., Li, L., Ahn, H. S. & Manthiram, A. Delineating the roles of Co$_3$O$_4$ and N-doped carbon nanoweb (CNW) in bifunctional Co$_3$O$_4$/CNW catalysts for oxygen reduction and oxygen evolution reactions. Journal of Materials Chemistry A 3, 11615–11623 (2015).
19. Yeo, B. S. & Bell, A. T. Enhanced activity of gold-supported cobalt oxide for the electrochemical evolution of oxygen. J. Am Chem Soc 133, 5587–5593 (2011).
This work was financially supported by National Natural Science Foundation (21575090), Beijing Municipal Natural Science Foundation (2162009), Scientific Research Project of Beijing Educational Committee (KM201410028006), Youth Talent Project of the Beijing Municipal Commission of Education (CIT&TD201504072), Scientific Research Base Development Program of the Beijing Municipal Commission of Education.
Author Contributions
T.Z. and Y.D. contributed to the experimental, data interpretation and wrote the manuscript. Y.L. conceived the study and experimental design. C.H. and F.S. contributed to the statistical analysis. M.W., L.P. and J.W. contributed to catalyst synthesis. All authors reviewed and approved of the final version of the manuscript.

Additional Information
Competing Interests: The authors declare no competing financial interests.

How to cite this article: Zhang, T. et al. Co3O4 nanoparticles anchored on nitrogen-doped reduced graphene oxide as a multifunctional catalyst for H2O2 reduction, oxygen reduction and evolution reaction. Sci. Rep. 7, 43638; doi: 10.1038/srep43638 (2017).

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/

© The Author(s) 2017