In-Situ Formation of Cobalt-Phosphate Oxygen-Evolving Complex-Anchored Reduced Graphene Oxide Nanosheets for Oxygen Reduction Reaction

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Oxygen conversion process between O₂ and H₂O by means of electrochemistry or photochemistry has lately received a great deal of attention. Cobalt-phosphate (Co-Pi) catalyst is a new type of cost-effective artificial oxygen-evolving complex (OEC) with amorphous features during photosynthesis. However, can such Co-Pi OEC also act as oxygen reduction reaction (ORR) catalyst in electrochemical processes? The question remains unanswered. Here for the first time we demonstrate that Co-Pi OEC does be rather active for the ORR. Particularly, Co-Pi OEC anchoring on reduced graphite oxide (rGO) nanosheet is shown to possess dramatically improved electrocatalytic activities. Differing from the generally accepted role of rGO as an "electron reservoir", we suggest that rGO serves as "peroxide cleaner" in enhancing the electrocatalytic behaviors. The present study may bridge the gap between photochemistry and electrochemistry towards oxygen conversion.
combining with support of reduced graphite oxide (rGO) nanosheet. A series of hybrid materials for use as ORR catalysts with high activity and stability has been synthesized, such as Co$_3$O$_4$/rGO$^{14,15}$, Co$_{1.8}$/rGO$^{16}$, MnCo$_2$O$_4$/rGO$^{17}$, FePt/rGO$^{18}$, MoS$_2$/rGO$^{19}$. The enhanced catalytic performance was attributed to the synergetic effect in catalyst/rGO support systems, where the interface boundary sites of catalyst/rGO support were believed to greatly influence the enhancement effect. Therefore, in our case, it is highly interesting to hybridize rGO nanosheet with Co-Pi to afford more efficient ORR catalysts (Figure 1). To this end, strong coupling of supported electrocatalysts to rGO is greatly needed$^{1+19}$, which can be obtained by in-situ electrodeposition technique. Herein, we report for the first time the in-situ synthesis of Co-Pi on rGO for ORR using an electrodeposition technique. The resulting Co-Pi anchored rGO nanosheet (rGO-Co-Pi) was found to be rather active for ORR in KOH solutions. The hybridization of rGO nanosheet leads to a clear enhancement in the electron-transfer kinetics of oxygen reduction especially at higher rotation rates. Furthermore, the present study provides us with a mechanism message on the novel role of rGO nanosheet for ORR as "peroxide cleaner", which is quite different from the widely accepted role as "electron reservoir".

**Results**

Co-Pi nanoparticles were electrodeposited potentiostatically onto the rGO nanosheet surface by placing a rGO nanosheet modified glassy carbon electrode into a 0.1 M potassium phosphate solution (pH 7) containing 0.5 mM CoCl$_2$ in a three-electrode electrochemical cell$^{7–12}$. For a comparison, sole electrodeposited Co-Pi layers were also synthesized on glassy carbon electrode in the same way in the absence of rGO. The resulting rGO-Co-Pi product was characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). Figures 2a and 2b show the representative SEM images of the as-prepared rGO-Co-Pi, disclosing that the rGO nanosheets are uniformly decorated with the electrochemically deposited Co-Pi nanoparticles with featureless shapes to form a spotted fabric-like structure. The observed sizes of Co-Pi nanoparticles in Figures 2a, b are about 50–200 nm. Using EDX analysis, it was found that C from rGO nanosheet, and Co, P, O, K from Co-Pi OEC are the principal elemental components (Figure 2c). The Co-Pi composition is consistent with the results obtained by other investigations$^{14}$. The recorded Cl signal could be due to the residual CoCl$_2$ physically bound to the surface of rGO nanosheet or Co-Pi. XPS was conducted to examine the compositions and element chemical states, and the full-scale spectrum is shown in Figure 2d, confirming the formation of rGO-Co-Pi hybrid. As illustrated in the high-resolution Co 2p and P 2p spectra, two peaks located at about 780.4 and 795.9 eV can be assigned to Co$^{2+}$ or Co$^{3+}$ bound to oxygen (Figure 2e), and the P 2p peak at 132.7 eV is consistent with phosphate (Figure 2f). The aforementioned characterizations point to that the resulted material contains similar Co-Pi structures found in previous studies$^{7–12}$.

The ORR catalytic activities of Co-Pi and rGO-Co-Pi were first evaluated through conventional three-electrode cyclic voltammetry (CV) in O$_2$ or N$_2$ saturated 0.1 M KOH aqueous solutions. Both Co-Pi and rGO-Co-Pi electrode materials show a substantial reduction process in the presence of O$_2$, whereas no obvious response was observed under N$_2$ (Figures 3a and 3b). The well-defined characteristic ORR peak for Co-Pi layer is centered at $–0.39$ V, while it shifts positively to around $–0.21$ V under the same condition upon hybridization with rGO nanosheets, indicating an easier ORR process on rGO-Co-Pi.

To further investigate the ORR performances, we carried out the linear sweep voltammetric (LSV) measurements on a rotating disk electrode (RDE) with sole Co-Pi layer and rGO-Co-Pi in an O$_2$-saturated 0.1 M KOH electrolyte solution (Figures 3c and 3d). At both lower rotating rate of 200 rpm and higher rotating rate of 1200 rpm, the onset potential for rGO-Co-Pi (ca. $–0.13$ V) is more positive that that for Co-Pi layer, which is at about $–0.27$ V, suggesting that the coupling with rGO nanosheets indeed leads to a significant enhancement in the catalysis for the ORR. The diffusion current density of rGO-Co-Pi is also notably stronger than that of sole Co-Pi layer over a large potential range ($–0.2––0.8$ V) with difference being widened at a higher rotating rate. Typical CV curves of the electrodes at other rotation rates also confirmed this tendency (vide post). Thus, it is clear that Co-Pi OEC can also work as electrocatalyst for ORR, with improved behaviors through forming hybrid with rGO nanosheets. Furthermore, the degree in enhancement of ORR activity is dependent on the rotational speed, which gives a clue to understanding the role of rGO nanosheet in ORR.

**Discussion**

To gain further insight into the ORR behaviors of Co-Pi and rGO-Co-Pi, the corresponding ORR kinetics were investigated, recording LSV curves at various rotation rates (Figures 4a and 4b). Compared with Co-Pi, rGO-Go-Pi gives more defined diffusion-controlled LSV waves. With increase in rotation rate, the limiting current density
Figure 2 | Characterization of rGO-Co-Pi. SEM images of spotted fabric-like rGO-Co-Pi obtained by direct electrodeposition technique at (a) low and (b) high magnification showing the uniform distribution of Co-Pi particles on rGO nanosheet; (c) EDX spectrum showing the elemental composition of the resultant rGO-Co-Pi; (d) XPS survey spectrum, (e) high resolution Co 2p and (d) P 2p spectrum for rGO-Co-Pi. Signals arising from rGO nanosheet and Co-Pi were mainly detected. The Cl signals are due to trace residual CoCl₂ on the surface.

Figure 3 | Electrochemical performance of Co-Pi and rGO-Co-Pi. CV curves of ORR on Co-Pi (a) and rGO-Co-Pi (b) in N₂- (solid) and O₂-saturated (dotted) 0.1 M KOH solutions at a scan rate of 20 mVs⁻¹. Cathodic peaks occur only in O₂-saturated solutions, and the peak position for rGO-Co-Pi hybrid is more positive, suggesting that rGO-Co-Pi more favors ORR. A weak peak marked with asterisk appears in the curve for rGO-Co-Pi, which is supposed to originate from Co-O. LSV curves at rotation speeds of 200 rpm (c) and 1200 rpm (d) for oxygen reduction in O₂-saturated 0.1 M KOH solutions. rGO-Co-Pi hybrid exhibits more positive onset potential and higher current density. Meanwhile, the difference in current density between the two electrodes is widened at a higher rotation speed.
also increases. Furthermore, the limiting current density of ORR on rGO-Co-Pi electrode is always higher than that on Co-Pi electrode at each rotation rate, suggesting better ORR activity on rGO-Co-Pi electrode. The transferred electron numbers per O\textsubscript{2} molecule involved in ORR at both Co-Pi and rGO-Co-Pi electrodes can be determined by Koutecky-Levich (K–L) equation as given below\textsuperscript{15–19}:

\[
\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B_0^{0.5}}
\]

Where \( j \) is the measured current density, \( j_k \) is the kinetic current, \( \omega \) is the electrode rotating rate. \( B \) could be determined from the slope of the K–L plots in Figures 4c and 4d based on the Levich equation:

\[
B = 0.2nF\text{Co}D_0^{2/3}\eta^{-1/6}
\]

Where \( n \) represents the transferred electron numbers per O\textsubscript{2} molecule, \( F \) is the Faraday constant (\( F = 96485 \text{ C mol}^{-1} \)), \( \text{Co} \) is the concentration of O\textsubscript{2} in the electrolyte (\( \text{Co} = 1.2 \times 10^{-6} \text{ mol cm}^{-3} \)), \( D_0 \) is the diffusion coefficient of O\textsubscript{2} (\( D_0 = 1.9 \times 10^{-5} \text{ cm}^{2} \text{s}^{-1} \)), and \( \eta \) is viscosity of electrolyte (\( \eta = 0.01 \text{ cm}^{2} \text{s}^{-1} \)). Using \( B \) factor, the numbers of electrons transferred associated with ORR for both Co-Pi and rGO-Co-Pi were calculated. As shown in Figure 4e,
the electron transfer number was found to be dependent on the potentials. The electron transfer numbers for Co-Pi layer from −0.5 V to −1.0 V were calculated to be between 1.79–1.92, thereby indicating that the ORR is dominated by a two-electron process under these voltages. However, the electron transfer numbers for rGO-Co-Pi are higher at 2.55–3.8 over the potential range, suggesting an oxygen reduction process with combined two-electron and four-electron reaction pathways. The higher electron transfer numbers indicate a more efficient ORR process over rGO-Co-Pi. In addition, the amount of the ORR reaction intermediate, peroxide, was determined using the current potential curves recorded at the disk and the ring at 1200 rpm in O2 saturated solution based on the equation 3: (Figure 4f).

\[ \text{H}_2\text{O}_2(\%) = 200 \times I_d / (N \times I_r + I_d) \]

Here \( I_d \) and \( I_r \) is the disk current and ring current, respectively, and \( N \) is the collection efficiency (0.37) of the ring electrode. The calculated peroxide yield is about 10% for rGO-Co-Pi hybrid over the range from −0.4 V to −1.0 V vs SCE, while it is beyond 50% for sole Co-Pi layer. These results further indicates that the rGO-Co-Pi is more favorable for ORR than the sole Co-Pi layer.

Very recently, rGO has been used as an effective support for certain nanoparticles such as FePt, Fe3O4 and Co3O4 to improve ORR catalytic activity and stability14-19. It has been reported that metal oxide/metal or rGO alone has little ORR catalytic activity, while the resulting strongly coupled hybrid exhibits much increased ORR activity than free metal oxide/metal, free rGO and even their physical mixture. In previous reports, the improved behavior was attributed to rGO working as an “electron reservoir” to trap electrons from electrocatalysts, and therefore charge transfer across the metal oxide/metal-rGO interface was supposed to be the main reason for the synergetic enhancement effect15. Based on our experimental results, we propose a different electrocatalytic mechanism where the role of rGO acts as a “peroxide cleaner” in our system. The average electron transfer number, 1.79–1.92 and 2.55–3.8 for Co-Pi and rGO-Co-Pi, respectively, suggests that 2-electron reduction pathway plays an important role in the reduction of oxygen for both the two materials. In this case, peroxide is the main reaction intermediate for the ORR, and its further reaction is an essential factor for the complete reduction of oxygen. When the rotation rate is low, the reaction rate and concentration of generated peroxide is low, and correspondingly rGO has a relatively less effect on ORR activities. The increase in rotation rate may result in speed up of the reaction and accumulation of the intermediate peroxide, and afterwards peroxide might be adsorbed to the surface of electrocatalysts, which probably blocks the active sites for further dissociating adsorption of oxygen. Therefore the removal speed of peroxide is a rate-limiting factor for the ORR. If the rGO could effectively catalyze the reduction of peroxide as a “peroxide cleaner”, the ORR activity would be largely enhanced20,21. A controlled experiment was performed to confirm the above inference on the role of rGO. Figure 5 shows CVs for rGO nanosheets in N2-saturated 0.1 M KOH (solid line) and 0.1 M KOH + 0.2 M H2O2 solution (dotted line). A broad, relatively large reduction peak was observed at about −0.32 V on the cathodic scan in KOH + H2O2 solution corresponding to the reduction of peroxide catalyzed by rGO nanosheets, while no such peak appears in KOH solution, which corroborates that the rGO nanosheets does play a role as “peroxide cleaner”.

In summary, we have described the first design of rGO-Co-Pi as efficient electrocatalysts for the ORR. As Co-Pi material is also an excellent oxygen-evolving complex during photosynthesis, this novel material can undergo two pairs of oxygen conversion process (electrochemical and photochemical) as a bifunctional catalyst. Compared to Co-Pi OEC, the rGO-Co-Pi exhibits much enhanced electrocatalytic activity for the ORR in O2-saturated KOH solution. The ORR activity enhancement induced by the addition of rGO shows dependence on the rotational speed. Possible mechanisms are proposed for the ORR reaction of rGO-Co-Pi hybrid, in which rGO nanosheets could play a role as “peroxide cleaner” to speed up the ORR rates. This work demonstrates that the rGO-Co-Pi may serve as a novel class of bifunctional catalyst material that is applicable to future optoelectronic integrated energy conversion devices. The present study may also bridge the gap between photochemistry and electrochemistry towards oxygen conversion.

**Methods**

**Synthesis of G-Co-Pi.** Co-Pi OEC nanoparticles were electrodeposited potentiostatically onto the reduced graphene oxide (rGO) surface via chronoamperometry technique by placing an rGO nanosheet-modified glassy carbon electrode under static conditions reported by Nocera et al14. A three-electrode cell was used with an rGO nanosheet-modified glassy carbon electrode as the working electrode. An SCE electrode and Pt foil were used as reference and counter electrode, respectively. 1.1 V was applied in a solution of 0.5 mM CoCl2 in 0.1 M KH2PO4 at pH 7. The amount of Co-Pi OEC nanoparticles deposited can be controlled by the deposition time, which ranged between 200 and 500 s. Current densities were typically about 0.05 to 1.5 mA cm−2 during deposition.

**Characterization.** Field emission scanning electron microscopy (FE-SEM) analysis was performed on a FEI Quanta 400 FEG field emission scanning electron microscope. Energy-dispersive X-ray spectra (EDS) were collected from an attached Apollo 40 SDD energy-dispersive spectrometer fixed on a FEI Quanta 400 FEG field emission scanning electron microscope. X-ray photoelectron spectra (XPS) were acquired on an X-ray photoelectron spectroscope (Thermo Escalab 250, a monochromatic Al Kα X-ray source). The binding energies obtained were corrected for specimen charging by referencing C 1 s to 284.4 eV. Electrochemical measurements were carried out on an electrochemical workstation (Autolab PEmstat 302N Auto 84082) using a conventional three-electrode test cell. A platinum wire was used as counter-electrode and saturated calomel electrode (SCE) as reference electrode. The geometric area of the working electrode is 0.2475 cm2. The Pt ring electrode was polarized at 0.50 V for oxidizing H2O2 intermediate.

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**Author contributions**

Z.G.Z. conceived the experiments, analyzed the results, and wrote the paper. Z.G.Z., J.Z., Y.Y.Y., H.L. and Y.Y.T. performed the experiments. D.W. and Q.W.L. helped with data analysis. All authors reviewed the paper.

**Additional information**

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