Co$_3$O$_4$ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction

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NATURE MATERIALS
DOI: 10.1038/NMAT3087
INTRODUCTION

❖ Catalysts for oxygen reduction and evolution reactions are at the heart of key renewable-energy technologies including fuel cells.

❖ The current bottleneck of fuel cells lies in the sluggish ORR on the cathode side.

Direct 4 e- reduction

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (acidic media)} \]

\[ O_2 + 4H^+ + 4e^- \rightarrow 4OH^- \text{ (basic media)} \]

Series 4 e- reduction

\[ O_2 + e^- \rightarrow O_2^- \]

\[ O_2^- + 2H^+ + e^- \rightarrow H_2O_2 \text{ (ACIDIC MEDIA)} \]

\[ H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \]

\[ O_2^- + H_2O + e^- \rightarrow HO_2^- + OH^- \]

\[ HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \text{ (BASIC MEDIA)} \]

❖ Pt or its alloys are the best known ORR catalysts.

❖ OER or water oxidation plays an important role in energy storage such as solar fuel synthesis.

❖ 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.
Manganese oxide was shown to be a bi-functional catalyst for ORR and OER.

It is highly challenging but desirable to develop efficient bi-functional catalysts for both ORR and OER, particularly for unitized regenerative fuel cells.

*In this report,*

Co$_3$O$_4$ 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.

**Method:**

Mildly oxidized GO (mGO): Hummers method.
Reduced mGO (rmGO): Hydrothermal reduction
N-rmGO: ammonia added during reduction

Co(OAc)$_2$ was used as precursor.
TEM images of Co$_3$O$_4$- N-rmGO (left) and Co$_3$O$_4$rmGO hybrid catalysts
XPS spectrum of Co$_3$O$_4$- N-rmGO hybrid catalysts
C K-edge XANES of N-rmGO (blue curve) and Co3O4=N-rmGO hybrid (red curve)
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 0.1M KOH (dash line).
CVs of Co$_3$O$_4$ nanocrystal, rmGO, N-rmGO, Co$_3$O$_4$/rmGO and Co$_3$O$_4$/N-rmGO on glassy carbon electrodes in oxygen (solid) or argon (dash) saturated 0.1 M KOH.
Rotating-disk CV of Co$_3$O$_4$- rmGO hybrid catalyst in O$_2$-saturated 0.1M KOH with a sweep rate of 5mV/s at different rotation rates
Rotating-disk CV of Co$_3$O$_4$- N-rmGO hybrid catalyst in O$_2$-saturated 0.1M KOH with a sweep rate of 5mV/s at different rotation rates.
Tafel plots of $\text{Co}_3\text{O}_4$-rmGO and $\text{Co}_3\text{O}_4$-N-rmGO hybrids derived by the mass-transport correction of corresponding RDE data.
Koutecky-Levich equation

\[
\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K}
\]

\[J_K = nFkC_0\]

\[B = 0.62nFC_0(D_o)^{2/3}\nu^{1/6}\]

\(J = \text{the measured current density}\)

\(J_K\) and \(J_L\) : kinetic- and diffusion-limiting current densities

\(C_0\) : bulk concentration of \(O_2\)

\(n\) : transferred electron number, \(F\) : Faraday constant

\(\nu\) : kinematic viscosity of the electrolyte

Mass-transport correction of RDE : 

\[J_K = \frac{J \times J_L}{(J_L - J)}\]
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.
ORR performance and stability of catalysts

Oxygen reduction polarization curves of $\text{Co}_3\text{O}_4$-rmGO, $\text{Co}_3\text{O}_4$-N-rmGO and a high quality commercial Pt/C catalyst dispersed in $\text{O}_2$-saturated 1M KOH and 6M KOH electrolytes.
Co$_3$O$_4$/graphene hybrid bi-functional catalyst for ORR and water oxidation (OER)

Oxygen evolution currents of Co$_3$O$_4$-N-rmGO hybrid, Co$_3$O$_4$-rmGO hybrid and Co$_3$O$_4$ nanocrystal loaded onto Ni foam

Tafel plots of OER currents
Co$_3$O$_4$/graphene hybrid catalyst is synthesized and shown to be one of the rare and highest performance bi-functional catalysts for ORR and water oxidation/OER.

Co$_3$O$_4$ or graphene oxide alone have little catalytic activity for ORR, their hybrid materials exhibit unexpected, surprisingly high ORR activities.

Synergistic coupling of nanomaterials opens up a brand new approach to advanced catalysts for energy conversion.