Co_3O_4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction

Yongye Liang, Yanguang Li, Hailiang Wang
Jigang Zhou, Jian Wang, Tom Regier and Hongjie Dai.

Department of Chemistry, Stanford University, Stanford, California 94305, USA
Canadian Light Source Inc., Saskatoon, Saskatchewan S7N 0X4, Canada

NATURE MATERIALS
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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- → $2H_2O$ (acidic media)

O_2 + 4H+ **+** 4e- → 4OH- (basic media)

Series 4 e- reduction

O_2 **+** e- → O_2-

O_2- **+** 2H+ **+** e- →H_2O_2(ACIDIC MEDIA)

H_2O_2 **+** 2H+ + 2e- → $2H_2O$

O_2- **+** H_2O **+** e- → HO_2- + OH-

HO_2- **+** H_2O **+** 2e- → 3OH- (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,

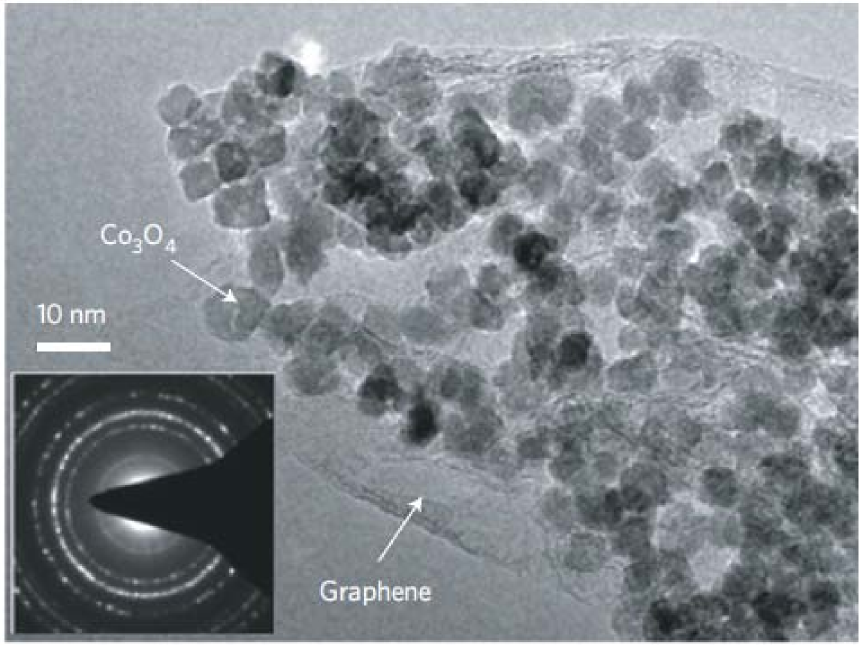
❖ **Co_3O_4 nanoparticles, a material with little ORR activity by itself, when grown on reduced mildly oxidized graphene oxide (rmGO) exhibits surprisingly high performance in both ORR and OER in alkaline solutions.**

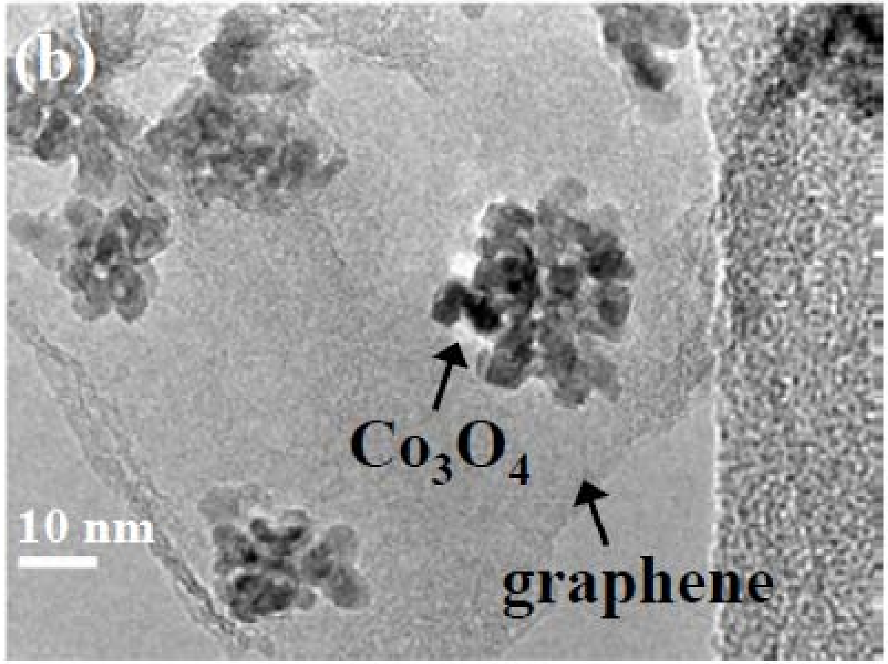
Method:

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

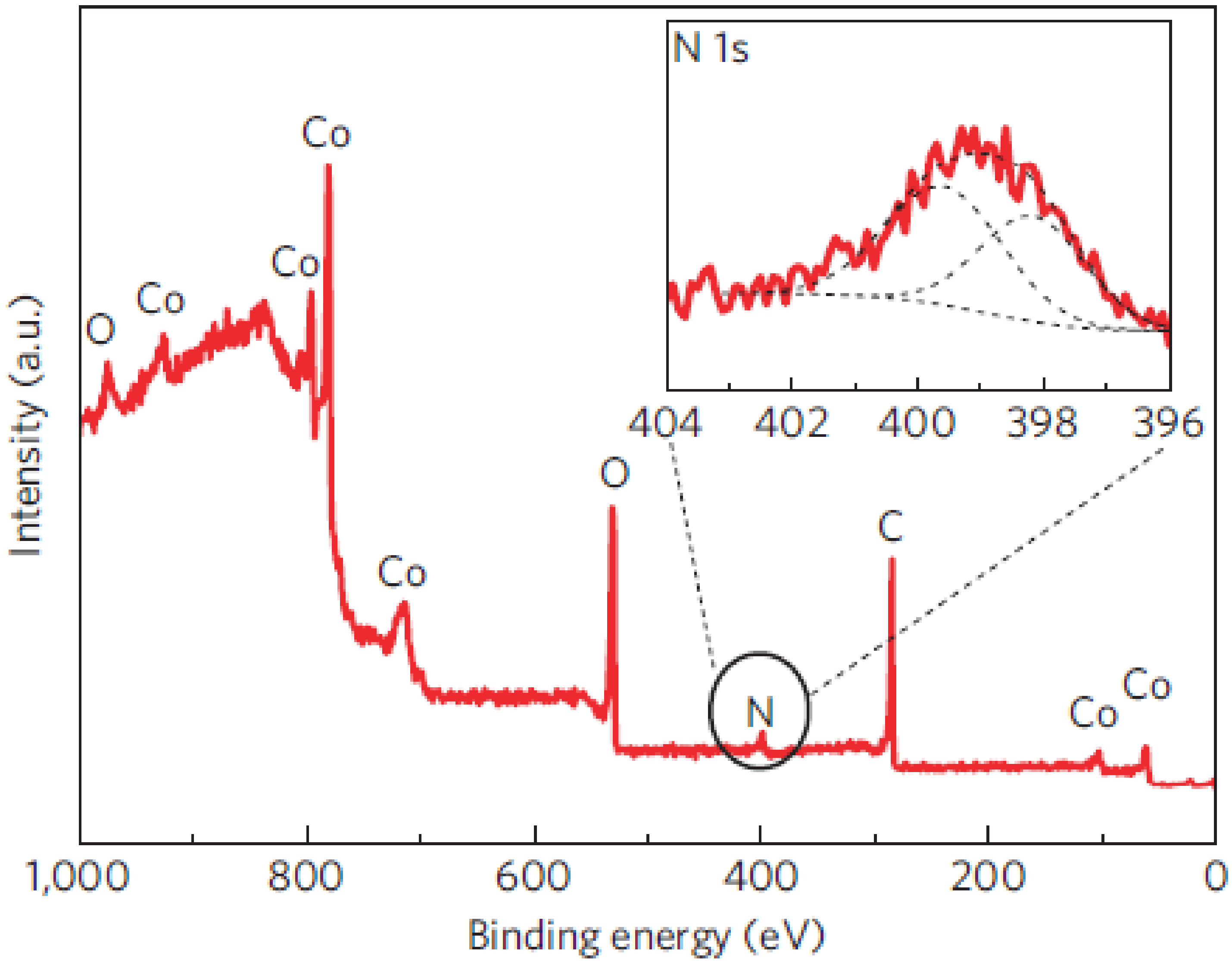
$Co(OAc)_2$ was used as precursor

TEM images of Co_3O_4- N-rmGO (left) and Co_3O_4rmGO hybrid catalysts

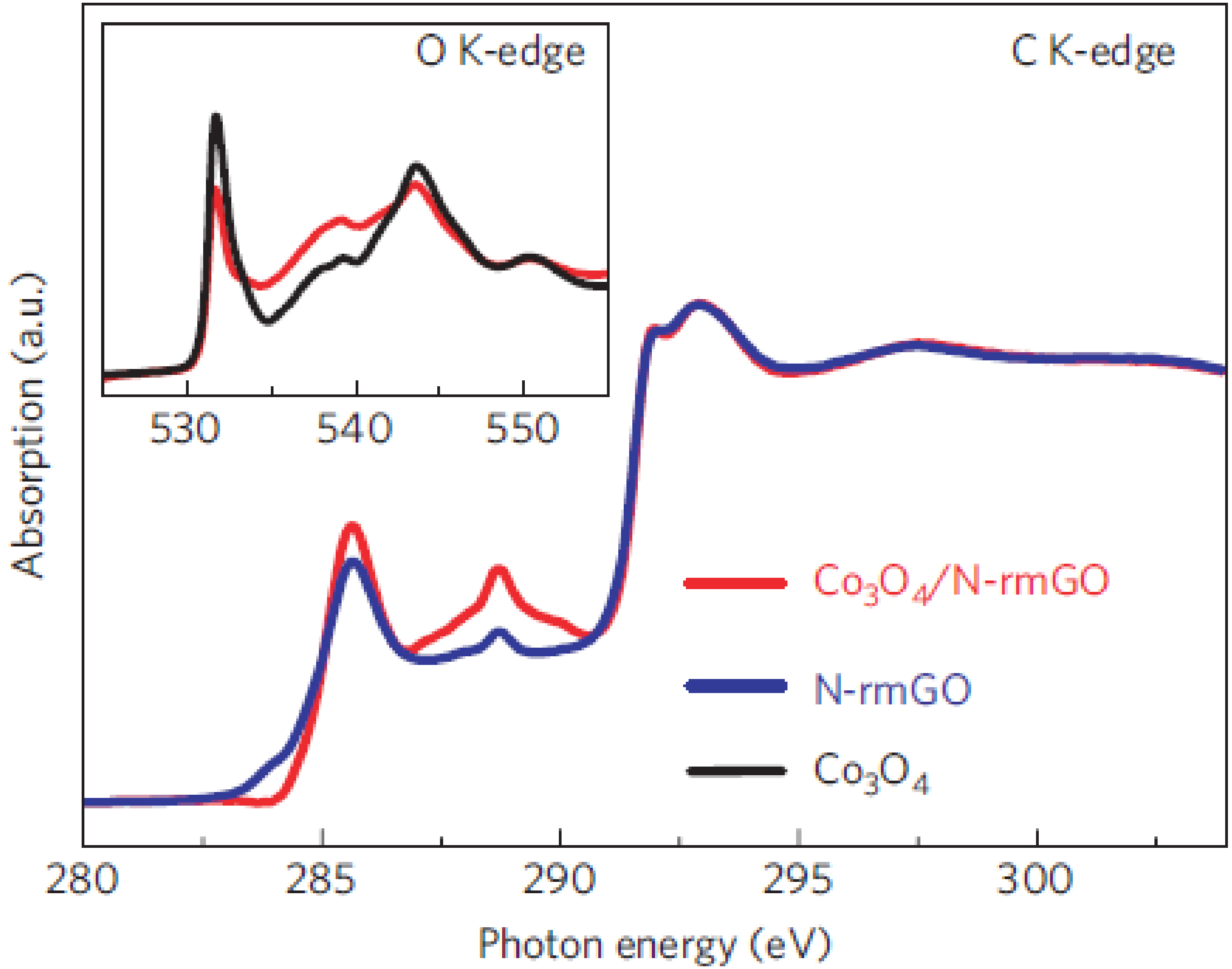




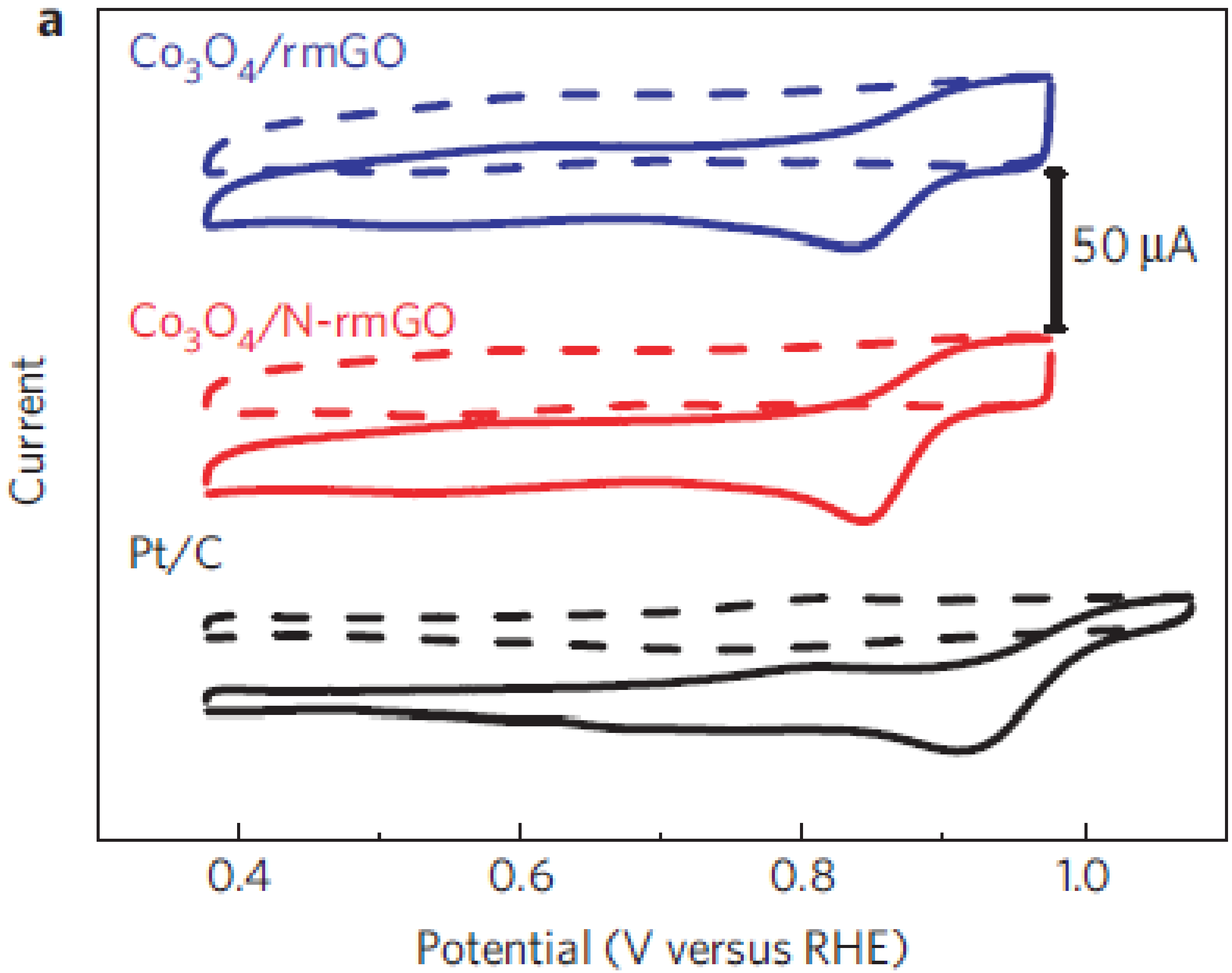
XPS spectrum of Co_3O_4- N-rmGO hybrid catalysts



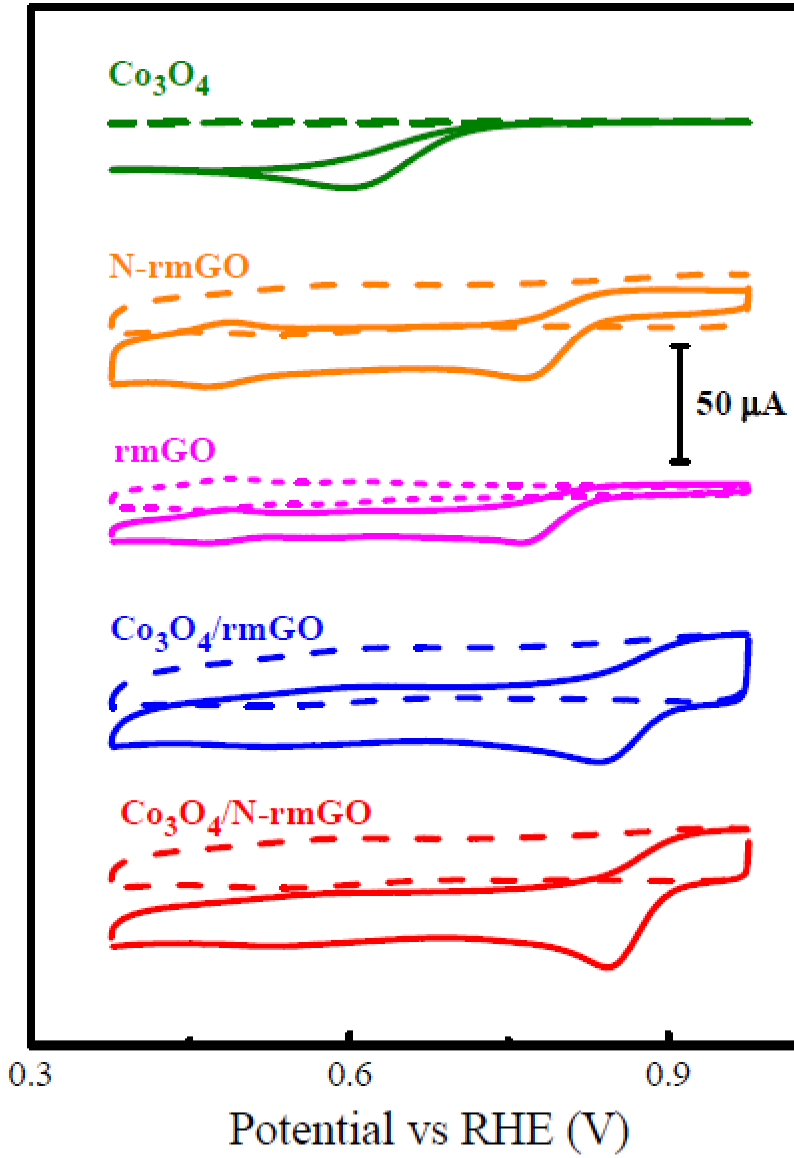
C K-edge XANES of N-rmGO (blue curve) and Co3O4=N-rmGO hybrid (red curve)



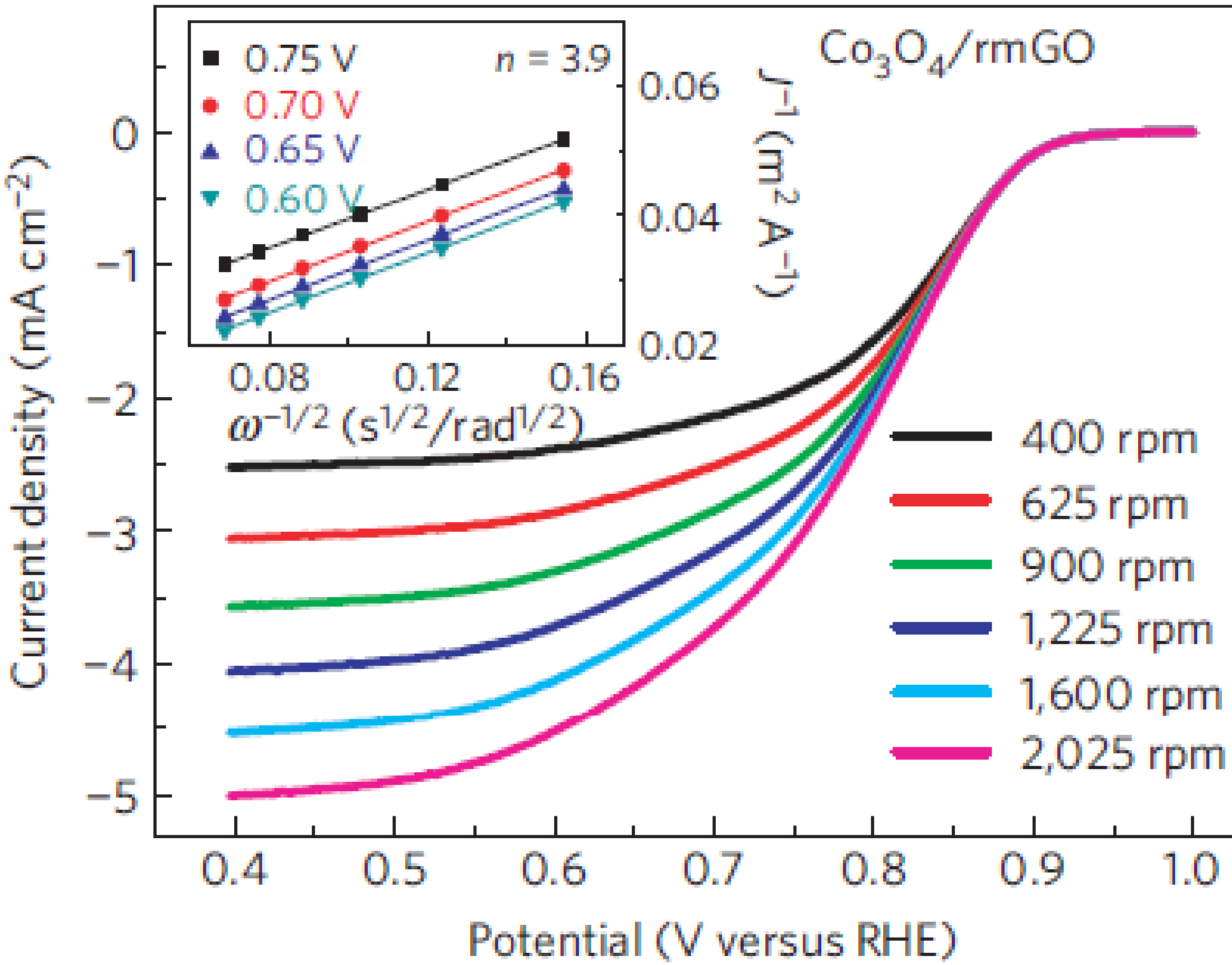
CV curves of Co_3O_4-rmGO hybrid, Co_3O_4-N-rmGO hybrid and Pt/C on glassy carbon electrodes in O_2-saturated (solid line) or Ar-saturated 0.1MKOH (dash line).



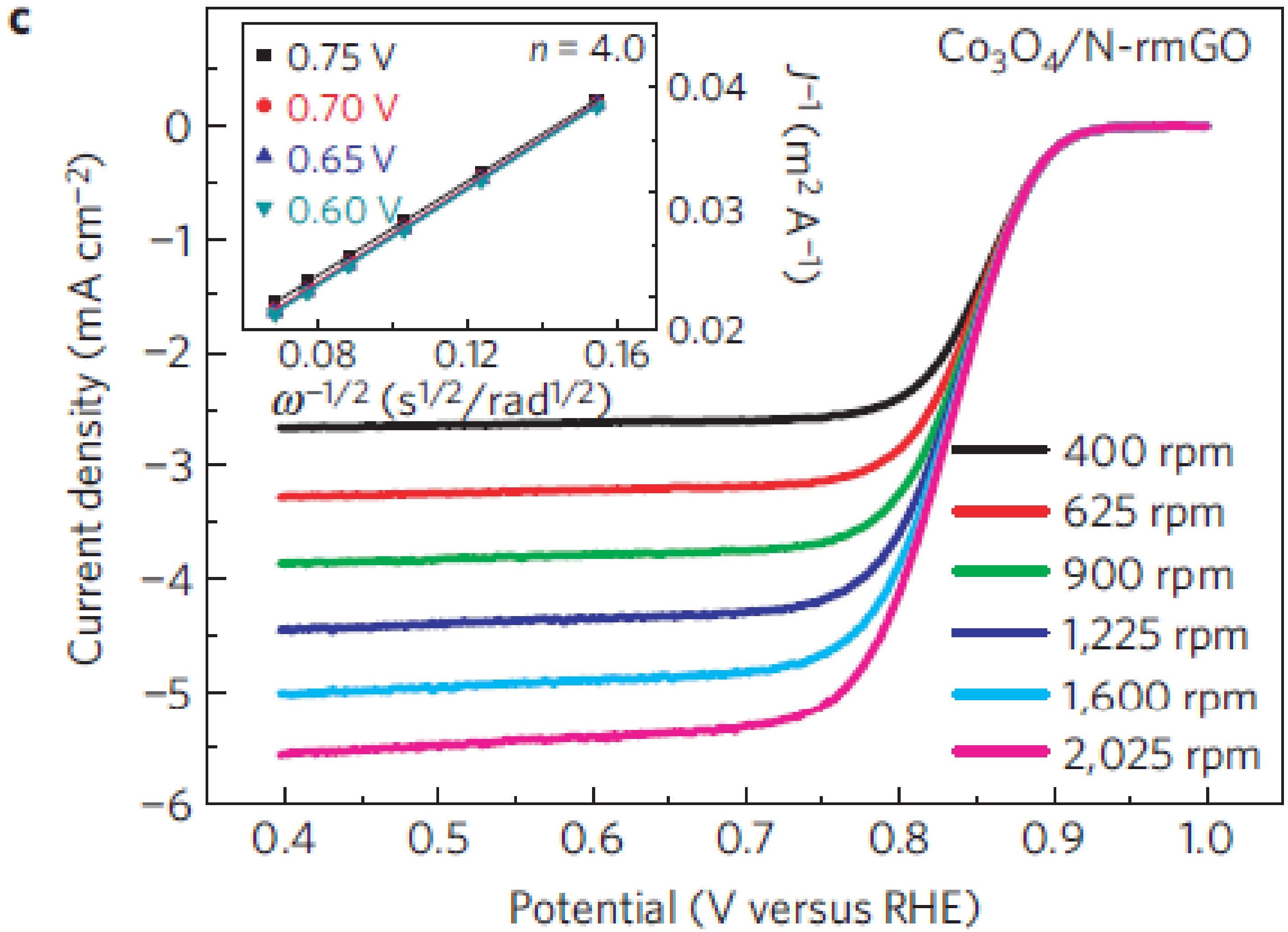
CVs of Co_3O_4 nanocrystal, rmGO, N-rmGO, Co_3O_4/rmGO and Co_3O_4/N-rmGO on glassy carbon electrodes in oxygen (solid) or argon (dash) saturated 0.1 M KOH.



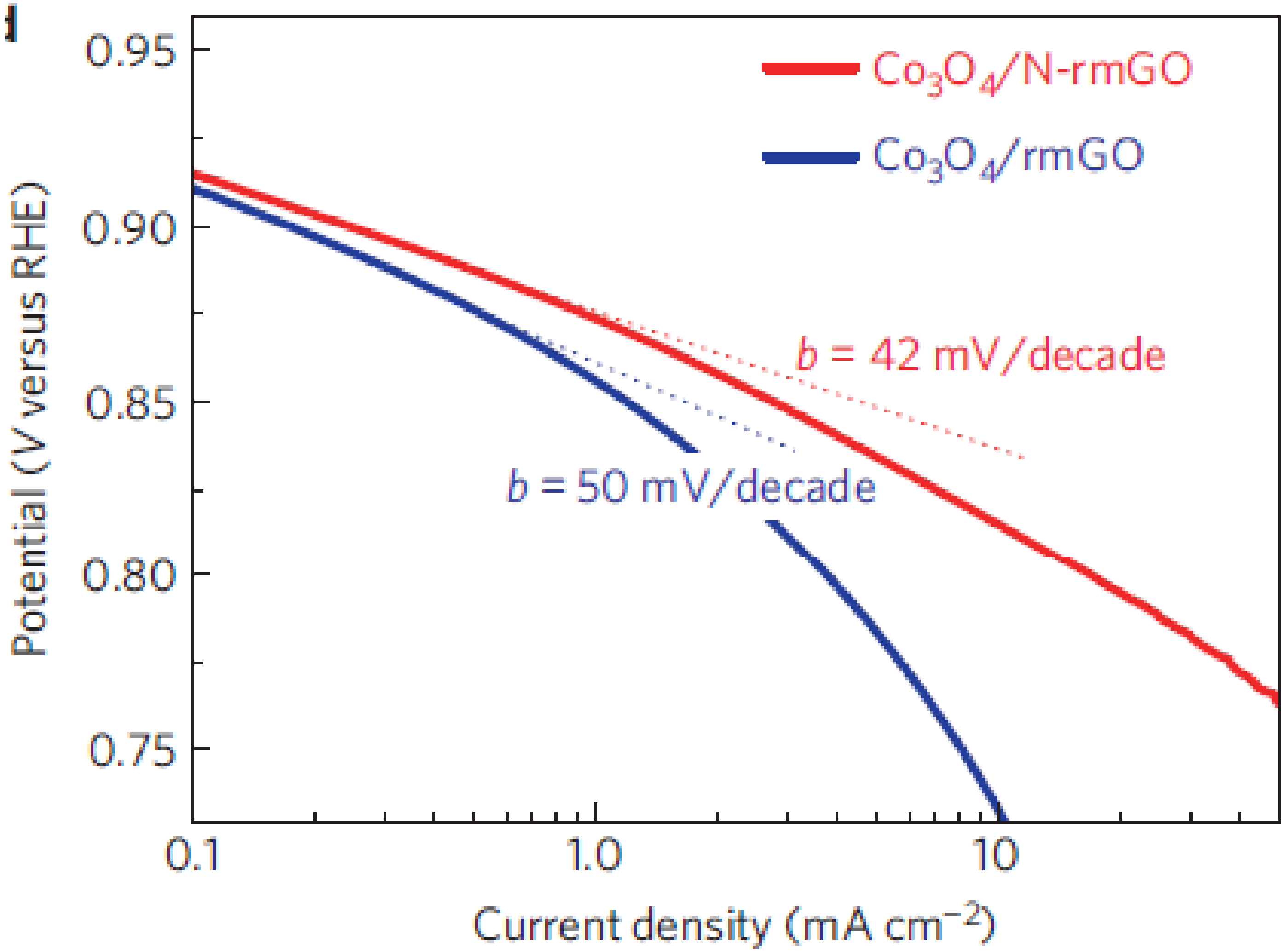
Rotating-disk CV of Co_3O_4- rmGO hybrid catalyst in O_2-saturated 0.1M KOH with a sweep rate of 5mV/s1 at different rotation rates



Rotating-disk CV of Co_3O_4- N-rmGO hybrid catalyst in O_2-saturated 0.1M KOH with a sweep rate of 5mV/s1 at different rotation rates



Tafel plots of Co_3O_4-rmGO and Co_3O_4-N-rmGO hybrids derived by the mass-transport correction of corresponding RDE data



Koutecky-Levich equation

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

$$J_K = nFkC_o$$

$$B = 0.62nFC_o(D_o)^{2/3}\nu^{-1/6}$$

J = the measured current density

JK and JL : kinetic- and diffusion-limiting current densities

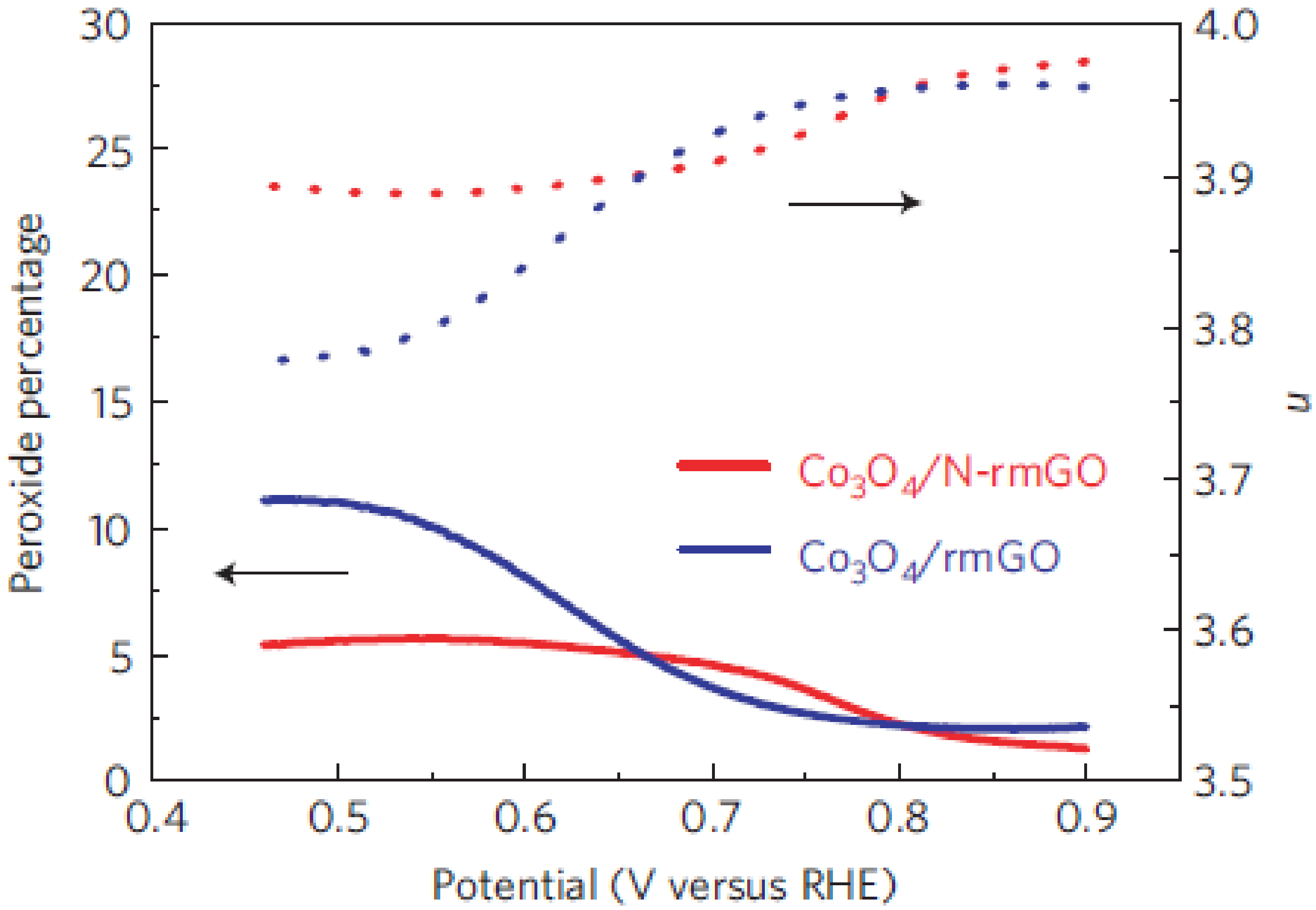
C_0 : bulk concentration of O_2

n : transferred electron number, F : Faraday constant

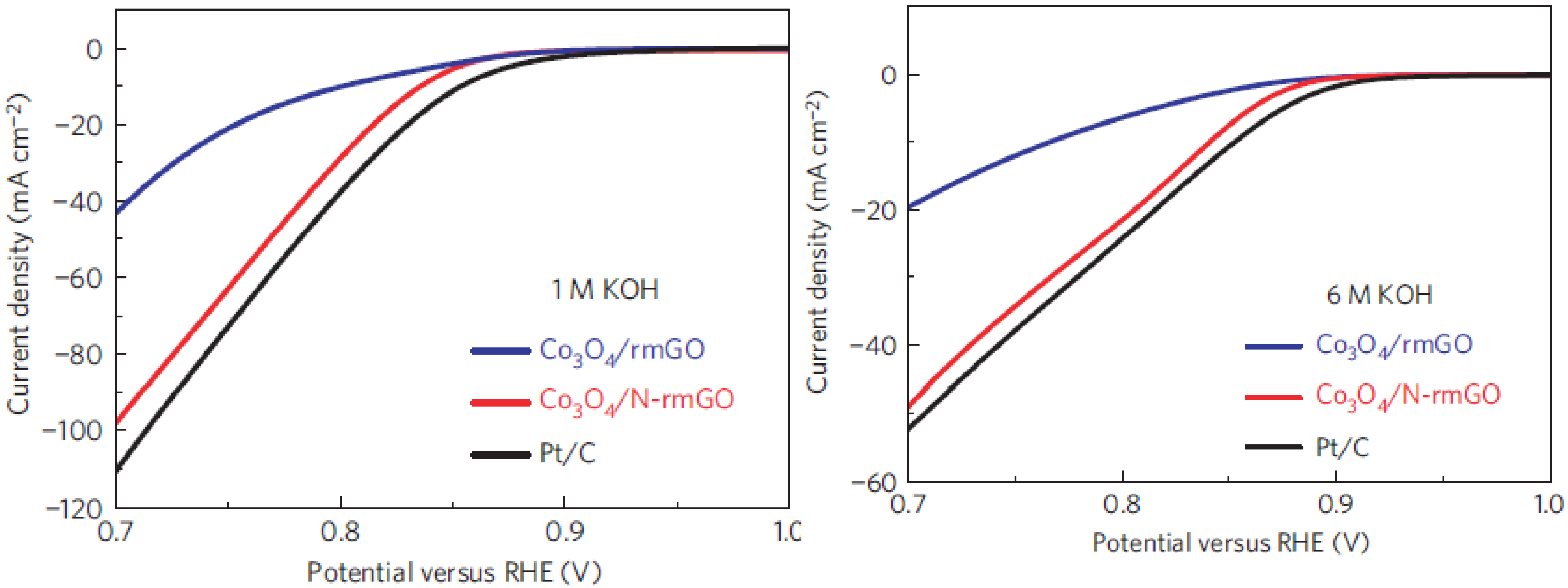
v : kinematic viscosity of the electrolyte

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_3O_4-rmGO and Co_3O_4-N-rmGO hybrids at various potentials, based on the corresponding RRDE data

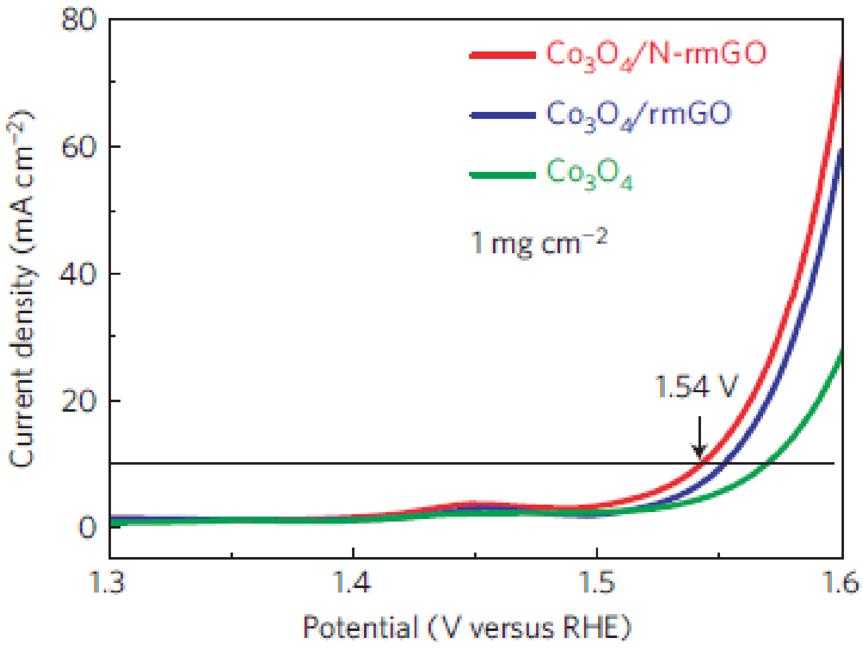


ORR performance and stability of catalysts

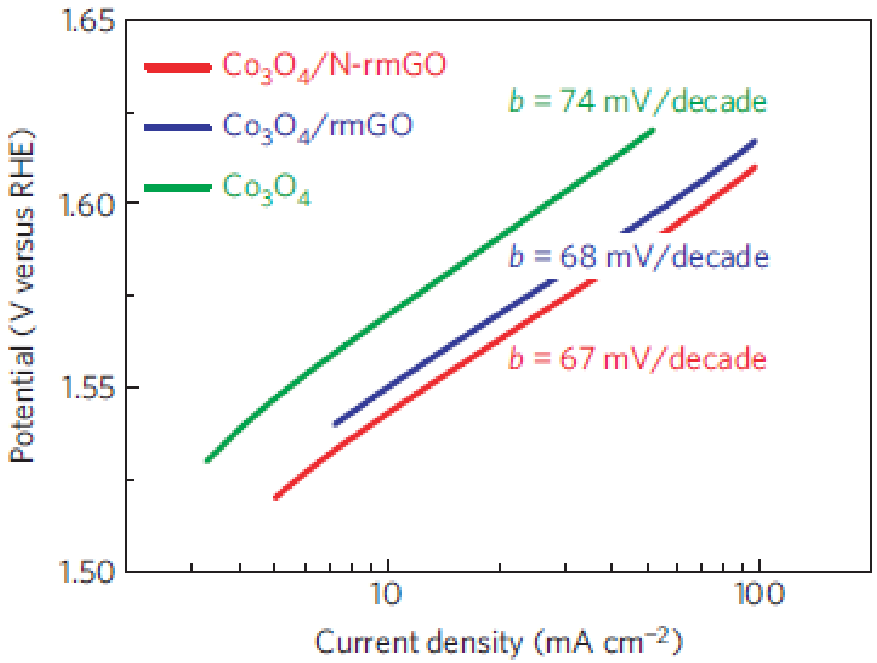


Oxygen reduction polarization curves of Co_3O_4-rmGO, Co_3O_4-N-rmGO and a high quality commercial Pt/C catalyst dispersed in O_2-saturated 1M KOH and 6M KOH electrolytes.

Co_3O_4/graphene hybrid bi-functional catalyst for ORR and water oxidation (OER)



Oxygen evolution currents of Co_3O_4-N-rmGO hybrid, Co_3O_4-rmGO hybrid and Co_3O_4 nanocrystal loaded onto Ni foam



Tafel plots of OER currents

CONCLUSIONS

- **Co_3O_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_3O_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.**