Promoting electrocatalytic oxygen reduction in a model composite using selective metal ions

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Supporting Information

List of Contents

S1: Material synthesis

S1.1: Synthesis of FePH Nanocomposite (FePO/PRGO)

S1.2: Synthesis of phosphorous doped reduced graphene oxide (PRGO)

S2. Computational details

S2.1 Theoretical models

S3: ORR performance of Co (II) ions on Phosphorous doped reduced graphene oxide (PRGO)

S4: Tafel plots of $\gamma\textsc{-NiFePH}$ and $\gamma\textsc{-MnFePH}$ catalysts

S5: RDE curves of the FePH on stoichiometric Ni (II) ions addition

S5.1: RDE curves of FePH on stoichiometric Mn (II) ions addition

S6: RDE curves of FePH and LSV comparison of different metal ions M (II) addition on FePH

S7: RDE curves of FePH on stoichiometric Co (II) ions addition

S8: SEM-EDX analysis of γ -CoFePH and δ -CoFePH.

S9: The K-L plots of FePH, γ-MnFePH, and γ-NiFePH

Table.S1: K-L plot parameters of FePH, γ-MnFePH, γ-NiFePH, and γ-CoFePH

S10: Methanol tolerance test of Pt/C

S11: TEM/HRTEM of catalyst γ -CoFePH after electrochemical stability measurement

Table.S2: Electrochemical ORR performance parameters of all the electrocatalysts

S12: The current-time (i-t) responses of FePH, γ-MnFePH, and γ-NiFePH

S13: XPS analysis of γ-CoFePH

S14: Transmission electron microscopy (TEM) image of γ-CoFePH

S14.1: SEM-EDX images of γ -CoFePH showing uniform distribution of nanoparticles throughout the PRGO sheet

S15: BET analysis of FePH and γ-CoFePH composite

Table.S3: Total energy and adsorption energy of all the systems

S1: Material synthesis.

S1.1 Synthesis of FePH nanocomposite (FePO,/PRGO).

The FePH Nanocomposite was synthesized by adding 60 mg of FeSO₄.7H₂O through vigorous stirring into 30 ml graphene oxide dispersion (1mg/mL) for 10 min, followed by dropwise addition of 1 ml orthophosphoric acid (3 M H₃PO₄). The reaction mixture was then stirred for 30 min and hydrothermally treated at 180°C for 12 h. The obtained hydrogel was lyophilised for 24 h and washed with distilled water repeatedly using Nylon membrane.

S1.2 Synthesis of phosphorous doped reduced graphene oxide (PRGO).

Synthesis of phosphorous doped reduced graphene oxide (PRGO) was carried out with the same procedure as mentioned in the previous section without adding FeSO₄.7H₂O in the GO dispersion.

S2. Computational details

All the calculations have been performed using density functional theory using Vienna abinitio simulation package (VASP) and all the energies are calculated with generalized gradient approximation (GGA) using Perdew-Burke Ernzerhof exchange-correlation functional.¹² The convergence threshold for energy is set at 10⁴ eV. Structures are optimized using selective dynamics as can be implemented in VASP. The supercell of planar graphene sheet of 98 atoms with dimensions a=17.08 Å, b=14.79 Å, and c=15 Å is used for the above calculation. The 15 Å length along the c crystallographic direction is the vacuum added to the graphene layer to avoid the interaction between the periodic layers of graphene. The supercell is tested for energy convergence and accordingly, the plane wave cut-off energy has been set to 550 eV with 7×7×1 gamma-centered K-mesh.

S2.1 Theoretical models

Adsorption of oxygen molecule on the layered two-dimensional p-doped graphene in the presence of iron phosphate and cobalt has been investigated using density functional theory.

We have constructed the theoretical model of slabs of PRGO for the adsorption of oxygen at different sites for ORR. Initially, a 2D layered graphene has been taken and oxygen is adsorbed on its surface as depicted in Figure. S1 (a) with the $E_{sat} = 51.79$ kcal/mol.³ For p-doped graphene, oxygen has been placed at two different sites, over carbon and phosphorus atoms and it was found that oxygen gets readily adsorbed on the phosphorus sites (Figure. S1b)



Figure. S1: Relaxed geometries of oxygen adsorption on (a) graphene surface and (b) p-doped graphene surface.

Different sites have been explored for the adsorption of oxygen on PRGO surfaces such as Coatom and Fe-atom of iron phosphate. Initially, the position and distance of the cobalt atom from the p-doped graphene surface are optimized. The oxygen molecule is now adsorbed on the cobalt atom as shown in Figure.S2.



Figure. S2: Optimized geometry of (a) cobalt atom on the p-doped graphene surface, (b) side views of oxygen adsorption on Co-atom placed on PRGO surface in two different orientations.

Further, iron phosphate is added to the already optimized PRGO with the cobalt adsorbate and again the geometry is relaxed (Figure. S3). The oxygen molecule is now adsorbed on both cobalt and iron atoms individually (Figure.S4).



Figure. S3: (a) Lateral and (b) top view of iron phosphate on cobalt attached p-doped graphene surface.



Figure. S4: Oxygen molecule adsorption at (a) Fe-atom and (b) Co-atom.

The oxygen molecule adsorption on Fe-site in FePO₄+PRGO system was also studied in the absence of Co atoms Figure. S5



Figure. S5: Oxygen molecule adsorption at Fe-atom in FePO₄ + PRGO system.

S3: ORR performance of Co (II) ions on Phosphorous doped reduced graphene oxide (PRGO).

An experiment was carried out where Co (II) ions were infused in metal-free PRGO ink, to study the independent role of Co (II) ions on ORR activity. A similar trend was observed, but the enhancement of ORR performance emerges from Co (II) ions is not great when compared to γ -CoFePH.



Figure. S6: (A) Linear sweep voltammogram (LSV) curve of PRGO at different rotations in O₂-saturated 0.1 M KOH (B) LSV comparison of Co (II) ions added PRGO with different concentrations at 1600 rpm: scan rate 10 mV s³.

(A) RRDE curve and electron transferred number in γ-CoPRGO.

The ring current detects the oxidation of peroxide ions generated as a by-product in the oxygen reduction reaction. The higher the ring current along with low disk current, the maximum n value obtained in this case is 3.18, the higher the possibility of occurring undesirable two-step ORR mechanism.⁴



Figure. S7: Ring and Disk curve of γ-CoPRGO at 1600 rpm in 0.1 M KOH (inset) describe the corresponding electron transfer number per O_imolecule.

S4: Tafel plots of γ-NiFePH and γ-MnFePH catalysts.

The Tafel analysis can be used to evaluate ORR kinetics and O₂-adsorption mechanism on the catalyst's surface.⁵ The Tafel plot was obtained using an equation is given below

$\eta = a + b \log (j)$

Where η is the overpotential, j is measured current density, a is a constant, and b is the Tafel slope expressed in mV/decade. The Tafel slope values of γ -MnFePH and γ -NiFePH at 1600 rpm were found to be 70 mV/dec and 76 mV/dec respectively.



Figure. S8: Tafel slope of γ -MnFePH and γ -NiFePH at 1600 rpm.

S5. RDE curves of FePH on stoichiometric Ni (II) ions addition.

The LSV curves at different rotation rates obtained after adding 0.001 (α), 0.002 (β) and 0.003 (γ) mmol of Ni (II) to the FePH nanocomposite and their comparison at 1600 rpm.



Figure. S9: Linear sweep voltammogram (LSV) curves recorded at different rotation rates (400 to 3000 rpm) (A) α (B) β (C) γ -NiFePH (D) LSV comparison at 1600 rpm in O, saturated 0.1 M KOH solution: scan rate 10 mV s³.

S5.1 RDE curves of FePH on stoichiometric Mn (II) ions addition.

The LSV curves at different rotation rates obtained after adding 0.001 (α), 0.002 (β) and 0.003 (γ) mmol of Mn (II) to the FePH nanocomposite and their comparison at 1600 rpm.



Figure. S10: Linear sweep voltammogram (LSV) curves recorded at different rotation rates (400 to 3000 rpm) (A) α (B) β (C) γ-MnFePH.(D) LSV comparison at 1600 rpm in O₂ saturated 0.1 M KOH solution: scan rate 10 mV s².

S6: RDE curves of FePH and LSV comparison of different metal ions M (II) addition on FePH.

The LSV curve of FePH nanocomposite at different rotation rates in 0.1 M KOH solution and LSV comparison after 0.003 (γ) mmol of M (II) (M= Ni, Mn, and Co) addition to FePH nanocomposite at 1600 rpm.



Figure. S11: (A) Linear sweep voltammogram (LSV) curves of FePH recorded at different rotations (400 to 3000 rpm) (B) LSV comparison at 1600 rpm of (M(II)) added FePH in O, saturated 0.1 M KOH solution: scan rate 10 mV s³.

S7: RDE curves of FePH on stoichiometric Co (II) ions addition.

The LSV curves at different rotation rates obtained after adding 0.001 (α), 0.002 (β) and 0.004 (δ) mmol of Co (II) to the FePH nanocomposite and their comparison at 1600 rpm.



Figure. S12: Linear sweep voltammogram (LSV) curves recorded at different rotations (400 to 3000 rpm) (A) α (B) β (C) δ -CoFePH (D) LSV comparison at 1600 rpm in O₂ saturated 0.1 M KOH solution: scan rate 10 mV s³.

S8: SEM-EDX analysis of γ -CoFePH and δ -CoFePH.

Unlike γ -CoFePH, SEM images of δ -CoFePH showing agglomerated Co which is not incorporated within the pores of FePH. Also, EDX spectra evidence the excess of Co (II) ions that are not getting into graphitic lattice rather gets agglomerated on the surface.







Figure. S13: (A) SEM image of γ -CoFePH and (B) δ -CoFePH and EDX-spectra of (C) γ -CoFePH and (D) δ -CoFePH

S9: The K-L plots of FePH, γ-MnFePH, and γ-NiFePH.

The K-L plot reflects a linear relationship between the inverse of obtained current density (j), kinetic current density (j_k) and the reciprocal of the square root of rotation speed. The smooth and linear fitting of the K-L plots indicate the first-order reaction kinetics towards the dissolved oxygen in electrolyte.⁶







Figure. S14: The K-L plots of (A) FePH (B) γ -MnFePH and (C) γ -NiFePH at different potentials.

Table. S1: K-L plot parameters of FePH, γ-MnFePH, γ-NiFePH, and γ-CoFePH.

(A) FePH

| Potential | Slope | Intercept | n | Jĸ |
|-----------|-------|-----------|------|-------|
| -0.40 V | 3.49 | 0.090 | 2.42 | 11.01 |
| -0.45 V | 3.33 | 0.0820 | 2.54 | 12.19 |
| -0.50 V | 3.16 | 0.0794 | 2.68 | 12.59 |
| -0.55 V | 2.79 | 0.0903 | 3.03 | 11.07 |
| -0.60 V | 2.73 | 0.077 | 3.10 | 12.98 |

(B) γ-MnFePH

| Potential | Slope | Intercept | n | J |
|-----------|-------|-----------|------|------|
| -0.40 V | 1.83 | 0.165 | 4.61 | 6.03 |
| -0.45 V | 1.87 | 0.158 | 4.52 | 6.32 |
| -0.50 V | 1.88 | 0.155 | 4.50 | 6.45 |
| -0.55 V | 1.90 | 0.150 | 4.45 | 6.66 |
| -0.60 V | 1.85 | 0.147 | 4.50 | 6.80 |

(C) **γ-NiFePH**

| Potential | Slope | Intercept | n | J |
|-----------|-------|-----------|------|-------|
| -0.40 V | 3.9 | 0.0864 | 2.17 | 11.57 |
| -0.45 V | 3.6 | 0.0955 | 2.35 | 10.47 |
| -0.50 V | 3.37 | 0.107 | 2.51 | 9.34 |
| -0.55 V | 3.06 | 0.1206 | 2.68 | 8.30 |
| -0.60 V | 2.81 | 0.1254 | 3.01 | 7.80 |

(C) γ-CoFePH

| Potential | Slope | Intercept | n | J |
|-----------|-------|-----------|------|-------|
| -0.40 V | 2.22 | 0.089 | 3.79 | 11.24 |
| -0.45 V | 2.20 | 0.082 | 3.85 | 12.19 |
| -0.50 V | 2.18 | 0.076 | 3.87 | 13.16 |
| -0.55 V | 2.10 | 0.076 | 4.02 | 13.16 |
| -0.60 V | 2.02 | 0.075 | 4.18 | 13.34 |

S10: Methanol tolerance test of Pt/C.

In Direct Methanol Fuel Cell (DMFC), methanol crossover takes place through proton exchange membrane which poison the ORR process and degrades its efficiency drastically, the phenomenon is commonly observed when Pt-based electrocatalysts are employed in the fuel cell.⁷



Figure. S15: CV curve of Pt/C before (Solid) and after adding 3M methanol (Dotted) to O₂-saturated 0.1 M KOH solution: scan rate 50 mV s⁴.

S11: TEM/HRTEM of catalyst γ-CoFePH after electrochemical stability measurement.

The electrocatalyst γ -CoFePH was recovered from the glassy carbon surface after 40,000 s of i-t chronoamperometric measurement. The TEM/HRTEM analysis shows retention of (103) facet of Fe_{1.176} (PO₄)(OH)_{0.57}(H₂O)_{0.43} with fringe width 0.33 nm demonstrating the structural durability of the catalyst.



Figure. S16: TEM/HRTEM image of γ -CoFePH after chronoamperometric (i-t) stability measurement of 40000 s.

| Electrocatalysts | E _{onset} , (V) Vs. | $\mathbf{E}_{_{1/2}}(\mathbf{V})$ Vs. | Limiting current density |
|------------------|------------------------------|---------------------------------------|-------------------------------------|
| | Ag/AgCl | Ag/AgCl (-3mA | (mAcm ²) at 1600 rpm (- |
| | | cm ²)at 1600 rpm | 0.90V) |
| PTC-20% | | -0.19 | -5.45 |
| FePH | -0.12 | -0.60 | -4.38 |
| α-СоFеРН | -0.10 | -0.32 | -5.29 |
| β-СоFеРН | -0.10 | -0.30 | -5.49 |
| ү-СоFеРН | -0.10 | -0.29 | -5.87 |
| δ-СоFеРН | -0.12 | -0.32 | -5.03 |
| α-MnFePH | -0.08 | -0.46 | -5.46 |
| β-MnFePH | -0.09 | -0.37 | -5.10 |
| γ-MnFePH | -0.09 | -0.30 | -5.46 |
| α-NiFePH | -0.13 | -0.64 | -4.86 |
| β-NiFePH | -0.13 | -0.63 | -4.70 |
| γ-NiFePH | -0.13 | -0.64 | -4.81 |

Table.S2: Electrochemical ORR performance parameters of all the electrocatalysts.

S12: The current-time (i-t) responses of FePH, γ-MnFePH, and γ-NiFePH.

The long term stability of the FePH, γ -MnFePH, and γ -NiFePH were evaluated using chronoamperometric measurements at -0.60 V with 1600 rpm under constant oxygen flow to the 0.1 M KOH electrolyte. The FePH retains 84.9 % of initial current density whereas, γ -MnFePH and γ -NiFePH retained only 52.7 and 73 % of the initial current density after 40,000 s of the measurements.



Figure. S17: The Current vs Time (Chrono-amperometric response) at -0.60 V of FePH, γ-MnFePH, and γ-NiFePH recorded with 1600 rpm under continuous oxygen flow.



Figure. S18: (A) Fe 2p and (B) Co 2p spectrum of γ -CoFePH

S14: Transmission electron microscopy (TEM) image of γ-CoFePH.

S17



Figure. S19: The TEM image of γ -CoFePH

S14.1: SEM-EDX images of γ -CoFePH showing uniform distribution of nanoparticles throughout the PRGO sheet.



Figure. S20: (A) The SEM image of γ -CoFePH and Elemental mapping of (B) carbon (C) Iron (D) oxygen (E) cobalt and (F) phosphorous contents

S15: BET analysis of FePH and γ-CoFePH composite

For BET isotherm, FePH and γ-CoFePH were degassed at 150 ° C for 6 h before analysis. The pore-size distribution was determined by applying 52the BJH model.



Figure. S21: Nitrogen adsorption-desorption of isotherm of (A) FePH and (B) γ -CoFePH with inset showing the pore size distribution of respective catalysts.

| Surface | Total Energy (eV) | Adsorption energy (eV) |
|------------------------------------|-------------------|------------------------|
| Graphene | -910.82 | 2.25 |
| (O ₂ on C-site) | | |
| PRGO | -906.70 | -1.96 |
| $(O_2 \text{ on } P\text{-site})$ | | |
| PRGO + Co | -908.51 | -1.69 |
| (O ₂ on Co-site) | | |
| PRGO + Co + FePO ₄ | -1058.57 | 0.88 |
| (O ₂ ontop of Fe-site) | | |
| PRGO + Co + FePO ₄ | -1061.31 | -1.85 |
| (O ₂ on top of Co-site) | | |
| FePO ₄ + PRGO | -1056.30 | +1.18 |
| (O ₂ on top of Fe-site) | | |
| 0. | -9.87 | |
| Со | -7.11 | |
| RGO | -903.20 | |
| PRGO | -894.87 | |
| PRGO + Co | -896.94 | |
| PRGO + Co + FePO ₄ | -1049.59 | |
| PRGO + FePO4 | -1047.62 | |
| | | |

Table.S3: Total energy and adsorption energy of all the systems.

References;

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