## **Electronic Supplementary Information**

Cobalt phosphate nanoparticles decorated with nitrogen-doped carbon layers as highly active and stable electrocatalysts for oxygen

## evolution reaction

Cheng-Zong Yuan, Yi-Fan Jiang, Zhou Wang, Xiao Xie, Zheng-Kun Yang, Ammar Bin Yousaf and An-Wu Xu\*

Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China.

\*To whom correspondence should be addressed. Email: <u>anwuxu@ustc.edu.cn</u>

**Table S1.** OER performance of noble metal-free electrocatalysts in alkaline media.

Catalyst	Overpotential (mV) (@10 mA cm <sup>-2</sup> )	Tafel slope (mV/dec)	Electrolyte (KOH)	Ref.
Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> @N-C	317	62	1 M	This work.
Co <sub>3</sub> O <sub>4</sub> -NA/Cu foil	290	70	0.1 M	J.Am.Chem.Soc., 2014, <b>136</b> , 1392. <sup>1</sup>
Ni-Co LDH/CP	367	40	1 M	Nano Lett., 2015, <b>15</b> , 1421. <sup>2</sup>
Mn <sub>3</sub> O <sub>4</sub> /CoSe <sub>2</sub>	450	49	1 M	J.Am.Chem.Soc., 2012, <b>14</b> , 2930. <sup>3</sup>
Fe-mCo <sub>3</sub> O <sub>4</sub>	380	40	1 M	Chem.Commun., 2014, <b>50</b> , 10122. <sup>4</sup>
Co-P film	345	47	1 M	Angew.Chem.Int.Ed. , 2015, <b>54</b> , 6251. <sup>5</sup>
Co <sub>x</sub> O <sub>y</sub> /NC	430	74.8	0.1 M	Angew.Chem.Int.Ed. , 2014, <b>53</b> , 8508. <sup>6</sup>



**Fig. S1.** (a) XRD patterns of the precursor of  $Co_3(PO_4)_2$ @N-C, (b)  $Co_3(PO_4)_2$ @N-C annealed at 300 °C, 400 °C and 500 °C, respectively.



Fig. S2 (a) SEM images of the precursor of  $Co_3(PO_4)_2$ @N-C, (b)  $Co_3(PO_4)_2$ @N-C-300, (c)  $Co_3(PO_4)_2$ @N-C-400, (d)  $Co_3(PO_4)_2$ @N-C-500 (e)  $Co_3(PO_4)_2$ . Scale bars: 1µm. (f) Corresponding EDS analysis of  $Co_3(PO_4)_2$ @N-C-400.



**Fig. S3** TGA curves of  $Co_3(PO_4)_2$  (a)N-C in air atmosphere.



**Fig. S4** (a) OER polarization curves for  $Co_3(PO_4)_2@N-C$  catalyst with different loadings on the glass carbon electrode, (b) polarization curves for  $Co_3(PO_4)_2@N-C$  catalysts annealed at different temperature, respectively.

The electrocatalytic activity of the catalysts for OER was investigated in 1 M KOH solution saturated with  $O_2$ , where glass carbon (GC) coated by catalysts was applied as working electrode. To know the best catalytic properties of the cobalt phosphate catalyst for OER, we firstly studied the change of OER current density with the loading of  $Co_3(PO_4)_2$ @N-C catalyst per unit area. It was found that the OER current density did not vary with catalyst loading proportionally. As shown in Fig. S4a, the OER current density loading and as the catalyst loading mass became 0.3 mg cm<sup>-2</sup>, the catalyst showed the highest OER current density.

The reason for this result might be that relatively thick catalyst layer reduced mass transport and made the bottom of the catalyst layer unuseful.<sup>7,8</sup> Except the loading mass, annealing at different temperature is another influencing factor of the catalytic activities. Fig. S4b shows the polarization curves for  $Co_3(PO_4)_2$ @N-C catalysts annealed at different temperature (300 °C, 400 °C and 500 °C), respectively. It was informed that the  $Co_3(PO_4)_2$ @N-C catalyst annealed at 400 °C possessed the best catalytic activity. Therefore, in this work, we chose  $Co_3(PO_4)_2$ @N-C annealed at 400 °C (denoted as  $Co_3(PO_4)_2$ @N-C for convenience) as the catalyst and a catalyst loading mass of 0.3 mg cm<sup>-2</sup> to study the OER activities of the catalysts.



**Fig. S5** (a) CVs of  $IrO_2$  measured in 1 M KOH at scan rates of 2 to 10 mV s<sup>-1</sup>. (b) A plot of the current density at 1.14 V vs. the scan rate.

To determine the double layer ( $C_{dl}$ ) of the IrO<sub>2</sub> catalyst, the CVs were recorded at different scan rates (2 to 10 mV s<sup>-1</sup>) in a potential region of 1.10 to 1.15 V in 1 M KOH solution. It is generally supposed that charge transfer electrode reactions are negligible and the current is resulted from electrical double layer charging and discharging, in this potential region.<sup>9,10</sup> Fig. S5a shows that the CVs are rectangular shape of an electrical double layer capacitor. Fig. S5b shows that the plot of current density at 1.14 V vs. RHE against scan rate has a linear relationship and its slope is the double layer capacitance ( $C_{dl}$  20mF cm<sup>-2</sup>), which clearly demonstrates that  $Co_3(PO_4)_2$ @N-C has much larger amount of active sites for OER.



**Fig. S6** (a) (b) CVs of  $Co_3(PO_4)_2$ @N-C and  $Co_3(PO_4)_2$  measured in 1 M KOH at scan rates of 40 to 200 mV s<sup>-1</sup>. (c) Plots of the current density at 1.14 V vs. the scan rate of  $Co_3(PO_4)_2$ @N-C and  $Co_3(PO_4)_2$ . (d) OER polarization curves for  $Co_3(PO_4)_2$ @N-C and  $Co_3(PO_4)_2$  measured under the condition of keeping the same electrochemically active surface area.

To further verify our conclusion, we used high scan rates, 40, 80, 120, 160, and 200 mV s<sup>-1</sup> to obtain the capacitance current. The results were shown in Fig. S6 a-c, and the same conclusion was obtained that  $Co_3(PO_4)_2$ @N-C has a much larger number of active sites. Actually, in the small potential range of 1.05-1.15 V, no redox reaction occurs, therefore, the faradic current is small enough to be neglected. Therefore, although different scan rates were taken, the same conclusion was obtained. Fig. S6d shows the OER polarization curves for  $Co_3(PO_4)_2$ @N-C and  $Co_3(PO_4)_2$ , which were measure by keeping the same active surface area but with different loading mass of  $Co_3(PO_4)_2$ @N-C (0.1 mg cm<sup>-1</sup>) and  $Co_3(PO_4)_2$  (0.5 mg cm<sup>-1</sup>). The results clearly demonstrate that the  $Co_3(PO_4)_2$ @N-C is more effective than  $Co_3(PO_4)_2$ .

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