Supporting Information

Phosphate-assisted efficient oxygen evolution over finely dispersed cobalt particles supported on graphene

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Note S1. Measurement of electrochemically active surface area (ECSA).

ECSA was obtained by performing CV measurements at different scan rates (20 to 160 mV/s) in a non-faradaic potential range (-0.2 to -0.1 V vs Ag/AgCl) as illustrated in Figure S1. The current density difference of the anodic and cathodic branch at -0.15 V vs Ag/AgCl was extracted. The current density difference was linearly fit to the scan rate (Figure S2), and half of the slope of the fitting line is the double layer capacitance (C_{dl}) of the electrode. The ECSA was then calculated by the following formula,

$$ECSA = \frac{C_{dl}}{C_s} \times S_{geo}$$

 C_{dl} is the double layer capacitance; C_s is the capacitance of a smooth planar surface, C_s = 0.040 mF cm⁻² was used for calculation;¹ S_{geo} is the geometric surface area of the electrode (0.126 cm²).



Potential / V vs. Ag/AgCl

Figure S1. CV measurements at different scan rates (20 to 160 mV/s) in a non-faradaic potential range (-0.2 to -0.1 V vs Ag/AgCl).



Figure S2. The current density difference as a function of the scan rate. The dots are experimental results and the dashed line represents the fitting result.

Note S2. Determination of the solution resistance (R_s) and the charge transfer resistance (R_{ct}) , and normalization of the Nyquist plot.

 R_s and R_{ct} were extracted from the Nyquist plot (Figure S3). R_s is the real impedance at the left endpoint of the Nyquist plot (high frequency end), and the sum of R_s and R_{ct} is the real impedance at the right endpoint (low frequency end). The Nyquist plots reported in this paper were normalized by the ECSA using the following formula,

 $\vec{R_n}(\Omega \ cm^2) = \vec{R}(\Omega) \times ECSA(cm^2)$

 $\vec{R_n}$ is the normalized impedance, \vec{R} is the measured impedance, and ECSA is the electrochemically active surface area.



Figure S3. Nyquist plot. Z_{real} is the real impedance and Z_{im} is the imagine impedance.



Figure S4. Normalized Nyquist plot. Z_{real} is the real impedance and Z_{im} is the imagine impedance.

Note S3. Calculation of current density.

The current densities based on the geometric surface area of the electrode, ECSA, and the mass of cobalt were calculated by the following formulas, respectively.

Current density based on the geometric surface area of the electrode, $j_g = \frac{I}{S_{geo}}$

 J_g is the current density normalized by the geometric surface area of the electrode; I is current; S_{geo} is the geometric surface area of the electrode.

Current density based on ECSA, $j_e = \frac{I}{ECSA}$

 J_e is the current density normalized by ECSA; I is current; ECSA is electrochemically active surface area.

Current density based on the mass of cobalt,
$$j_m = \frac{I}{m_{Co}}$$

 J_m is the current density normalized by the mass of cobalt; I is current; m_{Co} is the mass cobalt loaded on the electrode. The mass percent of cobalt in Co/Gr was calculated based on the feed for preparation instead of XPS result.



Figure S5. OER reaction mechanism in acid (a) and base (b), respectively. Reproduced with permission from Ref. ². Copyright © 2015 Elsevier B.V.

Catalyst	Catalyst loading	Electrolyte	η_{10}	Tafel slope
	$(mg \ cm^{-2})$		(V vs RHE)	(mV dec ⁻¹)
Co/Gr ^a	0.24	1.0 M KOH +	1.58	48
		0.244 M Na ₃ PO ₄		
Co/Gr ^a	0.24	1.0 M KOH	1.63	58
Nanostructured Co ₃ O ₄ ^a	0.24	1.0 M KOH +	1.59	48
		0.244 M Na ₃ PO ₄		
Co ₃ O ₄ nanocube ³	0.50	0.1 M kOH	1.78	~60
Co ₃ O ₄ nanooctahedra ³	0.50	0.1 M KOH	1.84	~60
$Co_3O_4^4$	1.00	1.0 M KOH	1.59	n.a.
CoMnO ₂ ⁵	0.284	1.0 M KOH	1.62	95
CoMnP ⁵	0.284	1.0 M KOH	1.56	61
CoSe ₂ bulk ⁶	0.142	0.1 M KOH	1.82	108
CoSe ₂ nanosheets ⁶	0.142	0.1 M KOH	1.55	44
Co ₂ P ⁵	0.284	1.0 M KOH	1.60	128
N-Co/C ⁷	0.714	0.1 M KOH	1.66	393
N-Co/C/NRGO ⁷	0.714	0.1 M KOH	1.75	292
NiFe@C ⁸	0.250	1.0 M KOH	1.50	57

Table S1. Comparison of the apparent OER activity with the state of the art catalysts.

^a This work.

Note S4. OER mechanism proposed by Doyle et al.⁹

$SOH_2 + OH^- \rightarrow SOH^- + H_2O$	(Eq. S1)
$SOH^- \rightarrow SOH + e^-$	(Eq. S2)
$SOH + OH^- \rightarrow SO^- + H_2O$	(Eq. S3)
$SO^- \rightarrow SO + e^-$ $SO + OH^- \rightarrow SOOH + e^-$	(Eq. S4) (Eq. S5)
$SOOH + OH^- \rightarrow SO_2 + H_2O + e^-$	(Eq. S6)
$SO_2 + OH^- \rightarrow SOH^- + O_2$	(Eq. S7)

S represents a surfaquo group attached to the hydrous oxide surface by bridging oxygen ligands.



Figure S6. XPS spectra of the Na₃PO₄ activated catalyst. XPS was performed on a Phi5000 VersaProbeII spectrometer. The spectra were obtained by an aluminum anode (hv(Al K α) = 1486 eV) operated at 50 W and a spot size of 200 μ m. The binding energies were referenced to C 1s at 284.8 eV.



Figure S7. P 2p core level XPS spectra of the Na₃PO₄ activated catalyst. XPS was performed on a Phi5000 VersaProbeII spectrometer. The spectra were obtained by an aluminum anode (hv(Al K α) = 1486 eV) operated at 50 W and a spot size of 200 μ m. The binding energies were referenced to C 1s at 284.8 eV.

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