Supporting Information for

# Accelerating Water Splitting Kinetics of CoP Microcubes Anchored on Graphene Electrocatalyst by Mn Incorporation

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#### **Experimental Section**

#### **1. Material Synthesis**

*Preparation of graphene oxide (GO) and reduced GO (rGO).* Firstly, the graphene oxide (GO) was synthesized through chemical exfoliation of graphite powders using a modified Hummers' method (*ACS Nano*, **2010**, *4*, 4806). Then the obtained GO was washed with water several times and freeze-dried for 48 h. After that, the product was heated at 400 °C for 2 h with a heating speed of 3 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere to get rGO.

*Preparation of MnCo Prussian blue analogues (PBA) anchored on graphene oxide (Mn<sub>0.6</sub>Co<sub>0.4</sub> PBA-GO).* In a typical synthesis, 3 mmol of Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 1.2 g PVP and GO (100mg) was added into the 400mL of water/ethanol mixture (200/200 mL) to get a homogeneous solution (2 mg mL<sup>-1</sup>) to form solution A. The solution A was stirred for 60 min to achieve the electrostatic adsorption of Mn<sup>2+</sup> on GO. Then 2 mmol of K<sub>3</sub>[Co(CN)<sub>6</sub>]<sub>2</sub> was dissolved in 50 mL of deionized water to form solution B, which was then added dropwise into solution A under magnetic stirring. The obtained mixture was aged for 3 h at room temperature. The as-prepared beige precipitate was collected and washed with water several times. Finally, the product was freeze-dried for 48 h to get MnCo PBA-GO. For comparison, Mn<sub>0.4</sub>Co<sub>0.6</sub> PBA-GO, Mn<sub>0.2</sub>Co<sub>0.8</sub> PBA-GO, and CoCo PBA-GO were also prepared under same condition by adjusting the Mn:Co ratio in the raw materials.

Preparation of  $Mn_{0.6}Co_{0.4}P$  nanocubes anchored on reduced GO ( $Mn_{0.6}Co_{0.4}P$ -rGO). In a typical synthesis, the  $Mn_{0.6}Co_{0.4}$  PBA-GO (50 mg) and  $NaH_2PO_2$  powder (1000 mg) were put at two adjacent porcelain boats and loaded into a tube furnace with  $NaH_2PO_2$  powder at the upstream side of the furnace. The furnace was heated at 400 °C for 2 h with a heating speed of 3 °C min<sup>-1</sup> under a Ar atmosphere to get the  $Mn_{0.6}Co_{0.4}P$ -rGO. For comparison,  $Mn_{0.4}Co_{0.6}P$ -rGO,  $Mn_{0.2}Co_{0.8}P$ -rGO, and CoP-rGO were also prepared under same condition using corresponding MnCo PBA-GO precursors.

*Preparation of*  $Mn_{0.6}Co_{0.4}P$  *nanocubes*. MnCo PBA nanocubes precursor was first synthesized by a simple precipitation method that is similar to the synthesis of  $Mn_{0.6}Co_{0.4}$  PBA-rGO as

described above except for no GO was used. The MnCo PBA was then thermally converted into  $Mn_{0.6}Co_{0.4}$  PBA nanocubes at 400 °C for 2 h using NaH<sub>2</sub>PO<sub>2</sub>.

#### 2. Structure Characterizations

X-ray diffraction (XRD) of all the prepared materials was performed on a Rigaku Ultima IV diffraction instrument (Rigaku Co., Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.54$  A°) under a voltage of 35 kV and a current of 35 mA. The morphologies of the samples were characterized by scanning electronic microscope (SEM) using a Zeiss SIGMA microscope (Carl Zeiss Co., Germany) and transmission electron microscope (TEM) using a Tecnai F30 microscope (FEI Co., US). Quantachrome instruments Quadrasorb SI (US) was used to measure the Brunauer-Emmett-Teller (BET) surface areas of the samples at liquid nitrogen temperature (77.3K).

## 3. Oxygen Evolution Reaction (OER) and Hydrogen Evolving Reaction (HER) Electrocatalysis

All electrochemical measurements were conducted on an electrochemical analyzer (CHI 660E, CH Instruments, Inc., China) in 1 M KOH using a standard three-electrode system, where the catalysts loaded on carbon paper as the working electrode, a Pt plate electrode for OER (or a graphite rod for HER) as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode, respectively. For the fabrication of the working electrode, 10 mg of the assynthesized catalyst was mixed with 100 µL Nafion solution (5% Nafion in ethanol) and 900 µL ethanol. The mixture was sonicated for 60 min. Then the suspension was pipetted out and dropped onto a piece of carbon paper. The mass loadings of the catalyst were about 2-2.5 mg cm<sup>-</sup> <sup>2</sup>. Polarization curves were obtained using linear sweep voltammetry (LSV) at a scan rate of 1 mV s<sup>-1</sup>. The long-term durability test was performed using chronopotentiometric measurements. Before each test, the electrodes were cycled until a stable cyclic voltammetry (CV) was achieved. All potentials were measured against SCE and converted to the reversible hydrogen electrode (RHE) according to the Nernst equation ( $E_{\rm RHE} = E_{\rm SCE} + 0.059 \times pH + 0.2415$ ). The electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 10<sup>-2</sup> to 10<sup>5</sup> Hz with an AC voltage amplitude of 10 mV. Unless otherwise noted, all current densities presented were IR corrected.

#### 4. Fabrication of RuO<sub>2</sub> and Pt/C electrodes

10 mg of commercial RuO<sub>2</sub> or 20 wt.% Pt/C was mixed with 100  $\mu$ L Nafion solution (5% Nafion in ethanol) and 900  $\mu$ L ethanol to form a homogeneous ink, which was then drop casted onto a piece of carbon paper. The typical catalyst loading was ~2.5 mg cm<sup>-2</sup>.

#### 5. Overall water splitting electrocatalysis

Overall water splitting electrocatalysis were conducted using a potentiostat (CHI 660E, CH Instruments, Inc., China) using a two-electrode system. The  $Mn_{0.6}Co_{0.4}P$ -rGO loaded on carbon paper was used as both the positive and negative electrodes. The polarization curves were recorded using linear sweep voltammetry (LSV) in 1.0 M KOH at a scan rate of 1 mV s<sup>-1</sup>. The long-term durability test was performed using chronoamperometric measurements. All polarization curves presented were IR corrected.

#### 6. Faradaic efficiency determination

The quantitative measurement of  $O_2$  and  $H_2$  was carried out using displacement method. The water splitting experiment was performed in an airtight diaphragm cell. The  $Mn_{0.6}Co_{0.4}P$ -rGO loaded on carbon paper was used as both the positive and negative electrodes, which were inserted into each side of the cell. The volume of each side of the cell is about 25 mL. Prior to the test, each side of the cell was filled with 15.0 mL of 1.0 M KOH aqueous solution. A constant current of 45 mA was applied between positive electrode and the negative electrode for 120 min.

#### 7. Turn-over frequency (TOF) calculations

The values of TOF were calculated assuming all the Mn and Co atoms in the catalysts are active and contribute to the catalytic reaction:

$$TOF = \frac{J}{z \times F \times n}$$

Here, J (A cm<sup>-2</sup>) is the measured current density at an overpotential of 100 mV (for HER) or 300 mV (for OER); the number of z means z electrons transfer in electrode reaction (z = 2 for HER and z = 4 for OER); F is Faraday constant (96485.3 C mol<sup>-1</sup>), and n is the molar number of active metals calculated from the mass loading density (mg cm<sup>-2</sup>) of catalyst.

## Additional Figures and Data



Fig. S1. Low magnification SEM images of (a) MnCo PBA-GO and (b)  $Mn_{0.6}Co_{0.4}P$ -rGO.



**Fig. S2.** Low magnification SEM images of (a) CoP-rGO, (b) Mn<sub>0.2</sub>Co<sub>0.8</sub>P-rGO, (c) Mn<sub>0.4</sub>Co<sub>0.6</sub>P-rGO, (d) Mn<sub>0.6</sub>Co<sub>0.4</sub>P-rGO.



Fig. S3. A typical SEM image of  $Mn_{0.6}Co_{0.4}P$  nanocubes obtained by thermal phosphorization of MnCo PBA at 400 °C.



Fig. S4. EDX spectrum of the  $Mn_{0.6}Co_{0.4}P$ -rGO.



Fig. S5 XPS survey spectrum of the Mn<sub>0.6</sub>Co<sub>0.4</sub>P-rGO.



**Fig. S6**  $Mn_{0.6}Co_{0.4}P$ -rGO loaded on carbon paper for (a,b) OER and (c,d) HER electrocatalysis in 1 M KOH along with  $Mn_{0.6}Co_{0.4}P$  for comparison. (a,c) *IR*-corrected polarization curves and (b,d) the corresponding Tafel plots.



**Fig. S7** Nyquist plots of  $Mn_{0.6}Co_{0.4}P$ -rGO,  $Mn_{0.6}Co_{0.4}P$ , and rGO catalysts. The inset shows the enlarged Nyquist plots in high frequency region.



**Fig. S8** Turnover frequency (TOF) values of  $Mn_xCo_{1-x}P$ -rGO at (a)  $\eta_{OER} = 300$  mV and (b)  $\eta_{HER} = 100$  mV.



**Fig. S9** Cyclic voltammograms of (a) CoP-rGO, (b)  $Mn_{0.2}Co_{0.8}P$ -rGO, (c)  $Mn_{0.4}Co_{0.6}P$ -rGO, and (d)  $Mn_{0.6}Co_{0.4}P$ -rGO in the region of 0.069-0.169 V vs. RHE in 1 M KOH.



**Fig. S10** Cyclic voltammograms of (a)  $Mn_{0.6}Co_{0.4}P$ -rGO, (b)  $Mn_{0.6}Co_{0.4}P$  nanocubes. (c) The difference in current plotted against scan rate showing the extraction of the double-layer capacitances, which allow the estimation of the electrochemically active surface area (ECSA).



Fig. S11 (a) OER and (c) HER polarization curves of the  $Mn_{0.6}Co_{0.4}P$ -rGO electrodes recorded before and after 5000 cycles. Chronoamperometry curves of the  $Mn_{0.6}Co_{0.4}P$ -rGO electrodes under (b) 1.54 V and (d) -0.14 V.



**Fig. S12** High resolution XPS spectra of (a) Mn  $2p_{3/2}$ , (b) Co  $2p_{3/2}$ , and (c) P 2p regions of the post-HER and post-OER Mn<sub>0.6</sub>Co<sub>0.4</sub>P-rGO electrodes.



Fig. S13 TEM image of Mn<sub>0.6</sub>Co<sub>0.4</sub>P-rGO after the OER.



Fig. S14 Electrocatalytic HER performance of  $Mn_{0.6}Co_{0.4}P$ -rGO loaded on carbon paper in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 1.0 M KOH, and 1.0 M PBS (pH =7.2).

### **Supplementary Tables**

Catalyst	Mn/Co/P ratio
Mn <sub>0.6</sub> Co <sub>0.4</sub> P-rGO	0.596:0.413:1
Mn <sub>0.4</sub> Co <sub>0.6</sub> P-rGO	0.387:0.619:1
Mn <sub>0.2</sub> Co <sub>0.8</sub> P-rGO	0.196:0.811:1
CoP-rGO	0:1.06:1

Table S1. Atomic ratio of Mn/Co/P in samples as determined by ICP-OES.

**Table S2.** Comparison of the OER activity of the  $Mn_{0.6}Co_{0.4}P$ -rGO in 1 M KOH and other recently reported high-performance OER catalysts.

Catalyst	Tafel slope (mV dec <sup>-1</sup> )	η <sub>10</sub> (mV)	Reference
Mn <sub>0.6</sub> Co <sub>0.4</sub> P-rGO	65	250	This work
RuO <sub>2</sub>	97	270	This work
Ni-Co Mixed Oxide Cages	50	381	Adv. Mater. 2016, 28, 4601.
CoP/rGO	70	340	Chem. Sci. 2016, 7, 1690.
CoMnP Nanoparticles	61	330	J. Am. Chem. Soc. 2016, 138, 4006.
Co@CoO/N-Doped Graphene	73	309	J. Mater. Chem. A 2016, 4, 12046.
Ni <sub>2</sub> P Hollow Microspheres	40.4	270	Chem. Mater. 2017, 29, 8539.
Ni <sub>3</sub> Se <sub>2</sub> Films <sup>b</sup>	97.1	310	Energy Environ. Sci. 2016, 9, 1771.
Carbon/NiP Nanoplates	64	291	Energy Environ. Sci. 2016, 9, 1246.
Co-P	47	345	Angew. Chem. Int. Ed. 2015, 54, 6251.
FeCoP Alloy	33	303	ACS Nano, 2018, 12, 158.
Co-P/Pi Thin Films	65	300	Adv. Mater. 2015, 27, 3175.
Phosphonate Co-P-C	64	267	ACS Catal., 2017, 7, 6000.
Ni–Co Hydroxide <sup>c</sup>	145	460	Adv. Funct. Mater. 2014, 24, 4698.
Cobalt/Iron Phosphides	58	260	ACS Appl. Mater. Interfaces 2017, 9, 362.
Co <sub>x</sub> -Fe-B	62.6	298	ACS Appl. Mater. Interfaces, 2017, 9, 40333.
Co <sub>3</sub> O <sub>4</sub> /CoP	70	287	Inorg. Chem. 2017, 56, 1742.
Co-Doped NiSe <sub>2</sub> /Ni <sub>3</sub> Se <sub>4</sub> /C	63		J. Mater. Chem. A 2016, 4, 15148.
CoP Nanosheets	85	300	ChemElectroChem 2017, 4, 1840.
NiSe Nanowire	64	~250	Angew. Chem. Int. Ed. 2015, 54, 9351.
Fe-Doped CoP	67	230	Adv. Mater. 2017, 29, 1602441.
Ni-Mo Hollow Nanorods	47	310	J. Mater. Chem. A, 2015, 3, 20056.

<sup>a</sup>N-doped graphene/Co-embedded porous carbon polyhedron.

<sup>b</sup>in 0.3 M KOH.

cin 0.1 M KOH.

Catalyst	Tafel slope (mV dec <sup>-1</sup> )	η <sub>10</sub> (mV)	Reference
Mn <sub>0.6</sub> Co <sub>0.4</sub> P-rGO	63	54	This work
20 wt.% Pt/C	26	31	This work
Ni <sub>x</sub> P/S/Se Nanosheets	48	55	ACS Appl. Mater. Interfaces, 2017, 9, 41347.
Mo <sub>6</sub> Ni <sub>6</sub> C	33.49	51	ACS Energy Lett. 2018, 3, 78-84.
FePO4 Nanosheet*	104.9	123	Adv. Mater. 2017, 1704574.
NC@W <sub>x</sub> C/NRGO	58.4	100	ChemSusChem 2017, 10, 2402.
CoP Nanowires	129	209	J. Am. Chem. Soc. 2014, 136, 7587.
NiCo <sub>2</sub> N Nanosheets	79	180	ChemSusChem 2017, 10, 4170.
NiFe Oxyfluoride Nanoporous	96	253	ACS Catal. 2017, 7, 8406.
Ni <sub>2</sub> P/Ni/Ni Foam	72	98	ACS Catal. 2016, 6, 714.
Ni–P Films	43	93	<i>ChemCatChem</i> <b>2016</b> , <i>8</i> , 106.
Ni <sub>2</sub> P Hollow Microspheres	86.4	98	Chem. Mater. 2017, 29, 8539.
Ni <sub>1/3</sub> Co <sub>2/3</sub> Se <sub>2</sub> **	40.1	131	Electrochim. Acta 2016, 200, 142.
Co <sub>9</sub> S <sub>8</sub> -MoS <sub>2</sub> /CNFs**	110	190	Adv. Mater. 2015, 27, 4752.
CoS <sub>2</sub> Nanowires**	51.6	145	J. Am. Chem. Soc. 2014, 136, 10053.
CoP/Ti**	50	72	Angew. Chem. Int. Ed. 2014, 53, 5427.
Co-Doped NiSe <sub>2</sub> /Ni <sub>3</sub> Se <sub>4</sub> /C	81	90	J. Mater. Chem. A 2016, 4, 15148.
CoP Nanosheets	60	52	ChemElectroChem 2017, 4, 1840.
NiSe Nanowire	120	96	Angew. Chem. Int. Ed. 2015, 54, 9351.
Fe-Doped CoP	75	128	Adv. Mater. 2017, 29, 1602441.
Ni-Mo Hollow Nanorods	76	92	J. Mater. Chem. A, 2015, 3, 20056.
Ni-Mo Sheets	45	35	Small 2017, 13, 1701648.

Table S3. Comparison of the HER activity of the  $Mn_{0.6}Co_{0.4}P$ -rGO in 1 M KOH and other recently reported high-performance HER catalysts.

\*in 0.5 M H<sub>2</sub>SO<sub>4</sub> \*\*in 0.5 M H<sub>2</sub>SO<sub>4</sub>

Catalysis	η <sub>10</sub> (V)	η <sub>100</sub> (V)	Reference
Mn <sub>0.6</sub> Co <sub>0.4</sub> P-rGO	1.55	1.77	This work
$Pt/C \parallel RuO_2$	1.55	1.80	This work
CoP Nanorod Bundles	1.6		Electrochim. Acta 2017, 242, 355.
Co-Doped NiSe <sub>2</sub>	1.61	~1.85	J. Mater. Chem. A 2016, 4, 15148.
FeP Nanotubes	1.62		Nano Energy <b>2017</b> , <i>4</i> , 327.
FePO <sub>4</sub> Nanosheet	1.54		Adv. Mater. 2017, 1704574.
Co-P/N-Doped carbon matrices	~1.7		Chem. Mater. 2015, 27, 7636.
NiFe LDH/NF	1.70		Science 2014, 345, 1593.
Ni <sub>3</sub> Se Nanoforest/NF	1.61		Nano Energy <b>2016</b> , 24, 103.
NiCo <sub>2</sub> O <sub>4</sub> Hollow Microcuboids	1.65		Angew. Chem. Int. Ed. 2016, 55, 1.
NiCo LDH-rGO	1.51		Adv. Funct. Mater. 2017, 1704594.
CoP/RGO	1.70		Chem. Sci. 2016, 7, 1690.
EG/Co <sub>0.85</sub> Se/NiFe-LDH	1.67	~1.73	Energy Environ. Sci. 2016, 9, 478.
Ni <sub>2</sub> P/NiO <sub>x</sub>	~1.63		Energy Environ. Sci. 2015, 8, 2347.
Co-Doped NiSe <sub>2</sub> /Ni <sub>3</sub> Se <sub>4</sub> /C	1.60		J. Mater. Chem. A 2016, 4, 15148.
CoP Nanosheets	1.60		ChemElectroChem 2017, 4, 1840.
NiSe Nanowire	1.63	~1.90	Angew. Chem. Int. Ed. 2015, 54, 9351.
Fe-Doped CoP	1.60		Adv. Mater. 2017, 29, 1602441.
Ni-Mo Hollow	1.64		J. Mater. Chem. A, 2015, 3, 20056.

**Table S4.** Comparison of the electrochemical performance of  $Mn_{0.6}Co_{0.4}P$ -rGO and other recently reported high performance electrocatalysts for overall water splitting in 1 M KOH.