Electronic Supplementary Information

Hollow CoP nanopaticle/N-doped graphene hybrids as highly active and stable bifunctional catalysts for full water splitting

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Experimental Section

Chemicals. Grapehene sheets with a thickness of about 0.8 nm were purchased from Nanjing XFNANO Material Tech Co., Ltd. (Nanjing City, China). Other regants were purchaged without further treatment.

Preparation of catalysts. The CoP_h/NG hybrids were synthesized as follow: The graphene sheets were treated at 700^{o}C for 3 h under an NH_3 flow and then NG was obtained. 36 mg of NG was dispersed into 72 mL ethanol, and 200 mg of cobalt acetate was added. After sonication for 10 min, 3.6 mL distilled water and 2 mL ammonia were then added. The mixture above was sealed in a flask and kept at 80^{o}C for 10 h under stirring. The precipitates were washed with distilled water and dried through a freeze-drying process. The obtained powder (powder A) was thermally treated at 325^{o}C for 2 h under an Ar/H_2 flow, and then was further treated in a furnace at 200^{o}C for 2 h under air atmosphere. After cooling to room temperature, the obtained powder denoted as powder B. The powder B was mixed with sodium hypophosphite by a weight ratio of 1 : 20, and then the mixture was annealed at 350^{o}C for 2 h at Ar flow. The CoP_h/G hybrids were synthesized under the similar conditions except that NG was replaced with the pristine graphene. The CoP_s/NG hybrids were synthesized by direct phosphatization of powder A.

Electrochemical measurements. Electrochemical measurements were carried out with a CHI 660D electrochemical analyzer (CH Instuments, Inc., Shanghai) in a standard three-electrode system using CoP-based catalysts on carbon paper as the working electrode, a graphite rod as the counter electrode and an Ag/AgCl electrode as the reference electrode.

Carbon paper electrode: The preparation of the working electrode was described below: the catalysts were dispersed in N-methyl-2-pyrrolidone solvent containing 7.5 wt% PVDF under sonication, in which the weight ratio of the catalyst to PVDF is 8:1. Then the slurry was coated onto a piece of carbon paper. The loading density of the catalyst was around 2.5 mg cm^{-2}.

Glassy carbon disk electrode: 2 mg of catalyst powders was dispersed in 0.5 mL of 3:1 (volume:volume) water/ethanol mixed solvents along with 20 μL of a Nafion solution (5 wt%), and the mixture was sonicated for 30 min. Then, 2.7 μL of the above solution dripped onto the surface of a glassy carbon disk electrode at a catalyst loading of around 0.15 mg cm^{-2}. The as-prepared catalyst film was dried at room temperature .

Electrochemical measurements of the catalysts were measured in 1 M KOH solution after purging the electrolyte with N_2 gas for 30 min. Polarization curves were obtained using Linear sweep voltammetry (LSV). The long-term stability test was carried out using chronopotentiometric measurements. All potentials measured were calibrated to RHE using the following Equation: $E_{(\mathrm{RHE})} = E_{(\mathrm{Ag/AgCl})} + 0.21\ \mathrm{V} + 0.059 \times \mathrm{pH}$. All current densities presented are corrected against ohmic potential drop.

The TOF calculation. The number of active sites (n) was first examined employing cyclic voltammograms with phosphate buffer (pH = 7) at a scan rate of 50 mV s^{-1}. Then the number of the voltammetric charges (Q) could be determined after deduction of the blank value. n (mol) could be determined with the following equation

$$n\ (\mathrm{mol}) = Q\ /2F\ (\mathrm{HER});\ n\ (\mathrm{mol}) = Q\ /4F\ (\mathrm{OER})$$

where F is Faraday constant. TOF (s^{-1}) could be calculated with the following equation

$$\mathrm{TOF}\ (\mathrm{s}^{-1}) = I\ /2nF\ (\mathrm{HER});\ \mathrm{TOF}\ (\mathrm{s}^{-1}) = I\ /4nF\ (\mathrm{OER})$$

where I (A) was the current of the polarization curve obtained by LSV measurements.

Structure characterizations. XRD data were performed on a X'Pert Pro diffractometer with Cu $K\alpha$ radiation (λ=1.5418Å). TEM measurements were carried out on a transmission electron microscope (FEI Tecnai-F20) with an accelerating voltage of 200 kV. XPS data were accuired on a X-ray photoelectron spectrometer (ESCALAB 250, Thermofisher Co.)with Mg $K\alpha$radiation.The binding energy was calibrated with the C 1s position of contaminant carbon in the vacuum chamber of the XPS instrument (284.6 eV).

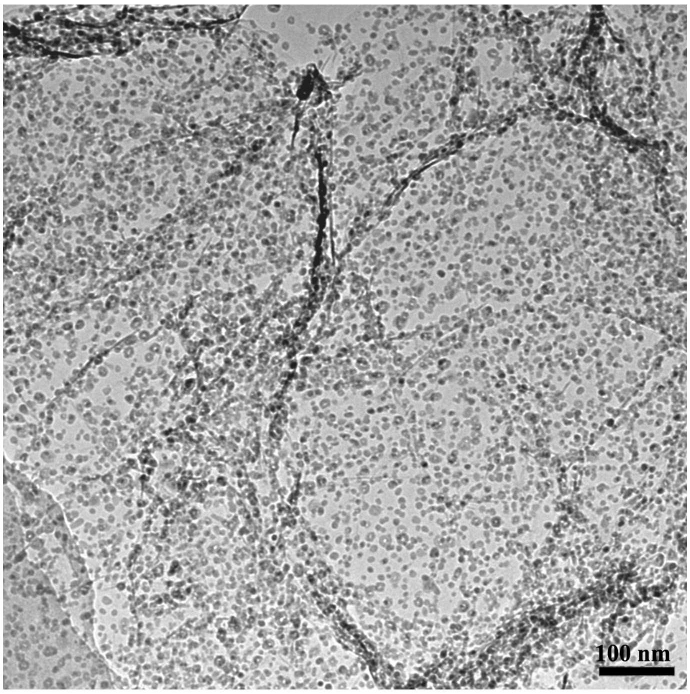

Figure S1. High-magnification TEM images of the CoP_h/NG hybrids composite.

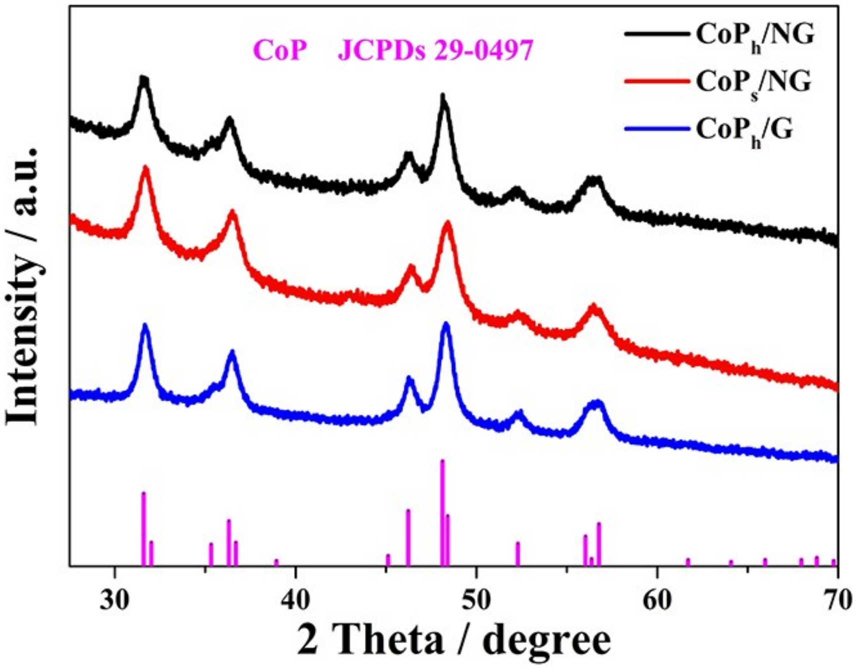

Figure S2. XRD spectra of the powder CoP_h/NG (black), CoP_s/NG (red) and CoP_h/G (blue). The lines correspond to standard XRD patterns of CoP (pink, JCPDS card No. 29-0497).

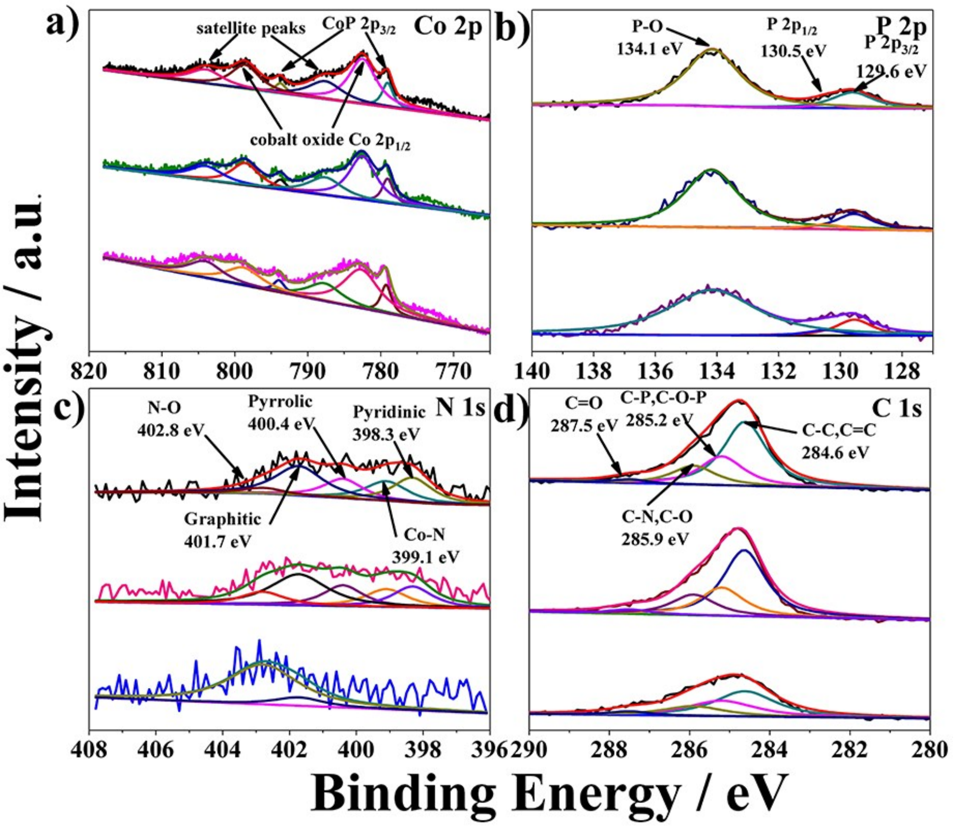

Figure S3. XPS spectra of a) Co 2p, b) P 2p, c) N 1s, d) C 1s in the power CoP_h/NG, CoP_s/NG, CoP_h/G, respectively.

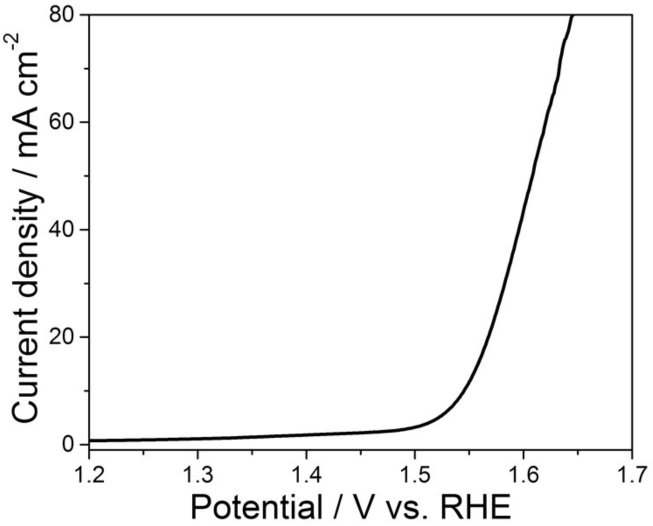

Figure S4. The polarization curve of CoP_h/NG loaded on glassy carbon disk electrode toward OER in 1.0 M KOH with a scan rate of 10 mV s^{-1}.

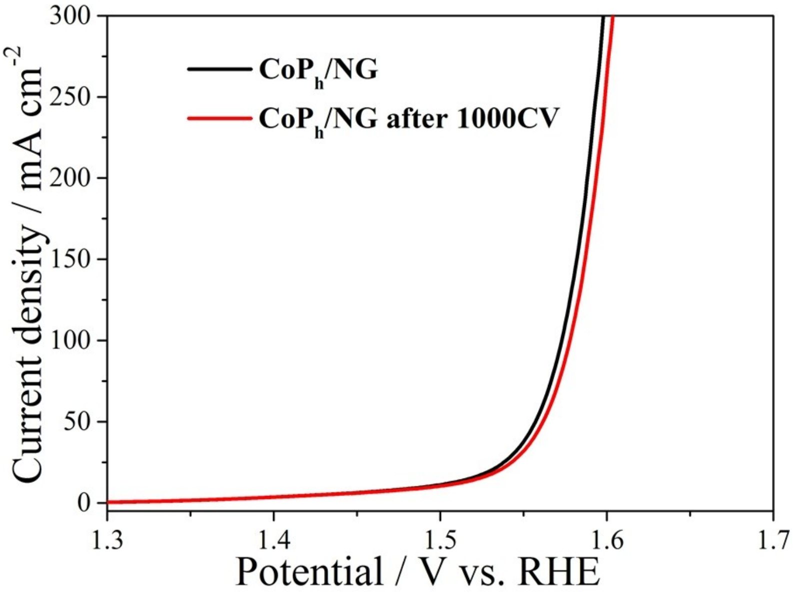

Figure S5. Stablity test for the CoP$_h$/NG hybirds by CV scanning for 1000 cycles in 1.0 M KOH solution at a scan rate of 50 mV s^{-1}.

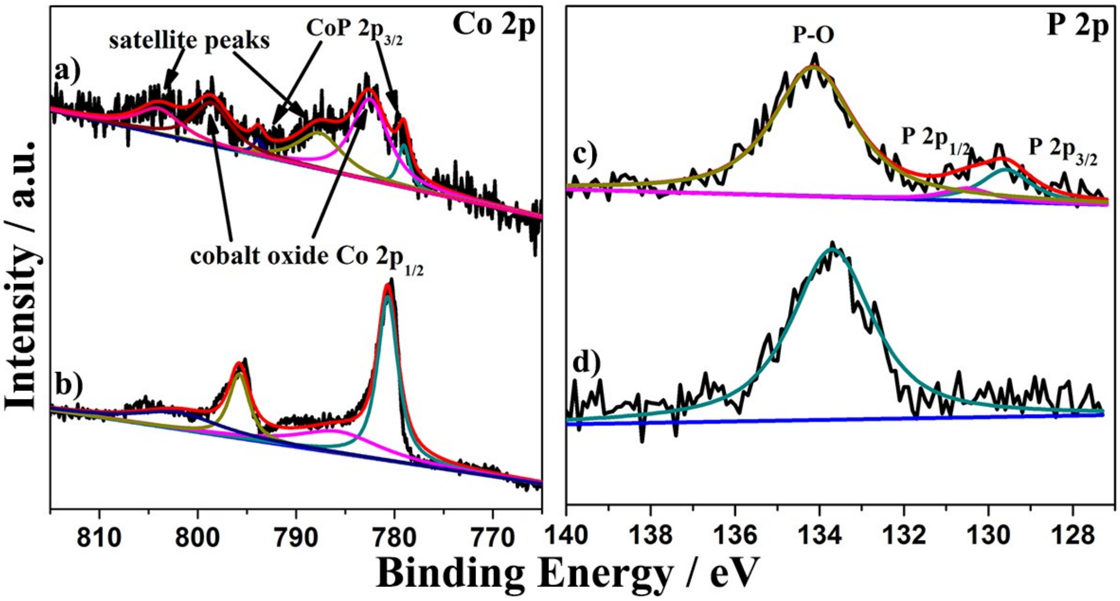

Figure S6. XPS spectra of Co 2p and P 2p in CoP$_h$/NG electrodes. a, c) The as-prepared CoP$_h$/NG electrode film without test. b, d) The as-prepared electrode after OER process for 3 h.

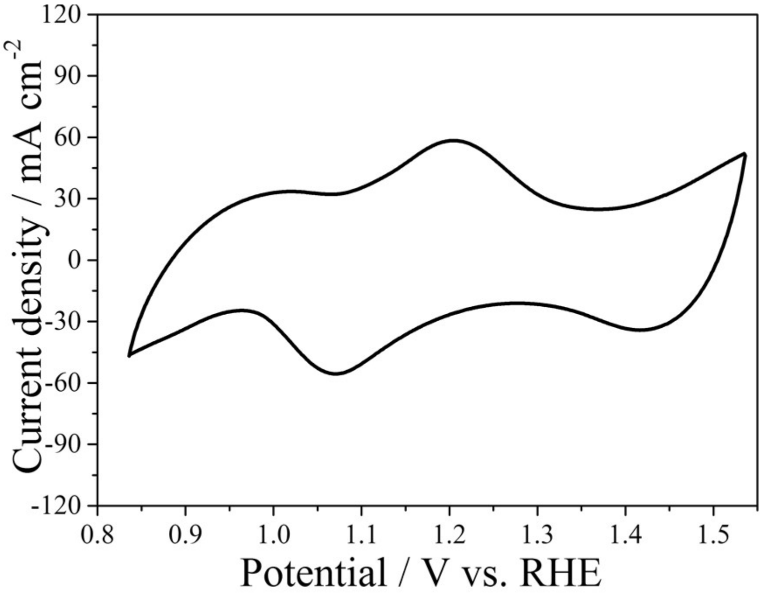

Figure S7 The CV curve of CoP_h/NG electrodes at a scan rate of 50 mV s^{-1}.

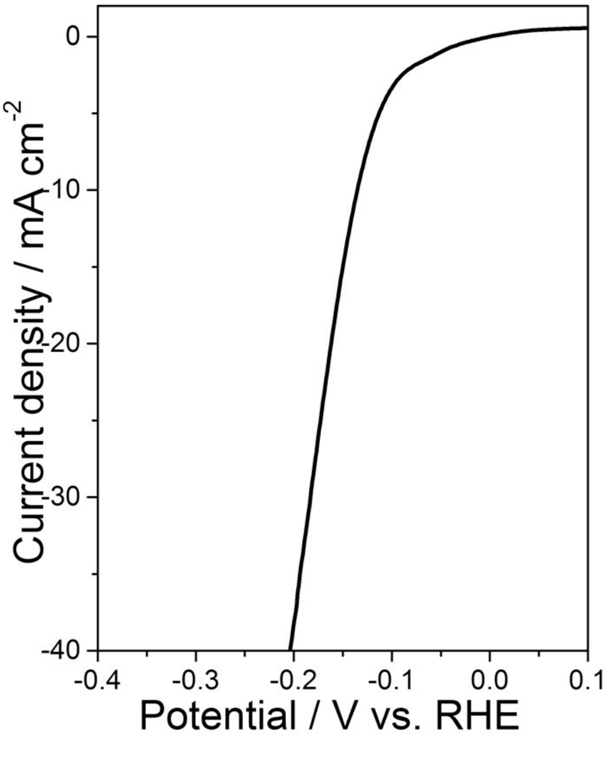

Figure S8. The polarization curve of CoP_h/NG loaded on glassy carbon disk electrode toward HER in 1.0 M KOH with a scan rate of 10 mV s^{-1}.

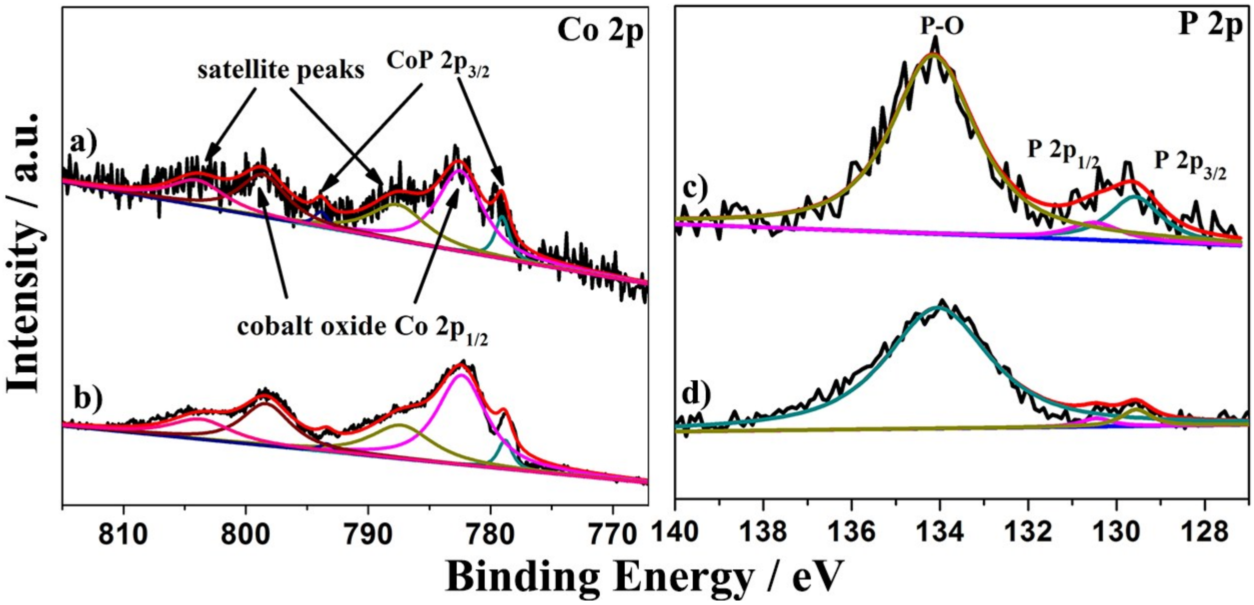

Figure S9. XPS spectra of Co 2p and P 2p in CoP_h/NG electrodes. a, c) The as-prepared CoP_h/NG electrode film without test. b, d) The as-prepared electrode after HER process for 3 h.

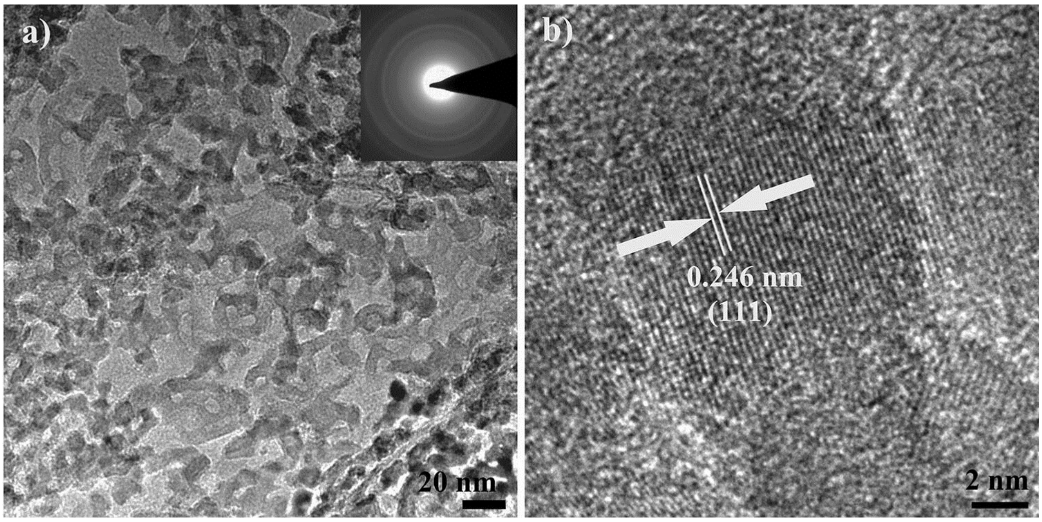

Figure S10. a) High-magnification TEM, and b) HRTEM images of the CoP_s/NG hybrids composite. The inset of a) shows the corresponding SAED pattern.

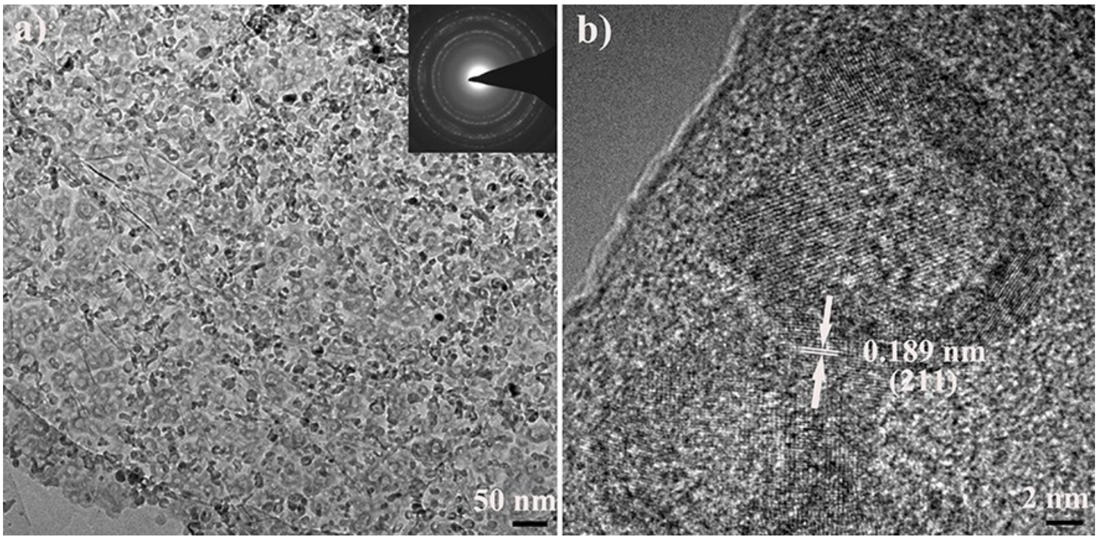

Figure S11. a) High-magnification TEM, and b) HRTEM images of the CoP_h/G hybrids composite. The inset of a) shows the corresponding SAED pattern.

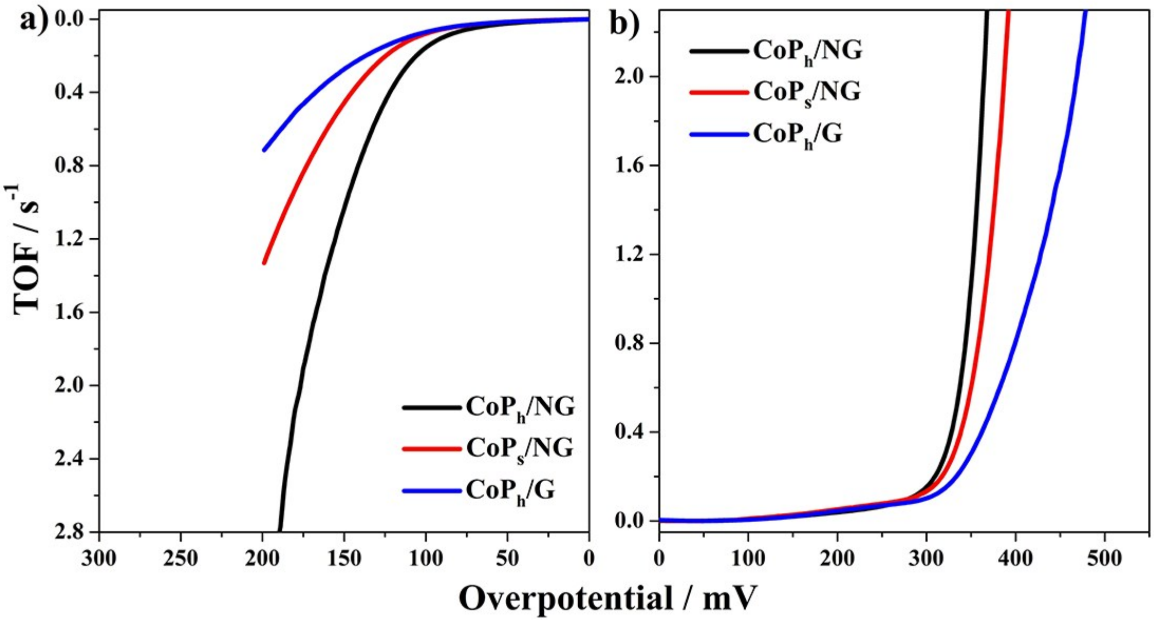

Figure S12. Calculated turnover frequencies for the CoP_h/NG, CoP_s/NG and CoP_h/G electrode films at pH = 14 for a) HER and b) OER process.

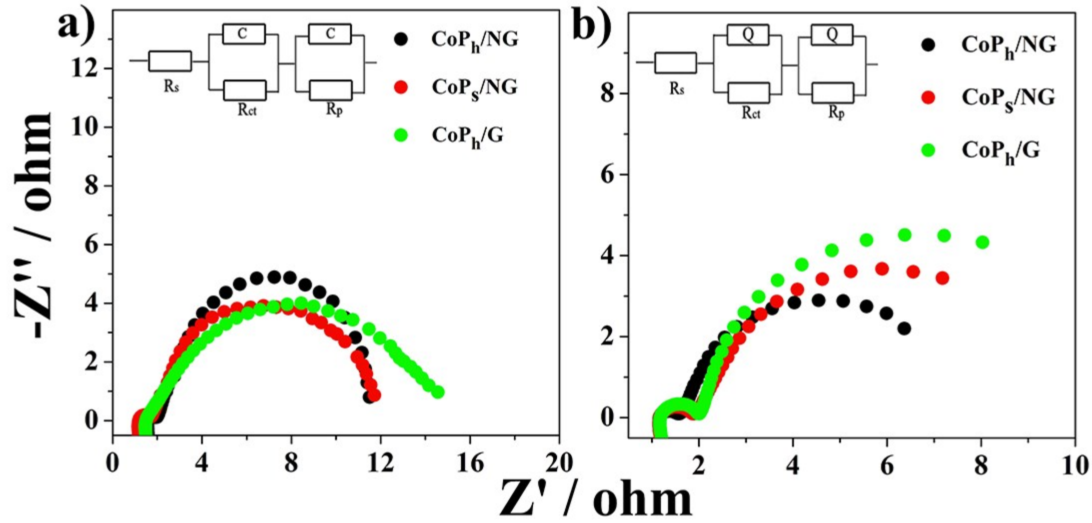

Figure S13. Nyquist plots for CoP$_h$/NG, CoP$_s$/NG and CoP$_h$/G electrode a) for HER under the overpotentials of 200 mV and b) for OER under the overpotentials of 306 mV.

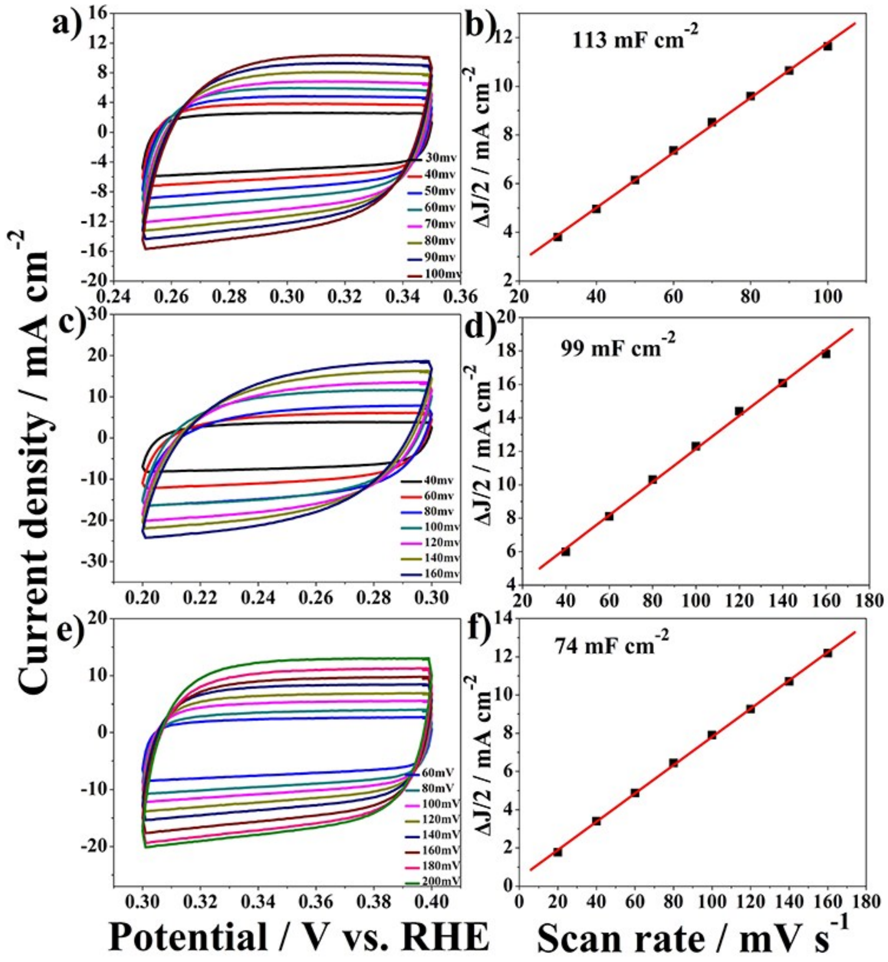

Figure S14. Cyclic voltammograms in the region of 0.3-0.4 V vs. RHE for a) CoP$_h$/NG, c) CoP$_s$/NG and e) CoP$_h$/G electrodes. The differences in current density ($\Delta J/2$) at 0.35 V vs.

RHE plotted against scan rate fitted to a linear regression allows for the estimation of C_{dl} for b) CoP_h/NG, d) CoP_s/NG and f) CoP_h/G electrodes.

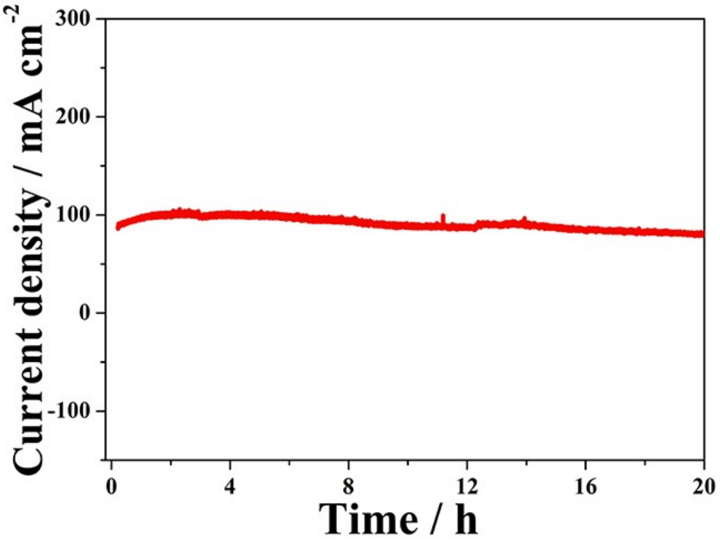

Figure S15. Time-dependent current density curve for CoP_h/NG–CoP_h/NG electrodes are tested under the cell voltage at 1.75 V over 20 h.

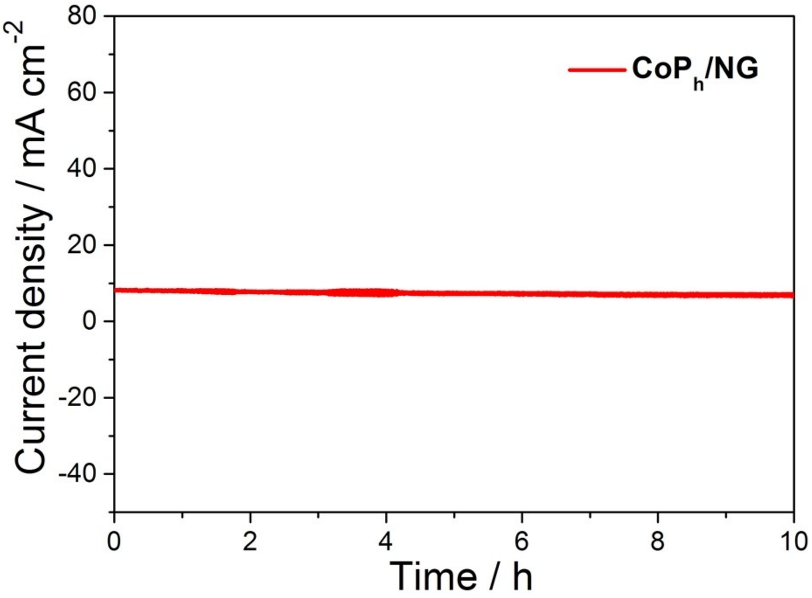

Figure S16. Time-dependent current density curve for CoP_h/NG–CoP_h/NG electrodes are tested under the cell voltage at 1.42 V over 10 h.

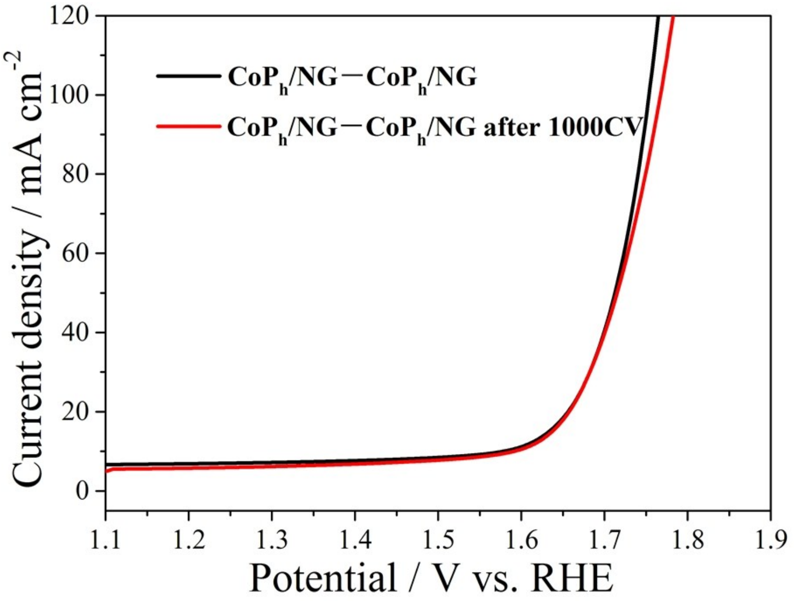

Figure S17. Stablity test for the CoP$_h$/NG-CoP$_h$/NG electrodes by CV scanning for 1000 cycles in 1.0 M KOH solution at a scan rate of 50 mV s^{-1}.

Table S1. Comparison of the OER activities of the CoP$_h$/NG, CoP$_s$/NG and CoP$_h$/G catalysts in 1.0 M KOH with recently published results.

Catalysts	Tafel slope (mV dec^{-1})	Overpotential at 10 mA cm^{-2} (mV)	Overpotential at 100 mA cm^{-2} (mV)	Electrolyte	Refs.
Cobalt-Phosphorous-Derived Films	47	345	413	1M KOH	*Angew. Chem. Int. Ed.*, 2015, 54, 6251-6254.
Co phosphide/phosphate thin film	65	～290	—	1M KOH	*Adv. Mater.*, 2015, 27, 3175-3180.
Co-P/ N-doped carbon matrices (Loading 0.283mg cm^{-2})	—	354	～410	1M KOH	*Chem. Mater.*, 2015, 27, 7636-7642.
Co-P/ N-doped carbon matrices (Loading 1.0mg cm^{-2})	52	319	～400	1M KOH	*Chem. Mater.*, 2015, 27, 7636-7642.
Ni_2P nanoparticles	59	290	—	1M KOH	*Energy Environ. Sci.*, 2015, 8, 2347-2351
Co_9S_8@MoS_2/carbon nanofibers	61	430	—	1M KOH	*Adv. Mater.*, 2015, 27, 4752-4759
Reduced Mesoporous Co_3O_4 Nanowires	72	～400	—	1M KOH	*Adv. Energy Mater.*, 2014, *4*, 1400696
CoP nanoparticles/Carbon	99	340	—	1M KOH	*ACS Catal.*, 2015, 5, 6874-6878
CoP nanorods/Carbon	71	320	—	1M KOH	*ACS Catal.*, 2015, 5, 6874-6878
Co_3O_4 Nanoflakes	59	380	—	1M KOH	*ACS Appl. Mater. Interfaces*, 2015, 7, 3306−3313
Nickel-Cobalt Binary Oxide (10 at% Co)	44	325	—	1M NaOH	*ACS Nano*, 2014, 8, 9518-9523
Nickel-Cobalt Binary Oxide (40 at% Co)	39	333	—	1M NaOH	*ACS Nano*, 2014, 8, 9518-9523
CoP$_h$/NG **CoP$_s$/NG** **CoP$_h$/G**	**54** **68** **98**	**262** **289** **292**	**343** **369** **409**	**1M KOH**	**This work**

Table S2. Comparison of the HER activities of the CoP_h/NG, CoP_s/NG and CoP_h/G catalysts in 1.0 M KOH with recently published results.

Catalysts	Tafel slope (mV dec^{-1})	j_0 (μA cm^{-2})	η_{10} (mV)	η_{100} (mV)	Electrolyte	Refs.
Cobalt Phosphide Nanowire Arrays	129	—	209	～510	1M KOH	*J. Am. Chem. Soc.*, 2014, 136, 7587-7590
Cobalt-Phosphorous-Derived Films	42	—	94	158	1M KOH	*Angew. Chem. Int. Ed.*, 2015, 54, 6251-6254.
Co phosphide/phosphate thin film	—	—	~360	—	1M KOH	*Adv. Mater.*, 2015, 27, 3175-3180.
Co-P/ N-doped carbon matrices (Loading 0.283mg cm^{-2})	—	—	191	277	1M KOH	*Chem. Mater.*, 2015, 27, 7636-7642
Co-P/ N-doped carbon matrices (Loading 1.0mg cm^{-2})	51	—	154	234	1M KOH	*Chem. Mater.*, 2015, 27, 7636-7642
CoP/Carbon Nanotubes	54	130	122	—	0.5M H_2SO_4	*Angew. Chem. Int. Ed.*, 2014, 53, 6710-6714
CoP/Ti Plate	43	—	90	146	0.5M H_2SO_4	*Chem. Mater.*, 2014, 26, 4326-4329
Cobalt phosphide nanorods	71 —	— —	134 ~150	— —	0.5M H_2SO_4 1M KOH	*Nano Energy*, 2014, 9, 373-382
CoP/RGO	104.8	40	~260	—	0.5M H_2SO_4	*J. Mater. Chem. A*, 2015,3, 5337-5343
CoP nanowires **CoP nanosheets** **CoP nanoparticles**	54 61 87	160 32 54	110 164 221	— — —	0.5M H_2SO_4	*J. Mater. Chem. A*, 2014, 2, 14634-14640
CoP nanotubes	60	—	129	—	0.5M H_2SO_4	*J. Mater. Chem. A*, 2014, 2, 14812-14816
CoP/Nitrogen-Doped Carbon	42	160	91	—	0.5M H_2SO_4	*ChemCatChem* 2015, 7, 1920-1925
CoP_h/NG **CoP_s/NG** **CoP_h/G**	**57** **68** **78**	**416** **262** **347**	**83** **109** **109**	**140** **190** —	**1M KOH**	**This work**

Table S3. Contents of various types of N in CoP$_h$/NG, CoP$_s$/NG and CoP$_h$/G catalysts.

	N-O 402.8 eV	**Graphitic 401.7 eV**	**Pyrrolic 400.4 eV**	**Co-N 399.1 eV**	**Pyridinic 398.3 eV**
CoP$_h$/NG	**0.2**	**1.2**	**0.6**	**0.7**	**0.8**
CoP$_s$/NG	**0.38**	**1.2**	**0.55**	**0.5**	**0.55**
CoP$_h$/G	**1.75**	**0.25**	**0**	**0**	**0**

Table S4. Comparison of R_{ct} and R_s among the CoP$_h$/NG, CoP$_s$/NG and CoP$_h$/G catalysts for HER and OER under the overpotentials of -200 mV and 306 mV,respectively. Unit: Ω cm^{-2}

Overpotential **R (Ω cm^{-2})**		**-200 mV(HER)**	**306 mV (OER)**
R_{ct} (Ω cm^{-2})	**CoP$_h$/NG**	**9.9**	**5.7**
	CoP$_s$/NG	**10.2**	**6.9**
	CoP$_h$/G	**12.4**	**8.8**
R_s (Ω cm^{-2})	**CoP$_h$/NG**	**1.648**	**1.218**
	CoP$_s$/NG	**1.264**	**1.242**
	CoP$_h$/G	**1.544**	**1.238**

Table S5. Comparison of the overall water splitting for CoP$_h$/NG–CoP$_h$/NG, CoP$_s$/NG–CoP$_s$/NG, CoP$_h$/G–CoP$_h$/G in 1.0 M KOH with recently published results.

Catalysts	Voltage at 10 mA cm^{-2} (V)	Electrolyte	Refs.
CoP nanoparticles/Carbon	1.587	1M KOH	*ACS Catal.*, 2015, 5, 6874-6878
Co-P/ N-doped carbon matrices	～1.7	1M KOH	*Chem. Mater.,* 2015, 27, 7636-7642
NiSe Nanowire/ Nickel Foam	1.63	1M KOH	*Angew. Chem. Int. Ed.,* 2015, 54, 9351-9355
NiCo$_2$S$_4$ nanowires array	1.68	1M KOH	*Nanoscale*, 2015, 7, 15122-15126
CoP$_h$/NG	1.58	1M KOH	**This work**
CoP$_s$/NG	1.635		
CoP$_h$/G	1.651		