

## Electronic Supplementary Information (ESI) for

### Cobalt nanoparticles embedded in porous N-rich carbon as an efficient bifunctional electrocatalyst for water splitting

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#### Experimental section

##### Materials

Cobalt nitrate hexahydrate, 2-methylimidazole, methanol, were purchased from Kelong Chemical Reagents Company (Chengdu, China). All reagents and chemicals were of analytical grade and used without further purification

##### Synthesis of the ZIF-67 crystals

In a typical synthesis of the ZIF-67 crystals, two solutions were first prepared by dissolving 4 mmol of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 16 mmol of 2-methylimidazole in 25 mL of methanol, respectively. The latter solution was poured into the former solution and magnetically stirred for 1 h. The mixture was then aged at room temperature for 48 h. The purple solid was collected by centrifugation, and washed three times with methanol and dry at 60 °C for 12 h.

##### Synthesis of the PNC/Co by direct carbonization of ZIF-67 crystals

To synthesize PNC/Co, the ZIF-67 powders were calcined under an argon atmosphere at 600 °C for 5 h. The temperatures inside the furnace were gradually increased from room temperature to the target temperatures with a heating rate of 5 °C·min<sup>-1</sup>.

##### Characterization

The powder X-ray diffraction (XRD) measurements were recorded on a Rigaku Dmax/Ultima IV diffractometer with monochromatized Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm). The morphology was observed with a Hitachi SU8010 field emission scanning electron microscope (FESEM) and a transmission electron microscope (TEM, FEI Tecnai G20). The elemental composition of the samples were characterized by energy-dispersing X-ray spectroscopy (EDS, Oxford instruments

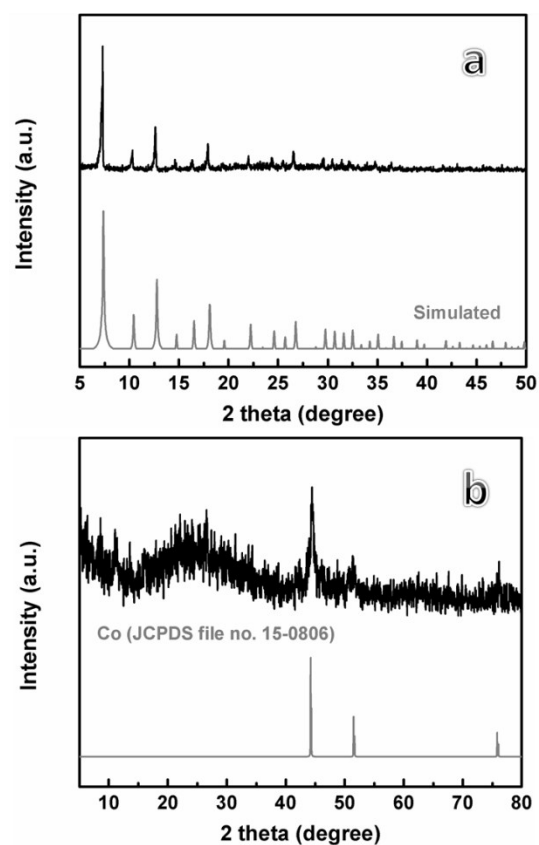
X-Max). X-ray photoelectron spectroscopy (XPS) measurements were recorded on a Perkin-Elmer PHI 5000C spectrometer using monochromatized Al K $\alpha$  excitation. All binding energies were calibrated by using the contaminant carbon (C<sub>1s</sub> = 284.6 eV) as a reference. The Brunauer-Emmett-Teller (BET) surface area and porous structure were measured using an ASAP 2020 V4.00 G apparatus (Micromeritics Instrument Corp., USA) from the nitrogen adsorption and desorption isotherms at 77 K.

### Electrochemical measurements

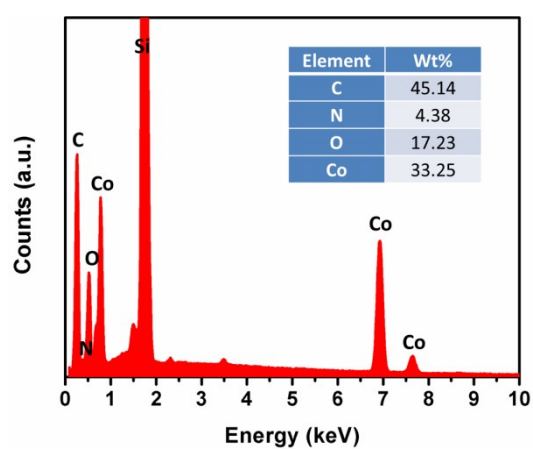
All the electrochemical measurements were carried out at room temperature using a conventional three-electrode system on an electrochemical workstation (CHI 660E, CH Instruments, Inc., Shanghai) with an electrolyte solution of 1.0 M KOH, using a glassy carbon electrode (GCE) modified with various catalysts as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. For the fabrication of the working electrode, 5 mg of the as-synthesized catalyst was dispersed in mixture of distilled water and ethanol (3:1 v/v, 1 mL). Then, 10  $\mu$ L 5 wt% Nafion was added to the above solution. The mixed solution was sonication at least 30 min to form a homogeneous ink. 5  $\mu$ L of the mixed solution was drop-casted onto the glassy carbon electrode with the diameter of 3 mm for the electrochemical measurements. All electrodes were prepared by depositing the same loading mass of active materials on GCE using the same method for OER and HER. All potentials measured in this work were referenced to the reversible hydrogen electrode (RHE) scale according to the Nernst equation:  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \text{ pH}$ .

To evaluate the OER and HER activities of the PNC/Co in 1.0 M KOH solution, linear sweep voltammetry (LSV) was carried out at 5 mV s<sup>-1</sup> for the polarization curves and Tafel plots. The catalyst was cycled 10 times by CVs with a scan rate of 100 mV s<sup>-1</sup> until a stable CV curve was obtained before LSV testing. The stability evaluation was accessed by potential cycling at a sweep rate of 100 mV s<sup>-1</sup> for 1000 cycles. Chronopotentiometry responses were obtained at 10 mA·cm<sup>-2</sup> in 1.0 M KOH. All currents presented are corrected against ohmic potential drop.

The overall water splitting was performed in 1.0 M KOH using a two-electrode cell using PNC/Co coated nickel foam as both anode and cathode. For the fabrication of the working electrode, PNC/Co ink was prepared by dispersing 10 mg catalyst in dispersed in mixture of distilled water and ethanol (3:1 v/v, 1 mL) with 10  $\mu$ L of 5 wt % Nafion solution. Then 50  $\mu$ L of the catalyst ink was loaded onto nickel foam surface and air-dried at room temperature. A catalyst loading on nickel foam is 1 mg cm<sup>-2</sup>.



**Fig. S1** XRD patterns of ZIF-67 (a) and PNC/Co (b).



**Fig. S2** EDS spectrum of the PNC/Co.

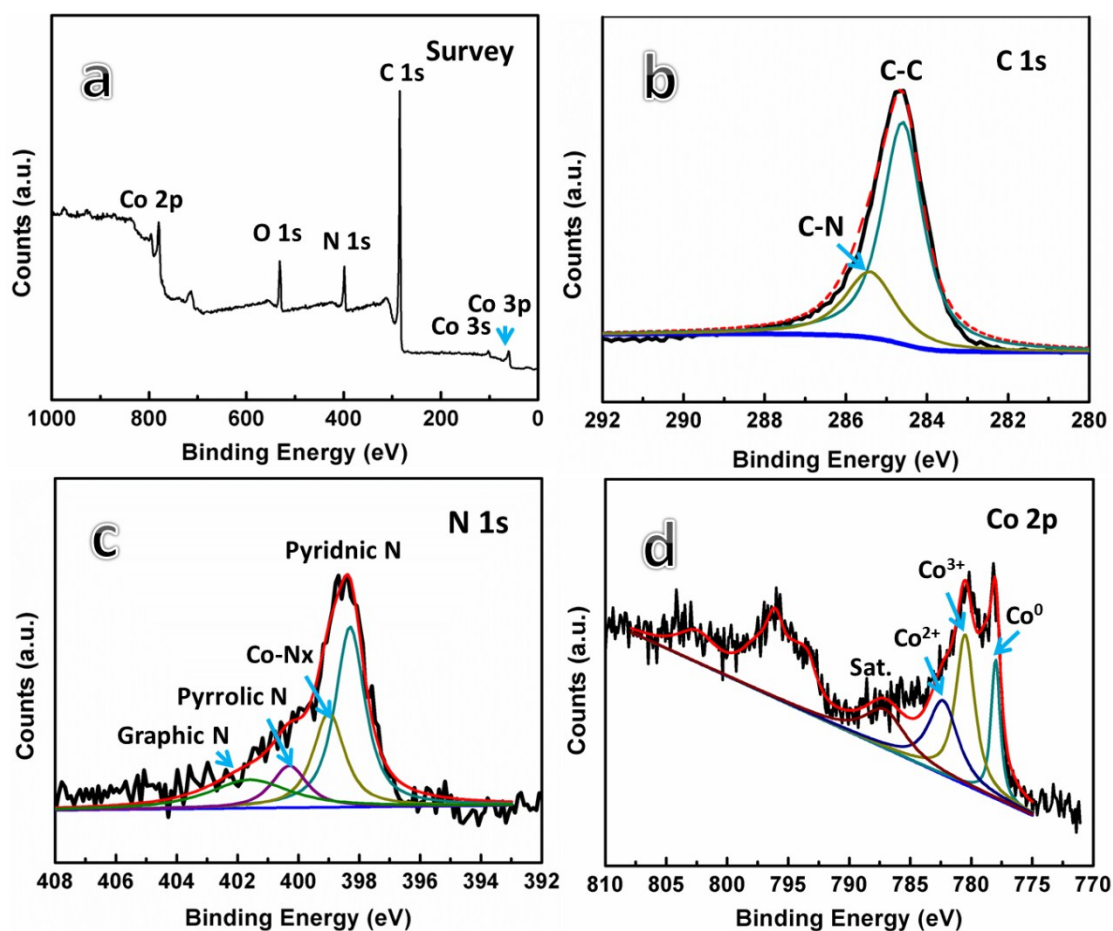
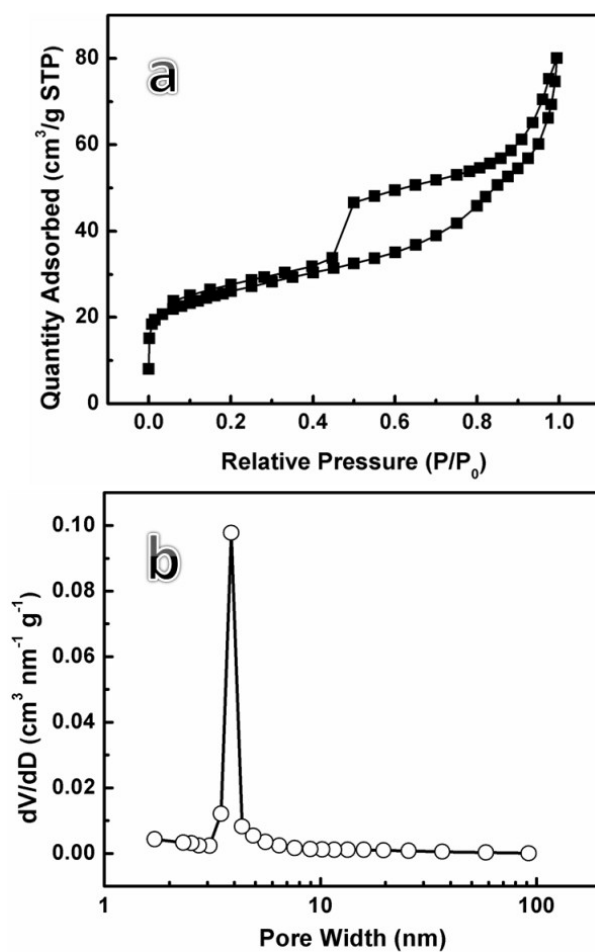
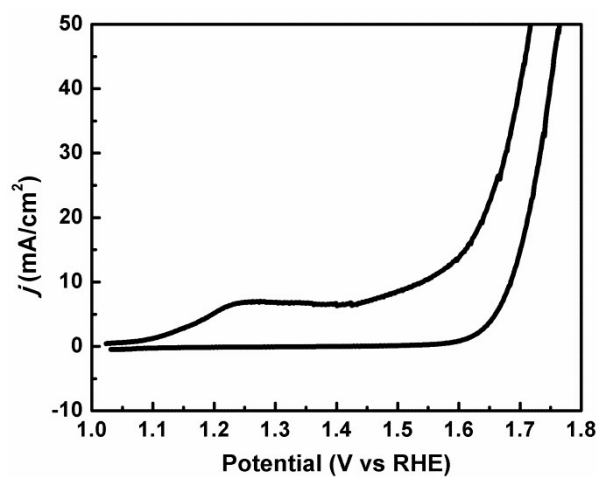


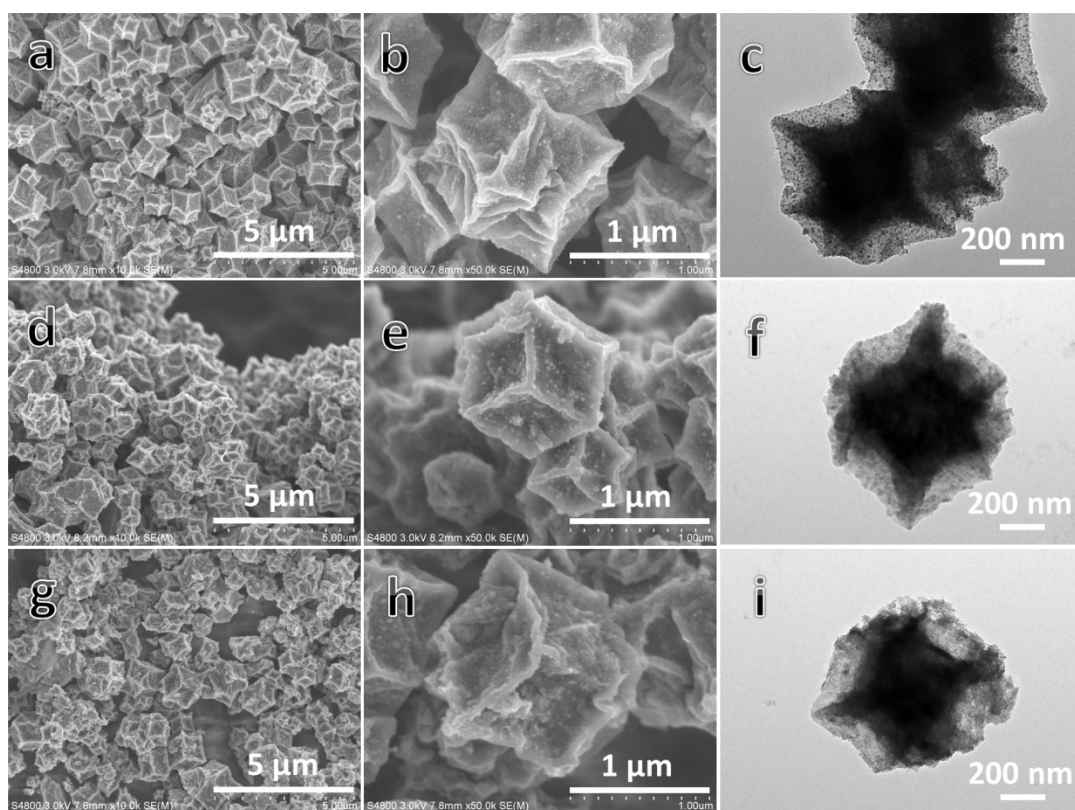
Fig. S3 XPS spectra of the PNC/Co: (a) survey, (b) C 1s, (c) N 1s, and (d) Co 2p.



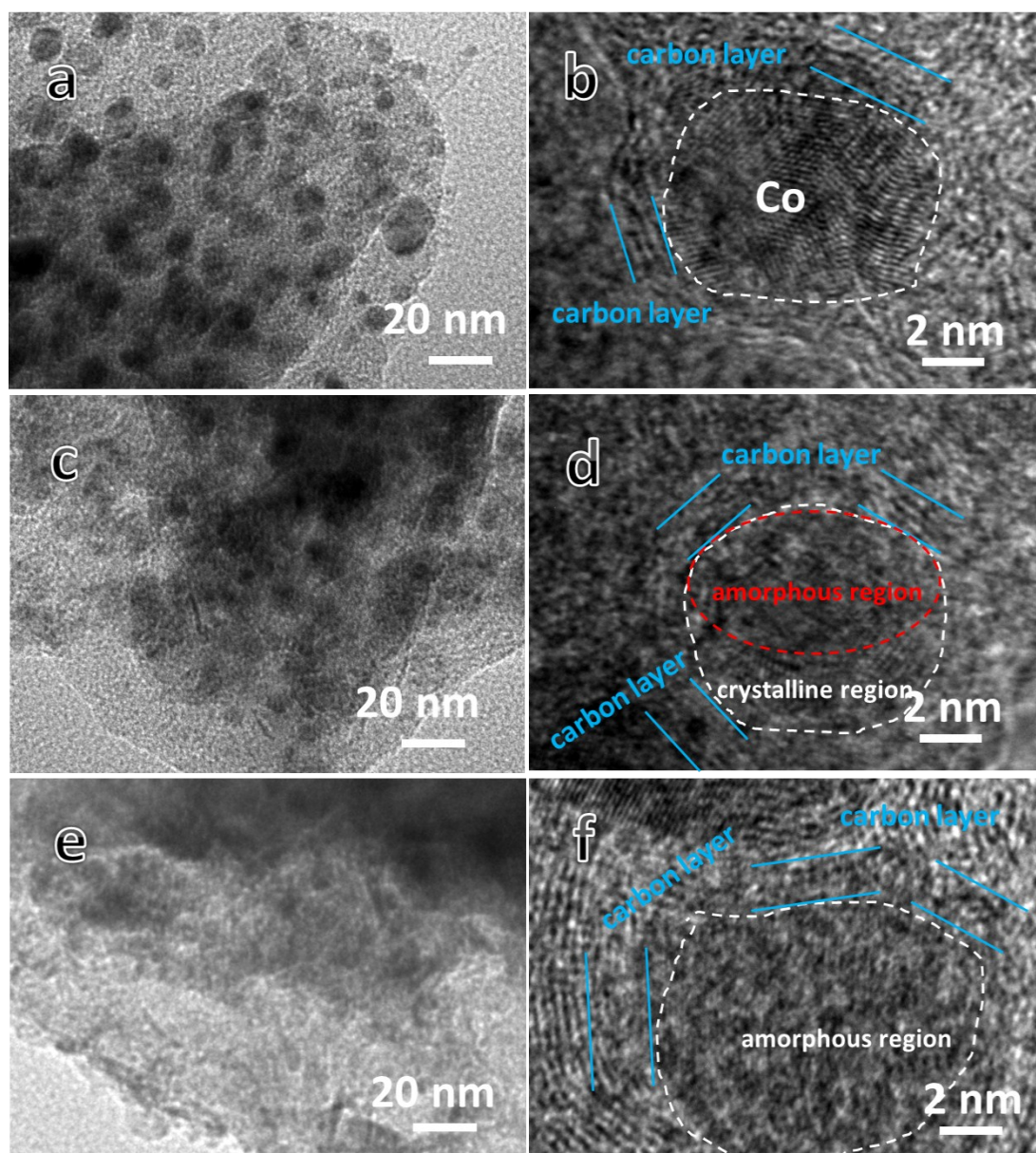
**Fig. S4**  $N_2$  adsorption-desorption isotherms (a) and pore distribution (b) of PNC/Co



**Fig. S5** Cyclic voltammograms of the PNC/Co on glassy carbon electrodes recorded at a potential sweep rate of  $100 \text{ mV s}^{-1}$  in  $1.0 \text{ M KOH}$  solution.

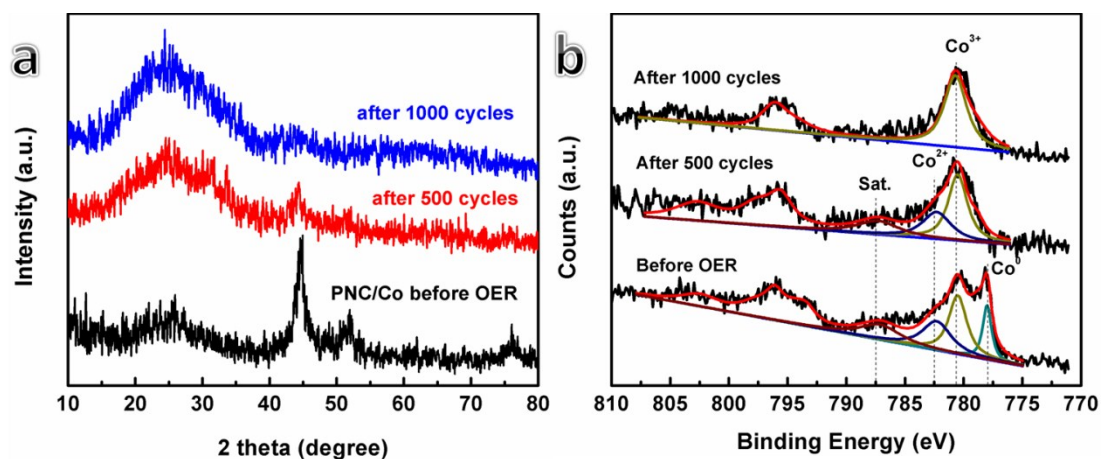


**Fig. S6** SEM and TEM images of the PNC/Co before (a-c) and after 500 (d-f) and 1000 CV (g-i) cycles for OER catalysis.

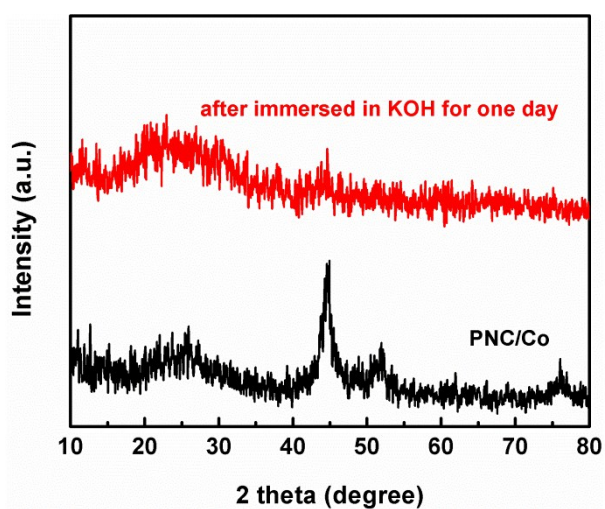


**Fig. S7** HRTEM images of the PNC/Co before (a,b) and after 500 (c,d) and 1000 CV (e,f) cycles for OER catalysis.



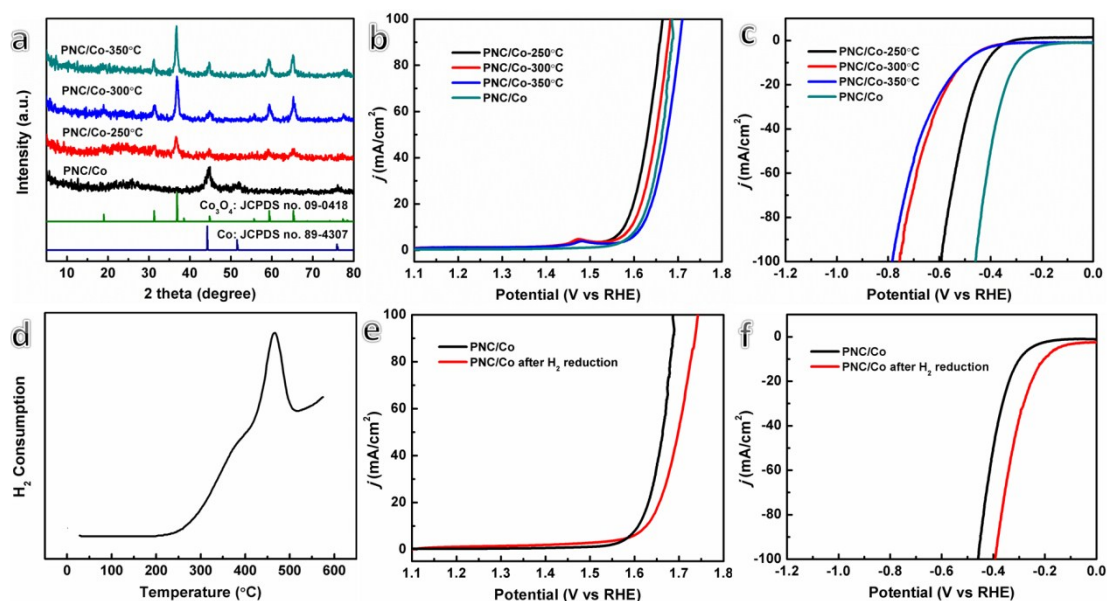


**Fig. S8** XRD patterns (a) and Co 2p XPS spectra (b) of the PNC/Co before and after 500 and 1000 CV cycles for OER catalysis.

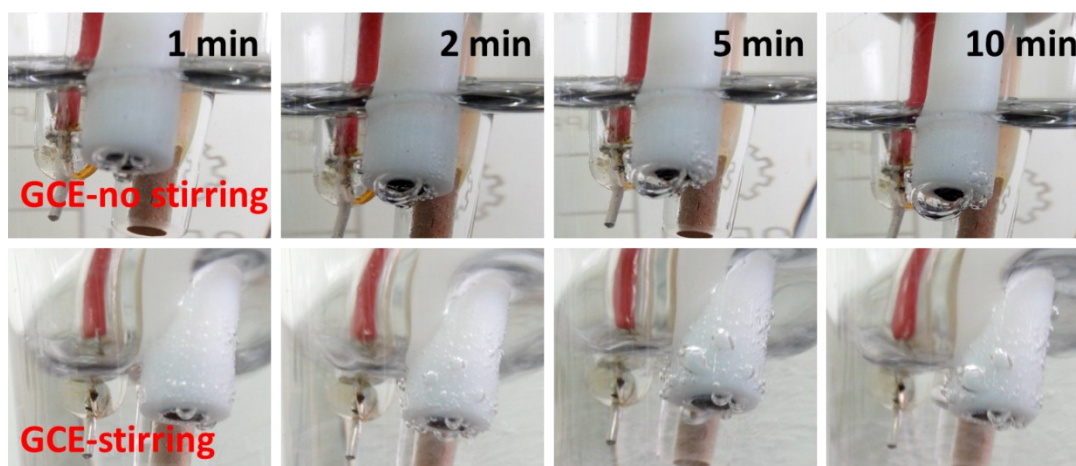


**Fig. S9** XRD patterns of the PNC/Co before and after immersed in 1.0 M KOH solution for one day.

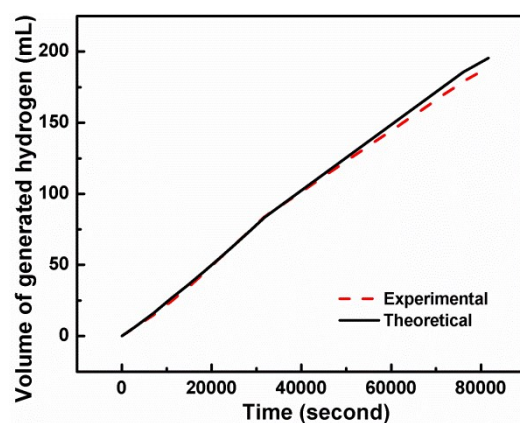




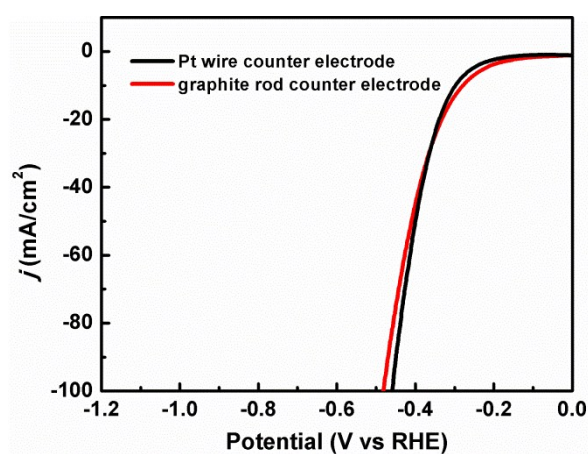
**Fig. S10** (a) XRD patterns of the PNC/Co calcined at different temperatures to create a certain amounts of oxidized Co. Anodic (b) and cathodic (c) polarization curves of the PNC/Co calcined at different temperatures with a scan rate of  $5 \text{ mV s}^{-1}$  in  $1.0 \text{ M KOH}$  solution. (d) TPR curve of the PNC/Co indicating the reduction of Co cations to metallic Co. Anodic (e) and cathodic (f) polarization curves of the PNC/Co before and after  $\text{H}_2$  reduction.



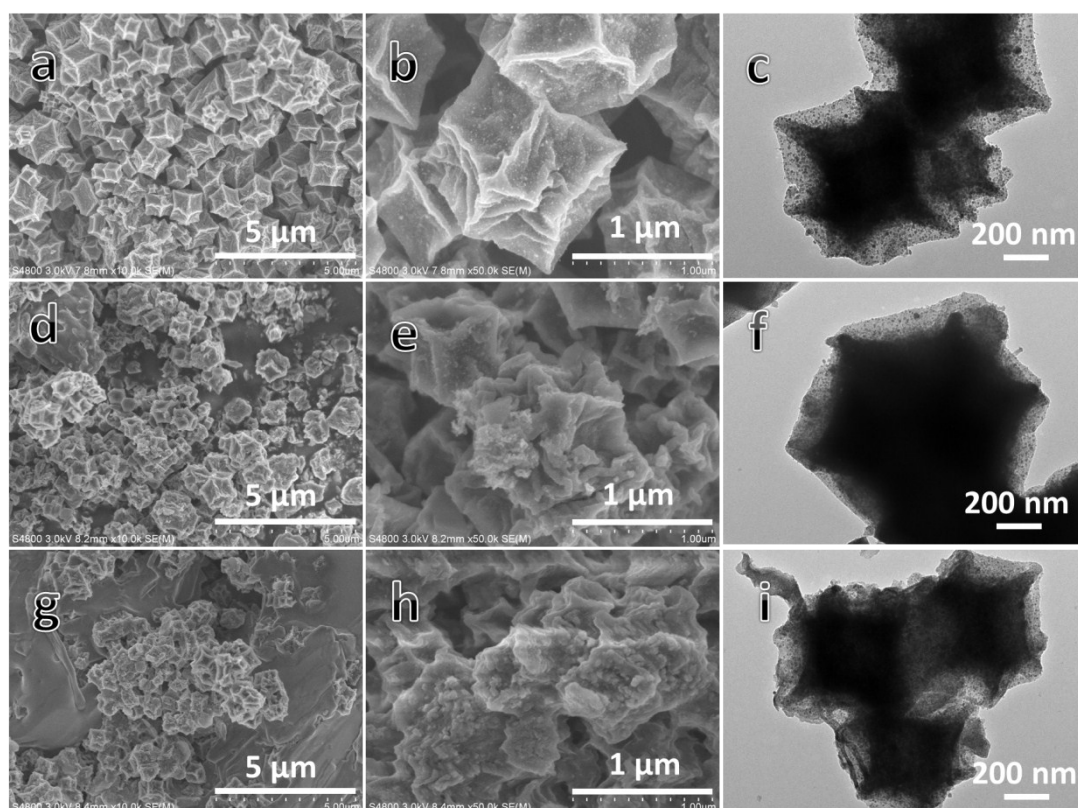
**Fig. S11** Optical photograph of the PNC/Co-modified GCE to generate oxygen bubbles under non-stirring and stirring conditions.



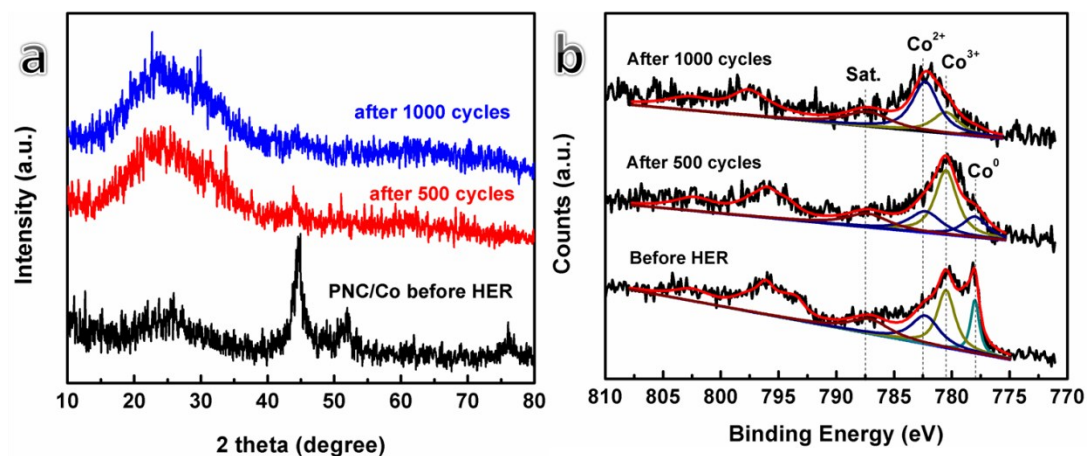
**Fig. S12** The theoretically calculated (solid line) and experimentally measured (dash line) amount of evolved oxygen versus time for the PNC/Co during electrolysis.



**Fig. S13** Cathodic polarization curves of the PNC/Co by using Pt wire and graphite rod as the counter electrode, respectively, with a scan rate of  $5 \text{ mV s}^{-1}$  in  $1.0 \text{ M KOH}$  solution.

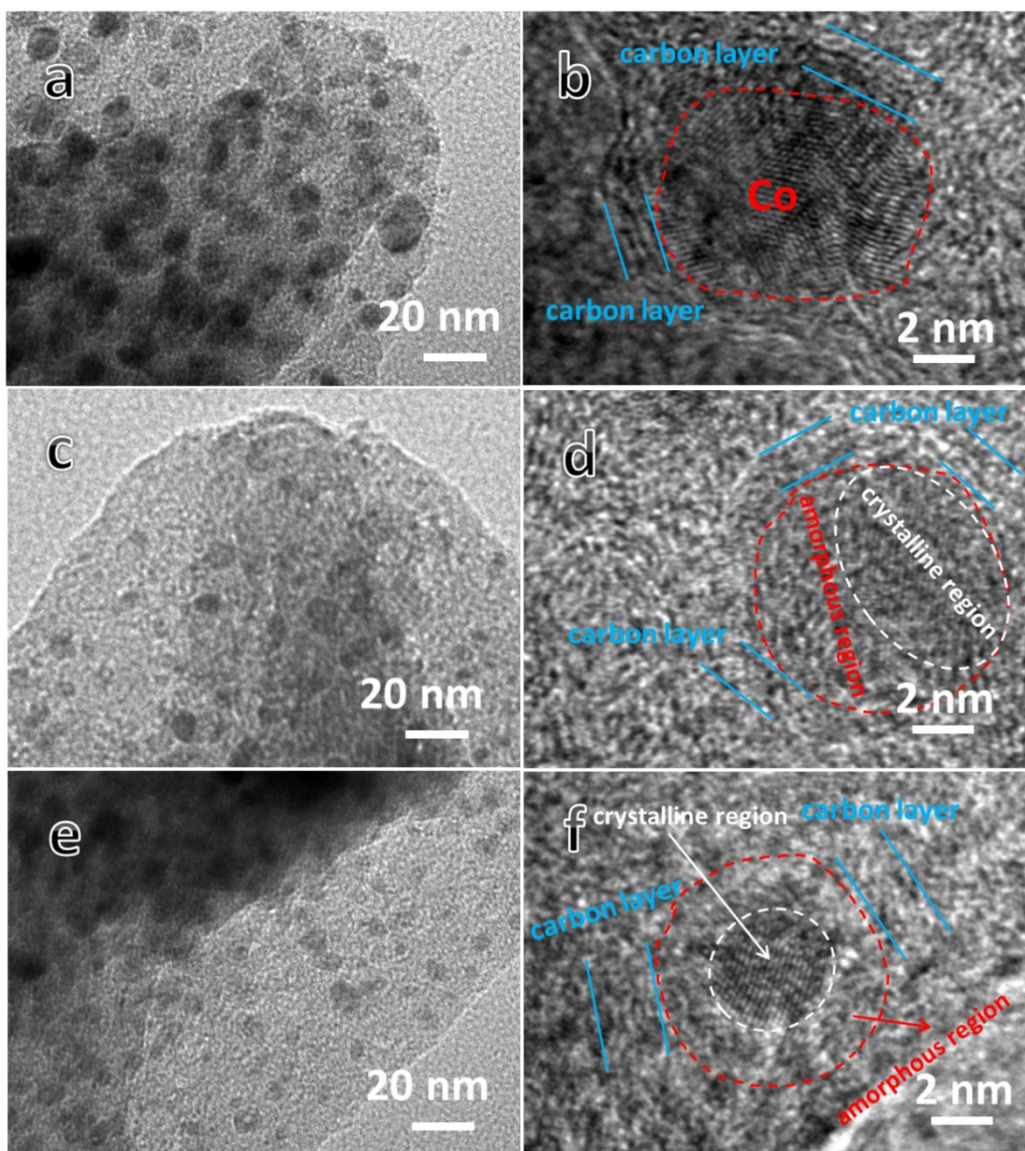


**Fig. S14** SEM and TEM images of the PNC/Co before (a-c) and after 500 (d-f) and 1000 CV (g-i) cycles for HER catalysis.

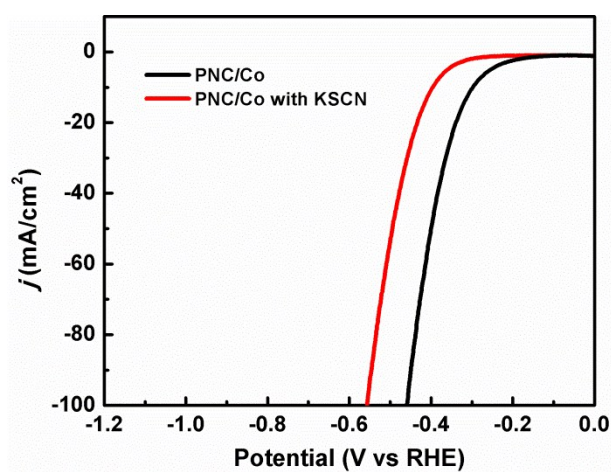


**Fig. S15** XRD patterns (a) and Co 2p XPS spectra (b) of the PNC/Co before and after 500 and 1000 CV cycles for HER catalysis.

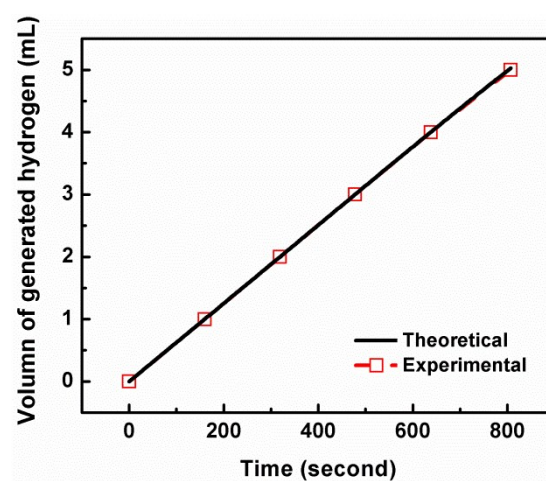




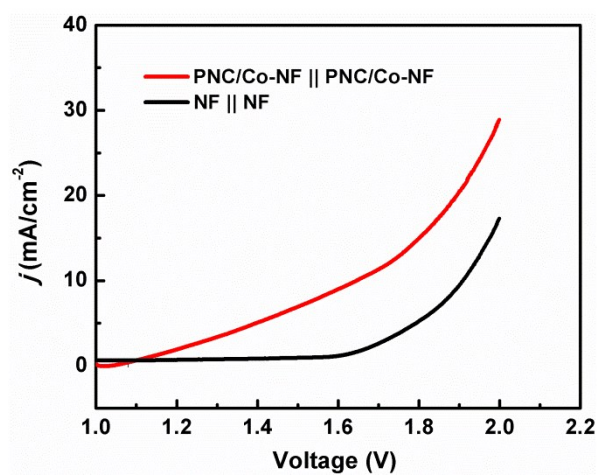
**Fig. S16** HRTEM images of the PNC/Co before (a,b) and after 500 (c,d) and 1000 CV (e,f) cycles for HER catalysis.



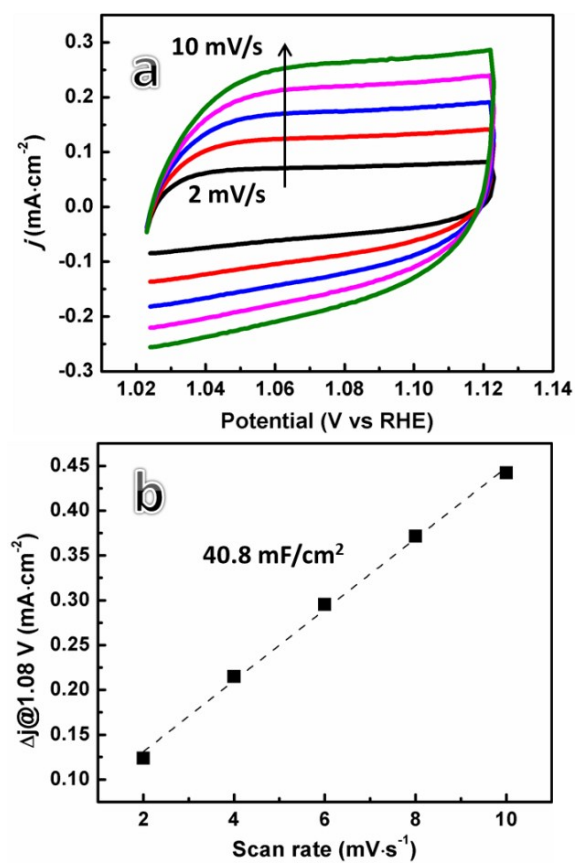
**Fig. S17** HER performances of the PNC/Co with and without the addition of KSCN in 1.0 M KOH.



**Fig. S18** The theoretically amount (solid line) of gas and experimental hydrogen evolution of the PNC/Co during electrolysis.



**Fig. S19** LSV curves of water electrolysis on the PNC/Co-nickel foam (NF) (loading:  $\sim 1 \text{ mg cm}^{-2}$ ) as both anode and cathode in 1.0 M KOH.



**Fig. S20** (a) CVs of the PNC/Co measured at different scan rates from 2 to 10 mV s<sup>-1</sup> (b) Capacitive currents at 1.08 V as a function of scan rate for the PNC/Co.

**Table S1** Comparison of electrocatalytic performance of the PNC/Co with other previously reported electrocatalysts for overall water splitting in a two-electrode cell

Catalyst	Electrolyte	Voltage@10 mA cm <sup>-2</sup> (V)	Reference
<b>PNC/Co</b>	1.0 M KOH	1.64	This work
<b>Co-P</b>	1.0 M KOH	1.65	Angew. Chem. Int. Ed., 2015, 54, 6251
<b>CoP</b>	1.0 M KOH	1.587	ACS Catal., 2015, 5 doi:10.1021/acscatal.5b02076
<b>Ni<sub>2</sub>P</b>	1.0 M KOH	1.63	Energy Environ. Sci., 2015, 8, 2347
<b>Ni<sub>5</sub>P<sub>4</sub></b>	1.0 M KOH	1.7	Angew. Chem. Int. Ed., 2015, 127, 1
<b>CoSe</b>	1.0 M KOH	1.65	Chem. Commun., 2015, 51 doi:0.1039/C5CC06892D
<b>NiCo<sub>2</sub>S<sub>4</sub></b>	1.0 M KOH	1.68	Nanoscale, 2015, 7, 15122
<b>NiMo alloy</b>	1.0 M KOH	1.64	J. Mater. Chem. A, 2015, 3, 20056
<b>Ni<sub>3</sub>Se<sub>2</sub></b>	1.0 M KOH	1.65	Catal. Sci. Technol., 2015, 5, 4954-4958
<b>CoO<sub>x</sub>@CN</b>	1.0 M KOH	1.55 (20 mA cm <sup>-2</sup> )	J. Am. Chem. Soc., 2015, 137, 2688