Supporting Information

Co_2P Quantum Dot Embedded N, P Dual-doped Carbon Self-supported Electrodes with flexible and binder-free properties for Efficient Hydrogen Evolution Reaction

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Experimental section

Materials

Aniline, H_2SO_4 and ethanol were purchased from Aladdin Reagents Ltd. (China). HCl and HNO_3 were purchased from Beijing Chemical Works Ltd. $Co(NO_3)_2 \cdot 6H_2O$ was purchased from Xinglong Chemical Corp. Ltd. Phytic acid (PA), Pt/C (20 wt. %) and Nafion (5 wt. %) were purchased from Sigma-Aldrich. All the reagents were analytical grade and used without further treatments. The deionized water used throughout the whole experimental process was purified through a Millipore system.

Preparation of carbon cloth (CC): CC was cleaned with mixed aqueous solutions of HCl (19 wt. %) and HNO_3 (10 wt. %), followed by washing with deionized water repeatedly.

Preparation of Co_2P@NPC: The preparation of Co_2P@NPC was obtained by a simple electrodeposition in a three-electrode system consisting of carbon cloth (CC) as working electrode, Ag/AgCl as reference electrode and carbon rod as count electrode at room temperature. The PANI-PA was electropolymerized onto the CC in the electrolyte. The solution was formed by dissolving 8 mL HCl in 50 mL H_2O and then adding 4.6 g aniline and 10 g phytic acid under stirring for 30 minutes. A potential of 0.8 V was constantly applied to the working electrode for 30 min. And then, PANI-PA/CC was washed with deionized water, followed by drying at 60 ^oC for half an hour and then immersed in $Co(NO_3)_2 \cdot 6H_2O$ solution at 40 ^oC for 2 h, followed by drying at 80 ^oC for 4 h. A temperature programmed reduction process was then carried out at 700, 800, 900 ^oC in H_2 for 2h. The heating rate is 5 ^oC per min. After cooling down to room temperature, the samples were entirely transformed into N, P co-doped carbon structure. The NPC was prepared in a similar way without the soaking step.

Structural characterizations

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku X-ray diffractometer equipped with a Cu Kα radiation source. The morphology and structure were characterized by scanning electron microscopy (SEM: XL30 ESEM FEG) and transmission electron microscopy (TEM: JEM-2100F). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALABMK II X-ray photoelectron spectrometer. Raman shifts were recorded on a LabRAM Aramis Raman spectrometer instrument using an Ar ion laser with an excitation wavelength of 633 nm.

Electrochemical measurements

All electrochemical measurements are performed on a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode with a two-compartment cell. The acidic (0.5 M H_2SO_4) and electrochemical measurements were performed using a saturated calomel electrode (SCE) as the reference electrode. The graphite rod was used as the counter electrode in all measurements. Polarization data were obtained at a scan rate of 2 mV s^{-1}. In all measurements, the reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE). All polarization curves were iR-corrected. Electrochemical impedance spectroscopy (EIS) measurements were carried out in the frequency range of 100 kHz–0.01 Hz.

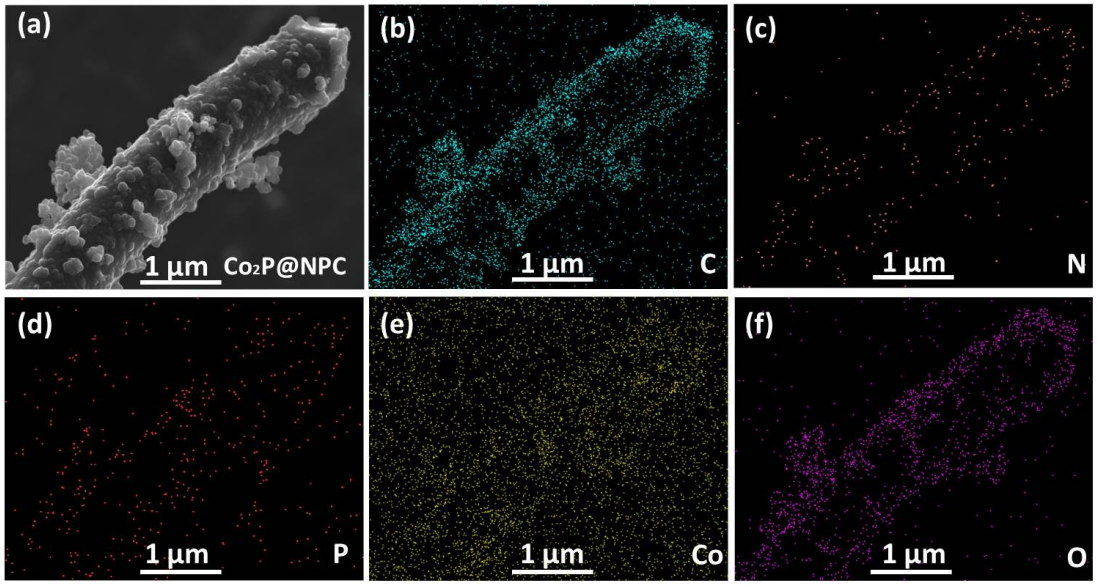

Figure S1. EDX element mapping images of (a) Co_2P@NPC-800 coated on CC, (b) C, (c) N, (d) P, (e) Co and (f) O.

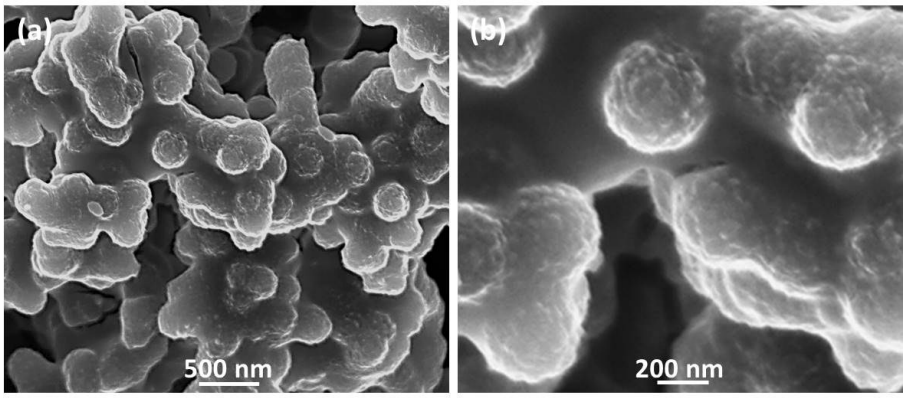

Figure S2. (a, b) SEM images of Co_2P@NPC-700.

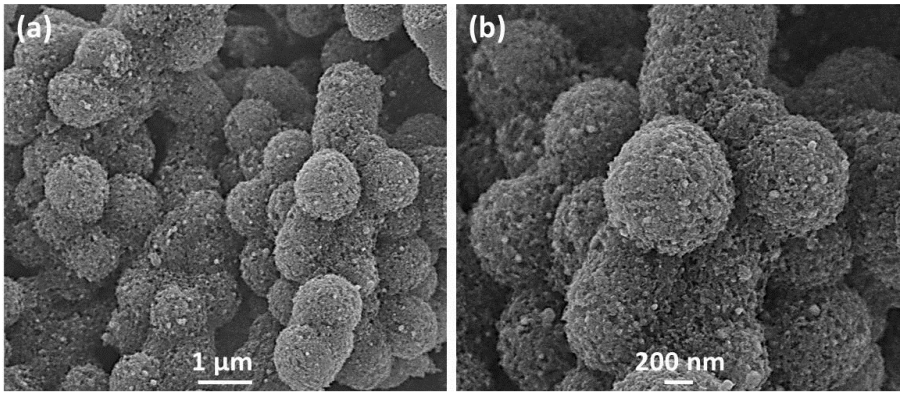

Figure S3. (a, b) SEM images of Co_2P@NPC-900.

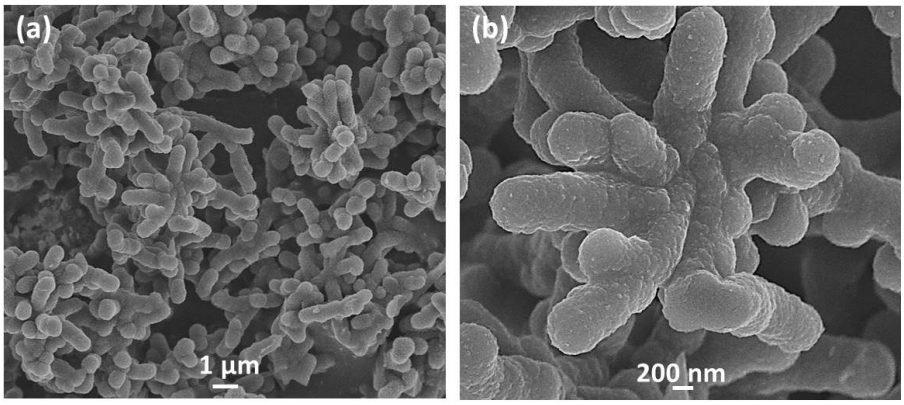

Figure S4. (a, b) SEM images of NPC.

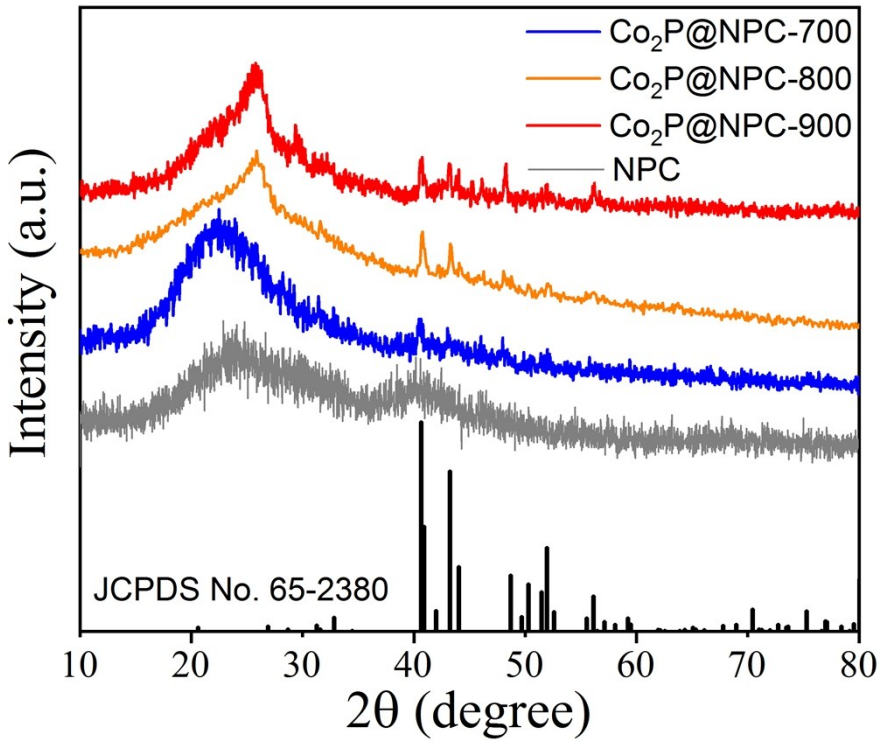

Figure S5. XRD pattern of NPC, Co_2P@NPC-700, Co_2P@NPC-800 and Co_2P@NPC-900.

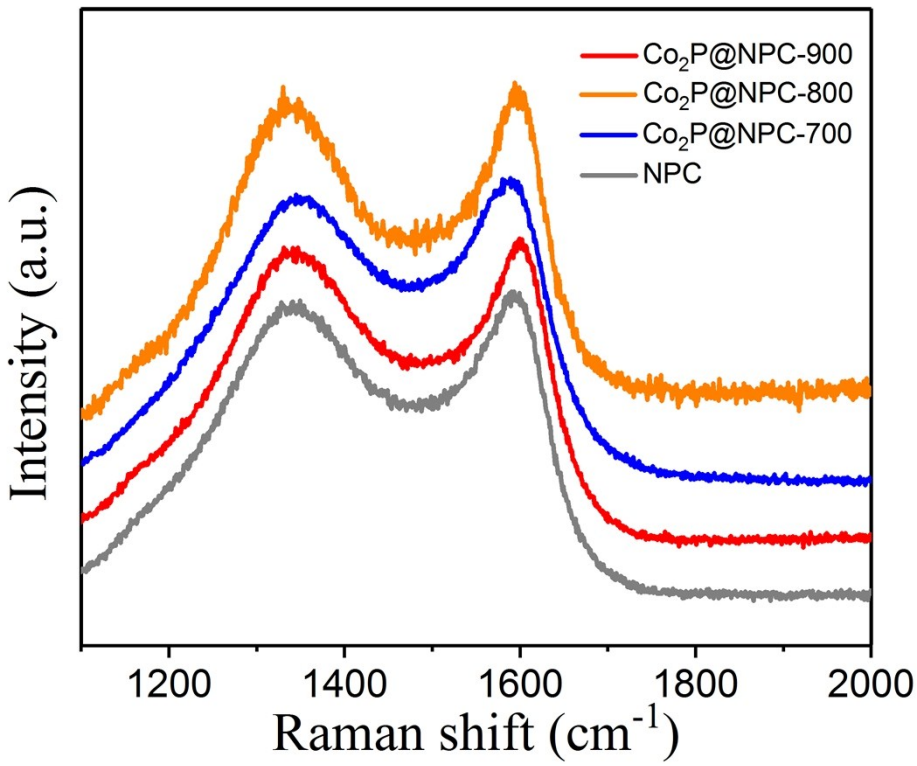

Figure S6. Raman spectrum of NPC (I_D/I_G=0.9771), Co_2P@NPC-700 (I_D/I_G=0.9620), Co_2P@NPC-800 (I_D/I_G=0.9914) and Co_2P@NPC-900 (I_D/I_G=0.9764).

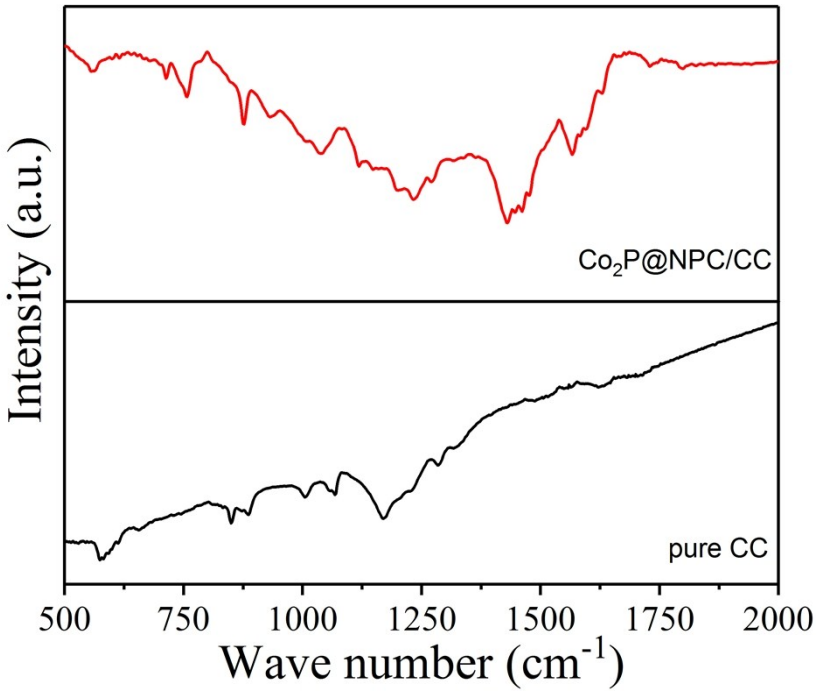

Figure S7. FTIR spectrum of Co_2P@NPC and the pure CC.

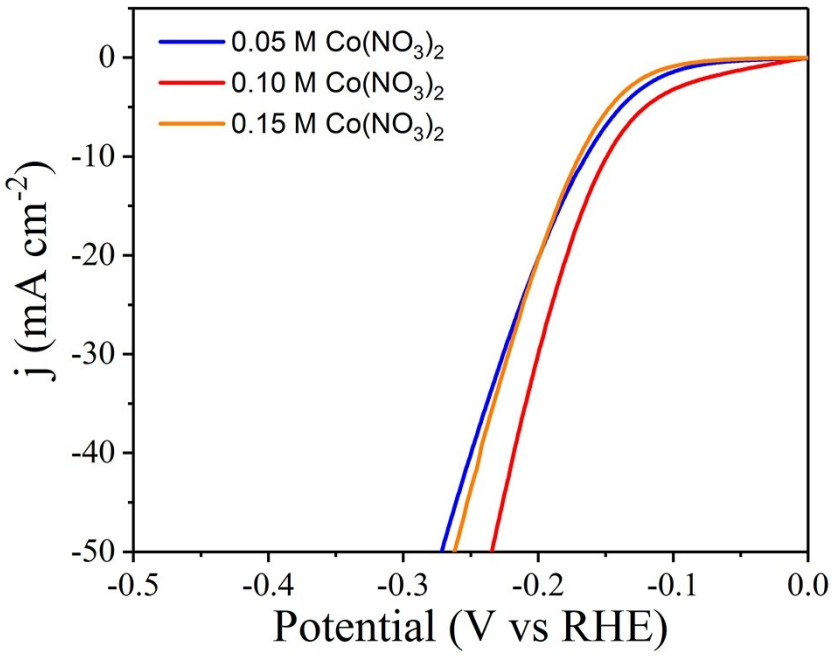

Figure S8. Effect of metal contents on the electrocatalytic activity of Co_2P@NPC. Polarization curves (without iR-correction) for HER were carried out in 0.5 M H_2SO_4 for Co_2P@NPC-800 with different Co contents.

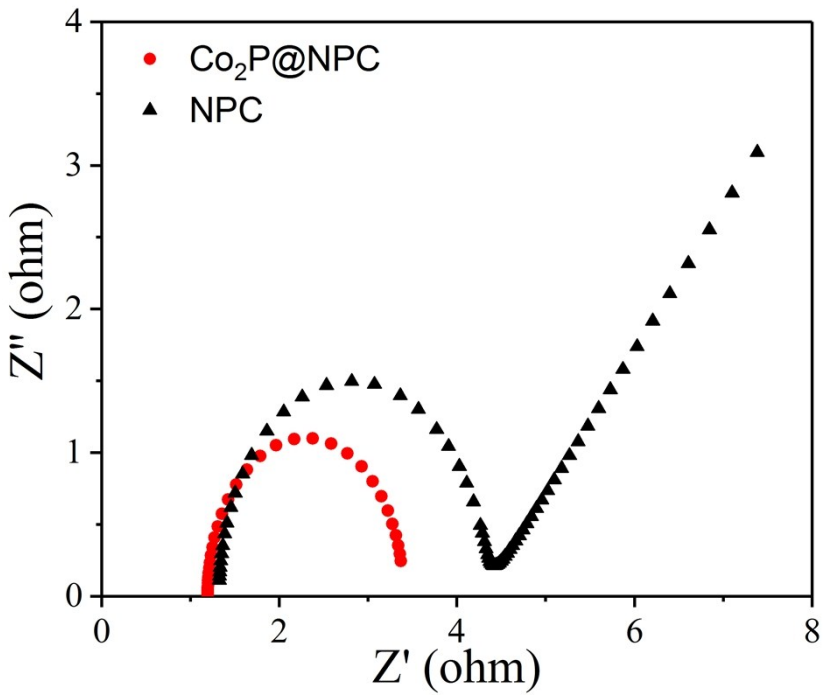

Figure S9. Nyquist plot of Co_2P@NPC and NPC.

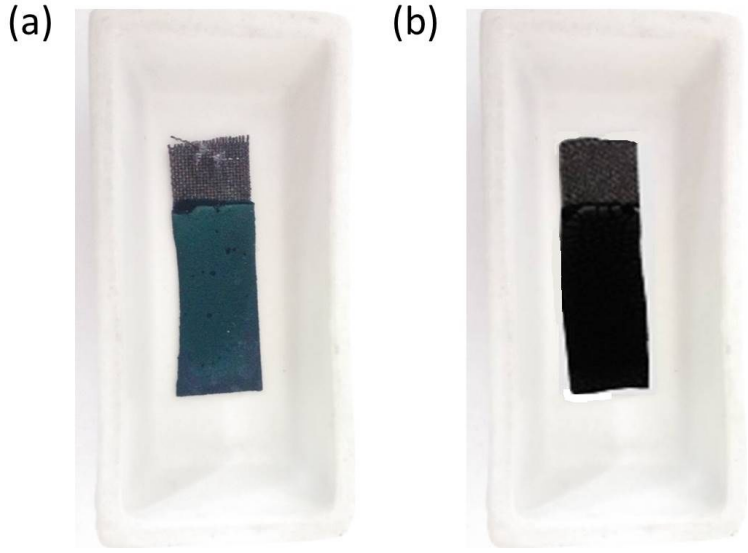

Figure S10. Photograph of (a) the precursor coated on CC after electrolytic deposition and (b) the Co_2P@NPC/CC.

Table S1. Comparison of HER performance of Co_2P@NPC with other recently reported catalysts in 0.5 M H_2SO_4.

Catalyst	Current density (j, mA cm^{-2})	Overpotential at the corresponding j (mV)	Ref.
Co_2P@NPC	10	116	This work
CoP/CNT	10	122	[1]
CoP hollow NPs	20	80	[2]
CoP nanotubes	10	129	[3]
Co_2P/Ti	10	100	[4]
Co_2P@N,P-PCN/CNTs	10	126	[5]
Co_2P@NPG	10	103	[6]
CoP/CNT	10	122	[7]
Ni_2P	10	137	[8]
FeP NPs@NC	10	130	[9]
CoP/rGO	10	105	[10]
CoP Hollow Polyhedron	10	159	[11]
CoP/carbon nanotubes	10	139	[12]
Mo_2C/CC	20	193	[13]
Porous Ni_2P Polyhedrons	10	158	[14]
Co_2P/C	10	125	[15]

Table S2. Comparison of HER performance of Co_2P@NPC with other recently reported catalysts in 1 M KOH.

Catalyst	Current density (j, mA cm^{-2})	Overpotential at the corresponding j (mV)	Ref.
Co_2P@NPC	10	129	This work
CoP/CC	10	209	[16]
CoP@NC	10	210	[17]
FeP NPs/CC	10	218	[18]
Co-NRCNTs	10	370	[19]
Co_2P@NPG	10	165	[6]
CoP_2/RGO	10	88	[20]
Co_2P nanorods	20	171	[21]
FeP NTs/CC	10	120	[22]
Co-P film	10	94	[23]
CoP_3	10	119	[24]
NiCoP quasi-hollow nanocubes	10	150	[25]
NiCoP Hollow QuasiPolyhedra	10	124	[26]
CuCoP/nitrogendoped carbon	10	220	[27]
Ni-Co mixed phosphide/nitrogendoped carbon	10	116	[28]
FeP2/Fe foil	10	189	[29]
Co@NG	10	337	[30]

Table S3. Elemental content analysis result of Co_2P@NPC

Element	Mass Conc (wt. %)
P	2.63
Co	6.10
C	83.28
N	3.16

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