Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

B, N-codoped and C-coated Co_2P Composite Derived from Phytate Derivatives as High Efficiency HER Electrocatalyst

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The calculation process of C_{dl}:

First, we measured CV in a range of 0.05 V to 0.2 V vs. Ag/AgCl (0.5 M H_2SO_4 solution) at different scan rates (20, 40, 60, 80 and 100 mV/s). Under each scan rate, the measurements were repeated three cycles to reduce errors. The measured CV results of Co_2P@BNC and Co_2P@NC are presented in . Fig. 5(b) and (c).

Second, the double-layer capacitance C_{dl} was estimated by plotting the Δj (Y-axis in Fig. 5d) = (j_a − j_c) at 0.12 V (where j_c and j_a are the cathodic and anodic current densities, respectively) against the scan rate (X-axis in Fig. 5d) for Co_2P@BNC and Co_2P@NC, in which the slope was twice that of C_{dl}.

Take Co_2P@BNC as an example：

The following are the j_a and j_c values for Co_2P@BNC (at 0.12 V and different scan rates 20, 100 mV/s.):

$j_a(20)$ = 1.30 mA/cm^2, $j_a(100)$ = 5.81 mA/cm^2;

$j_c(20)$ = -1.48 mA/cm^2, $j_c(100)$ = -6.04 mA/cm^2;

Δj = (j_a - j_c) values： Δj(20) = 2.78 mA/cm^2, Δj(100) = 11.85 mA/cm^2，

$$\Delta j = \frac{\Delta j\ 100 - \Delta j\ 20}{100 - 20} \times \frac{1}{2} = 0.0566875 F\ cm^{-2}$$

C_{dl} = 0.0566875 F cm^{-2} × 1000 ≈ 56.69 mF cm^{-2}

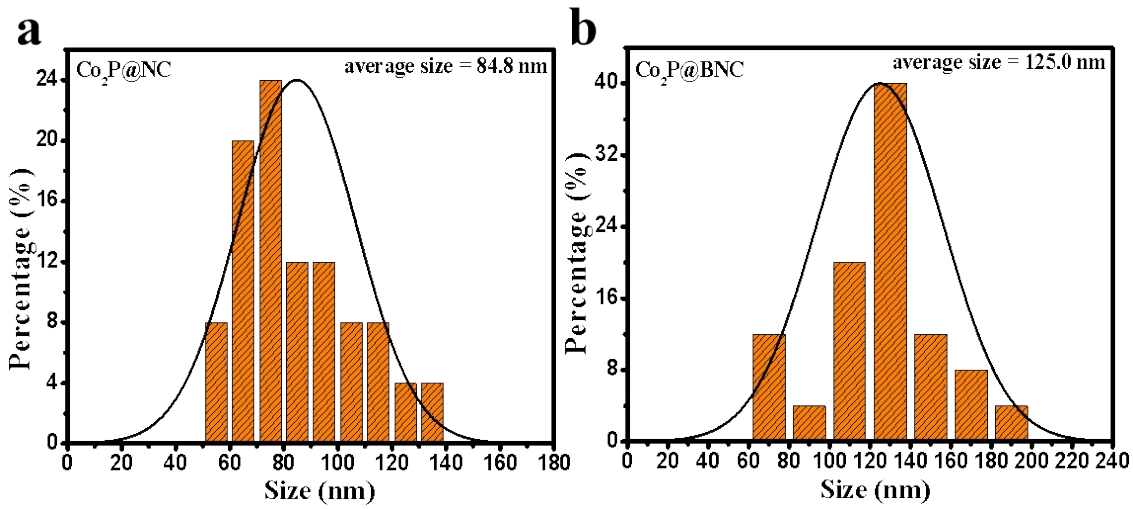

Fig. S1 Corresponding size distribution of (a) Co_2P@NC and (b) Co_2P@BNC.

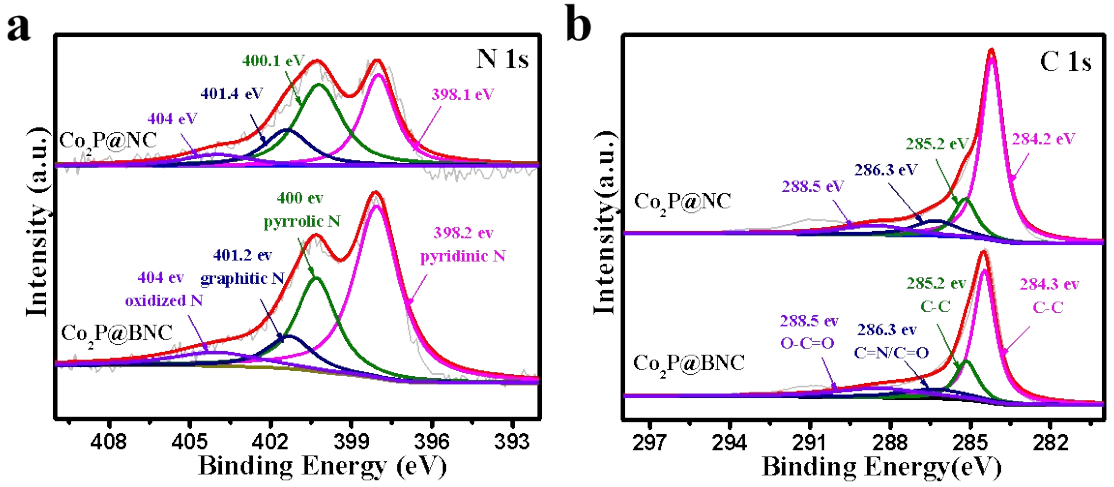

Fig. S2 High-resolution XPS spectra of N 1s (a), C 1s (b) for Co_2P@NC and Co_2P@BNC.

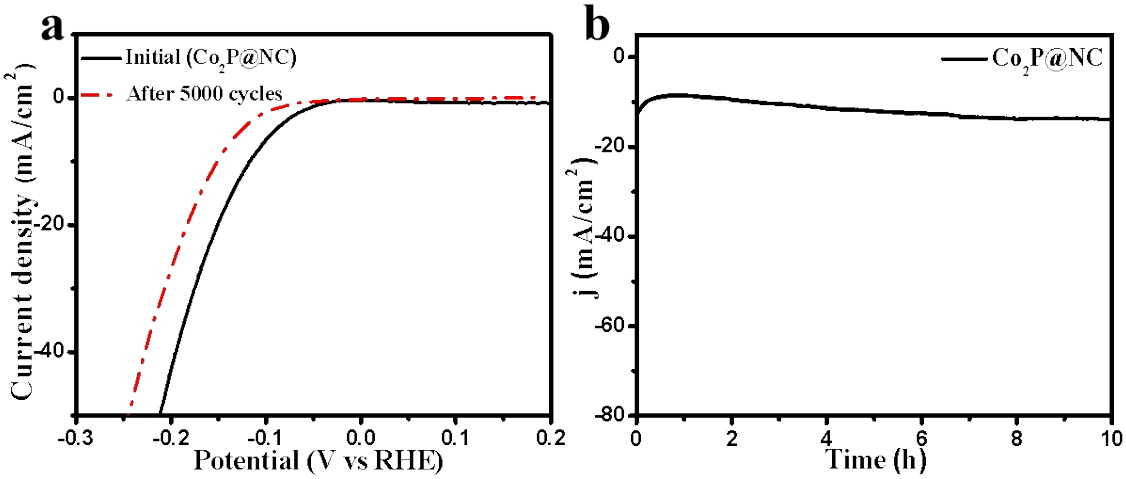

Fig. S3 (a) Polarization curves for Co_2P@NC initial and after 5000 CV scanning between - 0.3 and 0.2 V vs. RHE. (b) Timedependent current density curve for Co_2P@NC under a current density of 10 mV/cm^2 for 10 h.

Table S1 Comparison of HER performance for Co_2P@BNC with recently reported TMP-based and state-of-theart metallic electrocatalysts in acidic media.

Catalysts	Electrolytes	η@10mA·cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Reference
Co_2P@BNC	0.5 M H_2SO_4	75	56	This work
CoP/S	0.5 M H_2SO_4	107	57	Appl. Catal. B: Environ. 2019, 251, 213.

MoP/SNG-20	**0.5 M H_2SO_4**	**99**	**54.41**	**ACS Catal. 2017, 7, 3030.**
Ni-CoP/HPFs	**0.5 M H_2SO_4**	**144**	**52**	**Nano Energy 2019, 56, 411.**
NiCoP NS/NF	**0.5 M H_2SO_4**	**80**	**-**	**J. Am. Chem. Soc. 2018, 140, 5241.**
$NiCo_2Px$	**0.5 M H_2SO_4**	**104**	**59.6**	**Adv. Mater. 2017, 29, 1605502.**
Fe−Co_2P/NCNTs	**0.5 M H_2SO_4**	**104**	**68**	**ACS Appl. Mater. Interfaces 2016, 8, 13890.**
CoP/NCNHP	**0.5 M H_2SO_4**	**140**	**53**	**J. Am. Chem. Soc. 2018, 140, 2610.**
CoP@PS/NCNT	**0.5 M H_2SO_4**	**80**	**53**	**Adv. Energy Mater. 2018, 1702806.**
CoP/CNTs	**0.5 M H_2SO_4**	**76**	**67**	**Adv. Funct. Mater. 2017, 1606635.**
CoP-CNTs hybrids	**0.5 M H_2SO_4**	**139**	**52**	**Small 2017, 13, 1602873.**
CoP/CNTs	**0.5 M H_2SO_4**	**122**	**54**	**Angew. Chem. Int. Ed. 2014, 53, 6710.**
S-MoP NPL	**0.5 M H_2SO_4**	**86**	**34**	**ACS Catal. 2019, 9, 651.**
$Co_{0.6}Fe_{0.4}P$/CNTs	**0.5 M H_2SO_4**	**67**	**57**	**Adv. Funct. Mater. 2017, 27, 1606635.**
$Co_{0.59}Fe_{0.41}P$ nanocubes	**0.5 M H_2SO_4**	**72**	**52**	**Nanoscale. 2015, 7, 11055.**
MoP@C	**0.5 M H_2SO_4**	**88**	**50.4**	**Adv. Energy Mater. 2018, 8, 1801258.**
MoP@PC	**0.5 M H_2SO_4**	**153**	**66**	**Angew. Chem. Int. Ed. 2016, 55, 12854.**
Co-Fe-P nanotubes	**0.5 M H_2SO_4**	**80**	**72**	**Nano Energy 2019, 56, 225.**

Abbreviations: SN = Sulfur and nitrogen dual-doped; G = Graphene; HPFs = hollow polyhedron frames; NS = nanosheet; NF = nickel foam; CNT = Carbon nanotube; NCNHP = N-doped carbon nanotube hollow polyhedron; NPL = nanoporous layer; C = Carbon; PC = Porous carbon.