Phosphorus-doped carbon spheres supported CoP nanocatalyst for electrochemical hydrogen evolution

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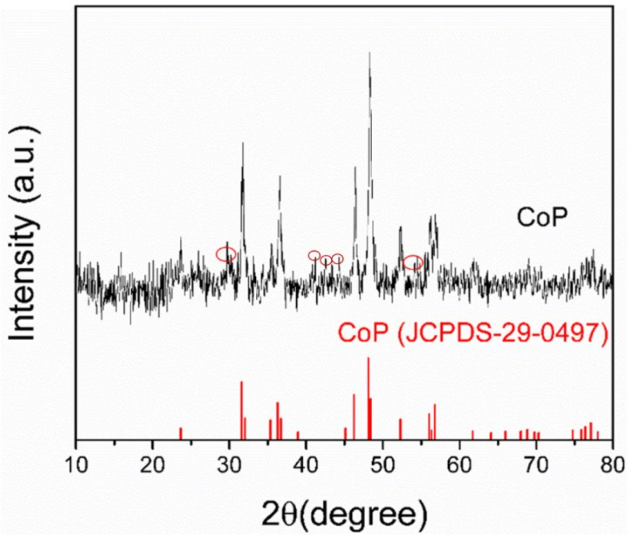

Fig. S1 XRD pattern of bare CoP.

As shown in Fig. S1, the XRD pattern of bare CoP is consistent with the characteristic peaks of CoP (JCPDS-29-0497). There are also some weak characteristic peaks (marked with red ring) of metallic cobalt can be observed in the pattern possibly due to the reduction action of hydrogen which will be produced during the low temperature decomposition of sodium hypophosphite. But, this phenomenon is not obvious for CoP/CSs possibly due to the relatively low content and small particle size of the matter.

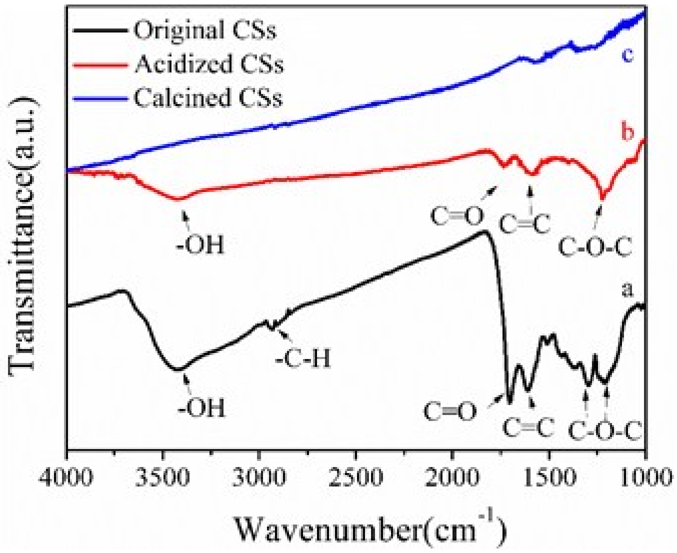

Fig. S2 FTIR spectra of CSs with different treatment processes original CSs (a), acidized CSs (b), calcined CSs (c).

The FTIR test was used to investigate the effects of different treatment processes of carbon spheres (CSs). It can be seen from Fig. S2a that there are many hydroxyl, carboxyl and oxygen-containing functional groups exist in the FTIR of original CSs. However, these functional groups are hard to be detected after calcination. With respect to the acidized CSs, there are few of functional groups can be detected. It is reported that Co^{2+} could readily adsorb on graphene oxide due to the interactive electrostatic attraction between Co^{2+} and oxygen-containing functional groups.[1] Therefore, the absorption and growth of cobalt salt on original CSs is easier than the acidized or calcined CSs.

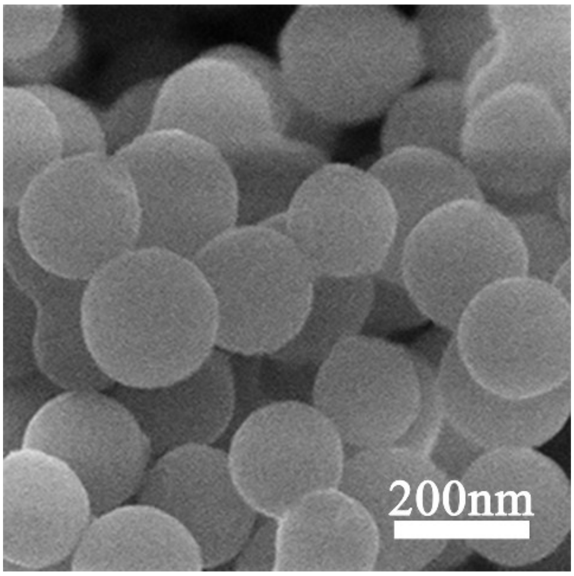

Fig. S3 SEM image of original CSs.

As shown in Fig. S3, the original CSs present a regular spherical structure with a diameter of about 180 nm.

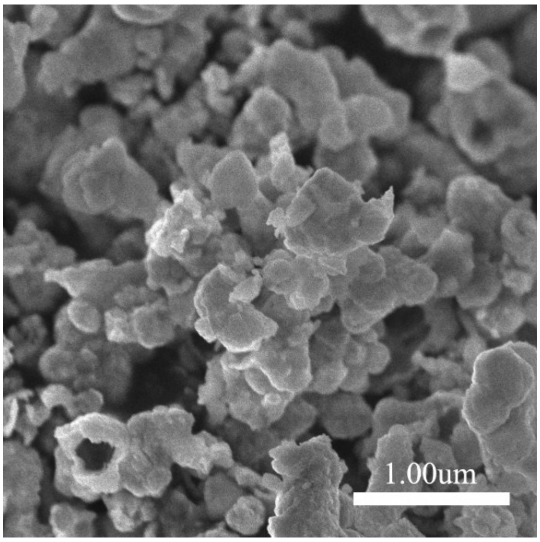

Fig. S4 SEM image of CoP.

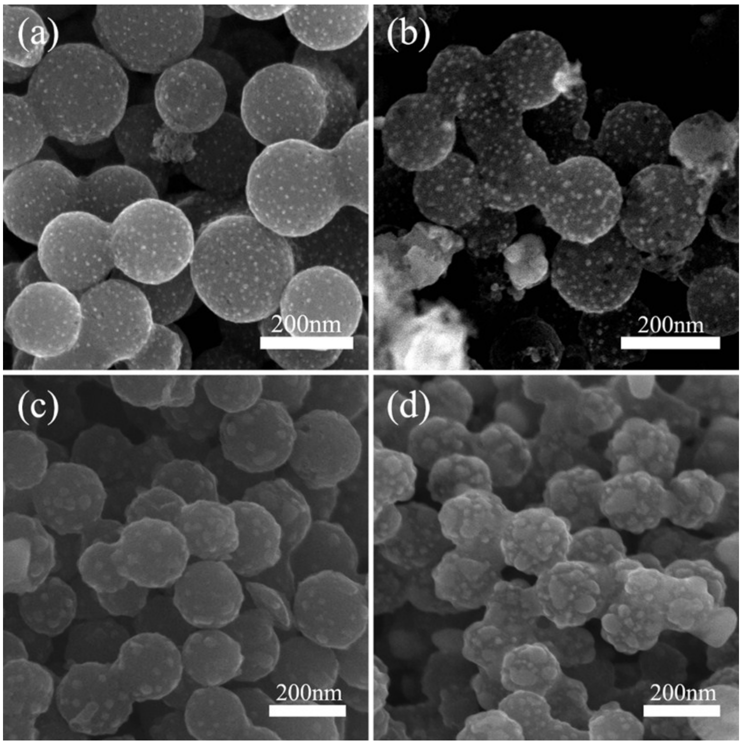

Fig. S5 SEM images of CoO/CSs-0.03 (a), CoO/CSs-0.07 (b), CoP/CSs-0.03 (c) and CoP/CSs-0.07 (d).

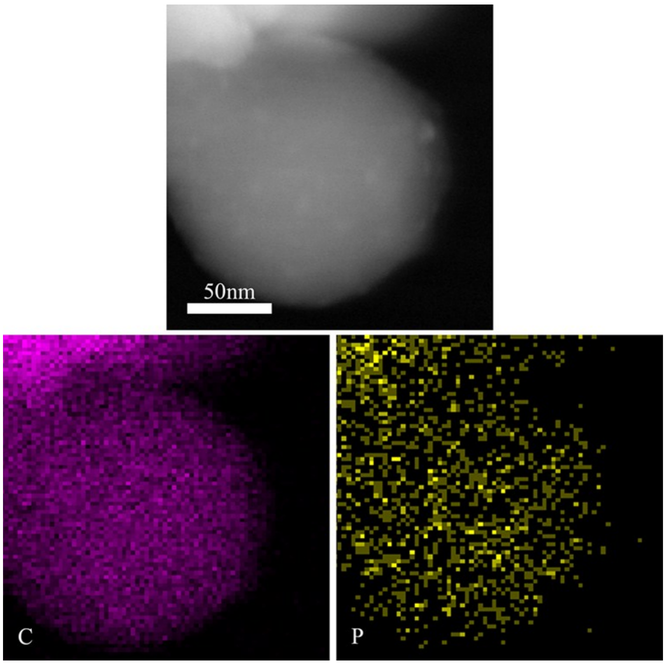

Fig. S6 HAADF-STEM image of P-doped CSs and elemental mappings of C, P.

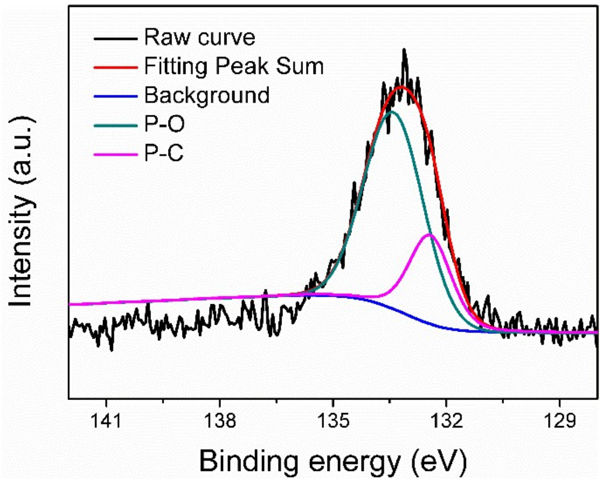

Fig. S6. XPS spectrum of bare CSs.

Fig. S7 shows the high resolution P 2p spectrum of bare CSs treated by phosphorization process which are same with the preparation of CoP/CSs. The peaks located at 133.7 eV and 132.4 eV are assigned to P-O bonding and P-C bonding, respectively.

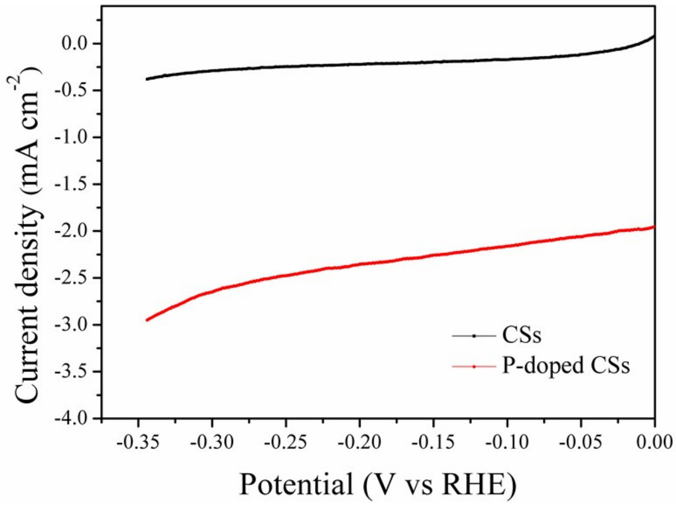

Fig. S8 Polarization curves of CSs and P-doped CSs in 0.5 M H_2SO_4 solution with a sweep rate of 3 mV s^{-1}

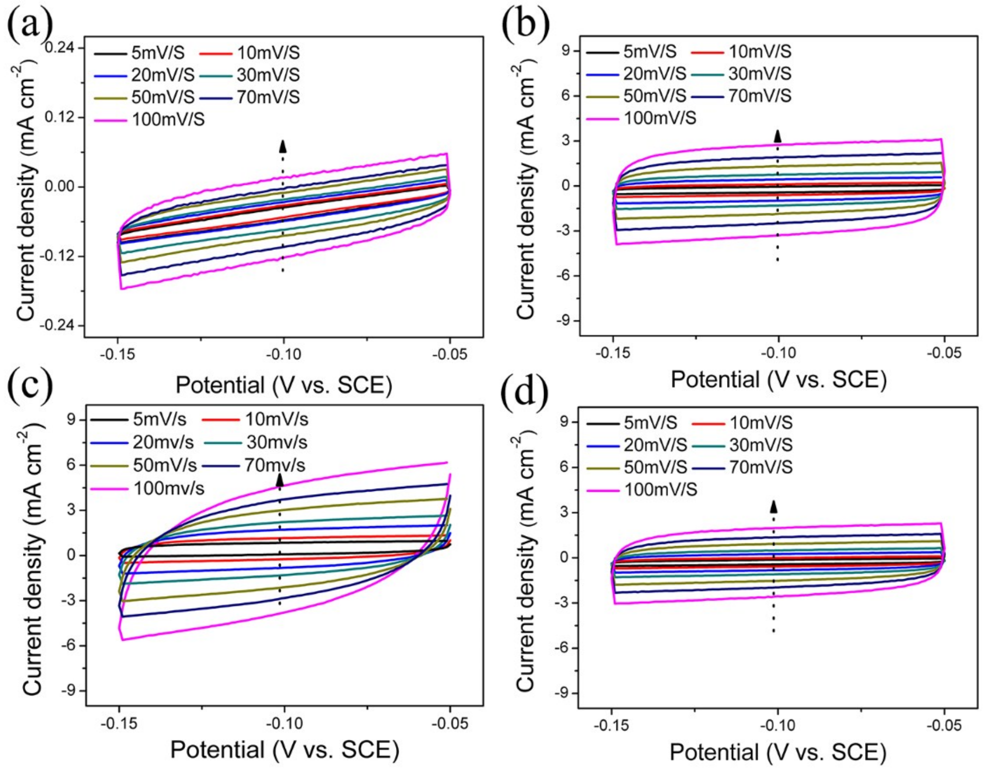

Fig. S9 Electrochemical double-layer capacitance (EDLC) measurements of CoP electrode (a), CoP/CSs-0.03(b), CoP/CSs-0.05(c), CoP/CSs-0.07(d).

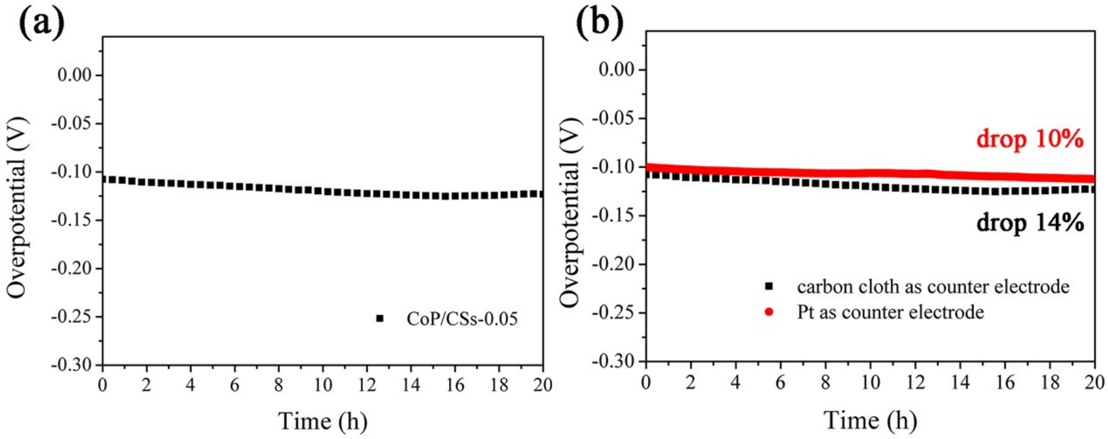

Fig. S10 Time dependence of the overpotential for CoP/CSs-0.05 at a static current density of 10 mA cm^{-2} for 20 h: (a) carbon cloth as counter electrode, (b) carbon cloth or Pt as counter electrode.

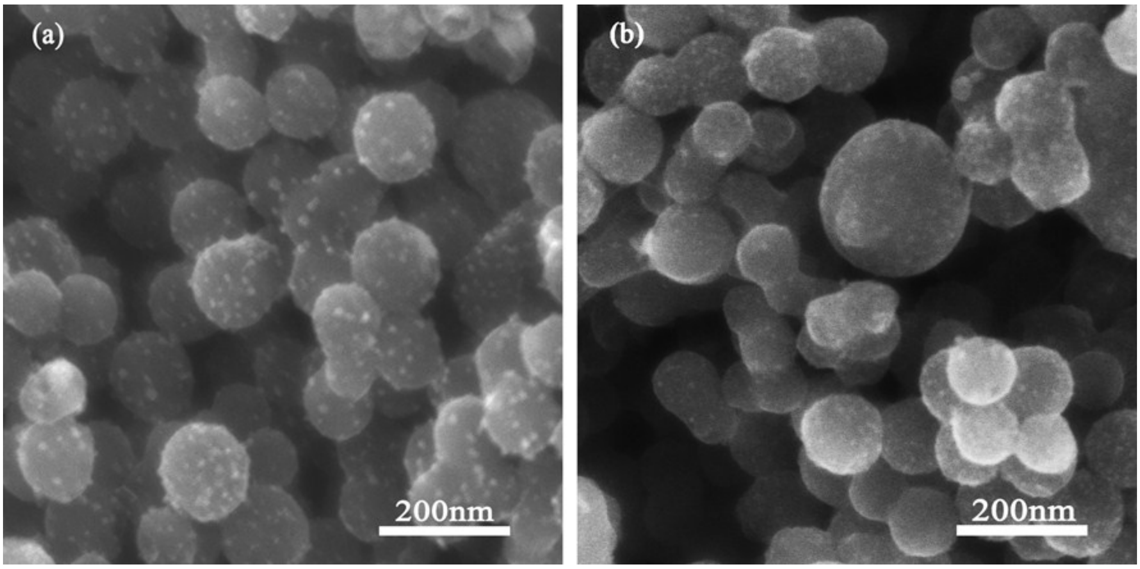

Fig. S11 SEM images of CoP/CSs-0.05 before (a) and after (b) stability test.

Table S1. HER performances of various non-precious metal catalysts and our sample in 0.5 M H_2SO_4.

Catalyst	Onset overpotential	Current density (mA cm^{-2})	Overpotential (mV)	Exchange current density (mA cm^{-2})	Ref.
Ni_2P nanoparticles	46	10	116	0.033	3
MoP/RGO	16	10	119	0.178	4
Cu_3P	62	10	143	0.18	5
Carbon-Shell-Coated FeP	-	10	71	-	6
WP NPs@NC	40	10	102	0.25	7
Branched CoP/Ti	-	10	100	-	8
CoP NWs	30	10	89	-	9
CoP/NPCFs	45	10	135	1.37×10^{-3}	10
CoP/CC	38	10	67	0.288	11
CoP/OMC	77.7	10	112.1	0.161	12
CoP/RGO	118.9	10	156.9	0.057	12
CoP/CNTs	-	10	165	0.068	13
CoP/NCNTs	32	10	79	0.32	13
CoP/GA	28	10	121	0.105	14
CoP/BMHNC	7	10	95.8	0.1182	15
CoP/NSGO	45	10	130	0.0176	16
CoP/CNTs	40	10	122	0.13	17
CoP/CSs	34	10	94	0.275	This work

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