

**Synergistically coupling ultrasmall PtCu nanoalloys with highly porous CoP nanosheets as enhanced electrocatalyst for electrochemical hydrogen evolution**

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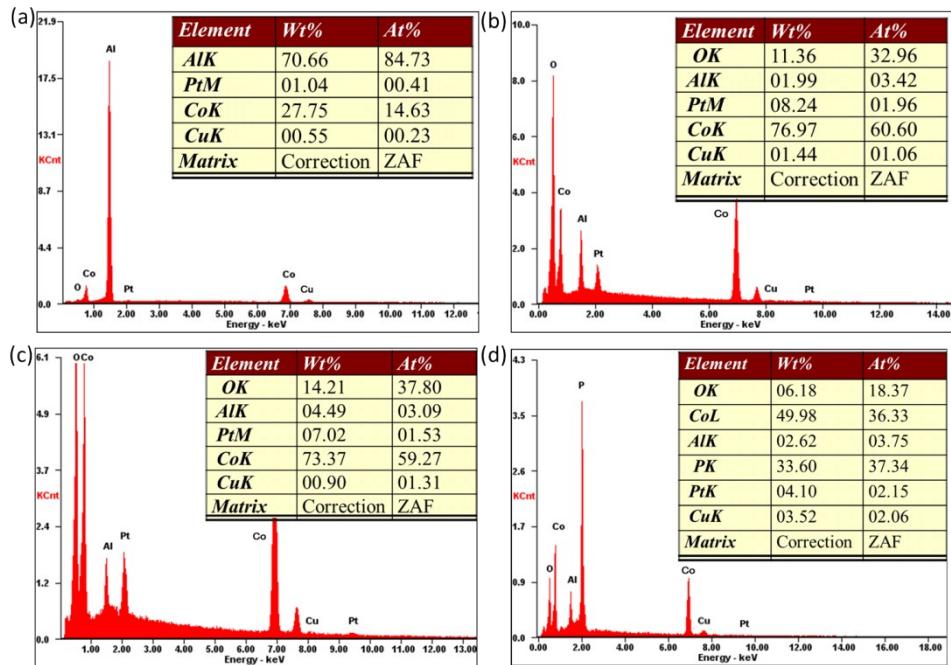
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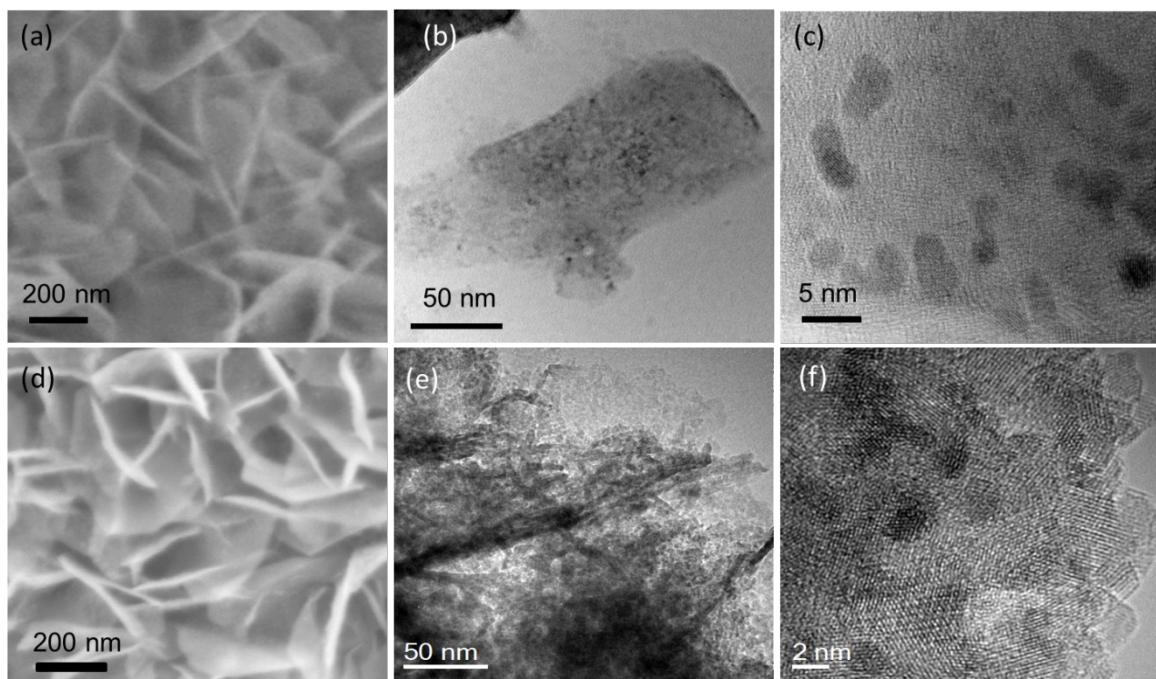
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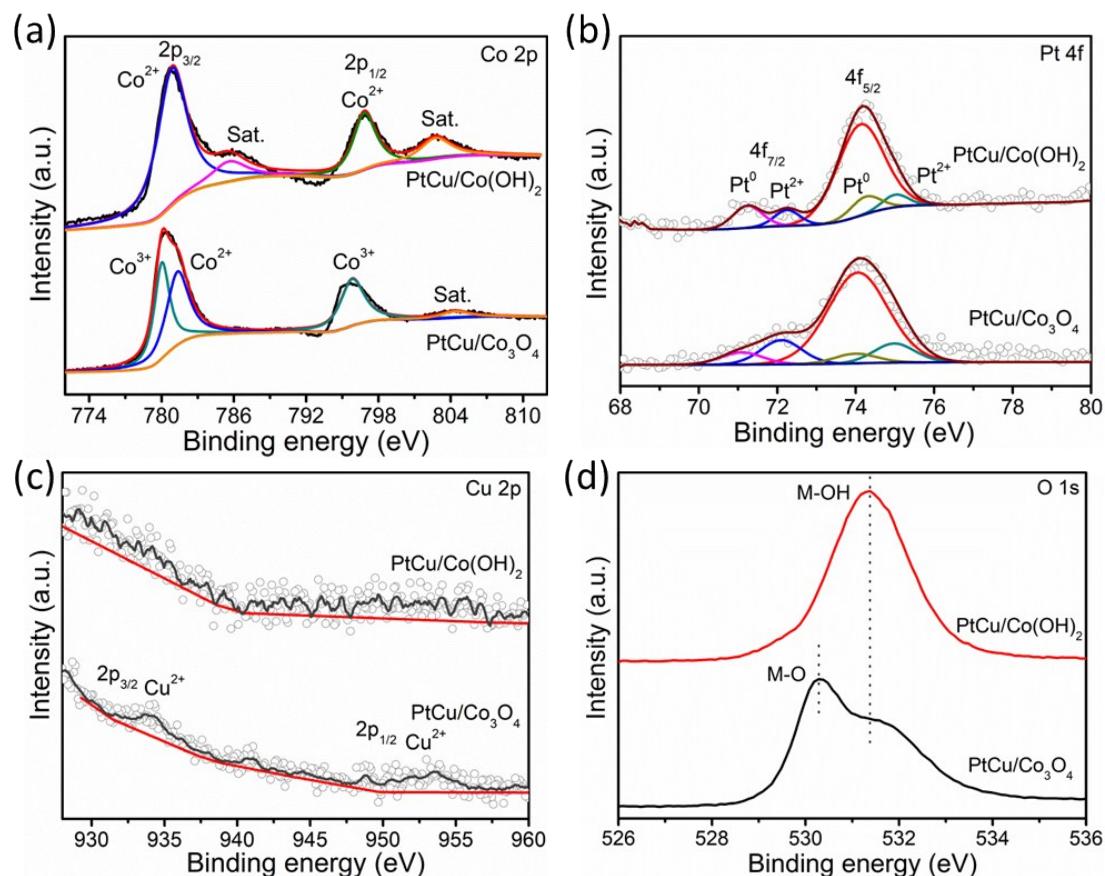
J.G. and X.T. contribute equally to this work.



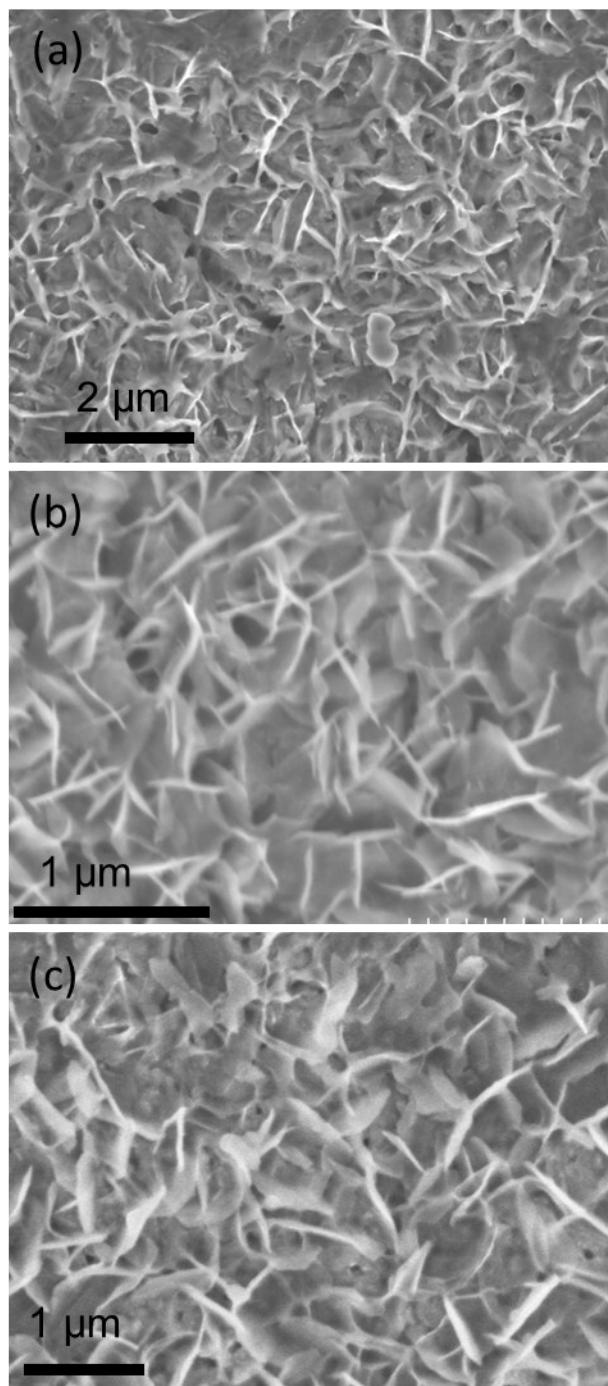
**Fig S1.** EDS spectrum of (a) AlCoPtCu precursor alloy, (b) freshly dealloyed PtCu/Co(OH)<sub>2</sub>, (c) PtCu/Co<sub>3</sub>O<sub>4</sub>, and (d) PtCu/CoP.



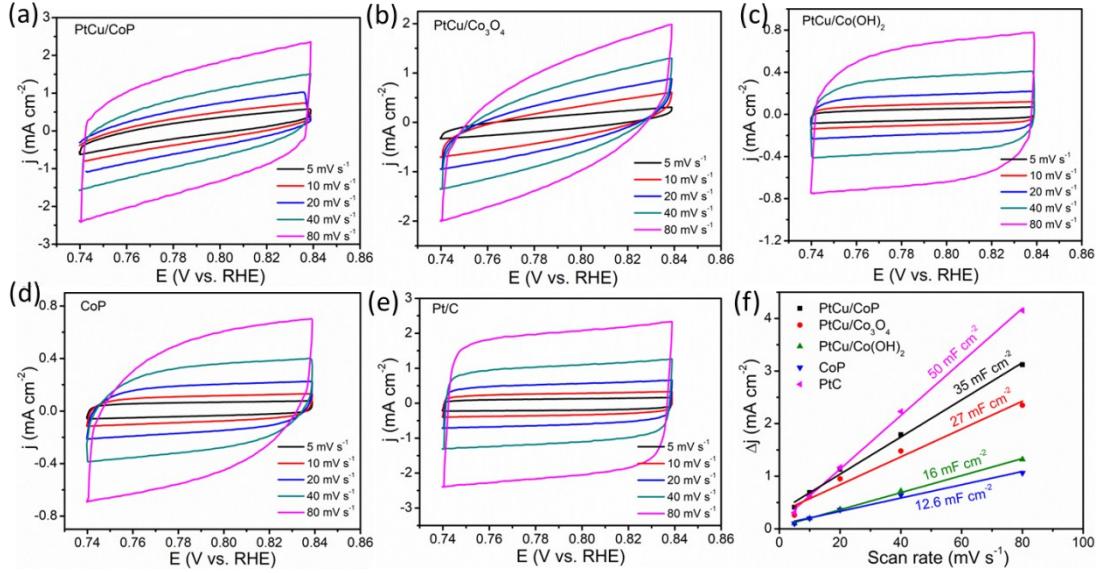
**Fig S2.** (a) SEM and (b, c) TEM images of the PtCu/Co(OH)<sub>2</sub>. (d) SEM and (e, f) TEM images of the PtCu/Co<sub>3</sub>O<sub>4</sub>.



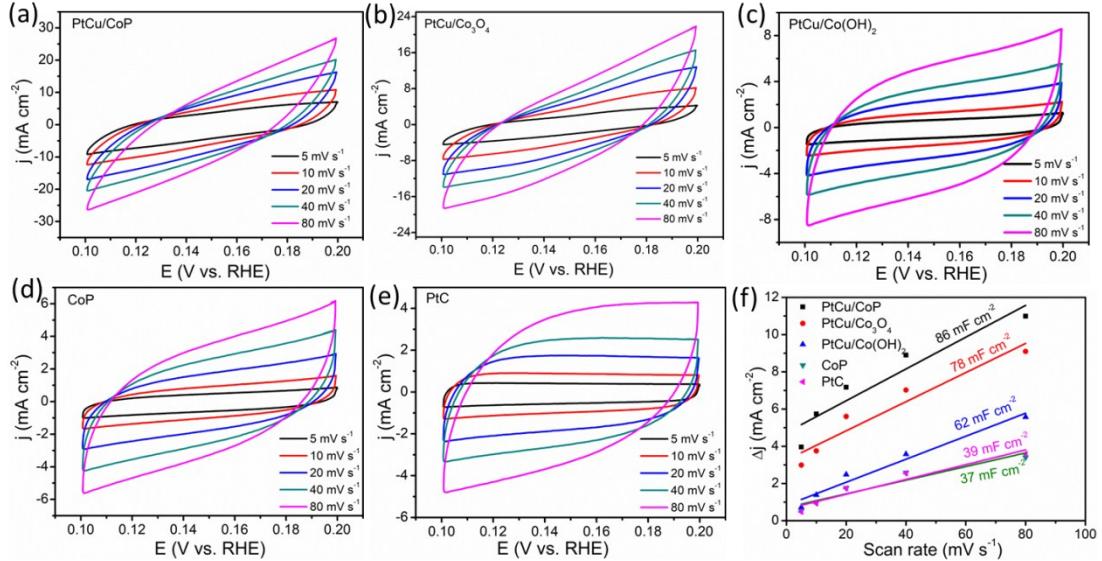
**Fig S3.** XPS spectra of (a) Co 2p, (b) Pt 4f, (c) Cu 2p and (d) O 1s of PtCu/Co(OH)<sub>2</sub> and PtCu/Co<sub>3</sub>O<sub>4</sub>.



**Fig S4.** SEM images of the (a) CoP, (b) Pt/CoP, (c) Cu/CoP.



**Fig S5.** Typical CV curves of (a) PtCu/CoP, (b) PtCu/Co<sub>3</sub>O<sub>4</sub> (c) PtCu/Co(OH)<sub>2</sub>, (d) CoP and (e) commercial Pt/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> with different scan rates (5, 10, 20, 40 and 80 mV s<sup>-1</sup>). (f) The current densities at 0.79 V with respect to scan rates for above five catalysts.



**Fig S6.** Typical CV curves of (a) PtCu/CoP, (b) PtCu/Co<sub>3</sub>O<sub>4</sub> (c) PtCu/Co(OH)<sub>2</sub>, (d) CoP and (e) commercial Pt/C catalysts in 1.0 M KOH with different scan rates (5, 10, 20, 40 and 80 mV s<sup>-1</sup>). (f) The current density at 0.15 V with respect to scan rate for above five catalysts.

**Table S1.** Comparison of the PtCu/CoP with some recently reported HER electrocatalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

Catalysts	Tafel slope (mV dec <sup>-1</sup> )	$\eta$ @10 mA cm <sup>-2</sup> (mV)	References
Pd/Cu-Pt	25	22.8	<i>Angew. Chem. Int. Ed.</i> <b>2017</b> , 56, 16047 –16051
ALD 50 Pt/NGNs	29	40	<i>Nat. Commun.</i> <b>2016</b> , 7, 13638
Ru@GnP	30	13	<i>Adv. Mater.</i> <b>2018</b> , 30, 1803676
PdP <sub>2</sub> @CB	29.5	27.5	<i>Angew. Chem. Int. Ed.</i> <b>2018</b> , 57, 14862 –14867
Ru@CN	30	22	<i>Nat. Nanotech.</i> <b>2017</b> , 12, 441–446
Au@PdAg	30	26.2	<i>J. Am. Chem. Soc.</i> <b>2016</b> , 138, 1414–1419
PtCoFe@CN	32	45	<i>ACS Appl. Mater. Interfaces</i> , <b>2017</b> , 9, 3596–3601
400-SWNT/Pt	38	27	<i>ACS Catal.</i> <b>2017</b> , 7, 3121–3130
PdCu@Pd NCs	35	68	<i>ACS Appl. Mater. Interfaces</i> <b>2017</b> , 9, 8151–8160
Pt-MoS <sub>2</sub>	40	53	<i>Nat. Commun.</i> <b>2013</b> , 4, 1444
<b>PtCu/CoP</b>	<b>28</b>	<b>15</b>	<b>This work</b>

**Table S2.** Comparison of the PtCu/CoP with some recently reported HER electrocatalysts in 1.0 M KOH solution.

Catalysts	Tafel slope (mV dec <sup>-1</sup> )	$\eta$ @10 mA cm <sup>-2</sup> (mV)	References
Pt/NiO@Ni/NF	40	34	<i>ACS Catal.</i> <b>2018</b> , 8, 8866-8872
RuP <sub>2</sub> @NPC	69	52	<i>Angew. Chem. Int. Ed.</i> <b>2017</b> , 56, 11559 -11564
Ru@GnP	28	22	<i>Adv. Mater.</i> <b>2018</b> , 30, 1803676
PdP <sub>2</sub> @CB	42.1	35.4	<i>Angew. Chem. Int. Ed.</i> <b>2018</b> , 57, 14862 -14867
N,P-doped Mo <sub>2</sub> C@C	71	47	<i>ACS Nano</i> <b>2016</b> , 10, 8851–8860
H-NiCoP NWAs/NF	38.6	44	<i>Small</i> <b>2018</b> , 14, 1800421
CoP-400-E15	86	73	<i>Adv. Energy Mater.</i> <b>2018</b> , 8, 1802445
CoP/NCNHP	66	115	<i>J. Am. Chem. Soc.</i> <b>2018</b> , 140, 2610-2618
Co <sub>2</sub> P/Co-Foil	59	157	<i>J. Mater. Chem. A</i> <b>2017</b> , 5, 10561-10566
MoP@C	54	49	<i>Adv. Energy Mater.</i> <b>2018</b> , 8, 1801258
<b>PtCu/CoP</b>	<b>49</b>	<b>40</b>	<b>This work</b>