Supporting Information for:

# A Highly Efficient Electrocatalyst Based on Amorphous Pd-Cu-S Material for Hydrogen Evolution Reaction

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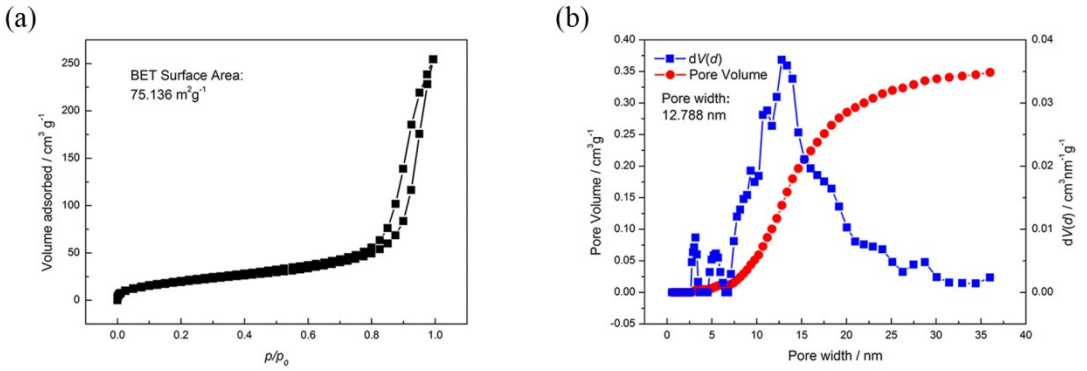


**Fig. S1.** $N_2$ adsorption–desorption isotherms (a) and pore size distribution (b) of the Pd-Cu-S catalyst.

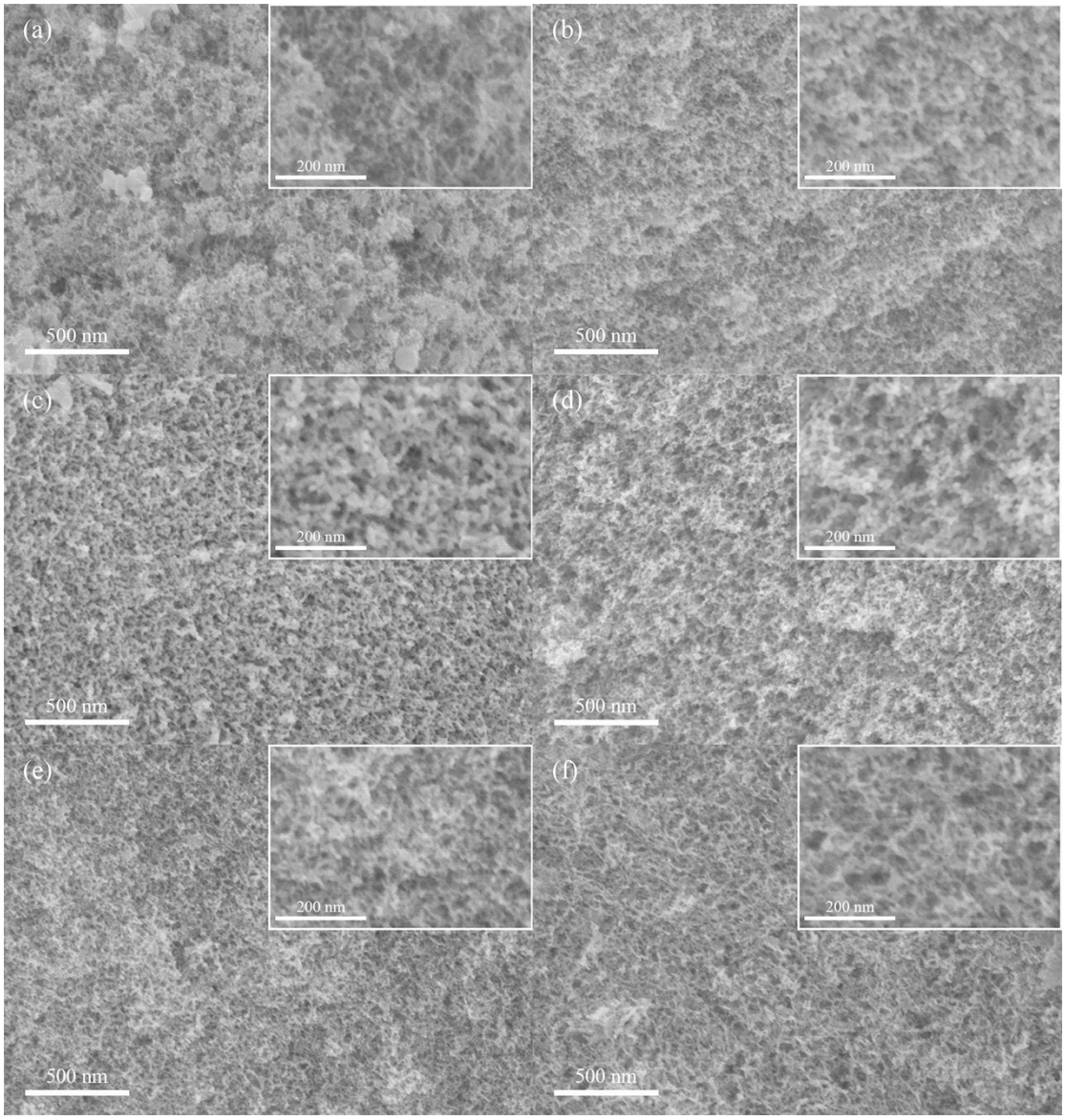


**Fig. S2.** SEM images of the as-prepared Pd-Cu-S samples for 12 h (a), 24 h (b), 36 h (c), 48 h (d), 60 h (e) and 72 h (f), respectively.

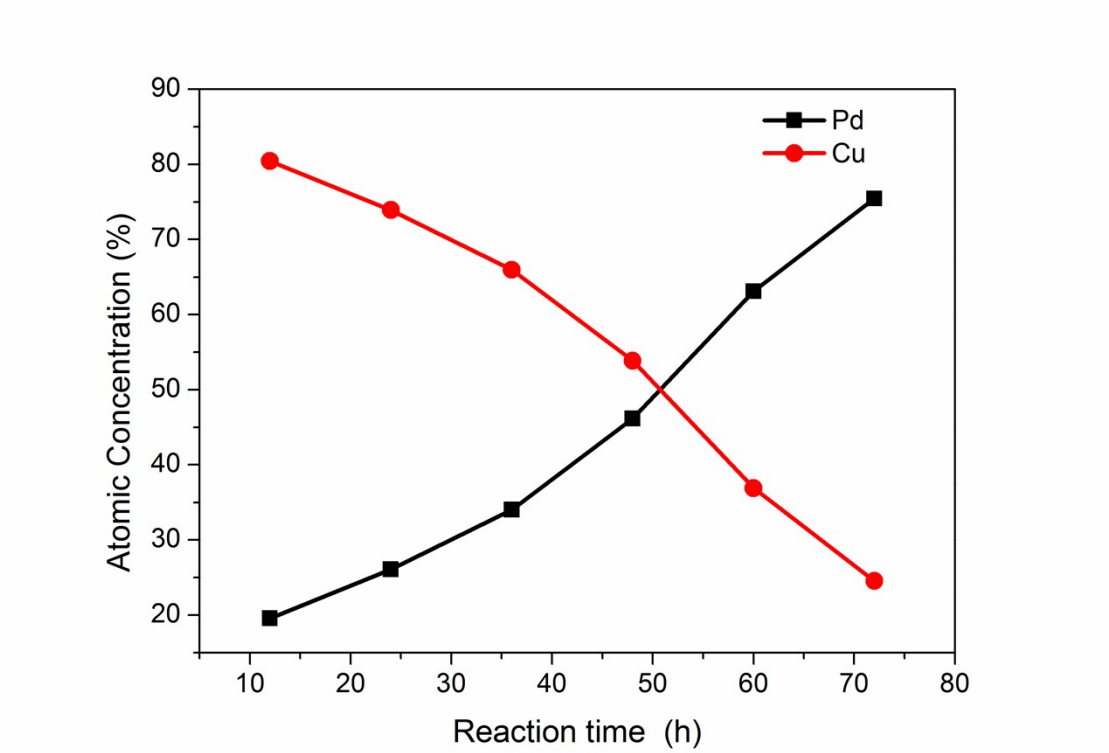


**Fig. S3.** Atomic concentration of the as-prepared Pd-Cu-S materials for different reaction times.

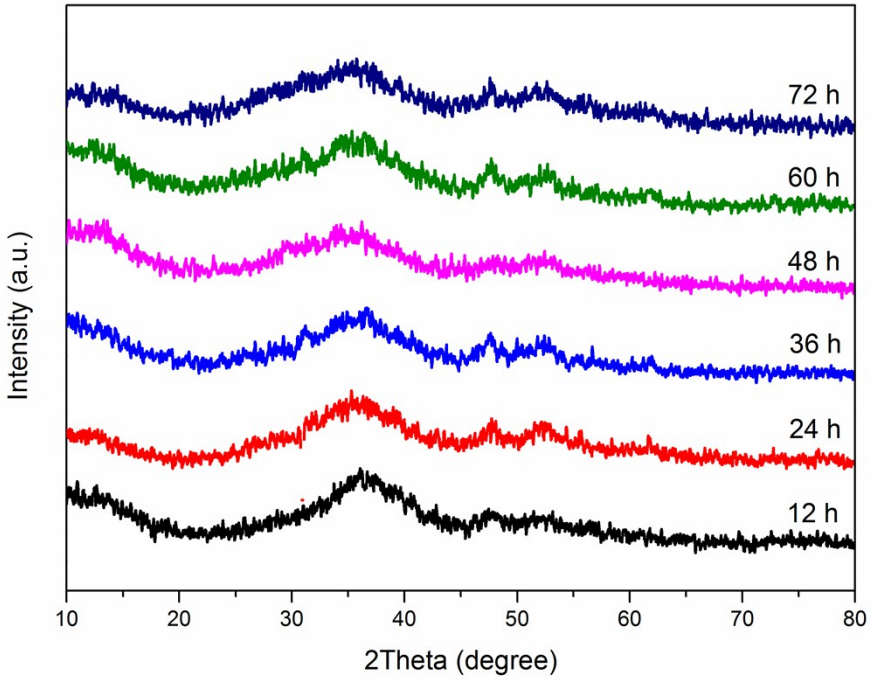


**Fig. S4.** XRD patterns of the as-prepared Pd-Cu-S materials.

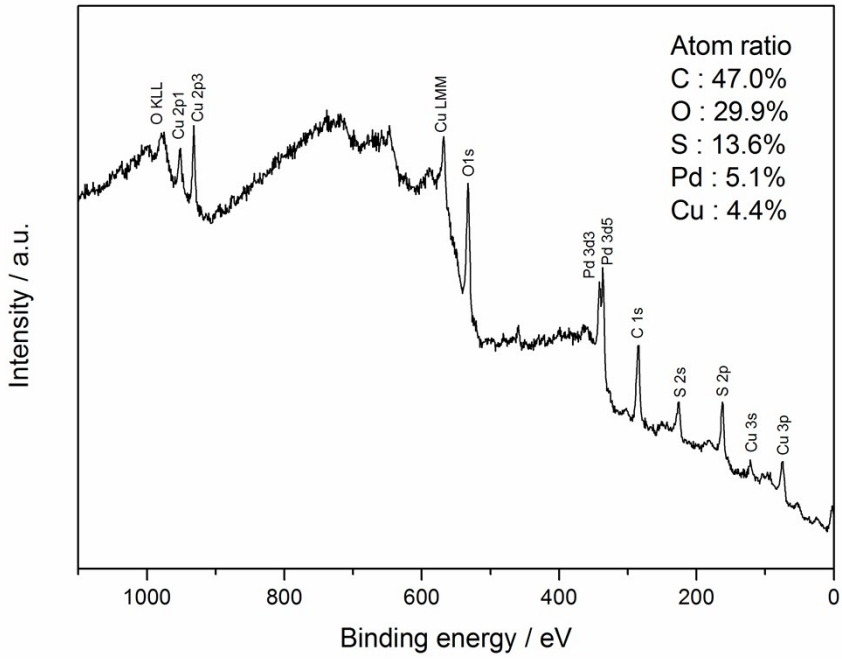


**Fig. S5.** XPS survey spectrum of Pd-Cu-S material prepared for 48 h.

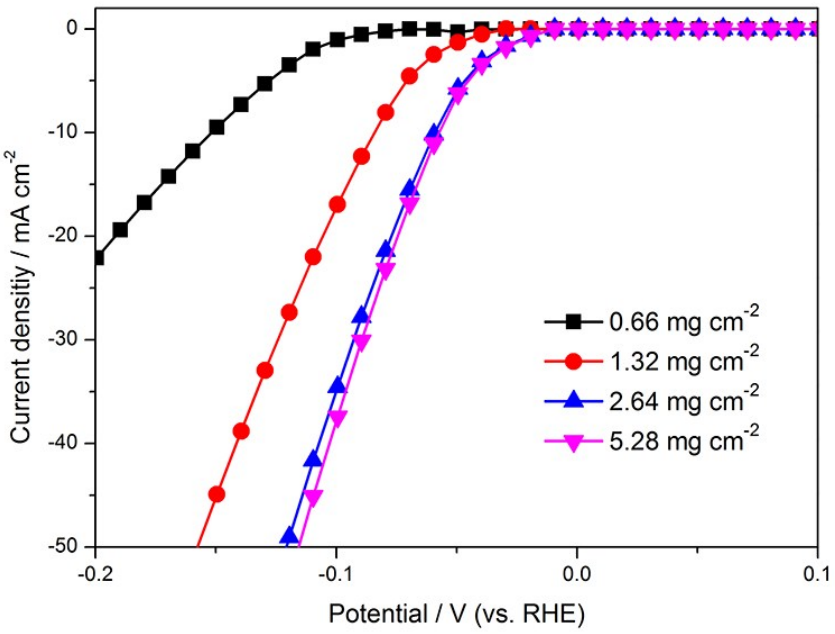


**Fig. S6.** Polarization curves of Pd-Cu-S catalyst with different loading amounts.

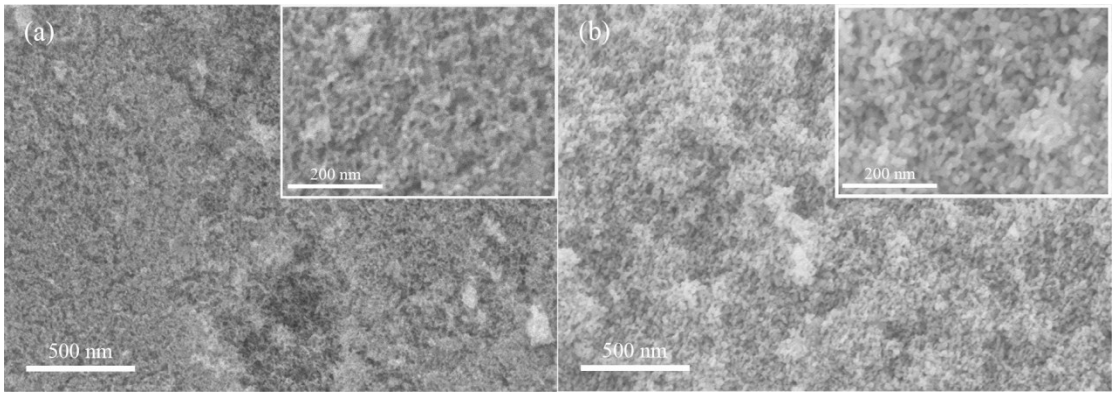


**Fig. S7.** SEM images of nanoporous Pd (a) and nanoporous Pd-S (b) catalyst.

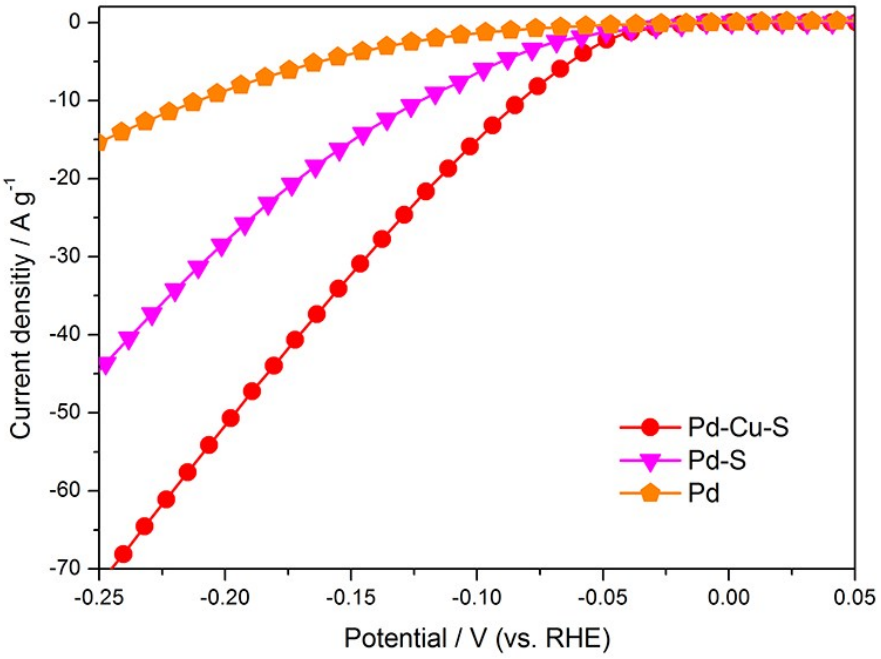


**Fig. S8.** Polarization curves normalized by the mass of Pd.

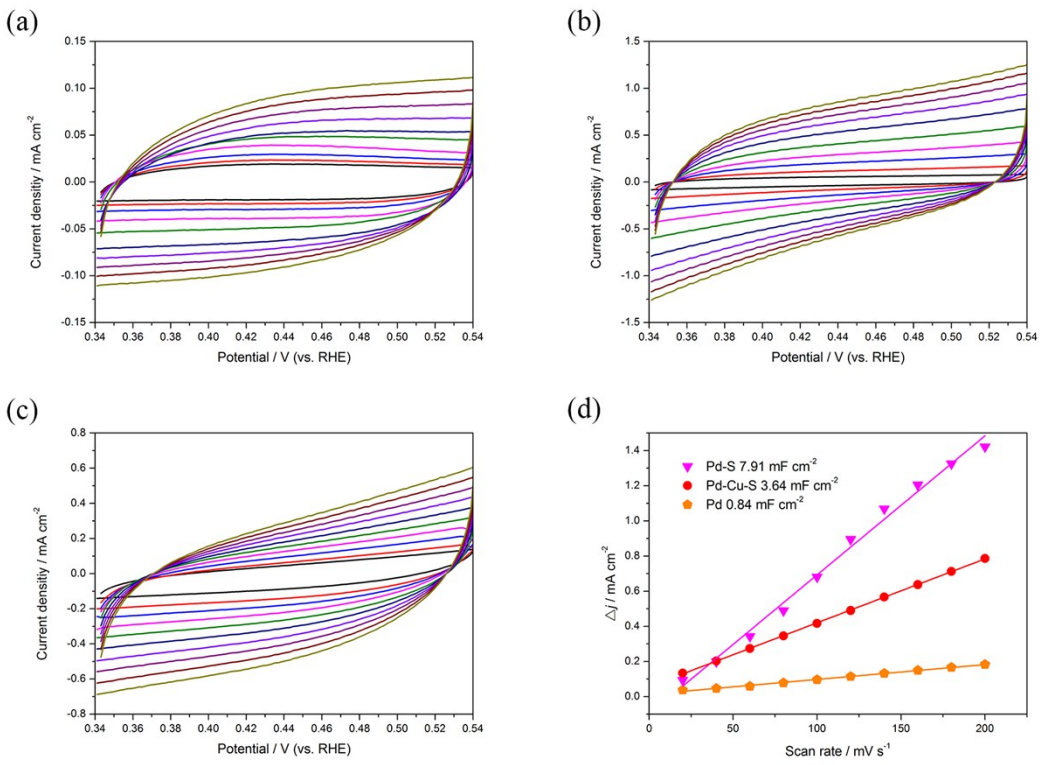


**Fig. S9.** CV curves for Pd (a), Pd-S (b) and Pd-Cu-S (c) catalysts at in 0.5 M $H_2SO_4$ from 0.34 V to 0.54 V using scan rate of 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mV $s^{-1}$. (d) Plots showing the extraction of the double layer capacitance for different catalysts.

The difference in the current density between the forward and reverse scan at 0.44 V is named as $\Delta j$. A linear trend is observed for $\Delta j$ as a function of scan rate. The slope represents geometric double-layer capacitance $C_{dl}$, which is linearly proportional to the electrochemistry surface area (ECSA). Hence, the ratio among $C_{dl}$ of different catalyst can be used to estimate ECSA [1].

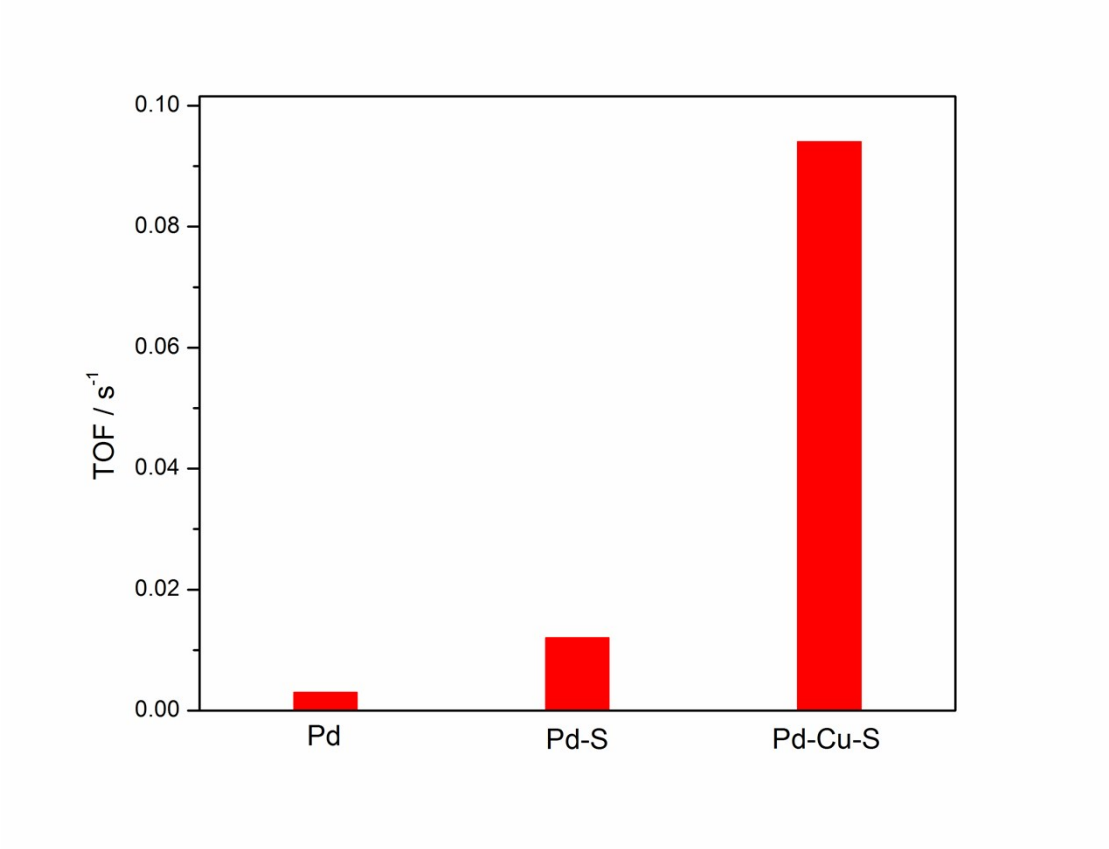


**Fig. S10.** Calculated TOF values of the as-prepared Pd-based materials.

Because the nature of the active sites of the catalyst is not clearly understood yet, the turnover frequencies (TOF) of the as-prepared materials were calculated by the amount of substance (Eq. 4), not the amount of active sites, therefore the TOF values of all the samples might be underestimated in this work.

$$\mathrm{TOF}_{\mathrm{mole}} = \frac{I}{2\mathrm{F}m} \qquad (1)$$

Where I is the current of the catalysts at a overpotential of 200 mV in the linear sweep measurement, F is the Faraday constant, m is the number of moles of catalyst that are deposited onto the electrodes and the factor 1/2 used by taking into account that two electrons are required to form one hydrogen molecule from two protons.

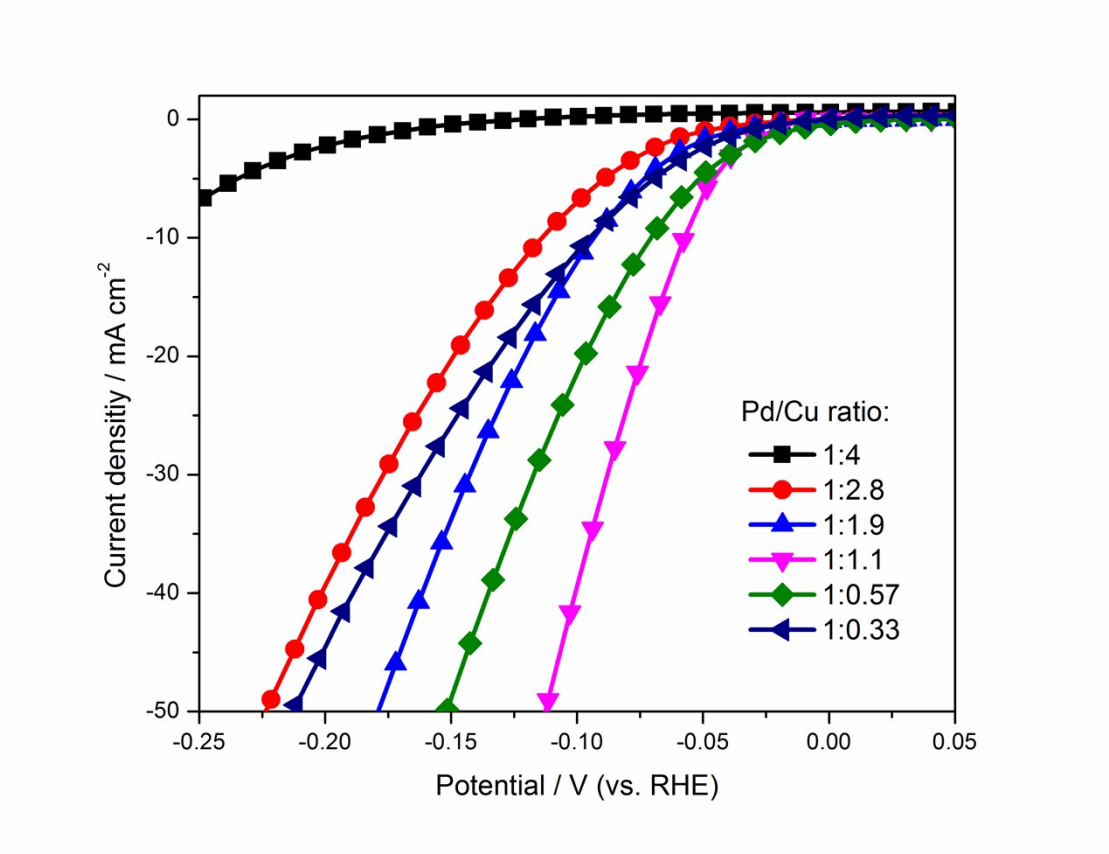


**Fig. S11.** Polarization curves of the Pd-Cu-S catalysts for different Pd/Cu ratio.

**Fig. S12.** Photograph of the hydrogen bubbles generated on the working electrode during the long-term test in 0.5 M $H_2SO_4$ at 200 mV vs RHE.

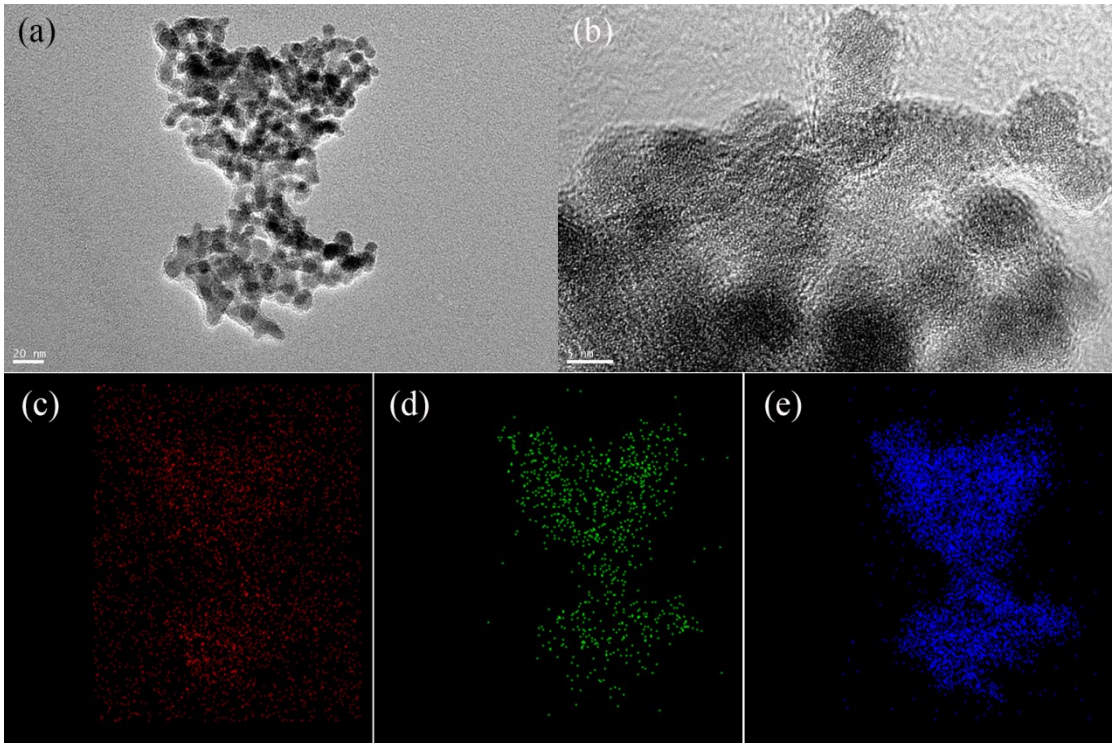


**Fig. S13.** TEM (a) and HRTEM (b) images of the Pd-Cu-S catalysts prepared by $Ti_{30}Cu_{68}Pd_2$ amorphous alloys for 48 h after the durability test. (c), (d) and (e) are the distribution of Cu (c), Pd (d) and S (e) shown by the TEM-EDX maps.

**Table S1.** Summary of the electrocatalytic properties of as-prepared based catalyst and other recently reported high performance HER catalysts in 0.5 M $H_2SO_4$.

| Catalyst | Loading amount (mg $cm^{-2}$) | $\eta_{10}$ (mV vs RHE) | Tafel slope (mV $dec^{-1}$) | $j_0$ (μA $cm^{-2}$) | Reference |
|---|---|---|---|---|---|
| Defect-rich $MoS_2$ nanosheets | 0.285 | 190 | 50 | 8.91 | [1] |
| np-$Mo_2C$ NWs | 0.21 | 123 | 53 | - | [2] |
| $Ni_{12}P_5$/Ti | - | 107 | 63 | - | [3] |
| $WS_2$/CC | 1.5 | ~250 | 50 | - | [4] |
| $CoSe_2$ nanoparticles/CP | - | 147 | ~40 | 4.9 | [5] |
| $CoS_2$ nanowires | - | 145 | 51.6 | 15.1 | [6] |
| $Cu_3P$ nanowire | - | 143 | 67 | 180 | [7] |
| MoP nanoparticles | 0.36 | 125 | 54 | 86 | [8] |
| CoPS nanoplates | - | 48 | 56 | 984 | [9] |
| $NiP_{1.93}Se_{0.07}$ nanoflakes | - | 84 | 41 | 20 | [10] |
| $C_3N_4$@N-Graphene films | 0.57 | 80 | 49.1 | 430 | [11] |
| CoP | ~0.3 | 180 (100 mA $cm^{-2}$) | 46 | - | [12] |
| AlNiP-TT | 54.1 | 111 | 65 | 600 | [13] |
| H-$MoS_2$ | 1.0 | 167 | ~70 | 36 | [14] |
| H-$WS_2$ | 1.0 | 157 | ~60 | 38 | [14] |
| np-Pd-Cu-S | 2.64 | 58 | 35 | 310 | This work |
| np-Pd | 2.64 | 151 | 89 | 198 | This work |
| np-Pd-S | 2.64 | 98 | 64 | 282 | This work |

**Table S2.** Summarization of the fitting results of the EIS at -50 mV vs. RHE of the as-prepared samples.

| Sample | $R_H$ | $R_L$ |
|---|---|---|
| Pd | 11.53 | 1.652 |
| Pd-S | 3.89 | 1.105 |
| Pd-Cu-S | 2.744 | 1.216 |

**Reference**

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