Supplementary Information for

Electron beam-assisted synthesis of porous Cu_2MoS_4 nanocubes for efficient all-pH electrocatalytic hydrogen evolution

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Preparation of Cu_2O Nanocrystals

All chemical reagents used in this experiment are analytically pure and can be used without further purification. The synthesis of Cu_2O nanocrystals was similar to the previous reports with minor modifications (J. Mater. Chem., 2009, 19, 5220). In a typical synthesis, 3.3 g of polyvinyl pyrrolidone (PVP) was dissolved in a dihydrate copper chloride solution (0.01 M, 100 mL), and then 10 mL of NaOH aqueous solution (2 mol/L) was added dropwise to the above-prepared transparent light green solution. During the addition process, the color of the solution changed from turbid blue-green to dark brown. After stirring for 30 min, ascorbic acid solution (10 mL, 0.6 mol/L) was added dropwise to the above solution. At this time, the color of the solution changed from dark brown to reddish brown, and then the mixture was aged for 3 hours. All processes were carried out at a constant speed, temperature stirring, and heated in a water bath at a given temperature. Then, it was centrifuged by centrifuge, washed with deionized water 3 times and anhydrous ethanol 2 times to remove the residue, and finally placed in a 60 °C vacuum drying oven for 6 h to obtain the target product.

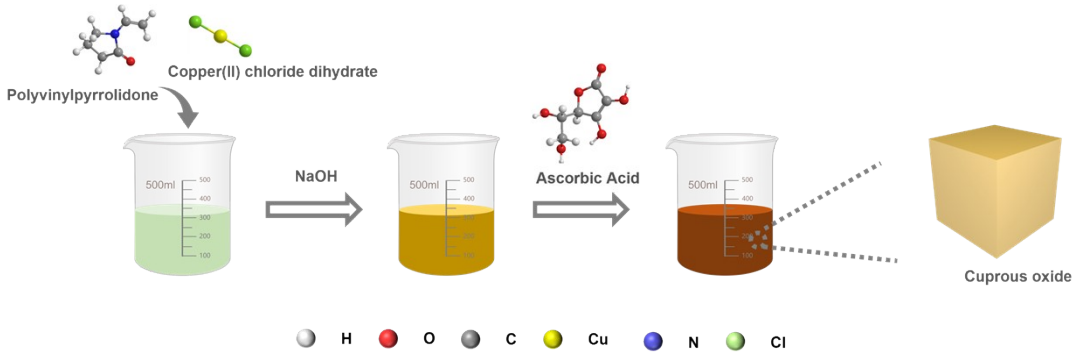

Fig. S1 Schematic diagram of hydrothermal synthesis of Cu_2O nanocubes.

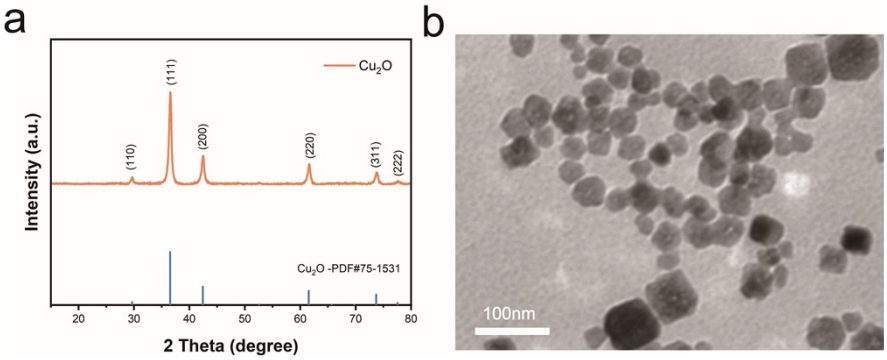

Fig. S2 XRD pattern (a) and TEM image (b) of the Cu_2O nanocubes.

Solvothermal Synthesis of Cu_2MoS_4

The solvothermal preparation of Cu_2MoS_4 was slightly modified according to previous studies[1]. 3.3 mg of the prepared Cu_2O template powder was dispersed in a mixed solution of 30 mL of ethylene glycol and water (EG : H_2O = 2 : 1), stirred and ultrasonicated for 10 min, then 10 mg of thioacetamide and 5 mg of sodium molybdate were added to the mixed solution, stirred for 30 min, and then the solution was transferred to a polytetrafluoroethylene-lined autoclave (45 ml) and kept at 160°C for 12 h. After the reaction was completed and cooled to room temperature, it was centrifuged, washed on both sides with deionized water and anhydrous ethanol, and dried in vacuum at 60°C for 8 h to obtain the target product of black powder, which was recorded as Cu_2MoS_4-R.

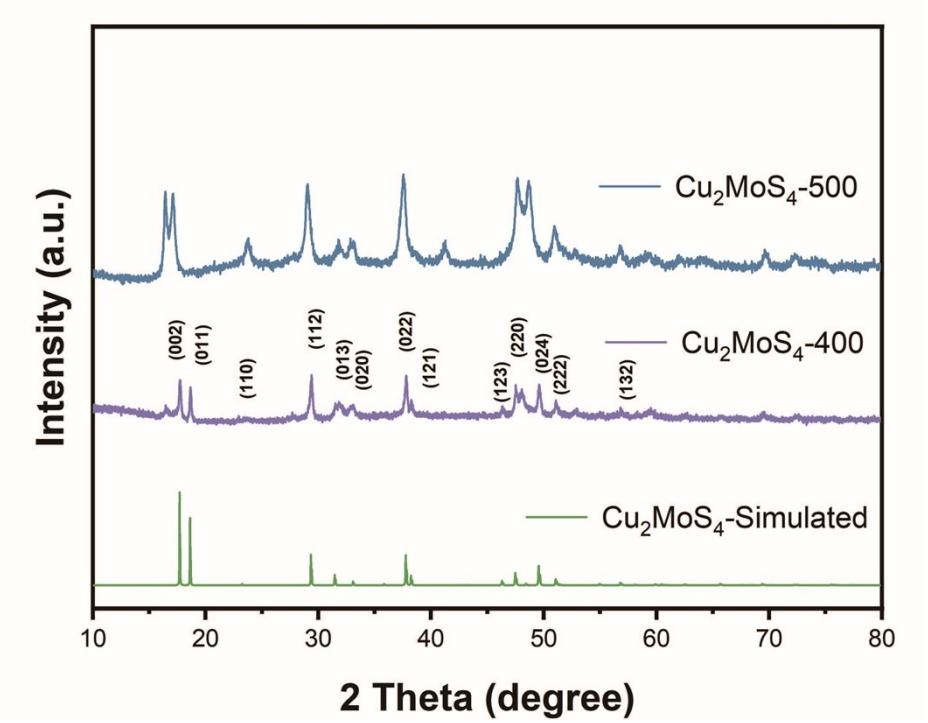

Fig. S3 XRD patterns of the Cu_2MoS_4-400 and Cu_2MoS_4-500 samples.

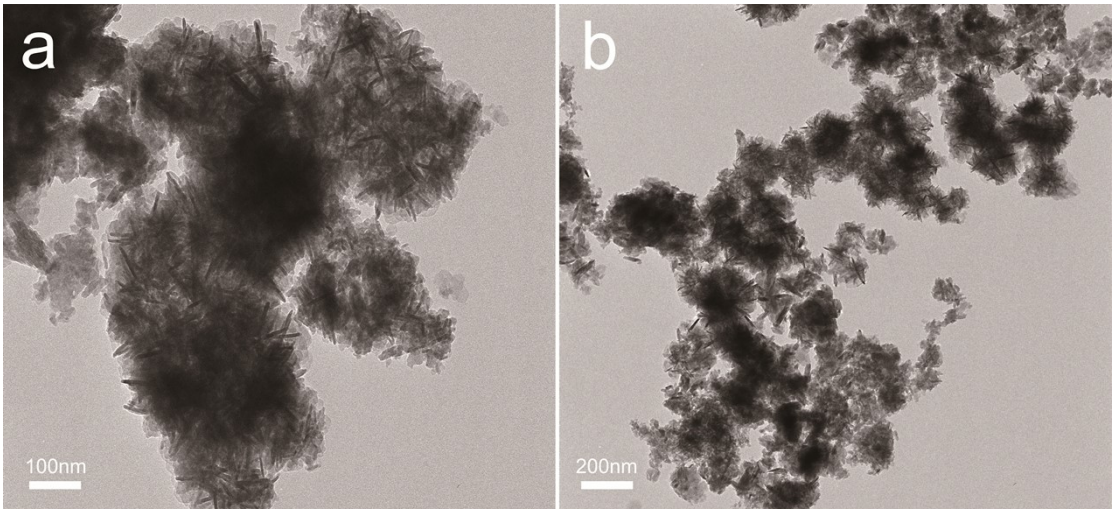

Fig. S4 TEM image of the sample before irradiation

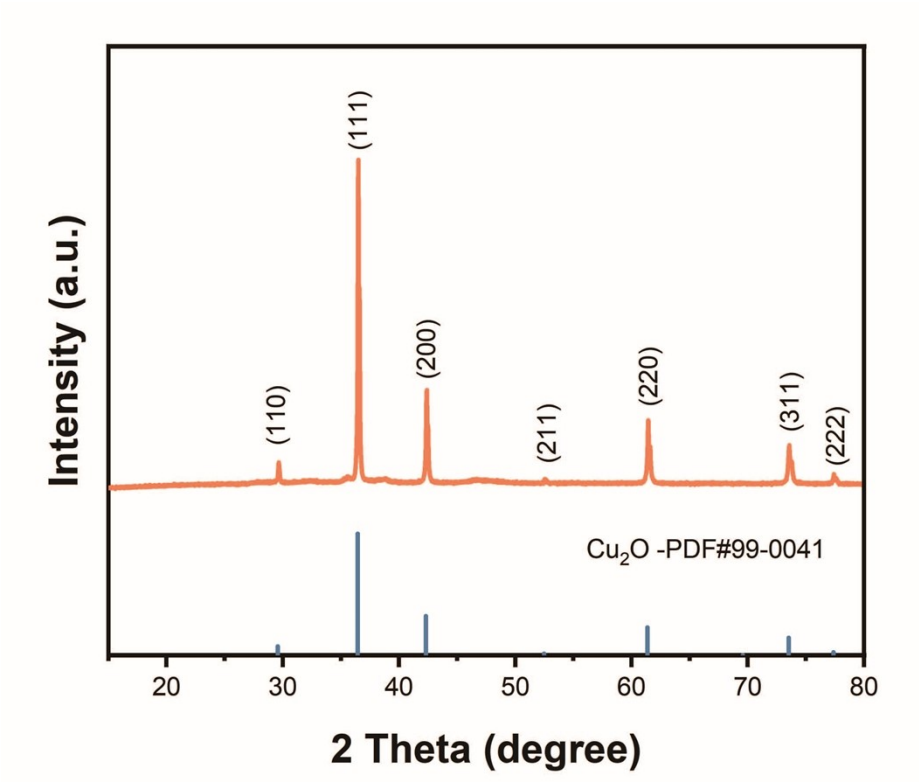

Fig. S5 XRD pattern of the resulting sample without EBI irradiation.

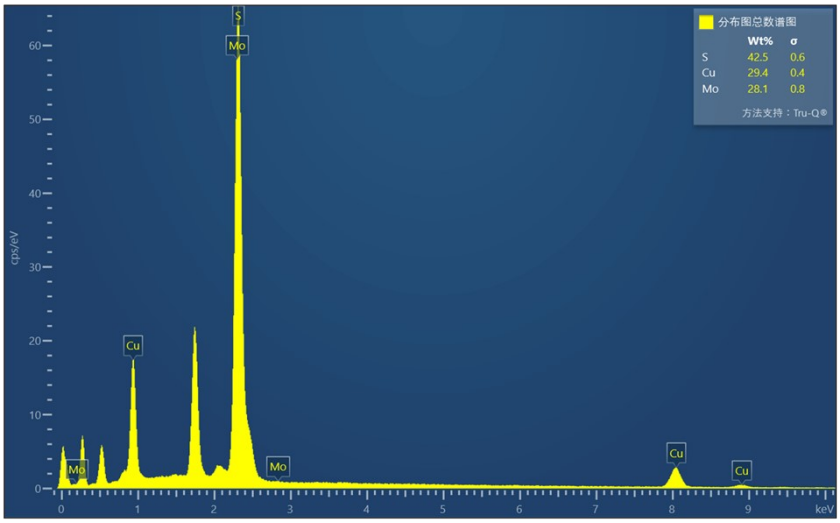

Fig. S6 Energy dispersive X-ray spectrum of the Cu_2MoS_4-300 nanocubes.

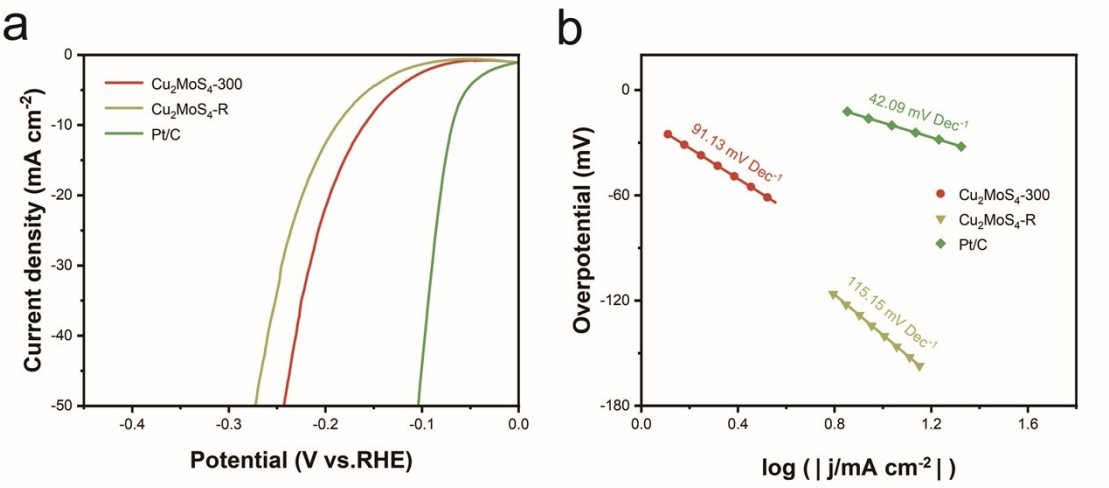

Fig. S7 (a) HER polarization curves of Cu_2MoS_4-300, Cu_2MoS_4-R and Pt/C in 0.5 M H_2SO_4; (b) Corresponding Tafel curves.

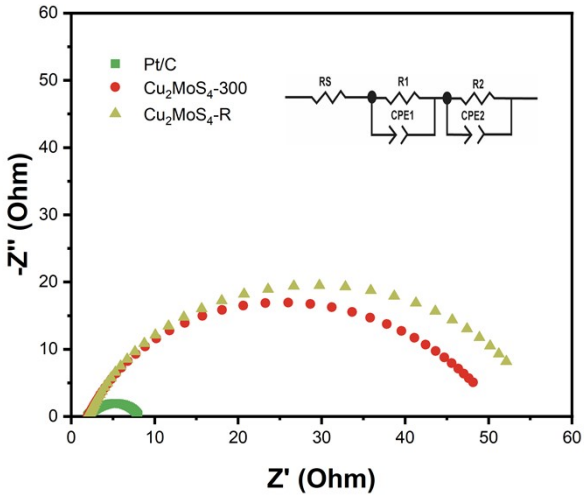

Fig. S8 EIS spectrum of Cu_2MoS_4-300 in 0.5 M H_2SO_4.

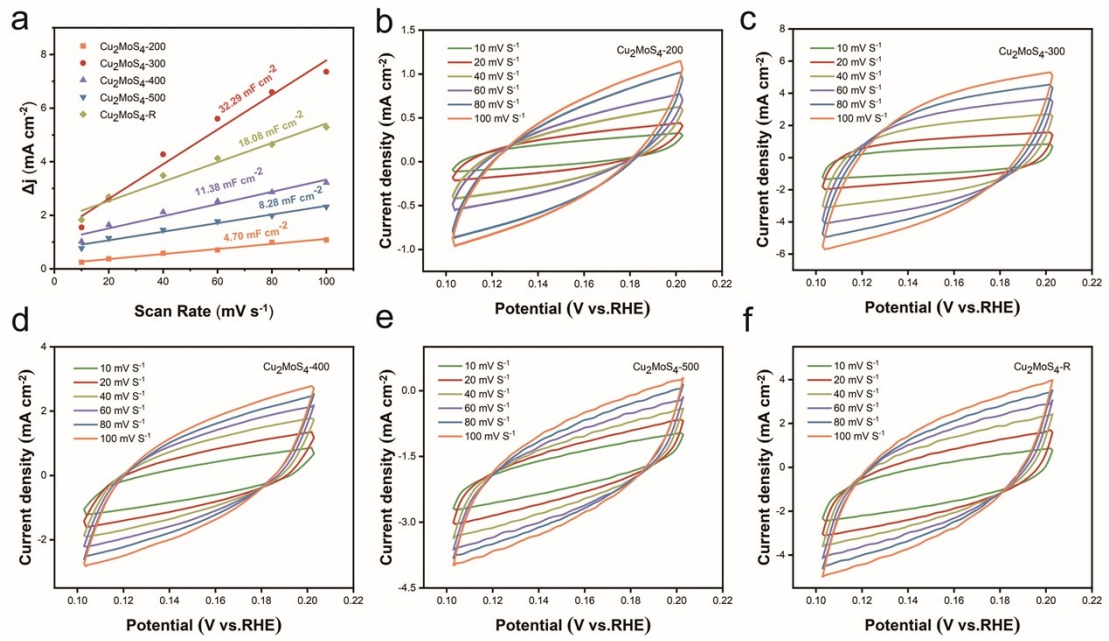

Fig. S9 (a) Double layer capacitance curves of different catalysts in 0.5 M H_2SO_4; (b-f) Cyclic voltammetry curves of the catalysts at different scan rates.

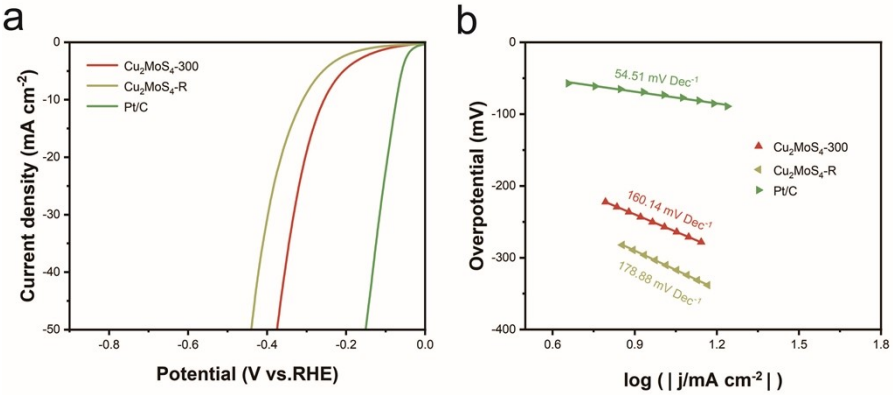

Fig. S10 (a) HER polarization curves of Cu_2MoS_4-300, Cu_2MoS_4-R and Pt/C in 1 M PBS; (b) Corresponding Tafel curves of samples in 1 M PBS.

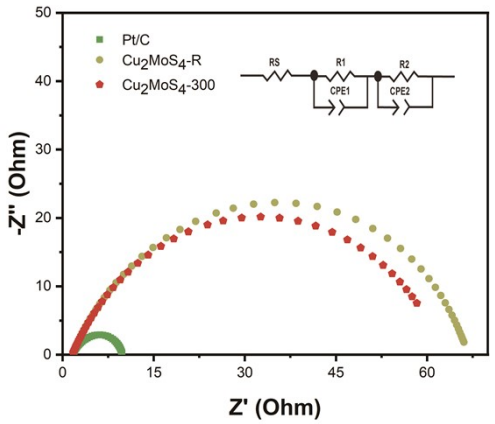

Fig. S11 EIS spectra of Cu_2MoS_4-300 in 1 M PBS.

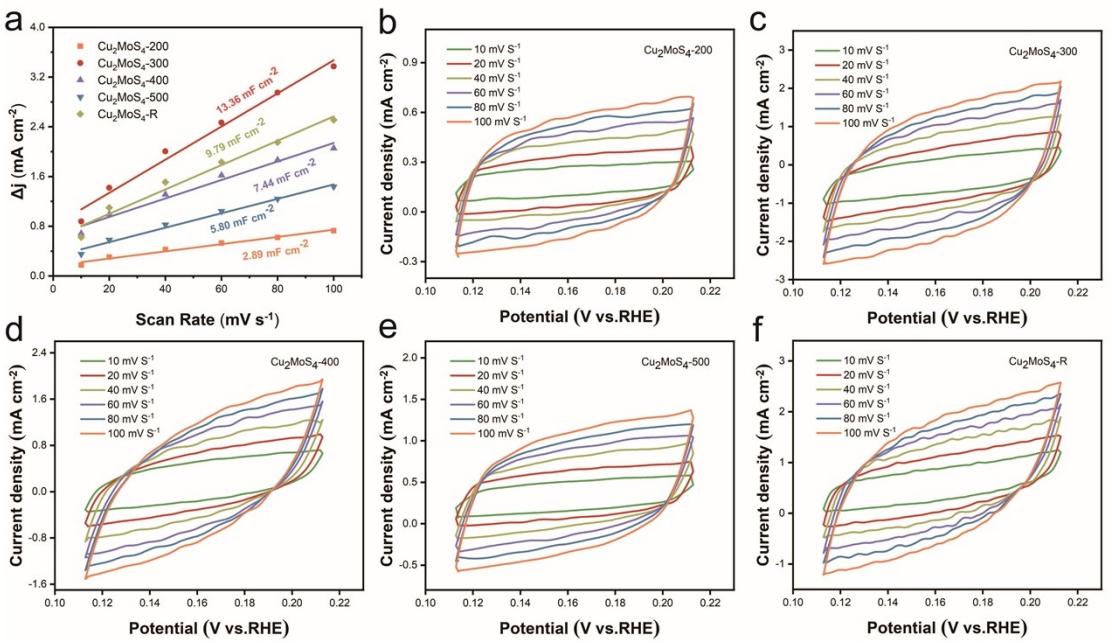

Fig. S12 (a) Double layer capacitance curves of catalysts in 1 M PBS; (b-f) Cyclic voltammetry curves of different catalysts at different scan rates.

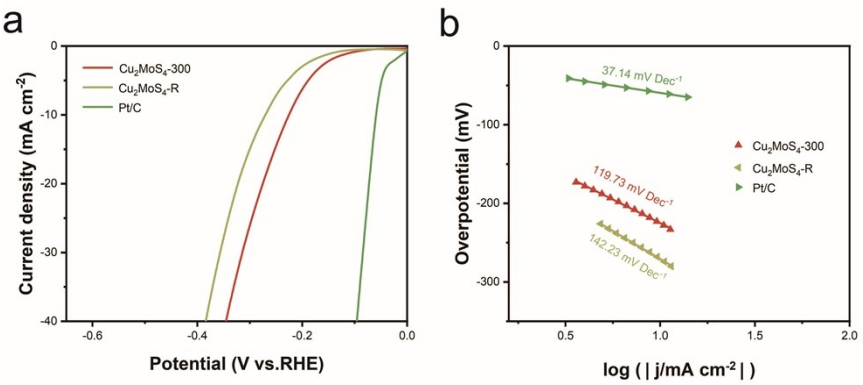

Fig. S13 (a) HER polarization curves of Cu_2MoS_4-300, Cu_2MoS_4-R and Pt/C in 1 M KOH; (b) Corresponding Tafel curves of the samples in 1 M KOH.

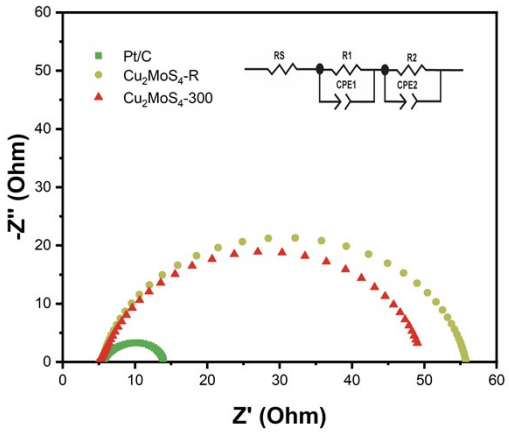

Fig. S14 EIS spectrum of the as-synthesized Cu_2MoS_4-300 nanocubes in 1 M KOH.

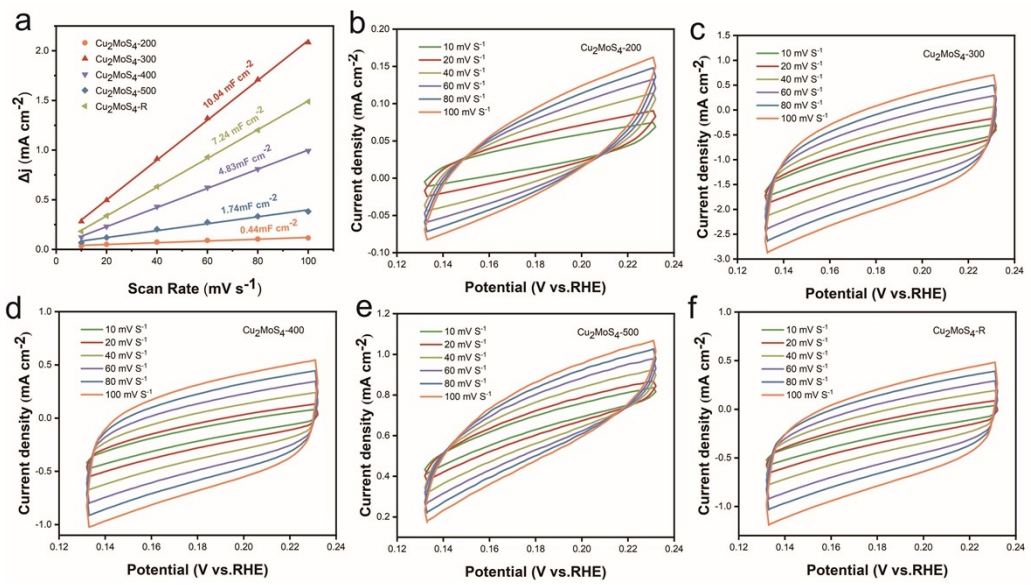

Fig. S15 (a) Double layer capacitance curves of Cu_2MoS_4-ralated catalysts in 1 M KOH; (b-f) Cyclic voltammetry curves at different scan rates.