Supporting Information

Precisely Controlled Synthesis of Hybrid Intermetallic-Metal Nanoparticles for Nitrate Electroreduction

Jiaqi Yu[1], Anna F. Kolln[2], Dapeng Jing[3], Jinsu Oh[2], Hengzhou Liu[4], Zhiyuan Qi[5], Lin Zhou[2], Wenzhen Li[4], Wenyu Huang[1,2]

[1]Department of Chemistry, Iowa State University, Ames Iowa 50011, United States

[2]Ames Laboratory, The U.S. Department of Energy, Ames, Iowa 50011, United States

[3]Materials Analysis and Research Laboratory, Iowa State University, Ames, Iowa 50010, United States

[4]Department of Chemical and Biological Engineering, Iowa State University, Ames Iowa 50011, United States

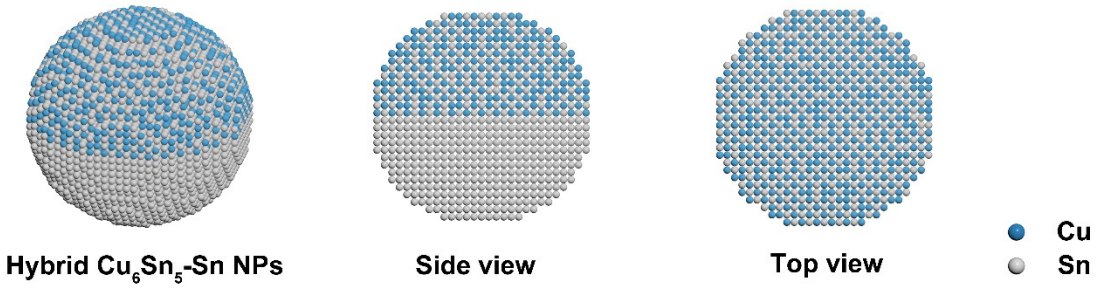
[5]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

Corresponding author

Email: whuang@iastate.edu

Table S1. Experimental synthesis conditions of different Cu_6Sn_5-Sn NPs.

Sample	$SnCl_2$, mmol	$Cu(acac)_2$, mmol	$Cu(acac)_2$ / OAm			Cu to Sn feeding ratio
			Conc., mM	Volume, mL	Inj. rate, mL/min	
Sn NPs	0.5	None				None
Cu_6Sn_5-Sn 1/4	0.5	0.125	125	1	0.5	1/4
Cu_6Sn_5-Sn 1/2	0.5	0.25	125	2	0.5	1/2
Cu_6Sn_5-Sn 1/1	0.5	0.5	125	4	0.5	1/1
Cu_6Sn_5	0.5	1	125	8	0.5	2/1



Scheme S1. 3D model of hybrid Cu_6Sn_5-Sn NPs and the projections from different directions.

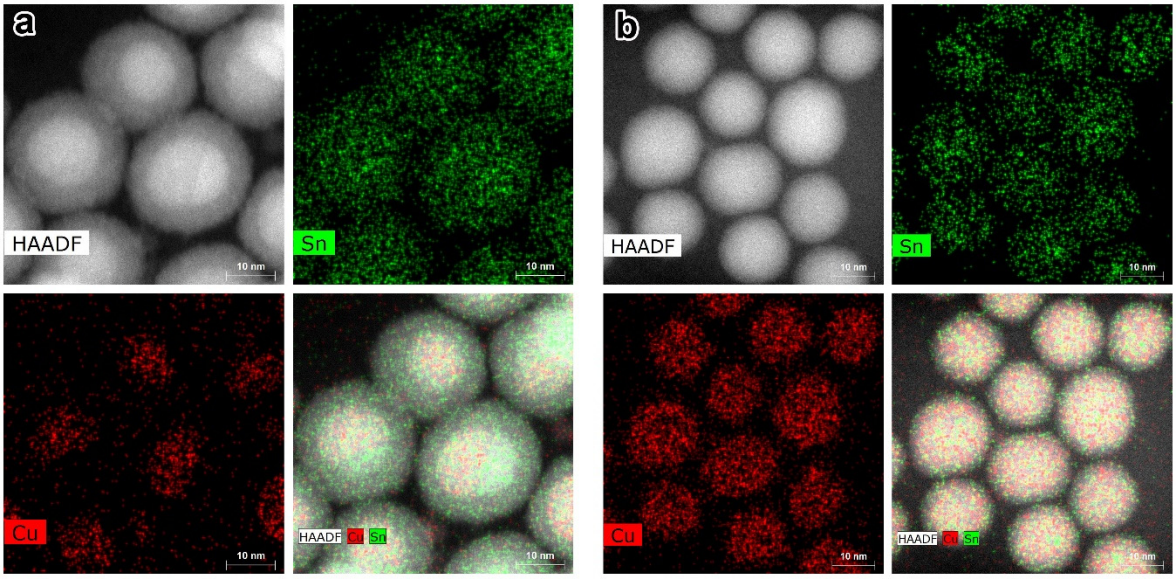


Figure S1. HAADF-STEM and EDS mapping images of (a) hybrid Cu_6Sn_5-Sn 1/2 and (b) Cu_6Sn_5 NPs.

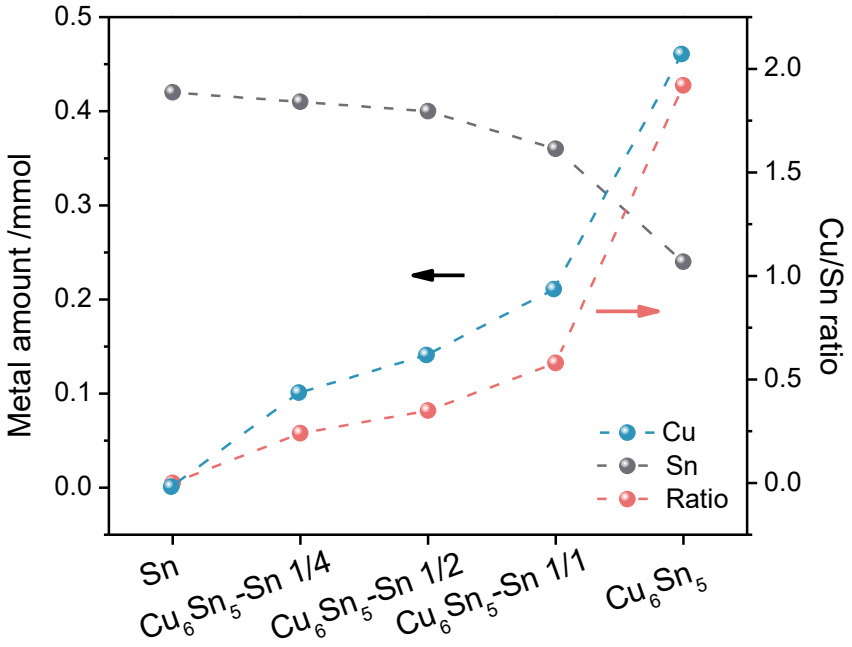


Figure S2. Elemental quantification of Sn and different Cu-Sn samples by ICP-MS analysis. Blue and grey dots represent Cu and Sn amount in mmol, respectively. Red dots represent Cu/Sn ratios at corresponding nanoparticle compositions.

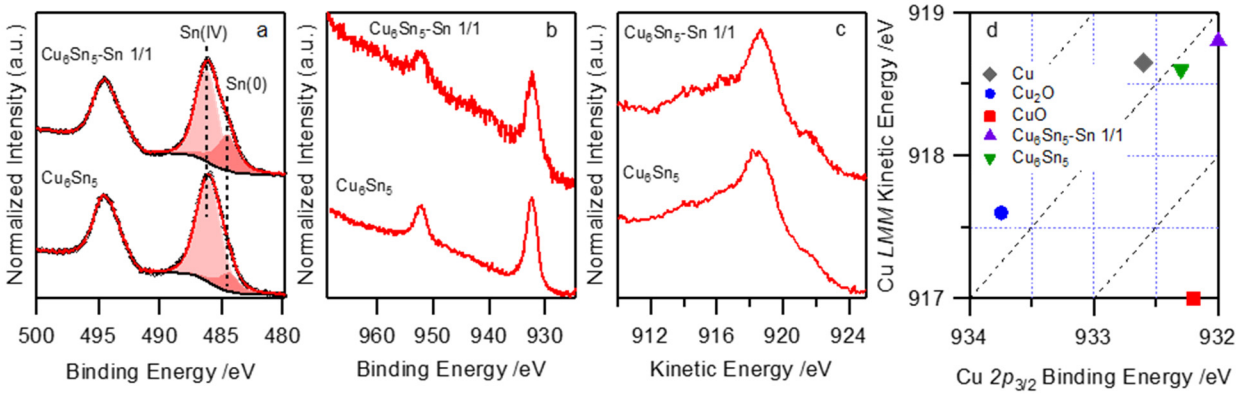


Figure S3. XPS spectra of (a) Sn *3d*, (b) Cu *2p,* and (c) Cu *LMM* of samples Cu_6Sn_5-Sn 1/1 and Cu_6Sn_5; (d) Wagner plot showing the chemical state of Cu from the same two samples together with Cu, Cu_2O, and CuO standards.

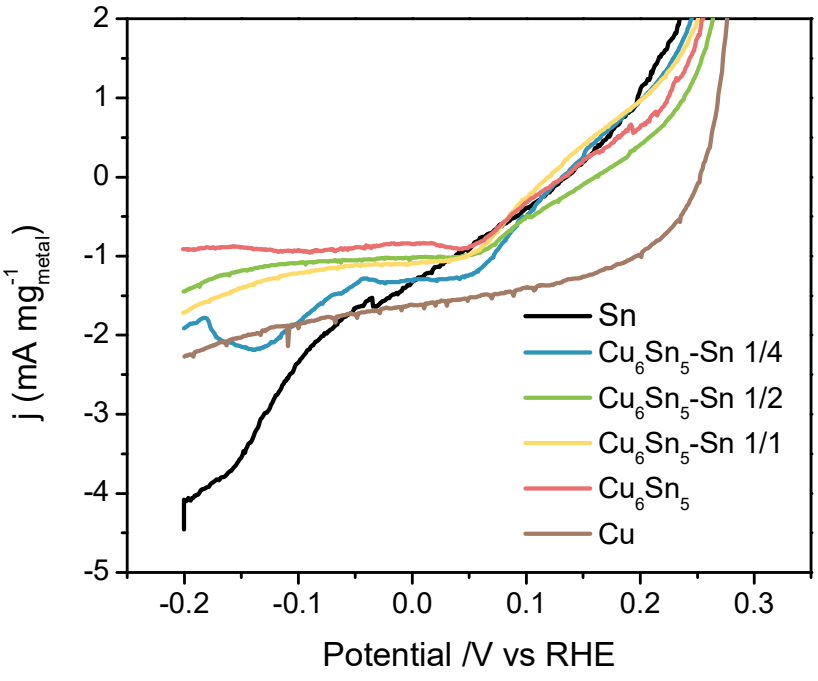


Figure S4. LSV of blank test in 1 M KOH for the hydrogen evolution character study.

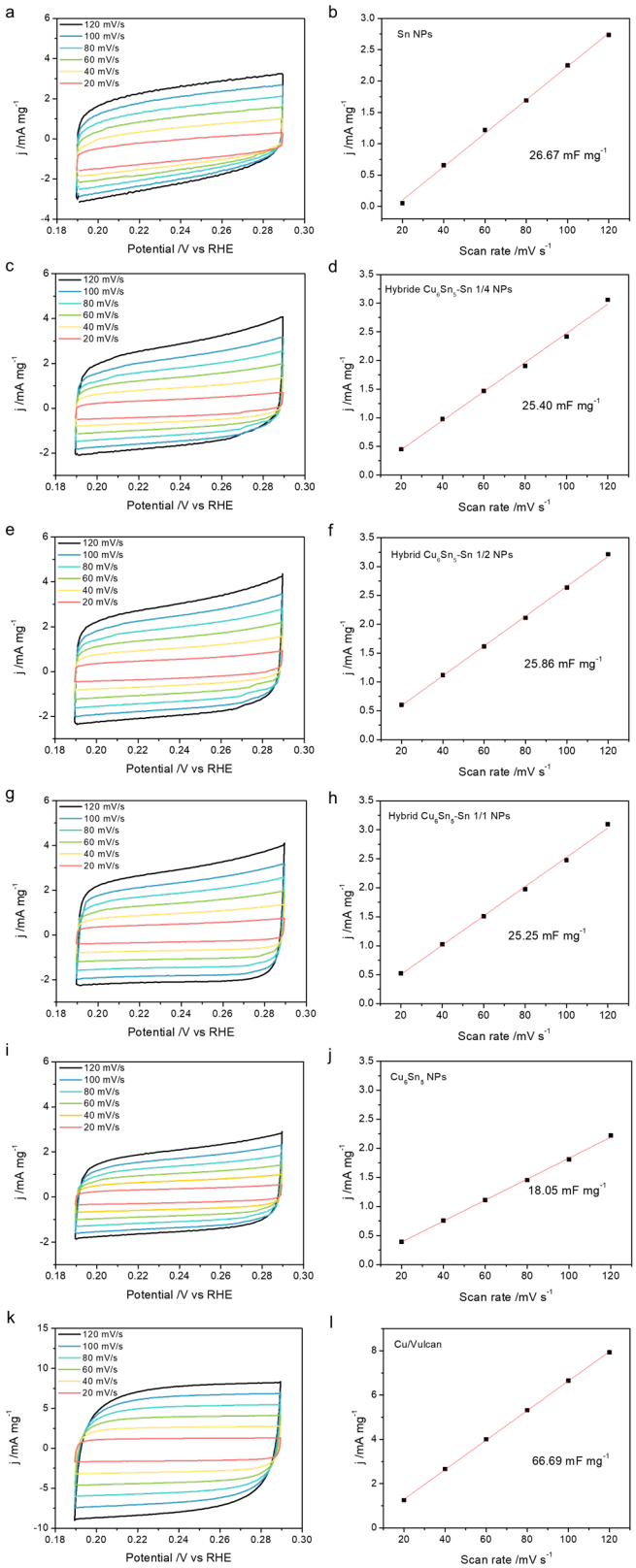


Figure S5. ECSA measurement. (a,c,e,g,i,k) CV profile of Sn, bimetallic Cu-Sn NPs and Cu; (b,d,f,h,j,l) linear fitting of current density vs scan rate to calculate double layer capacitance.

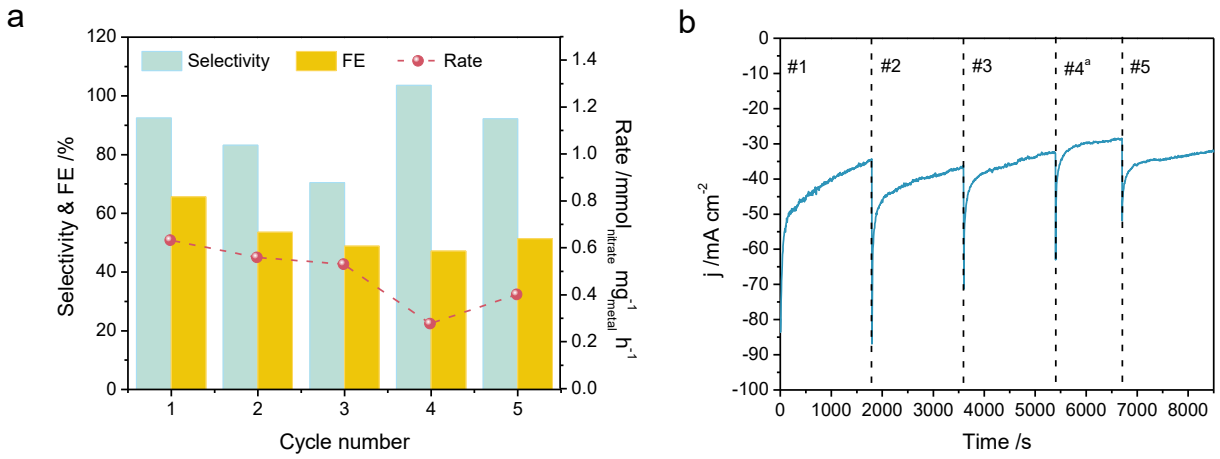


Figure S6. Recycle test of nitrate electroreduction with Cu_6Sn_5-Sn 1/1 NPs. a) selectivity and FE of nitrite, nitrate consuming rate with 5 cycles; b) Chronoamperometry (CA) curve of the 5 cycles test. Test condition: tested at -0.2 V vs RHE, 12 mL 0.1 M KNO_3 + 1 M KOH in cathode; change electrolyte every 30 min; Cu_6Sn_5-Sn 1/1 NPs/Vulcan loading on carbon fiber paper 2.5 mg cm^{-2}; continuously 400 rpm stir and He flow. [a] During 4th cycle, test stopped at 1300 s due to the instrument issue.

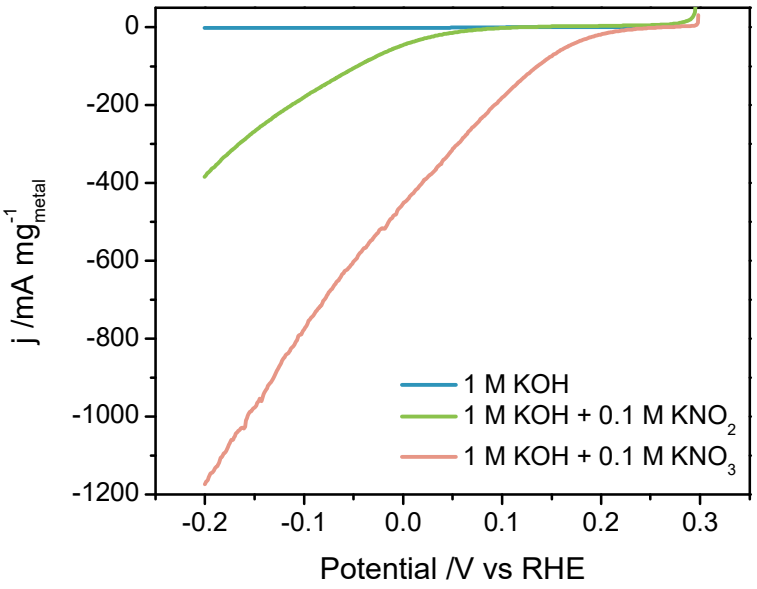


Figure S7. LSV profile of hybrid Cu_6Sn_5-Sn 1/1 NPs in different electrolytes (1 M KOH, 0.1 M KNO_2 + 1 M KOH, and 0.1 M KNO_3 + 1 M KOH).

Table S2. Selectivity and FE comparison for products in nitrate and nitrite electroreduction catalyzed by hybrid Cu_6Sn_5-Sn 1/1 NPs.

Reactant [a]	Reaction time	Conversion	Select. NH_4^+	Select. gas N-species	FE NH_4^+
0.1 M KNO_3 [b]	5 h	36.1%	0.9%	6.9%	2.4%
0.1 M KNO_2	5 h	5.1%	27.6%	72.4%	10.4%

[a] Reaction solution is 0.1 M KNO_3 + 1 M KOH or 0.1 M KNO_2 + 1 M KOH; potential is -0.2 V vs RHE.

[b] Selectivity and FE for nitrite are not listed in nitrate electroreduction.

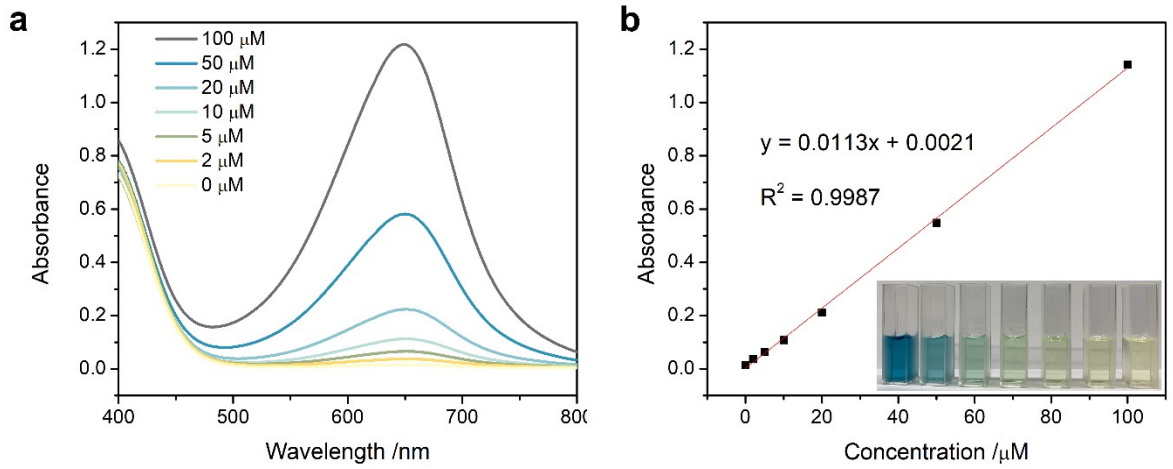


Figure S8. Calibration of ammonia detected with indophenol method. (a) UV-vis spectra of the solution with different ammonia concentrations. (b) The linear fitting of absorbance at 665 nm wavelength light with concentration. The inset in b is the picture of prepared ammonia calibration standards.

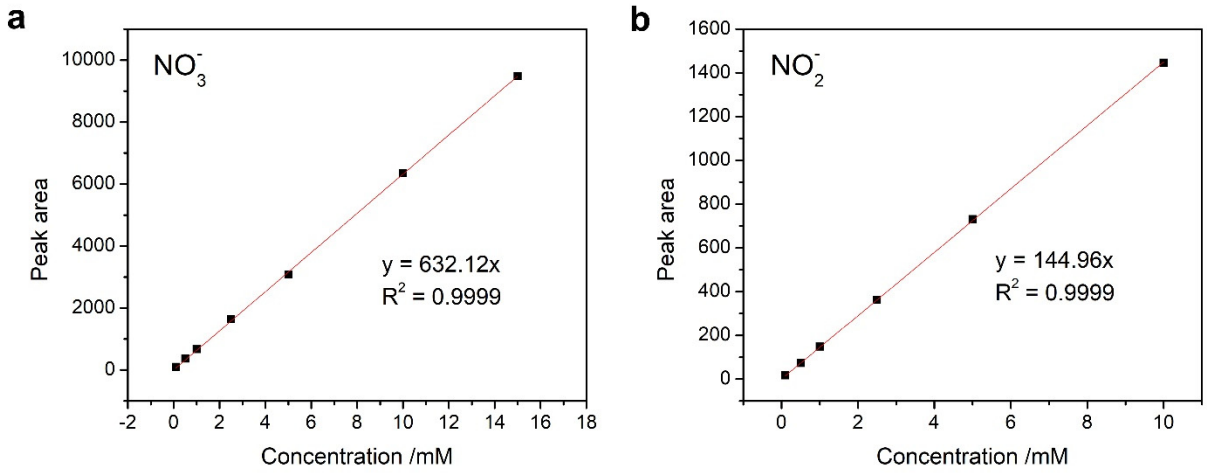


Figure S9. Calibration curves of (a) nitrate and (b) nitrite detected by LC with a UV detector.

Synthesis of Cu/Vulcan (20 wt. %)

Cu/Vulcan was synthesized through a wetness impregnation method. 36.59 mg copper nitrate ($Cu(NO_3)_2 \cdot 2.5H_2O$, Fisher Chemical) dissolved in 5 mL H_2O was added in 50 mg Vulcan XC-72 dispersed in 5 mL EtOH. The mixture was sonicated for 10 min and dried in a 80 °C oil bath for 24 h. Then, the powder of Cu^{2+} embedded on Vulcan was reduced at 500 °C for 4 h under 50 mL/min 10% H_2/Ar.

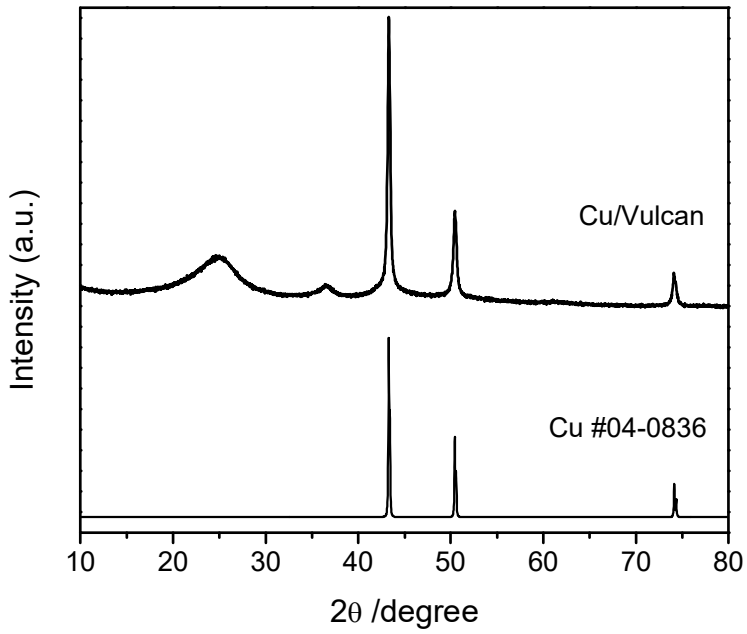


Figure S10. PXRD pattern of as-synthesized Cu/Vulcan.