

Supporting Information for

In-situ Generating Cu₂O/Cu Heterointerfaces on Cu₂O Cube Surface to Enhance Interface Charge Transfer for Rochow Reaction

Fei Tang,^{a,b} Jing Li,^{b,*} Yongxia Zhu,^b Yongjun Ji,^c Huifang Li,^b Hezhi Liu,^b Xueguang Wang,^{a,*} Ziyi Zhong,^{d,e} and Fabing Su^{b,f*}

^a State Key Laboratory of Advanced Special Steel, School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

^b State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

^c School of Light Industry, Beijing Technology and Business University, Beijing 100048, China

^d College of Engineering, Guangdong Technion Israel Institute of Technology (GTIIT), 241 Daxue Road, Shantou, 515063, PR China

^e Technion-Israel Institute of Technology (IIT), Haifa 32000, Israel

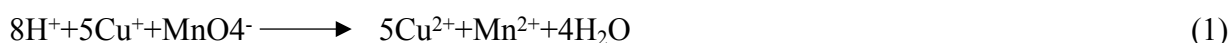
^f Institute of Industrial Chemistry and Energy Technology, Shenyang University of Chemical Technology, Shenyang 110142, China

*To whom correspondence should be addressed. E-mail address: lijing17@ipe.ac.cn (J. li);

wxc228@shu.edu.cn (X. Wang); fbsu@ipe.ac.cn (F. Su).

Part I: Supplementary Note

Supply note 1: Chemical titration analysis was used to determine the content of Cu, Cu₂O components within a sample. Typically, 0.3 g of sample was put into a flask containing 120.0 mL of acetonitrile (CH₃CN, 95%), followed by adding 40.0 mL of dilute HCl (18.5 wt.%). After vigorous rocking for 20 s, the mixture was filtered immediately. Subsequently, 160.0 mL of deionized water was added into the filtrate, which was then titrated with 0.02 mol·L⁻¹ of KMnO₄ aqueous solution (≥99.5%) (Eq. (1)). The residual solid precipitate was dissolved in 20.0 mL of FeCl₃ solution (0.1 mol·L⁻¹), which was kept at 50 °C in water bath and then cooled down to room temperature (Eq. (2)). Afterwards, 20.0 mL of MnSO₄ solution (0.7 mol·L⁻¹) and 100.0 mL of deionized water were introduced, which was again titrated with 0.02 mol·L⁻¹ of KMnO₄ solution (Eq. (3)). The content of Cu₂O in the sample can be calculated by the consumed amount of KMnO₄ according to Eq. (1), and the content of Cu is calculated through the amount of ferrous iron derived from consumed amount of KMnO₄ according to Eq. (3).



Supply note 2: Put 2 g of the contact masses after the reaction into a flask containing 10.0 mL of nitric acid (HNO₃, 65%) and kept at room temperature for 10 h. Then the resulting solid precipitate was recovered by filtration, washed with deionized water. Finally, the products were dried in oven at 50 °C for 10 h.

Part II: Supplementary Figures

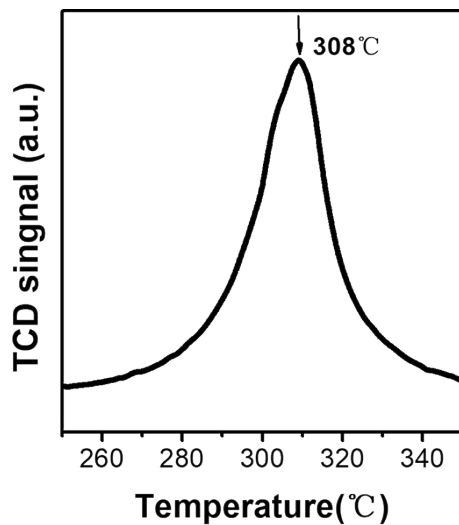


Fig. S1. CO-TPR profiles of cubic Cu₂O

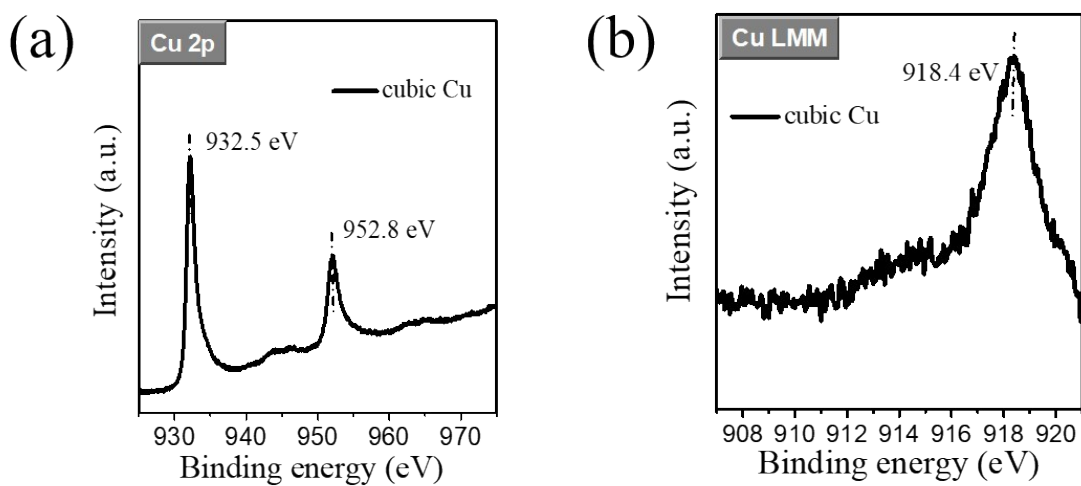


Fig. S2. XPS spectra of Cu 2p (a), Cu LMM (b) for cubic Cu.

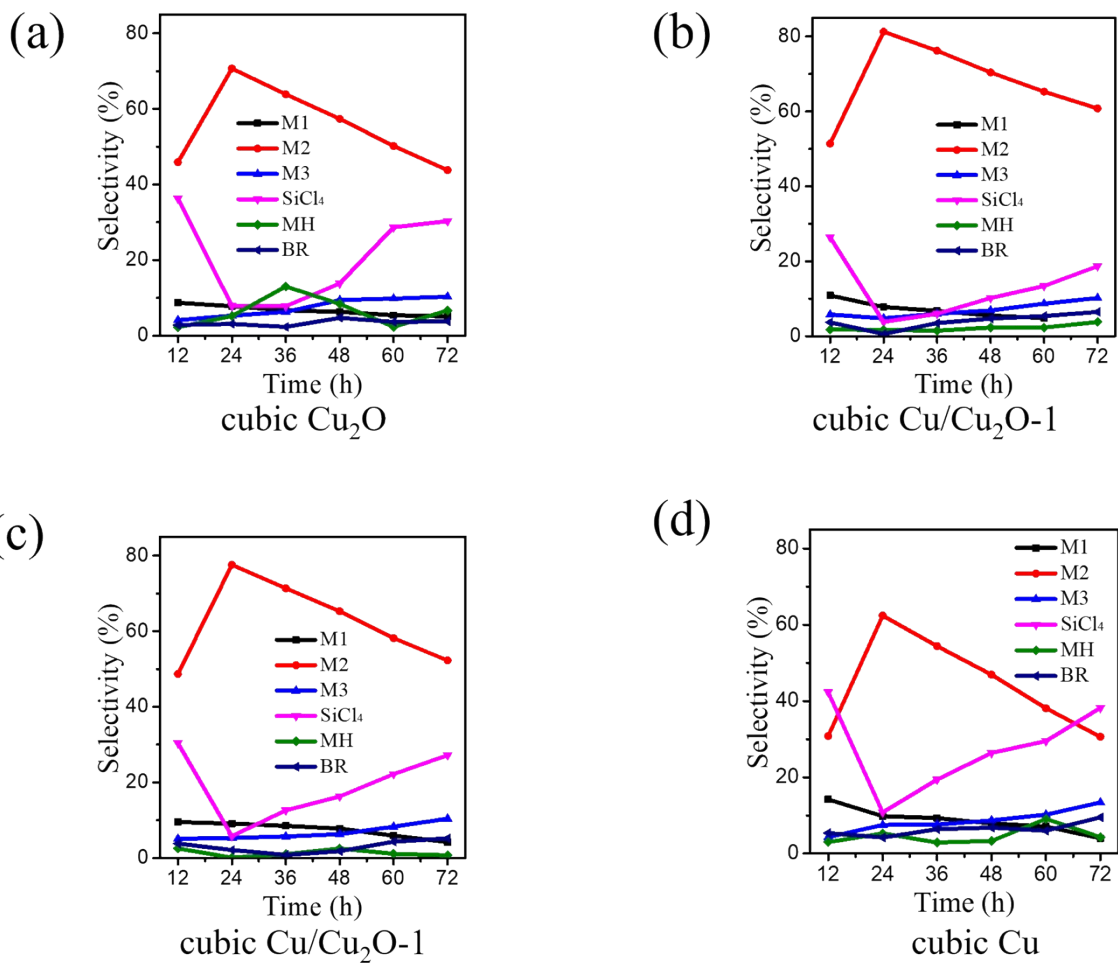


Fig.S3. Analysis of the catalytic products distribution with Time: (a) cubic Cu₂O ; (b) cubic Cu/Cu₂O-1 ; (c) cubic Cu/Cu₂O-2 (d) cubic Cu

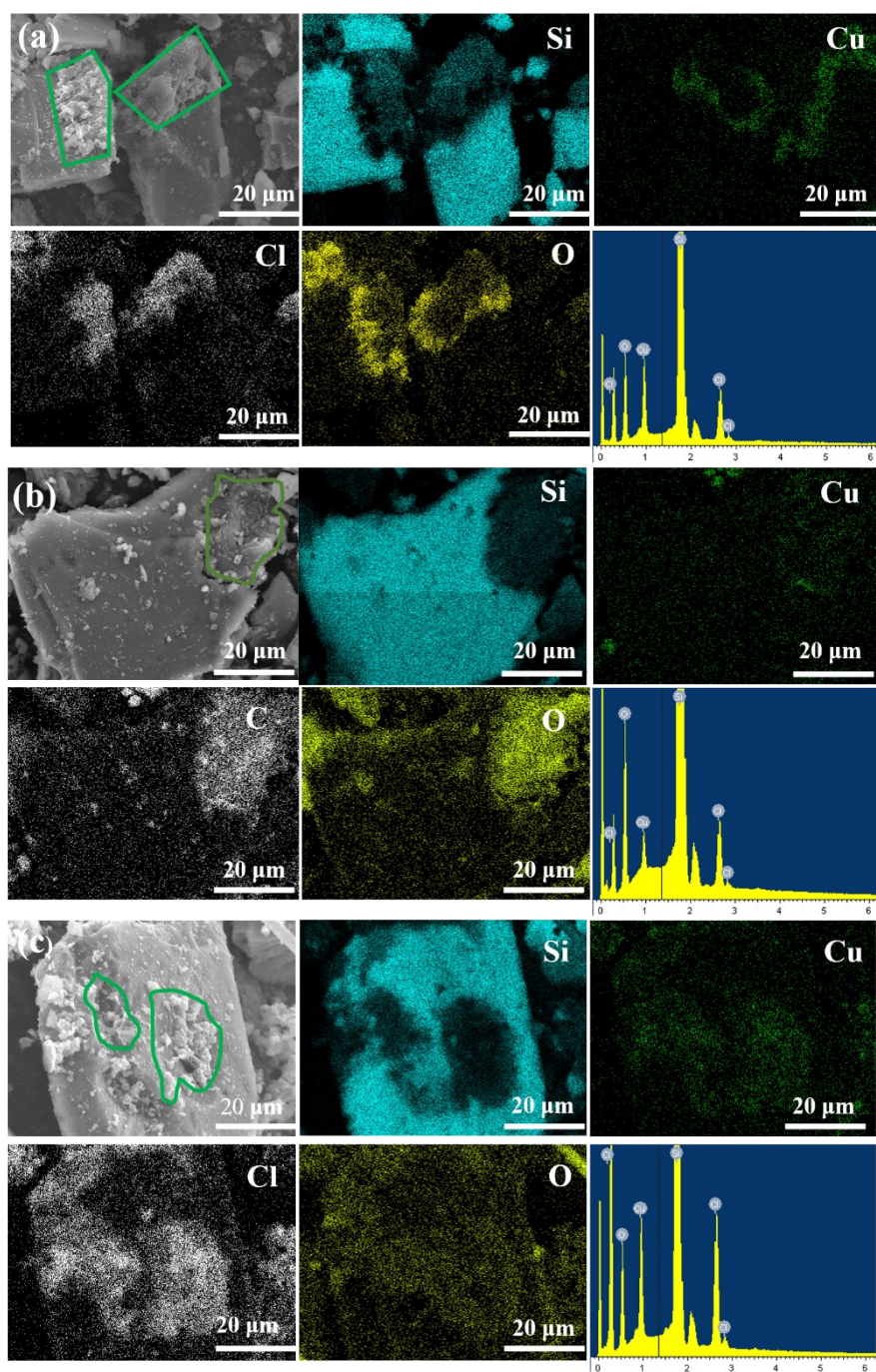


Fig. S4. SEM and the corresponding EDS mapping images, as well as EDS spectra of the Si particle surface after the reaction in the presence of cubic Cu (a), cubic Cu/Cu₂O-2 (b), cubic Cu (c).

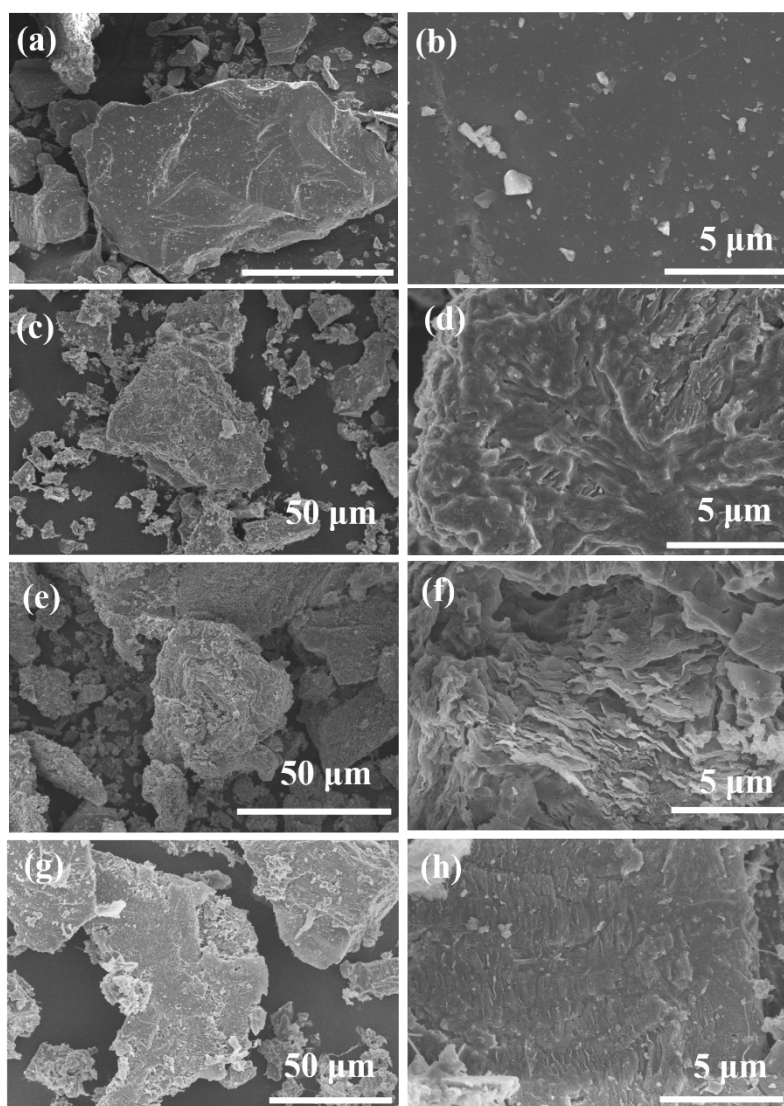


Fig. S5. SEM images of pure Si particles after 72 h reaction in the presence of cubic Cu_2O (a, b), cubic $\text{Cu}/\text{Cu}_2\text{O}$ -1 (c, d), cubic Cu (e, f) nanoparticles after removing surface copper species.

Part III: Supplementary Tables

Sample	(111)	(220)	(311)
cubic Cu ₂ O	53.4%	30.5%	15.1%
cubic Cu/Cu ₂ O-1	48.2%	23.9%	27.9%
cubic Cu/Cu ₂ O-2	49.2%	28.2%	22.6%
cubic Cu	50.7%	34.2%	16.1%

Table S1 Intensity ratio of crystal planes for the waste contact masses from XRD patterns