Supporting Information for

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

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Part I: Supplementary Note

Supply note 1: Chemical titration analysis was used to determine the content of Cu, Cu$_2$O components within a sample. Typically, 0.3 g of sample was put into a flask containing 120.0 mL of acetonitrile (CH$_3$CN, 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 KMnO$_4$ aqueous solution (≥99.5%) (Eq. (1)). The residual solid precipitate was dissolved in 20.0 mL of FeCl$_3$ 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 MnSO$_4$ 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 KMnO$_4$ solution (Eq. (3)). The content of Cu$_2$O in the sample can be calculated by the consumed amount of KMnO$_4$ according to Eq. (1), and the content of Cu is calculated through the amount of ferrous iron derived from consumed amount of KMnO$_4$ according to Eq. (3).

$8H^+ + 5Cu^+ + MnO_4^- \rightarrow 5Cu^{2+} + Mn^{2+} + 4H_2O$  

$Cu + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+}$  

$8H^+ + 5Fe^{2+} + MnO_4^- \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$  

Supply note 2: Put 2 g of the contact masses after the reaction into a flask containing 10.0 mL of nitric acid (HNO$_3$, 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 Cu$_2$O

![Graph showing CO-TPR profile with a peak at 308°C.](image)

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

![XPS spectra graphs](image)
**Fig. S3.** Analysis of the catalytic products distribution with Time: (a) cubic Cu$_2$O; (b) cubic Cu/Cu$_2$O-1; (c) cubic Cu/Cu$_2$O-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/Cu$_2$O-2 (b), cubic Cu (c).
Fig. S5. SEM images of pure Si particles after 72 h reaction in the presence of cubic Cu$_2$O (a, b), cubic Cu/Cu$_2$O-1 (c, d), cubic Cu (e, f) nanoparticles after removing surface copper species.
### Part III: Supplementary Tables

<table>
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<th>Sample</th>
<th>(111)</th>
<th>(220)</th>
<th>(311)</th>
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<tbody>
<tr>
<td>cubic Cu₂O</td>
<td>53.4%</td>
<td>30.5%</td>
<td>15.1%</td>
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<tr>
<td>cubic Cu/Cu₂O-1</td>
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<td>23.9%</td>
<td>27.9%</td>
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<tr>
<td>cubic Cu</td>
<td>50.7%</td>
<td>34.2%</td>
<td>16.1%</td>
</tr>
</tbody>
</table>

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