

## Supporting information

### **Hopper-like framework growth evolution in cubic system: a case study of Cu<sub>2</sub>O**

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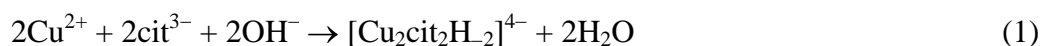
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## SI-1 Chemical roles of sodium citrate

Sodium citrate serves as ligand, reducing reagent, and weak base in our hydrothermal synthesis of Cu<sub>2</sub>O microcrystals.

### (1) Ligand

Citric acid, with one hydroxide and three carboxylic acid moieties, can form a variety of complexes with copper ions through mono- and polydentate complexation.<sup>[1]</sup> Three p*K* values of citric acid are given in Table S1. In the presence of Cu<sup>2+</sup> ions and high pH, the hydrogen of the hydroxyl group can deprotonate, and the citrate ion may become quadruply ionized (Fig. S1).<sup>[2,3]</sup> Citrate and Cu<sup>2+</sup> can form [Cu<sub>2</sub>cit<sub>2</sub>H<sub>-2</sub>]<sup>4-</sup> complex at high pH.



The dimer, [Cu<sub>2</sub>cit<sub>2</sub>H<sub>-2</sub>]<sup>4-</sup>, can have a structure with two equivalent copper(II) ions, both coordinated to three carboxylate and one alcoholate groups.<sup>[3,4]</sup> The dimer [Cu<sub>2</sub>cit<sub>2</sub>H<sub>-2</sub>]<sup>4-</sup> becomes dominant at pH values greater than 5.<sup>[1-3]</sup>

Table S1. p*K* values of the three acidities of citric acid

Deprotonation form	p <i>K</i>
[H <sub>2</sub> cit] <sup>-</sup>	3.2
[Hcit] <sup>2-</sup>	4.8
[cit] <sup>3-</sup>	6.4

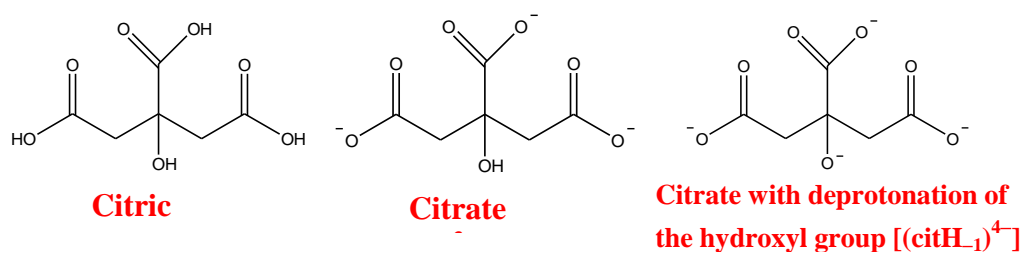


Figure S1. Structures of citric acid and its deprotonation forms.

The formation of  $[\text{Cu}_2\text{cit}_2\text{H}_2]^{4-}$  complex can be proved by the UV-vis spectra of the reaction solution (Fig. S2). In most experimental conditions ( $\text{pH} > 5$ ), the UV-vis spectra did not change upon different pH.

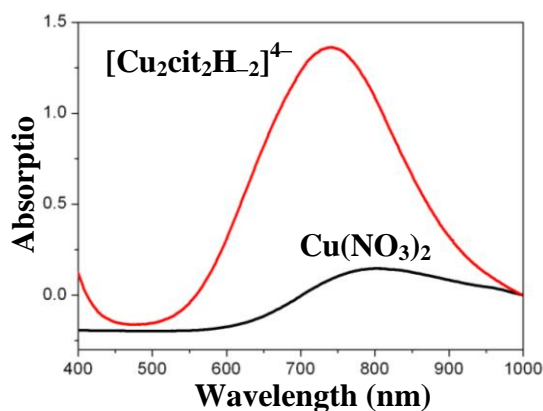


Figure S2. UV/vis spectra confirm that citrate can form  $[\text{Cu}_2\text{cit}_2\text{H}_2]^{4-}$  complex with  $\text{Cu}^{2+}$ .

## (2) Reducing reagent

Citrate (or citric acid) has been widely used as reducing agent in the synthesis of Au and Ag nanocrystals at room temperature or low temperature.<sup>[5,6]</sup> The chemical reaction of citrate has been proposed as reaction (2) and shown in Figure S3.<sup>[6]</sup>



Redox potential of citrate is  $E(\text{ADE}, \text{CO}_2/\text{citrate}) < -0.01\text{V}$  at  $\text{pH} > 8$ .<sup>[6]</sup>

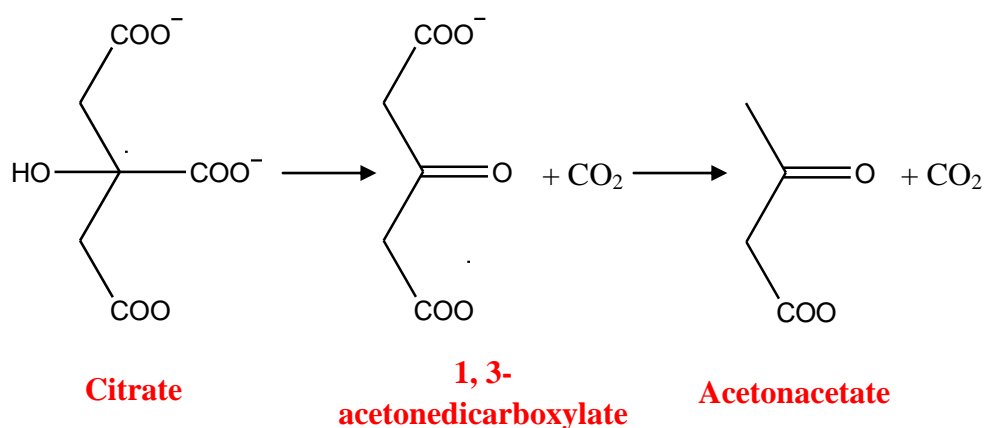
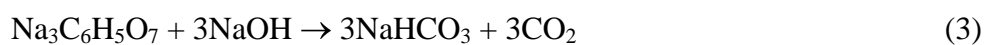


Figure S3. Degradation pathway of citrate as reducing agent in the synthesis of Ag nanocrystals.

The reduction of  $\text{Ag}^+$  by citrate is thermodynamically allowed because redox potential of  $\text{Ag}^+$ ,  $E(\text{Ag}^+/\text{Ag}) = 0.7996 \text{ V}$  vs NHE, is larger than that of citrate. The reaction is extremely slow at room temperature, thus it should proceed at elevated temperatures. Because of redox potential of  $\text{Cu}^{2+}/\text{Cu}_2\text{O}$ ,  $E(\text{Cu}^{2+}/\text{Cu}_2\text{O}) = 0.203 \text{ V}$  vs NHE,<sup>[7]</sup> is low than that of  $\text{Ag}^+/\text{Ag}$ , the redox reaction of  $\text{Cu}^{2+}$  and citrate should proceeds at elevated temperature ( $>160^\circ\text{C}$ , mostly at  $190^\circ\text{C}$ ).

In our hydrothermal condition, citrate can take place following reaction.



The reaction product of citrate mainly includes  $\text{NaHCO}_3$ , which was proved by the XRD data (Fig. S4).

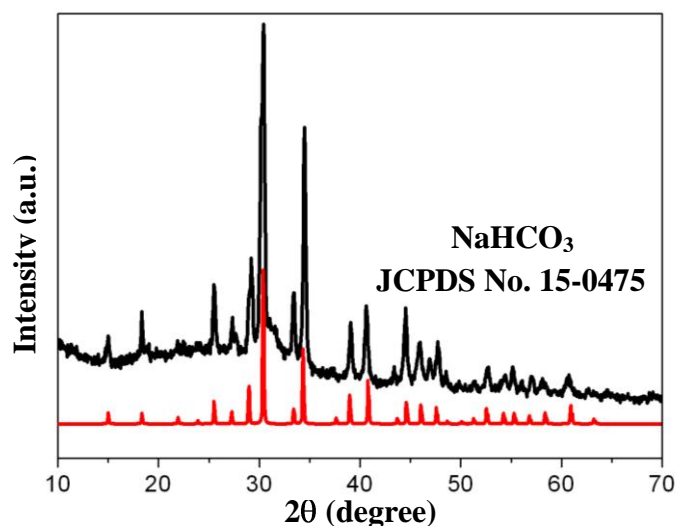


Figure S4. XRD patterns show the oxidation product of citrate after hydrothermal reaction.

### (3) Weak base

In addition, sodium citrate also serve as weak base, and can adjust the pH of Cu(NO<sub>3</sub>)<sub>2</sub> solution. The complexation, redox reaction and precipitation reaction are pH-dependent. Therefore, the different Na<sub>3</sub>cit/Cu<sup>2+</sup> ratios can affect the dynamics of chemical reaction by influencing its reduction power and pH-dependent properties.

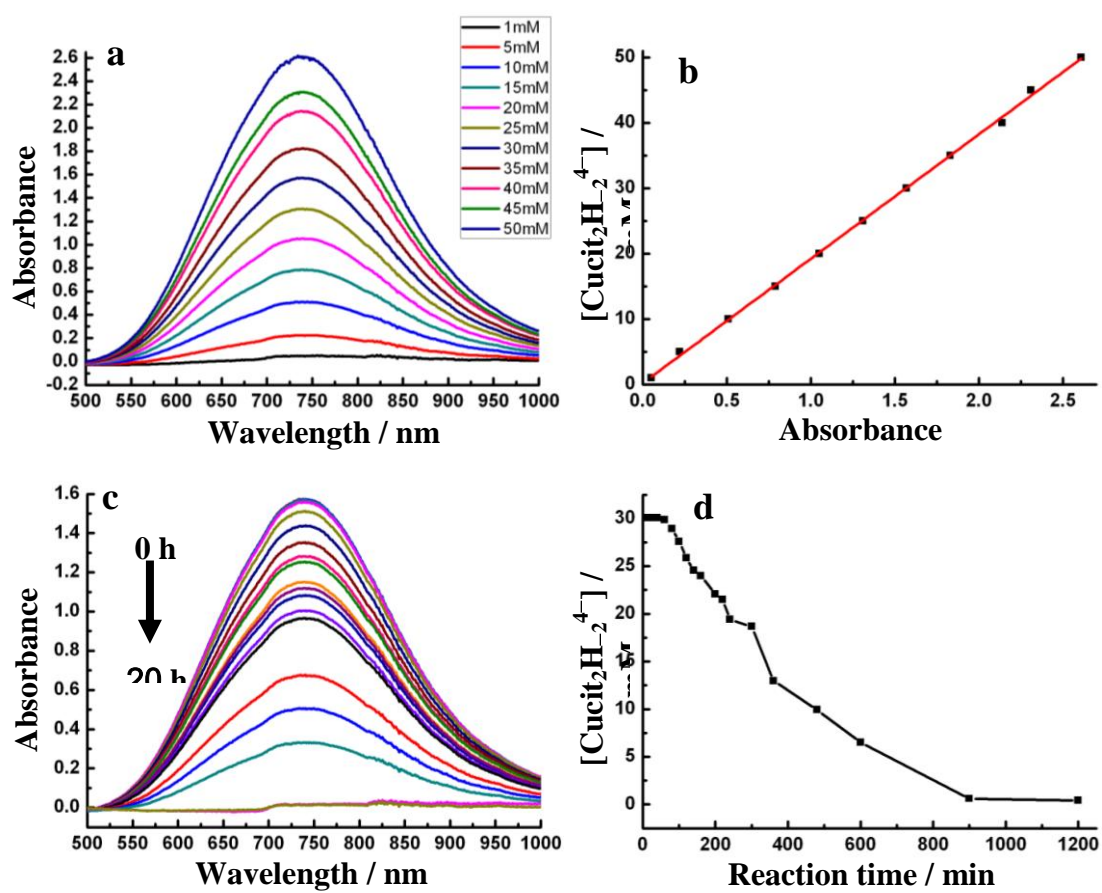
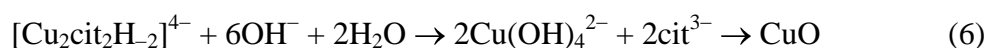
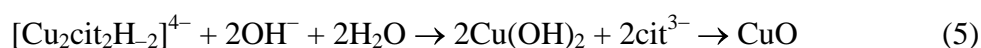
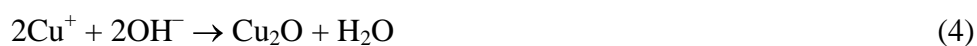


Figure S5. (a,b) UV-vis spectra of standard concentration of Cu(II) complex. (c,d)

UV-vis spectra of Cu(II) complex ions at different reaction time intervals.

## SI-2 Chemical roles of NaOH

NaOH can be used to control the thermodynamics and dynamics of chemical reaction, because  $\text{OH}^-$  ions participate in the redox reaction that forms  $\text{Cu}_2\text{O}$  and can complex with  $\text{Cu}^{2+}$  to form  $\text{Cu}(\text{OH})_2$  or  $\text{Cu}(\text{OH})_4^{2-}$  at high pH, and it can adjust the electrochemical potential of  $\text{Cu}^{2+}$  and citrate.



According to reaction (4), higher pH favors the fast reaction rate which can be proved by the reaction time of disappearance of blue  $\text{Cu}^{2+}$  color (Table S2).

Table S2. Reaction transformation time of disappearance of blue  $\text{Cu}^{2+}$  color at 190°C

NaOH: $\text{Cu}^{2+}$ ratio	Transformation time (disappearance of blue $\text{Cu}^{2+}$ color)
0	11h
0.67	11h
1.67	8h

Table S3. Stability constants for copper-citrate and copper-NaOH complexes at 298 K and corresponding NaOH: $\text{Cu}^{2+}$  ratio.

Species	NaOH: $\text{Cu}^{2+}$ ratio	Stability constant, $\log K_f$
$[\text{Cu}_2\text{cit}_2\text{H}_{-2}]^{4-}$	0	5.87

$[\text{Cu}_2\text{cit}_2]^{2-}$	0	14.43
$\text{Cu}(\text{OH})_2$	2	13.68
$\text{Cu}(\text{OH})_3^-$	3	17.00
$\text{Cu}(\text{OH})_4^{2-}$	4	18.50

According to reactions (5) and (6), and Table S3, CuO can form when NaOH:Cu<sup>2+</sup> ratio is between 2 and 4. Our experimental result show that NaOH:Cu<sup>2+</sup> ratio of 1.33 is the turning point of formation of intermediate CuO phase, and NaOH:Cu<sup>2+</sup> ratio of 2.67 is the turning point of formation of final CuO product.



Figure S6. Photograph shows solution color and precipitation formation after reacted at 80 °C for 2h. The concentrations of NaOH are: 20mM, 60mM, 100mM, 120mM, 140mM (from left to right). NaOH:Cu(NO<sub>3</sub>)<sub>2</sub> ratios are 0.67, 2, 3.33, 4, 4.67 (from left to right).

It is proved that the formation of CuO at high pH values is thermodynamic favorable.



### SI-3 Hopper cube structure

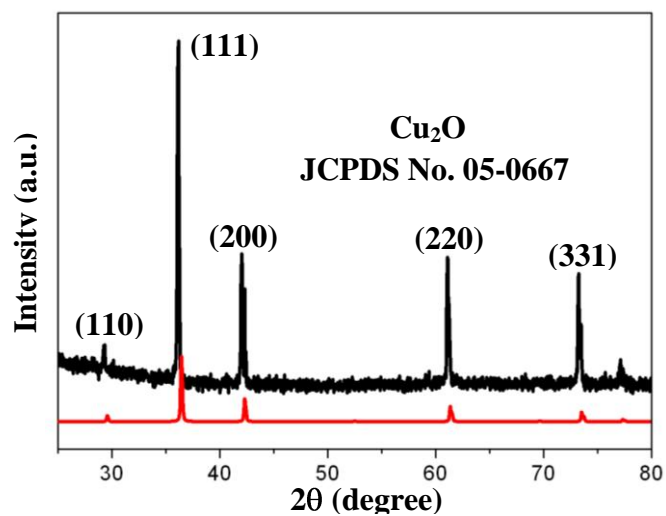


Figure S7. XRD patterns of the products after hydrothermal reaction. It is proved that the obtained red precipitations are phase-pure Cu<sub>2</sub>O crystals.

#### SI-4 Citrate controls crystal morphology

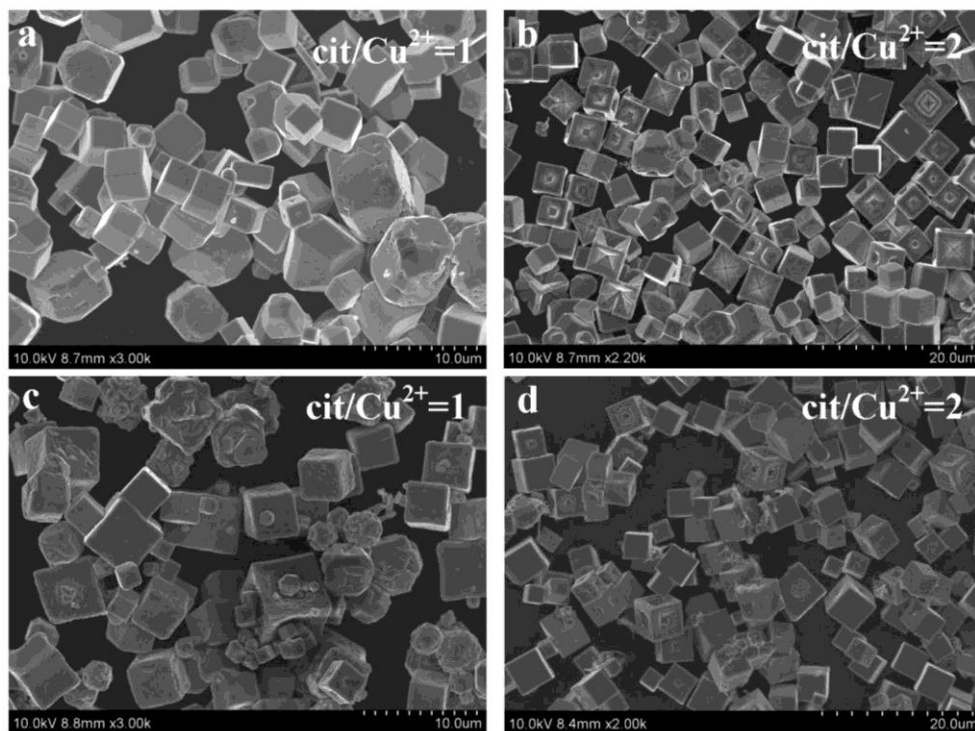


Figure S8. SEM images of  $\text{Cu}_2\text{O}$  microcrystals synthesized with different  $\text{Na}_3\text{cit}/\text{Cu}^{2+}$  and  $\text{NaOH}/\text{Cu}^{2+}$  ratios: (a and c)  $\text{cit}/\text{Cu}^{2+}=1$ ; (b and d)  $\text{cit}/\text{Cu}^{2+}=2$ .  $\text{NaOH}/\text{Cu}^{2+}$  ratio is set as 1.33 (a and b) and 0 (c and d). The concentration of  $\text{Cu}^{2+}$  is 30 mM.

## SI-5 Cu<sub>2</sub>O crystals synthesized with different NaOH/Cu<sup>2+</sup> ratios

(1) NaOH/Cu<sup>2+</sup> < 1.33

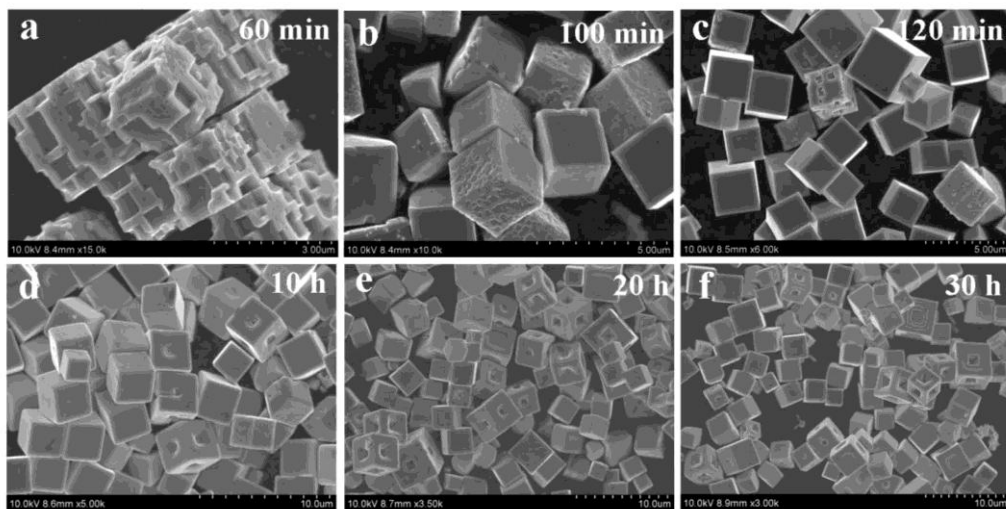


Figure S9. FESEM images of Cu<sub>2</sub>O obtained at different time intervals with NaOH/Cu<sup>2+</sup> = 1. The experiment conditions are set as Na<sub>3</sub>cit/Cu<sup>2+</sup>=3, [Cu<sup>2+</sup>]=30mM.

(2)  $1.33 < \text{NaOH}/\text{Cu}^{2+} < 2.67$

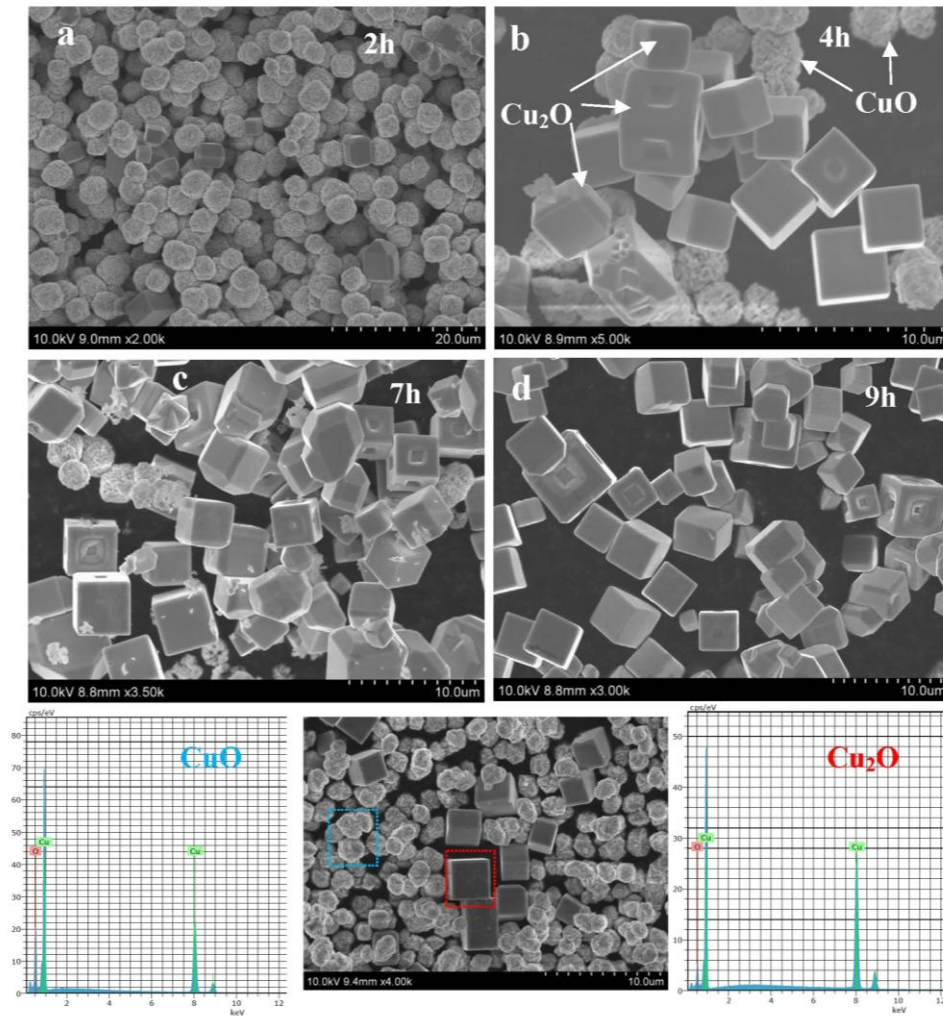


Figure S10. FESEM images and EDS show morphologies and compositions of products synthesized at different time intervals. The experiment conditions is set as  $\text{Na}_3\text{cit}/\text{Cu}^{2+}=3$ ,  $\text{NaOH}/\text{Cu}^{2+} = 1.33$ ,  $[\text{Cu}^{2+}]=30\text{mM}$ .

(3)  $\text{NaOH}/\text{Cu}^{2+} > 2.67$

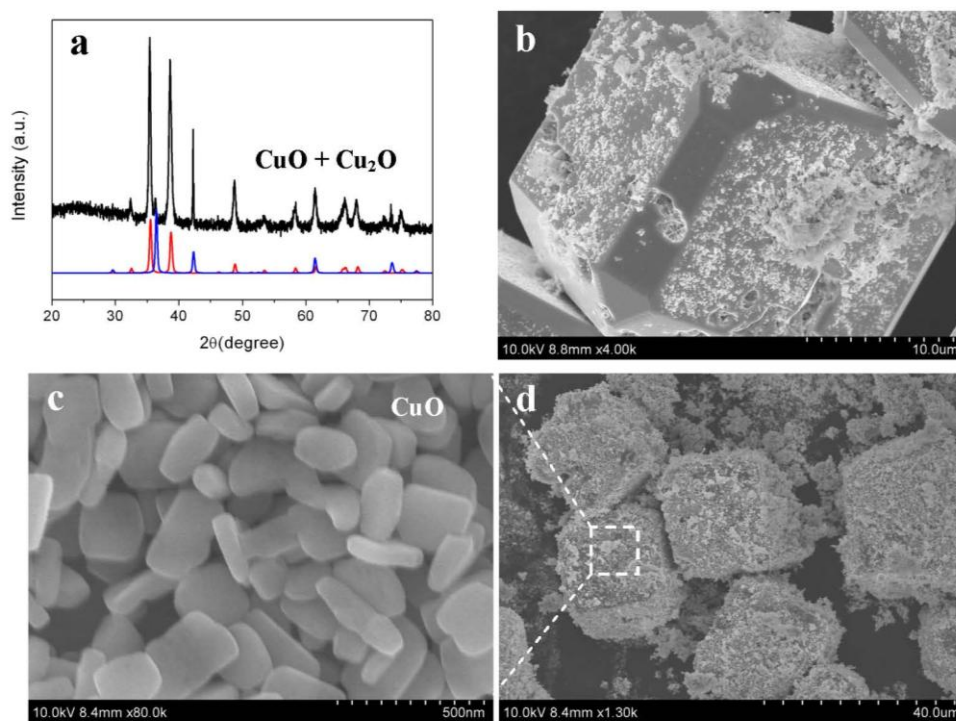


Figure S11. XRD pattern and FESEM images show  $\text{Cu}_2\text{O}$  microcubes and  $\text{CuO}$  nanoplates obtained at  $\text{NaOH}/\text{Cu}^{2+} = 2.67$ . The experiment condition is set as  $\text{cit}/\text{Cu}^{2+}=3$ ,  $[\text{Cu}^{2+}]=30\text{mM}$ .

## References

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