Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A


Supporting Information

# Scalable synthesis of hollow $Cu_2O$ nanocubes with unique optical properties via a simple hydrolysis-based approach

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## 1. Raw CuCl micropowder.

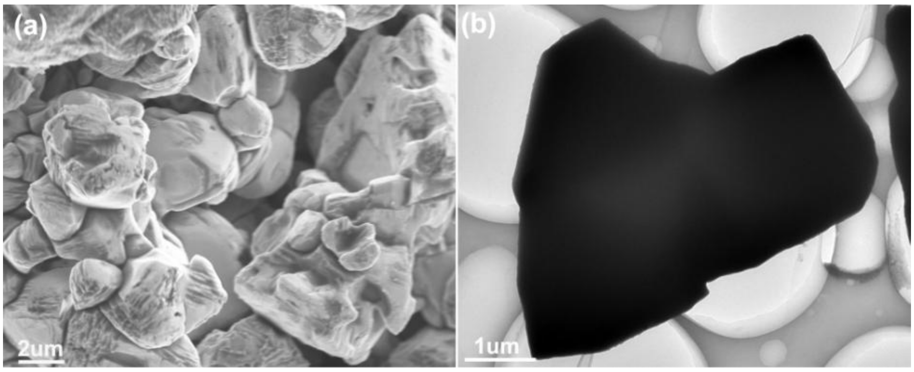


Figure S1. (a) SEM and (b) TEM images of raw CuCl micro-powder used as initial material.

## 2. Characterizations of hollow $Cu_2O$ nanocubes.

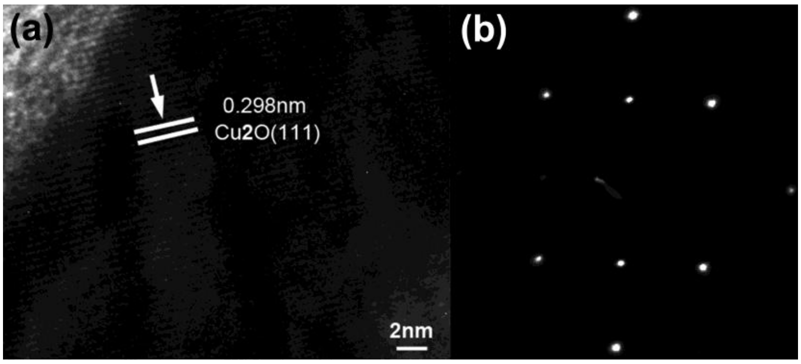


Figure S2. (a) HRTEM image and SAED pattern (b) of the shell of a hollow $Cu_2O$ nanocube.

## 3. Calculation of the pH threshold value for the complexation of CuCl in aqueous solutions.

The dissolution of CuCl in aqueous HCl proceeds in accordance with the following reactions:

Ionization $CuCl \leftrightarrow Cu^{+} + Cl^{-}$ (1)

Complexation $CuCl + x\,HCl \leftrightarrow H_xCuCl_{1+x}$ ($x$=1, 2) (2)

Therefore, the total solubility (**S**) of CuCl can be represented as the sum of several soluble Cu-containing species: [1]

$$S = c_{Cu^+} + c_{CuCl(aq)} + c_{CuCl_2^-} + c_{CuCl_3^{2-}}$$

$$= c_{Cu^+} + \beta_1 c_{Cu^+} c_{Cl^-} + \beta_2 c_{Cu^+} \cdot c_{Cl^-}^2 + \beta_3 c_{Cu^+} \cdot c_{Cl^-}^3$$

$$= K_{sp}(1/c_{Cl^-} + \beta_1 + \beta_2 c_{Cl^-} + \beta_3 c_{Cl^-}^2) \quad (3)$$

where $K_{sp}$ is the equilibrium constant, $c_{Cu^+}$ and $c_{Cl^-}$ are the concentrations of $Cu^+$ and $Cl^-$ ions, respectively. $\beta_1, \beta_2,$ and $\beta_3$ are the cumulative stabilization constants of CuCl, $CuCl_2^-$, and $CuCl_3^{2-}$, respectively ($\beta_1 = 2.43\times10^{-3}$, $\beta_2 = 6.91\times10^{4}$, $\beta_3 = 4.55\times10^{5}$). [1]

When the pH value of the aqueous solution is adjusted by adding HCl, two effects can influence the solubility of CuCl. As the added amount of HCl increases, first the common-ion effect takes place, where the increase of $Cl^-$ ion concentration can lower the solubility of CuCl, and the concentration of Cu-containing species reaches a minimum value. Further addition of HCl can cause the other effect, complexation,

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where HCl can react with CuCl, giving rise to soluble $H_xCuCl_{1+x}$ and thus improving the solubility of CuCl.

Therefore, the lowest concentration of Cu-containing species (or the minimum solubility of CuCl) corresponds to the concentration of $Cl^-$ ions at which the complexation reaction begins to proceed. This value can be determined by:

$$dS/dc_{Cl^-} = K_{sp}(-1/c_{Cl^-}^2 + \beta_2 + 2\beta_3 c_{Cl^-}) = 0 \quad (4)$$

which gives $c_{Cl^-(min)} = 3.72\times10^{-3}$ M

The ionization constant of CuCl is $1.72\times10^{-7}$, which is much lower than that of HCl in water. Hence, most of $Cl^-$ ions originate from the ionization of HCl. As a result, the concentration of $H^+$ ions is nearly equal to that of $Cl^-$ ions.

$$pH = -\lg c_{H^+} = -\lg 3.72\times10^{-3} = 2.43$$

Therefore, the complexation reaction takes place when pH is below 2.43.

## 4. Calculation of the lower pH limit for the alkaline hydrolysis of CuCl in aqueous solution.

The ionization constant ($K_a$) of CuCl can be calculated based on the ionization reaction [equation (1)]:

$$K_a = \frac{c_{Cu^+}\cdot c_{Cl^-}}{c_{CuCl}} \quad (5)$$

where, $K_a = 1.72\times10^{-7}$ for CuCl in water.

The saturated solubility of CuCl in water ($s_{CuCl}$) is $6.061\times10^{-4}$ M,[2] and

$$c_{CuCl} = s_{CuCl} - c_{Cu^+}$$

$$c_{Cu^+} = c_{Cl^-}$$

According to the above, the concentration of $Cu^+$ ions in the saturated CuCl aqueous solution is determined as $c_{Cu^+} = 1.0124\times10^{-5}$ M.

The corresponding pH value of the saturated CuCl aqueous solution is then calculated as follows. A hydrolysis equilibrium exists in the saturated CuCl aqueous solution

$$H_2O + Cu^+ \leftrightarrow CuOH + H^+ \quad (6)$$

The dissolution equilibrium constant $K_{sp6}$ of reaction (6) follows:

$$K_{sp6} = \frac{c_{H^+} \cdot c_{CuOH}}{c_{Cu^+} - c_{H^+}} = \frac{c_{H^+} \cdot c_{H^+}}{c_{Cu^+} - c_{H^+}} \quad (7)$$

The constant $K_{sp6}$ for the hydrolysis of CuCl is unknown. However, equation (6) can be departed into two basic equations:

$$H_2O \leftrightarrow OH^- + H^+ \quad (8)$$

$$CuOH \leftrightarrow Cu^+ + OH^- \quad (9)$$

Occasionally, both of them have the same dissolution equilibrium constant (see ref.[2]) presented below:

$$K_w = K_{sp9} = 1\times10^{-14}$$

Since Equation 6 = Equation 8－Equation 9, the dissolution equilibrium constant of Equation 6 can be obtained as:

$$K_{sp6} = \frac{K_w}{K_{sp9}} = 1 \quad (10)$$

The following equation can be obtained by combing Equation 6 with Equation 10:

$$(c_{H^+})^2 + c_{H^+} - c_{Cu^+} = 0 \quad (11)$$

$$c_{H^+} = 1.0124 \times 10^{-5}\,\mathrm{M}$$

The pH value of the saturated CuCl aqueous solution is then determined as:

$$pH = -\lg c_{H^+} = 4.995$$

5. **Characterization of the product of the reaction of CuCl with water at different pH values**

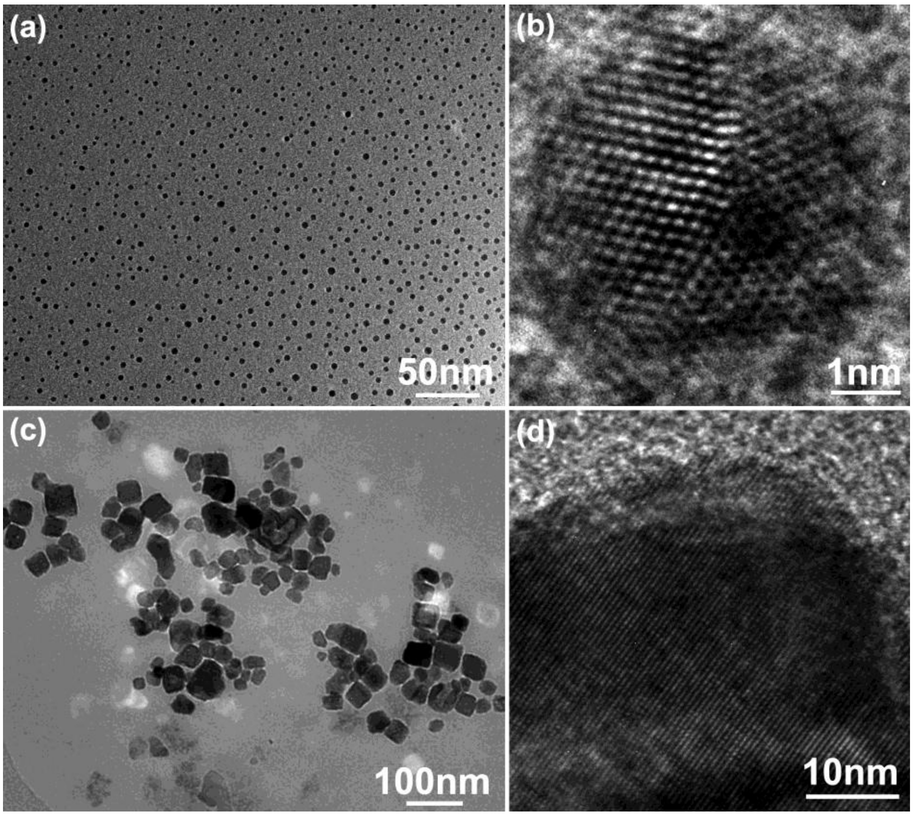


Figure S3. TEM images of the product of the reaction between CuCl and water at different pH values, (a) 4.3, (c) 8.5. HRTEM images of the product of the reaction of CuCl with water at different pH values, (b) 4.3, (d) 8.5.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A


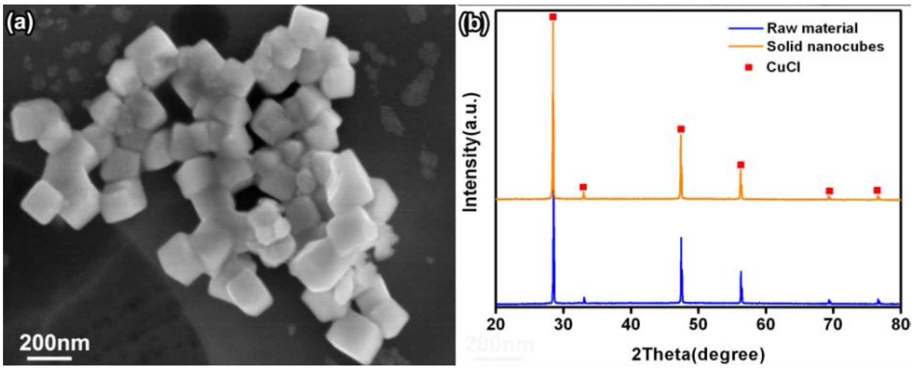


Figure S4. SEM image (a) and XRD pattern (b) of the CuCl nanocubes obtained after the dissolution of CuCl micro-powder in acidic water (pH= 0.5) followed by an increase in pH to 6.5 for a few seconds.

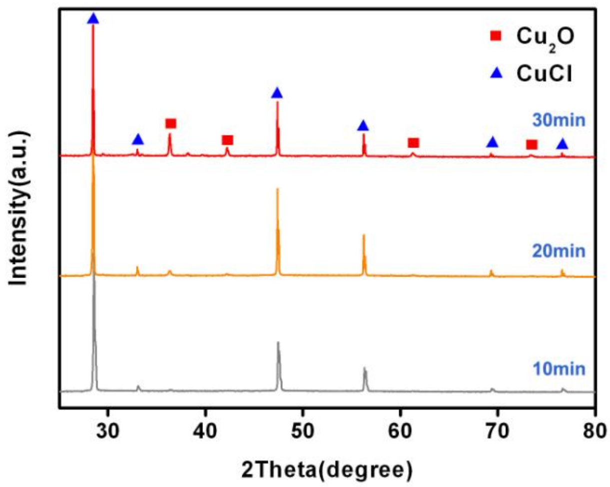


Figure S5. XRD patterns of the product after the reaction of CuCl with water (pH 6.5) for different times.

6. **TEM images of the intermediate products of the reaction of CuCl with water at pH of 6.5 for different times.**

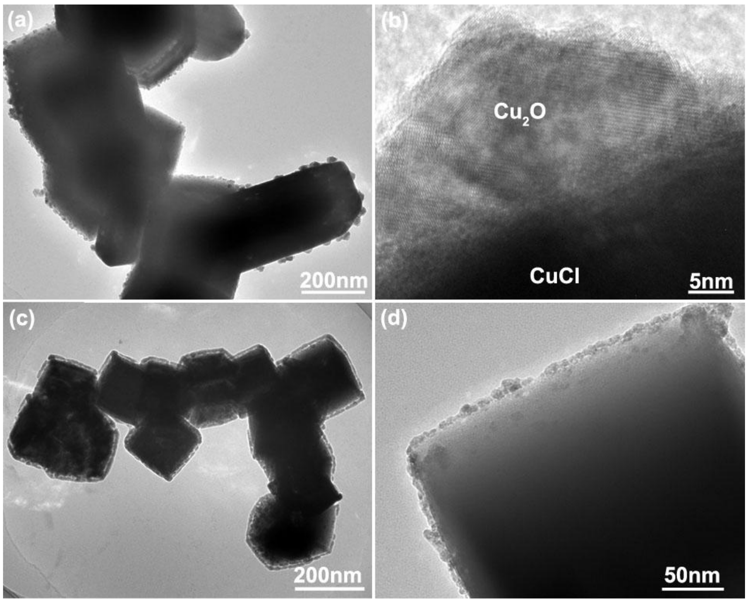


Figure S6 TEM images of the intermediate products obtained through the reaction of CuCl with water at pH of 6.5 for different times. (a) the product obtained after 2 min reaction, (b) high resolution TEM image of a $Cu_2O$ nanoparticle on a CuCl nanocube in (a), (c) the product obtained after 5 min reaction, (d) high magnification TEM image of a CuCl nanocube in (c).

## 7. Characterization of the conjunction of hollow $Cu_2O$ nanocubes with RhB

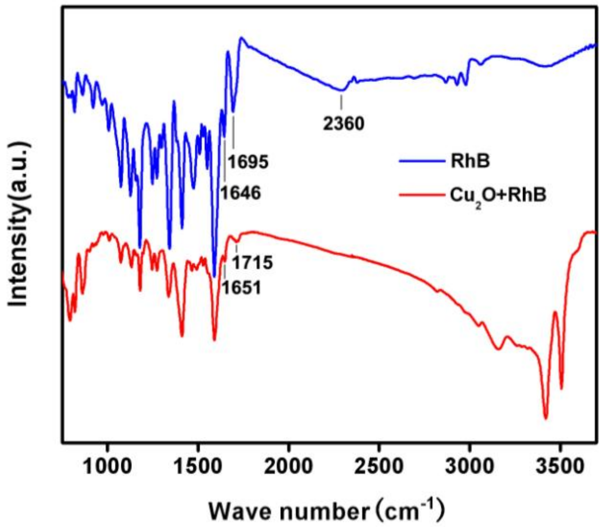


Figure S7. FTIR spectra of RhB and a mixture of hollow $Cu_2O$ nanocubes and RhB.

**References**:

[1] D. F. Liu, L.T. Huang, and W. Dong, *Inorganic Chemicals Industry* 2008, **40**, 27-29.
[2] J. A. Dean, *Lange's Handbook of Chemistry*, 15th.ed. **1999**.