Electronic Supplementary Information

A surfactant free synthesis and formation mechanism of hollow Cu_2O nanocubes using Cl^- ions as the morphology regulator

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Part I. Estimation of mass transfer in the morphology evolution from solid CuCl cubes to hollow Cu_2O cubes.

We take the hollow Cu_2O nanocube shown in Fig. 1c as the representative example. According to the TEM image, the outer length of the hollow Cu_2O nanocube is 116.4 nm, the interior size is ca. 105.6 nm, and the thickness is 10.8 nm. We suppose that such a hollow Cu_2O nanocube is transformed from a solid CuCl, the size of which is equal to the interior size of hollow Cu_2O. Then we can judge the rationality of our hypothesis by estimating mass transfer in the morphology evolution from solid CuCl cubes to hollow Cu_2O cubes. The detailed calculation processes are shown in the following equations.

$$V_i = (d_i)^3 \qquad \text{Equation 1}$$

$$V_{shell} = V_{total} - V_{interior} \qquad \text{Equation 2}$$

$$n = n_{\circ} \times \frac{V_i}{V_{\circ}} \qquad \text{Equation 3}$$

The volume of a single hollow Cu_2O particle could be seen as three parts, which are the total, shell and interior, respectively. V_i is the specific volume of each part (total or interior), and d_i is the side length. We take the hollow Cu_2O nanocube displayed in Fig. 1c as the representative example. The d_i of total particle and the interior is 116.4 nm and 105.6 nm, respectively, according to our measured results. From the equation 1, we can get the volume of total particle part and interior part, which are 1.58×10^6 nm^3 and 1.18×10^6 nm^3 respectively. The volume of shell (V_{shell}) could be calculated by the difference between the total volume of single particle (V_{total}) and the volume of interior ($V_{interior}$), as shown in the equation 2, which is 0.40×10^6

nm^3. Finally, the number of specific kind of molecules could be figure out via the equation 3, where V_o, n_o and n stand for the volume of crystal cell, the number of molecules in each cell and the total molecule number, respectively. The V_o of Cu_2O and CuCl are 77.83 Å^3 and 158.87 Å^3, and the n_o are 2 and 4, respectively. According to the equation 3, the total molecular number n of CuCl and Cu_2O are finally calculated to be 2.97×10^7 and 1.03×10^7, respectively. In theory, 2.97×10^7 CuCl can result in the formation of 1.48×10^7 Cu_2O. Our calculation result basically matches the theoretical one, which indirectly confirms our hypothesis that the hollow Cu_2O nanocubes should be transformed from CuCl in this case.

Part II. Supplementary results

Fig. S1 (a) SEM image and (b) corresponding XRD pattern of blue colloidal precursors obtained with 0.9 mmol NaOH.

Fig. S2 SEM and TEM images of hollow Cu_2O nanocubes obtained with (a,b) 5 mmol NaCl and (c,d) 7 mmol.

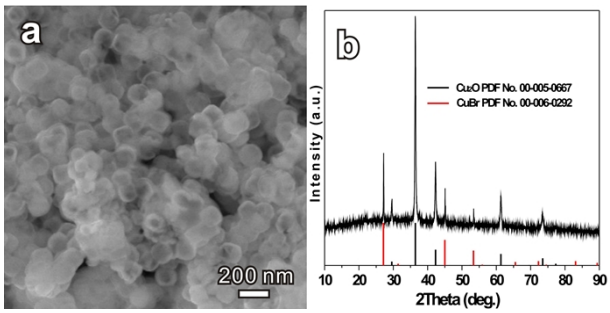

Fig. S3 (a) SEM image and (b) corresponding XRD pattern of as-prepared products when NaCl was replaced with 3mmol NaBr and copper nitrate used as copper source.

Fig. S4 Low magnification SEM and TEM images of products obtained after (a,b) 1 min and (c,d) 5 min.

Fig. S5 (a) SEM image and (b) corresponding XRD pattern of blue colloidal precursors obtained with 5 mmol NaOH.