Formation of Colloidal CuO Nanocrystallites and Their Spherical Aggregation and Reductive Transformation to Hollow Cu_2O Nanospheres

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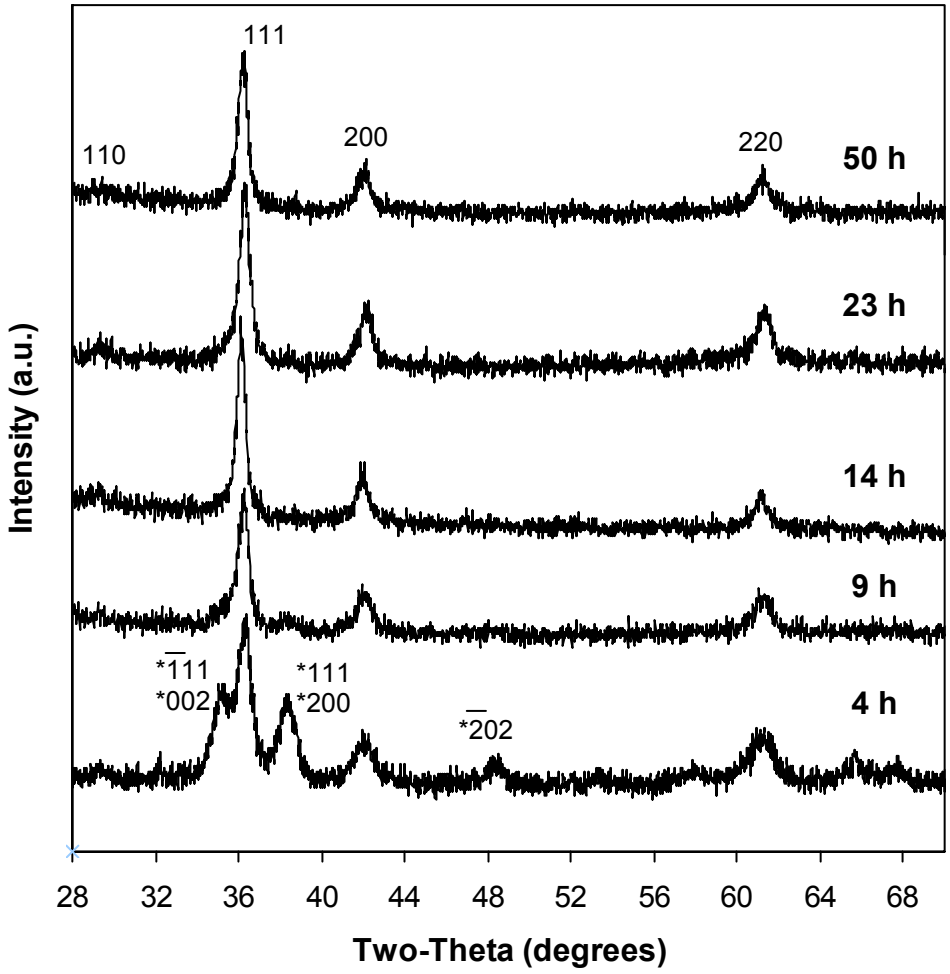
SI-1 A list of experiments conducted in the present work*

Sample No.	$[Cu^{2+}]$	Temperature (^{o}C)	Time (h)
1	0.010	150	4
2	0.010	150	9
3	0.010	150	14
4	0.010	150	23
5	0.010	150	35
6	0.010	150	50
7	0.010	160	2
8	0.010	160	4
9	0.010	160	10
10	0.010	160	15
11	0.010	160	27
12	0.010	160	40
13	0.010	170	1.5
14	0.010	170	3.25
15	0.010	170	4
16	0.010	170	6
17	0.010	180	2
18	0.010	180	3
19	0.005	180	4
20	0.010	180	4
21	0.010	180	7
22	0.010	180	8
23	0.010	180	9
24	0.010	180	10
25	0.010	180	12
26	0.010	180	13
27	0.010	180	14
28	0.010	180	15
29	0.010	180	17
30	0.010	180	20
31	0.010	180	25
32	0.010	180	30
33	0.010	180	33
34	0.010	180	36
35	0.010	150 + 180	22 + 8
36	0.010	150 + 180	22 + 10
37	0.010	150 + 180	22 + 11
38	0.010	150 + 180	24 + 8
39	0.010	150 + 180	24 + 10
40	0.010	150 + 180	24 + 11
41	0.010	150 + 180	26 + 42
42	0.010	140 + 180	40 + 8

* A series of experiments with copper ion molar concentration $[Cu^{2+}] > 0.010$ M had also been conducted in the present work. However, they could not produce nano-sized Cu_2O products, and these data are therefore not included in the above table.

SI-2 XRD results of samples synthesized at 150 °C

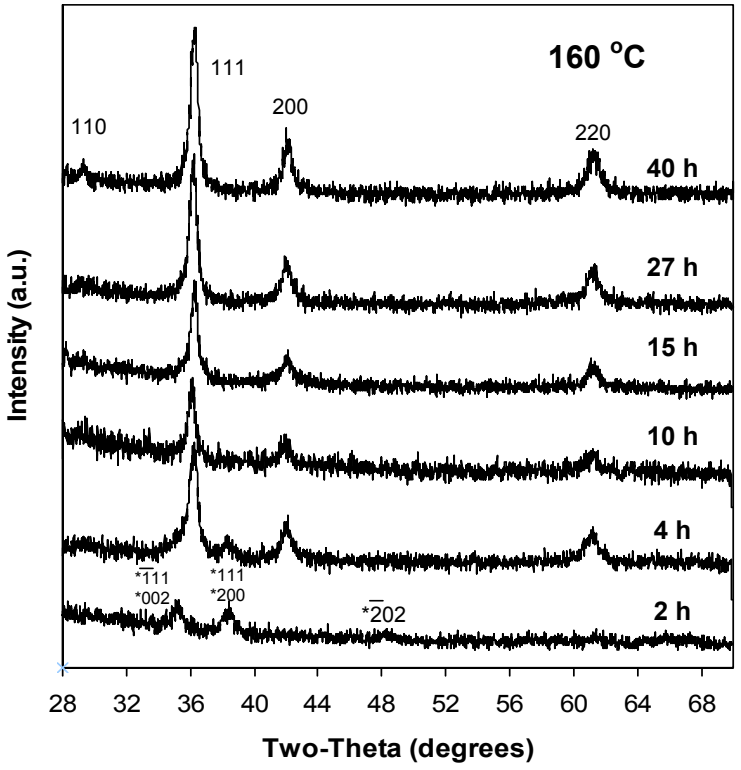
The following XRD patterns show the phase transformation of CuO to Cu_2O at 150 °C. Synthetic conditions: the samples were prepared after different reactions times (4 h to 50 h) at 150 °C with 30 mL of starting solution ($[Cu^{2+}]$ = 0.010 M). Symbol * indicates the diffraction peaks from unconverted CuO phase.

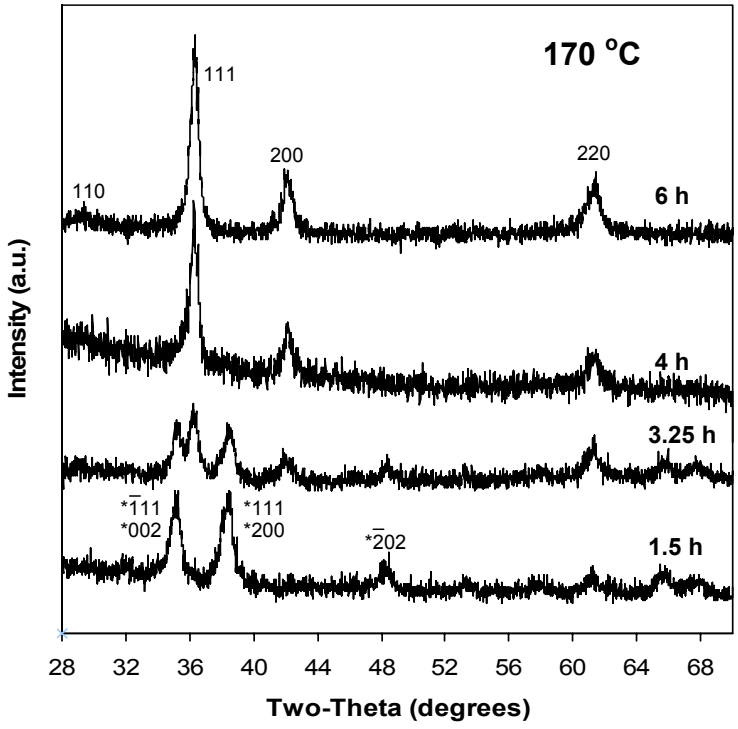


SI-3 XRD results of samples synthesized at 160 and 170 °C

The following XRD patterns show the phase transformation of CuO to Cu_2O at 160 and 170 °C respectively. Synthetic conditions: the samples were prepared after different reactions times at 160 and 170 °C respectively with 30 mL of starting solution ($[Cu^{2+}]$ = 0.010 M).

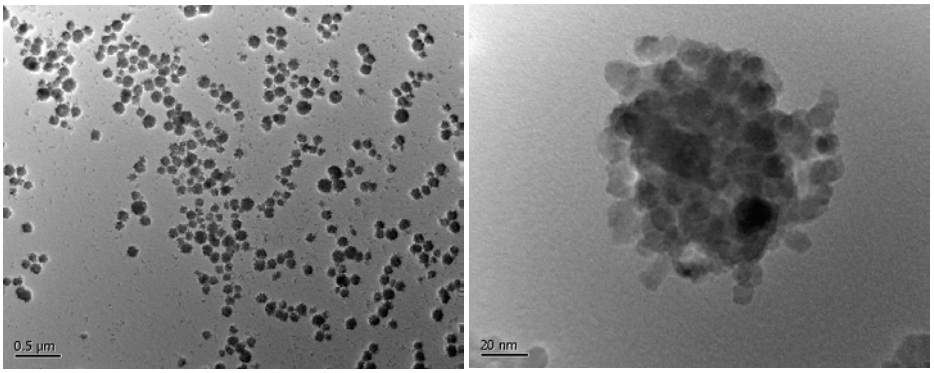
Symbol * indicates the diffraction peaks from initial CuO phase.



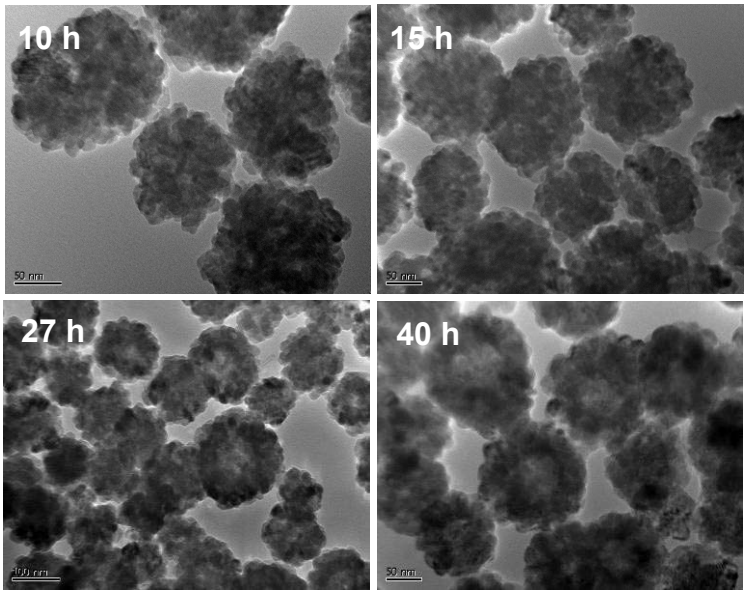


SI-4 TEM results of samples synthesized at 160 and 170 ^{o}C

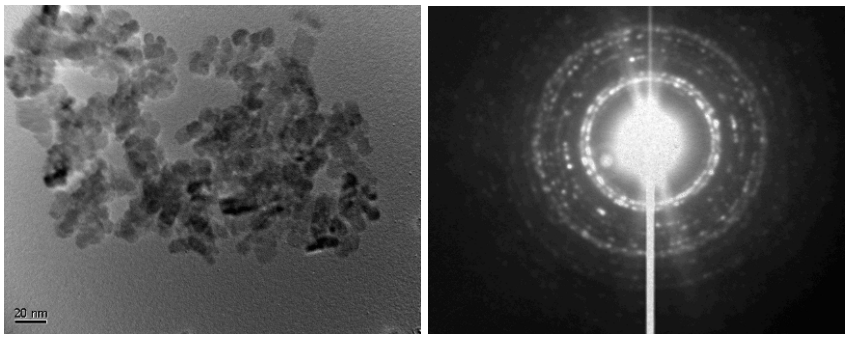
The following TEM images show morphological changes of the prepared sample at 160 and 170 ^{o}C respectively; refer to the above XRD results (SI-3) for their respective crystallographic information. Synthetic conditions: the samples were prepared after different reactions times at 160 and 170 ^{o}C respectively with 30 mL of starting solution ([Cu^{2+}] = 0.010 M).



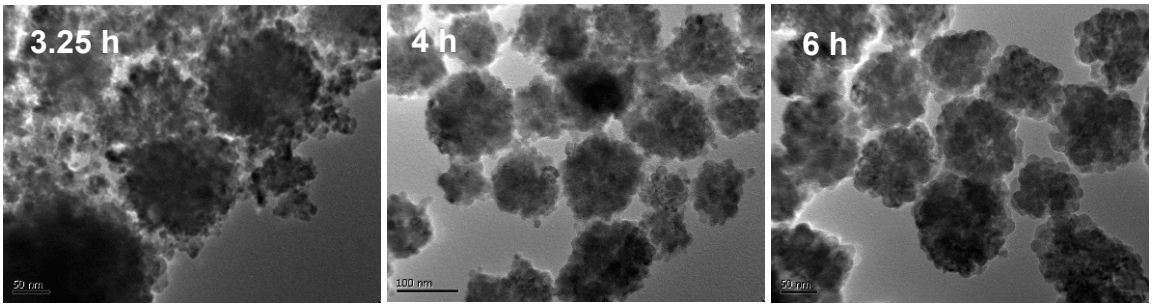
Experimental condition: 160 ^{o}C for 4 h.
Solid phases: Cu_2O (major) + CuO (XRD results, SI-3).
Left image: overall distribution of the aggregates.
Right image: an individual aggregate (one of those in the left image) which contains smaller crystallites.



Experimental conditions: 160 ^{o}C for 10 h, 15 h, 27 h, and 40 h.
Solid phase: Cu_2O (XRD results, SI-3).
All images: a hollowing process of the Cu_2O nanospheres.



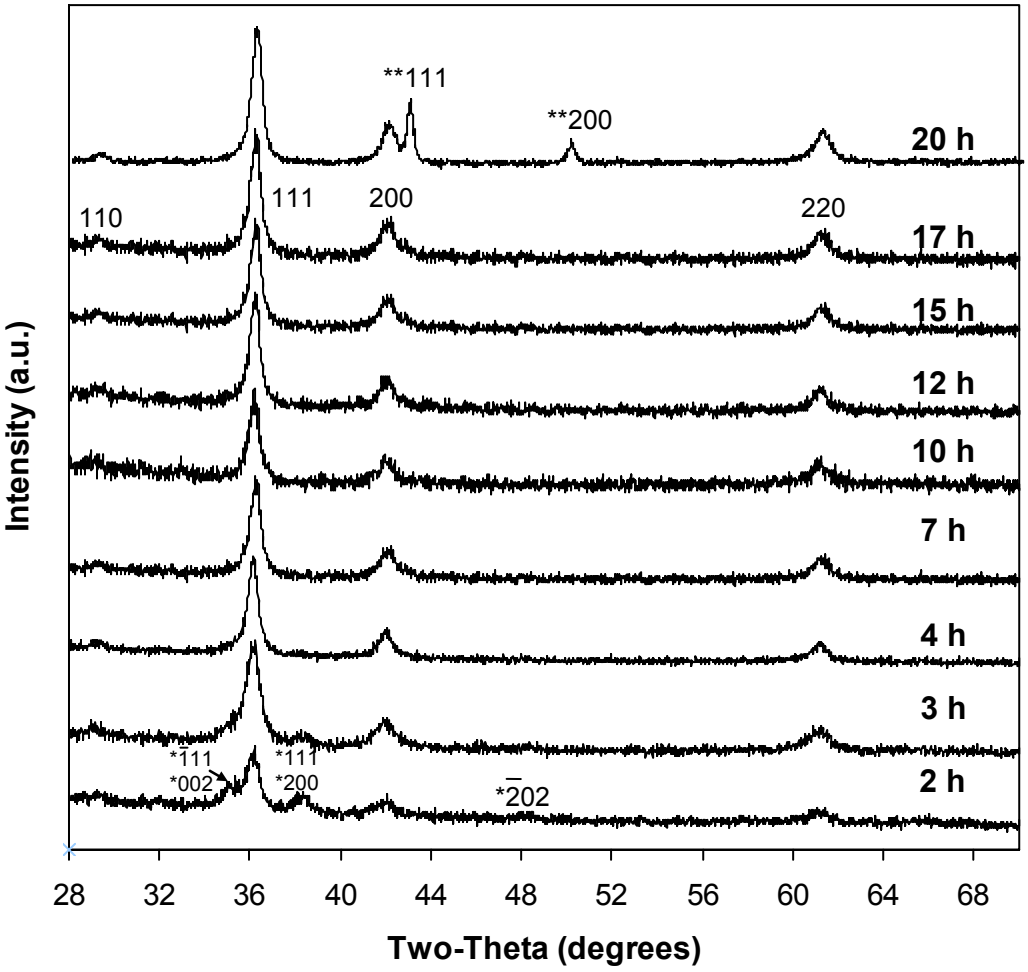
Experimental condition: 170 ^{o}C for 1.5 h.
Solid phase: CuO (also see XRD results, SI-3).
Left image: weakly aggregating CuO crystallites.
Right image: a SAED pattern of the CuO crystallites.



Experimental conditions: 170 ^{o}C for 3.25 h, 4 h, and 6 h.
Solid phase(s): Cu_2O + CuO (3.25 h); Cu_2O (4 h and 6 h; see XRD results, SI-3).
All images: an aggregation process for formation of solid Cu_2O nanospheres.

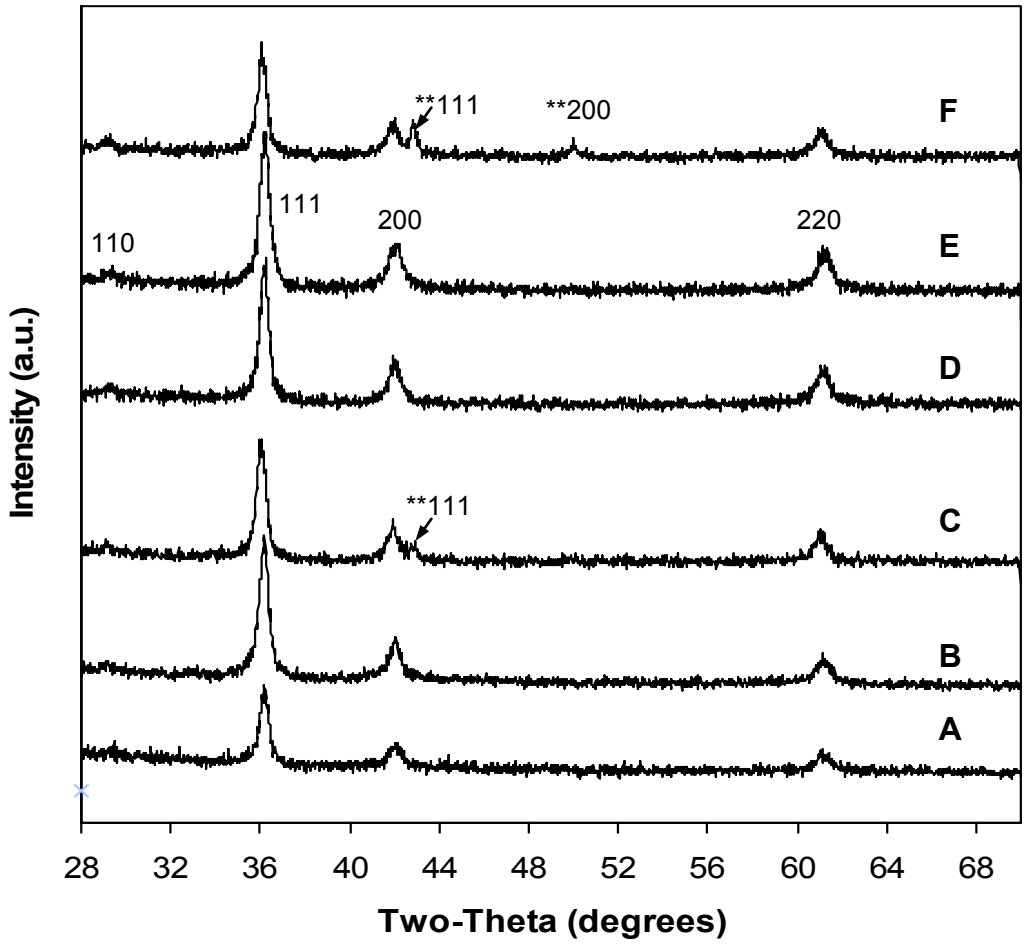
SI-5 XRD results of samples synthesized at 180 °C

The following XRD patterns show the phase transformation of CuO to Cu_2O at 180 °C. Synthetic conditions: the samples were prepared after different reactions times (2 h to 20 h) at 180 °C with 30 mL of starting solution ($[Cu^{2+}]$ = 0.010 M). Symbol * indicates the diffraction peaks from initial CuO phase, and symbol ** indicates the diffraction peaks from the metallic Cu phase formed during the final deep reduction.



SI-6 XRD results of samples synthesized with the two-step approach

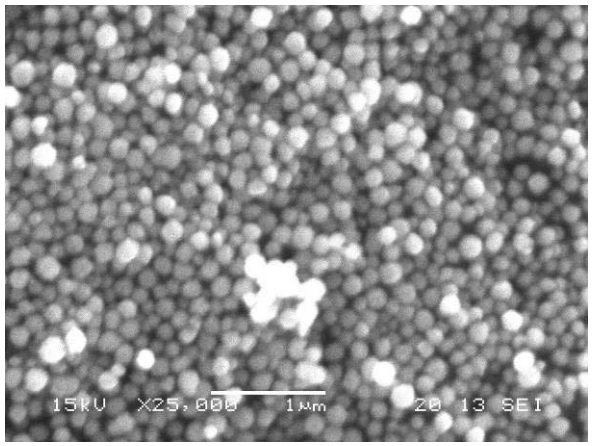
Representative XRD patterns of hollow Cu_2O nanospheres synthesized with the two-step method: (A) 150 °C for 22 h + 180 °C for 8 h; (B) 150 °C for 22 h + 180 °C for 10 h; (C) 150 °C for 22 h + 180 °C for 11 h; (D) 150 °C for 24 h + 180 °C for 8 h; (E) 150 °C for 24 h + 180 °C for 10 h; and (F) 150 °C for 24 h + 180 °C for 11 h. Symbol ** indicates the diffraction peaks from the metallic Cu phase formed during the final deep reduction. Synthetic conditions: starting solution $[Cu^{2+}]$ = 0.010 M, 30 mL.



SI-7 SEM observations for samples synthesized with single-step and two-step approaches: 100% morphological yield in hollow Cu_2O nanospheres

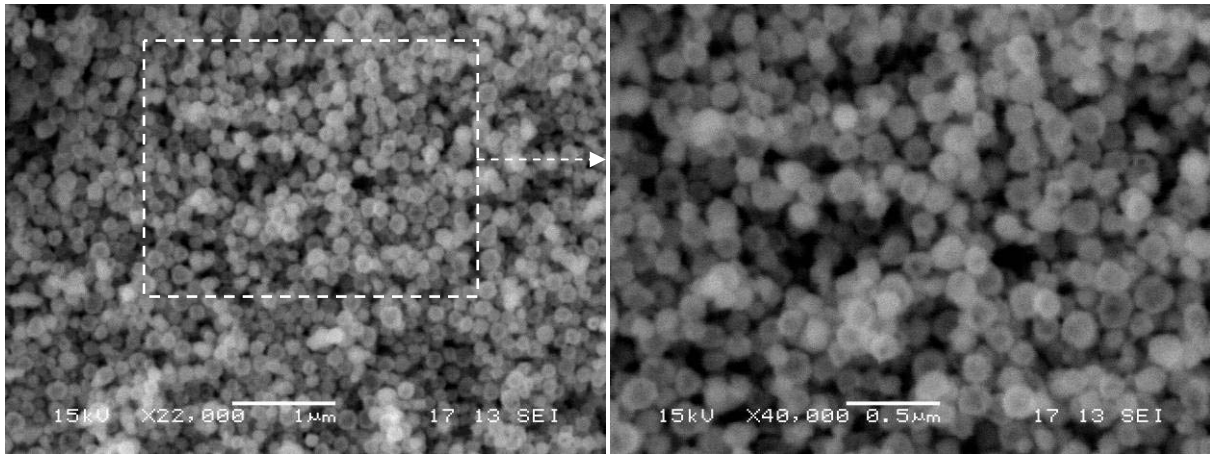
Single-step synthesis:

The following SEM image shows that the phase-pure Cu_2O hollow nanospheres (Its XRD pattern is shown in SI-2: 50 h) are highly regulated with a 100% morphological yield. Synthetic condition: the sample was prepared with a single-step heating routine at 150 ^oC for 50 h; starting solution $[Cu^{2+}]$ = 0.010 M, 30 mL.



Two-step synthesis:

The following two SEM images also show that the Cu_2O hollow nanospheres are also highly regulated with a 100% morphological yield even with a small amount of metallic cupper detected by XRD (F, SI-6). Synthetic condition: the sample was prepared with a two-step heating routine at 150 ^oC for 24 h + 180 ^oC for 11 h; starting solution $[Cu^{2+}]$ = 0.010 M, 30 mL.



SI-8 UV-Visible absorption spectra

The following representative UV-Visible absorption spectra were measured for four Cu_2O samples synthesized at 180^{o}C for 4, 7, 10, and 14 h, respectively (also see Figure 6B in the main text). The samples were dilute in ethanol solvent in these measurements.