The facile synthesis of Cu@SiO₂ yolk-shell nanoparticles via the disproportionation reaction of silica-encapsulated Cu₂O nanoparticle aggregates

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Supporting information



Figure S1. Control of the size of the Cu_2O NPAs by varying the PVP-10,000 concentration: (a) 80 g/L (~260 nm), (b) 60 g/L (~480 nm), (c) 40 g/L (~700 nm), and (d) 20 g/L (~900 nm). All of the scale bars represent 500 nm.



Figure S2. Characterization of the Cu₂O NPAs with (a) SEM, (b) XRD, (c) TEM, and (d) SAED analyses.

Highly spherical Cu₂O NPAs (~500 nm, Figure S2a) were synthesized in nearly 100% yield at room temperature in less than a minute in air. The XRD pattern (Figure S2b) indicated an averaged crystallite size of ~4.8 nm, which is consistent with the result from the TEM image (Figure S2c). The SAED pattern (Figure S2d) shows highly diffusive and weak diffraction rings, indicating poor crystallinity of the aggregate and small sizes of the crystallites.



Figure S3. TEM images of the encapsulated Cu_2O NPAs taken from the reaction solution at different reaction times. (a) 0 h, (b) 0.5 h, (c) 2 h, (d) 4 h, (e) 8 h, (f) 12 h, and (g) 24 h. The concentration of Cu_2O NPAs, TEOS, H₂O and NaOH were 0.5 g/L, 3.0 mM, 18 wt% and 1.0 mM, respectively. All of the scale bars represent 200 nm. (h) Shell thickness as a function of time curve during the encapsulation of Cu_2O NPAs.



Figure S4: EDX spectrum of Cu₂O@SiO₂.



Figure S5. SEM (a and b) and TEM (c and d) images of the encapsulated Cu_2O NPAssynthesized with the PAM surfactant. The NaOH concentration for images a and c was0.5 mM, and the NaOH concentration for images b and d was 1.0 mM. The Cu_2O NPAs,TEOS, and H_2O concentrations were 0.1 g/L, 5 mM, and 18 wt%, respectively. All ofthescalebarsrepresent500nm.

Due to the poor solubility of PAM in ethanol, we increased the amount of H_2O from 18 wt% to 54 wt% to prevent aggregation of the NPs. However, SiO₂ still cannot deposit on the surface of the Cu₂O NPAs due to the poor chemical affinity between PAM and SiO₂.



Figure S6. SEM (a and b) and TEM (c and d) images of the encapsulated Cu_2O NPAs obtained using the PAM surfactant. The NaOH concentration for images a and c was 0.5 mM, and the NaOH concentration for images b and d was 1.0 mM. The Cu_2O NPAs, TEOS, and H₂O concentrations were 0.1 g/L, 5 mM, and 54 wt%, respectively. All of the scale bars represent 200 nm.

The Cu₂O NPAs were quickly etched by $NH_3 \cdot H_2O$ in the conventional Stöber silica encapsulation process (Figure S7).



Figure S7. Photographic images of the reaction solution recorded one minute after the addition of different amounts of $NH_3 \cdot H_2O$ as follows: (a) 0 mL, (b) 2.23 mL, and (c) 6.68 mL. The Cu₂O NPAs, TEOS, and H₂O concentrations were 0.25 g/L, 3.0 mM, and 18 wt%, respectively.



Figure S8. TEM image of the Cu₂O@SiO₂ NP.

The difference between the theoretical and actual weight loss of the product was determined in $Cu_2O@SiO_2$ with a shell thickness of 60 nm after the disproportionation reaction.

The relative amount of Cu₂O (\sim 70 wt%) in the Cu₂O@SiO₂ NPs was calculated from their hollow SiO₂ NPs, which were synthesized using dilute HCl (0.05 M).

The theoretical weight loss of the product after the disproportionation reaction (Cu₂O $+ 2H^+ = Cu + Cu^{2+} + H_2O$) for these NPs was 39 wt%, which was calculated using the following equation:

 $\frac{\text{The percentage by weight of } Cu_2O}{M_{Cu2O}} \times (M_{Cu} + M_O) \times 100\%$ Equation (a)

The percentage by weight of Cu₂O: 70%

M_{Cu2O}: 144 g/mol

M_{Cu}: 64 g/mol

Mo: 16 g/mol.

After the Cu₂O@SiO₂ NPs, which had a shell thickness of 60 nm, were treated with 0.25 M H_2SO_4 , the weight loss of the product in the experiment was 42 wt%, which was similar to the theoretical weight loss (39 wt%) of the product.



Figure S9. EDX spectrum of the Cu@SiO₂ yolk-shell NPs.



Figure S10. $Cu_2O@SiO_2$ NPs with a shell thickness of 60 nm were treated with H_2SO_4 (0.25 M). Scale bar represents 500 nm.



Figure S11. $Cu_2O@SiO_2$ NPs with a shell thickness of 34 nm were treated with H_2SO_4 (0.25 M). Scale bar represents 200 nm.



Figure S12. Cu₂O@SiO₂ NPs with a shell thickness of 34 nm were treated with HCl (0.1 M). Both the scale bars represents 500 nm.



Figure 13. Cu₂O@SiO₂ NPs with a shell thickness of 34 nm were treated with 20 wt% of ascorbic acid. Scale bar represents 500 nm.



Figure S14. Hollow SiO₂ NPs synthesized from the Cu₂O@SiO₂ NPs with a shell thickness of 34 nm using 0.5 wt% ascorbic acid before (a) and after (b) purification of the product. Both of the scale bars correspond to 500 nm.



Figure S15. EDX spectrum of the hollow SiO_2 NPs with a shell thickness of 34 nm.