Supporting Information

## Fast synthesis of hierarchical yolk-shell copper hydroxysulfates at room-temperature with adjustable sizes

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Fig. S1 SEM images of some yolk-shell spheres in low magnification.



Fig. S2 (a) An overall SEM image of the yolk-shell products prepared using C<sub>3</sub>H<sub>6</sub>(NH<sub>2</sub>)<sub>2</sub> with a concentration of 0.4 M, (b) SEM image of the broken yolk-shell products after vigorous ultrasonication.



Fig. S3 SEM image of the products prepared using Cu(NO<sub>3</sub>)<sub>2</sub> as initial solution.



Fig. S4 SEM image of the products synthesized for different reaction time maintaining temperature at

5 °C, (a) 2 min; (b) 5 min; (c) 10 min; (d) 120 min. The products in Fig. S3c were destroyed by ultrasonic cell disruptor and in Fig. S3d were destroyed under vigorous ultrasonication.



Fig. S5 SEM image of the yolk-shell products prepared in a large-scale experiment.

**Table S1** Performance of the products for the oxidation of styrene by TBHP. ( $C_{bzh}$ , selectivity of benzaldehyde; $C_{so}$ , selectivity of styrene oxide;  $C_o$ , selectivity of other by-products)

| Reaction time | Conversion (%) | $C_{bzh}$ (%) | $C_{so}(\%)$ | $C_{0}(\%)$ |
|---------------|----------------|---------------|--------------|-------------|
| 3h            | 91.9           | 78.2          | 12.2         | 9.6         |
| 6h            | 93.6           | 76.9          | 12.4         | 10.7        |
| 9h            | 95.9           | 74.1          | 14.9         | 11.0        |

Reaction conditions: Styrene (1 mmol), catalyst (10 mg) and TBHP (5 mmol) dispersed in CH<sub>3</sub>CN (5 mL) at 60  $^{\circ}$ C.

**Table S2** Recyclability of the products for the oxidation of styrene by TBHP. ( $C_{bzh}$ , selectivity of benzaldehyde; $C_{so}$ , selectivity of styrene oxide;  $C_o$ , selectivity of other by-products)

| Run | Conversion (%) | $C_{bzh}(\%)$ | $C_{so}(\%)$ | C <sub>o</sub> (%) |
|-----|----------------|---------------|--------------|--------------------|
| 1   | 91.3           | 74.4          | 14.3         | 11.3               |
| 2   | 90.5           | 79.1          | 11.1         | 9.8                |
| 3   | 88.4           | 78.4          | 13.4         | 8.2                |
| 4   | 87.4           | 81.0          | 9.1          | 9.9                |
| 5   | 86.5           | 78.9          | 10.8         | 10.3               |

Reaction conditions: Styrene (1 mmol), catalyst (10 mg) and TBHP (5 mmol) dispersed in CH<sub>3</sub>CN (5 mL) at 60  $^{\circ}$ C for 6 h.

**Table S3** Performance of the products synthesized using different concentration of  $C_3H_6(NH_2)_2$  for the oxidation of styrene by TBHP. ( $C_{bzh}$ , selectivity of benzaldehyde;  $C_{so}$ , selectivity of styrene oxide;  $C_o$ , selectivity of other by-products)

| Products with different size | Conversion (%) | $C_{bzh}$ (%) | C <sub>so</sub> (%) | C <sub>o</sub> (%) |
|------------------------------|----------------|---------------|---------------------|--------------------|
| 7 μm                         | 93.8           | 78.8          | 12.6                | 8.6                |
| 5.5 μm                       | 94.1           | 75.3          | 13.7                | 11.0               |
| 4 μm                         | 95.3           | 75.7          | 12.2                | 12.1               |

Reaction conditions: Styrene (1 mmol), catalyst (10 mg) and TBHP (5 mmol) dispersed in CH<sub>3</sub>CN (5 mL) at 60  $^{\circ}$ C for 6 h.

![](_page_3_Figure_1.jpeg)

**Fig. S6** Conversion of styrene, as well as the selectivity of benzaldehyde versus the size of the yolk-shell products catalyzed by yolk-shell copper hydroxysulfates. Reaction conditions: Styrene (1 mmol), catalyst (10 mg) and TBHP (5 mmol) dispersed in CH<sub>3</sub>CN (5 mL) for 6 h.