Electronic Supplementary Information (ESI†)

Droplet-oriented construction of metal oxide hollow microspheres and their assembly into superstructures

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1. Supplementary experiment

1.1 Materials

The analytical reagents including NiSO$_4$·6H$_2$O, CoSO$_4$·7H$_2$O, MnSO$_4$·H$_2$O, MgSO$_4$·7H$_2$O, Al$_2$(SO$_4$)$_3$·18H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, AgNO$_3$, NaOH, Na$_2$CO$_3$, concentrated ammonia water (25 wt.%), ammonium carbonate, polyacrylic acid (PAA, 30 wt.%), polyvinyl pyrrolidone (PVP) K30, absolute ethanol and acetone were applied as received without further purification. And the titanium sulfate was chemically pure reagent, and also was used without further purification. Deionized (DI) water was employed for all preparation and treatment processes.

1.2 Preparation of samples

The illustration of the experimental setup for the wet-chemical preparation of hollow materials was shown in Scheme 1a. The novel spray reactor system consisted of an ultrasonic nebulizer at 1.7 MHz (YUYUE 402AI, Shanghai, China), a reaction vessel, a inflator pump (0.01MPa) and pipes. Based on acid-base reaction, the hollow precursors in this study were synthesized through the novel droplet-oriented strategy.

1.2.1 Synthesis of hollow Co$_x$ microspheres. Similarly, 5.0 g of CoSO$_4$·7H$_2$O was dissolved in 20.0 g of water. 75.0 g of absolute ethanol, 2.5 g of NaOH and 3.0 g of Na$_2$CO$_3$ was added to the reaction vessel. After atomization, 300.0 g of water was slowly added to the reaction vessel. Next, the mixture was maintained at 80°C for 10 h. The collected precursor was calcined at 450°C for 2 h, the resulting oxides of cobalt can be denoted as CoO$_x$.

1.2.2 Synthesis of hollow TiO$_2$ microspheres. Similarly, 2.5 g of Ti(SO$_4$)$_2$ and 0.25 g of PAA (30 wt.%) aqueous solution were dissolved in 10.0 g of hot water, followed by vigorous stirring. 40.0 g of absolute ethanol mixed with 3.0 g of concentrated ammonia water and 3.0 g of ammonium carbonate was added to the reaction vessel. Then, 160.0 g of water was slowly added to the reaction vessel. Next, the mixture was maintained at 60°C for 8 h. Analogously, the resulting precursor was calcined in an oven at temperature of 450°C with a heating rate of 10 K/ min for 2 h to obtain corresponding TiO$_2$ hollow microspheres.

1.2.3 Synthesis of hollow MgO microspheres. Similarly, 6.0 g of MgSO$_4$·7H$_2$O was dissolved in 20.0 g of hot water, followed by vigorous stirring until clarification. 75.0 g of absolute ethanol mixed with 0.06 g of PVP-K30, 4.0 g of NaOH and 3.0 g of ammonium carbonate was added to the reaction vessel. After atomization, the reaction mixture was stirred until the reaction was complete. Then, 300.0 g of water was slowly added to the reaction vessel. Next, the mixture was maintained at 80°C for 2 h. The resulting calcined product (450°C for 2 h) was MgO hollow microspheres.

1.2.4 Synthesis of hollow MgO/Al$_2$O$_3$ microspheres. Similarly, 3.0 g of MgSO$_4$·7H$_2$O and 3.0 g of Al$_2$(SO$_4$)$_3$·18H$_2$O were dissolved in 20.0 g of DI water, followed by vigorous stirring. 75.0 g of absolute ethanol mixed with 0.06 g of PVP-K30, 2.0 g of NaOH and 3.0 g of ammonium carbonate was added to the reaction vessel. After
atomization, 300.0 g of DI water was slowly added to the reaction vessel. Then, the mixture was maintained at 80°C for 3 h. The resulting calcined product (450°C for 2 h) was hollow MgO/Al₂O₃ microspheres.

1.5 Synthesis of hollow NiO/Ag microspheres. Similarly, 6.0 g of NiSO₄·6H₂O and 0.9 g of AgNO₃ were dissolved in 20.0 g of DI water, followed by vigorous stirring. 75.0 g of absolute ethanol mixed with 2.0 g of NaOH and 4.0 g of NaCO₃ was added to the reaction vessel. Then, the hollow NiO/Ag microspheres were synthesized and operated through the similar processes as the MnOₓ-450.
2. Supplementary figures and tables

**Fig. S1** XRD patterns of the micron-sized monometallic oxide products, including (a) NiO, (b) CoO\textsubscript{x}, (c) MnO\textsubscript{x}, (d) TiO\textsubscript{2}, (e) MgO and (f) Al\textsubscript{2}O\textsubscript{3}-AW microspheres. All of these hollow calcined samples were treated at 450°C.
**Fig. S2** TEM images of the precursor (NiO-P) of nickel oxide microspheres (a, b, c) and the resulting nickel oxide microspheres (d, e, f) with different magnification.

**Fig. S3** Optical microscope photographs of the micron-sized precursor of the NiO (labeled as NiO-P) (a), the as-obtained nickel oxide (labeled as NiO-450) (b), respectively; particle size distribution of the NiO-P (c); particle size distribution of the corresponding NiO-450 (d).
Fig. S4 SEM images of the precursor of MnO$_x$ (labeled as MnO$_x$-P) with different magnification.

Fig. S5 Corresponding BJH pore size distributions of (a) NiO, (b) CoO$_x$, (c) MnO$_x$, (d) TiO$_2$, (e) MgO and (f) Al$_2$O$_3$-AW hollow microspheres prepared using a novel spray reaction method.
Fig. S6 XRD patterns (a) of the sample after spray reaction (NiO-S) and the resulting precursor after aging (NiO-P); TGA curves (b) of NiO-S and NiO-P; Energy dispersive X-ray spectrum (EDS) of the NiO-S (c).

Fig. S7 TEM images of the as-obtained hierarchical hollow alumina using aluminum sulfate as aluminum source.
Fig. S8 SEM images of the as-obtained alumina using aluminum sulfate as aluminum source which its precursor was aged for 1 h.

Fig. S9 SEM images of the precursor of $\text{Al}_2\text{O}_3$-AN using aluminum nitrate (a, b and c); XRD pattern of the calcined $\text{Al}_2\text{O}_3$-AN (d); low-temperature $\text{N}_2$ adsorption-desorption isotherms (e) of the as-obtained alumina using aluminum nitrate ($\text{Al}_2\text{O}_3$-AN) and the corresponding pore size distribution derived from the desorption branches using BJH model (f).
Fig. S10 XRD pattern of the precursor of the hollow MgO/Al$_2$O$_3$ microspheres (a) and the MgO/Al$_2$O$_3$ (b), N$_2$ adsorption-desorption isotherms (c) and corresponding BJH pore size distribution (d) of the hollow MgO/Al$_2$O$_3$ microspheres.

Fig. S11 XRD pattern of the hollow NiO/Ag microspheres.
Table S1 Texture parameters of the resulting metal oxide hollow spheres and other reported metal oxides.

<table>
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<th>Samples</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>Total pore volume (mL/g)</th>
<th>Average pore size (nm)</th>
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References


