Supporting Information

Experimental section:

Synthesis of YS-Au@Ph-PMOs nanocomposites:

Gold nanoparticles were synthesized as follows. A 20 mL aqueous solution containing 2.5×10^{-4} M HAuCl₄ and 2.5×10^{-4} M trisodium citrate was prepared in a conical flask. Next, 0.6 mL of ice-cold, freshly prepared 0.1M NaBH₄ solution was added to the solution while stirring. The solution turned pink immediately after adding NaBH₄ solution, indicating particle formation. The obtained pink solution was continuous stirred for 2 h. And then, an aqueous solution of PVP10 (12.8 g/L, 0.5 mL) was added to the colloidal gold solution to modify the surface of gold nanoparticles to facilitate silica coating. The solution was stirred for 24 h at room temperature. The PVP-modified gold nanoparticles were collected by centrifugation and re-dispersed in 6.0 mL water. For silica coating, the above gold colloid aqueous was added into a mixture of ethanol (32 mL) and ammonium (0.93 mL). Then 1.5 mL of TEOS was added under vigorous stirring and stirred for another 6 h. The resultants were collected by centrifuging and then cleaned three times with water and ethoanol.

100 mg of the as-prepared Au@SiO₂ nanospheres were homogeneously dispersed in a mixture containing 22 mL of water and 11 mL ethanol by ultrasonication for 30 min. After the addition of 0.12 g of CTAB and 4 mL of ammonium aqueous solution (25–28%), the resultant mixture was further stirred at room temperature for 30 min. And then, 0.3 mL of organosilane BTEB was solwly dropwise added. After completely hydrolysis of BTEB, the as-obtained white mixture was transferred to a stainless steel autoclave with a Teflon container and hydrothermally treated at 100 °C for 24 h. The YS-Au@Ph-PMOs nanospheres were collected by centrifugation and then washed with water and ethanol several times. The surfactant CTAB was removal by refluxing 0.5 g of as-made material in 100 mL of ethanol containing 1.5 g of concentrated HCl aqueous solution for 6 hours.



Figure S1. FT-IR spectra of unextracted (a) and extracted (b) Et-HPMOs nanospheres.



Figure S2. Solid-state ¹³C NMR spectrum of Et-HPMOs nanospheres.



Figure S3. High-magnification TEM images of Et-HPMOs nanospheres prepared with different amount of organosilane BTEE: (a), 0.15 mL, (b), 0.27 mL.



Figure S4. Small-angel XRD patterns of hollow PMOs nanospheres prepared with different amount of organosilane BTEE: (a), 0.15 mL; (b), 0.27 mL.



Figure S5. SEM image of Ph-HPMOs nanospheres prepared under the same condition for Et-HPMOs nanospheres.



Figure S6. Nitrogen sorption isotherm and pore size distribution curve of Ph-HPMOs nanospheres.



Figure S7. FT-IR spectrum (a) and solid-state ¹³C NMR spectrum (b) of Ph-HPMOs nanospheres.



Figure S8. High-magnification TEM image of the sample prepared by using inorganic precursor TEOS under the same condition for Et-HPMOs nanospheres.



Figure S9. Low and high-magnification TEM images of the samples prepared with strong alkaline reagent NaOH: (a), (b), 0.2 mL 1M NaOH solution, (c), (d), 0.3 mL 1M NaOH solution; (e), (f), TEM images of the samples prepared with weak alkaline reagent $NH_3 \cdot H_2O$ and low alkalinity (1 mL 25% $NH_3 \cdot H_2O$). What the white arrows directed in (b) and (d) are ultrasmall fragments inside void space.



Figure S10. TG curves of (a), Et-HPMOs nanospheres, (b), Ph-HPMOs nanospheres.



Figure S11. (A), Small-angel XRD pattern of YS-Au@Et-PMOs nanocomposites; (B), wide-angel XRD patterns of Au@SiO₂ core-shell nanocomposite (a) and YS-Au@Et-PMOs nanocomposites (b).



Figure S12. (a), SEM image of as-made YS-Au@Ph-PMOs nanospheres; (b), SEM image of calcinated YS-Au@Ph-PMOs nanospheres; (c), TEM image of calcinated YS-Au@Ph-PMOs nanospheres. These images indicate that the hydrophilic YS-Au@SiO₂ nanospheres could be obtained after calcination of

as-made YS-Au@Ph-PMOs nanospheres at 550 °C for 6 hours. Because of the confinement of the hollow shell, the Au nanoparticles did not aggregate.



Figure S13. Time-dependent UV-Vis absorption spectral changes of the reaction mixture catalyzed by amphiphilic YS-Au@Ph-PMOs (A) and hydrophilic YS-Au@SiO₂ (B).