Supporting Information

Simultaneous Chemical Modification and Structural Transformation of Stöber Silica Spheres for Integration of Nanocatalysts

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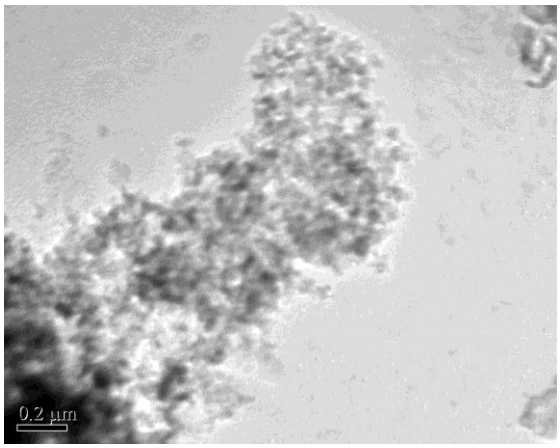
SI-1 The roles of PDDA polyelectrolyte

PDDA-modified SiO_2 spheres were entirely dissolved in NaOH



Experimental condition:

0.10 g of SiO_2 spheres was dispersed in 10 mL of 1% PDDA (poly(diallyldimethylammonium chloride)) solution by ultrasonication and stirred for 30 min for surface modification. The surface-modified SiO_2 spheres and 0.02 g of $Zn_4CO_3(OH)_6{\cdot}H_2O$ were dispersed in 20.0 mL of 0.01 M NaOH solution again by ultrasonication. Afterwards, the hydrothermal treatment was carried out at 180^{o}C for 4 h.

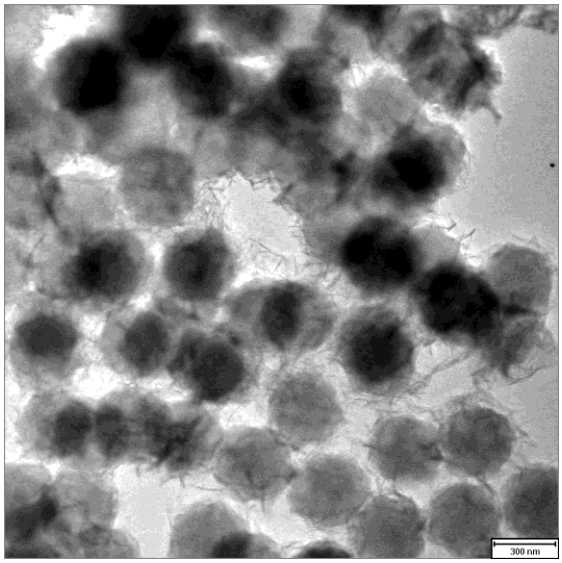
Note: This experiment shows that PDDA was not a protecting agent in our synthesis and the silica spheres (see Figure 2a,b in the main text) were entirely broken down in NaOH.

SI-2 XFS compositional analysis of porous Zn-SiO_2 spheres (atomic ratio)

Spectrum Label	Calc	Pos.X	Pos.Y	Pos.Z	Zn:Si Ratio
Spectrum 3	YES	40001	19120	0	0.028241
Spectrum 4	YES	40723	19120	0	0.028737
Spectrum 5	YES	41399	18476	0	0.025281
Spectrum 6	YES	39693	18240	0	0.022831
Spectrum 7	YES	40569	18920	0	0.02973
Spectrum 9	YES	39777	19534	0	0.030626
Average					**0.027574**

SI-3 Growth investigations of hollowing process

(a) Insufficient surface modification of PDDA on SiO_2 spheres

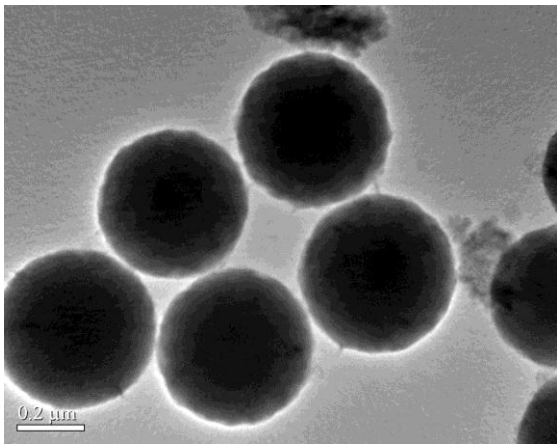


Experimental condition:

0.05 g of SiO_2 spheres was dispersed in 10 mL of 1% PDDA (poly(diallyldimethylammonium chloride)) solution by ultrasonication and stirred for 30 min for PDDA adsorption. The PDDA-adsorbed SiO_2 spheres and 0.03 g of $Zn_4CO_3(OH)_6{\cdot}H_2O$ were dispersed in 20.0 mL of de-ionized water by ultrasonication. Afterwards, the hydrothermal treatment was carried out at 180^{o}C for 6 h.

Note: This experiment shows that an insufficient amount of PDDA on the SiO_2 surface cannot attract sufficient hydroxyl ions and serve as template for shell formation. In such a case, the Zn-SiO_2 thin flakes could not form complete shells.

(b) Attraction between hydroxyl ions and PDDA in bulk solution



Experimental condition:

0.10 g of SiO_2 spheres (510 nm) was dispersed in 10 mL of 2% PDDA (poly(diallyldimethylammonium chloride)) solution by ultrasonication and stirred for 30 min for PDDA adsorption. The PDDA-coated SiO_2 spheres and 0.025 g of $Zn_4CO_3(OH)_6{\cdot}H_2O$ were dispersed in 20.0 mL of 1% PDDA solution (instead of 20.0 mL of de-ionized water) by ultrasonication. Afterwards, the hydrothermal treatment was carried out at 180^{o}C for 4 h.

Note: This experiment shows that hydroxyl ions were not attracted to the PDDA-adsorbed SiO_2 spheres. Instead, they were attracted to the positive PDDA present in the bulk solution phase.

(c) Experimental conditions for Figures 5 and 6 (main text):

Figure 5(a): 0.10 g of SiO_2 spheres (510 nm) was dispersed in 10 mL of 2% PDDA (poly(diallyldimethylammonium chloride)) solution by ultrasonication and stirred for 30 min for PDDA adsorption. The PDDA-adsorbed SiO_2 spheres and 0.03 g of $Zn_4CO_3(OH)_6{\cdot}H_2O$ were dispersed in 20.0 mL of de-ionized water by ultrasonication. Afterwards, the hydrothermal treatment was carried out at 180^{o}C for 4 h.

Note: This experiment shows that Zn-SiO_2 core-shell spheres are highly monodisperse and they can be arranged into a two-dimensional hexagonal superlattice.

Figure 5(b): 0.10 g of SiO_2 spheres (510 nm) was dispersed in 10 mL of 2% PDDA (poly(diallyldimethylammonium chloride)) solution by ultrasonication and stirred for 30 min for PDDA adsorption. The PDDA-adsorbed SiO_2 spheres and 0.03 g of $Zn_4CO_3(OH)_6{\cdot}H_2O$ were dispersed in 20.0 mL of de-ionized water by ultrasonication. Afterwards, the hydrothermal treatment was carried out at 180^{o}C for 4 h.

Note: This experiment shows that Zn-SiO_2 core-shell spheres are highly monodisperse and they can be arranged into a two-dimensional hexagonal superlattice.

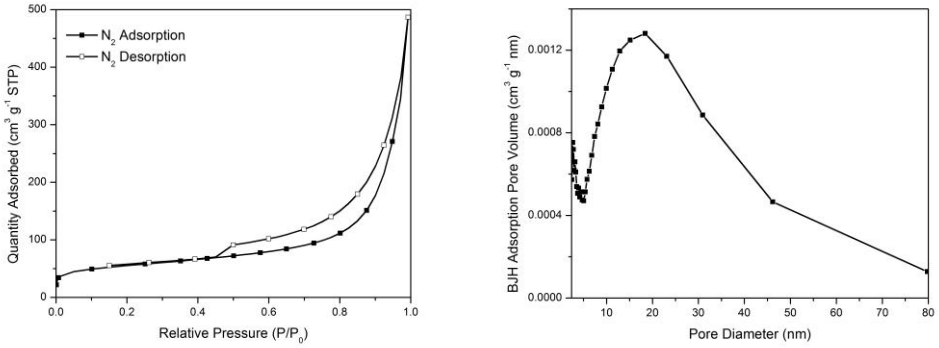
Figure 6(a): 0.05 g of SiO_2 spheres (260 nm) was dispersed in 10 mL of 2% PDDA (poly(diallyldimethylammonium chloride)) solution by ultrasonication and stirred for 30 min for PDDA adsorption. The PDDA-adsorbed SiO_2 spheres and 0.04 g of $Zn_4CO_3(OH)_6{\cdot}H_2O$ were dispersed in 20.0 mL of de-ionized water by ultrasonication. Afterwards, the hydrothermal treatment was carried out at 180^{o}C for 4 h.

Note: This experiment shows that small hollow spheres (diameter = 150 nm) of Zn-SiO_2 can also be attained with this approach.

Figure 6(b): 0.05 g of SiO_2 spheres (330 nm) was dispersed in 10 mL of 2% PDDA (poly(diallyldimethylammonium chloride)) solution by ultrasonication and stirred for 30 min for PDDA adsorption. The PDDA-adsorbed SiO_2 spheres and 0.03 g of $Zn_4CO_3(OH)_6 \cdot H_2O$ were dispersed in 20.0 mL of de-ionized water by ultrasonication. Afterwards, the hydrothermal treatment was carried out at 180°C for 4 h.

Note: This experiment shows that small hollow spheres (diameter = 250 nm) of Zn-SiO_2 can also be attained with this approach.

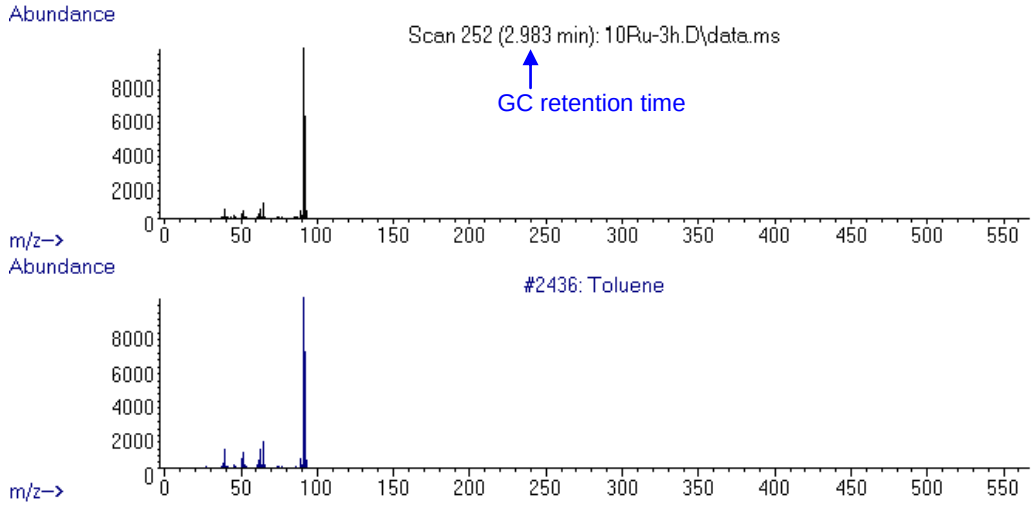
SI-4 BET/BJH analytical results of porous Zn-doped SiO_2 (Zn-SiO_2) spheres

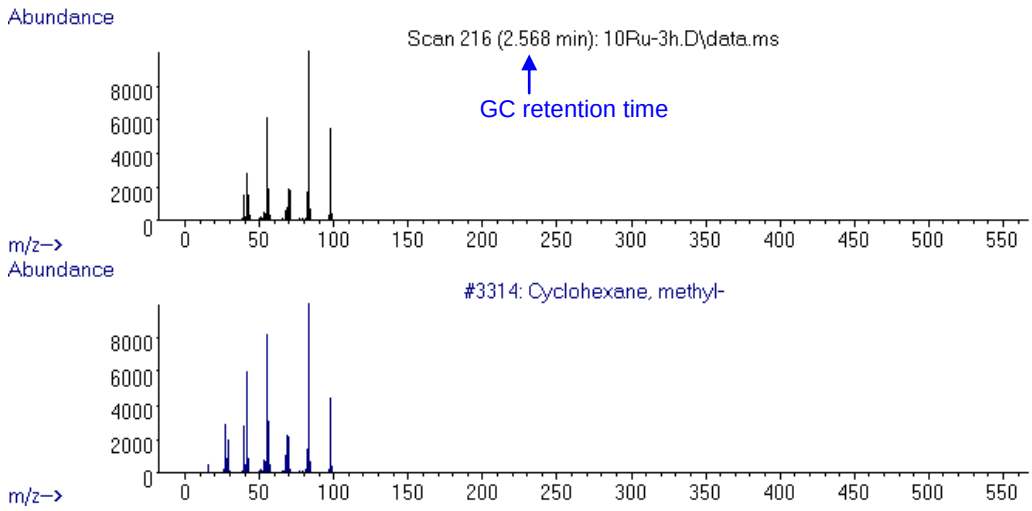


(a) Nitrogen adsorption-desorption isotherms (for BET analysis), and (b) pore volume curve and pore size distribution profile calculated from desorption isotherm (with BJH method).

SI-5 Arene hydrogenation reactions

Sample data of GC-MS analysis in toluene hydrogenation reaction





Note: Toluene was converted entirely to methyl-cyclohexane in this reaction (i.e., 100% selectivity)

SI-6 Morphology of used catalysts of Ru/ZnO/Zn-SiO_2

Low resolution TEM image; sample from Entry 6 of Table 1 in the main text (after the 5th run of toluene hydrogenation reaction)