Supplementary Material (ESI) for Chemical Communications

Controlled Synthesis of Mesoporous $SiO_2/Ni_3Si_2O_5(OH)_4$ Core-shell Microspheres with Tunable Chamber Structures via a Self-template Method

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Experimental Section

In a typical synthesis, a 245 ml of concentrated ammonia aqueous solution was added into the aqueous EtOH solution (EtOH 225 ml, H_2O 10 ml) and the resulting solution was stirred vigorously for 30 min. Then 21 ml of TEOS (tetraethylorthosilicate) was added in the solution and was stirred for 4 hrs. The mixture was centrifuged, decanted and dried in 100°C. $Ni(Ac)_2 \cdot 4H_2O$ was dissolved in 40 ml deionized water containing 0.1g silica (keeping constant in all experiments) sol particles and the resulting mixture was ultrasonically irradiated for 50 min to form uniform solution (Kunshan, KQ-50E, 40 kHz, controlled temperature range from 0°C to 80 °C). The obtained uniform solution was transferred to a Teflon- line stainless steel autoclave, which was sealed and maintained at 180 °C for 24 h, and then air-cooled to room temperature. The resulting precipitate was collected, washed with distilled water, and dried in air at room temperature.

The crystal structures of the resulting products were characterized by X-ray powder diffraction (XRD, D/MAX-500 X-ray powder diffractometer with Cu Kα radiation, λ=1.5418 Å at 40 kV and 70 mA). The morphologies and sizes of the resulting products were determined by field-emission scanning electron microscopy (FE-SEM, JSM 6700F), transmission electron microscopy (TEM, JEM-2000EX), and BET surface area analysis was determined using Micromeritics Tristar-3000 analyzer, respectively.

The X-ray diffraction patterns of mesoporous $SiO_2/Ni_3Si_2O_5(OH)_4$ core- shell microspheres and mesoporous $Ni_3Si_2O_5(OH)_4$ hollow microspheres are shown in Figure S1 a and b, respectively. Most of the diffraction peaks in Figure 1a can be exactly indexed to the end-centered $Ni_3Si_2O_5(OH)_4$ with lattice constants a = 5.270 Å, b = 9.171 Å, c = 14.74 Å, and β = 92.05, which are in good agreement with the literature values (JCPDS 49-1859). In addition, a diffraction peak at 26.2° corresponds to amorphous silica. As the molar ratios of Ni and Si is increased to 2 : 1, diffraction peak of amorphous silica disappears, indicating that mesoporous $Ni_3Si_2O_5(OH)_4$ hollow microspheres are formed.

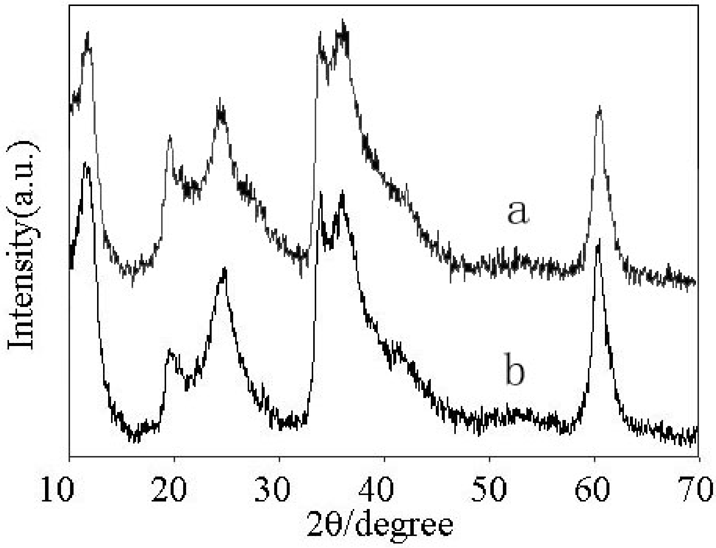
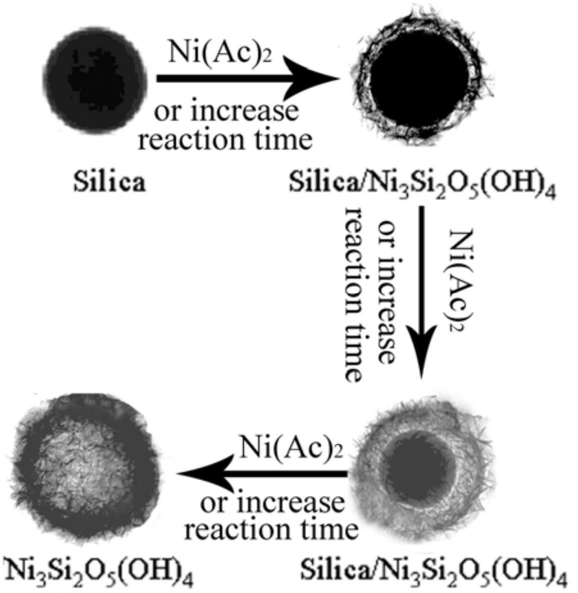


Fig. S1 XRD patterns of different microspheres: (a) mesoporous $SiO_2/Ni_3Si_2O_5(OH)_4$ core-shell microspheres with tunable chamber structures; (b) mesoporous $Ni_3Si_2O_5(OH)_4$ hollow microspheres.

Scheme S1 shows the overall procedure used to synthesize $SiO_2/Ni_3Si_2O_5(OH)_4$ core-shell microspheres and $Ni_3Si_2O_5(OH)_4$ hollow microspheres. Before the reaction, SiO_2 microspheres were dispersed in $Ni(Ac)_2 \cdot 4H_2O$ solution by ultrasound vibration. Under hydrothermal conditions, $Ni(Ac)_2 \cdot 4H_2O$ can react with SiO_2 to produce $Ni_3Si_2O_5(OH)_4$ at the surface of SiO_2 microspheres. The in situ reaction between SiO_2 and $Ni(Ac)_2$ may be expressed as follows [55-57]:

$2SiO_2 + 3Ni^{2+} + 5H_2O === Ni_3Si_2O_5(OH)_4 + 6H^+$



Scheme S1 Schematic procedure used to synthesize $SiO_2/Ni_3Si_2O_5(OH)_4$ core-shell microspheres and $Ni_3Si_2O_5(OH)_4$ hollow microspheres

In the reaction process, as the molar ratios of Ni and Si is 2 : 1, with the reaction proceeding (from 0 to 24 h), the diameter of SiO_2 microspheres decreases gradually because SiO_2 takes part in the reaction, so $SiO_2/Ni_3Si_2O_5(OH)_4$ core-shell microspheres and $Ni_3Si_2O_5(OH)_4$ hollow microspheres are obtained. As the molar ratio of Si and Ni decreases from 4 : 3 to 1 : 2 (keeping reaction time is 24 h), with the reaction proceeding, $SiO_2/Ni_3Si_2O_5(OH)_4$ core-shell microspheres and $Ni_3Si_2O_5(OH)_4$ hollow microspheres are obtained. In summary, $SiO_2/Ni_3Si_2O_5(OH)_4$ core-shell microspheres and $Ni_3Si_2O_5(OH)_4$ hollow microspheres are formed by adjusting the molar ratios of Si and Ni or controlling the reaction time.

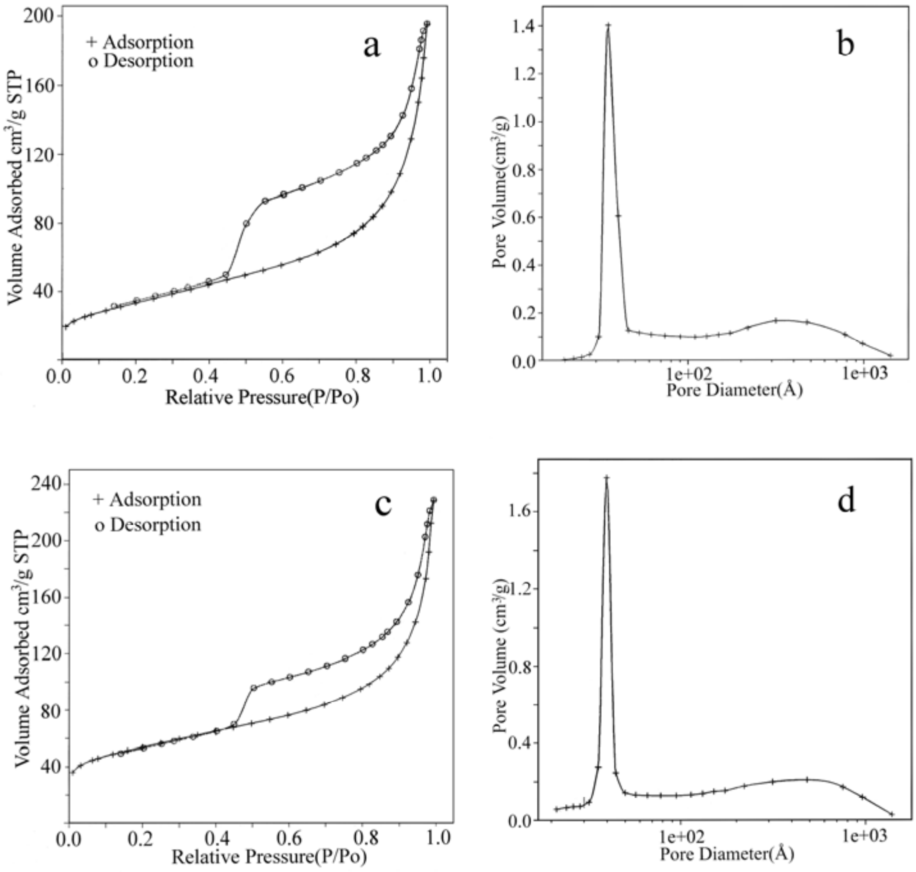


Figure S2. N_2 adsorption/desorption isotherm and pore diameter distribution: (a) N_2 adsorption/desorption isotherm with the molar ratios of Si and Ni = 1 : 1; (b) pore diameter distribution with the molar ratios of Si and Ni = 1 : 1; (c) N_2 adsorption/desorption isotherm with the molar ratios of Si and Ni = 1 : 2; (d) pore diameter distribution with the molar ratios of Si and Ni = 1 : 2.