

Core-Shell SiO₂@LDHs with Tuneable Size, Composition and Morphology

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1. Experimental details

Preparation of silica spheres

The monodispersed silica spheres were synthesised using a modified literature method. Tetraethyl orthosilicate (TEOS, 98%, Sigma-Aldrich) was added to a mixed solution of ammonia (35 wt%, Fisher Scientific), deionised water and ethanol. The white suspension was left to stir vigorously for 17 h. The volume of deionised water and ethanol remained constant (30 and 50 mL, respectively). The volume of TEOS and ammonia was varied to achieve the desired size of silica sphere (13.7, 9.15 and 3 mL of TEOS with 15, 10 and 5 mL of ammonia for 850, 550 and 250 nm silica spheres, respectively.) The final solid was washed with ethanol thoroughly followed by drying under vacuum overnight.

Preparation of SiO₂@LDH nanoparticles

The SiO₂@LDH particles were synthesised via an *in situ* co-precipitation method. SiO₂ spheres (100 mg) with the desired size were dispersed in deionised water (20 mL) using ultrasound treatment. After 30 minutes, the sodium carbonate (Na₂CO₃, 0.96 mmol, Acros Organics) was added to the solution and a further 5 minutes of sonication was carried out to form solution A. An aqueous solution (19.2 mL) containing magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, 0.96 mmol, Sigma-Aldrich) and aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O, 0.48 mmol, Sigma-Aldrich) was added at a rate of 60 mL/h to solution A under vigorous stirring. The pH of the reaction solution was controlled with the addition of 1 M NaOH by an autotitrator. The obtained suspension was stirred with or without heating for 1 h. The obtained solid was collected and then re-dispersed in deionised water (40 mL) and stirred for 1 h. The collection and re-dispersion was repeated once. The solid samples were then dried under vacuum.

In order to obtain a LDH with Mg:Al ratio of 1:1, the procedure described above was repeated with the exception that an aqueous solution (19.2 mL) containing Mg(NO₃)₂·6H₂O (0.72 mmol) and Al(NO₃)₃·9H₂O (0.72 mmol) was added at a rate of 60 mL/h to solution A under vigorous stirring. For the synthesis of LDH with Mg:Al ratio of 3:1, the aqueous solution (19.2 mL) contained Mg(NO₃)₂·6H₂O (1.08 mmol) and Al(NO₃)₃·9H₂O (0.36 mmol).

2. Characterisation

The morphology of the samples described in this work was observed using Transmission Electron Microscopy (TEM) analysis performed on a JEOL 2100 microscope with an accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) data were collected on a PANAnalytical X'Pert Pro diffractometer at 40 kV and 40 mA using Cu K α radiation ($\alpha_1 = 1.54057 \text{ \AA}$, $\alpha_2 = 1.54433 \text{ \AA}$, weighted average = 1.54178 \AA). The reflections at $2\theta = 43 - 44^\circ$ and 50° are produced by the XRD sample holder. The solid state NMR spectroscopy (^{29}Si ^{27}Al) were recorded on a Varian Chemagnetics CMX Infinity 200 (4.7 T). Samples were packed in 7.5 mm zirconia rotors. A double resonance MAS probe was used for all measurements and a MAS rate of 4 kHz for ^{29}Si , whereas MAS rate of 6 kHz was used for ^{27}Al . ^{27}Al MAS NMR spectra were acquired with a single pulse excitation applied using a short pulse length (0.7 μs). Each spectrum resulted from 2000 scans separated by 1 s delay. The ^{27}Al chemical shifts are referenced to an aqueous solution of $\text{Al}(\text{NO}_3)_3$ ($\delta = 0 \text{ ppm}$). In order to obtain the quantitative ^{29}Si DPMAS NMR spectra, 5000 transients were typically acquired with an acquisition time of 68 ms (1024 data points zero filled to 16 K) and recycle delay of 30 s. All ^{29}Si spectra were externally referenced to kaolinite (taken to be at $\delta = -91.7 \text{ ppm}$ on a scale where $\delta(\text{TMS}) = 0 \text{ ppm}$) as a secondary reference. Thermogravimetric analysis (TGA) measurements were collected using a Netzsch STA 409 PC instrument. The sample (10 - 20 mg) was heated in a corundum crucible between $30 \text{ }^\circ\text{C}$ and $800 \text{ }^\circ\text{C}$ at a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ under a flowing stream of nitrogen. Energy dispersive X-ray spectroscopy (EDX), carried out on from JSM-6610LV low vacuum SEM with an accelerating voltage of 20 kV, was used to determine the relative quantities of constituent elements on the surface of the sample. Brunauer–Emmett–Teller (BET) specific surface areas were measured from the N_2 adsorption and desorption isotherms at 77 K collected from a Micromeritic TriStar.

3. Results

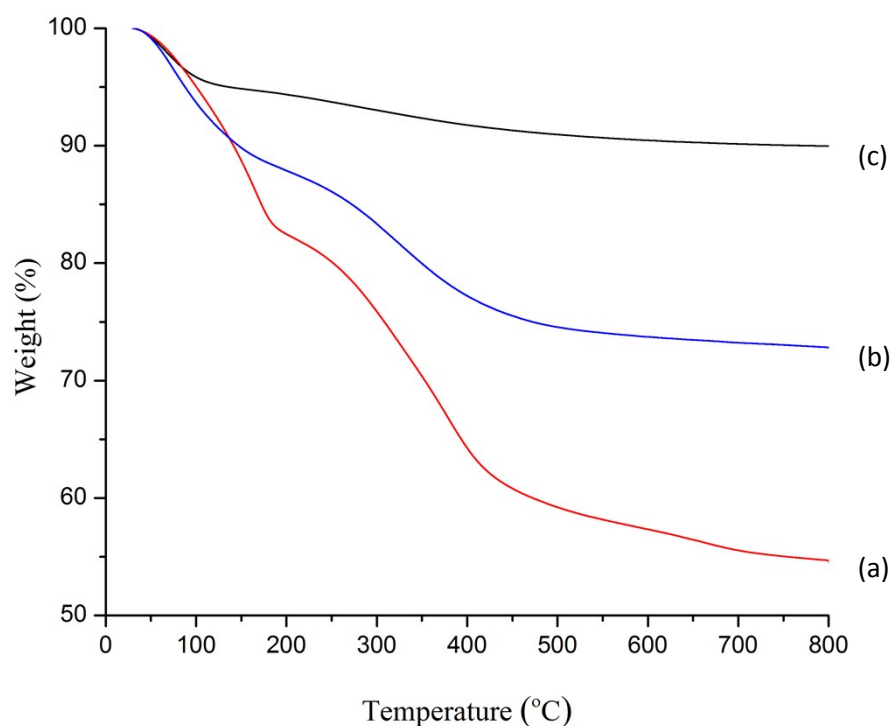


Fig. S1 Percentage weight loss of (a) LDH, (b) SiO₂@LDH and (c) silica nanoparticles.

Table. S1 Silicon environments in the SiO₂ and SiO₂@LDH samples as determined by ²⁹Si solid state MAS NMR.

Sample	Assignment ^a	δ (ppm)
SiO ₂ spheres	Q ⁴ (SiO) ₄ Si	-110
	Q ³ (SiO) ₃ SiOH	-101
SiO ₂ @LDH	Q ⁴ Si(2Al)	-111
	Q ³ (SiO) ₂ (AlO)SiOH	-85
	Q ² (SiO) ₂ Si(OH) ₂	-101
	Q ⁴ Si(1Al)	-101
	Q ³ (SiO) ₃ SiOH	-101
	Q ⁴ Si(0Al)	-111

^a Qⁿ(Si(*m*Al)) ; *n* refers to the number of bridging atoms around the central Si, and *m* refers to number of Al atoms substituting Si atoms in the first coordination sphere.

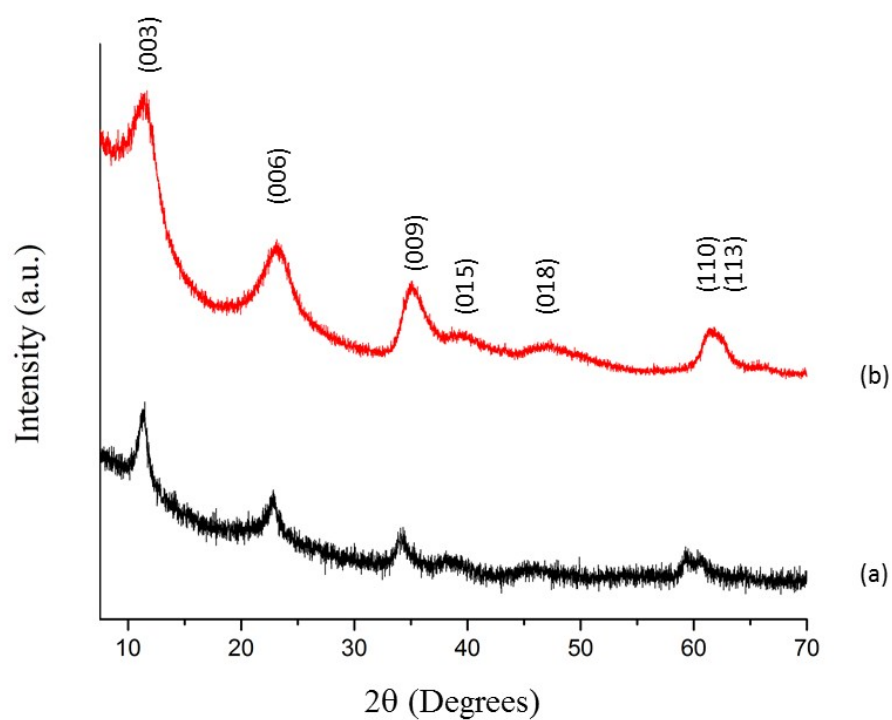


Fig. S2 XRD patterns of SiO₂@LDH samples prepared with Mg:Al ratios (a) 1:1 and (b) 3:1.

Table. S2 SEM-EDX data for SiO₂@LDH samples containing Mg/Al in different ratios.

Mg:Al theoretical ratio	Mg (atom %)	Al (atom %)	Mg/Al experimental ratio
1:1	0.32	0.30	1:0.94
2:1	0.56	0.28	2:1
3:1	0.57	0.19	3:1

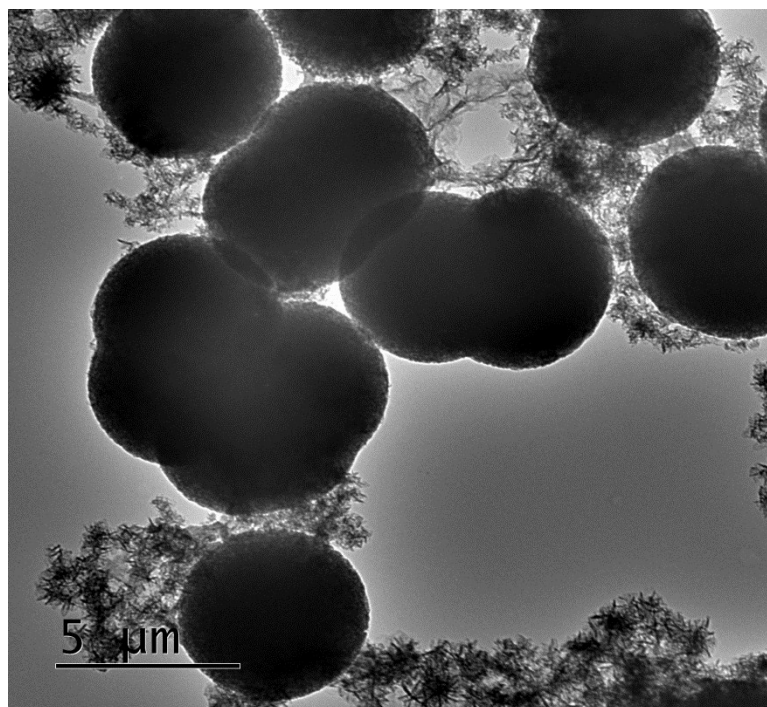


Fig. S3 TEM image of $\text{SiO}_2@\text{LDH}$ synthesized by pH 9 at room temperature.

Table. S3 Silicon environments in the SiO_2 and $\text{SiO}_2@\text{LDH}$ samples as determined by ^{29}Si solid state MAS NMR.

Sample	Assignment	δ (ppm)	Percentage
Solid core-shell $\text{SiO}_2@\text{LDH}$	$\text{Q}^4 \text{Si}(2\text{Al})$	-85	33.3%
	$\text{Q}^3 (\text{SiO})_2(\text{AlO})\text{SiOH}$		
	$\text{Q}^2 (\text{SiO})_2\text{Si}(\text{OH})_2$		
	$\text{Q}^4 \text{Si}(1\text{Al})$	-101	33.4%
	$\text{Q}^3 (\text{SiO})_3\text{SiOH}$	-111	33.3%
	$\text{Q}^4 \text{Si}(0\text{Al})$		
Yolk-shell $\text{SiO}_2@\text{LDH}$	$\text{Q}^4 \text{Si}(2\text{Al})$	-85	45%
	$\text{Q}^3 (\text{SiO})_2(\text{AlO})\text{SiOH}$		
	$\text{Q}^2 (\text{SiO})_2\text{Si}(\text{OH})_2$		
	$\text{Q}^4 \text{Si}(1\text{Al})$	-101	45%
	$\text{Q}^3 (\text{SiO})_3\text{SiOH}$	-111	10%
	$\text{Q}^4 \text{Si}(0\text{Al})$		

Table S4. N₂ BET surface area data for SiO₂@LDH samples.

	pH	Temperature (°C)	Surface area (m ² /g)
SiO ₂	-	-	17
LDH	10	RT	11
Solid core-shell SiO ₂ @LDH	10	RT	107
Yolk-shell SiO ₂ @LDH	10	40	118
Hollow-shell SiO ₂ @LDH	11	40	177

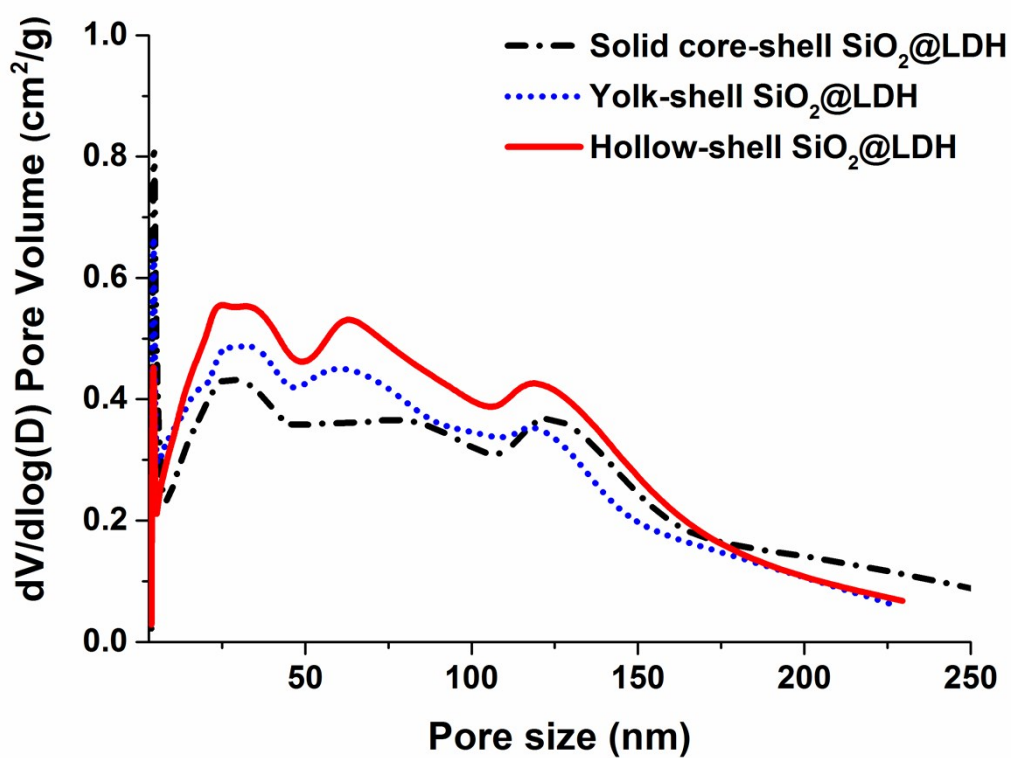


Fig. S4 Pore size distribution of SiO₂@LDH samples