

Electronic Supplementary Information

Facile one pot synthesis of mesoporous organic-inorganic hybrid aluminosilicate spheres with ultra-high aluminum contents and their enhanced adsorption behavior for methylene blue

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Experiment

2.1 Materials/Chemicals

Cetyltrimethylammonium bromide (CTAB), sodium aluminate, tetraethyl orthosilicate (TEOS, 99%), methylene blue (MB) were purchased from Sinopharm Chemical Reagent Co.(Shanghai, China), 1,2-Ethylenebis(trimethoxysilane) (BTME) was purchased from Sigma-Aldrich. Deionized water was used in all experiments.

2.2 Preparation of hybrid mesoporous aluminosilicate spheres (HMAS)

In the current synthesis of hybrid materials, we had utilized the static condition than the normally employed stirring condition. Typically, the synthesis procedure for aluminum-containing mesoporous organo aluminosilica materials was as follows: 1.05 g NaAlO_2 was dissolved in 40 ml of deionized water under stirring at room temperature, followed by addition of 1 g CTAB, the solution was stirred for 20 min, and then desired amount of BTME was quickly poured into the above transparent solution. The final mixture was stirring additional 50 seconds and subsequently kept static for 12 hours at ambient temperature. Finally, the white precipitate obtained was filtered off and washed with distilled water several times and finally dried at 60 °C overnight. The samples with different Si/Al molar ratios were denoted as HMAS_n, where n indicates Si/Al ratios in reacting mixture. The organic template was removed by mild alkaline system. Typically, 0.6 g of the as-synthesized material was added to

150 ml of ethanol containing 100 mg NH₄NO₃, the mixture was heated at 60 °C for 10 h. The process was repeated thrice to ensure complete extraction of the organic surfactant.

2.3 Characterization

TEM images were obtained on FEI Tecnai G2 F20 s-twin D573 field emission transmission electron microscope with an accelerating voltage of 200 kV. SEM images were obtained on a JEOL JSM-6700F field-emission scanning electron microscope. N₂ adsorption-desorption isotherms were obtained at -196 °C using a Micromeritics ASAP 2020M system. XRD data were collected on a Rigaku D/MAX 2550 diffractometer with Cu K α radiation (λ = 0.15418 nm). ²⁹Si MAS NMR and ²⁷Al MAS NMR spectra were recorded on a Varian Infinity Plus 400 spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS). The Si/Al ratio was determined by inductively coupled plasma (ICP) analysis (Perkin-Elmer 3300DV). Fourier transform infrared (FT-IR) spectra were recorded using a Bruker 66V FTIR spectrometer.

2.4 Adsorption experiment

Methylene blue (MB) adsorption experiment were carried out as follows: 20 mg HAMS₁ was added to 20 ml of MB solution of a predetermined concentration, then the solution were stewing in a thermostatically controlled water bath at constant temperature of 25 °C and constant rate 120 rpm. After a desired period of adsorption, the solution was removed out by centrifugation, and the concentration of filtrates was measured immediately. The initial PH of the solution of the solution was kept at PH 7 without changing. The determination of the MB concentration was done spectrophotometrically on a Perkin-Elmer Lambda 20 spectrophotometer by measuring absorbance at λ_{max} of 664 nm.

At any time, t , the adsorption capacity of MB adsorbed (Q_t) and the removal percentage of MB onto HMAS1 was calculated by the following mass-balance equation:

Adsorption uptake=capacit (mg g⁻¹)

$$Q_t = \frac{(C_0 - C_t)V}{M}$$

$$\text{Removal (\%)} : Q_t = \left(\frac{C_0 - C_t}{C_t} \right) \times 100$$

The amount of dye adsorbed onto the HMAS₁ and MCM-41 was calculated from the mass balance equation as:

$$Q_e = \frac{(C_0 - C_e)V}{M}$$

Where Q_e (mg g^{-1}) is the amount of MB adsorbed per gram of the HMAS₁ sample at equilibrium; C_0 (mg L^{-1}) and C_e (mg L^{-1}) are the initial and equilibrium liquid-phase concentrations of dye; V (L) is the volume of the solution and M (g) is the weight of the dry adsorbent.

The adsorption data for MB onto MCM-41 and HMAS₁ were analyzed by Langmuir equation to investigate the relationship between the adsorbate molecules and adsorbent species in solutions. The values of $1/Q_e$ are fitted against $1/C_e$ based on the Langmuir equation below:

$$1/Q_e = 1/Q_m + 1/(K_L Q_m C_e)$$

where C_e (mg L^{-1}) is the equilibrium concentration of MB in solution, Q_e (mg g^{-1}) is the adsorbed amount of MB at equilibrium concentration, Q_m (mg g^{-1}) is the monolayer capacity of adsorbent, and K_L (L mg^{-1}) is the Langmuir binding constant.

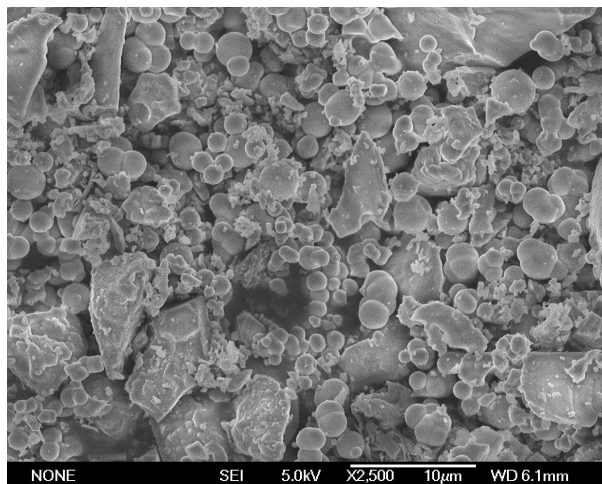


Figure S1. SEM image of the sample HMAS₁ obtained under stirring conditions.

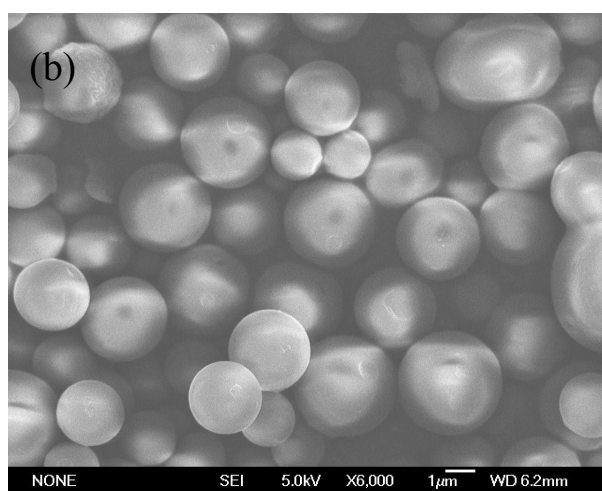
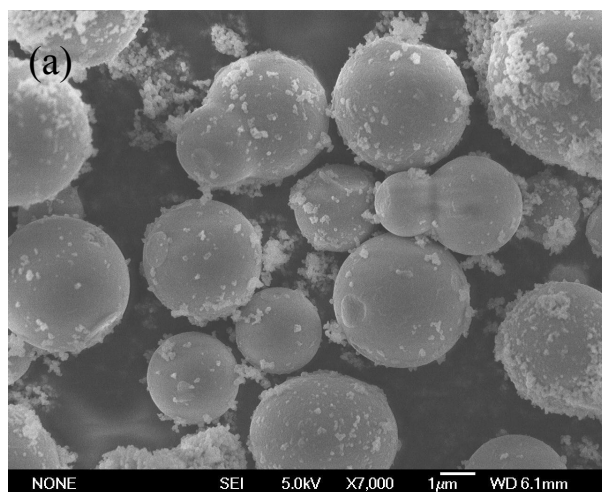


Figure S2. The sample HMAS₁ are synthesized with different amounts of water (a) 30 ml, (b) 50 ml.

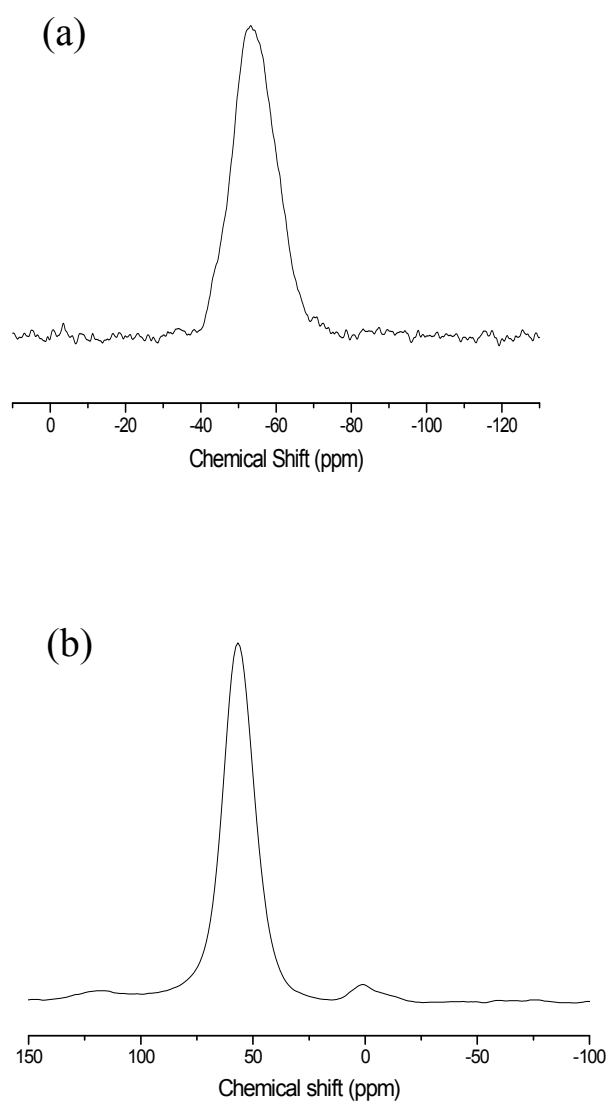


Figure. S3. The different MAS NMR spectra of template-free samples $\text{HMAS}_{0.67}$

(a) ^{29}Si -NMR and (b) ^{27}Al -NMR.

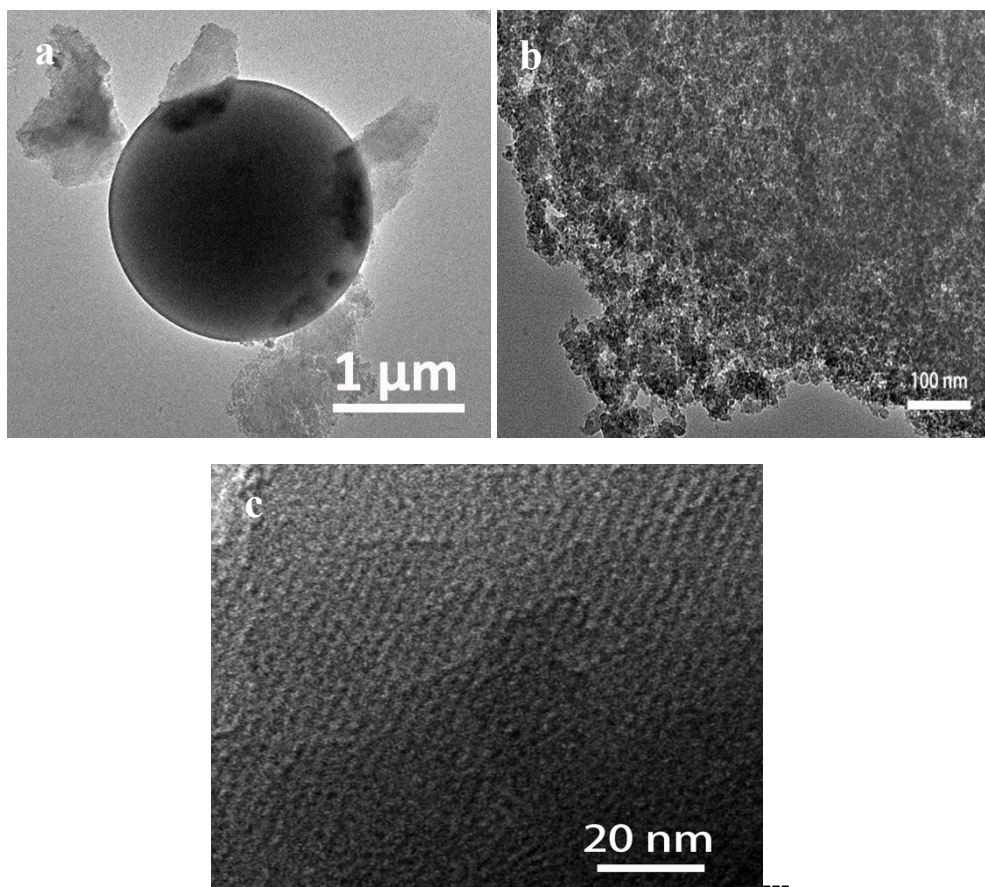


Fig. S4. TEM image of the sample HMAS_{0.67} (a) low- and (b), (c) high magnification.

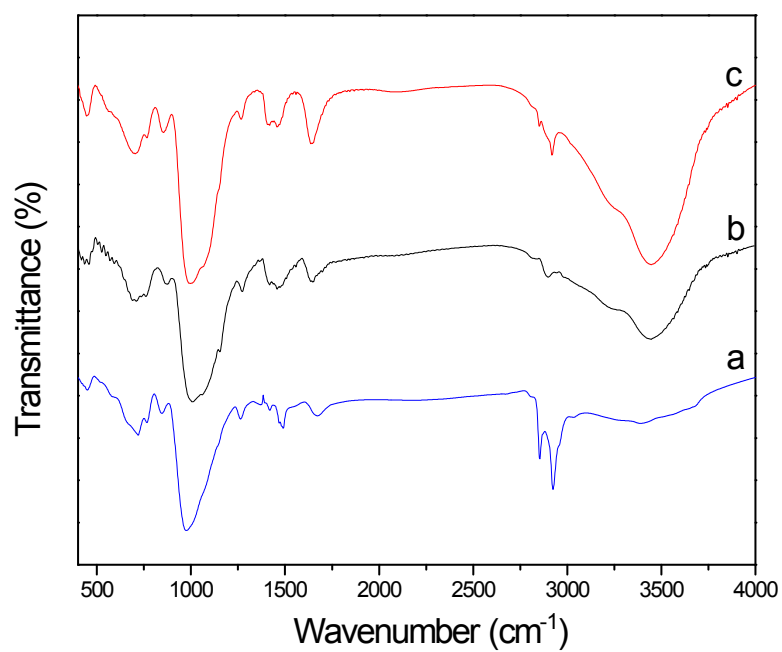


Fig. S5. IR spectroscopy of as-synthesized sample (a) HMAS₁ and template-extracted samples (b) HMAS₁, (c) HMAS_{0.67}.

Table S1. Comparison of the adsorption capacities of Methylene Blue onto various adsorbents

Adsorbent	Maximum adsorption capacities (mg g ⁻¹)	Ref.
Ordered Mesoporous Silica (OMS/OMS-NH ₂ /OMS-COOH)	54 / 90 / 113	9
Carboxylic acid functionalized mesoporous silicas	376	14
Carboxylate groups functionalized mesoporous silicas (C-MS-L)	159	15
AIMCM-41	278	45
AIMCM-41	0.208 mmol/g	31
SBA15/AISBA-15	45.08 / 79.82	32
Hybrid mesoporous aluminosilicates	397	This work

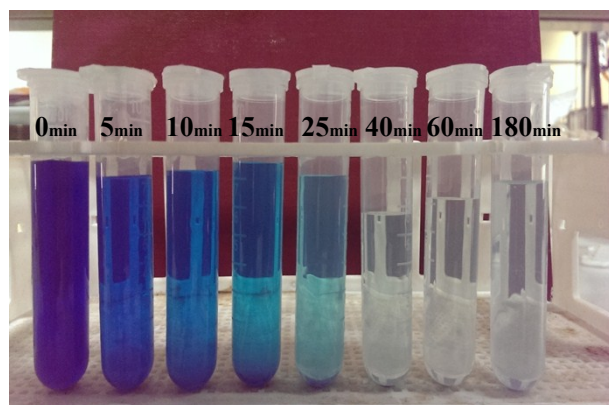


Figure S6. Photographs of the MB adsorption by the sample HMAS₁ with different contacts time 0, 5, 10, 15, 25, 40, 60 and 180 min.