Supporting Information

for

Superhydrophobic mesoporous silica nanospheres achieved via high level of organo-functionalization

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Chemicals and reagents

All of the reagents were of analytical grade and used as received without further purification. Cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich Company Ltd (USA). Tetraethoxysilane (TEOS) and ethyl acetate were obtained from Sinopharm Chemical Reagent Co., Ltd. TMB was obtained from Tianjing Guangfu Institute of Fine Chemical Industry. n-Propyltrichlorosilane, n-butyltrichlorosilane were purchased from Aladdin Industrial Corporation in Shang Hai (China). Diphenyldichlorosilane was obtained from Beijing OuHe Technology Co., Ltd. Methyl orange (MO) was commercially available from Tianjing Fuchen Chemical Reagent Co., Ltd. Other reagents were purchased from Shanghai Chemical Reagent, Inc. of the Chinese Medicine Group.

Preparation methods

Synthesis of propyl and butyl modified MSNs (C_3-MSN-0.5 and C_4-MSN-0.5):

In a typical synthesis, 0.1g cetyltrimethyl ammonium bromide (abbreviated as CTAB in the following paragraphs) was added to an aqueous solution (45 ml) of NaOH (0.35 mL, 2 M) at 70 ^{o}C. After dissolution of CTAB, TMB (0.284 ml) was added to the system. The mixture was sonicated for one hour for the formation of stable white emulsion. TEOS (0.5 mL) was added followed by the addition of ethyl acetate (0.4 mL). The mixture was stirred for 5~10 min, then a proper amount of chlorosilane (0.33 ml for n-propyltrichlorosilane and 0.37 ml for n-butyltrichlorosilane) was added to the system dropwise. The final chemical composition of the precursor solution was 1 CTAB : 2.6 NaOH : 7.5 TMB : 8.2 TEOS : 8.2 $RSiCl_3$: 9110 H_2O (molar ratio, R=C_3 and C_4). After being stirred for another two hours at 70 ^{o}C, the mixture was directly transferred to the autoclaves and kept aging at 100 ^{o}C for 24 h. After cooling to room temperature, the powder product was isolated by filtration, washed with ethanol and air-dried for 24 h.

To remove the surfactant, the as-synthesized materials (1g) were dispersed in a solution of 80 mg ammonium nitrate and 120 mL ethanol (95%) solution. The mixture was heated at 60 °C for 20 min and the process was repeated for three times.

Synthesis of Ph modified MSNs (Ph-MSN-x) with different phenyl content:

Ph-MSN-x were prepared at the same conditions with C_3-MSN-0.5 except that a proper amount of diphenyldichlorosilane (0.32, 0.47, 0.63, 0.71 ml) was added to the system, corresponding to the mole ratio of diphenyldichlorosilane (x) in the initial mixture varied from 0.33 to 0.75.

The as-made material Ph-MSN-0.5 was used directly without the surfactant removal steps mentioned above.

Synthesis of Phenyl grafted MSNs:

The pure mesoporous silica nanospheres were prepared according to the literature.[1] After removal of the surfactant, the MSNs were dispersed in 45 ml ethanol, followed by the addition of 0.47 ml Ph_2SiCl_2. The mixture was refluxed at 75 ^oC for 24 h, and then transferred to the autoclaves and kept aging at 100 ^oC for 24 h. After cooling to room temperature, the powder product was isolated by filtration, washed with ethanol and air-dried for 24 h.

Methyl orange (MO) adsorption

MO solution with a concentration of 0.1 g/L was prepared by dissolving 25 mg MO in water and diluted to 250ml. In a typical adsorption process, the MSNs material was divided into 10 copies. Each one contains 10 mg of MSNs, suspended in the MO solution of 2 mL. The resulting mixtures were continuously shaken with a speed of 160 rpm at 20 °C for 4 h, and was successively taken out at different times. Thereafter, the supernatant and solid material was separated by centrifugation. The concentration of MO was measured by UV-vis spectrophotometer at a wavelength of 465 nm, and the amount of MO loaded onto the MSN was calculated by subtracting MO in the supernatant from the total MO amount.

Characterization

N_2 sorption isotherms and vapor adsorption isotherms were carried out on a Micromeritics ASAP2020 volumetric adsorption analyzer. Before the sorption measurements, samples were out-gassed at 393 K for six hours. X-Ray powder diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation (λ=0.1541 nm). Transmission electron microscopy (TEM) was performed using HITACHI HT7700 at an acceleration voltage of 100 kV. Scanning electron microscopy (SEM) was performed on HITACHI S5500. UV-vis spectra were collected with a Shimadazu UV-2550 spectrometer. The thermo-gravimetric analysis (TGA) was performed using a NETZSCH STA 449F3 analyzer from 30 ^{o}C to 900 ^{o}C with a heating rate of 10 ^{o}C/min under air atmosphere. The solid-state NMR spectra were obtained with a Bruker DRX 400 spectrometer equipped with a magic-angle spin probe using a 4-mm ZrO2 rotor. ^{13}C and ^{29}Si signals were referenced to tetramethylsilane (TMS). The experimental parameters are as follows: 8 kHz spin rate, 3 s pulse delay, 4 min contact time, and 1000 scans. Water contact angle measurements were performed on KRÜSS DSA100, and the sample films were prepared via pressing the material powder at a pressure of 8 MPa on tablet press.

Reference:

1. J. Peng, J. Liu, J. Liu, Y. Yang, C. Li and Q. H. Yang, *J. Mater. Chem. A*, 2014, **2** , 8118 – 8125.

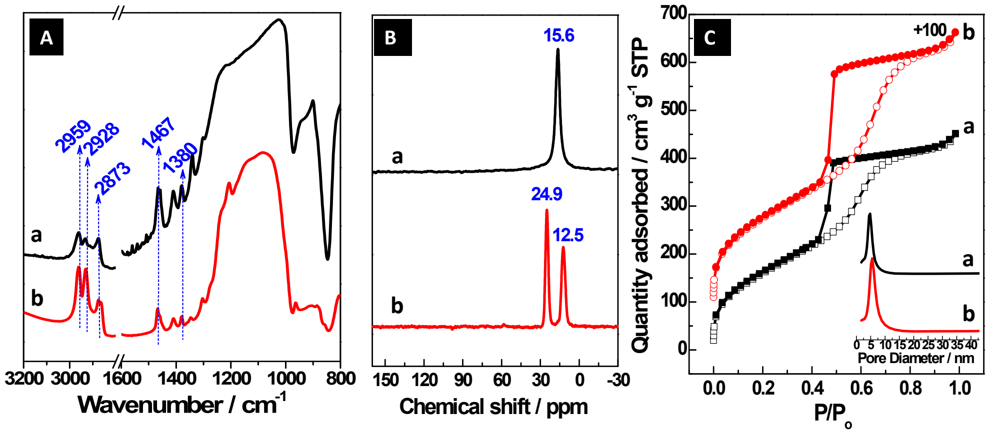


Figure S1. (A) FT-IR spectra, (B) ^{13}C CP/MAS NMR, (C) N_2 sorption isotherms of (a) C_3-MSN-0.5 and (b) C_4-MSN-0.5 (inset in C is the pore distribution of the corresponding materials)

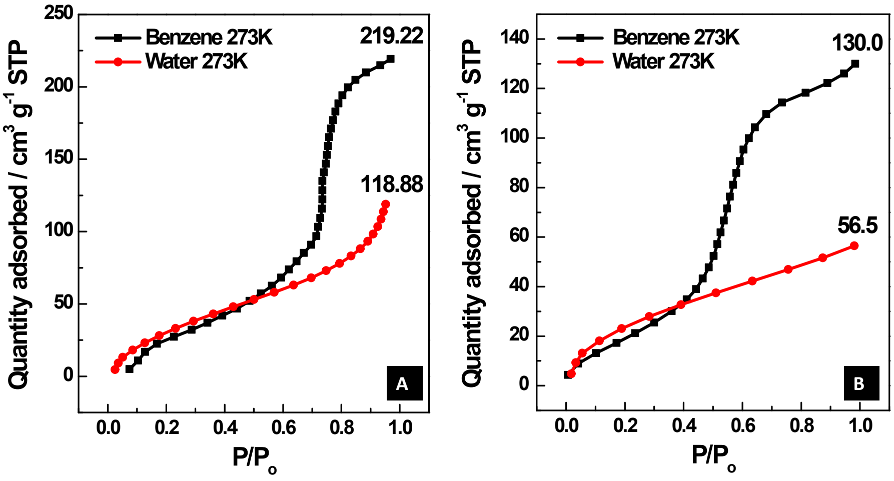


Figure S2. Benzene and water adsorption isotherms of (A) C_3-MSN-0.5 and (B) C_4-MSN-0.5.

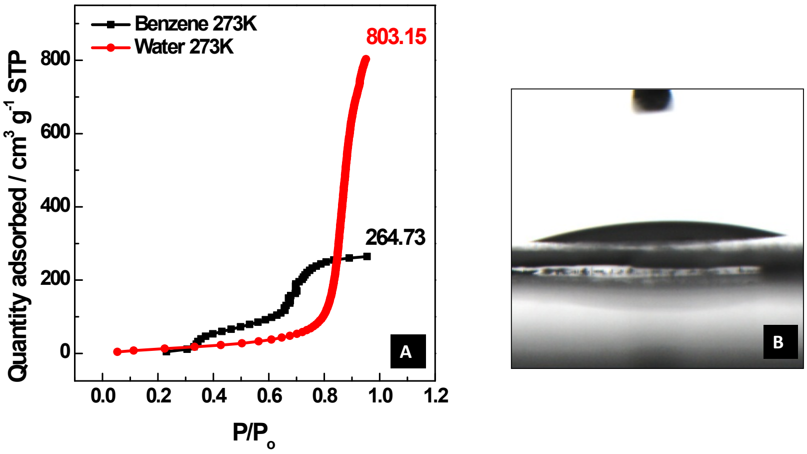


Figure S3. (A) Benzene and water adsorption isotherms and (B) Image of sessile water droplet on the material film made with pure mesoporous silica nanospheres.

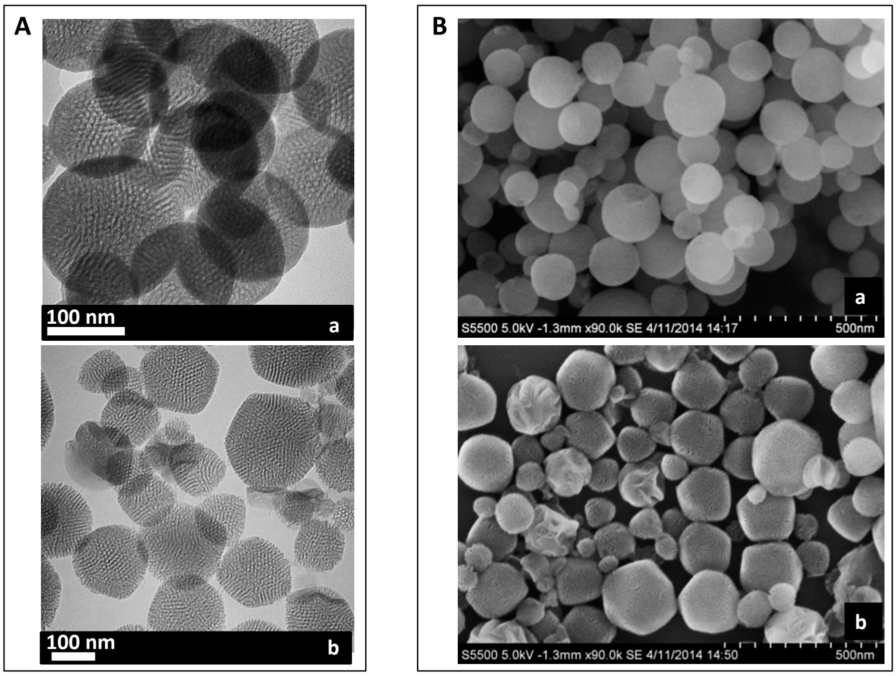


Figure S4. (A) TEM and (B) SEM images of (a) Ph-MSN-0.33 and (b) Ph-MSN-0.67.

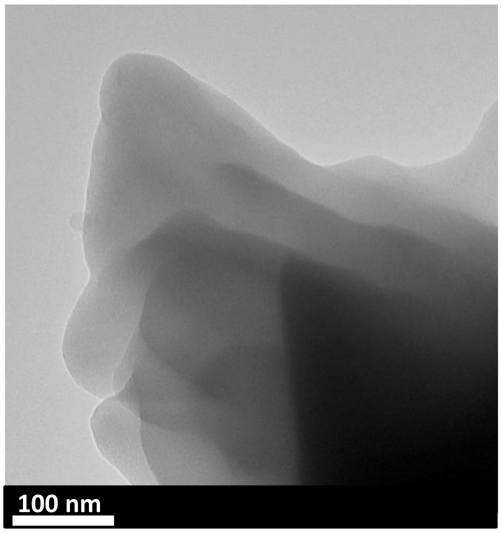


Figure S5. TEM image of the sample prepared using Ph_2SiCl_2 as precursor.

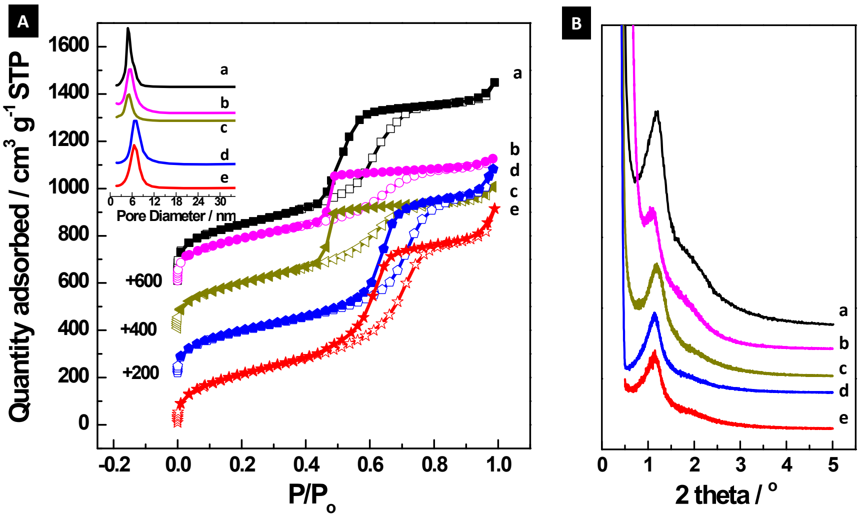


Figure S6. (A) N_2 sorption isotherms and (B) XRD patterns of (a) Ph-MSN-0, (b) Ph-MSN-0.33, (c) Ph-MSN-0.5, (d) Ph-MSN-0.67 and (e) Ph-MSN-0.75.

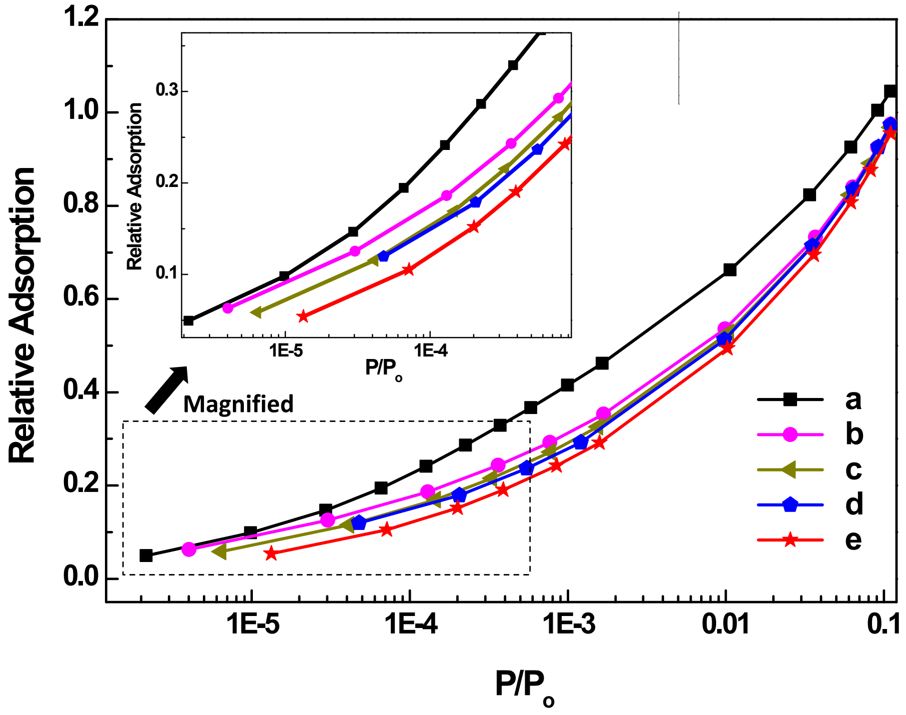


Figure S7. N_2 adsorption curves for Ph-modified MSNs with different phenyl content at low pressures: (a) Ph-MSN-0, (b) Ph-MSN-0.33, (c) Ph-MSN-0.5, (d) Ph-MSN-0.67 and (e) Ph-MSN-0.75.

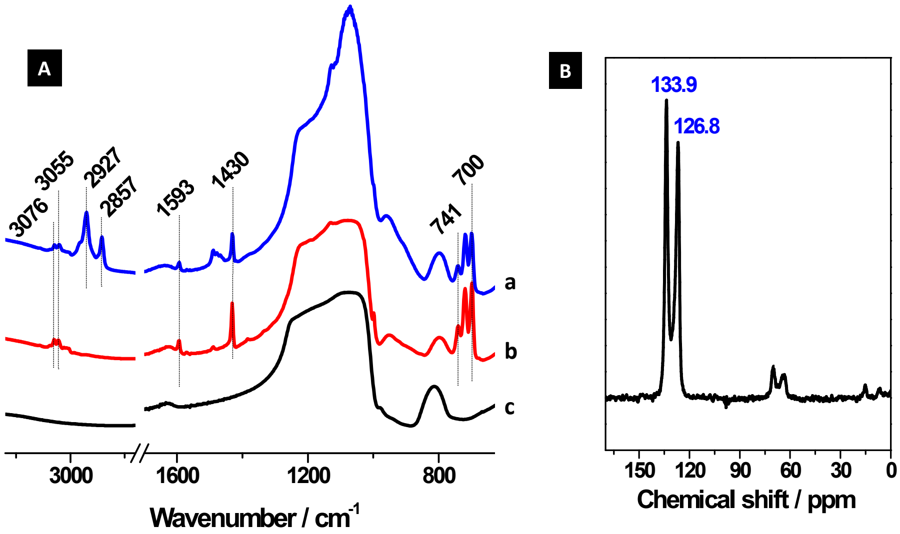


Figure S8. (A) FT-IR spectra of (a) Ph-MSN-0.5 mixed with additional CTAB, (b) as made Ph-MSN-0.5 and (c) pure silica. (B) ^{13}C-CP/MAS NMR spectrum of Ph-MSN-0.5.

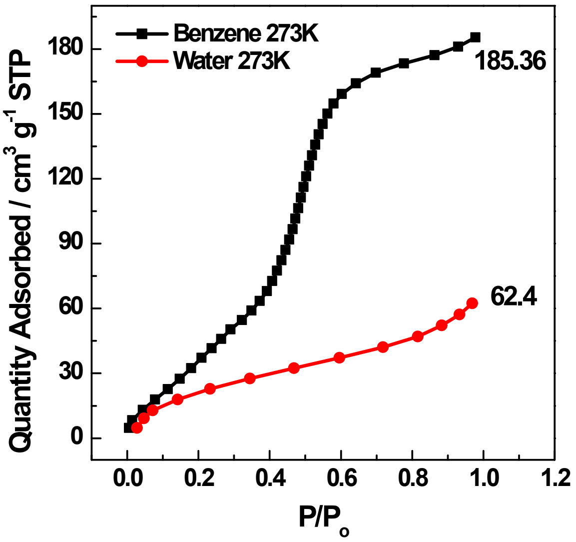


Figure S9. Benzene and water adsorption isotherms of Ph-MSN-0.75.

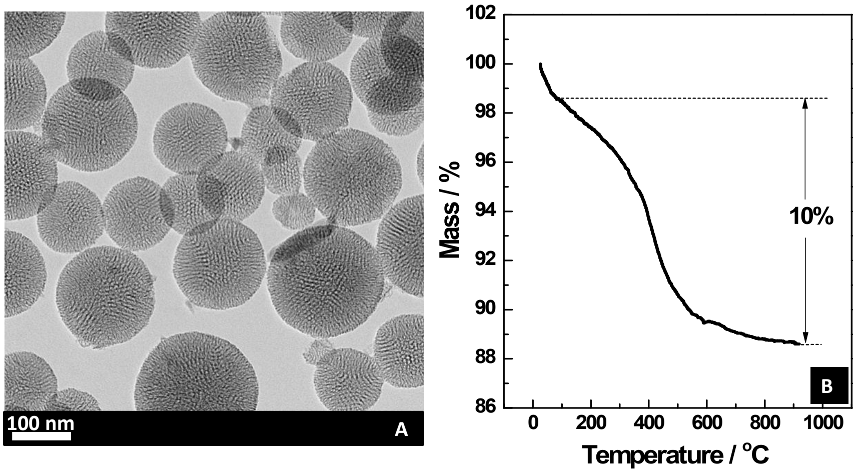


Figure S10. (A) TEM image and (B) TG curves of phenyl-functionalized MSNs prepared by grafting of Ph_2SiCl_2 onto MSNs.

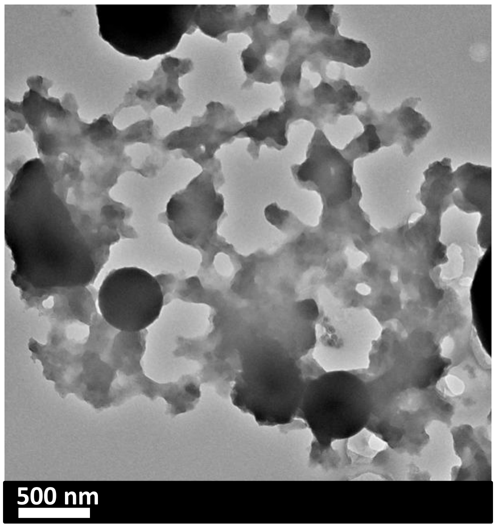


Figure S11. TEM image of the sample prepared under conditions similar to Ph-MSN-0.5 but without prehydrolysis of TEOS.

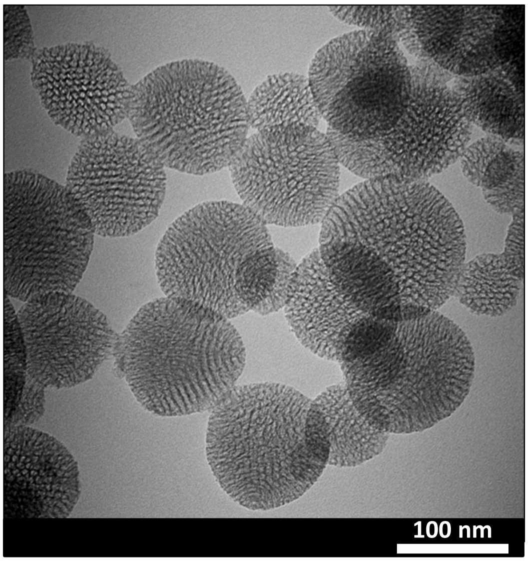


Figure S12. TEM image of the sample taken out at the initial 5 min during the synthetic process for Ph-MSN-0.5.

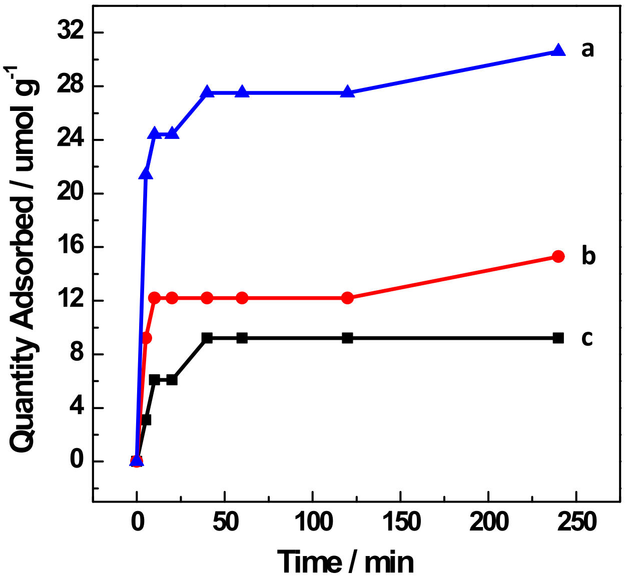
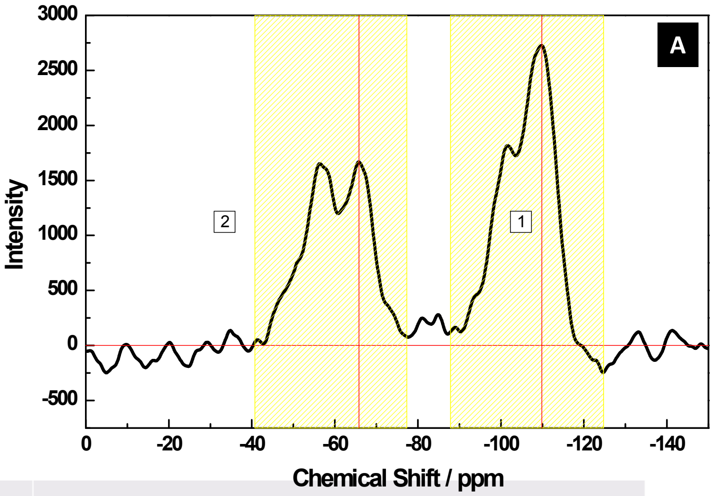
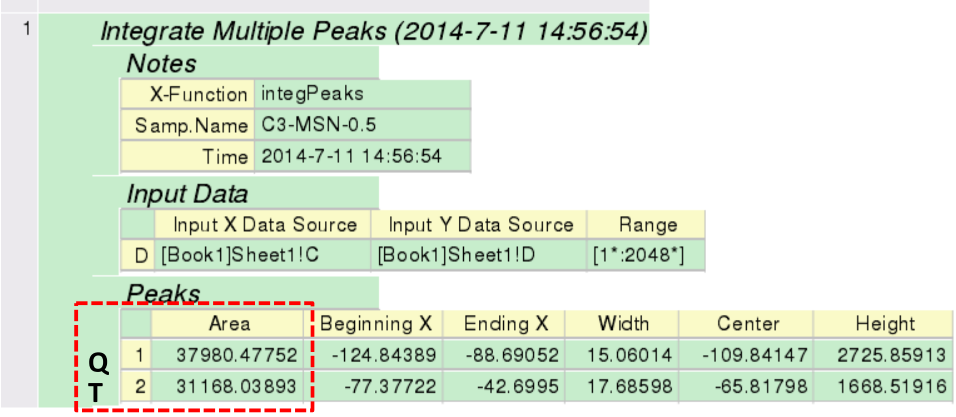


Figure S13. Adsorption curves of MO in water on (a) Ph-MSN-0.75, (b) C_3-MSN-0.5 and (c) pure MSN as a function of contact time





1 *Integrate Multiple Peaks (2014-7-11 14:56:54)*

Notes

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Time	2014-7-11 14:56:54

Input Data

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Peaks

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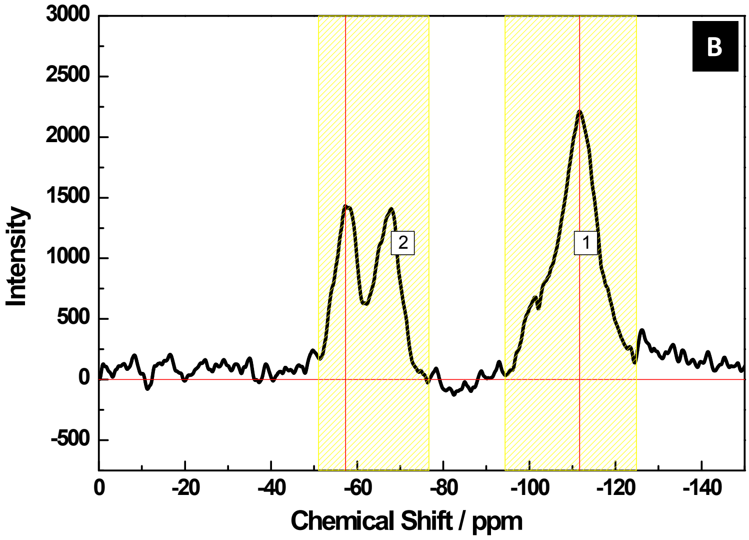

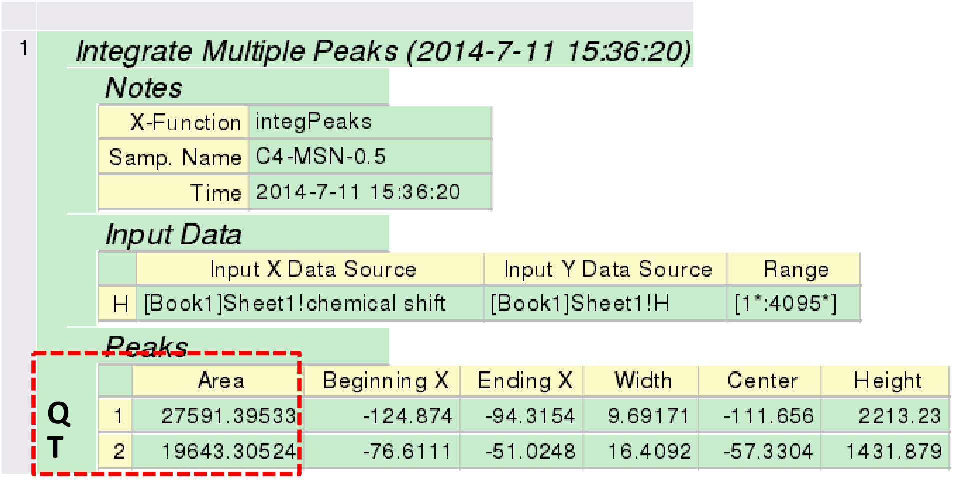

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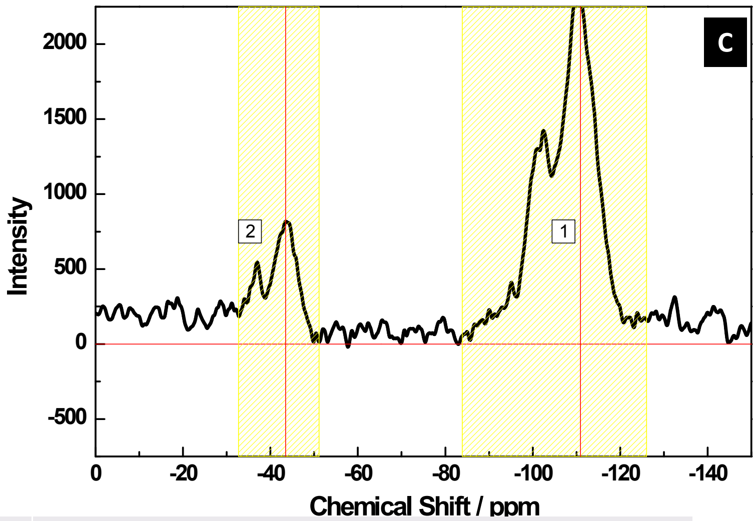

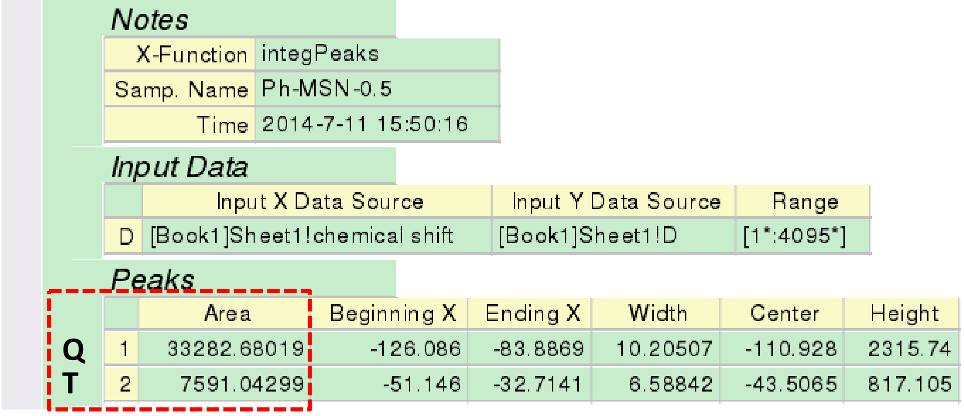

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Time	2014-7-11 15:50:16

Input Data

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Peaks

		Area	Beginning X	Ending X	Width	Center	Height
Q	1	33282.68019	-126.086	-83.8869	10.20507	-110.928	2315.74
T	2	7591.04299	-51.146	-32.7141	6.58842	-43.5065	817.105

Figure S14. ^{29}Si NMR spectrum with bands deconvolution and integral results of (A) C_3-MSN-0.5,(B) C_4-MSN-0.5,(C) Ph-MSN-0.5.