

A new strategy for surface functionalization of periodic mesoporous silica based on meso-HSiO_{1.5}

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Experimental Section

Synthesis of meso-HSiO_{1.5}. The synthesis of meso-HSiO_{1.5} was according to the procedure in the literature.¹ In a typical synthesis, 1.68 g of Pluronic-123 surfactant (BASF Co.), 1.2 mL of *n*-butanol (≥99.4 %, ACS) and 3.0 g of NaCl were dissolved in 60 mL of HCl_(aq) (0.1 M). After 1 h of continuous stirring, 4.5 mL of triethoxysilane (HSi(OEt)₃) (95%, Aldrich) was rapidly added to the homogeneous and clear aqueous solution. The mixture was constantly stirred at room temperature for 12 h, and the resulting white product precipitate was isolated by centrifugation. The surfactant was subsequently removed through Soxhlet extraction over ethanol/HCl for 24 h, and the solid was finally washed with 1.0 M HCl_(aq). The resulting white powder was dried in vacuum at 60 °C for 12 h and stored in vacuum prior to use to minimize hydrolysis and oxidation.

Synthesis of undecylenic acid (UA) grafted meso-HSiO_{1.5} (meso-HSiO_{1.5}@UA). 1.5 g meso-HSiO_{1.5} powder was dispersed in 50 ml decane by magnetic stir, then 5 ml UA and 200 μl 10 % H₂PtCl₆/isopropanol was added. The dispersing solution was put under N₂ and degassed by repeated freeze-pump-thaw cycles for 3 times. Once degassed, the mixture was heated to 170 °C and reacted overnight with stirring. The resulting product precipitate was isolated by centrifugation and repeatedly washed by *n*-hexane and ethanol to remove decane and un-grafted UA. Finally, the resulting powder was dried in vacuum at 60 °C for 12 h and stored in vacuum.

Synthesis of 3-allyloxy-2-hydroxy-1-propanesulfonic acid sodium salt (AHPSA) grafted meso-HSiO_{1.5} (meso-HSiO_{1.5}@AHPSA). 1.5 g meso-HSiO_{1.5} powder was dispersed in 50 ml ethanol or hexane by magnetic stir, then 5 ml AHPSA solution (40 % in H₂O) and 200 μl 10 % H₂PtCl₆/isopropanol were added. The dispersing solution was put under N₂ and degassed by repeated freeze-pump-thaw cycles for 3 times. Once degassed, the hydrosilylation reaction was initiated using a UV light source and the irradiation was sustained overnight. The resulting product precipitate was isolated by centrifugation and repeatedly washed by *n*-hexane and ethanol. Finally, the resulting powder was dried in vacuum at 60 °C for 12 h and stored in vacuum.

Materials Characterization. Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet700 FTIR spectrometer (USA Thermo Co.). Solid samples were mixed with KBr, ball

milled into a fine powder, and pressed into a dense pellet for analysis. X-ray photoelectron spectroscopy (XPS) was acquired using a PHI 5000 Versa Probe utilizing monochromatic Al K α radiation. The ^{29}Si high-power decoupling (HPDEC) MAS NMR and ^{13}C cross-polarized (CP) MAS NMR measurements were performed on a Bruker 400 MHz spectrometer. The thermo mass loss curve was obtained by thermo gravimetric analyzer (TGA) Pyris 1 DSC at N $_2$ atmosphere. The samples were pre-oxidized in oxygen atmosphere to transform Si-H bond to Si-OH or Si-O-Si bond, which avoided the loss of Si during TGA analysis. TEM images were obtained by JEM2000EX at 200 kV. Small Angle X-ray Scattering (SAXS) patterns of all samples were obtained by Bruker-AXS Nano STAR equipped with Cu K α radiation ($\lambda = 0.15406$ nm). Sorption experiments were performed by a Micromeritics ASAP2020 machine with N $_2$ as sorption gas. The Raman experiments were collected with a Renishaw Invia Reflex system equipped with Peltier-cooled charge-coupled device (CCD) detectors, a Leica microscope and a laser with excitation wavelength 532 nm.

Table S1. Atomic concentration of meso-HSiO $_{1.5}$, meso-HSiO $_{1.5}$ @UA, and meso-HSiO $_{1.5}$ @AHPSA from XPS.

sample element	meso-HSiO $_{1.5}$	meso-HSiO $_{1.5}$ @UA	meso-HSiO $_{1.5}$ @AHPSA
C	9.09	29.35	20.11
O	58.95	49.88	53.96
Si	31.96	20.77	21.20
S	-	-	2.12
Na	-	-	2.60

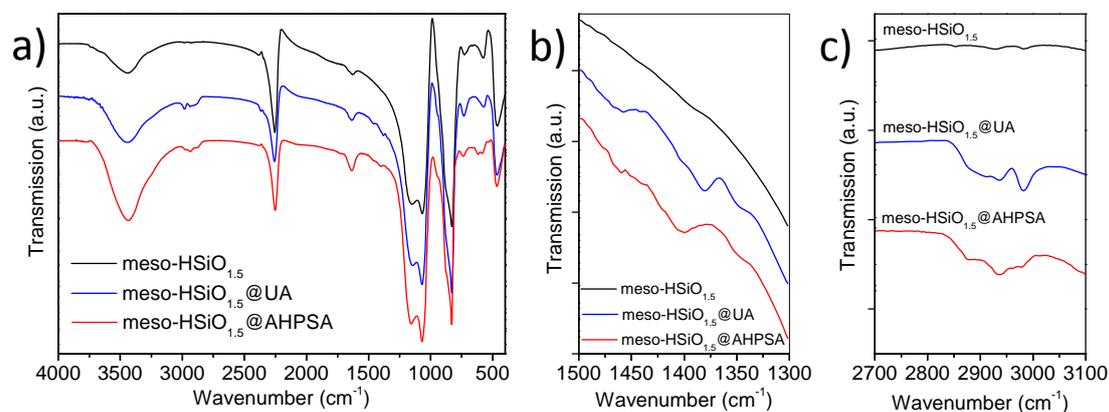


Figure S1: FTIR spectra of the modified meso-HSiO $_{1.5}$.

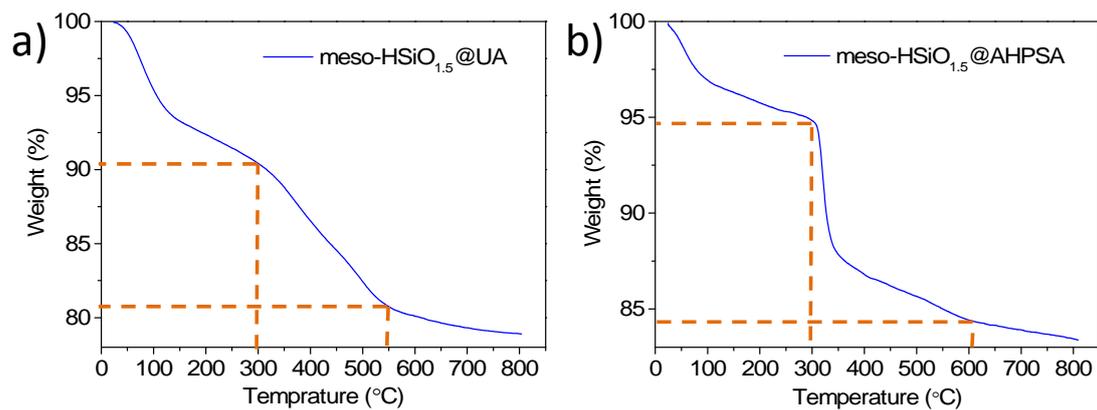


Figure S2: TGA curves of a) meso-HSiO_{1.5}@UA and b) meso-HSiO_{1.5}@AHPSA.

References

- (1) Xie, Z.; Henderson, E. J.; Dag, Ö.; Wang, W.; Lofgreen, J. E.; Kübel, C.; Scherer, T.; Brodersen, P. M.; Gu, Z.-Z.; Ozin, G. A. *J. Am. Chem. Soc.* **2011**, *133*, 5094.