Electronic Supplementary Information

Hierarchically Mesoporous Silica Nanoparticles: Extraction, Amino-functionalization and Their Multipurpose Potentials

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Part 1. The calibration curve of ibuprofen (IBU)

The solubility of IBU in pure water at 25 ^{o}C is ca. 0.086 mg/mL, but the solubility of IBU in phosphate-buffered saline (PBS, 137 mM NaCl, 2.7 mM KCl, 5.0 mM $Na_2HPO_4 \cdot 12H_2O$, 0.7 mM H_3PO_4 in ultrapure water, pH 7.2-7.4) is improved, and is at least 1.5 mg/mL. Four standard solutions of IBU in PBS were prepared, and shown in Table S1.

A calibration curve was obtained by plotting the absorbance of standard solution as a function of the IBU concentration between 0.1 and 1.5 mg mL^{-1}. The calibration curve fits well the Lambert and Beer's law

$$A = 1.6584\ C + 0.02439$$

where A is absorbance at 264 nm and C is the IBU concentration (mg mL^{-1}).

Table S1. Standard solutions of IBU in PBS and their UV-vis absorbances at 264 nm

Entry	IBU concentration (mg/mL)	Absorbance
1	0	0
2	0.1	0.191
3	0.5	0.87
4	1	1.721
5	1.5	2.481

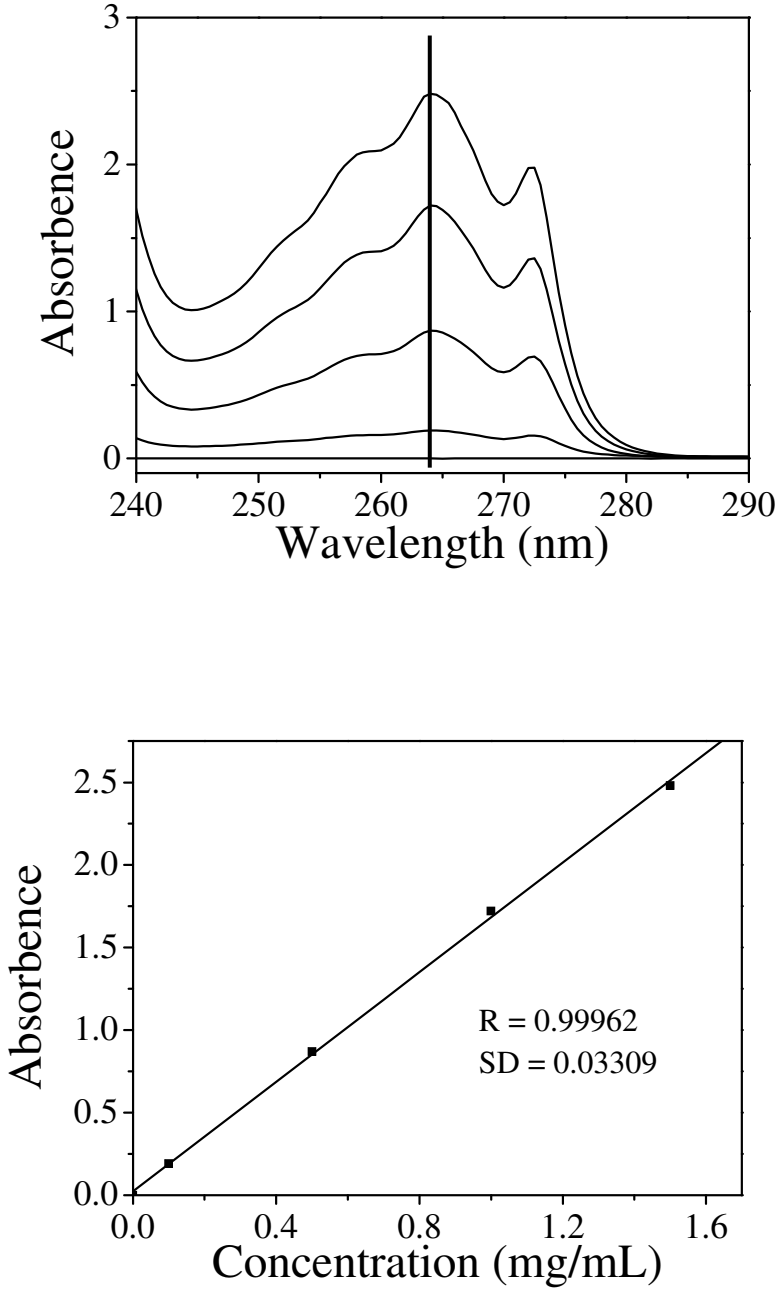

Figure S1. UV-vis spectra of IBU standard solutions in Table S1 and the calibration curve of the UV absorbance at 264 nm vs. the IBU concentration between 0 and 1.5 mg mL^{-1}.

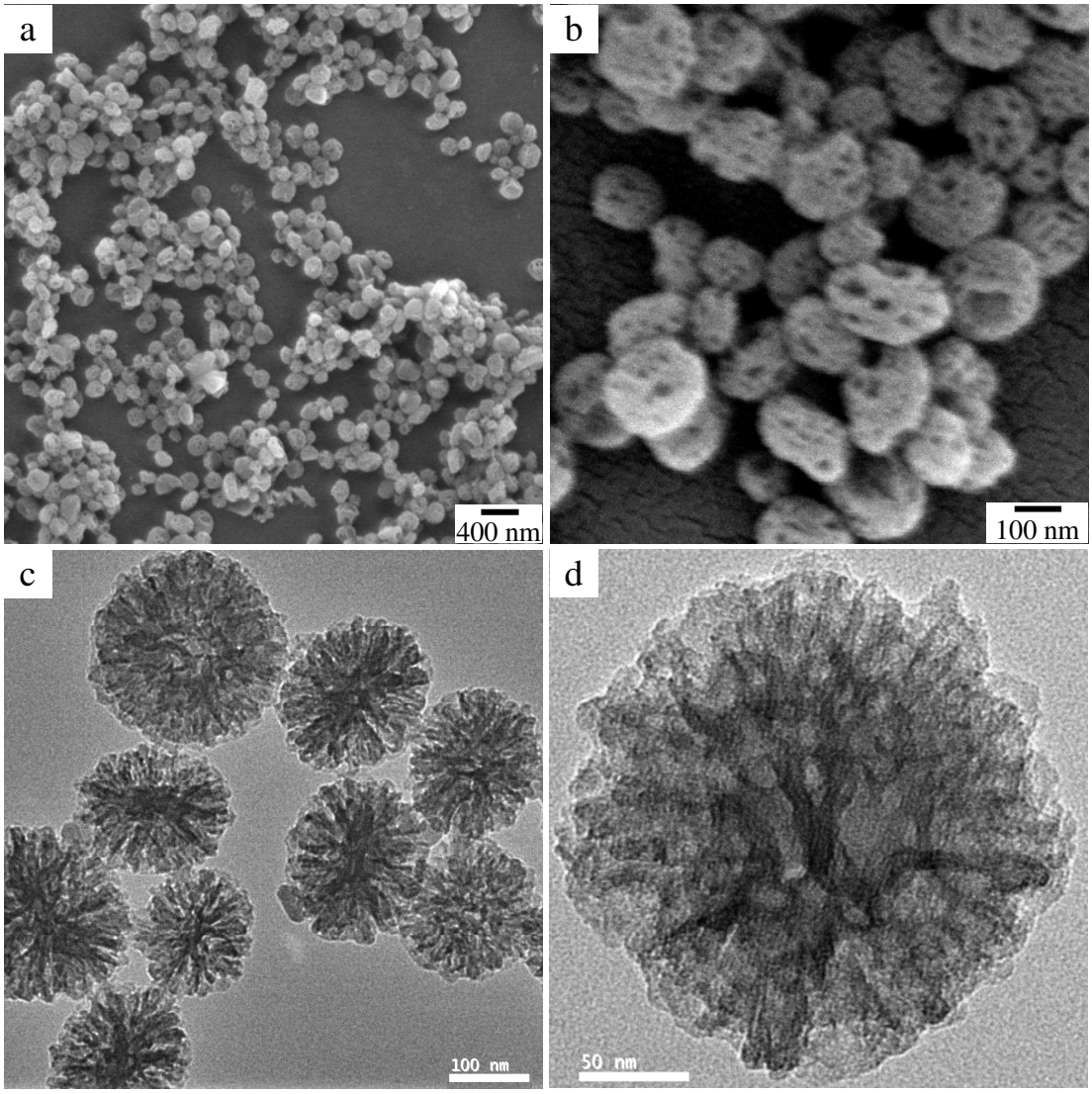

Figure S2. SEM (a,b) and TEM (c,d) images of as-HMSNs.

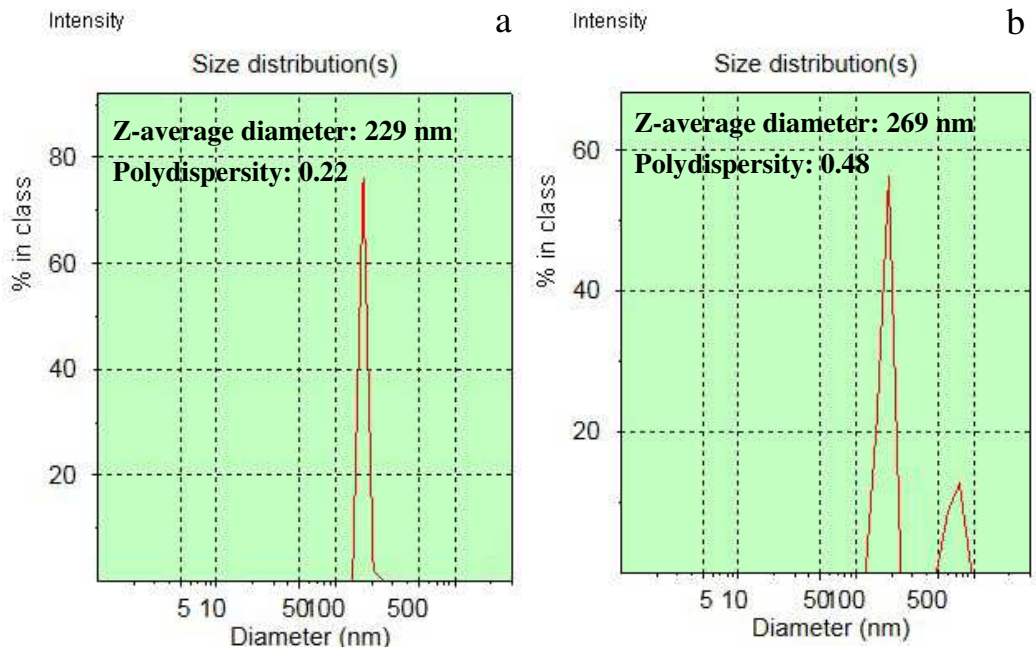

Figure S3. Particle size distributions of ext-HMSNs (a) and NH_2-ext-HMSNs fabricated by post-synthesis modification (b) by DLS measurements. Amino-functionalization results in a slight size increase from 229 to 269 nm and the appearance of a new distribution peak at ca. 600 nm, which indicates that NH_2-ext-HMSNs have a little aggregation.

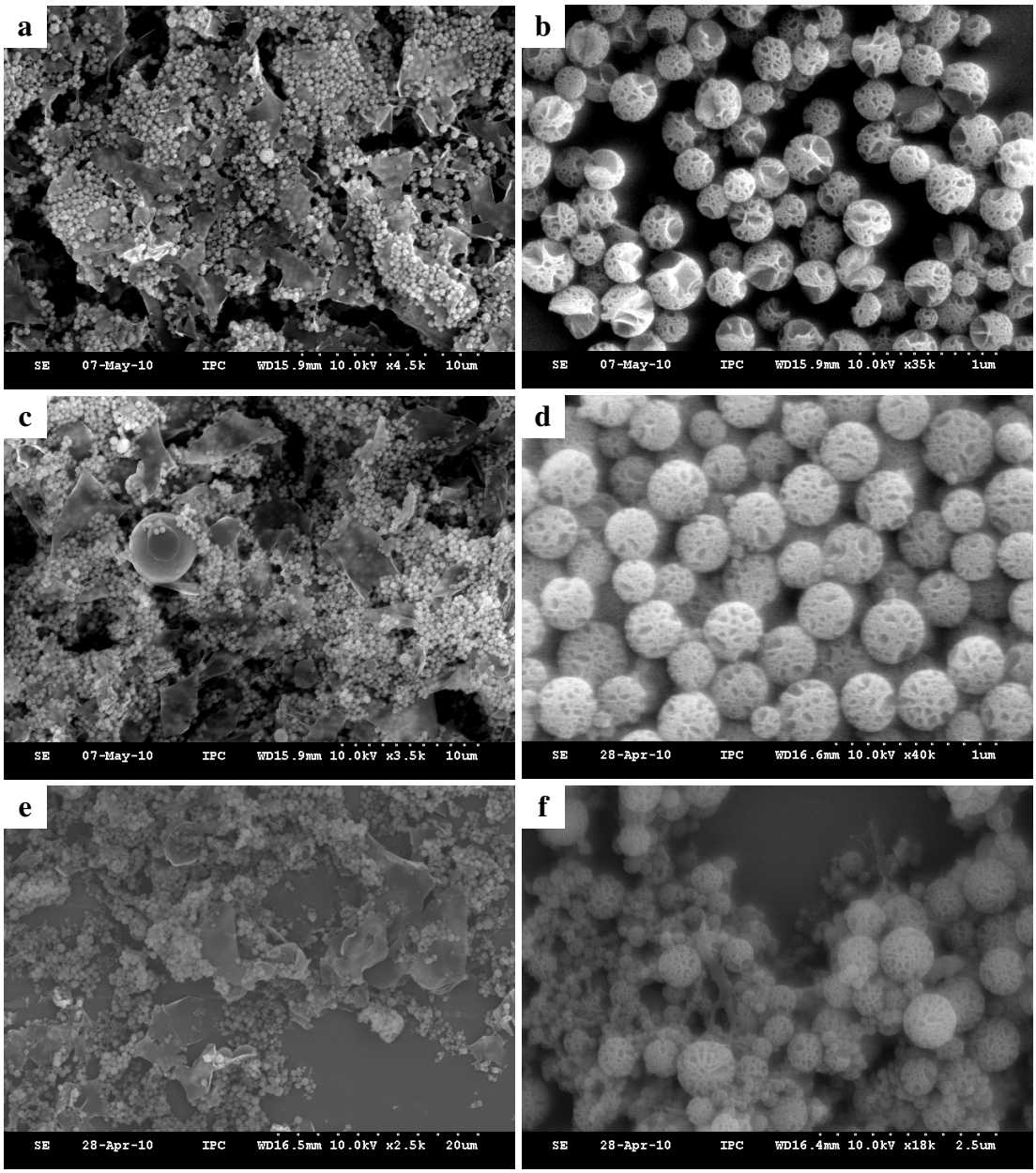

Figure S4. SEM images of products fabricated with addition of varied volumes of APMS as co-condensation precursor: 0.02 (a,b), 0.05 (c,d), and 0.2 mL (e,f).

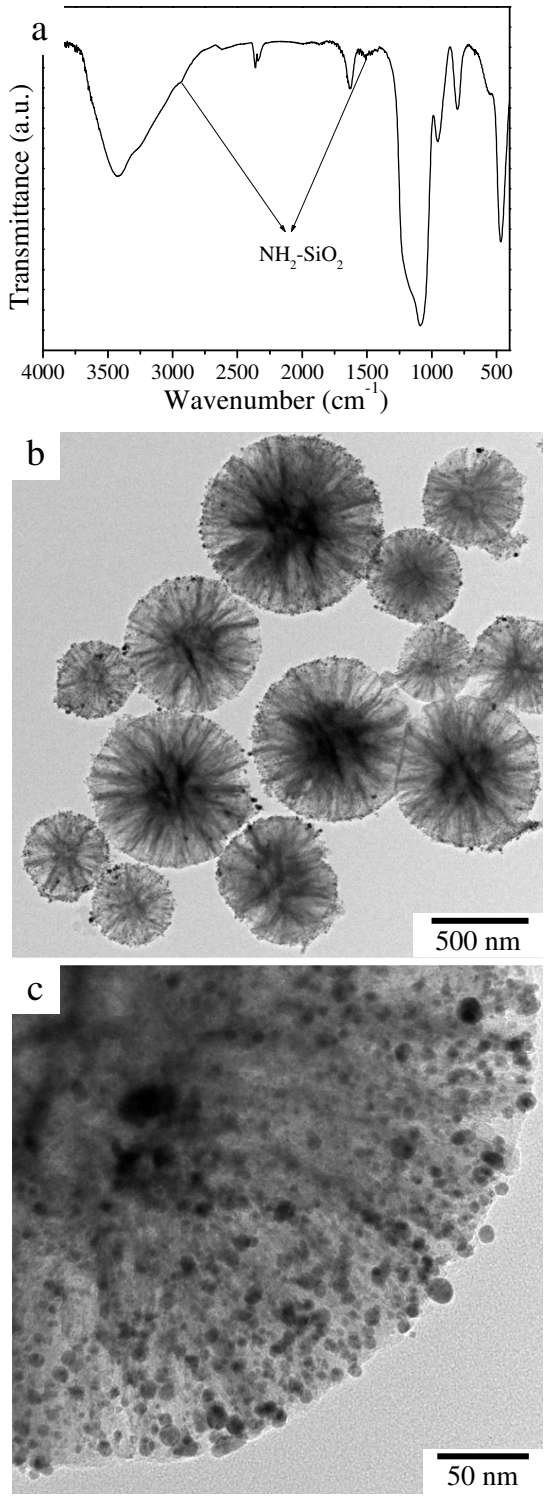

Figure S5. FTIR spectrum (a) of extracted NH_2-HMSNs fabricated with addition of 0.2 mL of APMS as co-condensation precursor. TEM images (b,c) of the extracted NH_2-HMSNs after loading with Au nanoparticles according to the process of experimental section.

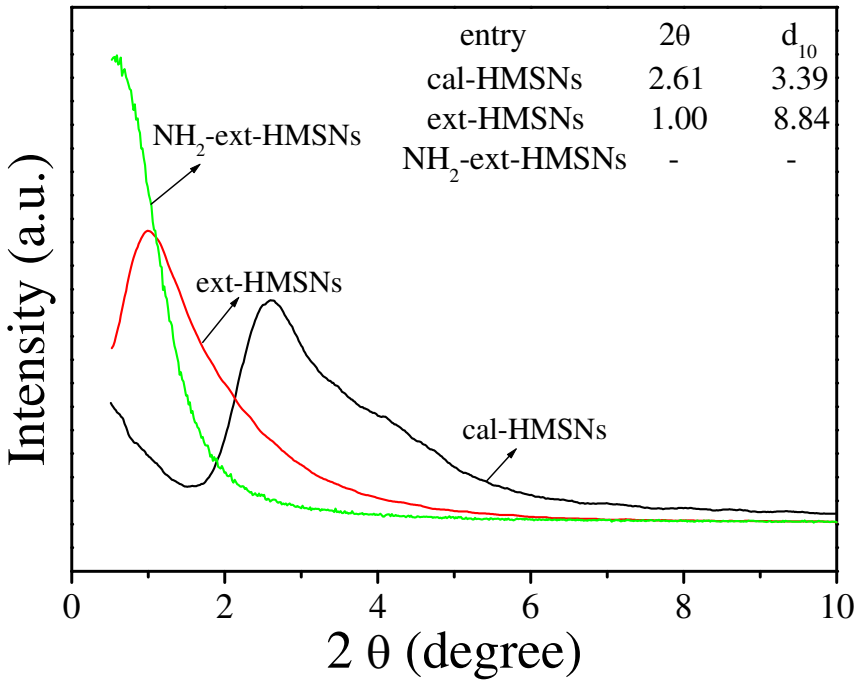

Figure S6 SAXRD patterns of cal-HMSNs, ext-HMSNs and NH_2-ext-HMSNs. The *d* spacings (d_{10}) were calculated from the XRD peaks of (10) diffraction.

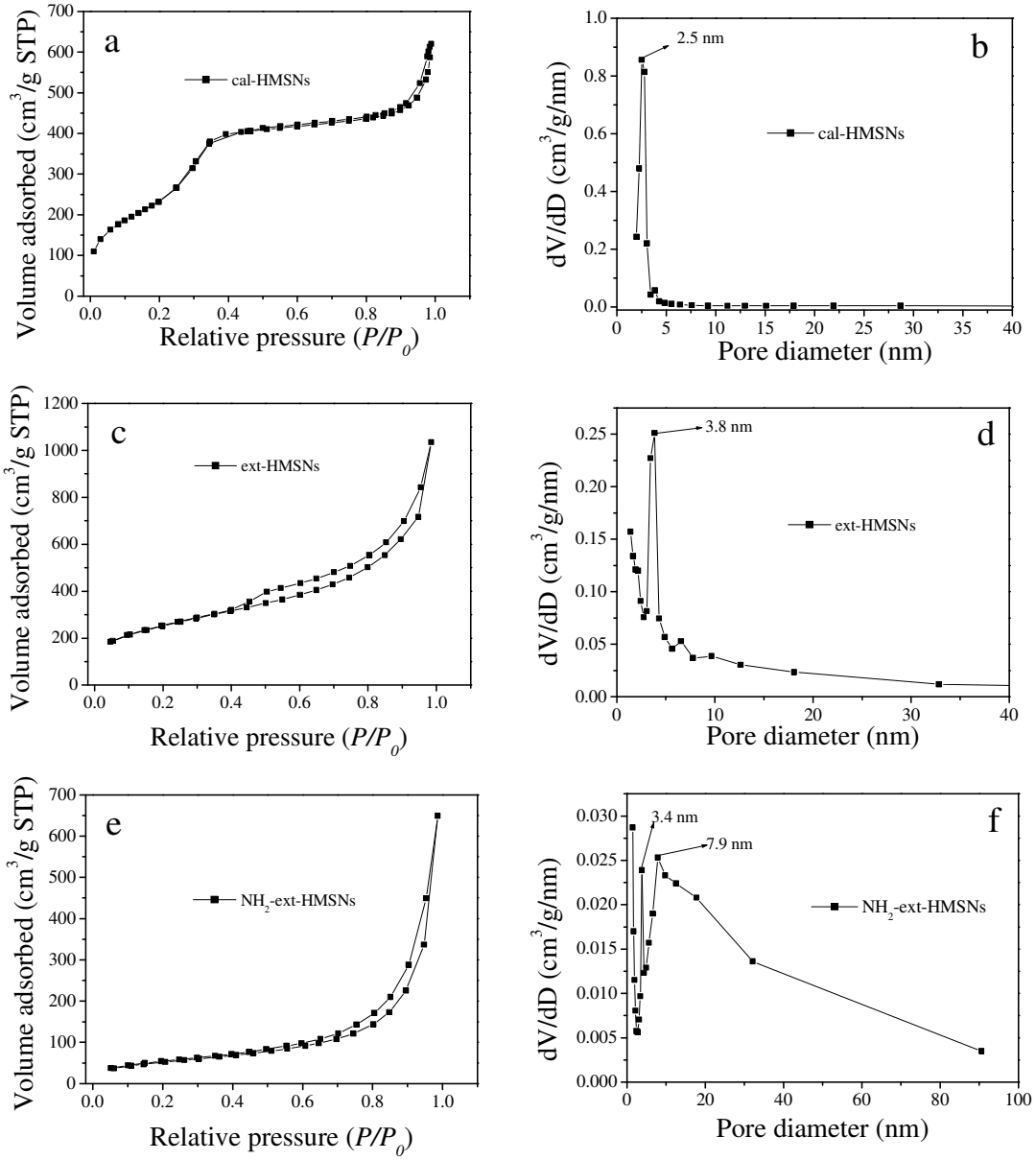

Figure S7 Nitrogen adsorption-desorption isotherms (a,c,e) and corresponding pore size distributions (b,d,f) obtained from desorption branches of cal-HMSNs (a,b), ext-HMSNs (c,d) and NH_2-ext-HMSNs (e,f).

Table S2 Physicochemical properties of prepared silica structures

Entry	d_{10} (nm)[a]	BET surface area (m^2 g^{-1})[b]	Pore diameter (nm)[c]	Pore volume (cm^3 g^{-1})[d]
cal-HMSNs	3.39	1078	2.5	1.01
ext-HMSNs	8.84	893	3.8	1.60
NH_2-ext-HMSNs	-	190	3.4, 7.9	1.01

[a] calculated from the SAXRD peak of (10) diffraction.

[b] calculated from the N_2 adsorption branch using the BET method.

[c] calculated from the N_2 desorption branch using the BJH method.

[d] estimated from the single-point amount adsorbed at $P/P_o = 0.98$.

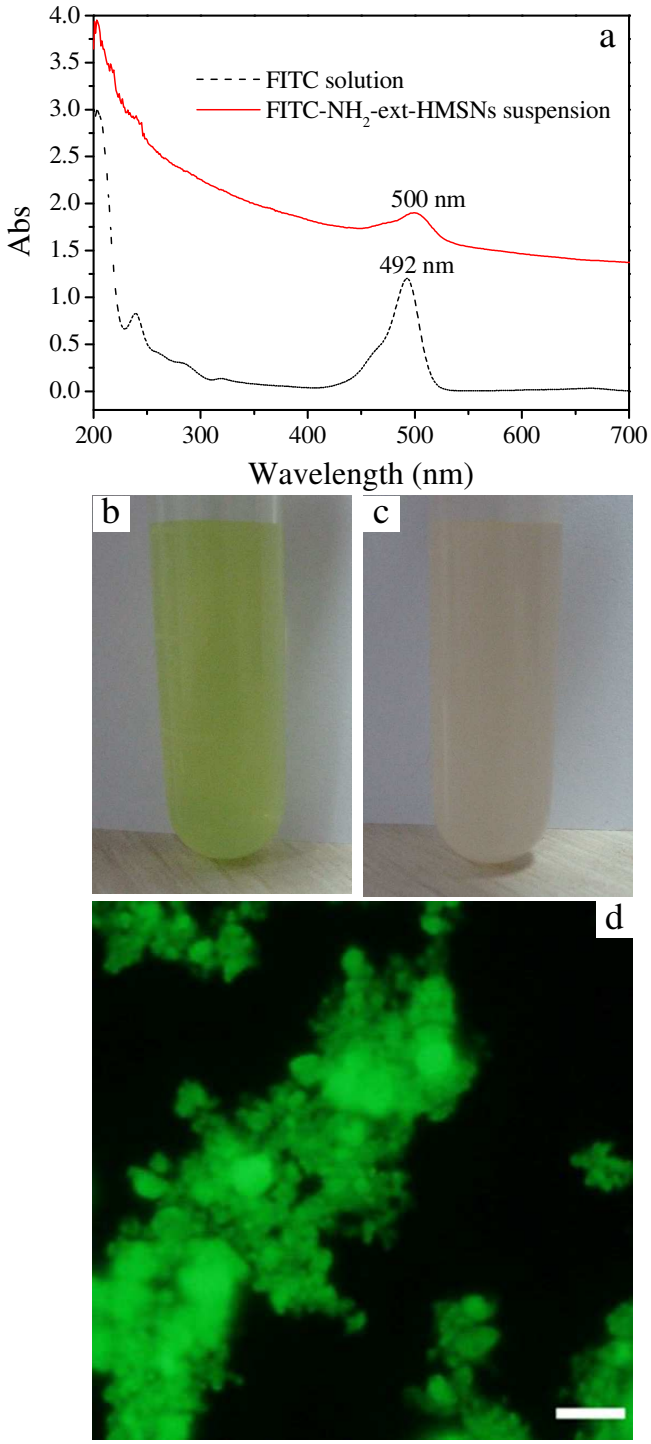

Figure S8. UV-vis absorption spectra (a) of FITC solution and FITC-NH_2-ext-HMSNs suspension, color digital images of FITC solution (b) and FITC-NH_2-ext-HMSNs suspension (c), and confocal microscopy image (d) of FITC-NH_2-ext-HMSNs. The scale bar in (d) is 5 μm.

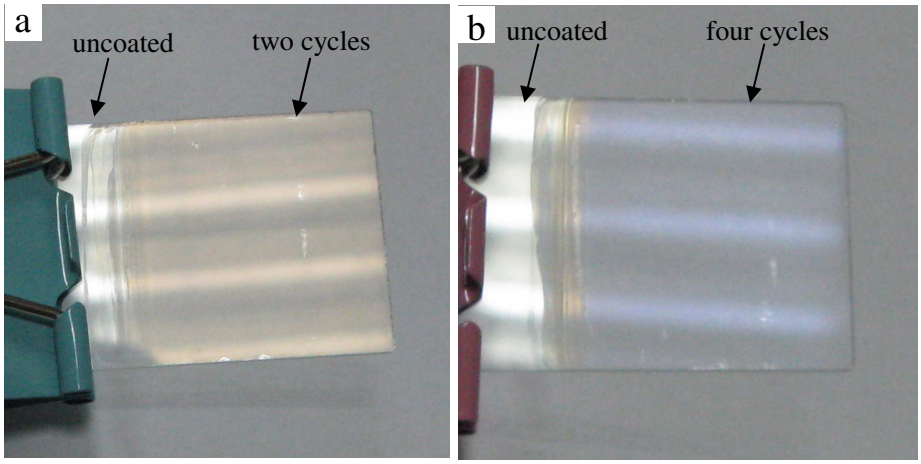

Figure S9. Digital images of slide glasses coated with two (a) and four (b) cycles of PDDA/ext-HMSNs showing the suppression of reflection.

After successful amino-functionalization of ext-HMSNs by post-grafting, NH_2-ext-HMSNs were dispersed in ultrapure water (ca. 0.5 wt%, pH=8.78) and were also used as building blocks to construct particulate coatings. Protonation of NH_2-ext-HMSNs results in pH increase from 3.46 (ext-HMSNs) to 8.78 (NH_2-ext-HMSNs). As NH_2-ext-HMSNs are positively charged, mutilayers of $(PDDA/PSS)_5$ were prepared, and were used as a primer and the particulate coating of $(PDDA/PSS)_5(NH_2\text{-ext-HMSNs/PSS})_3NH_2$-ext-HMSNs was prepared.

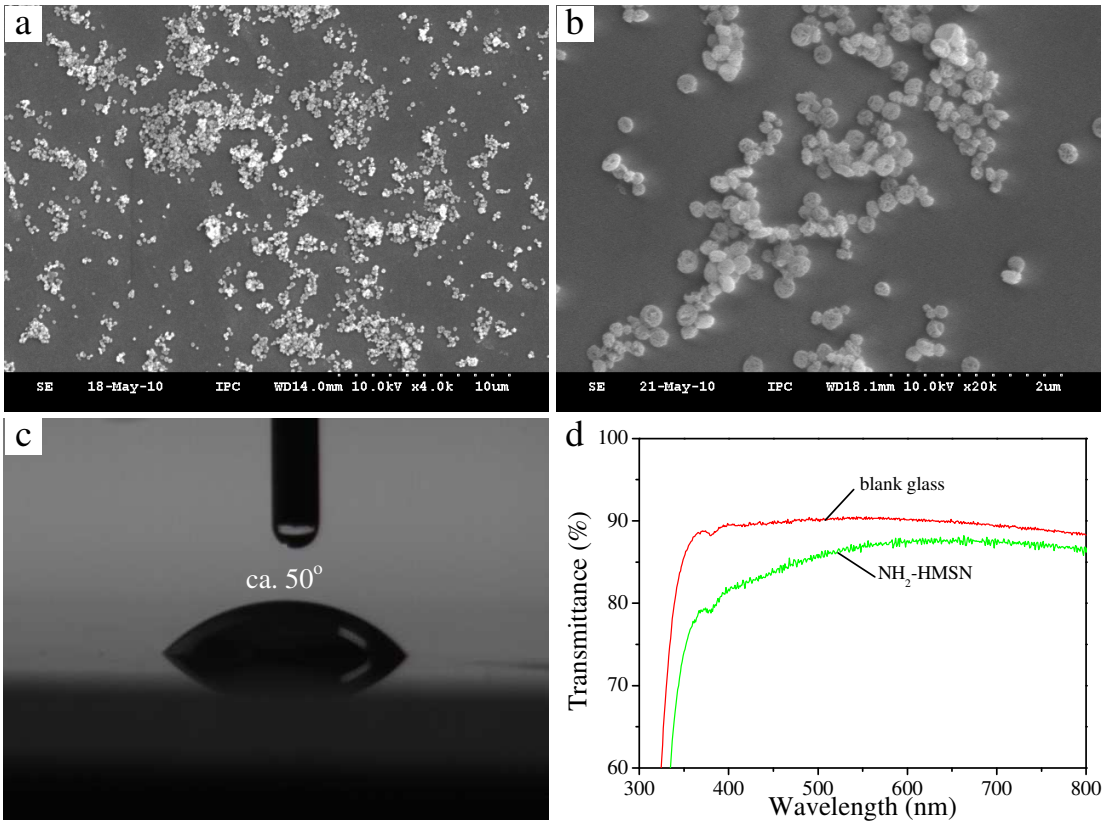

Figure S10. (a,b) SEM images of NH_2-HMSNs coatings on slide glasses by depositing four cycles of PDDA/NH_2-HMSNs. (c) Digital image of ca. 50° WCA on the NH_2-HMSNs coating. (d) Transmission spectra of blank slide glass and slide glass coated with four cycles of PSS/NH_2-HMSNs.

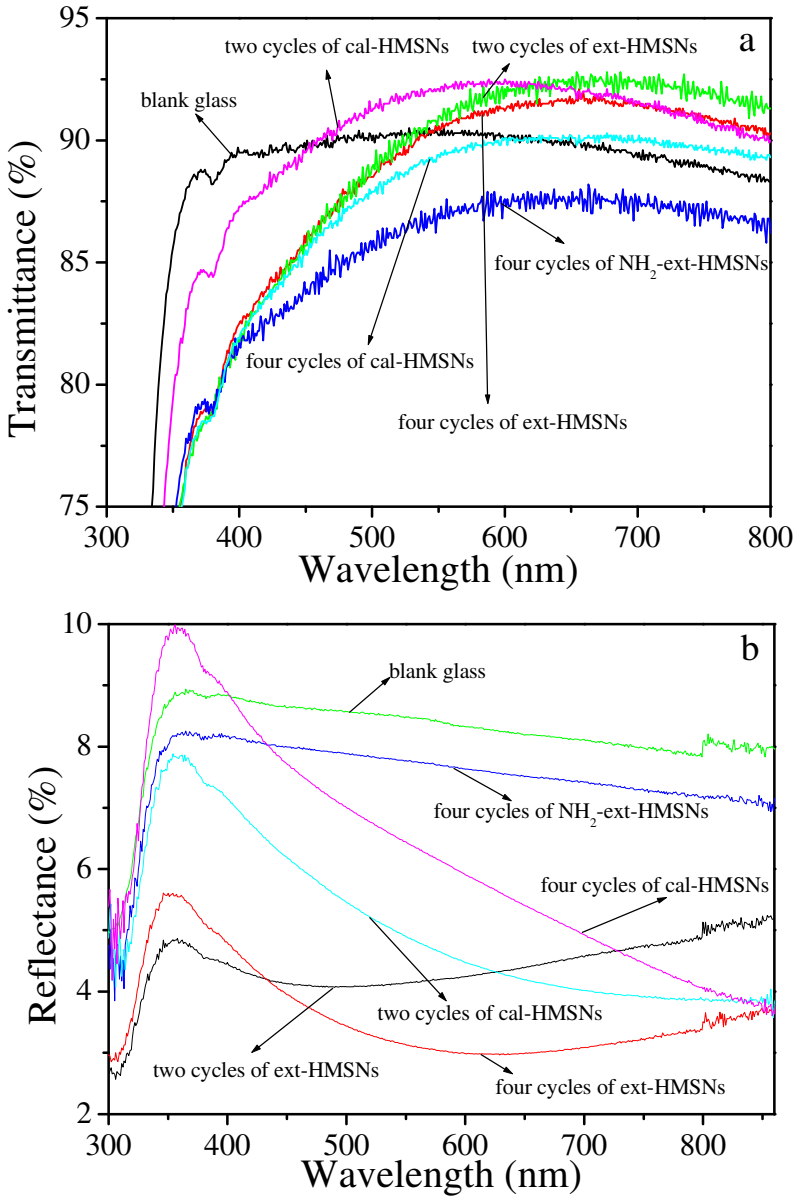

Figure S11. Transmission (a) and reflection (b) spectra of blank slide glass and slide glasses coated with varied particles: ext-HMSNs, cal-HMSNs and NH_2-ext-HMSNs.