Supporting Information

Amino-Modified High-Surface-Area Radial-Pore Silica Microspheres for Efficient Perfluorooctanoic Acid Removal

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Materials and Methods

Chemical and materials

Hexadecyltrimethylammonium bromide (CTAB, 99 %), tetraethyl orthosilicate (TEOS, AR), ammonia solution (~28 wt % NH_3 in water), triethanolamine (TEA) and ethanol were supplied by Sinopharm Chemical Reagent Co. Ltd. Tetrapropoxysilane (TPOS,97%), tetramethoxysilane (TMOS, 98%) was purchased from Sigma-Aldrich Trading Co., Ltd. (3-Aminopropyl) triethoxysilane (APTES), perfluorobutanoic acid (PFBA, 97%), perfluoro-n-pentanoic acid (PFPeA, 97%), perfluoroheptanoic acid (PFHpA, 97%), perfluorohexanoic acid (PFHxA, 97%), perfluorooctanoic acid (PFOA, 97%) and perfluorononanoic acid (PFNA, 97%) was purchased from Sigma-Aldrich Trading Co., Ltd.

Synthetic methods

Synthesis of radical-Pore Silica Microspheres

In a typical synthesis, 15.0 mL of water, 5.0 mL of ethanol, 0.04 g of CTAB and 0.45 mL of ammonia solution were mixed and stirred at room temperature for 30 min, named Solution A. Next, 0.5 mL of tetrapropoxysilane (TPOS) and 20.0 mL of ethanol were thoroughly mixed and then added to the Solution A, followed by continuous stirring at room temperature for 3 h. The products were collected by centrifugation and washed several times with distill water and ethanol. The as-synthesized porous silica microspheres were re-dispersed in a mix solution containing 120 mg NH_4NO_3 and 40 mL ethanol with ultrasonication treatment for 15 min and stirred gently a for 12 h to remove the organic templates. The products were collected by centrifugation and re-dispersed in a mix solution containing 120 mg NH_4NO_3 and 40 mL ethanol for 3 times. After removing the templates, the products were collected and air dried at 65 °C. The above-mentioned formulation corresponds to the case where TPOS is employed as the silicon source. The silicon source added can be substituted with equivalent molar amounts of tetramethoxysilane (TMOS) and tetraethyl orthosilicate (TEOS). The final products are denoted as MSSsR, where R equals 1, 2 and 3, representing the incorporation of TPOS, TEOS and TMOS as silicon source, respectively. The layer-by-layer growth strategy for fabricating larger-sized microspheres was achieved by

maintaining the total molar amount of silicon source while introducing different quantities of TPOS in batches at 2 h intervals. For instance, 2.8 μm microspheres were synthesized through sequential addition of 0.1 mL TPOS aliquots every 2 h until reaching a cumulative volume of 0.5 mL, followed by a final 3 h reaction period to complete the synthesis process.

Synthesis of the amino-MSSs

In a typical synthesis, the 100 mg of extracted MSSs1 dry powder were re-dispersed in 15 mL of anhydrous toluene with ultrasonication treatment for 40 mins and stirred vigorously. Subsequently, 3 mL of (3-Aminopropyl) triethoxysilane (APTES) was added to the toluene solution of MSSs1. The reaction was kept at 110 °C with reflux for 12 h. The products were collected by centrifugation and washed several times with ethanol to remove the residual reactants and air dried at 65 °C. The amino-functional products are denoted as MSSs1-NH_2.

Synthesis of the amino-functional mesoporous silica nanoparticles

Typically, 0.132 g of CTAB, 0.12 mL of (20 wt %) triethanolamine (TEA) solution and 7 mL of water were mixed and stirred gently at 80°C in a 25 mL round-bottom flask. Then, 1 mL of TEOS was carefully added to solution under mild stirring. The reaction was then kept at 80°C for 2 h.[1] The products were collected by centrifugation and washed several times with distilled water and ethanol. After the removal of the template and grafted amine groups using the aforementioned method, the products were collected and air dried at 65 °C. The amino-functional products are denoted as MSN-NH_2.

Synthesis of the amino-functional MCM-41 nanospheres

Typically, 0.40 g of CTAB, 1.4 mL of 2 mol/L NaOH solution and 192 mL of water were mixed and stirred gently at 80°C in a 500 mL round-bottom flask. Then, 2.68 mL of TEOS was carefully added to solution under mild stirring. The reaction was then kept at 80°C for 2 h[2]. The products were collected by centrifugation and washed several times with distilled water and ethanol. After the removal of the template and grafted amine groups using the aforementioned method, the products were collected and air dried at 65 °C. The amino-functional products are denoted as MCM-41-NH_2.

Characterizations

Transmission electron microscopy (TEM) imaging was implemented on FEI Tecnai G2 F20 S-TWIN Field Emission Transmission Electron Microscope with an accelerating voltage of 200 kV. The samples for TEM measurements were dispersed in ethanol, and then deposited and dried on a carbon film on a copper grid. Fourier transform infrared spectroscopy (FTIR) were collected a Nicolet iS10 FTIR Spectrophotometer from ThermoFisher. X-ray photoelectron spectroscopy (XPS) was performed using an AXIS LTRA DLD XPS system with MONO Al source (Shimadzu Corp). UV-vis-NIR absorption spectra were measured on a Epoch-Microplate Spectrophotometer (BioTek, USA). Nitrogen adsorption-desorption measurements were conducted to obtain information on the porosity. The measurements were conducted at 77 K with Micromeritics Tristar 2420. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and the Barrett-Joyner-Halenda (BJH) modelwas utilized to calculate the pore volumes and the pore size distributions derived from the adsorption branches of isotherms. Zeta potential of the samples were recorded by using Zetasizer Nano ZS apparatus (Malvern, UK). The data of PFOA batch adsorption experiments (the concentration of PFOA is between 1~2000 ppm) were obtained by high performance liquid chromatography (HPLC, LC-2030C 3D Plus, Shimadzu, Japan) with an UV-vis detector. The data of PFOA dynamic adsorption experiments (the concentration of PFOA is between 1~500 ppb) were obtained by ultra-performance liquid chromatography-high-resolution mass spectrometry (UPLC-HRMS, ACQUITY UPC2-Xevo G2-XS Tof, Waters, America).

Adsorption experiment

Adsorption batch experiment

PFASs batch adsorption experiment was performed in aqueous solutions with a ratio of m/V =2/3 (10 mg of adsorbents in 15 mL of PFAS solution) at pH = 3. After shaking for a certain time, 1.5 mL of aqueous samples were filtered with a 0.2 μm inorganic syringe filter (Collins) to remove the adsorbent. And then the PFAS concentration of the aqueous samples was measured by HPLC with an UV-vis detector.[3] The adsorption

capacity of PFAS was determined by equation below:

$$q = \frac{C_0 - C_t}{C_a}$$

Where q is the adsorption capacity at incubation time h (min), C_0 is initial concentration of PFAS, C_t is the concentration of PFAS in the sample at time t, C_a is the concentration of adsorbent.

Except for the adsorption kinetics experiments, the PFAS adsorption time is set to 6 h. The pH of solution was adjusted to 4, 5, 6 and 8 using sodium hydroxide (NaOH). The concentration of different ionic species is 200 ppm in the selective PFOA adsorption experiment.

Adsorption kinetic of PFOA

PFASs adsorption kinetic experiment was performed in aqueous solutions with a ratio of m/V =2/3 (10 mg of adsorbents in 15 mL of PFAS solution with an initial concentration of 500 ppm) at pH = 3. At each predetermined time of 2, 5, 10, 15, 30, 45 mins, 1, 2, 3, 4, 5 h, 1.5 mL of the solution mixture was collected for HPLC analysis for each sample. Adsorption kinetic data were fitted using two model below:

Pseudo-second-order kinetics model:

$$\frac{t}{q} = \frac{1}{k_2 * {q_e}^2} + \frac{t}{q_e}$$

Pseudo-first-order kinetics model:

$$\ln\left(q_e - q\right) = lnq_e - k_1 t$$

Where q is the adsorption capacity at incubation time h (min), q_e is the amount of PFOA that the adsorbent binds at equilibrium. k_2 is the pseudo-second-order kinetic adsorption rate constant (g mg^{-1} h^{-1}), k_1 is the pseudo-first-order kinetic adsorption rate constant (g mg^{-1} h^{-1}).

Adsorption isotherms of PFOA

PFASs adsorption isotherms experiment was performed in aqueous solutions with a ratio of m/V =2/3 (10 mg of adsorbents in 15 mL of PFAS solution) at pH = 3. A series concentration of PFOA stock solutions, with the initial concentrations of 50, 100, 300,

400, 500, 600, 700, 800, 1000 and 1500 ppm were prepared in Milli-Q water. The solution mixtures were placed on a shaker for 6 h, and 1.5 mL of the solution mixture was collected for HPLC analysis for each sample. Data were fitted using the two models below:

Langmuir isotherm model:

$$q_e = q_m \frac{bC_e}{1 + bC_e}$$

Freundlich isotherm model:

$$q_e = K_F C_e^{\frac{1}{n}}$$

Where C_e is the residual concentration of PFOA at equilibrium, q_e is the amount of PFOA that the adsorbent binds at equilibrium, q_m is the maximum adsorption capacity. b (L mg^{-1}) is the Langmuir equilibrium constant representing binding affinity, while K_F ((mg g^{-1}) (L mg^{-1})1/n) is the Freundlich constant and n is the adsorption intensity.

MSSs1-NH_2 regeneration and recycle experiment

MSSs1-NH_2 was regenerated by immersing in NaOH solution at pH = 10 for 3 h at room temperature. The recycling experiment was conducted by repeating the PFOA adsorption and desorption experiments successively.

PFOA dynamic adsorption experiment

The sorbents were contained within Pasteur glass pipettes with specific dimensions: cartridge length of 150 mm and cartridge inner diameter of 7 mm. Initially, a cotton layer was placed at the bottom of the column to support the adsorbents and prevent it from being carried away with the water. A 2000 mg·L^{-1} MSSs1-NH_2 suspension was utilized to form the adsorbent bed. Specifically, 15 mL of the suspension was pipetted into the column to create the adsorbent bed containing exactly 30 mg of MSSs1-NH_2. As the water passed through the cotton layer, the MSSs1-NH_2 was settled on top of it. Then, 110 mL of each PFOA solution was continuously pipetted from the influent side, and the filtrate was collected in 1 mL volumes, placed in HPLC vials, and analyzed using UPLC-HRMS.

Supplementary figures

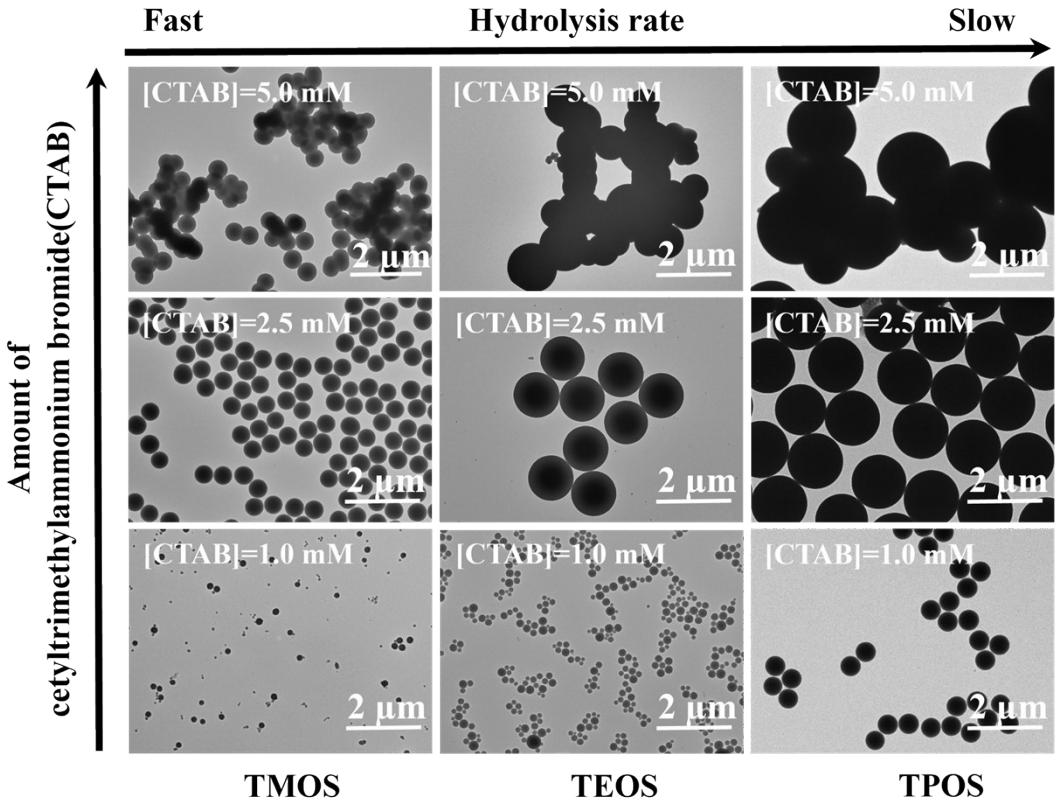

Fig. S1. TEM image of porous silica microspheres synthesized at various concentration of CTAB adding TMOS, TEOS and TPOS as silicon source.

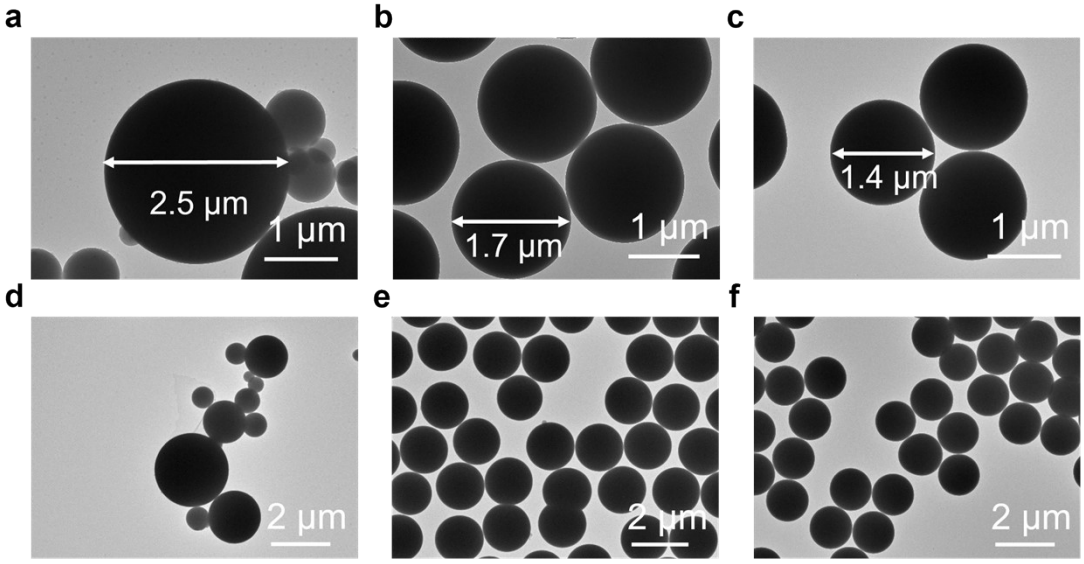

Fig. S2 TEM images of the micro-sized mesoporous silica spheres prepared by using TPOS and different concentrations of ammonia: (a, d) 0.032, (b, e) 0.16, and (c, f) 0.32 M, respectively.

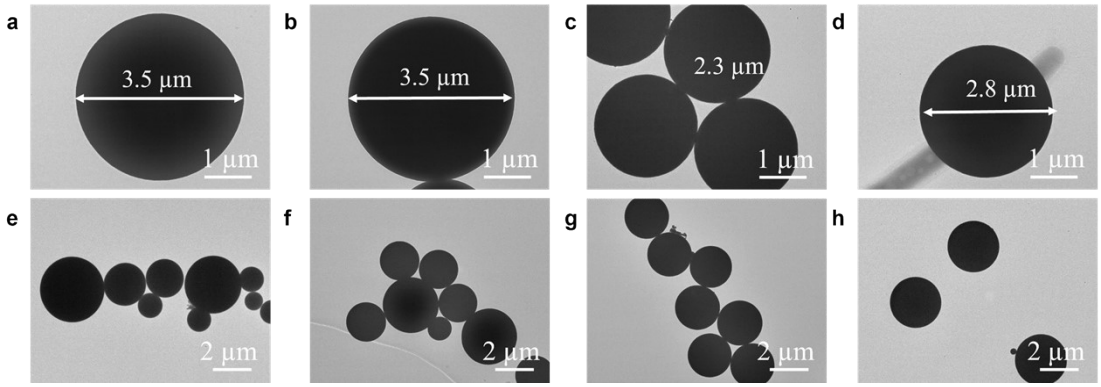

Fig. S3 TEM images of porous silica microspheres synthesized by maintaining a constant total molar amount of TPOS while introducing the precursor through sequential additions (a, e) 0.1 and 0.4 mL; (b, f) 0.1,0.1 and 0.3 mL; (c, g) 0.1,0.1, 0.1 and 0.2 mL; (d, h) 0.1, 0.1, 0.1,0.1 and 0.1 mL.

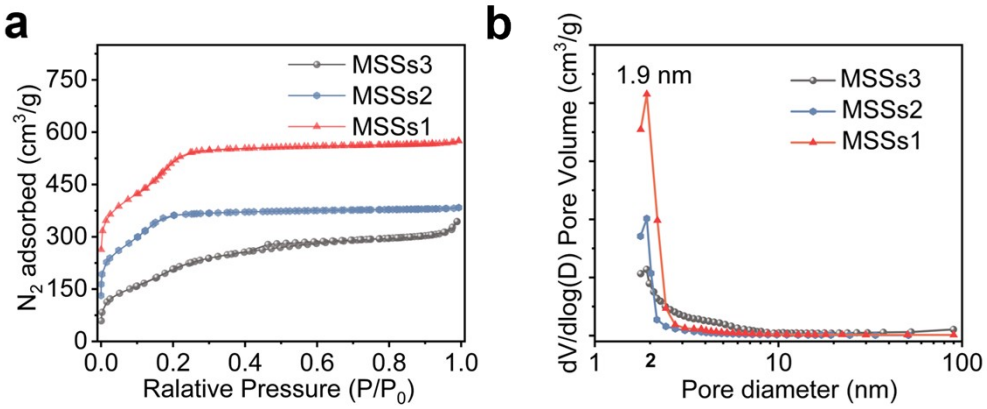

Fig. S4. (a) N_2 adsorption−desorption isotherms and (b) Pore diameter distribution curves of the silica microspheres synthesized with silicon sources of TPOS, TEOS and TMOS, respectively.

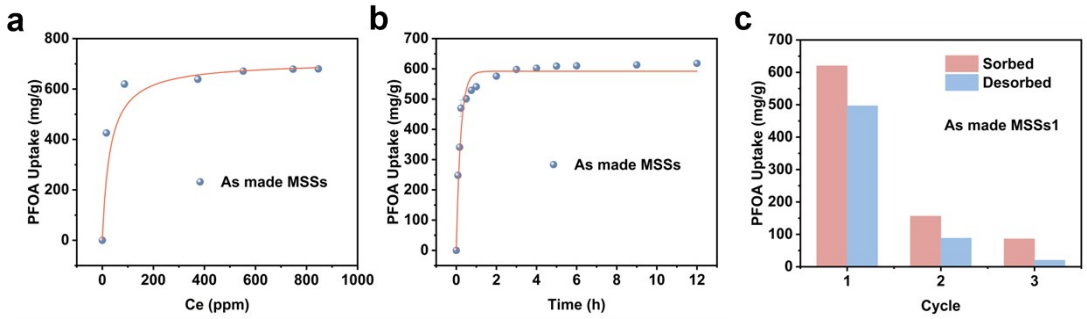

Fig. S5. (a) Equilibrium PFOA adsorption capacity as a function of equilibrium PFOA concentration (C_e) fitted with the Langmuir model. (b) Adsorption kinetics of PFOA with an initial concentration of 500 ppm fitted with the pseudo-second-order kinetics model. (c) PFOA uptake of as made MSSs1 after different cycles.

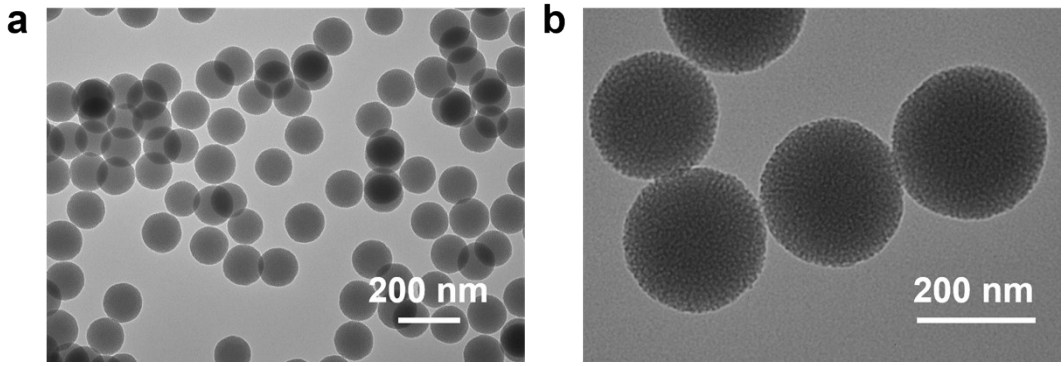

Fig. S6. TEM images of mesoporous silica nanoparticles (MSNs) with a particle size of ~130 nm.

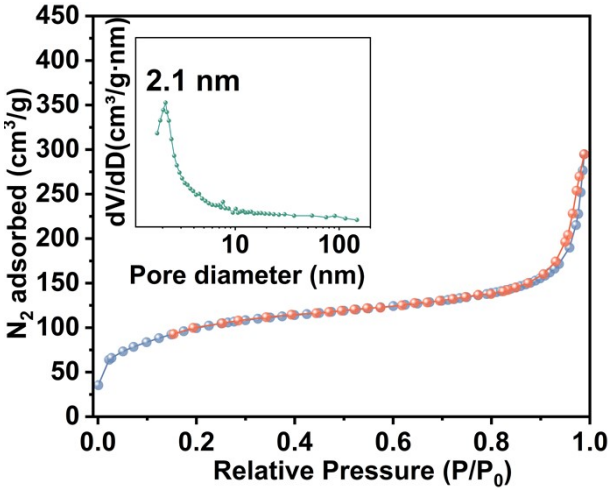

Fig. S7. N_2 adsorption−desorption isotherms of MSNs. (inset: the corresponding pore diameter distribution curves).

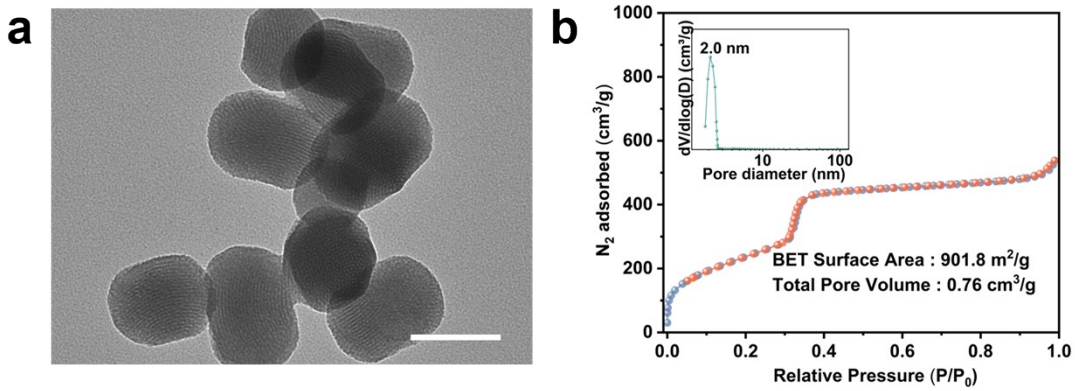

Fig. S8. The TEM image and the nitrogen adsorption–desorption isotherms of MCM-41.

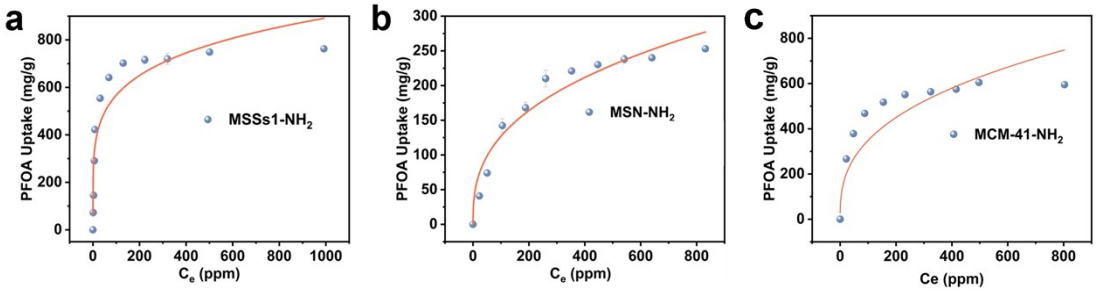

Fig. S9. Equilibrium PFOA adsorption capacity of (a) MSSs1-NH_2, (b) MSN-NH_2, (c) MCM-41-NH_2 as a function of equilibrium PFOA concentration (C_e) fitted with the Freundlich model.

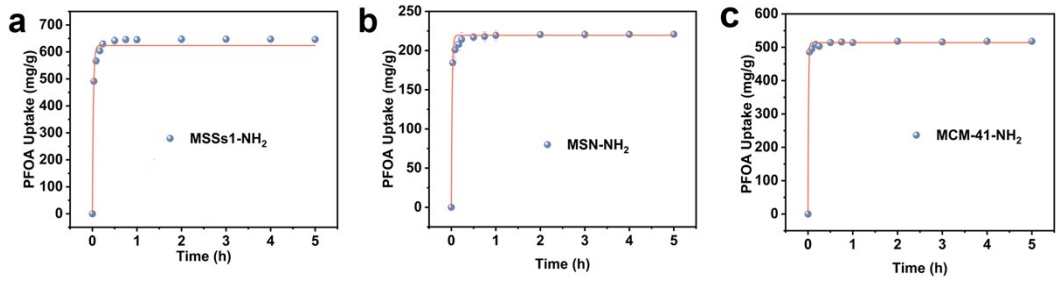

Fig. S10. Adsorption kinetics of PFOA of (a) MSSs1-NH_2, (b) MSN-NH_2 and (c) MSM-41-NH_2 with an initial concentration of 500 ppm, fitted with a pseudo-first-order model.

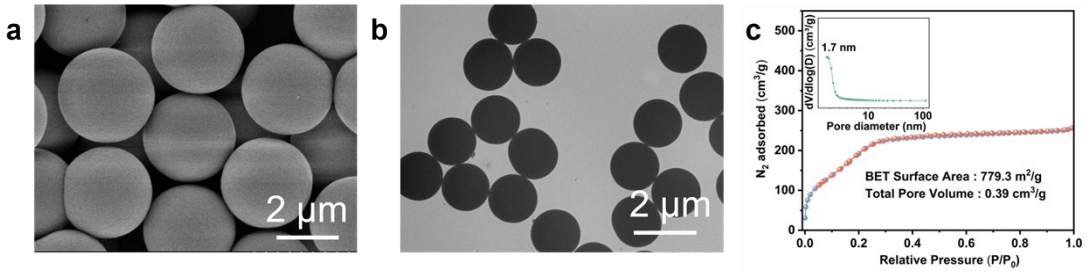

Fig. S11. (a) SEM image, (b) TEM image and (c) the nitrogen adsorption-desorption isotherm of MSSs1-NH_2 after 5 adsorption-desorption cycles (inset: pore distribution curve).

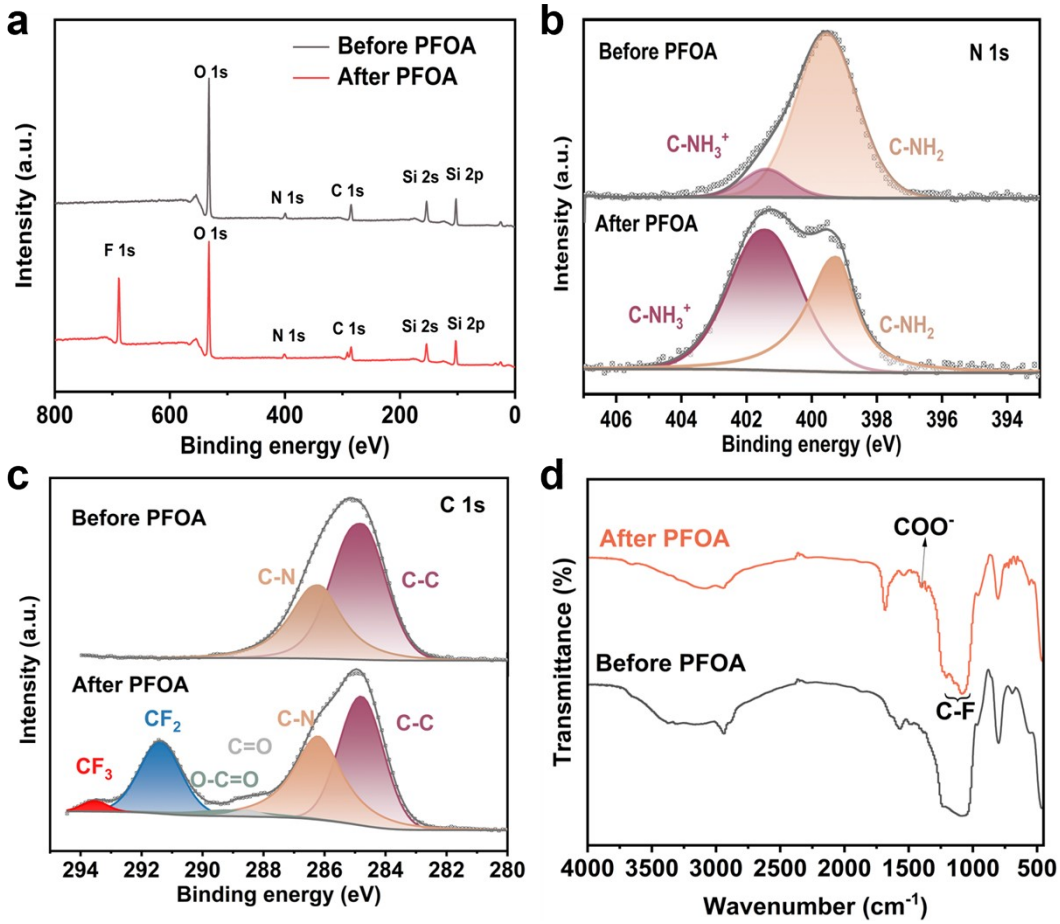

Fig. S12. X-ray Photoelectron Spectroscopy (XPS) of MSSs1-NH_2 before and after PFOA adsorption (a) XPS survey spectrum, and (b, c) high-resolution XPS spectra of N 1s and C 1s, respectively. (d) FTIR spectra of the MSSs1-NH_2 before (black) and after (red) PFOA adsorption.

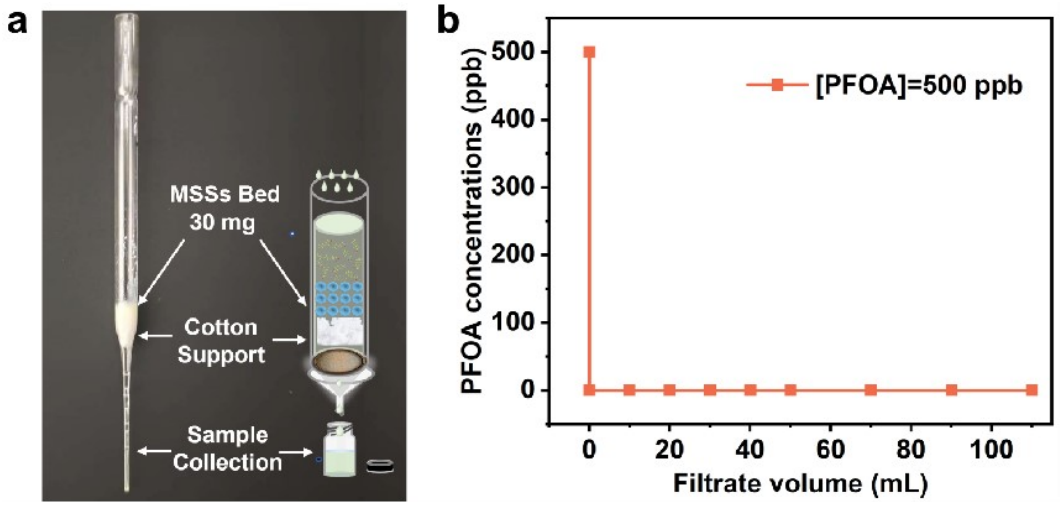

Fig. S13 (a) Schematic illustration of the PFOA dynamic adsorption experiments with the MSSs1-NH_2 column. (b) PFOA dynamic adsorption at 500 ppb PFOA concentration with water filtrate volume using the MSSs1-NH_2 column.

Table S1. Comparisons of adsorption performances for PFOA adsorption by previously reported silica-based catalysts with the MSSs1-NH_2 in this work.

Materials	Variable range	Sorption isotherm	Adsorption capacity (mg/g)	Ref.
MSSs1-NH_2	pH=3	Langmuir	775	This work
MSNs-NH_2	pH=3	Langmuir	292	This work
MCM-41-NH_2	pH=3	Langmuir	620	This work
HMSe	pH=5	Langmuir	6.2	[4]
AE-APTMS Nano-composite	pH=4	Langmuir	12.06	[5]
SBA-NH	pH = 3	Langmuir	649	[6]
Fe_3O_4@ SiO_2-NH_2&F_{13}	pH = 3	NR	13.2-111.1	[7]
OD-HMS	pH = 7	Sips	361.2	[8]
HY	pH = 7	Langmuir	33.3	[8]

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