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Amino Functionalized Ordered Mesoporous Silica SBA-15, a Rapid and Efficient Adsorbent for the Adsorption of (−)-Epigallocatechin Gallate from Green Tea Extract

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Supporting Information

Synthesis of SBA-15 with different pore size

The synthesis of SBA-15s with different pore size was prepared according to previous report[1]. In a typical synthesis of SBA-15, 1.6 g (0.32 mmol) of $EO_{20}PO_{70}EO_{20}$ (P123) and 2.2 g KCl were dissolved in 60 g of 2.0 M HCl at 40 ^oC. To this solution, 4.2 g (20 mmol) of TEOS was added under vigorous stirring. The final molar-composition of the reactants is 0.02P123/1.5 KCl/6 HCl/166 H2O/1TEOS. After stirring for 10 min, the mixture was kept in static conditions at the same temperature for one day, and then the mixture was transferred into an autoclave and heat at 100 ^oC or 140 ^oC for another 24 h. The solid product were collected by filtration and dried at 60 ^oC in air. The obtained samples were denoted as SBA-15-100 ^oC, SBA-15-140 ^oC. Sample SBA-15-40 ^oC was kept at 40 ^oC for 24 h. All materials were calcined at 350 ^oC before used.

Synthesis of SBA-15 functionalized with organic groups

Mesoporous slicas SBA-15 modified with different organic groups were prepared according to previous report[2,3]. For the synthesis of -SH, $-NH_2$ functionalized SBA-15, 0.01mol 3-mercaptopropyltrimethoxysilane or aminopropyltrimethoxysilane and 3.0 g SBA-15 were added to 60 mL toluene, the mixture was stirred at 110 ^oC for 12 h, then the solid was collected by filtration and dried at 60 ^oC in air. The obtained samples were denoted as SBA-15-SH, SBA-15-NH_2. For synthesis of SBA-15-COOH, 3-Cyanopropyltrimethoxysilane was used to modify the -CN group on the surface, and then the solid was filtrated and added to 100 mL 50% H_2SO_4 and stirred at 110 ^oC for

12 h to hydrolyze the -CN group.

Synthesis of NH_2 functionalized SBA-15 with different grafting amount.

0.0025, 0.005, 0.01mol aminopropyltrimethoxysilane and 3.0 g SBA-15-40 ^{o}C were added to 60 mL toluene, the mixture was stirred at 110 ^{o}C for 12 h, then the solid was collected by filtration and dried at 60 ^{o}C in air. The grafting amounts of amino groups were determined by element analysis.

Characterization of SBA-15s

Small angle powder XRD was conducted on Rigaku Ultima IV X ray diffraction. The BET specific surface area, average pore size, and pore volume of the SBA-15s were determined by N_2 adsorption/desorption isotherms at 77.15 K using a Micromeritics ASAP 2020 automatic surface area and porosity analyzer (Micromeritics Instrument Corp., Norcross, GA). FTIR spectra of SBA-15s were obtained on a FTIR spectrophotometer (Thermo Nicolet, NEXUS, TM) in the 3600−400 cm^{-1} region via the KBr pellet method. TEM micrographs were obtained with a Hitachi HT-7700 transmission electron microscope operating at 100 kV. Element analysis results were obtained with a Vario MICROCHN elemental analyser (EA)

Preparation of Green Tea Extract and Sample Solutions

Green tea (25 g) was refluxed with 200 mL of ethanol−water (60:40, v/v) solution at 363.15k for 1 h in triplicate. All of the extracts were filtrated and evaporated to a fluid extract by removing the solvent under reduced pressure in a rotary evaporator at 323.15 K. The obtained extracts were placed in a vacuum drying oven and dried at 313.15 K until the mass was constant. Then the dried extracts were ground to powder and stored in refrigerator at 277.15 K. Distilled water was added to obtain sample solutions of different concentrations.

Test of adsorption capacity

The adsorption capacities of EGCG and CAF on the SBA-15s were evaluated according to the following equation.

$Q= V_0 (C_0-C_e) /m$ (eq 1)

Where Q is the adsorption capacity (mg/g) toward EGCG or CAF at adsorption equilibrium.C_0 and C_e are the initial and equilibrium concentrations of EGCG or CAF solutions (mg/mL).m is the weight of SBA-15s (g).

Adsorption Kinetics

The adsorption kinetics curves of EGCG and CAF on the SBA-15s were studied according to the following operation mode: 100 mL of extract solution (C_0= 2.0 mg/mL) was incubated with 0.5 g SBA-15-NH_2s in a 250 mL flask. Then the mixture was stirring at 288.15, 298.15, and 308.15 K, respectively. Samplings (1.0 mL) were done in specific time intervals (from 0 to 200 min) after the addition of SBA-15-NH_2s. The samples were centrifuged at 5500 r/min for 10 min, and the concentration of EGCG and caffeine in the supernatants were analyzed by HPLC. In order to reveal the mechanism of the adsorption process and evaluate the performance of the adsorbents, we fit the experimental data to the pseudo-first-order (eq 2) and pseudo-second-order (eq 3) kinetic models respectively. The Intraparticle diffusion model is also employed for the porous adsorbent (eq 4).

Equation of pseudo-first-order kinetics model:

$\ln(Q_e - Q_t) = \ln Q_e - k_1 t$ (eq 2)

Equation of pseudo-second-order kinetics model:

$t/Q_t = 1/(k_2 Q_e^2) + t/Q_e$ (eq 3)

Intraparticle diffusion model:

$Qt = k_d t^{1/2}$ (eq 4)

where Qe and Qt are the adsorption capacity of EGCG or CAF onto the SBA-15 -NH_2s at equilibrium and at any time t (mg/g) respectively. The parameters k_1 (1/min), k_2 (g/(mg min^{-1})) and k_d (mg*min$^{-1/2}$/g) are the rate constants of the pseudo-first-order, pseudo-second-order and intraparticle diffusion models for the adsorption process, respectively.

Adsorption Isotherm

Extract solutions (10 mL) with different concentrations of EGCG and CAF (C_0= 1.0, 2.0, 6.0, and 8.0 mg/mL) were contacted with SBA-15-NH_2s (0.1 g) in conical flasks. The flasks were continually stirring for 3 h at 298.15 K. Then, the concentrations of EGCG and CAF in the solutions were analyzed by HPLC.

In order to describe the adsorption mechanism, we fit Langmuir (eq 5) and Freundlich (eq 6) isothermal models to the obtained data.

The Langmuir isotherm equation is represented as:

$Ce/Qe = K_L/Qm + Ce/Qm$ (eq 5)

$R_L = 1/(1 + Co/K_L)$

where Qe and Qm are the equilibrium and maximum adsorption capacity (mg/g) respectively. Ce is the equilibrium concentration of EGCG or CAF solution (mg/mL).

K_L is the parameter related to the adsorption energy (mg/mL).

The Freundlich isotherm equation is shown as:

$$\lg Qe = (1/n) \lg Ce + \lg K_F \qquad \text{(eq 6)}$$

K_F reflects the adsorption capacity of an adsorbent ($(\text{mg/g})(\text{mL/mg})^{1/n}$). The parameter n represents the adsorption affinity of the adsorbent for an adsorbate. Ce and Qe are the same as described above.

Figure S1 TEM images of SBA-15-100 ^{o}C a) before and b) after amino functionalized.

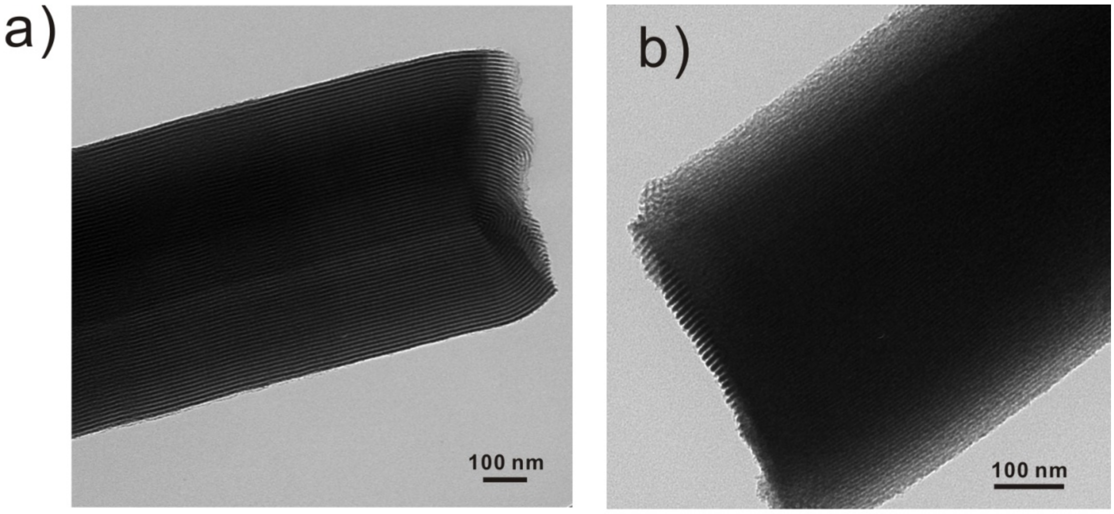

Figure S2 Pore size distributions of SBA-15-40 ^{o}C-NH$_2$, SBA-15-100 ^{o}C-NH$_2$ and SBA-15-140 ^{o}C-NH$_2$.

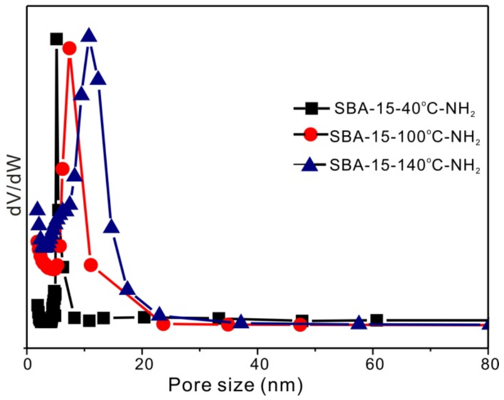

Figure S3 Intraparticle diffusion plots for the adsorption of EGCG on SBA-15-NH_2 with different pore size.

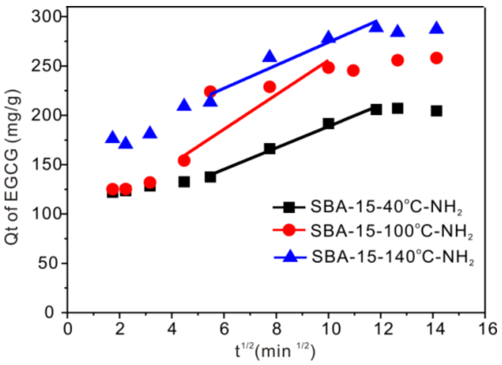

Table S1. Physiochemical characterization of SBA-15s and SBA-15 functionalized with different organic groups.

Samples	Surface area (m^2/g)	Pore diameter /(nm)	Pore volume (m^3/g)
SBA-15-40°C(-OH)	508.8	5.0	0.37
SBA-15-40 °C-SH	452.3	4.7	0.35
SBA-15-40°C-COOH	402.0	4.8	0.36
SBA-15-40 °C-NH_2	193.2	4.8	0.220
SBA-15-100°C-NH_2	389.9	7.4	0.55
SBA-15-140°C-NH_2	280.4	10.7	0.50

Table S2. The element analysis of SBA-15 functionalized with different organic groups.

Samples	N/%	C/%	H/%
SBA-15-40^{o}C(-OH)	0	1.16	1.88
SBA-15-40 ^{o}C-SH	0.04	2.19	1.84
SBA-15-40^{o}C-COOH	0.04	3.45	1.65
SBA-15-40 ^{o}C-NH_2(5%)	1.20	3.32	2.20
SBA-15-40 ^{o}C-NH_2(10%)	2.02	5.73	2.58
SBA-15-40 ^{o}C-NH_2(20%)	3.23	9.22	2.94
SBA-15-100 ^{o}C-NH_2(20%)	2.03	5.97	2.26
SBA-15-140 ^{o}C-NH_2(20%)	1.71	4.87	1.85

Reference

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2. Walcarius, A.; Etienne, M.; Lebeau, B., Rate of Access to the Binding Sites in Organically Modified Silicates. 2. Ordered Mesoporous Silicas Grafted with Amine or Thiol Groups. *Chem. Mater,* 2003, **15** (11), 2161-2173.

3. Ho, K. Y.; McKay, G.; Yeung, K. L., Selective Adsorbents from Ordered Mesoporous Silica. *Langmuir,* 2003, **19** (7), 3019-3024.