Fabrication of SiO_2@COF5 microspheres and its application in high performance liquid chromatography

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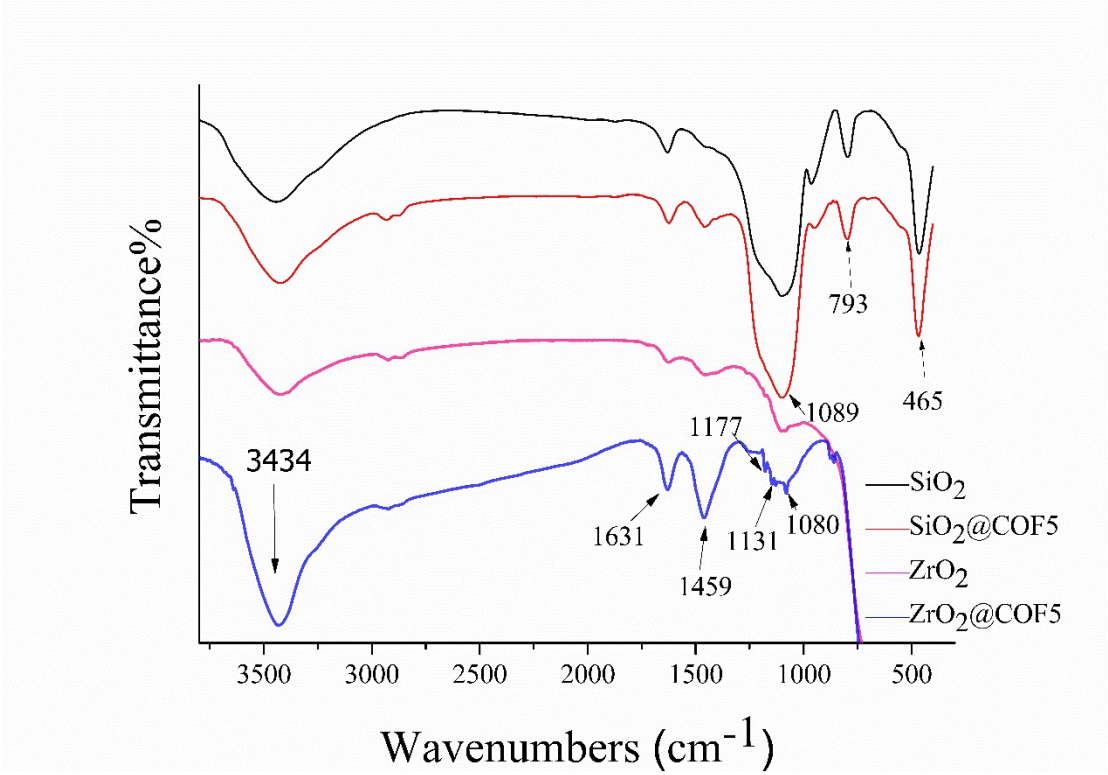

Figure S1. FTIR spectra of SiO_2, SiO_2@COF5,ZrO_2 and ZrO_2@COF5

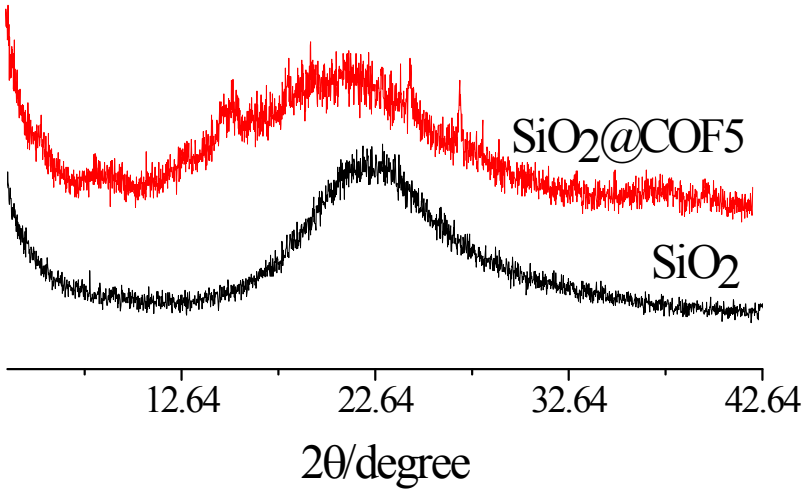

Figure S2. PXRD patterns of SiO_2 and SiO_2@COF5.

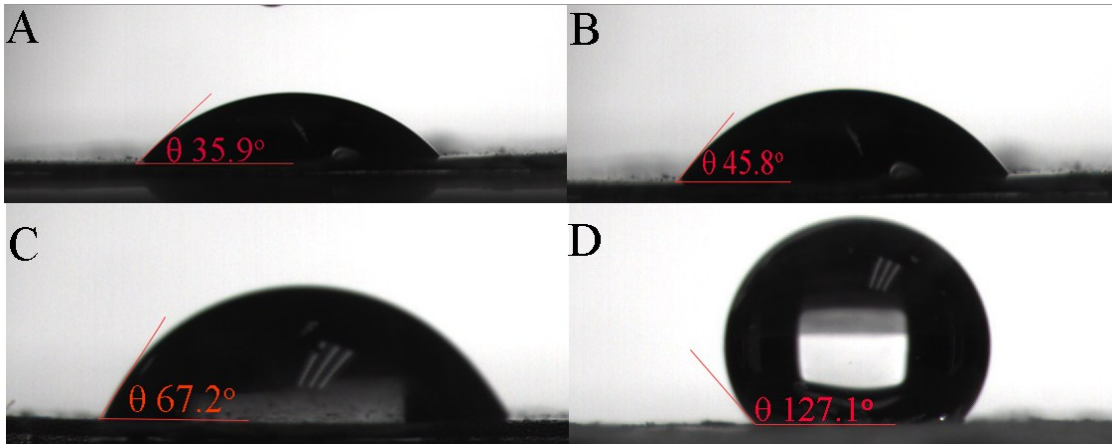

Figure S3. Water contact angels of (A) SiO_2, (B) SiO_2@APB, (C) SiO_2@COF5, and (D) C18.

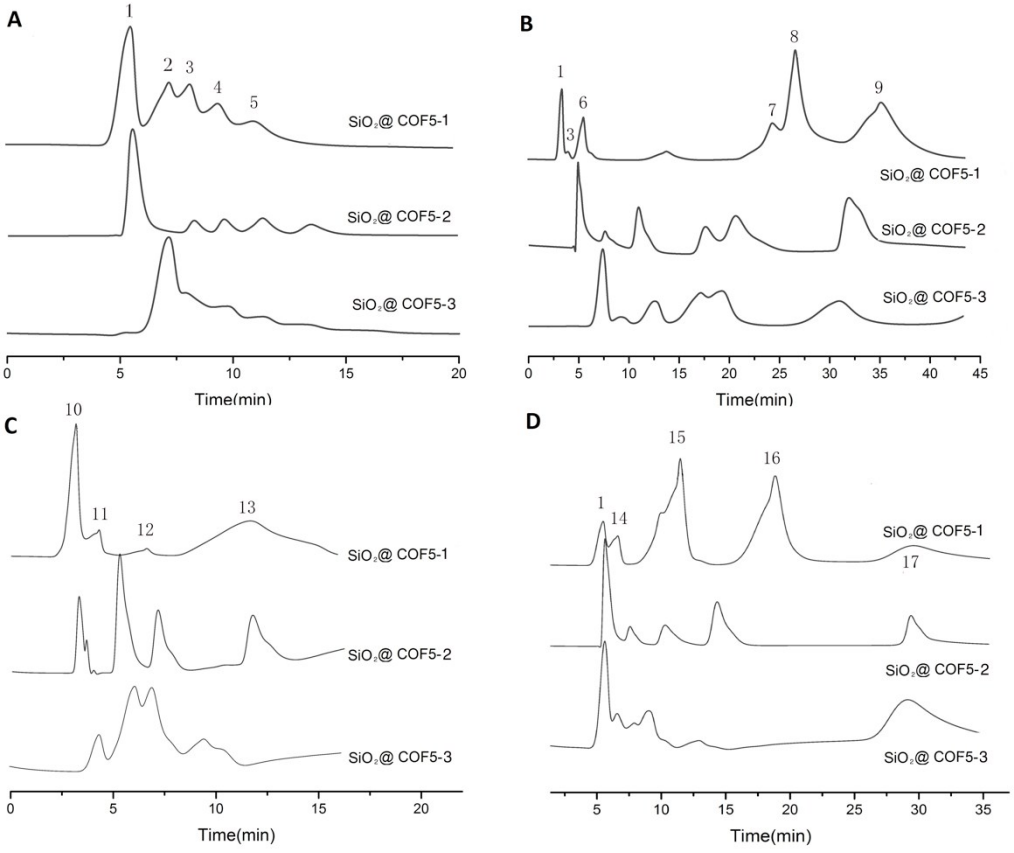

Figure S4. Chromatograms of alkyl benzenes, polycyclic aromatic hydrocarbons, anilines and acetophenones on the SiO_2@COF5-1 packed column, SiO_2@COF5-2 packed column, SiO_2@COF5-3 packed column. Conditions: flow rate: 0.1 mL·min^{-1}; UV wavelength: 254 nm; temperature: 25℃. Mobile phase: ACN-NH_4AC (pH=7.05), (A) 15% ACN; (B) 0–21 min, 20–40% ACN, 21–45 min, 40% ACN; (C) 0–8 min, 10–35% ACN, 8–16 min, 35% ACN; (D) 0–10 min, 10–20% ACN, 10–12 min, 20–35% ACN，12–35 min, 35% ACN. Samples: 1. thiourea, 2. benzene, 3. methylbenzene, 4. ethylbenzene, 5. cumene, 6. naphthalene, 7. acenaphthene, 8.

fluorene, 9. phenanthrene, 10. 2-aminoterephthalic acid, 11. aniline, 12. p-nitroaniline, 13. 1-naphthylamine, 14. phenol, 15. 2,4-dihydroxyacetophenone, 16. 1-(4-methylphenyl)-ethanone, 17. benzophenone.

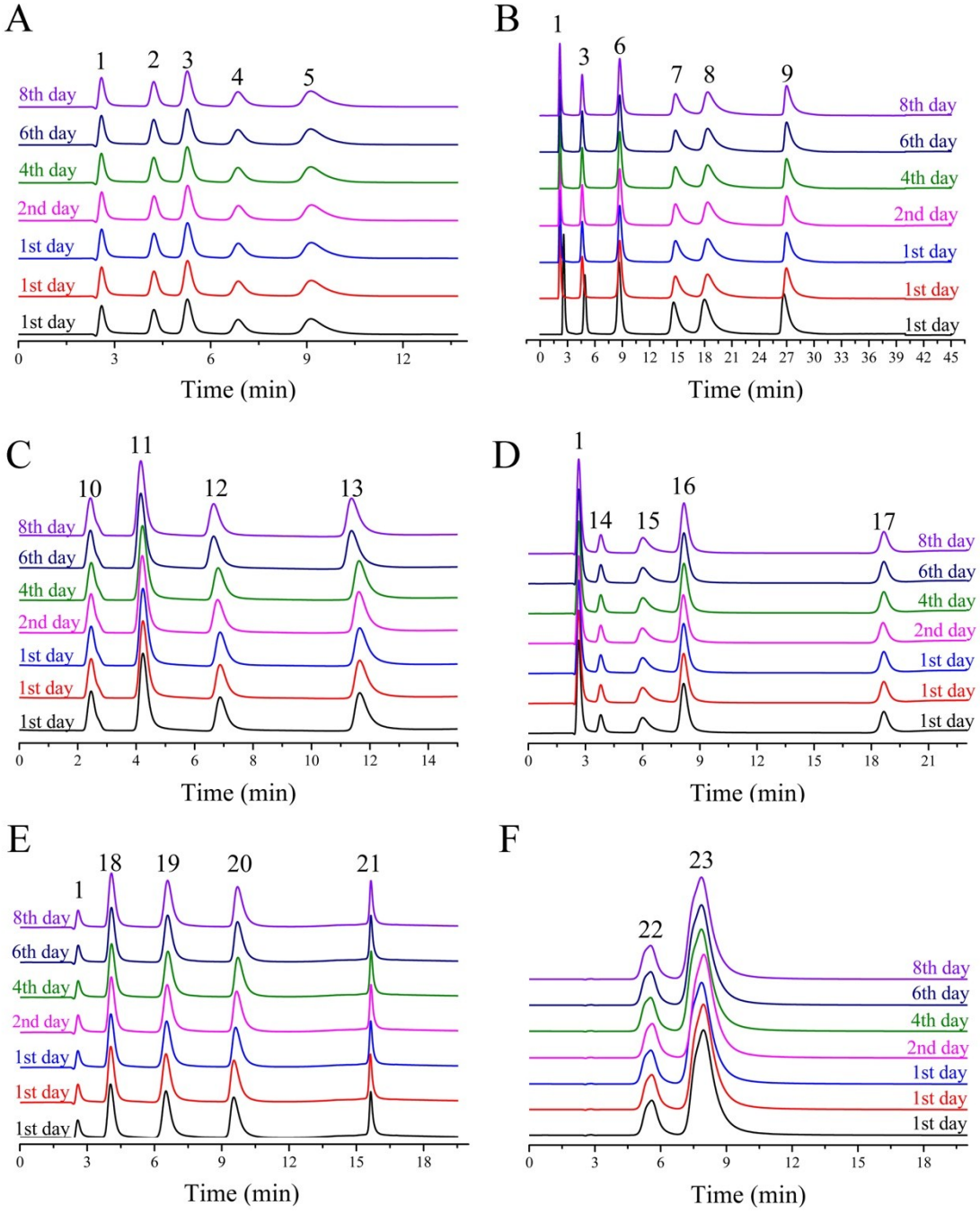

Figure S5. HPLC chromatograms on the SiO_2@COF5 packed column (150 mm ×2.1 mm). Conditions: flow rate: 0.2 mL·min^{-1}; UV wavelength: 254 nm; temperature: 25℃. Mobile phase: ACN-NH_4AC (pH=7.05), (A) 15% ACN; (B) 0–21 min, 20–40% ACN, 21–45 min, 40% ACN; (C) 0–8 min, 10–35% ACN, 8–16 min, 35% ACN; (D) 0–10 min, 10–20% ACN, 10–12 min, 20–35% ACN，12–21 min, 35% ACN. (E) 0–12 min, 10–60% ACN，12–19 min, 60% ACN; (F) 15% ACN. (A) 1. thiourea, 2. benzene, 3. methylbenzene, 4. ethylbenzene, 5. cumene; (B) 1. thiourea, 3.

methylbenzene, 6. naphthalene, 7. acenaphthene, 8. fluorene, 9. phenanthrene; (C) 10. 2-aminoterephthalic acid, 11. aniline, 12. p-nitroaniline, 13. 1-naphthylamine; (D) 1. thiourea, 14. Phenol, 15. 2,4-dihydroxyacetophenone, 16. 1-(4-methylphenyl)-ethanone, 17. Benzophenone; (E) 1. thiourea, 18. p-hydroxybenzaldehyde, 19. p-methoxybenzaldehyde, 20. p-dimethylaminobenzaldehyde, 21. 4- (N, N-diphenylamino) benzaldehyde;22.3-hydroxyacetophenone, 23.2-hydroxyacetophenone.

Table S1 Values of ΔH, ΔS, ΔG and correlation coefficients for alkyl benzenes and polycyclic aromatic hydrocarbons on commercial C18 column.

solutes	ΔH (kJ·mol^{-1})	ΔS (J·K^{-1}·mol^{-1})	ΔG (kJ· mol^{-1})	R^2
benzene	-2.8± 0.3	6.8 ± 0.9	-4.8 ± 0.6	0.961
toluene	-2.8 ± 0.2	10.3± 0.7	-5.9 ± 0.4	0.971
ethylbenzene	-2.8± 0.2	13.7 ± 0.6	-6.9 ± 0.4	0.984
cumene	-2.9± 0.2	16.1± 0.8	-7.7± 0.4	0.974
naphthalene	-3.7± 0.1	9.7 ± 0.1	-6.7 ± 0.1	0.980
acenaphthene	-4.3± 0.1	12.5 ± 0.1	-8.2 ± 0.1	0.995
fluorene	-5.0 ± 0.1	11.7 ± 0.1	-8.6 ± 0.1	0.997

Table S2 Capacity factor, asymmetry, the number of theoretical plates and resolution factors of different analytes on SiO_2@COF5 packed column and commercial C18 column.

Analytes	SiO_2@COF5 packed column				commercial C18 column			
	k'	As	N (plates m^{-1})	Rs	k'	As	N (plates m^{-1})	Rs
thiourea	—	2.15	6226	—	—	1.86	6619	—
benzene	0.83	1.58	11815	4.43	0.43	1.19	21182	4.77
methylbenzene	1.28	1.69	13529	2.42	0.59	1.17	2317	2.36
ethylbenzene	1.96	1.93	11711	2.83	0.78	1.17	22145	2.42
cumene	2.94	2.58	6704	2.53	0.97	1.97	24662	2.38
naphthalene	2.70	1.79	16121	6.95	2.92	1.25	23086	—
acenaphthene	5.31	3.80	10098	5.50	3.58	1.14	24265	4.85
fluorene	6.82	3.19	7351	1.91	6.40	1.07	33387	3.32
phenanthrene	10.46	4.45	46287	4.90	8.99	1.03	34536	3.65
2-aminoterephthalic acid	0.18	1.82	2820	2.69	0.18	0.36	9143	—
aniline	0.81	1.91	7018	2.97	0.41	0.51	22034	0.87
p-nitroaniline	1.94	2.33	10679	2.50	0.47	1.11	14819	2.08
1-naphthylamine	4.01	3.16	24778	13.84	0.67	1.26	10830	3.10
phenol	0.61	1.30	6938	—	0.39	1.14	33705	—
2,4-dihydroxyacetophenone	1.54	3.31	3778	2.97	0.56	1.27	36653	2.68
1-(4-methylphenyl)-ethanone	2.45	1.73	13975	2.50	0.88	1.19	42917	4.64
benzophenone	6.89	1.72	56728	13.84	1.43	1.10	39961	6.57
p-hydroxybenzaldehyde	0.75	1.75	6323	3.34	0.34	1.14	30066	—
p-methoxybenzaldehyde	1.83	1.96	9974	4.15	0.70	1.21	12139	3.85
p-dimethylaminobenzaldehyde	3.16	2.50	18935	4.42	1.20	1.14	40431	4.63

4-(N,N-diphenylamino)benzaldehyde	5.76	2.08	352495	12.15	1.56	1.36	46491	2.75
3-hydroxyacetophenone	1.35	0.74	1450	—	0.35	0.79	23095	—
2-hydroxyacetophenone	2.33	1.19	2259	2.04	0.69	1.23	19783	3.7

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90 Table S3. The comparison of SiO_2@COF5 microspheres to other COF materials

91 reported as stationary phase for chromatograph.

Materials	**Method**	**Surface area (m^2g^{-1})**	**Type**	***k′***	**R**				**N (plates m^{-1}, analytes)**	**Ref**
				alkyl benzenes, PAHs, basic, isomers	**alkyl benzenes**	**PAHs**	**basic molecules**	**isomers**		
LZU1	CEC	—	capillary column	—		—	—	—	7085-214106 (alkyl benzenes)	32
COF5	CEC	—	capillary column	—	2.2-3.3		—	—	50004-275467 (acid**molecules**)	33
TpBD@ SiO_2	HPLC	385	particulate - packedcolumn	3.8-5.4	—	—	—	—	—	34
TpPa-MA-co-EDMA	HPLC	224	monolithic column	0.6-7.8	—	4.7-5.4	1.6-1.8	—	17651-20920 (neutral molecules)	35
CTF–SiO_2	HPLC	359	particulate –packed column	0.5-3.6	0.7-3.6	—	1.4-2.3	1.3-2.0	21700-25600 (neutral molecules)	36
C18	HPLC	—	particulate –packed column	1.3-9.0	4.77	3.6-4.9	0.9-3.10	3.7	2317-46491	This work
SiO_2@ COF5	HPLC	374	particulate –packed column	0.6-10.5	2.5-4.4	1.90-7.0	2.3-6.6	1.5	6323-352495	This work

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