New Journal of Chemistry

Electronic Supplementary Material

Ionic Liquids Functionalized Graphene Quantum Dots-Bonded Silica as Multi-Mode HPLC Stationary Phase with Enhanced Selectivity for Acid compounds

Qi Wu [1,2], Yaming Sun [1,2], Jie Gao [1,2], Lixiao Chen [1,2], Shuqing Dong [1], Guoying Luo [1], Hui Li [1], Litao Wang[3], Liang Zhao [1,*]

[1] Key Laboratory of Chemistry of Northwestern Plant Resources and Key laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

[2] University of Chinese Academy of Sciences, Beijing 100039, China

[3] Department of Pharmacy, Jining Medical University, Rizhao, Shandong, China

* Correspondence author. Tel.: +86 931 4968261; fax: +86 931 8277088

Address: No.18, Tianshui Middle Road, Lanzhou, China.

E-mail address: zhaol@licp.cas.cn

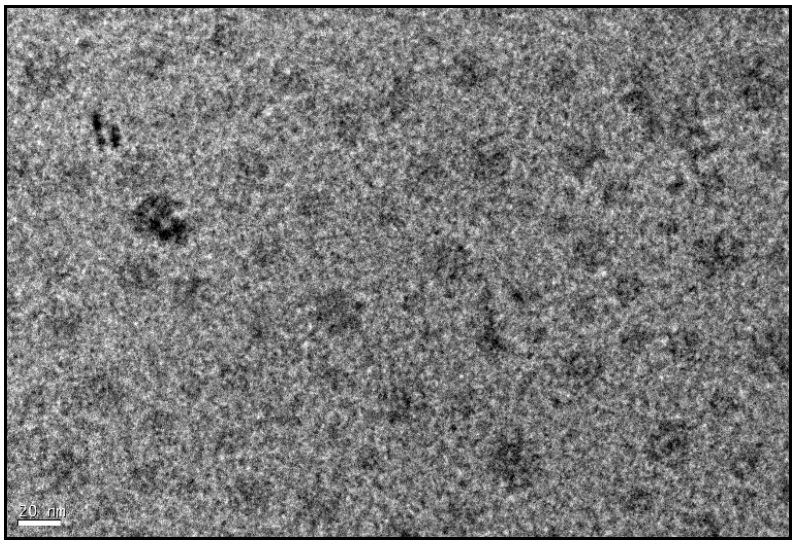

Fig. S1 TEM image of the prepared GQDs

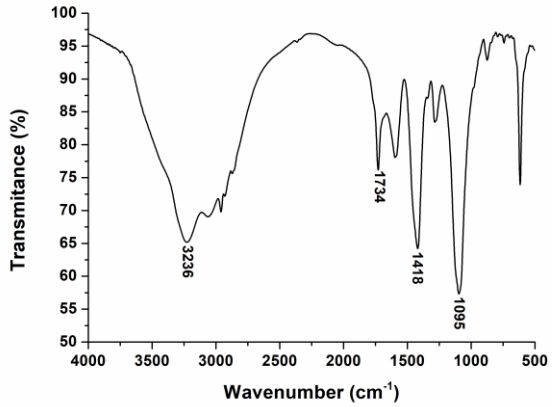

Fig. S2 FTIR spectra of the prepared GQDs

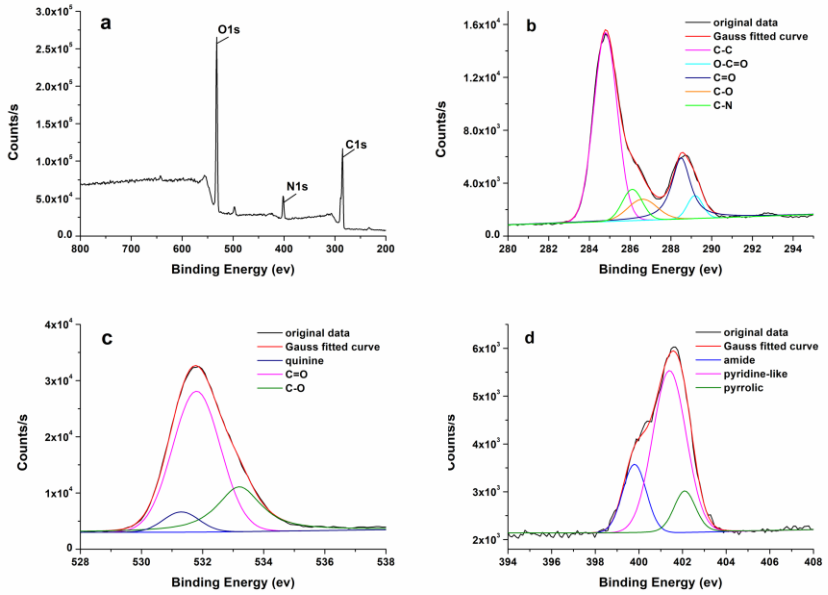

Fig. S3 XPS spectra of the prepared GQDs. (a) survey spectra; (b) C1s spectra; (c) O1s spectra; (d) N1s spectra

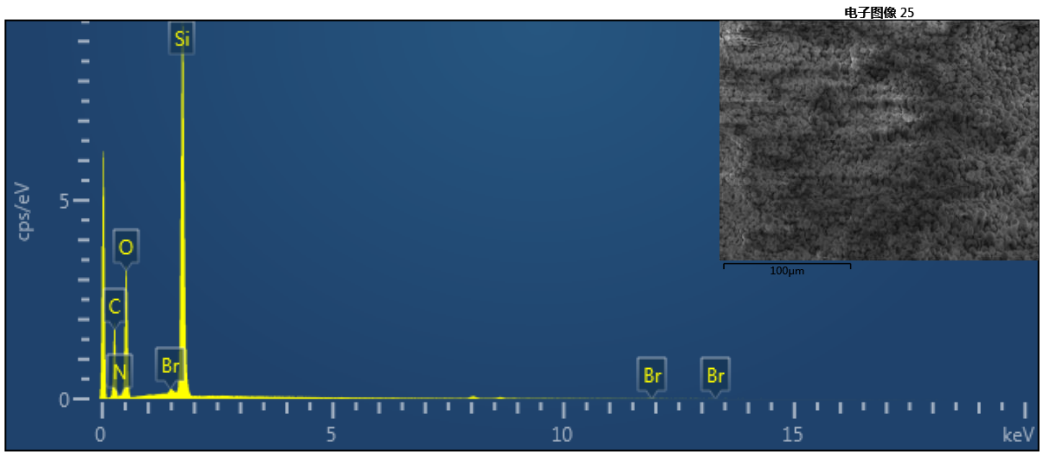

Fig. S4 EDS spectra of the prepared ILs/GQDs/SiO_2 composite

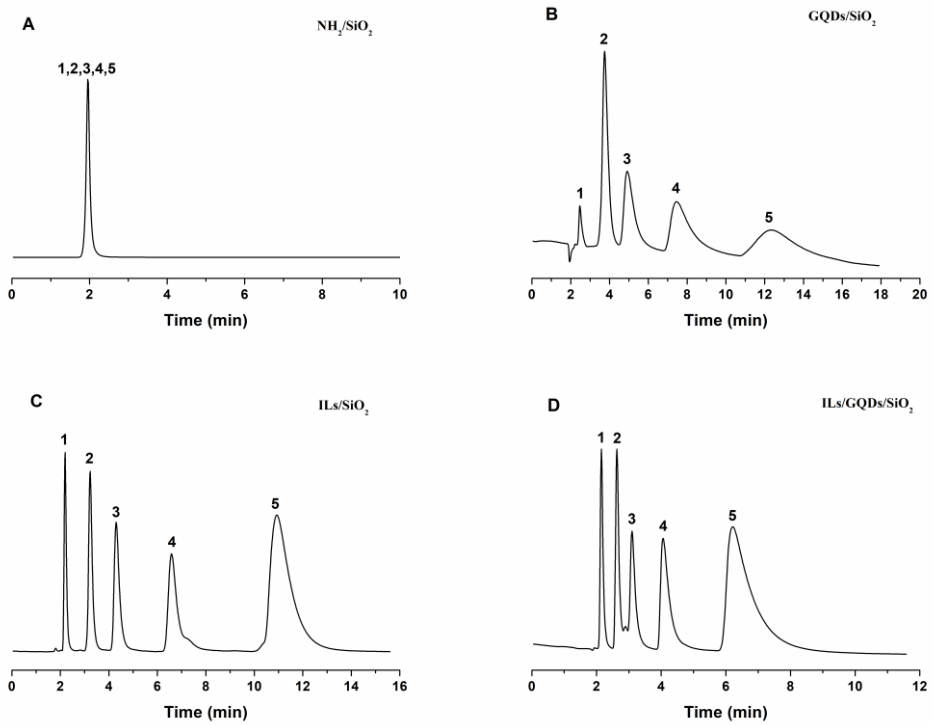

Fig. S5 Chromatograms for the separation of five PAHs on NH_2/SiO_2 column (A), GQDs/SiO_2 column (B), ILs/SiO_2 column (C) and ILs/GQDs/SiO_2 column (D). Analytes: (1) benzene, (2) naphthalene, (3) fluorene, (4) anthracene, (5) pyrene; mobile phase: (A) (C) (D) methanol/water (60/40, v/v), (B) methanol/water (40/60, v/v); flow rate: 1.0 mL min^{-1}; UV detection: 254 nm

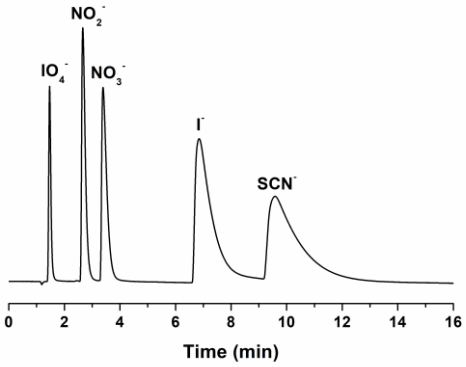

Fig. S6 Chromatography of separation of test mixture composed of: periodate (1); nitrite (2); nitrate (3); iodate (4) and thiocyanate (5). Mobile phase: 0.1 M phosphate buffer solution (pH 6.8); Flow-rate: 1.5 mL/min; Detection: UV at 200 nm.

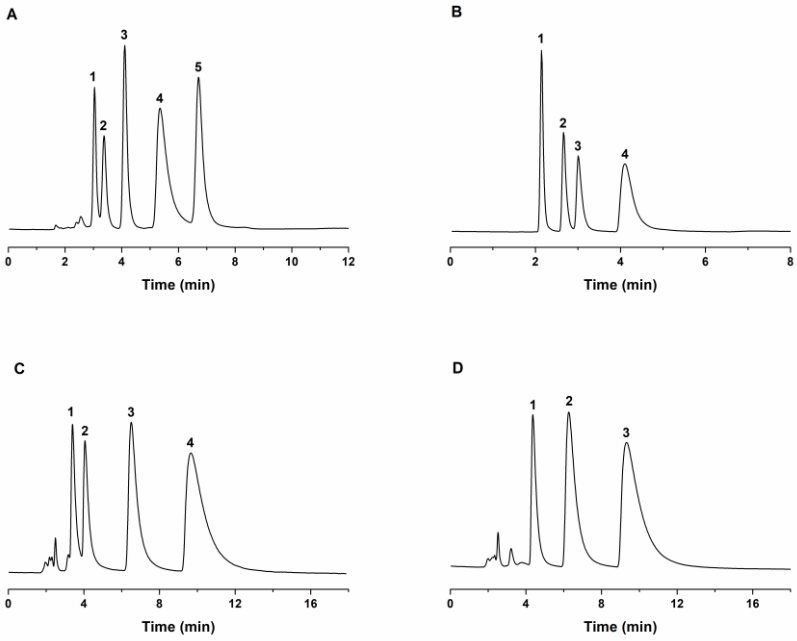

Fig. S7 Chromatograms for the separation of phenols (A), PAHs (B), amines (C) and nitroaniline isomers (D) on ILs/GQDs/SiO_2 column. Analytes: (A) (1) p-tert-butylphenol, (2) 3,5-dimethylphenol, (3) phenol, (4) 2-aminophenol, (5) p-nitrophenol; (B) (1) benzene, (2) naphthalene, (3) fluorene, (4) anthracene; (C) (1) 3,4-dimethylaniline, (2) aniline, (3) m-nitroaniline, (4) p-nitroaniline; (D) (1) o-nitroaniline (2) m-nitroaniline, (3) p-nitroaniline; mobile phase: (A) isopropanol/ n-hexane (30/70, v/v), (B) isopropanol/ n-hexane (0.5/95.5, v/v), (C) (D) isopropanol/ n-hexane (60/40, v/v); flow rate: 1.0 mL min^{-1}; UV detection: 254 nm

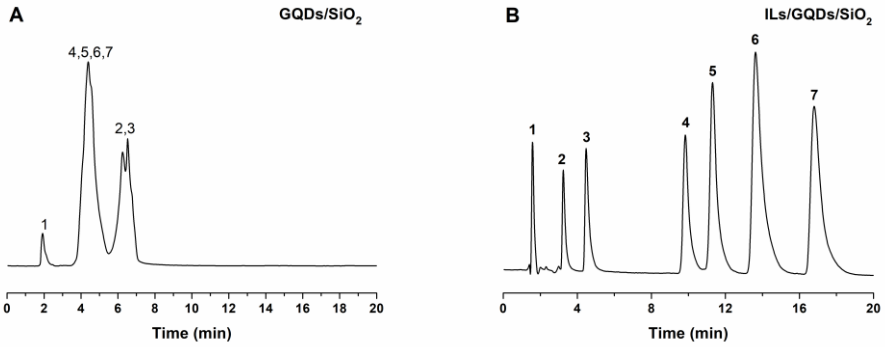

Fig. S8 Chromatograms of aromatic acids separated on GQDs/SiO_2 column (A) and ILs/GQDs/SiO_2 column (B). Analytes: (1) anthracene-9-aromatic acid, (2) phenylalanine, (3) tyrosine, (4) p-nitrobenzoic acid, (5) m-nitrobenzoic acid, (6) cinnamic acid, (7) benzoic acid; mobile phase: (A) acetonitrile/10 mM ammonium acetate (90/10, v/v), (B) acetonitrile/20 mM ammonium acetate (70/30, v/v); flow rate: 1.0 mL min^{-1}; UV detection: 254 nm

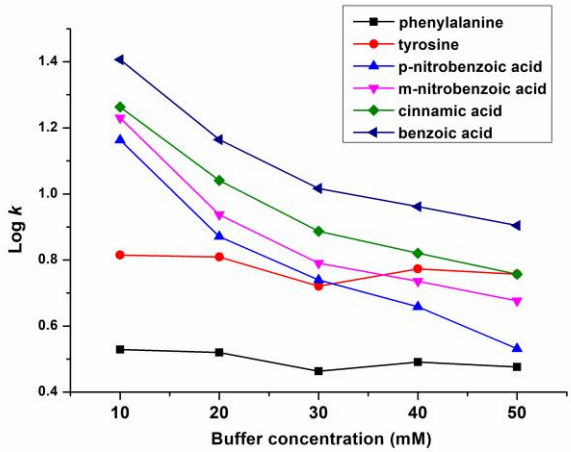

Fig. S9 Plot of log *k* versus buffer concentration. Mobile phase: 80% acetonitrile/20% ammonium acetate (10-50 mM), pH 6.8, flow rate: 1.0 mL min^{-1}

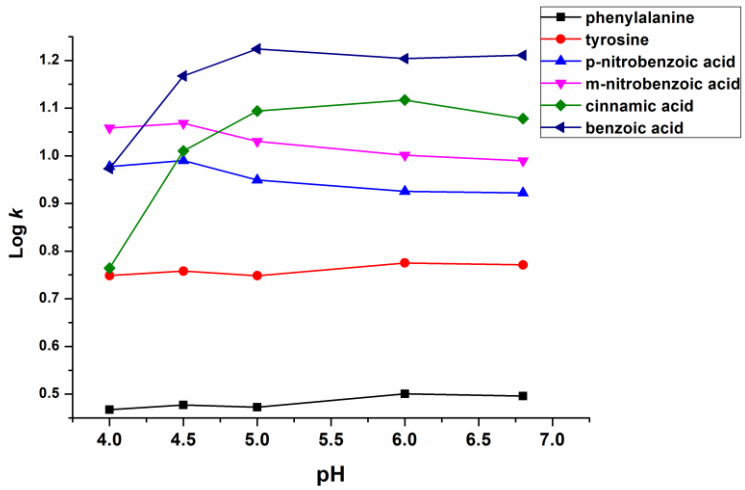

Fig. S10 Plot of log *k* versus buffer pH. Mobile phase: 80% acetonitrile/20% 20 mM ammonium acetate, flow rate: 1.0 mL min^{-1}.

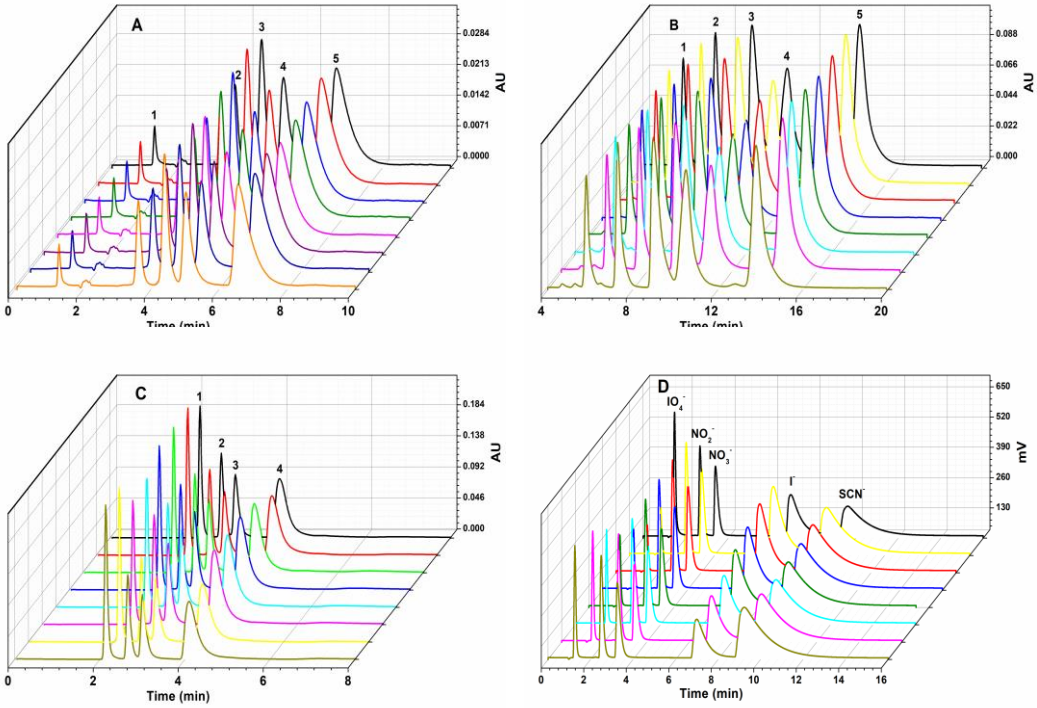

Fig. S11 The run-to-run repeatability tests of ILs/GQDs/SiO_2 column in RP (A), HILIC (B), NP (C) and IEC (D) modes. The test compounds and chromatographic conditions were identical to Fig. 5, Fig. 8B, Fig. S7B, and Fig. S6.

Table S1 LSER solutes, their descriptors and retention factors.

	Compound	E	S	A	B	V	D^-	D^+	Acid p*K*	Basic p*K*	Log *k*
1	Uridine	0.90	2.29	2.35	1.88	1.58	0.00	0.00	9.70		0.2902
2	Cytidine	2.09	2.21	0.87	2.62	1.62	0.00	0.02		4.40	0.5725
3	Cytosine	1.43	1.90	0.60	1.02	0.79	0.00	0.02		4.40	0.3906
4	Uracil	0.81	1.00	0.44	1.00	0.75	0.00	0.00	9.70		0.0354
5	Caffeine	0.50	1.72	0.05	1.28	1.36	0.00	0.00			-0.5137
6	Theophylline	1.50	1.60	0.54	1.34	1.22	0.00	0.00	8.70		-0.1809
7	Theobromine	1.50	1.60	0.50	1.38	1.22	0.00	0.00	9.90		-0.1380
8	Pyridine	0.63	0.84	0.00	0.52	0.68	0.00	0.07			-0.4722
9	Aniline	0.96	0.96	0.26	0.41	0.82	0.00	0.02		4.60	-0.8386
10	Phenol	0.81	0.89	0.60	0.30	0.78	0.00	0.00	10.30		-0.7084
11	Resorcinol	0.98	1.11	1.09	0.52	0.83	0.00	0.00	9.60		-0.3702
12	4-Nitrophenol	1.07	1.72	0.82	0.26	0.95	0.09	0.00	7.20		-0.7379
13	Phloroglucinol	1.36	1.12	1.40	0.82	0.89	0.00	0.00	9.00		0.0514
14	Pyrocatechol	0.97	1.07	0.88	0.47	0.83	0.00	0.00			-0.4685
15	Benzoic acid	0.73	0.90	0.59	0.40	0.93	0.99	0.00	4.10		0.3749
16	Cinnamic acid	1.14	1.00	0.58	0.57	1.17	0.99	0.00	4.20		0.1939
17	Ferulic acid	1.11	1.46	0.85	0.87	1.43	0.99	0.00	4.20		0.3759
18	p-Coumaric acid	1.13	1.39	1.07	0.79	1.23	0.99	0.00	4.20		0.4464
19	Salicylic acid	0.89	0.84	0.71	0.38	0.99	1.00	0.00	3.00		0.4838
20	Acetylsalicylic acid	0.78	0.80	0.49	1.00	1.29	1.00	0.00	3.50		0.4505
21	Tyrosine	1.18	1.60	1.28	1.29	1.37	1.00	1.00	2.10	9.10	0.7440
22	Phenylalanine	0.78	1.02	1.39	0.95	1.31	1.00	1.00	2.10	9.10	0.4558
23	Tryptophan	1.62	1.80	1.09	1.23	1.54	1.00	1.00	2.10	9.10	0.5241
24	Anisole	0.71	0.75	0.00	0.29	0.92	0.00	0.00			-1.4559
25	2-Naphthol	1.52	1.08	0.61	0.40	1.14	0.00	0.00			-0.9234
26	Nitrobenzene	0.87	1.11	0.00	0.28	0.89	0.00	0.00			-1.3399
27	Chlorobenzene	0.72	0.65	0.00	0.07	0.84	0.00	0.00			-1.4834

Table S2 Repeatability of ILs/GQDs/SiO_2 column.

	RSD (%)			
	RP[a]	NP[b]	HILIC[c]	IEC[d]
run-to-run (n=8)	0.60-0.83	0.86-1.31	0.25-0.39	0.90-1.28
day-to-day (n=3)	0.71-0.92	0.95-1.34	0.36-0.47	0.79-1.32

[a] The tested compounds and experimental condition were identical to Fig. 5

[b] The tested compounds and experimental condition were identical to Fig. S7B

[c] The tested compounds and experimental condition were identical to Fig. 8B

[d] The tested compounds and experimental condition were identical to Fig. S6