

Electronic supplementary information

Zeolite silica nanoparticles-supported open-tubular columns for isomer and chiral separation using capillary electrochromatography coupled with amperometric detection

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Synthesis and characterization of zeolite SiO₂NPs

Zeolite SiO₂NPs were prepared as described in the literature.¹ In a typical process, TPAOH, TEOS and deionized water were mixed firstly according to a certain molar ratio and hydrolyzed for a certain time at room temperature; then, the hydrolysate ethanol was evaporated in a water bath; finally, the white powder zeolite SiO₂NPs could be obtained by a series of filtration, washing and baking after hydrothermal crystallization. Two diameter sizes of zeolite SiO₂NPs (S-1, 50 nm; S-2, 400 nm) were selectively prepared in a certain molar ratio of TPAOH, TEOS, and deionized water, respectively.

The XRD patterns were collected on a Rigaku Ultima IV diffractometer with Cu-K α radiation ($\lambda=1.5405 \text{ \AA}$) in the 2θ angle ranging from 5 to 35°. The X-ray powder diffraction patterns of samples were shown in Fig. S1A. All the diffraction peaks of synthetic samples were in accordance with those of the standard sample of MFI, and there were no other peaks, which indicated that there were no mixed crystal phases, and that high purity of zeolite SiO₂NPs could be synthesized successfully at two different mole ratios of TPAOH, TEOS and deionized water. The SEM as shown in Fig. S1B further demonstrated that uniform zeolite SiO₂NPs with average crystallite sizes of 50 and 400 nm could be obtained when changing the molar ratio of TPAOH, TEOS, and deionized water.

References

1 B.J. Schoeman, *Micropor. Mesopor. Mat.*, 1998, **22**, 9-22.

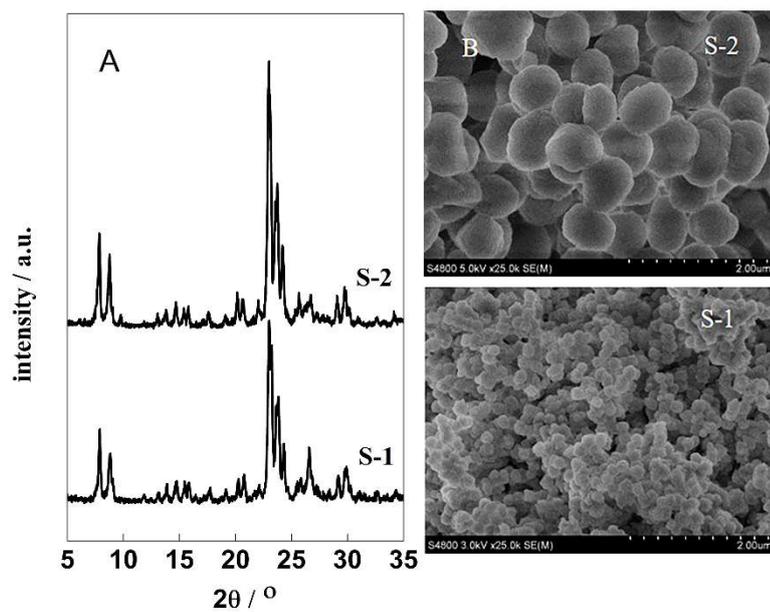


Fig. S1. (A) XRD and (B) SEM of zeolite SiO₂NPs with different diameters

The zeta potential values of zeolite SiO₂NPs at different pH values (3.00-11.00) was measured on a Zetasizer Nano ZSE instrument as shown in Fig. S2. Zeolite SiO₂NPs dispersions were prepared with 10 mM borate buffer adjusted by 0.1 M HCl or 0.1 M NaOH, respectively.

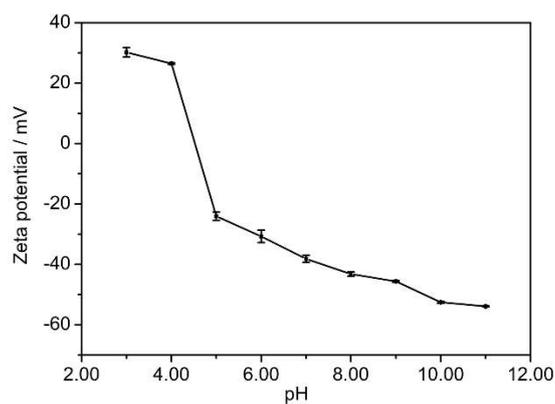


Fig. S2. Effects of pH values of the running buffer on the zeta potential values of zeolites SiO₂NPs. Experimental conditions: concentration of zeolites SiO₂NPs, 0.5 mg·mL⁻¹; and running buffer, 10 mM borate buffer (pH 3.00-11.00).

Optimization of heat time of Zeolite SiO₂NPs-OT column

The effects of heat time (1-4 h) for zeolite SiO₂NPs-OT columns on the resolution were also investigated, and propylparaben isomers were selected as the model molecules. The resolutions of propylparaben isomers on the zeolite SiO₂NPs-OT column with different heat time were shown in Fig. S3. The results showed with increasing the heat time, the resolution of the model isomers improved; the maximum resolution ($R=1.6$) was obtained when the heat time was maintained at 3 h. Therefore, 3 h was chosen as the optimal heat time.

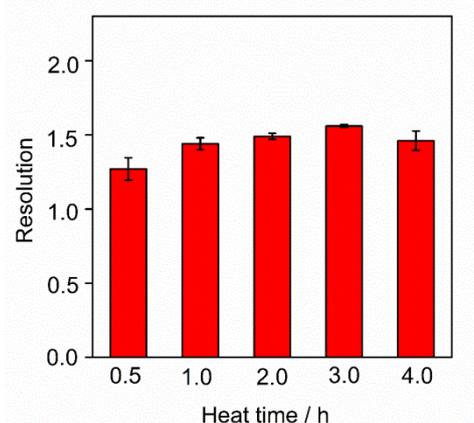


Fig. S3. Effects of heat time on the resolution of propylparaben isomers. Experimental conditions: running buffer, 80 mM borate buffer (pH 8.00); the length of OT column, 30 cm; separation voltage, 5 kV; injection time, 8 s (at 5 kV); working electrode, 300 μm diameter carbon-disk electrode; oxidation potential, +0.95 V (vs. SCE).

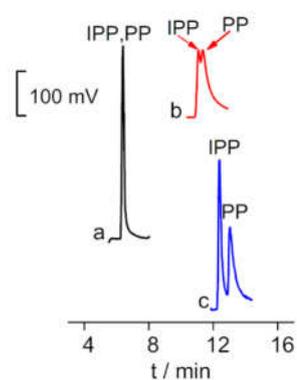


Fig. S4. Electropherograms of PP and IPP on (a) the bare capillary and zeolite SiO₂NPs-OT columns coated with (b) 400 nm and (c) 50 nm zeolite SiO₂NPs, respectively. The concentration of zeolite SiO₂NPs was 5.0 mg·mL⁻¹, and the other electrophoretic conditions were the same as Fig. S2.

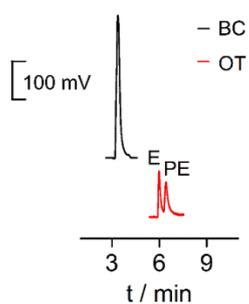
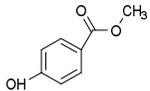
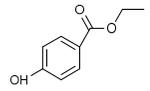
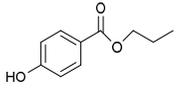
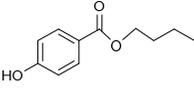
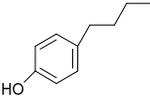
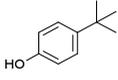
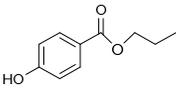
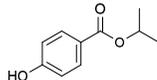
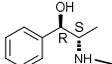
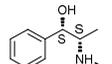
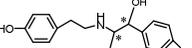
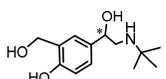


Fig. S5. Comparative electropherograms of E and PE in the BC and OT chiral columns. CE conditions: 10 mM borate buffer (pH 9.00); separation voltage, 5 kV; injection time, 8 s (at 5 kV); the length of OT column, 30 cm; working electrode, 300 μm diameter carbon-disk electrode; oxidation potential, +0.95 V (vs. SCE).

Table S1. Information of selected model molecules, resolution and their calculated theoretical plates based on this proposed method ^a

Model molecules	CAS No.	Structure	p <i>K</i> _a	Number of theoretical plates (m ⁻¹)	Resolution
Paraben homologous	MP (1)		8.31	107963	
	EP (2)		8.31	97690	<i>R</i> _{1/2} =4.9
	PP (3)		8.23	33433	<i>R</i> _{2/3} =2.6
	BP (4)		8.22	17633	<i>R</i> _{3/4} =1.9
Branched isomers	n-BP		10.11	39770	1.5
	t-BP		10.13	7433	
	PP		8.23	33433	1.6

	IPP	4191-73-5		8.40	77276	
Position isomers	3-Cl-4-MA (1)	95-74-9		3.97	80930	
	4-Cl-2-MA (2)	95-69-2		3.81	108200	$R_{1/2}=3.7$
	5-Cl-2-MA (3)	95-79-4		3.39	96510	$R_{2/3}=11.6$
Conformational isomers	MI	87-89-8		12.63	71050	1.6
	DI	643-12-9		12.63	84720	
Epimers	E	299-42-3		13.96	15270	1.6
	PE	90-82-4		13.96	10652	
Enantiomers	RIT	23239-51-2		/	26271/20499	1.8
	SAL	18559-94-9		9.99	14157/11622	1.5

^a The related information was cited from the web of <https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf>.

Table S2. Comparison of different OT-CEC methods for analysis of E and PE

Material	Column (id × effective length)	Detector	Running buffer	Analytical time /min	Real sample	LODs / ng·mL ⁻¹	Recovery	Performance	Ref.
Graphene oxide	75 μm×38 cm	UV	60 mM PBS - 10 mM SDS - 20%v/v methanol 10 mM borate -	15	Ephedra	605	/	Retention time: <2.05 % peak areas: <17.91 %	29
Homochiral MOFs	75 μm×30 cm	UV	15% v/v methanol (pH 9.3)	3	/	/	/	E: 12580 plates.m ⁻¹ PE: 9558 plates.m ⁻¹	34
Homochiral MOFs	100 μm×21 cm	DAD	75 mM borate (pH 9.4)	< 3	Ephedra	100	/	Retention time: < 2.65 % peak areas: < 4.52 %	33
Graphene oxide modified tentacle-ty- pe polymer	75 μm×41.5 cm	PDA	30 mM Na ₂ HPO ₄ - 50% v/v methanol (pH 8.5)	10	/	/	/	E: 184397 plates.m ⁻¹ PE: 196901 plates.m ⁻¹	35
Zeolite SiO ₂ NPs	50 μm×30 cm	AD	15 mM borate (pH 9.0)	< 8	Ephedra	29.2-55.1	86.4 – 105.8 %	Retention time: < 6.1 % peak areas: < 8.4 % E: 15270 plates.m ⁻¹ PE: 10652 plates.m ⁻¹	In this work

Table S3. Comparison of silica materials as stationary phases in CEC

Material	Partical size /nm	Column type (id × effective length)	Analyte	Analytical time /min	Detector	Performance	Ref.
PDMAEMA modified fibrous mesoporous SiO ₂ NPs ^a	200-300	OT column (50 μm×45 cm)	Three neutral molecules seven egg white proteins	20-40	UV	Retention time: <3.7% naphthalene: 76290 plates·m ⁻¹	[12]
Graphene / graphene oxide modified silica	110000	Packed column (100 μm×21 cm)	Three PAHs, three aromatic compounds fresh water	6-10	UV	Retention time: <3.8% naphthalene: 76290 plates·m ⁻¹	[13]
Stellate mesoporous silica nanospheres	90	Monolithic column (100 μm×32 cm)	Alkylbenzenes, anilines, naphthalenes and phenols	5-15	UV	N/m: 266000 R: <2%	[17]
Highly uniform mesoporous silica	/	PLOT column (50 μm×40 cm)	Basic, neutral samples and tryptic-digestion of proteins	10-25	UV	R: <6.2%	[18]
Organo-silica hybrid	245 ± 95	Monolithic column (100 μm×8.5 cm)	Alkyl benzenes, cresols and benzoic acid derivatives	2-15	UV	N/m: 140000 R: <14.2%	[19]
CDMPC modified MCM-41 mesoporous silica ^b	600	OT column (50 μm×50 cm)	Eight pairs of acidic, neutral and basic enantiomers	< 1	UV	Benzoin: 20700 plates·m ⁻¹	[20]

β -CD modified non-porous silica	800	Packed column (100 μm ×10 cm)	Four positional isomers five racemates five benzene series	12-25	UV	n-Propylbenzene: 170000 plates·m ⁻¹	[21]
SM- β -CD ^c Ordered mesoporous silica	4000-6000	Packed (100 μm ×48 cm)	Stereoisomer of flavanones and flavanone glycosides	12-25	UV	N/m: 39580-27010	[23]
Zeolite SiO ₂ NPs	50	OT column (50 μm ×30 cm)	Paraben homologues four groups of isomers one group of epimers two groups of enantiomers (0.25-40 $\mu\text{g}\cdot\text{mL}^{-1}$)	6-26	AD	Migration time: <6.1% peak area: <8.4% R: <6.3 % 4-Cl-2-MA: 108200 plates·m ⁻¹	In this work

^a PDMAEMA: polymer (Poly(2-(dimethylamino) ethyl methacrylate)).

^b CDMPC: cellulose tris(3,5-dimethylphenyl-carbamate), MCM: mobile crystalline material.

^c SM- β -CD: 3,5-dimethylphenylcarbamoylated β -CD modified spherical ordered mesoporous silica.