Supplementary Material

Carboxylated mesoporous carbon hollow spheres for efficient solid-phase microextraction of aromatic amines

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Materials and methods

Chemicals and reagents. All reagents were of analytical grade. Ammonia solution ($NH_3.H_2O$, 25wt%), hydrogen peroxide aqueous solution (H_2O_2, 30%), dichloromethane (DCM), methanol (MT), acetone (CP) and ethanol (EtOH) were bought from China Pharmaceutical Reagent Co. Ltd (Shanghai, China). Deionized water (18.2 MΩ cm^{-1}) was obtained by Milli-Q water purification system (Millipore, USA). Hydrofluoric acid (10%) was purchased from Fuchen Chemical Reagent Factory (Tianjin, China). Formaldehyde solution (37%) was purchased from Xilong Scientific Co. Ltd (Guangdong, China). Resorcinol, tetrapropyl orthosilicate (TPOS, 97%), standard solution of PCBs, naphthol, PAEs (the specific names and chemical structures was listed in Table. S1) and AAs including 2,3-dichloroaniline (2,3-DRA, 98%), 3,4-dichloroaniline (3,4-DRA, 98%), 1-naphthylamine (1-NA, 99%), 2-naphthylamine (2-NA, 99%) and 4-aminobipheny (4-ABP, 99%) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). All the AAs were formulated in acetone to obtained stock solutions (1000.0 ng mL^{-1}). Various concentrations of AAs solutions were prepared by stepwise diluting of the stock solution with water and stored at 4 °C before use.

Instruments. Transmission electron microscopy (TEM) images were obtained with Tecnai G2 F20 S-Twin (FEI, 200 kV); Scanning electron microscopy (SEM) images were recorded using a Verios G4 SEM instrument; The X-ray diffraction (XRD) pattern was defined by X′ Pert Pro MPD Diffractometer

(Philips, Netherlands); Fourier transform infrared (FT-IR) spectroscopy was carried out using a 360 Fourier infrared spectrometer (IR) (Nicololi, USA); The nitrogen adsorption-desorption isotherms and Brunauer-EmmettTeller (BET) surface areas of the material were obtained on an ASAP 2020 instrument (Micromeritics, USA); Water contact angles were acquired by DSA 100 (Krüss, German); ζ potentials of the adsorbent were measured on Zetasizer Nano ZS analyzer (Malvern, UK); The thermogravimetric analysis (TGA) experiments were performed on a TG 209 F3 Tarsus thermal gravimetric analyzer (Netzsch, Bavaria, Germany) in a nitrogen gas atmosphere at the heating rate of 10 °C min^{-1}; The surface elemental composition of the adsorbent was tested by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo); The carbon state was identified by a Renishaw Invia Raman spectrometer; An IKA RET magnetic stirrer (IKA, Guangdong, China) was used for the extraction experiment.

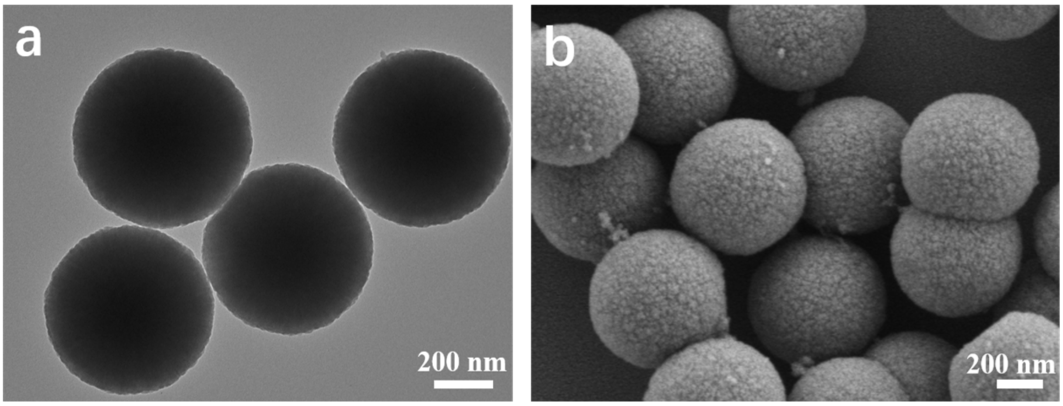


Fig. S1 (a)TEM image of $SiO_2@SiO_2$/RF precursor; (b) SEM image of $SiO_2@SiO_2$/RF precursor.

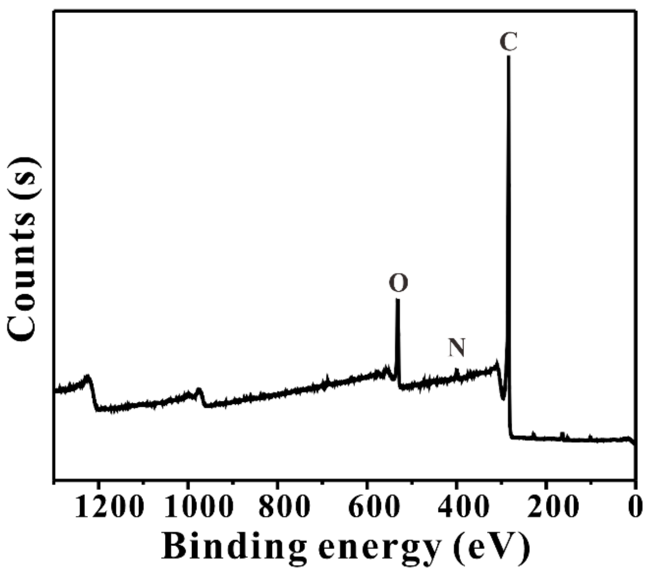


Fig. S2 XPS pattern of MCHS-COOH.

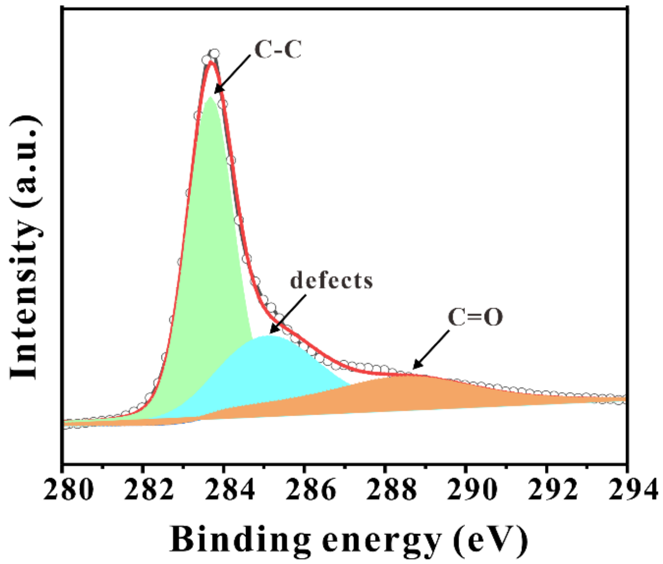


Fig. S3 XPS spectra of C 1s in MCHS-COOH.

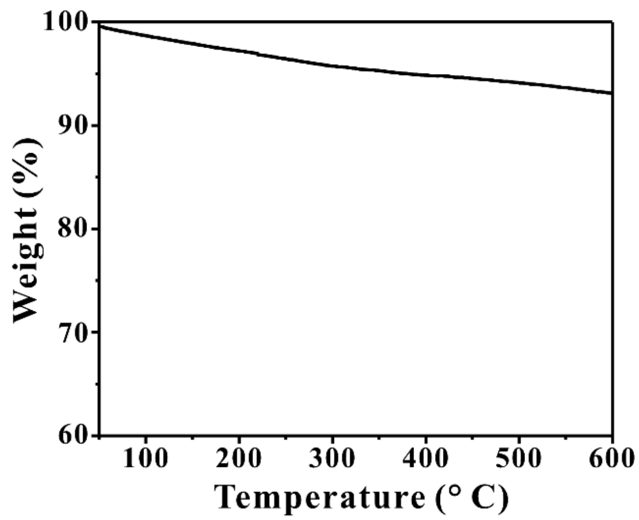


Fig. S4 TGA curve of the MCHS-COOH coating.

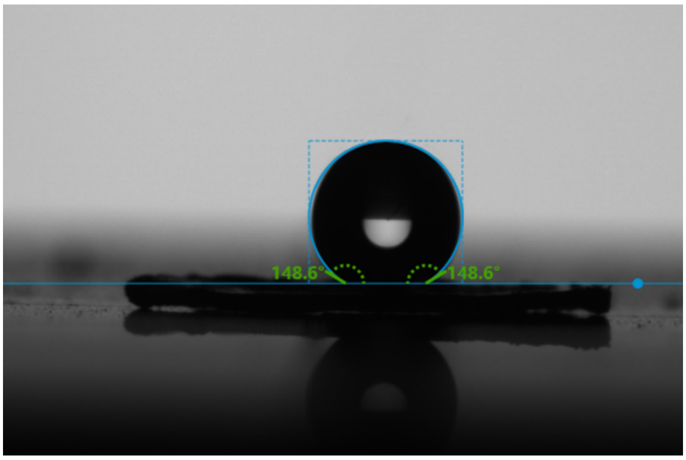


Fig. S5 The water contact angle image of MCHS.

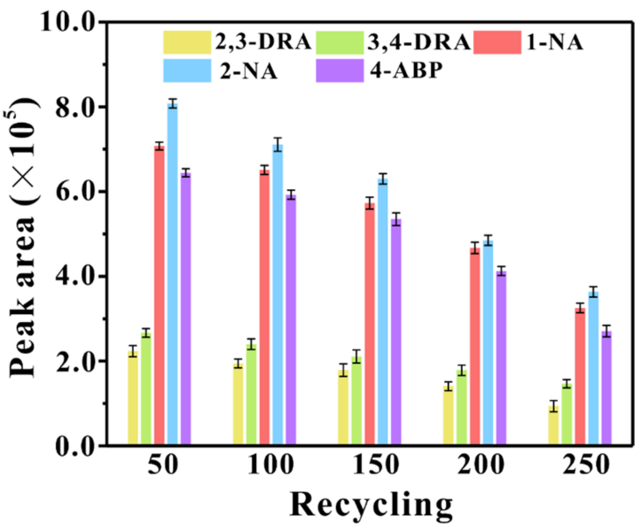


Fig. S6 Recyclability of MCHS-COOH-coated fiber for SPME of AAs. Error bars are ± SD (n = 3).

Table S1 The specific types and chemical structures of PCBs, naphthol and PAEs.

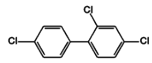
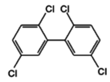
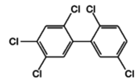
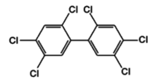
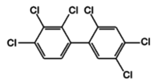
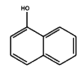
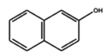
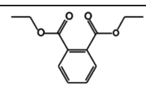
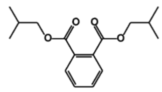
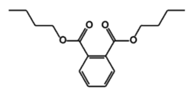
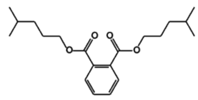
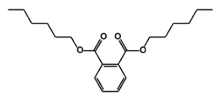
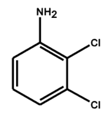
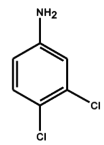
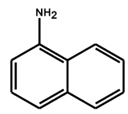
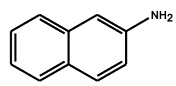
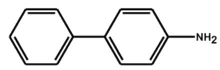
Type of compounds	Compounds	Molecular formula	Abbreviation	Structure
PCBs	2,4,4'-trichlorobiphenyl	$C_{12}H_7Cl_3$	PCB(28)	
	2,2',5,5'-tetrachorobiphenyl	$C_{12}H_6Cl_4$	PCB(52)	
	2,2',4,5,5'-pentachlorobiphenyl	$C_{12}H_5Cl_5$	PCB(101)	
	2,2',3,4,4',5'-hexachlorobiphenyl	$C_{12}H_4Cl_6$	PCB(153)	
	2,2',4,4',5,5'-hexachlorobiphenyl	$C_{12}H_4Cl_6$	PCB(138)	
Naphthol	α-Naphthol	$C_{10}H_8O$	1-Naphthol	
	β-Naphthol	$C_{10}H_8O$	2-Naphthol	
PAEs	diethyl phthalate	$C_{12}H_{14}O_4$	DEP	
	diisobutyl phthalate	$C_{14}H_{20}O_4$	DIBP	
	dibutyl phthalate	$C_{14}H_{20}O_4$	DBP	
	diisohexyl phthalate	$C_{20}H_{28}O_4$	DINOP	
	di-n-hexyl phthalate	$C_{20}H_{28}O_4$	DHXP	

Table S2 Chemical structures, retention time, collision energy and MS/MS transitions of AAs.

Analytes	Molecular formula	Ret. time (min)	MS/MS transitions		Structure
			Transition	Collision energy (Ev)	
2,3-DRA	$C_6H_5Cl_2N$	9.69	90.1→63.1[b] 161.0→90.1[a] 163.0→90.1[b]	8[b] 16[a] 16[b]	
3,4-DRA	$C_6H_5Cl_2N$	10.71	90.1→63.1[b] 161.0→99.1[a] 163.0→90.1[b]	8[b] 18[a] 16[b]	
1-NA	$C_{10}H_9N$	12.08	115.1→89.1[b] 116.2→115.1[b] 143.1→115.1[a]	14[b] 8[b] 20[a]	
2-NA	$C_{10}H_9N$	12.27	115.1→89.1[b] 116.2→115.2[b] 143.1→115.1[a]	14[b] 10[b] 22[a]	
4-ABP	$C_{12}H_{11}N$	14.53	167.2→166.1[b] 168.2→167.2[b] 169.2→168.2[a]	14[b] 10[b] 10[a]	

a: Quantitation transition

b: Confirmation transitio