A functional rattle-type microsphere with magnetic-carbon double layered shell for enhanced extraction of organic targets

Supplementary Information

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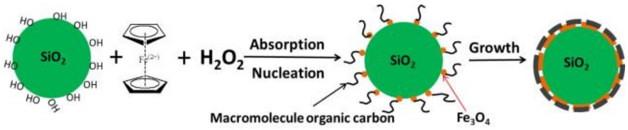
Experimental

Chemicals

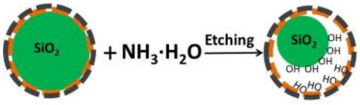
Fluoranthene (FluA), pyrene (Pyr), benzo(a)anthracene (BaA), benzo[b]fluoranthene (BbF), and benzo(a)pyrene (BaP) were obtained from AccuStandard (New Haven, CT). Standard stock solutions (100 μg L^{-1}) containing these compounds were prepared in acetonitrile and stored at 4 ^{o}C. HPLC-grade acetonitrile, toluene, and methanol were supplied by Fisher Scientific (Fair Lawn, NJ). Tetraethyl orthosilicate (TEOS) was obtained from Acros Organics (Morris Plains, NJ). Ammonia aqueous solution (25 %, w/w) was from Alfa Aesar (Ward Hill, MA). Octadecyltriethoxysilane was obtained from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Humic acid were obtained from Sigma-Aldrich (St. Louis, MO). Ferrocene, hydrogen peroxide (H_2O_2), and anhydrous ethanol were guarantee-grade reagents from Beijing Chemicals Co. Ltd. (Beijing, China). All chemicals were used as received without any further purification. Ultrapure water was prepared in the laboratory using a Milli-Q SP reagent water system from Millipore (Milford, MA).

Preparation of rattle-type SiO_2/Fe_3O_4-C/C_{18} microspheres

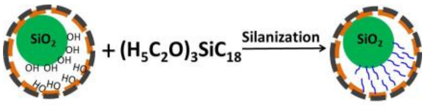
Monodispersed SiO_2 nanoparticles were firstly synthesized through the Stober method.[1] The core-shell SiO_2/Fe_3O_4-C microspheres were prepared by a modified hydrothermal approach.[2] Briefly, silica microspheres (100 mg) and ferrocene (200 mg) were dissoveld in actone (65 mL) with ultrasonic treatment for 30 min. Next, 2 mL H_2O_2 was dropwise added into the mixture and proceed with vigorous stirring for 1.5 h. The homogeneous yellow solution was then transferred into a Teflon-lined stainless-steel autoclave and sealed to heat at 210℃. After reaction for 48 h, the autoclave was cooled to room temperature. The obtained products were washed with acetone and ethanol three times respectively, and then dried under vacuum for 12 h.



To prepare rattle-type SiO_2/Fe_3O_4-C composites, 120 mg of the as-prepared core-shell SiO_2/Fe_3O_4-C microspheres were dispersed in 60 mL of ultrapure water contained 0.1 mL aqueous ammonia and allowed to proceed for 30 min under stirring at room temperature. The resultant product was transferred into a Teflon-lined stainless-steel autoclave again and heated to 150℃ for 6 h. After was separated and collected with a magnet, the product was washed with ultrapure water and methanol several times, followed by resuspension in toluene solution.



Finally, functionalization of the rattle-type materials with octadecyl groups were performed according to our previous reported methods.[3] 40 mL of the above mentioned rattle-type SiO_2/Fe_3O_4-C suspension and 0.15 mL of octadecyltriethoxysilane were mixed under ultrasonic radiation for 20 min. The mixture was then put into autoclave and heated at 120 ℃ for 9 h. The rattle-type SiO_2/Fe_3O_4-C/C_{18} microsphere was obtained after washing and drying.



Characterization

The size and morphology of the synthesized materials were surveyed by Hitachi S-5500 field-emission scanning electron microscope (FE-SEM, Tokyo, Japan), JEOL JEM-2010 high-resolution transmission electron microscope (HRTEM, Kyoto, Japan), and Tecnai G2 F20 HRTEM with a energy dispersive X-ray spectrometry (HRTEM-EDX, FEI, Netherlands); X-Ray diffraction studies (XRD, PANalytical X' Pert diffractometer, Almelo, Netherlands) were performed by using a monochromatized X-ray beam with nickel-filtered Cu Kα radiation with $0.4°min^{-1}$ scan rate. X-Ray photoelectron spectroscopy (XPS) measurements were conducted by applying a Thermo Scientific ESCA-Lab-200i-XL spectrometer (Waltham, MA) with monochromatic Al Kα radiation (1486.6 eV). FTIR spectra were taken in KBr pressed pellets on a Nicolet Thermo NEXUS 670 Infrared Fourier Transform Spectrometer (Waltham, MA). The magnetization curves of the products were measured with a LDJ9600 vibrating sample magnetometer (VSM, Troy, MI). Nitrogen sorption isotherms were measured at 77 K with a Quadrasorb™ SI Four Station Surface Area Analyzer and Pore Size Analyzer (Quantachrome Instruments, Boynton Beach, FL). Before measurements, the samples were degassed in a vacuum at 300 ℃ for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas using adsorption data in a relative pressure range from 0.05 to 1.0. By using the Barrett-Joyner-Halenda (BJH) model, the pore volumes and pore size distributions were calculated, and the total pore volumes were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.993.

Enrichment Procedure

First, 5 mg of rattle-type SiO_2/Fe_3O_4-C/C_{18} sorbents was added into 500 mL of a filtered water sample. The mixture was stirred vigorously for 10 min to help the sorbents dispersed uniformly and facilitate the adsorption of analytes. Subsequently, an Nd-Fe-B strong magnet was deposited at the bottom of the beaker to separate the sorbents from the solution after another 15 min of extraction. Next, the adsorbed analytes were eluted from the isolated sorbent with 12 mL of acetonitrile (4 mL × 3). Then, the eluate was concentrated with a stream of nitrogen at 50℃ to less than 1 mL and diluted to 1 mL with acetonitrile. Finally, 20 μL of this solution was injected into the HPLC-FLD system for analysis.

High Performance Liquid Chromatography - Fluorescence Spectrometry Analysis

The HPLC apparatus was a Dionex HPLC system (Sunnyvale, CA) composed of a

P680 pump, an ASI-100 automatic sampler, a DIONEX RF 2000 fluorescence detector and Chromeleon 6.70 software. PAHs were separated on a Diamonsil® C_{18} column (5 μm particle diameter, 4.6 mm i.d. × 250 mm length, Dikma Tech.). Gradient separation was carried out using water-acetonitrile (50:50) and pure acetonitrile as A and B solvents, respectively, and the flow rate was 1 mL min^{-1}. The linear gradient profile was as follows: B maintained at 80% in the first 15 min, and then linear gradient to 100% in 2 min and maintained for 5 min, after that, mobile phase was returned to initial conditions in 2 min. The PAHs were determined by using a fluorescence detector, and the time-programmed excitation/emission wavelengths were as following: 0 min, 252/370 nm; 6.7 min, 280/460 nm; 7.7 min, 270/390 nm; 11.0 min, 260/432 nm; 13.0 min, 290/410 nm; 22.3 min, 252/370 nm.

With a similar enrichment and analysis procedure, optimization of the extraction of PAHs with rattle-type SiO_2/Fe_3O_4-C/C_{18} sorbent was conducted by extracting spiked ultrapure water (20 ng L^{-1}) with 5 mg of the sorbents under a variety of experimental conditions, and the optimum conditions were established in terms of the recoveries of the target compounds. The influences of ionic strength, pH, humic acid and amount of sorbents on extraction of PAHs were also investigated.

Sample Collection and Analysis

All water samples were obtained from different districts of Beijing, China. Influent domestic wastewater sample was collected from the Gaobeidian wastewater treatment plant (Chaoyang district, Beijing) in October 2010. River water sample was collected from the Qinghe River (Haidian district, Beijing) in September 2012. Snow water was sampled in our institute (Haidian district, Beijing) in February 2013. Tap water sample was from our laboratory in the Haidian district, Beijing. All the samples were stored in 1 L methanol-rinsed and air-dried glass bottles and were filtered through 0.22 μm nylon membranes to remove suspended solids. The filtered samples were stored at 4 ^{o}C until analysis. All the samples were analyzed according to the above mentioned enrichment and HPLC-FLD analysis procedure within three days. The potential contamination from the collector, precleaned glass bottles, and containers used in the determination procedure were tested by running blank PAHs-free water. None of the target analytes were detected in the blanks.

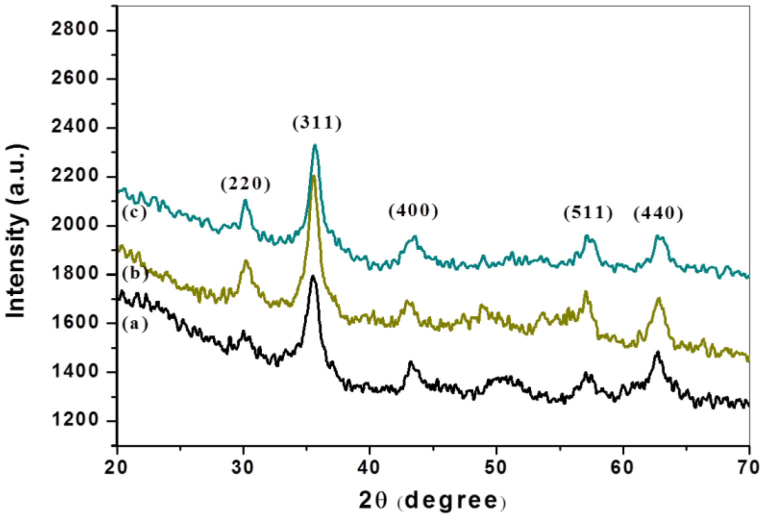


Figure. S1 XRD patterns of core-shell SiO_2/Fe_3O_4-C (a), rattle-type SiO_2/Fe_3O_4-C (b), and SiO_2/Fe_3O_4-C/C_{18} (c).

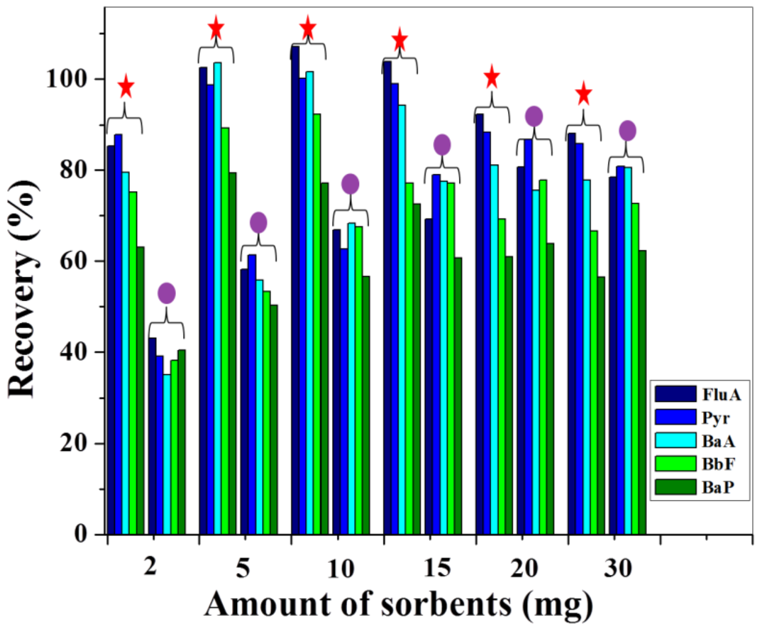


Figure S2 Comparison of the effects of rattle-type SiO_2/Fe_3O_4-C with (★) and without (●) the modification of C_{18} groups. Sorbents, 2 - 30 mg; loading volume, 500 mL; spiked concentration of PAHs, 20 ng L^{-1}; desorption, 3 mL× 4 acetonitrile with ultraphonic treatment.

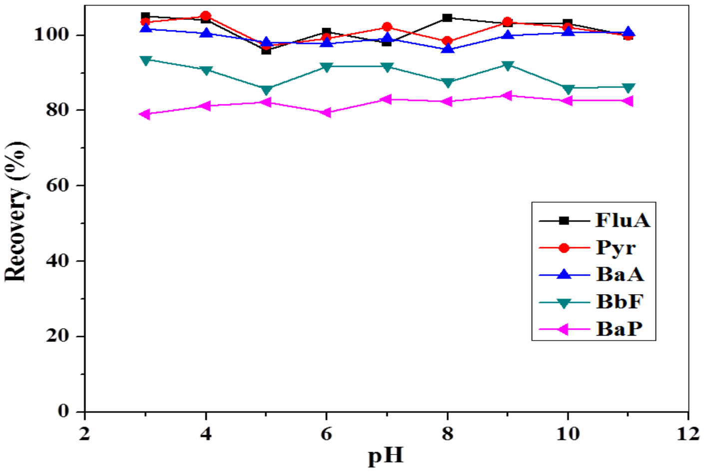


Figure S3 Effect of pH on the extraction of PAHs. Sorbents, 5 mg; loading volume, 500 mL; spiked concentration of PAHs, 20 ng L^{-1}; pH, 3 - 11; desorption, 3 mL× 4 acetonitrile with ultraphonic treatment.

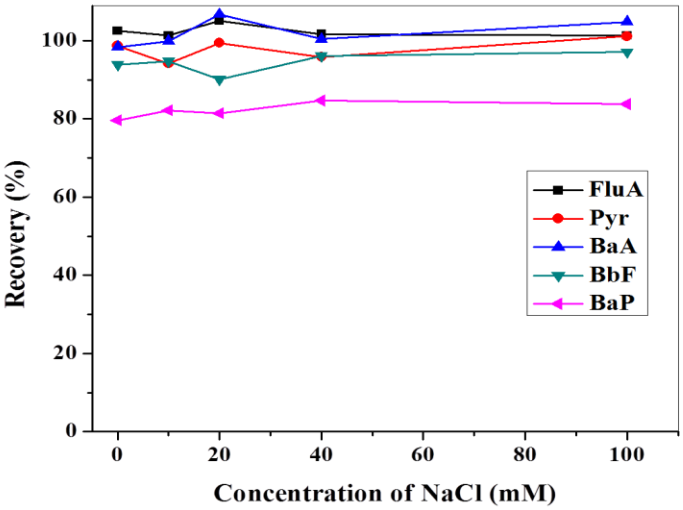


Figure S4 Effect of ionic strength on the extraction of PAHs. Sorbents, 5 mg; loading volume, 500 mL; spiked concentration of PAHs, 20 ng L^{-1}; concentration of NaCl, 0 - 100 mM; desorption, 3 mL× 4 acetonitrile with ultraphonic treatment.

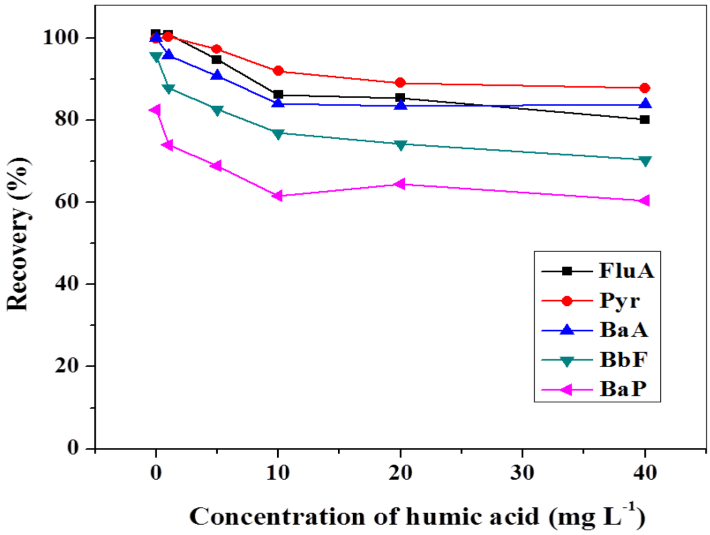


Figure S5 Effect of the concentration of humic acid on the extraction of PAHs. Sorbents, 5 mg; loading volume, 500 mL; spiked concentration of PAHs, 20 ng L^{-1}; concentration of humic acid, 0 - 40 mg L^{-1}; desorption, 3 mL× 4 acetonitrile with ultraphonic treatment.

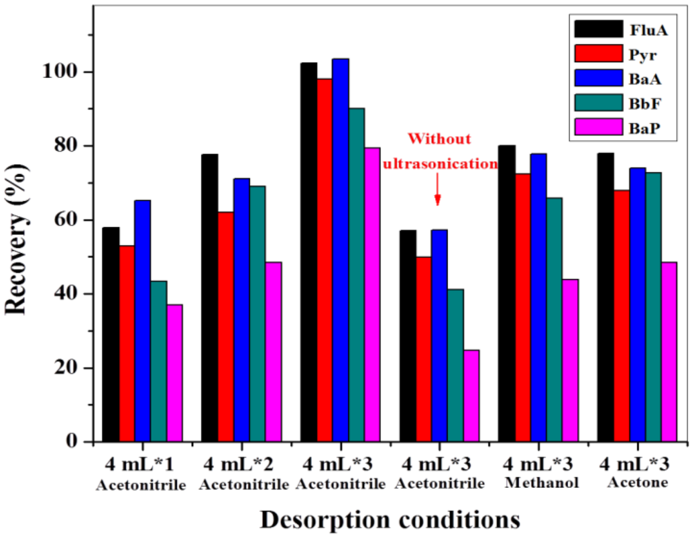


Figure S5 Effect of desorption condition on the extraction of PAHs. Sorbents, 5 mg; loading volume, 500 mL; spiked concentration of PAHs, 20 ng L^{-1}; desorption, different eluent with various volume, with and without ultraphonic treatment.

Table S1 Comparison of the amount and the extraction performance of different sorbents for the detection of PAHs

Sorbent	Sorbent amount (mg)	Sample volume (mL)	Detectiom technique	Limit of detection (LOD, ng L^{-1})	References
Fe_3O_4/C_{18}-barium alginate[4]	100	500	HPLC-FLD	2-5	4
C_{14} carboxylic Fe_3O_4 NPs[5]	200	350	HPLC-FLD	0.1-0.25	5
Fe_3O_4/carbon[6]	50	1000	HPLC-FLD	0.2-0.6	6
$Fe_3O_4/SiO_2/SiO_2$-C_{18}[7]	30	500	HPLC-FLD	0.27-0.84	7
Fe_3O_4/CTAB[8]	80	300	HPLC-FLD	0.33-8.3	8
Octadecylphosphonic Fe_3O_4 NPs[9]	50	10	GC-MS	16.5-64.4	9
Fe_3O_4/C_{18} NPs[10]	50	40	GC-MS	800-7900	10
Multiwalled carbon nanotubes[11]	100	100	HPLC-UV	5-58	11
Supelco ENVI-18 SPE cartridges[12]	1000	800	GC-ITMS	0.8-1.6	12
Rattle-type SiO_2/Fe_3O_4-carbon/C_{18}	5	500	HPLC-FLD	0.13-1.2	This work

Table S2 Analytical parameters of the proposed method

Target	Linearity range (ng L^{-1})	Calibration equation	Correlation coefficient (R^2)	Detection limit[a] (ng L^{-1})
FluA	2.0-200	$y = 0.1153x + 0.8666$	0.9996	0.13
Pyr	2.0-200	$y = 0.1994x + 1.8292$	0.9997	0.27
BaA	2.0-200	$y = 0.4319x + 0.2829$	0.9998	0.41
BbF	2.0-200	$y = 0.2032x - 0.2458$	0.9999	1.2
BaP	2.0-200	$y = 0.7740x - 1.7989$	0.9998	0.26

[a] The detection limits were calculated by using S/N = 3.

Table S3 Analytical results for the determination of PAHs in different water samples

Targets	Tap water		Snow water		River water		Waste water	
	Concentration[a] (ng L-1)	Recovery[b] (%)	Concentration (ng L-1)	Recovery (%)	Concentration (ng L-1)	Recovery (%)	Concentration (ng L-1)	Recovery (%)
FluA	nd[c]	98 ± 4	2.46	89 ± 3	2.07	71 ± 7	5.26	84 ± 4
Pyr	nd	104 ± 3	2.27	87 ± 5	16.56	86 ± 6	5.81	83 ± 4
BaA	nd	99 ± 7	2.33	106 ± 2	6.19	98 ± 3	3.47	97 ± 6
BbF	nd	99 ± 5	nd	103 ± 5	2.17	98 ± 4	0.88	94 ± 5
BaP	nd	93 ± 4	nd	107 ± 3	3.05	108 ± 4	nd	106 ± 3

[a] Mean value (n = 3). [b] Recoveries ± standard deviation (n = 3). [c] Not detected.

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