Supporting Information

Efficient enrichment of broad-spectrum pollutants by a double-shelled hollow ZnO/carbon nanocubes coated solid-phase microextraction fiber

Xingru Hu, Chaohai Wang, Rui Luo, Chao Liu, Junwen Qi, Xiuyun Sun, Jinyou Shen, Weiqing Han, Lianjun Wang, Jiansheng Li*

Key Laboratory of Jiangsu Province for Chemical Pollution Control and Resources Reuse, School of Environment and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
Tel: +(86) 025-84315351
E-mail: lijsh@njust.edu.cn

1. Enrichment procedure

The ZnO/C-F was mounted into a home-made SPME device reformed from a 5 μL GC microliter syringe and conditioned under helium at 250 °C for 60 min prior to use. For analysis, the headspace extraction was employed to perform the experiments, which can minimize the interference from the sample matrix. Each compound was dissolved in methanol to make the stock solution (1.0 $g \cdot L^{-1}$) and then stored in a refrigerator. The working sample was prepared by mixing the BTEX and CPs stock solutions with 10 mL of ultrapure water into a 20-mL headspace vial, which was covered with a polytetrafluoroethylene-coated septa. Then the ZnO/C-F was penetrated the septa under the protection of SPME device and used to extract the analytes by exposing the coating to the sample vapor for a certain period of time. In this process, the magnetic stirrer and thermostatic water bath were employed to control the extraction temperature and rate, respectively. After extraction, the fiber was withdrawn and placed in the injector of GC to thermally desorb the retained analytes.

The environmental samples of river and lake water were gathered from Youyi River and Xuanwu Lake (Nanjing, China), which need be filtered before use. The ZnO/C-F was used to extract the analytes with a headspace mode immediately. For the recovery assessment, 100 ng L^{-1} of the stock solution was added into the water samples.

2. Optimization of the extraction conditions

The extraction conditions were optimized prior to practical application. A working solution of 500 $\mu g \cdot L^{-1}$ was selected for the optimization. In the following sections, the peak area was used to evaluate the extraction efficiency of the ZnO/C-F.

Extraction temperature: In headspace (HS) SPME, the extraction efficiency is tied to the gas matrix partition coefficient. Here the influence of extraction temperature on the extraction efficiency was investigated ranging from 10 to 60 °C. As shown in the Fig. S5a, the peak area reached the maximum along with the temperature increasing to 30 °C. After that the extraction ability of the ZnO/C-F was reduced obviously. The high temperature could facilitate the evaporation of the analytes from the headspace to the fiber coating, accelerating diffusion rate. However, the temperature is too high to increase the partition coefficient because the extraction process is an exothermic adsorption. Therefore, 30 °C was chosen as the optimal extraction temperature.

Extraction time: The mechanism of SPME is the distribution process between the sample and the solid phase on the fiber. Therefore, the study of extraction time is essential for the extraction results. As shown in the Fig. S5b, the extracted amount of the analytes increased with the extraction time increasing from 4 to 12 min, then the peak area was decreased slightly. Taking into account the extraction sensitivity, the condition of 12 min was picked for the further experiments.

Desorption conditions: To avoid the carry-over effect and ensure the life time of the ZnO/C-F, the desorption conditions were optimized as follows. The desorption time in the range of 1 to 4 min was carried out. From Fig. S5c, the extraction efficiency was raised when increasing the desorption time to 2 min. The tendency of the peak areas based on the desorption temperature was examined from 220 to 270 ^{o}C. It was shown in Fig. S5d that the extraction was enhanced with an increase of the desorption temperature from 220 to 250 ^{o}C. Giving an overall consideration, the following desorption was performed at 250 ^{o}C for 2 min.

Ionic strength: Due to the salting-out effect, the solubility of the analytes can be reduced, which would lead to the improvement of extraction efficiency. On the other hand, adding the salt ions will hinder the mass transfer of the analytes. Therefore, the effect of ionic strength on the extraction efficiency was tested at various NaCl concentration from 0 to 20%. Fig. S5e showed that the peak areas of all the analytes increased as the NaCl concentration increased to 5% and after that started to decrease gradually. According to the results, 5% of NaCl was added into the working solutions.

3. SPE method for the determination of BTEX and CPs

The C18 SPE column (Shanghai ANPEL Scientific Instrument Co., Ltd., China) was selected for the concentration of BTEX. Prior to extraction, the cartridge was preconditioned with twice 5 mL dichloromethane. The sample solution (100 mL) was passed through the cartridge and the flow rate was less than 5 mL/min. Then the column was eluted with 2 mL dichloromethane for GC-MS analysis.

The Poly-Sery PSD SPE column (Shanghai ANPEL Scientific Instrument Co., Ltd., China) was used to extract the CPs from the water samples. Before use, the column was conditioned by 6 mL ethyl acetate, 6 mL methanol and 6 mL deionized water, respectively. 100 mL water sample was passed through the column at a flow rate of 5 mL/min. After that, 2×2.5 mL ethyl acetate was added to elute the analytes. 1.0 μL eluate was injected in GC-MS to analyze.

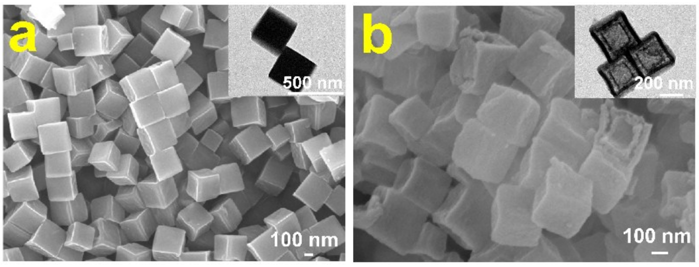


Fig. S1 (a) SEM image of ZIF-8 (inset: TEM image); (b) SEM image of DSH-ZIF-8 (inset: TEM image).

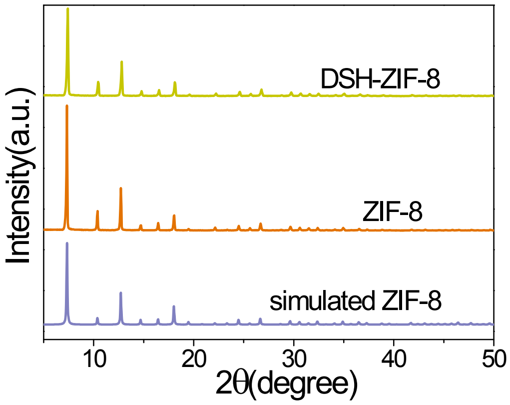


Fig. S2 XRD patterns of simulated ZIF-8, ZIF-8 and DSH-ZIF-8.

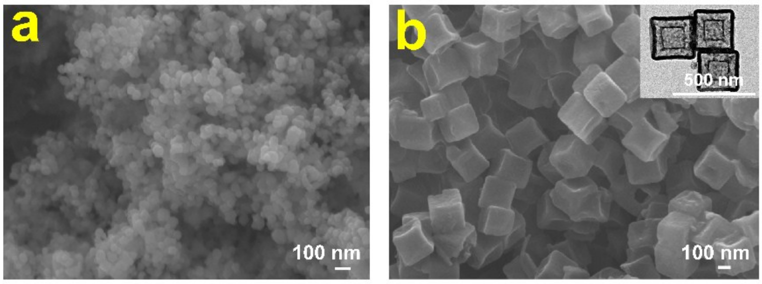


Fig. S3 (a) SEM image of ZnO; (b) SEM image of DSH-C (inset: TEM image).

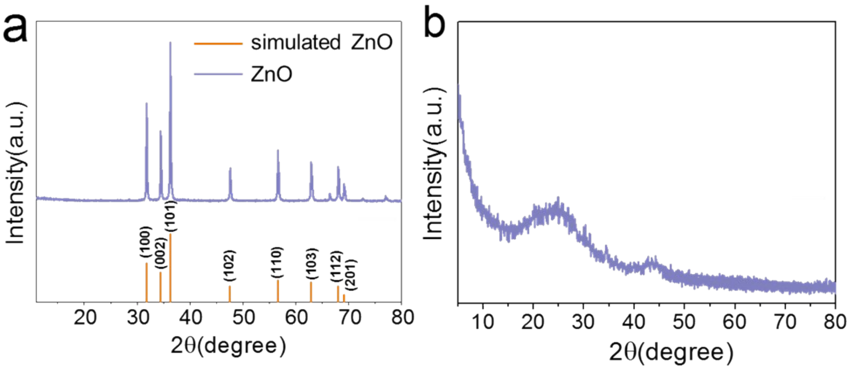


Fig. S4 XRD patterns of (a) simulated ZnO, ZnO and (b) DSH-C.

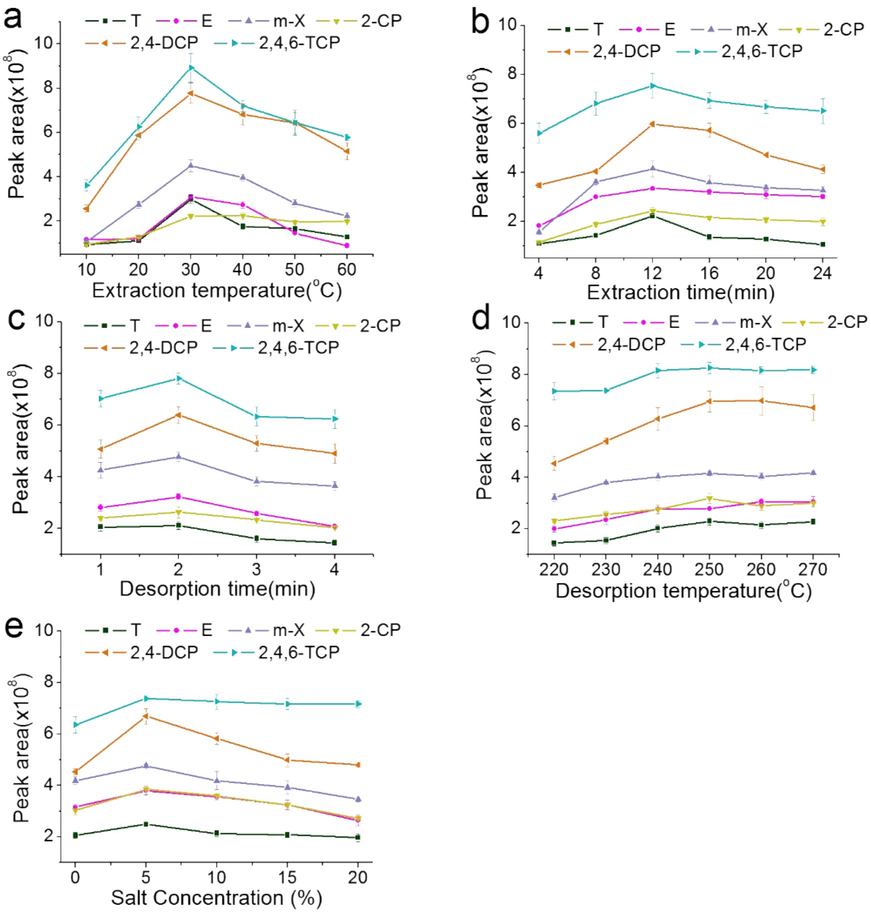


Fig. S5 Effects of SPME conditions on the extraction efficiencies of the ZnO/C-F for the selected analytes: (a) extraction temperature; (b) extraction time; (c) desorption time; (d) desorption temperature; (e) salt concentration.

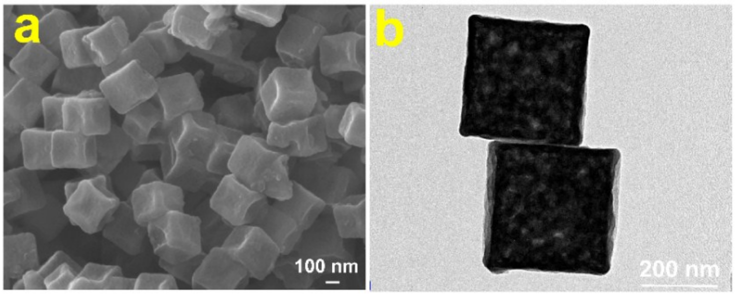


Fig. S6 (a) SEM and (b) TEM images of S-ZnO/C.

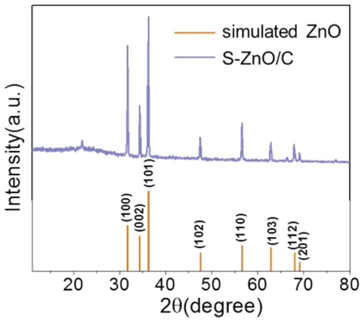
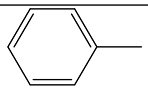
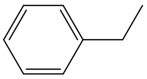
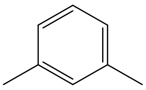
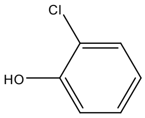
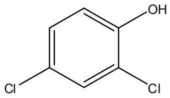
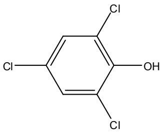


Fig. S7 XRD patterns of simulated ZnO and S-ZnO/C.

Table S1 Analytical Performance of BTEX and CPs

Analyte	Chemical Structure	Dipole [a]
T		0.32
E		0.28
m-X		0.30
2-CP		0.93
2,4-DCP		3.1
2,4,6-TCP		1.4

[a] From et al.[17]