Supporting Information

Magnetite/oxidized carbon nanotube composite used as adsorbent and matrix of MALDI-TOF-MS for the determination of benzo[a]pyrene†

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Experimental details

Chemicals and reagents. Benzo[a]pyrene (BaP) (2.0 mg/mL in Dichloromethane) was bought from J&K Chemical Ltd. Carbon nanotube (CNT) and oxidized carbon nanotube (OCNT) were purchased from Nanotech Port Co. (Shenzhen, China) and C60 was purchased from Yongxin Co. (Henan, China). 2,5-dihydroxybenzoic acid (2,5-DHB), α-cyano-4-hydroxycinnamic (CHCA), sinapic acid (SA) and trifluoroacetic (TFA) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Methanol, acetone and n-hexane were HPLC grade and purified water was obtained with a Milli-Q apparatus (Millipore, Bedford, Massachusetts, USA). The other chemical reagents were of analytical grade and were used without further purification.

Preparation of BaP solution. BaP was dissolved in acetone at a concentration of 1 ppm as storage solution, which was then diluted to different concentrations (500 μg/L, 100 μg/L, 50 μg/L, 10 μg/L) upon use. The volume of each diluted solution for MALDI analysis is 1 μL. Therefore, the amounts of the analyte are 500 pg, 100 pg, 50 pg, 10 pg, respectively. All storage solutions were stored at 4℃.

Synthesis grapheme (G) and graphene oxide (GO). Graphene oxide (GO) was synthesized from graphite powder by a modified Hummers and Offeman method[1], and Graphene was prepared using a low-temperature thermal reduction method[2]. Characterizations of the materials were described in our previous work[3].

Sample preparation for MALDI-TOF-MS. The CNT, OCNT and C60 were washed successively with acetone, methanol and water. Then, 2 mg of G, CNT and C60 was suspended in 1 ml of water/ethanol (1:1, v/v) with sonication for three minutes, while GO and OCNT were prepared in water. Similar to our previous work,[3] magnetite/oxidized carbon nanotube complex (Fe_3O_4@SiO_2/OCNT) was prepared by mixing 8 mg Fe_3O_4@SiO_2 and 2 mg OCNT in 1 ml water/N,N-Dimethylformamide (1:1, v/v). After washing with DMF and acetone, Fe_3O_4@SiO_2/OCNT was dispersive in 1 ml acetone. The same concentration of Fe_3O_4@SiO_2 was prepared in pure water for comparison. About 1 μL solution of matrix was applied to a stainless steel target probe, then 1 μL analyte solution was pipetted on the top of the matrix layer and dried at ambient conditions followed analysis by MALDI-TOF-MS.

Magnetic solid phase extraction procedure. The extraction procedure of BaP with Fe_3O_4@SiO_2/OCNT is as follows.

Extraction of BaP from n-hexane. 1 mL of n-hexane was spiked with stock solution to get final concentrations of BaP at 0.4, 2, 10, 50 μg/L. After 20 μL of Fe_3O_4@SiO_2/OCNT suspension were added into the solution, the suspension was vortexed vigorously for 10 min for extraction. Then the magnetic material-target conjugate was gathered to the bottom of the vial by applying an external magnet, and the supernatant was decanted. Finally, the magnetic materials were suspended in 2 μL methanol and 1 μL of the magnetic material-target conjugate was pipetted onto the stainless steel target probe.

Extraction of BaP from pure water. 10 mL of pure water were spiked with stock solution to get final concentrations of BaP at 50, 100, 500, 1000 ng/L. After 20 μL of Fe_3O_4@SiO_2/OCNT suspension were added into the solution, the suspension was incubated at 40℃ for 30 min. The following procedure was the same as the extraction of BaP from n-hexane.

Instrument conditions. MALDI-TOF-MS spectra were collected with an Axima TOF^2 mass spectrometry (Shimadzu, Kyoto, Japan). The instrument was equipped with a 337 nm nitrogen laser with a 3 ns pulse width. All the mass spectra were performed in positive ion reflector mode with an accelerating voltage of 20 kV. Typically, 100 laser shots were averaged to generate each spectrum. Nonmagnetic matrix was performed by using a laser energy of 60 μJ, while magnetic matrix was performed at 70 μJ.

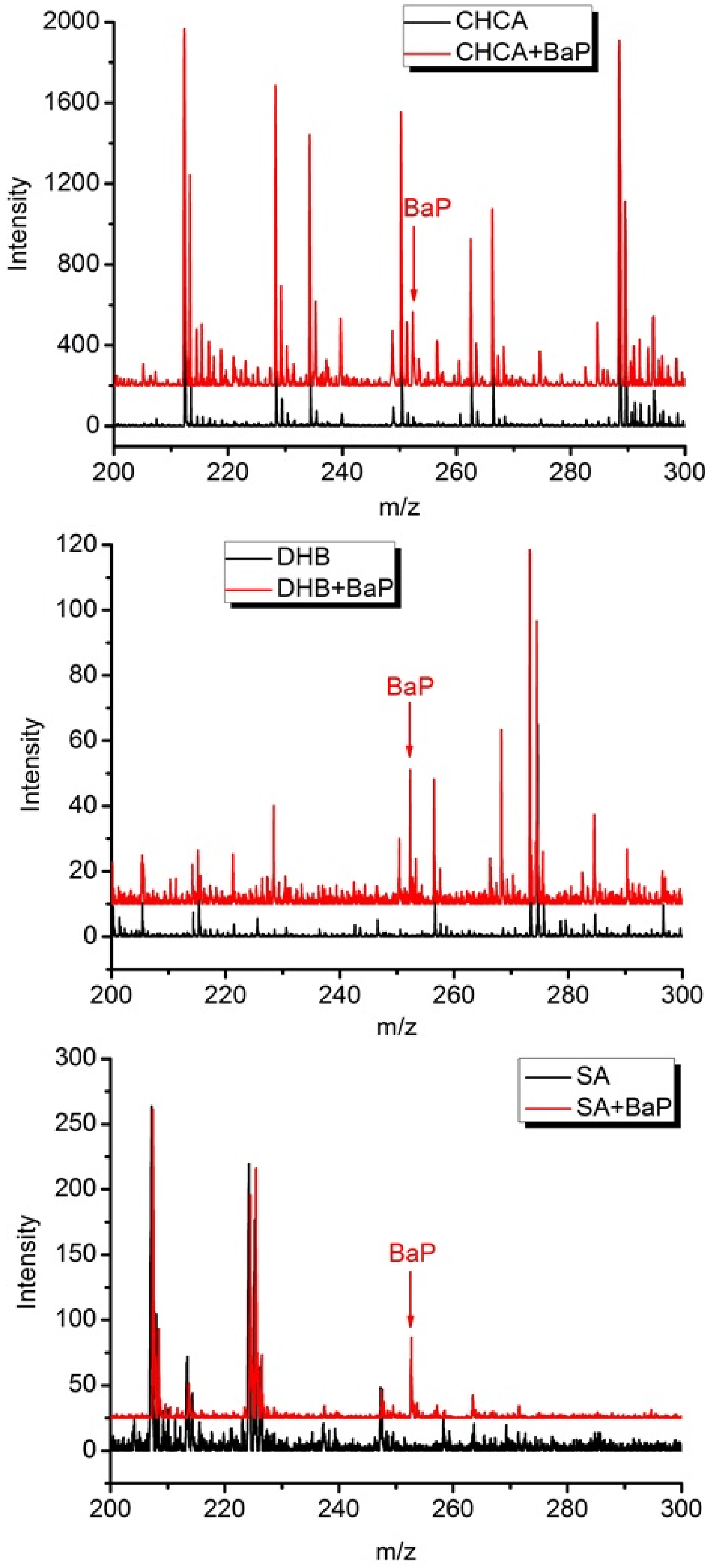

Figure S1. Mass spectra of BaP obtained by using CHCA, DHB, SA as the matrix of MALDI-TOF-MS.

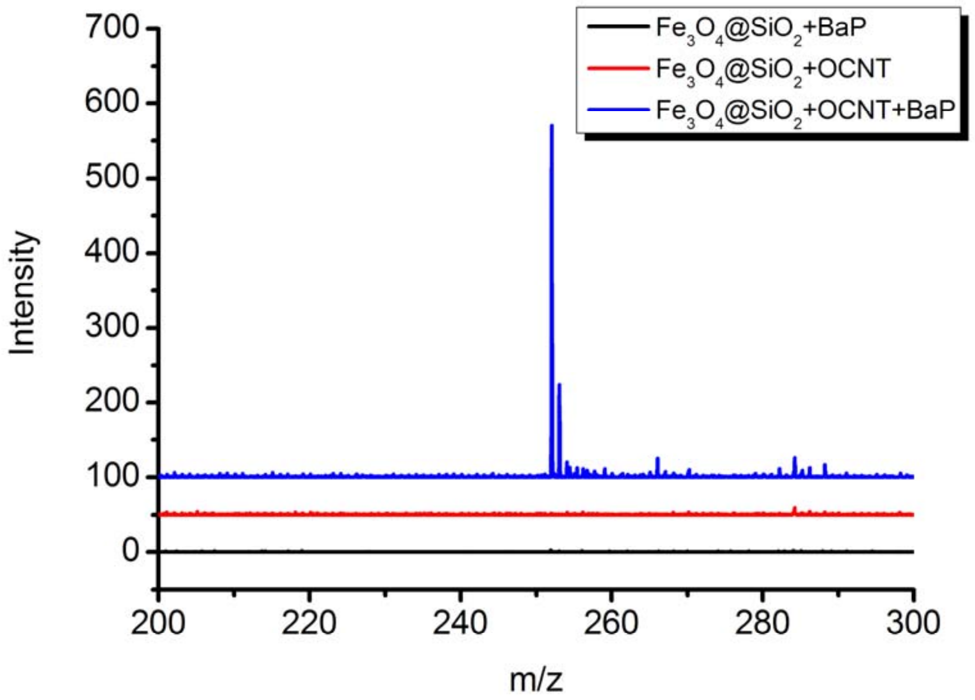

Figure S2. Mass spectra of BaP obtained by using Fe_3O_4@SiO_2 or Fe_3O_4@SiO_2/OCNT as the matrix of MALDI-TOF-MS.

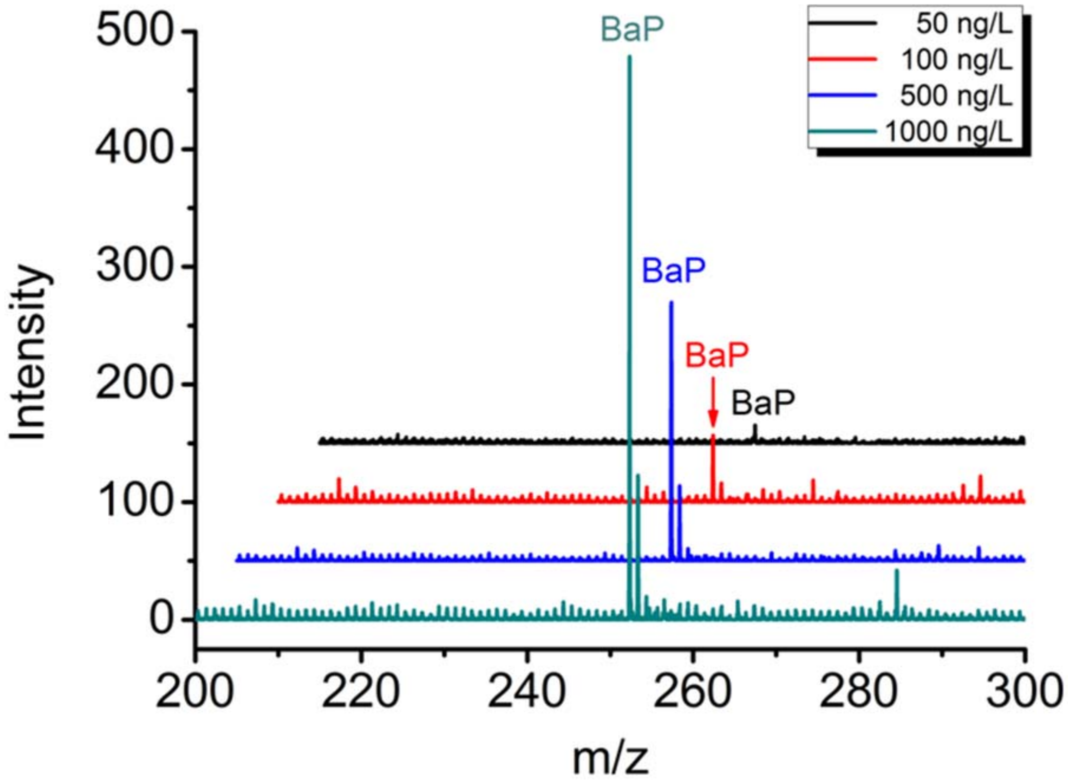

Figure S3. Mass spectra of BaP obtained after enrichment with $Fe_3O_4@SiO_2$/OCNT from 10 mL pure water.

References:

[1] Hummers W.S.; Offeman R.E. *J. Am. Chem. Soc.* **1958**, 10, 1339.

[2] Chen W.F.; Yan L.F. *Nanoscale* **2010**, 2, 559-563.

[3] Luo Y.B.; Shi Z.G.; Gao Q.; Feng Y.Q. *J. Chromatogr. A* **2011**, 1218, 1353-1358.