Supplementary Information

Graphene-based metal and nitrogen-doped carbon composites as adsorbents for high sensitive solid phase microextraction of Polycyclic Aromatic Hydrocarbons

Fuxin Wang, Yu Zheng, Junlang Qiu, Shuqin Liu, Yexiang Tong, Fang Zhu and Gangfeng Ouyang**

MOE Key Laboratory of Aquatic Product Safety/KLGHEI of Environment and Energy Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China.

E-mail: ceszhuf@mail.sysu.edu.cn (F. Zhu); cesoygf@mail.sysu.edu.cn (G. Ouyang).

Method S1. Instruments, SPME procedure, and preparation of the fiber

Instruments

An Agilent Technologies 6980 GC with 5975 MS equipped with a HP-5 MS capillary column (30 m ×0.32 mm i.d. × 0.25 μm) was used for analysis. The carrier gas was ultrapure helium at a constant flow rate of 1.2 mL/ min. The chromatographic separations were programed as follow: the initial oven temperature was set at 50 °C (held for 0.5 min). Next, it was heated at 20 °C/min to 150 °C and then 15 °C/min to 250 °C (held for 6 min). Finally, it was programmed at 30 °C/min to 270 °C (held for 8 min).

SPME procedure

Firstly, the fiber was aged in the GC injection at 250 °C for 30 min. For HP-SPME extraction process, the experiments were carried out with 10 mL of deionized water and PAH standard sample in a 20-mL vial. Next, the vial was placed in a magnetic stirrer, which could control the extraction temperature and agitation speed. The GERSTEL MPS autosampler inserted the fiber into the vial and fixed the fiber coating above the water sample. After a certain period of time, the fiber was removed from the vial and immediately inserted into the GC inlet for thermal desorption and analysis.

Preparation of the fiber

Before use, the stainless-steel wires with a length of 3 cm were ultrasonically cleaned in acetone, ethanol and water in turn. Then, it was transferred to an oven at 60 °C for 1 h. sol-gel approach was used to fabricate the fiber. About 1.0 g of neutral silicone sealant was added to a sample tube and then 2.0 mL of cyclohexane was added to the

sample tube as dispersing agent. The sample tube was ultrasonically for 20 min to obtain the appropriate sol-gel. Next, the cleaned steel wire was dipped into the sol-gel and then taken out. The wire was subsequently rotated in the powder of the prepared samples to acquire the single-layered sample coating. After that, the fiber was dried in the oven at 80 °C for 15 min. The final fiber was obtained by repeating the above steps for three times.

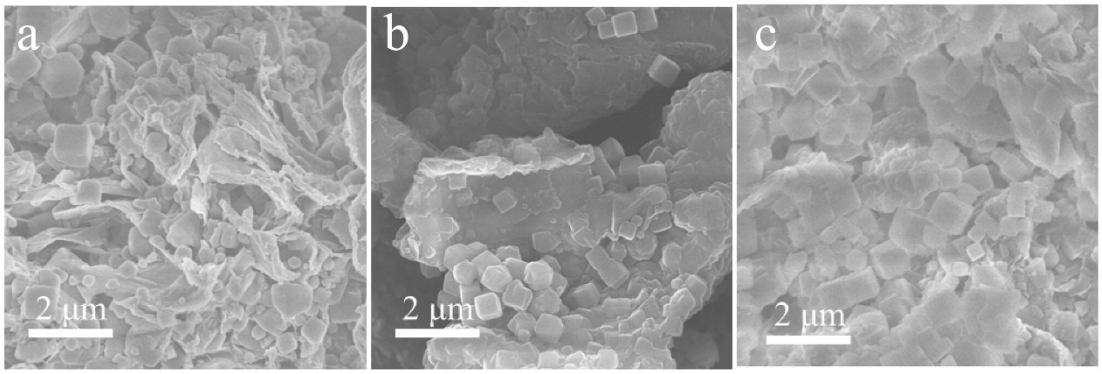

Figure S1. The synthesis conditions of different concentrations of GO (a) 32 g L^{-1} (b) 16 g L^{-1} and (c) 8 g L^{-1}.

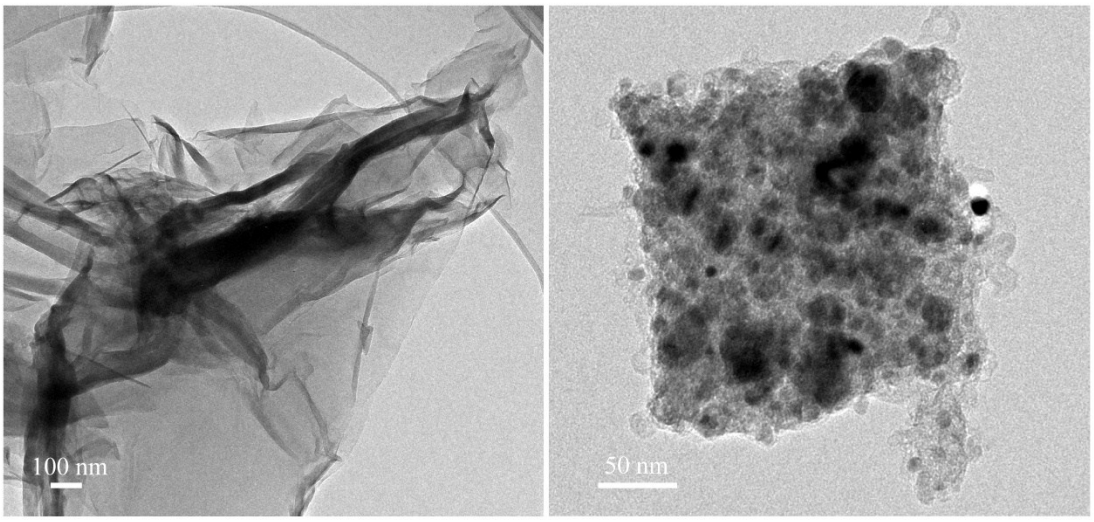

Figure S2. The TEM images of G and NC-Co sample.

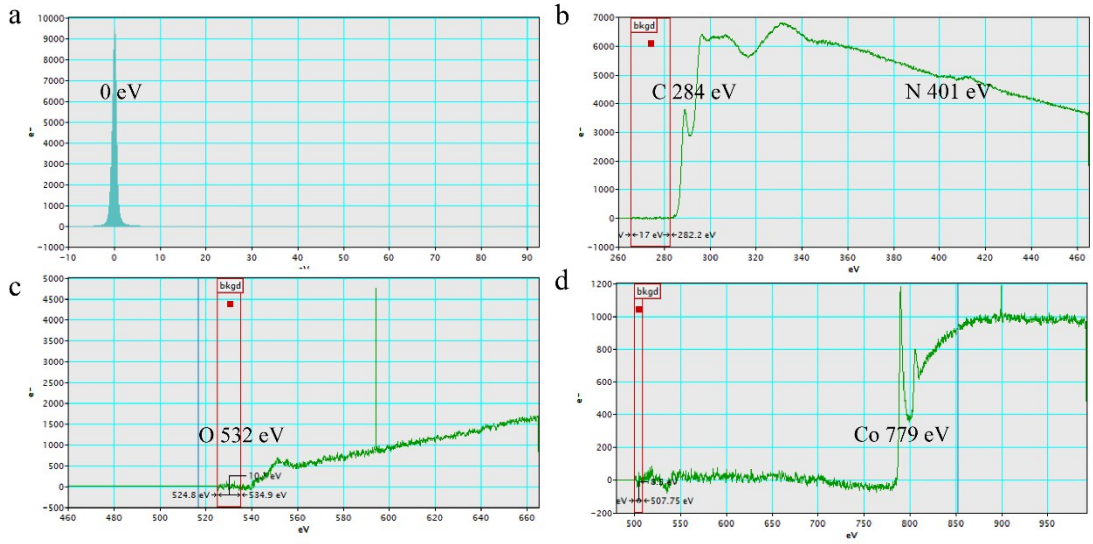

Figure S3. EELS spectrum of the GNC-Co sample

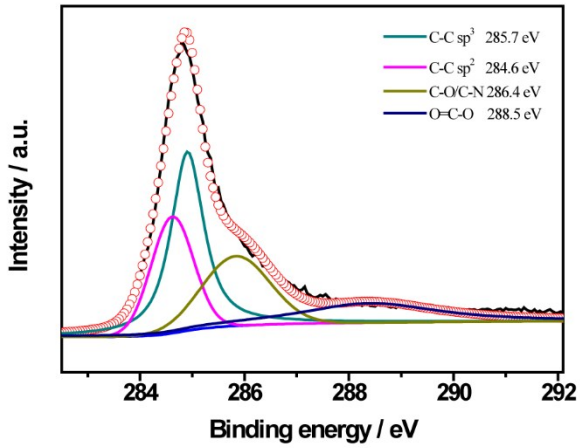

Figure S4. The C 1s core level XPS spectrum of GNC-Co sample.

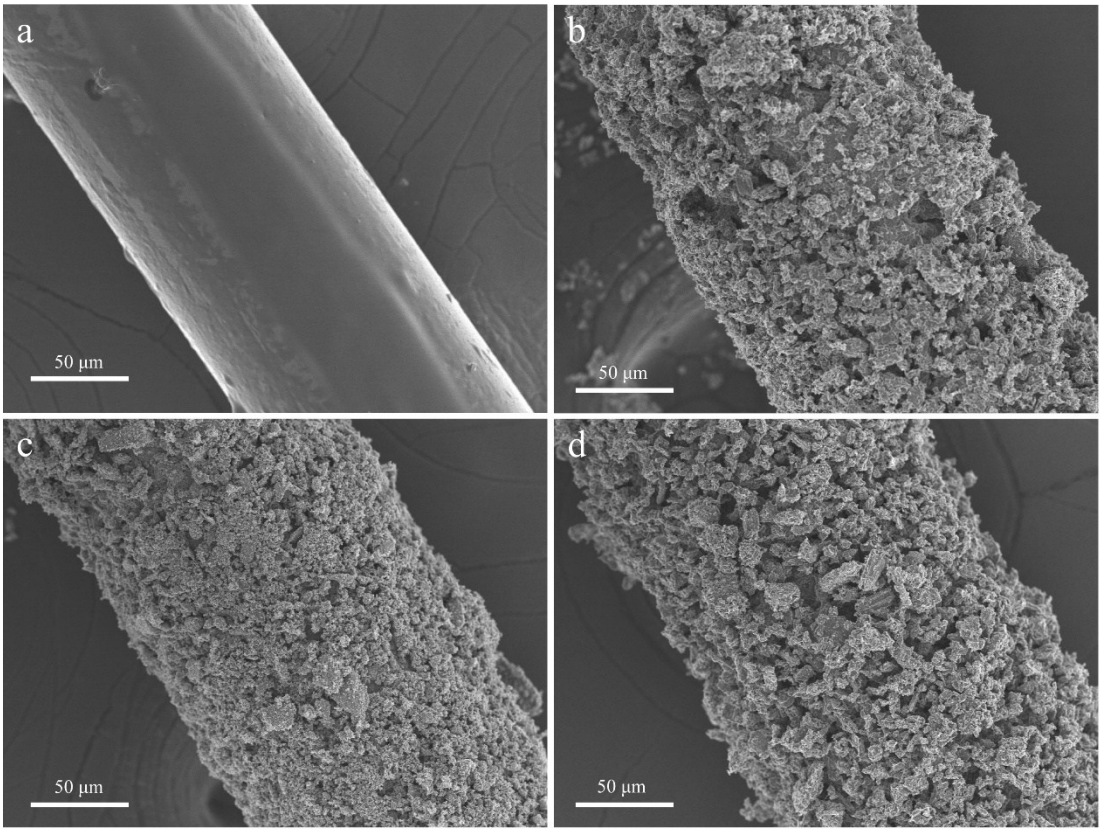

Figure S5. SEM images of (a) steel wire, (b) G, (c) NC-Co, and (d) GNC-Co fiber

Optimization of SPME parameters. In order to obtain the best extraction performance, SPME parameters, including extraction time, extraction temperature, desorption temperature and NaCl concentration, were optimized. The experiments were conducted at the concentration of 1 μg L^{-1} for PAHs. According to the result, the optimal conditions were as follow: extraction time 60 min, extraction temperature 45 °C, desorption temperature 270 °C, NaCl concentration 12 g / 100 mL.

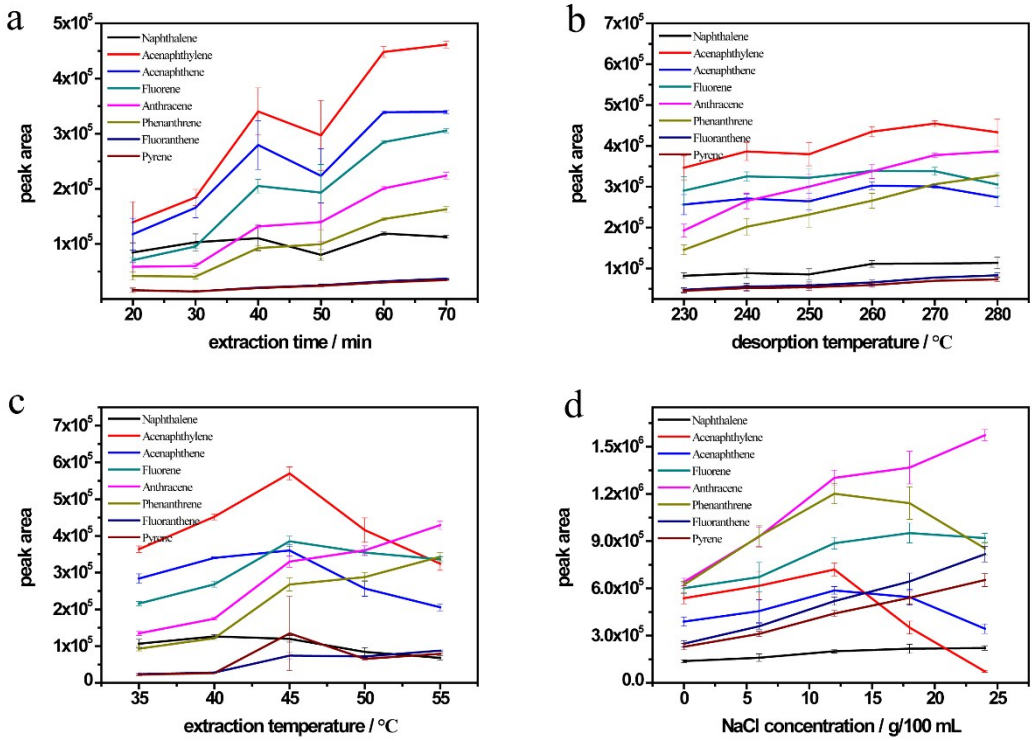

Figure S6. Effects of SPME conditions on the extraction efficiencies of GNC-Co fiber. (a) extraction time; (b) desorption temperature; (c) extraction temperature; (d) salt concentration.

Table S1. The Brunauer-Emmett-Teller results of samples

sample	BET Surface Area / m^2 g^{-1}	Average pore diameter / nm
G	21.0	13.0
NC-Co	261.1	4.9
GNC-Co	123.1	5.7

Table S2. The comparison of LODs between the GNC-Co fiber and the other work.

Compounds	LODs (ng L^{-1})				
	GNC-Co fiber	[1]	[2]	[3]	[4]
Naphthalene	0.01	10.0	75	18	5
Acenaphthylene	0.04			16	
Acenaphthene	0.13	9.0		18	20
Fluorene	0.14	5.0	40	15	10
Anthracene	1.52	2.0	25	16	10
Phenanthrene	2.47	4.0		13	10
Fluoranthene	0.88	2.0	5	10	
Pyrene	2.08	3.0		12	

1. S. Zhang, Z. Li, X. Yang, C. Wang and Z. Wang, *Rsc Adv.*, 2015, **5**, 54329-54337.
2. L. Xu, J. Feng, X. Liang, J. Li and S. Jiang, *J. Sep. Sci.*, 2012, **35**, 1531.
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4. X. Zhang, X. H. Zang, J. T. Wang, C. Wang, Q. H. Wu and Z. Wang, *Microchim. Acta*, 2015, **182**, 2353-2359.