Supplementary Information

Graphene oxide/β-cyclodextrin composite as fiber coating for high efficiency headspace solid phase microextraction of organophosphate ester flame retardants in environmental water

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Supplementary Information (SI)

The following information provides a more detailed optimization of HS-SPME conditions for OPFRs. Additional figures and tables are also presented to support the data described within the text.

3. Results and discussion

3.2 Optimization of HS-SPME conditions for OPFRs

a. Extraction temperature

Extraction temperature has prominent effect on the extraction efficiency of HS-SPME. On one hand, high temperature facilitates the analytes in water diffuse into the headspace to be adsorbed by the HS-SPME fiber, which can shorten the extraction time for equilibrium. On the other hand, high temperature decreases partition coefficients of the analytes from the headspace to the fiber, which is not favorable for extraction efficiency. The effect of temperature on the extraction efficiency was investigated ranging from 50°C to 100°C. As shown in Fig. S4a, the extraction efficiency increased with temperature rising from 50 to 80◦C for all the nine OPFRs, and then decreased. Thus, an extraction temperature of 80◦C was chosen for further experiments because the extraction capacity of all the analytes was the highest at this

temperature. Higher temperature did not significantly increase the extraction efficiency. Therefore, extraction temperature of 80°C was selected for the subsequent experiment.

b. Extraction time

The extraction time ranging from 10 to 50 min was investigated, and the result is shown in Fig. S4b. A time of 30 min was required for all OPFRs to reach equilibrium, considerably shorter than the hours required for PDMS/DVB fiber [1] because of the faster mass transfer of the analytes in the gel structure [2] and the thinner coating. Therefore, 30 min was selected as the preferred extraction time.

c. Volume of water sample

The volume ratio of the aqueous sample to its headspace also has important influence on the extraction efficiency of HS-SPME. Large volume of headspace facilitates the analytes escape from water into it headspace, which is good for extraction efficiency. However, too large volume of headspace would dilute the concentration of analytes and therefore decrease the analytical sensitivity. In this study, the volume of water sample ranging from 8.0 to 16.0 mL was investigated in a 20.0 mL sample vial, and the result is shown in Fig. S4c, the extraction efficiency increased increased with the increase of the volume of water from 8.0 to 14.0 mL, and

then decreased slightly. Hence, 14 mL water in 20 mL sample vial was selected as the optimal sample volume for the further experiment.

d. Stirring rate

Stirring can accelerate mass transfer and decrease the time required to reach thermodynamic equilibrium. In Fig.S4d, the extraction efficiency was very low when the extraction was performed without stirring and increased with an increasing stirring rate. Although the extraction efficiency still increased with the higher stirring rate of more than 600 rpm, poor reproducibility was observed, possibly because the rotating of the magnetic stirring bar was not very balanced when the stirring rate exceeded 600 rpm. 600 rpm was therefore selected for further experiments.

e. Ionic strength

Salt addition to the sample usually improves the extraction efficiency of analytes because high ionic strength decreases their water solubility. The influence of ionic strength was investigated by adding various amounts of NaCl from 0 to 30% (30% is the saturated solubility of NaCl in water). The result in Fig. S4e illustrates that the extraction efficiency increased with the addition of NaCl. Therefore, 30% (w/v) NaCl was used as the optimal content for subsequent studies.

f. Desorption time

Desorption time can prominently influence the responses of the target analytes, especially for compounds with high boiling point. A proper desorption time can ensure the complete desorption of analytes from the fiber and ensure the good reproducibilitys and accuracy. So optimization of desorption time is very important for SPME applications. Under certain desorption temperature at 270°C, the desorption time ranging from 1 to 6 min were investigated. As shown in Fig. S4f, the peak area reaches a maximum at 4 min for all analytes, so in this study all desorption processes were performed at 270 °C for 4 min.

Reference:

[1] M. Shah, J. Meija, B. Cabovska, J.A. Caruso, J. Chromatogr. A 1103 (2006) 329.
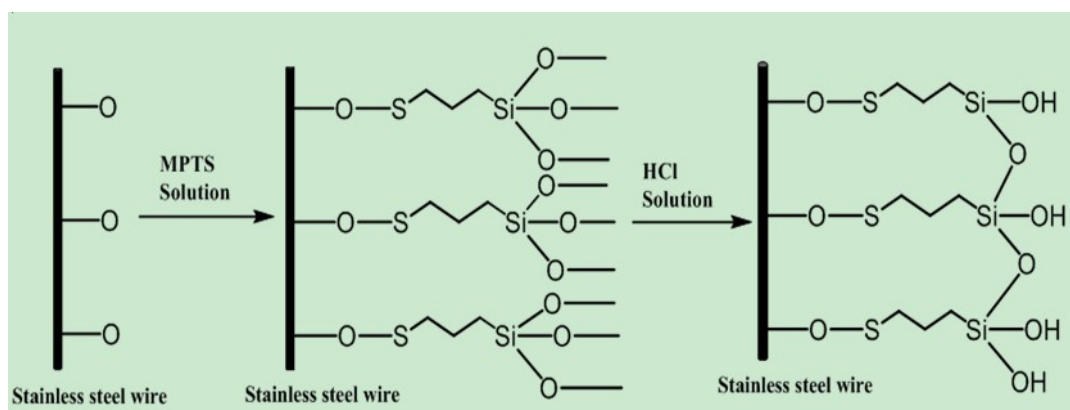[2] Z. Zeng, W. Qiu, Z. Huang, Anal. Chem. 73 (2001) 2429.

Additional Figures:

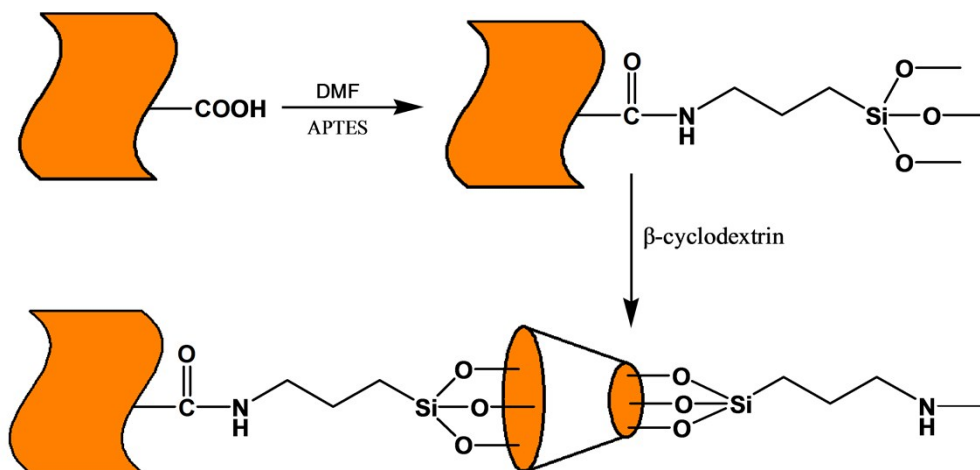**Fig. S1.** Schematic illustration of the surface modification processes for a stainless steel by MPTS.

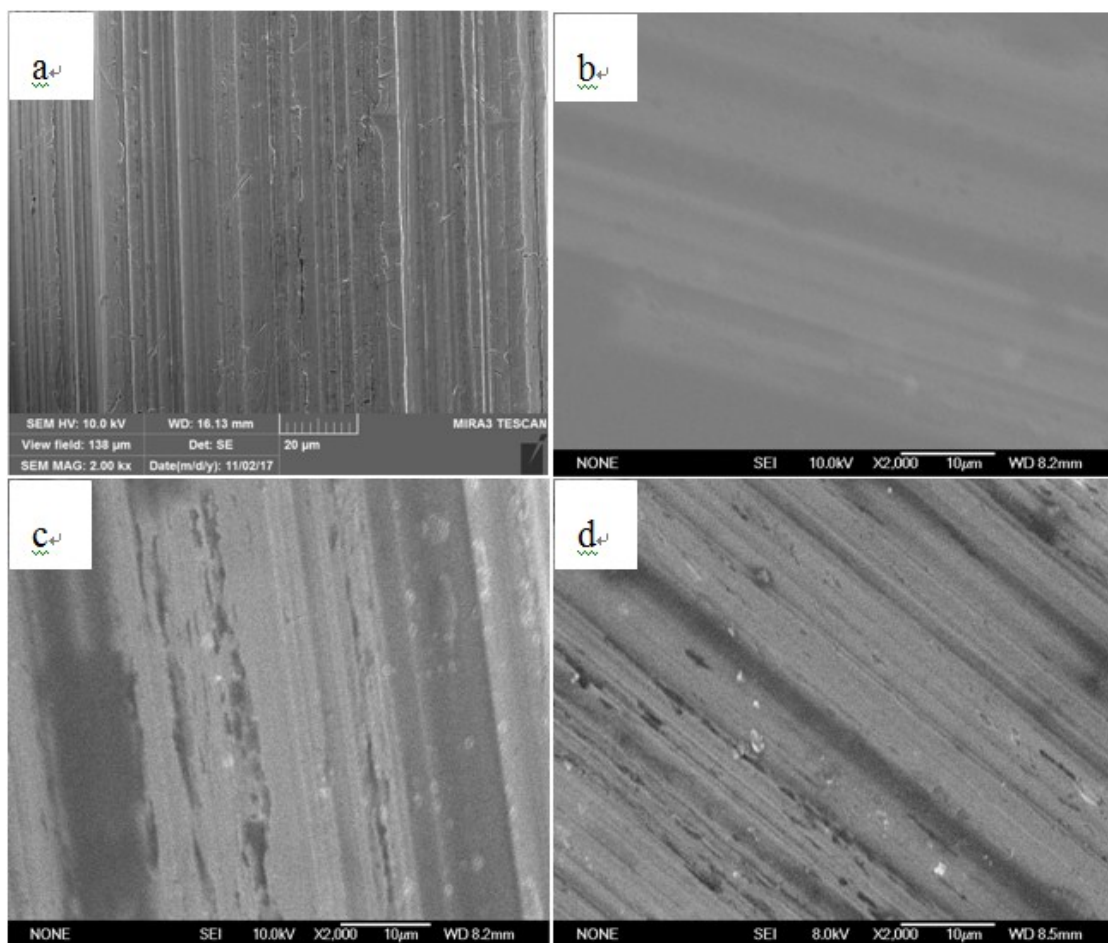**Fig. S2.** Schematic illustration of the synthesis processes for GO/β-CD composite.

Fig. S3. The SEM images of a stainless steel fiber (a×2000), β-CD sol-gel bonded stainless steel fiber (b×2000), GO-sol-gel bonded stainless steel fiber (c×2000), GO/β-CD sol-gel bonded stainless steel fiber (d×2000)
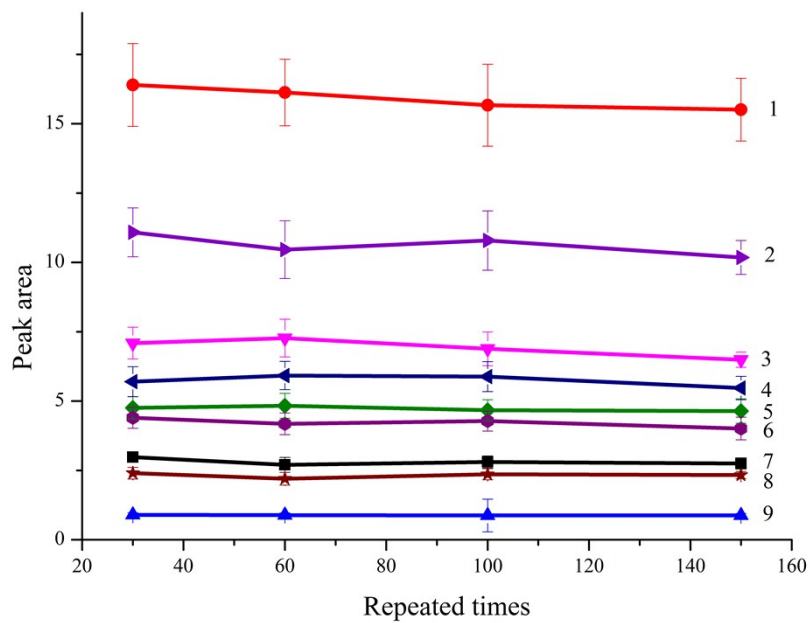
Fig. S4. The lifetime of the GO/β-CD sol-gel coating. Peak identifications: (1) TnBP; (2) EHDPP; (3) TCPP; (4) TPhP;(5) TDCP;(6) TEHP;(7) TPrP;(8) TCrP;(9) TCEP.
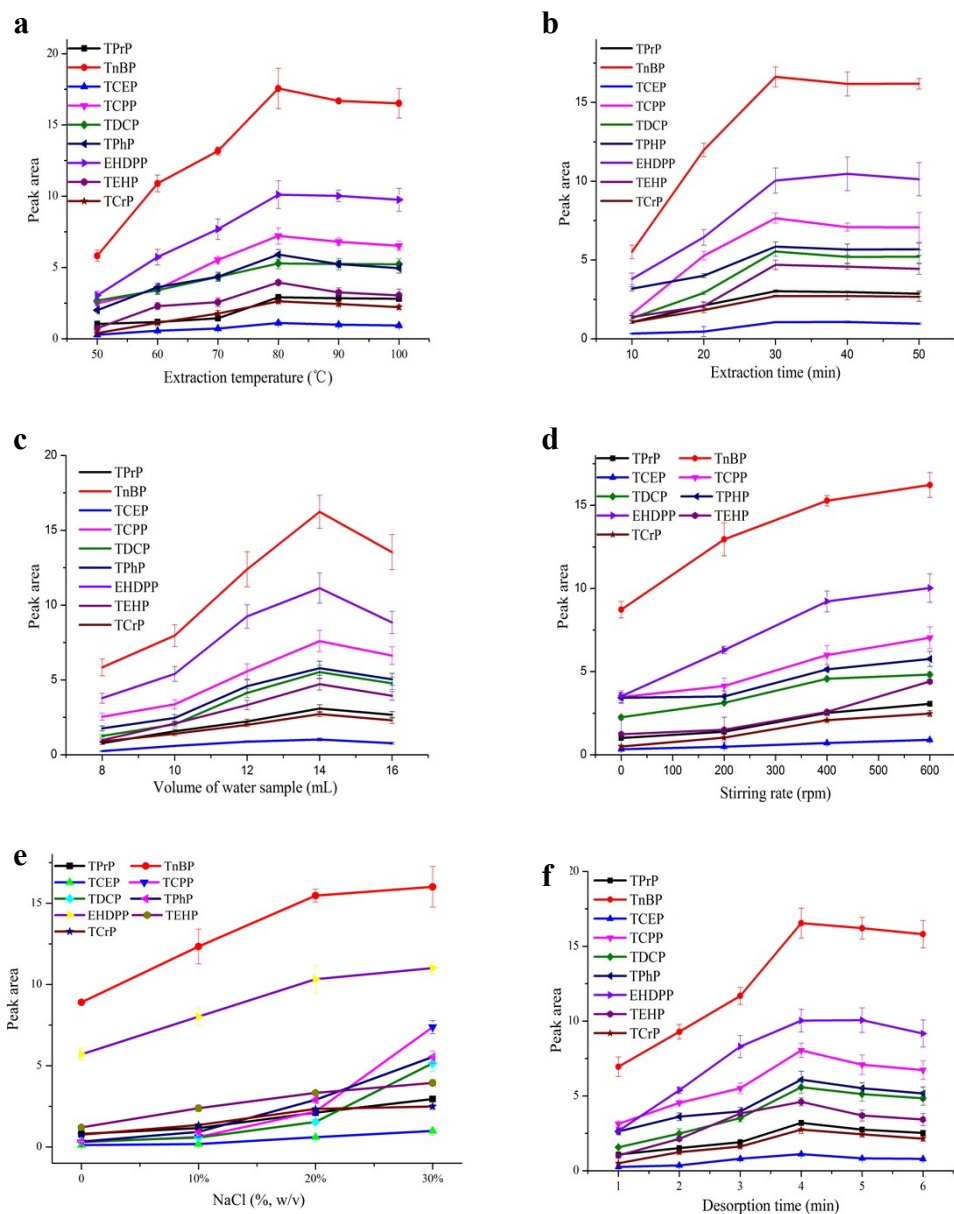
Fig. S5. Effect of the experimental conditions on extraction efficiency of the prepared GO/β-CD sol-gel coating fiber for OPFRs, including (a) extraction temperature. Experimental conditions: extraction time, 30 min; volume of water sample, 14 ml; stirring rate, 600 rpm; content of NaCl, 20% (w/v); desorption, 270 °C for 4 min; (b) extraction time. Experimental conditions: extraction temperature, 80 °C; volume of water sample: 14 ml; stirring rate, 600 rpm; content of NaCl, 20% (w/v); desorption, 270 °C for 4 min; (c) volume of water sample. Experimental conditions: extraction temperature, 80 °C; extraction time, 30 min; content of NaCl, 20% (w/v); stirring rate, 600 rpm; desorption, 270 °C for 4 min. (d) Stirring rate. Experimental conditions: extraction temperature, 80 °C; extraction time, 30 min; content of NaCl, 20% (w/v); stirring rate, 600 rpm; desorption, 270 °C for 4 min. (e) Ionic strength. Experimental conditions: extraction temperature, 80°C; extraction time, 30

min; content of NaCl, 20% (w/v); stirring rate, 600 rpm; desorption, 270 °C for 4 min; (f) Desorption time. Experimental conditions: extraction temperature, 80°C; extraction time, 30 min; volume of water sample, 14 ml; stirring rate, 600 rpm; content of NaCl, 20% (w/v); Analytes concentration, 50 μg L^{-1} TnBP, TPrP, TPhP, EHDPP, TCrP, TEHP and 250 μg L^{-1} TCEP, TCPP, TDCP.

Table. S1. Physicochemical properties of nine OPFRs
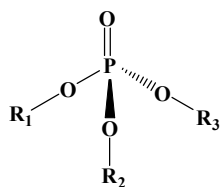
Acronym	Compound name	Substituents	Boiling point (at 760 Torr)	[a]Log K_{ow}
TCEP	Tri (2-chloroethyl) phosphate	$R_1=R_2=R_3=$	330∘C	1.44
TPrP	Tripropyl phosphate	$R_1=R_2=R_3=$	252∘C	1.87
TCPP	Tri(chloroisropyl) phosphate	$R_1=R_2=R_3=$	270∘C	2.59
TDCP	Tri(dichloropropyl) phosphate	$R_1=R_2=R_3=$	315∘C	3.65
TnBP	Tri-n-butyl phosphate	$R_1=R_2=R_3=$	289∘C	4.00
TPhP	Triphenyl phosphate	$R_1=R_2=R_3=$	245∘C	4.59
TCrP	Tricresyl phosphate	$R_1=R_2=R_3=$	265∘C	5.11
EHDPP	2-ethylhexyl diphenyl phosphate	$R_1=$, $R_2=R_3=$	375∘C	6.64
TEHP	Tri (2-ethylhexyl) phosphate	$R_1=R_2=R_3=$	215∘C	9.49

[a]Data taken from Syracuse Research Corporation database of physico-chemical properties
(http://www.syrres.com/eSc/physdemo.htm)

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