



# Graphenized pencil lead fiber: Facile preparation and application in solid-phase microextraction



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## ABSTRACT

Graphenized pencil lead fiber was facilely prepared by *in situ* chemical exfoliation of graphite in pencil lead fiber to few-layered graphene sheets via a one-pot, one-step pressurized oxidation reaction for the first time. This new fiber was characterized and demonstrated to be a highly efficient but low-cost solid-phase microextraction (SPME) fiber. The extraction performance of the fiber was evaluated with four bisphenol analogs [bisphenol A (BPA), bisphenol S (BPS), bisphenol AF (BPAF), and tetrabromobisphenol A (TBBPA)] as model analytes in direct SPME mode. Unlike commercially available fibers, the graphenized pencil lead fiber showed an excellent chemical stability in highly saline, acidic, alkaline and organic conditions due to its coating-free configuration. The fiber also showed a very long lifespan. Furthermore, high extraction efficiency and good selectivity for the analytes with a wide polarity range could be obtained due to the exceptional properties of graphene. The detection limits (LODs) for the analytes were in the range of 1.1–25 ng/L. The fiber was successfully applied in the analysis of tap water and effluent samples from a waste water treatment plant with spike recoveries ranging from 68.5 to 105.1%. Therefore, the graphenized pencil lead fiber provides a high performance, cheap, robust, and reliable tool for SPME.

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## 1. Introduction

Solid-phase microextraction (SPME) is a sample preparation technique with the advantages of simplicity, short extraction time, low/no consumption of solvents, ease of automation, and applicability in *in vivo* sampling [1]. Therefore, it has gained a remarkable progress over the years in both fundamental development and applications [2,3].

SPME is usually performed using a thin fiber with an adsorbent coating. Up to now, a series of commercial polymer-coated fibers are available for SPME, including polydimethylsiloxane (PDMS), polyacrylate (PA), divinylbenzene (DVB), carboxen (CAR), and their copolymers. However, the commercial fibers suffer from fragility of the fused silica substrate, insufficient chemical/thermal coating stability, high price, and limited range of polarity. To overcome these disadvantages, a number of lab-made coatings have been developed for SPME, such as nanomaterials [4], molecularly imprinted polymers [5], ionic liquids [6], mesoporous silica [7], etc. Besides, coating-free fibers have also been developed to eliminate the problems associated with coating stability, such as pencil lead [8–10], metal wires [11], and carbon monolith [12]. Despite that, the

performance of these fibers still needs to be further improved and new fibers are highly desired.

Graphene, a two-dimensional carbon nanostructure, has attracted tremendous interest in various areas due to its exceptional properties [13–15]. Using as sorbent in solid-phase extraction (SPE) and SPME is a very interesting application aspect for graphene due to its large surface area (theoretical value 2630 m<sup>2</sup>/g [16]), unique two-dimensional nanostructure and strong affinity for aromatic compounds [17–23]. To be applied in SPME, graphene needs to be integrated into macroscopic architectures such as fibers to realize the excellent properties of individual graphene sheets. Unfortunately, preparation of graphene fiber is still an extraordinary challenge due to irregular size and shape of graphene sheets and lack of effective assembly methods [24,25]. Dong et al. [26] prepared graphene fibers through dimensionally confined hydrothermal synthesis in a sealed pipeline, and Luo et al. [23] applied this fiber in SPME. In other reports, graphene was used to form sorbent coatings on silica or metal fibers [19–22]. However, preparation of graphene coatings involves complex procedures and the coating stability is often a serious concern. Especially under harsh conditions and long-term use, the coatings are easy to strip from the fibers, which may greatly reduce the extraction efficiency and shorten the lifespan of the fibers.

Inspired by the fact that graphite is both the main component of pencil lead and the precursor of graphene, we herein develop an *in situ* chemical exfoliation strategy to fabricate

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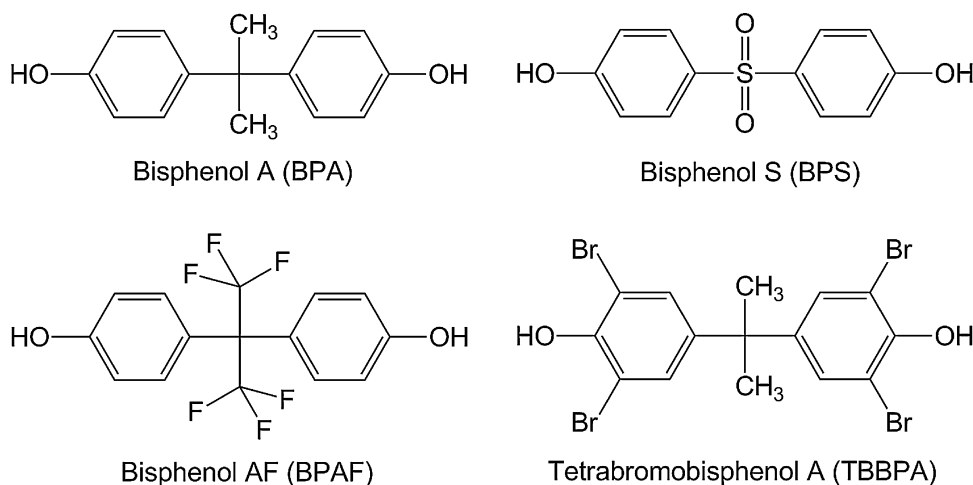


Fig. 1. Chemical structures of the analytes.

graphene-functionalized fiber using commercial pencil lead as starting material and show the application potential of this newly developed fiber in SPME. This method combines the low cost of pencil lead with the excellent extraction capability of graphene to produce high-performance but low-cost SPME fibers. The preparation process is very facile. Four bisphenol analogs (Fig. 1), i.e. bisphenol A (BPA), bisphenol S (BPS), bisphenol AF (BPAF) and tetrabromobisphenol A (TBBPA), were selected as model analytes to evaluate the performance of the fiber in direct SPME mode due to their wide use in consumer products and significant environmental and health risk [27–29]. Higher extraction efficiency and better selectivity were achieved than bare pencil lead and commercially available fibers. The as-prepared fiber displayed a long lifespan and good tolerance to harsh usage conditions and complex sample matrix.

## 2. Experimental

### 2.1. Chemicals and materials

Mechanical pencil leads (type 4H, 2H, HB, 2B, and 4B, diameter 0.5 mm, length 60 mm) were purchased from Mitsubishi Pencil Co. (Tokyo, Japan). Pure graphite fibers (diameter 0.7 mm) were bought from Zichen Graphite Co. (Shanghai, China). H<sub>2</sub>SO<sub>4</sub>, KMnO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> were from Beijing Chemical Works (Beijing, China). Hydrazine hydrate (85%) was from Sinopharm Chemical Reagent (Shanghai, China). BPA (>99.0%), BPS (>98.0%), BPAF (>98%) and TBBPA (>98.0%) were from TCI (Tokyo, Japan). Commercial SPME fibers of 100 μm PDMS and 85 μm PA were from Supelco (Bellefonte, PA). Ultrapure water was produced by a Milli-Q system (Millipore, Billerica, MA). All reagents were of analytical grade.

### 2.2. Preparation of graphenized pencil lead fibers

*In situ* exfoliation of pencil lead was achieved by a one-step, one-pot pressurized oxidation method derived from the Hummers method [30], which has also been used to synthesize graphene from graphite powder [31]. The procedure is depicted in Fig. 2. Briefly, pencil lead (PL) fibers were placed into a Teflon-lined stainless steel autoclave containing 30 mL of H<sub>2</sub>SO<sub>4</sub> and 3 g of KMnO<sub>4</sub>. The autoclave was cooled at 4 °C for 1.5 h, and then heated at 100 °C for 2 h. The obtained fibers were washed in sequence with 10 mL of H<sub>2</sub>O<sub>2</sub> (30%) (reducing the Mn species), 10 mL of HCl (removing the Mn(II) ions) and 10 mL of water (removing HCl and other ions). The products were denoted oxidized pencil lead (oPL) fibers. The oPL

fibers were then reduced in 10 mL of 5% hydrazine solution for 1 h to yield reduced pencil lead (rPL) fibers. The rPL fibers were thoroughly washed with water, air dried, cut into 1.0 cm pieces and stuck to a holder with epoxy resin for SPME.

### 2.3. Characterization of SPME fibers

SEM images were captured on a Hitachi SU-8020 field-emission scanning electron microscope (Tokyo, Japan) equipped with an IXRF Systems energy dispersive X-ray spectrometer (Austin, TX). XPS spectra were obtained on an AXIS Ultra DLD X-ray photoelectron spectrometer (Kratos, Manchester, UK) with Al K $\alpha$  X-ray radiation as the X-ray source excitation. FT-IR spectra were obtained on a JASCO FT/IR Fourier transform infrared spectrometer (Victoria, BC, Canada). The samples were mixed and ground with KBr and then pressed into transparent disks for measurement.

### 2.4. SPME procedure

The SPME was conducted in direct immersion mode as follows: the fiber was immersed into 10 mL of water sample (pH 3.0) with stirring at room temperature for 30 min, and then the analytes were eluted with 60 μL of acetonitrile (ACN) in a micro-insert in a 1.5 mL LC sample vial for subsequent HPLC–ESI-MS analysis.

### 2.5. Quantification

Quantification of the analytes were carried out on an Agilent 1290 Infinity LC coupled to an Agilent 6460 Triple Quadrupole mass spectrometer equipped with an ESI source working in negative ion mode. LC separations were achieved on a Dionex Acclaim PolarAdvantage C16 column (4.6 mm × 150 mm, 5 μm) at 40 °C. Isocratic elution was used with a mobile phase of 80% ACN/20% water and a flow rate of 0.5 mL/min. The sample injection volume was 10 μL. MS detection was performed in selective ion monitoring (SIM) mode. The optimized parameters are given in Table S1 in Supporting Information.

### 2.6. Analysis of environmental water samples

The tap water samples were collected in our lab (Beijing). The effluent samples were collected from Qinghe waste water treatment plant (WWTP) in Beijing. The collected water samples were filtered through a 0.45 μm Millipore glass membrane immediately after sampling and stored in amber glass bottles at 4 °C.

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