In-site and solvent-free exfoliation of porous graphene oxide from pencil lead fiber for solid-phase microextraction of cadmium ion before GF-AAS determination

Yang, Yuan; Lin, Yao; Deng, Yurong; Hou, Xiandeng; Yang, Lu; Zheng, Chengbin

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In-site and solvent-free exfoliation of porous graphene oxide from pencil lead fiber and its application in solid phase microextraction

Yuan Yang[1], Yao Lin[1], Xiandeng Hou[1,3], Lu Yang[2], Chengbin Zheng[1*]

[1]Key Laboratory of Green Chemistry & Technology of MOE, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

[2] National Research Council Canada, Ottawa, Ontario, Canada, K1A 0R6

[3] Analytical & Testing Center, Sichuan University, Chengdu, Sichuan 610064, China

Abstract

Graphene oxidized pencil lead fiber was greenly and facilely prepared by *in situ* oxidation and exfoliation of graphite contained in pencil lead fiber to porous graphene oxide structure *via* a one-step solvent-free dielectric barrier discharge (DBD) microplasma treatment for the first time. This new fiber was characterized and demonstrated to be used as a highly efficient and low-cost solid phase microextraction (SPME) fiber for the determination of toxic metal ions. The extraction performance of the fiber was evaluated by using cadmium as model analyte in a direct immersing SPME mode. Unlike commercially available and other lab-built fibers, the preparation of the graphene oxidized pencil lead fiber is environmentally friendly, low-cost and non-toxic without using any solvents. The fiber is also robust due to its coating-free configuration. Furthermore, high extraction efficiency and high sensitivity for Cd^{2+} could be obtained due to the abundant oxygen-containing functional groups on the surface of the novel fiber. The calibration curve for the cadmium ions was linear in a rage of 0.04–0.26 μg L^{-1} with a detection limit of 0.005 μg L^{-1}. A relative standard deviation (RSD, n = 5) of 2.1% was obtained at 0.1 μg L^{-1} of Cd^{2+}. The SPME fiber was successfully applied to analyze Cd in tap water, river water and pond water with spike recoveries ranging from 94 to 105%. Pipe network water samples were also analyzed to evaluate the cadmium release to drinking water due to the corrosion of tubes.

Keywords: Pencil lead, Solid phase microextraction, Open-air plasma, Grapheme oxide, *In-situ* exfoliation, Cadmium

Introduction

Solid-phase microextraction (SPME) is a novel sample pretreatment technology with advantages of simplicity, high sensitivity, and low/no consumption of solvents[1]. Therefore, it has been favored by scientists in many fields[2]. Although it has been widely used in various aspects, the application of SPME for the determination of metal ions has been limited[3]. Up to now, the analysis is limited to the determination of volatile organometallic complexes or a derivatization step was applied for metal-containing species to generate the corresponding derivatives, which then could be adsorbed onto a SPME fiber and desorbed by thermal or solvents[3]. There are still some heavy metals that cannot be derived, and their pollution to the environment is a major problem because they are toxic to humans and other life forms even at very low levels. Recently, a novel Polypyrrole/Carbon Nanotube/1, 10-Phenanthroline composite SPME fiber was prepared for the extraction of heavy metals in the direct immersion solid-phase microextraction (DI-SPME) mode for the first time.[4] Despite that, new fibers need to be fabricated to extent the application of SPME in metal ions extraction.

Fiber is a typical format of SPME based on the distribution of analytes among different phases, and fiber coating is the core which determines the sensitivity and selectivity of the developed method. In addition to its own physical and chemical properties, the extraction performance of the coating is closely related to the fiber preparation method. Up to now, various SPME fiber fabrication methods have been developed, including physical deposition[5], glue method[6], electrochemical deposition[7], polymerization[8], sol-gel method[9], chemical bonding[10], electrospun[11], *in situ* growth[12]. Although these fabrication procedures have yielded good results, almost all technologies involved steps often employing large volumes of hazardous organic solvents, strong acid/base and strong oxidizing/reducing agents except original pencil lead and glassy carbon rod, thus not only increase the cost but also generate adverse effect to operators and the environment. To meet the environmental friendly requirement in the development trend of Analytical Chemistry and realize greenness in the whole SPME process, the development of green preparation methods for new SPME fiber without solvents is highly desired.

The dielectric barrier discharge (DBD) plasma is a typical non equilibrium alternating current (ac) gas discharge with the advantages of simple construction, low power consumption, high molecular dissociation capability, and operation at atmospheric pressure and room temperature, which has been attracting increasing interest for SPME fibers fabrication and surface modification of materials. Luo et al. successfully prepared an efficient graphite SPME fiber by low-temperature nonthermal plasma using graphite rod as fiber precursor[13]. Our previous works demonstrated the use of the DBD plasma for a one-step *in situ* synthesis of PCs fibers on a metal

surface[14]. The method features environmental friendly, low cost and simple equipment. This method is relatively green compared to other methods, but still uses the organic reagent ethanol as the carbon source.

Pencil lead (PL), another carbon-based material, has gained attention because it is inexpensive and readily available, with uniform quality. Graphenized pencil lead fiber was facilely prepared by *in situ* chemical exfoliation of graphite in pencil lead fiber to few-layered graphene sheets [15]. Graphite, the main component of pencil lead, is a conductive material with low resistivity. Therefore, it can be used as an inner electrode instead of common metal rod in the DBD setup directly. Recently, Liu et al. realized the *in situ* exfoliation of graphene from carbon fibers using Ar plasma treatment, indicating that plasma could etch the amorphous carbon from the carbon fibers[16]. Inspired by the fact that graphite is the precursor of graphene(G) /graphene oxide (GO), we herein develop an *in situ* exfoliation and oxidation strategy by air plasma in a miniature DBD device to fabricate porous and GO-functionalized fiber using PL as the fiber substrate and demonstrate the application potential of this newly developed fiber in SPME. With only air and PL involved in the preparation step, the proposed method is a solvent-free method. Additionally, the new fiber integrates the supporter and the coating of the fiber into one part, which may obviate the coating to fall off the supporter due to its coating-free configuration. Under the ablation of plasma and oxidation of air plasma, graphene oxide may be produced on its surface. GO abounds with many oxygen-containing chemical groups across the basal planes, such as epoxy groups, hydroxyl groups, and carboxyl groups. These groups can bind with metal ions, especially the multivalent metal ions through both electrostatic and coordinate approaches[17]. It can be estimated that the new GO-functionalized fiber is an ideal adsorbing material for metal ions. Cadmium was selected as a model metal to evaluate the proposed method because Cd is one of the principal heavy metals of analytical interest due to its extreme toxicity even at relatively low concentration. It may release from leaching of metal or plastic pipes and then affect the quality of drinking water. Graphite furnace atomic absorption spectrometry (GFAAS) was used to determine cadmium duo to its advantage of low-cost, sensitive, and easy to be combined with microextraction techniques with low sample consumption (10–50 μL). To the best of our knowledge, the development of a solvent-free method for preparing a new fiber for DI-SPME and for the sensitive determination of trace Cd without derivatization or volatilization has not been reported.

Experimental

Reagents and materials

2B pencil leads (diameter 0.7 mm, length 100 mm) were bought from Duoqi Stationery Factory (Guangdong, China). Mechanical pencil leads (type 2H, HB, 2B, diameter 0.5 mm, length 60 mm) were purchased from Mitsubishi Pencil Co. (Tokyo, Japan) for type selection investigation. Pure graphite fibers (diameter 2 mm) were bought from Zichen Graphite Co. (Shanghai, China). All the reagents used in this work were of guaranteed grade. All solutions were prepared using 18.2 MΩ cm deionized water (DIW) produced by a water purification system (Chengdu Ultrapure Technology Co., China). Nitric acid (65% purity, Merck, Germany) was used in this experiment. High-purity ammonium hydroxide (25%–28%) was purchased from Kelong Chemical Factory (Chengdu, China). A stock solution of 1000 mg L^{-1} Cd^{2+} was purchased from the National Research Center for Standard Materials (NRCSM) of China. Nitrogen (N_2, 99.99%) and oxygen (O_2, 99.99%) were obtained from Qiaoyuan Gas Company (Chengdu, China).

Instrumentation

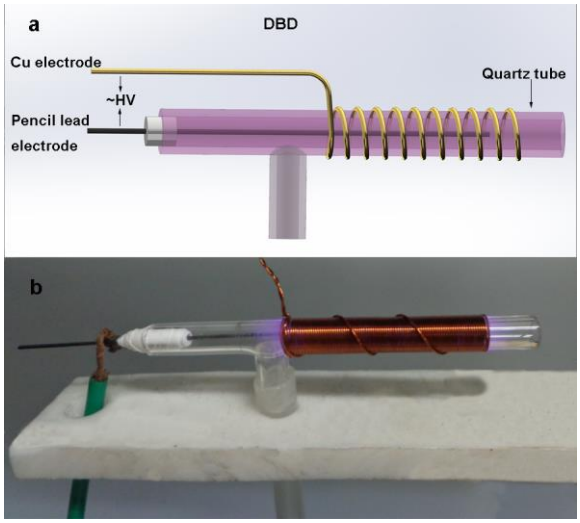

Fig. 1 (a) Experimental setup of the DBD plasma reactor used for *in situ* exfoliation of porous GO from pencil lead fiber; and (b) picture of the discharge process

In situ exfoliation and oxidation of pencil lead without solvents was achieved by a one-step DBD plasma surface treatment method. Fig. 1 provides a schematic and photo of the cylindrical laboratory-built DBD-synthesis system, which was constructed with a quartz tube (70 mm length × 2.5 mm i.d. × 4.0 mm o.d.), a pencil lead electrode (70 mm length × 0.7 mm diameter) and a copper electrode (0.4 mm diameter). The pencil lead fiber was directly used as a high-voltage inner electrode covered with the quartz tube and placed along the axis of the cylinder. The copper electrode was tightly and evenly wrapped around the outside of the quartz tube. A miniaturized ac power supply (Model NGB408BL, Jinshi Electronic Equipment Factory) was connected to the electrodes to provide high voltage for the generation of the DBD plasma. The discharge voltage was controlled by a variable transformers (TPGC2J-1, Shanghai Pafe Electronic Equipment Ltd. Co.) which connected to the power supply. Pencil lead acted as both the high voltage inner electrode and the substrate material for the generation of GO. The whole device was laid in an open place. After 40 min of discharge at 1.45 kV in air, the surface of pencil lead fiber become white and GO-functionalized PL fiber was achieved.

Quantification of the analytes were carried out on an Agilent 240Z AA atomic absorption spectrometer with graph-

ite furnace atomizer and Zeeman background correction. A cadmium hollow cathode lamp was used as a light source and operated at a current of 8 mA.

SPME-AAS

The SPME was conducted in direct immersion mode as follows: the GO-functionalized fiber was immersed into 15 mL of water sample (pH 8) with stirring at room temperature for 20 min, and then the Cd ions were eluted with 150 μL of 5% Nitric acid (HNO_3) in a 200 μL lab-made glass tube and then transferred to a 1.5 mL PE tube for subsequent GF-AAS analysis. The measurements were carried out at wavelength of 228.8 nm with a spectral band width of 0.7 nm. A high purity argon was used as a carrier gas. The sample injection volume was 15 μL in all experiments. The instrumental parameters and temperature program for the graphite atomizer are listed in Table S1 in Supporting Information.

Sample preparation

Water samples were collected from tap in our lab (Chengdu), Funan river in Chengdu city, Lotus pond in Sichuan University (Chengdu) and tap water samples from dormitories in Dong Yuan of Sichuan University. All the samples were collected in 50 mL glass bottles. The collected water samples were filtered through a 0.45 μm Millipore glass membrane immediately after sampling and stored in glass bottles at 4 ˚C.

Results and discussion

Synthesis and Characterization of fibers

Inspired by the fact that the pencil lead is conductive, and plasma can modify the surface of materials, we herein develop an solvent-free *in situ* exfoliation strategy to fabricate GO-functionalized fiber using commercial pencil lead as precursor. Only a coaxial cylindrical DBD for a one-step preparation of GO-functionalized fiber was introduced. After treating with Air plasma for 40 min, the surface of pencil lead fiber become white. The surface morphology of pencil lead after Air plasma treatment was observed by SEM characterization (Fig. 2). Compared to bare PL which has a flat surface, the surface of plasma-etched PL (P-PL) is porous and rough. The surface of P-PL also exhibited exposed and rich nanosheets. The SEM results show that plasma treatment can effectively etch the surface of the PL to produce porous structures. In a discharge, free electrons gain more energy from an imposed electric field. Energy transfers to the molecules lead to the formation of a variety of new species, such as metastable free radicals and ions, along with UV radiation and other photons[18]. Furthermore, these new species interact with the surface of the material and cause some physical and chemical changes, such as roughness, oxidation, and etching. To investigate the influence of discharge time on the morphology of pencil lead, pencil lead was treated with air plasma for different time (Fig. S1). With increasing plasma-etching time, the surface of the pencil lead became rougher, with more generated micro/nanosheets. After 40 min of air plasma treatment, the P-PL surface was compact and closely coated by highly porous GO nanosheets. However, the produced surface nanosheets have no differences if the treatment time exceeded 40 min. Thus, 40 min was selected as the discharge time for subsequent experiments. Voltage is another discharge condition that affects the structure and morphology of the synthesized fiber. As shown in Fig. S2, the roughness of the surface of the pencil lead increases with voltage increased from 1.09 kV to 1.45kV. When the discharge voltage was lower than 1.45 kV, only striped and dotted protrusions were observed rather than porous structure. In addition, lower discharge voltage cannot generate and maintain a stable plasma, whereas the stability of plasma was deteriorated when a higher voltage was used. A 1.45 kV of ac power supply was chosen as the optimal voltage to form rich porous structure which can provide more binding sites to Cd ions. The type of raw pencil lead plays an important role in fabricating porous P-PL fibers due to different content of graphite. We have tested pure graphite fiber and pencil leads of different types from 2H to 2B as raw materials. The content of graphite in pencil lead increases in the following order: 2H < HB < 2B. As shown in Fig. S3, no porous structure was observed on the surface of pure graphite fiber after plasma treating. With pencil lead fiber bought from Mitsubishi Pencil Co., only HB pencil lead has a partially uneven porous structure. For 2B pencil lead, it has a similar small hollow bump as 2B pencil lead bought from Duoqi Stationery Factory at lower discharge voltage. Therefore, it is possible that the plasma energy maybe not enough to make a porous structure for those with higher yield of graphene. Additionally, different morphology generated on PLs (2B) from different manufacturers indicates that the other components in pencil lead than graphite can help to form the porous structure of the fiber. To investigate the potential chemical reactions occurred during the plasma treatment, energy-dispersive X-ray spectroscopy (EDX) for the characterization of PL and P-PL was taken. The EDX (Table S2 and Table S3) show

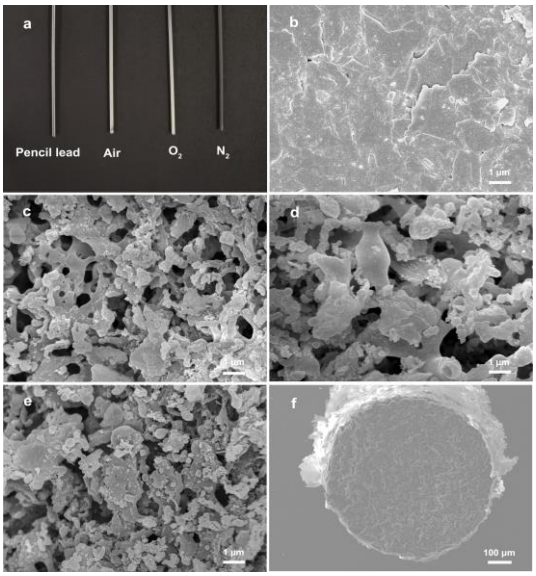

Fig. 2 (a) Photographs of different gases as the discharge gas; SEM images of (b) Pencil lead, (c) Air plasma treated pencil lead, (d) O_2 plasma treated pencil lead, (e) N_2 plasma treated pencil lead, (f) the cross-section image of the air plasma treated pencil lead. Experimental conditions: discharge voltage, 1.45 kV; and time, 40 min

that the elemental composition of the two kinds of PL have big

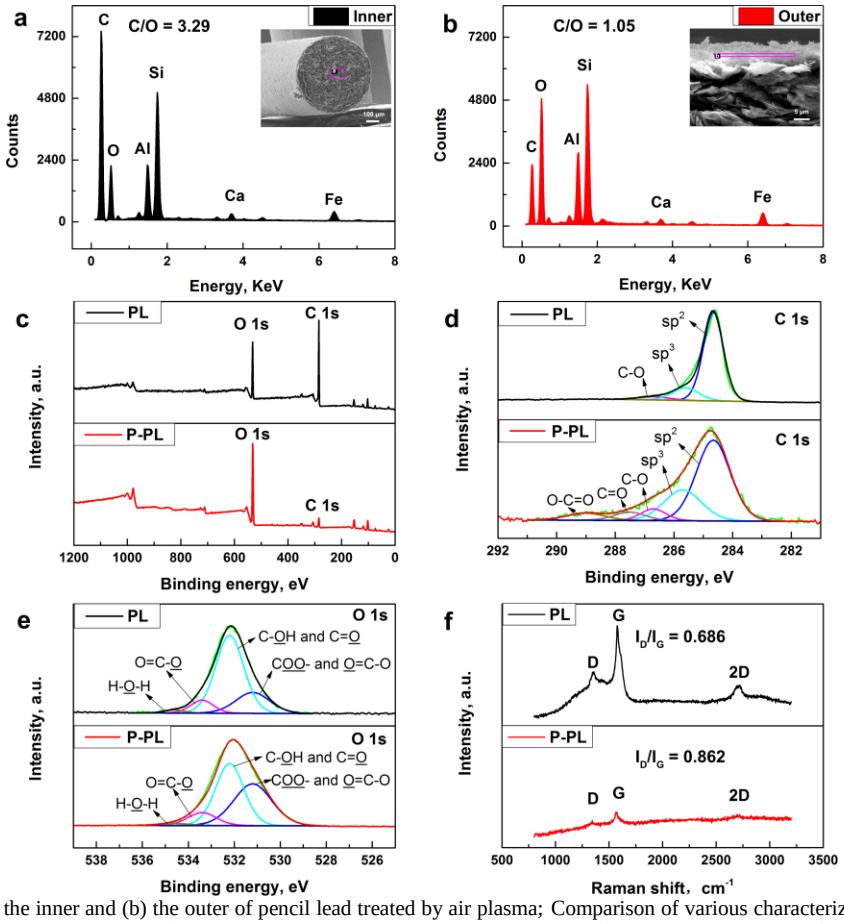

Fig. 3 EDX spectrum of (a) the inner and (b) the outer of pencil lead treated by air plasma; Comparison of various characterization results of PL and P-PL (c) XPS spectrum; (d) high resolution spectra of the C1s XPS peak; (e) high resolution spectra of the O1s XPS peak o; (f) Raman spectra. Experimental conditions: discharge voltage, 1.45 kV; and time, 40 min.

difference. The one from Mitsubishi Pencil Co. is cleaner than the other one, containing only four elements and 94.15% C (i. e. graphene). Although Duoqi pencil lead has a high carbon content, it contains more elements (Fe, Ca, Ti, Mg, K). It should be noted that the Fe amount accounts for 4.04%. As known, iron is an excellent catalyst, it might promote the physicochemical reaction induced by air plasma on the surface of the fiber to generate a porous structure. Thus, the following experiments were conducted with 2B Duoqi pencil lead. The two most dominant components in dry air are 21% (by volume) oxygen and 78% (by volume) nitrogen. To investigate their roles in forming P-PL, both pure O_2 and N_2 were used as discharge gas and the results are shown in Fig. 2. Under the reaction of oxygen plasma, the pencil lead turned white which was similar to the color obtained by air plasma, whereas it became black under N_2 plasma. This phenomenon indicates that the process of air plasma treating was mainly oxidation process, although O_2 accounts for a smaller proportion of air compared to N_2. Meanwhile, SEM images show porous structure under all tested gases. However, surprisingly, the product morphologies varied significantly when different discharge gases were used. A lot of lamellar loose accumulation, large, and rich pore structure were produced with O_2 as discharge gas, compared with shallow and small pores using N_2. The dense and deep pore structure generated by the air plasma indicates that it may be caused by both N_2 and O_2. In short, the synthetic conditions for P-PL are quite gentle with operation at room temperature, low power consumption (<10 W), relatively short reaction time (40 min), and simple operation. In addition, only air is used, avoiding the use of organic reagents and strong oxidation reagents, thereby greatly reduces the cost and environmental impact.

EDX measurement is shown in Fig. 3a and 3b, the carbon to oxygen ratio (C/O, atom) of inner black section of the P-PL fiber was higher than that of outer white layer, indicating a higher oxidation of graphite. As shown in Fig. S4, only 15 μm surface of the fiber rather than the entire P-PL fiber has been oxidized. The successful oxidation has also been confirmed by XPS (Fig. 3c). Both C1s and O1s peaks were observed in the survey spectra, and the O1s peak intensity in P-PL was much higher than that in PL. To further explore the bonding configuration, high resolution XPS spectra were collected, the results of which are shown in Fig. 3d and 3e. It is evident from the high resolution spectra of the C1s region of PL and P-PL that the content of sp^3 carbons increased in P-PL (Figure 3d), indicating more defects in P-PL. In addition, the content of C-O also increased, which may be induced from the oxidation of

carbon on the edge when exposed to air plasma. Most importantly, new oxygen-containing functional groups formed, including C=O and O=C-O, two main carbonyl groups, on P-PL. Those oxygen-containing groups are expected to form strong surface complexes with metal ions on the solid surfaces. The O1s peak (Figure 3e) indicates the content of carboxyl group or oxygen double bond and, in particular, the content of COO- and O=C-O increased after plasma-etching, which is consistent with the results from the high resolution spectra of C1s. To further confirm the structure of P-PL, Raman spectroscopy was carried out (Fig. 3f). The obvious bands at around 1580 and 1350 cm^{-1} are generally assigned as the G band (associated with the vibration of sp^2 carbon atoms in a graphitic 2D hexagonal lattice) and D band (related to the vibrations of sp^3 carbon atoms of defects and disorder). The weak and broad 2D peak at 2700 cm^{-1} is another indication of the disorder, due to the out of plane vibrational mode. The integrated intensity ratio of the D peak to the G peak (I_D/I_G) is usually used to evaluate the degree of disorder of carbon materials. The spectra of PL and P-PL have all these three bands. However, the D/G intensity ratio increased after air plasma treatment, which indicates an increase in defects, consistent with the results from the high resolution spectra of C1s. Although the degree of disorder has increased, the content of graphitized carbon is still greater than the content of amorphous carbon. The main carbon-containing compound on P-PL is GO. Overall, Air plasma treatment formed new structure, such as edges and defects, and functional groups, including carbonyl (C=O) groups and carboxylate (O=C-O) groups, on P-PL.

Preliminary studies and practicality of P-PL as SPME fiber for the detection of Cd

In this study, we synthesized the GO-functionalized PL fiber with rich oxygen-containing groups. Previous works showed that GO and these groups have impressive adsorption capacities toward metal ions[19,20]. Thus, the

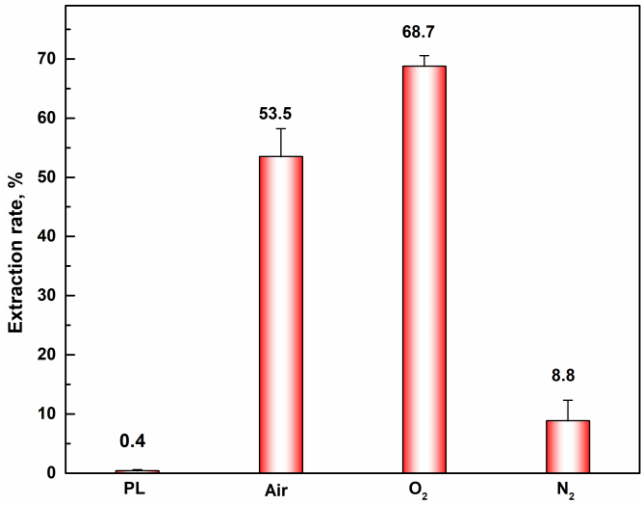

Fig. 4 The extraction rates of different pencil lead fibers treated with different discharge gas

new fiber may have excellent adsorption performance for heavy metals. Cadmium was used as a model metal to study the new P-PL fiber performance for metal adsorption. Preliminary experiments were carried out to study the adsorption/desorption of Cd on P-PL, and results are shown in Fig. S5a. The concentration of Cd before and after extraction were measured to investigate its extraction capacity. The concentration was reduced by 53.5% after extracting for 30 min, which means 53.5% of Cd in solution has been absorbed on P-PL, compared to 0.4% on PL. The high enhanced extraction rate of P-PL may due to its large surface area and lots of oxygen-containing functional groups. Comparisons were made with other pencil lead fiber treated by N_2 and O_2 (two main components of air) plasma (Fig. 4). As we can see, results from adsorption/desorption experiments show that the extraction capacity was in the order of O_2 > Air > N_2 > PL. This result further demonstrated that the carbonyl, carboxylate groups, and other oxygen-containing functional groups play an important role in the efficient adsorption of metal ions from aqueous solutions.

Optimization of experimental conditions for Cd extraction and desorption

All experimental conditions were optimized to obtain optimum response (Fig. S5). According to previous reports [21,22], the sorption of metal ions on GO is highly dependent on the solution pH, high pH is beneficial for the ionization of the oxygen-containing functional groups on the surface of GO. On the other hand, at high pH values, metal hydroxides can form precipitates or anionic species can be predominant. Fig. S5a shows the effect of pH on Cd(Ⅱ) sorption on the P-PL in different mix solutions of 0.1 M nitric acid and ammonium hydroxide. The absorbance value of Cd increased slowly at pH < 6, sharply increased at pH 6–8, and then decreases at pH > 8, indicating the sorption of Cd reaches its maximum at pH 8. Extraction time is another important parameter for Cd absorption efficiency with P-PL. Fig. S5b indicates that the amount of metal extracted increased dramatically from 10 min to 20 min and then rose slowly. The adsorption showed a slow kinetics. To compromise between high extraction efficiency and fast extraction time, the adsorption time was set to 20 min in all subsequent experiments. For GF-AAS analysis, HNO_3 was used as the eluent in this work. Thus, its concentration is important for desorption of the cadmium from the P-PL, which was studied in detail. The results show that 0.10 mol L^{-1} HNO_3 was sufficient for desorption of Cd from the surface of the fiber (Fig. S5c). Considering analyte concentration as large as possible, the size of fiber, and the craft of making glass tubes for collecting eluent, 150 μL of 0.10 M HNO_3 was used as reagent for desorption. Desorption time influences the degree of desorption and cross-contamination from reuse, so it was investigated and the results are shown in Fig. S5d. In contrast to absorption time, desorption in acid conditions was relatively fast with maximum response reached in less than 8 minutes. To ensure complete desorption, 10 min was selected as the optimum desorption time. It is important to note that shorter sorption and desorption times are possible to reduce the overall analysis time.

Analytical performance

Under the optimum experimental conditions, the analytical figures of merit for Cd(II) ions were obtained to evaluate the performance of P-PL fiber in DI-SPME and are summarized in Fig. 5 and Table 1. The developed method exhibited good linearity within the range of 0.04–0.26 μg L^{-1}, and the regression equation was $A = 3.4582\ C - 0.0359$, with a correlation coefficient of 0.9980. The enhancement factor (EF) was calculated in order to demonstrate that GF-AAS sensitivity can be enhanced by incorporating the SPME preconcentration procedure with the P-PL fiber. The parameter was determined as the slope ratio of calibration graphs with and without a preconcentration step. The EF value achieved was 25, which implies that the P-PL DI-SPME-GF-AAS system can offer an increase in the sensitivity for the determination of Cd by GF-AAS at the ultratrace level. Defined as the analyte concentration equivalent to three times the standard deviation of 11 measurements of a blank solution, the limit of detection (LOD) of Cd was 0.005 μg L^{-1} for P-PL extraction coupled with GF-AAS. The extraction on P-PL fiber showed good precision with the run-to-run RSD of 2.1% (n = 5). The RSD for fiber-to-fiber reproducibility was 5.6% when using three different fibers synthesized in the same way. To some extent, these results indicate that the P-PL fiber can be repeatedly and controllably prepared through the DBD plasma-based technique. A comparison of the developed method with other reported methods for the extraction and measurement of Cd is summarized in Table 2. It is clear, the LOD obtained by this work is higher than that preconcentrated by some types of SPE and LPME [23-27], and comparable with that obtained by MSPE and CPE [28,29], but lower than that achieved by DI-SPME using Polypyrrole/Carbon Nanotube/1, 10-Phenanthroline composite fiber, DSPE-SS, USAEME, DLLME and EC-SPME [30-33,4,34]. The EF value provided by DI-SPME with the new GO-functionalized pencil lead fiber is lower than values of MSPE, CPE, DMSPE, D-μ-SPE, LPME, USAEME and DLLME [30,31,23,26-28,32,29], which may due to limited absorbents of SPME, and comparable or better than the level of on-line solvent extraction preconcentration, SPE, and DSPE-DLLME [24,25,33]. The repeatability of the proposed method is better or comparable to that of other extraction methods.

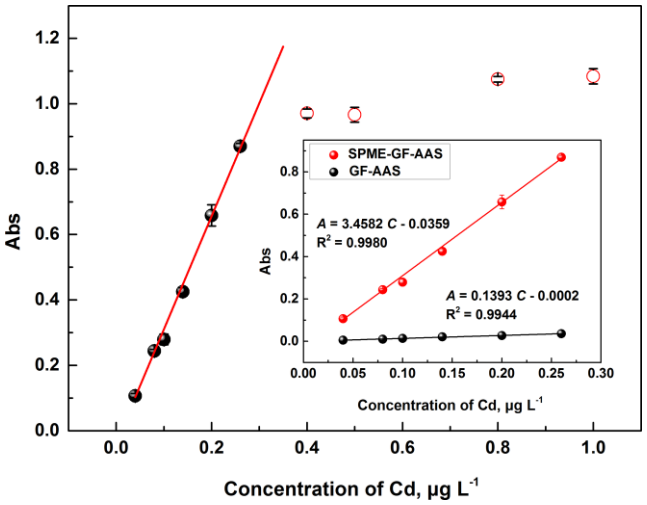

Fig. 5 Plots of the absorbance obtained from DI-SPME using P-PL fiber as a function of Cd concentration from 0.04 to 1.00 μg L^{-1}. Inset reveals calibration curves after and before extraction.

Table 1 Analytical Figures of Merits

Parameter	Analytical feature
Linear range (μg L^{-1})	0.04–0.26
r^2	0.9980
Limit of detection (μg L^{-1})	0.005
One fiber (%) (n=5)	2.1
Fiber to fiber (%) (n=3)	5.6
Enhancement factor[b]	25
Sample volume (mL)	15
Extraction time (min)	20

[b]Enhancement factor is the slope ratio of calibration graph after and before extraction.

Application in real water sample analysis

To verify the accuracy of the DI-SPME GF-AAS method with the new P-PL fiber for Cd quantitation in natural waters, spiked recoveries were evaluated with three types of water samples including tap water, river water, and pond water. The results are given in Table 3, the recoveries for spiked samples are in the satisfied range of 94–105%. These results confirm the validity of the proposed method. Additionally, the content of Cd in tap water is lower than that of river and pond water, possibly because water treatment plant can reduce heavy metal content. The proposed method was also applied to the determination of target metal ions in school dormitory pipe network water samples, and the results are summarized in Table 4. Among 11 tape water samples from Sichuan University dormitories, two of them were lower than the LODs of this method and were not detected, whereas the cadmium content in the remaining samples was up to 0.099 μg L^{-1}. Though a variety of faucets and pipes made of metal materials (copper, aluminum alloy, zinc alloy, and so on) can result in heavy metal pollution in drinking water, including cadmium, a few previous studies found that Cd concentrations from these sources are relatively low. The cadmium concentrations of the samples measured in this article are all lower than the permissible limits required by the regulatory authorities for drinking water, which is 5 and 3 μg L^{-1} for EPA and WHO, respectively.

Table 2 Analytical Performance in Comparison with Other Methods

Preconcentration	Detection method	Linear range ($\mu g\ L^{-1}$)	Sample consumption （mL）	LODs ($\mu g\ L^{-1}$)	RSD(%)	EF	ref.
DI-SPME	GF-AAS	0.04–0.26	15	0.005	2.1	25	This work
MSPE	GF-AAS	0.01–0.2	25	0.0061	4.0	50	[29]
CPE	GF-AAS	0–0.02	10	0.0059	2.1	50	[28]
LPME	GF-AAS	0.008–1	2	0.0035	4.5-5.2	450	[26]
On-line SE	GF-AAS	0.006–0.3	14	0.0028	3.2	24.6	[24]
SPE	GF-AAS	0.005–0.2	1.4	0.0014	2.4	19.8	[25]
DMSPE	HR-CS GFAAS	0.05–5	20	0.001	3	30	[27]
DSPE-SS	GF-AAS	0.125–1	20	0.0097	1.4-2.1	3.9	[33]
USAEME	GF-AAS	0.5–20	12	0.03	8	70	[32]
DLLME	GF-AAS	0.002–0.020	5	0.6	3.5	125	[30]
EC-SPME	GF-AAS	7–80	10	0.74	6.03	-	[34]
DI-SPME	ICP-MS	1–750	50	0.027	4.96	-	[4]
HF-SPME	ICP-MS	0.03–50	1	0.0067	7.8	10	[35]
D-μ-SPE	ICP-MS	0.01–0.5	50	0.0018	2.1	100	[23]

MSPE: magnetic solid-phase extraction; CPE: cloud point extraction; LPME: liquid phase microextraction; On-line SE: on-line solvent extraction; SPE: solid phase extraction; DMSPE: dispersive micro solid-phase extraction; DSPE-SS: dispersive solid-phase extraction- slurry sampling; USAEME: ultrasound-assisted emulsification microextraction; DLLME: dispersive liquid-liquid microextraction; EC-SPME: electrochemically controlled solid-phase microextraction ; D-μ-SPE: dispersive micro-solid phase extraction

Table 3 Determination of Cd in tap, river and pond water samples and relative recovery of spiked Cd in tap, river and pond water samples

Sample	Concentration of Cd^{2+} ($\mu g\ L^{-1}$)	Added Cd^{2+} ($\mu g\ L^{-1}$)	Found Cd^{2+} ($\mu g\ L^{-1}$)	Relative recovery (%)
Tap water	0.047 ± 0.004[a]	0.08	0.125 ± 0.005	98
Funan river	0.115 ± 0.021	0.08	0.199 ± 0.024	105
Lotus pond	0.131 ± 0.012	0.08	0.206 ± 0.006	94

[a]mean ± S.D. (n=3)

Table 4 Determination of Cd in tap water samples from dormitories in Dong Yuan of Sichuan University

Sample	Sample location	Concentration of Cd^{2+} ($\mu g\ L^{-1}$)
1	No. 1 Dormitory	0.076 ± 0.002[a]
2	No. 2 Dormitory	0.037 ± 0.001
3	No. 3 Dormitory	0.016 ± 0.003
4	No. 4 Dormitory	0.012 ± 0.004
5	No. 5 Dormitory	n.d.
6	No. 6 Dormitory	0.019 ± 0.005
7	No. 7 Dormitory	n.d.
8	No. 8 Dormitory	0.097 ± 0.002
9	No. 9 Dormitory	0.099 ± 0.005
10	No. 10 Dormitory	0.059 ± 0.009
11	No. 11 Dormitory	0.037 ± 0.004

[a]mean ± S.D. (n=3)
n.d., not detected

Conclusion

A novel solvent-free *in situ* plasma exfoliation and oxidation strategy for preparing GO-functionalized pencil lead fiber through a simple one-step air plasma treatment in a cylindrical dielectric barrier discharge setup with a pencil lead as the inner electrode, was successfully developed. The proposed GO-functionalized PL fiber preparation method is simple and environmental friendly (green) with only use of air without use of any organic solvents. In addition, pencil lead was used as both a central fiber support and a trigger, which has the advantages of low cost, non-toxicity, easy-to-get, and no coating falling off by integrating the support and the coating as one part. In this study, we have demonstrated an application of the prepared fiber in DI-SPME for the extraction of cadmium ions. This pretreatment technique avoids tedious operations such as derivatization, filtration and centrifugation. It is simple and easy to operate. In general, this work provides a potential green synthesis of SPME fiber and its application in metal determination, especially those metal ions that cannot be derived. The eco-friendly SPME fiber synthesis method and simpleness of SPME in metal analysis still need to be further explored.

Corresponding Author

* E-mail: abinscu@scu.edu.cn (C. Z.). Fax and Phone: +86 28 8541 0528; lu.yang@nrc-cnrc.gc.ca (L.Y.).

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