



Hierarchical Graphene coating for highly sensitive solid phase microextraction of organochlorine pesticides



Fuxin Wang, Shuqin Liu, Hao Yang, Juan Zheng, Junlang Qiu, Jianqiao Xu, Yexiang Tong, Fang Zhu*, 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, PR China

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ABSTRACT

Graphene, a novel class of carbon nanostructures, has received great attention as sorbents due to its fascinating structures, ultrahigh specific surface area, and good extraction ability. In this paper, a new type of hierarchical graphene was synthesized through employing a mild and environment-friendly method. Such 3D interconnected graphene own a high specific surface area up to $524 \text{ m}^2 \text{ g}^{-1}$, which is about 2.5 fold larger than the graphene, since the synthetic material has interlayer pores between nanosheets and in-plane pores. Then a superior solid-phase microextraction fiber was fabricated by sequentially coating the stainless steel fiber with silicone sealant film and hierarchical graphene powder. Since the novel hierarchical graphene possessed large surface area and good adsorption property, the as-prepared fiber exhibited good extraction properties of the organochlorine pesticides (OCPs). As for the analytical performance, the as-prepared fiber achieved low detection limits ($0.08\text{--}0.80 \text{ ng L}^{-1}$) and wide linearity ($10\text{--}30,000 \text{ ng L}^{-1}$) under the optimal conditions. The repeatability ($n=5$) for single fiber were between 5.1% and 11%, while the reproducibility ($n=3$) of fiber-to-fiber were range from 6.2% to 14%. Moreover, the fiber was successfully applied to the analysis of OCPs in the Pearl River water.

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1. Introduction

Solid-phase microextraction (SPME) is a simple pretreatment technique that possesses advantages of solvent-free, fast, sensitive, and easy coupling with GC and HPLC [1–4]. First developed by Pawliszyn's group in the 1990s [5–8], this technique has been considered as a promising pretreatment method and has been widely used in the fields of environment, food, biology, clinical medicine, toxicology and forensic medicine [9–17]. The mechanism of SPME is based on the distribution of analytes between the matrix and the fiber coating [18,19]. Hence, the stationary phase coated onto the fiber plays a key role in improving the sensitivity, mass transfer rate, and reproducibility of the SPME technique [20]. In the past decades, many efforts have been made to develop the novel SPME coating materials with remarkable chemical and thermal stability, enhanced sensitivity and selectivity for the specified analytes.

Carbon materials, such as single-walled carbon nanotubes [21], multi-walled carbon nanotubes [22], activated carbon [23] and

glassy carbon [24], are well known for their high adsorption capacity of organic compounds [25,26]. Graphene, an atomically thin honeycomb lattice of carbon atoms, has attracted great attention discovered shortly by Geim et al. in 2004 [27]. It is a one atom-thick planar sheet of sp^2 bonded carbon atoms arranged in six-membered rings and considered as the basic building block of all the graphitic materials [28]. In addition, with a high specific surface area, graphene displays excellent mechanical, electrical, optical, and thermal properties, which make it the most promising carbon-based nanomaterial due to its widespread applications like field-effect transistors, sensors, energy storage, and supercapacitors [29–32]. Furthermore, as a adsorbent, graphene has also been considered to be applied to extraction of benzenoid form compound, since it has a large delocalized π -electron system, which can form a strong π -stacking interaction with the benzene ring. For example, Chen et al [33]. used graphene as SPME fiber coating for the first time and extracted the pyrethroid pesticides from water samples. Li et al [18]. used graphene as fiber coating for the enrichment of polycyclic aromatic hydrocarbons.

So far, 3D hierarchical graphene materials with in-plane pores have attracted extensive attention, while the large voids can function as ion-buffering reservoirs, and the in-plane nanopores can shorten the ion transport length, directly reducing the response time of ion [34]. To fabricate the porous graphene

* Corresponding authors.

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

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materials, great efforts have been conducted [35], and the template methods, such as polystyrene sphere [36], nickel foams [37], and freeze-drying methods [38] are generally used. However, the results of these methods indicate that the material always hold the large pores (larger than 1 mm) or the low specific surface area (SSA) (less than $400 \text{ m}^2 \text{ g}^{-1}$). Since the theoretical surface area of the graphene is up to $2630 \text{ m}^2 \text{ g}^{-1}$ [39], it is urgent to find a mild and environment-friendly method to develop a graphene framework with an extremely large surface area.

In this study, we have developed a mild and environment-friendly method to efficiently construct a 3D continuous graphene framework, named as hierarchical pores graphene framework (HPGF), which has hierarchical pores of interlayer pores and in-plan nanopores. A novel HPGF coated SPME fiber was prepared by gluing the synthesized HPGF onto a stainless steel wire using neutral silicone sealant as binder. In order to examine the extraction performance and feasibility of HPGF as adsorbents for SPME, five OCPs were chosen as model analytes because of their acute toxicity and widespread environmental occurrence. It was shown that as-prepared fiber exhibited better extraction efficiencies toward OCPs than the commercial $85 \mu\text{m}$ PA fiber and $30 \mu\text{m}$ PDMS. Under the optimal conditions, the as-prepared fiber achieved the lower detection limits ($0.08\text{--}0.80 \text{ ng L}^{-1}$) and wider linearity ($10\text{--}30,000 \text{ ng L}^{-1}$).

2. Experimental

2.1. Reagents and materials

The stainless-steel wires (0.127 mm) were purchased from Component Supply Company (Fort Meade, MD, USA). Hexachlorobenzene (HCB) (99.5%), *trans*-chlordane (98.0%), *cis*-chlordane (99.6%), *o,p*-DDT (dichlorodiphenyltrichloroethane) (98.0%) and *p,p*-DDT (98.5%) were purchased from Dr. Ehrenstorfer GmbH (Germany). Methanol, anhydrous ethanol, sodium chloride (NaCl), acetone, graphite powder, concentrated sulfuric acid (H_2SO_4), concentrated nitric acid (HNO_3), concentrated hydrochloric acid (HCl), hydrogen peroxide (H_2O_2), potassium permanganate (KMnO_4), and sodium iodide (NaI) were purchased from Guangzhou Chemical Reagent Company (Guangzhou, China). Neutral silicone sealant was bought from Sikasil Ltd. (Guangzhou, China).

2.2. Synthesis of HPGF

Porous graphene framework was produced using the following procedures: Graphene oxide (GO) solution was firstly prepared by the oxidation of natural graphite powders based on a modified Hummer's method [40,41]. Then, 35 mL GO suspension (4 g L^{-1}) was transferred into a 50 mL Teflon-lined stainless steel autoclave. The sealed autoclave was further heated in an electric oven at $180 \text{ }^\circ\text{C}$ for 8 h. After being cooled down to room temperature, the as-prepared graphene hydrogel was obtained and then was transferred into the NaI-containing aqueous solution (1 g mL^{-1}) for filling NaI at $60 \text{ }^\circ\text{C}$ for 1.5 h. After that, it was dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ for 6 h. Next, thermal treatment was conducted under $800 \text{ }^\circ\text{C}$ for 3 h in nitrogenous atmosphere, in which the materials were washed by deionized water for three times and dried in the vacuum oven for 6 h. Thus 3D porous graphene frameworks were obtained. As a control experiment, a freeze-dried 3D graphene framework was prepared according to the literature [42].

2.3. Preparation of the HPGF-coated fiber

The stainless steel wires were firstly cut into a length of 3 cm ,

and then were ultrasonically cleaned in acetone, ethanol and water for 10 min, respectively. The cleaned wires were dried in an oven at $60 \text{ }^\circ\text{C}$ for 3 h. About 1.0 g of neutral silicone sealant with the main component of polydimethylsiloxane (PDMS) was dispersed in a sample tube by using 2.0 mL cyclohexane as dispersing agent and ultrasonically dissolved for 20 min. The cleaned steel wire was dipped into the mixture and taken out immediately. After being wiped by a piece of filter paper, a thin film of silicone sealant was left on the surface of the wire, and the wire was subsequently rotated in the powder of the synthesized HPGF to get the single-layered HPGF coating. Then the single-layered HPGF fiber was cured at $80 \text{ }^\circ\text{C}$ for 15 min. As a result, the three layered coating which was prepared by repeating the above coating steps was chosen for the following experiments.

2.4. SPME procedure and GC analysis

Before use, the prepared fibers and the commercial fibers were conditioned at $250 \text{ }^\circ\text{C}$ for 1 h in the GC injection port under nitrogenous atmosphere to avoid any contamination or carryover. The experiments were carried out on an Agilent Technologies GC–MS (6980-5975) equipped with a HP-5 MS capillary column ($30 \text{ m} \times 0.32 \text{ mm i.d.} \times 0.25 \mu\text{m}$). Helium was used as the carrier gas for GC–MS. The HPGF fiber was installed into a commercial device to conduct the direct immersion solid phase microextraction (DI-SPME). The sample solution was prepared by adding 10 mL deionized water and OCPs standard sample (10 mg L^{-1}) into a 10 mL sample vial. The extraction was conducted by a Gerstel MPS multipurpose sampler. DI-SPME parameters such as agitation speed, extraction temperature, extraction time and desorption temperature were optimized by the MPS sampler. After a certain extraction time, the fiber was directly transferred into the GC injector for desorption and analysis.

In GC analysis, desorption temperature was set at the optimized value under splitless mode. Helium was used as the carrier gas at a constant flow rate of 1.2 mL min^{-1} . The initial oven temperature was $50 \text{ }^\circ\text{C}$ (held for 0.5 min), and then increased to $150 \text{ }^\circ\text{C}$ at a rate of $20 \text{ }^\circ\text{C min}^{-1}$, held for 0 min, then increased to $250 \text{ }^\circ\text{C}$ at a rate of $15 \text{ }^\circ\text{C min}^{-1}$, held for 6 min, and finally increased to $270 \text{ }^\circ\text{C}$ at a rate of $30 \text{ }^\circ\text{C min}^{-1}$, held for 5 min. The total run time was 23.83 min.

2.5. Characterization

The morphologies, chemical compositions and the microstructures of the produces were characterized by field-emission scanning electron microscope (FE-SEM, JSM-6330F), Transmission electron microscopy (TEM, JEM2010-HR, 200 kV), X-ray Photoelectron Spectroscopy (XPS, ESCALab250, Thermo VG) and Raman spectroscopy (Renishaw inVia). N_2 adsorption measurement was carried out using a Micrometrics ASAP 2020 analyzer at 77 K. The pore size distribution of the sample was derived from the desorption branch by Barrett–Joyner–Halenda (BJH) theory combined with Kruk–Jaroniec–Sayari correction. The BET surface area (S_{BET}) was determined by BET theory.

3. Results and discussion

3.1. Characterization of as-synthesized HPGF

The HPGF synthesis procedure is schematically illustrated in Fig. 1. The whole synthesis procedure consists of four steps (Experiment section). The morphology was evaluated through scanning electron microscopy (SEM), Fig. S1 shows the low and high magnification SEM images of the GO and HPGF, clearly indicating

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