



Graphene aerogel based monolith for effective solid-phase extraction of trace environmental pollutants from water samples



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ABSTRACT

Graphene aerogel (GA), a typical kind of three-dimensional (3D) macroscopic assembly, not only provides inherently excellent properties of graphene sheets (GS), but also exhibits interesting characteristics of the 3D macroporous architecture including large and tunable pore volumes, high specific surface areas and fast mass transport kinetics. Thus, it is rational to expect GA to be an efficient adsorbent for solid-phase extraction (SPE). In this paper, a novel GA monolith based solid-phase extraction method was investigated in the application of environment analysis. The GA monolith based SPE cartridge was fabricated directly in the empty cartridge through template-free “sol-cryo” method. Due to the efficient mass transfer, more adsorption sites as well as effective retention for the analytes, the adsorption property of GA for bisphenol A revealed better performance than that of GS. What's more, GA also outperformed in loading and eluting for target analysis. On the basis of the above advantages, the obtained cartridge was applied for the separation of environmental pollutants from water samples. Taking endocrine disrupting chemicals and polychlorinated biphenyls as the polar and weak polar model analytes, optimizing several parameters influencing the recoveries, limits of detection in the range of 0.01–0.11 ng mL⁻¹ and 0.19–1.53 ng L⁻¹ for the two series of compounds were provided by the established methods. The satisfied sensitivity was accessed and recoveries ranging from 76.3 to 112.5% were obtained for all the analytes when the proposed methods were applied in real water samples analysis. The results revealed the potential of GA as an effective sorbent in sample preparation processes.

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1. Introduction

Sample preparation is an important step in the whole analytical procedures. Sorption-based extraction techniques [1] are currently the most widely used sample preparation techniques. The core component of the sorption-based extraction techniques is the adsorbent material, which dominates the selectivity and sensitivity of the method. Therefore, the development of new adsorbent material to meet different requirements is a hot research topic in sample preparation. Many kinds of materials have currently been developed for sample preparation, such as polymer materials [2,3], carbon nanotubes [4–6], metal-organic frameworks [7,8], and so on. Graphene, a new class of carbon nanomaterial, has been subjected to extensive studies in the past few years owing to its extraordinary physicochemical properties. Moreover, the novel nanomaterial possesses many intriguing properties such as ultra-

high specific surface area, superior chemical stability and excellent thermal stability, which evoke great interest and desire of exploration in separation science [9–13]. Our research group has made many investigations focused on the applications of graphene or its composites in sample preparation [14–18] and stationary phases [19].

Solid-phase extraction (SPE) is a powerful tool in sample pretreatment including preconcentration of trace analytes and elimination of matrix and interference components from a great variety of sample matrices. The previous researches focused on the application of graphene in SPE were, in general, directly packed graphene sheets (GS) into a cartridge though slurry-packed method [20,21]. However, the methods suffered from many problems. Firstly, the specific surface area of graphene which was synthesized through Hummers method is actually far less than the theoretical value (2630 m² g⁻¹). Secondly, the high pressure when sampling may lead polydisperse GS to irreversible aggregation or escape from the cartridge. Although many researches have made effective modification by the immobilization of GS on silica supporter through covalent bonding [9] or electrostatic interactions [22], the methods remained relatively cumbersome or the assemble amounts were

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extremely low. Finally, the density and homogeneity of the sorbents were difficult to manipulate by the method, thus resulted in a low mass transfer. Thereby, the effective utilization of graphene in SPE still needs further investigation.

Graphene aerogel (GA), a typical kind of three-dimensional (3D) macroscopic assembly, has recently become an intensively studied subject since its macroporous architecture can shift the intriguing properties of GS into a 3D interconnected framework. As a novel kind of functional materials, the 3D graphene architecture may not only provide inherently excellent properties of layered graphene materials, such as high electronic, optical and catalytical properties, but also exhibit interesting characteristics of the 3D macroporous architecture including large and tunable pore volumes, high specific surface areas and fast mass and electron transport kinetics, and thus actualize the exciting applications in energy storage and conversion [23,24], catalysis [25,26], biological and chemical sensors [27,28]. These intriguing properties also make it an ideal material for environmental remediation. GA based monoliths with a high porosity exhibit more advantages, including the improved absorption capability due to its high effective surface area, and the ease of separation from solution without auxiliary magnetic or centrifugation techniques, thereby making them easily recyclable. Qu and co-workers demonstrated that nitrogen-doped GA prepared by hydrothermal treatment of graphene oxide (GO) with pyrrole can act as efficient sorbent for gasoline [29] and the adsorption capacity can be as high as about 277 g g^{-1} with an average adsorption rate of 41.7 g per gram of GA per second, which is much higher than other typical carbonaceous sorbents. The 3D graphene-iron oxide nanoparticle aerogel composite showed outstanding absorption performance for the removal of As from contaminated water, which is due to its high surface-to-volume ratio and characteristic pore network in the 3D architecture [30]. In addition, the gas adsorption performance was investigated through GO composite aerogels. It was found that the H_2S adsorption capacities are as high as 63.5 and 46.7 mmol g^{-1} for two types of functional GO aerogels, being higher than those for activated carbon. The GO aerogels also exhibit high adsorption capacities towards the reducing gases of SO_2 and HI at ambient atmosphere and room temperature [31]. As mentioned above, many reports have explored the adsorption performance of GA for many pollutants, however, the use of GA in the analysis of environmental pollutants at trace levels has not been demonstrated to the best of our knowledge.

Based on the above statement, GA based monoliths with uniform pore size and high effective surface area could achieve a lower mass transfer resistance, and eventually realize the improved absorption capability and effective elution, it is rational to expect GA to be a more effective adsorbent than GS for SPE. In the present study, GA was directly synthesized in cartridges though template-free “sol-cryo” method for the application as SPE sorbent for the first time. GA in SPE compared with GS was investigated through dynamic adsorption for BPA as well as loading and eluting performance for the targets. Typical environmental pollutants including endocrine disrupting chemicals (EDCs) and polychlorinated biphenyls (PCBs) were selected as the polar and weak polar model analytes, respectively, to evaluate the analytical performance of the GA based SPE method. The parameters influencing the recoveries of the targets were optimized in details and the developed GA based SPE method was applied to real water samples.

2. Experimental

2.1. Chemicals and materials

Expanded graphite powder (100 mesh) was supplied by Xinghe Graphite Co., Ltd. (Qingdao, China). The chemicals applied in

synthesis graphite oxide were purchased from Beijing Chemical Works (Beijing, China). All of the organic reagents used for chromatographic analysis were of HPLC grade and purchased from Amethyst Chemicals (J&K Scientific, Beijing, China) and the water used for HPLC analysis was Wahaha purified water (Hangzhou, China). Target-free tap water was chosen for the evaluation of SPE and the figures of merit of the proposed method.

Four EDCs namely: estrone (E1), β -estradiol (E2), estriol (E3) and 17α -ethynylestradiol (EE2) were purchased from J&K Scientific (Beijing, China) and bisphenol A (BPA) were bought from Dima Technology TNC (CA, USA). These molecular structures are shown in Fig. S1. The individual standard stock solutions of the five EDCs (1000 mg mL^{-1}) were prepared in acetonitrile and the standard mixture was prepared at a concentration of 10 mg mL^{-1} . The standard of the seven PCBs (congener numbers: 28, 52, 101, 118, 138, 153 and 180) in isooctane solution (10 mg L^{-1}) was obtained from AccuStandard (New Haven, CT, USA) and was diluted to 1 mg L^{-1} by methanol. All the standards were stored at 4°C and fresh working solutions were obtained daily by appropriate dilution of the stock solutions.

2.2. Instrumental and analytical conditions

Scanning electron microscopy (SEM) images were collected on a field emission SU8010 system (Hitachi, Japan). Transmission electron micrographs (TEM) were taken out on an H-7650B (Hitachi, Japan) transmission electron microscope. X-ray photoelectron spectroscopy (XPS) data were collected using a PHI-5300 ESCA X-ray photoelectron spectrometer (PHI, USA). The analyses of EDCs and PCBs were performed on Shimadzu HPLC system and Shimadzu GC-MS QP2010 ultra system (Kyoto, Japan), respectively, and the chromatographic conditions were listed in Supplementary Material.

The SPE experiments were performed on a Win-SPE 12 with a VP30 vacuum pump. A Sepaths-C Evaporator was used to concentrate the analytes. The empty SPE cartridges (3 mL, polypropylene) and frits ($10 \mu\text{m}$, polypropylene) and the above mentioned equipments were all supplied by LabTech (Beijing, China).

2.3. Preparation of monolithic GA based SPE cartridges

Graphene oxide (GO) was synthesized from expanded graphite according to a modified Hummers' method [32]. The procedure is briefly described as follows. Potassium permanganate (36 g) was poured into a solution of frozen concentrated H_2SO_4 (720 mL) and H_3PO_4 (80 mL) mixture, then expanded graphite (6 g) was added to the above solution slowly with vigorous agitation to avoid a sudden increase of the temperature. The reaction kept at 50°C for 12 h, afterward, the mixture was poured into an ice-water mixture with the identical volume. $30\% \text{ H}_2\text{O}_2$ was added dropwise to all the slurry turn to golden yellow. The obtained slurry was rinsed with $10\% \text{ HCl}$ and water by centrifugation. Finally, it was purified by dialysis for one week to remove the remaining metal species.

After the dialysis, the slurry was transferred subsequent to the ultrasonication for 2 h, and the mass concentration of the as-prepared GO aqueous dispersion (13.3 mg mL^{-1}) was confirmed by drying certain volume of the above solution. The monolithic GA based SPE cartridges were performed by the reported template-free “sol-cryo” method [33] and the detailed process is illustrated in Fig. 1. Typically, the obtained homogeneous GO dispersion (1 mL) was added into the SPE cartridge which has been placed the lower frit. Because of the hydrophobic property of the frit, the dispersion could not leak through the frit. The cartridges were subjected to freezing and freeze-drying to form a porous GO aerogel (SEM in Fig. S3). The as-prepared aerogel was chemically reduced to GA by hydrazine vapor at 95°C for 24 h. After the reduction, the upper

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