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Three dimensional phytic acid-induced graphene as a solid-phase microextraction fiber coating and its analytical applications for nerolidol in tea

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A R T I C L E   I N F O

A B S T R A C T

In this work, three dimensional phytic acid-induced graphene coating was prepared by hydrothermal synthesis and fabricated on a stainless-steel wire using physical coating method as a solid phase microextraction (SPME) coating. The graphene coating revealed high specific surface area, extraordinary electrical conductivity and excellent chemical stability. Coupled with gas chromatography-flame ionization detector (GC-FID), the home-made phytic acid-induced graphene SPME fiber exhibited excellent extraction efficiency for the analysis of nerolidol in tea samples. Under the optimized conditions, the linear range of working curve was found to be 1–1000 ng/g, and the limit of detection of nerolidol was 0.18 ng/g. The coefficient variation of repeatability for each single fiber and reproducibility for fiber to fiber was less than 3.9% and 8.3%, respectively.

Graphene, a two dimensional single atomic layer of sp²-hybridized carbon atoms, has been found to be a promising material in a wide range of potential applications including energy storage, electronics, sensing and catalysis [1,2] owing to its large theoretical surface area, high electron mobility, superior thermal conductivity, remarkable optical transmittance and mechanical properties [3–6]. In addition, three-dimensional graphene (3D-graphene) materials with the structure of aerogel, sponge or foam present their characteristics comparing with those of two-dimensional graphene, such as larger specific surface area, higher mechanical strength, lower density, faster electron and mass transport kinetics [7]. Due to its unique properties, 3D-graphene has been widely used in the fields of catalysis, energy storage, environmental treatment, etc. [8,9]. Especially, the ultrahigh surface area, porous and unique structure of 3D-graphene makes it to be a good candidate in adsorption [10–12]. The further functionalization of graphene is critical to its fine-tune chemical and physical properties [13]. Graphene oxide, the precursor of the 3D-graphene, can be easily modified chemically due to the various functional groups containing hydroxyl, carboxyl, or epoxy.

Phytic acid, composed of six phosphate groups, provides an excellent characteristic for the modification of numerous substrates [14] owning to the predominant properties such as renewable, non-toxic, environment-friendly and easily obtained from cereals and beans [15,16]. For example, phytic acid can react with graphene oxide to import hydrophilic functional groups containing inositol triphosphate and phosphoric acid, which exhibits good capability of absorbing both water solutions and hydrophobic oil [17]. Ji et al. exhibited that phytic acid-stabilized Fe_3O_4-graphene oxide (GOPA@Fe_3O_4) was assembled by microwave-enhanced hydrothermal synthesis and was used as a sorbent for enrichment of eight polycyclic aromatic hydrocarbons (PAHs) from vegetable oils by magnetic solid-phase extraction (MSPE) [18]. Moreover, phytic acid has gain increasing attention for the anti-corrosion of metal [19], good antioxidant [20] and water treatment [14].

Solid phase microextraction (SPME) is considered as a simple, powerful, rapid and solventless sample preparation technique combining sampling, extraction and preconcentration, by which the desorption of total target compounds and sample introduction into a single step [21]. The key technique of SPME is the variety of fiber coating. SPME has attracted wide attention in the analysis of

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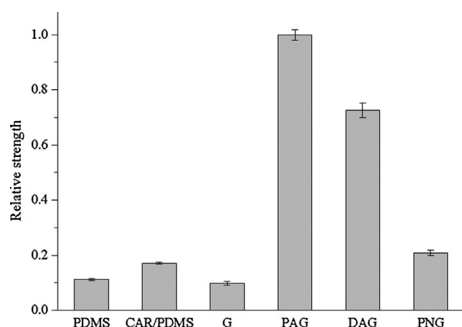
Fig. 1. Comparison of extraction efficiency towards nerolidol using different fibers. Error bars show the standard deviation of the mean (n = 3). G: graphene; PAG: phytic acid-induced graphene; DAG: dopamine-induced graphene; PNG: o-phosphorylethanolamine-induced graphene.

organic compounds. In the last years, different kinds of fiber coatings and their fabrication methods have been developed including sol-gel technology, electrospinning, electrodeposition, chemical grafting, liquid phase deposition, hydrothermal and physical adhesion approaches. Nerolidol (3,7,11-trimethyl-1,6,10-dodecatrien-3-ol) is a predominant sesquiterpene present in essential oils from plenty of plants [22]. It was approved as a fragrance ingredient and a food flavoring agent [23,24]. In general, terpenes are applied to enhance effective skin permeation and nerolidol has been found to be a good candidate for the enhancement of hydrophilic drug transdermal delivery [25]. Moreover, nerolidol exhibits several medicinal benefits such as antibacterial, antiulcer, antitumor and antischistosomal properties [22,26–28]. In particular, quantitative analysis of the volatile compound for nerolidol is considered as an indicator in the evaluation of tea qualities [29]. Ma *et al.* showed that higher grades of Wuyi rock tea possess higher content of nerolidol. It is beneficial to tea manufacturers in order to endow desirable flavour characteristics to tea and improve its quality. Therefore, to develop an effective and powerful tool for the analysis of nerolidol in tea samples is necessary.

In this work, a simple strategy to fabricate the 3D phytic acid-induced graphene (PAG) was performed by a hydrothermal method. The PAG was applied as SPME fiber coating. Its extraction performances were then evaluated and compared with those of 100 μm polydimethylsiloxane (PDMS) and 85 μm carboxen/polydimethylsiloxane (CAR/PDMS) fibers in the analysis of nerolidol in tea samples.

3D heteroatom doped graphene aerogel was prepared by a hydrothermal synthesis method in this work. Graphene oxide was prepared from graphite powders based on a Hummers method with some modification [30,31]. PAG was synthesized following the report [17]. In brief, 1 mL of phytic acid was mixed into a 15 mL of graphene oxide aqueous dispersion (2 mg/mL, $m_{grapheneoxide}$: $m_{phyticacid}$ = 1:19), and the mixture was sonicated for 40 min. The obtained mixture was sealed in a 30 mL Teflon-lined stainless steel

sealed vessel and maintained at 180 °C for 12 h. After the vessel was cooled to room temperature, the product was washed with ethanol and water several times, and then freeze-dried for 24 h. The fabrications of 3D dopamine-induced graphene (DAG) [32] and o-phosphorylethanolamine-induced graphene (PNG) were similar to the PAG, and the mass ratio of graphene oxide and dopamine or o-phosphorylethanolamine was 1:1 and 1:3, respectively. The resultant products exhibited an excellent adsorption ability for oil in these mass ratios [17,32]. All the chemicals, instruments used in this work and the detailed preparation solutions were shown in the Supporting information (section 1.1-1.4).

The fabrication of solid phase microextraction fiber was illustrated as following. Prior to the coating fabrication, the stainless steel wire (17 cm) was sequentially cleaned with acetone and ultrapure water by ultrasonicator for 5 min, and then dried at room temperature. The treated stainless steel wire (1.5 cm) was immersed into AB glue until it became sticky. The fiber was then placed into the PAG, DAG or PNG powder in a tube, rotated and drawn out to dry. The prepared fibers were dried at 80 °C in an oven overnight, and further heated at 220 °C under a nitrogen atmosphere for 30 min to avoid any residual.

The different 3D-graphene coated fibers were assembled into a 5 μL microsyringe. The target analyte was conducted from different sample solutions in a 20 mL glass vial equipped with a PTFE-lined septum cap. During extraction, the SPME fiber was directly immersed into the sample solution and the stirring rate was controlled at 900 rpm. After extraction, the fiber was pulled out and immediately introduced into the GC injector for the thermal desorption and analysis. The sample preparation process was shown in the Supporting information (section 1.5).

The morphology of PAG was characterized by SEM. As shown in Fig. S1a (Supporting information), the PAG coating possessed a rough and homogeneous surface from the low magnification. The coating thickness was approximately 60 μm as indicated in Fig. S1b (Supporting information), and the coating was tightly adhered to the stainless-steel wire. Due to the same coating fabrication procedures and conditions, the similar morphology and thickness of DAG or PNG fiber could be found. The three fibers revealed a little different surface from that of the pure graphene due to the phytic acid-, dopamine- or o-phosphorylethanolamine-induced (Fig. S1c-f in Supporting information). The X-ray diffraction (XRD) pattern of the different-induced graphene illustrated a broad diffraction peak at approximately 25° (Fig. S2 in Supporting information), which was belonged to the (002) plane of stacked graphene sheets in the XRD pattern. These results were in accordance with the reports [17,32].

In order to investigate the extraction ability toward nerolidol using the phytic acid-induced graphene coated fiber, two most commonly used commercial fibers (100 μm PDMS and 85 μm CAR/PDMS) and the other two different-induced graphene coated fibers (DAG and PNG) were chosen for the comparison. As shown in Fig. 1, the extraction efficiency of PAG, DAG or PNG coatings towards nerolidol was 5.9, 4.3 and 1.2 folds higher than that using the
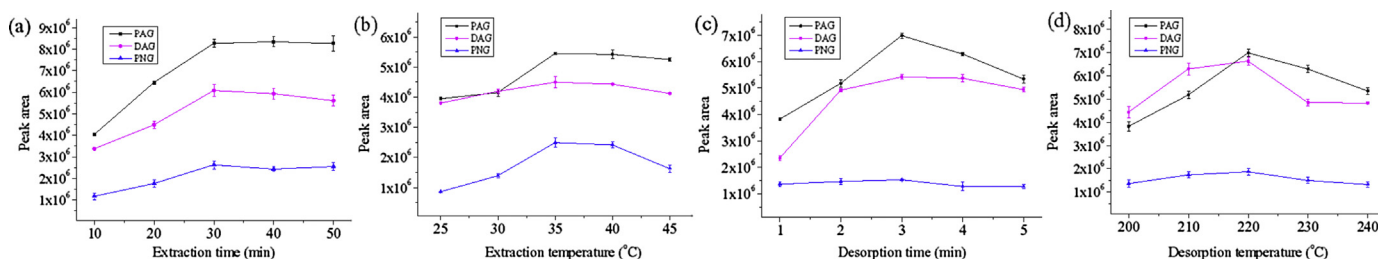

Fig. 2. (a) The effect of extraction time on the extraction capability. (b) The effect of extraction temperature on extraction efficiency. (c) The effect of desorption time on peak areas. (d) The effect of desorption temperature on extraction efficiency. Concentration of nerolidol was 50 ng/mL. Error bars show the standard deviation of the mean (n = 3).