



Covalent immobilization of graphene onto stainless steel wire for jacket-free stir bar sorptive extraction



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ABSTRACT

Stainless steel wire is a good substrate for jacket-free stir bar sorptive extraction (SBSE). In this work, we present the first example of chemical modification of graphene on stainless steel wire (SSW) for SBSE. Bio-inspired polydopamine was firstly modified on the SSW covalently; then graphene oxide was introduced and reacted with amino groups of polydopamine layer. The modification of polydopamine and graphene can be repeated by a layer-by-layer strategy, resulting in control of the thickness of graphene layer and increase of extraction capability. The prepared covalently immobilized graphene-stainless steel wire (G-SSW) exhibited good stability under stirring, ultrasonication and treatment with commonly used organic solvents, basic and acidic solutions. Application as stir bar for SBSE, G-SSW was found to possess good extraction efficiency towards pollutant polyaromatic hydrocarbons (PAHs), with enrichment factors from 10086 to 16896. After optimization of conditions, G-SSW based SBSE was coupled HPLC for determination of PAHs in environmental and food samples. The quantitative method has low limits of detection of 0.2–50 pg/mL, which is better than some reported SBSE-HPLC methods. The method shows wide linear range (200–5000, 10–1000 and 1–1000 pg/mL), good linearity ($r \geq 0.9950$) and good reproducibility (RSD $\leq 4.97\%$). The method has been applied to soil and food samples, with good selectivity and good recoveries ranging from 88.5–113.6%.

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1. Introduction

Determination of organic or inorganic compounds in complex matrices such as environmental, food and biological samples often requires sample pretreatment before separation or detection [1]. Green sample pretreatment techniques such as stir bar sorptive extraction (SBSE) and solid-phase microextraction (SPME) are desirable for they consume little organic solvent [2].

Stir bar sorptive extraction was first developed in 1999 [3]. In comparison with SPME, SBSE usually exhibits better extraction capability due to its larger volume and surface area. However, at present only a few kinds of stir bars such as polydimethylsiloxane (PDMS) and ethyleneglycol silicone-coated stir bars are commercially available, therefore, to develop stir bar with different kinds of sorbents is useful for the purpose of extending the application of SBSE [1,4]. Generally, stir bars consist of three essential parts:

a magnetic stirring rod, which rotates the stir bar, as well as the liquid sample; a thin glass jacket that covers the magnetic stirring rod and a layer of sorbent into which the analytes are extracted. The glass jacket is useful to immobilized sorbents onto the stir bar as its chemical activity. For example, for polymer sorbents, the glass jacket can be first silanized with 3-(trimethoxysilyl) propyl methacrylate (γ -MAPS), which can co-polymerize with monomers and resulting in immobilization of polymer sorbents [5]; and PDMS can be immobilized by sol-gel process [6]. However, the glass is fragile and easy to be broken during stirring and ultrasonication, which would lead to bad stability and reproducibility.

Stainless steel wire (SSW) can stir spontaneously under the magnetic force given by a commonly used magnetic stirring apparatus. Besides, they are easy to obtain and of high mechanical strength, making them good substrates for SBSE. However, as the stainless steel is chemically resistant, it is difficult to immobilize sorbents onto the surface of the stainless steel. Few works were reported to coat sorbents onto the stainless steel for SBSE. Conductive polymer was electrochemically deposited onto the surface of a stainless steel rod for SBSE [7]. However, as the sorbents were just coated physically, the immobilization was not firmly enough, and just a thin film of conductive polymer could be fabricated on

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the surface of the stir bar, it is difficult to increase the thickness of the sorbent for the purpose of increasing the extraction efficiency. Moreover, sorbents can be immobilized are also limited. The presence of chemical bonding between sorbents and the substrate can lead to high stability and lifetime [8]. However, to our knowledge, no work has been reported for covalent bond of sorbents onto stainless steel for SBSE.

Graphene is a typical two-dimension material that has been attracting considerable interest since its first discovery in 2004 [9–11]. Graphene possesses large delocalized π -electron system which can form a strong π -stacking interaction with aromatic compounds and their derivatives [12], along with its large surface area (theoretically about 2700 m²/g) [13] and ease of preparation [14,15], graphene has been used in extraction techniques in recent years, such as for solid-phase extraction (SPE), SPME and matrix solid-phase dispersion [8,16–19]. However, graphene as sorbent for SBSE has not been reported. The reason may be that conditions in SBSE such as stirring and ultrasonication are more damageable than that in SPE or SPME, so that methods for immobilization of graphene in SPE or SPME are not fit for SBSE.

Inspired by mussel's unique binding behavior onto rocks, dopamine was revealed to be essential to the binding [20] and a polydopamine method has been developed as a versatile surface modification protocol [21]. On the basis of this discovery, we have developed a method for immobilization of sorbents or stationary phase inside micro tubes in our previous works [16,22,23]. Polydopamine can "grow" on the surface of plastic tubes; the polydopamine layer is chemically active and can be used for binding of polymer sorbents or graphene. The functionalized polydopamine layer was found to be highly stable and we also testified the firm binding between the plastic surface and sorbents. However, the interaction between polydopamine and plastic surface is non-covalent, it is still not adequate to use for SBSE. Fortunately, the catechol group was found to covalently bond with metals [24]; the presence of catechol groups in polydopamine layer make it promising to covalently modify the stainless steel by the polydopamine method.

In this work, we proposed a simple chemical-bonding procedure to immobilize sorbents on SSW for SBSE. Bio-inspired polydopamine method was used to covalently functionalize SSW firstly. Graphene oxide (GO) was then introduced to react with polydopamine to form a layer of graphene-based sorbent. The process can be repeated by a layer-by-layer strategy to control the thickness of the sorbents of SBSE. In comparison with that for polyetheretherketone (PEEK) or polytetrafluoroethylene (PTFE) surfaces, polydopamine can covalently react with SSW, resulting in good stability of the proposed stir bar. The formation of multilayer graphene was characterized by Fourier transform infrared spectra (FTIR) and scanning electron microscopy (SEM). Extraction efficiency of the multilayer graphene-modified SSW stir bar was investigated and an SBSE-HPLC method has also been developed for determination of polyaromatic hydrocarbons (PAHs) in environmental and food samples. To the best of our knowledge, this is the first time that graphene is chemically modified onto metal surfaces for SBSE.

2. Experimental

2.1. Chemicals and materials

PAHs standards (fluoranthene (FLU), pyrene (PYR), benz[a]anthracene (B[a]AN), benzo[a]fluorathene (B[a]FL), benzo[a]pyrene (B[a]PY) and dibenz[a,h]anthracene (D[a,h]AN)) and dopamine hydrochloride were obtained from Sigma–Aldrich (MO, USA). Graphite powder (natural, 2–15 μ m, 99.9995%) was

purchased from Alfa Aesar (Tianjing, China). Acetonitrile (Tedia, OH, USA) was HPLC grade and water used was purified by a Milli-Q system (MA, USA). Stainless steel wires were purchased from a local store.

2.2. Instrumentation

A Shimadzu 20A HPLC system (Tokyo, Japan) was used, which equipped with two 20A pumps, a six-port valve and a 10A fluorescent detector. A column (C-18, 150 mm \times 4.6 mm i.d.) packed with 5 μ m particle size (GL Science, Tokyo, Japan) was used for chromatographic separation. Data collection and handling was performed on a Shimadzu LC Solution software. The detection wavelength of fluorescent detector was set at 300 nm (exciting wavelength) and 440 nm (emission wavelength). The temperature for HPLC separation was set at 30 °C, controlled by a thermostat controlled column compartment.

FTIR spectra was determined a by Thermo Nexus 470 FT-IR system (MA, UAS). The morphology of GO was investigated by a JEM-2100 (HR) transmission electron microscope (TEM) (JEOL, Tokyo, Japan), and the surface morphology of the graphene modified wires was characterized by a Quanta 200 scanning electron microscope (SEM, FEI, Holand). X-ray photoelectron spectroscopy (XPS) experiments were performed by a KRATOS XSAM800 XPS instrument (Manchester, UK).

2.3. Preparation of GO

Graphene oxide was prepared by a modified Hummers method [14,15]. The graphite powder was firstly preoxidized by H₂SO₄, K₂S₂O₈ and P₂O₅. It was then subjected to oxidation by Hummers' method. The GO product was suspended in distilled water to give a viscous, brown dispersion, which was subjected to dialysis to remove metal ions and residual acids. Exfoliation was achieved by dilution of the GO dispersion with deionized water (1/24, v/v), followed by sonication. GO sheets were obtained by centrifugation (10,000 rpm) and further dried in an oven (60 °C) for 12 h.

2.4. Fabrication of graphene-polydopamine modified SSW

SSW (3 cm) was washed sufficiently with ethanol to clean the surface, and then dried in an oven (60 °C) for further use. For polydopamine modification, dopamine solution (2 mg/mL, pH 8.5) was agitated with a vortex mixer for peroxidation. When the solution became slightly brown, the SSW was immersed and put under room temperature for 12 h. After drying in an oven (60 °C) for 3 h, polydopamine modified SSW was obtained. For graphene modification, GO aqueous solution (1 mg/mL) was prepared in a screw-cap vial, polydopamine modified SSW was then put into the solution. The vial was sealed and put into a water bath for reaction (65 °C, 10 h). After washing with ethanol and drying in the oven (60 °C, 3 h), graphene-polydopamine modified SSW was obtained. The above procedures were repeated for three times to obtain multilayer graphene modified SSW (G-SSW). The schematic is shown in Fig. 1.

2.5. SBSE procedures

SBSE was performed in a 100 mL beaker with a cover of parafilm. Sample solution of 30 mL (containing 1% acetonitrile, v/v) was added into the beaker with the G-SSW in the solution. G-SSW can stir by controlling with a magnetic stirring apparatus, at a speed of 300 r/min. After sample loading for 2 h, the wire was taken out of the sample solution and put into a small tube filed with 200 μ L acetonitrile, which was then sonicated for 5 min to desorb the

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