



# Graphene oxide reinforced ionic liquid-functionalized adsorbent for solid-phase extraction of phenolic acids



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## ABSTRACT

An environmental friendly sorbent of polymeric ionic liquids modified graphene oxide-grafted silica (PILs@GO@Sil) was synthesized for solid-phase extraction (SPE) of phenolic acids. The sorbent was prepared via a chemical layer-to-layer fabrication including amidation reaction, surface radical chain-transfer polymerization and in situ anion exchange. After modification with PILs, the silica surface had higher positive potential so that it would exhibit stronger electrostatic interaction for acidic compounds compared with GO@Sil. The adsorption performance of phenolic acids was investigated through the theoretical calculation and static, kinetic state adsorption experiments. Under the optimized conditions, wide linear ranges were obtained with correlation coefficients ranging from 0.9912 to 0.9998, and limits of detection were in the range of 0.20–0.50  $\mu\text{g L}^{-1}$ . Compared with other reported methods, the proposed PILs@GO@Sil-SPE-HPLC showed higher extraction efficiency. Finally, the black wolfberry yogurt and urine were analyzed as real samples and good recoveries spiked with standard solution were obtained.

## 1. Introduction

Phenolic acids are a class of secondary metabolites, which have drawn increasing attention due to their antioxidant properties and marked effects in the prevention of various oxidative stress associated diseases such as cardiovascular disease and cancer [1,2]. They widely spread throughout the plant kingdom including vegetables and fruits, and further exist in beverages as the food ingredient. Once ingested, most phenolic acids are extensively metabolized by the enzymes and partly adsorbed or excreted [3]. It is essential to enrich and purify before the instrumental analysis due to the low concentration of analytes and the interference of other complex substance in real samples. Therefore, sample pretreatment is one of the most important procedures in the whole analysis, especially for the analysis of biological and environmental samples with complex matrix [4], such as solid-phase extraction (SPE), solid-phase microextraction, liquid-phase microextraction, electromembrane extraction, microextraction by packed sorbents and so on. This stage would realize the pre-concentration of target compounds and elimination of most matrix interferences before introduction into the analytical instrument [5]. SPE is the most widely used separation and pre-concentration technique owing to its high chromatographic utility [6,7]. New various materials as adsorbents in

SPE have been exploited to extract organic and inorganic compounds from the complex media with higher adsorption capacity [8–10]. The studies indicated that nanosized SPE sorbents have high extraction capacities with rapid extraction kinetic performance [11]. Nanostructured materials, such as carbon-based nanomaterials, metal and metal oxide nanoparticles, electrospun nanofibers, and metal-organic frameworks, have gained great attention because of their physical and chemical properties including large surface area, desirable chemical and thermal stability, and favorable adsorption performance [4,12,13].

Graphene and its precursor graphene oxide (GO), as 2-dimensional nanoscale materials, have sparked intense research interest in sample preparation because of the outstanding properties. GO contains miscellaneous chemical functional groups on the basal planes and at the edges of GO sheets, such as hydroxyl, epoxy and carboxyl, which are expected to promote interfacial interactions between GO and adsorbate [14,15]. In the previous work, based on the excellent adsorption performance, GO-grafted silica was fabricated and used to determine trace phenolic acids in urine [16]. Besides, GO could be modified conveniently through the chemical fabrication procedure to improve the extraction yield and selectivity for some specific analytes [17,18].

Ionic liquids (ILs) are a class of organic salts composed entirely of organic cations (e.g. pyrrolidinium, pyridinium, imidazolium,

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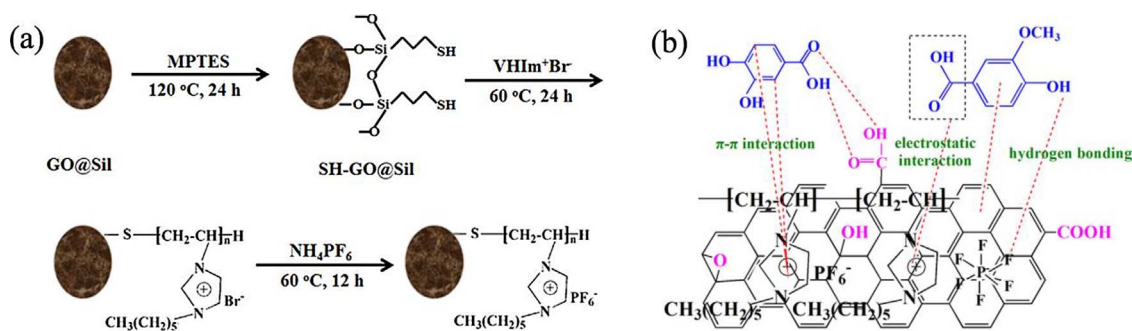


Fig. 1. Scheme of the synthetic route for poly(VHIm<sup>+</sup>PF<sub>6</sub><sup>-</sup>)@GO@Sil (a) and the interactions between the extraction material and analytes (b).

tetraalkyl ammonium or tetraalkyl phosphonium) and inorganic or organic anions (e.g. Br<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, NTf<sub>2</sub>, PF<sub>6</sub><sup>-</sup>). Due to the unique physicochemical properties, such as low vapor pressure, good chemical and thermal stability, wide viscosities range and miscibility with water and organic solvents, ILs have been used as promising solvents and materials in many fields [19–21]. Imidazolium IL, a member of ILs family, is widely used for sample preparation on the basis of the pentacyclic structure and the easily tuned property. In the previous reports, polymeric ionic liquids (PILs) modified GO-grafted silica exhibited high extraction efficiency for flavonoids because of its capacity of most types of interactions with analytes (e.g., π-π, n-π, hydrogen bonding, dispersive, dipolar, ionic/charge-charge) [22,23]. The satisfactory results indicated that the presence of GO would increase the overall extraction recoveries of analytes and bring an enhancement in analyte transport.

In this paper, the properties of an imidazolium-based PIL were tuned based on the reconstruction of its counter anion via in situ anion exchange. Firstly, poly(1-vinyl-3-hexylimidazolium hexafluorophosphate)-GO-grafted silica (poly(VHIm<sup>+</sup>PF<sub>6</sub><sup>-</sup>)@GO@Sil) was synthesized and characterized. Next, the adsorption performance of phenolic acids on the proposed adsorbent was investigated through the theory calculation and a series of adsorption experiments. Comparisons of extraction efficiency with other prepared materials were also performed. Under the optimum conditions, the proposed poly(VHIm<sup>+</sup>PF<sub>6</sub><sup>-</sup>)@GO@Sil-SPE-HPLC method was used to determine the selected phenolic acids in yogurt and urine.

## 2. Experimental

### 2.1. Chemicals and materials

Protocatechuic acid (ProA), vanillic acid (VanA), *N*-hydroxy succinimide (NHS) and *N*-(3-dimethylaminopropyl)-*N*-ethyl-carbodiimide (EDC) were obtained from Aladdin Chemical Reagent Co. (Shanghai, China). Syringic acid (SyrA) and salicylic acid were purchased from Energy Chemical (Shanghai, China). The chemical structures of the selected phenolic acids are shown in Fig. S1. VHIm<sup>+</sup>Br<sup>-</sup> was purchased from Shanghai Chengjie Chemical Co. (Shanghai, China). Ammonium hexafluorophosphate (NH<sub>4</sub>PF<sub>6</sub>) was purchased from Shanghai Tiancheng Chemical Co. (Shanghai, China). Azobisisobutyronitrile (AIBN) was obtained from Shanpu Chemical Co. (Shanghai, China). Dimethyl sulfoxide (DMSO) was obtained from J&K scientific LTD. (Beijing, China). 3-Aminopropyltriethoxysilane (APTES) and 3-mercaptopropyltriethoxysilane (MPTES) were purchased from Chemical Industrial Corporation of Gaizhou (Guangzhou, China). SPE empty column (3 mL), polyethylene frits (5 mm pore size) and the commercial C18 SPE column were purchased from Shenzhen Biocomma Biotech Co. (Shenzhen, China).

Stock solutions of phenolic acids were prepared in methanol with the concentration of 0.2 mg mL<sup>-1</sup>. Working solutions for extraction were freshly prepared by diluting the stock solutions with ultrapure

water (18.2 MΩ), which was collected from a Molecular water purification system.

### 2.2. Instrumentation and chromatographic conditions

The SPE procedure was performed on a HGC-8 numerical control solid phase extraction system (Hegong Scientific Instrument Co., Shanghai, China). HPLC analysis were performed on an Agilent 1100 Series modular HPLC system (Agilent Technologies, USA) with a high-pressure quaternary pump, a 20 μL sample loop and a UV-vis detector. Separation of the analytes was performed on a C18 column (Hypersil ODS2, 250 mm length × 4.6 mm i.d., 5 μm). The mobile phase was methanol and water with 0.25% acetic acid. The gradient elution condition was 0–23 min, 15–40% methanol; 23–30 min, 40–70% methanol. Flow rate was set at 0.8 mL min<sup>-1</sup> while the detection wavelength was 298 nm.

BET surface area was detected by a Micromeritics ASAP 2020 device. Surface properties of the prepared silica were characterized by scanning electron microscope (SEM, JSM-6701F, Japan). Energy dispersive spectrometry (EDS) was obtained on a low vacuum scanning electron microscope-X-ray energy dispersive spectrometer (JSM-5600LV, Japan). The zeta potential was determined with a Zetasizer Nano series ZS instrument (Malvern Instruments, United Kingdom).

### 2.3. Preparation of PILs/GO-modified silica

Hummers method was used to synthesize GO from the natural graphite [24].

Fig. 1 shows the preparation procedure of the PILs/GO-modified silica. Firstly, 8 g of silica was immersed in hydrochloric acid to be activated for 24 h and then rinsed with distilled water. The neutral silica and 8 mL of APTES were added in 100 mL of dry toluene to react and reflux at 120 °C. After 24 h, the obtained aminopropyl-modified silica (Sil-NH<sub>2</sub>), 10 mL of GO solution (0.1%, w/v), 100 mL of phosphate buffer solution (pH, 7.4), 0.05 g of EDC and 0.05 g of NHS were added into a 250 mL reaction flask. GO-grafted silica (GO@Sil) was obtained through the above amidation reaction.

Mercaptopropyl-modified GO-grafted silica (GO@Sil-SH) was prepared being similar to that of Sil-NH<sub>2</sub>, in which APTES was replaced by MPTES. The fabrication of poly(VHIm<sup>+</sup>PF<sub>6</sub><sup>-</sup>)@GO@Sil involved the following two processes (surface radical chain-transfer polymerization and in situ anion-exchange): (a) 8 g of VHIm<sup>+</sup>Br<sup>-</sup> and 0.4 g of AIBN were dissolved in 100 mL of DMSO and added into the conical flask with the prepared GO@Sil-SH, which was refluxed for 24 h at 60 °C under an N<sub>2</sub> atmosphere to obtain poly(VHIm<sup>+</sup>Br<sup>-</sup>)@GO@Sil particles; (b) after cooling, rinsed and dried, the poly(VHIm<sup>+</sup>Br<sup>-</sup>)@GO@Sil particles and 8 g of NH<sub>4</sub>PF<sub>6</sub> were added into a 250 mL three-neck round-bottomed flask with 150 mL of aqueous solution for reacting at 60 °C for 12 h. Finally, the obtained poly(VHIm<sup>+</sup>PF<sub>6</sub><sup>-</sup>)@GO@Sil was dried, stored, characterized and further used as the extraction material.

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