Journal of Chromatography A, 1299 (2013) 10–17

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Facile fabrication of reduced graphene oxide-encapsulated silica: A sorbent for solid-phase extraction

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ARTICLE INFO

Article history:
Received 16 March 2013
Received in revised form 15 May 2013
Accepted 15 May 2013
Available online 22 May 2013

Keywords:
Graphene
Solid-phase extraction
Chlorophenols
Peptides
Environmental water samples

ABSTRACT

In this study, a facile hydrothermal reduction strategy was developed for the preparation of reduced graphene oxide-encapsulated silica (SiO_2@rGO). Compared with other conventional methods for the synthesis of SiO_2@rGO, the proposed strategy endowed the obtained SiO_2@rGO with larger amount of immobilized rGO. The prepared functionalized silica shows remarkable adsorption capacity toward chlorophenols (CPs) and peptides. When it was used as solid-phase extraction (SPE) sorbent, a superior recovery could be obtained compared to commercial sorbents, such as C18 silica, graphitized carbon black and carbon nanotubes. Based on these, the prepared material was used as SPE sorbent for the enrichment of CPs, and a method for the analysis of CPs in water samples was established by coupling SPE with high performance liquid chromatography–ultra violet detection (SPE-HPLC/UV). In addition, the obtained SiO_2@rGO was further successfully extended to the enrichment of peptides in bovine serum albumin (BSA) digests.

1. Introduction

Graphene sheet is composed of two-dimensional carbon network with a honeycomb crystal structure, and is a basic unit for construction of carbonaceous materials [1]. Because it is an electron-rich, hydrophobic nanomaterial with large specific area and π–π electrostatic stacking property, graphene can serve as an extraordinarily good sorbent toward a variety of compounds [2–12]. Solid-phase extraction (SPE) is a powerful sample preparation technique due to its high recovery and high enrichment factor [13], so it is widely used in sample preparation for a great variety of samples with complicated matrices. Based on its exceptional properties, graphene has been used as a sorbent for SPE [5,8,9,13–18]. However, the escaping from SPE cartridge and irreversible aggregation of graphene may arise when direct use of graphene as SPE sorbent, which may not only reduce the sorption capacity and extraction efficiency of sorbent, but also result into the SPE cartridge blocking [13].

Immobilization of reduced graphene oxide (rGO) onto silica is a good solution to the issues as described above. For example, the rGO sheets were incorporated into silica matrix *via* silane [19,20]. Meanwhile, by using sol–gel method, silica-coated rGO (rGO@SiO_2) composites were synthesized by the hydrolysis and condensation of tetraethylorthosilicate under basic conditions [21–24]. However, for this type of materials, the plenty of adsorption sites of rGO were occupied by silica which were deposited on the surface of rGO sheets. To circumvent the problem and still maintain the advantageous properties of rGO, GO sheets were firstly immobilized on silica particles (SiO_2@GO) *via* electrostatic assembly or covalent bonding [13,25]. SiO_2@rGO was then prepared by reduction of SiO_2@GO. This type of SiO_2@rGO or SiO_2@GO materials have been widely applied in analytical sample preparation [13,26,27], *in vitro* fluorescence imaging [28], stationary phase of high performance liquid chromatography (HPLC) [29,30], sensor [31], lithium storage [25] and polymer composite [32,33]. However, to obtain SiO_2@rGO materials, GO was normally reduced by hydrazine, which was toxic and environmental unfriendly. Furthermore, only a single layer of rGO sheet was immobilized onto the silica surface, so the amount of immobilized rGO was low, which will hamper the performance of the graphene. In this respect, it is necessary to develop a facile synthesis strategy of SiO_2@rGO with large amount of immobilized rGO.

Herein, in current study, a facile hydrothermal reduction strategy for the preparation of SiO_2@rGO was developed. Chlorophenols (CPs) and peptides were selected as model analytes to evaluate the adsorption capacity of the resultant SiO_2@rGO due to their strong interaction with rGO *via* π–π interaction, H-bonding and hydrophobic interaction [8,13,27]. Because multiple layers of rGO sheets were immobilized on the silica surface, the prepared SiO_2@rGO material contains large amount of immobilized rGO, which was demonstrated to be highly efficient SPE sorbent for model analytes. Moreover, high performance of desalting

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http://dx.doi.org/10.1016/j.chroma.2013.05.036

for biological samples was achieved on the prepared SiO_2@rGO in matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS) analysis. Finally, by coupling SPE with high performance liquid chromatography–ultra violet detection (SPE-HPLC/UV), a method for the determination of CPs in water samples was proposed by using the prepared material as SPE sorbent.

2. Experimental

2.1. Chemicals and materials

Graphite powder (325 meshes, 99.9995%) was purchased from Alfa Chemicals (Bracknell, UK). Concentrated sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), potassium persulfate ($K_2S_2O_8$), phosphorus pentoxide (P_2O_5), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), and N,N-dimethyl formamide (DMF) were of analytical grade and purchased from Sinopharm Chemical Reagent (Shanghai, China). Acetonitrile (ACN) and methanol (MeOH) of HPLC reagent grade were obtained from Tedia (Fairfield, OH, USA).

The four CPs standards, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China) and stored in dark at 4 °C, and the working solutions were freshly prepared by diluting the stock solutions with MeOH/water (1/1, v/v). α-Cyano-4-hydroxycinnamic acid (CHCA), trifluoroacetic acid (TFA), and bovine serum albumin (BSA) were purchased from Sigma–Aldrich (St. Louis, USA). Sequencing grade trypsin was obtained from Promega (Madison, WI, USA). Ultra-pure water used throughout the study was purified using a Milli-Q apparatus (Millipore, Bedford, MA, USA).

Carbon nanotubes (CNTs, length 5.0–15 μm, diameter 10–20 nm) were obtained from Nanotech Port (Shenzhen, China). CNTs were washed with acetone to remove the impurities by wrapping with filter paper in reflux in Soxhlet extractor at 80 °C for 48 h. The resultant CNTs were dried under reduced pressure at 60 °C for 6.0 h before use. Aminosilica (NH_2–SiO_2, aminopropyl silica gel, 200–300 meshes), graphitized carbon black (GCB) and C18 silica sorbents used in this study were purchased from Weltech Co., Ltd. (Wuhan, China).

2.2. Preparation of SiO_2@rGO

GO was synthesized from graphite powder by a modified Hummers and Offeman method [3,10,34]. SiO_2@rGO was prepared by a hydrothermal reduction of SiO_2@GO. SiO_2@GO was fabricated *via* the electrostatic interaction between positively charged NH_2–SiO_2 and negatively charged GO in aqueous solutions.

The schematic illustration of the preparation strategy for SiO_2@rGO was shown in Fig. 1. Two strategies were developed to obtain SiO_2@rGO. In strategy A, 62.5 mL NH_2–SiO_2 dispersion was added into a 62.5 mL aqueous GO suspension (2.0 mg/mL) under stirring at room temperature. After 2 h, the mixture was sealed in a 200-mL poly tetrafluoro ethylene lined stainless-steel autoclave and maintained at 230 °C for 3 h. Then the autoclave was naturally cooled to room temperature. Finally, the SiO_2@rGO was obtained after free rGO removal by flotation with the aid of DMF. The SiO_2@rGO was washed with ethanol for three times, and dried at 60 °C before use. The as-prepared SiO_2@rGO was denoted as SiO_2@rGO-A.

In strategy B, before mixture was sealed in a poly tetrafluoro ethylene lined stainless-steel autoclave, the free GO sheets which were not encapsulated onto silica surface were firstly removed by flotation with the aid of DMF, and only SiO_2@GO was subjected to hydrothermal reduction process for comparison. The SiO_2@GO was washed with ethanol for three times, and dried at 60 °C. Then, 245 mg dried SiO_2@GO was added into 70 mL water, the mixture was sealed in a 100-mL poly tetrafluoro ethylene lined stainless-steel autoclave and maintained at 230 °C for 3 h. Then the autoclave was naturally cooled to room temperature. Finally, the product was washed with ethanol for three times, and dried at 60 °C before use. The as-prepared SiO_2@rGO was denoted as SiO_2@rGO-B. Meanwhile, rGO was obtained in an identical manner but in the absence of NH_2–SiO_2.

2.3. SPE procedures

SPE was performed on a CNW 12-port model SPE Vacuum Manifold (Dusseldorf, Germany). The SPE cartridges were packed as follows: the sorbents (20 mg) were packed into 1-mL polypropylene cartridge, and the material was retained by two polyethylene frits.

For the enrichment of CPs, the cartridge was firstly preconditioned by washing with 2.0 mL MeOH and 2.0 mL water. Then sample solutions (10 mL) were passed through the cartridge. At the end of extraction, the cartridge was washed with 1 mL of 5% (v/v) MeOH aqueous solution. It was then kept under vacuum until the washing solution was discarded. Finally the CPs were eluted from the cartridge by 1.0 mL alkaline MeOH. The alkaline MeOH was prepared by adding 0.3 mL of 1 M NaOH aqueous solution into 10 mL of MeOH. Prior to analyzing desorption solution by HPLC, the excess base in desorption solution was neutralized by 30 μL of 1 M HCl aqueous solution. For C18 silica sorbent, the desorption solution was 1 mL of MeOH, and desorption solution was directly analyzed by HPLC. Alkaline MeOH was favorable for the ionization of CPs, thus reducing their affinity for sorbents and facilitating the elution. However, CPs adsorbed on C18 silica sorbent can be easily eluted with pure MeOH [8,13]. So, different desorption solutions were adopted for the different sorbent materials.

For the enrichment of peptides, the cartridge was firstly preconditioned by washing with 1.0 mL 80% ACN in 0.1% TFA solution and 2.0 mL water. Then 4.0 mL BSA digests (10 nmol/L) were passed through the cartridge. At the end of extraction, the cartridge was

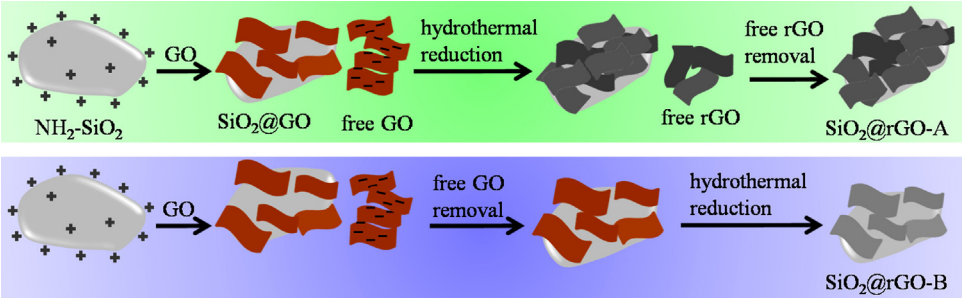

Fig. 1. Schematic diagram for the synthesis of SiO_2@rGO materials.