Graphene deposited onto aligned ZnO nanorods as an efficient coating for headspace solid-phase microextraction of gasoline fractions from oil samples

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ABSTRACT

The content of gasoline fraction in oil samples is not only an important indicator of oil quality, but also an indispensable fundamental data for oil refining and processing. Before its determination, efficient preconcentration and separation of gasoline fractions from complicated matrices is essential. In this work, a thin layer of graphene (G) was deposited onto oriented ZnO nanorods (ZNRs) as a SPME coating. By this approach, the surface area of G was greatly enhanced by the aligned ZNRs, and the surface polarity of ZNRs was changed from polar to less polar, which were both beneficial for the extraction of gasoline fractions. In addition, the ZNRs were well protected by the mechanically and chemically stable G, making the coating highly durable for use. With headspace SPME (HS-SPME) mode, the G/ZNRs coating can effectively extract gasoline fractions from various oil samples, whose extraction efficiency achieved 1.5-5.4 and 2.1-8.2 times higher than those of a G and commercial 7-μm PDMS coating respectively. Coupled with GC-FID, the developed method is sensitive, simple, cost effective and easily accessible for the analysis of gasoline fractions. Moreover, the method is also feasible for the detection of gasoline markers in simulated oil-polluted water, which provides an option for the monitoring of oil spill accident.

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1. Introduction

Gasoline fractions generally refer to a liquid hydrocarbon (C_4-C_{10}) mixture initially distilled at <200 °C from crude oil. In most crude oil, gasoline fractions are rich in content and generally occupy its total 20%-40% [1]. In addition, gasoline fractions contain abundant *n*-alkanes, isoparaffin, naphthenes, aromatics, etc. Therefore, the content of gasoline fractions is not only an important indicator for gasoline products, but also an indispensable fundamental data for oil refining and processing. At present, analytical methods commonly used for the analysis of petroleum include gas chromatography-flame ionization detection (GC-FID) [2,3], GC-mass spectrometry (GC–MS) [4] and GC-isotope ratio mass spectrometry (GC-IRMS) [5]. Generally, direct injection of crude oil into gas chromatograph is basically not recommended since the components with high boiling point will unavoidably remain on the column, thereby reducing the lifetime of the column and possibly causing contamination to subsequent analyses.

Therefore, prior to GC analysis, selection of appropriate sample pretreatment methods is critical for the analysis of gasoline fractions in oil samples.

Traditional sample preparation techniques include liquid–liquid extraction and solid-phase extraction [6–8]. Although these methods are easy to carry out in routine labs, they require a large amount of organic solvents. Purge and trap is a solvent-free technique particularly suitable for the sampling of volatile gasoline fractions but it requires a specialized device compatible to GC [9,10]. Single drop microextraction is another alternative feasible for gasoline extraction with very low solvent consumption [11,12]. Since the organic microdrop is not stable during the extraction, an extra operation care must be taken to reduce the extraction irreproducibility. In addition, the solvent peak might overlap with some hydrocarbons with low molecular weight. Headspace solid-phase microextraction (HS-SPME) is a sampling tool in which a fiber coated with a small amount of adsorbent is placed above the samples to extract volatile compounds from sample matrix. This technique is considered to be an ideal method for the extraction of gasoline fractions from oil samples, since these compounds (C_4-C_{10}) has a high vapor pressure and tend to exist as gaseous forms, while those of macromolecular hydrocarbons are present with trace level at headspace

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due to their low vapor pressure. To date, very few studies have been reported using HS-SPME for the extraction of gasoline fractions from oil samples with commercial PDMS fibers [1,13]. These commercial fibers provide good extraction reproducibility but suffer from being costly, fragile and nonresistant to organic solvent and high temperature. The purpose of this study is to tailor-make a SPME fiber, which is easy to prepare, chemically and mechanically stable, and more importantly, possesses high extraction efficiency towards gasoline fractions.

Since the gasoline fractions are mainly hydrophobic and volatile, our goal is to prepare SPME coatings with hydrophobic surfaces and high specific surface area. Aligned ZNRs have high specific surface area and they are easy to in-situ grown on a solid substrate using a hydrothermal method. However, the surface of ZNRs is considered as polar and so they show low efficiency towards nonpolar analytes [14]. Graphene (G) is an emerging two-dimensional carbon nano-material and it has been prepared as a SPME coating, which has proved to show excellent adsorption efficiency towards hydrophobic compounds due to its hydrophobicity and π-π localized system [15–17]. Our approach was to deposit a thin layer of G onto the surface of ZNRs as a composite SPME coating. By this means, the virtual surface area of G was effectively enlarged and the surface of ZNRs was changed from polar to non-polar. The G/ZNRs coated fiber was used to extract gasoline fractions from different kinds of oil samples and simulated oil-polluted sea water with HS-SPME mode, followed by the separation and detection with GC-FID.

2. Experimental

2.1. Reagents and solutions

All solvents were of analytical grade and used as received. Graphite powder, potassium permanganate, concentrated sulfuric acid, sodium nitrate, hexamethylene tetramine and zinc nitrate hexahydrate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Stainless-steel wires (SSWs) having O.D of 0.15 mm were provided by Shanghai Gaoge industry and Trade Co., Ltd. All oil samples were provided from the Shengli oil-field located at Dongying, China.

2.2. Instrumentation

All GC analyses were performed on a Varian CP-3800 gas chromatography (Varian, Inc., California, USA) equipped with a 50 m × 0.32 mm I.D., 0.32 μm HP-PONA capillary column and an FID system. The following column temperature program was used for the separation of gasoline fractions: 35 °C (10 min) → 0.5 °C min^{-1} to 60 °C → 2.0 °C min^{-1} to 200 °C (2 min). High-purity nitrogen (99.99%) was utilized as the carrier gas and maintained at a flow rate of 1.25 mL min^{-1}. The flow velocity of nitrogen (makeup gas), hydrogen and air were fixed at 30, 40 and 400 mL min^{-1}, respectively. The GC inlet and detector temperatures were set at 260 and 280 °C, respectively. A Hitachi S4800 field emission scanning electron microscope assembled with energy dispersive X-ray spectrometer (EDX) (Tokyo, Japan) was used to observe the morphology of the fiber coating.

2.3. Synthesis of G

The preparation and characterization of graphene oxide (GO) and G have been reported in our previous reports [18,19]. Briefly, graphite powder (0.5 g), NaNO$_3$ (0.5 g), and concentrated H$_2$SO$_4$ (23 mL) were mixed and stirred in an ice bath for 1 h. Then, 3 g of KMnO$_4$ was slowly added to the mixture, and it was stirred at room temperature (26 °C) for 2 h. Subsequently, 46-mL water was added into the mixture, and it was heated at 98 °C for 30 min. Then,

100 mL of water and 10 mL of H$_2$O$_2$ (30%) were sequentially added to eliminate excess of KMnO$_4$. The mixture was centrifuged and the sediment was washed in sequence with 10% HCl (V/V) aqueous solution and pure water for six times. The product was dried at 90 °C for 24 h and redispersed in water to make a 3 mg mL^{-1} GO solution. To prepare G, 50 g of ascorbic acid was added to a GO aqueous solution (3 mg mL^{-1}, 50 mL), and the mixture was heated at 80 °C for 3 h. During this process, the color of the solution changed from brown to black, indicating the formation of G. The G was centrifuged and washed with 150 mL of water for five times. Finally, a G aqueous solution (1 mg mL^{-1}) was prepared for further use.

2.4. Preparation of G, ZNRs and G/ZNRs coated fiber

For the preparation of G coated fiber, an end of SSW (1 cm) was vertically dipped into the G solution for 10 s. Then, the SSW was pulled out and placed into an oven heated at 120 °C for 1 min. Such steps were repeated for 20 times until a thin brown layer was formed on the surface of SSW. The ZNRs coated fiber was prepared using a hydrothermal method. Specifically, one end of the SSW (1 cm) was dipped into a mixture of hexamine (0.025 mol L^{-1}) and zinc nitrate (0.025 mol L^{-1}), which was then incubated at 90 °C for 4 h. For the preparation of G/ZNRs coated fiber, the same hydrothermal method was used for the preparation of ZNRs onto the SSW. Then, the G was coated on the ZNRs using the same steps as those described for the preparation of G. All fibers were assembled into laboratory-made SPME holders developed by our group [20].

2.5. Analysis of gasoline fractions using HS-SPME-GC

50 μL of oil sample was pipetted into a 20-mL vial which was then sealed with a cap. The vial was heated at 35 °C using a water bath. The needle of the SPME holder was used to penetrate the cap of the vial and then the fiber was pushed out making the coating hang above the oil sample. The extraction continued for 30 min and the fiber was retracted back to the needle and finally transferred to GC inlet for desorption at 260 °C for 4 min. The crude oil was diluted with sea water at a ratio of 10^6 to function as simulated oil-polluted water. The same HS-SPME-GC procedures were used for this application.

3. Results and discussion

3.1. Characterization of G, ZNRs and G/ZNRs coated fibers

G, ZNRs and G/ZNRs coated SPME fibers were prepared for comparison. As shown in Fig. 1a–b, a smooth and flat layer of G was coated onto the SSW. Fig. 1c–d shows that the ZNRs were well aligned on the SSW and they had hexagonal-like structures with a diameter of 200–300 nm. After depositing with G, a very thin layer was coated on the surface of ZNRs without changing their orientation and morphology (Fig. 1e–g). The EDS result (Fig. 1h) shows the presence of C (44.84%), Zn (38.72%) and O (16.44%) in one ZNR, further demonstrating the successful coating of G onto ZNRs. By increasing the cycles of coating G, its thickness can be further increased. As displayed in Fig. 1i–j, there were many honeycomb-like wrinkles existing on the surface of SSW. Fig. 1k further shows that there were many hexagonal-like bumps on the surface of coating, indicating G was effectively coated onto the ZNRs. The coating thickness was calculated to be about 5 μm based on the cross view of coating (Fig. 1l). This fiber was used for the subsequent gasoline extraction. By this approach, the virtual surface of G was effectively enlarged, while the surface polarity of ZNRs was changed from polar to non-polar. In addition, the ZNRs can be well protected by the mechanically and chemically stable G. It was found that the G/ZNRs coating was difficult to be scraped even using a knife. The G/ZNRs