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Renewable Reduced Graphene Oxide-Based Oil-Absorbent Aerosols: Preparation and Essential Oils Absorption Ability

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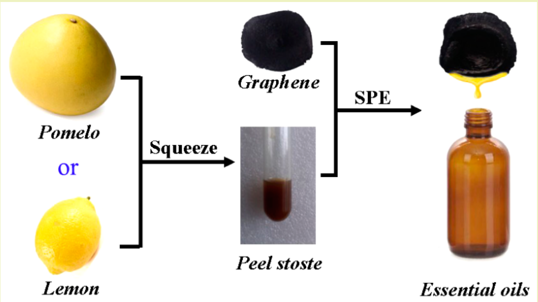

ABSTRACT: This study proposes a rapid solid-phase extraction (SPE) of essential oils from citrus, including pomelo and lemon, using graphene aerosol (GA) as sorbent based on a $\pi-\pi$ conjugative and hydrophobic interaction. The graphene aerosol was fabricated by the hydrothermal reduction low-temperature freeze-drying method, and its morphology and structures were analyzed by scanning electron microscopy (SEM) and X-ray photoclectron spectroscopy (XPS). The specific surface area and pore volume of the samples were measured using N_2 adsorption. The effects of amount of sorbent, extraction time, and extraction temperature on extraction were investigated. Maximal extraction yields of 2.70% and 2.47% were achieved under optimal conditions for pomelo and lemon, respectively. In addition, this extraction could be completed rapidly without adding another solvent and tedious processing steps such as centrifugation and evaporation of organic solvent. Besides, the sorbent also can be reused with heat treatment. This simple, rapid, environmentally friendly, and cost-effective method had been successfully applied to extract essential oils in two types of citrus. Meanwhile, it offers a potential application for extraction and analysis of essential oils from plants.

KEYWORDS: *Graphene aerosol, Solid-phase extraction, Essential oils, Citrus, Lemon, Pomelo*

■ INTRODUCTION

Essential oils obtained from citrus peel are complex mixtures of volatile substances, which can give people a fresh feeling. They also exhibit antioxidant and antimicrobial activity.[1−7] Therefore, they have been widely employed in the production of food, cosmetics, and household products. Recently, with an increasing demand for natural products, the demand for essential oils has also increased, but essential oils still cannot be chemically synthesized and cannot been replaced by the other flavors. Nevertheless, much peel is discarded that lies rotting in the field, resulting in a huge waste of resources, environmental pollution, and economic losses. Thus, it is critically important to develop a method to make full use of the byproducts and satisfy the high commercial demand.

Presently, there are a variety of methods for essential oil production, such as distillation, cold pressing, and solvents extraction.[8−13] However, these general methods use a large number of organic solvents and have long processing times and complex operation steps that limit their practical application. Nanomaterials have been widely used as absorbent in solid-phase extraction (SPE), which is used in processing large volumes of liquid samples due to large surface areas, short diffusion distances, high enrichment ratios and recovery rates, less organic solvent consumptions, and low cost.[14]

Since its discovery in 2004, graphene has received widespread attention of scientists all over the world. Graphene is composed of of carbon atoms with a sp^2 hybrid orbital and a hexagonal honeycomb lattice structure of two-dimensional nanomaterials, which is a new generation of carbon allotropes following carbon nanotubes. Graphene has high specific surface area, contains rich π electronics, and exhibits good chemical stability and thermal stability, which is expected to replace other carbon materials. Because of its high specific surface area, graphene is a superior adsorption material and has broad application in the field of sample preparation.[15−17] Also, due to its low density, small aperture, and microporous structure,[23−27] the 3D graphene structure, including hydrosol[18,19] and aerosols,[20−22] have attracted wide attention by researchers. Very recently Sun et al.[22] prepared total carbon aerogels by a low-temperature freeze-drying method, and they found that the aerosol showed super oil absorption ability and that it could rapidly absorb organic matter instead of water. 3D graphene was also prepared and used for oil spill cleanup. Li and colleagues found that 3D graphene still had a high adsorption capacity and rapid adsorption speed even under the high concentration of 100 g/g.[27] Graphene aerosol with high specific surface area can be synthesized and used as an adsorbent for plant essential oils.[28−32]

In the current study, we use graphite powder as the raw material to obtain a few layers of graphene oxide using the modified Hummer's method.[33] Hydrothermal reduction and low-temperature freeze-drying were used for the preparation of

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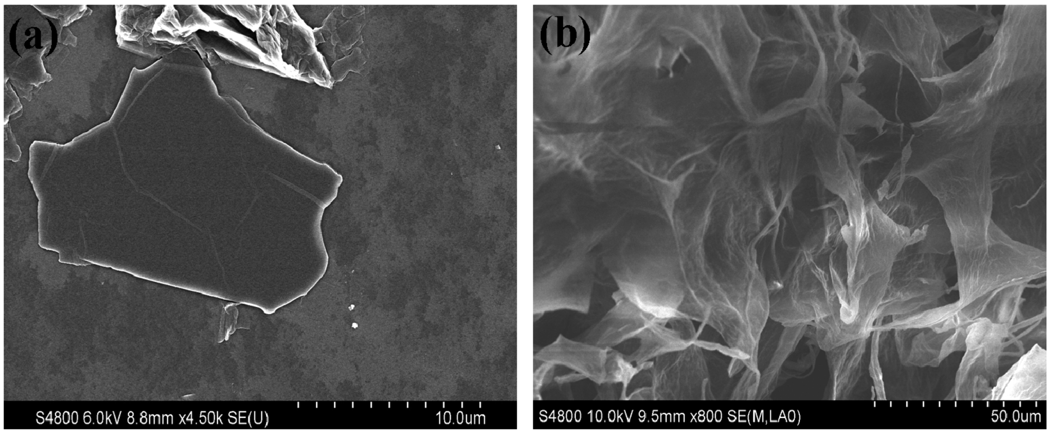


Figure 1. Scanning electron micrograph image of graphene oxide, (a) scale bar of 10 um, and graphene aerosol, (b) scale bar of 50 um.

the graphene aerosols. Moreover, the graphene aerosol was first used as sorbent for SPE of essential oil from peel pressing juice. Several parameters including dosing amount of sorbent, extraction temperature, and extraction time on the influence of peel essential oil extraction were investigated. Essential oils of plants are important natural sources of bioactive substances, and SPE is an innovative clean and efficient technology to produce them. We believe this simple, rapid, environmentally friendly, and cost-effective method can offer a potential application for extraction and analysis of essential oil from plants.

■ MATERIALS AND METHODS

Chemicals. Graphite powder was purchased from the National Medicine Group Chemical Reagent Co., Ltd. Sodium nitrate, potassium permanganate, hydrochloric acid, sulfuric acid, barium chloride, and hydrogen peroxide (30%) were purchased from Shantou West Long Chemical Co., Ltd. All chemicals were of analytical grade and used as received. The pomelo and lemon were purchased from a local supermarket and washed with water for further use. All aqueous solutions synthesized with graphene aerosol were prepared using ultrapure water (18 MU) from a Milli-Q system (Millipore).

Preparation of Graphene Oxide. Graphene oxide was prepared by the modified Hummer's method.[33] In detail, graphite (1.0 g) was added to concentrated sulfuric acid (23 mL) in a 1000 mL round-bottomed flask and stirred in an ice bath. Then, $NaNO_3$ (0.5 g) and $KMnO_4$ (3.0 g) were slowly added to the suspension at a constant temperature of (0 ± 1) °C. After that, the mixture was heated at (35 ± 3) °C for 30 min, and then water (46 mL) was injected into the mixture and maintained at 98 °C for 15 min, followed by addition of water (140 mL) and 30% H_2O_2 (2 mL) to end the reaction. Finally, the hot mixture was filtered and washed with 5% HCl and water several times to remove metal ions. The filter residue was dried at 70 °C under vacuum for 24 h.

Preparation of Graphene Aerosol. The obtained graphene oxide solid was dissolved in water aided by ultrasonication for 12 h to obtain a few layers of graphene oxide. Then, a 30 mL portion of 1.0 mg/mL homogeneous graphene oxide aqueous dispersion was sealed in a 100 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 6 h. After that, the black products were obtained and washed several times with water and then dried by vacuum freeze-drying for 2 days. The density was calculated by the weight of solid content without including the weight of entrapped air divided by the volume of aerosol.

Sample Collection. The peel was washed and dried by airing to get rid of water on the surface. Then, the inner white spongy material was shaved off by a knife, and the outer peel was pressed by a family manual oil press. The juice was collected and stored at 0 °C.

Graphene Aerosol-Based SPE Procedure. For essential oil extraction, the stoste (20 mL) was poured into a 100 mL beaker. The graphene aerosol was weighed, and then it was immersed in the stoste with magnetic stirring for a period of time. After that, the sorbent was immediately transferred to a small distilling flask and distilled at 100 °C. The drips were separated by a pear-shaped separatory funnel, with the upper portion considered as essential oil and stored at 0 °C. For the continued reuse of the sorbent, the graphene aerosol was washed with ethanol and dried at 150 °C for 60 min for use in the next extraction experiment.

Characterization. Scanning electron microscopy (SEM) was carried out on Hitachi S-4800, and the accelerating voltage was 10 kV. The samples were dissolved and dropped onto the silicon wafer, and the excess was removed with filter paper. This step was repeated three times. Finally, the silicon wafers were dried overnight for micrographic analysis. Surface area and porosities of graphene aerosol were performed on a TriStar II 3020 2.00 (Micromeritics Instrument Corporation). For nitrogen physisorption, all samples were degassed at 150 °C for at least 24 h prior to characterization. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). Raman spectrum was performed by using a laser Raman spectrometer (Renishaw inVia plus, U.K.). Structural characterization of graphene aerosol was performed by X-ray photoelectron spectroscopy using an apparatus (Thermo ESCALAB 250XI). The spectrum was obtained from the average of 21 scans at a resolution of 1 eV with a binding energy of 1361-0 eV. High-resolution, signal-averaged scans of the C 1s and O 1s regions were obtained using a monochromatic Al K Alpha and a step size of 0.05 eV under a flood gun to minimize charging.

■ RESULTS AND DISCUSSION

Characterization of Graphene Aerosol. In this paper, the graphene oxide was prepared by the modified Hummer's method. After dispersion in aqueous solution aided by ultrasonication, the mixture was transferred to a Teflon-lined stainless-steel autoclave under 180 °C hydrothermal reduction for 6 h to make reduced graphene oxide, after which the black product was then freeze-dried. The morphologies of graphene oxide and graphene aerosols were characterized using a scanning electron microscope (SEM). The results are shown in Figure 1. The graphene oxide (Figure 1a) was a thin lamellar structure. SEM images of graphene aerosol obtained by hydrothermal reduction and low-temperature freeze-drying is illustrated in Figure 2b. It is clearly illustrated that the graphene aerosol appears as a variety of macropores between layers that have a certain degree of bending. It can be concluded that graphene aerosol had formed. The graphene aerosol had a density of 9.8 mg cm^{-3}, which was calculated by the weight of the solid content without including the weight of entrapped air divided by the volume of aerosol.

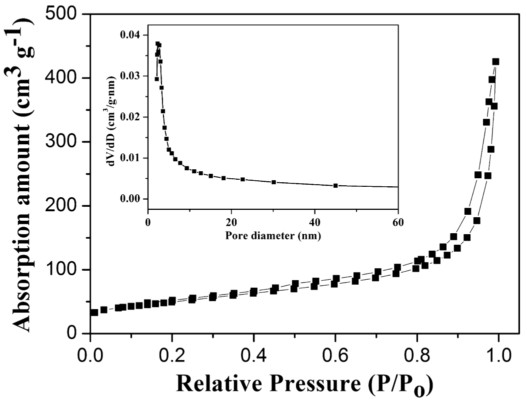


Figure 2. Nitrogen adsorption−desorption isotherms of graphene aerosol. Inset is pore distribution curve of graphene aerosol.

Not only the microscope observation but also the data suggested that the sample was composed of graphene walls with various pores. The nitrogen adsorption isotherm of graphene aerosol is presented in Figure 2, which exhibits a typical type IV curve at low relative pressure and a hysteresis loop at relative pressure from 0.2, indicating the presence of a special 3D structure, with average pore sizes of 8.9 nm and few macropores within. This was consistent with the SEM images shown in Figure 1b. The BET surface area of the graphene aerosol was 175.6 m^2/g, which was significantly lower than the theoretical surface area of 2630 m^2/g for monolayer graphene.[15] Despite some large pores, the majority pore sizes are narrowly distributed at 2.5 nm (Figure 2, inset). Graphene aerosol could be a good candidate as adsorbent for the extraction of essential oil from citrus because it is a mesoporous material with a π−π conjugative interaction and thin layer structure.

In order to further explore how the graphene aerosol surface groups change in the formation process, X-ray photoelectron spectroscopy (XPS) was used for graphene aerosol characterization. Figure 3a showed the XPS survey spectra of graphene aerosol within the binding energy range from 0 to 900 eV. Graphene aerosol is composed of elements C and O and mainly of carbon. As shown in Figure 3b, the high-resolution spectrum of C 1s was decomposed into three different peaks. The strong peak at 284.8 eV corresponds to the graphene C═C bond. The banding energy at 286.2 and 288.5 eV are respectively attributed to the graphene C−O and C═O bonds.[34,35] The oxygen-containing groups of graphene oxide had greatly reduced after hydrothermal reduction, but graphene aerosol still contained a small amount of surface oxygen groups, which made the graphene aerosol the SPE agent that was well infiltrated in the aqueous solution containing essential oil but not dissolved.

We studied the reduction degree of the GA using the Raman spectrum, and the original GO was also provided for comparison (Figure 4). The Raman spectra of the GA had two strong peaks at 1356 and 1586 cm^{-1} corresponding to the D and G bands, respectively. The ratio of D to G band intensity (I_D/I_G) of GA was relatively intense compared to that in GO, which was in agreement with previous results for graphene samples obtained from GO. This increase might be caused by the defects within the sp^2 carbon network that arose upon reduction of the exfoliated GO.

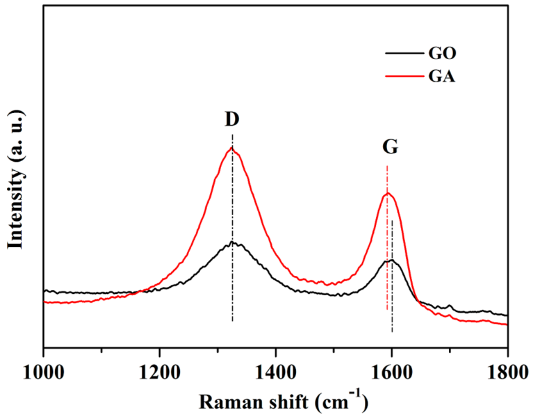


Figure 4. Raman spectrum of graphene oxide and graphene aesorol.

Parameters Affecting the Extraction Yield of Essential Oils. To estimate the feasibility of graphene aerosol for the extraction of essential oil from citrus, several parameters including the amount of sorbent, extraction time, and extraction temperature affecting the extraction were investigated in this study.

Under the conditions of extraction time and room temperature, according to the experimental steps, the dose of graphene aerosol for the effects of the essential oil absorption was inspected. As shown in Figure 5, the dose of graphene aerosol had an important influence on solid-phase extraction of essential oil. When too low of a dosage of sorbent was added, the essential oils could not be completely adsorbed onto the

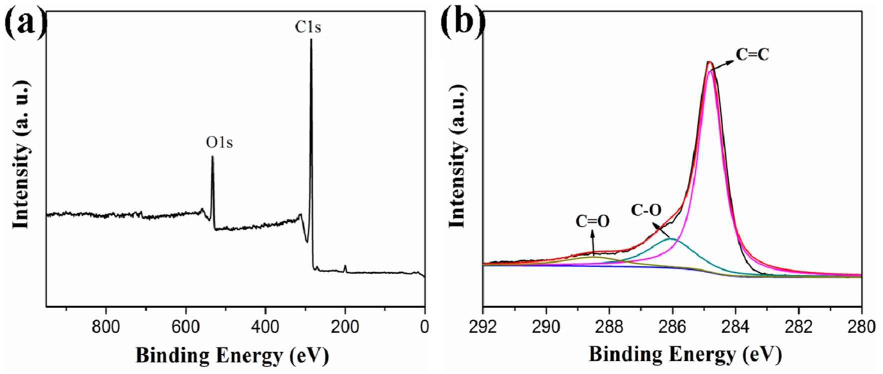


Figure 3. XPS spectrum (a) and high-resolution C 1s peak (b) of the freeze-dried graphene aesorol by hydrothermal treatment of graphene oxide (GO) aqueous.

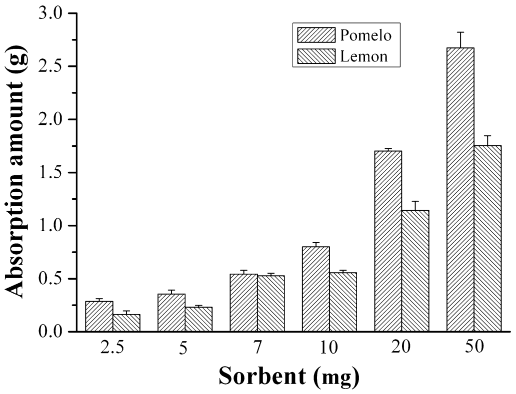


Figure 5. Influence of the dose of graphene aerosol on the extraction efficiency at the extraction time of 20 min and room temperature.

graphene aerosol resulting in low extraction efficiency. The absorption amount increased when the sorbent increased for Pomelo and Lemon. When we used double sorbent (20 mg to 10 mg), a double absorption amount (1.7 to 0.8 g, 1.14 to 0.56 g for pomelo and lemon) was obtained.When adsorbent dosage was too high an reached 50 mg, no multiple amount of adsorbed material was achieved. A large dose of sorbent can effectively isolate essential oils from the mixture, but too much of the sorbent disturbs the essential oil steaming out. So the optimal dosing quantity of graphene aerosol for solid-phase extraction essential oil was 10 mg.

The effect of contact time on essential oil extraction efficiency has been studied by many researchers previously,[11−13] and the results indicated that the contact time is directly related to essential oil extraction efficiency. The experiment about the effect of extraction time on extraction of essential oil was executed using the sorbent dose of 10 mg. The difference in efficiency caused by contact time ranging from 5 to 60 min is shown in Figure 6. It is shown that the essential oil absorption amount increases within the first 20 min, achieves a maximum absorption amount for pomelo, and rises slowly in the next 20 min for lemon. Upon conditions of 20 min contact time, the overall yields of the essential oils obtained was 2.70% and 2.47% from pomelo peel and lemon peel, respectively. The process of extraction needed in such a short time suggested that it was mainly physical adsorption between graphene aerosol and essential oils. This short equilibrium time indicated that GA has a strong potential application for essential oils extraction.

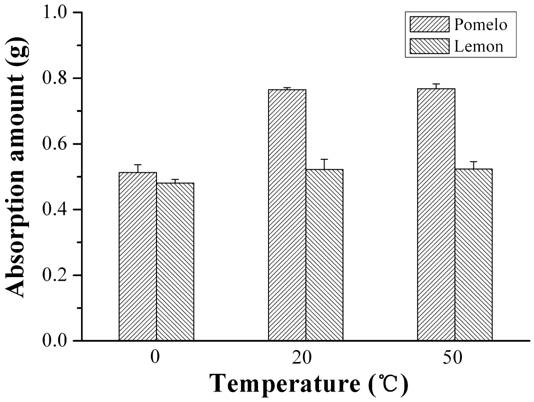


Figure 6. Influence of extraction time on the extraction efficency at the dose of 10 mg and room temperature.

The absorption amount of essential oil in relation to extraction temperature was carried out by varying the treatment temperatures from 0 to 50 °C for a 20 mL stoste with a dose of adsorbent of 10 mg and stirring for 20 min under optimum conditions. The results are presented in Figure 7. It was found that low temperatures are adverse to GA-based solid-phase extraction because of slow molecular motion and diffusion. There was no obvious effect for graphene aerosol solid-phase extraction essential oils by extraction temperature when the temperature increased to 20 °C. This temperature independence property was directly caused by the 3D structure of the graphene aerosol. Graphene aerosol has a large specific surface area and rich π electrons, making it easy for essential oil extraction at different temperatures. In practice, considering the factors including energy conservation and the yield of the extraction, room temperature was chosen as the optimum extraction temperature.

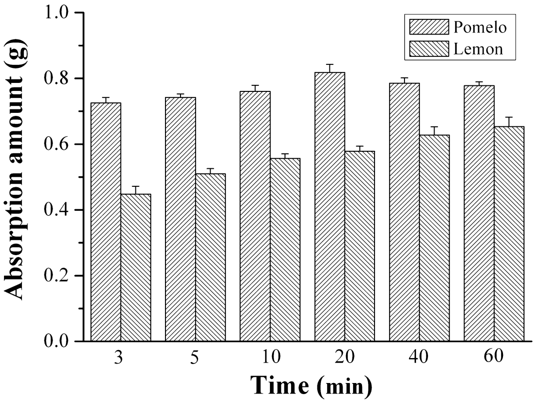
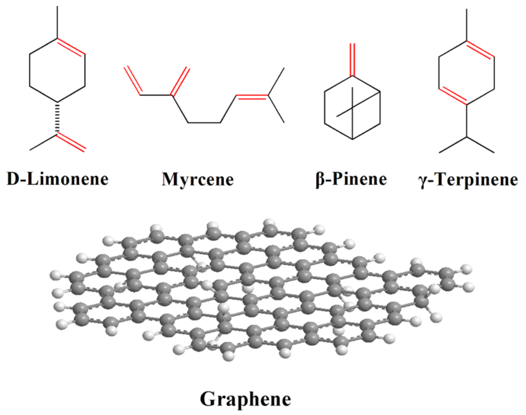


Figure 7. Influence of extraction temperature on extraction yield at the dose of 10 mg and extraction time of 20 min.

GA-Based Solid-Phase Extraction Mechanism. Scheme 1 shows the structures of D-limonen, myrcene, β-pinene, γ-terpinene, and graphene. There were a pair or more of π electrons in those compounds from essential oils, while a large π-conjugated system existed in the graphene layer. Our proposed mechanism for essential oil adsorption may due to π electron interaction and large specific surface area. Also, we

Scheme 1. Structures of Some Main Compounds of Essential Oils from Citrus and Graphene



found GA contained a small amount of oxygen groups that can make it well infiltrated in the mixture but not dissolved. The well infiltration of GA in the mixture increased the contact and also enhanced the extraction efficiency. Table 1 shows the comparison of GA with various 3D graphene materials for adsorbing oil from plants reported before. In addition, GA could be regenerated and reused without affecting its performance when heated to the temperature around the boiling point of absorbate.

Table 1. Applications of Typical Graphene Structures and Other Carbonaceous Materials for Plant Oil Adsorbtion

sorbent	plant oils	adsortion capacities[a] (times)	ref
graphene sponge	soybean oil	55	26
graphene sponge	caster oil	75	26
graphene aerogel	vegetable oil	17.5	27
carbonaceous nanofiber aerogel	vegetable oil	76	28
graphene capsules	vegetable oil	17.5−21	29
graphene framework	olive oil	470	30
graphene aerosol	essential oils	80	this work

[a] Adsortion capacities were calculated by the weight of adsorbed substances divided by adsorbent.

■ CONCLUSION

In summary, a SPE based on graphene aerosol as sorbent for essential oils extracted from two types of citrus was demonstrated. The proposed SPE was to be a simple, rapid, and effective method. The whole extraction procedure was quick and could be accomplished by simple magnetic stirring within 20 min. Maximal extraction yields of 2.70% and 2.47% were achieved under optimal conditions for pomelo and lemon, respectively, by this method. We believe that this simple, rapid, environmentally friendly, and cost-effective method might be a potential application for extraction and analysis of essential oils from other plants.

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Notes

The authors declare no competing financial interest.

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