



# High-yield exfoliation of graphene using ternary-solvent strategy for detecting volatile organic compounds



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## ABSTRACT

Despite the great progress in the theory and experimental verification we made in past decade, the practical application of graphene is still hindered by the lack of efficient, economical, scalable, ease-processing exfoliation method. Herein, we propose a facile, low-cost, and efficient liquid-phase exfoliation process using low boiling-temperature solvent mixture to fabricate few-layer graphene in large scale. The Hansen solubility parameter theory was applied to help optimize the composition of solvent mixture. Aqueous-based ternary-solvent mixture, for the first time, was adapted to exfoliate graphene. We demonstrate that the exfoliation efficiency using ternary-solvent mixture surpasses that from binary-solvent approach. The final product concentration after optimization was over 260  $\mu\text{g}/\text{ml}$ . The concentrated graphene dispersion was used to fabricate gas sensor for detecting volatile organic gases. Taking advantage of large surface area, large number of adsorption sites, and well-preserved basal plane, the mass-produced graphene nanosheets exhibited promising sensing potential toward ethanol and methanol vapors.

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## 1. Introduction

Graphene is a two-dimensional form of carbon based material existing as a single layer of carbon atoms arranged in honeycomb lattice [1,2]. It has emerged as a revolutionary material that possesses exceptional thermal, mechanical, electronic and optical properties due to its unique two-dimensional  $sp^2$ -bonded structure [3,4], which makes graphene an attracted material for many applications, including gas and energy storage, light-emitting device, solar cell, photodetector, touching screen, gas and bio sensor [5–11]. In past decade, world-wide researches were focused on the fundamental study of graphene, and great progress has been achieved. The commercialization of graphene in future is thus mainly dependent on how efficient we could fabricate graphene in large scale. Generally, two strategies are used to fabricate graphene up to now, those are so-called ‘bottom-up’ including chemical vapor growth and annealing silicon carbide substrate [12–15], and ‘top-down’ involving micro-mechanical cleavage, ball-milling of graphite, reduction of graphene oxide, and exfoliating graphite toward graphene [1,16–18]. In particular, graphite can be exfoliated in liquid environments assisted by ultrasound to extract individual graphene nanosheet. Unlike the reduction of graphene

oxide, which presents large number of irremovable defects, liquid-phase exfoliation mainly generates ‘pristine’ graphene nanosheets. Furthermore, liquid-phase exfoliation method is extremely versatile, eco-friendly, potentially up-scalable, and can be used to deposit graphene in a variety of environments and on different substrates that are not available using mechanical cleavage or growth methods.

Recently, numerous efforts have been devoted to the study on ultrasound assisted liquid-phase exfoliation method [19–23]. It was found that beside the ultrasonic dose, i.e. ultrasound time and power [24–26], the solvent mediums play the key role in exfoliation process. It was reported that the solvents with surface tension about 40  $\text{mJ}/\text{m}^2$  are the best mediums for dispersing graphene due to the minimized interfacial tension between graphene and solvent. However, those ‘best’ solvents, such as *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and ortho-dichlorobenzene (*o*-DCB), have toxic effects on multiple organs in human body. Furthermore, those solvents have high boiling temperature (NMP 203 °C, DMF 154 °C and *o*-DCB 181 °C) which are difficult to be removed with modest condition and also making them difficult to be handled during the next device processing [27]. Thus development of an efficient exfoliation method using low-boiling-temperature solvents is urgent and significant. However, most low-boiling-temperature solvents have a surface tension unsuitable for the direct exfoliation of graphene. Recently developed Hansen solubility parameters (HSP) strategy gives the potential to solve this problem. HSP is a semi-empirical

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correlation developed to explain dissolution behavior, and it has been widely applied to exfoliate graphene and other transition metal dichalcogenides [28,29]. In the HSP theory, three HSP parameters are used to describe the character of a solvent or solute:  $\delta_D$ ,  $\delta_P$ , and  $\delta_H$ , which are the dispersive, polar, and hydrogen-bonding solubility parameters, respectively. The dissolution of nanomaterials in liquids can be estimated by calculating the approximation degree ( $D_{\text{HSP}}$ ) of the three HSP values between the solvents and solutes:

$$D_{\text{HSP}} = \sqrt{(2\delta_{D,\text{solv}} - 2\delta_{D,\text{solu}})^2 + (\delta_{P,\text{solv}} - \delta_{P,\text{solu}})^2 + (\delta_{H,\text{solv}} - \delta_{H,\text{solu}})^2} \quad (1)$$

where solv and solu represent solvent and solute, respectively. The smaller the  $D_{\text{HSP}}$  value, the higher dissolution capability is. The HSP theory is also valid when the solvents are mixed each other. The three HSP parameters of solvent mixture are a linear function of composition, and the  $D_{\text{HSP}}$  of mixture can be derived by the following equation:

$$\delta_{\text{mixture}} = \sum \Phi_{n,\text{solv}} \delta_{n,\text{solv}} \quad (2)$$

where the  $\Phi$  represents the volume fraction of a single solvent, and  $n$  means one of the HSP parameters. Thus, combining Eqs. (1) and (2), one can brew 'best' solvent mixture for exfoliating graphene by mixing several 'poor' solvents.

On the other hand, graphene is considered as the talented gas and vapor sensor material since every atom of graphene is a surface atom capable of interacting with ambient molecules. The interaction introduces drastic change in the conductivity of graphene, and presents ultrasensitive sensor response. However, the study on gas sensor response of intrinsic graphene, especially to volatile organic compounds (VOCs) vapors is still in initial stage [30]. In this study, according to HSP theory, we developed a facile process to exfoliate graphene in an aqueous-based ternary-solvent mixture. The exfoliated product was carefully examined. We demonstrate that the ternary-solvent strategy is more efficient than that of binary-solvent approach. The mass-produced graphene was fabricated into thin film sensor and its detection ability toward VOCs gas (e.g. ethanol, methanol) was investigated.

## 2. Experiment details

### 2.1. Liquid-phase exfoliation of graphene

All chemical reagents were of analytical grade and were commercially obtained. Typically, 4 g of graphite powder (Sigma-Aldrich, 20  $\mu\text{m}$ ) was dispersed in 200 ml of a solvent mixture. The dispersion was then ultrasonically treated for 1 h using a horn probe sonic tip (Sonic VCX 750). To avoid the considerable ultrasound-induced heating effect, a cooling water system was used to keep the processing temperature below 5 °C throughout. The ultrasonic power was set to 600 W. Pulsed ultrasonic irradiation was performed for 20 s on and 10 s off to avoid damage to the ultrasonic processor and reduce solvent heating and resultant degradation of the graphene nanosheets. After the ultrasonic treatment, the black dispersion was transferred to vials and centrifuged at 1500 rpm for 30 min. After centrifugation, the top 20 ml (out of 25 ml) was carefully decanted and retained for next characterization. In order to determine the concentration of the product, 100 ml of graphene dispersion after centrifugation was transferred to a pre-weighted vial and dried in oven at 100 °C for 24 h.

For the characterization of the exfoliated product, a drop of solution containing the produced graphene nanomaterial was placed on a Si/SiO<sub>2</sub> substrate and then dried in a furnace at 100 °C for 6 h before it was observed by scanning electron microscope (SEM, JSM 7100F, operated at 15 KeV), atomic force microscopy (AFM, Bruker Nano N8 NEOS), and Raman spectroscopy (Nanobase Inc., XperRam 200 Raman Microscope, 530 nm). Transmission electron

microscopy (TEM) and selected area electron diffraction were taken with a JEOL 2100 operating at 200 KV.

### 2.2. VOCs sensing detection of graphene-based thin film sensor

Graphene dispersion was evaporated in an oven for 24 h with a moderate temperature (~45 °C) to improve the concentration of solute without introducing severe aggregation. Alumina substrates (4 mm × 4 mm) with interdigital Pt electrodes were carefully cleaned and placed on a hot-plate with a temperature about 100 °C. Concentrated graphene nanosheets solution was then drop-casted onto the sensor substrates with micro-pipettes. The thickness of the thin films was about 1  $\mu\text{m}$  and was controlled by the volume of the solution in the micro-pipettes. After coating, the alumina substrates were heated at 100 °C in oven for 1 h to eliminate the remaining solvent and then sintered at 200 °C in Ar gas for 1 h to improve the adhesion and contact.

The gas sensing test system was comprised of two parts: gas delivery system and conductance measurement system. The graphene-based thin film sensor was placed into a quartz chamber with a total volume of 5 cm<sup>3</sup>. Nitrogen (Daehan Gas Co., Ltd.) gas was used as a carrier gas. Manufactured standard ethanol and methanol gases (both 50 ± 1 ppm in nitrogen, Daehan Gas Co., Ltd.) as a target gas was diluted with carrier gas for the desired concentrations. The accurate concentration control of the target gases was done by using a mixing system equipped with mass flow controllers (MFC, Tylan 2900) and mass flow meters. All the measurements were conducted under ambient conditions. The total gas flow of the carrier and target gases was kept at 250 sccm throughout the measurement process. The electrical conductance signal of the sensor was collected and recorded by a data acquisition (Agilent 34970A) through a customized clamp and wire connector. The sensitivity was defined as

$$S = \frac{R_G}{R_N} \quad (3)$$

where  $R_N$  and  $R_G$  represented the resistance of the thin film sensor upon exposure to nitrogen and target gases, respectively. The response and recovery time were defined as the time taken by the sensor to achieve 90% of the total resistance change in the respective case of adsorption and desorption.

## 3. Results and discussion

### 3.1. Characterization of exfoliated graphene nanosheets

The liquid-phase exfoliation process typically involves two steps: (1) ultrasound-induced exfoliation and (2) solvent-induced balance. The ultrasound-induced effects, including shear force and cavitation, are from the growth and collapse of the micrometer-sized bubbles or void in liquids due to pressure fluctuations [31,32]. These effects are the driving force of exfoliation, and thus ultrasonic dose, i.e. ultrasound power and time, takes an important role in exfoliation results. After exfoliation, the inter-layer attractive force needs to be balanced by proper solvent-graphene interaction to avoid the restacking phenomenon. The proper solvent with matched surface energy can minimize the enthalpy of the exfoliation process, and facilitate the exfoliation process. Thus the match of the solvent and graphene is the key parameter in exfoliation process. In our study, this match work was done with the help of HSP strategy. As discussed above, mixing solvents may change the HSP distance between mixture and solute. Moreover, this quantitative value is assessable with variation of composite, making prediction and optimization of 'best' solvent mixture available.

Fig. 1 illustrates the calculated HSP distance by mixing water with two low-boiling-temperature solvents with different blending

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