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Green sonochemical synthesis of few-layer graphene in instant coffee

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HIGHLIGHTS

- Graphite exfoliation in coffee produces graphene with bandgap energy of 3.1 eV.
- "Red-edge effect" is demonstrated by our graphene/water solution.
- The thickness range of graphene is between 2 and 4 layers.
- About 25.6% presence of oxygen group is detected in the exfoliated graphene.
- The reported time exponent factor of 1.07 is higher than the typical value.

ARTICLE INFO

ABSTRACT

In this work, we reported for the first time the use of bath sonication of graphite in instant coffee to produce few-layered graphene flakes. The sonication of graphene in instant coffee allows facile production of graphene flakes in a green medium and avoids the application of commonly used organic exfoliating solvents such as Dimethylformamide or N, N methyl pyrrolidone. We verified the presence of graphene flakes in the resulting supernatant using local maximum UV spectrum (269 nm) and performed thickness and length measurements of said graphene flakes by atomic force microscopy and transmission electron microscopy. The defect and purity of exfoliated graphene flakes were investigated using Raman spectroscopy (I_D/I_G = 0.85) and X-ray photon spectroscopy (C/O = 2.6) meanwhile Fourier transform infrared spectroscopy was used to identify the functional group attached to graphene. The production of graphene flakes in coffee was shown to have a time exponent factor of 1.07, which impressively is higher than the time exponent factor for typical sonication in a solvent and surfactant.

1. Introduction

Graphene has been proposed as a future material for many major components in consumer applications such as electronics [1], medical [2], energy storage [3], polymer [4] and sensors [5] due to its unique intrinsic properties. In the production of graphene itself, there have been a countless number of graphene synthesis techniques that have been developed ever since the discovery of graphene in 2004 [6]. The available techniques fundamentally can be divided into two categories which are known as the bottom-up and top-down approaches. A bottom-up approach which is used for the preparation of defect-free graphene include methods such as pyrolysis [7], epitaxial growth [8], and chemical vapor disposition [9]. Mechanical cleavage [10], chemical exfoliation [11] and liquid-phase exfoliation [12] meanwhile are production methods of graphene that belong to the top-down approach and are commonly employed for the production of liquid or powdered graphene. In contrast to the limited scalability of a bottom-up approach, a top-down approach is more scalable and flexible for future mass production of graphene. Of all the presented methods, liquid phase exfoliation of graphite that can be accomplished either by sonication or shear exfoliation is considered the most facile method for production of low-defect graphene flakes.

In describing the sonication medium of few-layer graphene, organic solvents such as N-methyl-pyrrolidone (NMP), dimethylacetamide (DMA), and dimethylformamide (DMF) were frequently used as exfoliating solvents for graphite flakes [13–15]. The process involves sonication of graphite in a selected solvent where the exfoliation of graphite is majorly promoted by the cavitation energy introduced by the sonic transducer. Breaking the van der Waals forces of the used solvent results in a balancing of the inter-sheet attraction, thus preventing the graphene from re-aggregating in the resulting supernatant [16].

However, the properties of these mentioned solvents are considered

as a major drawback in the actual synthesis process of graphene flakes. A majority of these solvents have a high boiling point which ultimately results in the re-aggregation problem of graphene flakes during dropcasting if it is not well cleansed [17]. Importantly, these solvents are known as carcinogenic [18] and would cause a major environmental problem if a proper disposal system for these solvents is not well designed. Therefore, an alternative exfoliating medium for few-layer graphene must be proposed to avoid the usage of organic solvents for the sonication process of graphene.

Coffee generally has been available for human consumption as a beverage since 1000 years ago [19] and the commonly used bean for production of coffee are *Coffea arabica* and *Coffea canephora* [20,21]. In describing the chemical composition of coffee, caffeine which is well known as a chemical component of coffee is only accounted for 0.8%–1.4% whereas insoluble polysaccharides (46%–53%) and cellulose (41%–43%) become the major chemical constituents in coffee [20] besides chlorogenic acid. Aside from beverage, coffee has been reported to be a potential material for the production of ethanol [22], biodiesel [23] and fuel pellets [24]. However, until now there has never been any published work on the application of coffee as an exfoliating medium for direct synthesis of graphene although application of coffee solution as a reducing agent [25] has been reported previously. In this research, we demonstrate the effectiveness of intant coffee as a medium for direct liquid phase exfoliation of graphene assisted by bath sonication. Specifically, the properties and quality of the produced graphene is assessed using different characterization method. The distribution length, $< L >$ and layers, $< N >$ of the graphene were estimated, supported with Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). Defect level of graphene was evaluated using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) while the attached functional group to the graphene was identified using Fourier Transform Infrared spectroscopy (FTIR) in order to consider the active component responsible for the stability. We also presented the effect of process parameters to the graphene yield in order to prove the efficiency of instant coffee as a medium. The purpose and advantage of this work is to demonstrate the use of non-toxic, green, cheap and easily available instant coffee to produce graphene with the yield and quality rivaled the established solvents. This finding has increased the list of mediums for direct liquid phase exfoliation of graphene besides being proven to be scalable and environmental friendly.

2. Results and discussion

2.1. UV spectroscopy

Fig. 1a showed the collected UV spectrum of the graphene-coffee, G_C supernatant after bath sonication of graphite in coffee after 8 h. A presence of local maximum at 269 nm is corresponding to the π to π* transition of graphene and therefore could be used as proof of G_C presence in the resulting supernatant [26]. A change of instant coffee medium from brownish to dark black is also another strong indicator of suspended graphene in the colloidal supernatant (see Fig. 1b and c).

After multiple stages of washing, the graphene solution was subjected to freeze-drying for preparation of G_C in powder form. As shown in Fig. 1d, the obtained black powder showed no traces of silver-metallic graphite, which could be used to highlight the importance of coffee component as stabilizing agent against reaggregation of graphene to graphite after the exfoliation stage. The value of the absorption coefficient for G_C is 1267 mg^{-1}m^{-1}ml and is comparable with α magnitude from previously reported water dispersible graphene (see Table 1).

For evaluation of the effect of graphene functionalization on the electronic properties of our graphene, a calculation of bandgap energy values for the G_C was performed using the following Tauc equation (Equation (1)) [34].

$$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2} \tag{1}$$

where α is the obtained absorption coefficient, υ is the frequency, h is the Planck's constant, E_g is the computed bandgap energy and A is the mass constant of the graphene. The extrapolation of resulted tangential line for presented plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ in Fig. 1e shows the presence of bandgap energy of 3.1 eV for our graphene. This means that the liquid-phase exfoliation of graphene in coffee can be employed for electronic manipulation of zero-bandgap graphene through chemical functionalization with oxygenous function group in coffee [35]. Moreover, we notice that this value is not far from the reported value of bandgap energy for graphene oxide (GO), which suggest the possibility of bandgap tuning of graphene with lower plane-defect density as compared to GO [36]. This possibility potentially allows the application of our heterostructured graphene in many optoelectronics based applications such as light-emitting diodes [37], solar cell [38–40] and transparent electrodes [41] and thus, the changes of graphene electronic structure after exfoliation in coffee is crucial. To further identify the changes in electronics states of graphene, a photoluminescence (PL) study was performed on the graphene/water solution sample and the resulted plots are presented in Fig. 1f. Similar to PL behaviour of GO when dispersed in water, a "red-edge effect" is demonstrated by G_C suspension as the shift and broadening of fluorescence peak is observed after the increase of λ_{ec} from 400 to 450 nm. This effect is caused by solvent relaxation time that is longer than the fluorescence lifetime as the graphene itself is dispersed in water, which is a polar solvent [42]. It is also noticed that the presence of PL peak is located at 580 nm instead of 480 nm for G_C at $\lambda_{ec} = 350$ nm and this different certainly is attributable to the different in heterostructure of graphene in this work when compared to PL peak of GO although both materials is known to be dispersible in water.

For estimation of the distribution length ($< L >$) and thickness ($< N >$) of exfoliated G_C from our process, an in-situ measurement method of length (Equation (2)) and thickness of graphene flakes (Equation (3)) by UV-vis spectroscopy were used [29,43].

$$\langle L \rangle = 561 \left[1 - \left(0.64 - \frac{Abs_{min}}{Abs_{max}} \right)^{1.36} \right] \tag{2}$$

$$\langle N \rangle = 13.7 \times \alpha_{550}/\alpha_{max} - 1.2 \tag{3}$$

To achieve this objective, we centrifuged our graphene solution at different centrifugation speeds (4000, 5000, 6000, 7000, 8000, 9000, 10000 and 11000 rpm) with the volume and duration fixed at 10 ml and 1 h respectively. As can be seen from Fig. 2, the length range of our graphene flakes are measured between 260 nm–400 nm while for thickness, the value are varied in between 2 and 4 layers. From the result, we estimate that 62% from the sonicated graphene flakes are trilayer while the remaining can be either bi or four layers (few-layer) graphene.

The presented topography AFM image in Fig. 3a showed the height of the deposited graphene is about 2–3 nm which is within the layer thickness range for few-layer graphene flakes. As the effect of apparent height in AFM measurement was neglected in this work [44,45], the layer number for a typical AFM image is suggested as bilayers (2 nm + 0.95 nm). In term of flakes appearance, the obtained slender and fragmentized shaped of G_C flakes could be attributed to the intense sonication process during the exfoliation stage.

The shown TEM image of G_C at higher magnification in Fig. 3b meanwhile highlights the wrinkleless state of surface graphene after intense exfoliation stage. It is suggested that the sonication of graphite over 8 h did not introduce any defect to basal planes of graphene. Moreover, the transparency level of the graphene flakes in the TEM image is consistent with the proposed layer number of G_C from AFM evaluation. However, it is noted that there are multiple presence of folded edges along the graphene flakes, which probably has been caused by the exfoliation dynamic of graphene in coffee during the