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Facile method for liquid-exfoliated graphene size prediction by UV-visible spectroscopy

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Abstract. In this work, an application of UV spectroscopy for facile prediction of liquid –exfoliated graphene size is discussed. Dynamic light scattering method was used to estimate the graphene flake size ($\langle d \rangle$) whilst UV spectroscopy measurement was carried out for extinction coefficient value (ϵ) determination. It was found that the value of (ϵ) decreased gradually as the graphene size was further reduced after intense sonication time (7h). This observation showed the influence of sonication time on electronic structure of graphene. A mathematical equation was derived from log-log graph for correlation between ($\langle d \rangle$) and (ϵ) value. Both values can be expressed in a single equation as ($\langle d \rangle = (3.4 \times 10^{-2}) \epsilon^{1.2}$).

INTRODUCTION

The application of UV spectroscopy in the characterization of graphene can be widely found in large number of literatures [1, 2, 3]. The method is not a time consuming procedure, easy to be carried out and importantly can determine the presence of graphene in a mixed composition precisely. UV spectroscopy utilizes on a concept of quantum mechanics, where an excitation of electron for one material can be only initiated if the incoming energy possesses a certain frequency value and thus, allowing a change of molecules condition from ground to excited state by energy absorption ($E = h\nu$). During this phase, the energy is transported from highly occupied molecular orbit (HOMO) to lowest unoccupied molecular orbit (LUMO) by diffusion through sequential vibration in a group of molecules [4].

Considering the advantageous features of UV spectroscopy, we believe that we must optimize the technique in order to reduce the workload in liquid exfoliated graphene characterization strategy. We decide to investigate a viability of UV spectroscopy as a method that can be used to estimate a mean length value of graphene besides conventional application of transmission electron microscopy (TEM) and atomic force microscopy (AFM). TEM and AFM imaging are expensive and particularly require a special handling from an expert although both can measure a single graphene at its highest precision size. Dynamic light scattering method (DLS) is another approach that can be used to estimate the size of graphene by assuming of graphene geometry as sphere.

Based on the work by Loyta et al. [5], a graphene mean size measured by TEM can be related to graphene size measured from DLS by following equation

$$\langle L_{TEM} \rangle = (0.07 \pm 0.03) \alpha_{DLS} (1.5 \pm 0.15) \quad (1)$$

where α_{DLS} is the intensity primary peak of particle size distribution (PSD). From the report, a value of α_{DLS} was taken to represent intensity distribution curve because of bimodal peak existence in their data from DLS.

Based on this explanation, we decided to replace α_{DLS} unit with the mean diameter value $\langle d \rangle$. We believe that $\langle d \rangle$ can represent the graphene size obtained from DLS accurately more than α_{DLS} , whose value is only illustrates

a majority size of polydispersed graphene in a solution. Importantly, our measured PSD of graphene were shown to possess a mono distributive peak and free from any presence of foreign particle, dust or bubble. As far as we concern, $\langle d \rangle$ is totally independent from the refractive index of graphene, whose dimension is absolutely difficult to be precisely determined for number and volume calculation from Mie's theory. We also found that the refractive index of graphene is strongly influenced by mean layer thickness of graphene and thus, the value can be varied from sample to sample. To avoid the high uncertainties during the conversion of intensity PSD value to number and volume units; we were against the z-average data given by the built-in program and therefore used intensity PSD for representation of graphene size distribution in this work.

METHOD

Gum arabic ($M_w \sim 250000$) and graphite flakes (+100 meshes) with purity of 75% were obtained from Sigma Aldrich (Malaysia). Industrial ultrasonic (Branson) was used for the preparation of graphene at different duration of sonication. UV-vis spectra for each sample were recorded using a spectrophotometer (Shimadzu). A series of diluted dispersion volume was prepared by varying of graphene concentration. The determination of extinction coefficient (ϵ) was carried out accordingly to Lambert-Beer law

$$A = \epsilon Cl \quad (2)$$

where (A) represents the extinction value at wavelength of 660 nm, (C) is the concentration of graphene carefully weighted after filtration and washing and (l) is the length of optical path determined from width of used cuvette (10 mm). Statistical size distributions of graphene flakes were measured by dynamic light scattering technique (Malvern).

RESULT AND DISCUSSIONS

Using UV spectroscopy, we determined the value of extinction coefficient (ϵ) for each sample by calculation derived from Lambert-Beers law. We are interested to study the change of optical extinction properties of graphene liquid after different mixing time. We suspect an influence of graphene size on the above value because of the (ϵ) large variation (1390 to $6600 \text{ mg}^{-1} \text{ m}^{-1} \text{ ml}$) in previous reported works [6,7]. An extinction coefficient is composed of absorption and scattering coefficient. As the size of π -conjugated system increase, the amount of absorbed light will also be increased and vice versa [8]. The presence of scattering light during spectra measurement was minimized by incorporation of low graphene mass ($0.74 - 3.7 \text{ mg}$). A series of spectra measurement from UV-spectroscopy is presented in Figure-1.

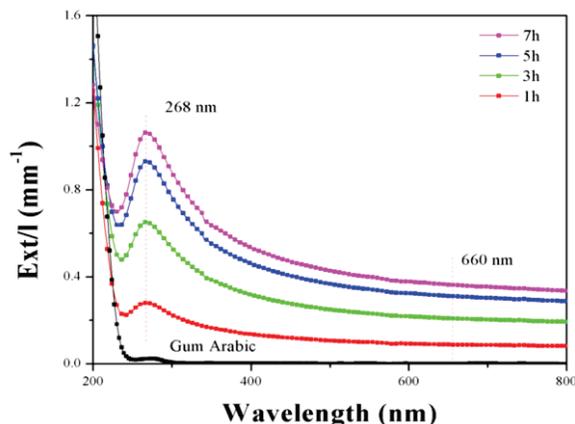


FIGURE 1. A collection of graphene spectra obtained from UV spectroscopy measurement after different sonication time. The extinction belongs to gum arabic is zero at the wavelength of 660 nm, thus enable a comparison of graphene spectra at the similar wavelength.

Contrary to our expectation, there is no shift of $\pi - \pi^*$ corresponded peak of graphene as sonication time was increased. After normalization of spectra at 268 nm however, we notice a sequential local minimum shift towards shorter wavelength for higher duration of sonication time (Figure-2). From this observation, we postulate that the prepared graphene size might have an influence on the electronic properties of graphene itself.

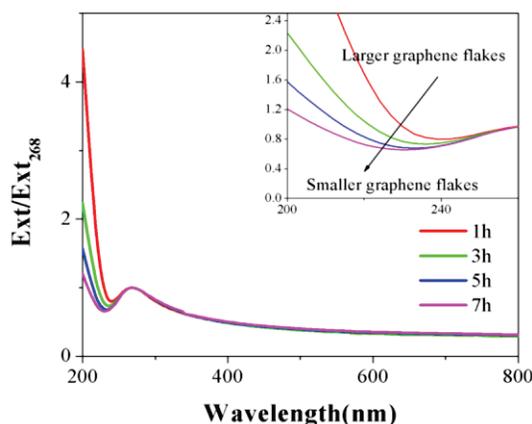


FIGURE 2. A series of normalized spectra at the wavelength of 268 nm. A significant shift of local minimum peak is observed, indicating an indirect effect of sonication time on electronic properties of graphene. We noticed on how this shift is directly related to the reduction of graphene dimension by comparison from dynamic light scattering methodology

Based on the determination of linear gradient from given samples with different mixing time, we observe that (ϵ) was reduced in value as the sonication time was increased from 1h to 7h (Figure-3). Our (ϵ) values are definitely in range with the values reported previously [6,7]. A direct exfoliation of graphene might be a factor that leads to this particular observation. We note a large difference of reported (ϵ) for reduced graphene oxide by ball milling ($2.67 \times 10^6 - 6.72 \times 10^6 \text{ mg}^{-1} \text{ m}^{-1} \text{ ml}$) [8].

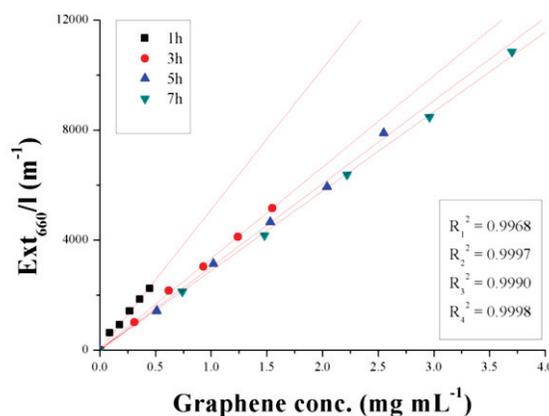


FIGURE 3. A series of function is used to represent a linearly correlation between extinction at 660 nm and sonication time. The highest value of (ϵ) was obtained at shortest sonication time (5115, 3325, 3023 and 2890 $\text{mg}^{-1} \text{ m}^{-1} \text{ ml}$). The decrease in value for (ϵ) for every reduced mixing time indicates an influence of graphene size on extinction.

Next, we examine the effect of sonication time on graphene size distribution from intensity PSD measurement (Figure-4). We find that the distribution of small graphene ($\leq 500 \text{ nm}$) is exponentially increased as the mixing time was prolonged to 7h (4.8%, 33.6%, 50.9% and 53%). In contrast, the value of $\langle d \rangle$ is decreased following the increased mixing time as expectedly (1026 nm, 685 nm, 526 nm and 511 nm). From this observation, we conclude that a higher sonication time is required to increase a portion of smaller size graphene in a batch volume.

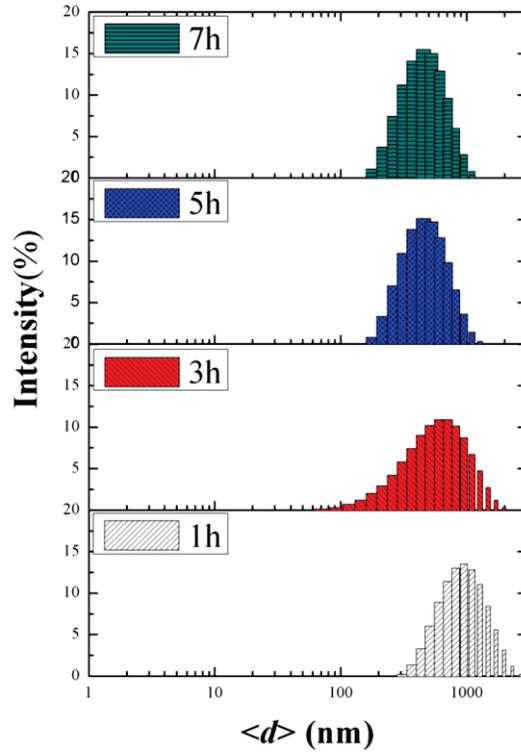


FIGURE 4. Stacked functions of intensity versus graphene PSD plotted from DLS data. In the measurement, the scattered graphene is assumed to possess a spherical geometry and is individually characterized from recorded mean diameter $\langle d \rangle$.

As far as we know, an absorbance of a solution at certain wavelength is strongly influenced by total absorption of a particles group with distinguished distributive size [9]. We also know that a preparation condition as well as centrifugation speed and time can strongly affect the dimension of collected graphene flakes [10]. Based on these facts, we attempt a correlation study between $\langle d \rangle$ and (ϵ) values to demonstrate a dependence of former on the latter. We however, chose to set our centrifugation parameter at a constant (ω) for each of mixing time as we were only interested to investigate the correlations between graphene flakes size and optical extinction in this study. From the plotted points of (ϵ) against $\langle d \rangle$ in log-log graph, a linear was obtained (Figure-5).

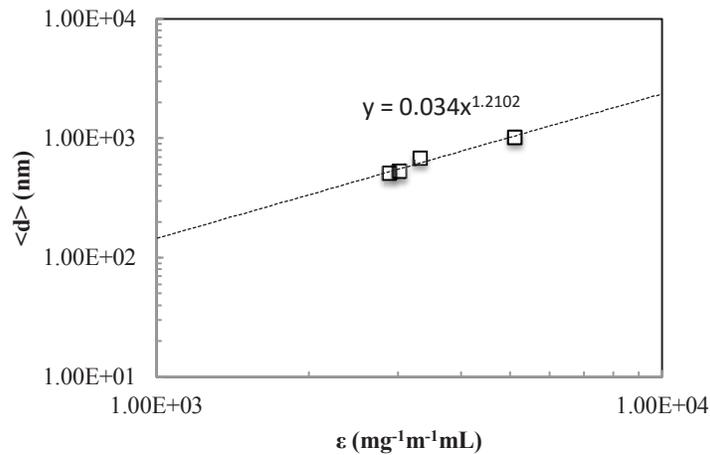


FIGURE 5. Mean diameter $\langle d \rangle$ values as function of optical extinction coefficient (ϵ). Based on the exponent of produced curve between $\langle d \rangle$ and (ϵ), we estimate that both parameters can be almost linearly represented ($\langle d \rangle \propto \epsilon^{1.2}$).

Based on the fitted line obtained from above plotted linear, we imply that $\langle d \rangle$ is related to (ϵ) by following equations:

$$\langle d \rangle = (3.4 \times 10^{-2}) \epsilon^{1.2} \quad (3)$$

Provided that centrifugation parameters are set at similar condition as ours, we propose that a $\langle d \rangle$ for a number of graphene flakes can be approximately estimated from (ϵ) value by UV spectroscopy measurement.

CONCLUSION

In this work, a novel approach for estimation of liquid-exfoliated graphene size by UV spectroscopy is presented. The relationship between extinction coefficient (ϵ) and graphene flakes dimension was in detail discussed. Finally, a mathematical estimation of mean size graphene $\langle d \rangle$ from (ϵ) value for easier characterization of graphene was generated.

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