Carbon 107 (2016) 733–738

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Relating the optical absorption coefficient of nanosheet dispersions to the intrinsic monolayer absorption

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A R T I C L E I N F O

Article history:
Received 30 March 2016
Received in revised form
14 June 2016
Accepted 16 June 2016
Available online 18 June 2016

A B S T R A C T

The concentration of nanosheet suspensions is an important technological parameter which is commonly measured by optical spectroscopy, using the absorption coefficient to transform absorbance into concentration. However, for all 2D materials, the absorption coefficient is poorly known, resulting in potentially large errors in measured concentration. Here we derive an expression relating the optical absorption coefficient of an isotropic dispersion of nanosheets to the intrinsic monolayer absorption. This has allowed us to calculate the absorption coefficients for suspensions of graphene, MoS_2 and other 2D materials, and to estimate the monolayer absorption for new materials from careful measurement of the suspension absorption coefficient.

1. Introduction

Liquid phase exfoliation of layered materials has become one of the most widely used methods to obtain nanosheets in an easily processable form [1–8]. Nanosheet suspensions (a.k.a. dispersions or inks) have been shown to be ideally suited to production of printed electronics [9,10], including devices such as LEDs, battery and supercapacitor electrodes [11–16], photo-detectors [17] and hydrogen evolution catalysts [18–23], as well as additives in composites [23–26]. While the production of these dispersions can be scaled to industrial levels [8], methods to reliably and rapidly characterise the material produced are limited. Measurement of the concentration of nanosheets in the dispersion is commonly achieved by optical absorption spectroscopy, through the application of the Beer-Lambert Law. Note that we use the term nanosheets throughout this paper to refer to objects consisting of 1 or more monolayers (generally fewer than 10), where for some materials (e.g. MoS_2) a monolayer may be more than one atom thick. While this has been widely used for a range of nanosheet dispersions, it requires an accurate value for the absorption coefficient (or more usefully the extinction coefficient [27]). This in turn is usually obtained by removing the liquid from the dispersion, either by filtering or evaporation, and weighing the resulting solid (taking account of any surfactant or solvent residues). Despite the simplicity of the procedure to obtain this important parameter, the values reported in the literature vary widely, from as low as 1043 ml mg^{-1} m^{-1} to as high as 6600 ml mg^{-1} m^{-1} for graphene [28,29]. Similar variation exists for other 2D materials such as MoS_2 (see SI). It is not clear which papers are correct, as theoretical values of the suspension absorption coefficient are not available.

However, this is a problem which should be easily addressed. For a number of 2D materials, notably graphene, the amount of incident light absorbed by a single monolayer is known experimentally. This intrinsic material property is the primary factor controlling the absorption coefficient of a dispersion of nanosheets. Once it is known, it should be straightforward to derive a relationship between these quantities. However, to date such a calculation has not been published. In the present paper, we derive an expression relating the absorption coefficient for dispersions of nanosheets to the optical absorption of a monolayer at normal incidence. This relationship will allow the calculation of dispersion absorption coefficients from theoretical estimates of monolayer absorption and the validation of experimental values of absorption coefficient. In addition, it will be possible to estimate the monolayer absorption from careful measurements of dispersion absorption coefficient.

2. Results and discussion

Optical spectrometers physically measure the transmission of light, T (defined as the ratio of transmitted, I, to incident, I_0, light

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http://dx.doi.org/10.1016/j.carbon.2016.06.043

intensity). However, the data is often outputted as the absorbance, which we will refer to here as A_T. In the absence of scattering (see below), this parameter is generally defined as $A_T = -log_{10}T$ and it is this quantity that is automatically outputted by the spectrometer software (i.e. not $-lnT$) [30]. The absorbance is useful because it is directly proportional to the quantity of absorbing material: $A_T = \alpha CL$ where C is the concentration of nanosheets, defined as the dispersed mass/dispersion volume. Although more typically applied to liquid solutions, with absorbing species truly dissolved in a solvent, it has been shown by several authors that this equation can also be applied to samples of 2D nanosheets dispersed in solvents [1,29,31–34]. Here the proportionality constant, α, is the absorption coefficient which tends to be poorly known (L is the cell length, the distance the beam travels through the vessel containing the liquid).

The simplest way to calculate α is via the absorption, A, which (in the absence of scattering) is the fractional light intensity change as the beam travels through the sample: $A = (T_0 - T)/T_0$, where T_0 is transmission in the absence of the sample. Neglecting reflections, we have $A = 1 - T$. For a dilute solution, where αCL is small, it is straightforward to show that $A = \alpha CL/log_{10}e$, where $e = 2.72$. Thus, calculation of the absorption will allow us to find the absorption coefficient (see SI for full derivation).

The absorption of a dispersion of nanosheets is simply the sum of the absorptions of all individual 2D nanosheets. To calculate this we must consider that, at any given instant, the nanosheets are randomly distributed throughout the liquid with isotropic orientation distribution. To calculate the total absorption, we consider a nanosheet whose orientation is defined by the polar angle, θ, and azimuthal angle, φ, associated with the unit vector normal to its basal plane, $\hat{\mathbf{n}}$ (see Fig. 1A). The contribution to the absorption from all nanosheets with this orientation is given by

$$dA = A_{NS}(\theta,\varphi)N_{\Omega}d\Omega \tag{1}$$

where $A_{NS}(\theta,\varphi)$ is the absorption of a single nanosheet of this orientation, N_{Ω} is the number of nanosheets per unit solid angle and $d\Omega$ is the differential solid angle defined by θ and φ, given by $d\Omega = \sin\theta d\theta d\varphi$ (Fig. 1B). N_{Ω} is the total number of nanosheets interacting with the beam, multiplied by the fraction of nanosheets per unit solid angle. The latter parameter is the nanosheet orientation distribution function, Γ_{NS}, which for an isotropic distribution is given by $\Gamma_{NS} = 1/2\pi$ (see SI). This allows us to write $N_{\Omega} = N_V \Lambda_{Beam} L/2\pi$ where N_V is the number of nanosheets per unit volume, Λ_{Beam} is the area of the beam in the x-y plane, and L is the cell length. This parameter can be written in terms of the nanosheet concentration:

$$N_{\Omega} = \frac{C\Lambda_{Beam}L}{2\pi\rho_{NS}\Lambda_{NS}t_{NS}} \tag{2}$$

where ρ_{NS}, Λ_{NS} and t_{NS} are the nanosheet density, area and thickness respectively.

This allows us to write the total absorption of the dispersion as

$$A = \frac{C\Lambda_{Beam}L}{2\pi\rho_{NS}\Lambda_{NS}t_{NS}} \int_{\theta=0}^{\pi} \int_{\varphi=0}^{\pi} A_{NS}(\theta,\varphi)\sin\theta d\theta d\varphi \tag{3}$$

As the absorption of a flake at $\varphi = \pi/2$ is equivalent to a flake at $\varphi = 3\pi/2$ (with $\theta = \pi$ in both cases), the upper limits of integration in equation (3) are therefore π. We therefore require an expression for $A_{NS}(\theta,\varphi)$, the absorption of the single nanosheet.

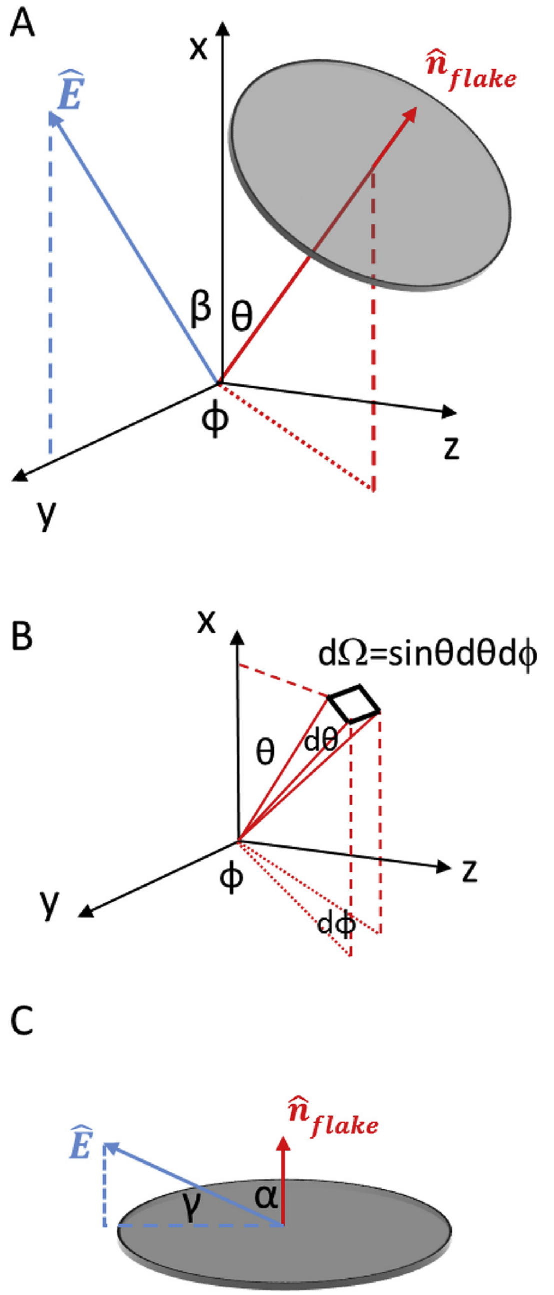

Fig. 1. A) Diagram showing geometry of flake orientation. Light is taken to propagate in the z-direction, with electric field vector making an angle β with the x-axis. The normal to the flake makes an angle θ with the x-axis, and φ with the y-axis. The flake is shown as offset from the origin for clarity. B) Schematic showing the construction of the differential solid angle dΩ. C) Diagram showing angle between the flake and electric field vector of the light. (A colour version of this figure can be viewed online.)

The value of A_{NS} varies with orientation for two main reasons. Firstly, the projected area the nanosheet presents to the beam depends on nanosheet orientation and, secondly, the amount of light the nanosheet absorbs depends on the square of the cosine of the angle between the nanosheet basal plane and the electric field vector of the light (essentially Malus' law, see SI).

The fraction of the total light intensity absorbed by a single nanosheet is given by the fraction of beam area occluded by the nanosheet, F_{Λ}, multiplied by the fraction of light intensity incident on the nanosheet that is absorbed [35]. This second parameter is given by $A_{||}\cos^2\gamma$, where $A_{||}$ is the intrinsic nanosheet absorption (i.e. when the electric field of the light is parallel to the nanosheet basal plane) and γ is the angle between the electric field vector and