ATOM PHYSICS AND PHYSICS OF CLUSTERS AND NANOSTRUCTURES

Conference materials
UDC 544.774.3; 544.77.03; 544.77.051.1; 661.666.2; 543.062
DOI: https://doi.org/10.18721/JPM.163.144

Optical extinction and electrical conductivity measurements as express techniques to estimate concentrations of graphene suspensions

T.S. Kalyakin [1, 2] ✉, E.A. Danilov [1]

[1] JSC Research Institute “Graphite”, Moscow, Russia;

[2] Mendeleev Russian University of Chemistry and Technology, Moscow, Russia

✉ t.s.kalyakin@gmail.com

Abstract. This article explores a method for determining the concentration of graphene dispersion using the integral optical technique based on the Beer-Lambert-Bouguer law for direct ultrasonic exfoliation method. The results showed nonlinear dependence of conductivity on concentration, indicating fundamental differences in the mechanism of exfoliation at different solid phase concentrations. Graphene dispersions in ethylene glycol also exhibited low transmittance in the visible region of the spectrum, which requires the use of other research methods for higher concentrations. Extinction coefficients were determined to calculate the concentration of graphene in the dispersion, which allows for the calculation of light absorption in the solution at a certain concentration and beam path length. The obtained results can be useful for further use of graphene in optoelectronic devices. Additionally, the concentration of few-layered graphene particles was calculated in the suspension obtained by liquid-phase exfoliation method with an initial graphite concentration of 6 mg/ml.

Keywords: graphene, Beer-Lambert-Bouguer law, concentration, exfoliation

Citation: Kalyakin T.S., Danilov E.A., Determination of graphene concentration in dispersions using integral methods, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (3.1) (2023) 248–253. DOI: https://doi.org/10.18721/JPM.163.144

Материалы конференции
УДК 544.774.3; 544.77.03; 544.77.051.1; 661.666.2; 543.062
DOI: https://doi.org/10.18721/JPM.163.144

Измерения оптической проницаемости и электропроводности как экспресс-методы оценки концентраций графеновых суспензий

Т.С. Калякин [1, 2] ✉, Е.А. Данилов [2]

[1] АО «НИИграфит», Москва, Россия;

[2] Российский химико-технологический университет им. Д.И. Менделеева, Москва, Россия

✉ t.s.kalyakin@gmail.com

Аннотация. В данной статье разработан способ определения концентрации графена в суспензии в этиленгликоле интегральным методом, основанным на законе Ламберта-Бугера-Бера. Результаты показали нелинейную зависимость электропроводности от концентрации, что указывает на принципиальные отличия механизма процесса эксфолиации при различных концентрациях твердой фазы. Суспензии графена в этиленгликоле имели низкую пропускную способность в видимой области спектра, что требует использования других методов исследования для более высоких концентраций. Для расчета концентрации графена в суспензии были определены коэффициенты экстинкции, которые позволяют рассчитать поглощение света в растворе при определенной концентрации и длине оптического пути. Полученные результаты могут быть полезны для дальнейшего использования графена в оптоэлектронике. Также, была рассчитана концентрация малослойных графеновых частиц в суспензии, полученной методом жидкофазной эксфолиации, с концентрацией исходного графита 6 мг/мл.

Ключевые слова: графен, закон Ламберта-Бугера-Бера, концентрации, эксфолиация

Ссылка при цитировании: Калякин Т.С., Данилов Е.А. Определение концентрации графена в суспензиях с использованием интегральных методов // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 3.1. С. 243–253. DOI: https://doi.org/10.18721/JPM.163.144

Introduction

Graphene is a unique material that attracts research attention worldwide due to its properties. High electrical conductivity, mechanical strength, as well as thermal and chemical stability allows graphene to be used in various fields of science and technology [1, 2]. Graphene was first obtained and described by Novoselov and Geim in 2004. They proposed a method called mechanical exfoliation, which involved repeatedly using adhesive tape to peel off layers of graphite. The starting material was highly oriented pyrolytic graphite. Although this method allows for the production of high-quality atomically thin layers, scaling it up is not feasible, and therefore its application in different devices is limited [3]. One practical area where graphene is of interest is optoelectronics, where it can be used as transparent electrode or light-absorbing material [4]. Liquid-phase exfoliation represents a scalable approach to graphene production. It involves only single technological step, maintains the integrity of graphene layer structure, and allows for the production of suspended graphene that is convenient for further use [5, 6]. However, this synthesis method requires refinement and optimization of particle analysis methods. It is important to know particle concentration in dispersions, as it can influence the properties of the resulting materials. One possible method for conducting this analysis is the integral optical method based on the Beer-Lambert-Bouguer law [7].

Materials and Methods

We used natural graphite (GE grade) and ethylene glycol (purified, JSC "ECOS-1") for graphene production. Graphite powder with an ash content of up to 10% by weight underwent thermal treatment in an industrial graphite furnace at 2800 °C and thermal treatment in a freon-12 atmosphere at 2200 °C (technology of JSC "VNIIEI"). After the treatment, the content of mineral impurities did not exceed 0.01% by weight, and the maximum particle size was 200 μm.

The concentration of the dispersed phase varied in the range of 0.01 to 20 mg/ml. Graphene was obtained by liquid-phase exfoliation using a Melfiz MEF-391 ultrasonic disperser with a horn-type probe. The dispersions were processed for 7 hours.

Centrifugation of the dispersions was performed using a Hettich EBA280 centrifuge (Austria). The processing was carried out for 30 minutes at 4000 rpm rotation speed.

Electrical conductivity was measured using a Seven Compact S230 compact conductivity meter (Mettler Toledo, Switzerland) with an InLab 710 sensor.

Optical spectra were obtained using a Cary 60 UV-Vis spectrophotometer (Agilent Technologies) in a quartz cuvette with an optical path of 1 cm.

Results and Discussion

The electrical conductivity of the dispersions obtained by the aforementioned method was studied over a wide range of concentrations (1–20 mg/ml). Based on the obtained data (Fig. 1), it can be concluded that there is a non-linear dependence of electrical conductivity on concentration in graphene dispersions in ethylene glycol (EG). This suggests that the mechanism of the graphene dispersion formation (exfoliation) and the emergence of electrical conductivity likely have fundamental differences at different concentrations of the solid phase. To further analyze and understand these results in more detail, additional research is needed.

For any types of dispersions manufactured using this method, it is necessary to determine the concentration of the obtained graphene. Since the processed dispersion becomes transparent after centrifugation, optical methods can be applied to determine the concentration. The presence of graphene and few-layered graphene particles in the suspensions after centrifugation has been confirmed in previous works by the authors [6, 8].

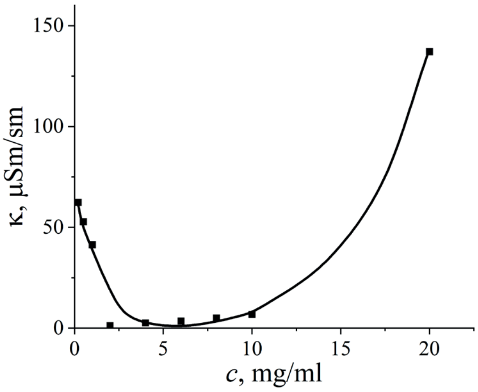

Fig. 1. Dependence of electrical conductivity on the concentration of the solid phase after 7 hours of ultrasonic treatment

Graphene dispersions in ethylene glycol exhibited low transmittance for the visible spectrum in the majority of the investigated concentration range. Due to this limitation, only low concentrations of graphene in the range up to 0.1 mg/ml were studied using the integral method. Other research methods will be required for higher concentrations. The spectra for concentrations of 0.1, 0.05, 0.025, and 0.01 mg/ml are presented below, which were used for the calculation (Fig. 2).

By applying the Beer-Lambert-Bouguer law, which is one of the fundamental optical laws used for measuring the concentration of solutions, we can establish a relationship between light absorption and solution concentration, as well as the path length of light through the solution.

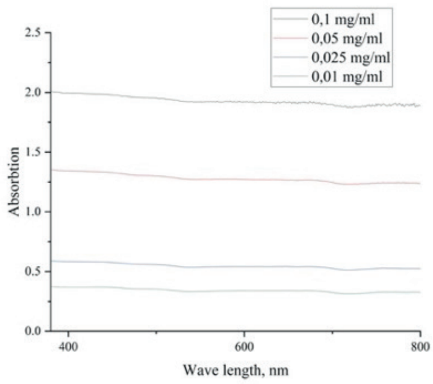

Fig. 2. Absorption spectra for the investigated concentrations

Initially, extinction coefficients were calculated, which serve as a measure of a substance's ability to absorb light of a specific wavelength. The extinction coefficient allows for the calculation of light absorption in the solution at a given concentration and optical path length.

$$A = \varepsilon l s \tag{1}$$

where A is light absorbtion, ε is extinction coefficient, l is distance traveled by light (1 cm), and c is concentration.

The obtained data is presented in Table 1.

To confirm the accuracy of the calculations and the validity of this method in general. a separate sample was chosen for which the light absorption was experimentally measured at a known concentration of graphene (~ 0.025 ± 0.002 mg/ml) (see Table 2).

Table 1

Calculation of extinction coefficients

Wave length, nm	Concentration, mg/ml	Concentration, mol/l	Absorbtion	Extinction coefficient, l·mol^{-1}·cm^{-1}
1050	0.010	0.000833	0.3927	277.46
	0.025	0.002083	0.5945	
	0.050	0.004167	1.3131	
	0.100	0.008333	2.2134	
950	0.010	0.000833	0.3429	245.41
	0.025	0.002083	0.5410	
	0.050	0.004167	1.2573	
	0.100	0.008333	1.9064	
850	0.010	0.000833	0.3250	241.66
	0.025	0.002083	0.5205	
	0.050	0.004167	1.2422	
	0.100	0.008333	1.8795	
750	0.010	0.000833	0.3260	244.04
	0.025	0.002083	0.5249	
	0.050	0.004167	1.2420	
	0.100	0.008333	1.9047	
650	0.010	0.000833	0.3389	246.44
	0.025	0.002083	0.5411	
	0.050	0.004167	1.2643	
	0.100	0.008333	1.9146	
550	0.010	0.000833	0.3329	247.32
	0.025	0.002083	0.5371	
	0.050	0.004167	1.2724	
	0.100	0.008333	1.9219	
450	0.010	0.000833	0.3680	241.66
	0.025	0.002083	0.5759	
	0.050	0.004167	1.3293	
	0.100	0.008333	1.9802	

The obtained concentration values indicate that this method is applicable for determining the concentration of graphene-based transparent dispersions. However, it should be noted that the data calculated based close to the UV-edge of the spectrum and its proximity are overestimated, therefore using them in this method is not appropriate.

Table 2

Calculation of the concentration of a separately prepared dispersion

Wavelength, nm	Absorption	Extinction coefficient, l·mol^{-1}·cm^{-1}	Concentration, mg/ml
1050	0.25314	277.46	0.0258
950	0.28367	245.41	0.0268
850	0.29503	241.66	0.0263
750	0.29322	244.04	0.0262
650	0.28272	246.44	0.0267
550	0.28464	247.32	0.0265
450	0.25911	256.39	0.0275

Thus, calculating of the concentration based on the optical absorption data indeed allows estimating the concentration of graphene dispersion within the selected range, and results are not highly dependent on the wavelength used.

For the dispersion with a concentration of pristine graphite 6 mg/ml, which visually appeared the darkest after centrifugation, the graphene content was calculated. By applying the determined coefficients, the corresponding values are obtained, as shown in Table 3.

Table 3

Concentration of graphene in the obtained dispersion

Wavelength, nm	Absorption	Extinction coefficient, $l \cdot mol^{-1} \cdot cm^{-1}$	Concentration, mg/ml	The percentage content relative to the amount of the initial graphite (6 mg/ml)
1050	0.83654	277.46	0.0362	0.60%
950	0.78824	245.41	0.0385	0.64%
850	0.77296	241.66	0.0384	0.64%
750	0.77925	244.04	0.0383	0.64%
650	0.80573	246.44	0.0392	0.65%
550	0.82730	247.32	0.0401	0.67%
		Average value	0.0385	0.64%

The average concentration value in the centrifuged dispersion was 0.0385 mg/ml, which corresponds to 0.64% of the initial graphite quantity.

Conclusion

The present study revealed nonlinear relationship between electrical conductivity and the concentration of graphene dispersion in ethylene glycol, indicating that accurately estimating the concentration of graphene dispersion is a crucial task for the development of conductive inks. An integral method for determining the concentration of graphene in the dispersion based on the Beer-Lambert-Bouguer law has been proposed, and corresponding calculations have been performed. It has been shown that low concentrations of graphene (up to 0.1 mg/ml) exhibit sufficient transmittance in the visible spectrum for analysis using the Beer-Lambert-Bouguer method. The results for the calculated concentrations have converged for different wavelengths, indicating that this method of determining dispersion concentration is acceptable and sufficiently accurate. Thus, a simple and fast optical absorption method is applicable for determining the concentration of graphene dispersion, where gravimetric or other standard types of analysis may lead to incorrect estimations.

In the ethylene glycol dispersions obtained by the liquid-phase exfoliation method described, the content of few-layered graphene particles was found to be less than 1% of the initial graphite quantity, amounting to 0.0385 mg/ml.

REFERENCES

1. **Geim A.K., Novoselov K.S.,** The rise of graphene, Nature Materials. 6 (3) (2007) 183–191.

2. **Choi W., Lahiri I., Seelaboyina R., Kang Y.,** Synthesis of Graphene and Its Application, Critical Reviews in Solid State and Materials Science. 35 (1) (2010) 52–71.

3. **Novoselov K.S., Geim A.K., Morozov S.V., Jiang D., Zhang Y., Dubonos S., Grigorieva I.V.,** Electric field effect in atomically thin carbon films, Science. 306 (2004) 666–669.

4. **Kozhitov L.V., Zaporotskova I.V., Kozlov V.V.,** Perspektivnye nanomaterialy na osnove ugleroda (Prospective carbon-based nanomaterials), Vestnik VolGU. 10 (4) (2009-2010) 63–85.

5. **Xu Y., Cao H., Xue Y., Li B., Cai W.,** Liquid-phase exfoliation of graphene: an overview on exfoliation media, techniques, and challenges, Nanomaterials. 8 (11) (2018) 942.

6. **Samoilov V.M., Danilov E.A., Nikolaeva A.V., Yerpuleva G.A., Trofimova N.N., Abramchuk S.S., Ponkratov K.V.,** Formation of aqueous suspensions using fluorinated surfactant-assisted ultrasonication of pristine graphite, Carbon. 84 (2015) 28–46.

7. **Landsberg G.S.,** Optics, M.: PhysMathLit. (2006).

8. **Danilov E.A., Samoilov V.M., Kalyakin T.S., Shakhnazarova A.B., Nakhodnova A.V.,** Properties of suspensions of few-layer graphene particles obtained by means of the direct exfoliation of natural graphite in polyatomic alcohols, Sorbtsionnye I Khromatograficheskie Protsessy. 22 (4) (2022) 453–465.

THE AUTHORS

KALYAKIN Timofey S.
t.s.kalyakin@gmail.com
ORCID: 0000-0002-8347-7028

DANILOV Egor A.
danilovegor1@gmail.com
ORCID: 0000-0002-1986-3936

Received 01.07.2023. Approved after reviewing 07.08.2023. Accepted 07.08.2023.