

## Study of graphene oxide solid films prepared by Langmuir – Blodgett technology

E. V. Seliverstova, N. Kh. Ibrayev, R. Kh. Dzhanabekova

Institute of Molecular Nanophotonics, Buketov Karaganda State University, Kazakhstan

genia\_sv@mail.ru

PACS 81.15.-z, 68.03.cd, 68.60.wm

DOI 10.17586/2220-8054-2016-7-1-65-70

The preparation of Langmuir – Blodgett (LB) films based on graphene oxide and the study of their structure and optical properties are presented. Graphene oxide dispersions were prepared in different solvents and the stability of each solution was studied. The measurements have shown that most stable dispersions were prepared in tetrahydrofuran, but in acetone, the concentration of graphene oxide is higher. Therefore, graphene oxide monolayers were formed from acetone dispersions. The physicochemical properties of graphene oxide monolayers at the water-air interface were studied. The LB films were deposited onto solid substrates according to Y-type (transfer during downward and upward stroke of substrate) and Z-type transfer (deposition during the upward stroke only). The absorption spectra of graphene oxide LB films exhibit a broad band in the ultraviolet and visible region of the spectrum. The optical density of the film obtained according to the Y-type transfer is greater than the optical density of the film prepared according to the Z-type transfer. The transparency of the films in the visible region of the spectrum is greater than 90 %. As it was shown by SEM images, the films obtained according to the Y-type transfer are more uniform in structure.

**Keywords:** graphene oxide, dispersion, Langmuir – Blodgett films, optical properties.

*Received: 20 November 2015*

### 1. Introduction

Currently, the wide use of inorganic solar cells is hindered by the relatively expensive manufacturing technology and processing of inorganic semiconductors, which requires high temperatures and high vacuum. In this regard, interest in organic materials to create new types of cheap solar cells is growing. Organic compounds, being carbon-based, usually do not contain rare chemical elements and can be very manufacturable, and therefore much cheaper in comparison to inorganic materials.

Graphene and its modified derivatives are a new class of carbon materials having high specific surface area and electron mobility, which makes them suitable for use as electrodes in dye-sensitized solar cells. In earlier work [1], it was shown that graphene has a high specific surface area and electron mobility, as well as having a higher oxidation potential than Pt. The wide variety of existing forms of graphene can improve the necessary parameters for counter electrodes. For example, reduced graphene oxide has a surface lattice defects, which implies a higher catalytic activity than the fully reduced defect-free graphene [2, 3]. Additionally, graphene production costs are cheaper than that of other carbon nanomaterials. This combines many useful properties necessary for effective modification of photovoltaical device design. In this aspect, the study of conditions for producing graphene oxide solid films with predictable properties, which is presented in this paper, is particularly relevant.

## 2. Experimental

Single layer graphene oxide was used for dispersion preparation (SLGO) (Cheaptubes, USA). Graphene oxide suspensions were prepared in acetone, chloroform, tetrahydrofuran (THF) and dimethyl formamide (DMF). All solvents were purchased from Sigma Aldrich and used without purification. The concentration of graphene oxide in solution was equal to  $6 \cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ . Suspensions were sonicated in ultrasonic bath. The dimensions of the graphene oxide particles were measured by dynamic light scattering method with Zetasizer nano analyzer (Malvern). The graphene oxide particle and film morphologies were obtained with scanning electron microscopy (TESCAN Mira-3) on a glass surface with FTO coating.

Solid films were obtained by Langmuir – Blodgett (LB) technology. Monolayers were formed on the surface of the subphase by spreading of solution throughout the LB trough. The deionized water was purified by AquaMax and was used as the subphase. The resistivity of the deionized water was equal to  $18.2 \Omega\cdot\text{m}^{-1}$ . The surface tension of water was equal to  $72.8 \text{ mN}\cdot\text{m}^{-1}$  at  $\text{pH} = 5.6$  and a temperature of  $22 \text{ }^\circ\text{C}$ .

## 3. Results and discussion

The conditions for preparation of graphene oxide dispersions were chosen to obtain highly concentrated and stable particle solutions. From the diagram of the size distribution of graphene oxide particles in DMF before sonication, one can see that about 80 % of the particles have a size of 2000 – 3000 nm. Particles with sizes of 2300, 2700 and 3000 nm predominate in the solution. A decrease in the size of the graphene oxide particles was observed after sonication of solution for 30 min: 60 % of particles have a size of 900 – 1000 nm, 15 % – from 850 nm and 17 % of particles – about 1100 nm. Further ultrasonic treatment of the solutions had virtually no effect on the decrease in the average size of particles or the scatter of sizes.

The dependence of the graphene oxide particle size distribution on the sonication time is shown in Fig. 1 (curve 1). At least five measurements were taken to plot the graph.

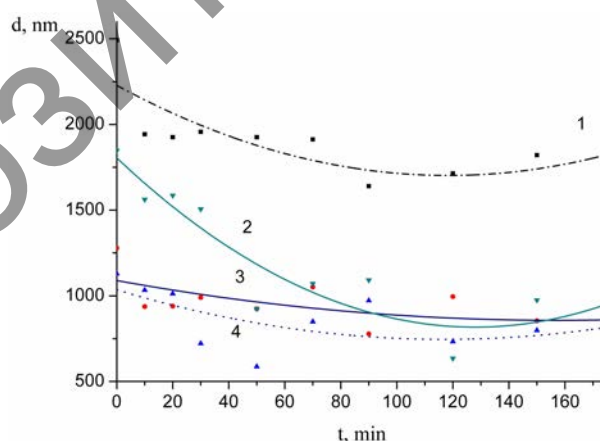


FIG. 1. Dependence of average size of graphene oxide particles over the sonication time in: 1 – DMF; 2 – chloroform; 3 – THF; 4 – acetone

Similar results have been obtained for other solvents. Thus, in THF the particle size also decreased from  $2.5$  to  $1.8 \mu\text{m}$  and from  $1.1 \mu\text{m}$  to  $750 \text{ nm}$  for acetone solution after sonication. In addition, for both solvents, the size of particles remained practically unchanged after 30 min of treatment. Characteristically, that in chloroform ultrasonic treatment of SLGO dispersions has the strongest influence on the particle size. The particle sizes were almost halved with 30 min

of treatment. This behavior for graphene oxide may be associated with the fact that as a result of chloroform's high density, the dissolved particles of SLGO were most strongly affected by the ultrasonic oscillation.

In addition, the size of particles was estimated from SEM images of graphene oxide films obtained by evaporation of SLGO solution in THF on a FTO layer-covered glass surface. Fig. 2 shows that upon drying, the graphene sheets rolled up to form spindle-shaped particles having an average size of  $\sim 320$  nm. The observed conformation of graphene is a result of thermal effects [4].

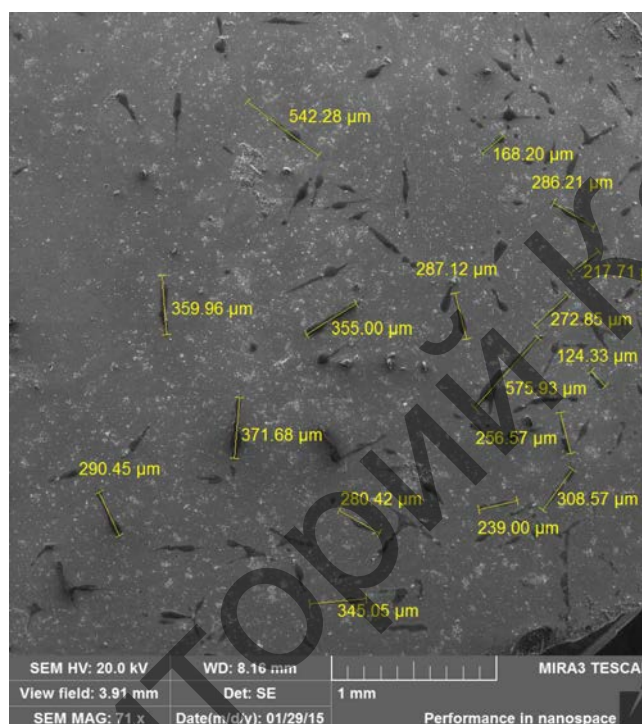


FIG. 2. SEM image of dispersed graphene oxide on the FTO surface

The stability of the graphene oxide dispersion was studied by measuring the optical density of the solutions over various time intervals. Absorption spectra were registered in the UV-Vis spectral region from 290 to 600 nm for DMF and THF and from 320 to 600 nm for acetone. The spectra of SLGO in DMF and THF exhibited a shoulder at  $\sim 300$  nm which was ascribed to  $n \rightarrow \pi^*$  transitions of C = O bonds [5]. The dependence of optical density of graphene oxide solutions upon time is shown in Fig. 3. Measurements have shown that the optical density change for graphene oxide in DMF and THF have similar behaviors. The absorption for SLGO in THF was practically unchanged for 48 h after sonication (curve 1). In DMF (curve 2), the optical density was reduced by 15 % within the first hour, additionally, this parameter was decreased by 40 % every 24 h. The strongest changes in the optical density of the graphene oxide solutions were registered for acetone (curve 3). During the first hour, the absorption decreased three-fold. Graphene oxide almost completely precipitated after 24 h of storage in acetone. The most unstable dispersions were obtained in chloroform – SLGO precipitated on the bottom of the cell within 1 hour after preparation.

Subsequently, acetone solutions were used to study the physicochemical properties of graphene oxide, since the solubility of graphene was highest in that solvent. Compression isotherms ( $\pi - A$  isotherms) for graphene oxide monolayers are shown on the Fig. 4. The

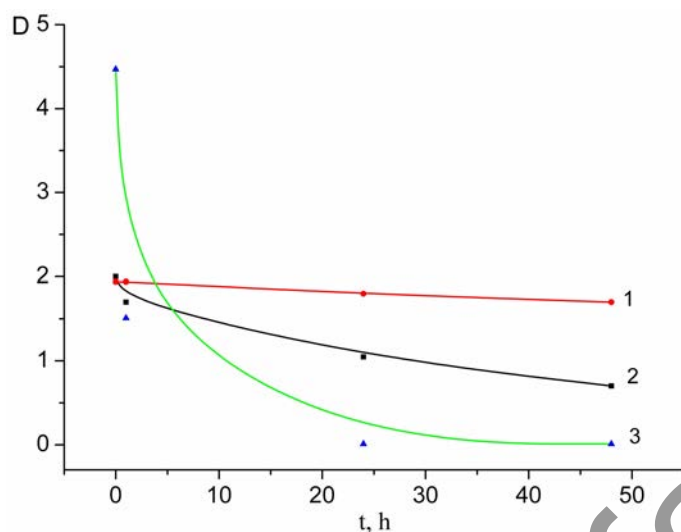


FIG. 3. Time dependence of optical density  $D$  of graphene oxide solutions ( $\lambda_{\text{reg}} = 340 \text{ nm}$ ) in: 1 – THF, 2 – DMF, 3 – acetone

minimum volume was deposited onto the subphase monolayer in the “gaseous” state [6] at surface pressures of  $2 - 2.5 \text{ mN}\cdot\text{m}^{-1}$  (curve 1). This means that the distance between graphene oxide particles on an aqueous surface is large. With further compression of the monolayer, the particles approach and the film becomes “liquid”. Moreover, this “liquid–expanded” state was preserved with additional compression of the monolayer up to its minimum area.

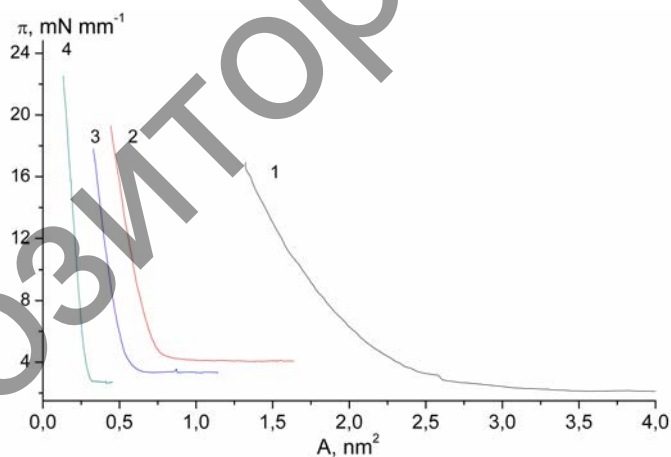


FIG. 4.  $\pi - A$  isotherms of monolayers based on graphene oxide. Monolayers were spreaded from acetone, ml: 1 – 0.5, 2 – 1.5, 3 – 3.5, 4 – 5

Spreading a greater volume of substances onto the surface of the subphase (1.5 ml) results in a dense packing of particles within the monolayer (curves 2–4). In this case, the film on the aqueous surface is also initially in the “gaseous” state (curve 2). Transitions of monolayer in “liquid–expanded” and “liquid–condensed” states were observed upon compression of film within the pressure range of  $5 - 9$  and  $9 - 19 \text{ mN}\cdot\text{m}^{-1}$ , respectively.

For monolayers formed from greater volumes of dispersion, an increase in the specific surface area was registered at higher SLGO concentrations. Fig. 5 shows that for the curve 1, the “gaseous state” had an area equal to  $1 \text{ nm}^2$ , and  $0.8$ ,  $0.5$  and  $0.3 \text{ nm}^2$  for the curves 2, 3 and 4, respectively. The change of phase states of monolayer upon compression occurs in the

same sequence as that for the curve 2. It should be noted that all monolayers had no collapse, despite the rather large amount of spread solution.

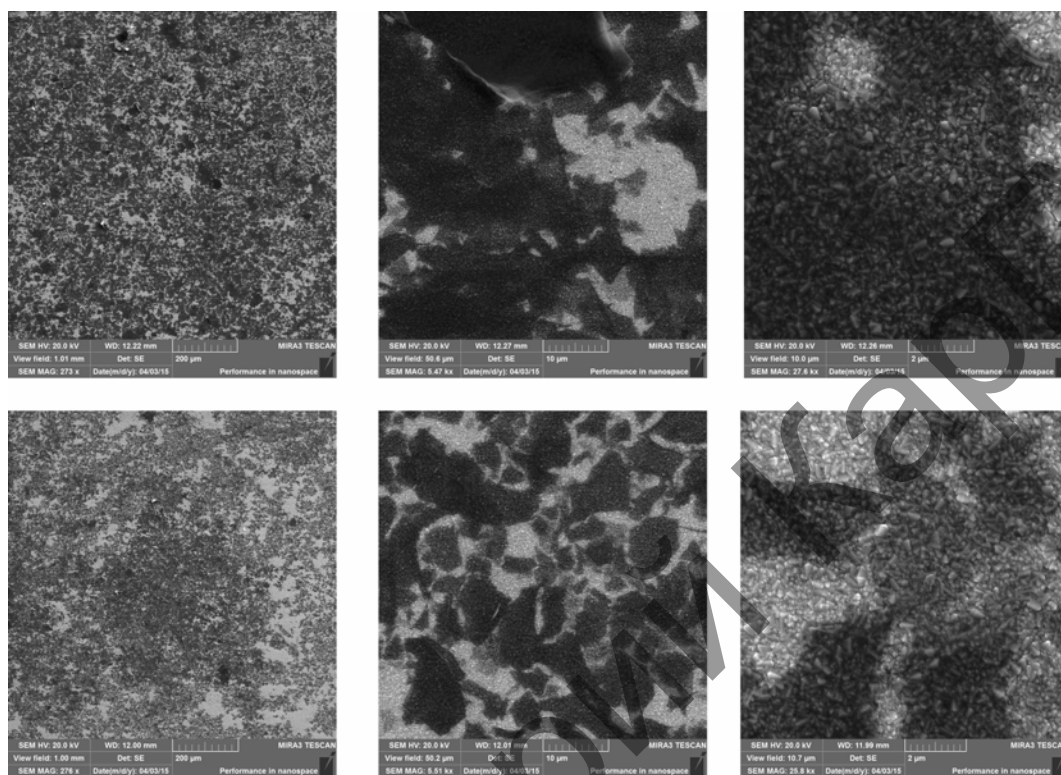


FIG. 5. SEM-images of graphene oxide LB films. At the top – Y-type, at the bottom – Z-type

SEM-images were obtained for graphene oxide LB films (Fig. 5). Monolayers were deposited onto solid substrates according to Z-type (transfer during the upward stroke only) and Y-type transfer (deposition during downward and upward stroke) at surface pressure  $\pi = 19 \text{ mN}\cdot\text{m}^{-1}$ . The thickness of the films consisted of 4 monolayers.

As can be seen from the figure, the SLGO films on a solid substrate have an island structure. The individual particles of graphene oxide could be distinguished in the SEM-images. Particles were distributed more uniformly across the substrate surface for the film obtained by Y-type transfer than in the film obtained by the Z-type transfer. Upon closer scrutiny, dark areas of varying intensity can be seen on the surface of the film. This fact is evidence for the presence of multilayer graphene oxide particles in the film.

The absorbance and transmittance of the LB films were measured (Fig. 6). Absorption spectra have a typical form and correspond to the spectra obtained by other authors [5]. For films prepared according to the Y-type transfer, the optical density at the maximum absorption band was approximately two times greater than the absorbance than the Z-type prepared films.

In the visible region of the spectrum, both films have high transparency – about 90 % in the wavelength ranging from 400 to 800 nm.

### 3.1. Conclusion

In this study, we investigated the stability of graphene oxide dispersions in different solvents. The suspensions of graphene oxide were prepared in acetone, chloroform, THF and DMF. Suspensions were sonicated in ultrasonic bath. By measuring the sizes of graphene oxide

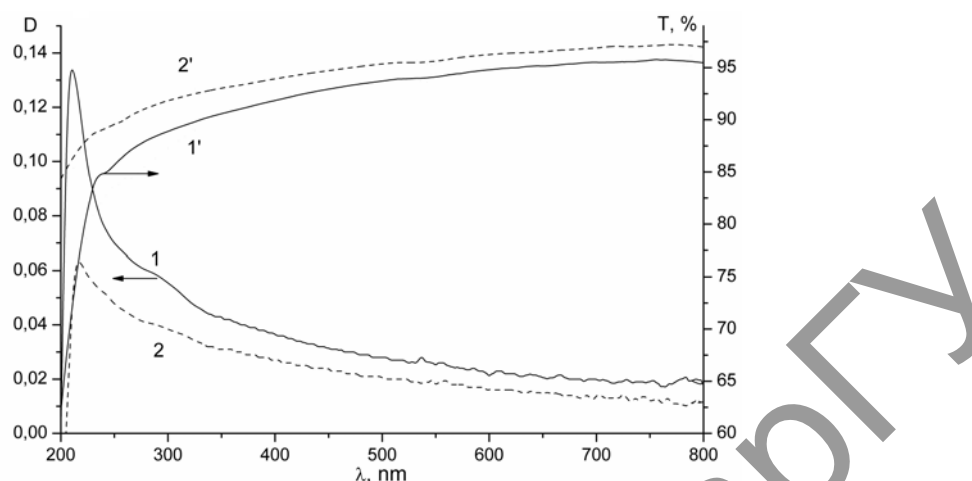


FIG. 6. Absorption  $D(1, 2)$  and transmittance  $T(1', 2')$  spectra of graphene oxide LB films, deposited according to Y-type (1, 1') and Z-type (2, 2') transfer

particles, it was shown that sonication for 30 min leads to a reduction in the size of graphene oxide particles. Further ultrasonic treatment of the solutions had virtually no effect on the average size of the particles and the distribution of particle sizes. Most stable dispersions of graphene oxide were prepared in THF.

The physicochemical properties of graphene oxide monolayers at the water – air interface were studied. From the compression isotherms of monolayers, it was found that for the pressures in the range of 0 to 2  $\text{mN}\cdot\text{m}^{-1}$  monolayer is predominantly in a gaseous state. With further compression of the monolayer, the particles approach and the film becomes “liquid”. Spreading a greater volume of graphene oxide onto the surface of the subphase results in a denser particle packing within the monolayer. For all monolayers, no collapse was registered, despite the rather large amount of the spread solution.

In the absorption spectra of graphene oxide LB films, a broad band was found in the ultraviolet and visible region of the spectrum with a maximum at 230 nm. The optical density of the film obtained according to the Y-type transfer is greater than the optical density of the film prepared according to the Z-type transfer. The transparency of the films is more than 90 % in the visible wavelength range (from 400 to 800 nm).

SEM-images show that the films have an island structure. In the pictures, the individual particles of graphene oxide are clearly distinguished. The films obtained according to the Y-type transfer were more uniform than films prepared according to than Z-type transfer, which makes them more promising in terms of their use as conductive coatings.

## References

- [1] Guo C.X., Guai G.H., Li C.M. Graphene Based Materials: Enhancing Solar Energy Harvesting. *Adv. Energy Mater.*, 2011, **1**, P. 448–452.
- [2] Roy-Mayhew J.D., Bozym D.J., Punckt C., Aksay I.A. Functionalized graphene as a catalytic counter electrode in dye-sensitized solar cells. *ACS Nano*, 2010, **4**, P. 6203–6211.
- [3] Cruz R., Tanaka D.A.P., Mendes A. Reduced graphene oxide films as transparent counter-electrodes for dye-sensitized solar cells. *Solar Energy*, 2012, **86**, P. 716–724.
- [4] Whitby R., Gun'ko V.M., et al. Driving forces of conformational changes in single-layer graphene oxide. *ACS Nano*, 2012, **6** (5), P. 3967–3973.
- [5] Sutar D.S. Spectroscopic studies of large sheets of graphene oxide and reduced graphene oxide monolayers prepared by Langmuir-Blodgett technique. *Thin Solid Films*, 2012, **520**, P. 5991–5996.
- [6] Adamson A. *Physical Chemistry of Surfaces*. A Wiley-Interscience Publication, New York, 1997, 785 p.