The influence of the preparation conditions on structure and optical properties of solid films of graphene oxide

E Seliverstova, N Ibrayev, R Dzhanabekova and V Gladkova
Institute of Molecular Nanophotonics, Karaganda 100028, Kazakhstan
E-mail: genia_sv@mail.ru

Abstract. In this study, we investigated the physico-chemical properties of graphene oxide monolayers at the interface water-air. Monolayers were formed by the spreading of dispersion of graphene oxide in acetone and THF. It was found than graphene monolayers are in the “liquid” state on the surface of subphase. Monolayers were transferred onto solid substrates according to Langmuir-Blodgett (LB) method. SEM images show that the films have an island structure. The films obtained from acetone solutions are more uniform, which makes them more promising in terms of their use as conductive coatings. Absorption spectrum of graphene LB films exhibits a broad band in the ultraviolet and visible region of the spectrum. The optical density of the film obtained from acetone solution is greater than the optical density of the film prepared from THF. In the visible region of the spectrum both films have high transparency.

1. Introduction
Currently, search and active use of new alternative energy sources in many developed countries accepted as vital, strategic resources needed to ensure the future development of these economies. However, despite of the promising results, alternative energy sources have not yet reached the level of optimal responsiveness of expectations of mass consumer. The most widely used silicon photovoltaic elements are very expensive. Therefore search of cheaper dye sensitized solar cells is carried on.

Intensive research worldwide is in pursuit of cheaper production methods of photovoltaic devices without compromising performance. Given that graphene production costs may be cheaper than other carbon nanomaterials, it’s single or few layered structure is nearly fully transparent, their conductivity, plus graphenes can be easily chemically altered, their physicochemical properties tuned and their 3-d structure manipulated, means that graphene possess many useful properties for the production of photovoltaic devices. The technology could be realized by casting graphene sheets into composite devices using Langmuir-Blodgett casting techniques.

Widespread and low-cost graphene can be used in the counter electrodes instead of platinum. In the works of [1, 2] was showed that graphene had high specific surface area and high mobility of electrons, having a higher oxidation potential than Pt. The wide variety of existing forms of graphene can improve the necessary parameters of counter electrodes. For example, reduced graphene oxide [3], has a surface lattice defects, which implies a higher catalytic activity than the fully reduced defect-free graphene [4-6]. Additionally, graphene production costs are cheaper than other carbon nanomaterials. This combines many useful properties necessary for effective modification of photovoltaics device.
design. Due to this aspect study of conditions for producing of graphene oxide solid films with predictable properties that is presented in this paper, it is particularly relevant.

2. Experiment
Single layer graphene oxide was used for dispersion preparation (SLGO) (Cheaptubes, USA). The suspension of graphene oxide was prepared in acetone and tetrahydrofuran (THF). All solvents were purchased from Sigma Aldrich and used without purification. Concentration of graphene in solution was $6 \times 10^{-4}$ mol L$^{-1}$. Suspensions were sonicated in ultrasonic bath during 50 min. The morphology of particles and films of graphene were obtained by scanning electron microscopy (TESCAN Mira-3) on the surface of glasses with FTO coating.

Solid films were obtained by Langmuir-Blodgett (LB) technology. Monolayers were formed on the surface of the subphase by the spreading of the solution in the Langmuir-Blodgett through. The deionized water was cleaned by AquaMax and was used as subphase. The resistivity of the deionized water was 18.2 MΩ/cm. The surface tension of water was equal to 72.8 mN/m at pH=5.6 and temperature 22 °C.

3. Results and discussion
Compression isotherms ($\pi$-A isotherms) of graphene oxide monolayers are shown on the Figure 1.

![Figure 1](image)

Figure 1. Compression isotherms of graphene oxide monolayers at subphase surface. Monolayer is formed from acetone solution at various volumes of solution, ml: 1 – 0.5; 2 – 1.5; 3 – 3.5; 4 – 5

Form minimal volume that was deposited onto subphase monolayer is in the “gaseous” state [7] at the surface pressures of 2-2.5 mN/m (curve 1). It means that the distance between the graphene particles on a surface of the water is large. With further compression of the monolayer the particles approaches and the film becomes “liquid”. Moreover, this “liquid-expanded” state preserved at further compression of the monolayer up to its minimum area.

Spreading of greater volume of substances onto the surface of the subphase (1.5 ml) results in a dense packing of particles within monolayer (curves 2-4). In this case film on the water 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 in the pressure range of 5-9 mN/m and 9-19 mN/m, respectively. From isotherms it also can be seen that the surface pressure equal to 18 mN/m the specific area of graphene has a smaller values than at the pressure equal to 9 mN/m. For monolayers that were formed from greater volumes of dispersion the increasing of specific surface
area was registered with the growth of SLGO concentration. It should be noted that all monolayers had no collapse, despite the rather large amount of the spreaded solution.

When the monolayer is formed from the dispersion of graphene oxide from THF similar phase states were observed upon compression of the films on the surface. Increasing of particle concentration in monolayer leads to shift of curve to the side of the little area, and the extent of “gaseous” and “liquid” phases is decreased.

In could be concluded, from the comparison of two $\pi$-A isotherms registered for different solvents, that behavior of monolayers for both solvents is similar. But in monolayers of graphene oxide, that were spreaded from acetone, packing of SLGO is denser, though average size of particle in solutions is nearly equal (Figure 2).

![Figure 2. Compression isotherms of graphene oxide monolayers at subphase surface. Monolayer is formed from: 1 – acetone; 2 – THF. Volume of solution is 0.5 ml.](image)

To maintain the required density of monolayers in the course of their transfer onto solid substrate the stability of films was studied [8]. The changing of surface pressure was fixed at constant area of monolayer during 120 minutes. For all monolayers a significant change of surface pressure was observed during 20 minutes at vaporation of solvents. The value of the surface pressure decreased on 2 mN/m times during all time of observation. This testifies that films formed from graphene oxide particles have high stability and could be transferred onto solid surface.

SEM-images were obtained for graphene oxide LB films (figure 3). Monolayers were deposited onto solid substrates according and Y-type (transfer during downward and upward stroke) at surface pressure of $\pi$=16 mN/m. The thickness of the films consisted of 4 monolayers.
As could be seen from the figure, the graphene films on a solid substrate have an island structure. In the pictures you can clearly distinguish the individual particles of graphene. Particles are distributed more uniformly across the substrate surface for the film obtained from acetone dispersion. At closer look at the surface of the film the dark areas of varying intensity can be seen. This fact is evidence about the presence of multilayer graphene particles in the film.

Absorption of the LB films was measured (figure 4). Absorption spectra have typical form and correspond to the spectra of other authors [9].

**Figure 3.** SEM-images (registered with detectors of secondary electrons and reflected electrons) of graphene oxide LB films prepared from solution in: 1 – acetone; 2 – THF

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**Figure 4.** Absorption spectra of graphene oxide LB films prepared from solution in: 1 – acetone; 2 – THF

For films prepared from acetone solutions the optical density at the maximum absorption band is higher about in several times than absorbance of the films prepared from THF. In the visible region of the spectrum both films have high transparency.

4. **Conclusion**

In this study, we investigated the physical-chemical properties of graphene monolayers formed from dispersion of SLGO in acetone and THF at the interface of water-air. From the compression isotherms of monolayers it was found that for the pressures in the range of 0 to 2 mN mm\(^{-1}\) monolayer is predominantly in a gaseous state. With further compression of the monolayer the particles
approaches and the film becomes “liquid”. But in monolayers of graphene oxide, that were spreaded from acetone, packing of SLGO is denser, though average size of particle in solutions is nearly equal.

Absorption spectrum of graphene LB films exhibits as broad band in the ultraviolet and visible region of the spectrum with a maximum at 230 nm. The optical density of the film obtained from acetone dispersion is greater than the optical density of the film prepared from THF solution. The transparency of the films is more than 90% in the 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 are clearly distinguished. The pictures are clearly visible single sheets of graphene. The films obtained from acetone dispersion are more uniform, which makes them more promising in terms of their use as conductive coatings.

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