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Effect of the Conditions of Transfer on the Structure
and Optical Properties of Langmuir Graphene Oxide Films
during Deposition on a Substrate

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Abstract—The effect the solvent and transfer pressure of graphene oxide (SLGO) Langmuir–Blodgett films on the physicochemical properties of monolayers, and on their structural and optical properties, is studied. Examination of the physicochemical properties of SLGO monolayers on subphase surfaces that are formed from SLGO dispersions in different organic solvents reveals that monolayer behavior is virtually independent of the solvent. Electron microscope and optical studies show that the monolayers formed from SLGO dispersions in DMF and acetone have the highest transfer coefficients. It is concluded that the structural heterogeneity of the surfaces of graphene oxide films results from simultaneous effect of electrostatic interactions between graphene oxide particles and Van der Waals interactions with the solvation shell of the particles. Studies focusing on the effect the pressure of transferring a graphene oxide monolayer onto the surface of a solid substrate has on structural features of LB films show that films produced at low surface pressures have more homogeneous structures.

Keywords: Langmuir–Blodgett films, graphene oxide, structure, optical properties

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INTRODUCTION

Modern nanotechnologies have become an integrated discipline that combines all aspects of the fabrication and application of nanomaterials. Advances in synthesizing many materials, including two-dimensional (2D) nanostructures (which are a unique object of study), have recently been achieved in this area. As with other nanostructures whose properties depend on size and morphology, 2D graphene has properties that differ from those of its 1D form (i.e., carbon nanotubes). The 2D structure of graphene makes it more compatible with planar substrates, offering a viable alternative for silicon replacement. In addition, the 2D structure and atomic size of graphene layers give them unique properties [1]. High specific conductivity and large specific surface area are the most prominent features of layered graphene nanostructures [2].

There are several ways of producing graphene nanostructures. Graphene films are typically manufactured via CVD [2], aerosol sputtering [3], and polyionic assembling [4]. The CVD technique and polyionic assembling are complex procedures that require us to prepare additional substrates and design templates for growing graphene films. There is also the

problem of controlling the thickness of the synthesized coatings.

The Langmuir–Blodgett (LB) technique allows us not only to control the thickness of films but also to predict the orientation of particles in them. The combination of varying the number of layers and the distance between individual graphene sheets enables us to control film conductivity and resistance, and to regulate the specific surface area of a film. This creates new prospects for fabricating highly efficient graphene layers for use in nanodevices.

Despite the popularity of graphene and graphene-based films, there have been few studies devoted to the effect different conditions of LB synthesis have on the properties of graphene films. The LB technique enables us to vary the mutual orientation of molecules and thus the specific molecular surface area of particles in a monolayer [5, 6]. Mironov et al. [7] showed that repeated monolayer compression yields a homogeneous film made of natural graphite particles that undergoes stages of particles approaching one another, the formation of contacts between them, and subsequent compression of the film.

In this work, we present results from studying the effect the solvent and surface pressure of deposition of

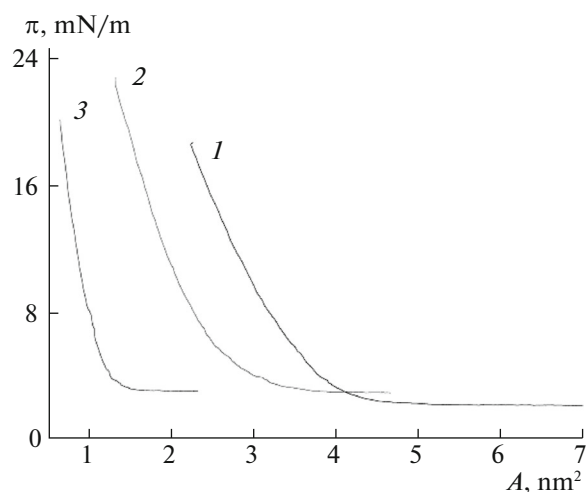


Fig. 1. Compression isotherms of a graphene oxide monolayer on an interface surface. THF was used as a solvent. The volume of the deposited solution was: (1) 0.1, (2) 0.5, and (3) 1 mL.

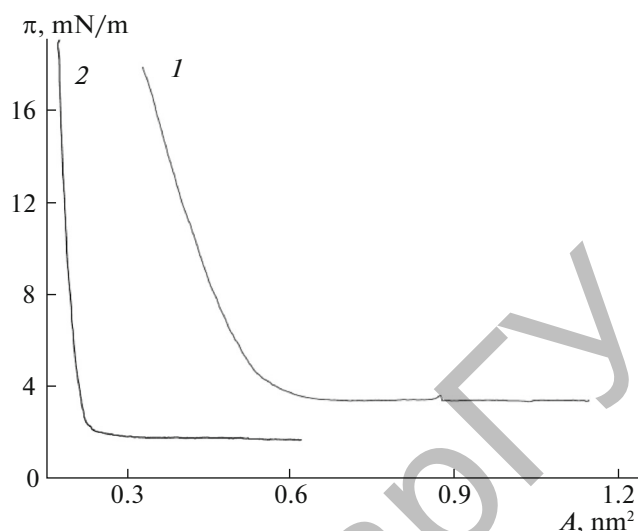


Fig. 2. Compression isotherms of a graphene oxide monolayer on an interface surface. The monolayer was deposited from (1) acetone and (2) DMF. The solution volume was 3.5 mL.

graphene oxide monolayers have on the structural and optical properties of solid LB films.

EXPERIMENTAL

Graphene oxide dispersions (SLGO, Cheaptubes) in acetone, tetrahydrofuran (THF), and dimethylformamide (DMF) were prepared. Solvents of special purity grade were purchased from Sigma Aldrich and used without additional purification. The concentration of SLGO in the solutions was 0.03 wt %. The graphene solutions were treated in an ultrasound bath for 60 min.

The monolayers under study were formed by spreading the solutions in a Langmuir bath (KSV Nima). Compression isotherms of graphene oxide monolayers on the surfaces of water–air interfaces were recorded and studied. To ensure stabilization, each monolayer was kept on a subphase for 40 min. Deionized water obtained using an AquaMax water purification system, was used as a subphase. The water's specific resistance was 18.2 MΩ/cm. The surface pressure was 72.8 mN/m at pH 5.6 and a temperature of 22°C. Solid Y-type films were prepared using the LB technique, since these films were shown earlier to have a more homogeneous structure than Z-type films [8]. The rate of substrate motion across each monolayer was 19 mm/min, and the monolayer compression rate was 5 mm/min.

The morphology of SLGO films on the surfaces of FTO-coated glasses was studied with a TESCAN Mira-3 electron scanning microscope. The optical properties of the films on quartz substrates were studied with a Cary-300 spectrophotometer (Agilent).

RESULTS AND DISCUSSION

Compression isotherms of graphene oxide monolayers deposited from acetone solution were presented in [8]. The compression curves of graphene oxide monolayers deposited from THF solutions onto interface surfaces are shown in Fig. 1.

As when using acetone, the gaseous SLGO monolayers became a liquid-expanded state upon compression at low volumes of the deposited solution [5] (Fig. 1, curve 1). The surface pressure changed to 18 mN/m without collapse of the monolayers. The increased number of particles in the monolayers shifted the curve toward smaller surface areas and reduced the lengths of the gaseous and liquid-expanded phases. Similar results were obtained upon compression of the monolayers formed from SLGO dispersion in DMF.

After comparing the curves recorded for different solvents (Fig. 2), we concluded that monolayer behavior was virtually the same for all of our solvents.

A phase change similar to the one described above was observed upon monolayer compression both for polar and nonpolar solvents, while the specific surface area of the particles within a film shrinks as the volume of the deposited solution grows. A comparison of the isotherms recorded for equal volumes of the deposited solution shows that the packing of SLGO particles in the monolayers prepared from graphene dispersion in acetone was denser than in the monolayers prepared from dispersions in THF and DMF (Fig. 2), even though the average size of particles in these solvents differ only slightly, as was shown in [8].

In order to determine whether we could maintain the required density of a monolayer when transferring

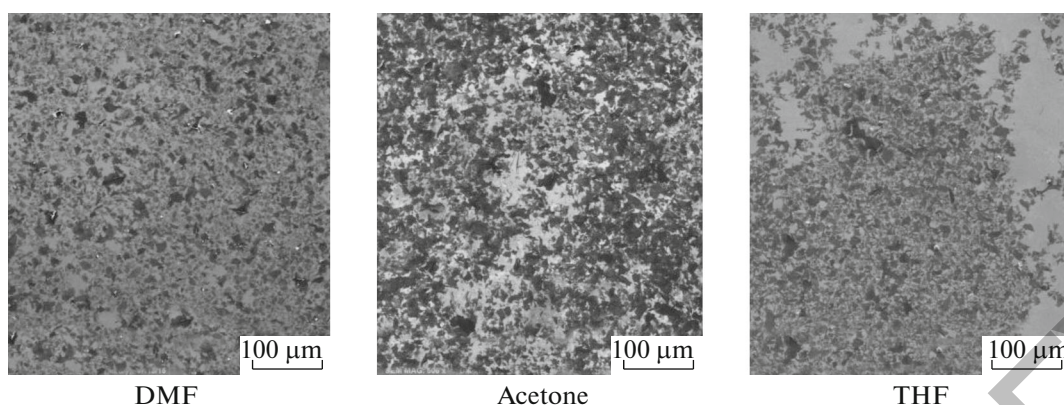


Fig. 3. SEM images of graphene oxide LB films deposited from different solutions.

it to a solid substrate, we monitored film stability on the subphase surface by detecting changes in the surface pressure at a constant monolayer density. The monitoring time was 120 min. No major changes in surface pressure were observed after the solvent evaporated. On average, it changed by 2 mN/m. These findings indicate that the stability of the films formed from graphene particles is relatively high and they can be transferred onto the surface of a solid substrate.

Monolayer stability was also studied via repeated compression. The shape and position along the x axis for the recorded curves remained virtually the same. This indicates that all of the processes that occur upon monolayer compression are reversible and there is no formation of aggregates [7, 9].

SEM images of the graphene oxide LB films were obtained. Figure 3 shows the SEM images of the films prepared at surface pressure $\pi = 16$ mN/m. The volume of the solution deposited onto the interface surface was 5 mL. There were three monolayers in the film. The coefficients of film transfer, determined from the ratio between changes in the monolayer's surface area and that of the film were 0.5, 0.7, and 0.86 for THF, acetone, and DMF, respectively.

Figure 3 shows that a graphene oxide film on a solid substrate has an island structure. Individual graphene particles can be seen clearly in the SEM images. In the films prepared from SLGO dispersion in DMF, the graphene particles were distributed more homogeneously (Fig. 3). In the LB film prepared from dispersion in acetone, particles were also homogeneously distributed over the substrate's surface. Upon closer examination of the film's surface, we can see dark areas of different intensities, indicating that the film contained multilayer graphene particles.

The structure and surface morphology of graphene oxide films is easily explained. Graphene oxides form colloid solutions, due to electrostatic repulsion between the negative carboxyl and phenol hydroxyl groups in the plane of a graphene oxide layer [10]. When a second graphene oxide layer is deposited onto

the surface of the first layer, it is likely that they will simultaneously repulse each other due to electrostatic interaction, and be attracted to each other due to Van der Waals forces [11]. Residual π -conjugated domains will also contribute to the attraction between graphene oxide layers. Attraction processes will therefore dominate, allowing us to prepare multilayer films. However, the graphene sheets in this case overlap; this can be in the SEM images as wrinkles and folds [12].

The solvation shell around SLGO particles also contributes to the interaction and stability of graphene oxide particles in solutions. The dipole moments of solvent molecules are known to diminish in the order DMF–acetone–THF [13]. Even though the solubility of SLGO in these solvents can be described using an inverse relationship, it results in a more homogeneous distribution of particles in DMF- and acetone-based films. The heterogeneity of the films prepared using THF can be attributed to weaker electrostatic interactions between the graphene layers in this solvent and the solvent's molecules.

We next measured the absorption spectra of the prepared LB films (Fig. 4). The profile of the absorption spectrum of LB films is typical of graphene oxide, and is consistent with the data in [12, 14].

A band with a maximum at 210 nm and poorly expressed shoulder at 250 nm emerge in the absorption spectrum of the films. For the films prepared from acetone and DMF solutions, the optical density at the absorption maximum was several times higher than that of the films prepared from THF solutions. Both films were highly transparent in the visible region of the spectrum. From 75 to 95% of the light in the 400–800 nm range was transmitted through the films prepared from DMF and acetone. The films prepared from THF allowed 90–95% of the incident light to pass through. The light transmission of the prepared films was 5% higher than for the similar objects obtained in [9, 15].

The effect surface pressure has on structure and optical properties of LB films SLGO was studied in

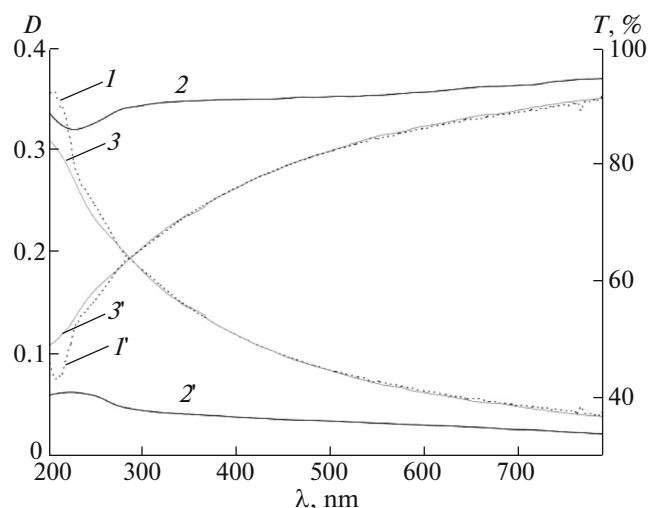


Fig. 4. (1–3) Absorption and (1'–3') transmission spectra of graphene oxide LB films prepared from dispersions in different solvents: (1, 1') acetone, (2, 2') THF, and (3, 3') DMF.

the second part of this work. We prepared monolayer films at surface pressures of 19, 15, and 8 mN/m. DMF was used to form monolayers. The SEM images of the resulting LB films are shown in Fig. 5. The images show that the film prepared at low surface pressure had a more homogeneous structure than the

one prepared at $\pi = 19$ mN/m. This difference in surface morphology was clearly the result of interparticle interaction that led to the formation of a multilayer structure. Analysis of the surface area occupied by the LB film on the substrate showed that all of the monolayers transferred onto the solid substrate occupied ~80% of it at high pressures. This value is consistent with the transfer coefficient of the films formed from SLGO dispersions in DMF (0.85).

The absorption and transmission spectra of the prepared LB films showed that the optical density at the absorption maximum diminished as the pressure of transfer fell from 19 to 8 mN/m (see table).

Similar results were also obtained for graphene oxide LB films prepared from SLGO dispersions in acetone.

CONCLUSIONS

Our investigation of the physicochemical properties of graphene monolayers prepared from SLGO dispersions in DMF, THF, and acetone on the surfaces of water–air interfaces showed that monolayer behavior was virtually independent of the solvent. The density of particle packing in the monolayers fell in the order DMF–acetone–THF, although the average particle size in the solutions for acetone and THF differed negligibly [8]. Electron microscopy studies demonstrated that SLGO LB films have an island

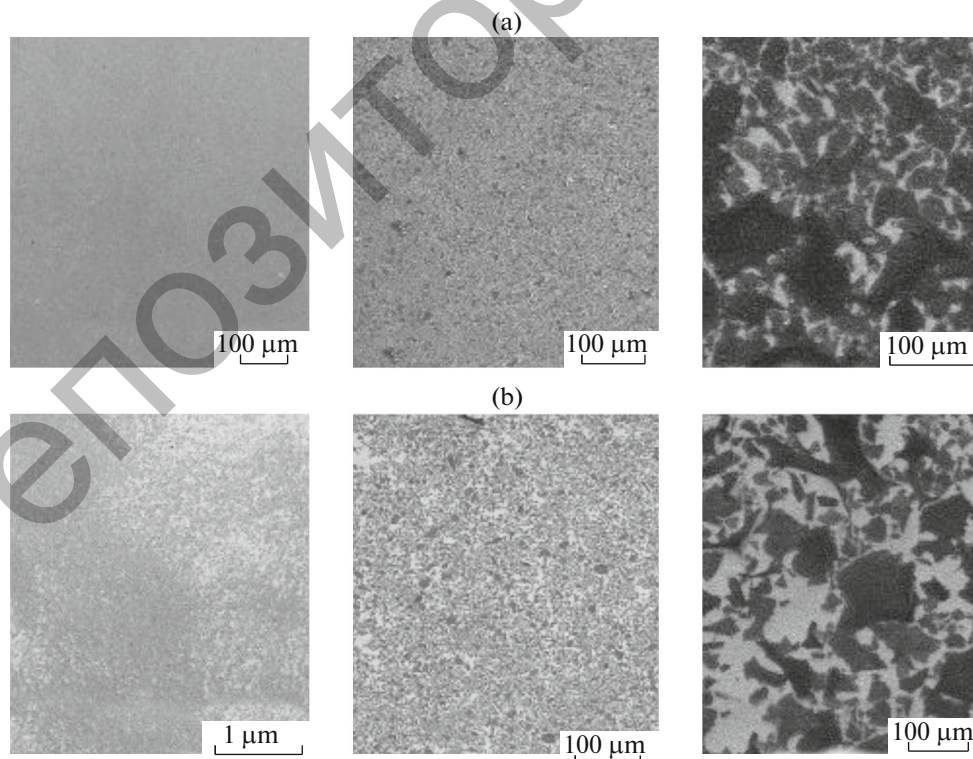


Fig. 5. SEM images of graphene oxide LB films transferred at different surface pressures: (a) 8 and (b) 19 mN/m.

Optical density (OD) and transmission coefficients (T , %) at different λ for graphene oxide LB films prepared at different transfer pressures (π)

π , mN/m	λ_{abs} , nm	OD	T , %		
			$\lambda = 400$ nm	$\lambda = 550$ nm	$\lambda = 800$ nm
8	230	0.25	92	86	77
15	210	0.3	92	85	76
19	230	0.38	86	78	67

structure. Individual graphene sheets were clearly seen in the SEM images. The films prepared using acetone and DMF were more homogeneous, making them more promising for use as conductive coatings.

The structural heterogeneity of a graphene oxide film's surface can be attributed to the simultaneous effect of electrostatic interactions between graphene oxide particles and Van der Waals forces. In addition, the solvation shell of an SLGO molecule makes its own contribution to the interaction and stability of graphene oxide particles in solutions. Since the dipole moments of solvent molecules diminish in the order DMF–acetone–THF, the particles in DMF- and acetone-based films are distributed more homogeneously. The heterogeneity of the films prepared using THF can be attributed to the weaker electrostatic interaction between graphene layers in this solvent, and with solvent molecules.

A broad band with a maximum at 210 nm was observed in the UV and visible region of the spectrum for graphene oxide films on solid substrates. The optical density at the absorption maximum of the films prepared using acetone and DMF solutions was several times higher than that of the THF-based films. The films were characterized by high transparency in the visible part of the spectrum.

Examining the effect of the pressure of graphene oxide monolayer transfer onto the surface of a solid substrate and the structural features of LB film revealed that the film prepared at low surface pressure had a more homogeneous structure, but its optical density was 30% lower than that of the film produced at high pressure. Analysis of the surface area occupied by the LB film showed that the monolayers transferred onto the solid substrate at high pressures occupied

~80% of it, which was consistent with the film transfer coefficient.

Our data can be used to develop the technology for manufacturing transparent graphene oxide films and its derivatives for molecular electronics and photovoltaics.

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