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OPTIMIZED DEPOSITION OF GRAPHENE OXIDE LANGMUIR-BLODGETT THIN FILMS

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Single sheet graphene (SG) is an innovative transparent material with high electrical and thermal conduction the use of which in transparent electrodes instead of traditional materials improves the performance of optoelectronic devices. In this study, graphene oxide (GO) has been obtained by a modified Hummer`s method followed by an advanced technique of water removal (lyophilisation). The Langmuir-Blodgett (LB) method was applied to transfer GO from suspension to substrate. To optimize the deposition process, as suspending and spreading solvents the benzene and benzene/methanol mixtures were chosen instead of previously studied water suspensions. The number of GO layers in suspension is reduced by exfoliation in order to obtain a single GO monolayer. For this purpose, sonication and centrifugation of GO sheets are carried out. Finally, the effect of variously treated glass substrate surfaces on the deposition efficiency has been studied. In the work, it is shown that ozonization of glass substrate improves the deposition outcome, while ozonization of indium tin oxide (ITO) glass substrate is necessary to perform such deposition. The obtained GO suspensions and LB thin films have been studied using a scanning electron microscope (SEM).

Keywords: *single sheet graphene, graphene oxide, Langmuir – Blodgett (LB) technology.*

1. INTRODUCTION

In the last decade a particular interest has been shown in the graphene materials for optoelectronic devices. Graphene has high optical transmittance and electrical conductivity, and, therefore, is considered an innovative and alternative material to produce transparent conductive films. The substrates covered with single-sheet graphene (SG) could be used in a wide variety of optoelectronic devices such as solar cells, optical communication and solid state lightning devices, etc.[1-6].

In this study, single-sheet graphene oxide – a 2D multifunctional material – is used for producing graphene-based materials. The graphene oxide (GO) was

obtained by a modified Hummer`s method [7] followed by GO-water gel lyophilization in order to remove water from the sample as completely as possible. Nonpolar benzene and benzene/methanol mixtures were chosen as suspending solutions to fully abandon the use of water suspensions. The Langmuir-Blodgett (LB) technique was applied for transferring GO from suspension to substrate. The deposition parameters and conditions were carefully chosen; nevertheless, further optimization of the deposition process is required. The obtained GO thin films have been characterized using SEM.

2.MATERIALS AND METHODS

GO synthesis and characterization

Graphite flakes (7-10 μm) were purchased from *Alfa Aesar*, while sulfuric acid (H_2SO_4, 96 %) and hydrogen peroxide (H_2O_2, 30 %) – from *Lach:ner*. Phosphoric acid (H_3PO_4, 80 %), potassium permanganate ($KMnO_4$) and hydrochloric acid (HCl, 37 %) were acquired at *Latvijas Kimija*.

Graphene oxidation was carried out using a modified Hummer`s method [7]. Graphite flakes (10 g) were mixed with conc. H_2SO_4 (490 ml) and conc. H_3PO_4 (60 ml), then $KMnO_4$ (50 g) was gradually added. The reaction mixture was stirred with magnetic stirrer for 19 h at ambient temperature. After that, distilled water (300 ml) and 30 % H_2O_2 solution (35 ml) was slowly added. The mixture was filtrated and then – using centrifugation (9000 rpm) – washed several times with 5 % HCl solution and distilled water. The obtained GO-water gel was sonicated in an ultrasound bath for 75 min and freeze-dried for 24 h.

Elemental analysis was performed using *Euro Vector AE 3000*. The water content in the samples produced was determined by Karl-Fischer's titration. The Fourier transform infrared spectroscopy (FTIR) spectrum was recorded on *PerkinElmer Spectrum 100* with a diamond attenuated total reflectance sampling accessory. The thermogravimetric analysis (TGA) was performed under a nitrogen flow (20ml/min) at the heating rate of 1ºC/min using *PerkinElmer STA 6000*. The SEM images were obtained by means of *Tescan Lyra3* at 5 kV.

GO exfoliation

GO suspension was prepared by adding 4.0 ml of benzene or benzene/methanol mixture (5:1) to the lyophilized GO (3.0 mg). After adding benzene, the solution was sonicated for 50 h using an ultrasound bath. Low-speed centrifugation was carried out at 1000 rpm for 10 min. The supernatant then underwent three high-speed centrifugation steps at 6000 rpm for 10 min. The GO sheets in suspension were characterized using SEM. The LB surface pressure – area isotherms for non-exfoliated and exfoliated GO suspensions were collected and analyzed.

Substrate surface treatment

Previous reports have shown that hydrophilic surfaces are preferable for effectively collecting the GO layers from a Langmuir film [8]; therefore, glass substrates were treated with H_2SO_4:H_2O (1:1) solution for 24 h to make them more wettable by water. The hydrophilized substrate was cleaned with deionized (DI)

water and dried at ambient conditions. Ozonization of hydrophilized glass substrates and ITO-covered substrates was carried out for 10 min.

GO deposition by Langmuir-Blodgett technique

The LB trough (150 × 700 mm) was carefully cleaned with chloroform and then filled with DI water. GO suspension was slowly spread onto the water surface drop-wise up to the total of 0.5-1.0 mL. The surface pressure was monitored using a tensiometer attached to a platinum Wilhelmy plate (20 mm). The monolayer was compressed step-by-step to the deposition pressure (in the range from 10 to 20 mN/m). Particularly, two barriers were moved together symmetrically by fraction (typically 1 mm) at a speed of 100 mm/min, then GO monolayer was allowed to relax until the surface pressure stabilized and then a next compression step proceeded. The obtained Langmuir layer of GO was transferred to substrate by dipping it fast (50 -100 mm/min) vertically into the trough and then slowly pulling it out (1 - 2 mm/min). The surface pressure – area isotherms were collected and analyzed. To evaluate the LB deposition efficiency, the GO monolayer area variations were recorded, while the surface pressure was kept constant.

3. RESULTS AND DISCUSSION

GO synthesis and characterization

Elemental analysis (Table 1) was made for a GO sample dried at ambient conditions (and not for a freeze-dried sample as this very quickly adsorbs water from air[*]).

Table 1

Elemental analysis of GO dried at ambient conditions

C (%)	H (%)	N (%)	S (%)	H_2O (%)	C/O molar ratio[**]
42.815	2.809	-	1.575	17.6[*]	1.7

As seen in Fig. 1*a*, GO exhibits characteristic IR absorbance bands at 3680-2400 cm^{-1} (O-H stretching of GO and adsorbed water molecules), 1730 cm^{-1} (C=O stretching), 1617 cm^{-1} (O-H bending), 1046 cm^{-1} (C-O stretching) and 975 cm^{-1}(C-O stretching of epoxy groups) as well as at 1408 cm^{-1} (S=O symmetric stretching of covalently bonded sulphates on GO surface) and 1221 cm^{-1} (S=O asymmetric stretching), which complies with literature data [9]. In the region 2250-1920 cm^{-1} a noise was recorded stemming from the spectrometer diamond attenuated total reflectance sampling accessory. The TGA data (Fig. 1*b*) show a weight loss at 190ºC of approx. 35 wt%, which is explained by the oxygen-containing group decomposition and is characteristic for GO [10]. The observed lyophilized GO flakes (Fig. 1*c*) ranged in size up to 100 μm were stacked in a multilayer, suggesting that further exfoliation of sample had to be performed before LB technology.

* Freeze-dried sample contains 3.8 wt% water.

** Adsorbed water and covalently bonded sulphuric acid was taken into account.

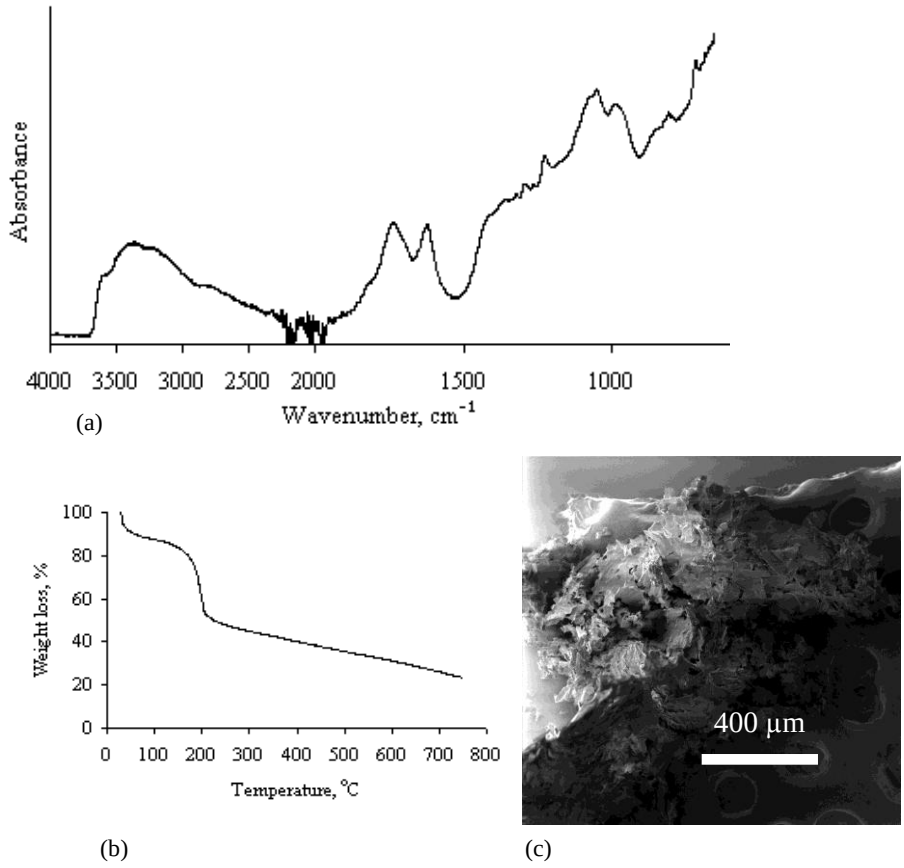
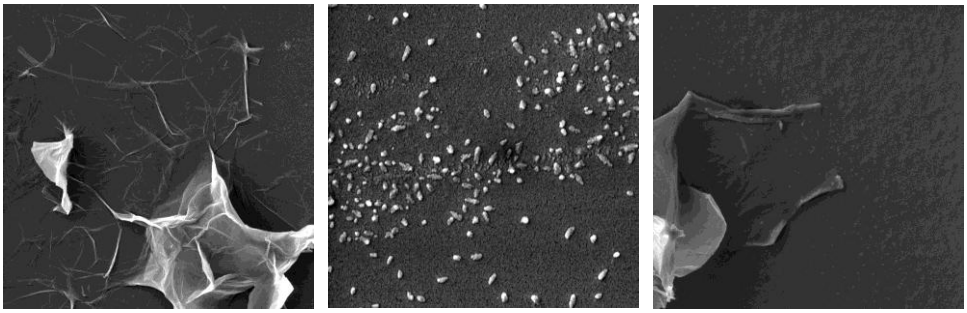


Fig. 1. Characterization of lyophilized GO:
(a) FT-IR spectra; (b) TGA curve; (c) SEM image.

GO exfoliation

Benzene and benzene/methanol mixtures were chosen as suspending and spreading solvents to avoid loss of material in water subphase. However, in some cases formation of colloidal stabilized emulsion was observed in the SEM analysis (Fig. 2*c*). Possible explanation was found in literature: according to [11], GO sheets are capable of stabilizing the oil-water interfaces to form particle-stabilized emulsions; these latter remained kinetically stable for many months since GO sheets are trapped at the oil-water interfaces (this effect is to be studied thoroughly in the future).

The number of sheet layers in suspended GO particles was controlled by additional exfoliation process in order to obtain a monolayer of GO sheets at the air-water interface. Sonication and centrifugation were carried out with particular attention paid to the sonication time and the centrifugation speed; as a result, GO particles with reduced number of sheet layers were obtained. During the GO synthesis and processing, the sheets were torn up into smaller pieces. As a result, the size of GO sheets was ranging from few nm to tens of μm.



(a) (b) (c)

Fig. 2. SEM images of sonicated GO suspension:
(a) non-uniform sheet of 10 μm;
(b) 100 nm sized particles;
(c) sheet covered in colloidal stabilized emulsion.

As shown in Fig. 2, sonication of GO suspension reduces the number of GO layers, producing a new fraction of 100 nm particles and promoting the formation of stabilized emulsion. The centrifugation significantly reduces the number of 10 μm sheets and removes conglomerates from suspension. The difference between the effects of low-speed and high-speed centrifugation was not observed. The equal volume of GO suspensions (1.0 mL) was spread on LB trough surface. As seen in Fig. 3, better spreading of GO Langmuir layer takes place for exfoliated GO suspensions. The trough area is corresponding to the start of surface pressure build, since the increased fraction of single (or few) sheet GO becomes larger with each exfoliation step.

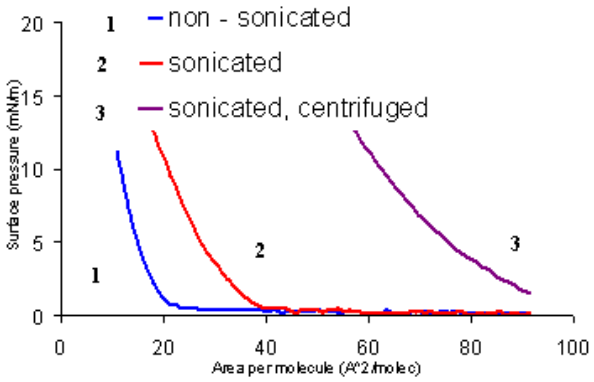
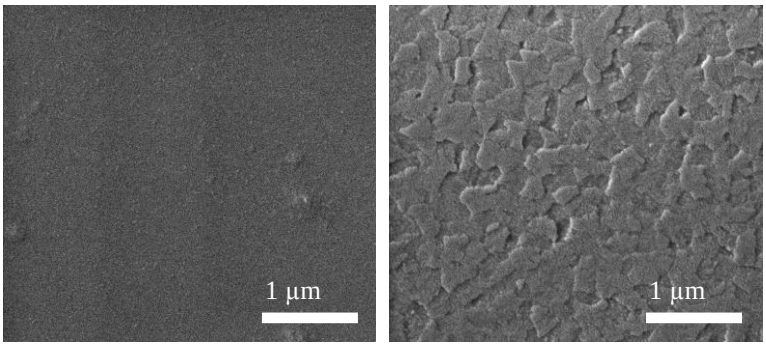


Fig. 3. Surface pressure - area isotherm of GO suspension before and after exfoliation (from left to right).

Substrate surface treatment

In our experiments we observed the effect of variously treated glass substrate surfaces (hydrophilized, ozonated). Our studies have shown that ozonization of glass substrate improves the deposition outcome; while ozonization of ITO covered glass substrate is needed to perform such deposition. As seen in Fig. 4, differences in deposition outcomes could be explained with a change of surface relief. Ozonating an ITO-covered substrate resulted in anisotropic plasma etching,

revealing sub-micron grains on the surface. Now, further research of substrate surface treatment is under way.

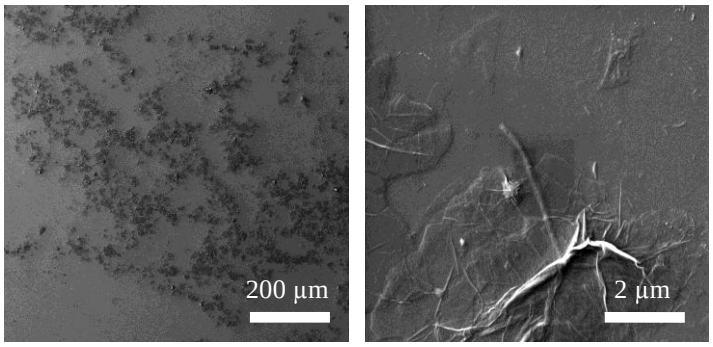


(a) (b)

Fig. 4. SEM images of glass substrate surface:
(a) ITO; (b) ITO after plasma ozonization.

GO deposition by Langmuir – Blodgett technique

Generally, GO consists of atomic carbon layers derivitized by phenol hydroxyl and epoxide groups on the basal plane and carboxylic acid groups at the edges. The hydroxyl functioning makes the sheet more hydrophilic, and the ionizable carboxylic acid groups induce an electrostatic repulsion between the sheets; this allows GO to readily form a stable single-layer dispersion [12]. Therefore, the Langmuir-Blodgett (LB) technique was selected for producing large-scale GO films, and mainly assemblies of GO multilayers were obtained. As shown in Fig. 5, in the case of non-exfoliated GO deposited on substrate, a multilayered structure instead of a monolayer was obtained, which is one more evidence for necessity of exfoliation. Non-uniform character of the deposited GO LB sheet (Fig. 5*b*) might be explained with the presence of particle-stabilized emulsion.



(a) (b)

Fig. 5. SEM images at different magnification of GO deposited on hydrophilized glass substrate by Langmuir - Blodgett technology (deposition pressure 10 mN/m).

4. CONCLUSIONS

In this work graphene oxide has been successfully obtained by modified Hummer`s method followed by lyophilization (an advanced water removal process). The non-polar aromatic benzene chosen as suspension solvent instead of water suspensions has shown a good performance. The use of Langmuir-Blodgett technique (usually applied to obtain large-scale GO assemblies) resulted mainly in GO multilayers produced by deposition. The carefully optimized sample and substrate preparation and deposition technique has also given a good result. Sonication and centrifugation have been proved to be appropriate methods for making exfoliation of GO layers. The intense GO benzene suspension sonication has resulted in a reduced number of GO layers, a new fraction of 100 nm particles, and formation of stabilized emulsion. Centrifugation of suspension significantly reduces the number of 10 μm sheets and removes the conglomerates. The quality of obtained GO suspensions and thin films has been estimated using SEM as high.

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GRAFĒNA OKSĪDA LENGMĪRA – BLODŽETAS PLĀNO KĀRTIŅU IEGŪŠANAS OPTIMIZĀCIJA

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K o p s a v i l k u m s

Vienslāņa grafēns ir inovatīvs gaismas caurlaidīgs materiāls, kam piemīt augsta elektrības un siltumvadītspēja, līdz ar to, tradicionālos elektrodus aizstājot ar grafēna monoslāni, tiktu paaugstināta optoelektrisko ierīču efektivitāte. Pētījumā grafēna oksīda (GO) iegūšanai izmantota modificēta Hammera (*Hummer*) metode un parauga liofilizācija, lai atbrīvotos no ūdens. Grafēna oksīda plānās kārtiņas uzklāšanai izvēlēta Lengmīra - Blodžetas (*Langmuir - Blodgett*) metode, kurai piedāvāts jauns paņēmiens GO monoslāņa iegūšanai uz gaisa/ūdens robežvirsmas. Pretēji iepriekš LB tehnoloģijā izmantotām GO suspensijām ūdenī parādīts, ka kā suspensijas un uznešanas šķīdinātājs var tikt izmantots benzols vai benzola/metanola maisījums. Lai samazinātu GO lokšņu skaitu Lengmīra kārtiņā, veikta GO slāņu papildus eksfoliēšana uznešanas šķīdinātājā, paraugu sonējot un centrifugējot. Novērota substrāta virsmas apstrādes ietekme - stikla substrāta hidrofilizēšana un ozonēšana uzlabo plānās kārtiņas uznešanas iznākumu, savukārt ar ITO (*indium tin oxide*) pārklāta stikla substrāta ozonēšana ir nepieciešama, lai varētu veikt uznešanu. Iegūtās GO suspensijas un plānās kārtiņas raksturotas ar skenējošo elektronu mikroskopiju.

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