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Preparation of graphene nanostructured films for photovoltaics

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Abstract. The results of the development of technology for the preparation of graphene films for solar photocells by the Langmuir-Blodgett method are presented. A comprehensive study of the dependence of structural, optical, electrophysical and photovoltaic properties on the chemical composition and conditions for the preparation of films based on graphene oxide, reduced graphene oxide and N-doped graphene oxide is carried out. It is shown that using the technology of applying graphene nanostructures to solid substrates by the Langmuir-Blodgett method leads to a decrease in the amount of platinum catalysts used for electrodes of solar devices.

1. Introduction

Modern nanotechnologies have become an integral science that includes all aspects of the preparation, fabrication and application of nanomaterials. Recently, in this field, success has been achieved in the synthesis of many materials, including two-dimensional (2D) nanostructures, which represent a unique target for research.

High conductivity and a high ratio of surface area to volume are the most significant characteristics of layered graphene nanostructures [1]. In addition, it was shown [2, 3] that graphene has a higher oxidation potential than Pt, which is a traditional material used in dye-sensitized solar cells (DSSC). Due to the variety of existing forms of graphene, it is possible to improve the necessary parameters of the counter electrodes in solar cells.

Typically, chemical vapor deposition (CVD) technology [1], aerosol spraying [2] and polyion assembly [3] are used for the deposition of graphene layers. Polyion assembly and CVD are a complicated procedure that requires additional preparation of substrates and a template for growing of graphene films. Furthermore, there is the problem of controlling the thickness of the synthesized coatings, which is a negative factor.

Langmuir-Blodgett technique allows you to control the thickness of the films, as well to predict the orientation of the particles within it. For this project, this means that the combination of possible variations in the number of layers and the distance between the individual graphene sheets enable to control not only the conductivity and resistance of the films, but also to adjust the surface area of the film. This opens up the possibility of creating a highly efficient catalyst graphene layer with high conductivity for using in photovoltaic cells.

This paper presents the results of the development of technology for the production of graphene films for solar cells by the Langmuir-Blodgett method (LB). A comprehensive study was carried out



on the dependence of the structural, optical, electrophysical, and photovoltaic properties of films on the chemical composition and preparation conditions. It is shown that the use of the technology of deposition of graphene nanostructures on solid substrates by the Langmuir-Blodgett method leads to a decrease in the amount of platinum catalysts used for electrodes of solar devices.

2. Experiment

Single-layer graphene oxide (SLGO, Cheaptubes), reduced graphene oxide (rGO, Cheaptubes), and nitrogen-doped graphene oxide (NGO) (Sigma-Aldrich) were used as the objects of the study. Monolayers of graphene derivatives were formed by spreading from a solution in the Langmuir trough (KSV Nima). The isotherms of monolayer compression at the water-air interface were measured and investigated. To stabilize the monolayer, it was held for 40 minutes. As a subphase, deionized water was used, purified using the AquaMax water purification system. The specific resistance of water was equal to 18.2 M Ω /cm. The surface pressure was equal to 72.8 mN/m at pH = 5.6 and a temperature of 22 °C.

From measurements of π -A isotherms, surface pressures were chosen as the pressure of monolayer transfer onto a solid substrate, when the sheets of the corresponding graphene derivative contact each other, but do not form significant folds and “wrinkles” on the surface of the film. In this case the monolayer is in a condensed liquid state [4-6].

For the SLGO, the method of preparation of films was used, which was described in detail in [4, 6]. The solid films were obtained by the Y-type transfer at 19 mN/m, since such films are more homogeneous in structure than the Z-type films [4]. The velocity of the substrate motion through the monolayer was equal to 8 and 19 mm/min, and the compression rate of the monolayers of 5 mm/min.

For the preparation of NGO films, data on the phase state of monolayers and their stability, published in [5], were used. In particular, it was established from the isotherms of compression of monolayers that the monolayer is predominantly in the gaseous state in the pressure range from 0 to 2 mN/mm. With further compression of the monolayer, the particles come closer to each other and the film becomes liquid. When comparing the curves recorded for NGO and SLGO, it can be concluded that the behavior of the monolayers for both derivatives of graphene is the same. Solid films of NGO were obtained by the LB method by the Y-type transfer at 10 mN/m. The monolayer was compressed at a barrier velocity of 5 mm/min, the substrate rate was equal to 2 mm/min, and the monolayer stabilization time was equal to 30 minutes.

The rGO films were transferred at a surface pressure of 10 mN/m. The thickness of the films was equal to 1 monolayer, transferred along the Z-type. The monolayer was compressed at a barrier velocity of 5 mm/min, the substrate rate was equal to 2 mm/min, and the monolayer stabilization time was equal to 30 minutes.

For the deposition of graphene films, glass plates coated with an FTO layer were used, on which 1 monolayer of SLGO, rGO or NGO was deposited, as well as layered films based on Pt catalysts+graphene oxides. A platinum catalyst was electrochemically applied from an ethanolic solution of H₂PtCl₆ (Sigma Aldrich).

The morphology of the films was studied with a Mira 3 (Tescan) scanning electron microscope (SEM). The absorption and transmission spectra of the films were measured with a Cary-300 (Agilent) spectrophotometer.

The preparation, assembly and measurement of DSSC cell parameters with graphene electrodes was carried out according to the procedure detailed in [7]. Measurements of the electrophysical properties were carried out on a Z-500PRO impedance meter (Elins, Russia) under irradiation of cells with standard simulated solar radiation (Air Mass (AM) 1.5).

3. Results and discussion

For the SLGO it was shown [4, 6] that the packing density of particles within monolayers of a single-layer graphene oxide decreases in the series of DMF-acetone-THF dispersions, although the average particle size in solutions of acetone and THF differs insignificantly. The structural heterogeneity of the

surface of graphene oxide films (figure 1 a) can be explained by the result of the simultaneous influence of electrostatic interactions between graphene oxide particles and Van der Waals forces.

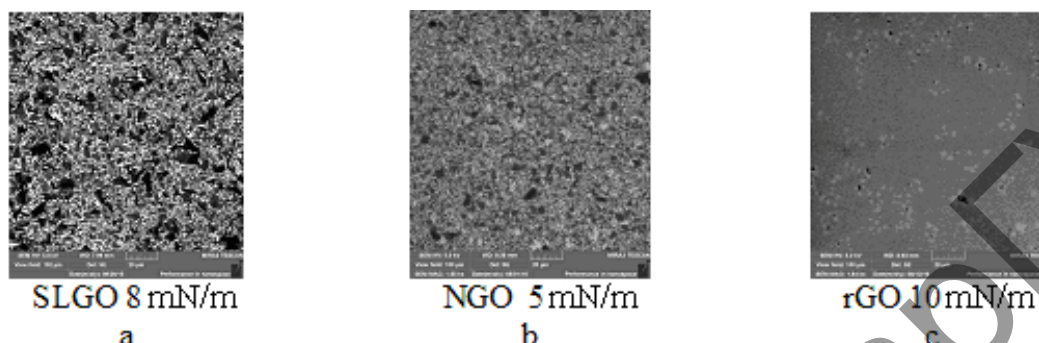


Figure 1. SEM images of the graphene oxide LB films

When studying the effect of transfer pressure of a monolayer of graphene oxide on the surface of solid substrates and the structural features of LB films, it was found [4] that the film obtained at low surface pressure is more homogeneous in structure, but its optical density was on 30% smaller than that of the film, obtained at high pressure.

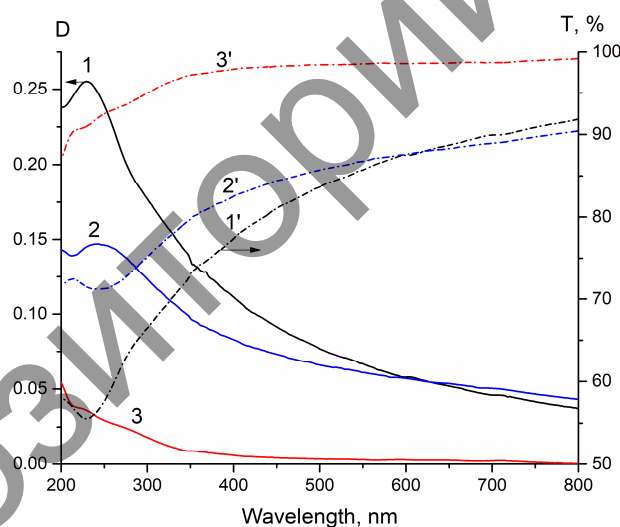


Figure 2. Absorption (1 – 3) and transmission (1' – 3') spectra of LB films based on SLGO (1, 1'), NGO (2, 2') and rGO (3, 3')

Also, the technology of films preparation by the Langmuir-Blodgett method on the basis of graphene oxide doped with nitrogen atoms was developed. SEM measurements showed (figure 1 b) that NGO forms island films. It is possible to distinguish multilayer structures formed by the imposition of individual sheets of NGO in the structure of films transferred at low surface pressures. The synthesized NGO films, like SLGO, have high transparency in the visible spectral range – from 80 to 90% (figure 2), which makes them attractive for various technological applications.

Studying the influence of the preparation conditions of LB films of reduced graphene oxide have shown that rGO forms uniform island films with clearly discernible clusters, whose density increases with increasing surface pressure of monolayer transfer onto solid substrate (figure 1 c). An increase in the surface pressure leads to an increase in the optical density of the absorption band of the reduced

graphene oxide. The synthesized rGO films have high transparency in the visible spectral range - from 87 to 96%.

The study of the electrophysical properties of LB films based on SLGO, rGO, and NGO, have shown that LB films prepared from rGO and SLGO with transfer pressures of 10 and 19 mN/m, respectively, have the best electrophysical and conductive parameters.

The obtained LB films were used as counter electrodes in DSSCs. As shown by the measurements (table 1), the use of composite electrodes Pt+graphene oxide is more promising compared to the counter electrodes based on pure derivatives of graphene oxide.

Table 1. Photovoltaic parameters of DSSC with various counter electrodes

Counter electrode	U_{oc} , V	J_{sc} , mA/cm ²	FF	Efficiency, %
Pt	0.67	9.7	0.67	4.4
SLGO	0.41	5.3	0.13	0.31
rGO	0.52	6.0	0.38	1.28
NGO	0.39	3.2	0.10	0.2
Pt+SLGO	13.61	0.262	0.400	3.72
Pt+rGO	13.72	0.404	0.753	3.94
Pt+NGO	13.70	0.505	0.484	2.44

Among the graphene oxide derivatives studied, the photocatalytic activity of composite electrodes decreases in the series of Pt –Pt+rGO – Pt+SLGO – Pt+NGO, which is associated with a low recombination coefficient and a long lifetime of electrons in composite electrodes.

4. Conclusion

Thus, the studies have shown that a graphene oxide film in combination with a platinum catalyst is more promising for photovoltaic cells, than neat graphene oxide electrodes. In our work, as well as in the works [8, 9] it was shown that a graphene-coated Pt composite film provides a large and superior conductive interface for significant improvement of Pt utilization efficiency and charge transfer, which, in turn, leads to a higher power conversion efficiency of the DSSC. As it was compared to a conventional Pt-coated counter electrode, the Pt loading of a composite electrode can be reduced by more than 60% while achieving even better performance.

Graphene oxide LB films, despite the advantages in electrotransport properties, have a sufficiently high resistance, which is reflected in the number of charge carriers injected into the semiconductor layer from dye molecules and in the complex decrease in the efficiency of solar cells.

When studying the photovoltaic properties of solar cells with counter electrodes based on SLGO LB films, it was clarified that the use of Pt + rGO composite electrodes is more promising than the counter electrodes based on pure SLGO or rGO. Among the graphene oxide derivatives represented, the photocatalytic activity of composite electrodes decreases in the series of Pt –Pt+rGO – Pt+SLGO – Pt+NGO, which may be due to the low recombination coefficient and the long lifetime of electrons in the composite electrodes.

Acknowledgments

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