

A BRIEF REVIEW OF METAL OXIDE (HYDROXIDE)-GRAPHENE NANOCOMPOSITES SYNTHESIS BY LAYER-BY-LAYER DEPOSITION FROM SOLUTIONS AND SYNTHESIS OF CuO NANORODS-GRAPHENE NANOCOMPOSITE

V.P. Tolstoy, I.A. Kodintsev, K.S. Reshanova and A.A. Lobinsky

Institute of Chemistry, St. Petersburg State University, St. Petersburg, 198504 Russia

Received: June 14, 2016

Abstract. Principle conditions for layer-by-layer synthesis of nanocomposite layers incorporating graphene and metal oxides or hydroxides are formulated in the review. Practical applications of such nanocomposites in the electrodes of lithium-ion batteries, supercapacitors, or electrochemical sensors, systems of water purification and environmental control, photocatalysts, etc, are considered. As an example of this method the synthesis of nanocomposite containing graphene nanosheets and CuO nanorods is described. This material was first synthesized in our study using $\text{Cu}[\text{NH}_3]_4(\text{OAc})_2$ solution and water suspension of graphene. Analysis of the synthesized thin films by SEM, XRD, and Raman spectroscopy have shown that the size of the graphene nanosheets in the films is about 2 μm and the size of the CuO nanorods is approximately 10-12 by 150-200 nm. This nanocomposite layers were deposited on the surface of nickel foam and their electrochemical properties were studied for application in supercapacitor electrode. It was shown that the capacitance of the supercapacitor is 700 F/g, and its value after 500 cycling is reduced by 6% only. Also some recommendations are given concerning potential applications of these layers in the electrodes of electrocatalysts or electrochemical sensors.

1. INTRODUCTION

It is well known that graphene is an allotropic modification of carbon, a two-dimensional material with hexagonal crystal lattice, with unique mechanical, electrical, optical and other properties and therefore an object of great interest of researchers in recent 10 years [1–3]. Among the variety of potential technological applications of graphene fairly significant is its use as a component of nanocomposites. The importance of the problem of design of such nanocomposites may be seen from growing number of publications in this field. Thus, according to the Scopus database there were only 17 articles on this topic published in 2008, whereas in 2012 there

were about 600 and in 2015 upwards of 1500 articles.

The analysis of literature shows that most attention is currently being paid to the composites of graphene with metals [4–6], polymers [7,8], and other carbon materials [9,10]. Also there are works devoted to composites containing metal-oxide compounds, which are intended for application in energy storage devices as a material for lithium-ion batteries and supercapacitors [11–13], in water purification systems and for removal of pollutants from the environment [14], in electrochemical sensors [17], etc. Such nanocomposites are produced mainly by electrochemical deposition techniques [18], sol-

Corresponding author: V.P. Tolstoy, e-mail: vptol@yandex.ru

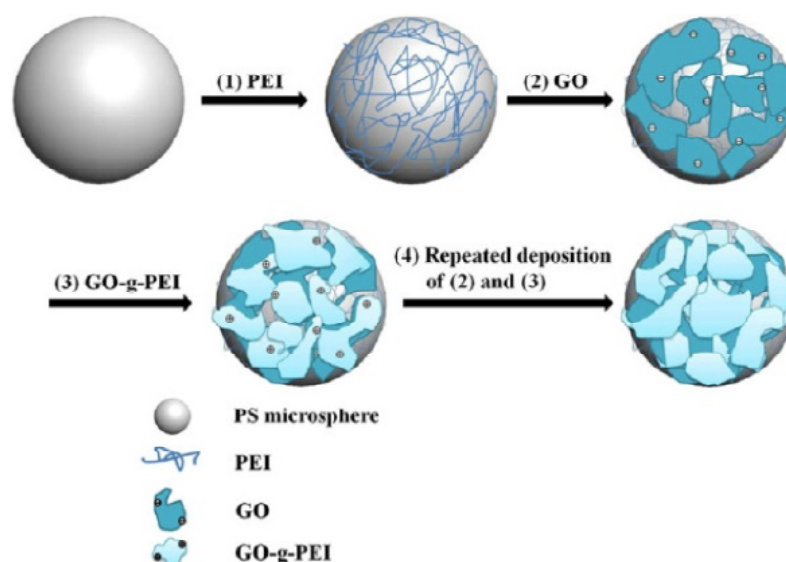


Fig. 1. Schematic illustration of oppositely charged GO onto PS microspheres via LbL assembly. Reproduced with permission from [24], © Copyright Cambridge University Press (2013).

gel process [19], hydrothermal [20], and microwave synthesis [21].

2. LAYER-BY-LAYER SYNTHESIS OF GRAPHENE – METAL-OXIDE (HYDROXIDE) NANOCOMPOSITES

Among the studies devoted to the synthesis of the graphene-based nanocomposites a matter of particular interest is the so called Layer-by-Layer (LbL) synthesis based on successive adsorption of precursors in the solution on a substrate surface, each successive adsorption cycle requiring subsequent removal of unreacted excess reagent. As a result, a film of the synthesized material is formed, which thickness grows proportionally to the number of the treatment cycles at multiple repetition of the adsorption reactions [22,23] (Fig. 1). This method allows to control precisely the thickness and composition of nanolayers even on the surface of complex shapes, as well as to synthesize so called “nanolaminates”, i.e. multilayers composed of layers with different composition.

Wide range of thin-layer materials was obtained previously by this method, for example, metal oxides [25,26], fluorides [27,28], sulfides [29,30] of metals, as well as nanoparticles of noble metals, such as gold [31], silver [32], etc.

The LbL synthesis of graphene nanocomposites became possible due to the ability of graphite nanosheets to form stable suspensions in solutions caused by their negative charge generated by dissociation of functional hydroxyl, carboxyl and other

groups in structure of nanosheets (Fig. 2). As was shown by numerous experiments, the magnitude of zeta potential of graphene nanosheets in an aqueous solution depends on the pH of the solution and is approximately -50 ~ -40 mV at pH 6.0 and -45 ~ -25 mV at pH 4.0 [33]. The value of the specific density of such charge increases as the surface area of graphene nanosheets decreases.

Since graphene nanosheets are negatively charged, the second component for the LbL synthesis must be taken a solution containing positively charged metal ions, polyelectrolytes or colloidal particles. In such syntheses the adsorption of reagents on the surface of a substrate is generally realized by formation of hydrogen bonds and the electrostatic interaction. A short summary of the results of these studies and the specification of the conditions of LbL synthesis are given in Table 1.

Among the variety of suitable reagents, solutions of polyelectrolytes and solutions of PDDA in particular, are most often used in the LbL synthesis. In reference [34] composite (PDDA-graphene/ Fe_3O_4)_n was shown to exhibit higher, compared to pure Fe_3O_4 , electrocatalytic activity with respect to $\hat{I}_{2/2}$ since the graphene sheets hamper aggregation of the Fe_3O_4 nanoparticles. Notably, the observed effect demonstrates excellent stability and reproducibility. Composite (PDDA/GO/PDDA/ TiO_x)_n studied in reference [35] can serve as a material for solar cells and microelectronic devices because it was found out that photoelectrons generated by TiO_x nanosheets in this multilayer under solar radiation are accumulated in reduced graphene oxide (rGO)

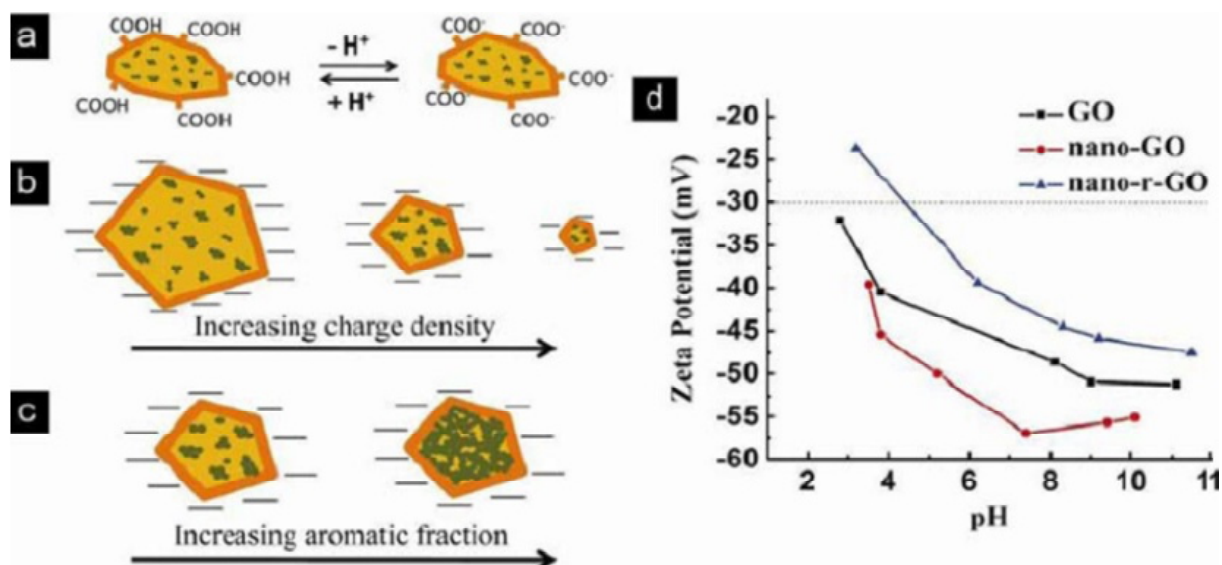


Fig. 2. Amphiphilicity of GO is dependent on pH, sheet size, and degree of reduction as shown schematically in *a*, *b*, and *c*, respectively. (*d*) Zeta potential measurements show the charge density (i.e., hydrophobicity) of GO increases with higher pH, smaller size (from regular micron-sized GO to nano-GO with diameter <100 nm) and lower degree of reduction (nano-rGO to nano-GO). Reproduced with permission from [33], © Copyright IUPAC (2011).

Table 1. Synthesis conditions and application fields of nanocomposites based on graphene and metal oxides prepared by the LbL technique.

Substrate	Reagent for LbL synthesis ("+" component)	Reagent for LbL synthesis ("- component)	Synthesized layer composition	Properties, application	Ref.
ITO glass	PDDA-GR	NPs of Fe ₃ O ₄	(PDDA-GR/Fe ₃ O ₄) _n	H ₂ O ₂ detection	[34]
	PDDA	GO, TiO	(PDDA/GO/PDDA/TiO) ₂₀	high photocurrent generation and good reversibility	[35]
PMMA	PEI	GO, Ti _{0.91} O ₂	(PEI/Ti _{0.91} O ₂ /PEI/GO) _n	photocatalysis, solar cells, supercapacitors and sensors	[36]
GO	b-PEI	Ti-BALDH (titanium bis(ammonium lactato)-dihydroxide), HAuCl ₄)	(b-PEI)/TiO ₂ /Au) _n	anode material for LIB	[37]
GO	b-PEI	Ti-BALDH (titanium bis(ammonium lactato)-dihydroxide), CuCl ₂)	(b-PEI)/Cu-Ti-O) _n	photocatalysis	[38]
quartz	PEI	GO, Ti _{0.91} O ₂	Ti _{0.91} O ₂ /GR	functional separation of charge transport and storage	[39]
PMMA	PEI	GO, TiO ₂	(PEI/TiO ₂ /PEI/GO) _n	solar cells and light-emitting diodes	[40]

graphene-deposited ITO quartz glass, ITO	[Co(NH ₃) ₆] ²⁺	H ₂ O ₂	Co ₃ O ₄ /GR	electrocatalysts	[42]
glass/stainless steel	nafion/MnO ₂	nafion/GR	MnO ₂ /GR	supercapacitor	[43]
FTO	MnSO ₄	GO, NaOH	GO/Mn ₃ O ₄	supercapacitor	[44]
ITO	TiO ₂ nanofibers	graphene quantum dots (GQDs)	(TiO ₂ /GQDs) _n	photovoltaic devices	[45]
PSF ultrafiltration membrane	PDDA, TiO ₂	GO	[GNS/TiO ₂] _n	supercapacitor	[46]
native yeast cells	TiO ₂	GO	(TiO ₂ -GO) _n	photocatalytic membrane	[47]
quartz glass, ITO	yeast-(GO-NH ₃ ⁺ /PSS ⁻) & yeast-(PDDA ⁺ /GO-COO ⁻)	Fe ₃ O ₄	(GO-NH ₃ /GO-COO/GO-NH ₃ /Fe ₃ O ₄ / GO-NH ₃ /Fe ₃ O ₄) _n	biosensors, biomedical devices and tissue engineering	[52]
Ti	PDDA	PSS-GS, MnO ₂	(PDDA/PSS-GS/PDDA/MnO ₂) _n	supercapacitor	[53]
interdigital electrode (N-type (100) oriented silicon with SiO ₂ and Ti/Au)	PDDA	GO, PMA	(PDDA/GO/PDDA/PMA) _n PMA=H ₃ PMo ₁₂ O ₄₀	anode for LIB	[54]
quartz slides, PET plates, and PET fabrics	PDDA	GO, ZnO-PSS	(PDDA/rGO/PDDA/ZnO) _n	HCHO gas-sensing	[55]
glass, Si	PDDA	GO	rGO/ZnO	water-adsorbent separation, treatments of oil spills and industrial effluent	[56]
Silicon, glass	PDDA	GO, Ti _{0.87} O ₂	GO _n -(Ti _{0.87} O ₂) _n (Ti _{0.87} O ₂) _n -GO _n	tunable hydrophilicity under UV irradiation, liquid transport engineering	[57]
quartz glass	PDDA	rGO, Ti(O _n Bu) ₄ (titanium tetrabutoxide)	(rGO) _n -(TiO ₂) _n	self-cleaning optoelectronic devices with long-term efficiency	[58]
quartz slides	PDDA	GO, Ti _{0.87} O ₂	(PDDA/GO/PDDA/Ti _{0.87} O ₂) _n	channel material	[59]
	PDDA	MnCoNiO ₂ , rGO	(PDDA/MnCoNiO ₂ /PDDA/rGO) _n	pseudocapacitor	[60]

nanosheets and then drift along the rGO nanosheets thus producing photocurrent. Photocurrent produced by the synthesized multilayer retains high stability after a comparatively large number of cycles of exposure to solar radiation, even when it is put in the natural ambient conditions.

Another polyelectrolyte that is also being used in the LbL synthesis is PEI since its molecules are characterized by the relatively high density of positive charge [36]. In references [36-40], for example, PEI is used for the synthesis of nanocomposites

based on graphene and titanium (III, IV) oxides. These composites exhibit enhanced electrical conductivity performance due to the synergistic effect of its components acting together. They are considered to be promising materials in photocatalysis [36], in lithium-ion batteries [37], in photovoltaic devices and solar cells [38,39].

At the same time, there are studies where graphene nanosheets in a water suspension are reported to have positive charge formed by implanted NH₂-groups and in this case the synthesis is car-

ried out using solutions of polyelectrolytes with anionic molecules, for example polystyrene sulfonate (PSS) [41].

Summarizing this short overview of the domain of LbL synthesis of multilayers employing polyelectrolyte solutions it should be mentioned that in some cases the presence of polyelectrolyte molecules in a layer deteriorates its performance. In particular, these molecules reduce the electrical conductivity of the layer or block out active centers in the layer. For this reason, a vital topic from our point of view is the synthesis of multilayers in which polyelectrolyte solutions are not involved. As the reagents in this case may be chosen the solutions containing salts of the metals whose cations can form chemical bonds with negatively charged graphene nanosheets or the colloidal particles bearing positive charge.

A number of works on this subject can be found in at present the literature [42–47]. A combination of two techniques, a LbL synthesis and electrophoresis, was used to fabricate a nanocomposite film in Ref. [42]. For this purpose graphene layer was deposited by electrophoresis on the surface of ITO substrate. During this process negatively charged graphene nanosheets migrate toward the positively charged ITO substrate thus forming a thin graphene layer. In the course of further treatment by the solution containing cobalt ammine complex ion the latter adsorbs on the negatively charged graphene, the adsorption being caused by electrostatic attraction. Next, the adsorbed $[\text{Co}(\text{NH}_3)_6]^{2+}$ ions are oxidized to CoOOH by way of dipping it into H_2O_2 solution. The oxidation process is accompanied by formation of NH_3^+ , water, and $\text{CoO}(\text{OH})$ that transforms into Co_3O_4 after exposure to oxygen of the air. It was shown that the obtained $(\text{Co}_3\text{O}_4/\text{graphene})_n$ nanocomposite layer may be used in electrocatalytic reactions with oxygen as a reactant and as a photoelectrode in various devices.

$(\text{Gr}/\text{MnO}_2)_n$ composite material was synthesized by adsorption of positively charged micelles of manganese oxide on the negatively charged graphene surface [43]. The micelles acquired their positive charge as a result of modification of the surface of the manganese oxide nanoparticles by a surface active agent (surfactant) in the conditions of microemulsion synthesis. Cationic CTAB (hexadecyltrimethylammonium bromide) was taken as a surfactant. The charge of such micelles depends on the value of pH of the solution. For example, their charge becomes positive at pH 10 and this was exactly the solution chosen for the synthesis in [43].

$(\text{GO}/\text{Mn}_3\text{O}_4)_n$ composite was produced employing ion-ion interaction between nanosheets of manganese oxide and graphene oxide [44] by means of successive immersions of the substrate in the solutions of graphene oxide and manganese sulfate MnSO_4 for 40 and 20 s, respectively. This composite exhibits high specific capacity (344 F/g) and energy (93 W h/kg) as well as high stability at 3000-cycle trials. This is likely to be a result of blocking by the graphene nanosheets the dissolution of the Mn_3O_4 nanoparticles in the solution of electrolyte during the rapid charge-discharge cycles.

Layers composed of graphene and titanium dioxide nanofibers were synthesized on FTO substrate by the authors of [45], their photoelectric properties were also investigated in this study. It was established that the highest values of photocurrent could be recorded in the range of wavelengths 450–480 nm and above 520 nm. The authors suppose that photocurrent generated in the composite layer is a result of a transfer of the radiation-excited electrons from Gr into the conduction band of TiO_2 and their further migration to the surface of FTO substrate.

The authors of [46] in their investigation of specific capacity of a supercapacitor electrode made of $(\text{graphene}/\text{TiO}_2)_n$ nanocomposite multilayer made a conclusion that its value increases in the following order: $(\text{graphene})_{15} < (\text{TiO}_2)_{15} < (\text{graphene})_{15} + (\text{TiO}_2)_{15} < (\text{graphene}/\text{TiO}_2)_{15}$, the value corresponding to the last term of this chain being 2.3 times higher than the value corresponding to the second one. Furthermore, this last composition retains excellent, about 98%, stability after 1500 charge-discharge cycles.

An interesting feature of the research reported in [47] is that the authors took as a substrate a polysulfonic membrane modified by a composite based on graphene oxide and titanium dioxide. At the first step of the synthesis TiO_2 nanoparticles were adsorbed of surface of the membrane with the formation of Ti-O bonds between Ti^{4+} and sulfo groups and/or the formation of hydrogen bonds between hydroxyl groups of TiO_2 and sulfo groups. After this the membrane was treated in the suspension of graphene oxide, which formed a layer on its surface due to bonding of carboxyl groups and the active centers of titanium oxide. Examination of this membrane indicated that the synthesized layer enhanced water flow through the membrane as a result of photocatalytic promotion of its hydrophilicity. In addition, 60–80% increase of photodegradation rate of methylene blue under UV illumination was observed and 3–4-fold increase under visible light.

Considering the studies related to the synthesis of nanocomposites of graphene and metal hydroxides some investigations may be pointed out devoted to the synthesis of composites based on layered double hydroxides (LDH) [48–51] (Table 2). These compounds are perspective materials for electrodes of supercapacitors and photovoltaic devices.

Minimal thickness of the (CoAl LDH/GO)_n nanocomposite layer obtained in [48] was 4 nm, corresponding approximately to one monolayer of LDH and one monolayer of GO. Specific electrical capacity of such layer increased proportionally to the number of bilayers and at the rate of 5 mV/s its values were 19, 38, 55, and 70 F/m² for the films consisting of 10, 20, 30, and 40 bilayers, respectively. After reduction of GO to rGO by its treatment at 200 °C in hydrogen atmosphere the capacity per unit area reached 23, 51, 67, and 70 F/m² for the films of 10, 20, 30, and 40 bilayers, respectively, and the specific capacity increased from 900 F/g up to 1200 F/g.

In reference [49] the authors concluded that formation of the composite layer in their study was promoted by a pre-treatment of graphene with nitric and sulfuric acids. As a result the graphene surface was functionalized by the chemical groups which were active centers for precipitation of Co²⁺ and Al³⁺ ions attracted by the graphene nanosheets via electrostatic and Van der Waals forces. The synthesized samples demonstrated high specific capacity equal to 974.1 F/g at the scan rate 10 mV/s.

For the synthesis of (Co-Al-NO₃ LDH/ PVA/GO/ PVA)_n nanocomposite [50] reactions of adsorption of polyvinyl alcohol (PVA) with graphene oxide and LDH were used stimulated by hydroxy-, epoxy-, and carboxy-groups on the GO surface and by hydroxyl groups on the LDH surface, while for the synthesis of (graphene/TSCuPc/ MgAl LDH)_n nanocomposite [51] were used adsorption reactions of TSCuPc (3,4',4'',4'''-copper(II) phthalocyanine-tetrasulfonic acid tetrasodium salt) with the graphene surface via non-covalent π-π interaction and with LDH via electrostatic interaction.

The purpose of the present study was to examine the conditions of the LbL synthesis of the films composed of graphene and copper oxide. The first attempt of this synthesis was made in [61]. It has been previously shown that such nanocomposites are promising for use as anode material for lithium-ion batteries [62] and photocatalysts [63].

3. EXPERIMENTAL

Graphene suspension in water was obtained by electrochemical exfoliation of graphite EC-12 in (NH₄)₂SO₄ 1 M solution [64]. A solution of Cu[NH₃]₄(OAc)₂ was prepared by dissolving dry analytical grade salts Cu(OAc)₂·5H₂O (C = 0.01 M) and NH₄OAc (C = 0.1 M) in deionized water. The pH of the solution was 9.5 and adjusted by addition of NH₄OH solution. All reagents were obtained from Vekton LLC. As a substrates were used a polished

Table 2. Synthesis conditions and application fields of nanocomposites based on graphene and layered double hydroxides of metals prepared by the LbL technique.

Substrate	Reagent for LbL synthesis ("+" component)	Reagent for LbL synthesis ("- component)	Synthesized layer composition	Properties, application	Ref.
ITO, PET	Co-Al LDH-NS	GO	(Co-Al LDH-NS/GO) ₁₀₋₄₀	flexible electrode for supercapacitor	[48]
ITO	PDDA, mixture of 0.1 M CoCl ₂ ·6H ₂ O and 0.1 M AlCl ₃ ·6H ₂ O solutions	GNS, NH ₄ OH (pH=12)	(GNS)/cobalt aluminum (CoAl) layered double hydroxide (LDH)	electric double-layer (EDL) capacitance, pseudocapacitance	[49]
quartz glass slides	PVA	GO, Co-Al-NO ₃ LDH	(LDH/PVA/GO/PVA) _n	controllable electrode and switches, magnetic-electric sensors	[50]
ITO	P D A D M A C , LDH	GR	G/LDH	visible-light-driven-photovoltaic material	[51]
	P D A D M A C , LDH	G/TSCuPc	G/TSCuPc/LDH		

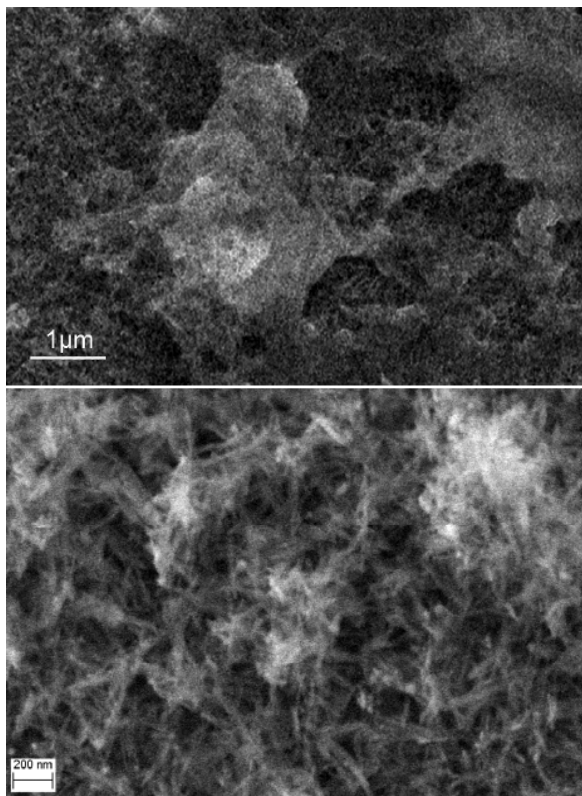


Fig. 3. SEM images of the nanocomposite layer on the silicon surface.

single crystalline silicon wafers with orientation $\langle 100 \rangle$ and resistance of 30–40 Ohm and nickel foam (NF) plates (110 PPI). Before the synthesis all substrates underwent preliminary preparation by the techniques described in [65]. One cycle of the LbL synthesis was formed by sequential treatment of the substrate in $\text{Cu}[\text{NH}_3]_6(\text{OAc})_2$ solution, distilled water, graphene suspension, and again distilled

water. The above sequence of the treatments was repeated from 30 to 60 times on a special “home made” automated setup.

Raman spectra were obtained on a SINTERRA Raman microscope. Vibrational modes were excited by a laser with $\lambda = 532 \text{ nm}$. The electron microscopy images of the synthesized samples were obtained via a Zeiss Auriga Laser scanning electron microscope at an accelerating voltage of 1 keV. XRD was applied on a Rigaku MiniFlex II diffractometer using the $\text{Cu K}\alpha$ -line as a source of monochromatic X-ray radiation.

Electrochemical characterization of the films was made by cyclic voltammetry and galvanostatic charge-discharge methods. Electrochemical measurements were made by Elins P-30I potentiostat in a three-electrode cell with a platinum plate as counter electrode and Ag/AgCl reference electrode with 1M KOH solution as an electrolyte. Cyclic voltammograms were recorded at with a potential sweep range between 0 and 0.8 V. Specific capacitance (C) of a nickel foam electrode with LDH layer was determined according to [30] as $C = I/(\Delta V/\Delta t) \times m$ (where I is a galvanostatic current, ΔV is the potential window, Δt is the discharge time of a cycle and m is the mass of the electroactive material in the film electrode).

4. RESULTS AND DISCUSSION

As it follows from the results of SEM analysis of the synthesized layers (Fig. 3) in the bulk of the nanocomposite one may distinguish nanosheets up to $2 \mu\text{m}$ in size and nanorods 10–12 nm in diameter and 150–200 nm long. Analysis by Raman spec-

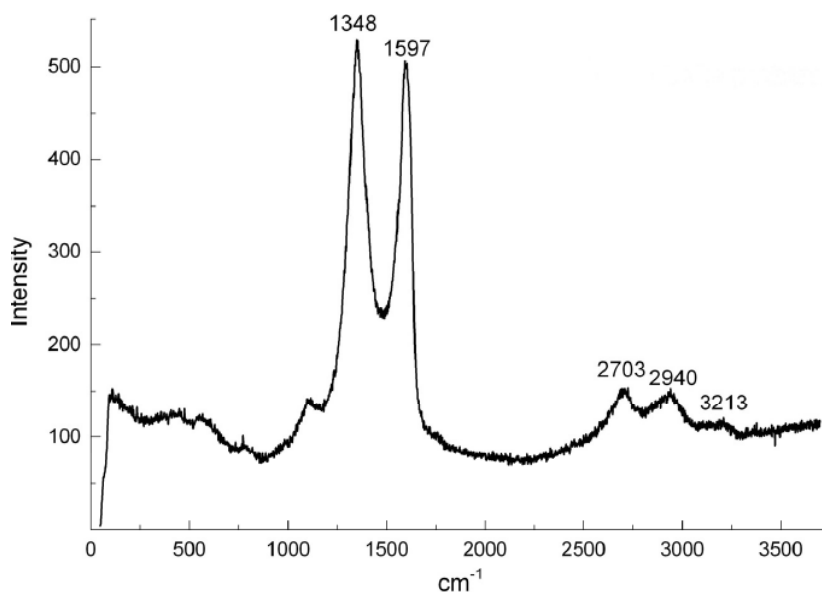


Fig. 4. Raman spectrum on the nanocomposite layer on the silicon surface.

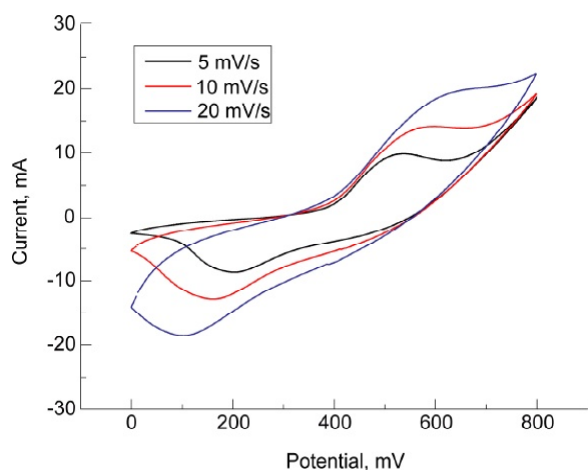


Fig. 5. Cyclic voltammograms of NF electrode, covered by graphene-CuO film, recorded at different scan rates. Current is normalized by square root of scan rate.

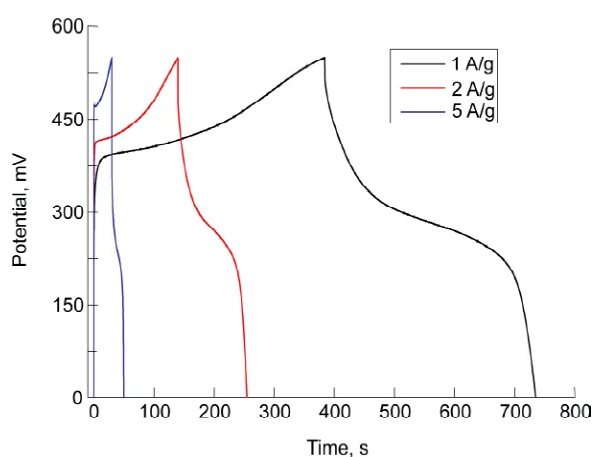


Fig. 6. Galvanostatic charge-discharge curves of NF electrode, covered by graphene-CuO film, recorded at different current densities.

troscopy (Fig. 4) makes possible identification of graphene layers in the films using 1348 and 1597 cm^{-1} peaks, while EDX spectroscopy and XRD method (not shown on figures) indicate the presence of CuO oxide with monoclinic crystalline structure.

Using these results the nanosheets could be attributed to graphene and nanorods – to copper oxide.

To interpret the observed processes of formation of the nanocomposite layer it may be supposed that when the silicon substrate is immersed in the solution of $\text{Cu}[\text{NH}_3]_4(\text{OAc})_2$ a layer of adsorbed ammine complexes of copper is formed on its surface. During subsequent rinsing of the substrate in water ammonium molecules are replaced by water molecules and hydroxyl groups. This substitution pro-

cess leads to formation of hydrate-hydroxyl complexes of copper and as a result of self-assembly these complexes form the nanorods of hydrated copper oxide with monoclinic crystalline structure. On the next stage of the synthesis procedure, when the substrate is dipped into the graphene suspension these nanorods become the centers of adsorption of the graphene nanosheets due to the reactions of interaction with the carboxyl groups of graphene and as a result a nanolayer of the composite forms.

To evaluate the potential applications in supercapacitors, Graphene-CuO layers has been used to make electrodes and characterization cyclic voltammograms and galvanostatic charge/discharge methods. As demonstrated in Fig. 5, two redox processes takes place in the layer, including $\text{Cu}^{1+} \rightarrow \text{Cu}^{2+}$ transformation at 560-600 mV and $\text{Cu}^{2+} \rightarrow \text{Cu}^{1+}$ transformation at 100-200 mV. Charge-discharge curves of nickel foam/Gr-CuO electrode at different polarizing currents (Fig. 6) allow one to determine it capacitance. For instance, specific capacitance of a sample, formed by 50 LbL cycles, is 700 F/g at current density 1 A/g. Prolonged cycling for 500 charge-discharge cycles demonstrates 6% capacitance fade relative to the initial values.

Electrodes based on layers obtained by LbL method, possess a higher specific capacity. These results can be explained by the formation of very fine nanocrystals (with 10-12 nm size) with high the specific capacity.

We believe that the layers of such morphology, composition and thickness may find application as a material for electrodes of supercapacitors and electrochemical sensors or electrocatalysts.

5. CONCLUSION

Summarizing the above discussion it should be noted that nowadays a new methods of the synthesis of graphene-based nanocomposites have emerged in the preparative chemistry, this methods are making use of the possibility to choose aqueous suspensions of graphene as one of the reagents. These suspensions may be used for preparation of nanocomposites both in the mixture mode, using such methods as sol-gel, co-precipitation, etc., and in the LbL synthesis in the course of successive and multiple treatment of the substrate by a number of reagents, which forms by interaction a layer of poorly soluble compound on the surface. The analysis of literature have shown that LbL synthesis with water suspensions of graphene usually employing in fabrication of nanocomposites contain-

ing metal-oxygen compounds and these compounds are of great interest for development of new photoelectrocatalysts, membranes, electrodes in electrochemical sensors, chemical power sources.

In particular, it was first demonstrated in the present study that multiple successive treatment of the silicon substrate with the solution of $\text{Cu}[\text{NH}_3]_4(\text{OAc})_2$ and aqueous graphene suspension results in the formation of a layer on its surface consisting of graphene nanosheets and copper oxide nanorods measured 10-12 nm in diameter and up to 200 nm in length. The study by cyclic voltammetry and galvanostatic charge-discharge techniques showed that the capacitance of the supercapacitor with such electrode is 700 F/g, and after 500 cycling it is reduced only by 6%. In our opinion the layers of this nanocomposite also may find application as constituents of electrodes of electrochemical sensors or electrocatalysts.

ACKNOWLEDGMENTS

This work was financially supported by the SPbSU grant (project # 12.38.259.2014). Some experiments was carried out as a part of RFBR grant (project # 15-03-08253). The synthesized samples were studied at the Resource Centers for X-ray Diffraction Studies, the Interdisciplinary Center for Nanotechnologies, and the Optical and Laser Materials Research, St. Petersburg State University.

REFERENCES

- [1] C.N.R. Rao, K.S. Subrahmanyam, H.S.S. Ramakrishna Matte, U. Maitra, K. Moses and A. Govindaraj // *Int. J. Mod. Phys. B* **25** (2011) 4107.
- [2] O.C. Compton and S.T. Nguyen // *Small* **6** (2010) 711.
- [3] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **34** (2013) 1.
- [4] Y.V. Konakov, I.A. Ovid'ko and A.G. Sheinerman // *Rev. Adv. Mater. Sci.* **37** (2014) 83.
- [5] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **38** (2014) 190.
- [6] V.G. Konakov, I.A. Ovid'ko, N.V. Borisova, E.N. Solovyeva, S.N. Golubev, O.Yu. Kurapova, N.N. Novik and I.Yu. Archakov // *Rev. Adv. Mater. Sci.* **39** (2014) 41.
- [7] I.A. Ovid'ko // *Rev. Adv. Mater. Sci.* **34** (2013) 19.
- [8] J.-F. Dai, G.-J. Wang, L. Ma and C.-K. Wu // *Rev. Adv. Mater. Sci.* **40** (2015) 60.
- [9] Q. Zheng, B. Zhang, X. Lin, X. Shen, N. Yousefi, Z.-D. Huang, Z. Li and J.-K. Kim // *J. Mater. Chem.* **22** (2012) 25072.
- [10] T. Liu, K. Wang, S. Song, A. Brouzgou, P. Tsiakaras and Y. Wang // *Electrochim. Acta* **194** (2016) 228.
- [11] Z.-S. Wu, G. Zhou, L.-C. Yin, W. Ren, F. Li and H.-M. Cheng // *Nano Energy* **1** (2012) 107.
- [12] Y. Ma, H. Chang, M. Zhang and Y. Chen // *Adv. Mater.* **27** (2015) 5296.
- [13] A. Ghosh and Y.H. Lee // *ChemSusChem* **5** (2012) 480.
- [14] K. Lü, G. Zhao and X. Wang // *Ch. Sci. Bull.* **57** (2012) 1223.
- [15] W.-J. Ong, L.-L. Tan, S.-P. Chai, S.-T. Yong and A.R. Mohamed // *Nanoscale* **6** (2014) 1946.
- [16] R.K. Upadhyay, N. Soin and S.S. Roy // *RSC Adv.* **4** (2014) 3823.
- [17] S.G. Chatterjee, S. Chatterjee, A.K. Ray and A.K. Chakraborty // *Sens. and Act. B: Chem.* **221** (2015) 1170.
- [18] B. Liu, X. Ouyang, Y. Ding, L. Lou, D. Xu and Y. Ning // *Talanta* **146** (2016) 114.
- [19] C. Fu, T. Chen, W. Qin, T. Lu, Z. Sun, X. Xie and L. Pan // *Ionics* **22** (2015) 555.
- [20] M. Onyszko, K. Urbas, M. Aleksandrak and E. Mijowska // *Pol. J. Chem. Technol.* **17** (2015) 95.
- [21] J. He, Y. Liu, Y. Meng, X. Sun, S. Biswas, M. Shen, Z. Luo, R. Miao, L. Zhang, W.E. Mustain and S.L. Suib // *RSC Adv.* **6** (2016) 24320.
- [22] V.P. Tolstoy // *Russ. Chem. Rev.* **62** (1993) 237.
- [23] T. Lee, S.H. Min, M. Gu, Y.K. Jung, W. Lee, J.U. Lee, D.G. Seong and B.-S. Kim // *Chem. Mater.* **27** (2015) 3785.
- [24] W. Fan, C. Zhang, W.W. Tjiu and T. Liu // *J. Mater. Res.* **28** (2013) 611.
- [25] K. Semishchenko, V. Tolstoy and A. Lobinsky // *J. Nanomater.* (2014) ID 632068.
- [26] L.B. Gulina and V.P. Tolstoy // *Thin Sol. Films* **440** (2003) 74.
- [27] V.P. Tolstoy and B. Altangerel // *Mater. Lett.* **61** (2007) 123.
- [28] B.S. Zhuchkov, V.P. Tolstoy and I.V. Murin // *Sol. State Ionics* **103** (1997) 165.
- [29] D.S. Dhawale, D.P. Dubal, M.R. Phadatare, J.S. Patil and C.D. Lokhande // *J. Mater. Sci.* **46** (2011) 5009.

- [30] L.B. Gulina and V.P. Tolstoy // *Russ. J. Gen. Chem.* **69** (1999) 1528.
- [31] L.B. Gulina, A.A. Pchelkina, K.G. Nilolaev, D.V. Navolotskaya, S.S. Ermakov and V.P. Tolstoy // *Rev. Adv. Mater. Sci.* **44** (2016) 46.
- [32] L.B. Gulina, G. Korotcenkov, B.K. Cho, S.H. Han and V.P. Tolstoy // *J. Mater. Sci.* **46** (2011) 4555.
- [33] L.J. Cote, J. Kim, V.C. Tung, J. Luo, F. Kim and J. Huang // *Pure Appl. Chem.* **83** (2010) 95.
- [34] X. Liu, H. Zhu and X. Yang // *Talanta* **87** (2011) 243.
- [35] H.-B. Yao, L.-H. Wu, C.-H. Cui, H.-Y. Fang and S.-H. Yu // *J. Mater. Chem.* **20** (2010) 5190.
- [36] W.G. Tu, Y. Zhou, Q. Liu, Z. Tian, J. Gao, X. Chen, H. Zhang, J. Liu and Z. Zou // *Adv. Funct. Mater.* **22** (2012) 1215.
- [37] B. Hao, Y. Yan, X. Wang and G. Chen // *Nanoscale* **5** (2013) 10472.
- [38] X. Wang, Y. Yan, B. Hao and G. Chen // *Dalton Trans.* **43** (2014) 14054.
- [39] K.K. Manga, Y. Zhou, Y.L. Yan and K.P. Loh // *Adv. Funct. Mater.* **19** (2009) 3638.
- [40] S. Bao, Z. Hua, X. Wang, Y. Zhou, C. Zhang, W. Tu, Z. Zou and M. Xiao // *Opt. Express* **20** (2012) 2233.
- [41] R. Ma and T. Sasaki // *Acc. Chem. Res.* **48** (2015) 136.
- [42] B.H.R. Sutyanto, X. Lu and C. Zhao // *J. Mater. Chem. A* **1** (2013) 12726.
- [43] D. Zhai, B. Li, H. Du, G. Gao, L. Gan, Y. He, Q. Yang and F. Kang // *Carbon* **50** (2012) 5034.
- [44] G.S. Gund, D.P. Dubal, B.H. Patil, S.S. Shinde and C.D. Lokhande // *Electrochim. Acta* **92** (2013) 205.
- [45] X. Wang, D. Ling, Y. Wang, H. Long, Y. Sun, Y. Shi, Y. Chen, Y. Jing, Y. Sun and Y. Dai // *J. Mater. Res.* **29** (2014) 1408.
- [46] W. Liu, X. Yan and Q. Xue // *J. Mater. Chem. C* **1** (2013) 1413.
- [47] Y. Gao, M. Hu and B. Mi // *J. Membrane Sci.* **455** (2014) 349.
- [48] X. Dong, L. Wang, D. Wang, C. Li and J. Jin // *Langmuir* **28** (2012) 293.
- [49] Y. Kim and S. Kim // *Electrochim. Acta* **163** (2015) 252.
- [50] D. Chen, X. Wang, T. Liu, X. Wang and J. Li // *ACS Appl. Mater. Interfaces* **2** (2010) 2005.
- [51] Q. Yang, J. Yang, F. Jiang and H. Zhao // *Adv. Eng. Mater.* **18** (2016) 141.
- [52] S.H. Yang, T. Lee, E. Seo, E.H. Ko, I.S. Choi and B.S. Kim // *Macromol. Biosci.* **12** (2012) 61.
- [53] Z. Li, J. Wang, X. Liu, S. Liu, J. Ou and S. Yang // *J. Mater. Chem.* **21** (2011) 3397.
- [54] F. Xia, X. Hu, Y. Sun, W. Luo and Y. Huang // *Nanoscale* **4** (2012) 4707.
- [55] X. Li, J. Wang, D. Xie, J. Xu, R. Dai, L. Xiang, H. Zhu and Y. Jiang // *Sens. Actuator B-Chem.* **221** (2015) 1290.
- [56] J. Wang, T. Tsuzuki, B. Tang, L. Sun, X.J. Dai, G.D. Rajmohan, J. Li and X. Wang // *Aust. J. Chem.* **67** (2014) 71.
- [57] P. Sun, M. Zhu, R. Ma, K. Wang, J. Wei, D. Wu, T. Sasaki and H. Zhu // *RSC Adv.* **2** (2012) 10829.
- [58] J. Zhu, Y. Cao and J. He // *J. Colloid Interface Sci.* **420** (2015) 119.
- [59] X. Cai, R. Ma, T.C. Ozawa, N. Sakai, A. Funatsu and T. Sasaki // *Nanoscale* **6** (2014) 14419.
- [60] M. He, L. Kang, C. Liu, Z. Lei and Z.H. Liu // *Mater. Res. Bull.* **68** (2015) 194.
- [61] I.A. Kodintsev, K.S. Reshanova and V.P. Tolstoy // *AIP Conference Proceedings* **1748** (2016) 040005.
- [62] B. Wang, X.-L. Wu, C.-Y. Shu, Y.-G. Guo and C.-R. Wang // *J. Mater. Chem.* **20** (2010) 10661.
- [63] B. Zeng, and H. Long // *Nanomater. Nanotechnol.* **6** (2016) 1.
- [64] K. Parvez, Z.-S. Wu, R. Li, X. Liu, R. Graf, X. Feng and K. Mullen // *J. Am. Chem. Soc.* **136** (2014) 6083.
- [65] L.I. Kuklo and V.P. Tolstoy // *Russ. J. Gen. Chem.* **85** (2015) 2528.