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Structural Properties of Graphene Oxide Materials Synthesized Accordingly to Hummers, Tour and Modified Methods: XRD and Raman Study

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Graphene oxide colloidal solutions were synthesized by Hummers and Tour methods and also accordingly to modified protocol. Hydrazine- and microwave-assisted routs of reduction procedure were used for each type of graphene oxides. A detailed comparative study of the structural arrangement was done for all obtained materials by XRD and Raman spectroscopy. The application of modified method for the graphene oxide synthesis which involves increasing the pH of the reaction medium at the stage of graphite oxidation using microwave-assisted reduction procedure allows obtaining reduced graphene oxide with the particles consisting of 2 - 3 graphene layers (particle's thickness is about 0.8 nm and the lateral size of about 7.6 nm).

Keywords: graphene oxide, reduced graphene oxide, structure, XRD, Raman spectroscopy.

Introduction

Carbon nanomaterials have an extrawide range of practical applications in all spheres, from medicine [1] to electrochemistry [2]. The main reason for its poly-functionality is the electronic structure peculiarities that allow obtaining of 2D- and 3D functional materials (graphene, multilayered structures) with unique properties. At the same time, large-scale production of such materials is complex and expensive. Reduced graphene oxide in some cases may become an affordable alternative of graphene, primarily for nanocomposite materials preparation [3, 4].

Graphene oxide (GO) is formed as a result of graphite powder oxidation and exfoliation of packages composed of graphene layers. For example, most widely used Hummers method involves the usage of $NaNO_3$ and KMnO4 solution in concentrated sulfuric acid [5]. There are a lot of Hummers method improvements and one of the most important changes was proposed by [6], where

graphite and $KMnO_4$ without $NaNO_3$ were treated in the mixture of H_2SO_4 and H_3PO_4. This approach allows obtaining respectively larger hydrophilic oxidized graphite material compared to Hummers method with fewer defects in the basal plane [7]. GO consisting of packages of hydrophilic graphene layers with interplanar distances from 0.6 to 1.2 nm embedded water molecules are obtained [8]. The ratio of C : O for graphite oxide is 1.6 - 2.57 [9] whereas for GO this parameter is 3 - 4 [10] and higher.

According to the most widely used and well-founded Klinowski-Lerf model [11] carbon atoms on the surface of graphene sheets form covalent bonds with oxygen-containing epoxy and hydroxyl groups located on the basal plane of the sheets, and also carboxyl, carbonyl and lactone groups localized on the edges of sheets [12]. GO is also hydrophilic due to surface hydroxyl groups presence and forms stable aqueous solutions with concentration up to 14 mg/ml [13]. Generally GO has amphiphilic properties caused by hydrophilic and hydrophobic groups localized at the edges of sheets and

in the basal plane, respectively. The amphiphilic properties of GO depend on the ionization degree of -COOH groups found at the edges of the graphene planes and on the pH value of the dispersion. The hydrophilicity of the GO packages rises with the increasing pH of the GO solution [14]. The most adopted approaches for reduced graphene oxide (rGO) obtaining are chemical [15], thermal [16], and microwave [17]. The properties of GO and rGO depend on many factors: the peculiarities of graphite oxidation, the degree of exfoliation of graphene sheets, the method and degree of reduction process. The improving of existing and the developing of new synthesis methods allow obtaining the functional materials with a controllable characteristics. In this work the comparative study of GO synthesized by Hummers and Tour methods and also accordingly to modified protocol has been accomplished. Two different variants (chemical and microwave-assisted) for obtaining solid-phase reduced graphene oxide were tested.

I. Experimental details

Synthetic graphite (Aldrich, # 282863) with particle sizes <20 μm was used as the starting material at GO synthesis.

GO synthesis details
Hummers (H) method

Graphite powder (4 g) was added to 180 ml of H_2SO_4 cooled to 0° C with continuous stirring for 4 hours, and with the subsequent addition of $NaNO_3$ solution. Potassium permanganate $KMnO_4$ (24 g) was added at the next stage at solution temperature less 5 °C with stirring for 20 - 25 minutes The resulting mixture was heated to 35 – 40 °C for 2 hours. The water (180 ml) and H_2O_2 (30 % aqueous solution) were added dropwise and the solution change color to yellow. The water (180 ml) was again added to the reaction medium. The obtained colloidal solution was ultrasonicated for 1 hour. Micrometric graphite particles were separated by centrifugation. The resulting material was repeatedly (5 - 7 times) washed with distilled water. The partially sedimented precipitate was washed with a HCl solution and ethanol to reach the pH value of about 6.5 - 7.0.

Tour (T) method

Graphite powder (4 g) was added to a mixture of H_2SO_4 (150 ml) and H_3PO_4 (30 ml), the resulting colloidal solution was cooled to 0°C with continuous stirring for 4 hours. $KMnO_4$ (24 g) was added at solution temperature less 5 °C with stirring for 20 - 25 minutes The resulting mixture was heated to 35 – 40 °C for 2 hours. Water (180 ml) and H_2O_2 (30 % aqueous solution) were added dropwise until the solution changed color to yellow. The water (180 ml) was added again. The obtained sol was ultrasonicated for 1 hour, large graphite particles were separated by centrifugation. The resulting material was washed with distilled water, HCl solution and ethanol to reach a pH of about 6.5 - 7.0.

Modified (M) method

Graphite powder (4 g) was added to 180 ml of H_2SO_4 cooled to 0 °C with continuous stirring for 4 hours. Potassium permanganate $KMnO_4$ (24 g) was added at the next stage at solution temperature less than 5 °C with stirring for 20 - 25 min. The resulting mixture was heated to 35 - 40° C for 2 hours. The water (180 ml) was added dropwise, the mixture was kept at room temperature for 2 hours with continuous stirring. The water (180 ml) was gradually added again and after that H_2O_2 (30 % aqueous solution) was added up to solution color change to yellow with next stirring for 30 min. At this stage, 30 % aqueous solution of NaOH (8 - 10 ml) was added with pH increased to 2.0 - 2.2 The obtained solution was ultrasonicated for 1 hour, and large particles were separated by centrifugation. The resulting material was washed with distilled water, HCl solution and ethanol to reach the pH value of about 6.5 - 7.0.

GO reduction details

Chemical and microwave-assisted methods of GO reduction were performed. GO colloidal solutions ultrasonicated for 2 hours before reductions. Chemical reduction involved the interaction of a colloidal GO solution (50 ml) with hydrazine hydrate (5 ml). The reducing agent was added dropwise to the GO solution with continuous stirring. The mixture was transferred into a Teflon-lined autoclave and heated at 120 ºC for 12 hours. The relatively low temperature of the reaction medium affirmed that it can be argued that a chemical method of GO reduction was realized. The resulting precipitate was washed with distilled water and ethanol, centrifuged and dried at 85 °C. The resulting material had the form of a fine-grained powder.
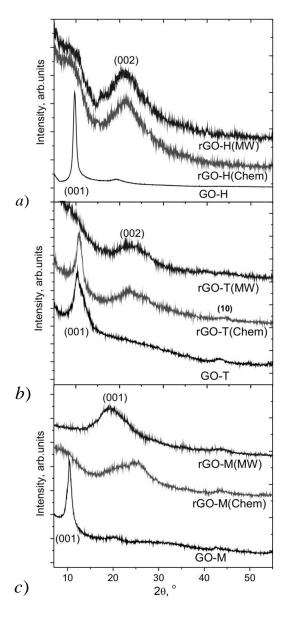
The microwave-assisted reduction was performed by placing dehydrated graphene oxide (brown-yellow film fragments) in a Teflon cup on a ceramic substrate with the next treatment in a microwave oven (Panasonis NN-SD382S, radiation power of 950 W). The irradiation consisted of 5 sessions for 20 seconds with idle intervals of 30 s. The resulting material had the form of a fine-grained powder with the morphology close to pyrogenic silica. The materials obtained by chemical reduction showed hydrophilic properties At the same time the microwave-assisted method causes the formation of hydrophobic rGO particles.

Graphene oxide samples were marked as GO-H, GO-T and GO-M for materials obtained by Hummers, Tour and modified protocols, respectively. rGO samples were marked with "Chem" or "MW" accordingly to the type of used reduction procedure.

Powder XRD patterns were obtained with DRON-3 (Cu Kα radiation, Bragg-Brentano focusing scheme, 30 kV x-ray tube voltage). Raman spectra were measured with T64000 Jobin-Yvon spectrometer (1800/mm, resolution of about 1 cm^{-1}) in reverse dispersion geometry, using an argon-krypton laser (λ = 488 nm). Laser irradiation power was less than 1 mW/cm^2 so the local overheating of samples was avoided.
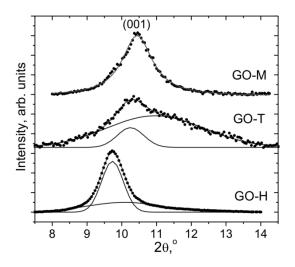
II. Results and discussion

Intense peaks at 2θ of about 10.07,11.28 and 10.44° were observed in XRD patterns of GO-H, GO-T and GO-M samples, respectively, that correspond to (001) diffraction reflex of the distorted graphite oxide lattice

a)

b)

c)

Fig.1. XRD patterns of GO samples synthesized according to Hummers, Tour and modified protocols as well as the XRD patterns of the materials obtained after reduction of these samples with chemical and microwave methods.

Fig.2. Deconvoluted (001) reflexes of GO samples synthesized according to Hummers, Tour and modified protocols.

(Fig. 1) [7].The approximation of symmetrical (001) reflexes for GO-H and GO-T samples with Gaussian functions (Fig. 2) allows to determining two most probable values of interplanar distance $d_{(001)}$ for these materials perpendicularly to the basal plane of graphene packages (Table 1). (001) reflexes for GO-M was symmetrical and approximated by one Gaussian functions only. The interplanar distances for GO depend on multiply factors, including the oxidation degree, the number of water molecules into the interlayer space as well as the lateral dimensions of the packages and the presence of chemisorbed functional groups on the graphene layers [18]. The distance between the basal planes for bulk graphite is 0.335 nm [19].

Two fraction of GO particles with the average $d_{(001)}$ values of 0.91 and 0.88 nm and also 0.86 and 0.81 nm was separated for GO-H and GO-T samples, respectively. Scherer's formula allow calculating the average size D of packages in the direction perpendicular to the (001) plane using the analysis of component's position (θ, rad) and its full width at half maximum (β, rad): $D = \dfrac{K\lambda}{\beta\cos\theta}$, where K=0.89. It was learned, that GO-H sample is formed by two types of packages – "thick" with an average thickness of about 12.5 nm which consist of 14 - 15 graphene layers and "thin" with the D value of 3.6 nm which consist of about 5 layers (content about 40 %).
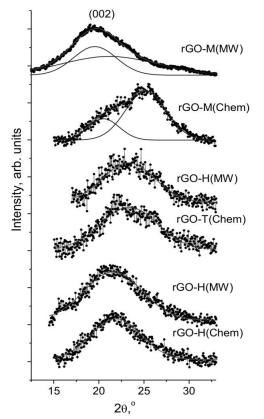
The two fractional composition was also observed for GO-T sample, but in this case "thin" particles with an average thickness of about 2.8 nm consisting of about 4 - 5 layers were dominant (about 85 mass %) compared to "thick" particles with a D value of about 10.3 nm (13 layers in package). The average values of $d_{(001)}$ for GO-H samples are relatively higher in comparison with the GO-T when the thickness of the packages is relatively larger.

Only one particle's fraction was observed for the GO-M sample that for $d_{(001)}$=0.85 nm and D = 7.5 nm corresponds to the average number N = 9 - 10 layers in

Table 1

Structural characteristics of GO samples obtained by Hummers, Tour and modified methods

GO-H				GO-T				GO-M			
$d_{(001)}$, nm	D, nm	N	Cont., %	$d_{(001)}$, nm	D, nm	N	Cont., %	$d_{(001)}$, nm	D, nm	N	Cont., %
0.91	12.5	14-15	59.6	0.86	10.3	13	14.6	0.85	7.5	9-10	100
0.88	3.6	5	40.4	0.81	2.8	4-5	85.4				

Fig.3. Deconvoluted (002) reflexes of rGO of rGO materials obtained after chemical and microwave reduction of GO samples synthesized using Hummers, Tour and modified protocols.

the package. The obtained results are generalized in Tab. 1.

The GO reduction consist of removing oxygen functionalities from graphene sheets. The main advantages of chemical reduction is the possibility of better process control. The hydrazine will react essentially with hydroxyl or epoxy groups when the reduction of carbonyl groups is less likely [20]. The hydrazine-assisted GO reduction is preferred for functionalities located at the interior of an aromatic domain of GO and the edges of an aromatic domains. At the same time the chemical reduction is a respectively slow process and the evolution of GO-rGO transition in hydrazine hydrate continues for tens of hours [21]. Microwave-assisted reduction is much faster but the process control and reproducibility of results are problematical. The comparative study of the structural arrangement of rGO samples obtained on the base of GO materials synthesized subsequently via different methods

was performed. The broadened peaks in the range of $2\theta = 15 - 35^{\circ}$ that corresponds to (002) reflex of rGO structure were observed for all XRD patterns. The presence of (001) reflex at $2\theta = 10.72^{\circ}$ in the XRD pattern of rGO-T(Chem) sample indicate the incomplete chemical reduction of this material. XRD data analysis applied to (002) reflexes with Gaussian functions (Fig.2, 3) allow estimation of the average values of $d_{(002)}$ and D for rGO particles (Tab. 2).

It was found that rGO samples obtained from GO-H and GO-T as a starting material regardless of the recovery procedure type are formed by particles with an average thickness of about 1.3 - 1.4 nm containing 4 - 5 graphene layers. The material obtained by on the base of the GO-T sample have relatively higher reduction degree (relatively less $d_{(002)}$ values) compared to GO-T-based rGO sampes.
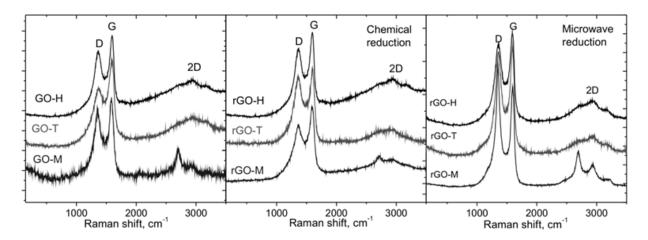
In contrast two fractions of particles were observed for GO-M-based rGO materials. Particles with an average thickness of 1.8 nm (5 - 6 graphene layers in package) are dominant for GO-M(Chem) sample when another part of the material is formed by the particles with an average thickness of about 2.3 nm which consist of about 6 - 7 layers. MW reduction of GO-M sample causes the formation of particles with an average thickness of about 0.8 nm (2 - 3 graphene layers in the package, fraction content of about 60 %) and 1.7 nm (4 - 5 graphene layers in the package). The reduction degree of these materials is the highest among the whole series: $d_{(002)}$ interplanar distances for particles with the smallest thickness (0.35 nm) are close to the bulk graphite characteristics (0.33 nm).

Raman spectroscopy allows to obtaining independent data about the structural arrangement of GO and rGO samples. Typical first-order Raman spectra of material consist of E_{2g} modes at about 1580 cm^{-1} that corresponds to in-phase vibration of the graphite lattice (G band) and peak at about 1350 cm^{-1} caused by the disordered structure of graphene sheets that represents the breathing mode of aromatic rings arising due to the defect formation (D band) [22]. The 2D peak at around 2700 cm^{-1} corresponds to double resonance transitions resulting in the formation of two phonons with opposite momentum. In contrast to the D peak which is observed ;at the presence of defects only, the 2D peak is active even in the defect free graphene lattice. This band is sensitive to the stacking order along the c-axis and the number of graphene layers in a package. Defect-activated D+G mode is also visible at around 2950 cm^{-1}. Raman spectra of GO samples synthesized according to Hummers, Tour and modified protocols, as well as the

Table 2

Structural characteristics of rGO materials obtained after chemical and microwave reduction of GO samples synthesized using Hummers, Tour and modified methods

	GO-H				GO-T				GO-M			
	$d_{(002)}$, nm	D, nm	N	Cont. %	$d_{(002)}$, nm	D, nm	N	Cont. %	$d_{(002)}$, nm	D, nm	N	Cont. %
Chem	0.40	1.4	4-5	100	0.38	1.3	4-5	100	0.43	2.3	6-7	25
									0.35	1.8	5-6	75
MW	0.41	1.3	4-5	100	0.38	1.4	4-5	100	0.45	1.7	4-5	40
									0.35	0.8	2-3	60

Fig. 4. Raman spectra of GO samples synthesized according to Hummers, Tour and modified protocols (a), as well as the Raman spectra of the materials obtained with the reduction these samples by chemical (b) and microwave (c) routs.

spectra of the rGO samples obtained with the reduction by chemical and microwave route are presented in Fig. 4.

The ratio between D and G bands integral intensity (I_D / I_G) is inversely proportional to the in basal (002) plane crystallite size of graphite [23]:

$$L(nm) = (2.4 \times 10^{-10}) \lambda^4 \left(\frac{I_D}{I_G} \right)^{-1} ,$$

where λ is the laser excitation wavelength. D and G bands were fitted using with two Lorentzian peaks (Fig. 5, a, c, e). This allows obtaining I_D and I_G and estimation of the lateral size of the GO and rGO particles. The obtained results are generalized in Table 3.

It was determined that the average lateral size of GO particle samples is about 8 nm regardless of the synthesis method. The reduction process causes the most considerable decrease in lateral sizes for a case of rGO materials obtained by the chemical method. In general, reduction-induced decreasing of particle's lateral sizes for rGO samples obtained from GO synthesized accordingly to modified protocol is respectively smaller than in materials obtained from GO samples synthesized with Hummers and Tour protocols.

Table 3

The ratios of D and G Raman bands integral intensities and lateral sizes of GO flakes synthesized according to Hummers, Tour and modified methods and also rGO particles obtained by chemical and microwave reductions

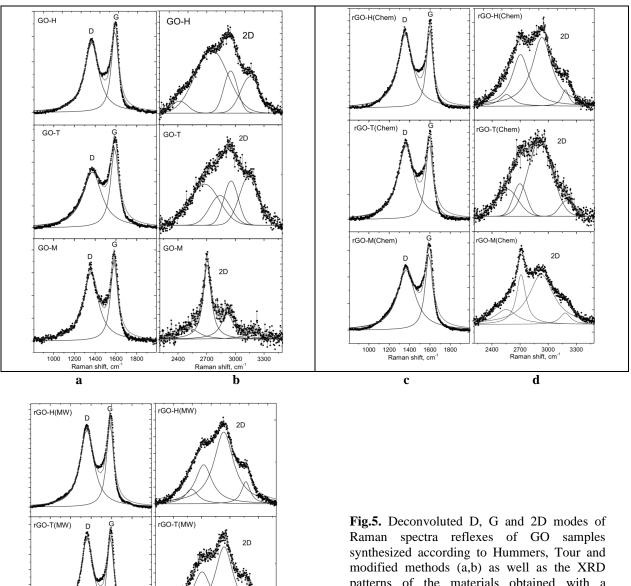| Sample	Hummers methods		Tour methods		Modified methods	
	I_D/I_G	L, nm	I_D/I_G	L, nm	I_D/I_G	L, nm
GO	1.70	8.0	1.66	8.2	1.81	7.5
rGO (Chem)	2.21	6.2	2.14	6.3	1.94	7.0
rGO (MW)	1.85	7.4	1.81	7.5	1.78	7.6

The formation and intensity changes of 2D Raman mode are caused by zone boundary phonons that do not satisfy the Raman fundamental selection rules and can be observed only in resonant conditions. As a result the analysis of 2D Raman mode allows obtaining the information about the number of graphene layers in the GO or rGO particles.
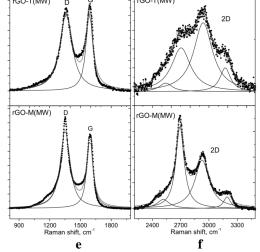
The number of constituent components of 2D mode is sensitive to the number of graphene layers in particles. For monolayer graphene D-band has a singlet structure but for a material where particles consist of 2-4 graphene layers D-band has a complex structure and splits into several components [24]. The next increase in the number of layers initiates the transition to the doublet structure of the D-band. At the same time the decreasing of of the number of layers causes the shift of the maximal intensity component position to a smaller wavenumber [25].

In our case the best results were obtained when 2D bands in Raman spectra of GO and rGO materials were fitted using four Lorentzian peaks (Fig. 5, b, d, f). The presence of an intensive and respectively narrow component in 2D bands of rGO materials obtained from GO synthesized accordingly to modified method corresponds to XRD data about the smallest number of graphene layers forming their particles. At the same time a close to doublet structure of the 2D band for GO-M sample indicate the respectively high numbers of graphene layers that is also consistent with the XRD data.

Conclusions

The comparative analysis of structural properties of graphee oxide samples synthesized accordingly to Hummers, Tour and modified methods was done. The main features of the proposed method of synthesis are the absence of $NaNO_3$, the controllable increase of the pH value of reaction media up to 2.0 - 2.2 at a stage of graphite powder oxidation and another algorithm of system dilution. It was determined that graphene oxides obtained accordingly to Hummers and Tour consist of

Fig.5. Deconvoluted D, G and 2D modes of Raman spectra reflexes of GO samples synthesized according to Hummers, Tour and modified methods (a,b) as well as the XRD patterns of the materials obtained with a reduction of these samples by chemical (c,d) and microwave (e,f) methods

two fraction of particles that are composed of about 13 - 15 and 5 - 6 graphene layers with a lateral size of about 8 nm. Graphene oxide obtained by the modified method consists of particles that are formed by 9 - 10 graphene layers with a lateral size of about 7 nm. Both chemical (hydrothermal treatment with hydrazine hydrate) and microwave-assisted reduction procedure applied to graphene oxide synthesized accordingly to Hummers and Tour causes the formation of particles consisting of 4 - 5 graphene layer with lateral sizes of about 6 - 7 nm. Chemical and microwave reduction of graphene oxide

synthesized accordingly to modified protocol causes the formation of materials with two fraction of particles. Particles with an average thickness of 1.8 nm consisting of 5 - 6 graphene layers are dominanting after the chemical reduction procedure. The microwave reduction of this graphene oxide causes the formation of the dominant fraction of particles with an average thickness of about 0.8 nm (2 - 3 graphene layers) with a high reduction degree as evidenced by the interplanar distance values close to bulk graphite characteristics. The reduction-induced decreasing of particle's lateral sizes

for rGO obtained from the graphene oxide synthesized by modified method is smaller compared to materials obtained from GO samples synthesized by Hummers and Tour methods.

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Структура оксидів графену, синтезованих методами Хамерса, Тоура та модифікованим способом: дослідження методами рентгенодифракційного аналізу та раманівської спектроскопії

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Колоїдні розчини оксиду графену синтезувалися методами Хаммера і Тоура, а також відповідно до розробленого оригінального протоколу. Кожен типу оксиду графену відновлювався хімічним (гідротермальна обробка з гідратом гідразину) та мікрохвильовим методами. На основі результатів, отриманих методами рентгенівської дифрактометрії та раманівської спектроскопії здійснено детальний порівняльний аналіз структурного впорядкування для всіх синтезованих матеріалів. Застосування модифікованого методу синтезу оксиду графену, який передбачав підвищення рН реакційного середовища на стадії окислення графіту, дозволив отримати в результаті процедури мікрохвильової обробки відновлений оксид графену з частинками, що складаються з 2 - 3 графенових шарів (товщина частинок становить близько 0,8 нм, латеральні розміри близько 7,6 нм).

Ключові слова: оксид графену, відновлений оксид графену, структура, рентгеноструктурний аналіз, раманівська спектроскопія.