



Multi-layer graphene oxide alone and in a composite with nanosilica: Preparation and interactions with polar and nonpolar adsorbates



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ABSTRACT

Freeze-dried multi-layer graphene oxide (MLGO), produced from natural flake graphite using ionic hydration method, demonstrates strong interactions of functionalized carbon sheets with polar or nonpolar adsorbates or co-adsorbates depending on the characteristics of dispersion media. Interactions of MLGO with a mixture of water and *n*-decane in chloroform media provide specific surface area (S_u) in contact with unfrozen liquids greater than 1000 m²/g corresponding to stacks with 3–5 carbon layers. Electrostatic interactions between functionalized carbon sheets in dried MLGO are very strong. Therefore, nonpolar molecules (benzene, decane, nitrogen) cannot penetrate between the sheets. Water molecules can effectively penetrate between the sheets, especially if MLGO is located in weakly polar CDCl₃ medium. In this case, *n*-decane molecules (co-adsorbate) can also penetrate into the sheet stacks and locate around nonpolar fragments of the sheets. The S_u value of MLGO being in contact with unfrozen water can reach 360 m²/g, but upon co-adsorption of water with decane $S_u = 930$ m²/g, *i.e.*, hydrophobic interactions of the mentioned fragments with decane are stronger than with co-adsorbed water. Water alone (0.25 or 0.5 g/g) bound to MLGO in a mixture with fumed silica A-300 in air or CDCl₃ media can provide $S_u = 30–50$ m²/g. Pores in wetted MLGO or MLGO/A-300 mainly correspond to mesopores. Nanosilica does not provide significant opening of the MLGO sheet stacks during their mechanical mixing.

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1. Introduction

Various carbons are important materials for industrial, medicinal and other applications [1]. Among them graphenes such as single (SLG) and multi (MLG) layer graphenes, single (SLGO) and multi (MLGO) layer graphene oxides are the most promising materials for applications in industry and medicine [1–10]. However, these materials remain relatively expensive (especially SLG and SLGO) despite significant reduction of their cost during last years. Therefore, searching of less expensive pathways of preparation of materials of graphene family is of great practical importance. One of these ways could be based on natural cheap raw and relatively pure

materials such as natural flake graphite treated, *e.g.*, using relatively cheap modified methods of preparation of graphite oxide [11,12]. An additional way to reduce the final cost can be based on preparation of composites with graphene materials and other cheaper materials, *e.g.*, fumed silica, natural disperse minerals, polymers, *etc.* Note that previous investigations of carbon materials in combination with fumed silica showed that carbon layers can practically completely cover the silica surface [13]. Note that graphene materials are effectively used in composites with various metal oxides [14–18].

In composites based on the graphene materials, their fundamental properties, caused by a specific 2D structure, relatively large sizes of carbon sheets, and significant amounts of O-containing functionalities in SLGO and MLGO, play an important role in adsorption of polar or nonpolar, low- or high-molecular weight compounds, reactions in the gas and liquid phases, electro-physical

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properties (e.g. anisotropic electro-conductivity), etc. [19–34]. Surface O-containing functionalities in SLGO or MLGO determine the behavior of these carbons in both gaseous and liquid media or composites [35–50]. Therefore, the efficiency of applications of the graphene materials depends strongly on control of the interfacial phenomena at their surfaces because these materials are very flexible and soft and can be collapsed and agglomerated or disagglomerated during heating, evacuation, changes in pH value of the solutions, presence of bound oxide or metallic nanoparticles, etc. [1–5,19,20,51–58]. Composites with graphene oxide and various metal oxides can be used as effective catalysts, adsorbents, polymer fillers, etc. [59–73], and interfacial phenomena play an important role in these composites per se and, therefore, in their applications. Preparation of a monolayer (or close) carbon coverage of the matrices (carriers) is of interest from both theoretical and practical points of view because the matrices are cheaper than SLGO or MLGO.

Interactions of the graphene materials with water and various aqueous solutions and suspensions are of importance because these materials are frequently used in the aqueous media. Features of these interactions depend on many factors such as types of dispersion media (humid air, aqueous or more complex media, pH, and salinity), content and structure of solutes or adsorbates and co-adsorbates, temperature, mechanical loading, etc. Therefore, investigations of the interfacial phenomena are of importance to control the properties of the graphene materials, including a thin layer of MLGO located at a surface of nanooxides, in different media, and these investigations were aimed in the present work for a deeper insight into the mentioned above problems.

MLGO produced from flake graphite as a precursor was studied alone and in a mechanical mixture with nanosilica A-300 located in different media (air, aqueous, CDCl_3 pure and with addition of CD_3CN , trifluoroacetic acid F_3CCOOD (TFAA), and non-deuterated *n*-decane), as well as adsorption of water, benzene, toluene, dimethylsulfoxide (DMSO), *n*-hexane, and *n*-decane and evaporation of water, *n*-hexane, and *n*-decane bound to MLGO. A variety of conditions, adsorbates and methods used allows us to accumulated information for better understanding the properties of MLGO studied.

2. Materials and methods

2.1. Materials

Multi-layer graphene oxide (MLGO) was prepared using natural flake graphite (Zaval'evsk coal field, Ukraine; flake sizes <0.2 mm) as a precursor using a modified method of ionic hydration described in detail elsewhere [11,12]. Briefly, a solution of concentrated H_2SO_4 (0.65 L) was added to 20 g of flake graphite, heated at 45 °C to appearance of blue color of graphite bisulphate and cooled to 10–15 °C. KMnO_4 (72 g) was added by small portions during constant stirring at 20 °C. The mixture was heated to 400 °C. It was stirred to a slurred state and then aged for 20 h at room temperature. Water (120 mL) was added with constant stirring at 45 °C. The mixture was maintained at 45 °C for 1 h, cooled to 10–15 °C, and 1 L of water was added, and then 70 mL of 28% H_2O_2 was added by small portions with constant stirring. The obtained mixture of light yellow color was centrifuged. The residue was suspended in 3% aqueous solution of HCl (2 L) and again centrifuged. The residue was suspended in bidistilled water and centrifuged, and this procedure was repeated four–five times to neutral pH of the suspension. The dried residue after final centrifugation was freeze-dried at –24 °C to 10^{-3} Torr. The MLGO samples were also dried and degassed by evacuation up to 10^{-3} Torr (this sample was studied only by DSC method). The final dry MLGO has very low bulk density and light brown color similar to that of commercial MLGO or SLGO (Cheap

Tubes, Inc.) used in comparative investigation with MLGO produced from natural flake graphite.

Fumed silica A-300 (Pilot plant of Chuiko Institute of Surface Chemistry, Kalush, Ukraine, $S_{\text{BET}} = 285 \text{ m}^2/\text{g}$, bulk density $0.045 \text{ g}/\text{cm}^3$) was used to prepare a mechanical mixture with MLGO (4:1 w/w) carefully stirred in a porcelain mortar. This A-300/MLGO ratio was selected because it provides the carbon amount enough to prepare a surface layer close to a monolayer coverage of nanosilica [13,53,54].

2.2. ^1H NMR

The ^1H NMR spectra were recorded at 200–285 K using a Varian 400 Mercury spectrometer of high resolution with the 60° probe pulses with the duration of 1 μs and a bandwidth of 20 kHz. The temperature of samples was controlled by means of a Bruker VT-1000 device with relative mean errors of ± 1 K. Relative mean errors smaller than $\pm 10\%$ for ^1H NMR signal intensity were determined for samples in different dispersion media. To prevent supercooling of the systems, the temperature dependences of concentration of unfrozen water and decane were determined on heating of samples pre-cooled to 200–210 K. The signals of water molecules from ice or frozen decane did not contribute the ^1H NMR spectra recorded here because of features of the measurement technique using static samples and narrow bandwidth [54]. Some details of the low-temperature ^1H NMR spectroscopy used are described in electronic Supplementary Information (SI) file.

Deuterated organic compounds (solvents CDCl_3 and CD_3CN) and trifluoroacetic acid F_3CCOOD (TFAA) and non-deuterated *n*-decane were used in low-temperature ^1H NMR spectroscopy measurements with static samples. Deuterated compounds were used to prevent their contribution into ^1H NMR signals of water and decane bound to MLGO or MLGO/A-300.

2.3. DSC

Differential scanning calorimetry (DSC) investigations of interactions of MLGO and A-300/MLGO with nonpolar (benzene, toluene, and *n*-decane) and polar (water and DMSO) or a mixture of water and decane adsorbates were carried out using a PYRIS Diamond (Perkin Elmer Instruments, USA) differential scanning calorimeter calibrated at different heating rates using standard samples such as distilled water (melting temperature $T_m = 0^\circ\text{C}$) and indium ($T_m = 156.6^\circ\text{C}$) supplied by the producer and using the recommended standard calibration procedure (see also the SI file).

On the basis of the methods sensitive to transition of phase (such as ^1H NMR and DSC), different versions of cryoporometry, relaxometry and thermoporometry were developed to study the structural and textural (specific surface area, S , pore volume, V , pore size distributions, PSD) characteristics of a variety of solid and soft materials and bioobjects in non-dried states [54,74–86].

2.4. Adsorption and desorption

To analyze the adsorption characteristics of MLGO, the adsorption of water and benzene was studied using an adsorption apparatus with a McBain–Bark quartz scale at 293 K. Samples were evacuated at 10^{-3} Torr and 473 K for several hours to a constant weight, then cooled to 293 ± 0.2 K, and the adsorption of water or benzene was studied at varied relative pressures p/p_s . The measurement accuracy was 1 ± 10^{-3} mg with a relative mean error of $\pm 5\%$.

Low-temperature (77.4 K) adsorption-desorption of nitrogen was measured using a Micromeritics ASAP 2420 adsorption analyzer.

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