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Chemistry of graphene oxide. Reactions with transition metal cations

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ABSTRACT

The main advantage of graphene oxide (GO) over its non-oxidized counterpart, is its ability to form stable solutions, due to exfoliation to single-atomic-layer sheets. At present day, the fine chemical structure of GO remains ambiguous, while the traditional characterization methods have exhausted their potentials in revealing GO chemistry. Here we employ the NMR relaxation method to monitor reactions between GO and the three transition metal cations Mn^{2+}, Gd^{3+} and Fe^{3+} while in solution phase. We demonstrate that interaction between GO and metal cations is chemical in its nature. The GO functional groups serve as ligands replacing water molecules from the metal cations' first coordination sphere. The functional groups interacting at different pH values have been identified and quantified. At least part of the functional groups interacting with metal cations in neutral and basic solutions are alcohols that have acidic character. The metal ion induced rearrangement of the oxygen functional groups on GO platform points at the highly dynamic nature of GO, confirming the main standing points of our earlier proposed Dynamic Structural Model. For Fe^{3+}, the polynuclear complexes with hydroxide ion bridges form on the surface of GO; the process of the seeding the nanoparticles on GO surface is recorded.

1. Introduction

Graphene oxide (GO) became one of the most intensively studied materials of the last decade, being successfully tested for numerous applications. In particular, nanocomposites of GO with several metals found being promising in energy storage, fuel cells and catalysis [1]. These composite materials consist of nanometer-scale particles of metals and/or metal oxides anchored to GO sheets. Despite numerous papers reporting formation and use of such nanocomposites, the mechanism of their formation remains elusive. It is not even clear if any interaction between GO and metal cations takes place prior to the nanoparticle grow. Understanding of these interactions, from one side, would help to control the process, and subsequently the parameters of as-grown nanoparticles. From another side, this would shed additional light on GO chemistry that remains ambiguous despite intensive research.

The classical way of learning about chemical structure of any new substance is studying how it behaves being subjected to certain chemical reactions. Thus, thorough investigation of chemical reactions, their correct interpretation would help in understanding the actual chemical structure of GO. Since the pioneering work by Lerf et al. [2], up to the present day, substantial body of the studies on GO chemical properties were focused on attempts of covalent functionalization of GO [3–6]. Despite the large number of publications claiming such functionalization, solid and unambiguous demonstration of covalent bonding between GO and reacting species is very difficult [6]. First of all, different functional groups on GO platform cross-influence each other, changing the chemical behavior from that described in classical organic chemistry textbooks. Secondly, even if such functionalization takes place, it is difficult to confirm. Strictly, formation of covalent bonds can be demonstrated only spectroscopically by elimination of original GO bands and rise of the new ones. With multifunctional GO this is very difficult [6], especially by the commonly used methods that analyze solid GO samples.

One of the main advantages of GO, making it different from its non-oxidized counterpart and other 2D materials, is its ability to form stable solutions, by exfoliating to single-atomic-layer sheets. Thus, a successful chemical reaction involving GO should be conducted in solution phase to provide easy and unimpeded access to GO surface. To investigate such reactions, one needs the instrumental techniques applicable to solutions. Note, today most of the traditional instrumental methods, used for GO characterization (^{13}C SSNMR, FTIR, TGA, Raman etc.), investigate the solid material; they miss a crucial information about the chemistry of GO in solution. In our opinion, traditional spectroscopic methods, broadly used for

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GO characterization, have exhausted their potential for revealing GO chemical structure. As an additional argument for this statement, the intensive and extensive studies of the last decade, despite some progress, have not brought us substantially closer to understanding GO chemistry. New, nontraditional approaches are needed today for studying GO chemistry.

In this report we investigate interaction of GO with three transitional metal cations in aqueous solutions. In contrast to the majority of GO related studies, we do not employ a solid GO product as a main indicator of chemical reaction. Instead, we monitor the reactants, while they are still in solution phase. More specifically, we use NMR relaxation method to monitor the environment of the three metal cations Mn^{2+}, Gd^{3+} and Fe^{3+}. This method was rarely used, if at all, in GO chemistry studies before. A few papers on this topic were focused mostly on preparing new contrast agents for MRI, but not on the chemistry of GO [7,8].

In this work, we investigate two different ranges of ratios between GO and metal cations. The ranges of equimolar ratios are studied by the NMR relaxation. The ranges with an excess of the metal salts were used to determine the upper limit uptake of the metals by GO; the as-prepared metal-GO composites, were investigated by traditional characterization methods.

2. Experimental part

2.1. Materials

All the reagents have been used as received, without additional purification. Sulfuric acid was from "Shchekinoazot" Trading House, LLC, Russia; nitric acid, hydrochloric acid, sodium hydroxide were from CJSC "TatHimProduct", Russia; potassium permanganate was from MCD Company, Russia. Manganese(II) chloride, manganese (II) nitarte, gadolinium(III) nitrate, iron (III) nitrate were all the "pure for analysis" grade.

2.2. Preparation of GO

GO was synthesized by the modified Hummers method according to the following procedure. Graphite flakes (10 g, 832 mmol) were dispersed in 96% sulfuric acid (680 mL) at room temperature using a mechanical stirrer. After 10 min of stirring, 1 wt equiv of $KMnO_4$ (10 g, 63.2 mmol) was added. The mixture became green due to the formation of the oxidizing agent MnO_3^+. Additional portions of $KMnO_4$ (10 g, 63.2 mmol each) were added when the green color of MnO_3^+ was diminished, indicating that the oxidizing agent was consumed. A total of 4 wt equiv of $KMnO_4$ were sequentially added. The end of the oxidation was always determined by the disappearance of the green color after each $KMnO_4$ addition. After complete consumption of $KMnO_4$, the reaction was quenched with 1400 mL of ice-water mixture, and 16 mL of 30% H_2O_2 solution was added to convert manganese by-products to soluble colorless Mn (II) ions. The reaction mixture was centrifuged 15 min at 8900 rpm to separate GO from acid. For purification, the GO precipitate was redispersed in DI water, stirred 30 min, and centrifuged 20 min at 8900 rpm to separate purified GO from washing waters. This constituted one purification cycle. Four more purifications were performed consecutively: one time with DI water and three times with 4% HCl. The GO precipitate after the last washing was dried in air. 18.2 g of air-dry GO was obtained.

2.3. NMR relaxation measurements

All the experiments and measurements were conducted at 298 K. "ThermoOrion 420A+" (Thermo Electron) pH-meter was used to measure acidity values of solutions, and was calibrated using standard buffers (pH 4.01, 7.00 and 9.00). Proton relaxation times $T_{1,2}$ were measured using pulsed NMR-relaxometer Minispec MQ20 from Bruker with operational frequency of 19.65 MHz by applying standard radio frequency pulse sequences: inversion-recovery method (spin-lattice relaxation time T_1) and Carr-Purcell sequence modified by Meiboom-Gill (spin-spin relaxation time T_2) with measuring accuracy error smaller than 3%. The temperature was maintained using Haake DC10 (Thermo Electron) cryo thermostat. The solutions for the relaxivity measurements were prepared by introducing certain amount of the 33% GO aqueous paste into the stock metal salt solution, and diluting the resulted solution in the volumetric flask to achieve the 0.5 mM concentration by metal cation. The concentration of metal ions in resulted solution was always 0.5 mM; the content of GO varied from 0.05 wt% through 0.40 wt%.

The as-prepared solutions, formed by mixing metal salts and GO, had pH~3, which is typical for aqueous GO solutions. To explore a broader pH range, small amounts of either HCl or NaOH solutions were added to the as-prepared metal-GO solutions, and the relaxivity at a given pH values was measured.

The experimentally measured relaxation times $(T_{1,2})_{obs}$, were inverted to the relaxation rates $\left(\frac{1}{T_{1,2}}\right)_{obs}$. The latter is the sum of the two main contributions: the relaxation of the protons located in the first coordination sphere of the paramagnetic ion $\left(\frac{1}{T_{1,2}}\right)_p$ (paramagnetic component), and the relaxation of protons in bulk water $\left(\frac{1}{T_{1,2}}\right)_d$ (diamagnetic component):

$$\left(\frac{1}{T_{1,2}}\right)_{obs} = \left(\frac{1}{T_{1,2}}\right)_d + \left(\frac{1}{T_{1,2}}\right)_p \tag{1}$$

The diamagnetic component for pure water is ~0.4 s^{-1}. Addition of GO into pure water increases this parameter up to 0.9 s^{-1} in the tested GO concentration region. The contribution of the diamagnetic component to the overall relaxation is small. In our experiments, for the neutral solutions, the contribution of the diamagnetic component to the overall relaxation rate was 1–2%. In the highly acidic and highly basic conditions it can increase up to 10% mainly due to the lowering the absolute value of the paramagnetic component. The paramagnetic component, $\left(\frac{1}{T_{1,2}}\right)_p$, was calculated as the difference between the measured relaxation rate $\left(\frac{1}{T_{1,2}}\right)_{obs}$ (measured for the metal-GO-water system), and the diamagnetic component $\left(\frac{1}{T_{1,2}}\right)_d$ (measured for GO-water). The value of the paramagnetic component, adjusted to the concentration of the paramagnetic metal cation, C_M, is usually denoted as the relaxivity, $R_{1,2} = \frac{1}{C_M(T_{1,2})_p}$. This parameter is used below to characterize the state of the metal ions (Mn^{2+}, Gd^{3+}, Fe^{3+}) in GO solutions.

2.4. Preparing highly metal-loaded M-GO composites

To prepare the M-GO composites, the metal salts and GO were mixed in the ratio where one metal cation was used toward two carbon atoms of GO framework.

To prepare high-Fe-GO, the 20.0 g of the 0.25M $Fe(NO_3)_3$ solution was added with stirring into the 20.0 mL of the 1.0% GO solution. The GO solution immediately turned opaque due to coagulation of GO flakes in the high ionic strength solution. The mixture stirred for 1 h. Next, the solution was centrifuged 30 min at