The scalable production of high-quality nanographite by organic radical-assisted electrochemical exfoliation.

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Abstract: One of the promising ways to produce graphene is the technology of graphite splitting or exfoliation, both by physical or mechanical and chemical, including electrochemical methods. The product of electro exfoliation is nanographite, which is transformed into multigraphene at the subsequent stage of liquid-phase mechanical and ultrasonic disintegration. This approach demonstrates a successful method of obtaining multigraphene from available graphite raw materials. Since, already at a potential of 1.23V, during the electrolysis of water on a graphite anode, the hydroxyl anion is discharged with the formation of a very active hydroxyl radical oxidizer, it is not surprising that when the graphite electro exfoliation process is overvolted at 10V, graphite oxidation products are formed. In order to control the defectiveness of the graphene lattice by oxidation products, we carried out processes of graphite exfoliation in the presence of both a number of reducing agents ascorbic acid, sodium borohydride, hydrazine hydrate, and in the presence of industrial antioxidants radical traps (2,2,6,6-tetramethylpiperidine-1-yl)oxyl (TEMPO), (2,2,6,6-tetramethyl-4 oxopiperidine-1-yl)oxyl (IPON), a mixture of 5,8,9-bis isomers[(2,2,6,6-tetramethyl-4 oxopiperidine-1-yl)]–[5,8,9-1,1’-bi(cyclopentylidene)]-2,2’,4,4’-tetraene (YARSIM-0215). It should be noted, that the best result of preventing the oxidation of nanographite in electro exfoliation technology in our studies is the ratio of carbon to oxygen (C/O) about 69.

1. Introduction
The uniquely high mobility of carriers, exceptional mechanical and optical properties, and high thermal conductivity have advanced graphene as a precursor material for new opto and nanoelectronics [1]. One of the limiting factors in the use of graphene in electronics and other areas of use is the lack of industrial scalable, inexpensive methods for the production of graphene derivatives (multigraphenes) with low defects. One of the promising ways to produce graphene is the technology of graphite splitting or exfoliation, both by physical or mechanical and chemical, including electrochemical methods.

At the initial stage of the technology, graphite undergoes electrochemical exfoliation in an aqueous solution of ammonium sulfate at DC and a voltage of 10 V in a potentiostatic mode. The product of electro exfoliation is nanographite, which is transformed into multigraphene at the subsequent stage of liquid-phase mechanical and ultrasonic disintegration. This approach demonstrates a successful
method of obtaining multigraphene from available graphite raw materials [2]. Such physical methods of graphite exfoliation as: grinding in ball mills, cleavage with adhesive tape, make it possible to obtain relatively low-defect graphene, but with a very low yield at the level of units of percent. Chemical exfoliation methods are usually based on modified Hammer methods and are used to produce graphene oxides. These methods are easily scaled, the output of products is close to quantitative. However, these chemical methods have a number of significant drawbacks. The result of exfoliation is oxidized graphene derivatives that do not possess graphene properties due to the strong defectiveness of the graphene lattice with oxygen. Even after the reduction stage, the so-called reduced graphene oxide contains a significant amount of oxygen, which is not completely removed.

2. Experiment

2.1. Electrochemical exfoliation

The exfoliation process was carried out on a homemade installation in which GRAFLEX graphite foil was used as the anode, and platinum foil was used as the cathode at a constant current, voltage of 10 volts in a potentiostatic mode. A 3M aqueous solution of ammonium sulfate electrolyte with antioxidant additives was used as the electrolyte. Such as ascorbic acid, hydrazine, sodium borohydride, dimethyl sulfoxide (DMSO), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), 2,2,6,6-tetramethyl-4-one-piperidin-1-yl)oxyl (IPON), Dimer (2,2,6,6-tetramethylpiperidin-1-yl)oxyl-fulvalene (YARSIM-0215). In acidic electrolytes, anions intercalate into the graphite anode, causing its cleavage. Along with splitting, the processes of decorating the graphite structure with oxygen are underway, including radical processes involving hydroxyl radical [3].

The exfoliated graphene sheets were then transferred onto a Si/SiO2 substrate using the Langmuir−Blodgett method. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EMF) by means electron microscopes SUPRA-40 and QUANTA 300i were used to study the morphology of graphene flakes on the SiO2 surface, the size of hundreds of micrometers, and the carbon and oxygen content in the sample. In general, the efficient intercalation of electrolyte into graphite interlayer and the subsequent gas eruption are the key factors governing graphite exfoliation. Since, already at a potential of 1.23V, during the electrolysis of water on a graphite anode, the hydroxyl anion is discharged with the formation of a very active hydroxyl radical oxidizer, it is not surprising that when the graphite electro exfoliation process is overvolted at 10V, graphite oxidation products are formed.

3. Results and discussion

3.1. A mechanism of anodic exfoliation

The mechanism of exfoliation of anodic graphite in an aqueous solution of (NH4)2SO4 was proposed by Parvez et al. in 2014 [3] (figure 1). Hydroxyl anions formed during electrolysis of water at the anode (OH-) are a strong nucleophile that enters into nucleophilic substitution of hydrogen at the sp2 carbon atoms of the aromatic ring at the grain boundaries, forming two vicinal phenolic OH (1) groups. The series-parallel reactions 2 and 3 are dehydration reactions with the formation of oxyrane cycles and carbonyl groups, respectively. Reactions 4 - 6 are channels of gas formation of oxygen and carbon dioxide contribute to the expansion of the interlayer space of graphite layers and the advancement of ions deep into the graphite crystal.

The scheme of the graphite exfoliation process in the presence of a radical scavenger (nitroxy radical trap TEMPO.) was illustrated in figure 2.
These gases also assist in the exfoliation of the graphite layers [3]. Along with reaction 1, a hydroxyl radical strong oxidizer (SHE) = -2.8 V was generated at the anode at an overvoltage of 10 V by reaction 6. Reaction 7 of radical addition of hydroxyl radical by the double bond of the aromatic core lead to products similar to reaction 1. In our previous study [4], we identified the products of electrochemical exfoliation of graphite as oxidized nanographite with 20-30 graphene layers. In order to control the defectiveness of the graphene lattice by oxidation products, we carried out processes of graphite exfoliation in the presence of both a number of reducing agents ascorbic acid, sodium borohydride, hydrazine hydrate, and in the presence of radical traps (2,2,6,6-tetramethylpiperidine-1-yl)oxyl (TEMPO), (2,2,6,6-tetramethyl-4 oxo-piperidine-1-yl)oxyl (IPON), a mixture of 5,8,9-bis isomers\{(2,2,6,6-tetramethyl - 4 oxo-piperidine-1-yl)\}–{5,8,9-[1,1' bi(cyclopentylidene)]-2,2',4,4'-tetraene}(YARSIM-0215).

3.2. Experimental data
The G-band of Raman scattering spectra for sp2 carbon atoms is observed as a single or multiplicative peak near the frequency of 1585 cm\(^{-1}\) for all carbon structures of sp2 hybridization. The G\(^1\) - band is also defined by sp2 carbon atoms as a single peak or a multi-peak structure in the range of 2500-2800 cm\(^{-1}\) in figure 3.
The sensitivity to the details of the sp2 structure makes this band a powerful indicator for determining the number of layers of graphene layers in a stack. The Raman spectrum of disordered graphene shows two new sharp peaks around 1350 cm\(^{-1}\) peak D and 1620 cm\(^{-1}\) peak D\(^1\). These inter-valley D and intra-valley D\(^1\) defect-induced resonant scattering processes are mainly responsible for electron decoherence in the optical and transport phenomena of sp2 carbon atoms. These bands are also blurred and, therefore, their actual positions depend on the laser excitation energy. D-band basic Raman frequency sp2, attributed to disorder and defects. Since absolute intensity is rarely used in Raman spectroscopy, the normalized I\(D\)/I\(G\) intensity is widely used for quantitative measurements of the degree of defect (disorder). Equation 1, obtained for determining the size of the crystal regions of graphene L\(_a\) and the defect density, or in other words, the distance between the defects, depending on the energy of the exciting radiation used in the visible range [5,6]

\[
L_a(\text{nm}) = \frac{560}{E_{laser}^{1/4}} (I_D/I_G)^{1/4} = (2.4 \times 10^{-10}) E_{laser}^{1/4} (I_D/I_G)^{1/4}
\]

For a laser with a wavelength of 532 nm, the defect density \(n_D\) can be represented by equation 2.

\[
n_D \left( \text{cm}^{-2} \right) = (2.16 \times 10^{11}) \frac{I(D)}{I(G)}
\]

For a honeycomb ideal lattice, the number of carbon atoms is \(N_c = 3.82 \times 10^{15} \text{ cm}^{-2}\). If you normalize the number of defects in equation 2 by \(N_c\), you can get the concentration of defects per cm\(^{-2}\) in millionths (ppm). The Table 1 shows the results of processing the spectra of graphite samples obtained under various exfoliation conditions.

| \(n\) | D/\(\lambda_{max}\) | G/\(\lambda_{max}\) | G\(^1\)/\(\lambda_{max}\) | I\(_D\)/I\(_G\) | I\(_G\)/I\(_G\) | \(N_D/N_c\) (ppm) | Reaction conditions |
|------|-----------------|-----------------|-----------------|----------|----------|----------------|-------------------|
| 1    | 495  1346 cm\(^{-1}\) | 523  1581 cm\(^{-1}\) | 152  2711 cm\(^{-1}\) | 0.95     | 0.29     | 53             | no additives       |
| 2    | 368  1346 cm\(^{-1}\) | 391  1581 cm\(^{-1}\) | 120  2711 cm\(^{-1}\) | 0.94     | 0.31     | 53             | Ascorbic acid 0.4% by weight |
| 3    | 506  1346 cm\(^{-1}\) | 472  1581 cm\(^{-1}\) | 165  2711 cm\(^{-1}\) | 1.07     | 0.35     | 60             | Hydrazine Hydrate 0.4% w |
| 4    | 495  1346 cm\(^{-1}\) | 523  1581 cm\(^{-1}\) | 152  2711 cm\(^{-1}\) | 0.95     | 0.29     | 53             | Sodium borohydride 0.4% w |
| 5    | 210  1346 cm\(^{-1}\) | 518  1581 cm\(^{-1}\) | 177  2711 cm\(^{-1}\) | 0.41     | 0.34     | 23             | TEMPO 0.4% w         |
| 6    | 367  1346 cm\(^{-1}\) | 806  1581 cm\(^{-1}\) | 261  2711 cm\(^{-1}\) | 0.46     | 0.32     | 26             | DMSO 0.4% w           |

\(^{a}\)The density of graphene structure defects according to Equation 3 in ppm

The analysis of the results of Table 1 clearly demonstrates the dependence of the conditions for the electro-exfoliation of graphite on the size and density of defects in the crystal lattice (the basal plane of graphene) of graphite. Thus, carrying out the process without oxidation inhibitors, but with reducing agents: ascorbic acid, hydrazine hydrate, sodium borohydride leads to approximately the same result. That is, it does not significantly affect the density of defects, in contrast to the fact that the use of TEMPO and DMSO significantly reduces the density of defects by 2.5 to 3 times. Probably, a noticeable decrease in the defect density was associated with the blocking of the hydroxyl radical as an oxidizing agent of the basal plane of the graphene crystal lattice by scavengers of radicals by DMSO or TEMPO molecules.

| Graphene products | Approaches | C/O ratio |
|-------------------|------------|-----------|
| Original graphite foil «graflex» | | 48.11 |
| Exfoliated graphene | Pt electrode | 16.95 |
| Electrochemical | 0.05M (NH\(_4\))\(_2\)SO\(_4\) | |
The main mechanism of hydroxyl radical formation is the neutralization of the hydroxyl anion on the graphite anode, and since it has a high oxidation potential, it is necessary to use radical traps to bind the attacking radical.

It should be noted, if the molecules of industrial antioxidants (TEMPO, IPON) interaction with hydroxyl radical in accordance with the scheme shown in Figure 2 and are practically not consumed in the oxidation reduction cycle, whereas DMSO is consumed during the reaction, forming a neutral non-radical compound methanesulphinic acid through a series of successive stages.

4. Conclusion
A method of electrochemical exfoliation of graphite in an aqueous solution of an electrolyte of 3M ammonium sulfate by DC at a voltage of 10 V in a potentiostatic mode has been developed. The exfoliation product is a high-quality nanographite with a good yield close to quantitative. The use of antioxidants in the process allows you to regulate the degree of oxidation and bring the carbon/oxygen ratio to 69. Commercially available and inexpensive reagents, a fast process, and the absence of by-products make such a process promising for industrial scale.

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References
[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 J. Science 306 666
[2] Parvez K, Wu Z-S, Li R, Liu X, Graf R, Feng X and Müllen K 2014 J Am Chem Soc 136 6083-91.
[3] Yang S, Brüller S, Shuai Wu Z, Liu Z, Parvez K, Dong R, Richard F, Samori P, Feng X and Müllen K 2015 J. Am. Chem. Soc. 137 13927–32.
[4] Savinsky N G, Melesov N S, Parshin E O, Vasiliev S V, Bachurin V I and Churilov A B 2020 Bulletin of the Russian Academy of Sciences: Physics 84 N 6732–735.
[5] Paton K R et al 2014 Nat. Mater. 13 624.
[6] Eckmann A, Felten A, Mishchenko A, Britnell L, Krupke R, Novoselov K S and Casiraghi C 2012 Nano Lett. 12 3925–30.