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Analysis of Properties of Oxidized Graphene Dispersions for 2D Printing Obtained by Electrochemical Exfoliation of Graphite

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Abstract. Due to its unique properties, graphene is a promising material for a wide range of applications, including for printed electronics. Suspensions of graphene and reduced graphene oxide (rGO) are in demand for creating conductive layers for 2D and 3D printing. Currently, technologies for the preparation of suspensions and inks from these materials are being actively developed. In this paper we consider a rather simple method for obtaining suspensions of oxidized graphene for 2D printing using a dispersant and analyzing the comparison of the structural and electrophysical characteristics of the obtained samples with samples in obtained using ultrasound.

INTRODUCTION

2D printing is characterized by low cost of the technological process, the ability to print on different substrates, including flexible ones. It is a cheap approach, alternative to technologies based on the use of lithography, allowing the creation of electronic components of instrumentation devices. The creation of structures based on graphene and reduced graphene oxide opens up new opportunities for future electronics. Currently, the application areas of this technology include touch screens, various sensors, radio frequency identifiers and labels, photovoltaic elements, light emitting diodes and electronic textiles, supercapacitors and thin-film batteries and much more [1, 2, 3, 4]. The paper[5] shows the electrochemical exfoliation of graphite in an aqueous solution of ammonium sulfate with different concentrations in combination with ultrasound. In this technique, the oxidation and exfoliation take place simultaneously and a high yield of exfoliation flakes is provided for a short time [6, 7]. It was found that the degree of oxidation of graphene is not monotonically dependent on the concentration of electrolyte. At electrolyte concentration 0.15 M was found to have the lowest oxidation degree. Thus, the suspension obtained at an electrolyte concentration of 0.15 M looks most promising for use, such as a water-based ink for the creating of conductive layers in flexible electronic and photonic devices. However, the search for new ways to synthesize suspensions for 2D printing is relevant. It is interesting to compare the properties of suspensions obtained by electrochemical exfoliation combined with ultrasound and a dispersant.

METHODS

In [5], the electrochemical exfoliation of graphite was carried out in an electrolyte on the basis of an aqueous solution of ammonium sulfate $(NH_4)_2SO_4$ at a concentration of 0.15 M and sonicated (IL100-6 / 3, 750 W) for 1 hour. In this paper, after electrochemical exfoliation of graphite, the suspension was treated, instead of ultrasound, with a dispersant (IKA Ultra-Turrax T18 digital) at 15,000 rpm for 2 hours. In both samples, an industrial electrode was used as the graphite electrode and the samples was filtered through a track-etched membrane with the pore size of 0.4 μm. According to the literature, the inks for inkjet printing require the thickness of the flakes in inks less than a few nanometers to obtain smooth films, and the lateral dimensions should be approximately 50 times smaller than the

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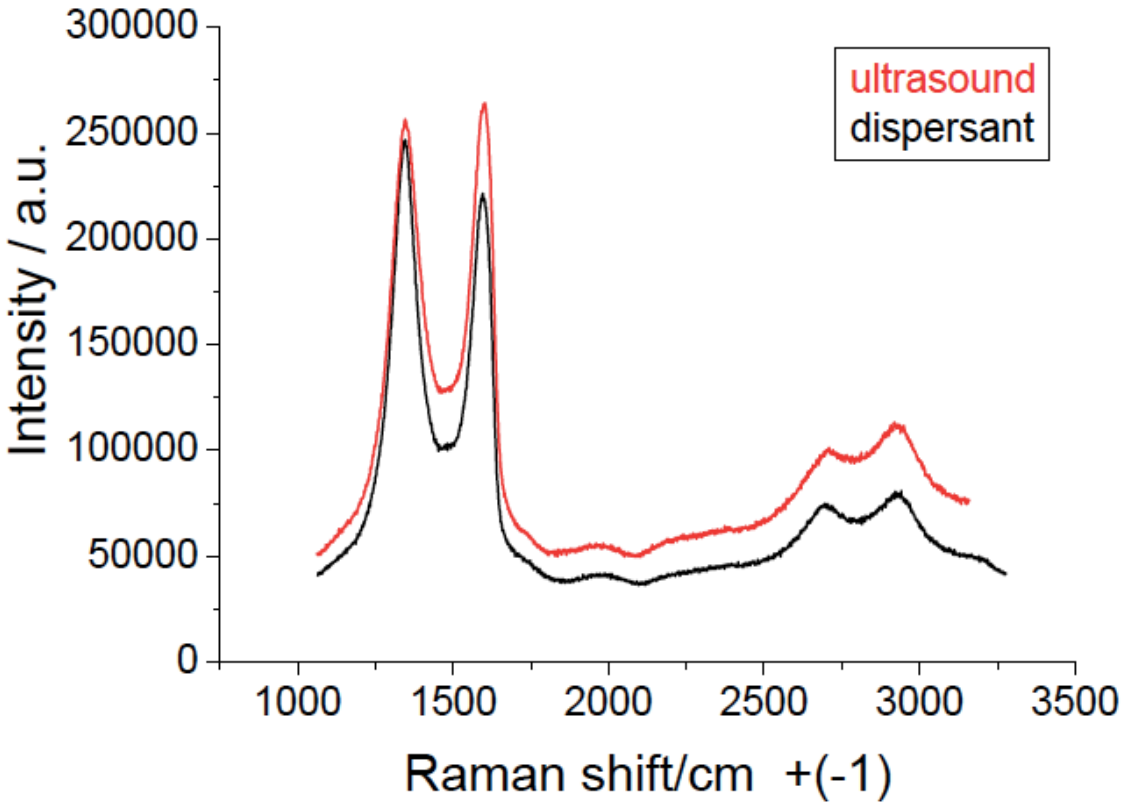

FIGURE 1. Raman spectra of samples obtained using ultrasound and dispersant.

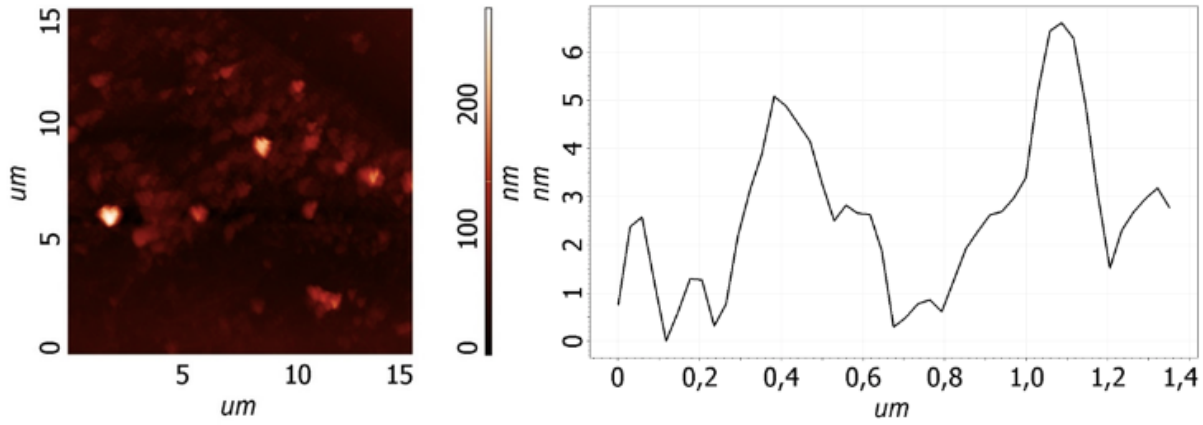

FIGURE 2. AFM image of flakes of oxidized graphene obtained using a dispersant and a height profile drawn through individual particles.

nozzle diameter to avoid the printer nozzle clogging. A Solver Next (NT-MDT) atomic force microscope (AFM) in the non-contact scanning mode was used to determine the thickness and lateral dimensions of the flakes. The Raman spectra were measured by the setup Ntegra Spectra (NT-MDT) at the green laser excitation with the wavelength of 532 nm. To study the thermal reduction and the conductivity of the films obtained by the drop casting method on the SiO_2/Si substrate from suspensions. To measure the volt-ampere characteristics, ohmic contacts were formed on the films from silver paste, and then a complex of automatic determination of the electrophysical parameters of ASEC-03 materials was used to diagnose the films.

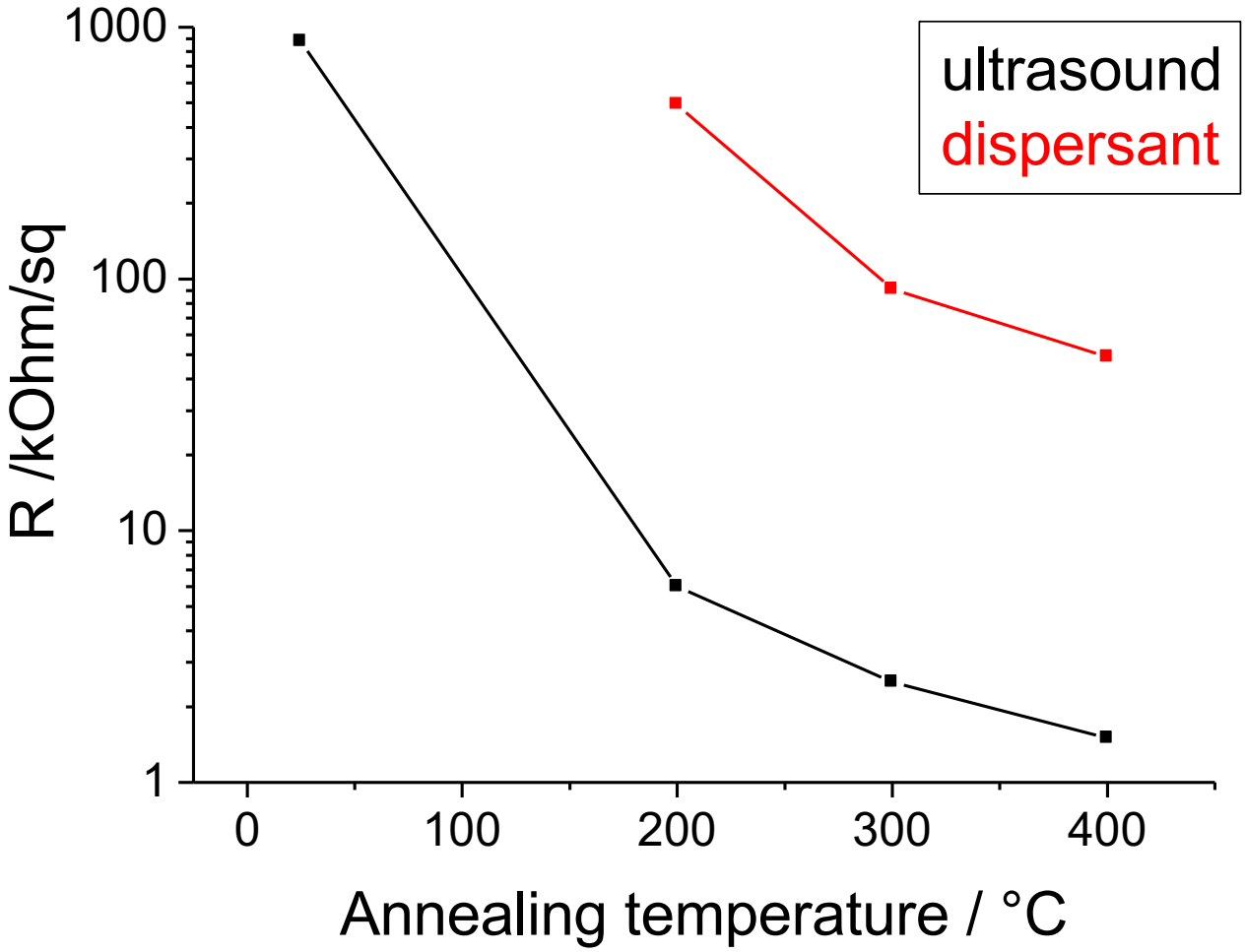

FIGURE 3. Dependence of resistance on annealing temperature.

RESULTS AND DISCUSSION

It is well known that the Raman spectra of graphene have several features: the G band (1580 cm-1) corresponds to the primary in-plane vibration mode; the D band (about 1350 cm^{-1}) is known as a disorder band or defect band and the 2D band (about 2700 cm^{-1}) is the second order of D band. Only the G and 2D bands are presented in the Raman spectrum of ideal graphene and graphite. The D band is not presented because it requires defects to be activated.

Such defects may be grain boundaries, edges, other defects of the crystal lattice and sites with the state of sp^{3-} hybridization. Some carbon atoms in GO are well known to include oxygen functional groups or. In other words,

they have sp^{3-} hybridization states. It is reflected in the appearance of intense D band and the decrease of 2D band intensity [5]. Figure 1 shows the Raman spectra of the samples. The Raman spectra of both samples differ little. The ratio between the intensities of D band and G band ID/IG is often used to estimate the defect density in graphene sheets [8, 9]. It can be seen from figure 1 that the ratio of ID / IG intensities is slightly higher in the sample using a dispersant, this may indicate that in this flakes the defect is more.

Figure 2 shows an AFM image of sample flakes with a dispersant. The lateral dimensions of flakes are less than 1 micron, and their thickness varies from nanometers to several tens of nanometers. Thus, in samples of ultrasound [5] and dispersant application, the lateral dimensions and thicknesses of the flakes can be considered to be practically the same.

Figure 3 shows the electrical resistance curves from the reduction temperature. It can be seen that in the sample of using a dispersant, the sample has a greater resistance than in the sample of ultrasound. At room temperature, the sample with the dispersant had too much resistance, on the graph it is not reflected. At a temperature of 400° C, the sample with ultrasound has a resistance of 1.5 $kOhm/kq$ [5], with a dispersant - 49 $kOhm/kq$. The difference in resistances in both samples may be due to the difference in film thicknesses and the different oxidation of graphene flakes.

CONCLUSION

Thus, in samples of ultrasound and dispersant application for delamination of graphite, the lateral dimensions and thicknesses of flakes are almost identical. The difference in resistance may be due to the different defects, oxidation of graphene flakes and film thicknesses in both sample and requires further research.

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