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# Electrical conductivity and optical properties of water-based graphene/AgNWs hybrid inks for flexible electronics

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**Abstract.** The present study provides the description of water-based inks made of hybrid graphene-silver nanoparticles conductive fillers in a wide concentration range for printed electronics applications. Aqueous graphene suspensions were manufactured via ultrasonic exfoliation of pristine graphite, whereas polyol synthesis was used to obtain silver nanowires. Hybrid suspensions were centrifuged to improve transmittance while retaining electrical conductivity. As a result, we successfully manufactured conductive transparent films with transmittance up to 96%.

**Keywords:** conductive ink, graphene, silver nanowires, flexible electronics

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# Электропроводность и оптические свойства гибридных чернил на основе графена и серебряных наностержней в водной среде для гибкой электроники

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**Аннотация.** В настоящем исследовании представлено описание гибридных чернил, изготовленных из проводящих графеновых частиц и наночастиц серебра в широком диапазоне концентраций. Водные суспензии графена были изготовлены путем ультразвуковой эксфолиации исходного графита; для получения серебряных наностержней был использован процесс полиольного синтеза. Гибридные суспензии подвергались центрифугированию для повышения оптического пропускания при сохранении уровня электропроводности. В результате были успешно изготовлены проводящие прозрачные плёнки с коэффициентом пропускания до 96%.

**Ключевые слова:** электропроводящие чернила, графен, серебряные наностержни, гибкая электроника

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## Introduction

Flexible electronics have shown great potential for applications in various areas of human life. Applications include flexible printed circuit boards [1], flexible electrodes for displays [2–4], antennas [5], wearable skin sensors [6], etc [7]. The growing need in printed electronics causes increased interest in manufacturing of new materials that meet optical and electrical requirements.

Since the most common and simple method for flexible electronics production is inkjet printing technology, there are also specific requirements for inks in terms of particle size and other important parameters to consider, such as viscosity, adhesion, sintering temperature and so on [8]. In particular, the solvent must dry sufficiently quickly, but not so fast as to clog the nozzle.

Thus, manufacturing inks with suitable properties is a challenging task. Firstly, the choice of conductive filler must be made. Among suitable materials are conducting polymers, carbon nanotubes (CNTs), graphene and metal nanoparticles (MNPs) of various shapes [9]. Despite its advantages, all of the abovementioned inks have their shortcomings.

Currently, the most widely used inks are based on silver nanoparticles or nanowires due to their excellent electrical conductivity [10]. Another commonly used option is graphene-based ink because of its excellent electronic and mechanical properties [11]. However, both of these ink types have limitations as well. Specifically, high concentration of AgNPs and high sintering temperature are required to achieve desired conductivity values, or low conductivity of pure graphene ink that limits its widespread use. Moreover, high cost of Ag increases processing cost. Combination of graphene and AgNWs solves cost-effectiveness problems by reducing the concentration of AgNWs. Simultaneously, it increases conductivity, and graphene improves the mechanical performance of AgNWs for flexible electronic applications.

Further questions arise regarding the solvent used in inks. This choice can serve as a separate topic for research because of its importance [12], since the ability to use inkjet printing technology depends mostly on the properties of the solvent. For example, it must have the required viscosity and surface energy. Moreover, it is necessary for the solvent to have low boiling point in order to apply inks on plastic substrates. Many options are often limited by toxicity and cost, therefore, the use of water is most environmentally friendly and economically viable way. Thereby, in this work water was chosen as a suitable option for graphene exfoliation, while polyol synthesis in particular requires ethylene glycol.

## Experimental section

Graphene suspensions were obtained using the ultrasonic exfoliation technique described in [13]. As a precursor, 300 mg of pristine graphene GE-1 (GOST 17022-81) was used and added to 50 ml of water. Due to the hydrophobic nature of graphene, exfoliating graphite in water is particularly challenging and requires the aid of surfactants. Therefore, in the obtained graphite suspension (6 mg/ml) has been added 0.6 mg/ml of ZONYL BA-L surfactant. The suspension was then subjected to a 7.5-hour ultrasonic exfoliation on an ultrasonic homogenizer with an acoustic power of 100 W at a frequency of 22.5 kHz, which led to stable conductive suspensions of graphene. Further sonication hardly changes particle size distributions.

Suspensions of AgNWs were manufactured via polyol process. The main advantage of this process is the ability to vary wide number of parameters to obtain the required result [14]. In this study, 150 mg of silver nitrate was reduced with ethylene glycol (EG) at 178 °C in the presence of KBr, AgCl and polyvinylpyrrolidone ($10^6$ g/mol).

In order to determine the effect of the mass ratio of graphene on the characteristics of the resulting suspensions, 7 hybrid suspensions were made with different mass graphene loadings: 15, 25, 35, 50, 75, 85 wt.%, the volume of each was 20 ml. All hybrid suspensions were then placed in an ultrasonic bath with operating frequency of 35 kHz and sonicated for 30 minutes in order to achieve homogeneity.

For the purpose of transparent and free of agglomerates hybrid suspensions, 10 mL of suspensions were sonicated in an ultrasonic bath for 10 minutes and subjected to centrifugation for 45 minutes on centrifuge Hettich EBA 280 with 2000 rpm. Transparent suspensions and the sediment remaining on the walls of the flasks were separated from each other.

Conductivity measurements were made using SevenCompact Cond meter S230 and conductivity sensor InLab 710 (Mettler Toledo). Measurements of initial suspensions of graphene and silver were taken immediately after the synthesis. Initial hybrid suspensions were measured after sonication, while centrifuged suspensions' conductivity measurements were made directly after centrifugation in order to eliminate the influence of agglomeration on conductivity.

Before measuring properties, suspensions were sonicated in an ultrasonic bath for 10 minutes in order to reduce possible agglomeration. Particle size distributions for initial suspensions were measured using laser diffraction method on Microtrac SYNC (Microtrack MRB). For measuring size of smaller particles of suspensions after centrifugation Zetasizer Nano (Malvern) was used.

Thin films were made by drop-casting 0.4 ml of ink on glass substrate with dispenser and drying for 1 hour at 100 °C. Sheet resistance was calculated using precision source-measuring unit b2901a (Agilent) from current-voltage curves (linear region slopes) in a four point-probe cell.

Optical characteristics, e.g. transmittance and absorbance, were measured for centrifuged suspensions, both in liquid and in films, via UV-Vis absorption spectrophotometry (Agilent Cary 60).

**Results and discussion**

Graphene/AgNWs hybrid inks with graphene content 0, 15, 25, 35, 50, 75, 85 and 100 wt.% were prepared and then centrifuged in order to achieve satisfactory transparency and dispose of agglomerates. The resulting properties for initial and centrifuged inks are shown in table 1.

Table 1

**Graphene/AgNWs hybrid inks conductivity**

| Graphene content, wt.% | | 0 | 15 | 25 | 35 | 50 | 65 | 75 | 85 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|
| Conductivity, μS/cm | Initial | 110.7 | 161.0 | 192.2 | 222.6 | 240.1 | 278.9 | 300.1 | 264.3 | 67.9 |
| | Centrifuget | 105.9 | 188.2 | 231.1 | 274.0 | 327.4 | 356.0 | 348.4 | 280.8 | 121.3 |

As can be seen from the Table 1, centrifugation increases the conductivity of suspensions, apart from AgNWs' suspension. This may be due to the removal of agglomerates and thus obtaining smaller and better conducting particles. The best conductivity among the initial suspensions is observed at a mass content of graphene of 75%. However, after centrifugation this peak shifts to 65%, although the difference in conductivity is rather small.

Results (Fig.1) show that the particle size obtained is small enough to meet the basic requirements necessary for a non-clogging printer nozzle. Centrifugation reduces the particle size by several times and at the same time increases the conductivity of the suspensions.

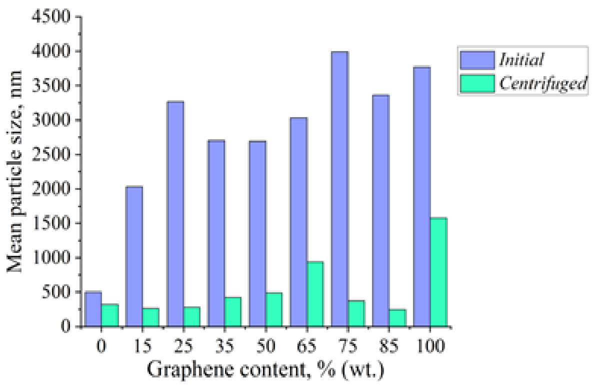


Fig. 1. Particle size distribution depending on graphene content for initial and centrifuged suspensions

In addition to reducing the size and increasing the conductivity, centrifugation provided sufficient transparency; Figure 2 presents UV-visible absorption spectra of the produced inks. The results for optical characteristics are given for the most conductive of the suspension, as well as for centrifuged AgNWs and graphene.

As can be seen from the spectra and Table 1, although transparency is lowest for 75 wt.% suspension, its conductivity is the highest of all hybrid suspensions. However, the 65 wt.% suspension that differs fairly little in conductivity, has excellent transparency.

Although it is expected that the absorption of the films will correlate with the absorption of suspensions, the obtained results (Fig. 3) show a different dependency.

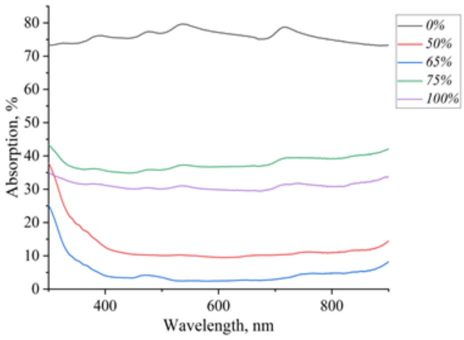


Fig. 2. Suspensions' absorption depending on graphene content

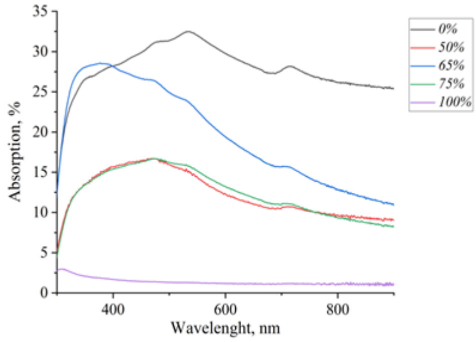


Fig. 3. Films absorption depending on graphene content

For example, better transmittance instead of 65% hybrid is obtained for hybrids with 50 and 75 wt.% graphene content. In general, obtaining hybrids in the form of films increases their transmission, although it should be taken into account that one layer is not enough for printed paths to be conductive.

Hybrids in the form of films are distinguished by the presence of an absorption peak in the region of 400–450 nm. This local maximum of absorbance indicates the presence of silver nanoparticles. The obtained absorption spectra are similar to the spectra obtained by the authors [15] for similar graphene-silver hybrids.

This difference in absorption for films and suspensions can be explained by the obvious drawbacks of the film deposition method. Despite the fact that the same amount of ink is applied to the substrate, the distribution of the liquid over the surface is always different. This leads to the need to work on improving the adhesion of suspensions to the substrate.

Sheet resistance was measured for films obtained from initial suspensions, since even multilayer deposition of centrifuged suspensions has not yet given satisfactory results in terms of conductivity. Obtained characteristics are shown in the table below.

Table 2

**Sheet resistance of films from initial suspensions**

| Graphene content, wt.% | 15 | 25 | 35 | 50 | 65 | 75 | 85 |
|---|---|---|---|---|---|---|---|
| Sheet resistance, $10^{-3}\cdot\Omega$/sq | 48.0 | 28.6 | 3.1 | 4.5 | 11.3 | 48.9 | 5.7 |

Despite the fact that suspensions with a graphene content of 65–75% have the highest conductivity, we obtained the best sheet resistance of $3.1\cdot10^3$ Ω/sq for film with 35 wt.% graphene content. An inconsistent result may be associated with the measurement method that damages the films. This, in turn, leads to the conclusion that ways to increase film adhesion for more adequate measurement resukts are needed.

## Conclusion

In this work, we manufactured water-based graphene/AgNWs hybrid inks. Their electrical conductivity and optical transmittance were measured. Best conductivity value of 356 μS/cm and excellent transparency up to 96% obtained for centrifuged suspension with 65% graphene mass content. However, the highest transparency in the form of films has the one made from 75% hybrid suspension, that is only 2.5% less conductive than 65 wt.% graphene content hybrid. The best sheet resistance for drop casted thin films of $3.1\cdot10^3$ Ω/sq is observed in the film with 35% graphene mass content.

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