

Stability of graphene suspensions in an aqueous based multi-component medium

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Abstract

The stability of multi-component graphene based ink solutions for its optimization and alignment with complex requirements of inkjet printing technologies is considered in the present study. Stable compositions of a four-component suspension (graphene, water, ethanol, and ethylene glycol) were analyzed with the use of Hansen solubility parameters and their experimental corrections. Realization of a set of the stable suspension composition showed that the droplet forming conditions at inkjet printing were fulfilled in all cases. From the point of view of printed layer drying and suppression of the coffee ring effect, it was found that the ethylene glycol concentration has to be lower than 20%. Printing by inks, which fit the optimal composition in all respects, has demonstrated good electrical characteristics, namely, the layer resistance of 3 – 15 k Ω /Y for lines with a 20-40 nm thickness. Copyright © 2018 VBRI Press.

Keywords: Inkjet printing, graphene suspension, stability of ink solutions, printed layers properties.

Introduction

The increase in the number of materials used in printed electronics is one of the main approaches in electronic industry, allowing creating cheap lightweight electronic devices for a wide range of applications [1]. Printing technologies have several attractive features such as mask-free patterning, purely additive operation, compatibility with proven materials, and scalability for large-area production [2]. Currently, the two-dimensional (2D) printing technology for fabricating devices is an important trend in the development of modern electronics and photonics [2,3]. Moreover, 2D printing technologies are the basis for the development of flexible, foldable, wearable, and transparent electronics [1,2,4,5].

Two-dimensional layered materials such as graphene and reduced graphene oxide are widely used as conductive layers on flexible substrates due to their excellent mechanical properties. Graphene is a well-known material that is stretchable up to 25% [6]. Generally, for the past few years, graphene-based materials have attracted tremendous scientific interest because of their unusual mechanical, optical and electronic properties. To make full use of these materials there is a need for methods of mass production which allow advancing from the conceptual laboratory research to large-scale applications [7].

In the present study the stability of multi-component graphene – water-based ink solutions for its optimization and alignment with complex requirements of inkjet printing technologies is considered. As a result, stable compositions of a four-component suspension were

found, printed layers were created. The study of structural and electrical properties demonstrates excellent properties of printed layers.

Basic foundation of graphene suspension stability for 2d printing technologies

Stability of multi-component solutions

The lifetime of the ink is directly related to the issue of stability of the material particles in the selected solution and the presence of surfactants or organic solvents used in particles exfoliation [8]. In the case of an unstable solution, all flakes precipitate on the bottom, resulting in a reverse process, the formation of clusters and/or their clogging. To avoid this phenomenon, the surface-active substances (surfactants) are used to encapsulate flakes, preventing them from clogging and resulting in the system stabilization. It is known, that surfactants degrade the properties of printed layers; moreover, to eliminate surfactants it is necessary to apply annealing at 200^oC and higher [9].

Graphene flakes are stable in fluids having similar surface energies (surface tensions σ) [10], the Hildebrand solubility parameter δ [11] or more detailed Hansen Solubility Parameters (HSP) [12]. But almost all liquids satisfying these conditions are organic; they greatly deteriorate the electric properties of particles and sometimes functionalize graphene, thus, drastically changing its properties [13].

Materials dispersion in liquids can be described by a semiempirical theory of Hansen solubility parameters [14–16]. The dispersion is described with three

parameters: δd , δp , and δh , which relate to the energies from dispersion, intermolecular forces and hydrogen bonds between molecules, respectively. Thereat, the degree of the solution stability is characterized by similar HSP parameters of substance and solution (the lesser the difference of individual parameters is, the better the stability is). Furthermore, the Hildebrand parameter is expressed through HSP (equation 1), and substances with a similar Hildebrand parameter have a good solubility/stability.

On the other hand, there is an analogous situation with substances having similar surface tensions: the lesser the difference between the surface materials is the more stable the suspension is.

Difficulties arise when trying to choose a solution, consisting of several components, to stabilize the material. Handling Hansen and Hildebrand solubility parameters in this case is easier, as the resulting parameters may be presented as a linear combination of components (equations 2 and 3). In the case of surface tension, it is difficult to use this approach, since it is impossible to present a surface tension function as a linear sum of fractions.

In this work, using the semiempirical theory of Hansen, we have calculated suspensions that are optimal from the point of view of stability and consist of four components: graphene, water, ethanol, and ethylene glycol (EG) and, having created such suspensions, we came up to printed layers and investigated their structural and electrical characteristics. Water was chosen as a basic medium due to its minimal influence on electrical properties of the graphene flakes, compared to organic media. The EG was added to avoid the coffee-ring effect [8]. Ethanol was added in an EG-containing solution, to optimize the printed layer drying process.

Theory background of graphene suspension stability in different solutions

Knowing the Hansen parameters for the material and the solution, we can estimate the intermolecular distance R_a in Hansen space between molecules of the material and the liquid according to equations 1, 3 [14]. The smaller the R_a value is, the higher the stability of the suspension is. It is known that the composition with minimum R_a found using this theory does not give an accurate value and requires experimental adjustments to determine the optimal composition. The parameters of the solution consisting of several components are their linear combination (equation 2) [15].

$$\delta^2 = \delta d^2 + \delta p^2 + \delta h^2 \quad (1)$$

$$\delta_{\text{solvent}} = \sum_i \phi_{i,\text{component}} \delta_{i,\text{component}} \quad (2)$$

$$R_a = [4(\delta_{d,\text{material}} - \delta_{d,\text{solvent}})^2 + (\delta_{p,\text{material}} - \delta_{p,\text{solvent}})^2 + (\delta_{h,\text{material}} - \delta_{h,\text{solvent}})^2]^{\frac{1}{2}}, \quad (3)$$

where ϕ is the volume fraction of each component in the solution (mixture), and the parameters are δ_d , δ_p and δ_h .

The surface tensions of graphite and graphene are 46.7 and 54.8, respectively [17]. In case of the particles as against a continuous film, we have found out that a decrease in the particle size leads to an increase in surface tension.

Thus, in our case, the water based suspension with the multigraphene flakes with a size lower 400 nm was stable for a week, whereas, the suspension with the flakes of larger sizes was stable without special additives only for few minutes.

Table 1. Parameters of graphene and different medium.

Material	Hansen parameters (MPa ^{1/2})			R _a (MPa ^{1/2})	Hildebrand parameter (MPa ^{1/2})	Surface tension (mN/m)
	δd	δp	δh		δ	σ
Graphene	18.0	9.3	7.7	0	21.7	47
NMP	18.0	12.3	7.2	3.0	23.0	41
DMF	17.4	13.7	11.3	5.8	24.9	18
Water	17.3	18.8	16.7	13.1	30.5	73
Ethanol	15.8	8.8	19.4	12.5	26.5	22
EG	17.0	11.0	26.0	18.5	33.0	46
Toluene	18.0	1.4	2.0	9.7	18.2	29

In **Table 1** one can see the details of HSP, Hildebrand for different fluids and the correlation between the literature data on the values of HSP and surface tension. Thus, the most stable medium for the graphene dispersion is N-Methyl-2-pyrrolidone (NMP) [18]. It is clear that this fluid has minimum R_a , weak difference between the Hildebrand parameters, and a surface tension similar to that of graphene. It is well known and widely used for producing graphene suspensions.

However, there are some contradictions between the two points of view; the EG has the highest R_a , but its surface tension is similar to that of graphene; but with all this, it is reported that graphene is stable in the EG medium. There are also stable media in a reverse situation; graphene flakes are stable in N,N-Dimethylformamide (DMF) and toluene solutions, but they have an almost 2 times smaller surface tension than that of graphene, and R_a is quite small [19].

These two viewpoints assumingly describe different mechanisms of interaction. This needs the analogy with a comparison of crystal lattice constants at the substrate and the epitaxial grown material. If materials have similar values of the parameter, the growth will happen without any complications, otherwise the additional external influence is necessary.

We have performed simulation of a three-component solution and graphene as a suspension material. Since the solution consists of three components, the R_a depends on two variables (the third component of the composition is determined through $1 - x - y$). It means that the result may be presented in as a plane (**Fig. 1a**). The plane cross sections for an easy use and discussion, using the concentration of ethanol and water as a variable parameter for different curves presented in **Fig. 1b, c**. Based on

these calculations of minimum values of interatomic distances, we have determined the optimal solutions with different component ratios.

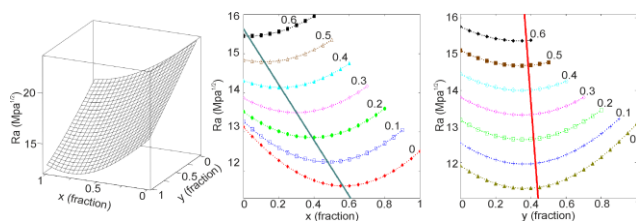


Fig. 1. (a) Parameter R_a as a function of ethanol (x) with water (y) concentrations with the EG (1-x-y) concentration. (b) Parameter values R_a at the plane cross sections as a function of ethanol concentration with the EG given as a parameter on the curves and water concentrations (1-x-y). (c) Parameter values R_a at the plane cross sections as a function of water concentration with EG given as a parameter on the curves and ethanol concentrations as (1-x-y). The volume fractions of EG are given near the curves in (b) and (c) as a parameter. The change in the position of the R_a minimum is marked in (b) and (c) with a line.

Thus, arrays of stable solutions have been found and that necessitated their testing in practice and introducing corrections if needed. The analysis of R_a minima with increasing concentrations of EG has shown (**Fig. 1b**) that the minimum position R_a changes linearly; so, it has been suggested, that in the practical case the linear dependence of the minimum is maintained. It follows that practically finding a stable solution based on the used component enables a determination of the entire array of stable solutions adjusted compositions.

Experimental

Graphene suspension was created with use of electrochemical exfoliation in the liquid phase in environmentally safe media, such as water (H_2O), and the mixture of ethanol with water, followed by centrifugation and ultrasonic treatment. Electrochemical exfoliation of graphite occurred in the acid water solution and allowed obtaining graphite flakes in a wide range of lateral sizes and thicknesses. The carbon source was highly oriented pyrolytic graphite (HOPG). The electrolyte, in which the cleavage occurred, was an acid solution $(NH_4)_2S_2O_8$ with low concentration when oxidation of graphite flakes is negligible. After obtaining the graphene suspension the solution was replaced by water.

After the electrochemical exfoliation of graphite the flakes dimensions lie in a wide range that is not suitable for their use for printing. Therefore, to further reduce the flake size the suspensions were additionally treated using share mixer, ultrasound and centrifugation, which increases the efficiency of the presented method. It is important that the flakes obtained by electrochemical exfoliation contain a large number of intercalated gases, which greatly facilitates their subsequent exfoliation. In the course of additional processing the solution was added with surface active materials (surfactants) to improve the size reduction efficiency and/or use a ethanol water solution.

Experimental results and discussion

Experimental examination of simulation results

The composition of ethanol with water, without EG, was chosen for experimental verification. Solutions were prepared to have a 20 ml water volume with 5% increment on ethanol. One gram of dispersed graphene flakes was added to each of the solutions. All tubes were maintained for two weeks, and the result is shown in **Fig. 2a**. The optimal composition of a stable solution corresponds to the ratio of ethanol and water 65/35, whereas the calculation gave the ratio of 57/43. The adjusted dependences of R_a are shown in **Fig. 3**.

Additional verification of several empirically corrected compositions has shown that the assumption on linear dependences was correct. A photograph of the suspension at the EG concentration of 30% is shown in **Fig. 2b**. Thus, we have identified a set of compositions of 4-component stable suspensions used in further experiments.

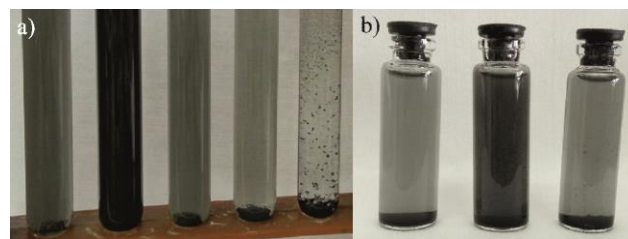


Fig. 2. (a) Photograph of graphene suspensions after 3 days with a different ethanol/water ratio: from left to right: 60/40, 65/35, 70/30, 75/25, 80/20 (b) Photograph of solutions with the EG concentration of 30% and a different ethanol/water ratio: from left to right: 40/30, 32/38, 27/43 after 3 days.

It is worth mentioning that the coefficient 4 in equation (4) before difference δd is a correction factor added after an accurate matching of the theoretical and practical results in the case of polymer solutions solubility [14]. In the general case, this coefficient has to be equal to 1 [12]. Therefore, if we recalculate the solubility of graphene in water with alcohol, it turns out that the minimum point for R_a is at alcohol/water ratio 63/37. This relation perfectly corresponds to the experimental curves given in **Fig. 3**. The change in the constant value does not affect the qualitative form of the function. So, the position of the minimal R_a remains a linear function of the content.

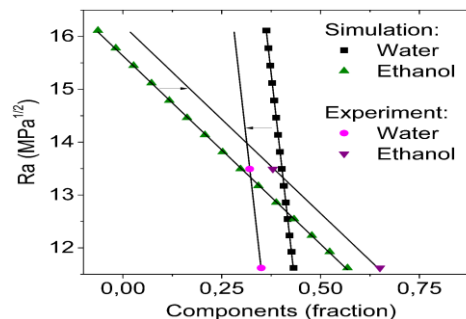


Fig. 3. Changing the position of the minimum depending on the substance fraction in the solution.

Droplet formation during the printing process by chosen ink compositions

Except for stability, here is a necessity for fulfilling the conditions of the droplets forming in the printing process. This property is described by parameter Z [9].

$$Z = (\gamma\rho d)^{1/2}/\eta \quad (3)$$

where η is the dynamic viscosity, γ is the surface tension, and ρ is the ink density. If $1 < Z < 14$, the droplets formation process at printing is optimal. For $Z < 1$, the droplets are not formed and, at $Z > 14$, there is ink-spraying and the formation of secondary droplets during printing. The viscosity and surface tension for our solutions were measured with the use of a viscometer and capillary effect.

Therefore, to optimize the parameter Z for the found boundary and intermediate stable solutions it was necessary to experimentally determine the surface tension, density, dynamic viscosity and the calculated parameter Z . The results are shown in **Table 2**. It is interesting that all stable inks are found to be in the range of the parameter Z values corresponding to the optimal printing.

Table 2. Parameters of solutions: composition, solution density ρ , dynamic viscosity η , surface tension γ and parameter Z .

EG/Water/Ethanol	ρ (kg/m ³)	η (m \cdot c \cdot P)	γ (mN/m)	Z
0/35/65	890	2,6	25	8
15/34/51	917	3,2	28	7
35/32/33	1005	4,3	35	6
50/30/20	1018	5,0	35	5
70/28/2	1063	5,6	46	6

Coffee-ring effect for films printed by stable suspension

After the analysis given above it is essential to verify the optimality of the ink composition from the point of view of the coffee-ring effect in printed layers drying. A series of stable suspensions was created and separate drops were printed (**Fig. 4**) on a substrate of SiO₂/Si with a APTES monolayer (chemical formula H₂N(CH₂)₃Si(OCH₃)₃) on the surface to ensure the surface hydrophilicity. For printing we used a printer FUJIFILM Dimatix DMP-2831 with the resolution of 25 microns and a drop volume of 10 pL (nozzle diameter of 21 μ m), and the substrate was heated to the temperature of 60°C.

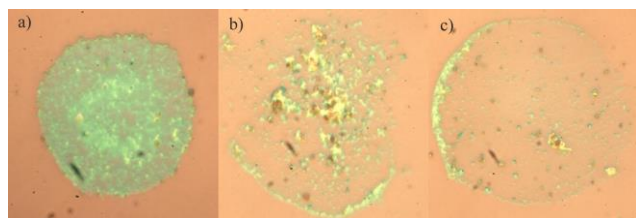


Fig. 4. Optical images of the drops obtained by printing for compositions EG/Water/Ethanol (a) 05/35/60 (b) 20/33/47 (c) 30/32/38 (see Table 2).

The selection of interest lies in a region with a small amount of EG because, in spite of its stabilizing properties and ability to suppress the coffee-ring effect, it is an undesirable organic additive. It is shown in the drops optical images that the coffee ring effect occurs when the concentration of EG is in the range of 10-25%.

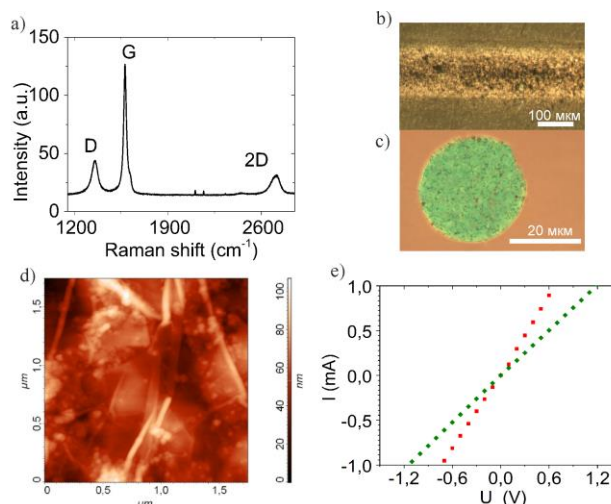


Fig. 5. (a) Raman spectrum for the film printed by one stable suspension with the composition EG/Water/Ethanol 15/34/51. (b, c) Optical images of the printed line and drop on the paper substrate. (d) AFM images of the printed layer. (e) Current-voltage characteristics for two printed lines with the thickness of 25 nm and a different length.

Structure and properties of layers printed by optimal suspension composition

Graphene flakes were obtained by HOPG electrochemical exfoliation with a subsequent refining of the suspension using a laboratory disperser. As a result, flakes with a thickness of 1-2 monolayers were obtained and, after the suspension filtration through a track membrane, the particles lateral size did not exceed 400 nm. The Raman spectrum for the film printed using one of the stable suspensions, shown in **Fig. 5a**, demonstrates the quality of the used material. The source material was HOPG, and the electrochemical exfoliation with a subsequent mechanical exfoliation by the disperser was used for exfoliation. The full width of G peak at a half maximum (FWHM) is 34 cm⁻¹ (for graphene FWHM of the G peak is equal to 14 cm⁻¹ for comparison). The amplitude of the D peak associated with defects is relatively small. It is also worth recalling that the graphene suspension was obtained through the electrochemical exfoliation followed by dispersing, and as can be seen from the Raman spectrum, the technological process does not introduce additional defects, with the exception of the edge ones.

In **Fig. 5b, c** are the optical images of the printed line and drop without the coffee-ring effect, and in **Fig. 5d** is the AFM image of the printed layer. In the AFM image there are only the transparent flakes which correspond to graphene or few-layered graphene in the printed layers. The similar solutions are used for carrier mobility analyses in the printed layers [20]. The current-voltage characteristics, measured using contacts of silver paste and picoammeter Keithley 6485 to determine the

resistances of the printed layers are presented in **Fig. 5e**. The resistance value for lines with a thickness of 20 - 40 nm after annealing at 300°C for 30 min is found to be 3 – 15 kΩ/μ.

The use of a silicon substrate as a gate allows measuring the transferring transistor characteristics that served to determine the carriers mobility in the printed films. The carriers mobility was found to be 30 – 50 cm²/Vs. The obtained characteristics show that not only stable water-based graphene suspensions, but good electrical parameters of the printed layers have been obtained.

Conclusions

The semi-empirical theory of Hansen solubility parameters and the experimental correlation of the obtained results served to find arrays of stable compositions of a four-component suspension (graphene, water, ethylene glycol, and ethanol). The correction factor in the theory of Hansen solubility parameters was found to be equal to 1 instead of 4 widely used in the case of polymer solutions. It has been shown that for a set of variants of these stable suspensions, the condition of forming droplets at printing is fulfilled in all cases. From the point of view of the printed layers drying, the coffee ring effect disappears for an ethylene glycol concentration in the range of 10-25%. Printing by ink, which fits the optimal composition in all respects, has demonstrated good electrical characteristics, namely the layer resistance of 3 –15 kΩ/μ for lines with a thickness of 20-40 nm.

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