2D printing technologies using graphene-based materials

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Contents

1.	Introduction	204
2.	Graphene-based materials used in printing technologies	205
	2.1 Preparation of graphene suspensions; 2.2 Suspensions of graphene derivatives and other 2D materials	
3.	Physical and chemical basis of creating inks based on graphene suspensions. Preparation of substrates	207
4.	Properties of layers produced using 2D printing technologies	207
5.	Commercially available inks based on graphene and graphene oxide	211
6.	Examples of implementing devices created with the use of 2D printing technologies	212
7.	Conclusions. Prospects for the development of 2D printing technologies	216
	References	217

<u>Abstract.</u> This paper reviews major research into the use of graphene and other monolayer materials in 2D printing technologies for fabricating modern electronics and photonics devices. The paper discusses methods for preparing suspensions, properties of printed layers, examples and parameters of specific printed devices, and major trends in the field. Special emphasis is placed on the conceptual change in graphene suspension preparation from using organic liquids to utilizing water-based solutions for delaminating graphite and fabricating liquid ink. The paper also considers the trend towards the use of increasing graphene-rich ink, an approach whereby highly conductive printed layers can be obtained. The expansion of the range of materials employed is also discussed.

Keywords: printing technologies, graphene and graphene oxide suspensions, suspensions of fluorinated graphene, preparation and parameters of suspensions, graphene-based inks, properties of printed layers, instrument structures, development directions

1. Introduction

With the development of technologies for the preparation of graphene and other 2D materials, a significant advance is observed in the manufacturing of components of printed and, in particular, flexible electronics, as well as a noticeable expansion of the fields of their application [1-3]. The printing technologies represent a cheap alternative approach to technologies based on the use of lithography, which makes it

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Uspekhi Fizicheskikh Nauk **187** (2) 220–234 (2017) DOI: https://doi.org/10.3367/UFNr.2016.03.037783 Translated by S N Gorin; edited by A Radzig possible to create electronic components for many devices. At present, the fields of application include sensory displays [4], various sensors [5–7], radio-frequency identification tags and labels [8], photovoltaic elements [9], light-emitting diodes [10], electronic textiles [11], supercapacitors [12], and thin-film energy-storage devices [13].

The application of the so-called functional inks possessing the properties of conductors, semiconductors, and dielectrics in combination with the methods of contemporary polygraphy makes it possible to substantially reduce the cost of electronic engineering goods and to increase the efficiency of their production. Just recently, the basic materials for printed electronics were organic materials [14], which have low performance characteristics (first of all, a limited service life) but are cheap in production.

Another important component of printed electronics is liquid compositions based on metallic nanoparticles, for example, silver (with resistivity $\rho = 1.6 \times 10^{-6} \Omega$ cm) of the bulk material, and copper ($\rho = 1.7 \times 10^{-6} \Omega$ cm) [2, 15]. However, the typical values of the resistivity of layers printed using such inks are $(5-35) \times 10^{-6} \Omega$ cm and are inferior to the characteristics of this material prepared by traditional methods.

In 2009, the NanoGram company (United States) developed inks based on silicon nanoparticles [16]. For transistors fabricated using silicon ink, a mobility of approximately $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was obtained, which exceeds the mobility in amorphous silicon (20–30 cm² V⁻¹ s⁻¹) which is widely used for the transistors in display motherboards [17].

At present, significant attention in the field of printing technologies is focused on the oxides of metals and, first of all, on zinc oxide, mainly for the formation of transparent conducting layers of coatings in the production of passive and active components of displays and solar cells, thin-film lasers, etc. [18]. This is far from a complete list of the possible applications of this material.

As is expected, the appearance of a new class of substances, namely, inks based on graphene and its chemical modifications, should cause a significant breakthrough in printed electronics from the viewpoint of the expansion of the functional potential of printed layers and an improvement in the performance characteristics of the implemented instrument structures. On the whole, it is assumed that 2D printing technologies represent one of the most needed and promising trends in the development of modern materials science. The amount of funding in this field has grown severalfold in recent years [19].

In this review, we consider the basic achievements in the field of printed electronics provided by using the materials based on graphene, chemically modified graphene, and other 2D materials.

2. Graphene-based materials used in printing technologies

2.1 Preparation of graphene suspensions

Several basic approaches that at present are applied to create suspensions can be mentioned. The first is based on the intercalation of organic substances into particles of dispersed graphite. The solvents that are most widely used for the intercalation are N-methyl-pyrrolidon (NMP) and dimethylformamide (DMF), since it is assumed that these solvents give the greatest yield of single-layer particles of graphene in suspensions [20, 21]. A number of other organic substances can also be employed to obtain graphene suspensions [22, 23]. After intercalation, such technological steps as prolonged (tens and hundreds of hours) sonication and centrifugation follow. A drawback of the thus obtained suspensions is a large spread in the sizes and thicknesses of particles (thicknesses from one monolayer to 100 nm; sizes from tens of nanometers to several microns). Large particles, naturally, can be removed by centrifugation, but in this case a significant reduction in the concentration of graphene in the suspension occurs. Moreover, to further use the suspension, as a rule, a replacement of the solution and the removal of the organic solvent are required [24].

On the whole, numerous ways have been found to exfoliate graphite with the employment of different additives, intercalants, etc., which make it possible to obtain relatively good suspensions [25–28]. Typical values of the sheet resistances of films obtained from suspensions vary, depending on the thickness, from 0.1 to $10^4 \text{ k}\Omega/\text{sq}$; the latest developments make it possible to reach values from a few to tens of Ω/sq [28, 29].

Besides organic solvents, graphene suspensions can be prepared using an aqueous solution of ethanol with an optimum content of 70% ethanol [30]. This method does not lead to oxidation; it does not require intercalation or frequent replacement of the solvent. The basic technological stage is sonication, the time of which, as a rule, does not exceed 10 h. It is precisely this version that recently has been most widely applied by both leading groups of researchers and firms that produce graphene ink. The sheet resistance of the films obtained from such suspensions is 150–200 k Ω /sq before the annealing, and 5–12 k Ω /sq after annealing (for 30 min at 300 °C), depending on the medium in which the annealing occurs.

Another approach exploits thermo-expanded graphite, which is then exfoliated into layers with the aid of sonication and other additional treatments [31–33]. This approach makes it possible to obtain relatively thick particles of the suspension, 3–7 nm [32, 34]. Furthermore, the lateral size of the particles in this case is, as a rule, varied from several microns to several dozen microns. The decrease in the lateral

sizes of the particles (to less than 400 nm), which is necessary for the application of the suspension as the ink, requires significant additional effort. The conductivity of the layers obtained from commercially available graphene suspensions reaches 200 Ω/sq .

Recently, several new and very promising approaches to the preparation of suspensions have appeared. The first consists of the electrochemical exfoliation of graphite [13, 35]. This approach is based on the formation of gas bubbles at a graphite electrode; as a result, its exfoliation occurs, which provides a rapid formation of the graphene suspensions with a high content (up to 88%) of particles with a thickness of 1– 3 monolayers, but with large lateral sizes (to several dozen microns). The time for the process of exfoliation of a piece of graphite takes 10–20 min. The films produced from such suspensions have a high conductivity (from 11 Ω /sq to 1 k Ω /sq) and good mobility of charge carriers, to 98 cm² V⁻¹ s⁻¹. In measurements of the mobility of carriers inside one particle, the authors of Refs [13, 35] obtained values to 310 cm² V⁻¹ s⁻¹.

The possibility of using a shear-mixer [36] and even a kitchen blender [37] for grinding and exfoliating graphite particles has been demonstrated. Figure 1 presents some data taken from Ref. [36]. According to the data obtained by the Raman spectroscopy, the use of a rotary shear-mixer makes it possible not only to rapidly prepare a large amount of graphene suspension, but also to ensure a relatively low concentration of defects in the flakes of such a suspension, in spite of the high rotation speed of the shear-mixer rotor [36]. The characteristic times of treatment using a shear-mixer or a blender last 1–2 h. The operating principle is based on the creation of shear strains in the particles of graphite placed in an organic solution (for example, NMP) or, most importantly, in an aqueous solution with the addition of surfactants.

The authors of Ref. [36] emphasized the role of the liquid component of the solution: for a liquid with a surface energy close to the surface energy of graphene, a minimum energy would be required for the exfoliation of the graphene and, correspondingly, minimum shear strains and a minimum rate of rotor rotation. According to the model constructed by Paton et al. [36], which is based on local shear strains, the concentration C of graphene nanolayers in the solution must be proportional to the initial concentration C_i of graphite in the solution, the time t of the treatment by the shear-mixer, the volume V of the liquid, the rotor diameter D, and the speed N of rotor rotation. The authors of Ref. [36] empirically obtained the following dependences: $C \sim C_1 t^{0.66} N^{1.13} D^{2.28} V^{-0.68}$ for graphene suspensions in NMP, and $C \sim C_i t^{1.08} N^{2.54} D^{3.34} V^{-0.47}$ for graphene suspensions in water with the addition of a surfactant. On the whole, this approach significantly simplifies the graphite exfoliation process and makes it possible to move to industrial volumes of obtaining graphene suspensions, as well as of suspensions of other layered materials (such as dichalcogenides of transition metals: MoS₂, WS₂, etc.).

It should be noted that the methods have recently been applied increasingly more widely, in which no organic solvents are employed for the exfoliation of graphene. Thus, instead of NMP, DMF, and other similar substances, various salt solutions are increasingly more frequently utilized, which are less dangerous, e.g., the aqueous solution of ethanol or water with additives of surfactants.



Figure 1. (a–d) Preparation of a graphene suspension with the aid of a shear-mixer. (e) Image of a suspension in a transmission electron microscope. (f) Particle-thickness distribution (the inset shows a Raman spectrum of the suspension). (g) Sheet resistance of a film obtained from a suspension as a function of the film thickness. The figure panels are based on data taken from Ref. [36].

Furthermore, there are a large number of additional methods for obtaining thinner and smaller particles for 2D printing. For example, putting into practice the sonication in combination with ozonication makes it possible to additionally exfoliate the particles and to change their aspect ratios [38]. Thus, a 30-min treatment led to a decrease in the thickness of the suspension particles by approximately an order of magnitude (from 11 to 1.2 nm). In this case, a partial oxidation of multigraphene occurred, which made the waterbased suspension stable. After thermal treatment at 400 °C, directed toward the restoration of graphene, the authors of Ref. [38] obtained a sheet resistance of $\sim 3 \text{ k}\Omega/\text{sq}$ at the thickness of the printed film equal to 220 nm. Thinner layers (~ 6 nm) had a sheet resistance of $7 \times 10^5 \Omega/sq$, and the transparency of the layer reached 93%. The typical value of the resistance of similar layers of reduced graphene oxide was equal to $2 \times 10^7 \Omega/\text{sq}$ [39].

2.2 Suspensions of graphene derivatives and other 2D materials

Chemically modified graphene (graphene oxide, fluorinated or hydrogenated graphene), as a rule, becomes insulating. The most common and widely used derivative is graphene oxide [40]. The technology of preparation of a suspension of graphene oxide (modified Hummers method) is based on the chemical oxidation and exfoliation of graphite. This is a welldeveloped and relatively low-cost technology. However, the graphene oxide is not used for creating a dielectric layer, since its properties easily change upon annealing above 100 °C, running a current, intensive illumination, and other actions as a result of partial reduction. The layers of thermally or chemically reduced graphene oxide are widely utilized as conductive layers [40, 41].

Recently, a method was proposed for the fluorination of a graphene suspension by adding an aqueous solution of hydrofluoric acid to it [42, 43]. It was reported that in the process of the fluorination a mechanically stimulated exfoliation of the flakes of the suspension occurs, with a simultaneous decrease in their lateral sizes. It was also revealed that in the process of fluorination of the suspension, layers with quantum dots of graphene inserted into the matrix of the fluorographene were obtained. In the case of a higher degree of fluorination, dielectric layers are obtained, which are characterized by the formation of an extremely low charge in the film and in the surface states (density of states $\sim 10^{10}$ cm⁻²) and by a low (1.2) dielectric constant. Furthermore, a hybrid approach was shown to be promising, in which the graphene grown by the method of chemical vapor-phase deposition or mechanically exfoliated graphene is either transferred onto the layers of the graphene oxide or of fluorographene obtained from the suspensions, or is encapsulated by them [44].

It was also shown recently that the formation of vertical heterostructures with the use of layers of graphene and other 2D materials, such as hexagonal boron nitride (h-BN) and dichalcogenides of transition metals (MoS₂, WS₂, etc.), makes it possible to create a wide spectrum of electronic and photonic devices [45-48]. These developments stimulated interest in the search for methods of obtaining suspensions of 2D materials and their use for creating heterostructures with the aid of printing technologies [49-52]. In particular, it was demonstrated that the exfoliation of BN, MoS₂, and WS₂, just as of graphene, occurs efficiently in 40-60%solutions of ethanol in water [50]. To date, many methods of preparing suspensions for printing technologies have been developed, and prospects of this approach for preparing heterostructures have been discussed [51, 52]. For the preparation of suspensions of NB, MoS₂, WS₂, and many other materials, just as for graphene, the shear-mixer described in Ref. [36] can be used.

3. Physical and chemical basis of creating inks based on graphene suspensions. Preparation of substrates

To move from suspensions to inks, it is necessary to solve a number of problems.

The first requirement deals with the limitation on the lateral sizes and thickness of the suspension particles. For producing flat films, the thickness of particles must be no more than several nanometers, and their lateral sizes must be approximately 50 times less than the diameter of the nozzle in order to avoid clogging of the printhead nozzles [53]. With a nozzle diameter of 20 μ m, this corresponds to lateral sizes of ≤ 400 nm.

Second, for successful printing it is necessary to ensure the stability of the ink solution. Suspensions are stable if their Gibbs energy satisfies the condition $\Delta G_{\text{mix}} =$ $\Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \leq 0$, where ΔS_{mix} is the change in the entropy (in the case of graphene, ΔS_{mix} is small); ΔH_{mix} is the enthalpy of the mixture; the solvent must have a surface energy close to that of graphene [53]. Such properties are characteristic, for example, of N-methyl pyrrolidone (NMP) and of the aqueous solution of ethanol; that is the reason why they are widely used not only for the exfoliation of graphite but also for the stabilization of solutions. The addition of NMP, even in a small concentration, just as the addition of ethanol, stabilizes the solution of graphene in water. Ethanol makes it possible to regulate the surface tension of a suspension (and, correspondingly, the Gibbs energy) over wide limits. One more stabilizer that is frequently used for the suppression of clustering of the suspension particles is ethylcellulose (EC). This additive prevents the adhesion of graphene particles to each other.

Furthermore, the stabilization of suspensions is achieved by using: surfactants; special additives which accelerate the drying of printed layers; hygroscopic additives which prevent the evaporation of water and clogging of the inkjet nozzles of the printer, and some organic additives which permit regulating the electrical conductivity of the solution and the surface tension. Among the special additives, it is again necessary to mention NMP whose addition not only stabilizes the suspension, but also prevents the clogging of the printhead nozzles and increases the electrical conductivity of the solution. It is obvious that these additives in the final analysis can also influence the conductivity of the printed layers and the mobility of charge carriers in them, thus limiting the permissible concentrations of the additives.

It is also necessary to ensure a specific combination of such parameters of the suspension as the surface tension γ , the viscosity η of the solution, its density ρ , and the diameter α of the nozzle. To this end, as a rule, the parameter $Oh = \eta/(\gamma \rho \alpha)^{0.5}$ or Z = 1/Oh is used. The optimum condition is believed to be satisfied when Z = 1-14; if Z < 1, the droplets will not flow out from the inkjet nozzles of the printer; as Z > 14, numerous additional small droplets appear [53].

Graphene oxide is a hydrophilic material; therefore, its suspensions are always obtained in water, and no significant effort is required for the stabilization of the suspensions and prevention of their layering; however, for the suppression of clusterization of particles, some surfactants are usually added. Similarly to graphene oxide, fluorographene also possesses hydrophilic properties and does not require a large number of additives to obtain water-based inks.

Graphene constitutes a hydrophobic material; therefore, its stable suspension can most easily be obtained in organic liquids (in NMP, terpineol, cyclohexane, etc.); however, the layers prepared from such suspensions require annealing at temperatures of 250-400 °C, depending on the specific composition. In a water-based suspension, graphene precipitates easily into a sediment, and water-based graphene inks can be obtained only upon the introduction of different stabilizing and special additives. Usually, such inks contain no fewer than ten different additives.

In the case of printing with the aid of water-based inks, the surface of the substrate must also be hydrophilic. Thus, for example, to guarantee adhesion on Si and SiO₂/Si substrates, a monolayer of (3-aminopropyl)trimethoxysilane (APTES) or a thin film of polyvinyl alcohol (PVA) can be practised. This is also necessary on the hydrophilic surface of silicon, because its surface in air is immediately covered with a layer of natural oxide and becomes hydrophobic. APTES (chemical formula $H_2N(CH_2)_3Si(OCH_3)_3$) forms a monolayer as a result of the attachment of its molecules to silicon atoms on the surface. Flexible substrates are also covered with additional layers to ensure the required adhesion. Thus, the Lomond firm (Great Britain) produces films of polyethyleneterephthalate (PET) with an adhesive coating for printing with water-based inks using inkjet printer nozzles.

In the case of printing using inks with a liquid composition consisting of organic substances, the substrate must be hydrophobic. To this end, the surface of the substrates can be coated, for example, by a layer of hexamethyldisilazane (HMDS) described by a chemical formula $[(CH_3)_3Si]_2NH$.

4. Properties of layers produced using 2D printing technologies

In the first work on the creation of printed structures, a reduced graphene oxide (rGO) [54–57] was utilized, since the technology of preparing a suspension of graphene oxide was developed earlier than that of a graphene suspension (Table 1). The layers of graphene oxide were reduced either via annealing (300–1000 °C) or chemically (with the use of hydrazine, ascorbic acid, hydroiodic acid, etc.); the layers obtained had, especially in the latter case, rather low resistivity (up to 4 k Ω /sq [56]) and low mobility of charge carriers (from 0.1 to 1.2 cm² V⁻¹ s⁻¹) [54]. Higher values of

	, , , , , , , , , , , , , , , , , , , ,									
Material	$ \begin{array}{c c} \rho, k\Omega/sq; & \mu, cm^2 V^{-1} s^{-1} \\ \sigma, S m^{-1} \end{array} \begin{array}{c} Comments \end{array} $		References							
rGO	$\sigma = 0.1$			[54] Wang et al., 2008						
rGO	rGO $\rho = 1.7 - 3.4$ $\sigma = 6 \times 10^4$ 1: 5.4(h) 1.1(e); 2: 50(h) 10(e); 3: 92(h) 51(e)Composition of the reduction at 1000 °C spincouter; thickness (3) 1.6-2.4 nm; prin		Composition of the suspension: GO, 15 mg ml ⁻¹ ; reduction at 1000 °C; size, $> 25 \ \mu\text{m}$; applied using a spincouter; thickness: (1) 0.5–0.8 nm, (2) 0.8–1.6 nm, (3) 1.6–2.4 nm; printed layers, thickness of 50–100 nm	[55] Wang et al., 2010						
rGO	$\sigma = 400 - 900$		Composition of the ink: GO, 5–9 mg ml ⁻¹ ; reduction at 400 °C; flexible substrates	[56] Huang et al., 2011						
rGO	ho = 107		Chemical reduction (printing of 6 layers of GO and of 1 layer of ascorbic acid); layer thickness, 300–400 nm; substrate, PET	[89] Kim et al., 2014						
rGO	$\rho = 150 (10 \text{ nm}) \rho = 10 (30 \text{ nm}) \rho = 4 (60 \text{ nm})$		Chemical reduction of GO; layer thickness, 10–100 nm; substrate, PET	[57] Rogala et al., 2015						
WGO	$\sigma = 4.2 \times 10^4$		Weak oxidation during the exfoliation of graphite; reduction at 100 °C	[67] Su et al., 2013						
	Graphene, thin films (inkjet printing)									
G	$ ho = 30 \ \sigma = 10^2$	95	Composition of the ink: graphene, 0.11 mg ml ⁻¹ ; NMP; layer thickness, 25 nm; annealing, at 170 °C; substrate, HMDS/SiO ₂ ; ON/OFF ~ 10	[53] Torrisi et al., 2012						
G	$\rho = 0.3$ $\sigma = 2.5 \times 10^4$ Composition of the ink: graphene, EC, ethanol, terpineol; layer thickness, to 140 nm; annealing, at 250 °C; substrate, polyimide film		[68] Secor et al., 2013							
G	$\rho = 2.1$ $\sigma = 3 \times 10^3$		Composition of the ink: graphene, 6 mg ml ⁻¹ ; layer thickness, 160 nm; printing temperature, 70 °C; substrate, PET	[69] Finn et al., 2013						
G	$ ho = 0.81 \ \sigma = 9 imes 10^3$		Composition of the ink: graphene, 1 mg ml ⁻¹ , EC, cyclohexane; layer thickness, 30–100 nm; annealing, at 300 °C; substrate, PET	[70] Gao et al., 2014						
G	$\rho = 0.6$ $\sigma = 1 \times 10^4$		Composition of the ink: graphene in ethanol, 10 mg ml ⁻¹ , EC, terpineol; layer thickness, \sim 170 nm; annealing, at 250 °C	[71] Secor et al., 2014						
G	ho = 60		Composition of the ink: graphene, 1 mg ml ⁻¹ , EC, terpineol; laser annealing	[72] Del et al., 2015						
G	$\rho = 0.2 - 0.4$ $\sigma = 2.5 \times 10^4$		Composition of the ink: graphene, 20 mg ml ⁻¹ , EC, terpineol; thickness of one printed layer, 380 nm before annealing, and 190 nm after annealing; annealing by pulsed xenon lamp	[73] Secor et al., 2015						
			Graphene, thick films							
G	$ ho=0.055 \ \sigma=1.8 imes10^4$		Composition of the ink: graphene, 80 mg ml ⁻¹ , EC, terpineol; layer thickness, $\sim 1 \mu m$; application through a stencil, resolution, 40 μm ; annealing at 300 °C	[74] Hyun et al., 2014						
G	$\rho = 0.0038$ $\sigma = 4.3 \times 10^4$		Layer thickness, $\sim 6 \ \mu m$; compression of the printed layer	[75] Huang et al., 2015						

Table 1. Properties of printed graphene layers: G, graphene; GO, graphene oxide; rGO, reduced graphene oxide; WGO, weakly oxidized graphene; ρ , sheet resistance; σ , conductivity; μ , charge mobility; h, holes, and e, electrons.

mobility were observed only in the layers prepared from coarse particles reduced at high temperatures, which are not attainable with contemporary technologies, especially for flexible electronics [55]. Among the methods for the chemical reduction of graphene oxide, the use of such a safe substance as ascorbic acid should be noted, which gives the smallest resistance of the reduced layers [57].

In Fig. 2, the resistances of the rGO films prepared using suspensions of graphene oxide and of hybrid layers obtained with additions of metallic particles into the suspensions [58] are compared. The addition of metallic nanoparticles is one of

the most common ways of decreasing resistance of the rGO films, which is especially important for creating transparent electrodes. An increase in the transparency of a layer corresponds to a decrease in its thickness. It follows from the data shown in Table 1 and in Fig. 2 that, depending on the specific features of obtaining and reducing the graphene oxide, the resistance of a sheet can change in wide limits [54–67], but the smallest resistances are obtained when adding metallic nanoparticles.

An interesting approach to producing weakly oxidized graphene (WGO) was proposed by Su et al. [67], who used a



Figure 2. Dependence of the sheet resistance on the transparency to light with a wavelength of 550 nm for films of reduced graphene oxide (rGO), graphene (G), and rGO with additives of metallic nanoparticles obtained from suspensions (according to Ref. [58]).

concentration of the oxidizer (KMnO₄) decreased twofold in the solution. As a result, after reduction at a temperature as low as only 100 °C, the authors managed to obtain sufficiently thin particles (1.2 nm) and conducting films. The conductivity of the films with a thickness of more than 200 nm amounted to 4.2×10^4 S m⁻¹.

The main parameters of the printed layers of graphene are presented in Table 1 and in Fig. 3 [68–75]. Among the studies of such layers, the work by Torrisi et al. [53] should be emphasized. The authors showed to what extent the proper preparation of the substrate was important: the application of a monolayer of HMDS can decrease the conductivity of the layer by four orders of magnitude in comparison with a layer applied onto a substrate treated in an oxygen plasma. The reason is that in work [53] thin printed layers (with a thickness to 25 nm), whose properties are directly affected by the substrate, were investigated.

The minimum resistance of the thin printed layers (~ 0.3 k Ω /sq) was obtained by Secor et al. [68]. In their work, the suspension was prepared via the exfoliation of graphite in an aqueous solution of ethanol with the addition of EC to ensure the stability of the solution and of terpineol to guarantee the necessary viscosity. One consequence of the introduction of organic additives is the need to use thermal treatments of the printed layers at temperatures of 250–300 °C to achieve a sufficiently low resistance of the sheet (Fig. 4). Figure 5 depicts data on the conductivity of sheets from the same study [68] obtained after the substrate was subjected to bending. A distinguishing feature of this testing was the formation of sharp kinks in the flexible substrate, which, as turned out, did not really affect the conductivity of the printed layers of graphene.

When carrying out a comparison of different studies on the preparation of graphene inks and of the properties of printed layers, two basic features can be noted:

(1) a move to methods of producing graphene inks without the use of organic additives or with a reduced content of organic substances. This leads to a reduction in the temperatures of annealing or drying of the printed layers from 300-400 °C to 250 °C when using EC and terpineol, and to 60-80 °C when using water-based inks.

(2) the tendency towards obtaining thicker films, from hundreds of nanometers to a few microns. This requires ever more concentrated inks and makes it possible to reach a lower resistance of the sheet.



Figure 3. (a) Thickness of a graphene film as a function of the number of printed layers. (b, c) Resistance and conductivity of layers, depending on their thickness and on the treatment of the SiO_2/Si substrate. (d) Transparency of the layer depending on the sheet resistance [53].



Figure 4. Resistivity of layers printed using inks based on graphene with additives of EC, ethanol, and terpineol on a polyimide film as a function of (a) temperature, and (b) annealing time; (c) thickness of a line, and (d) its resistivity depending on the number of printed layers after annealing for 20 min at 250 °C [68].

On the whole, it is necessary to note a reduction in the resistance of the printed layers with the development of technologies for suspension preparation and with the refinement of the composition of graphene-based inks. Since graphene and reduced graphene oxide are used at present mainly for the production of conducting layers, the basic purpose of most works has been an increase in the conductivity of the sheets, even simply due to an increase in the thickness of the printed layer.

Hyun et al. [74] have demonstrated the possibility of using a stencil made of a thin silicon plate (with a thickness of 90 μ m, with slots 50–5 μ m wide, made by lithography) in lithographic printing by graphene inks with the addition of EC and terpineol. It was shown that the resolution achieved with this approach was 40 μ m. The characteristic thickness of the graphene layer is 0.5–2.0 μ m, which gives a low resistance, approximately 50–60 Ω /sq.

The presence of organic additives in graphene inks requires the optimization of the annealing regimes of the films. In Refs [72, 73], the annealing was performed using a laser beam (at a power of 500 mW; wavelength 532 nm; intensity 55 MW cm⁻²; pulse duration 1–4 ms) and also with a pulsed xenon lamp. In the case of irradiation by a laser light, the resistivity of the printed

layers decreased from 200 to 60 k Ω /sq; simultaneously, the transparency at the wavelength of 550 nm increased by 40% and the roughness of the surface relief decreased significantly.

A more noticeable effect was observed with the employment of a flash xenon lamp in Ref. [73]. Figure 6 illustrates the basic results obtained in the last work. It can be seen that, by fitting the intensity of illumination, the same resistance of sheets as in the case of optimized thermal annealing can be obtained; however, because of the different rates of heat extraction, the required intensity depends, in particular, on the type of substrate. The use of an HMDS coating makes is possible to obtain, all other conditions being equal, narrower printed lines, with a resolution of approximately 50 μ m. In Fig. 6c are the results of a comparison of the sheet conductivity of printed layers made of various materials (for references, see paper [73]).

Above, we mainly considered the results of using inkjet printing to create devices of printed electronics. However, the lowest-cost, higher-speed, and most high-performance type of printing (of electronic materials as well) is rolling printing. Recently, inks based on graphene and graphene oxide that can be used for rolling printing as well have been developed [76, 77].



Figure 5. Characteristics of layers created on a flexible KaptonTM polyimide substrate (based on polyimide film, DuPont, United States). The relative resistance of a graphene strip depending on (a) the number of bending cycles, (b) radius of curvature r_c , and (c) bending in accordance with figure (e) or flattened (d) [68].



Figure 6. (a) Sheet resistance as a function of the density of radiation energy from a xenon lamp used for annealing the films printed on different substrates. The following substrates were used: polyethylene terephtalate (PET); polyethylene naphthalate (PEN); polyimide film (PI), and glass. (b) The width of the printed strip depending on the spacing between the droplets during printing and the type of substrate. (c) Map of the conductivity of the printed layer (after a single printing step) depending on the concentration of graphene in the ink. For comparison, data for a conducting polymer (PEDOT:PSS) and carbon nanotubes (CNT) are given. (The figure was borrowed from Ref. [73].)

5. Commercially available inks based on graphene and graphene oxide

types of inks and suspensions based on graphene solution in water [78]:

At present, there are several types of commercially available inks. The GRAPHOS company (Italy) has developed two (1) G-Ink, with a concentration of graphene to 4 mg ml⁻¹ and with a lateral size of particles to 1 μ m (with an average size of 80 nm) and a thickness of 1–3 nm. At a layer thickness

to 20 μ m, its resistance reaches 70 Ω /sq. Additives are introduced to the composition of the inks, ensuring a combination of the parameters necessary for printing with an inkjet printer. These are additives that provide the stability of the inks (up to several months) and regulate their viscosity and surface tension.

(2) Sol-G, with a concentration of graphene equal to 0.4 mg ml⁻¹, a lateral particle size to 30 μ m (with an average size of 150 nm), a thickness of 2–4 nm, and excellent electrical and mechanical properties. At a layer thickness of ~ 50 μ m, its sheet resistance comes to 15 Ω /sq.

The GRAPHOS firm also produces graphene oxide-based inks (Sol-GO) with a concentration of $0.01-2 \text{ mg ml}^{-1}$, which contain 80% single-layered particles.

The Sigma-Aldrich firm (United States) sells three types of graphene suspensions [79]:

(1) Graphene with additives of EC in cyclohexane and terpineol (798983). After annealing for 30 min at 250 °C and at a film thickness of more than 100 nm, the resistivity of the layer ranges 0.003–0.008 Ω cm. The lateral dimensions of the particles are less than 3 μ m.

(2) Graphene with additives of EC in terpineol (798963). After annealing for 30 min at 300 °C and at a film thickness of more than 100 nm, the resistivity of such sheets is also $0.003-0.008 \ \Omega$ cm, and the lateral sizes of the particles are less than 3 μ m.

(3) Suspensions of graphene in water (799092) with a concentration of 1 mg ml⁻¹ and sheet conductivity of 10 Ω /sq at a layer thickness equal to 25 μ m.

There are also suspensions for lithographic printing (796115) and suspensions based on graphene oxide in water (796034).

On the whole, it is necessary to note a change in the basic concept of the ink composition. A transition occurred from the preparation of inks produced using graphene suspensions on an organic base to water-based inks. The water-based graphene inks appeared quite recently and in the open press there are still no publications concerning an analysis of the properties of the printed layers or instrument structures implemented with the use of such inks, except, possibly, for work [69].

6. Examples of implementing devices created with the use of 2D printing technologies

According to estimates by Intel (United States), the need in devices for printed electronics in 2006 comprised 2 billion devices; in 2015, it increased to 15 billion devices; and in 2020, it is expected the need will be 50 billion devices. An increase in the printed-electronics market, according to the data of J Daniel (Palo Alto Research Center, United States), is evaluated to grow from \$1.9 billion in 2009 to \$57 billion in 2019 [81].

Figure 7 displays comparative data on the conductivity of the sheets of various materials used for printed and flexible electronics (the data are borrowed from Table 1 and from Z Yang's report [82]). It can be seen that the conductivity of the sheets obtained using graphene-based inks are inferior only to metallic films and only in the case of utilizing nanometer-thick films.

Some of the basic fields of the application of printing technologies are flexible electronics and optoelectronics. Printing making use of inks based on graphene or on reduced graphene oxide on different flexible substrates, and on paper



Figure 7. Comparison of properties of various conducting layers produced by printing and by deposition. ITO stands for indium tin oxide.

as well, leads to the creation of layers whose conductivity barely changes with any bending treatments (see, e.g., Ref. [83]). The relatively thin (of a nanometer thickness) layers of graphene and, particularly, of graphene oxide have high transparency (80–90%), which makes the structures obtained with the use of printing technologies very promising for transparent electronics [84, 85]. And the mechanical properties of graphene-based materials, as is known, are also promising for stretchable electronics.

Table 2 demonstrates examples of the use of graphenebased printing technologies for various device applications [84-95]. One of the possible applications is transparent electrodes, which are manufactured, as a rule, from rGO. Figure 8 gives data by Li et al. [84], in which the dependences of the transparency on the resistance are reported for films which consist of different numbers of printed graphene layers. As usual, one should search for a compromise between the transparency and resistance, since at the high transparency the resistance proves to be too high. If a low resistance $(\sim 10-20 \Omega)$ is necessary in combination with a high transparency (~90–95%), i.e., properties comparable to those of indium-tin oxide (ITO), then to guarantee the sufficiently high conductivity it is necessary to employ a composite or two-layered structures with metallic nanoparticles or nanowires [58, 85].

Transistor structures made on printed graphene layers [67, 84] and on reduced graphene oxide layers [53, 54] with SiO₂/Si substrates as gate and under-gate dielectric materials, demonstrate low characteristics as a rule. Figure 9 gives data for such a structure borrowed from Ref. [84]. At a layer thickness of less than 50 nm and with the use of the terpineolbased inks, a low mobility (0.12 cm² V⁻¹ s⁻¹) of charge carriers in the channel and a large spread of the resistances of the channel, from a few k Ω to 1 M Ω , were obtained. Such parameters are most likely connected with the incomplete annealing of the organic component in the printed layers, since in the case of printed layers of reduced graphene oxide (with no organic substances being added to the inks in a high concentration) substantially better parameters were observed (see Table 1). A maximum electron mobility of $4.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the printed channel of a transistor structure was reached in the case of graphene oxide locally reduced in ascorbic acid by additional printing of the layer [89].

Graphene-based sensors, including gas sensors, various biosensors, electrochemical sensors, and sensors of humidity

Application	Material	Comments	References
Transparent electrodes	Graphene	Five printed layers: 80% transparency at the wavelength of 550 nm with sheet resistance equal to 30 k Ω /sq; 90% transparency with sheet resistance of 200 k Ω /sq	[84] Li et al., 2013
Transparent electrodes	GO on Ag nanowires	Approximately twofold decrease in the resistance of electrodes made of an Ag nanowire with the retention of transparency; transparency equal to 83% with the sheet resistance equal to $30 \Omega/sq$	[85] Moon et al., 2013
Electrodes for electrochemical cells	Graphene	Electroactive redox electrodes for a number of biologically important analytes	[86] Randviir et al., 2014
Electrodes for organic transistors	rGO/PVA	Electrodes made of an rGO–polyvinyl alcohol composite increased the mobility of charge carriers in the transistor channel from 0.0019 (Au electrodes) to 0.23 cm ² V ⁻¹ s ⁻¹	[87] Lim et al., 2012
Transparent electrodes in organic light-emitting diodes	rGO	Reduction of graphene oxide by ferric chloride or ascorbic acid in the process of printing; transmission of 40–50% at the sheet resistance of 100–900 k Ω /sq; operative OLED structures*	[89] Kim et al., 2014
Transistors	Graphene	Suspension with EC and terpineol, six layers, thickness of ~ 30 nm. Ag contacts; resistance of the channel from 1 k Ω to 1 M Ω ; mobility of charge carriers of 0.12 cm ² V ⁻¹ s ⁻¹	[84] Li et al., 2013
Transistors and biosensors	rGO	Reduction in graphene oxide by ascorbic acid locally in the process of printing. Ag contacts; conductivity of the channel from 8000 Sm^{-1} ; mobility of holes and of electrons equal to 0.7 and 4.4 cm ² V ⁻¹ s ⁻¹ , respectively	[88] Su et al., 2015
Supercapacitors	Graphene	Electrodes for supercapacitors, printing at silver electrodes; capacitance increased from 0.2 (Ag) to 0.6 mF cm ⁻² (Ag + G)	[51] Li et al., 2014
Supercapacitors	Graphene – poly- aniline	Specific capacitance of 82 F g^{-1} ; energy density of 74 kW k g^{-1} ; recharging more than 10 ³ cycles	[90] Xu et al., 2014
Flexible supercapacitors	GO/rGO	Specific capacitance of 140 F g^{-1} ; recharging more than 2×10^3 cycles	[91] Xue et al., 2015
Chemical sensors	rGO	Gas sensor, rGO resistor with an organic framing for detecting aggressive media; sensitivity of a few ppm	[92] Dua et al., 2010
Biosensors	rGO	Detection of DNA with a sensitivity of 10 fM without using aptamers; shift of the transfer characteristics of a transistor	[93] Cai et al., 2014
Biosensors, biomarkers, and other biological applications	rGO, graphene	Survey of the implementations of printing technologies, including graphene and graphene oxide, for a wide spectrum of biological applications	[3] Magliulo et al., 2015
Humidity sensors	Graphene+ poly- vinyl pyrrolidon	Testing the humidity in a range of 40–60% at temperatures of 25–70 $^{\circ}\mathrm{C}$	[94] Santra et al., 2015
Anticorrosion coatings	rGO	Low-cost protective coatings for iron against aggressive chlorine-containing media	[95] Mayavan et al., 2013
* OLED — organic light-emitting	diode.		

Table 2. Application of	printing technologi	es for the creation of	f electronic and	photonic devices
11				1

and pressure, etc., constitute an extensive field of applications of the above materials. (see, e.g., Refs [96–99]). The sensors most widely used at present are those based on rGO. Thus, the rGO layers printed on PET have shown a high sensitivity (a few ppm) for a wide spectrum of gases (NO₂, CO, Cl₂, SO₂) and aggressive organic substances (CH₃OH, C₂H₅OH, CH₂Cl₂, NH₃) [92]. It has been established that the layers printed on PET possess a maximum sensitivity in comparison with unsupported layers with a thickness of 700 nm or with layers created from droplets.

Of great interest is the opportunity (revealed by Cai et al. [93]) of detecting DNA without the use of aptamers. The capture of DNA leads to a shift of the transfer characteristics of a transistor structure in which the silicon substrate is utilized as a gate. This ensures simplicity of fabrication and a high sensitivity of the biosensor (~ 10 fM).

A humidity sensor with a high sensitivity was implemented on the printed composite layers of graphene in isopropyl alcohol with additions of polyvinyl pyrrolidon (PVP) introduced for the stabilization of inks [94]. The conductivity of this film was determined by the percolation conductivity of graphene in the PVP matrix, while a change in the humidity led to a swelling of the PVP owing to its hygroscopicity, which decreased the film conductivity. It has been shown that the conductivity of the film is described by the expression $\phi \sim (v - v_0)^i$, where ϕ is the number of conducting paths, v and v_0 are the fraction of the volume of graphene particles and the critical fraction of the graphene volume, respectively, with $v_0 = 27\pi d^2 t / 4(d + d^*)^3$, where d and t are the size and the thickness of graphene flakes, respectively, and d^* is the spacing between the flakes [100]. A critical distance for the electron hop is considered to be 10 nm [101]. As a result, it was



Figure 8. (a) Optical images of structures consisting of one to six printed graphene layers. (b) Image obtained by the method of scanning electron microscopy from a structure consisting of six printed layers. (c) Raman spectra of the above-mentioned structures. (d) Transmission of light with a wavelength of 550 nm depending on the sheet resistance of printed layers [84].



Figure 9. (a, d) Optical images of a structure consisting of 15 graphene layers (top) and of a transistor structure based on 6 graphene layers (bottom) created on (a) a Kapton polyimide film (Kapton, DuPont, United States) and (d) a silicon substrate. All markers correspond to 10 μ m; the drain and the source in (d) were formed using silver inks. (b) Current–voltage characteristics of resistors with a length of 250 μ m with different numbers of layers. (c) Resistance of a resistor depending on its length. (e) Transfer transistor characteristics of a 6-layer transistor on an SiO₂/Si substrate; V_d is the drain–source voltage. (f) Current in the open state and the ratio between the open and closed states currents (ON/OFF) depending on the length L_c of the transistor channel [84].



Figure 10. Supercapacitor printed on a Kapton polyimide film (Kapton, DuPont, United States): (a) printed silver collector; (b) printed graphene electrodes (8 layers); (c) current–voltage characteristics measured in an aqueous Na_2SO_4 solution for the structures shown in figures (a, b); (d) dependence of the capacitance on the scan rate of the voltage for the structures shown in figures (a, b) [84].

possible to test the humidity in the range from 10 to 80% at temperatures of 25-70 °C. The value of the response (change in the resistance of the film) did not exceed 10%; the response time of the system lasted 16 min for dry air (10%) and decreased to 6-8 s at a higher humidity; the recovery time of a sensor was 60-70 s at a humidity below 50%, and it increased to 300 s at 80%.

Figure 10 schematically displays the fabrication of electrodes for a supercapacitor printed on a flexible substrate [50, 84]. The printed silver collector was covered with graphene (8 layers); as a result, the capacitance of the capacitor in an aqueous solution of Na₂SO₄ increased from 0.2 mF cm⁻² for Ag to 0.6 mF cm⁻² for the two-layered electrodes. With the use of a polymeric electrolyte and Au/graphene electrodes, Xue et al. [91] fabricated a flexible supercapacitor with a specific capacity of 140 F g⁻¹. The potential to recharge such a capacitor to more than 2×10^3 cycles was shown. At present, these are the highest parameters for printed flexible supercapacitors.

Figure 11 depicts the results of an investigation into a photodetector printed using MoS₂-based inks on an Si/SiO₂ substrate [102]. The sheet resistance of the MoS₂ film 50 nm thick was $2 \times 10^{11} \Omega$ /sq; the characteristic response time was 0.6 s. The processes of switching the current in the photo-detector upon illumination by light with different wavelengths are shown in Fig. 11b; the magnitude of the photoresponse is 37 μ A W⁻¹. This is approximately an order of magnitude lower than that characteristic of MoS₂ layers [103], but it is comparable to the results obtained for graphene [104, 105].

Recently, the possibility of preparing micro- and nanowires from an rGO suspension with the use of 3D printing was demonstrated [106]. It was shown that, by controling the velocity of the suspension jet outflowing from the printhead nozzle in the range from 1.2 to 140 μ m s⁻¹, it is possible to obtain (if water is evaporated from the meniscus) an rGO thread with a diameter from 625 to 150 nm. This nanowire was formed with the aid of a micropipette with an orifice diameter equal to 1.3 μ m. The suspension in this case consisted of relatively large flakes with a lateral size of a few microns in water or in organic solvents.

Figure 12 illustrates the dependence of the nanowire diameter on the velocity of the suspension escape from the inkjet printer nozzle and the exterior view of the nanowires of various diameters. This wire is capable of being extended significantly and having its length restored without changing its resistance. Thus, the resistance of a wire with a diameter of 400 nm and a length of 30 μ m was $2.0 \times 10^5 \Omega$, and it did not change under stretching up to a length of 310 μ m. Figure 12 also demonstrates the possibility of using such a nanowire as a gas sensor.

It would be desirable to note one more application of inks with a high content of graphene, namely, their use for 3D printing of scaffolds—three-dimensional substrates for the subsequent growing of bones, future cellular organs, or their parts for transplants. In Ref. [107], it is proposed to create scaffolds from graphene composite (60 vol.%) and polylactide-co-glycolide (biocompatible elastomer). Graphene ensures the required mechanical properties and, first of all, the elasticity of the scaffold, its biocompatibility with a human body, and the potential to grow soft tissues (organs) and bones. The high conductivity of this material makes it possible to also apply it to create bioelectronic devices (for example, heart pacemakers). The printed 75%-porous material from Ref. [107] had a resistivity of 0.114Ω cm (conductivity of 875 S m^{-1}), which is an order of magnitude better than the parameters of the structures created earlier with the use of composite materials [108, 109].



Figure 11. (a) Printed photodetectors made of MoS₂ on an Si/SiO₂ substrate. At the top, an Al₂O₃ film 50 nm thick is applied for passivation; the contacts are made of Ag. (b) Switching of current in the photodetector upon illumination by light of various wavelengths at different gate voltages V_g ; the illumination pulse was repeated every 5 s. (c) Photoresponse of the structure upon illumination by white light at $V_g = 0$. The drain–source voltage was 1 V in all cases [102].



Figure 12. (a) Dependence of the diameter of a nanowire on the velocity of the suspension ejection from a micropipette for three types of suspensions with different characteristic dimensions of the particles. (b) A change in the resistance of a nanowire with a diameter of 400 nm in the presence of carbon dioxide in air. (c–e) SEM images of an unsupported nanowire with a diameter of 625, 400, and 150 nm, respectively [106].

7. Conclusions. Prospects for the development of 2D printing technologies

As has already been noted, the main focus of implications of products made by printing technologies is the designing of sensors and medical and household devices. These are socalled portable electronics, ultrathin consumer electronics, smart clothing, and flexible medical or touch-sensitive detectors, namely, this is the spectrum of applications connected with flexible, transparent, and stretchable electronics on the whole. The appearance of a new class of materials based on graphene and other 2D structures gave hope for a breakthrough in improving the performance characteristics of printing technology devices. This is, first of all, an increase in the lifetime of the devices of printed and flexible electronics, an increase in the sheet conductivity and mobility of carriers in the channel of transistors, and the use of thin-film vertical heterostructures with a high sensitivity as various sensors, photodetectors, etc. It is also necessary to note that the employment of the 2D or 3D printing methods for creating graphene-based materials for biological or medical applications is one of the most actively developing fields, in which composite materials with a high content of graphene are already being used. Thus, at present, rapid progress can be observed in the development of printed micro-, nano-, and bioelectronics and photonics.

The observed progress includes the development of technologies to prepare suspensions of 2D materials and a change in the concept concerning the composition of inks, namely, the passage from liquid compositions with organic fillers to water-based inks with insignificant amounts of organic additives. A decrease in the adoption of such additions or the complete rejection of organic fillers leads to a decrease in the temperatures of the required thermal treatments or makes any thermal treatment completely unnecessary. As a result, a substantial improvement in the parameters of printed layers is observed. The spectrum of materials employed for printing is enlarged significantly: apart from reduced graphene oxide and a regular graphene, research is carried out on the application of MoS₂, NB, WS₂, and fluorographene. Technologies for preparing suspensions and inks from these materials are being developed at present, and studies of the new potential for their use separately or in combination with graphene are being carried out. This enlarges the spectrum of the functional properties of films produced with the application of 2D printing technologies, and in the nearest future it will make it possible to move to printing different heterostructures suitable for a wide spectrum of applications.

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