

Graphene Suspensions for 2D Printing

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Abstract—It is shown that, by processing a graphite suspension in ethanol or water by ultrasound and centrifuging, it is possible to obtain particles with thicknesses within 1–6 nm and, in the most interesting cases, 1–1.5 nm. Analogous treatment of a graphite suspension in organic solvent yields eventually thicker particles (up to 6–10 nm thick) even upon long-term treatment. Using the proposed ink based on graphene and aqueous ethanol with ethylcellulose and terpineol additives for 2D printing, thin (~5 nm thick) films with sheet resistance upon annealing ~30 M Ω/\square were obtained. With the ink based on aqueous graphene suspension, the sheet resistance was ~5–12 k Ω/\square for 6- to 15-nm-thick layers with a carrier mobility of ~30–50 cm²/(V s).

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At present, the use of 2D printing technologies for device production is an important area in the development in modern electronics and photonics [1, 2]. The most attractive features of 2D printing is low cost of the technological process, possibility of assembling devices on flexible substrates, and hybrid approach to using organic materials. The discovery of graphene and other 2D materials possessing unique properties gives hope that one can significantly improve the quality of materials for 2D printing, create new important and promising materials for this technology, and expand the range of its applications [3].

The main requirements for graphene suspensions for 2D printing are conductivity of ink and the lateral dimensions and thickness of particles in suspension. The thickness of particles should not exceed several nanometers, while their lateral sizes must be about 50 times as small as the printer jet nozzle diameter [1, 2]. At a nozzle diameter of 20 μm , this implies a lateral particle size of ≤ 400 nm. A no less important property is the ability of ink material to retain conductivity upon dispersion. As is known, the exfoliation and dispersion of particles may be accompanied by their oxidation and defect formation [4, 5]. Both these processes affect the conductivity of ink layers. In addition, the use of organic additives (e.g., ethylcellulose as a suspension stabilizer and terpineol as a viscosity-controlling agent) requires subsequent annealing for their removal and ensuring desired functional properties of printed layers. Typical values of conductivity in the printed layers of graphene-based ink range from 700 Ω/\square up to several hundred k Ω/\square [1, 6]. Recently, it was shown [7] that a graphene suspension can be obtained using an electrochemical process for graphite exfoliation and dispersion into small particles without oxidation.

In the present work, we have implemented a quite simple method of obtaining graphene-based ink for 2D printing with the use of electrochemical exfoliation of graphite and the creation of suspensions in ethyl alcohol (ethanol) and/or water with the aid of ultrasonic processing and centrifuging. For comparison, we have also prepared graphene suspension in an organic solvent—N-methylpyrrolidone C₅H₉NO (NMP). It was found that the most effective exfoliation of graphite was achieved in ethanol and water. The conductivity of obtained multigraphene particles was retained at a rather high level of 5–12 k Ω/\square and allowed nanometer-thick conducting layers to be obtained.

Electrochemical exfoliation of graphite was carried out in an electrolyte based on an aqueous solution of ammonium persulfate (NH₄)₂S₂O₈. The initial material was high-oriented pyrolytic graphite (HOPG) or natural graphite used as the anode. The electrochemical exfoliation process is based on the formation of gas bubbles on the anode surface. This electrolysis for several minutes allowed HOPG to be delaminated and yielded a suspension of graphite particles of various thicknesses below 100 nm and lateral dimensions within several microns (below 5 μm). In contrast to a conventional method used for the chemical exfoliation of graphite powder and preparation of graphene suspension, which involves the use of organic solvents and many hours of ultrasonic treatment, the proposed electrolysis for several minutes yields approximately the same result and, which is especially important, does not involve organic additives.

Figure 1a shows a typical atomic force microscopy (AFM) image of particles present in a suspension obtained by electrochemical exfoliation of graphite.

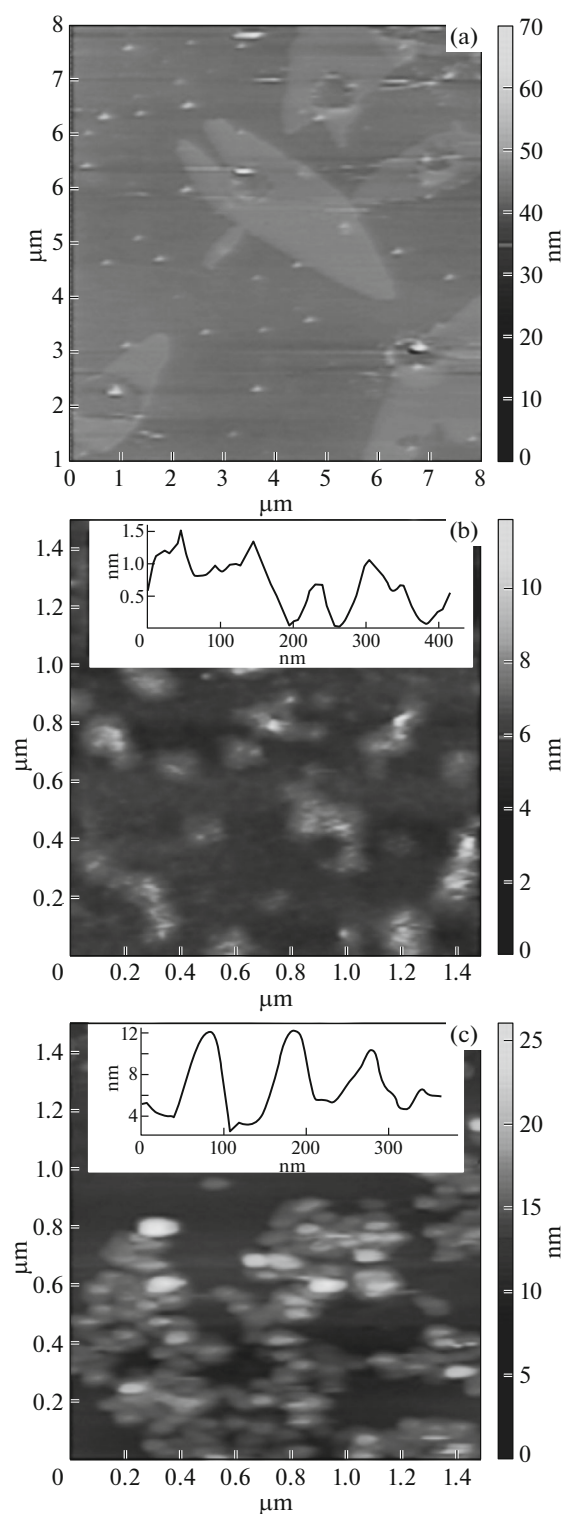


Fig. 1. AFM images of graphene particles deposited from suspension on a SiO_2/Si substrate: (a) immediately upon the electrochemical exfoliation of graphite; (b, c) upon three cycles of 30-min ultrasonic treatment and 30-min centrifuging in ethanol-based and NMP-based suspensions, respectively. The insets show the surface reliefs used to estimate the thickness and lateral sizes of particles. The AFM measurements were performed on a Solver PRO (NT-MDT) instrument.

The image was obtained by depositing washed particles onto a SiO_2/Si substrate surface with an oxide thickness of 300 nm. The results of AFM measurements showed that the particle thickness varied from several nanometers up to several dozen nanometers. Measurements of the sheet resistance of deposited films on SiO_2/Si substrates gave a value of $\sim 20 \Omega/\square$ for an $\sim 200\text{-nm}$ -thick film and $\sim 500 \Omega/\square$ for an $\sim 100\text{-nm}$ -thick film. These measurements were performed using a Jandel four-point-probing head (with interprobe spacing of $\sim 1 \text{ mm}$), so that the resistance was averaged over a sufficiently large area.

The particles obtained by electrochemical exfoliation of graphite were washed, filtered, and transferred to other solutions. First, the particles were mixed with NMP—an organic solvent that is widely used for the preparation of graphene suspensions and conventionally believed to ensure the maximum yield of monolayer graphene particles [8]. In the second case, suspensions were prepared in water and ethanol with various special additives. Then, all suspensions were subjected to three cycles of relatively soft ultrasonic processing (180 W, 30 min) in combination with centrifuging (10 000 rpm, 30 min). Suspensions obtained upon these treatments were applied onto SiO_2/Si substrate (Figs. 1b, 1c). The surface relief of particles from various suspensions (see insets to Figs. 1b, 1c) can be used to estimate their thicknesses. As can be seen from these data, the particle thicknesses in the NMP suspension range within 6–20 nm, while those in the ethanol solution are significantly smaller and vary from one monolayer ($\sim 0.4 \text{ nm}$) to 1–1.5 nm. In the aqueous suspension, the particle thickness varied from 0.4 nm to 6–12 nm. The lateral dimensions of particles in all cases were rather close ($\sim 100 \text{ nm}$). Relatively thick (100–200 nm) layers deposited from graphene suspensions in water and ethanol had upon drying a sheet resistance of 170–200 Ω/\square . Analogous layers deposited from the NMP suspension and measured upon annealing at 150–180°C had a sheet resistance of 200–400 $\text{k}\Omega/\square$.

The more effective electrochemical exfoliation of graphite suspensions in aqueous and ethanol solutions as compared to the well-known NMP suspension is probably related to the significantly higher viscosity of the latter solution, which decreases the efficiency of centrifuging. At the same time, according to [8], the NMP intercalation into interlayer space of graphite particles must favor exfoliation during ultrasonic processing, but the efficiency of this process is insufficiently high. The use ethanol and aqueous solutions significantly facilitates and accelerates graphite exfoliation. In addition, these suspensions do not require taking special measures for the removal of organic components. It should be noted that, according to [9], the most effective graphite exfoliation was observed for 70% aqueous ethanol solution, while not at all taking place in pure water and ethanol.

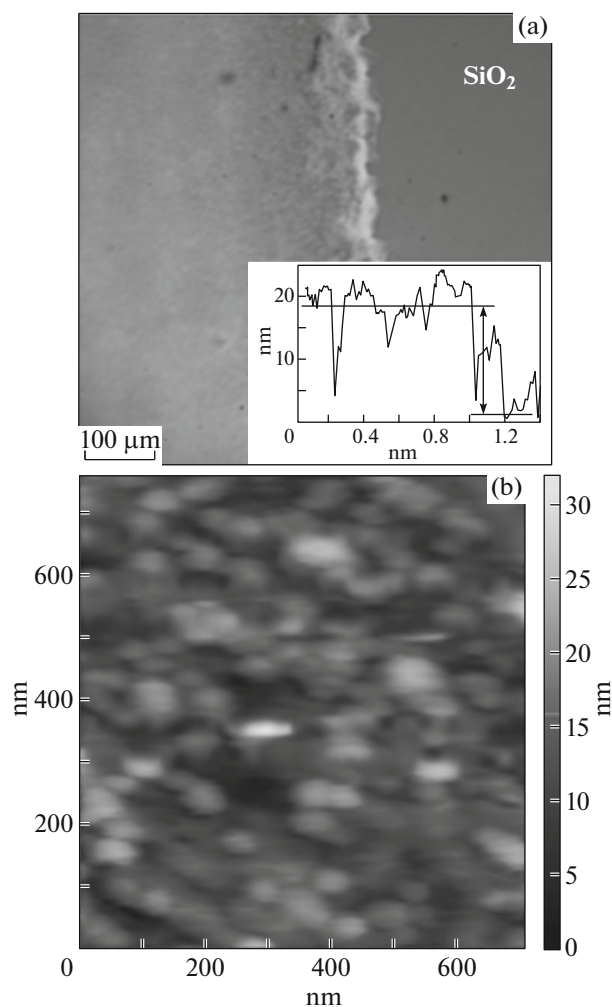


Fig. 2. (a) Optical image of the edge of a 20-layer film printed on a SiO_2/Si substrate using an Epson Status Photo R220 jet printer adapted for working with graphene ink. The inset shows the surface profile measured by AFM near the edge of the printed layer (horizontal lines indicate average height levels in the film and substrate used for determining the printed film thickness; vertical arrow shows the average height drop on the passage from film to substrate). (b) AFM image of the same film.

The graphene suspensions in aqueous and ethanol solutions are unstable and require using special additives or solution replacement during 2D printing. The problem of instability was solved by adding ethylcellulose and terpineol or some surfactants to the ink.

In the first variant of ethanol-based suspension stabilization and use for 2D printing, we used ethylcellulose and terpineol additives. The introduction of ethylcellulose prevents the coalescence of graphene particles, while the addition of terpineol ensures required viscosity of the ink. Figure 2 shows optical and AFM images of a film comprising 20 printed layers with total thickness estimated at ~ 17 nm (see height drop in the insert to Fig. 2a). In order to remove ethylcellulose and

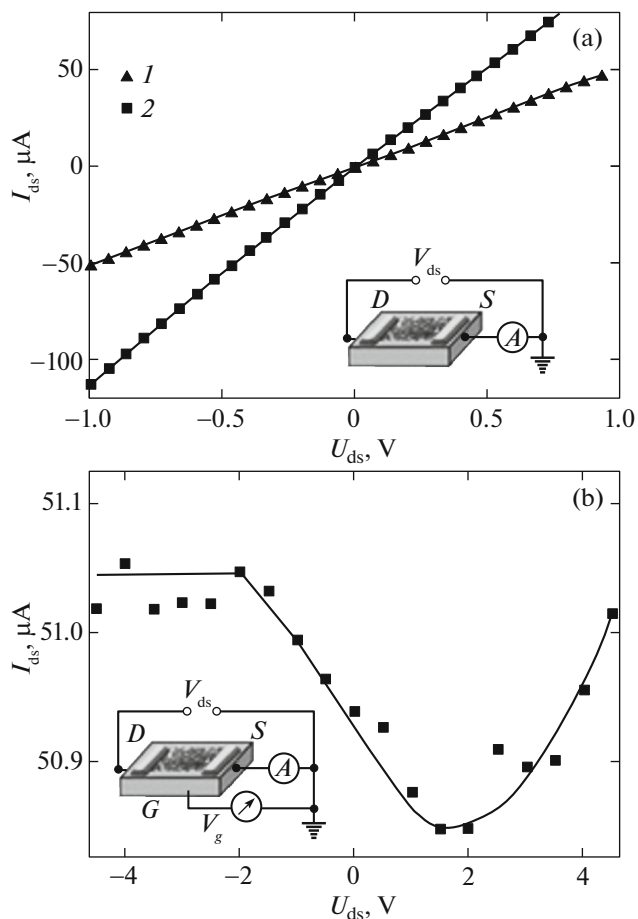


Fig. 3. (a) Current–voltage characteristics measured on (1) ~ 6 -nm-thick and (2) 12-nm-thick printed stripes; (b) transfer characteristic of the 12-nm-thick printed stripe in a transistor structure on a silicon substrate acting as the gate with silver paste contacts. The measurements were performed using a Keithley 6485 picoammeter in the scheme depicted on the inset.

terpineol from the printed film, it was annealed for 1 h at 400°C in an argon–hydrogen atmosphere. As a result of this annealing, the total film thickness decreased to about 5 nm. The sheet resistance of the film upon annealing amounted to ~ 30 $\text{M}\Omega/\square$, which corresponded to a resistivity of 15 Ω cm and was three orders of magnitude higher than the resistivity of pure graphene. The high resistance of printed layers was most probably explained by their small thicknesses and loose structure formed (according to AFM data) after removal of the organic additives.

The most interesting variant of ink was obtained using surfactant additives to aqueous graphene suspensions. Figure 3a (curve 1) shows the current–voltage (I – U) characteristic measured on ~ 6 -nm-thick stripes printed using an aqueous suspension, which had a sheet resistance of ~ 12 $\text{k}\Omega/\square$. In thicker layers (8–12 nm), the sheet resistance decreased to 4–5 $\text{k}\Omega/\square$ (Fig. 3a, curve 2), while 4-nm-thick layers

had a resistance of ~ 570 k Ω . Figure 3b shows a transfer characteristic of the 12-nm-thick printed stripe in a transistor structure on a silicon substrate acting as the gate, measured using a scheme depicted in the inset. The carrier mobility amounted to 50 cm²/(V s) for holes and 40 cm²/(V s) for electrons. In the case of thinner (6–8 nm thick) printed layers, the mobility decreased to 10–30 cm²/(V s).

In concluding, it was demonstrated that a relatively short-term processing of graphite suspension in aqueous ethanol with special additives by ultrasound in combination with centrifuging allows the electrochemical exfoliation of suspended particles to thicknesses within 0.4–6 nm. The exfoliation proceeds more effectively as compared to the process carried out in the organic (NMP) solvent, where the typical particle thicknesses upon analogous processing amounted to 6–10 nm. The conductivity of both aqueous and ethanol suspensions remained sufficiently high and the films with thicknesses within 100–200 nm had a sheet resistance of 170–210 Ω/\square . The replacement of liquid component by terpineol with ethyl cellulose additives provided a stable suspension for 2D printing. However, layers printed with this ink required annealing at a relatively high temperature (400°C) for the removal of organic components and possessed a high resistance. The best result in terms of conductivity was obtained by printing with aqueous

and ethanol suspensions with additives of surfactants. In this case, films of 6–12 nm thickness possessed sheet resistances from 12 to 5 k Ω/\square and a carrier mobility within 30–50 cm²/(V s).

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