Inkjet printing of liquid-exfoliated, highly conducting graphene/poly(3,4 ethylenedioxythiophene):poly(styrenesulfonate) nanosheets for organic electronics

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In this work, highly dispersive graphene inks are demonstrated by liquid-phase exfoliation of the bulk graphite crystal in the solvent *N*-methyl-2-pyrrolidone (NMP). In order to make the inks suitable for inkjet printing, an avenue to tailor the viscosity of the NMP-based ink has been developed through the addition of the organic additive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). The use of PEDOT:PSS with graphene inks shows the solutions to exhibit high dispersion densities as deciphered through optical absorbance measurements, while the inkjet printed structures themselves show a uniform microstructure and typical resistivity values of approximately $0.26 \, m\Omega \, m$ on average with graphene/PEDOT:PSS inks and can be improved further with the modification of ink properties. PEDOT:PSS as a conductive surfactant enhances the electrical conductivity of graphene patterns, and a viscosity of about 12 cP which is ideal for inkjet printing can be achieved by adding a very small amount (0.25 wt. %) of PEDOT:PSS to NMP as compared to higher amounts of nonconductive surfactants like ethyl cellulose needed to obtain similar levels of viscosity. PEDOT:PSS is a workhorse of the organic electronics industry, and this work on graphene/PEDOT:PSS composite inks provides new directions to the organic electronics industry to incorporate two-dimensional layered materials in device platforms. © *2017 American Vacuum Society*.
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I. INTRODUCTION

Graphene, a two-dimensional (2D) form of carbon, has found importance in a range of applications since its discovery in 2004. Graphene consists of just one sheet of carbon atoms arranged in a honeycomb lattice and is the thinnest 2D material known.[1–4] Specifically, some of its applications include printed electronics,[5–7] flexible displays,[8] fuel cells,[9] and solar cells[10] and also a range of other applications due to its high strength and good thermal and electrical properties. Other 2D noncarbon based layered materials have similar characteristics in that they have a strong in-plane covalent bonding within the layers but a weak out-of-plane bonding through the van der Waals interaction bonding.[11]

Given the weak van der Waals bonding, 2D layered materials can be exfoliated easily in which individual crystal planes are sheared from their neighbors to yield monolayer or few layer dispersions for the production of thin atomic 2D nanosheets.[12–15] Liquid-phase exfoliation refers to exfoliation in suitable solvents. It is a versatile, scalable, and sustainable route for the production of 2D nanosheets. There are four widely used methods of liquid exfoliation, which include oxidation and subsequent dispersion in a suitable solvent, ion intercalation, ion exchange, and sonication-assisted exfoliation.[16] Sonication-assisted exfoliation is the most popular among the techniques commonly used to make inks, which includes techniques such as aerosol jet printing

and inkjet printing.[17,18] In this process, a bulk layered material, e.g., graphite, is added to a solvent and the resultant solution is exposed to ultrasonic waves. These waves generate cavitation bubbles that collapse into high-energy jets breaking up the layered crystallites and producing exfoliated nanosheets. If the surface energy of solvent is similar to that of the layered material, there is no driving force for reaggregation of exfoliated nanosheets after sonication, and this will thus lead to stable dispersions of 2D nanosheets. Therefore, a good solvent for exfoliating a layered material is the one with surface energy similar to the layered material undergoing exfoliation.[19] Once the stable exfoliated solution of 2D nanosheets is prepared, the inkjet printing technique can be used to print desired structures from the 2D materials.

Inkjet printing is a material-conserving deposition technique used for printing patterns and devices using liquid–phase materials.[20–23] It finds importance in various applications like thin-film transistors,[24] light-emitting devices,[25] solar cells,[26] sensors, and detectors.[27] The present challenges in printed electronics include finding an appropriate common solvent for exfoliation and printing, obtaining highly conductive and uniform graphene patterns, preventing nozzle clogging and nonuniform spread of ink on the substrate, promoting adsorption, and preventing absorption of inks.[28–31]

2D materials can be printed with an adequate resolution using inkjet printing when the viscosity of inks is in the desired range (around 12 cP for DMP-2800 Fujifilm Dimatix Materials Printer). Good solvents for exfoliating graphene

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15 mg/ml graphite powder in NMP

48 hours
Bath Sonication

Addition of 0.25 weight% PEDOT:PSS

1 hour Magnetic Stirring at 100 rpm

Final Ink
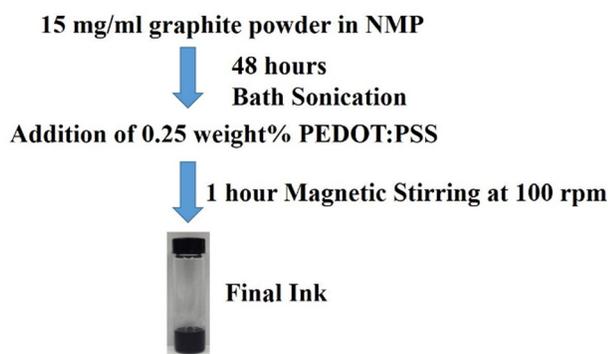
FIG. 1. (Color online) Schematic representation of the ink preparation procedure.

like *N*-methyl 2-pyrrolidone (NMP) and dimethylformamide have viscosity significantly less than 12 cP. In order to obtain a viscosity of about 12 cP, which is ideal for inkjet printing, either a highly viscous solvent in an appropriate amount can be added to exfoliating solvent or an additive such as a surfactant can be used. The former often leads to the reaggregation of dispersed nanosheets. The latter involves the use of surfactants which are comparatively stable. Surfactants can be divided into two categories—conductive and nonconductive. Both promotes the stabilization of dispersed 2D nanosheets;[32–34] however, the use of a conducting polymer like poly(3,4 ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), as a surfactant helps in enhancing electrical conductivity in applications where high electrical conductivity is desired.[35] Graphene/PEDOT:PSS inks have found applications in gas, electrochemical, and biochemical sensing.[36–38] This work utilizes the conductive property of the PEDOT:PSS polymer surfactant to demonstrate the good electronic transport properties of graphene/PEDOT:PSS inkjet printed films and promotes inkjet printing as a scalable approach to yield printed features with the desired high electrical transport properties.

II. EXPERIMENT

Graphite powder in the amount of ~15 mg/ml was obtained by breaking the graphite rod (Sigma Aldrich #496553) and placed in a glass vial, and 10 ml of NMP (Sigma Aldrich #270458) was then added. The solution was sonicated in a Branson 2800 bath sonicator for 48 h. PEDOT:PSS of 0.25 wt. % was then added to the solution and magnetically stirred for 1 h at 100 rpm. This was our final conductive ink. The ink preparation procedure is shown in Fig. 1. PEDOT:PSS used in the present study was 1.1 wt. % PEDOT:PSS in water solution (Sigma Aldrich #739332).

PEDOT:PSS was added primarily to obtain a viscosity of about 12 cP which is ideal for inkjet printing. It also prevents particle agglomeration and improves suspension stability. Graphene/PEDOT:PSS ink was characterized by optical absorption spectroscopy using a CARY 5000 spectrophotometer. A DMP-2800 series Fujifilm Dimatix Materials Printer with a printhead consisting of 16 inkjet nozzles was used to print various patterns in this work. Annealing of printed patterns was done at 250 °C for 2 h to remove solvents. A cartridge temperature of 30 °C and a platen temperature of 60 °C were used during all the printing work. Raman spectroscopy was performed on annealed samples using LabRAM HR Evolution. Tungsten probe tips were used to contact the inkjet printed patterns. All the electrical measurements were performed using a micromanipulator 450PM-B probe stage equipped with a precision semiconductor parameter analyzer 4156A.

III. RESULTS AND DISCUSSION

The optical absorption study was conducted to observe the effectiveness of the exfoliation and dispersion, where the absorption measurements of the graphene/PEDOT:PSS solutions were conducted in the visible range (400–700 nm). NMP was used as the reference sample. High values of optical absorbance were found, indicating good uniform dispersibility and high concentration of graphene and PEDOT:PSS in NMP as shown in Fig. 2(a). These high values of absorbance are attributed to nanodispersions of graphene and PEDOT:PSS particles, which was confirmed by optical micrographs of the annealed graphene/PEDOT:PSS printed line as shown in Fig. 2(b).
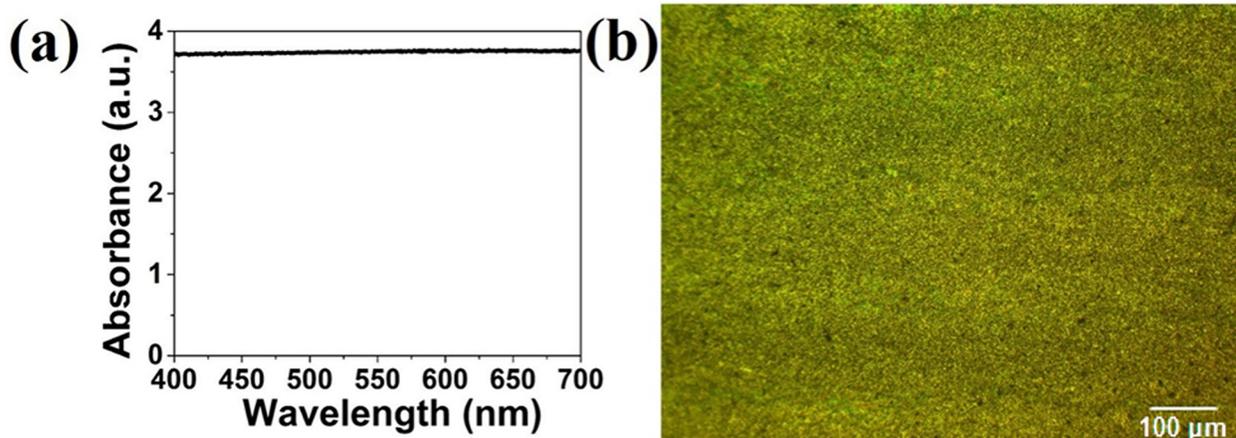
FIG. 2. (Color online) (a) Optical absorption spectra of graphene in NMP sonicated for 48 h, and (b) optical micrograph showing graphene/PEDOT:PSS nanosheets.
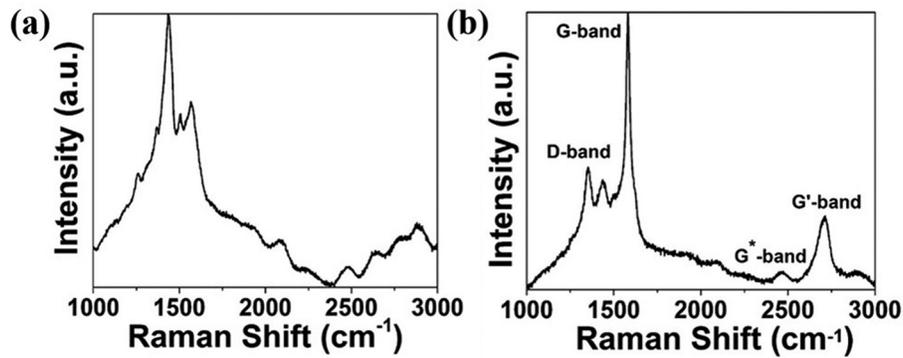
FIG. 3. (a) Raman spectra of annealed printed PEDOT:PSS, and (b) Raman spectra of annealed printed graphene/PEDOT:PSS.

Raman spectroscopy is a widely used spectroscopic technique for the identification of various materials.[39–43] The Raman spectra of annealed printed PEDOT:PSS showed a strong peak at about $1436\,cm^{-1}$, which is ascribed to C=C stretching as shown in Fig. 3(a).[44] The Raman spectra of annealed printed graphene/PEDOT:PSS showed the D-band, G-band, G*-band, and G′-band of graphene and the peak at about $1436\,cm^{-1}$ of [Fig. 3(b)], indicating uniform mixing of graphene and PEDOT:PSS nanoparticles. The D-band is attributed to the in-plane A_{1g} zone-edge mode and can be used to monitor the defect distribution.[45] The G-band arises from stretching of C–C bonds in graphitic materials.[46] The G′-band is indicative of exfoliation in graphitic materials. The higher G′-band implies better exfoliation. No other significant peaks were observed as NMP solvent was removed completely by annealing at a temperature of 250 °C for 2 h, which is well above its boiling point.

Lines of 5 mm length and 1 mm width were printed first with 2.5 wt. % PEDOT:PSS in NMP [Fig. 4(a)] and then with graphene/2.5 wt. % PEDOT:PSS in NMP [Fig. 4(b)] followed by annealing at 250 °C for 2 h to remove NMP solvent. Good resolution and uniform printability were observed during printing of both inks. This was done to study and compare the optical and electrical behavior of PEDOT:PSS in NMP inks with and without graphene. Lines of different lengths (1, 5, 10, 15, 20, and 25 mm) with 50 numbers of printing passes [Fig. 4(c)] were printed to show the good dimensional accuracy and scalability of the inkjet printing process.

Electrical measurements of annealed printed patterns were carried out to compare the electrical behavior of graphene/PEDOT:PSS and only PEDOT:PSS printed films. Figure 5(a) demonstrates that 0.25 wt. % PEDOT:PSS is not conductive by itself even up to 50 numbers of printing passes. Graphene/PEDOT:PSS annealed printed patterns showed good conductivity up to 0.7 mA with 50 numbers of printing passes at a 5 mm length scale or probe separation distance [Fig. 5(b)]. The response of current was inversely proportional to the length. The values of current increased with decreasing lengths [Fig. 5(c)]. It can be observed that high values of current (around 0.2 mA) can be obtained even at length scales of 25 mm which is significantly higher in the electronics industry. The resistance of printed graphene/PEDOT:PSS annealed films showed inverse proportionality with the number of printing passes and direct proportionality with the length of printed patterns. It decreased with the increasing number of passes when the length was kept constant at 5 mm [Fig. 5(d)] and increased with the line length when the number of printing passes was constant at 50 [Fig. 5(e)]. Resistances as low as 1.36
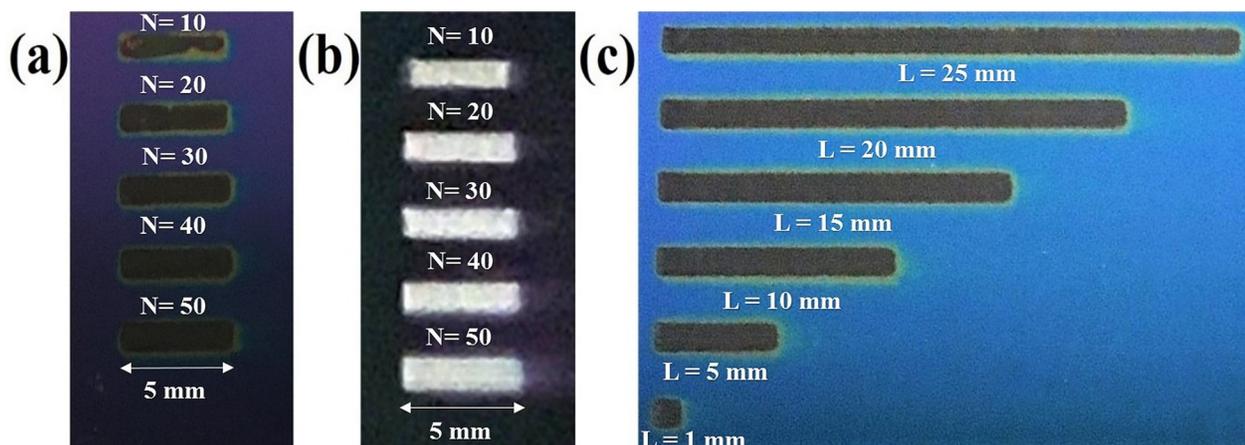
FIG. 4. (Color online) (a) and (b) Line patterns of 5 mm length and 1 mm width of annealed (a) PEDOT:PSS, (b) graphene/PEDOT:PSS with different numbers of passes (N = 10, 20, 30, 40, and 50), and (c) printed lines with 50 numbers of passes of annealed graphene/PEDOT:PSS of varying lengths (L = 1, 5, 10, 15, 20, and 25 mm).
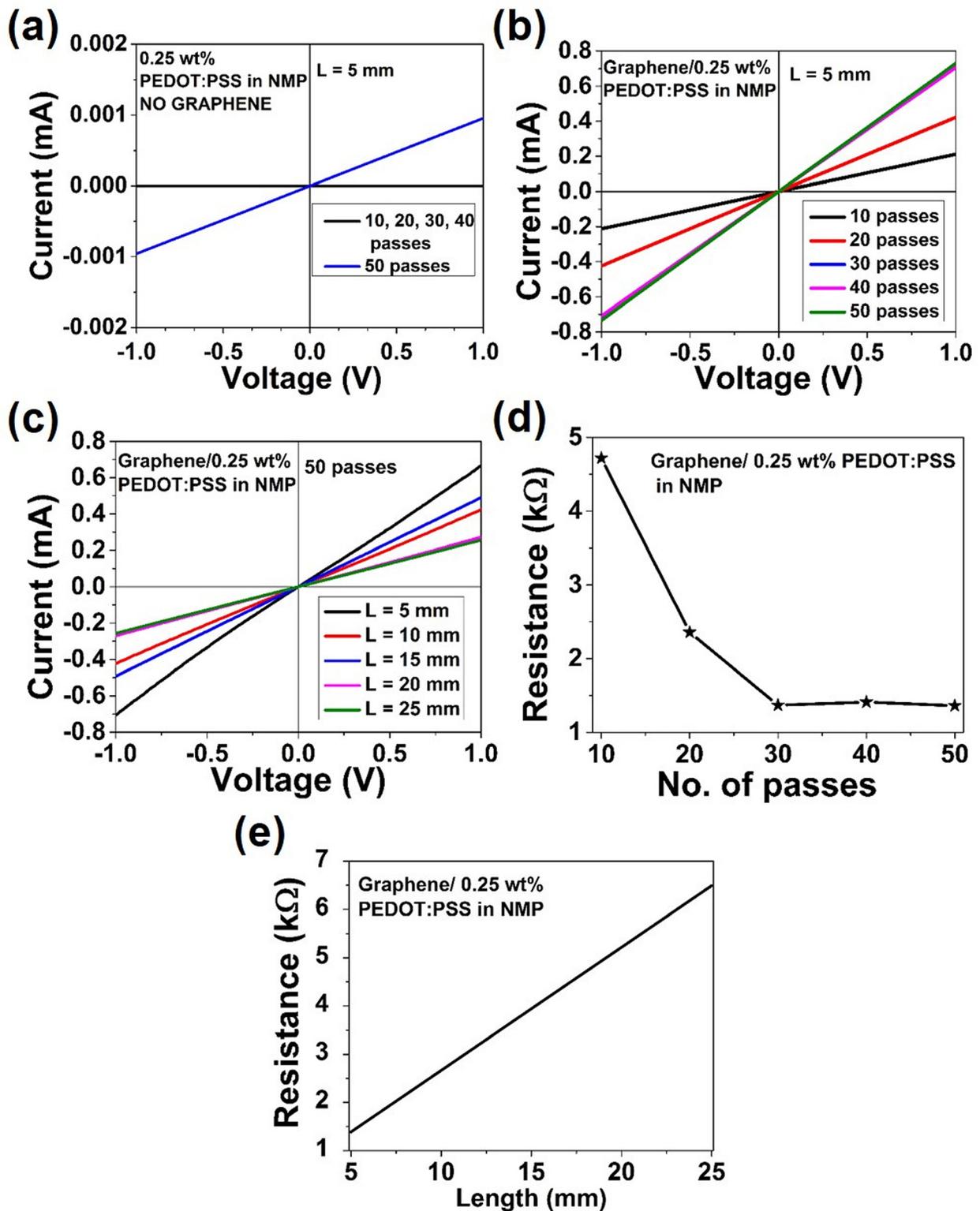
Fɪɢ. 5. (Color online) (a)–(c) Variation of current with voltage for (a) PEDOT:PSS at a length of 5 mm, (b) graphene/PEDOT:PSS at a length of 5 mm, and (c) graphene/PEDOT:PSS at varying lengths (5, 10, 15, 20, and 25 mm), (d) variation of resistance with the number of printing passes, and (e) variation of resistance with the printing pattern length.

and 6.49 kΩ at lengths of 5 and 25 mm were achieved with just 50 numbers of printing passes. Higher electrical conductivity can be achieved by either increasing numbers of printing passes, decreasing pattern lengths, or using higher initial graphite concentrations.

IV. SUMMARY AND CONCLUSIONS

High absorbance values were obtained indicating highly concentrated and dispersed graphene particles in NMP. Raman spectra confirmed the presence of both PEDOT:PSS

and graphene in printed patterns. Graphene/PEDOT:PSS highly conductive patterns were successfully printed with a good resolution using NMP as the solvent. High values of currents and low values of resistance were obtained, which promotes inkjet printing as a material-conserving and simple method for device fabrication. The scalability of the inkjet printing process has also been demonstrated. This work will aid researchers in the organic electronics industry to make better conductive devices with graphene/PEDOT:PSS solution.

ACKNOWLEDGMENTS

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