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Inkjet printing of graphene

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The inkjet printing of graphene is a cost-effective, and versatile deposition technique for both transparent and non-transparent conductive films. Printing graphene on paper is aimed at low-end, high-volume applications, i.e., in electromagnetic shielding, photovoltaics or, e.g., as a replacement for the metal in antennas of radio-frequency identification devices, thereby improving their recyclability and biocompatibility. Here, we present a comparison of two graphene inks, one prepared by the solubilization of expanded graphite in the presence of a surface active polymer, and the other by covalent graphene functionalization followed by redispersion in a solvent but without a surfactant. The non-oxidative functionalization of graphite in the form of a donor-type graphite intercalation compound was carried out by a Birch-type alkylation, where graphene can be viewed as a macrocarbanion. To increase the amount of functionalization we employed a graphite precursor with a high edge to bulk carbon ratio, thus, allowing us to achieve up to six weight percent of functional groups. The functionalized graphene can be readily dispersed at concentrations of up to 3 mg ml\(^{-1}\) in non-toxic organic solvents, and is colloidally stable for more than 2 months. The two inks are readily inkjet printable with good to satisfactory spreading. Analysis of the sheet resistance of the deposited films demonstrated that the inks based on expanded graphite outperform the functionalized graphene inks, possibly due to the significantly larger graphene sheet size in the former, which minimizes the number of sheet-to-sheet contacts along the conductive path. We found that the sheet resistance of printed large-area films decreased with an increase of the number of printed layers. Conductivity levels reached approximately 1–2 k\(\Omega\) \(\square\)\(^{-1}\) for 15 printing passes, which roughly equals a film thickness of 800 nm for expanded graphite based inks, and 2 M\(\Omega\) \(\square\)\(^{-1}\) for 15 printing passes of functionalized graphene, having a film thickness of 900 nm. Our results show that ink preparation and inkjet printing of graphene-based inks is simple and efficient, and therefore has a high potential to compete with other conductive ink formulations for large-area printing of conductive films.
1 Introduction

Manufacturing large-area graphene thin films is an important step towards the commercialization of graphene based technologies. The inkjet printing of graphene is one method for the controlled deposition of large-area transparent or non-transparent conductive films. In comparison with other approaches such as chemical vapor deposition (CVD), inkjet printing is a poor competitor. This holds true especially for transparent graphene thin films, where high conductivity and high transparency, together with precise control over the number of layers and defect density is required. Nevertheless, the printing of graphene has a very high potential for applications, where non-transparent but highly conductive patterns are required. Examples of such low-end, high-volume applications could be radio frequency identification tags (RFID tags), electromagnetic shielding, or devices where graphene printing of conductive patterns can be effectively utilized.

Graphene inks made from graphite have the potential to revolutionize the field of printed conductors by replacing metallic inks while at the same time reducing biological hazards and production costs.

There are several reports on graphene-based inks encompassing different preparation routes, including the oxidation of graphite to graphite oxide, and extended ultrasonication of graphite with or without a surfactant. The majority of studies on non-oxidized graphene report a relatively low graphene concentration, poor conductivity and rather low ratio of graphene to surfactant. Recently, the successful non-oxidative functionalization of graphene was shown, leading to slightly improved dispersibility in a number of solvents. Functionalization seems to be very promising for graphene inks as it allows the use of surfactants for colloidal stabilization to be avoided, which in turn has been made responsible for decreasing the conductive properties of a printed layer by increasing the sheet-to-sheet contact resistance. Unfortunately, the previously demonstrated amount of graphene functionalization and, thus, product dispersibility, is far from ideal, a point which this paper will address.

In this paper we describe two methods for the preparation of graphene-based inks. First, a simple, efficient and up-scalable method is presented, starting from raw graphite and avoiding any oxidation steps to preserve the conductive properties of the graphene throughout the entire process. Second, a non-oxidative covalent functionalization of graphene is presented resulting in a final product dispersibility of up to 3 mg ml$^{-1}$ in non-toxic solvents. Subsequently we studied the printability of the two inks using two paper substrates, namely FS3 and LumiForte special application papers, which are widely used as substrates for the inkjet and screen printing of conductive patterns. Furthermore, the performance of the two inks was evaluated by means of sheet resistance measurements of large printed areas as a function of the number of printed layers.

2 Experimental

2.1 Preparation of expanded graphite (EG) from Li–THF–GIC

The synthesis of a ternary graphite intercalation compound with Li in THF (Li–THF–GIC) was performed using the procedure of Nomine and Bonnetain. Briefly, 1.28 g of naphthalene C$_{10}$H$_{8}$ (0.01 mol, Alfa Aesar, USA) was dissolved in
100 ml of freshly distilled tetrahydrofuran (THF) by vigorous stirring, followed by
the addition of 0.12 g of freshly cut metallic lithium (0.017 mol, Alfa Aesar, USA).
Then 0.5 g of −10 mesh graphite (0.042 mol, Alfa Aesar, USA or Asbury Graphite,
USA) was added to the reaction mixture at once. The reaction flask was then
sealed and left stirring for another 72 hours. The Li–THF–GIC was separated from
the side products by decantation followed by rinsing with freshly distilled THF.
The residue was filtered and dried in ambient conditions for 20 minutes.

The freshly prepared GIC was placed at the bottom of a Vitreosil quartz
 crucible ensuring that all of the particles were in mutual contact. The crucible was
placed in a 2450 MHz 700 W home appliance microwave oven and exposed to
irradiation for 1 minute. The as-prepared expanded graphite (EG) was used
without any further treatment.

2.2 EG ink preparation with Plasdone S-630
EG (1.4 mg ml\(^{-1}\)) was added to a glass vial containing 5 mg ml\(^{-1}\) of a 60 : 40
copolymer of N-vinyl-2-pyrrolidone and vinyl acetate (Plasdone S-630, Ashland
Inc., USA) dissolved in a mixture of isopropanol (IPA) and \(n\)-butanol (\(n\)-BuOH)
with a volume ratio of 1 : 3. The slurry was ultrasonicated (Branson 1510DTH SB)
in ice water for 30 minutes. The as-obtained dispersion was used without any
further treatment.

2.3 Functionalization of graphite platelet carbon nanofibers (GCNFs)
The synthesis and functionalization of graphite via a potassium intercalation
compound (C\(_8\)K GIC) were performed in a N\(_2\) glovebox with an O\(_2\) concentration
<0.1 ppm and H\(_2\)O <0.1 ppm.

Preparation of NaK. A liquid NaK alloy was prepared similarly to ref. 18. Briefly,
freshly cut and dry pieces of Na and K with a mass ratio of 1 : 7.4 were pressed
together and agitated with a spatula to obtain a liquid state alloy.

Preparation of C\(_8\)K GIC. Graphite platelet carbon nanofibers (100 mg, 0.0083
mol, Strem Chemicals, USA) were added to a 50 ml round bottom flask containing
20 ml of absolute THF, followed by the addition of 0.29 ml of freshly prepared NaK
alloy. The reaction mass was stirred for 3 days to obtain a dark blue to green
dispersion. Next, 0.9 g of \(p\)-nitrobenzylbromide (0.00416 mol, Merck Chemicals,
Germany) was dissolved in 10 ml of absolute THF and added to a GIC dispersion
by 0.5 ml every 1.5 hours. After addition the reaction mixture was additionally
agitated for 1 day. Afterwards the sample was taken out of the glovebox, followed
by quenching with isopropanol (5 ml), ethanol (5 ml), and finally water (5 ml). The
reaction mass was then centrifuged at 8000 rpm for 30 minutes and the super-
natant was discarded. The product was redispersed in a THF–H\(_2\)O (3 : 1) mixture
and centrifuged under the same conditions as described above. The washing
procedure was repeated with the following solvent mixtures: IPA–H\(_2\)O (3 : 1),
EtOH–H\(_2\)O (3 : 1), EtOH–H\(_2\)O (1 : 3), and H\(_2\)O. The washed product was finally
redispersed in H\(_2\)O and filtered through a 0.45 μm pore size PTFE membrane and
dried under vacuum at 50 °C to yield a black powder of \(p\)-nitrobenzyl functional-
alized graphite platelet carbon nanofibers (PNB–GCNFs). This material was used
for the preparation of graphene inks without further treatment.
2.4 Ink preparation with PNB–GCNFs
PNB–GCNF powder (3 mg ml\(^{-1}\)) was added to a vial containing propylene glycol diacetate (PGDA, The Dow Chemical Company, USA) and ultrasonicated (Branson 1510DTH SB) in ice water for 2.5 h. The as-prepared dispersion was used for printing without further treatment.

2.5 Printing conditions
Printing tests were performed on a Dimatix DMP 2800 system (Dimatix-Fujifilm Inc., USA), equipped with a 10 pl drop volume cartridge (DMC-11610). The print head contained 16 parallel square nozzles with a diameter of 30 \(\mu\)m. The dispersion was printed at a voltage of 13 V, using a frequency of 5 kHz and a customized waveform. FS3 paper (Felix Schoeller, Germany) and LumiForte paper (Stora Enso, Finland) were used as substrates. The distance between the printing head and substrate was set to 200 \(\mu\)m. The following patterns were printed: dots (3 lines, 200 \(\mu\)m drop spacing), rectangles of 5 \(\times\) 35 mm in size, and 3 pixel wide lines with a 20 \(\mu\)m line distance. In the case of the functionalized graphene inks with propylene glycol diacetate as the solvent, the substrate temperature was optimized to 50 °C.

2.6 Thermal gravimetric analysis conditions
TGA measurements were performed using a TGA Q500 (TA Instruments, USA) in the temperature range 35–600 °C under a \(\text{N}_2\) gas flow with a heating rate of 10 °C min\(^{-1}\).

2.7 X-ray photoelectron spectroscopy conditions
X-ray photoelectron spectroscopy (XPS) measurements were carried out with a K-Alpha, Thermo Scientific spectrometer using an aluminum anode (Al K\(_{\alpha}\) = 1486.3 eV) operating at 510 W with a background pressure of 8 \(\times\) 10\(^{-9}\) mbar. The spectra were recorded using the VGX900 data system collecting 40 scans. The spectra were acquired at a take-off angle of 0° relative to the surface normal, corresponding to a probe depth of around 10 nm.

2.8 X-ray diffraction conditions
X-ray diffractograms were obtained on a Bragg–Brentano Rigaku Geigerflex diffractometer with CuK\(_{\alpha}\) irradiation using Lindemann capillaries with an internal diameter of 3 mm.

2.9 Sheet resistance measurement conditions
The sheet resistance was measured with a four-point probe setup (source: Keithley 237 High Voltage Measure Unit, resistance meter: Keithley 6517A High Resistance Meter) with an interprobe distance of 5 mm, in a range of currents from 10 nA to 1 mA.
3 Results and discussion

3.1 Preparation of ink with expanded graphite

The ink preparation workflow starts with a donor-type intercalation of raw graphite as shown in Fig. 1. The donor-type intercalation compound (IC) is formed by donating electrons to the graphite matrix, thus, making it negatively charged, and accompanied by the insertion of positively charged species to sandwich a graphene layer between two layers of intercalants (stage 1 IC).\textsuperscript{18,19} In contrast to oxidation, \textit{i.e.}, the withdrawal of electrons from a graphite matrix, such an approach prevents the formation of any functional groups, and hence, preserves the conductive properties of graphene. The formed stage 1 donor-type IC slowly decomposes upon exposure to ambient conditions into mixtures of a higher stage IC.\textsuperscript{20} For instance, the IC flake shown in Fig. 1b exhibits charging effects at the edges and planes which can be attributed to lithium salts deintercalating from the graphite matrix. Therefore, the intercalated materials were analyzed or used immediately after their synthesis.

To increase the distance between graphene layers and to promote layer separation, the IC was subjected to high-speed thermal expansion by means of microwave irradiation. Rapid heating of the GIC results in an abrupt conversion of the intercalated species into the gas phase, thus, causing expansion of the graphite planes along the \textit{c}-axis.\textsuperscript{21,22} The resulting expanded graphite (EG) has a porous worm-like structure, as shown in Fig. 1c, with a significantly increased specific volume (more than 300 times larger compared to the initial IC). In the next step, EG with concentrations of up to 1.4 mg ml\textsuperscript{-1} was dispersed in a mixture of i-propanol and \textit{n}-butanol to obtain a colloidally stable dispersion (Fig. 1d). For ink formulation we opted for the highest graphene content \textit{vs.} a reasonable colloidal stability. We found experimentally that at a graphene concentration of 1.4 mg ml\textsuperscript{-1} against 5 mg ml\textsuperscript{-1} of surfactant, the ink is colloidally stable for more than 9 months, whilst also providing a maximum graphene to surfactant ratio.

Fig. 1 The preparation of graphene inks from raw graphite via intercalation. (a) The overall scheme showing: (i) graphite intercalation, (ii) thermal expansion, and (iii) liquid phase exfoliation; (b) a scanning electron micrograph of a Li(THF) graphite intercalation compound; (c) a scanning electron micrograph of expanded graphite; (d) a graphene dispersion with a concentration of 1.4 mg ml\textsuperscript{-1} prepared from expanded graphite.
3.2 Preparation of ink with functionalized graphene

As an alternative to the surfactant-based graphene ink formulation, we also developed a functionalized graphene ink (Fig. 2a). To date, there have been several studies on graphene functionalization\textsuperscript{14,16,23,24} based on the chemistry of donor-type graphite intercalation compounds. Nevertheless, most approaches demonstrate only a very low amount of functionalization (thus poor dispersibility), which is in good agreement with the early works of Bergbreiter and Killough.\textsuperscript{25} According to ref. 25, in a donor-type IC the reactivities of edge and bulk carbon atoms are different, with edge atoms undergoing the desired two-electron Birch-type alkylation, while bulk carbon can just give up an electron via a single electron transfer, thus acting as a catalyst for the undesired Wurtz-type coupling. This has led to the conclusion that the edge-to-plane ratio of carbon atoms plays a significant role in functionalization efficiency. Therefore, instead of commonly used micrometer-sized graphite, which has a low edge-to-plane carbon ratio, we used platelet-type, \textit{i.e.} graphitic, carbon nanofibers (GCNFs). This type of graphite, with graphene sheet sizes of only 10–60 nm, assures a high edge-to-plane carbon ratio (Fig. 2b).

According to the above concept, a high degree of functionalization can significantly improve the dispersibility of small sheet graphene due to an increased number of interaction sites between functional groups and solvent associates. Thus, we synthesized a potassium graphite intercalation compound with GCNFs as the starting material for further functionalization. Next, we functionalized the as-obtained GCNF IC with \textit{p}-nitrobenzylbromide using an approach similar to the one described by Garst, Barbas, and Barton.\textsuperscript{26} In order to minimize the formation of undesired Wurtz-type dimerization side products, the

![Diagram of ink preparation process]

**Fig. 2** Preparation of functionalized graphene inks from graphitic carbon nanofibers (GCNFs). (a) Scheme of GCNF functionalization (i) preparation of potassium–GCNF IC, (ii) functionalization of potassium–GCNF IC with \textit{p}-nitrobenzylbromide, and (iii) liquid phase exfoliation; (b) a transmission electron micrograph of the starting GCNF; (c) a transmission electron micrograph of the cast-dried functionalized GCNF; (d) a PNB–GCNF dispersion with a concentration of 3 mg ml\textsuperscript{-1} in propylene glycol diacetate.
concentration of alkyl radicals in solution had to be kept much lower than the concentration of the substrate. Such conditions can be achieved by a slow alkylhalide vapour diffusion into the reaction medium or, as utilized in our procedure, by the stepwise addition of a very dilute (see experimental) alkylhalide solution. Upon the addition of alkylhalide we observed a significant volume expansion of the graphite phase indicating in situ exfoliation. The dried reaction product was found to be dispersible in a number of solvents including ethanol, i-propanol, chlorinated solvents and others. Transmission electron microscopy of a cast dried dispersion revealed that most of the GCNFs had been exfoliated into platelets which were prone to agglomeration, as shown in Fig. 2c.

We also performed dispersibility tests in order to find an appropriate solvent for inkjet printing. Our criteria for the final formulation included non-toxicity of the solvent, combined with a high solid content vs. colloidal stability, and printability. Experimentally we found that an optimal solvent for p-nitrobenzyl functionalized GCNFs (PNB–GCNFs) was propylene glycol diacetate (PGDA), allowing a solid content of 3 mg ml\(^{-1}\) without the use of surfactants (Fig. 2d). PGDA is a common solvent used for inkjet printing, with a viscosity of 2.6 mPa s (at 25 °C) and a surface tension of 32.9 mN m\(^{-1}\) (at 20 °C). The downside of this solvent is the rather low relative evaporation rate of 0.04 (n-butyl acetate = 1.0), which might extend the drying process.

3.3 Analysis of the functionalized graphene

The functionalized GCNF graphene was subjected to thermal gravimetric analysis (TGA). In an inert atmosphere this technique revealed (Fig. 3a) a sharp

Fig. 3 Analysis of p-nitrobenzyl functionalized carbon nanofibers. (a) Thermal gravimetric analysis in dry N\(_2\) with a heating rate of 10 °C min\(^{-1}\); X-ray photoelectron spectra of (b) C 1s, (c) N 1s, and (d) O 1s.
decomposition peak amounting to about 6 weight percent, which was attributed to the presence of functional groups (p-nitrobenzyl), relating to approximately one per 166 carbon atoms. This hypothesis was supported by X-ray photoelectron spectroscopy (Fig. 3b–d). Here, XPS analysis confirmed the presence of carbon covalently bonded to a strong electron withdrawing group, i.e., C–NO₂ (Fig. 3b). Further, XPS showed the presence of nitrogen, presumably in a nitro group (–NO₂), as well as in reduced form –NHₓ (possibly including the hydroxylamine form), which can be explained by the partial reduction of nitro groups by the NaK alloy (Fig. 3c). Also the XPS spectra of oxygen show the presence of a strong electron withdrawing oxygen containing group such as –NO₂. Quantification of the XPS data by peak area adjusted with relative sensitivity factors gave a relative carbon to nitrogen ratio of approximately 99 to 1. This corresponds to a functionalization degree of one p-nitrobenzyl group per 92 carbon atoms or theoretically 11 wt%. The observed discrepancy between the TGA and XPS data can be attributed to several factors, such as probing depth, and the sample surface roughness of the latter. Nevertheless, the results found by both techniques are comparable when the margins of error are taken into account. Considering all of the above results, combined with the significantly improved dispersibility of the final product, we concluded that functionalization had been successful.

3.4 Inkjet printing of graphene-based inks onto paper substrates

Printing tests of the developed inks were performed on commercially available paper substrates, namely FS3 and Lumi. FS3 is a glossy, polymer-coated paper and Lumi is a matt and rougher paper. The presence of a polymer coating on the FS3 minimizes the surface roughness, making it similar to polymeric foil substrates such as polyethylene terephthalate (PET), and it improves the adhesion of the printed layers. Nevertheless, even with a coating on top, FS3 still maintained its absorbing properties towards solvents, and quickly separates the non-soluble components from soluble ones.

To analyze the spreading behavior of the inks, arrays of dots were printed. In Fig. 4a–d optical micrographs of the corresponding shapes of the printed dots are shown. It can be clearly seen that, independent from the ink formulation, the two substrates have different spreading behavior. Dots printed on FS3 paper have a round shape with sharp edges and no significant signs of any “coffee stain” effects are observed. Contrary to FS3, both of the inks printed on Lumi paper demonstrate extensive spreading with an increase in dot size. In addition, the printed dots have irregular shapes with ill-defined edges, thus significantly lowering the resolution of the printed features. All of the above indicates clearly that independent from the ink formulation, both substrates have different spreading properties, with the FS3 paper suppressing any expansion of the droplet while it is drying and adsorbing, whereas on the Lumi paper the droplet is spreading while it is drying or being absorbed.

An important characteristic of evaluating ink-substrate compatibility is the edge resolution and the ink spreading over large printing areas. To this end, rectangles of 5 x 35 mm in size were printed with 1, 5, 10 and 15 printing passes on both paper substrates. In Fig. 4e–l optical micrographs of the corners of the printed rectangles are presented. The corners of the rectangles printed on FS3...
paper (Fig. 4e, g, i and k) have sharp edges in the printing direction and perpendicular to it, demonstrating a fair printing definition. In the case of EG + Plasdone S-630, it can be seen that the corners are rounded for the ink printed on Lumi paper (Fig. 4f and j), which can be explained by extensive spreading of the ink over the substrate. Overall the ink covered the substrate uniformly. Optical micrographs of the functionalized graphene ink printed on Lumi paper (Fig. 4h and l) also demonstrate a reasonable printing resolution, with a distinct edge roughness, probably caused by the slow solvent evaporation and an increase of the Marangoni flow within a layer.

We found that ink spreading depends not only on the substrate but also on the ink characteristics. The formulation based on expanded graphite with a polymeric surfactant printed on the FS3 substrate (Fig. 4e and i) demonstrated a good spreading and uniform particle distribution. This ink was formulated with a solvent mixture of highly volatile i-propanol and n-butanol, that evaporates quickly (evaporation rate of i-propanol = 2.9, n-butanol = 0.4, n-butyl acetate = 1.0), thus, minimizing any particle segregation and producing a homogeneous layer. For the same ink, a similar behavior was observed in the case of the Lumi paper (Fig. 4f and j), where the ink spreads rather uniformly with minimal drying artefacts. The ink formulation based on functionalized graphene (PNB–GCNF)

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**Fig. 4** Graphene based inks printed on FS3 (a, e, i and c, g, k) and Lumi (b, f, j and d, h, l) papers. Expanded graphite with Plasdone S-630 dots (a and b), and large-area rectangles (e, i and f, j), 10 printing passes. p-Nitrobenzyl functionalized graphene dots (c and d), and large-area rectangles (g, k and h, l), 10 printing passes. Scale bars: (a–d) – 20 μm, (e–l) – 500 μm.
printed on FS3 paper (Fig. 4g and k) demonstrated a non-uniform though regular particle segregation into lines parallel to the printing direction. This behavior is most likely caused by the slowly evaporating solvent and the ink's instability at locally high concentrations. This creates a pattern where lines of segregated material are poorly connected with each other, potentially causing anisotropy of the conductive properties. The spreading of the PNB–GCNF ink on the Lumi substrate (Fig. 4h and l) was very complex, with particle segregation not only along the printing direction but also perpendicular to it. This demonstrates that extensive spreading in combination with slow drying decreases the printing resolution and overall printing quality.

3.5 Sheet resistance evaluation of inkjet printed graphene films on paper substrates

Along with the printability of inks, another highly important characteristic is the conductivity of the printed layers. We performed four point probe sheet resistance measurements of printed large-area rectangles with different numbers of layers, i.e., 1, 5, 10 and 15 printing passes. We found that in all cases, single-pass printed rectangles were not conductive, indicating that the achieved coverage of conductive particles was below the percolation threshold. However, after subsequent printing passes, a significant increase in the conductivity of the printed layers was observed (Fig. 5).

We observed a significantly lower sheet resistance ($R_s$) for the ink prepared from expanded graphite and polymeric stabilizer than for the functionalized graphene based ink. As can be seen from Fig. 5, the trend continued with an

![Graph showing sheet resistance vs. number of printed layers.](image)

Fig. 5  Sheet resistance of $5 \times 35$ mm printed rectangles as a function of the number of printing passes.
increase in the number of printing passes for both inks resulting in decreasing sheet resistance. This results, for 15 printing passes, in a film sheet resistance of approximately 1–2 kΩ m−1 for the EG + Plasdone S-630 ink (800 nm thickness) and ~2 MΩ m−1 for the PNB–GCNF ink (900 nm thickness). Remarkably, in the case of EG with Plasdone S-630, we did not notice any significant difference in Rs for the two paper substrates, which is in good agreement with the observed spreading of the ink (Fig. 4e, i and f, j). However, we found a significant (~2 times) difference in Rs for the PNB–GCNF ink, which correlates with the difference in spreading and drying of the ink (Fig. 4g, k and h, l) described earlier. Thus, inkjet printed films with uniform material distribution demonstrate lower and isotropic sheet resistance, whilst printed films with a non-uniform particle distribution show higher and anisotropic sheet resistance.

From the observed sheet resistance data we hypothesize that the size of the graphene sheets plays a role in the conductive properties. If we assume that the Rs of a graphene film scales with the resistance of the contact between two flakes (R(CR)) and the resistance of the graphene flake itself (R(GF)), then the number of contacts would give a major contribution to the overall resistance. Here we assume that Rf for a flake is approximately constant for all sizes as it depends on the defect density,31–33 or doping,34–40 etc. Since the large (90% of population >1 μm) graphene flakes of EG + Plasdone S-630 assemble into a layer with fewer contacts between each other compared to a layer of the PNB–GCNF graphene (90% of population <60 nm), then the overall sheet resistance of the former film (on both substrates) is much lower than that of the latter.

4 Conclusions

In this paper we demonstrated two approaches for graphene ink formulation: first, based on the solubilization of graphene with a surface active polymer, and, second, based on covalent graphene functionalization. In the first route, we used a donor-type graphite intercalation compound as an intermediate prior to thermal expansion to avoid any oxidation of the graphene. We experimentally found that the presence of a surface active polymer (60 : 40 copolymer of N-vinyl-2-pyrrolidone and vinyl acetate, Plasdone S-630) facilitated efficient graphene exfoliation allowing stable colloidal dispersions with concentrations of up to 1.4 mg ml−1 at a polymer concentration of 5 mg ml−1 in a mixture of non-toxic solvents. The formulated ink was printable on substrates including plastic foils and paper.

In the second route, we synthesized a potassium graphite intercalation compound with graphitic carbon nanofibers as a precursor and utilized it as an intermediate for covalent functionalization. We confirmed the hypothesis that high ratios between edge and bulk carbon atoms would increase the Birch-type alkylation efficiency with p-nitrobenzylbromide, allowing up to six weight percent of functional moieties. The functionalized graphene was readily dispersible in a number of solvents at high concentrations including alcohols, ethers, and chlorinated solvents. We found that the optimal solvent was propylene glycol diacetate, which can disperse up to 3 mg ml−1 of solid material with a colloidal stability of up to several months.

Both inks were printable on FS3 and Lumi paper substrates with good to satisfactory spreading. From our observations of spreading and drying behavior,
we concluded that the optimal combination is an ink of expanded graphite with Plasdone S-630 printed on FS3 paper, as the ink forms a uniform layer with a reasonable print resolution. Further, we analyzed the conductive properties of the inks by measuring the sheet resistance of large-area printed rectangles. The evaluation of sheet resistance as a function of the number of printing passes showed a significant (up to 2000 times) difference between the two inks in favor of the one containing expanded graphite. We hypothesize that this difference could be due to a much smaller number of sheet-to-sheet contacts, and that the overall resistance mainly depends on the resistance of the graphene itself. In contrast to that, for a functionalized graphene printed film, the number of sheet-to-sheet contacts is much larger, therefore, the resistance of the film is limited by inter-layer contact resistance. Such a hypothesis is a task for further investigation. Finally, we found that the sheet resistance decreases with an increase of the number of printing passes, providing the opportunity that further increasing the printed layer thickness could lower the sheet resistance to reach the conduction values achieved by metal based inks. Taking into account the simplicity and cost-effectiveness of our method, we believe that inkjet printing of graphene based inks is a good alternative for the mass production of conductive films and devices on paper.

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