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Plasma Jet Printing and *in situ* Reduction of Highly Acidic Graphene Oxide

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Abstract

Miniaturization of electronic devices and the advancement of Internet of things pose exciting challenges to develop technologies for patterned deposition of functional nanomaterials. Printed and flexible electronic devices and energy storage devices can be embedded onto clothing or other flexible surfaces. Graphene oxide (GO) has gained much attention in printed electronics due its solution processability, robustness and high electrical conductivity in the reduced state. Here we introduce an approach to print GO films from highly acidic suspensions with *in situ* reduction using an atmospheric pressure plasma jet. A low temperature plasma of a He and H₂

mixture was used successfully to reduce highly acidic GO suspension ($\text{pH} < 2$) *in situ* while deposition. This technique overcomes the multiple intermediate steps required to increase the conductivity of deposited GO. X-ray spectroscopic studies confirmed that the reaction intermediates and the concentration of oxygen functionalities bonded to GO have been reduced significantly by this approach without any additional steps. Moreover, the reduced GO films showed enhanced conductivity. Hence, this technique has a strong potential for printing conducting patterns of GO for a range of large scale applications.

Keywords: graphene oxide, reduction, plasma jet, printing, flexible electronics, functionalization, and surface coating,

Recently there has been an increased interest in the fabrication of printed and flexible electronics for diverse applications including sensors¹, batteries², solar cells³, supercapacitors⁴, displays⁵ and many more.^{6–8} Printing nanostructured materials from colloidal solution (ink) on various substrates possesses some challenges for the development of these technologies.⁶ In particular, commercial printed electronics should be electrically, optically and mechanically

robust, with materials and components meeting properties such as low resistivity, high transparency and substrate independence. This combination of requirements poses great challenges to use or adapt existing low-cost mass-manufacturing approaches.

Graphene based technology might deliver benefits in terms of both cost effectiveness and desirable properties and performance. Graphene oxide (GO) suspension has attracted significant interest since it is best known for its electronic properties but is hard to disperse in common solvents.^{9,10} The dispersibility in solvents provides GO an added advantage for spin coating, drop-casting and spraying on the required substrates. Liquid phase exfoliation of GO from oxidation of graphite using processes proposed by Brodie, Staudenmaier, Hofmann and Hummers is common for high yield synthesis of graphene oxide suspensions.¹¹ Studies by Poh *et al.*¹² revealed that GO prepared by these techniques possesses different chemical structure and material properties. According to them, Hummers method yields better quality GO in terms of higher heterogeneous electron transfer rate and enhanced electrochemical response. Though this technique results in high yield production, the strong oxidation introduces defects into the graphitic lattice. The sp^2 network of the honeycomb structure is strongly disrupted by the oxygen moieties.¹³ Per Lerf–Klinowski model, the basal plane of GO is decorated with epoxide and hydroxyl groups, whereas carbonyl or carboxylic acid groups are located at the edge sites.¹⁴ These induced defects adversely affect the electrical properties of GO, and subsequent deoxygenation is required to recover the electrical conductivity. The other issue with using strong acids is that the reaction products need to be dispersed in de-ionized water for several cycles to neutralize the pH and to make it suitable for the desired application, printing in this case. Sonication based exfoliation and shear exfoliation of graphite have also been implemented to produce graphene inks. Paton *et al.*¹⁵ reported the synthesis of unoxidized defect-free

graphene using shear exfoliation. However, these processes require special solvents whose surface energy should be well matched to that of graphene. Additionally, these solvents have high boiling point; for example, *N*-Methyl-2-pyrrolidone (NMP) has to be annealed in forming gas at high temperatures needing an extra step which is not an environmental friendly process.¹⁶ In some cases, polymer stabilizers like ethyl cellulose are added to the mix to keep the graphene ink stable, which needs to be decomposed to achieve optimal electrical performance.¹⁷

Several approaches have been reported so far to print patterned structures using graphene oxide ink such as micro-moulding in capillary (MIMIC) method¹⁸, gravure printing¹⁹, screen printing²⁰ and ink jet printing.^{21–24} The first two suffer from limited scalability while screen printing has the lowest resolution among all techniques. Hence, inkjet technology is the most accepted for fabrication of devices.²⁴ Present ink jet printing technologies, which are substrate dependent, suffer from the need for various post-processing steps. The major issue with GO based inks is the need for reduction after printing, which is done either by high temperature annealing²⁵ or by reducing agents like hydrazine vapour.²⁶ Other techniques include UV reduction²⁷ and annealing in Ar/H₂ atmosphere.²⁸

Tailoring the ink plays a key role for a successful printing process. Properties like viscosity, surface tension and density of the ink are important and need to be designed dependent on the substrate.²⁹ Most inks, including graphene inks, require sophisticated pre-and post-processing steps. Thus, there is a strong drive to develop a robust technique that is independent of the ink in use and has the ability to perform any additional processing steps *in situ*. Plasmas, both low pressure and especially atmospheric pressure, possess considerable potential in functionalization of carbon based materials.³⁰ Plasma discharges can allow the fixation of different chemical species of the same element to the graphene structure. Ostrikov *et al.*³¹

presented a detailed overview on applications of plasmas in nanomaterial synthesis, deposition on substrates, surface functionalization, etching, sputtering, conformal coating *etc.* Atmospheric pressure plasma jets (APPJs) can be an ideal solution to overcome the issues of conventional printing techniques. The rich physical and chemical properties of APPJs makes it suitable for applications in medicine, health care, materials processing and nanotechnology. A detailed discussion about the fundamental physics of cold atmospheric-pressure plasma jets can be found in the review article by Lu *et al.*³² In this work, we demonstrate that an APPJ with He and H₂ plasma can print GO from a highly acidic precursor and reduce it simultaneously. The printed films were further treated with plasma (in what we call an extended print) to enhance their properties. High throughput deposition of reduced graphene oxide patterns can be achieved with this technique on a varied range of substrates including polymer and silicon. This process effectively negates some of the intermediate steps involved in Hummers method as shown in Figure 1 in addition to printing. The surface chemical and electronic properties of these films were studied using X-ray photoelectron and near edge X-ray absorption spectroscopy to confirm the effectiveness of this process. Raman spectroscopy was used to understand the changes in the graphitic structure of GO. Electrostatic force microscopy (EFM) was used to show the evolution of conductivity with plasma printing and treatment of these GO films.

Figure 1. Proposed plasma bypass using an APPJ.

Results and Discussion

A schematic of the plasma printing setup is shown in Figure S1. Four types of samples were studied in order to understand the effectiveness of the plasma printing process (Figure S2): (a) GO suspension (as-synthesized) drop cast on to silicon (sample1); (b) aerosolized deposition of GO without *in situ* plasma treatment (sample 2) where the mist created by the nebulizer is carried through to the substrate by the carrier gas without being subjected to any plasma (aerosolized); (c) aerosolized GO carried through to the plasma, reacts with the plasma and

printed using the plasma jet termed as printed (sample 3); and (d) post plasma treatment of the printed sample *i.e.* (extended print). The post plasma treatment is not a post process actually; after achieving the desired deposition, just the flow of the aerosolized GO was stopped while the plasma remained on. The entire process of treatment was continuous keeping all the conditions same. The deposited GO film was exposed to the plasma jet for an additional duration of 1 min.

(Sample 4).

Figure 2 . (a) Raman spectra of different GO films (samples 2, 3 and 4) normalized to the G band. (b) Variation in I_D/I_G values from Raman spectra.

Figure 2 (a) shows Raman spectra of the different graphene oxide samples. The spectra consist of two peaks D band and G band, typical of GO. The G band originates from the in-plane vibrations of E_{2g} phonons at the Brillouin zone centre while the D peak stems from the breathing modes of sp^2 rings having A_{1g} symmetry and requires a defect for its activation.³³ For all the GO samples, the disorder induced D band is located approximately at 1350 cm⁻¹.³⁴ This D band is

absent for pristine graphite, while a prominent G peak features at 1581 cm^{-1} . Both the G band and D band show appreciable broadening, resulting in an overlapped feature.

The aerosolized sample (sample 2) shows a G peak at 1600 cm^{-1} . This peak exhibits a red shift of about 20 cm^{-1} for sample 3, which is *in situ* reduced and plasma printed. Further post-treatment with plasma (sample 4) results in additional red shift by $\sim 5\text{ cm}^{-1}$. The dissipated heat from the laser source of the Raman spectrometer will cause a maximum shift of only 2 cm^{-1} in the G band position.³⁵ The only viable reason for this red shift can be linked to the recovery of the hexagonal network within the graphitic framework, mentioned as graphitic “self-healing” by Kudin *et al.*³⁴ The ratio between the D and G bands intensity is often used as a measure of defect levels in graphitic systems and is also linked to the average size of graphitic domains. To estimate these values, all the three spectra were normalized with respect to the G band. Respective intensity ratios are presented in Figure 2 (b). The ratio increased after printing and post treatment, from 0.96 to 0.98 and then to 1.04. Both the shift and increased I_D/I_G ratio are consistent with the formation of graphitic domains during printing and plasma treatment, but are smaller in size with respect to synthesized GO. This finding can be correlated with those of Stankovich *et al.*³⁶ where the reduced GO showed an increase in I_D/I_G ratio. However, the effect of the D' peak cannot be neglected as well, as it tends to overlap with the G peak for highly defective graphitic system.³⁷

X-Ray photoelectron spectroscopy (XPS) was used to understand the surface chemical properties of all the samples (1)–(4). The C1s spectra for the drop cast GO is shown in Figure S3 and represents the XPS spectrum of as-synthesized GO (sample1). The binding energies in XPS are strongly dependent on the chemical environment of the carbon atom. Due to stronger electronegativity, C=O in COOH occurs at higher B.E ($\sim 289\text{ eV}$), whereas ketone and aldehydes

are found at lower energies.³⁸ Thus, the strong presence of carboxyl (O-C=O) moieties can be seen in this spectrum owing to the strong acidic suspension (pH<2) of GO. The peak around 292 eV (trace X) is not obvious for GO and might be attributed to the presence of reaction intermediates in the form of carbonates or dicarboxylic acid functionalities. This feature may also arise due to strong ionic bond between K^+ and carboxylic acid functionalities, leading to a shift toward higher binding energy. The spectral signatures for the aerosolized sample (sample 2) as shown in Figure 3 (a) are quite different with respect to the drop cast (sample 1) as in Figure S3. The sample 2 shows an increased concentration of single bonded oxygen moieties (phenol, epoxides) around ~ 287 eV with respect to the drop cast GO.³⁸ This may be due to the air-induced agitation promoting chemical reactivity during the aerosol formation. The presence of potassium (K2p ~ 294 eV) is also evident in both samples (1) and (2), and is mainly due to the use of $KMnO_4$ during the synthesis.³⁹ The K^+ ions are bound at the GO surface as the probability of intercalation within the graphite interlayers is low.⁴⁰ Dimiev and Tour⁴¹ reported that molecules of H_2SO_4 and the oxidizing agent (Mn_2O_7) diffuse into the interlayer spacing of graphite during GO formation and are stable unless large amounts of water have been added. Both aerosolized and as-synthesized GO (ink stock) have high concentration of oxygen but in different bonding environments. However, both these samples are the same *i.e.* graphene oxide from the perspective of the printing process. In Figure 3 (b) and (c), K 2p is absent for samples (3) and (4) after the printing and plasma treated process. Potassium on the carbon surface can migrate into the carbon matrix at temperatures greater than 650 K and potassium was found to evaporate from the carbon surface at 1,123 K.⁴² Such high temperatures are unlikely here as all plastic tubes and connectors would have melted. Hence, the possible explanation might include (a) likely oxidation and hydroxidation of potassium since the reactor is an open flow system at

atmospheric pressure with abundant possibility of air and water vapour contamination; for example, the GO was dispersed in water and (b) desorption of potassium from the surface during the printing process. Future work involving detailed plasma diagnostics studies using *in situ* mass spectroscopy and optical emission spectroscopy is essential to understand the reasons and plasma chemistry in general.

For the *in situ* reduced and printed GO film (sample 3), the concentration of carbonyl (C=O) functionalities is reduced considerably with respect to sample 2. For sample 4 (exposure to the plasma after printing), the concentration of single bonded oxygen (~287 eV) moieties is reduced as well. Table 1 presents the fitting parameters of the individual components in the carbon spectra, as shown in Figure 3. Full width at half maxima (FWHM) of both the oxygen functionalities (C-O, C=O) have decreased by ~0.5 eV for sample 4. Alongside this, the main C-C peak at 284.5 eV had a FWHM of 2.4 eV for both aerosolized (sample 2) and printed GO (sample 3) but decreased to 2 eV after printed and plasma treated (sample 4). According to Ganesan *et al.*⁴³ defects (sp^3 carbon) in the sp^2 structure broaden the C-C line shape. Hence, the decrease in FWHM of C-C can be correlated to the increase in sp^2 domains of the graphitic lattice. Figure 3 (d) presents the ratio between the spectral weights of carbon bonded to carbon and carbon bonded to oxygen. There is a significant decrease in the oxidized carbon species after the completion of the process. The presence of excited states of hydrogen and helium in the plasma might also contribute to this effect. When the aerosolized GO interacts with the plasma, it is exposed to ions (He^+ and H^+), hydrogen radicals and neutral molecules (H_2 and He). Except for He , all of the other species will accelerate the deoxygenation of GO. Studies by Lee *et al.*⁴⁴ and Li *et al.*⁴⁵ provide insight into the efficient reduction of GO films using $Ar+H_2$ plasma. But both these studies showed that plasma-reduced graphene possesses enhanced properties either in

electrochemical performance or as a transparent conductor. It is evident from the XPS results that all the steps involved in the printing process influence the chemistry of GO. To the best of our knowledge, none of the available printing technologies can do this. From the XPS spectra, we attribute that the carboxylic acid undergoes reduction to form C-O groups during deposition. Post treating the deposited film further reduces the C-O moieties, consequently recovering the

sp^2 structure of the graphitic lattice. While zero oxygen content is the desired goal, films with higher amount of oxygen that is controllable could find use in fluorescence applications.

Figure 3 C 1s XPS spectra of (a) aerosolized (sample 2), (c) plasma printed (sample 3), (d) printed and post treated sample (sample 4) .

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements were also carried out to understand the local electronic structure as well as chemical composition and coordination environment. Additionally, a limited number of final states are allowed (governed by dipole selection rule) in NEXAFS. Thus, the overlapped structures in XPS can be easily resolved in NEXAFS.⁴⁶ Carbon *K*-edge (*1s*→*2p* transition of unoccupied states) spectra presented in Figure 4 were acquired at 54.7° (magic angle) incidence of the X-ray beam to eliminate the effects of any preferential orientation. The low energy peak at 285.5 eV and the intense peak around 293 eV correspond to the *1s*→ π^* and *1s*→ σ^* transitions of *sp*² derived carbon structure.⁴⁷ The absence of a core-exciton peak around 291.65 eV reflects to the highly defective *sp*² structure of the graphene, which is consistent with the Raman spectra.⁴⁷ The relative intensities of these two resonances *i.e.* I_{π^*}/I_{σ^*} can be used as a measure of the restoration of π -conjugated network upon plasma induced reduction of GO.⁴⁸ For defect free graphene, the I_{π^*}/I_{σ^*} ratio has been calculated to be 1.30 and the ratio of integrated peak areas to be 1.49.⁴⁹ For the GO samples under study, the I_{π^*}/I_{σ^*} has almost doubled after the printing and post treatment as shown in the inset of Figure 4. Here, corresponding I_{π^*}/I_{σ^*} values for aerosolized, printed and post treated samples were calculated to be 0.25, 0.37 and 0.48 respectively. This indicates to the restoration of the π -conjugated *sp*² frame work of the graphitic lattice resulting from the removal of oxygen functionalities. These findings are in good agreement with those of Raman measurements where the recovery of *sp*² framework is also reflected.

In Figure 4, the region between the π^* and σ^* resonances is occupied by three distinct features, discernible at ~286.9 eV, ~289 eV and ~290 eV for all the three samples (samples 2-

4). The aerosolized GO (sample 2) shows a strong resonance feature at 289 and 290 eV (marked b and c) corresponding to C1s to π^* transitions of C=O symmetry in carboxylic acid (–COOH) and carbonyl (C=O) moieties, respectively.⁴⁸ The peak at 286.9 eV (marked a) results from the core level transitions to π^* symmetry of carbon singly bonded to oxygen in phenol (C–OH) configuration.⁵⁰ Going from aerosolized (sample 2) to printed plus treated GO (sample 4), the intensity of C=O moieties decreases considerably, while the phenol groups increases in intensity and hence concentration. The presence of highly reactive hydrogen species results in reduction of carboxylic acid functionalities to phenol groups. This can be attributed to the *in situ* reduction by plasma

For the aerosolized GO sample (sample 2), two additional distinctive features at 297.6 eV and 300.2 eV are visible. These features arise from $2p_{3/2}$ and $2p_{1/2}$ states at the potassium *L*-edge respectively.⁴⁷ However, these potassium *L*-edge peaks are shifted by 3 eV with respect to the reported values for potassium *L* edges at 294.6 eV and 297.3 eV.⁵⁰ This shift to higher energy value is due to the formation of strongly ionic bonds of potassium probably with carboxylate groups ($K^+ - RCOO^-$) during the strong oxidation of graphite. Similar shift at the potassium *L*-edge has been reported by Lee *et al.* for KOH/hydrazine-reduced graphene oxide.⁵⁰ This result confirms the formation of ion pairs ($K^+ - MnO_4^-$) during the oxidative exfoliation of graphite using $KMnO_4$. However, these potassium features are absent for the plasma-printed GO for the reasons speculated earlier. It is likely potassium in the RCOOK complex might have underwent hydroxylation due to the presence of H^+ , OH^- ions in the plasma, as shown in equation 1.

Figure 4. Carbon K edge NEXAFS spectra of aerosolized GO and plasma printed and treated GO films (samples 2, 3 and 4).

Electrical transport measurements are often used to measure the changes in conductivity of graphene oxide films. The conductivity values thus obtained result from the entire film and cannot provide direct information about the local changes.⁵¹ Hence, a complete picture of the plasma-induced *in situ* reduction of GO can be obtained by studying the local conducting properties. EFM has evolved as a fast and non-invasive technique to determine the change in conductivity of graphene oxide upon reduction. Gomez-Navarro *et al.*⁵² showed that EFM can be used as an *in situ*, fast and contactless technique to evaluate the conductivity of chemically

derived graphene layers. Similarly, Jeong *et al.*⁵¹ also reported that EFM can be used with high spatial resolutions to study the evolution of conductance in GO as it is reduced. Kulkarni *et al.*⁵³ studied the reduction of individual graphene oxide sheets using EFM and were able to directly monitor the surface charge distribution of individual graphene oxide flakes during chemical reduction. On the other hand, Yalcin *et al.*⁵⁴ carried out EFM measurements to observe the propagation of charge carriers along the conducting pathways in reduced graphene oxide (rGO).

The removal of oxygen functionalities will have a definite effect on the electronic properties of the GO films. Tu *et al.*⁵⁵ reported that GO can be transformed between *p* type and *n* type states with progressive thermal reduction. EFM is typically a two-step process. In the first step, the standard topography of the sample is recorded as in AFM. In the second step, the AFM tip with an applied dc bias (V_t) is lifted to a desired height above the sample to negate the influence of van der Waals force on the electrical measurements. During this process, only changes in the electrostatic force between the tip and the sample surface influence the phase and amplitude signals of the oscillating tip. During EFM, the biased tip scanning over the substrate is subjected to a capacitive force. This force induces phase shifts in the tip oscillations. The dependence of the phase shift on the electrostatic force between the tip and substrate can be represented as follows:

$$\Delta \Phi = \frac{Q}{2k} \frac{d^2 C}{dz^2} (V_t - \phi) \quad (2)$$

In the above equation, $\Delta\Phi$ represents the phase shift, Q and k are the quality factor and the spring constant of the cantilever respectively, C is the capacitance of the system, V_t is the tip

bias and ϕ is the surface potential. Thus, it will be possible to differentiate between conductive and insulating GO films by measuring the phase shift of the cantilever.⁵¹

In this experiment, EFM was used to map the sample surface with respect to the phase shift of the cantilever ($\Delta\Phi$), a lag between the drive frequency and the cantilever oscillation.⁵⁶ If the bias on the tip is kept constant along with the distance between the tip and the sample, then the measured variation in electrostatic force corresponds to the changes in surface potential distribution. Due to the presence of lone pair of electrons on the oxygen atoms for GO, the oxygen functionalities such as hydroxyl, epoxy and carboxyl are known to decrease the surface potential. Thus, for a positively biased tip, $V_t - \phi$ (phase-lag) will be more for highly oxygenated GO and should progressively decrease with deoxygenation. Figure 5 (a), (b), (c) presents the potential map of the three samples *i.e.* (i) aerosolised GO (sample 2), (ii) printed GO (sample 3), (iii) printed and treated GO (sample 4). These maps show a clear contrast between the different GO samples. From Figure 5 (d), representing the average value of the phase shift over the measured area, it is clear that the phase shift has considerably dropped with plasma treatment (~ 0.5 to 0.1 degrees). Also, the increased contrast between the EFM map of these samples confirms the increase of conductivity of the films.⁵¹ However, due to non-uniformity of the surface, regions of residual oxide moieties exist which can be seen in the phase maps of the treated sample.

Note that the z-scale in the EFM phase map presented here has been normalized to unity *i.e.* 0 to 1 degree. There have been various approaches reported so far to depict the change or difference in conductivity using EFM. Kulkarni *et al.* presented their data with a z-scale of 0 to 3 degrees.⁵³ while Panchal *et al.*,⁵⁷ Yalcin *et al.*⁵⁴ and Vasić *et al.*⁵⁸ reported their EFM

measurements on graphene related materials at a z-scale of 6.5 to 8.5, -1 to +1 and 0 to 10 degrees respectively. As a matter of fact, the Z-scale of the EFM phase images is set to visually perceive the changes in conductivity with the contrast difference. Kulkarni *et al.* measured the phase change of gradually reduced (chemically) GO flakes with respect to the silicon substrate.⁵³ Their EFM-phase contrast between a graphene oxide flake and surrounding silicon substrate increased by an order of magnitude, $\sim 0.20^\circ$ to 2.1° with 100 seconds of exposure to hydrazine vapour. Here, a 60 sec plasma treatment resulted in phase change from 0.5° to 0.1° degree, with a Z-scale of 0° to 1° .

The sheet resistivity of all the four samples was measured by four probe technique using Jandel RM3000 test unit. The dropcast and aerosolized samples did not show any sheet resistivity values possibly due to higher sheet resistance than the instrument limit of 5×10^8 ohm/sq. Previously reported values suggest that the deposited GO films have sheet resistance $> 10^9$ ohm/sq and after chemical reduction drops to $> 10^7$ ohm/sq.⁵⁹ The average sheet resistance value for plasma printed (sample 3) was found to be 87×10^6 ohm/sq which dropped by one order of magnitude to 9×10^6 ohm/sq. with post plasma treatment (sample 4).

Figure 5. EFM phase map of (a) aerosolized GO (sample 2), (b) Printed GO (sample 3), (c) Post-treated GO (sample 4), (d) average phase shifts for these three samples.

Conclusion

We have successfully demonstrated that a plasma jet can reduce *in situ* highly acidic GO without the need for external post processes. No other printing technique has achieved this till now. XPS results confirm that the reaction intermediates during synthesis of GO can be eliminated by introducing reducing gases in the plasma. Both XPS and NEXAFS results confirm that during

deposition, carboxylic acid functionalities are reduced to phenol groups and the oxygen content at the surface is reduced with extended exposure to the plasma jet further yielding reduced graphene oxide films. Importantly, this reduction process aids in the recovery of sp^2 structure of the graphitic lattice. The I_{π^*}/I_{σ^*} ratio calculated from the carbon K -edge spectra is almost doubled with plasma treatment (~ 0.25 to ~ 0.5) and is in accordance with the 25 cm^{-1} red shift of the G band in the Raman spectra. Both these findings are fingerprint of the recovery of sp^2 structure. Finally, EFM phase maps showed a distinguishable increase in contrast with plasma treatment. The decrease in phase shift confirms the increase in conductivity of the GO films at the nanoscopic level. Further studies need to be carried out to confirm this observation, along with fabrication of prototype devices exclusively using the plasma jet.

Methods

Graphene oxide was prepared following modified Hummers method.¹² The steps involved including process parameters are given in **Table 2**. For the *in situ* plasma reduction and printing process here, we followed up to step 6. The suspension from step 6 was then centrifuged at 8,000 rpm for 15 min, and the supernatant was extracted to remove the unreacted graphite flakes. Note that no excess water was added to this suspension to increase the pH. This suspension with pH < 2 was then used as ink for the plasma jet printer, as described previously.⁶⁰

The plasma jet printer consists of two units as shown in Figure S1. First is the print head in the form of a glass nozzle where the plasma is generated in a dielectric barrier discharge configuration and second is the ink reservoir. The colloidal suspension is aerosolized using a nebuliser and carried through to the plasma using the carrier gas (He). In this work, a pneumatic nebulizer was used instead of piezoelectric nebulizer to produce droplet size of 1-10 microns. This aerosolized ink interacts with the plasma and is deposited on a silicon oxide substrate by the

plasma jet. The plasma jet was operated with a gas mixture of He (1,600 sccm) and H₂ (100 sccm) and the aerosol was carried to the plasma by the carrier gas (He, 500 sccm) through the ink reservoir. Samples studied in order to understand the plasma printing process has been described in the discussion section. SEM images reveal GO flakes with an average size of 5 microns as seen in Figure S4. The film thickness of the deposited GO is of the order of 80 nm measured (see Figure S5) using confocal microscopy.

Near edge X-ray absorption fine spectroscopy (NEXAFS) and X-ray photoelectron spectroscopy (XPS) measurements were performed at the bending magnet source beamline 8–2 at Stanford Synchrotron Radiation Lightsource (SSRL) equipped with a spherical grating monochromator.⁶¹ For NEXAFS intensity of the incoming flux, (I_0) was monitored using a Au grid placed just after the refocusing optics. This measured intensity was used for normalising individual spectra, a standard protocol used to negate any unwanted features arising from beam instability. All samples were mounted on an aluminium stick using a conductive carbon tape and analysed in ultrahigh vacuum conditions ($\leq 10^{-9}$ mbar). Spectra were acquired in total electron yield (TEY) mode, *via* the sample drain current. The analysis chamber is equipped with a PHI 15–255G double pass cylindrical mirror analyser. Carbon *K*-edge spectra were first divided by the incoming flux (I_0) and then normalized 30–40 eV above the ionization potential. For NEXAFS measurements the energy of the incident beam was calibrated at the carbon dip (284.7 eV), arising from the carbon contaminations on the beamline optics. The total energy resolution is 0.3 eV. XPS binding energies were referenced to *C 1s* of HOPG taken at the same time as GO. All XPS spectra were fitted with a mixture of Gaussian and Lorentzian line shape function along with Shirley background subtraction algorithm.

Raman spectra were measured using Horiba Jobin-Yvon LabRAM HR evolution spectrometer using Ar^+ laser with 514.5 nm line as the excitation source. The laser power was kept at ~ 0.5 mW for these measurements to minimize any effect of heating. Atomic force microscopy (AFM) and EFM were carried out using an Asylum Research MFP-3D with Pt-Ir coated conducting silicon probes (PPP-EFM-10, Nanosensors) with nominal force constant of 2.8 N/m were used for this measurement. The tip was biased at +3 V during EFM scan with a drive amplitude of 300 mV. The image parameters were set at a scan size of $25\text{ }\mu\text{m}^2$, scan rate of 1 Hz, 512 points and lines.

Tables

GO sample	component	% concentration	FWHM
Drop cast (sample 1)	C-C	33.2	2.45
	C-O	28.6	3
	C=O	26.8	3
	X	8.7	3
	K $2p_{3/2}$	2.7	3
Aerosolized (sample 2)	C-C	26.4	2.40
	C-O	40.4	2.90
	C=O	22.6	2.80
	X	8.2	2.5
	K $2p_{3/2}$	2.4	2.5
Printed (sample 3)	C-C	43.2	2.40
	C-O	47.7	2.60
	C=O	9.1	2.80
	X	0	0
	K $2p_{3/2}$	0	0
Printed & treated (sample 4)	C-C	58.9	2.0
	C-O	33.1	2.4
	C=O	8	2.5
	X	0	0
	K $2p_{3/2}$	0	0

Table 1. Components used to fit carbon $1s$ spectra of GO and other plasma functionalized GO samples as shown in **Figure 3** and **Figure S3**.

Step	Process	Comments
1	3 g graphite flakes + 1.5 g NaNO_3 + 100 ml 98% H_2SO_4	Stirred at 0 °C in an ice bath
2	9 g of KMnO_4 added to suspension	Vigorous stirring
3	Ice bath removed	Temperature maintained at 30 ± 3 °C for 30 mins.
4	138 ml of DI water added slowly	Violent effervescence, temperature rises to 98 °C.
5	After 15 mins, 200 ml DI added	To Dilute
6	30 ml of 30% H_2O_2 added	Reduces the residual permanganate to soluble manganese sulfate.
7	Filtered and washed	Till pH reaches ~7 (Neutral)
8	Centrifuged at 8000 rpm for 10 min	To extract GO

Table 2 Process steps for the synthesis of graphene oxide (GO).

Associated Content

The Supporting Information is available free of charge on the ACS Publication website at DOI:

Figures related to the experimental setup, SEM images of samples and XPS data for the dropcast sample.

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