Laser Direct Writing of Heteroatom (N and S)-Doped Graphene from a Polybenzimidazole Ink Donor on Polyethylene Terephthalate Polymer and Glass Substrates

DOI:

[10.1002/sml.201803143](https://doi.org/10.1002/sml.201803143)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Huang, Y., Zeng, L., Liu, C., Zeng, D., Liu, Z., Liu, X., Zhong, X., Guo, W., & Li, L. (2018). Laser Direct Writing of Heteroatom (N and S)-Doped Graphene from a Polybenzimidazole Ink Donor on Polyethylene Terephthalate Polymer and Glass Substrates. *Small*, 14(44), [1803143]. <https://doi.org/10.1002/sml.201803143>

Published in:

Small

Citing this paper

Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights

Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy

If you believe that this document breaches copyright please refer to the University of Manchester's Takedown Procedures [<http://man.ac.uk/04Y6Bo>] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.

Laser Direct Writing of Heteroatom (N and S) Doped Graphene from a Polybenzimidazole (PBI) Ink Donor on Polyethylene Terephthalate (PET) Polymer and Glass Substrates

Yihe Huang^{1*}, Lei Zeng², Chongguang Liu², Desen Zeng², Zhu Liu^{2,1}, Xuqing Liu², Xiangli Zhong², Wei Guo² Lin Li^{2*}

¹Laser Processing Research Centre, School of Mechanical, Aerospace and Civil Engineering, The University of Manchester, Manchester, M13 9PL, UK

²School of Materials, The University of Manchester, Manchester, M13 9PL, UK

*Corresponding authors:

yihe.huang@postgrad.manchester.ac.uk

lin.li@manchester.ac.uk

Abstract

In this paper we report, for the first time, a laser direct writing technique to form S and N doped graphene patterns on thin (0.3 mm thickness) polyethylene terephthalate (PET) and glass substrates from a specially formulated organic Polybenzimidazole (PBI) ink, without thermally affecting the substrates and without the need for a metallic precursor. Unlike standard graphene ink printing, post curing at high temperatures is not needed here, thus avoiding potential substrate distortion and damages. A UV laser beam of 355 nm wavelength was used to generate photo-chemical reactions to break the C-S bond (2.8 eV) from Dimethyl Sulfoxide (DMSO, a component of the PBI ink) and the C-N bond (3.14 eV) of PBI and form N and S doped graphene on the substrates. The sheet resistance of the laser induced graphene was as low as 12 Ω/sq on PET, matching that of indium tin oxide (ITO). The laser-written doped graphene showed hydrophilic characteristic, unlike pristine graphene. The S and N doped graphene allowed the tailoring of band gaps and thus controlling electrical and chemical properties. The optical transparency of the written graphene is below 10% that could be improved in the future. Potential applications include printing of flexible circuits and sensors, and smart wearables.

Keywords: Laser Direct Writing (LDW), graphene, ink, growth, PET, polymer, liquid, nano-crystallization, sheet resistance

1. Introduction

The next generation displays, imbedded sensors and smart wearable are heavily dependent on formation of transparent or non-transparent, durable, conducting circuits on flexible, polymeric substrates. Indium Tin oxide (ITO) is currently the most commonly used transparent conducting material because of its outstanding light transmittance ($T > 90\%$) and low sheet resistance (approx. $10 \Omega/\text{sq}$). However, due to the dependence a rare earth element, indium, largely from one country, the availability and price of ITO are unpredictable [1, 2]. Additionally, ITO as a ceramic material is brittle and is easily damaged at relatively low strains of 2-3% [3], which is unsuitable to flexible or wearable devices [2, 4, 5]. The sputtering process used to coat ITO film is also highly inefficient, typically wasting 70% of the ITO material [6].

Conducting polymers such as poly(3,4-ethylenedioxythiophene) – PEDOT, and Polystyrene sulfonates (PSS) have good optical transparencies up to 97%, but they have inferior electrical properties (e.g. typical sheet resistance at $240 \Omega/\text{sq}$), and thus not yet good enough to replace ITO [7].

The electrical conducting properties of metallic nano-materials can be better than ITO [8]. Silver micro/nano flakes and nanowire based conducting inks are commonly used as conductive elements [9, 10]. The printed ink tracks can reach $13 \text{ m}\Omega/\text{sq}$ at 85% optical transmittance and the metal nanofibers can reach $1.3 \pm 0.2 \Omega/\text{sq}$ at 90% optical transmittance [8, 10]. Silver nanoparticles have been shown to give similar resistivity at about $4 \mu\text{m}$ ink thickness [11]. However, the synthesis and purification of mono-dispersed nanoparticles would increase the cost of Ag based conducting inks by 3 to 4 times. The poor mechanical properties due to weak grain boundaries after thermal sintering (230°C) is a common disadvantage of the silver nano material based conducting inks [12, 13], although silver MOD (Metal-Organic-Decomposition) ink was designed for lower curing

temperatures (e.g. 150°C) [14]. In addition, the stability of Ag based conducting material over time due to oxidation is often a problem causing changes in the material electrical conductivity, although silver oxidation shield can reduce scattering effect[15].

Copper is more abundant than silver. Cu nanowires have similar electrical properties as Ag nanowire based inks (26 Ω /sq at an optical transmittance of 80%). Cu nanowires can be grown from spherical copper seeds in an aqueous solution of NaOH, ethylenediamine, $\text{Cu}(\text{NO}_3)_2$ and hydrazine. The drawback of the copper nanowires is highly sensitive to oxidation and water [16].

Carbon nanotubes (CNTs) are highly conductive. However, it is difficult to obtain bulk quantities of CNTs with suitable purity. Various impurities include catalyst particles, and amorphous and non-tubular carbon. Normally, carbon nanotubes are dispersed in an organic solvent or a super acid. The solvent can be a dispersing agent such as surfactants, and dispersants. The most critical problem of these solvents is reducing electrical conductivity.

The boiling points of the organic solvents are typically 150 °C higher than the thermal deformation temperature. Therefore, it is difficult to remove these solvents once applied to a polymer substrate. The functionalized CNTs have been shown to help with drying out the inks leaving a high concentration of CNTs and bundles. The functionalization procedure, however, induces defects on CNTs, which reduces the electrical conductivity significantly [5].

Graphene based inks are commonly made by exfoliating graphite and suspension with organic solvents. They typically have an electrical sheet resistance of 3560 Ω /sq [17]. The post process required for the organic solution removal at over 150 °C induces thermal deformation or decomposition of the commonly used flexible materials, such as PET(70 °C) and PEEK(140 °C)[18]

Laser direct writing is capable of treating materials with little thermal damage to the substrates with precise control of laser energy, beam/material interaction time and heat penetration depths [19, 20]. Conventionally, laser irradiation was regarded as a source of the thermal reaction for chemical vapour deposition (CVD), which was commonly adopted for large area graphene growth.

Hazardous gases, like CH₄ and H₂ gases were typically used as carbon sources at a 5:2 ratio. The number of graphene layers grown could be controlled by a pulsed laser or a continuous wave laser and laser scanning speeds. These processes require a metallic precursor such as Cu and Ni. Monolayer or bilayer graphene were achievable from a Ni/Cu alloy metal precursor, and deposition of graphite to them, followed by laser heating to over 1000 °C [21-23]. Solid carbon coating on Cu or Ni, instead of the use of hazard gas, was developed for graphene growth combined with laser writing [24-26]. The high temperature process (typically over 1000 °C) would cause certain damages to the polymer substrates and removal of metallic coating subsequently was an additional process either chemically or the use of laser ablation. Graphene can also be transferred from CVD growth on copper foils to a substrate surface. The adhesion of the transferred graphene to the substrate is often a challenge [25, 27]. The Rice University research [20] showed that a continuous wave CO₂ laser (with a wavelength of 10.6 μm) infrared irradiation of Polyimide (PI) and Polyetherimide (PEI) solid sheets could thermally change them into graphene without the use of Cu or Ni. This process, however, also required high temperatures.

Inkjet-printed wearable electronics using graphene inks on fabrics with a PET coating was demonstrated by the Cambridge University researchers. Post process annealing at 100°C for 1 hour enhanced the electrical property of the graphene ink and a water proof polyurethane-protective layer was hot pressed around at 120 °C for 5s. This improved adhesion between the graphene ink and PET. The printed graphene features remained after 20 cycles of washing [28].

In this paper, we report, for the first time, a pulsed UV laser direct writing technique to form S and N doped graphene patterns on polymer (PET) and glass substrates, from a specially formulated organic ink, without thermally affecting the substrates and without the need for a metallic precursor. The UV laser beam was used to generate photo-chemical reactions to break certain molecular bonds of the organic ink and form doped graphene on a substrate without damaging the polymer substrate.

2. Results and Discussion

2.1. Surface morphology and Raman Spectra

Figure 1 shows a pattern written using the laser direct writing technique on PET. The laser irradiated tracks appeared black. The typical morphology of the graphitized PBI ink after the laser

irradiation on PET is shown in

Figure 1 taken with a FEG-SEM. It is clear that a porous structure was formed.

Figure 1: Optical (bottom left) and SEM (bottom right) images of graphene grown on PET irradiated at a $0.013\text{J}/\text{cm}^2$ laser fluence. The top left image is the PBI ink written on PET before the laser irradiation and the top right image is the graphene pattern on PET after the laser irradiation on the ink track.

To form graphene from the 5% PBI ink, laser fluence was increased gradually from $6\text{ mJ}/\text{cm}^2$ to $14\text{ mJ}/\text{cm}^2$ on the PET substrate and $7\text{ mJ}/\text{cm}^2$ to $45\text{ mJ}/\text{cm}^2$ on glass. The enhanced degree of carbon crystallization was demonstrated by the increasing ratios of Raman spectrum D peak (1350 cm^{-1}) over the G peak, i.e. $I(D)/I(G)$ at the laser fluence range of $6\text{ mJ}/\text{cm}^2$ - $13\text{ mJ}/\text{cm}^2$. A higher D peak indicates higher proportion of defects. A reduction of $I(D)/I(G)$ and the presence of 2D peaks at 2700 cm^{-1} on both glass and PET sheets demonstrated the formation of graphene and a reduction of disordered carbons.

Figure 2 shows the 2D Raman spectrum mapping of the laser formed graphene from the PBI ink. The colour intensity as the ratios of $I(2D)/I(G)$ and $I(D)/I(G)$ demonstrated the uniformity of the graphene tracks formed. The mean values of $I(2D)/I(G)$ ratio were around 0.3 for the graphene formed on PET and 0.1 for the graphene on glass. The overlapping areas processed by the laser tracks had relatively higher values of $I(2D)/I(G)$ indicating the possibility of improving graphene

quality through laser annealing. The overlapping of laser scanned tracks processing reduced graphene layer thickness, but more defects would be produced by introducing thermal effects[29].

Figure 2: A selection of 2D Raman spectrum mapping for graphene formed on (a) PET sheet and (b) glass and correlation of the sheet resistances (c) with laser induced graphene thickness at various laser fluences and various concentrations of the PBI in the ink on PET

2.2. Crystallographic characteristics of the graphene formed and effect of laser wavelength

There were two sharp peaks centred at $2\theta=22.7^\circ$ and $2\theta=25.9^\circ$ in the XRD spectra Figure3(a) for the graphene generated at the 13mJ/cm² laser power. An interlayer spacing (I_c) of 3.4Å at $2\theta=25.9^\circ$ indicated a high degree of graphitization. An interlayer spacing (I_c) of 3.74Å at $2\theta=22.7^\circ$ indicated

the loss of interface forces from a turbostratic structure, which might be due to element penetration during graphene generation from the recombination of benzene rings [30]. The in-plane structure was associated with the (100) reflection peak at $2\theta=43^\circ$, which was intensified with the increase of laser fluence from 7 mJ/cm^2 to 13 mJ/cm^2 (Figure 3(a-c)) [31].

Figure 3: XRD spectra of the specimen processed at (a) 13 mJ/cm^2 , (b) 10 mJ/cm^2 and (c) 7 mJ/cm^2 laser power.

A picosecond laser (Edgewave, having a pulse length of 10 ps) with an ultraviolet (UV) wavelength of 355 nm was used and was compared with processing at a 1064 nm wavelength from the same laser. Under self-gas protection generated from the imide structure, the 355 nm laser wavelength has a photon energy of 3.49 eV, which would allow both photochemical and Photothermal processes to take place when interacting with the PBI ink to enable customized sulphur and nitrogen doping at low laser powers and avoid thermal damages to the substrate[20, 32, 33]. The specific bonding and doping structure between the sulphur and carbon ring originated from bond breaking by the pulsed UV laser and the polar aprotic solvent selection (sulphur element from DMSO). The C-S bond energy (2.8 eV) from the DMSO (a component of the PBI ink) and the C-N bond energy (3.14 eV) of PBI are lower than the laser photon energy. The electrical and electrochemical processes can be promoted through orbital hybridization from sulphur, nitrogen bonding and controlled doping.

From the XPS spectra shown in Figure 4(b), the peaks for the specimen processed with the 355 nm wavelength laser at 163.9 eV and 165.18 eV demonstrated a $\text{S}2\text{p}_{3/2}$ and $\text{S}2\text{p}_{1/2}$ -S-C-S- covalent

bond of the thiophene -S owing to their spin-orbit couplings[34]. The peak for the specimen processed with the 1064 nm wavelength laser at 163.9 eV was relatively weaker, which demonstrated less heteroatom structures between sulphur and carbon. The N 1s spectrum was indicated by an intense pyrrolic N (400.1 eV) peak shown from the 355 nm laser wavelength processed sample. The absence of the pyrrolic N peak from the specimen processed by the 1064 nm laser demonstrated the occurrence of photochemical bond break for samples processed with the 355 nm wavelength laser. The peaks from oxidized N (402 eV) and pyridinic N (400 eV) were from the gas oxidization and strong C=N bond energy of 6.33 eV, which was higher than 355 nm wavelength photon energy (3.49 eV). The 355 nm wavelength was able to break the C-S bond (2.8 eV) from the DMSO (a component of the PBI ink) and C-N bond (3.14 eV) of PBI. The dominated pyrrolic N and oxidized N from 1064nm laser treated specimen in Figure 4(c) were instead of graphitic N, much less pyrrolic N and oxidized N. It was assumed that S=O was reduced to S by 355nm wavelength laser or free radical HN, which was freed from the PBI by the 355 nm wavelength laser irradiation. Corresponding to the 164 eV peak, the C-S thiophene bond from 355 nm laser irradiated

specimen C1s shown in

Figure (a) above vanished from the 1064 nm laser irradiated specimen C1s in Figure 4(a) below.

Figure 4: (a) C, (b) S and (c) N XPS spectra of the specimen processed by 355 nm wavelength laser above and 1064nm wavelength laser below and DFT calculations (d) of (d₁) polymerization after photochemical bond break by the 355 nm laser irradiation (d₂) polymerization after thermal effect from the 1068 nm laser irradiation

Density Functional Theory (DFT) calculation was used to show the possibility of the related structure formation as shown in Figure 3d for both the 355 nm and 1064 nm laser wavelength irradiation of the PBI ink. It was conducted on Quantum Espresso [35]. GGA-PBE[36] methods were applied to describe the exchange-correlation function between electrons. Ultra-soft potential was used. Considering the material used was a polymer and the reaction is highly localised, the calculation was conducted on a monomer of given structure to accelerate the calculation. As the reaction path was complex and not highlighted, the energy of a possible reaction pattern was selected and compared with the final product. The energy of each possible free radical from the PBI ink irradiated by the laser was calculated. From Figure 3d₁, the 18.95Ha energy reduction demonstrates that it is possible to link the free radicals to a possible ring structure containing

sulphur, which corresponds with the thiophene generation in a membered ring structure. However, considering that one free radical is fixed in the polymer chain and has poor mobility, it is possible that the reaction was caused by direct collision of molecules. The thiophene structure of sulphur bonding conformed to the DFT calculation result. However, calculation on this aspect did not support the assumption that DMSO can replace the NH group in a polymer N-ring structure, as shown in Figure 4(d₂). Overlapping ring and ripple-like wrinkled graphene structures were formed, as shown in the high-resolution TEM image in Figure 5(a). This structure could improve the electrochemical performance of devices [37]. The abundant hexagon, pentagon ring structures in

Figure (c) originated from the benzene ring and polymerization process after the photochemical bond breaks. In the polymerization process, the N or S free radicals and residual bonds built the pentagon rings and caused different porous structure on graphene [38]. Sulphur showed a bonding behavior in the s-defect as shown in Figure 5(d). The doping energy showed clear dependence on

CN and the most favourable defect was the d-defect (CN=4), whose dimension is 0.35 nm, as

Figure (c) around pentagon ring. A certain amount of charges (or holes from defects) on graphene could shift the Fermi level.

Figure 5: TEM images of laser induced graphene with 2nm scale bar obtained with a laser power of 0.87 W (a) the edge of a laser induced graphene showing a few-layer wrinkled feature and an overlapping ring structure (b) a selected area from the Cs-TEM image taken at the edge of a laser induced graphene (LIG) flake (c) hexagon, pentagon ring structure and dimension of defect around pentagon ring (d) s and d defect from element penetration in graphene generation

Heteroatom doped graphene has a tailored band gap, which is different from pristine graphene that does not have a band gap. This structure changes its electric and electrochemical properties, providing electrochemically active sites and increasing applicability for graphene [39]. Two reasons for the increase of charge carrier density are that the structure would free more electrons of the

sulfur and nitrogen penetration and structural defects[40]. The n-type doping normally results in an increase of charge carrier density. The charge carrier density of p-type doping is normally lower than that of n-type doping, but the capacitive performances were also improved[41]. The defect types and number of holes from various bonding behaviour always have a great effect on the activation energy. The energy barrier increases with holes added and decreases with charges added, which also increases charge carrier density from less energy waste.

2.3. Electrical and electrochemical performances

It was found that the sheet resistance (R_s) was gradually reduced to 28 Ω /square on the PET and 48 Ω /square on the glass substrate when laser fluence increased to 14mJ/cm² for PET and 45 mJ/cm² on glass. Further increase of laser fluence induced damages on PET and the sheet resistance increased, which may be caused by oxidation [31]. As shown in in Figure 2(c), when the PBI concentration in the polymer ink was increased from 1% to 10%, the sheet resistance, R_s dropped to 12 Ω /square on laser-induced graphene (LIG) on PET processed at the 13 mJ/cm² laser fluence. This is comparable to commercial ITO and Ag conductive inks. The corresponding electrical conductivity was 50 S/cm when the thickness of graphene was about 15 μ m, which is higher than those of laser-reduced graphene oxide GO[42], commercial graphene inks and laser induced graphene from PI [31].

The degree of graphitization from the PBI ink depended also on the number of laser irradiation passes and the concentration of PBI ink. To investigate the effect of conductive line printing, various widths of lines (0.05 mm to 0.2 mm) were prepared using the 5% PBI ink with laser fluences ranged from 10mJ/cm² to 30m J/cm². More laser irradiation passes on wider lines had lower electrical resistances for line drawing as shown in Figure 6 (The electrical resistance was measured across a 20 mm line distance using two standard long needles multi-meter with microscopy). More graphitization volume, demonstrated by the rise trend of 50um track thickness in Figure 5(a), had a lower resistance with the increase of laser fluence when the width of track was 50um one laser pass. Much less dropping rate of sheet resistances and thicknesses as shown in

Figure 6(b) and Figure 6(c) could prove that 0.2 and 0.1mm width tracks with laser passes overlapping was fully graphitized with low laser fluences. The lowest sheet resistance of 0.1 mm line was 8 ohm/square as shown in Figure 6(a) when the laser pass line spacing was 0.05 mm and the laser fluence was 13 mJ/cm².

Figure 6: Thickness of lines in (c) and sheet resistances for lines with different parameters (a) laser pass gaps from 0.05 to 0.2 mm, (b) laser fluence from 0.01 to 0.03J/cm² (d) illustration for lighting with aid of the graphene made by PBI ink for electrical circuit on flexible PET

2.4. Bonding with the substrate

To understand the characteristics of bonding the laser-generated graphene on the polymer substrate, the following investigation was carried out. In most aromatic systems, the cation- π interaction has primary contributions to the electrostatic interactions, so van der Waals forces are able to ensure tight interactions between graphene and the PET. As a π bond conjugated polymer, Polydopamine (PDA) had a great potential to be utilized as a medium to improve bonding between the graphene and PET. Various thicknesses PDA (from 1 nm to 15 nm) were polymerized on PET for 12 to 48

hours. The bending 5% strain was calculated from a 2.8 mm radius rod and the 0.3 mm PET plus PDT. With the thickness increase of the PDA, the laser fluence threshold for the PDA damage increased from 10 to 20 mJ/cm². The higher degree of graphitization generated higher surface area of porous morphology, which can effectively eliminate damages on graphene as illustrated in Figure 7(b₁-b₃). So a sheet resistance increase, related to strain from 2 to 5%, was ranged from 9% to 18% after bending in both directions for 1000 cycles. It was demonstrated for the specimen with 36 hours of PDA coating as shown in Figure 7(a). After 36 hours of polymerization, the PDA coating on PET was saturated and the maximum thickness of PDA was approached at constant of about 15 nm. The sheet resistance of the specimen with 48 hours of PDA coating was not lower than that of 36 hours PDA coating in Figure 7(a).

Figure 7: R/R_0 ratio, sheet resistance changes (a) of graphene growth on different polymerization time PDA coating on PET and different strains from 2-5% after 1000cycles bending test. The AFM images show the different thickness PDA and SEM images shows graphene morphology changes on different thickness PDA after 1000cycles bending test corresponding to polymerization time (12hours(b₁), 24hours(b₂) and 48hours(b₃))

2.5. Potential for inkjet printing and cathode printing

To understand the printability of the PBI ink, the ink fluid characteristics were investigated. A stable droplet generation is related to the reciprocal of Ohnesorge number, which can be characterized by groupings of physical constants as shown in the following equations[43] :

$$\text{Re} = \frac{v\rho a}{\eta} \quad (1)$$

$$\text{We} = \frac{v^2\rho a}{\gamma} \quad (2)$$

$$\text{Z} = \frac{1}{\text{Oh}} = \frac{\text{Re}}{\sqrt{\text{We}}} = \frac{\eta}{(\gamma\rho a)^{1/2}} \quad (3)$$

Where ρ , η and γ are the density (1.1g/cm³, 1.11g/cm³ and 1.12 g/cm³ for the 1%, 5% and 10% PBI solution), dynamic viscosity (3.5 mPa.s, 13 mPa.s and 52 mPa.s for 1%, 5% and 10% PBI solution) and surface tension of PBI solution (38mN/m). v is the velocity and a is the radius of the ink printer nozzle orifice. The Z value dropped from 10.4 to 0.6 with the 10 pl printer head when the 1% PBI solution concentration increased gradually to 10%. The high viscosity prevented droplet from ejecting with a low Z value and a large number of satellite droplets when the Z value was over 10. The Z value of the 1 to 5% PBI solution ranged from 0.6 to 2.7. As illustrated in **Error! Not a valid bookmark self-reference.**, the 1% PBI solution was printable with the Fujifilm Dimatrix inkjet printer , whose viscosity and surface tension threshold are 10-12mPa.s and 25-40mN/m [44].

Figure 8: 1% PBI ink droplet from a FujiFilm Dimatrix Drop watcher image

Figure 9 shows the variation of water contact angles of the graphene produced from the PBI inks at different laser power levels. It is clear that the surfaces became hydrophilic ($< 90^\circ$) and high volume of the mesoporous and macro porous as laser power increased. This is different from the standard graphene water contact angle of around 90° and generally hydrophobic. It is known that nitrogen-doped carbon can improve the wettability of carbon materials. These properties may be useful in favour of the impregnation of electrolytes for lithium sulphur batteries. In addition to the potential applications for flexible displays, graphene based sensors and smart wearables, another potential application of the laser direct writing of S and N doped graphene can be coated and loading sulphur on cathode in the lithium-sulphur batteries. Lithium-sulphur batteries(LI-S) have a great potential to become the next generation power source for electric vehicles, mobile phones, computers and smart grid community systems [45, 46], due to its high operating voltages, high power density ($2600 \text{ mA h kg}^{-1}$), low self-discharge and high energy capacity (1672 mA h g^{-1})[47]. Nitrogen and sulphur-doped graphene could improve both electrical conductivity and the capture of soluble polysulfide [48]. Moreover, the enhanced interface adsorption of the heteroatom (nitrogen and sulphur) doped porous carbon/graphene could suppress diffusion of polysulfide into the electrolyte and thus could shorten the transport pathway for both ions and electrons, which would benefit the battery life and charging time [49].

Figure 9: Water contact angles of laser generated graphene from PBI inks at various laser power ratings (100% = 1 W)

3. Conclusion

We have demonstrated a novel laser direct writing technique to form heteroatom (S, N) doped graphene on PET polymer and glass and potentially on any substrates without causing any heat damages to the substrates and without the use of Ni and Cu and without post-process curing. With the use of a UV laser wavelength, a controllable heteroatom doping with a high functionalized bond was realised within very short interaction time of a few milliseconds. The conductivity of the laser induced heteroatoms doped graphene was as high as 50 S/cm, matching that of ITO and higher than commercial conducting inks and graphene inks. The printed doped graphene showed hydrophilic characteristic, different from pristine graphene. A very thin layer (around 15 nm) of Polydopamine (PDA) allowed better graphene adhesion to the PET substrate, even after 1000 bending cycles. Potential applications of this technology may include roll-to-roll printing of flexible electronics, imbedded sensors, smart wearables and lithium ion batteries. The optical transparent of the printed graphene is still very low and further work is needed to improve this. The reported technology is under patent protection (UK patent application: GB1811466.0).

Experimental Section

Formulation of the Graphene Forming Organic Ink and Substrates Used

Polybenzimidazole (PBI) was dissolved in Dimethyl Sulfoxide (DMSO), which is a high polar aprotic solvent, at 1%, 5%, 10% and 15% PBI concentrations prepared with 1 hour stirring at 30 °C. The major driving forces for the intramolecular interactions are hydrogen bonding, electrostatic interactions and hydrophobic interactions. The inter-chain hydrogen bonding plays an important role for the conformational transition and aggregation process [50]. PBI with proton donor(-NH-) and proton acceptor(-N=) hydrogen bonding sites can be dissolved in a polar aprotic solvent [51]. The strong covalent sp^2 bonds were built by carbon atom hybridization with neighbouring carbon's atomic orbitals.

Then, 0.1 ml of the PBI ink was selectively deposited with 0.02 ml droplets using a 100 μ m diameter micropipette on a 20 mm x 20 mm glass sheet of 1 mm thickness and polyethylene terephthalate (PET, DuPont) substrates of 0.2 mm thickness.

The crystallization and the thermal decomposition temperatures of the PBI ink were determined from a Thermogravimetric Analysis (TGA) to be around 50 °C and 530 °C respectively, as shown in Figure 10. The quantity of the ink dropped quickly when the temperature was over 50 °C.

Figure 10: Thermogravimetric analysis and transmittances of 1%, 5% and 10% PBI solution.

The optical transmission and absorption characteristics of the PBI ink depended on the concentration of the PBI as shown in Figure 10. As the amount of the PBI increased, light

absorption also increased. An interesting characteristic was that the light transmission increased with the increase of wavelength particularly towards the infrared spectrum.

Laser Writing Procedure

Laser direct writing in ambient condition was carried out using the Edgewave picosecond laser with a laser fluence 0.006-0.045 J/cm², a pulse repetition rate of 3372.8 kHz and a scanning speed of 100 mm/s using a galvo x-y scanner. The focused beam spot size was 40 µm on the target surface. The laser beam scanning line spacing was 0.02 mm. A hotplate was used to dry the deposited PBI ink coating in a few minutes and the droplets in a few seconds at about 60 °C to avoid liquid flowing during laser processing. This could be replaced with an infrared non-contact heater or the ink is left to dry in air.

Surface modification of PET by PDA: PDA was self-polymerized on PET at ambient temperature by dissolving dopamine solution (2 mg/mL) in Tris-HCl buffer solution (1.2 mg/mL). For the thin layer of PDA, PET films were immersed in PDA solution for 12h and 24h, and then PET was rinsed by distilled water and dried. For the thick layer of PDA, after immersing in PDA solution for 24 hrs, the PET films were taken out and immersed in fresh made dopamine and Tris-HCl solution. PDA coating process was continued to polymerise PET films for another 12 hrs (for 36 hr-PDA-PET) and 24 hrs (for 48h-PDA-PET).

Material characterisation

The laser-processed samples were analysed using Raman spectrometry with a single excitation wavelength of 514 nm. Field Emission Gun - Scanning Electron Microscopy (FEG-SEM, Zeiss Sigma VP Field Emission Gun Scanning Electron Microscope), transmission electron microscopy (TEM), Thermogravimetric analysis (TGA), and Energy Disperse Spectroscopy (EDS, Zeiss Merlin SEM with Gemini II). X-ray Photon-Spectrometry (XPS) and X-ray Diffraction (XRD) were used to understand the atomic structures of the materials. Sheet resistances were determined using a 4-point contact probe method with 0.4 mm electrodes separated by a distance of 1 mm. The resistance

of tracks were determined using two point contact probe, which was allocated at the each end of the track by an optical microscope. A 6220 current source (Keithley Instruments, Cleveland, OH, USA) was used to record the resistivity (R) and the resistance (R) of tracks, which was transferred into sheet resistance (R_s) through:

$$R_s = \frac{2\pi}{\ln 2} \times R \quad (4)$$

$$R_s = \frac{RL}{W} \quad (5)$$

where L , W are the length and the width of the track. The optical transmissions of the materials were examined using an optical spectrometer. The wettability of the laser direct writing graphene from PBI ink was investigated with a water contact angle analyser (DSA25 from Kruss).

References

1. Zhang, X.Y., et al., *Ultrathin lanthanide oxides nanomaterials: synthesis, properties and applications*. Science Bulletin, 2016. **61**(18): p. 1422-1434.
2. Park, S.K., et al., *Mechanical stability of externally deformed indium-tin-oxide films on polymer substrates*. Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers, 2003. **42**(2A): p. 623-629.
3. Cairns, D.R., et al., *Strain-dependent electrical resistance of tin-doped indium oxide on polymer substrates*. Applied Physics Letters, 2000. **76**(11): p. 1425-1427.
4. Xue, J., et al., *Nanowire-based transparent conductors for flexible electronics and optoelectronics*. Science Bulletin, 2017. **62**(2): p. 143-156.
5. Hecht, D.S., L.B. Hu, and G. Irvin, *Emerging Transparent Electrodes Based on Thin Films of Carbon Nanotubes, Graphene, and Metallic Nanostructures*. Advanced Materials, 2011. **23**(13): p. 1482-1513.
6. Rathmell, A.R., et al., *The Growth Mechanism of Copper Nanowires and Their Properties in Flexible, Transparent Conducting Films*. Advanced Materials, 2010. **22**(32): p. 3558-+.
7. Xue, J., et al., *Nanowire-based transparent conductors for flexible electronics and optoelectronics*. Science Bulletin, 2017. **62**(2): p. 143-156.
8. De, S., et al., *Silver Nanowire Networks as Flexible, Transparent, Conducting Films: Extremely High DC to Optical Conductivity Ratios*. Acs Nano, 2009. **3**(7): p. 1767-1774.
9. Jang, J., et al., *Rapid production of large-area, transparent and stretchable electrodes using metal nanofibers as wirelessly operated wearable heaters*. Npg Asia Materials, 2017. **9**.
10. Im, H.G., et al., *A high-performance, flexible and robust metal nanotrough-embedded transparent conducting film for wearable touch screen panels*. Nanoscale, 2016. **8**(7): p. 3916-3922.
11. Yin, W.W., et al., *Screen printing of silver nanoparticle suspension for metal interconnects*. Korean Journal of Chemical Engineering, 2008. **25**(6): p. 1358-1361.
12. Kell, A.J., et al., *Versatile Molecular Silver Ink Platform for Printed Flexible Electronics*. Acs Applied Materials & Interfaces, 2017. **9**(20): p. 17227-17238.
13. Kim, K.S., W.R. Myung, and S.B. Jung, *Adhesion Characteristics of Silver Tracks Screen-Printed on Polyimide with an Environmental Reliability Test*. Journal of Nanoscience and Nanotechnology, 2012. **12**(7): p. 5769-5773.

14. Dong, Y., et al., *Facile synthesis of high silver content MOD ink by using silver oxalate precursor for inkjet printing applications*. Thin Solid Films, 2015. **589**: p. 381-387.
15. Kim, S.W., et al., *A Full-Visible-Spectrum Invisibility Cloak for Mesoscopic Metal Wires*. Nano Letters, 2018. **18**(6): p. 3865-3872.
16. Rathmell, A.R., et al., *The Growth Mechanism of Copper Nanowires and Their Properties in Flexible, Transparent Conducting Films*. Advanced Materials, 2010. **22**(32): p. 3558-3563.
17. Lee, J.H., et al., *One-Step Exfoliation Synthesis of Easily Soluble Graphite and Transparent Conducting Graphene Sheets*. Advanced Materials, 2009. **21**(43): p. 4383-+.
18. Chien, C.H., et al., *Thickness Effects on the Thermal Expansion Coefficient of Indium Tin Oxide/Polyethylene Terephthalate Film*. Experimental Techniques, 2014: p. n/a-n/a.
19. Gautam, G.D. and A.K. Pandey, *Pulsed Nd:YAG laser beam drilling: A review*. Optics & Laser Technology, 2018. **100**: p. 183-215.
20. Lin, J., et al., *Laser-induced porous graphene films from commercial polymers*. Nature Communications, 2014. **5**: p. 8.
21. Park, J.B., et al., *Transparent interconnections formed by rapid single-step fabrication of graphene patterns*. Applied Physics Letters, 2011. **99**(5).
22. Park, J.B., et al., *Fast growth of graphene patterns by laser direct writing*. Applied Physics Letters, 2011. **98**(12).
23. Jiang, J., et al., *Graphene synthesis by laser-assisted chemical vapor deposition on Ni plate and the effect of process parameters on uniform graphene growth*. Thin Solid Films, 2014. **556**: p. 206-210.
24. Ye, X., et al., *Laser Controllable Growth of Graphene via Ni-Cu Alloy Composition Modulation*. Lasers in Manufacturing and Materials Processing, 2015. **2**(4): p. 219-230.
25. Xiong, W., et al., *Single-Step Formation of Graphene on Dielectric Surfaces*. Advanced Materials, 2013. **25**(4): p. 630-634.
26. Xiong, W., et al., *Direct writing of graphene patterns on insulating substrates under ambient conditions*. Scientific Reports, 2014. **4**.
27. Baraton, L., et al., *On the mechanisms of precipitation of graphene on nickel thin films*. Epl, 2011. **96**(4).
28. Carey, T., et al., *Fully inkjet-printed two-dimensional material field-effect heterojunctions for wearable and textile electronics*. Nature Communications, 2017. **8**: p. 11.
29. Lin, Z., et al., *Thinning of large-area graphene film from multilayer to bilayer with a low-power CO₂ laser*. Nanotechnology, 2013. **24**(27).
30. Tian, Z.S., et al., *Facile synthesis of highly conductive sulfur-doped reduced graphene oxide sheets*. Physical Chemistry Chemical Physics, 2016. **18**(2): p. 1125-1130.
31. Lin, J., et al., *Laser-induced porous graphene films from commercial polymers*. Nature Communications, 2014. **5**.
32. Wang, L., et al., *Formation of Deep-Subwavelength Structures on Organic Materials by Femtosecond Laser Ablation*. Ieee Journal of Quantum Electronics, 2018. **54**(1).
33. Arnold, N. and N. Bityurin, *Model for laser-induced thermal degradation and ablation of polymers*. Applied Physics a-Materials Science & Processing, 1999. **68**(6): p. 615-625.
34. Wang, C., et al., *Application of sulfur-doped carbon coating on the surface of Li₃V₂(PO₄)₃ composites to facilitate Li-ion storage as cathode materials*. Journal of Materials Chemistry A, 2015. **3**(11): p. 6064-6072.
35. Giannozzi, P., et al., *Advanced capabilities for materials modelling with QUANTUM ESPRESSO*. Journal of Physics-Condensed Matter, 2017. **29**(46).
36. Perdew, J.P., K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple (vol 77, pg 3865, 1996)*. Physical Review Letters, 1997. **78**(7): p. 1396-1396.
37. Zhu, Y.W., et al., *Carbon-Based Supercapacitors Produced by Activation of Graphene*. Science, 2011. **332**(6037): p. 1537-1541.
38. Ma, J., et al., *Stone-Wales defects in graphene and other planar sp²-bonded materials*. Physical Review B, 2009. **80**(3).
39. Singh, S.P., et al., *Sulfur-Doped Laser-Induced Porous Graphene Derived from Polysulfone-Class Polymers and Membranes*. ACS Nano, 2018. **12**(1): p. 289-297.

40. Song, B.Q. and L.D. Pan, *Penetration of the first-two-row elements through mono-layer graphene*. Carbon, 2016. **109**: p. 117-123.
41. Jeong, H., *Nitrogen-doped graphene for high performance ultracapacitors and the importance of nitrogen-doped sites at basal-planes*. Abstracts of Papers of the American Chemical Society, 2012. **243**: p. 1.
42. Strong, V., et al., *Patterning and Electronic Tuning of Laser Scribed Graphene for Flexible All-Carbon Devices*. Acs Nano, 2012. **6**(2): p. 1395-1403.
43. Derby, B., *Inkjet Printing of Functional and Structural Materials: Fluid Property Requirements, Feature Stability, and Resolution*. Annual Review of Materials Research, Vol 40, 2010. **40**: p. 395-414.
44. Derby, B., *Inkjet Printing of Functional and Structural Materials: Fluid Property Requirements, Feature Stability, and Resolution*, in *Annual Review of Materials Research, Vol 40*, D.R. Clarke, M. Ruhle, and F. Zok, Editors. 2010, Annual Reviews: Palo Alto. p. 395-414.
45. Erickson, E.M., C. Ghanty, and D. Aurbach, *New Horizons for Conventional Lithium Ion Battery Technology*. Journal of Physical Chemistry Letters, 2014. **5**(19): p. 3313-3324.
46. Bogart, T.D., et al., *Lithium Ion Battery Performance of Silicon Nanowires with Carbon Skin*. Acs Nano, 2014. **8**(1): p. 915-922.
47. Mei, J., T. Liao, and Z.Q. Sun, *Two-dimensional metal oxide nanosheets for rechargeable batteries*. Journal of Energy Chemistry, 2018. **27**(1): p. 117-127.
48. Chen, D., et al., *One-pot fabrication of nitrogen and sulfur dual-doped graphene/sulfur cathode via microwave assisted method for long cycle-life lithium-sulfur batteries*. Journal of Alloys and Compounds, 2018. **746**: p. 116-124.
49. Xu, G.Y., et al., *High performance lithium-sulfur batteries: advances and challenges*. Journal of Materials Chemistry A, 2014. **2**(32): p. 12662-12676.
50. Pedersen, C.J., *THE DISCOVERY OF CROWN ETHERS (NOBEL LECTURE)*. Angewandte Chemie-International Edition, 1988. **27**(8): p. 1021-1027.
51. Sannigrahi, A., et al., *Aggregation behavior of polybenzimidazole in aprotic polar solvent*. Macromolecules, 2007. **40**(8): p. 2844-2851.

Acknowledgement

Mr. yihe Huang acknowledges the University of Manchester for his research scholarship.