

# Chemical Fabrication and Characterization of Graphene for Water-Based Inks used in Screen-Printing

Mathias Kirkholt Laursen

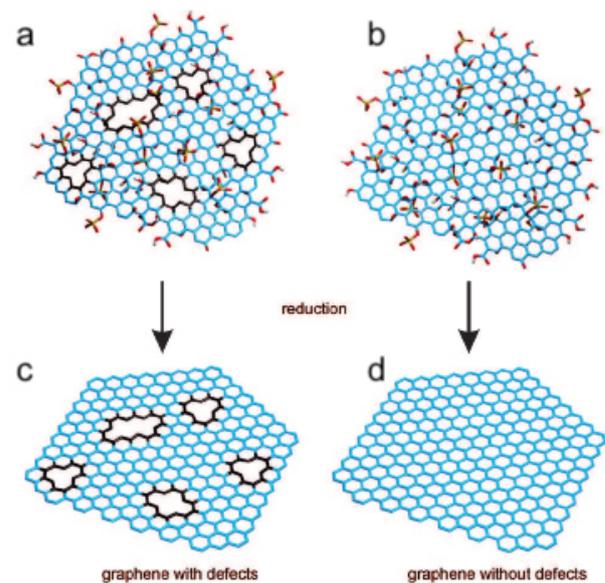
Submitted June 2018, accepted July 2018

Graphene exhibits a range of interesting properties such as high optical transmittance, good thermal conductivity, high Young's modulus, and good electrical conductivity. Graphene can serve as a component in conductive applications and potentially replace the expensive conductive materials, such as indium tin oxide (ITO), that are used today. In this article the graphene derivatives graphene oxide (GO) and reduced graphene oxide (rGO) are synthesized. The reduction of GO is done by either microwave assisted reduction, intense light reduction or chemical reduction with hydrogen iodide. The structures of the synthesized compounds are characterized and analyzed using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Based on the synthesized GO, a GO-ink is formulated and screen-printed on a polymer-based polyethylene terephthalate (PET) substrate, from which a sheet resistance of  $0.4 \text{ k}\Omega \text{ sq}^{-1}$  is measured. This work suggests that the synthesized GO can be used in production of conductive circuits or serve as a precursor for future scalable conductive films.

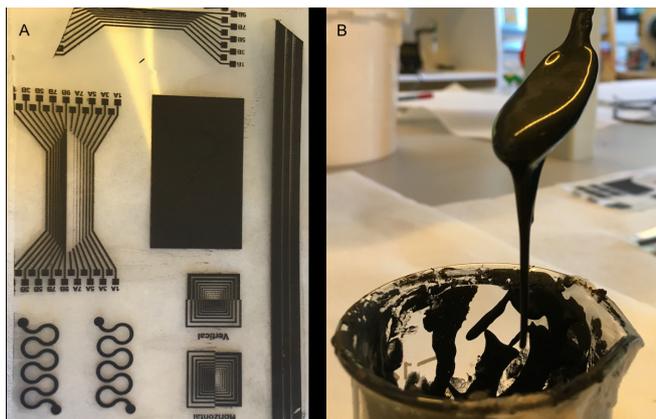
## 1 Introduction

Graphene has been the subject of intense research in the last decade due to its application possibilities which includes chemical sensors,<sup>1</sup> micro-supercapacitors,<sup>2</sup> semi-transparent conductive films,<sup>3-4</sup> and many more. The application possibilities with graphene are vast due to several factors such as the large theoretical specific surface area, high Young's modulus, good thermal conductivity, high optical transmittance and good electrical conductivity. These attributes arise from the molecular structure of graphene, which is shown in figure 1d.<sup>5</sup> Graphene consists of a two dimensional carbon structure, which is build up by  $sp^2$ -hybridized carbon atoms positioned in a honeycomb lattice. A Nobel price was given in 2010 to Andre Geim and Kostya Novoselov for formulating graphene through mechanical exfoliation.<sup>6</sup> Although, graphene was first synthesized in 1860<sup>7</sup> by Brodie, it is today still almost impossible to synthesize without lattice defects and functional groups.<sup>5</sup> Even though chemical vapor deposition produces a high quality of graphene the downsides to this method is the cost and that it is not scalable. In this article the graphene derivative graphene oxide(GO) is synthesized using the improved Hummers method.<sup>8</sup>

To synthesize GO, a precursor of natural graphite is needed to be separated into single sheets. This is done in two steps, first intercalation of the graphite sheets using sulfuric acid, then exfoliation of the sheets with a sonicator. GO is a single layer of graphene with functional



**Fig. 1** Theoretical molecular structures of a) graphene oxide (GO) b) GO-without lattice defects, c) reduced graphene oxide (rGO), with lattice defects d) graphene. The figure is taken from article [5].



**Fig. 2** In picture a), the synthesized GO-ink is shown. The print is made using the printing setup described in the experimental section. In picture b), the viscosity of the GO-ink used in picture a) is presented. The GO-ink was made using a water-based ink and the synthesized GO. The precise mixture of the ink can be found in the supporting information.

groups such as epoxy, hydroxyl and carbonyl groups some of which can be seen in figure 1a and 1b. These functional groups on GO disturb the electronic properties of graphene, and to enhance the conductive nature it is advantageous to remove these groups. This challenge is thoroughly researched and there are several reports that attempt to remove the functional groups and synthesize the reduced-graphene-oxide(rGO).<sup>9-10</sup> The rGO samples synthesized in this article are achieved with either microwave assisted reduction (MW-rGO),<sup>11</sup> intense-light reduction (IL-rGO)<sup>1</sup> or chemical reduction using hydrogen iodide (HI-rGO).<sup>10</sup> The goal of these reduction processes is to remove any functional groups from the GO, and restore the hybridized carbon lattice as seen in figure 1b to 1d. The rGO exhibit characteristic of the perfect graphene lattice and single rGO flakes can become visible in an optical microscope. However, rGO is often synthesized only to find a defective carbon lattice due to holes, additional atoms or lattice frameshifts. The reasons behind these defects are often either an over-oxidation in the initial synthesis, or a too hard reduction resulting in decarboxylation with the release of CO<sub>2</sub> from the GO. This article presents a high quality of rGO from different reduction methods in addition to discussing the effectiveness of the reduction agents.

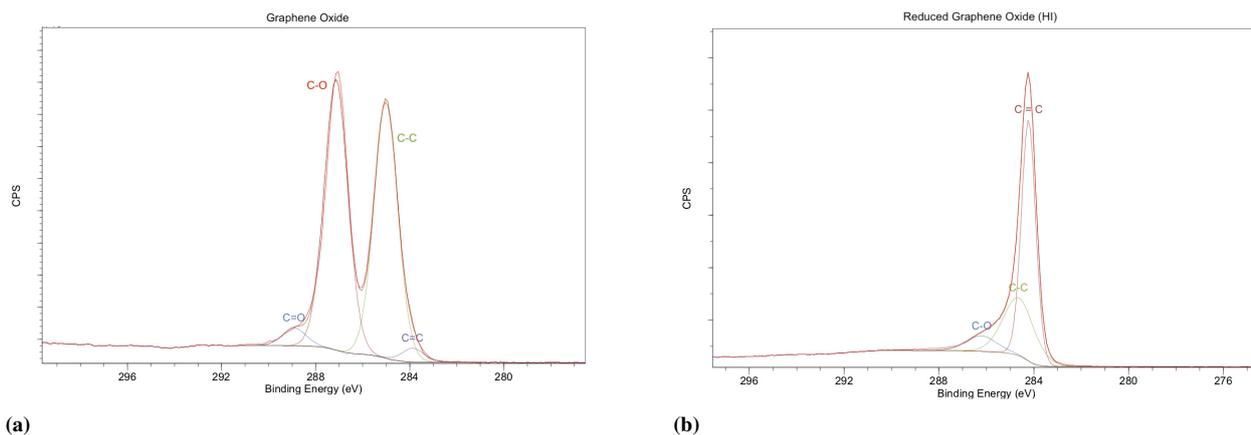
Printed films have many applications such as flexible touch screens and displays, printable electronics and film heaters.<sup>4</sup> The conductive films in production today, use metal nanoparticles, metal nanowires or transparent conductive oxides such as indium tin oxide.<sup>12</sup> These materials, comes at a high price, and cannot meet the global consumer demands.<sup>3</sup> A water-based ink is preferable as

it is less toxic and less expensive than commercial available inks.<sup>13</sup> Therefore, a GO-ink application has attracted a great deal of interest as it could either directly replace the films in production today or be a component in the production of conductive films.<sup>3</sup> The GO synthesized in this paper, is formulated into a graphene oxide ink (GO-ink) using water as the solvent. In figure 2 the formulated GO-ink is shown. This ink-application can be transferred to a roll-to-roll (R2R) production line used on a flexible and transparent polymer substrate. This technique allows for mass production of low-cost fully printed devices.

## 2 Results and discussion

The synthesis method used in this article is referred to as the improved Hummers method,<sup>8</sup> as first described by Eigler.<sup>14</sup> Here natural graphite is the starting material, for a scalable production of GO. Sulfuric acid and permanganate is used to synthesize the GO, where it is desirable to prevent an overoxidation of the graphite as it leads to the release of CO<sub>2</sub>. The decarboxylation of the GO leaves holes or defects in the graphene lattice, creating irreversible damage to the lattice, ultimately reducing the conductivity of the GO material. To prevent this, the reaction is kept at a low temperature, and the permanganate is added slowly to prevent local heating. To synthesize GO one needs to overcome the Van der Waals  $\pi - \pi$  stacking interaction of the carbon sheets. In this article exfoliation with a sonicator, as described in the experimental section, is used to overcome these interactions and create monolayers of graphene sheets. This procedure of producing GO, which is fully described in the experimental section, allows for an almost intact carbon lattice throughout the synthesis, and serves as the precursor for further processing. A theoretical picture of the synthesized GO is shown in figure 1b.

To investigate and further understand the effects of different reduction techniques X-ray photoelectron spectroscopy (XPS) measurements were performed. The GO examined by XPS consists of several peaks as seen in figure 3a. By decomposing the XPS C1 spectral lines, each peak correspond to specific bonds. The C=O, C-O, C-C and C=C each has a specific binding energy and is presented in figure 3. The peaks provide details about the binding state of the carbon in the sample. The two very intense peaks at energies 287 eV and 285 eV correspond respectively to the C-O and C-C bonds. Furthermore, peaks at binding energies 289 eV and 284 eV correspond to the bonds C=O and C=C. This allows for calculating the composition of the carbon in the GO sample and each of the rGO samples. Using the XPS measurements the chemical binding states of the GO and rGO samples was determined and compared. All XPS measurements are shown



**Fig. 3** In each figure the CPS corresponds to the intensity in arbitrary units. a) In this figure, the XPS data from the synthesized GO is shown. b) In this figure, the XPS data, from the HI-rGO is presented. The reduction process for this figure was done using hydrogen iodide(HI). In table 1, all data from the XPS measurements can be found.

**Table 1** XPS spectroscopy data

Samples		Composition of the sample in %				Composition of the carbon in %			
		C	O	N	S	C-O	C-C	C=O	C=C
GO	On SiO <sub>2</sub>	67	27.1	2.5	3.4	46.5	42.1	5.0	6.4
rGO-MW	powder	15.8	56.6	11.2	16.4	42.7	49.3	8.0	<1.0
rGO-IL	On SiO <sub>2</sub>	86.3	13.1	<1.0	<1.0	6.1	30.5	<1.0	63.41
		C	O	I	Traces of N and S	C-O	C-C	C=O	C=C
rGO-HI	On SiO <sub>2</sub>	90.2	6.5	2.3	<1.0	8.3	31.5	<1.0	60.2

in table 1. Each C-O peak corresponds to carbon atoms bound to either a hydroxide group (C-OH) or an epoxide group (C-O-C). After the chemical reduction with hydrogen iodide(HI), a major reduction in the C-O level is observed. Furthermore, the content of C=O, and thus the carbonyl groups (C=O), is no longer measurable and is determined to be less than 1%. These measurements indicate the effectiveness of the chemical reduction technique, as the amount of carbon-oxygen functional groups have decreased drastically. Additionally, the amount of C=C bonds and thus the sp<sup>2</sup> hybridization of carbon increase significantly, which is expected to be caused by the reconstruction of the carbon lattice network. The chemical reduction with HI is believed to follow an E1 elimination reaction mechanism.<sup>15</sup> This would remove functional groups from the graphene oxide and would explain the reconstruction of hybridized carbon lattice. However, as graphene is a big two-dimensional carbon network, with each carbon atom affecting the next one, the mechanism for this reaction is not completely understood and further research is needed in that area.

In this article the reduction of GO is done with by either MW-reduction, IL-reduction, or chemical reduction using HI. In the case of MW-reduction and IL-reduction, it is believed that the energy supplied, either by the microwave or the light introduced on the sample, forces the chemical binding to the functional groups to become unstable. However, if too much energy is dispersed to the carbon lattice, an irreversible decarboxylation of the carbon lattice would occur followed by the release of CO<sub>2</sub>.

The XPS measurements of the synthesized GO and reduced GO derivatives are displayed in table 1. The traces of sulfur are believed to be from the sulfuric acid used in the synthesis method<sup>8</sup> and the nitrogen is estimated to be due to contamination in each sample. However, it is worth noticing that the contamination levels decrease after reduction of the sample, except for the MW-rGO. When synthesizing the MW-rGO, arcs were observed when the sample was exposed to microwaves, which indicates a violent reduction of the sample. It can be argued that the microwaves energy was too high, and a lot of the GO was reduced to CO<sub>2</sub> due to decarboxylation. This would also

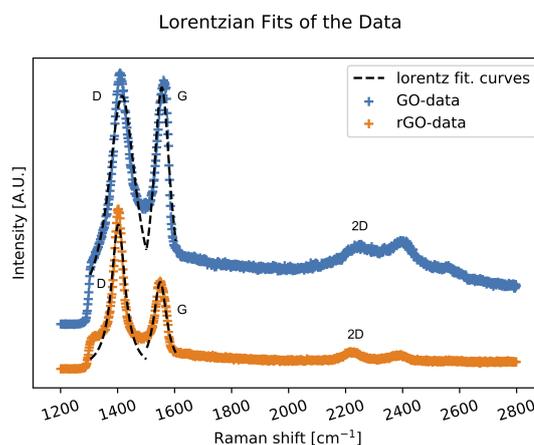
**Table 2** An average of the Raman Data

Sample	D-Band	G-Band	2D-Band	Intensity ratio, $I_D/I_G$
	Peak, $\text{cm}^{-1}$	Peak, $\text{cm}^{-1}$	FWHM, $\text{cm}^{-1}$	
GO-MeOH	1406.1	1559.6	432.4	1.439
GO-MiliQ	1404.9	1560.8	404.1	1.411
rGO-MeOH	1405.4	1551.0	164.1	1.770
rGO-MiliQ	1407.8	1551.6	177.6	1.799

explain the high oxygen level in the MW-rGO sample and that is believed to have completely ruined the graphene lattice.

It is believed that the contamination in the samples decrease after reduction because several functional groups are removed from the GO. As seen in table 1, a significant decrease in both oxygen, nitrogen and sulfur is observed when comparing rGO-HI, and rGO-IL with the GO sample. Furthermore, after both the chemical- and light reduction, the carbon-oxygen bonds have decreased significantly as well. In addition, the C=C bonds after reduction shows a major increase. These indications both demonstrate that the reduction of GO was successful. The carbon lattice in these samples should have a low density of defects and serve effectively as a conducting material. The best and most efficient reduction technique is determined to be the intense light reduction. This is evident from the XPS data in table 1 showing a high decrease in C-O bonding compared to the other reduction methods. Additionally, the intense light reduction technique could be further refined by targeting the binding of specific functional groups. The energy supplied by the intense light is determined by the distance to the sample, the exposure time, and the wavelength of the mercury lamp. A way to improve the IL-reduction method would be to target specific functional groups by exposing the sample with light at a specific energy. Another possible way to improve the reduction of GO is to combine the chemical reduction with the light reduction. Both methods could potentially create an even higher quality of rGO. In this work the IL-reduction is performed with a mercury lamp for about 1-2 seconds and the sample was about 1 cm from the light source.

The improved Hummers method<sup>8</sup> is used to synthesize the GO in this article. To determine the quality and whether the chemical reduction had any influence on the quality, Raman spectroscopy was performed on the synthesized compounds. The spectroscopy measurements were done on a GO and a chemically reduced rGO sample. The full width at half maximum (FWHM) of the 2D band and the intensity ratio  $I_D/I_G$ , in the Raman spectroscopy, are correlated to the amount of defects in the carbon lattice. Typical Raman spectra of graphene displays three characteristic peaks; a D-peak, a G-peak and a 2D-peak.<sup>5</sup> All



**Fig. 4** The Raman spectroscopy data represented here is from both of the GO and the chemically reduced rGO sample. There is an offset between the two curves. The characteristic peaks of D, G and 2D for GO and rGO, are indicated on each data sets and a Lorentzian function have been fitted to the D and G peak. Furthermore, a FWHM calculation was made on the 2D peak.

peaks are visible in figure 4 where the D-peak is around  $1400 \text{ cm}^{-1}$ , the G-peak is approximately at  $1555 \text{ cm}^{-1}$ , and the 2D-peak around  $2200 \text{ cm}^{-1}$ . The intensity ratio,  $I_D/I_G$ , indicates the quality of the carbon lattice in the sample and is displayed in table 2. As described by Eigler<sup>16</sup> the FWHM of the 2D peak and intensity ratio  $I_D/I_G$  are correlated (this trend can be seen in supplementary information figure S4). At the measured FWHM of the 2D peak in this work, the intensity ratio  $I_D/I_G$  is believed to increase with a lower density of defects.

The Raman measurements done on the samples reports a small increase in the intensity ratio after chemical reduction with HI on GO. This increase in intensity ratio  $I_D/I_G$  can be explained by the restructure of the carbon lattice. The HI is believed to restore the conjugated system in the carbon lattice structure when removing functional groups. This is also indicated by the drop in the 2D-peak FWHM-calculation when comparing GO and rGO samples. After chemical reduction the peak is more defined and resembles the peak of pure single sheet graphene. Thus, it can be derived from the Raman spectroscopy data that the chemi-

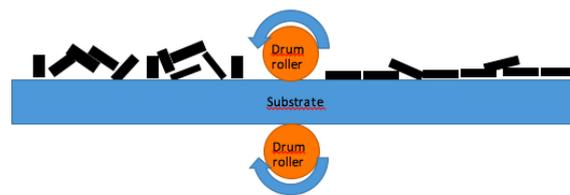
**Table 3** Sheet resistance of the different GO-inks

Sample	$R_s$ $k\Omega$ $sq^{-1}$
GO-ink	10.4
rGO-ink	0.7
rGO-ink pressed	0.4
rGO-(Cellulose)-ink	20.2

cally reduced rGO decreases the density of defects.

The synthesized graphene oxide inks (GO-ink) were printed with a woven polyester screen onto a polymer based polyethylene terephthalate (PET) substrate. The GO and rGO were each applied, to a water based graphene ink and tested with a screen-printing method. The synthesized GO proposes a challenge, as the oxygen levels in the GO sample measured to almost 30%. In addition, 50% of the carbon in the GO sample is bound either to a hydroxide group, an epoxide group or a carbonyl group. Since there are many functional groups and defects in the lattice structure of the synthesized GO, the GO is expected to have a high resistivity. The conductivity of the all GO-inks were tested using a probe station which measures the resistance of a sample. This is used to calculate the sheet resistance ( $R_s$ ) of each sample. In table 3, an average of the various sheet resistances of all synthesized inks are presented. As expected, the GO has a very high sheet resistance which is deemed due to the high oxygen level in that sample.

In an attempt to optimize the GO-ink different GO derivatives were tried. Firstly, the GO was chemically reduced using HI (rGO-ink), then the sample was pressed using a pressing drum (rGO-ink pressed). This resulted in a low sheet-resistance of  $0.4 k\Omega sq^{-1}$ . However, the pressure applied to the ink, resulted in a very fragile ink which fractured at a low force. Thus, another ink was synthesized using a mixture of rGO and hydroxyethyl cellulose which acted as a binding agent. The print results were visibly of much higher quality, which can be seen in figure 2A, where the print with hydroxyethyl cellulose is displayed. Even though the hydroxyethyl cellulose print was of high quality, the downside of using hydroxyethyl cellulose is proven to be a high sheet resistance. The increase in sheet resistance observed in the last print is believed to be caused by the insulating nature of the hydroxyethyl cellulose. To see whether the surface tension of the substrate had any effect on the quality of the prints, the polymer substrate was treated with oxygen plasma before applying the ink. This made a major visual improvement on the last print where the oxygen plasma was applied. This illustrates that each composition of ink, should be paired with a specific substrate, as surface tension of the substrate is vital to the finished printing result. However, it is believed that the oxygen plasma applied to the substrate only helps with the visual result, not the conductivity of the print.



**Fig. 5** Here the theoretical effect of pressing the GO-ink is shown. The black boxes represent the GO-flakes in the ink and before applying the pressure the GO-flakes are randomly dispersed. After the pressure is applied the GO-flakes are flat and connected.

The print with hydroxyethyl cellulose shows that if a correct binding agent is added to the GO-ink, it could result in a visually high quality print, and the result with the pressed rGO-ink shows that a high conductivity can be achieved. If a binding agent can be found that combines these results, then it would be possible to synthesize a fully conductive and flexible ink. The low sheet resistance measured from the pre-pressed rGO-ink is believed to be caused by the alignment of graphene flakes in the sample. This pressure effect is presented in figure 5.

To potentially improve the conductivity of the ink one could try and reduce the GO-ink by either thermal reduction or light reduction after printing. Another improvement could be to try to induce some conductive properties with dopants. Furthermore, the optimal print conditions are yet to be found so there is room for improvement in that area as well.

It is difficult to directly compare the commercially available ITO-ink<sup>12</sup> with the synthesized GO-ink because of the difference in film thickness.

### 3 Conclusion

In conclusion, the synthesized GO in this article works as a precursor for water-based conductive screen-prints. The GO was synthesized using the improved Hummers method,<sup>8</sup> for a high quality GO and then reduced using either chemical, microwave, or light-reduction. As in previous work,<sup>1</sup> the light reduction was very successful with the lowest measured oxygen level as shown in table 1. The Raman spectroscopy measurements of the samples with HI indicated a high quality of GO with a clear 2D-peak after chemical reduction of GO. This showed that with chemical reduction of GO, the GO would reconstruct the graphene lattice through an E1-like elimination reaction mechanism.

The synthesized GO was mixed with ink and printed onto a polymer substrate. Both the GO, rGO, and pre-pressed rGO, was measured for their conductivity using a probe station. The print with the lowest sheet resistance

---

proved to have a sheet resistance of  $0.4 \text{ k}\Omega \text{ sq}^{-1}$ . This is in line with previous work.<sup>4</sup> However, in this article the prints are scalable and inexpensive to produce. Furthermore, there are several options to improve the conductivity of the prints by either dopants or either thermal or light reduction of the prints.

This work proves that the synthesized GO can either serve as a precursor for other conductive applications, or be printed with the screen-printing method shown in this work.

## 4 Experimental

The synthesis of GO was done using a method described by Eigler.<sup>8</sup> The starting point of the synthesis is natural graphite. Here 2.01 g of large flaked graphite ( $<300\mu\text{m}$ ), was loaded into a large round beaker. The beaker was put in an isolating box, where it was constantly cooled by a mixture of dry ice and water, and stirred at a moderate tempo. 50 mL of a 95% sulfuric acid solution was added to the beaker. When the graphite was completely suspended in the acid, 4 g of potassium permanganate was added over 4 hours. The solution was continuously stirred and cooled for 12 hours while the reaction with potassium permanganate occurred. Then 100 mL of diluted 20% sulfuric acid was added at a rate of 40 mL per hour. This was followed by the addition of 240 mL of miliQ water at a rate of 8 mL per hour. Then, 160 mL of 20% hydrogen peroxide was added over 12 hours. The beaker was kept cool and with a moderate stirring during every step. The obtained suspension of GO was sonicated with a Hielscher UPS400 (400 W) ultrasonic processor at an amplitude of 55% with 0.5 cycle for 4 minutes total. Finally, the GO solution was washed 4 times using cold ( $5^\circ\text{C}$ ) miliQ water and centrifugation at 9000 RPM for an hour. After each cycle the supernatant was replaced and the precipitate was resuspended. The pH was measured to be approximately 7 with pH paper after the washing. To remove small particles from the GO solution it was centrifuged 3 times at 2000 RPM for 16 minutes, and the precipitate was removed after each cycle. To further clean the solution and remove small graphene-like particles, the GO suspension was centrifuged at 9000 RPM 4 times for 45 minutes, each time replacing the supernatant.

Chemical reduction of GO was made using HI. The GO was placed on a silicon oxide wafer in drops of about 50  $\mu\text{L}$ . The drops of GO were added each day for a total of 4 straight days, each time the GO layer was allowed to dry in atmosphere. Before adding the GO, the silicon oxide wafer was cleaned using acetone, ethanol and isopropanol, and then prepared using a base piranha solution which consist of 1/4 ammonia, 1/4 hydrogen peroxide and 1/2 miliQ water. The silicon-wafer, was now placed in a gas chamber

with a single drop of HI. Next, the gas chamber was heated to  $60^\circ\text{C}$  for 30 minutes. This should reduce the GO and create reduced graphene oxide (rGO).

Physical reduction of GO was done using microwave.<sup>11</sup> GO was centrifuged at 9000 RPM for one hour. The excess water was removed from the GO solution and about 10 mL of thick GO solution remained. This was now freeze dried using a cold trap (for details on the method see supplementary information). The dry GO was now mildly reduced by thermal annealing at  $300^\circ\text{C}$  for one hour under a flow of nitrogen. The mildly reduced GO was placed in a glass beaker, which was filled with nitrogen or argon and sealed. The beaker with GO was placed inside a microwave oven, and heated at 800 W for 1-2 seconds. Arcs from the GO were observed which suggests an extremely fast annealing process where the GO is heated to a couple of thousands degrees Celsius within a few milliseconds. The MW-rGO was finally allowed to rest for some minutes.

Light reduction of GO was done using light from a mercury lamp.<sup>1</sup> A drop of GO from the stock solution was added to a silicon oxide wafer. The wafer was cleaned and prepared as in the chemical reduction part above. The mercury lamp was allowed to heat up for 5 minutes before exposing the samples to the light. The GO-samples on the wafers were held using a tweezer about 1 cm from the light source for 1-2 seconds. This should reduce the GO and form the intense light reduced graphene oxide (IL-rGO).

Graphene oxide was printed on a PET substrate. The print was done using a mixture of the stock GO solution and a water based ink. The stock GO solution was high speed centrifuged at 9000 RPM and excess water was removed. The remaining GO was then mixed with the ink and stirred for 10 minutes, then a highly viscous solution was achieved. About 15 mL of the GO-ink solution was needed for each print.

The screen-printing with GO was done using a mesh consisting of a tightly woven polyester yarn. The mesh used in this article had mesh openings between  $57 \mu\text{m}$  and  $77 \mu\text{m}$ . For each print the GO-ink solution was added to the mesh and a squeegee was used to press it through the mesh and onto the substrate. The print thickness could be varied by changing the number of print passes, varying the pressure from the squeegee, varying the angle from the squeegee to the mesh, and changing the viscosity of the GO-ink solution. Further information about the screen print can be found in supplementary information.

Raman spectroscopy was performed on GO and the chemically reduced rGO. A silicon oxide wafer was prepared as described earlier.  $5 \mu\text{L}$  of the stock GO solution was spin coated on the silicon wafer. The spin coating was done at 3000 RPM for 30 seconds. Some of the GO samples were then reduced using the chemical reduction technique as described previously. The sample was placed

upside down on an Olympus IX71 microscope. The laser was aimed directly at flakes on the sample. The measurement performed by the Raman setup were done with a 543 nm laser. For the precise Raman setup and all Raman data see the supplementary information

X-Ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra-DLD instrument. Samples were prepared on the silicon wafers as described previously. XPS measurements were performed on both the GO and different rGO samples. The rGO samples were produced either by microwave assisted reduction, intense-light reduction, or by chemical reduction using HI. The MW-rGO was a fluffy material which was compressed to a powder and then XPS was performed on that sample. For further information about the X-Ray see supplementary information.

Vapor deposition was performed on the finished screen prints to form gold electrodes. The bottom side of the screen printed polymer substrates, were fastened to a silicon wafer. These were then lowered into a vacuum tank where gold electrodes were deposited on the ink using a mask. A picture of the gold electrodes can be seen in the supplementary information.

The sheet resistance of each print was measured using a probe station, where a current was induced from the outer electrodes. The voltage drop over the inner electrodes was then measured. The sheet resistance for the material could then be calculated using the equation<sup>17</sup>  $R = R_s \cdot L/W$  where  $R_s$  is the sheet resistance,  $R$  is the resistance measured,  $L$  and  $W$  is the length and width of the sample.

## 5 Acknowledgements

I would like to thank my supervisor Kasper Nørgaard and Marc H. Overgaard, Martin Kühnel, Ramus K. Jakobsen, Jens R. Frandsen for valuable discussions. I would also like to thank Nico Bovet and Tom Vosch for the XPS and Raman measurements done in this article.

## References

- 1 S.-J. Choi, S.-J. Kim and I.-D. Kim, *NPG Asia Materials*, 2016.
- 2 Y. M. Shulga, S. A. Baskakov, Y. V. Baskakova, A. S. Lobach, E. N. Kabachkov, Y. M. Volkovich, V. E. Sosenkin, N. Y. Shulga, S. I. Nefedkin, Y. Kumar and A. Michtchenko, *Journal of Alloys and Compounds*, 2018, **730**, 88–95.
- 3 M. H. Overgaard, M. Kuhnel, R. Hvidsten, S. V. Petersen, T. Vosch, K. Nørgaard and B. W. Laursen, *Advances Materials Technologies*, 2017.
- 4 L. He and S. C. Tjong, *Journal of Materials Chemistry C*, 2016, **4**, 7043–7051.
- 5 S. Eigler and A. Hirsch, *Angewandte Chemie-International Edition*, 2014, **53**, 7720–7738.
- 6 A. K. G. . K. S. Novoselov, *Nature Materials* ., 2007, **Vol. 6**, year.
- 7 B. C. Brodie, *Proceedings of the Royal Society of London*, 1860, **10**, 11–12.
- 8 E. Siegfried, E. Michael, G. Stefan, H. Philipp, K. Wolfgang, G. Andreas, D. Christoph, R. Michael, X. Jie, P. Christian, L. Ole, S. HansPeter, M. Paul and H. Andreas, *Advanced Materials*, 2013, **25**, 3583–3587.
- 9 F. T. Johra, J.-W. Lee and W.-G. Jung, *Journal of industrial and Engineering Chemistry*, 2014, **20**, 2883–2887.
- 10 S. Eigler, S. Grimm, M. Enzelberger-Heim, P. Muller and A. Hirsch, *Chem. Commun.*, 2013, **49**, 7391–7393.
- 11 D. Voiry, J. Yang, J. Kupferberg, R. Fullon, C. Lee, H. Y. Jeong, H. S. Shin and M. Chhowalla, *SCIENCE*, 2016, **353**, 1413–1416.
- 12 M. sung Hwang, B. yong Jeong, J. Moon, S.-K. Chun and J. Kim, *Materials Science and Engineering: B*, 2011, **176**, 1128 – 1131.
- 13 H. 1 2 3 4 Kipphan, *Handbook of print media*., technologies and production methods (Illustrated ed.), 2001, vol. pp. 130–144, ISBN 3-540-67326-1.
- 14 S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, **45**, 1558 – 1565.
- 15 J. E. McMurry, *Organic Chemistry*, Brooks/Cole, 8th edn, 2012.
- 16 S. Eigler, F. Hof, M. Enzelberger-Heim, S. Grimm, P. Mueller and A. Hirsch, *Journal of Physical Chemistry C*, 2014, **118**, 7698–7704.
- 17 J. G. Webster, *Electrical Measurement, Signal Processing, and Displays, Chapter 7 "Electrical Conductivity and Resistivity*, CRC Press, 2003.