

Improvements in electronic structure and properties of graphene derivatives

Velram Balaji Mohan^{1*}, Dongyan Liu², Krishnan Jayaraman¹, Manfred Stamm^{3,4} and Debes Bhattacharyya¹

¹Centre for Advanced Composite Materials (CACM), Department of Mechanical Engineering, The University of Auckland, Auckland, New Zealand

²Institute of Metal Research (IMR), Chinese Academy of Sciences (CAS,) Shenhe District, Shenyang City, Liaoning Province, China

³Leibniz Institute of Polymer Research Dresden (IPF), Department of Nanostructured Materials, Dresden, Germany

⁴Technische Universität Dresden, Physical Chemistry of Polymer Materials, Dresden, Germany

*Corresponding author. Tel: (+64) 93737599; Fax: (+ 64) 9-3737005; E-mail: vmoh005@aucklanduni.ac.nz

Received: 30 August 2015, Revised: 03 February 2016 and Accepted: 01 May 2016

ABSTRACT

This article focuses on the reduction of graphene oxides using different reductants and conditions systematically varying the chemical and physical structure, surface topography and chemistry and film thickness of reduced graphene oxide (rGO) films, with a focus on how these influence the property of most interest: electrical conductivity. The reduction process restores graphene oxide to a graphene-like structure, improving electrical conductivity while creating changes such as increased roughness, film thickness and new surface functionality. Films with smooth surfaces and minimal thicknesses have been shown to possess higher electrical conductivity. There have been minor changes in d-spacing and improvements in crystal perfection and orientation could be concluded from XRD patterns. Through XPS analysis, a significant decrease in the amount of oxygen functional groups at the surface has been noticed as the films get thinned. Copyright © 2016 VBRI Press.

Keywords: Reduced graphene oxide; flexible films; electronic structure; chromatic confocal imaging; electrical conductivity.

Introduction

Graphene is an exciting material being widely investigated today [1, 2] for its potential applications in a wide range of areas such as flexible electronic devices, catalysis, sensors and energy conversion and storage [3]. A major reason that graphene research has progressed fast, compared to other areas, is that the laboratory procedures enabling us to obtain high-quality graphene are relatively simple and cheap [3]. Electrical conductivity is important in the applications of nano-electronics, such as super-capacitors, transparent conductors, sensors, storage cells, and actuators [4, 5]. In addition, it has been demonstrated that chemically modified graphene, and its derivatives can be reinforced in a polymeric or inorganic matrix with better dispersion to make electrically conducting composites that have many potential practical applications [6].

In this study, detailed comparisons of physical structure, chemical composition, specific surface area, d-spacing phenomenon and surface characteristics of different reduced graphene oxide (rGO) materials together with graphite, graphene oxide (GO) and graphene as reference materials are provided. The above results are analysed with reference to their effects on the electrical conductivity of the rGO films. XRD is used to analyse structural changes, especially d-spacing variations in rGO layers at different reduction conditions. Scanning electron microscopy (SEM) has been used to characterise the changes in microstructure of rGO [6].

Characterisation of graphene derivatives by Raman spectroscopy and X-ray diffraction demonstrate the chemical reduction mechanisms at different reduction conditions. Moreover, the difference in the quality of rGO films has been established by using Raman spectroscopy [7].

Understanding the surface topography of films of graphene oxide (GO) and its analogues helps to identify their influence on electrical and physio-chemical properties. In particular, film thickness, roughness, and functionality (such as OH and COOH groups) influence electrical conductivity, one of the most interesting properties for use in practical applications. This would provide the relationship and interpretation of how electrical conductivity (σ , S/cm) changes due to the various combinations of surface roughness and thickness of graphene oxide (GO) and reduced graphene oxide (rGO) films.

Thickness dependency of the electrical conductivity of lanthanum strontium ferrite ((La, Sr)FeO₃) films [8] showed that the total apparent conductivity of the thin layer was found to increase with increased film thickness in a certain range, which further encouraged us to carry out this study. For this analysis, the GO and rGO films were mechanically exfoliated using adhesive tape. X-ray photoelectron spectroscopy was carried out to quantify the elemental composition, providing further information on how electrical conductivity was affected by this property.

X-ray photoelectron spectroscopy has been used for elemental analysis of rGOs.

The main objective of this study is to understand the influence of various factors on the electrical properties of graphene derivatives. This paper identifies these factors and helps in understanding their interactions which allow the production of rGO that has both high conductivity and can be produced in realistic volumes for use in practical devices.

Experimental

Materials details

Graphite flakes and hydroiodic acid (HI), sodium borohydride (NaBH_4) were purchased from Sigma-Aldrich, New Zealand with hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) being supplied by Macron Chemicals, USA. Potassium permanganate (KMnO_4) and hydrogen peroxide (H_2O_2) were obtained from J. T. Baker, Netherlands and ECP Chemicals, New Zealand, respectively. Hydrobromic acid (HBr) was bought from Scharlau, Spain. All these chemicals are of analytical reagents grade. Dextrose was bought from TREC nutrition (Pharmaceutical grade). Graphene was purchased from Emfutur, Spain.

Synthesis and reduction of graphene oxide

GO was synthesised via a modified Hummers and Offenman's method [11] using H_2SO_4 , NaNO_3 , and KMnO_4 . Typically, the oxidation process took 2 hours for adding all the chemical components, and the final mixture was left overnight for overall completion. Adding water and subsequent addition of hydrogen peroxide (H_2O_2) made the manganese salts soluble and the yellowish intermediate graphite oxide formed was purified by washing. The suspension from the synthesis was then ultrasonicated and dried to form films on a petri-dish in an oven, maintained at 50 °C for reduction. The films need to be removed carefully to avoid cracks and physical hole. This chemical synthesis gave GO, which was further treated with reducing agents to remove oxygen functional groups. These groups lower the conductivity of GO as they disrupt the delocalization of the pi-system with their electron withdrawing properties since they break the extended aromaticity of the graphite/graphene sheet and the removal of these functional groups was necessary. The GO films obtained by drying out the suspension in a petridish were reduced by HBr, N_2H_4 , HI, NaBH_4 and dextrose for up to 72 hours. Graphene purchased from the commercial market has been used as reference material to compare with the rGOs. The molar populations of these and the level of the desired reduction determine the amount of reductant that needs to be used. It has been suggested in the literature that 150 mmol is needed to reduce the groups present in 420 mmol (0.42 mol) of GO to a large extent [6].

Mechanical exfoliation

The thickness of each selected GO/ rGO film was carefully measured with a digital point micrometer. Then the films were exfoliated mechanically by using an adhesive tape (Ladedah Washi brand) placed on both sides of the film and slowly peeling off both ends of the tape. This procedure

was repeated until the smallest possible thickness of a film was achieved.

Characterization of graphene derivatives

Raman spectroscopy of rGO films was obtained using a Renishaw System. The samples were analysed in back scattered mode on the stage of a Leica microscope with a 20x magnification. The gratings groove density was 2400 mm^{-1} with 4 cm^{-1} resolution. A holographic notch filter (HNF) was configured for removal of Rayleigh scattered light. The Raman excitation radiation was detected using 488 nm line of an air-cooled Argon ion laser operating at 30 mW. The removal of spikes of cosmic rays and a manual multi-point baseline correction (for fluorescence background subtraction) were used.

X-ray diffraction analyses were performed on rGO powders in P2 Phaser Bruker with XFlash silicon drift detector Kindat the elemental range and energy resolution of K to Hf (~ 3 to 20 keV) and <180 eV (Cu $K\alpha$) at 100,000 CPS.

Brunauer-Emmett-Teller (BET) specific surface area measurements were carried out in an 'Autosorb-1 Quanta-chrome der Firma', USA in a volumetric working device an under nitrogen gas adsorption-desorption isotherms at 77 K. The samples were dried at 80 °C for 36 hours before the measurement.

X-ray photoelectron spectroscopy (XPS) elemental analysis of rGO samples was carried out using X-ray photoelectron spectroscopy. The instrument was an ESCALAB 220i (Vacuum Generator, UK) spectrometer, equipped with two X-ray sources for monochromatic Al K-alpha and non-monochromatic Mg K-alpha X-ray irradiation and a He capillary discharge light source. Photoelectron spectrometer AXIS ULTRA (Kratos Analytical, UK) was equipped with an X-ray source for non-monochromatic Mg K-alpha X-ray irradiation and monochromised X-ray sources for Al K-alpha and Ag L alpha X-ray irradiation. The take-off angle of the photoelectrons was 90°. High-resolution spectra of the Ce 3d, O 1s, C 1s, N 1s and Li 1s core level regions were recorded with pass energy of 20 eV and for wide scan measurement (energy range 1100-0 eV), 160 eV was used. The data processing (peak fitting) was performed using CasaXPS software. The binding energies were corrected by setting the C 1s hydrocarbon ($-\text{CH}_2-\text{CH}_2-$ bonds) peak at 285.0 eV for the samples.

Scanning electron microscopy (SEM) was carried out with Philips XL30S FEG (Field Emission Gun), the Netherlands, equipped with EDS Detector (Si-Li drifted) with a super ultra-thin window). The sputter coater used for standard SEM samples was a Quorum Q150RS sputter coater. It is designed to give a very thin, minimal metal coating suitable for SEM viewing and the normal target used was Pt or Au.

Electrical conductivity values of graphene derivatives were measured by the four-probe method, also known as four-terminal sensing or 4T sensing [9].

Characterization of GO and rGO films

Chromatic confocal imaging was carried out with MicroGlider® 600 instrument (FRT, Germany) with a

measuring range of 600×600 mm in the “xy” directions and $600 \mu\text{m}$ on the “z” direction. The roughness/flatness can be measured with a resolution of $2 \mu\text{m}$ in the lateral and 6 nm on the vertical directions. The maximum speed of the measuring head was 300 mm/s with a load capacity of 40 kg [10].

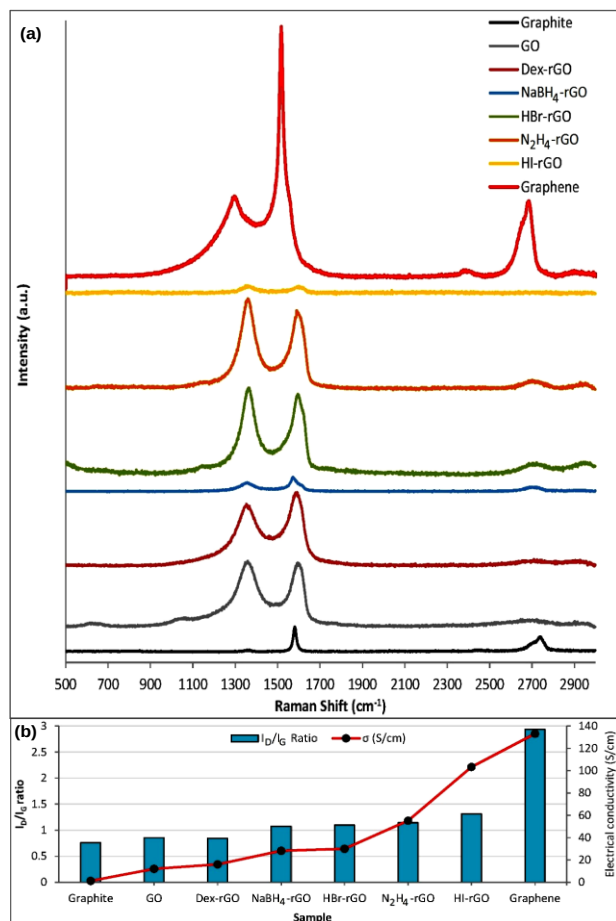


Fig. 1. (a) Raman spectra of graphene derivatives, (b) I_D/I_G ratio.

Results and discussion

Raman spectroscopy

The intensity ratios of the D and G peaks have been used as the metrics of disorders in graphene, such as edges, charged impurities and the presence of domain boundaries [5]. For edges, the intensity of the D peak depends on the edge structure; it is weak at the zigzag edge and strong at the armchair edge, and the 1580 cm^{-1} band of graphite is known as the G band [12]. From the literature [12], it has been noted that highly ordered graphite has only a few Raman-active bands visible in the spectra (Fig. 1a), the (weak) disorder band caused by the graphite edges called D band at approximately 1355 cm^{-1} as well as the in-phase vibration of the graphite lattice called G band at 1575 cm^{-1} as found for our samples (1350 cm^{-1} and 1580 cm^{-1}).

From the Raman spectrum in Fig. 1a, GO to rGOs structural transformation shows topological defects (Stone-Wales defects). Along the graphite-GO-rGOs route, the Raman spectra undergo vast changes that are similar to those observed in the graphite to amorphous carbon transition [6]. Specifically, D and G bands of rGOs reduced

at 72 hours broaden and shorten significantly and display a shift to higher frequencies with growing in intensity. In our spectrum of GO, both D and G bands shift to higher frequencies during graphite amorphisation. The rGOs from different reduction period as well as the different reducing agent exhibit same scenario of gradual decrease of the intensity ratio of D and G bands (I_D/I_G ratio). The increase in reduction time and the nature of reducing agents have distinct effects on I_D/I_G [13]. When comparing closely with this I_D/I_G behaviour and electrical conductivities obtained from these rGOs show that shorter and broader the D and G bands, higher the electrical conductivity.

From our Raman spectra, the defect induced (weak) disorder band caused by the graphite edges [12], are referred to as D and G peaks and can be found at around 1340 cm^{-1} and 1580 cm^{-1} , respectively [7] (assignment of peak positions to functional groups were referred from Mohan *et al.* [6]). The different intensity ratios of D and G bands of rGOs are different at different reducing conditions as the extent of reduction gives varying populations of oxygen containing functionalities and graphene sheet defects, such as interruptions in aromaticity/ π -bonding. The peculiar dispersion of the π electrons in graphene derivatives is the fundamental reason why Raman spectroscopy in carbons is always resonant and, thus, a powerful and efficient probe of their electronic properties [14]. The changes apparent from comparing our graphite, GO, and rGO samples show the variation in functionalisation caused by using different reducing agents. The variation of the relative intensities of G (an analogous vibration mode of sp^2 carbon atoms or graphitic carbon) and D (vibrational mode for disordered carbon) bands in the Raman spectra of the GO during the reduction reveals the change degree of the conjugation [15].

Higher disorder in graphite leads to a broadening of the G and D bands and an increase in the relative intensity of the D band by comparison to the G band [16, 17]. Based on this argument, and the observed narrower D and G bands, HI-rGO has a more ordered and regular structure. Based on the proposed mechanisms for conductivity [17], it would be expected that HI-rGO will have higher conductivity than those of the samples produced using HBr and N_2H_4 . Moreover, highly ordered graphite has few couple of Raman-active bands visible in the spectra: the in-phase vibration of the graphite lattice (G band) at 1575 cm^{-1} as well as the (weak) disorder band caused by the graphite edges (D band) at approximately 1355 cm^{-1} [6].

The main differences among Dex/ NaBH_4 /HBr/ N_2H_4 /HI-rGOs are that the shift between 950 and 1250 cm^{-1} is much smaller for HI-rGO than those for HBr-rGO and N_2H_4 -rGO. The signal at 1050 cm^{-1} is believed to arise from single C-C vibrational modes and is, therefore, in HI-rGO higher in intensity compared to the intensities found for Dex/ NaBH_4 /HBr/ N_2H_4 -rGOs [7]. The rGOs from different reduction period as well as the different reducing agent exhibit same scenario of gradual decrease of the intensity ratio of D and G bands (I_D/I_G ratio). Firstly, the I_D/I_G gradually increased as reduction “reorders” the system [13]. Fig. 1a presents Raman spectra of all the graphene derivatives.

From Fig. 1b shows the absolute values of I_D/I_G ratio of all the rGOs comparing with electrical conductivity and the

values for graphite and GO are 0.76 and 0.86 respectively. The ratio of I_D/I_G provides a measure of the degree of disorder and crystallite size of the graphitic materials. It can also be noticed that I_D/I_G of all rGOs increases from 0.2 to 0.3 over graphite. This happens due to the increasing amounts of new graphitic crystallites formed because of the restoration of the p-conjugated system when the oxygen-containing functional groups are reduced/removed [18].

When comparing the I_D/I_G behaviour and electrical conductivities obtained from these rGOs we can see that the shorter and broader the D and G bands are, the higher the electrical conductivity is. When compared to the I_D/I_G ratio of GO and rGO (graphene oxide reduced by Lawesson's reagent) prepared by Liu *et al.* [18] the behaviour of increasing I_D/I_G ratio is similar after reduction with the difference being in the absolute values, rather than the relative shift. The rGO from their work reaches a higher electrical conductivity, compared with other rGOs prepared by them. This further supports the argument of higher I_D/I_G ratio correlating with higher electrical conductivity. As in our work, HI-rGO has the highest electrical conductivity with highest I_D/I_G ratio.

From the above discussion, Raman spectroscopy can be used to measure the 'quality' [19] of graphene layers by the shape, width, and position of the D peak. In Fig. 1b changes in Raman peak intensities have been compared with peak positions, corresponding to different physical structures of the various rGO samples. Qualitatively, the positions and intensities of all samples would indicate inter-defect distances of around 1 nm in the samples (supplementary data provided in [7]). This suggests that for HI-rGO, there may be clusters of defects but with smaller overall populations compared to the other two samples. This should result in HI-rGO having a higher conductivity than N_2H_4 -rGO and HBr-rGO.

X-ray diffraction (XRD)

The initial oxidation of graphite causes the functionalisation of the individual sheet surfaces, preventing the carbon sheets from remaining close to each other and resulting in a measurable increase in d-spacing for GO over graphite. Subsequent reduction removes many of these oxygen-containing functional groups that are repulsing the GO layers and lets the sheets stack closer due to partially obstructed π -stacking [20]. This gives rGO an approximate structure of graphene, with corresponding physical and electronic properties and facilitates electron motion through the sheet and increases electrical conductivity [21].

XRD patterns of rGOs are shown in Fig. 2a together with those of GO and graphite. The XRD pattern of HI-rGO exhibits much smaller peaks indicating a higher level of reduction than those of Dex/NaBH₄/HBr/ N_2H_4 -rGOs. Standard diffraction peak for graphite occurs at $2\theta=26.5$ with a corresponding d-spacing of 3.36 Å. The peak positions for HBr, N_2H_4 , and HI-rGOs decrease with reduction process. The diffraction line for HI-rGO occurs at a smaller 2θ value of 24.03°, corresponding to a larger d-spacing of 3.70 Å compared to other rGOs. Supporting Ruoff's [23] observations, the quality of HI-rGO films are found to be better even when d-spacing is relatively higher

than those of Dex/NaBH₄/HBr/ N_2H_4 -rGOs at different reduction periods examined (shown in Fig. 2b), and this also demonstrates that d-spacing has less influence on electrical conductivity in these experiments. It is likely that high defect rates in N_2H_4 -rGO and HBr-rGO are obscuring d-spacing effects. From XRD graphs, it can be seen that the interlayer spacing for all HI-rGOs increases with increasing reduction time and increasing concentrations of different reducing agents. This increase in d-spacing is due to the intercalation of water molecules and generation of oxygen functionality in the interlayer spacing of graphite [20].

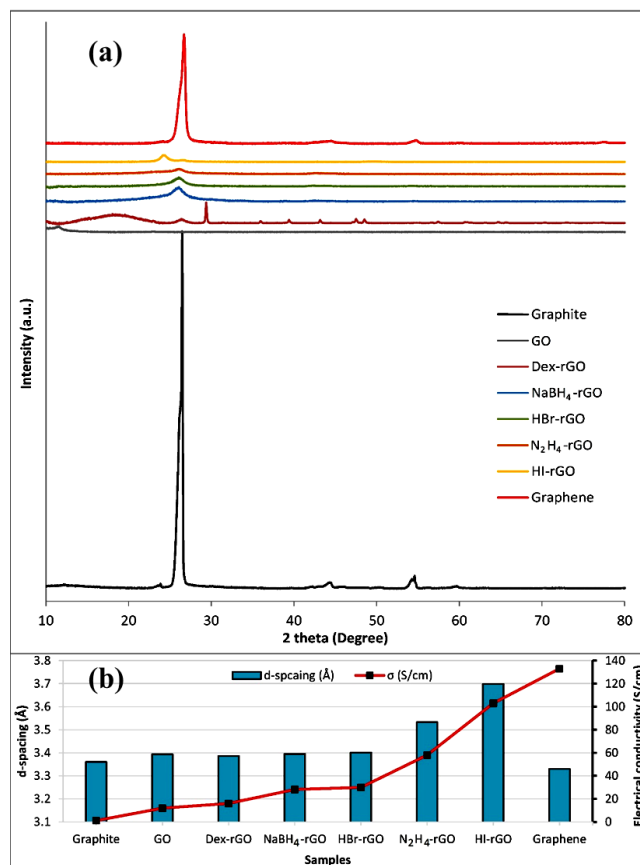


Fig. 2. (a) XRD patterns of GO, (b) d-spacing vs. σ .

It is proposed that this happens due to the weaker interaction of water with HI-rGO than with the other two samples, as it has a higher degree of reduction and, therefore, lower number of oxygen functionalities (which would bind more strongly to H₂O). It is also possible that the slightly larger d-spacing in HI-rGO allows more H₂O molecules to pack between sheet edges or possibly even between sheets, as these are not perfectly aligned [22–24]. The weaker rGO-H₂O interaction and the higher d-spacing of the HI-rGO sample, compared to the other samples, indicate that HI-rGO contains fewer oxygen functionalities. It is, therefore, more completely reduced, and so it would be expected that the conductivity of HI-rGO will be higher than those of Dex/NaBH₄/HBr/ N_2H_4 -rGOs, ignoring other factors. It would be assumed that N_2H_4 -rGO, NaBH₄-rGO, and HBr-rGOs, with d-spacing closer to graphite than to HI-rGO, would have similar problems with electron transfer and therefore low conductivity. Likewise, increases

in d-spacing during the reduction process would indicate increasingly complete restoration of the sheet structure and increasing conductivity. This is also observed for N_2H_4 -rGO and HI-rGO but not HBr-rGO, Dex-rGO and NaBH_4 -rGO. However, d-spacing of rGO sheets is not entirely responsible for electrical conductivity.

Specific surface area analysis (SSA)

BET specific surface area (SSA) can be used to evaluate the similarity of the bulk structure of rGO samples and pure graphene. **Fig. 3a** compares SSA and electrical conductivity, and **Fig. 3b** shows a clear correlation between SSA and d-spacing of graphene derivatives. However, discrepancies arise due to defects in rGO, especially physical holes causing “bends” in extended pi-systems/sheets. This accounts for why d-spacing and SSA does not correlate when graphene (**Fig. 3c**) is included in the comparison: holes distort local sheet structure from planar and give a larger-than-expected d-spacing for reduced graphene oxides.

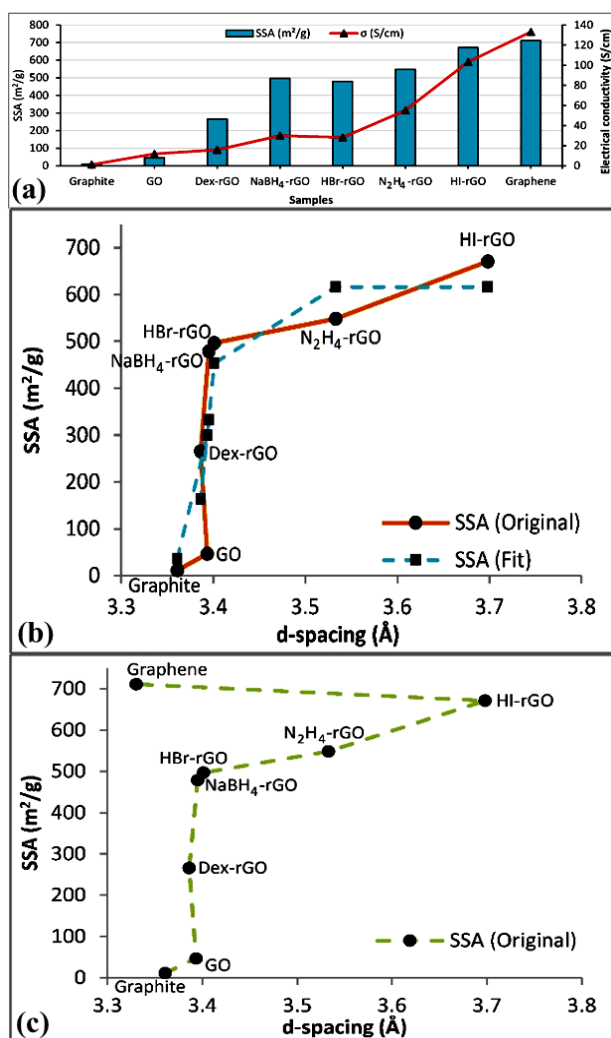


Fig. 3. (a) Specific surface area vs. σ , (b) correlation in SSA vs. d-spacing in the absence of graphene with sigmoid fitting, (c) absence of correlation in SSA vs. d-spacing in the presence of graphene.

Plotting the SSA vs. the d-spacing for the rGO and graphene samples gives a growth curve with an asymptote

around $670 \text{ m}^2/\text{g}$, close to that of pure graphene ($712 \text{ m}^2/\text{g}$). As the inter-sheet distances increase the available surface area also increases, suggesting incremental exfoliation of the samples rather than a sudden change in total sample structure from graphite-like to graphene-like. Conductivity follows a very similar trend, demonstrating that bulk properties, as measured by SSA and electrical conductivity, arise from microscopic properties (sheet distances, local defects, sheet microstructure).

The simultaneous exfoliation and reduction of graphene oxide by rapid chemical reduction and functionalisation gives increases in electrical conductivity. These high SSAs have been attained followed modification by reduction and chemical functionalisation. This work suggests a number of further research pathways for energy storage in particular, such as adjusting d-spacing to optimise gas-storage properties of rGO, tailoring inter-sheet distances for improving materials for use in batteries or minimising costs of conducting composites.

Sigmoid curve fitting **Fig. 3b** was done on the assumption that the SSA would gradually and incrementally increase as the inter-sheet distance increased from an underlying base of no available surface area (graphite) with growth and saturation occurring when the rGO structure reached that of graphene. To this end a sigmoid curve was modified as follows:

$$f(t) = g_0 + \frac{k_g}{(1 + e^{-\Delta g(t-t_i)})}$$

where, ' g_0 ' is the baseline, ' Δg ' is the amount of growth, ' t_i ' is the inflection point and ' k_g ' is the rate of growth.

X-ray photoelectron spectroscopy (XPS)

The C1s peak at 287.7 eV decreased in intensity following hydro-bromic reduction, with subsequent further decreases for hydrazine reduction and hydriodic reduction. The O 1s peak at 532.8 eV is observed for all the rGO samples, indicating that from the changes in % O, we see the significant removal of oxygen from the rGO samples after reduction by the various reagents. These changes represent the reduction of groups such as C O and CO_2H back to alcohols [17] and subsequent further removal of most of the oxygen to give graphene-like structures (especially for HI) [25].

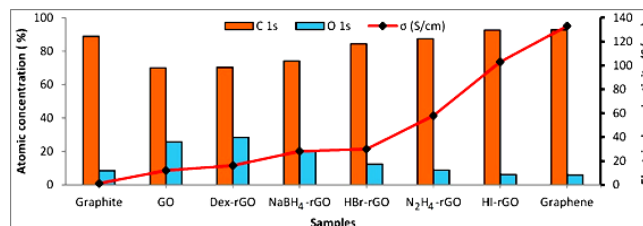


Fig. 4. Atomic concentration vs. σ .

After the HI reduction, this peak nearly disappears. The decrease of this peak indicates loss of oxygen and possibly carbon. The O 1s/C 1s ratio obtained from the XPS study (**Fig. 4**) is highly dependent on reducing agents, which also indicates a partial reduction of the graphene oxide;

however, HI reduction is efficient compared to the other two.

The peaks corresponding to those oxygen functional groups in the spectrum of rGO around 532 eV were significantly lowered by the hydroiodic reduction than those of N_2H_4 and HBr-rGOs. The elemental analysis and XPS spectra suggest that the degree of reduction of rGOs is lower in N_2H_4 and HBr-rGOs compared to that in HI-rGO.

Film roughness-thickness vs. electrical conductivity

GO, HBr-rGO, and HI-rGO films were considered for this part of the study as they possess considerably different surface roughness and electrical conductivities.

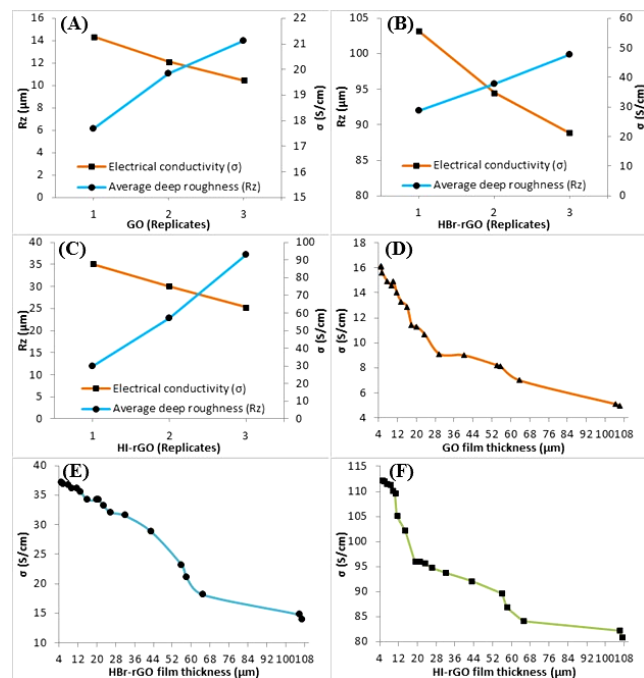


Fig. 5. (A, B & C) Electrical conductivity vs. average deep roughness and (D, E & F) thicknesses.

Roughness vs. σ

A perfect graphene sample would consist of macro-scale defect-free sheets of graphene arranged in totally parallel layers, which are in perfect contact and free of defects. The surface of the graphene film would be atomically smooth and exhibit no roughness or irregularities above this scale. Deviations from this level of perfection can be determined from the surface roughness of the sample. Roughness would arise from imperfections such as physical holes (removal of C from the sheet), un-reduced oxygen-containing groups (incomplete reduction) and irregular distribution of sheet/particle sizes caused by the oxidation and reduction processes.

Larger-scale distortions of the rGO sheets (crenulation) would be due to the irregular packing of rGO sheets, defects causing “bending” and interactions between the sheets caused by un-reduced oxygen containing groups. Increasingly “rough” samples should, therefore, be increasingly poor facsimiles of pure graphene, with correspondingly poor electrical properties compared to

pure graphene. Based on these arguments we propose that the conductivity of samples should correlate with surface roughness, which in turn will also be related to the reduction process used.

Roughness data are obtained from the confocal imaging for three films (GO, HBr-rGO, and HI-rGO). In those experiments, the roughness values are averaged laterally over typically 2 μm while height resolution is 6 nm. For comparative analysis, both sides of the films were examined, and the experiments were triplicated. The surface of the sample (which faces the atmosphere during drying of GO suspension) should be rougher than that of the bottom surface, and this is observed for the samples examined.

The parameters provided are averaged over the height profile: R_a (arithmetic average), R_q (root mean square of roughness), R_k (roughness core area) and R_{lr} (profile length ratio). The roughness increases significantly after the reduction process but also varies with the nature of the reducing agent. Significant differences in the roughness values of GO, HBr-rGO to HI-rGO films have been detected which is highly related to the reduction completeness with HBr and HI. The HBr reduction is particularly severe, and the surfaces of these films are rougher than those of HI reduced samples.

Similar behavior has been found in electrical conductivity measurements. For this analysis single side (top side of the film) data have been used, since the behaviour for both sides was the same. The correlation coefficients for the linear fits are 0.99 in all the cases, meaning that roughness has a clear correlation with conductivity as samples with higher surface roughness have a lower conductivity.

Different sides of one sample show differences in roughness, but the change in surface roughness values before and after the reduction process are very similar. The top side of a GO film is identified as the smoothest surface while the surfaces of the HBr-rGO films show the highest roughness. These structural parameters are determined by the structure of the surface such as size, the geometry of flakes, irregularities, waviness, and orientation. High surface roughness indicates that the samples may possess increased holes and defects which may cause reduced electrical contact between flakes and may influence the reduction of oxygen functional groups resulting in decreased electrical conductivity. **Fig. 5** shows conductivity vs. average deep roughness (A, B & C) for GO, HBr-rGO, and HI-rGO films.

Surface roughness can also cause an increase the hydrophobicity of the materials which then influences the wetting properties of reducing agents and in this way can lower the rate of reduction. Comparatively, HBr-rGO films possess higher surface roughness and lower conductivity than HI-rGO. The electrical conductivity values of GO and rGO samples have been compared with “average deep roughness (R_z)” of the respective samples in order to understand their influence on the conductivity which is shown in **Fig. 6** (A, B & C). Therefore, surface roughness and conductivity are linked, due to the fact that surface roughness is a result of a defective surface. Due to functionalisation, electron traps are in the bulk, and there is a loss of delocalisation in general. These factors lower the

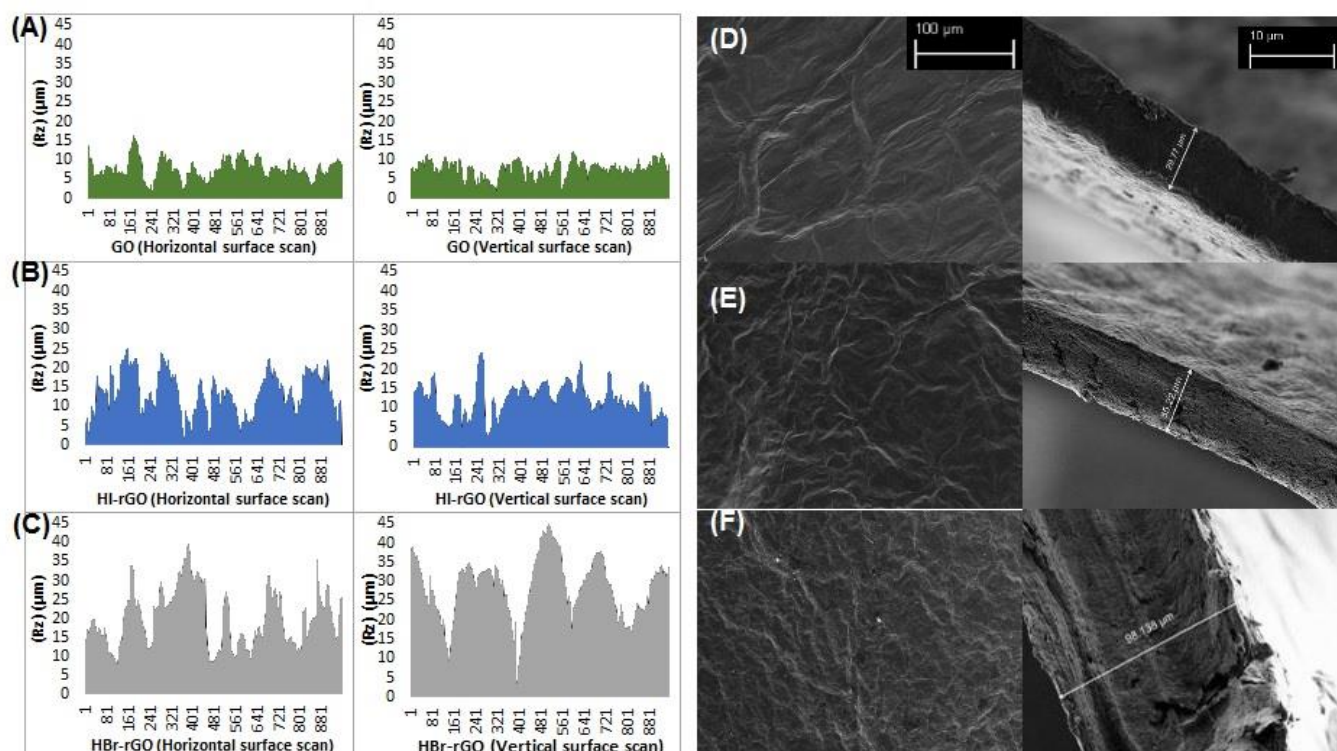


Fig. 6. Microglider Rz data (A, B & C) and SEM images (D, E & F) of GO, HI-rGO, and HBr-rGO (Surface and thickness)

conductivity by reducing the free path length of electrons or by trapping the electrons at functional sites.

Correlation coefficients for the linear fits are around 0.99 in all cases, meaning roughness and conductivity are strongly correlated. This supports the hypothesis proposed earlier: increasing surface roughness in rGO is symptomatic of increasing deviation from pure graphene properties. This roughness is due to different effects including chemical functionalisation of graphene flakes, which produce electron traps in the bulk sheets, reduce electrical contact between different flakes and cause a general loss of delocalisation of the extended pi-system. These factors then lower the conductivity.

Thickness vs. σ

It has been identified that after reduction process the thickness of films increases. Comparatively, reduction using HBr, instead of HI, makes the films much thicker due to the greater incorporation of oxygen and carbonyl functional groups. This can be visualised from SEM images shown in **Fig. 6**. In addition, the surface is heavily corrugated with HBr-rGO films, indicative of a less extended π -system, which leads to a lower level of electrical conductivity.

It can be observed that GO shows the smallest thickness while it increases with HI and HBr-rGOs. However, HBr-rGO shows lots of cracks and pores in the walls as well as on the surface with the highest thickness amongst all the films examined which signifies that the particular reduction process produces a lot of damages between the layers of the film. From **Fig. 5 (D, E & F)**, it is evident that the conductivity is increasing as thickness decreases.

From the aforementioned discussion, it is clear that an increasing film thickness results in decreasing conductivity, possibly because films are more porous, and the graphene layers have greater numbers of oxygen functional groups. It could also be attributed to the fact that the mechanical action of exfoliation aligns the stacking flakes more uniformly, giving a longer path length for electron flow. It is also likely that there could be the removal of more functional groups close to the film surface during exfoliation which could increase the conductivity of thinner films as well. It can be observed in all the films that there is a considerable jump in the conductivity on the removal of the first rough surface layer to further exfoliation. This clearly indicates that there is a correlation between the surface roughness and bulk thickness on the film's electrical conductivity.

Surface elements on exfoliated GO/rGO films of different thickness

The amount of oxygen present in the rGO samples has been analysed using XPS of samples of 5, 40 and 100 μm thickness. It should be mentioned that XPS is sensitive for a surface layer of only typically 7 nm, which means that in the samples used only the surface composition is probed by this technique. The C 1s peak at 287.7 eV decreases in intensity following hydrobromic reduction, with a subsequent further decrease for hydroiodic reduction. An O 1s peak at 532.8 eV is observed for all the rGO samples but with significant differences in intensity, showing that mechanical peeling results in the removal of oxygen from the rGO samples. The differences between GO and rGO samples are also due to varying effects of reduction on groups such as C=O and CO₂H [17, 25].

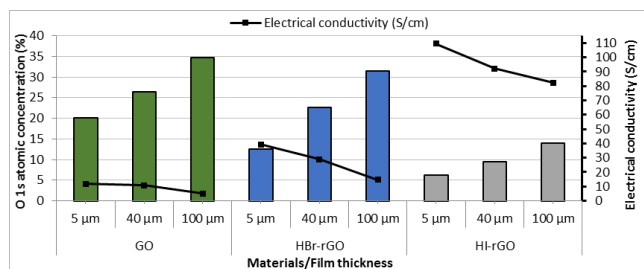


Fig. 7. Film thickness vs. electrical conductivity with respect to oxygen concentration.

The O 1s/C 1s ratio obtained from the XPS study is highly dependent on reducing agents, which also indicates a partial reduction of the graphene oxide only; however, with the thickness of the films also the oxygen concentration varies which can be noticed from **Fig. 7**. There it is compared the atomic concentration C 1s and O 1s of GO, HBr-rGO and HI-rGO films of 5, 40 and 100 μm thickness values which also shows that surface oxygen functional groups are less as a film becomes thinner and vice versa with carbon functional groups. The peaks corresponding to those oxygen functional groups in the spectrum of rGO around 532 eV were significantly lowered by the hydroiodic reduction compared to by HBr-rGO. Assuming that this result also holds for the entire film, one can correlate this finding with conductivity. **Fig. 7** compares the electrical conductivity of the films with respect to thickness and oxygen concentration, which shows that conductivity increases with both thickness and oxygen concentration decreasing. This analysis also suggests that the degree of reduction is lower in HBr-rGO compared to that in HI-rGO [6].

Considering the entire data set and individual GO/rGO sample data sets it can be seen that as samples are exfoliated (made thinner), the proportion of oxygen in the remaining film consistently decreases. At the same time, the d-spacing decreases and the conductivity increases. As discussed before this increase in conductivity can be related to decreasing defect density and better contact between flakes with decreasing oxygen content.

These observations describe a process of the preferential removal of highly-oxidised GO and rGO nano-particles over their less-oxidised counterparts. This results in increasingly large proportions of graphene-like nano-particles with correspondingly higher conductivity. Intriguingly this suggests a way forward to develop a simple technique that can be used for large-scale “purification” of low-cost, low-quality rGO films/tapes to make higher quality rGO films/tapes.

Conclusion

Raman spectra and XRD results demonstrate that the HI reduction method gives highly orientated two-dimensional graphene-like layers with a uniform chemical structure that allows comparatively unimpeded movement of electrons. The closeness of this structure to that of graphene explains the higher electrical conductivity values of the HI-rGO films compared to rGO films obtained by other methods. The results of this study show simple methods for reducing

GO result in an improved electrical conductivity of rGO films due to the high completeness of reduction and back-reaction to a graphene-like structure. Electrical conductivity is dependent on the reducing agent, reduction time and to the amount of oxygen functional groups (and hence reduction efficiency) and not solely to d-spacing, which is often used as a de-facto measure of “closeness to graphene”.

From non-contact chromatic confocal imaging study, it has been found that in both GO and rGO, the influence of surface topography on electrical conductivity is similar: the rougher the surface, the lower the conductivity. The MicroGlider operation allows comparison of the surface before and after its topographic and chemical modification (reduction). Film thicknesses also have a major impact on the electrical conductivity with thinner films having higher conductivity. XRD studies have been carried on the films of 5, 40 and 100 μm thicknesses and show that the crystal perfection, crystallinity and possibly orientation of crystals of the films improve as they get thinner. XPS studies reveal that amount of oxygen present in thinner films made from exfoliation of thicker films is less which likely leads to higher conductivity. The differences that arise in electrical conductivity due to structural and chemical changes is very high. The key finding of the influence of roughness and thickness has been clearly verified. These results demonstrate how complex interaction between different chemical and physical mechanics affects conductivity and, for practical use, shows that reduced graphene oxide materials can have electrical properties “tuned” by reduction reagents, conditions, and mechanical post-processing.

Future research will focus on the possible applications of these materials in graphene/polymer composites for mechanical applications with the potential for in-situ testing and use as sensors. Further work is being carried out to optimise mechanisms for processing and production parameters to obtain graphene materials in bulk.

Acknowledgements

The authors would like to thank the Ministry of Business, Innovation, and Employment, New Zealand for the financial support under the Sustainable Composites research grant. The first author is grateful to German Academic Exchange Service (DAAD) for a fellowship. Both first and last authors are thankful to IPF for support. The authors are grateful to Dr. Reuben Brown for assistance in interpretation.

Authors contributions

Conceived the plan: VBM, DB, MS; Performed the experiments: VBM, DL; Data analysis: VBM, KJ, DB, DS; Wrote the paper: VBM, KJ, DB, DL, MS. Authors have no competing financial interests.

Reference

- Geim, AK.; Novoselov, KS.; *Nat. Mater.*, **2007**, 6, 183.
DOI: [10.1038/nmat1849](https://doi.org/10.1038/nmat1849)
- Rao, C. ; Biswas, K.; Subrahmanyam, K.; Govindaraj, A; *J. Mater. Chem.*, **2009**, 19, 2457.
DOI: [10.1039/B815239J](https://doi.org/10.1039/B815239J)
- Novoselov, KS.; Falko, VI.; Colombo, L.; Gellert, PR.; Schwab, MG.; Kim, K; *Nature*, **2012**, 490,192.
DOI: [10.1038/nature11458](https://doi.org/10.1038/nature11458)
- Becerril, HA.; Mao, J.; Liu, Z. ; Stoltenberg, RM.; Bao, Z. ; Chen Y; *ACS Nano*, **2008**, 2, 463.
DOI: [10.1021/nn700375n](https://doi.org/10.1021/nn700375n)

5. Zhu, Y.; Murali, S.; Cai, W.; Li, X.; Suk, J. W.; Potts, JR.; Ruoff, RS., *Adv. Mater.* **2010**, 22, 3906.
DOI: [10.1002/adma.201001068](https://doi.org/10.1002/adma.201001068)
6. Mohan, VB.; Brown, R.; Jayaraman, K.; Bhattacharyya, D; *Mater. Sci. Eng., B*, **2015**, 193, 49.
DOI: [10.1016/j.mseb.2014.11.002](https://doi.org/10.1016/j.mseb.2014.11.002)
7. Eigler, S.; Enzelberger-Heim, S.; Grimm, S.; Hofmann, P.; Kroener, W.; Geworski, A.; Dotzer, C.; Röckert, M.; Xiao, J.; Papp, C.; Lytken, O.; Steinrück, HP.; Müller, P.; Hirsch, A; *Adv. Mater.*, **2013**, 25, 3583.
DOI: [10.1002/adma.201300155](https://doi.org/10.1002/adma.201300155)
8. Mosleh, M.; Pryds, N.; Hendriksen, PV; *Mater. Sci. Eng., B*, 2007, 144, 38.[9]
DOI: [10.1016/j.mseb.2007.07.089](https://doi.org/10.1016/j.mseb.2007.07.089)
9. Montgomery, H; *J. Appl. Phys.* **1971**, 42, 2971.
DOI: [10.1063/1.1660656](https://doi.org/10.1063/1.1660656)
10. FRTG FRT, Bergisch-Gladbach, Germany.
(www.frt-gmbh.com/en/microglider-600.aspx- Assessed on 01.03.2015)
11. Hummers, WS.; Offeman RE; *J. Am. Chem. Soc.*, 1958, 80, 1339.
DOI: [10.1021/ja01539a017](https://doi.org/10.1021/ja01539a017)
12. Hummers, WS.; Offeman R E. *J. Am. Chem. Soc.*, **1958**, 80, 1339.
DOI: [10.1021/ja01539a017](https://doi.org/10.1021/ja01539a017)
13. Kudin, KN.; Ozbas, B.; Schniepp, HC.; Prud'homme, RK.; Aksay, IA.; Car, R; *Nano Lett.*, **2007**, 8, 36.
DOI: [10.1021/nl071822y](https://doi.org/10.1021/nl071822y)
14. Diez-Betriu, X.; Alvarez-Garcia, S.; Botas, C.; Alvarez, P.; Sanchez-Marcos, J.; Prieto, C.; Menendez, R.; de Andres, A; *J. Mater. Chem. C*, **2013**, 1, 6905.
DOI: [10.1039/c3tc31124d](https://doi.org/10.1039/c3tc31124d)
15. Ferrari, AC; *Solid State Commun.*, **2007**, 143, 47.
DOI: [10.1016/j.ssc.2007.03.052](https://doi.org/10.1016/j.ssc.2007.03.052)
16. Z Zhang, J.; Yang, H.; Shen, G.; Cheng, P.; Zhang, J.; Guo, S; *Chem. Commun.*, **2010**, 46, 1112.
DOI: [10.1039/B917705A](https://doi.org/10.1039/B917705A)
17. Srivastava, I.; Mehta, RJ.; Yu, ZZ.; Schadler, L.; Koratkar, N; *Appl. Phys. Lett.*, **2011**, 98, 063102.
DOI: [10.1063/1.3552685](https://doi.org/10.1063/1.3552685)
18. Pei, S.; Zhao, J.; Du, J.; Ren, W.; Cheng, HM; *Carbon*, **2010**, 48, 4466.
DOI: [10.1016/j.carbon.2010.08.006](https://doi.org/10.1016/j.carbon.2010.08.006)
19. Liu, H.; Zhang, L.; Guo, Y.; Cheng, C.; Yang, L.; Jiang, L.; Yu, G.; Hu, W.; Liu, Y.; Zhu, D; *J. Mater. Chem. C*, **2013**, 1, 3104.
DOI: [10.1039/c3tc00067b](https://doi.org/10.1039/c3tc00067b)
20. Pimenta, MA.; Dresselhaus, G.; Dresselhaus, MS.; Cancado, LG.; Jorio, A.; Saito, R; *Phys. Chem. Chem. Phys.*, **2007**, 9, 1276.
DOI: [10.1039/b613962k](https://doi.org/10.1039/b613962k)
21. Kuila, T.; Bose, S.; Mishra, AK.; Khanra, P.; Kim, NH.; Lee JH; *Prog. Mater. Sci.*, **2012**, 57, 1061.
DOI: [10.1016/j.pmatsci.2012.03.002](https://doi.org/10.1016/j.pmatsci.2012.03.002)
22. Park, S.; An, J.; Potts, JR.; Velamakanni, A.; Murali, S.; Ruoff, RS; *Carbon*, **2011**, 49, 3019.
DOI: [10.1016/j.carbon.2011.02.071](https://doi.org/10.1016/j.carbon.2011.02.071)
23. Moon, IK.; Lee, J.; Ruoff, RS.; Lee, H; *Nat. Commun.*, **2010**, 1, 73.
DOI: [10.1038/ncomms1067](https://doi.org/10.1038/ncomms1067)
24. Stankovich, S.; Dikin, DA.; Piner, R. D.; Kohlhaas, KA.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, ST.; Ruoff, RS.; *Carbon*, **2007**, 45, 1558.
DOI: [10.1016/j.carbon.2007.02.034](https://doi.org/10.1016/j.carbon.2007.02.034)
25. Shen, J.; Hu, Y.; Shi, M.; Lu, X.; Qin, C.; Li, C.; Ye, M; *Chem. Mater.*, **2009**, 21, 3514.
DOI: [10.1021/cm901247t](https://doi.org/10.1021/cm901247t)
26. Yang, D.; Velamakanni, A.; Bozoklu, G.; Park, S.; Stoller, M.; Piner, RD.; Stankovich, S.; Jung, I.; Field, DA.; Ventrice Jr, CA.; Ruoff, RS; *Carbon*, **2009**, 47, 145.
DOI: [10.1016/j.carbon.2008.09.045](https://doi.org/10.1016/j.carbon.2008.09.045)



A Monthly Journal

Publish your article in this journal

Advanced Materials Letters is an official international journal of International Association of Advanced Materials (IAAM, www.iaamonline.org) published monthly by VBRI Press AB from Sweden. The journal is intended to provide high-quality peer-review articles in the fascinating field of materials science and technology particularly in the area of structure, synthesis and processing, characterisation, advanced-state properties and applications of materials. All published articles are indexed in various databases and are available download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review article, research article, notes, letter to editor and short communications.

Copyright © 2016 VBRI Press AB, Sweden

www.vbripress.com/aml