

CHARACTERISATION AND FUNCTIONAL PROPERTIES OF REDUCED GRAPHENE OXIDE AND ITS NANOCOMPOSITES

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Abstract

Graphene, a single layer consisting of hexagonally bonded carbon atoms is an attractive material because of its excellent electronic properties. Graphene and its derivatives can be used as functional reinforcements in polymers for applications, such as sensors, flexible devices, packaging, and functional nanocomposites. This article focuses on the modified synthesis method, reduction using hydrobromic (HBr), hydrazine hydrate (HH), hydroiodic acid (HI), sodium borahydride (SBH) and dextrose (Dex) and characterization using Raman spectroscopy and X-ray diffraction (XRD) of reduced graphene oxide in order to identify an electronic structure that possesses higher electrical conductivity. Conductivity measurements were made using four-probe method and thermo gravimetric analysis was carried out to identify the difference in weight percentage caused by different reducing agents as well reduction hours. Hydroiodic acid reduced graphene oxide (rGO) shows the highest electrical conductivity of about 103 S/cm with a highly oriented and uniform chemical structure. A nanocomposite prepared using this highly conductive rGO and LLDPE has been found to improve the conductivity of the system but it is not significant due to agglomeration of rGO particles. The issue of higher rGO loading in rGO based nanocomposites resulting in reduced conductivity is currently being re-examined from a compatibility perspective.

Keywords: Graphene oxide, Reduction, Raman spectroscopy, Electrical conductivity, Nanocomposites.

1. SYNTHESIS AND REDUCTION OF GRAPHENE OXIDE

Graphene oxide has been synthesised by the “modified” Hummers and Offenman’s method [1] using H_2SO_4 , $NaNO_3$ and $KMnO_4$. Typically the reaction takes 2 hours for overall completion. Adding water and subsequent addition of hydrogen peroxide (H_2O_2) make the manganese salts soluble. The yellowish intermediate graphite oxide formed can be purified by washing procedures to yield GO after sonication. The suspension from the synthesis was then ultrasonicated and dried to form films.

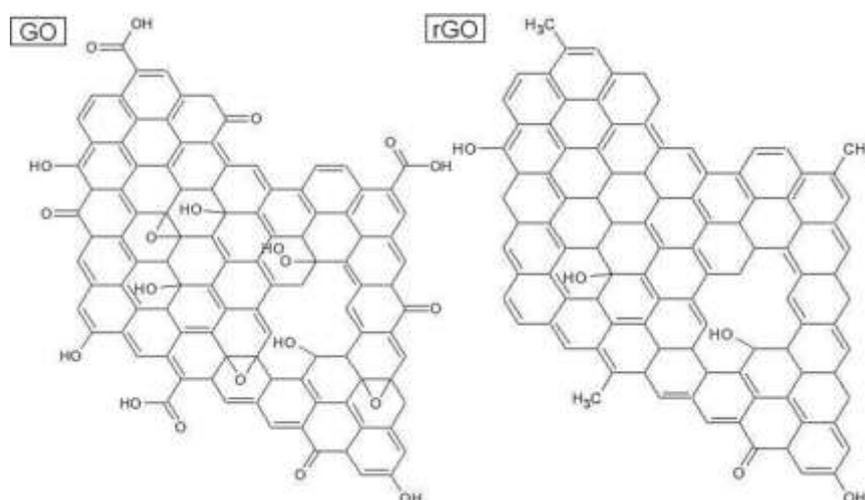


Figure 1. Chemical structures of GO and rGO

Graphene oxide (GO) has been reduced at three reduction periods (24, 48 and 72 hours) with the five reducing agents (HI, HH HBr, SBH and Dex). With almost all three reducing agents, the electrical conductivities increased when reduction time progressed to 72 hours. After 72 hours the films got corrugated and no significant increases in conductivity could be observed. The reduction procedure removes functional groups, such as ROH, R=O, ROOH and ROR (depicted in Figure 1). It is assumed that the oxidation of graphene to graphene oxide involves the initial formation of epoxides, then alcohols (highly populated compared to other groups) and eventually ketones/ aldehydes/carboxylic acids (along edges and defects) [2-4]. The molar populations of these and the level of desired reduction determine the amount of reductant that needs to be used [5, 6], e.g. 150 mmol is needed to reduce 420 mmol (0.42 mol) of GO. All the three reducing agents react 1:1 with a COH, C=O or COOH group, reducing them back to CH₂ or COH or CO, respectively [3].

2. RESULTS AND DISCUSSION

2.1 Raman spectroscopy and FTIR analyses:

Raman spectroscopy is used to directly determine the defect density in graphene-like materials. The defect induced (weak) disorder band caused by the graphite edges [7], so called, D and G peaks can be found at around 1340 cm⁻¹ and 1580 cm⁻¹, respectively [8]. It can be observed from Figure 2 (a) that 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 variation of the relative intensities of G and D bands in the Raman spectra of the GO during the reduction usually reveals the change in degree of the conjugation [9]. Based on this argument, and the observed D/G broadening, HI-rGO has a more ordered and regular structure. Based on the proposed mechanisms for conductivity [3], it would be expected that HI-rGO will have a higher conductivity than those of the samples produced using HBr, HH, SBH and Dex.

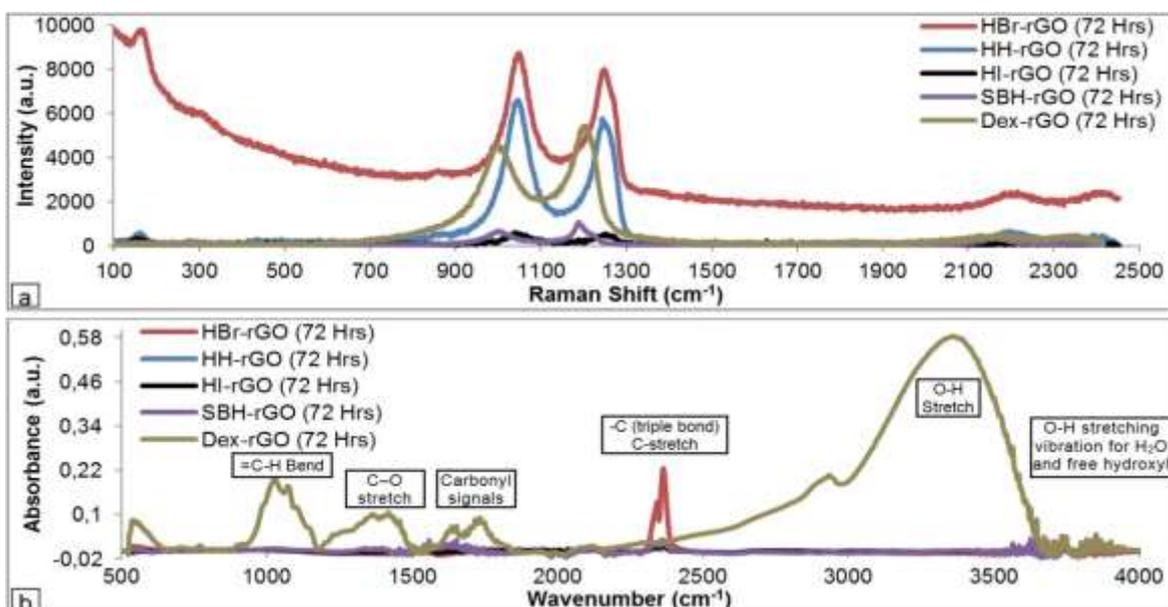


Figure 2 (a) Raman spectra and (b) FTIR of rGOs

Moreover, it is known that highly ordered graphite has only a couple of Raman-active bands visible in the spectra: the in-phase vibration of the graphite lattice (G band) at 1575 cm⁻¹ and the (weak) disorder band caused by the graphite edges (D band) at approximately 1355 cm⁻¹ [48]. The main differences among HBr-rGOs, HH-rGOs and HI-rGOs are that the shift between 950 and 1250 cm⁻¹ is much smaller for HI-rGO than those for HBr, HH, SBH and Dex-rGOs, Figure 2 (a). 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 other rGOs [8].

From the FTIR peaks depicted in Figure 2(b), it can be identified that HI has very small vibrational signals for all the functional groups in comparison to other rGOs. Dex-rGO has a lot of O-H stretching and carbonyl groups present which obviously has the lowest conductivity among all rGOs.

2.2 XRD and thermal analyses:

The proposed mechanism behind variation in d-spacing is that the reduction removes oxygen containing functionalities that are repulsing the GO layers. Removing these repulsive groups helps in restoring the physical and electronic structure of rGO [2] to an approximation of graphene, facilitates electron motion through the sheet and hence increases electrical conductivity [3]. XRD patterns of rGOs are shown in Figure 3 (a). HI-rGO exhibits much smaller peaks indicating a higher level of reduction than those of HBr-rGOs and HH-rGOs. The peak positions for all rGOs decrease with increasing reduction time. The diffraction line for HI-rGO (reduced for 72 hours) occurs at a smaller 2θ value of 24.03° , corresponding to a much smaller d-spacing of 3.70 Å.

From XRD graphs, it can be seen that the interlayer spacing for all HI-rGOs increase with increasing reduction time (up to 72 hours) and increasing concentrations of different reducing agents. It may be assumed that SBH-rGO, HH-rGO and HBr-rGO, with d-spacing moving more towards that of graphite compared to HI-rGO, would have similar problems with electron transfer and therefore lower conductivity. Dex-rGO has a lot of defects and poor structure which can be noticed from its pattern. However, it is to be noted that for electrical conductivity, d-spacing of rGO sheets is not the only factor that is responsible. The extent of the restoration of the π -system and the presence of remaining oxygen groups are also critical as the defects affect both path length and trapping factors which are important in electrical conductivity [4].

Thermo gravimetric analysis (TGA) has been used to further assess the level of reduction with HBr, HH, HI, SBH and Dex-rGOs at 72 hours. Figure 3 (b) displays the TGA thermograms of rGOs which indicates weight loss as a function of temperature along with GO and it reveals that HI-rGO has the least amount of functional groups followed by HH, HBr, SBH and Dex-rGOs, respectively. This confirms that a rGO material with less amount of function groups possess better electrical conductivity.

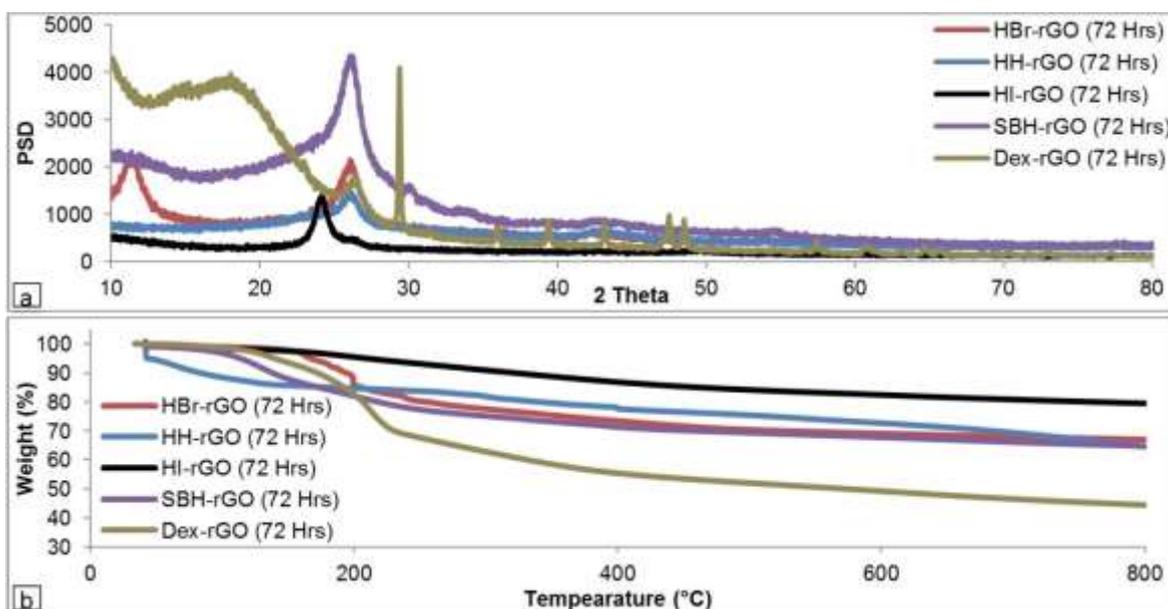


Figure 3 (a) XRD patterns and (b) thermograms of rGOs

2.3 Electrical conductivity of rGOs:

From the presented results and discussion, it may be hypothesised that the conductivity in rGOs depends on the combination of d-spacing, lower corrugation, low numbers of oxygen functional groups and a final structure with few missing carbons. Comparing conductivity of the rGO samples, Figure 4, it can be seen that, not all those factors influence the electrical conductivity. Because, HI-rGO has the highest electrical conductivity which also has the lowest amount of functional groups, but, higher d-spacing. Hence, the most influencing factor is the amount of functional groups present in the samples.

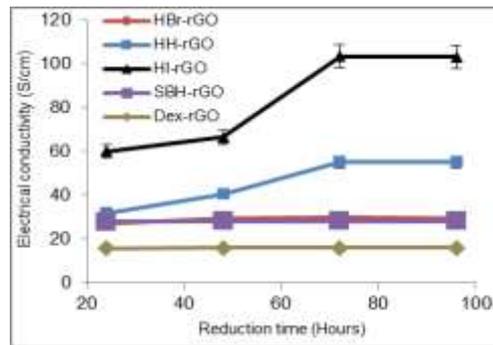


Figure 4 Electrical conductivity [16]

2.4 Conductivity of rGO/LLDPE nanocomposites

Preliminary experiments on rGO/LLDPE nanocomposites prepared (via melt blending, followed by compression moulding) using highly conductive HI-rGO did not reach the practical performance criteria. The conductivity values for rGO/LLDPE were too low due to agglomeration of rGO particles, Figure 5. It clearly shows that, the conductivity does not improve beyond 4% loading of rGO.

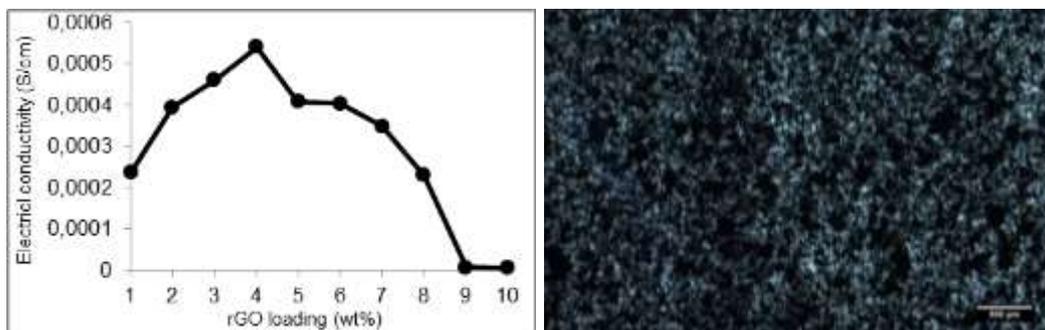


Figure 5 Conductivity of HI-rGO/LLDPE nanocomposites prepared by melt blending and optical microscope image of a sheets showing agglomerates at 5% rGO loading

2.4.1 Mixture analysis

Mixture analysis was performed in order to predict suitable combinations of the blends which could control the right amount of rGO loading. A quadratic model with 4 design points, 3 lack of fit points and 3 replicates has been considered. There are certain well defined criteria to check the fit and adequacy of the fitted models. The first criterion is R^2 , which should be close to 1.0, but it does not always explain the adequacy of the model as the value of R^2 increases with additional parameters. Hence, an adjusted R^2 criterion should be used as an additional check, as it decreases with addition of non-significant parameters. Therefore, a model is well-fitted if both R^2 and R^2_{adj} are close to 1.0 with a slight difference. A well fitted model should also be the one which can accurately predict the responses of the unseen values of the input parameters. So predicted R^2 is the third criterion which measures the variation in new data, should also be considered. R^2_{pred} should also be close to 1.0, and

in practice, if the difference between R^2_{pred} and R^2_{adj} is less than 0.2, the response surface model is acceptable. For this model R^2 is 0.982 and R^2_{adj} is 0.98760062. In addition, p-value that determines the overall validity of the significance of the model should also be considered for model selection [5, 6]. The lack of fit value for this model is 0.1043.

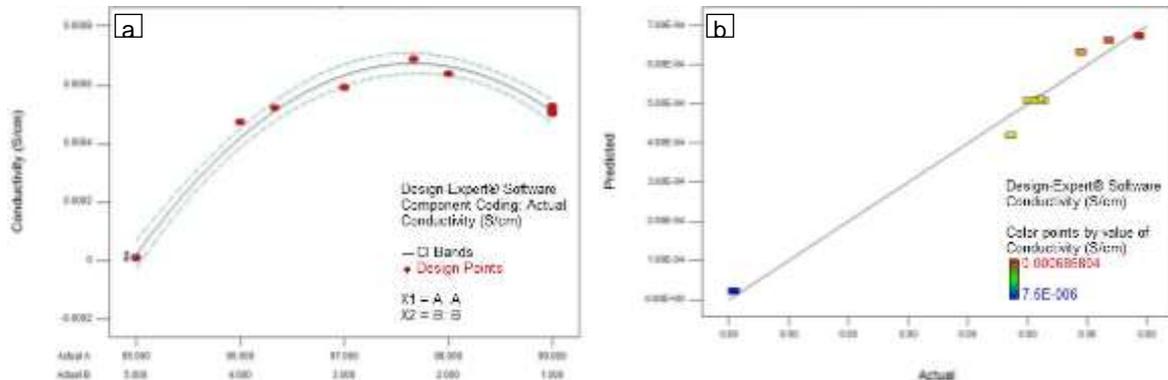


Figure 6 Mixture analysis model graphs: (a) lack of fit (b) predicted vs. actual response

From predicted response values versus the actual response values and lack of fit (LOF) graphs, Figure 6, it can be seen that the model fits the data with reasonably low sum of squares. It helps to detect a value, or group of values, that are not easily predicted by the model. LOF value and the curve define the suitability of the model. In this case, the “lack of fit F- value” of 5.16 implies that the LOF is not significant relative to the pure error. Non-significant lack of fit shows the model is good [6]. The model provides the sub-optimised blends of LLDPE/rGO (Table 1) and their electrical conductivity results have been depicted in Figure 7. The results have been sub-optimised in terms of rGO loading with electrical conductivity. Before the model was built, the highest conductivity was achieved at rGO loading of 4%. With the help of the model it has been identified that the maximum conductivity could be achieved at the 3.6% rGO loading. It can also be observed that this conductivity value is higher than the conductivity at 4% which further clarifies that agglomeration of rGO particles is reduced with a difference of 0.4%.

Table 1 Sub-optimised blends from the mixture model

Blend	LLDPE (wt %)	rGO (wt %)
1	99	1
2	99	1
3	97.67	2.33
4	96	4
5	95	5
6	95	5
7	98	2
8	96.34	3.66
9	99	1
10	97	3

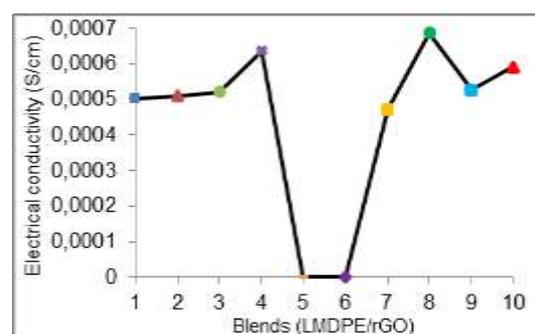


Figure 7 Electrical conductivity of the sub-optimised blends

3. CONCLUSIONS

The electronic and physical properties of rGO films depend highly on the efficiency of reducing agents and reduction time. Raman spectra and XRD results show that the HI reduction method gives highly orientated two-dimensional graphene-like layers with uniform chemical structure that allows unimpeded movements of electrons. The mechanism of conductivity is directly related to electron charge transport properties of graphene layers [2, 7], which in turn depends on the structural defect,

functionality and layer disorder. It also shows that how close the rGO structure is to that of graphene, despite having defects in it, e.g. physical holes due to oxidation removing carbon atoms or alkyl/H groups. The results of this study show that a relatively simple but efficient method of reducing GO gives improved electrical conductivity of rGO films due to the high level of reduction. The Nanocomposites of HI-rGO/LLDPE prepared by melt-blending, has the maximum conductivity of 5×10^{-3} S/cm at the rGO loading of 3.6% and the conductivity drops with 4% loading due to the agglomeration of rGO particles. A mixture analysis model has been built to sub-optimize the LLDPE/rGO blends and the results are in agreement with the actual electrical conductivity measurements of LLDPE/rGO blends.

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