



## Short Communication

## Dispersion behaviour of graphene oxide and reduced graphene oxide

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## ABSTRACT

The dispersion behaviour of graphene oxide (GO) and chemically reduced GO (rGO) has been investigated in a wide range of organic solvents. The effect of the reduction process on the GO solubility in eighteen different solvents was examined and analysed, taking into consideration the solvent polarity, the surface tension and the Hansen and Hildebrand solubility parameters. rGO concentrations up to ~9 µg/mL in chlorinated solvents were achieved, demonstrating an efficient solubilization strategy, extending the scope for scalable liquid-phase processing of conductive rGO inks for the development of printed flexible electronics.

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## 1. Introduction

Graphene is an atomically thin layer of sp<sup>2</sup>-bonded carbon atoms, stacked in a two-dimensional (2D) honeycomb lattice, forming the basic building block for carbon allotropes of any dimensionality [1]. Since its isolation as a monolayer, graphene has attracted an extraordinary amount of interest due to its potential application in the fastest growing scientific fields, such as supercapacitors [2], biosensors [3], photovoltaics [4] and touch panels [5].

Chemical vapour deposition (CVD) [6] and micromechanical exfoliation of graphite are the most widely used fabrication methods of less defective graphene films. However, the CVD deposition of uniform large area graphene films on arbitrary substrates at low temperatures is not possible and furthermore this method is incompatible with roll to roll mass production processes. At the same time, the exfoliated graphene exhibits very low solubility in common organic solvents [7], due to the essential addition of a stabilizer as the exfoliation liquid medium [8].

On the other hand, exfoliated graphene oxide (GO) is the ideal alternative for the production of solution processable graphene, as it can be synthesized in large quantities from inexpensive graphite powder and can readily yield stable dispersions in various solvents [9]. GO is an oxidized graphene sheet having its basal

planes decorated mostly with epoxide and hydroxyl groups, in addition to carbonyl and carboxyl groups located at the edges [10].

The covalent character of C–O bonds disrupts the sp<sup>2</sup> conjugation of the hexagonal graphene lattice, making GO an insulator. Nevertheless, GO can be partially reduced to conductive graphene-like sheets by removing the oxygen-containing groups [11–13]. In this way the conjugated structure of graphene can be recovered, resulting in reduced graphene oxide (rGO) with important electrical properties partially restored [14].

However, the preparation of dispersed form of graphene for applications in printed flexible electronics is not a straightforward process, since its stability in various solvents is a critical point. In this context, the solubility of GO in various solvents has been recently examined by several groups [9,15,16]. However, there is a gap in the literature on the direct comparison on solubility values on GO and rGO, which in principle they are different. Therefore, the knowledge on how conductive rGO stable solution can be obtained in common organic solvents is vital.

In this work, the dispersion behaviour of GO and chemically rGO is compared, aiming to get an insight into how the removal of oxygen containing groups during the reduction process affects its dispersion quality. The solubility/dispersibility of rGO is investigated in eighteen different solvents and directly compared with the pristine GO. In this way, critical solubility values are recorded aiming at the application of conductive rGO inks on printed flexible electronic devices [17].

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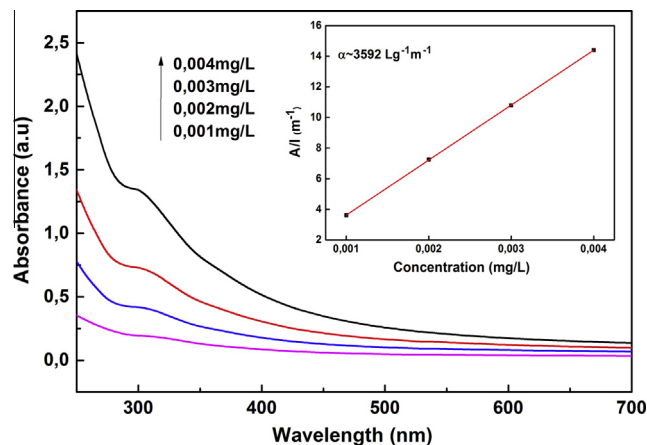
## 2. Results and discussion

For the preparation of GO and rGO dispersions, the products prepared as described in the [Experimental Section \(SI\)](#), were first grounded with a mortar and pestle. In order to compare the dispersion behaviour in the different solvents, the same quantity of GO and rGO powder ( $\sim 1$  mg) was added to a given volume of solvent ( $\sim 2$  mL), with an initial concentration of 0.5 mg/mL. GO and rGO dispersions were tested in the following organic solvents: (DI) water, acetone, methanol, ethanol, 2-propanol, ethylene glycol, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), n-hexane, dichloromethane (DCM), chloroform, toluene, chlorobenzene (CB), o-dichlorobenzene (o-DCB), 1-chloronaphthalene (CN), acetylacetone, diethyl ether. The dispersions were sonicated in an ultrasound bath cleaner (Elmasonic S30H) for 1 h and then mildly centrifuged at 500 rpm for 90 min (Alegria X-22) to remove the large aggregates. Afterwards, the supernatant was collected for analysis.

For the estimation of solubility values for GO and rGO in different solvents, UV–Vis spectroscopy was performed on a Shimadzu UV2401PC UV–Vis spectrometer. Using the 2 weeks left suspensions, the dispersibility of GO and rGO in each solvent was examined from the linear relationship between the absorbance ( $A$ ) and the concentration ( $C$ ) of a compound in a solution, given by the Lambert–Beer law ( $A = \alpha l C$ ). It is necessary to determine the absorption coefficient ( $\alpha$ ), which is related to the absorbance per unit path length  $A/l$  and it is an important parameter in characterizing any dispersion. For this purpose, a calibration line was constructed by measuring the absorbance at 660 nm of four GO and rGO solutions with different, low concentrations ([Fig. 1](#)). The procedure was repeated for each solvent. The observed values divided by the cuvette length ( $l = 1$  cm) were plotted versus the known concentration values, allowing to estimate the absorption coefficient for its suspension. Using  $\alpha$  values, the maximum solubility of GO and rGO in each solvent could be extracted ([Table 1](#)).

Treating GO with hydrazine causes an enormous structural change with the recovery of the conjugated system, through the removal of oxygen containing groups. The morphology, structure and composition of GO and rGO were characterized by Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and Thermogravimetric Analysis (TGA).

Raman spectroscopy is a powerful tool, which can be used to characterize carbonaceous materials and particularly for distinguishing the disorder in the crystal structures of carbon. In the Raman spectrum of GO and rGO ([Fig. 2a](#)), two prominent peaks



**Fig. 1.** UV–Vis spectra of GO dissolved in water at different concentrations. The inset shows the linear relationship between the absorbance per unit path length and the concentration of GO.

are clearly visible, corresponding to the so-called D and G bands. In particular the Raman spectrum of GO exhibited a D band peak at  $1330\text{ cm}^{-1}$ , that corresponds to the breathing mode of  $\kappa$ -point phonons of  $A_{1g}$  symmetry and a G band peak at  $1592\text{ cm}^{-1}$ , due to the first-order scattering of the  $E_{2g}$  phonons [18]. The corresponding D and G bands in the Raman spectrum of rGO appeared at  $1341\text{ cm}^{-1}$  and  $1598\text{ cm}^{-1}$ , respectively. The intensity of the D band is related to the size of the in-plane  $sp^2$  domains and the relative intensity ratio ( $I_D/I_G$ ) is a measure of the extent of disorder [18]. After the reduction of GO, the intensity ratio ( $I_D/I_G$ ) was increased significantly and the higher intensity of D band suggests the presence of more isolated graphene domain in rGO compared to GO and removal of oxygen groups from the latter [19].

[Fig. 2b](#) shows the FTIR spectra of GO and rGO. The peaks at  $\sim 3400\text{ cm}^{-1}$  (O–H stretching vibrations), at  $\sim 1700\text{ cm}^{-1}$  (C=O stretching vibrations), at  $\sim 1600\text{ cm}^{-1}$  (skeletal vibrations from unoxidized graphitic domains), at  $\sim 1200\text{ cm}^{-1}$  (C–O–C stretching vibrations), at  $\sim 1050\text{ cm}^{-1}$  (C–O stretching vibrations) are characteristic for the GO. The removal of oxygen-containing groups during the reduction is confirmed from the decrease (almost disappearance) of the bands of C=O stretching, C–O–C stretching, C–O stretching. The relative decrease in the intensity of O–H stretching band indicates that C–OH still exist, but in lower proportion.

**Table 1**

Dipole moments, surface tensions and Hildebrand parameters of solvents and GO, rGO solubility values for all solvents studied.

Solvents	Dipole moment	Surface tension (mN/m)	$\delta_T$ (MPa <sup>1/2</sup> )	GO Solubility ( $\mu\text{g/mL}$ )	rGO Solubility ( $\mu\text{g/mL}$ )
Di water	1.85	72.8	47.8	6.6	4.74
Acetone	2.88	25.2	19.9	0.8	0.9
Methanol	1.70	22.7	29.6	0.16	0.52
Ethanol	1.69	22.1	26.5	0.25	0.91
2-propanol	1.66	21.66	23.6	1.82	1.2
Ethylene glycol	2.31	47.7	33	5.5	4.9
Tetrahydrofuran (THF)	1.75	26.4	19.5	2.15	1.44
N,N-dimethylformamide (DMF)	3.82	37.1	24.9	1.96	1.73
N-methyl-2-pyrrolidone (NMP)	3.75	40.1	23	8.7	9.4
n-Hexane	0.085	18.43	14.9	0.1	0.61
Dichloromethane (DCM)	1.60	26.5	20.2	0.21	1.16
Chloroform	1.02	27.5	18.9	1.3	4.6
Toluene	0.38	28.4	18.2	1.57	4.14
Chlorobenzene (CB)	1.72	33.6	19.6	1.62	3.4
o-Dichlorobenzene (o-DCB)	2.53	36.7	20.5	1.91	8.94
1-Chloronaphthalene (CN)	1.55	41.8	20.6	1.8	8.1
Acetylacetone	3.03	31.2	20.6	1.5	1.02
Diethyl ether	1.15	17	15.6	0.72	0.4

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