

# Synthesis of hexamethylene diisocyanate-functionalized graphene oxide for solar cell applications

J A Luceño<sup>1</sup>, A M Díez-Pascual<sup>1</sup>, R Peña<sup>2</sup> and P García-Díaz<sup>2</sup>

<sup>1</sup>Analytical Chemistry, Physical Chemistry and Chemical Engineering Department

<sup>2</sup>Signal Theory and Communications Department, Alcalá University, 28871, Madrid, Spain

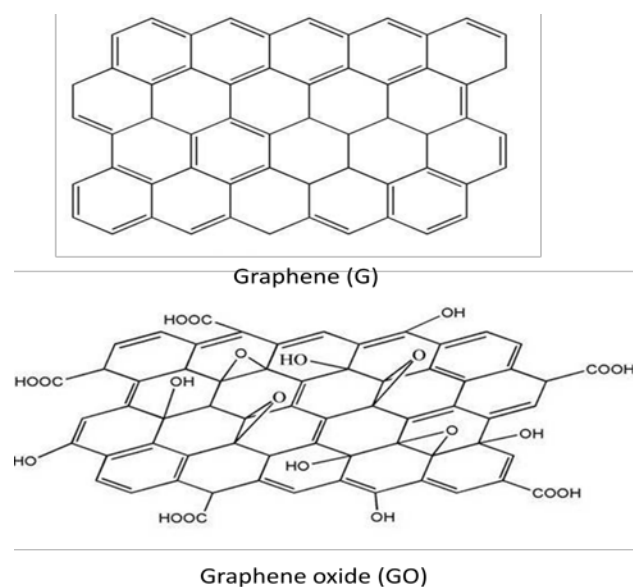
**Abstract.** Graphene (G), an allotrope of carbon with exceptional optical, electronic, thermal and mechanical properties, and its oxidized form graphene oxide (GO), show huge potential for a broad range of applications. In particular, their high conductivity, transparency, flexibility, and abundance make them suitable for polymer solar cells (PSCs). However, their insolubility in common organic solvents hinders their applications. Consequently, novel functionalization approaches are pursued. The present work is devoted to the preparation of hexamethylene diisocyanate-functionalized graphene oxide (HDI-GO). The synthesized nanomaterial shows a highly hydrophobic nature and can be dispersed in organic non-polar solvents, hence is a prospective candidate to be combined with conjugated polymers for solar cell applications.

## 1 Introduction

Graphene (G), an allotrope of carbon like diamond, graphite and fullerenes, has attracted a lot interest in recent years both for fundamental studies and potential applications [1]. It is a flat, atomically thick 2D sheet composed of sp<sup>2</sup> carbon atoms arranged in a honeycomb structure (Figure 1). It presents superior electronic, thermal and mechanical properties, very large surface area and the highest electrical conductivity known at room temperature [2]. Besides, G is believed to be the strongest material on earth, with an elastic modulus of 1 TPa [3], tensile strength of ~150 GPa and a breaking strength 200 times higher than steel [4]. Its extremely high carrier mobility, broad absorption spectral range, high optical transparency and abundance make it a suitable candidate for application in optoelectronic devices such as displays, light-emitting diodes, and solar cells [5,6]. In this regard, a lot of effort is currently focused onto the development of polymer solar cells (PSCs) with G or its derivatives [7]. They have great potential to be used as transparent conductive electrodes (anode, cathode or both of them), as additives at the interfacial layers (cathode buffer or hole transporting layers) and as acceptor additives to donor-acceptor materials in bulk heterojunction (BHJ) organic photovoltaic cells [8].

Several routes have been reported for the preparation of G, including chemical vapor deposition (CVD) of hydrocarbons onto transition metal surfaces, micromechanical exfoliation of graphite, epitaxial growth on electrically insulating substrates like SiC wafers, electrochemical intercalation, thermal exfoliation or chemical reduction of graphite oxide [9,10]. However,

these methods lead to very small amount of nanomaterial. Further, G is insoluble in common solvents, which hinders its applications. G can be oxidized following the Hummers' method [11] to yield graphene oxide (GO, Figure 1), a water-soluble nanomaterial since comprises epoxide, hydroxyl and carbonyl groups on the basal planes and carboxylic acids on the edges. Thus, upon sonication in aqueous media, GO easily exfoliates into colloidal suspensions of single layers. However, the hydrophilic nature of GO hinders its dispersion in common organic solvents, which limits the preparation of polymer/GO nanocomposites. To solve this drawback, novel functionalization strategies are pursued.



**Figure 1.** Schematic representation of G and GO

G and GO have been functionalized via covalent and non-covalent approaches [12,13]. When organic molecules are covalently attached onto the G (or GO) surface, its aromatic pi system is perturbed, which allow to control its electronic properties. In particular, the development of a band gap by means of chemical doping is a potent way to prepare G for use in nanoelectronic devices [14]. This type of functionalization includes two main routes: covalent bonding between free radicals or dienophiles and the C=C bonds of G and bonds between organic functional groups and the surface oxygenated moieties of GO. The covalent functionalization includes amidation, esterification, and introduction of negatively charged carboxylic or sulfonic groups. However, it typically introduces defects on the G network that have detrimental effect on the properties, in particular the electrical and mechanical.

The non-covalent functionalization is an interesting method since provides the possibility of anchoring functional groups to G without disturbing the electronic network. It involves the use of surfactants and/or polymers that wrap around G to facilitate dispersion via hydrophobic,  $\pi - \pi$  and ionic interactions [15]. It is believed that the hydrophobic regions cover the majority of the surface of the G sheets, whilst the hydrophilic tails stretch out into the aqueous solution where the flakes are dispersed [16]. Hence, the size and geometry of the resulting surfactant-wrapped G will significantly differ from that of pristine G.

An interesting approach is the isocyanate functionalization proposed by Stankovich *et al.* [17] that facilitates GO dispersion in polar aprotic solvents such as dimethylformamide (DMF), N-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO). However, isocyanate-functionalized GO cannot be dispersed in non-polar solvents, and this restricts its use in organic polymers-based BHJ solar cells

In this regard, the present work focuses on the synthesis of hexamethylene diisocyanate (HDI)-functionalized graphene oxide. This nanomaterial possesses a highly hydrophobic nature and can be

suspended in organic non-polar solvents such as benzene, toluene, chlorobenzene, tetrahydrofuran (THF), etc. Therefore, theHDI-GO sheets can be dispersed with organic materials, in particular conjugated polymers used for solar cell applications.

## 2 Experimental Section

### 2.1 Reagents

Natural graphite was obtained from Bay Carbon, Inc. (Michigan, USA).  $\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4$ ,  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{H}_2\text{O}_2$  (30 wt % in water), toluene, triethylamine (TEA) and hexamethylene diisocyanate (HDI) were purchased from Sigma-Aldrich and used as received. Dichloromethane (DCM) (analytical grade), acetone (99.9%), hexane (96%), pentane (99%), Tetrahydrofuran (THF) (HPLC grade); Dimethyl sulfoxide (DMSO) (99.5% anhydrous); N,N-dimethylformamide (DMF) (99.8% anhydrous); N-methyl-2-pyrrolidone (NMP) (99%), methanol (99.8%), ethanol (analytical grade) and 2-propanol (99.5%) were purchased from Scharlau S.L. The aqueous solutions were prepared using ultrapure water obtained from a Milli-Q system (Millipore, Milford, USA).

### 2.2 Synthesis of graphene oxide (GO)

GO was prepared using a modified Hummers' method from flake graphite [11,18]. Briefly, graphite powder,  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{S}_2\text{O}_8$ , and  $\text{P}_2\text{O}_5$ , were heated at 80 °C for 5 h. After cooling, deionized water was added to the mixture and it was stirred overnight. The resulting product was then filtered, dried under air and oxidized again via addition of  $\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4$  and water in an ice-water bath. Following to dilution with water, excess  $\text{KMnO}_4$  was decomposed by addition of 30 wt %  $\text{H}_2\text{O}_2$  aqueous solution and then 5 wt % HCl aqueous solution.

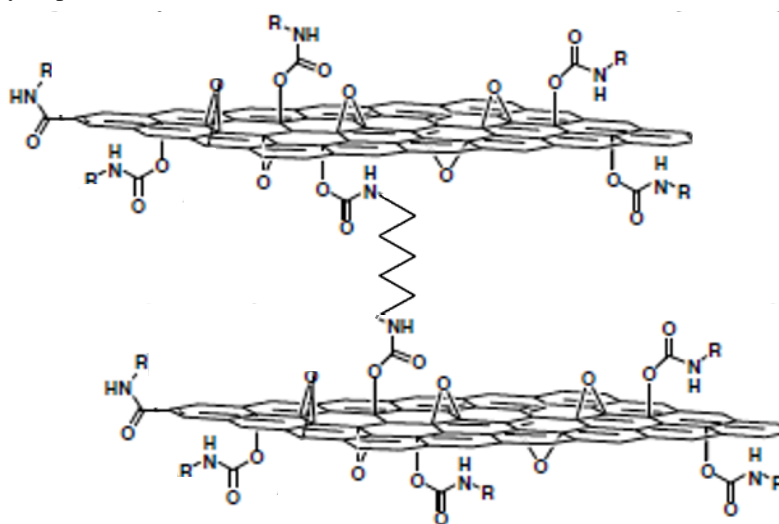


Figure 2. Schematic representation of HDI-functionalized GO

The product was filtered again and purified by repeating the following cycle: centrifugation, removal of the supernatant liquid, addition of aqueous solution of  $H_2SO_4$  (3 wt %)/ $H_2O_2$  (0.5 wt %) and bath ultrasonication for 30 min at a power of 140 W. Then it was washed several times with deionized water and finally freeze-dried.

### 2.3 Synthesis of hexamethylenediisocyanate-functionalized graphene oxide (HDI-GO)

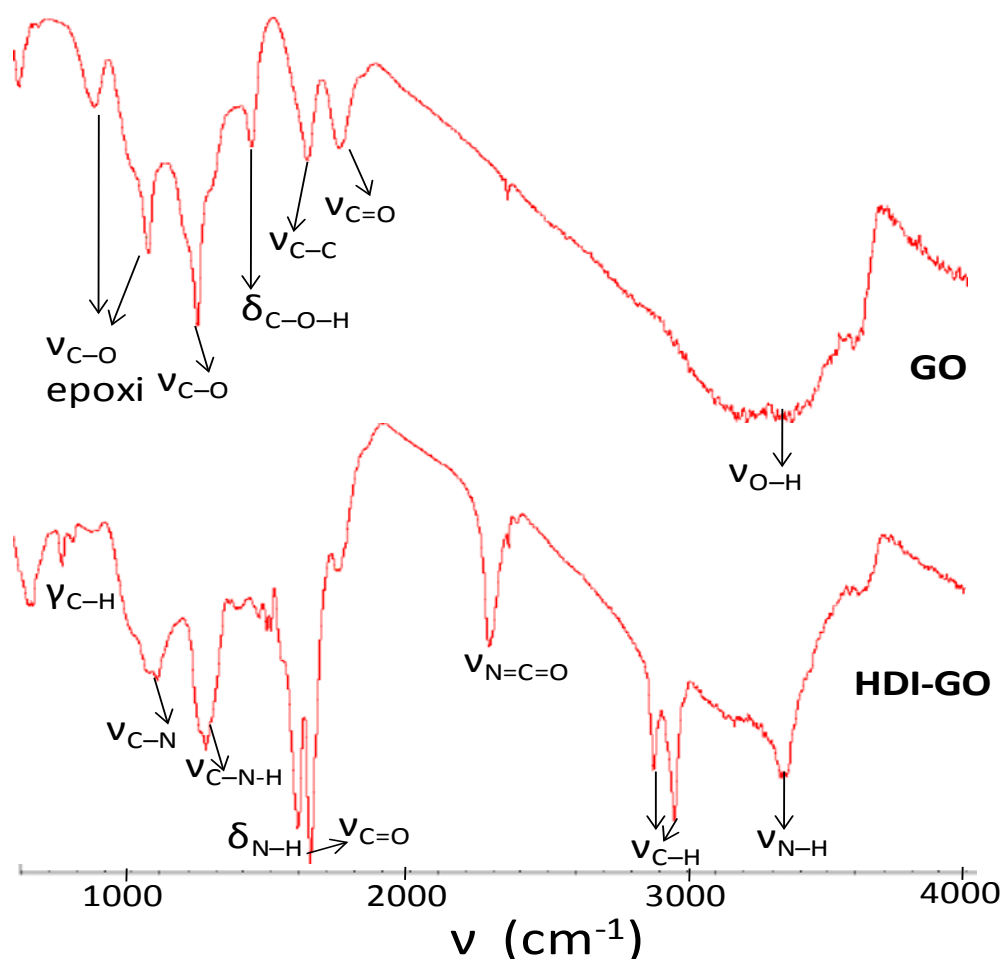
1 g of purified GO powder was added to 100 mL of toluene, ultrasonicated in an ultrasonic bath for 2 h, and then transferred to a reactor equipped with mechanical agitator, thermometer and reflux condenser. Then 35 mL of TEA and 20 mL of HDI were added to the system, the last one dropwisely. The solution was heated to 60 °C and vigorously stirred overnight under an inert atmosphere of argon. The mixture was then poured into methylene chloride to coagulate the product. Finally, the reaction product was filtered, washed thoroughly with methylene chloride and dried under vacuum to yield HDI-GO (Figure 2).

### 2.4 Instrumentation

An ultrasonic bath (Selecta, Spain) and a Hielscher UP400S ultrasonic probe (Hielscher Ultrasonics GmbH, Germany) equipped with a titanium sonotrode ( $\varnothing = 7$  mm,  $l = 100$  mm) was used to prepare the nanomaterial dispersions in the different solvents. Elemental analysis was carried out with a LECO CHNS-932 elemental analyser. Infra-red spectrum was obtained with a Perkin Elmer Frontier FT-IR Spectrometer.

### 3. Results and discussion

Similar to pristine GO, the HDI-functionalized GO consisted in a black powder. However, unlike GO, it was insoluble in water or other polar solvents including DMF, NMP, or DMSO. This is in contrast to the results reported for GO functionalized by monoisocyanates, which were found to be soluble in polar aprotic solvents [17]. The insolubility of HDI-GO is likely ascribed to its higher hydrophobic character and the crosslinking between the GO sheets that are randomly covalently bonded by HDI to each other. Conversely, the synthesized nanomaterial was found to be soluble in organic non-polar solvents like benzene, toluene, chlorobenzene, THF, acetone, pentane, hexane, heptane and cyclohexane.



**Figure 3.** FT-IR spectra of GO (top) and HDI-functionalized GO (bottom)

The treatment of GO with isocyanates can lead to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides or carbamate esters [17], respectively. The chemical changes that occurred upon treatment of GO with HDI was investigated by Fourier transform infrared spectroscopy (FT-IR), since both GO and its derivative display characteristic IR spectra (Figure 3).

GO contains epoxide and hydroxyl functional groups on both sides of its basal plane and carboxyl moieties at the edge sites. The strong broad band centred at  $\sim 3520\text{ cm}^{-1}$  corresponds to the O–H stretching vibrations and that near  $1750\text{ cm}^{-1}$  corresponds to the C=O stretching of the carboxylic groups. The band at  $1600\text{ cm}^{-1}$  can be assigned to the aromatic C=C stretching, that at  $\sim 1400\text{ cm}^{-1}$  corresponds to the O–H deformation and those at approximately  $1260$ ,  $1050$  and  $850\text{ cm}^{-1}$  are related to epoxy C–O stretching vibrations [18].

Upon treatment with HDI, the intensity of the O-H stretching band was strongly reduced, and a band appeared at  $2280\text{ cm}^{-1}$  ascribed to the isocyanate group [19]. Further, a peak appeared at  $3320\text{ cm}^{-1}$  due to N-H stretching vibrations, and those at  $2850$  and  $2950\text{ cm}^{-1}$  arise from C-H stretching vibrations of the methylene chain of HDI. Intense bands are found at  $1630$  and  $1585\text{ cm}^{-1}$ , attributed to the C=O stretching and N-H bending vibrations of the urethane or carbamate ester group [19]. The band ascribed to the O-H bending and those attributed to epoxy C–O stretching vibrations almost disappeared, indicating that the isocyanate reacted with both hydroxyl and epoxide groups of the surface of GO to form carbamate esters. Further, the band close to  $1110\text{ cm}^{-1}$  is likely related to C(=O)-O and C-N stretching vibrations of the urethane groups, and that at around  $720\text{ cm}^{-1}$  is ascribed to the rocking of the methylene groups of HDI. Overall, the FT-IR spectra confirm the successful reaction of GO with the organic diisocyanate.

Assuming that the formation of carbamate esters through reaction of HDI with the OH or epoxide groups of GO is the hydroxyls or epoxies is the unique reaction pathway, the nitrogen-to-carbon atomic ratio can be used to roughly estimate the functionalization degree (FD). In particular, FD can be expressed as moles of carbamate ester unit incorporated per mol of carbon atoms of GO. Taking into account the results from elemental analysis of GO: C, 41.93%; O, 51.96%; H, 3.44%; S, 2.67% and HDI-GO: C, 56.68%; O, 28.22%; H, 5.82%; N, 8.00%; S, 1.28%, the calculated FD was 16.32%, higher than that reported for other isocyanate functionalized GO [17]. It should be noted that this value corresponds to a lower bound of functionalization; in the case of amide formation, which seems less feasible according to the FTIR spectrum, the FD would be higher since there is a loss of carbon (as carbon dioxide) from the isocyanate reagent.

## 4 Conclusions

Hexamethylene diisocyanate-functionalized graphene oxide (HDI-GO) has been prepared following a two-step approach: firstly, GO was prepared using a modified

Hummers' method from graphite, and secondly GO was treated with HDI in toluene to yield the modified nanomaterial. HDI-GO was found to be soluble in organic non-polar solvents like benzene, toluene, chlorobenzene, THF, acetone, pentane, hexane, heptane and cyclohexane. The comparison of the elemental analysis and FT-IR spectra of GO and HDI-GO corroborated the successful synthesis of the functionalized GO. Future work will focus on the characterization of HDI-GO by UV-vis spectroscopy, X-ray diffraction, atomic force microscopy, scanning electron microscopy, transmission electron microscopy and Raman spectroscopy. Further, mixture of these derivatives with different types of conductive polymers will be tested, with the aim to use them in photovoltaic cells.

## Acknowledgments

Financial support from Fundación Iberdrola España via an Energy Research Grant 2017 is gratefully acknowledged. We would also like to thank to Alcalá University for making possible this research.

## References

1. Geim A K and Novoselov K S 2007 *Nat. Mater* **6** 183
2. Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y and Dubonos S 2004 *Science* **306** 666
3. Lee C, Wei X, Kysar J W and Hone J 2008 *Science* **321** 385
4. Novoselov K S, Falko V I, Colombo L, Gellert P R, Schwab M G and Kim K 2012 *Nature* **490** 192
5. Dubacheva G V, Liang C K and Bassani D M 2012 *Coord. Chem. Rev.* **256** 2628
6. Iwan A and Chuchmała A 2012 *Prog. Polym. Sci.* **37** 1805
7. Manzano-Ramirez A, Lopez Naranjo E J, Soboyejo W, Meas-Vong Y and Vilquin B 2015 *J. nanomaterials* **2015** 406597
8. Xiao-Feng L, Zi-Yan Z, Zhong-Ke Y, Jing L, Xiao-Fen X, Wei H, Xu-Dong C and Ding-Shan Y 2016 *Chinese Chem. Lett.* **27** 1259
9. Park S J and Ruoff R S 2009 *Nature Nanotechnol.* **4** 217
10. Steurer P, Wissert, Thomann R and Mulhaupt R 2009 *Macromol. Rapid Comm.* **30** 316
11. Hummers W S and Offeman R E 1958 *J. Am. Chem. Soc.* **80** 1339
12. Díez-Pascual A M, Gómez-Fatou M A, Ania F and Flores A 2015 *Prog. Mater. Sci.* **67** 1
13. Texter J 2014 *Curr. Opin. Coll. Interf. Sci.* **19** 163
14. Niyogi S, Bekyarova E, Itkis M E, Zhang H, Shepperd K, Hicks J, Sprinkle M, Berger C, Ning Lau C, de Heer W A, Conrad E H and Haddon R. C. 2010 *Nano Lett.* **10** 4061

15. Díez-Pascual A M, Hermosa C, San Andrés M P, Valiente M and Vera S 2017 *J. Phys. Chem. C* **121** 830
16. Mateos R, Vera S, Valiente M, Díez-Pascual A M, and San Andrés M. P. 2017 *Nanomaterials* **7** 403.
17. Stankovich S, Piner R D, Nguyen S T and Ruoff R S 2006 *Carbon* **44** 3342
18. Diez-Pascual A M and Diez-Vicente A L 2016 *ACS Appl Mater Interfaces* **8** 17902
19. Silverstein R M, Webster F X and Kiemle D J 2005 *Spectrometric Identification of Organic Compounds*, 7<sup>th</sup> edition (John Wiley & Sons, Inc, Hoboken, USA) p. 72-126