Conference paper

Synthesis and characterization of graphene oxide derivatives via functionalization reaction with hexamethylene diisocyanate

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Abstract: Graphene oxide (GO), the oxidized form of graphene, shows unique properties such as strong mechanical strength, high electrical and thermal conductivity, amphiphilicity and surface functionalization capability that make it very attractive in various fields ranging from medicine to optoelectronic devices and solar cells. However, its insolubility in non-polar and polar aprotic solvents hinders some applications. To solve this issue, novel functionalization strategies are pursued. In this regard, the current study deals with the preparation and characterization of hexamethylene diisocyanate (HDI)-functionalized GO. Different reactions conditions were tested to optimize the functionalization degree (FD), and detailed characterization was conducted via Fourier-transformed infrared (FT-IR) spectroscopy to confirm the success of the functionalization reaction. The HDI-GO could further react with other organic molecules or polymers via the remaining oxygen groups, which makes them ideal candidates as nanofillers for high-performance GO-based polymer nanocomposites.

Keywords: **g**raphene oxide; hexamethylene diisocyanate; functionalization degree; solubility; infrared spectroscopy

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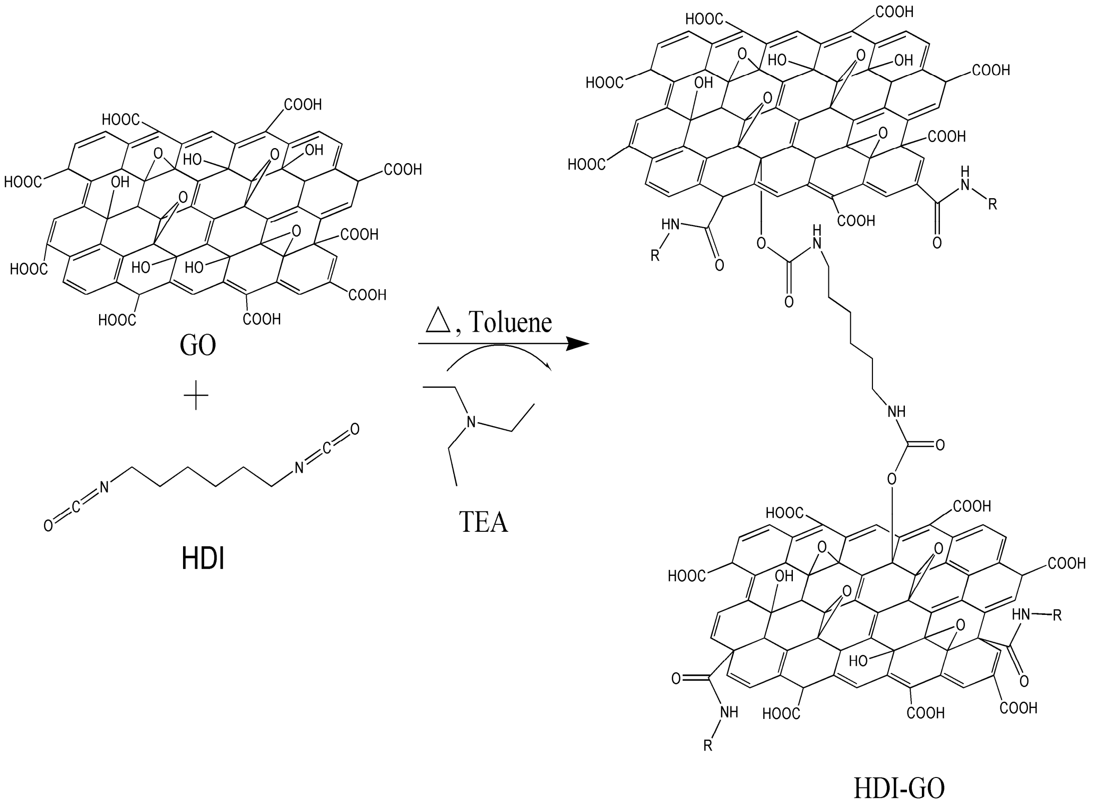
1. Introduction

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^2 carbon atoms arranged in a honeycomb structure. It presents superior electronic, thermal and mechanical properties, very large surface area and the highest electrical conductivity known at room temperature [2]. Its extremely high carrier mobility, broad absorption spectral range, high optical transparency and abundance make very attractive material in various fields ranging from medicine [3] or high-performance composites [4] to chemical sensors [5] and solar cells [6].

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 [7]. However, these approaches lead to a low production yield and are time consuming. Further, G is insoluble in common organic solvents, which hinders its applications. In this context, graphene oxide (GO), originated from the exfoliation of graphite oxide or the chemical oxidation of G [8], has been studied in many researches as an alternative to G. The established advantages of GO in production yield and cost make it an attractive candidate as nanofiller in polymer composites. GO is 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, it easily exfoliates and forms stable colloidal suspension due to its strong hydrophilicity [9]. However, the exfoliation of GO in organic solvents is hindered due to strong hydrogen bonding interactions between the adjacent GO layers that prevent the penetration of organic molecules into the interlayer spaces. The hydrophilicity of GO has been regarded as a drawback to develop high-performance polymer/GO nanocomposites in organic solvents. To solve this issue, novel functionalization strategies are pursued. An interesting approach is the isocyanate functionalization proposed by Stankovich et al. [10]. In their work, reactions between different organic isocyanates and the hydroxyl and carboxyl groups of GO were tested to reduce the amount of hydrogen bonds with donor groups on GO sheets, thus reducing the nanomaterial hydrophilicity. As a result, the isocyanate-treated GO samples could be exfoliated in some polar aprotic solvents such as N,N-dimethylformamide (DMF), after a mild ultrasonication. However, they could not be dispersed in non-polar solvents, and this still restricts its use in certain applications like polymeric-based solar cells.

In this regard, the present work focuses on the synthesis and characterization of hexamethylene diisocyanate (HDI)-functionalized GO. In our approach, GO was first prepared using a modified Hummers′ method from flake graphite [8] and then reacted with HDI in the presence of triethylamine (TEA) as a catalyst to yield functionalized HDI-GO nanosheets (**Scheme 1**). Different reactions conditions were tested in order to optimize the functionalization degree (FD), and characterization was conducted to confirm the successful functionalization of HDI on the GO surface.



Scheme 1. Schematic representation of the synthesis procedure of HDI-functionalized GO.

2. Results and Discussion

The reaction conditions, namely reaction temperature, reaction time, GO/HDI/TEA ratio, tip/bath sonication cycles and solvent volume, were varied in order to determine their effect on the product yield. The conditions of each experiment and nomenclature of the different HDI-GO samples obtained herein are detailed in **Table 1**.

Table 1. Nomenclature and reaction conditions for the synthesis of the different HDI-GO samples.

Sample	Reaction time (h)	Reaction temperature (ºC)	GO/HDI/TEA weight ratio	Tip/Bath sonication time (min)	Solvent volume (ml)
GO	–	–	–	–	–
HDI-GO 1	12	60	1/1/1	0/120	25
HDI-GO 2	12	60	0.5/1/1	0/120	25
HDI-GO 3	48	60	1/1/1	0/120	25
HDI-GO 4	12	90	1/1/1	0/120	25
HDI-GO 5	12	60	1/1/1	5/120	50
HDI-GO 6	12	60	1/1/1	5+5+5*/120	50

*3 probe sonication cycles with 5 min of break between cycles

The chemical changes that occurred upon treatment of GO with HDI were monitored by FT-IR spectroscopy, since both GO and the derivatives display characteristic IR spectra (**Figure 1**). As mentioned earlier, GO contains epoxide and hydroxyl functional groups on both sides of its basal plane and carboxyl moieties at the edge sites. The most characteristic features in the IR spectrum of GO are the strong broad band centred at ~3430 cm^{-1} corresponding to the O–H stretching vibrations, the peaks at around 2925 and 2845 cm^{-1} attributed to sp^2 and sp^3 C-H stretching bands produced at defects sites of the graphene network, the peak at ~1730 cm^{-1} arising from the C=O stretching of the carboxylic acid groups, the band at 1620 cm^{-1} assigned to the aromatic C-C stretching, that at ~1400 cm^{-1} corresponding to the O–H deformation [11] and the C–OH stretching at 1260 cm^{-1} [3].

Upon treatment with HDI, the intensity of the O-H stretching band was reduced, decreasing gradually with increasing FD, and also shifted towards lower wavenumbers, due to the overlapping with the N-H stretching vibrations of the carbamate groups. Further, the peaks at 2845 and 2925 cm^{-1} originating from symmetrical and asymmetrical stretching vibrations of -CH_2- became more intense upon raising FD, due to increased number of methylene chains arising from the HDI. A new band appeared in the samples with low FD at 2280 cm^{-1} ascribed to unreacted N=C=O group [12], suggesting the absorption/intercalation of the organic isocyanate between the GO flakes. However, this band can hardly be detected in the HDI-GO 5 and HDI-GO 6 samples, corroborating that the -N=C=O groups of HDI reacted completely with the hydroxyl groups of GO. Further, the C=O stretching appearing at 1730 cm^{-1} in pristine GO is hidden by a new peak at ~1710 cm^{-1} ascribed to the C=O stretching of the carbamate ester groups [10]. This peak becomes more intense and shifts gradually towards lower wavenumbers with increasing FD. Besides, new intense bands can be observed at ~1648 cm^{-1} and 1580 cm^{-1}; the first can be assigned to the coupling of the C=O stretching with in-phase N–H bending and the second to the coupling of the N–H bending with the C–N stretching vibration [12]. These bands could originate from either amide or carbamate ester groups, although in the first case they typically appear at 1660 and 1550 cm^{-1}, whilst for carbamate esters the bands are closer together due to the stronger π-π interaction between the carbonyl group and the nitrogen lone pair electrons, and the amide II band appears at higher frequency [13]. These two peaks also turn out to be stronger and move to lower wavenumbers with increasing FD, which could be indicative of increased H-bonding interactions between carbamate esters closely located [14]. Another bands become visible at around 1110 cm^{-1}, likely related to -C(=O)-O and C-N stretching vibrations of the carbamate groups, at 885 cm^{-1} attributed to C-H out-of-plane bending vibrations of substituted aromatic rings and at around 720 cm^{-1}, ascribed to the rocking of the methylene groups of HDI. On the basis of all the aforementioned observations, it can be concluded that GO was successfully functionalized with the organic HDI reactant and that the functionalization route via carbamate ester formation predominates.

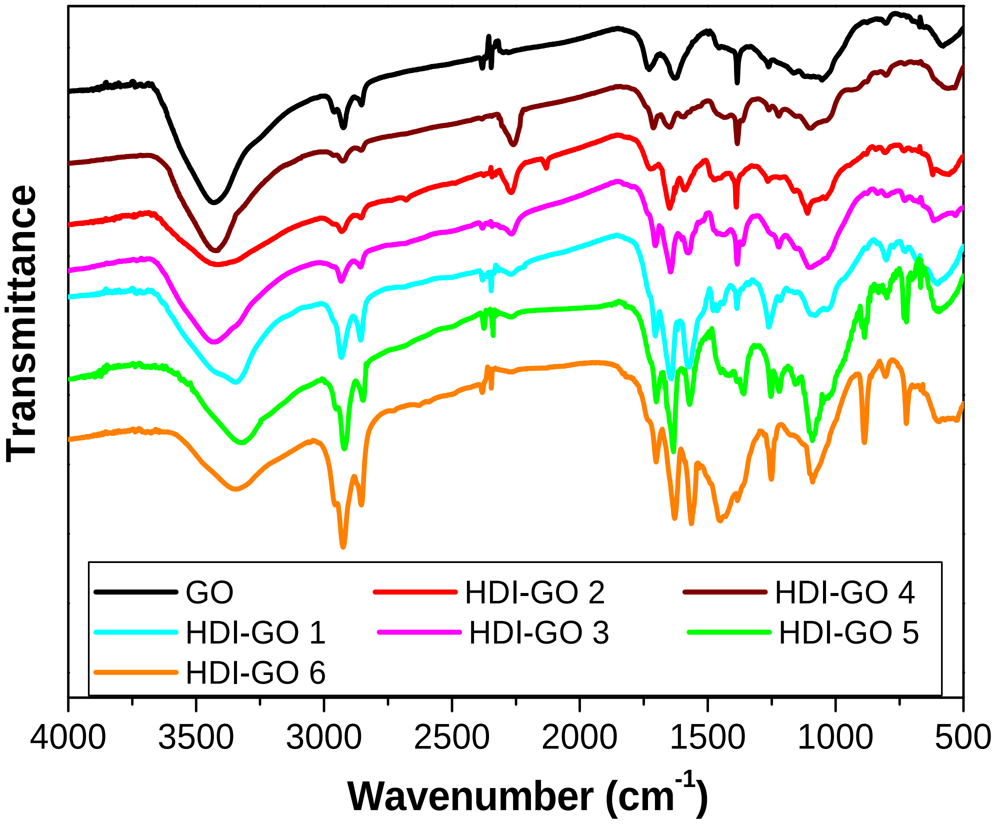


Figure 1. FT-IR spectra of raw GO and the different HDI-GO samples

3. Materials and Methods

2.1. Reagents

Natural graphite was obtained from Bay Carbon, Inc. (Michigan, USA). H_2SO_4, $KMnO_4$, P_2O_5, $K_2S_2O_8$ and H_2O_2 (30 wt % in water) were purchased from Sigma-Aldrich and used as received.

Hexamethylene diisocianate (HDI, >99%, $C_8H_{12}N_2O_2$ M_w = 168.196 g/mol) was acquired from Acros Organics). Triethylamine (TEA, >98%, $N(CH_2CH_3)_3$, M_w = 101.193 g/mol) was obtained from Fluka Analytical. All the organic solvents were HPLC grade and were purchased from Scharlau S.L. Toluene was dried and purified with a MBRAUN solvent purification system. Ultrapure water was obtained from a Millipore Elix 15824 Advantage 15 UV purification system.

2.2. Synthesis of graphene oxide (GO)

GO was prepared using a modified Hummers′ method from flake graphite [3,8]. Briefly, graphite powder, H_2SO_4, $K_2S_2O_8$, and P_2O_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 H_2SO_4, $KMnO_4$ and water in an ice-water bath. Following to dilution with water, excess $KMnO_4$ was decomposed by addition of 30 wt % H_2O_2 aqueous solution and then 5 wt % HCl aqueous solution. 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 vacuum freeze-dried before use.

2.3. Synthesis of hexamethylene diisocyanate-functionalized graphene oxide (HDI-GO)

The whole process was carried out under inert atmosphere of argon in order to avoid contamination during the functionalization reaction. In a typical experiment, GO powder (c.a. 250 mg) was weighed and loaded into a 100-mL round-bottom flask, followed by addition of dried toluene (25 mL) under Ar atmosphere. The suspension was then ultrasonicated in an ultrasonic bath for 2 h; in some experiments, the bath sonication was preceded by probe sonication cycles (5 min on/5 min off, 40% amplitude). The sonication conditions were chosen according to preliminary studies carried out in the group [15]. The GO dispersion was then transferred to a reactor equipped with mechanical agitator, thermometer and reflux condenser. Subsequently, TEA (c.a. 8.75 mL) and HDI (5 mL) were added dropwise via a dropping funnel. The mixture was heated to 60 ºC and stirred at 350 rpm overnight under inert atmosphere. The resultant slurry reaction mixture was then poured into methylene chloride to coagulate the product, and finally filtered, washed thoroughly with methylene chloride and dried under vacuum to yield HDI-GO. A schematic representation of the synthesis procedure of functionalized HDI-GO is shown in **Scheme 1.**

2.4. Instrumentation

FTIR spectra were recorded with a Perkin Elmer Frontier FTIR spectrophotometer equipped with an Attenuated Total Reflection (ATR) sampling accessory. Spectra were recorded at room temperature, in the wavenumber range of 4000-500 cm-1, with an incident laser power of 1 mW and a minimum resolution of 4 cm-1. Prior to the measurements, the powder samples were mixed and ground with KBr, and the mixtures were then pressed into a round transparent pellet in a pellet-forming die.

4. Conclusions

Hexamethylene diisocyante-functionalized graphene oxide (HDI-GO) derivatives with different functionalization degrees have been synthesized following a two-step approach: firstly, GO was prepared using a modified Hummers´ method from graphite, and secondly GO was treated with HDI in the presence of TEA catalyst to yield the modified nanomaterial. The FT-IR and Raman spectra corroborated the success of the reaction and that the functionalization route via carbamate ester formation predominated. Future work will focus on the reaction of HDI-GO with other organic molecules or polymers via the remaining oxygen groups, in order to develop high-performance GO-based nanocomposites.

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Conflicts of Interest: The authors declare no conflict of interest.

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