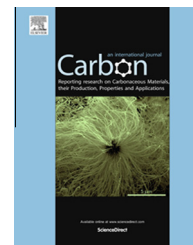


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# Photochemistry of covalently functionalized graphene oxide with phenothiazinyl units

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## ARTICLE INFO

### Article history:

Received 1 December 2013

Accepted 5 March 2014

Available online 13 March 2014

## ABSTRACT

Phenothiazinyl units have been covalently attached to graphene oxide (GO) by nitrene insertion onto C=C bonds. Laser flash photolysis of this material indicates that tethering of phenothiazinyl units to GO enhances significantly the interaction with respect to mixtures of both components, leading to the observation of photoinduced electron transfer.

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## 1. Introduction

Covalent functionalization of carbon nanoforms with organic units or metal complexes is a general methodology to introduce response in a material vs. external stimuli [1]. Covalent derivatization has been extensively used to modify the properties of fullerenes and carbon nanotubes (CNTs) [2]. Considering the remarkable properties of graphene (G)-based materials and their easy availability [3], covalent attachment of responsive units is also of interest in this case to produce modified G materials with enhanced response. Herein, we describe the synthesis and photochemical properties of a modified graphene oxide (GO) having pendant phenothiazinyl units [4]. Considering the large variety of functional groups present in GO, its large reactivity and the easy of reduction, GO is an ideal starting material for covalent functionalization that subsequently can be reduced towards G of similar electrical conductivity as conventional G obtained from Hummers oxidation of graphite, subsequent exfoliation of graphite oxide to GO and final reconstitution. It is known that the quality of reduced G obtained from graphite is lower than G films obtained from CVD, but its availability in large amounts and affordability makes still modified reduced G appealing for a broad range of applications.

Due to its low oxidation potential, phenothiazine and its derivatives are excellent electron donors that have been widely used as electron donor unit in photoinduced electron transfer [5]. Photoinduced charge separation is a phenomenon commonly observed upon photoexcitation of fullerenes [6] and CNTs [7] and it has also been reported to occur for some G materials [8]. Typically, the lifetime of charge separation can be increased if the system comprises units that can trap electrons ( $e^-$ ) or holes ( $h^+$ ) by forming relatively stable radical ions. In view of these precedents, it would be of interest the synthesis of a G material containing phenothiazinyl units to study its photochemical properties.

There are examples in the literature showing that covalent functionalization of G with photoresponsive units leads to materials in which efficient photoinduced electron transfer takes place, generating the corresponding radical ions [8–11]. Considering the high electron mobility in G, photoresponsive modified G can find a wide application in optoelectronics and sensing. The present work reports the preparation of an analogous photoresponsive material based on graphene suited for photoinduced electron transfer due to the excellent electron donor ability of phenothiazinyl.

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<http://dx.doi.org/10.1016/j.carbon.2014.03.011>

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## 2. Experimental

### 2.1. Reagents and techniques

All reagents were purchased from commercial firms and were employed without extra purification. Raman spectra were recorded at ambient temperature with a 514 nm laser excitation on a Renishaw In via Raman spectrometer equipped with a CCD detector. IR spectra were recorded with a Bruker ATR spectrometer. TEM images were recorded in a Philips CM300 FEG system with an operating voltage of 100 kV. XPS spectra were recorded on a SPECS spectrometer equipped with a Phoibos 150 9MCD detector using a non-monochromatic X-ray source (Al and Mg) operating at 200 W. The samples were evacuated in the prechamber of the spectrometer at  $1 \times 10^{-9}$  mbar. The materials were exfoliated in water by ultrasonication of samples at 0.001 mg/ml during 4 h and prior to laser experiences. Laser flash photolysis (LFP) experiments were performed by using a Q-switched Nd:YAG laser (Quantel Brilliant, 355 nm, 20 mJ per pulse, 5 ns fwhm) coupled to a mLFP-111 Luzchem miniaturized equipment. This transient absorption spectrometer includes a ceramic xenon light source, 125 mm monochromator, Tektronix 9-bit digitizer TDS-3000 series with 300 MHz bandwidth, compact photomultiplier and power supply, cell holder and fiber optic connectors, fiber optic sensor for laser-sensing pretrigger signal, computer interfaces, and a software package developed in the LabVIEW environment from National Instruments. The LFP equipment supplies 5 V trigger pulses with programmable frequency and delay. The rise time of the detector/digitizer is  $\sim 3$  ns up to 300 MHz (2.5 GHz sampling). The monitoring beam is provided by a ceramic xenon lamp and delivered through fiber optic cables. The laser pulse is probed by a fiber that synchronizes the LFP system with the digitizer operating in the pretrigger mode. All transient spectra were recorded using 10 mm  $\times$  10 mm quartz cells with a capacity of 4 mL and were bubbled for 30 min with Ar before signal acquisition. The absorbance of the samples was 0.2 (0.001 mg/mL) at the laser excitation wavelength (355 nm).

### 2.2. Synthesis procedures

#### 2.2.1. Delamination of GO

GO was suspended in water (1 mg/mL) and ultrasonicated during 6 h at 25 °C. The whole suspension was then submitted to lyophilisation. This process affords a material that can be suspended better in organic solvents, particularly DMF, and NMP.

#### 2.2.2. Preparation of 1

The reaction is performed at 1 mg/mL (DMF 99.8%) concentration (200 mL) to obtain stable suspensions, under these conditions dimethylamine impurities (40 mg) are responsible of the amine presence in blank material. GO was suspended in DMF (1 mg/mL, 200 mL) and ultrasonicated for 5 h, then N-(2-azidoacetyl)phenothiazine (200 mg) prepared according to the literature [12] were added and the suspension was heated at 130 °C for 24 h with strong stirring observing a color change from brown to black. After this time the solution was cooled to 25 °C. The reaction mixture was filtrated over a Nylon

membrane (0.2  $\mu$ m pore diameter) and washed with DMF (3  $\times$  30 mL). The resulting material was suspended in water by means of ultrasonication and filtrated again. This procedure was repeated 4 more times. Then the remaining materials was suspended in the small quantity of water (100 mL) with ultrasonication and lyophilized to afford 1 as a black powder (180 mg). The corresponding combustion analysis afforded: H: 4.495% C: 50.124% N: 3.283% S: 3.643%.

## 3. Results and discussion

The synthesis of the phenothiazinyl-derivatized G material (1) was carried out as indicated in Fig. 1. The key reaction is the generation of a nitrene intermediate by thermal decomposition [13–15] in DMF of N-(2-azidoacetyl)phenothiazine [12,16,17] (2) that should insert into the C=C double bonds of GO. Nitrene insertion onto C=C double bonds is one of the general reactions used to modify covalently carbon nanoforms and is well documented in the literature [2]. However, in the present case and considering the large variety of functional groups that can be present in GO, the possibility that the nitrene intermediates react with other types of functional groups present in GO besides C=C cannot be ruled out, but would lead in any case to the covalent linkage. Suspensions of GO in DMF were obtained by Hummers oxidation of graphite [18,19] followed by ultrasound exfoliation in this solvent. AFM of the GO sample at this stage showed that the material was constituted by single layer GO in the conditions of covalent functionalization. For the sake of comparison, we prepared a control material 3 in which GO was submitted to the same treatment, but in the absence of N-(2-azidoacetyl)phenothiazine. It should be commented that, unless G films of electronic quality are used, there is no advantage of employing reduced G obtained from graphite, since GO is the precursor of this type of material.

GO and materials 1 and 3 were characterized by combustion chemical analysis (Table 1). In particular, the increase in the S content from GO to 1 was used to quantify the content of phenothiazinyl units that was estimated as 28 wt% that is a remarkably high percentage compared to those loadings for covalent functionalization achieved using G as starting material of in CNTs. Starting from G, loadings of photoactive subunits in the range of 3–7% have been typically reported [9–11] and, with respect to the amount of attached subunits, the strategy based on the use of GO is considerably more advantageous due to its higher reactivity [19]. Interestingly, the S content already present in GO should derive from the large excess of H<sub>2</sub>SO<sub>4</sub> employed in the Hummers oxidation that could remain as –OSO<sub>3</sub>H attached to the GO sheet [20]. It has been found that these –OSO<sub>3</sub>H units are labile and can be removed in part by extensive CH<sub>3</sub>OH washings and G reconstitution [21]. This should be the most likely reason why control material 3 is free from S, since the DMF heating at 130 °C acts apparently as a cleaning process removing the –OSO<sub>3</sub>H groups and leading to G reconstitution, reducing the imperfection in the G sheet. Comparison of material 1 with control 3 suggests that also for material 1 this structure healing should have take place in similar extent leading to detachment of –OSO<sub>3</sub>H groups.

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