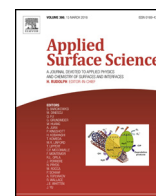




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## Self-propagating solar light reduction of graphite oxide in water

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### ABSTRACT

Graphite Oxide (GtO) is commonly used as an intermediate material for preparation of graphene in the form of reduced graphene oxide (rGO). Being a semiconductor with tunable band gap rGO is often coupled with various photocatalysts to enhance their visible light activity. The behavior of such rGO-based composites could be affected after prolonged exposure to solar light. In the present work, the alteration of the GtO properties under solar light irradiation is investigated. Water dispersions of GtO manufactured by oxidation of natural graphite via Hummers method were irradiated into solar light simulator for different periods of time without addition of catalysts or reductive agent. The FT-IR analysis of the treated dispersions revealed gradual reduction of the GtO with the increase of the irradiation time. The XRD, FT-IR and XPS analyses of the obtained solid materials confirmed the transition of GtO to rGO under solar light irradiation. The reduction of the GtO was also manifested by the CV measurements that revealed stepwise increase of the specific capacitance connected with the restoration of the  $sp^2$  domains. Photothermal self-propagating reduction of graphene oxide in aqueous media under solar light irradiation is suggested as a possible mechanism. The self-photoreduction of GtO utilizing solar light provides a green, sustainable route towards preparation of reduced graphene oxide. However, the instability of the GtO and partially reduced GO under irradiation should be considered when choosing the field of its application.

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### 1. Introduction

Graphite oxide (GtO) firstly synthesized in 1855 [1] has received enormous attention in the recent years due to the fact that this material can be utilized as an intermediate for preparation of novel 2D graphene and graphene-containing heterostructures. Its exfoliated reduced form known as reduced graphene oxide (rGO) is widely used as graphene substitute [2] in order the costly preparation procedures of pure graphene monolayers [3,4] to be avoided. Currently, the synthesis of GtO is mostly carried out via Hummers' [5] and Staudenmayer's [6] routes that offer the advantage of scalable oxidation using cheap natural graphite powder. Although the rGO has more structural defects than non-oxidized graphene which mainly impact its electrical properties [7,8], this material is highly preferred due to the presence of covalently bonded oxygen functionalities on the GtO sheets. The attached carbonyl, carboxyl, epoxy and hydroxyl groups not only increase the interlayer distance between the GtO sheets, but also endow hydrophilic properties of

the atomic thick layers, making them dispersible in water after sonication [9]. Such dispersions with one- or few-layered sheets known as graphene oxide (GO) are often the starting point for reduction and/or functionalization toward specific rGO applications. Graphene-based materials were reported effective as electroactive materials for supercapacitors [10–12] and  $Li^+$  batteries [13], photoactive materials for  $CO_2$  reduction to solar fuels [14–16], various pollutants degradation in combination with  $TiO_2$  [17–20],  $ZnO$  [21],  $CdS$  [22,23], etc.

Characteristic features of the GtO are the lamellar, inhomogeneous and non-stoichiometric structure, which are preserved after the partial removal of the functional groups. Traditionally, the reduction of GtO is performed mainly by: (i) high temperature (up to  $\sim 1000^\circ C$ ) treatment usually in absence of oxygen [24] (ii) chemical treatment with reductive agents such as hydrazine [25], ammonia borane [26], hot sulfuric acid [27], hydroiodic acid [28], etc. Both thermal and chemical reduction routes harvest graphene oxide with high level of deoxygenation and electrical conductivity close to the pure non-oxidized graphene. However, the rapid uncontrollable extend of reduction and the defects created on the graphene sheet (holes, edges), as well as the hazardness of the

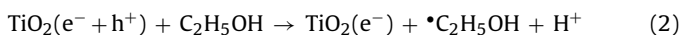
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reagents/wastes and the elevated time and energy costs, triggered the search for alternative eco-friendly reductive techniques.

Lately, reduction of graphene oxide has been achieved by solvo/hydrothermal treatment [29,30], spray pyrolysis [31], supercritical ethanol processing [32], electrochemical reduction [33], nature-based reducing agents like vitamins, plant extracts etc. [34]. Also, rGO have been obtained employing various types of irradiation such as microwave [35,36], far infrared [37], pulsed laser [38,39] irradiation, UV [40,41] and visible [42] light. Besides the green environmental approach, these techniques have the advantage of gradual, controllable reduction of graphene oxide films and suspensions to a desired level and, in case of light assisted reduction, masking/treating of selected areas for manufacture of flexible electronic devices.

In general, the photoreduction strategies have been categorized as: (i) catalytic/catalysts-free photochemical reduction (ii) photothermal reduction (iii) solid state/in-solution laser reduction with the later one being a combination of (i) and (ii) [43]. It has been established that the photoreduction of GO via photocatalysts (semiconductors, metal nanoparticles) or reducing agents (solvents, additives) occurs through photochemical reactions. For example, in presence of photocatalyst  $\text{TiO}_2$  as  $e^-$  donor and ethanol as  $h^+$  scavenger the (1)–(3) photochemical reactions take place [43,44] upon UV irradiation:



Following similar pathway, GO has been reduced under visible light irradiation utilizing the surface plasmon resonance effect of Ag nanoparticles (AgNPs) for  $e^-$  generation and presence of dimethylformamide (DMF) as  $h^+$  scavenger which reduce them back to metallic Ag [42]. In the same work, it was noted that the GO can not be reduced by visible light if one of the components AgNPs or DMF is not present.

In absence of photocatalysts, self-photoreduction of GO under UV light has been performed with assistance of sacrificing agent ( $e^-$  donor) [42] as well as in  $\text{H}_2$  or  $\text{O}_2$  atmosphere at room temperature [41]. It was found that the epoxy (C–O–C) groups can be destroyed by UV light releasing  $\text{O}_2$  and forming large  $\text{sp}^2$  domains. Also, self-photoreduction of free-standing GO films with Xenon lamp providing mainly visible light has been reported [45] where the deoxygenation process was assigned to photothermal reactions. Similarly, paper-like GO has been exposed to sunlight irradiation and bilayer GO/reduced GO structure was obtained due to self-photoreduction of the irradiated side of the paper. It was affirmed that UV part of the solar radiation is critical for the GO photoreduction [46].

In water solutions, the self-reduction mechanism is influenced by the high temperature which increase the dissociation constant creating thus more reactive environment for the deoxygenation, i.e. dehydration of GO [40]. In this case, where UV light and no catalysts/sacrificing agent were employed, the self-photoreduction was attributed to both photothermal and photochemical reactions. Usage of visible light for treatment of water solutions of GO has also been reported, but with addition of triethanolamine as sacrificial  $e^-$  donor, where stable aqueous dispersions of graphene sheets were obtained via photochemical reactions [47].

The above described cases reveal the constantly increasing plethora of pathways for controllable GO photoreduction. The mechanism of this environmentally benign process, as well as the role of the UV, visible or solar (UV and visible) irradiation in absence of photocatalyst or reducing agent are still not well known. Taking into account the estimated 3.2 eV energy threshold for GO reduction and the insufficient energy of the visible light alone to

overcome this threshold [43], it is important to further investigate the process of photoreduction of GO in water dispersion without addition of photocatalyst or sacrificial substance. In addition, undesired reduction of rGO under prolonged solar light irradiation needs to be explored as important stability issue of rGO-containing composites has been raised [48].

In the present work, the partial reduction of GtO under solar light irradiation is investigated. The process was conducted in aqueous solutions without addition of catalysts or sacrificing agent in sealed glass flasks. The alteration of the structural and electric properties of the initial GtO and the irradiated rGO was examined in relation to the illumination time. Mechanism of functional groups removal under solar light is suggested.

## 2. Materials and methods

### 2.1. Materials and preparation of the samples

Graphite oxide was initially prepared by oxidation of graphite. Natural graphite powder briquetting grade 100 mesh, Alfa Aesar 99.9997% was used. For the oxidation, Hummers method was employed that uses a combination of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$  [5]. The slightly modified preparation procedure that was followed in our experiment is schematically presented Fig. 1a. Briefly, 2 g of natural graphite and 1 g of  $\text{NaNO}_3$  (Sigma Aldrich) were mixed with 80 mL of concentrated  $\text{H}_2\text{SO}_4$  (97%, Riedel de Haen) under stirring in an ice bath. Then, 6 g of  $\text{KMnO}_4$  (Sigma Aldrich) were slowly added to the mixture while keeping the temperature at around 10 °C. After the addition of  $\text{KMnO}_4$ , the solution was removed from the ice bath and kept at 35 °C for 90 min under strong stirring. 100 mL of deionized (DI) water were added dropwise causing a rise in temperature. The solution was kept at ~95 °C for 30 min. Then, 90 mL of 3%  $\text{H}_2\text{O}_2$  (Sigma Aldrich) were added. Finally, the solution was diluted by adding a large amount of DI water and left to rest for 24 h. The supernatant was removed and the precipitant was washed with DI water and centrifuged at 3000 rpm repeatedly until pH ~5. Paper-like graphite oxide was obtained by deposition of the GtO slurry on glass surface and drying at room temperature. The material was nominated as sample GtO. Photographs of free-standing GtO paper are given in Fig. 1b–d.

Subsequently, water solutions of GtO with concentration 0.5 mg/mL were prepared using homogenizer “Hielscher” UIP 1000 hd. The duration of the sonication was 20 min and the total energy input was  $E = 0.0041$  kWh. The resulting light brown dispersions were irradiated under stirring in order uniform exposure of the GO sheets to light to be ensured. SUNTEST XLS apparatus with irradiation spectrum similar to the solar and intensity  $765 \text{ W/m}^2$  that is ~8 times higher than the natural solar irradiation for Southern Europe, was employed. Irradiation time between 0.5 h and 30 h was applied. The dispersions were treated in closed flasks to prevent water evaporation. Finally, all the treated solutions were dried at room temperature and the samples obtained were designated as rGO-x, where  $x = 0.5, 2, 10, 15, 20, 30$  according to the irradiation time in hours [h].

### 2.2. Characterization methods

The structural changes in the GtO caused by the solar light irradiation treatment were investigated via X-ray Diffraction analysis, Transmission electron microscopy (TEM), UV-vis, FT-IR, Raman and XPS spectroscopies, while the electrochemical behavior of the initial and the reduced graphite oxide was studied using Cyclic Voltammetry (CV).

The UV-vis absorption spectra of the GtO and the rGO solutions in the 200–700 nm range were recorded using UV-2100 Shimadzu

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