



## Pulsed laser irradiation for environment friendly reduction of graphene oxide suspensions



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### ARTICLE INFO

#### Article history:

Received 5 November 2013

Received in revised form 4 February 2014

Accepted 8 February 2014

Available online 18 February 2014

#### Keywords:

Graphene

Nanostructures

Pulsed laser irradiation

Green synthesis

### ABSTRACT

Graphene oxide (GO) sheets were synthesized through a modified Hummers' method. Using high resolution transmission electron microscopy the thickness of the GO sheets in a multilayer structure of stacked GO sheets was found  $\sim 0.8$  nm. A nanosecond pulsed laser (with wavelength of 532 nm and average power of 0.3 W) was applied for effective and environment friendly reduction of the GO sheets in an ammonia solution (pH  $\sim 9$ ) at room temperature conditions. The deoxygenation of the GO sheets by the pulsed laser reduction method was confirmed by using UV–visible, Fourier transform infrared, X-ray photoelectron spectroscopy (XPS) and thermo gravimetric analysis. Based on XPS analysis, the O/C ratio of the GO sheets decreased from 49% to 21% after 10 min laser irradiation. This reduction efficiency was comparable with the efficiency achieved by hydrazine which yielded the O/C ratio of 15% at 80 °C after 10 min. Using Raman spectroscopy it was found that the pulsed laser reduction method resulted in nearly no aggregation of the reduced GO sheets in the ammonia solution. These results can help to further promotion and application of pulsed lasers in environment friendly reduction of GO.

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### Introduction

Graphene (as a single atomic layer with  $sp^2$ -hybridized carbon atoms in a perfect hexagonal lattice structure) has opened up the possibility of enormous progresses in various fundamental [1–6] and technological [7–13] areas. Hence, environment friendly mass production [14] and consequently high consumption of graphene (especially in bio-nanotechnological fields such as nanomedicine [15,16]) is highly demanded in soon future. One of the most usual methods for mass production of graphene is chemical exfoliation of graphite followed by reduction of the obtained graphene oxide (GO) sheets into reduced graphene oxide (rGO) ones [17–21]. In fact, the graphene oxide synthesized by this method usually contains epoxide and hydroxyl groups on their basal plane, and carbonyl as well as carboxyl groups on their edges [22]. Although, the

chemically synthesized GO sheets show high water-dispersibility, we often require a subsequent reduction to obtain rGO sheets with, e.g., much better electrical conductivity ( $\sim$ five orders of magnitude [23]). At first, GO sheets were reduced by strong chemical reductants such as hydrazine ( $N_2H_4$ ) [24] and sodium borohydride ( $NaBH_4$ ) [25] and/or heating in a reducing ambient [26,27]. However, the high temperatures needed in the thermal reductions (usually  $>500$  °C) restrict applications of this method. On the other hand, the strong chemical reductants, e.g. hydrazine, are known as hazardous agents for human's life and environment. For instance, hydrazine exhibits highly corrosive, explosive and toxic properties [28]. In addition, reduction by hydrazine resulted in formation of  $sp^3$  C–N bonds as disorders on surface of the reduced sheets. Such disorders prevent obtaining graphene sheets with high electrical conductivities [29]. Therefore, achieving environment friendly as well as effective low-temperature methods for reduction of GO is highly demanded, especially in mass production of graphene.

So far, some environment friendly methods for reduction of GO such as flash photo reduction [30], hydrothermal dehydration [31], solvothermal reduction [32], catalytic [33] and photocatalytic

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[34,35] reductions have been suggested as suitable substitutions for the common reduction methods. Moreover, replacing the toxic reductants (e.g., hydrazine) by some green as well as biocompatible reducing agents such as vitamin C (L-ascorbic acid) [36], melatonin [37,38], sugar [39], glucose [40], polyphenols of green tea [41,42], protein bovine serum albumin (BSA) [43], L-glutathione [44], ginseng [45], and even bacteria [46–48] was also proposed for effective reduction of GO. Recently reduction of GO by laser has been also attracted the attention of researchers, because it is not only a safe reduction method, but also a fast one (takes only few minutes) [49]. For example, Abdelsayed et al. [50] developed a facile laser reduction method for synthesis of laser converted graphene from graphite oxide. Huang et al. [51] reported pulsed laser assisted reduction of GO with the electrical sheet resistance ( $R_s$ ) value of 53.8 k $\Omega$ /sq. Zhang et al. [52] reported reduction of patterned graphene oxide microcircuits (down to 39% remaining oxygen groups) by femtosecond laser. They also showed that the electrical resistivity of the graphene microcircuits can be easily adjusted in a certain range by altering the output power of laser. Very recently, Trusovas et al. [53] reported reduction of GO films to rGO ones using picosecond pulsed laser irradiation. Direct formation of graphene through liquid-phase pulsed laser exfoliation of highly ordered pyrolytic graphite was also reported [54]. However, no systematic investigation regarding comparison between the reduction efficacies obtained by the pulsed laser irradiation methods and hydrazine (as a standard and strong chemical reductant) has been reported.

In this work, chemically exfoliated GO sheets suspended in an ammonia solution (pH  $\sim$ 9) were reduced at room temperature condition using nanosecond pulsed laser irradiation (as a fast, facile, and environment friendly method) without any aggregation of the reduced sheets in the solution. The effect of irradiation time on the reduction level of the GO sheets was also studied. Moreover, the reduction efficacy achieved by the pulsed laser irradiation method was compared to the efficacy obtained by hydrazine.

## Experimental

### Synthesis of GO

Graphite flakes (Sigma-Aldrich, cat #332461, 150  $\mu$ m lateral dimensions) were used as the raw materials for synthesis of graphite oxide using a modified Hummers method. Concerning this, at first, 3 g graphite was dissolved in a solution containing 180 mL  $H_2SO_4$  and 20 mL ortho- $H_3PO_4$  to promote the oxidation of the graphite. Then, 18 g  $KMnO_4$  along with 6 g  $KCrO_4$  was added slowly to the mixture. Adding  $KCrO_4$  resulted in more effective oxidation and more hydrophilic graphene oxide with a lower risk of explosion (high concentrations of  $KMnO_4$  in  $H_2SO_4$  ( $\sim$ 7 wt%) can cause explosion upon heating [55]). Although temperature of the exothermic reaction was 40–45  $^\circ$ C, the mixture was heated to 55  $^\circ$ C and stirred for 10 h. Then, the mixture was cooled to room temperature followed by cooling in an ice bath. The reaction was completed by adding 6 mL  $H_2O_2$  (30%) into the mixture. The solution was centrifuged at 6000 rpm for 6 h to eliminate the supernatants. The remaining solid material was washed by 250 mL distillate water (with resistivity  $>$ 18 M $\Omega$ -cm) three times, 250 mL of HCl (30%) one time, and 250 mL ethanol two times. Each washing process was completed by centrifuging at 6000 rpm for 20 min, and removing the supernatants. Then, the obtained materials were dispersed in distillate water and sonicated at power of 260 W for 4.5 h. Then the sonicated aqueous suspensions were again centrifuged at 6000 rpm for 5 h and the supernatants were removed. Then the obtained materials were coagulated with 150 mL di-ethyl ether and filtered by using a poly tetrafluoroethylene membrane (0.45  $\mu$ m pore size).

The filtered materials were dried in a vacuum oven at pressure of 35 mmHg and temperature of 65  $^\circ$ C overnight.

### Pulsed laser reduction of GO

For reduction of GO suspension by laser irradiation, 1 g of the prepared GO powder was dispersed in 50 mL conc. ammonia solution (pH  $\sim$ 9) and the suspension was sonicated for 60 min. pH of the solution was determined using a S-3C model pH meter (Shanghai Precision Scientific Instrument Co.). An ND:YAG pulsed laser system (Quantel, Brilliant b class4 with 532 nm wavelength, 5 ns pulse duration, 10 Hz repetition rate, 0.3 W power, and 300 mJ maximum pulse energy in 7 mm beam diameter) was applied at its second harmonic for reduction of the GO suspension at room temperature condition. The laser beam was directed towards a quartz tube containing 12 mL GO suspension stirred using a magneto stirrer without using any focusing lens to obtain a large irradiation area. The total time of laser irradiation was considered 3, 5, 7 or 10 min, so that the temperature of the quartz tube containing the suspension showed no significant change. To compare the reduction efficacy of the pulsed laser irradiation method with that of hydrazine (as a common and standard reducing agent), the GO suspension was also reduced by hydrazine (with 5 mM concentration) at 80  $^\circ$ C for 10 min. The ammonia solution was also used to adjust the pH of the hydrazine-rGO suspension to  $\sim$ 9.

### Material characterization

High-resolution transmission electron microscopy (HRTEM, FEI Tecnai F30) was employed to study the morphology of the graphene sheets. Optical absorption spectra were recorded using a Perkin Elmer UV-vis spectrometer. Fourier transform infrared (FTIR) spectra were acquired on a Nicolet 6700 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was utilized to study the chemical state variations of the GO sheets under applying the pulsed laser irradiation. The data were obtained through a hemispherical analyzer supplied by an Al  $K\alpha$  x-ray source ( $h\nu = 1486.6$  eV) operating at a vacuum better than  $10^{-7}$  Pa. For quantitative analyses, the XPS peaks were deconvoluted by using Gaussian components after a Shirley background subtraction. Quantitative elemental compositions were obtained based on peak area ratio of the XPS core levels modified by the sensitivity factor of each element in XPS. Thermo gravimetric analysis (TGA) were performed simultaneously using a SDT Q600 under  $N_2$  flow rate of 40 mL/min and heating rate of 5  $^\circ$ C  $min^{-1}$ . Raman spectra were acquired using a Dispersive Raman Microscope Senterra-2009 at excitation wavelength of 785 nm. To study current-voltage ( $I$ - $V$ ) properties of the graphene sheets, they were deposited (through drop-casting the desired graphene suspension) between two Au electrodes (coated on a  $SiO_2$ (300 nm)/Si(100) substrate by using electron-beam evaporation). The thickness and width of the electrodes were about 200 nm and 120  $\mu$ m, respectively. The average distance between the electrodes was  $\sim$ 0.5  $\mu$ m. After graphene deposition, the samples were heated in a vacuum ( $\sim$ 0.8 Pa) at 250  $^\circ$ C for 30 min. The number of graphene sheets randomly deposited between the two Au electrodes was counted by using an optical microscope. The data of  $I$ - $V$  curves were gathered by using a Keithley 485 Autoranging Picoammeter. A SEM image concerning the electrodes and some graphene sheets located between them was previously presented elsewhere [23].

## Result and discussions

Morphological and structural features of the synthesized GO powders were investigated by HRTEM. Fig. 1 shows the TEM image

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