Pulsed versus continuous-wave Laser deoxygenation of graphene oxide suspensions

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Abstract. We report on a comparative study of laser deoxygenation of graphene oxide (GO) suspensions in pure water (pH ∼ 7) using pulsed (nanosecond with wavelength 532 nm and fluence ~ 0.15 J/cm²) and continuous-wave (CW) (of wavelength 448 nm and power density ~ 0.25 MW/cm²) lasers at room temperature. Such comparison was not performed previously for GO suspensions. Concentrated GO colloidal suspensions were prepared by a modified Hummer’s method. The presence of oxide groups in GO was proved using X-ray diffraction and Fourier transform infrared (FTIR). The laser deoxygenation processes were verified by means of UV-visible, FTIR and micro-Raman spectroscopies. The impact of changing the laser irradiation time for both lasers has been investigated using the characteristic Raman bands (D and G) of GO as markers to assess the degree of reduction as well as the structural defects of the resulting laser RGO.

Keywords: Graphene oxide suspensions, laser reduction, Raman spectroscopy, reduced graphene oxide

1. Introduction

Graphene oxide (GO) is one of the most significant graphene byproducts utilized for mass production of graphene [1-4]. Its structure is like a graphene and characterized by a random allocation of oxygen functional groups attached at sp³ hybridized carbon atoms (C-sp³) in what is called oxidized area. Merged with this region are non-oxidize domain constituted by hydrophobic π-conjugated C-sp². The former region contains epoxy and hydroxyl groups at the basal planes, while edges are linked to carboxyl and carbonyl groups [5]. This structure of GO makes it poor electrical conductivity that restricts its applications in microelectronics. Deoxygenation of GO affords another pathway to graphene-like sheets [6]. GO can be reduced chemically with reducing agents [7] or through annealing at relatively high temperatures [8], as well as using photo-thermal reduction, or elective reduction by straightforward laser writing [9, 10]. Selection of the reduction method of GO is decisive where it determines the properties of the resultant reduced graphene oxide (RGO) material [11].

The laser deoxygenation of GO allows creation of conductive domains with improved optical properties, which can be appropriate in photo-electronics devices, such as in organic photovoltaic devices, and biological sensors etc. [12-15]. As well, laser reduction of GO is appealing owing the ability to control the extent of reduction process depending on the experimental parameters as GO concentration and irradiation conditions. In addition, this method has an advantage like other photo-irradiation processes, that it does not depend on utilizing chemicals or high temperatures. The production of a homogeneous colloidal suspension of electrically and thermally conductive graphene sheets in solvents that allows their broad use for both essential examination and in applications is a basic interest [16-19]. However, studies concerning the use of lasers in the reduction processes of GO suspensions are mainly through pulsed laser of high power [20, 21]. Continuous-wave (CW) laser never used before in the reduction process of GO suspensions [22].

In this work, we provide visible laser reduction of GO suspensions by both pulsed and CW laser. The method offers a suspension production of individual RGO sheets in water under ambient conditions. The structure of GO was investigated and characterized using X-ray diffraction (XRD), UV-Vis, Fourier transform infrared (FTIR) spectroscopy as well as micro-Raman spectroscopy. Micro-Raman spectroscopy is a powerful
technique for studying crystallographic defects and local stress distribution [23, 24]. Also this spectroscopy is omnipresent technique for examining sp² domain size of GO, lattice order, functionalization, and sheet-stacking arrangement [25]. Therefore, we have employed Raman spectroscopy to assess and compare the impact of irradiation time on the reduction process by both pulsed and CW lasers

2. Experimental

2.1 GO preparation

Modified Hummer’s method was used to prepare GO [26]. In a typical method, 46 mL of concentrated H₂SO₄ was mixed up with 1 g graphite powder with stirring in an ice bath. To fix the mixture temperature lower than 20 °C, the oxidizing agent KMnO₄ (3.0 g) was added bit by bit under strong stirring. Consecutively, the ice bath was removed, and the reaction system was vigorously stirred for 0.5 h at about 35 °C. Next, 100 mL water was added gently, and the solution was stirred for 15 min at 95 °C. Then, the solution was poured into 250 mL water followed by a dropwise addition of 5 mL H₂O₂ (30%), changing the color of the solution from dark brown to yellow brown. The suspension was held uninterrupted overnight where GO precipitated. The washing stage starts with removing excess metal ions by adding 1:9 HCl aqueous solution (250 mL) to the precipitated GO and centrifuged at 7000 rpm. Recurrent washing using distilled water was performed until the pH was ~7. The resulting GO precipitates were dried at room temperature for 24 h.

2.2 Laser reduced GO

A yellow homogeneous dispersion of GO was obtained by sonicating 1 mg of dried GO powder in 10 mL of deionized water. Two experiments for GO suspension irradiation were conducted using two different lasers. The first is a second harmonic (λ= 532 nm) pulsed Nd/YAG laser of pulse width 9 ns and repetition rate = 20 Hz at low pulse fluence ~ 0.15 J/cm² whereas the second is a CW laser of λ= 448 nm at power density 0.25 MW/cm². The irradiation time (τ) varies according to the laser used, starting at 5 up to 60 minutes for 532 nm lasers, while for 448 nm laser the irradiation time begins at 60 minutes up to 300 minutes.

2.3 Characterization

XRD pattern of GO was collected at room temperature by a Philips diffractometer (X’pert MPD) using Cu Kα (λ= 1.54 Å) radiation source. Absorption spectra were picked up employing UV-Vis spectrophotometer. Oxidation and deoxygenation processes were assessed by FT-IR spectroscopy using Bruker alfa II system in the range 500 to 4000 cm⁻¹ in the transmission mode by the aid of KBr (IR grade). The structures of the GO and RGO were studied by micro-Raman spectroscopy (LabRam HR Evolution-Horiba spectrometer) using 532 nm laser line as an excitation source.

3. Results and Discussion

The XRD pattern (Lorentzian fit) of the dried GO powder is shown in Fig. 1. The diffractogram shows a sharp peak centered at 2θ = 11.5°, which is a characteristic peak of GO corresponding to the (001) inter-planar (d) spacing of 7.69 Å calculated by Bragg’s equation. This value of interlayer distance is larger than twice of the original graphite (3.34 Å) [27]. This increase of inter-planar distance is attributable to the entrapping of oxygen functional groups between the graphene oxide sheets confirming the oxidation process [28]. The broad peak centered around 2θ = 26° can be attributed to the residual non-oxidized graphite, while the weak peak centered at 20 = 42° is related to the in-plan crystallinity.

Figure 2 (a – c) shows the UV–vis spectra of unirradiated, CW laser irradiated (τ = 300 min) and pulsed laser irradiated (τ = 60 min) GO suspensions, respectively. The position of the absorption peak of the spectra is deemed as an indication of the deoxygenation degree. The π → π* transition in the aromatic bands is clearly observed in the GO suspension spectrum through the strong absorption peak at ~231 nm [29]. Also, the existence of the carbonyl groups is verified by the obvious shoulder at about 300 nm corresponding to n → π* transitions. The laser irradiation provokes a reclamation of the electronic conjugation inside the RGO sheets.
This is in harmony with the change in color of the suspension from yellow for the GO to black for the CW and pulsed laser-RGO obtained after 300- and 60-min irradiation respectively, as displayed in the inset of Figure 2. Also, the red shift of the strong absorption peak from 231 to $\sim 261$ nm is caused by further $\pi - \pi^*$ transitions in the aromatic bands of the restored sheets which has become in need to less energy for the electronic transition. Furthermore, the disappearance of shoulder peak ($\sim 300$ nm) in the spectra of the laser irradiated suspensions indicates the elimination of the carbocyclic and carbonyl groups from the surface of the laser irradiated GO sheets.

Figure 3 shows FT-IR spectrum of GO (a) together with those spectra of RGO under the influence of laser irradiation with CW laser for 300 min (b) and pulsed laser for 60 min (c). The GO spectrum reveals a clear existence of oxygen containing functional groups as an evidence of the successful oxidation process. The characteristic bands include a broad peak at $\sim 3420$ cm$^{-1}$ corresponding to the stretching of OH group [31], a strong band at 1725 cm$^{-1}$ related to the C=O stretching vibrations of the carboxyl groups, and the C$\equiv$O stretching of epoxide group at 1178 and1079 cm$^{-1}$ [32]. The band which reflects the C=C stretching in graphene structure appears at 1630 cm$^{-1}$. The intensity of this band relative to the intensities of the characteristic bands corresponding to oxygen functional groups can be used to assess the deoxygenation process [31]. Most of these bands have entirely disappeared from the spectra of suspensions treated with both lasers at the specified irradiation time used for each as shown in Fig. 3 (b & c). Such results confirm the significant deoxygenation of GO following pulsed as well as CW laser irradiation under the previously mentioned conditions.

The Raman spectrum of GO in the range 1100 – 1800 cm$^{-1}$ is displayed in Fig. 4a. This spectrum shows the characteristic first order peaks (G and D bands) of the exfoliated GO. The one-phonon process of $E_{2g}$ optical phonon known as G - band is attributed to the in-plane vibration of the C atom sp$^2$ network [33]. While the D-band is a breathing mode of $A_{1g}$ symmetry induced by structural sp$^3$ defects [34]. The G-band appears at 1588 cm$^{-1}$ which is broadened and blue-shifted from that of the graphite G-band shown in the inset of Fig. 4. The D-band that be seen at $\sim 1350$ cm$^{-1}$ has a considerably higher intensity and broadening relative to that of graphite. The considerable broadening of the apparent G band could be referred to the existence of an overlapped defect activated band D'. This band has been ascribed to phonon confinement effect provoked by defects. Besides the D to G (actual band) intensity ratio ($I_D/I_G$) which is $\sim 0.14$ for graphite increases to be $\sim 1.43$ for GO. These pronounced variations are related to significant defects and structural disorder caused by various oxygen functional groups present in the basal plane and terminating the edges.
Fig. 3 FTIR spectra of (a) unirradiated, (b) CW laser irradiated ($\tau = 300$ min) and (c) pulsed laser irradiated ($\tau = 60$ min) GO

The Raman spectrum of the 448 nm CW laser irradiated GO ($\tau = 300$ min) is presented in Fig. 4b. The spectrum shows a stronger and little resolved G – band ($\sim 1580$ cm$^{-1}$) relative to that of GO without noticeable narrowing of the apparent band. This slight resolution allows a weak appearance of the $D'$ band as a broad shoulder that indicate a small reduction of the width of the G band. The D-band also appears around 1350 cm$^{-1}$ with reasonable intensity; however, $I_D/I_G$ decreases to be $\sim 0.96$. Figure 4c shows the Raman spectrum of GO irradiated with 532 nm pulsed laser ($\tau = 60$ min). There is a clear narrowing of the G band with further red shift ($\sim 1575$ cm$^{-1}$) allows the observation of $D'$ as a small shoulder around 1610 cm$^{-1}$. Furthermore, a pronounced reduction of D band width and intensity is observed in the Raman spectrum shown in Fig. 4c, where the ratio $I_D/I_G$ decreases to be $\sim 0.4$. Generally, the narrowing of G band and D bands point to the existence of fewer defects in the structure because of lower oxygen content [35]. The intensity ratio $I_D/I_G$ is used as a quality assessment of the of the graphitic structures, it reflects how extent is sp$^2$ domain. The variation of this ratio as a function of irradiation time $\tau$ for pulsed and CW laser irradiated GO are shown in Figure 5 (a & b) respectively. The continuing decrease of this ratio with increasing $\tau$ implies expansion of sp$^2$ domain which indicates more conversion of GO into graphene [36].
Fig. 4 Raman spectra of (a) unirradiated, (b) CW laser irradiated (τ = 300 min) and (c) pulsed laser irradiated (τ = 60 min) GO (the inset is the Raman spectrum of graphite)

Figure 5 The variation of $I_D/I_G$ ratio as a function of irradiation time for pulsed (a) and CW (b) laser irradiated GO

4. Conclusion

In conclusion, CW laser (448 nm) of relatively low power density (0.25 MW/cm$^2$) as well as pulsed laser (532 nm) of least pulse fluence (0.15 J/cm$^2$) used in this study can deoxygenate GO suspensions. The results of UV-Vis as well as FTIR reveal that under these conditions the deoxygenation process of GO using CW laser needs irradiation period up to 300 min to produce comparable results to those obtained using pulsed laser of 60 min irradiation time. However, Raman spectroscopy offers other comparisons to distinguish between RGOs produced due to irradiation by both lasers through their structural properties. The larger drop in $I_D/I_G$ in case of pulsed laser reduced GO may be an indication to more efficient conversion of GO into graphene. More Raman investigations regarding comparing crystallite size, defect density and type of defects of the RGO suspensions formed by these lasers are going to be presented in the forthcoming work.

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