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Infrared reduction, an efficient method to control the non-linear optical property of graphene oxide in femtosecond regime

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Abstract

Graphene Oxide (GO) has been prepared by modified Hummers method and it has been reduced using an IR bulb (800-2000 nm). Both as grown GO and reduced graphene oxide (RGO) have been characterized using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Raman spectra shows well documented D-band and G-band for both the samples while blue shift of G-band confirms chemical functionalization of graphene with different oxygen functional group. The XPS result shows that the as-prepared GO contains 52% of sp^2 hybridized carbon due to the C=C bonds and 33% of carbon atoms due to the C-O bonds. As for RGO, increment of the atomic % of the sp^2 hybridized carbon atom to 83% and rapid decrease in atomic % of C=O bonds confirm an efficient reduction with infrared radiation. UV-Visible absorption spectrum also confirms increment of conjugation with increased reduction. Non-linear optical properties of both GO and RGO are measured using single beam open aperture Z-Scan technique in femtosecond regime. Intensity dependent non-linear phenomena are observed. Depending upon the intensity, both saturable absorption and two photon absorption contribute to the non-linearity of both the samples. Saturation dominates at low intensity (~ 127 GW/cm^2) while two photon absorption become prominent at higher intensities (from 217 GW/cm^2 to 302 GW/cm^2). We have calculated the two-photon absorption co-efficient and saturation intensity for both the samples. The value of two photon absorption co-efficient (for GO~ 0.0022-0.0037 cm/GW and for RGO~ 0.0128-0.0143 cm/GW) and the saturation intensity (for GO~57 GW/cm^2 and for RGO~ 194GW/cm^2) is increased with reduction. Increase in two photon absorption coefficient with increasing intensity can also suggest that there may be multi-photon absorption is taking place.

Keyword: Graphene Oxide, Reduced graphene oxide, optical nonlinearity, femtosecond z scan.

1. Introduction

Graphene, two-dimensional nanostructure of carbon, has become a potential candidate in photonics [1] and optoelectronic [2] application for its unique linear and non-linear properties [3], broadband absorption and band filling effect [4]. However Graphene oxide (GO), an important member of grahene family, which can be thought of as pristine graphene decorated with chemical functionalization possesses non-linear optical property [5]. GO have attracted much attention due to the ease of making procedure [6] and potential for being used in laser and photovoltaic applications due to its unique electrical and optical properties [7,8]. Complete reduction of GO can lead to the physical structure of graphene [9].In this paper, we have used a green reduction technique to manipulate the nonlinear property of GO.

We use novel infrared (IR) induced reduction technique to prepare the samples, because it is a relatively slow process allowing us to measure easily the optical nonlinearity at each step. Chemically synthesized GO sample has been used to prepare various RGO samples with increasing degree of reduction. Nonlinear absorption properties of these samples measured by femtosecond z scan.

2. Experimental Section

An aquaous solution of graphene oxide (GO) is made from graphite powder using oxidation, sonication and centrifugation by following modified Hummer's method [10]. GO concentration is kept at 0.8 mg/ml.Reduced graphene oxide (RGO) has been produced by incubating the GO solution with exposure of a broadband IR

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source (800-2000nm). Distance between the GO solution and the IR-source is kept at 5 cm with exposure time of 180 min at an intensity of 0.64 W/cm^2 [8].

The samples are characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe II,ULVAC-PHI, INC., Japan) and UV-Visible absorption spectroscopy (Perkin ElmarLamda-900) to verify the degree of reduction of GO. Non-linear optical measurement is carried out by single beam z scan measurement [11]. Open aperture z-scan measurement is performed with laser pulse of 150 fs at 1 kHz repetition rate at wavelength of 808 nm. GO in aqueous dispersion has been taken into 1 mm path length quartz cuvette. Laser spot is focused at the beam waist of 58 μm with a 20 cm plano-convex lens. GO Dispersion kept in the cuvette is moved across the focus through a motorized delay stage (Thorlab, LTS-150). Rayleigh range (z_0) is 1.13 cm which is much greater than the path length. Input pulse power has been varied with the combination of half-wave plate and a plate polarizer. Reference and the transmitted laser pulses area detected with two Si-photodiode. Data is taken through a lock-in amplifier for better signal to noise ratio. Lock-in amplifier is triggered with 1kHz signal from SDG. Schematic of the experimental set up is shown in figure 1.

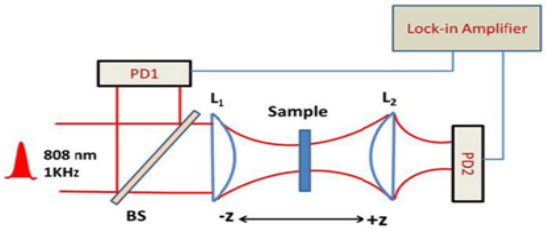


Figure 1. Schematic diagram for z scan experiment

3. Results and Discussion

X-ray photoelectron spectroscopy (XPS) data for GO and RGO is shown in figure 2. The de-convoluted peaks of the C1s spectra from XPS for as-prepared graphene oxide is attributed to C=C/C-C bonds (284.6 eV), epoxy (C-O)/hydroxyl (C-OH) bonds at 286.6 eV, carbonyl (C=O) bonds at 287.9 eV and carboxyl (C (=O)-OH) bonds at 289.2 eV. The result shows that the as-prepared GO contains 52% of sp2 hybridized carbon due to the C=C bonds and 33% of carbon atoms due to the C-O bonds. As for RGO, increment of the atomic % of the sp^2 hybridized carbon 83% and rapid decrease in atomic % of C=O bonds confirm an efficient reduction with infrared radiation.

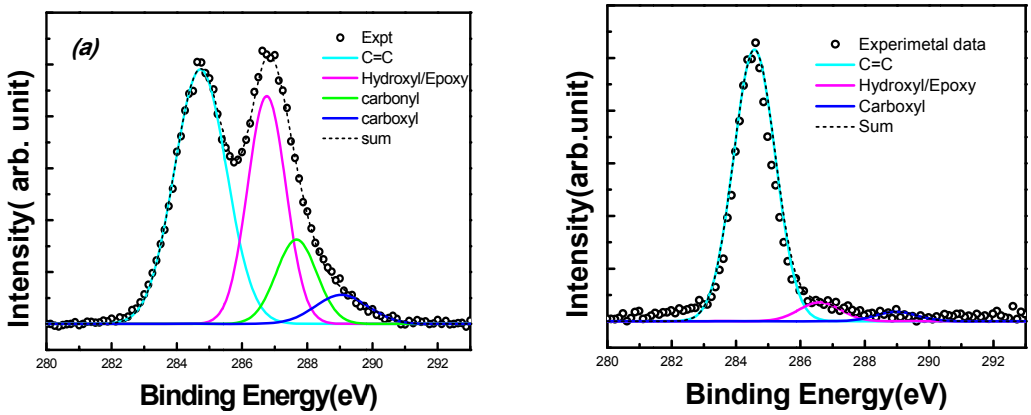
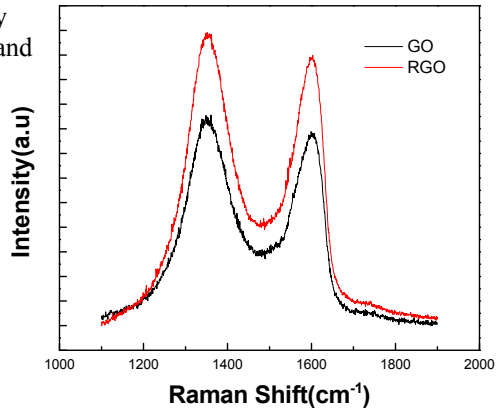


Figure 2. (a) High–resolution C1s XPS spectra of as-synthesized GO (b) High–resolution C1s XP spectra of RGO

Raman spectra shows well documented D-band and G-band for both the samples while blue shift of G-band confirms chemical functionalization of graphene with different oxygen functional groups [12]. D-band and G-band of GO are observed at 1350 cm^{-1} and 1600 cm^{-1} respectively. The intensity ratio of D band and G band (ID/IG) remains almost constant from GO to RGO which may be attributed to removal of oxygen functional group as well as the evolution of C-atoms in the form of CO_2.



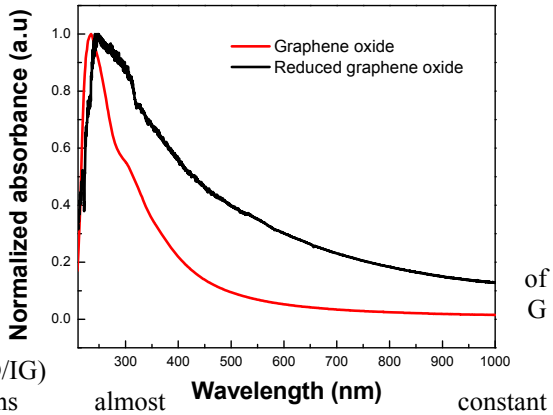


Figure 3. Raman spectra of GO and RGO pumped at 514 nm Figure 4. UV-VIS absorption spectra for GO and RGO

The results of UV-VIS absorption measurement for GO and RGO are shown in figure 3. Absorption peak of as prepared GO at 230 nm is attributed to plasmonic π-π* transition of C=C bond. But for RGO this peak is red shifted and overall absorption is also increased which suggest restoration of electronic conjugation.Non-linear optical measurement is carried out by single beam z scan measurement. Open aperture z-scan measurement is performed with laser pulse of 150 fs at 1 kHz repetition rate at wavelength of 808 nm coming out from a Ti:Sapphire mode-locked laser. Aqueous dispersion of GO and RGO has been taken into 1 mm path length quartz cuvette. Laser spot is focused at the beam waist of 58 μm with a 20 cm plano-convex lens. Open aperture (OA) z scan is performed on GO and RGO in four different input intensities, 127 GW/cm^2, 217 GW/cm^2, 255 GW/cm^2 and 302 GW/cm^2. Intensity dependent non-linear phenomena are observed. Depending upon the intensity, both saturable absorption and two photon absorption contribute to the non-linearity of both the samples.

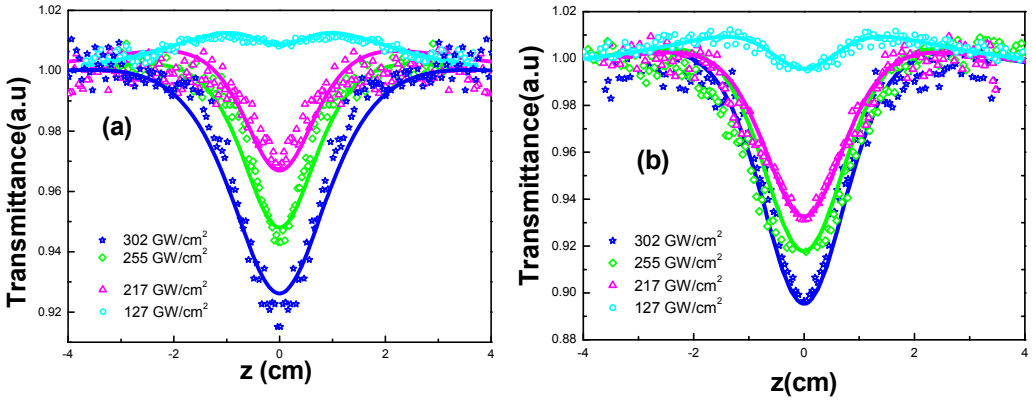


Figure 5. OA z scan curve for (a) GO and (b) RGO

Saturation dominates at low intensity (~ 127 GW/cm^2) while two photon absorption become prominent at higher intensities (from 217 GW/cm^2 to 302 GW/cm^2). Experimental data have been fitted with considering both saturation and two photon absorption in the total absorption coefficient,

where, I_{Sat} is the saturation intensity and β_{eff} is the two photon absorption coefficient. The transmittance of the incident power of laser beam is obtained by solving the intensity equation with the intensity dependent absorption coefficient and it is fitted with the experimental curve. From the fitted parameters, we have calculated the two-photon absorption co-efficient and saturation intensity for both the samples. The value of two photon absorption co-efficient (for GO~ 0.0022-0.0043 cm/GW and for RGO~ 0.0128-0.0143 cm/GW) and the saturation intensity (for GO~57 GW/cm^2 and for RGO~ 194GW/cm^2) increase with reduction. Increase in two photon absorption coefficient with an increase in the intensity also suggests the possibility of multi-photon absorption.

4. Conclusion

GO is efficiently de-oxygenated to obtain RGO by irradiation of IR beam. Reduction is confirmed by high resolution XPS measurements. Optical nonlinearity of GO reduced at different degrees are measured by open aperture Z-scan with a femtosecond laser pulse at 808nm. Saturation power and two-photon absorption coefficients are determined and are found to increase with the degree of reduction.

5. References

(1) Bonaccorso,F.; Sun,Z.; Hasan, T. and Ferrari, A.C. Graphene Photonics and Optoelectronics. *Nat. Photonics* 2010, 4, 611-622.

(2) Bao,Q. and Loh,K.P. Graphene photonics, plasmonics, and broadband optoelectronic devices. ACS nano 2012, 6, 3677-3694.

(3) Zhang, H., Virally, S., Bao, Q., Ping, L.K., Massar, S., Godbout, N. and Kockaert, P. Z-scan measurement of the nonlinear refractive index of graphene. Optics letters 2012,37,1856-1858.

(4) Liu, Z.; Wang, Y.; Zhang, X.; Xu, Y.; Chen, Y. and Tian, J. Nonlinear Optical Properties of Graphene Oxide in Nanosecond and Picosecond Regimes. *Appl. Phys. Lett.* 2009, 94, 021902.

(5) Lim, G.K.; Chen, Z.L.; Clark, J.; Goh, R.G.; Ng, W.H.; Tan, H.W.; Friend, R.H.; Ho, P.K. and Chua, L.L. Giant broadband nonlinear optical absorption response in dispersed graphene single sheets. Nature photonics, 2011, 5, 554-560.

(6) Loh, K. P.; Bao, Q.; Eda, G. and Chhowalla, M. Graphene Oxide as a Chemically Tunable Platform for Optical Applications. Nat. Chem. 2010, 2, 1015-1024.

(7) Jung, I.; Dikin, D.A.; Piner, R.D. and Ruoff, R.S. Tunable Electrical Conductivity of Individual Graphene Oxide Sheets Reduced at Low Temperatures. Nano Lett. 2008, 8, 4283-4287

(8) Maiti, R.; Midya, A.; Narayana, C. and Ray, S. K. Tunable Optical Properties of Graphene Oxide by Tailoring the Oxygen Functionalities using Infrared Irradiation. Nanotechnology. 2014, 25, 495704.

(9) Pei, S. and Cheng, H.M. The reduction of graphene oxide. Carbon 2012, 50, 3210-3228.

(10) Hummers, J.; William, S. and Offeman, R. E. Preparation of Graphitic Oxide. J. Am. Chem. Soc. 1958, 80,1339-1339.

(11) Sheik-Bahae, M.; Said, A.A.; Wei, T.H.; Hagan, D.J. and Van Stryland, E.W. Sensitive Measurement of Optical Nonlinearities Using a Single Beam. IEEE J. Quantum Electron. 1990, 26, 760-769.

(12) Kang, H.; Kulkarni, A.; Stankovich, S.; Ruoff, R.S. and Baik, S. Restoring Electrical Conductivity of Dielectrophoretically Assembled Graphite Oxide Sheets by Thermal and Chemical Reduction Techniques. Carbon. 2009, 47, 1520-1525.