

Investigation on photoluminescence emission of (reduced) graphene oxide paper

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Abstract. In order to contrastively investigate optical properties of graphene oxide (GO) and reduced graphene oxide (rGO) paper, GO is prepared by improved Hummer method and controlled reduced using hydration hydrazine to obtain good dispersive rGO in organic solvent. Finally, GO and rGO paper are obtained by vacuum filtration method. Samples morphology and optical properties are analyzed by scanning electron microscopy (SEM) images, Raman spectra, absorbance spectra and photoluminescence (PL) spectra. Results indicate that there are large numbers of localized states in both GO and rGO paper, and optical gaps of two samples are 0.62 eV. In PL spectra of GO paper, we observe three emission peaks at 565, 578 and 608 nm, respectively whose intensity decreases evidently after reduced, which is due to the decrease of oxide functionalized groups and expansion of sp^2 clusters. PL emission will gradually decrease during GO are reduced.

1. Introduction

Graphene has attracted a lot of research interest since its discovery in 2004 [1]. As a semiconductor material with zero band gaps, it has excellent mechanical, thermal, optoelectronic property, superior electrical conductivity and special electron transport property. It possesses many important applications in field effect transistor, photovoltaic cells, liquid crystal display, nanocomposite materials, field emitter, sensors, and save energy materials *etc* [2]. For optical properties, Bao et al. [3] reported that, compared with the traditional semiconductor material, single-layer graphene has lower light absorbance saturation and higher light carrier density. This means that it is very easy to attain saturation under illumination from visible to infrared light wave band, which can be used as saturated absorption layer of fiber laser device to produce ultra-quick laser.

Graphene oxide (GO) is a graphene sheet modified with oxygen functional groups [4], it exhibits interesting steady-state photoluminescence (PL) properties [5-7]. Such as, Luo et al. [8] reported the visible light band from solid GO and discussed its possible band gap mechanism. Eda et al. [9] observed a narrow peak at 390 nm and a similar peak at 440 nm in PL spectra of GO prepared by chemical method. Mei and Zhang [10] synthesized GO sheets with strong PL and proposed a fluorescence on-off mechanism. In addition, PL can also be observed in chemical decoration GO [11].

Generally, optical properties of materials are closely related to their structures and component. Both GO and reduced graphene oxide (rGO) mainly contained carbon functional groups related to sp^2 (graphite) and sp^3 (oxide functional groups). At the same time, the sp^3 carbon regions divide the graphite into sp^2 carbon clusters with different sizes and shapes, and wraps the sp^2 clusters to make them localized. GO has similar structures with amorphous carbon, while the atoms used to form hybrid sp^3 functional groups are different. In GO and rGO, each carbon atom in the lattice has a π



orbital that contributes to a delocalized network of electrons. At present, properties of GO and rGO raw materials have been gradually mastered. So we want to comparatively investigate optical properties of GO and rGO paper. GO and rGO paper are synthetic material based on graphite raw materials. They have light weight, good strength and high hardness. In addition, they have better flexibility than steel, and they are also environmentally friendly materials.

In this paper, GO is prepared by improved Hummer method and controlled reduced using hydration hydrazine to obtain good dispersive rGO in organic solvent. Finally, GO and rGO paper are obtained by vacuum filtration method. The morphology and optical properties are analyzed by using scanning electron microscopy (SEM) images, Raman spectra, absorption spectra and PL spectra.

2. Experimental details

Native graphite powder (3 g) is mixed with concentrated H_2SO_4 (12 mL), $\text{K}_2\text{S}_2\text{O}_8$ (2.5 g), and P_2O_5 (2.5 g), and then incubated at 80 °C for 5 h. The product is cooled to room temperature and diluted with deionized water and then set aside for one day. The mixture is filtered using 0.45 μm microspores to remove the remaining acid and dried in vacuum at room temperature to get a preoxidized graphite powder. The preoxidized graphite powder is placed in concentrated H_2SO_4 (120 mL) at 0 °C and stirred quickly. KMnO_4 (15 g) is added gradually with stirring while keeping the temperature of the mixture below 20 °C. The mixture is dispersed into 250 ml of water and then stirred at 35 °C for 2 h, followed by the addition of water (700 mL) and 30% H_2O_2 (20 mL), and stir for 2 h. The GO brilliant-yellow mixture is filtered and washed with 10 wt.% HCl aqueous solution (1000 mL) to remove metal ions and wash repeatedly with H_2O to remove the acid until the pH of the filtrate is neutral. The resulting GO slurry is dried in a vacuum oven at 60 °C. Then, 100 mg of the as-prepared GO powers are dispersed into 200 mL of water under mild ultrasound for 1 h. Then, the GO solvents are centrifuged with 4800 rpm/min for 30 min to obtain even and stabilized GO with transparent yellow-brown suspension. The above solution (20 mL) is mixed with water (20 mL), and then add hydrazine hydrate (17.5 μL) and ammonia (313.6 μL) and stir 10 min. The mixture is transferred into a 100 mL flask equipped with a condenser and stirred for 2 h at 95 °C, and then cooled to room temperature to obtain rGO solution, then filtered repeatedly, and dried in vacuum at 60 °C to obtain rGO. Finally, GO paper and rGO paper are prepared by vacuum suction filtration.

SEM images are characterized by a FEI Quanta 250 scanning electron microscope under 10K magnification. Raman spectra are investigated using a JY LabRAM HR800 laser Raman spectrometer. The absorption spectra are measured by using a Jasco V-570 UV/VIS/NIR spectrophotometer. PL spectra are carried out by a SENS-9000 fluoroSENS fluorescence spectrometer under the 278 nm excitation wavelength. All spectra are measured at room temperature.

3. Results and discussion

Figure 1 shows the photos of GO (left) and rGO paper (right). As prepared GO paper and rGO paper are circle with a diameter of 3 cm. The surface is flat and brittle.

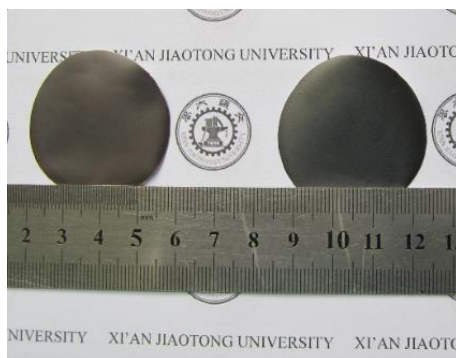


Figure 1. Photos of GO (left) and rGO paper (right).

Figure 2 presents cross-sectional SEM images of GO (a) and rGO (b) paper. The GO paper exhibits a curly graphene layer. The cross-sectional view of rGO paper clearly shows the superposition of the lamellar structure.

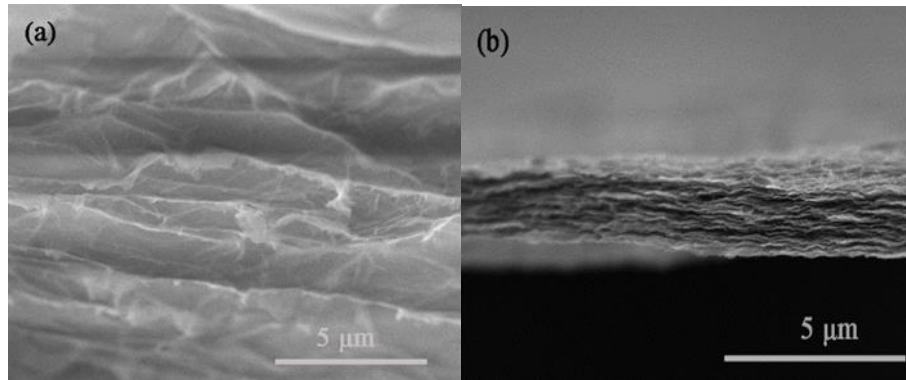


Figure 2. Cross-sectional SEM images of GO (a) and rGO (b) paper.

Raman Spectra is used to widely investigate the bonding structure of various carbon materials. Disordered carbon material exhibit the regular two peaks at 1350 and 1587 cm^{-1} corresponding to the D and G peaks, respectively. Figure 3 presents Raman spectra of GO and rGO paper. Two strong D and G peaks located at 1329 and 1593 cm^{-1} , respectively, are observed, which indicates that both GO and rGO paper have high disorder structures. The D peak is due to the presence of structural disorders in graphene sheets. The G peak attributes to optical E_{2g} phonons at the Brillouin zone center, whereas the ratio of the intensity of the G-band to the D-band is related to the in-plane crystallite size [12]. Besides, the intensity ratio of I_G/I_D is widely used to characterize the defect quantity in graphene and a low ratio indicates a great disorder arising from structural defects [13]. As shown in figure 3, the intensity ratio I_G/I_D of rGO (0.79) is larger than that of GO (0.70) paper, indicating that structural defects in GO paper are partially repaired.

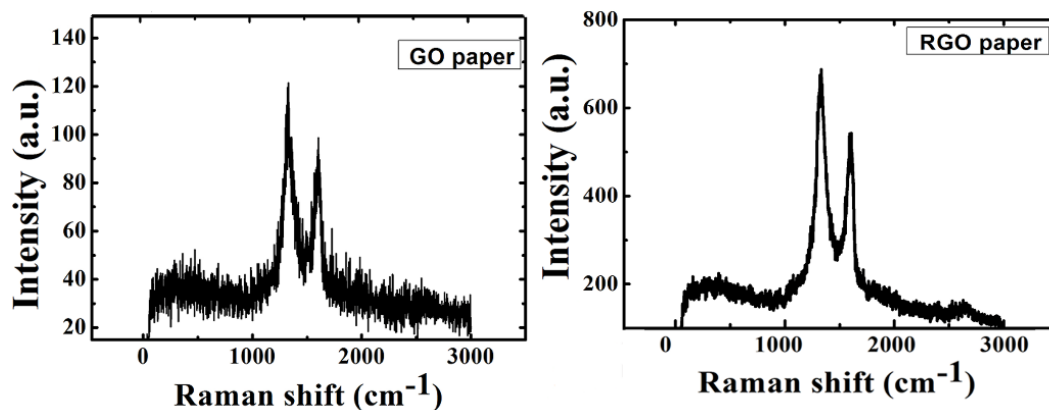


Figure 3. Raman spectra of GO (left) and rGO paper (right).

In order to calculate optical band gap of GO and rGO paper, we use the following formula [14]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

Where, α is absorption coefficient, A is a constant, h is Planck's constant, ν is the photon frequency, E_g is the optical band gap, n is an exponent which have values of $1/2$ for direct-band semiconductors. As can be seen from figure 4, both plots are basically same and E_g values are about 0.62 eV .

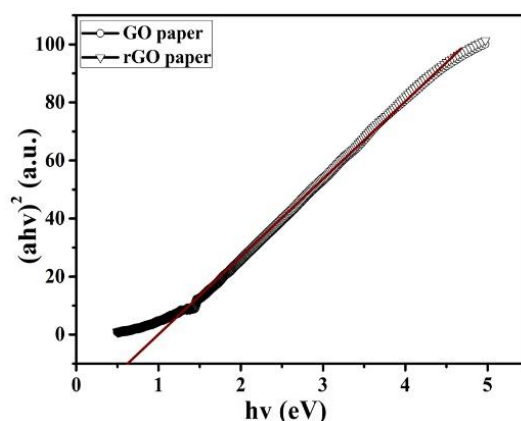


Figure 4. $(ahv)^2$ vs. $h\nu$ plots of GO and rGO paper.

Figure 5 shows PL spectra of GO and rGO paper. Graphite is semiconductor material with zero band gap and do not own luminescence properties. However, as its size is decreased to nano-scale, band gap will be opened due to quantum effect. In the GO and rGO sheets, oxide functional group and carbon vacancies will cut the graphene to form some nano-carbon cluster, which makes them show semiconductor properties and occur luminescence phenomenon. Three emission peaks located at 565, 578 and 608 nm, respectively, are observed in GO paper and they are attributed to the recombination of electron-hole pairs in local state of sp^2 carbon cluster embedded in sp^3 matrix [15]. Compared with GO paper, PL intensity of rGO decreases rapidly. The peak at 578 nm shows blue shift. As GO is reduced, oxide functional groups decrease and sp^2 carbon cluster expand. GO gradually transform into graphene structures and PL emissions decrease and even disappear.

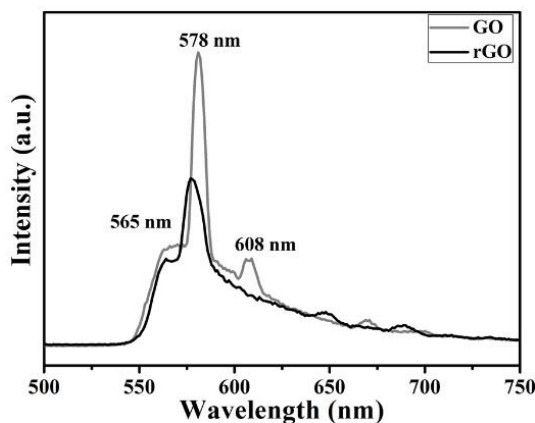


Figure 5. PL spectra of GO and rGO paper.

4. Conclusions

GO and rGO paper are prepared by Hummer method and vacuum suction filtration. Surface micrograph and optical properties are characterized using SEM images, Raman spectra, absorption spectra and PL spectra. Results indicated that rGO shows separated, flake-like graphene layer, and both samples have high disorder. Three emission peaks located at 565, 578 and 608 nm, respectively, are observed in GO paper and they are attributed to the recombination of electron-hole pairs in local state of sp^2 carbon cluster embedded in sp^3 matrix. Compared with GO paper, PL intensity of rGO decreases rapidly. The peak at 578 nm shows blue shift. As GO is reduced to become rGO, oxide functional groups decrease and sp^2 carbon cluster expand. GO gradually transform into graphene structures and PL emissions decrease and even disappear.

Acknowledgment

This work is supported by the National Natural Science Foundations of China (Grant No. 11447116), Natural Science Basic Research Plan in Shaanxi Province of China (Grant No. 2016JQ5037), Special Program for Scientific Research of Shaanxi Educational Committee (Grant No. 16JK1601), Doctoral Scientific Research Startup Foundation of Xi'an Shiyou University (Grant No. 2016BS12) and Creative Scientific Research Group of XSYU (Grant No. 2014KYCXTD02).

References

- [1] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV and Firsov AA 2004 Electric field effect in atomically thin carbon films *Science* **306** 666-669
- [2] Tombros N, Jozsa C, Popinciuc M, Jonkman HT and Van Wees BJ 2007 Electronic spin transport and spin precession in single graphene layers at room temperature *Nature* **448** 571-574
- [3] Bao QL, Zhang H, Wang Y, Ni ZH, Yan YL, Shen ZX, Loh KP and Tang DY 2009 Atomic-layer graphene as a saturable absorber for ultrafast pulsed lasers *Adv. Funct. Mater.* **19** 3077-3083
- [4] Cai WW, Piner RD, Stadermann FJ, Park S, Shaibat MA, Ishii Y, Yang DX, Velamakanni A, Sung JA, Stoller M, An J, Chen DM and Ruoff RS 2008 Synthesis and solid-state NMR structural characterization of ^{13}C -labeled graphite oxide *Science* **321** 1815-1817
- [5] Gokus T, Nair RR, Bonetti A, Bohmler M, Lombardo A, Novoselov KS, Geim AK, Ferrari AC and Hartschuh A 2009 Making graphene luminescent by oxygen plasma treatment *ACS Nano* **3** 3963-3968
- [6] Lu J, Yang JX, Wang IZ, Lim A, Wang S and Loh KP 2009 One-pot synthesis of fluorescent carbon nanoribbons, nanoparticles, and graphene by the exfoliation of graphite in ionic liquids *ACS Nano* **3** 2367-2375.
- [7] Pan DY, Zhang JC, Li Z and Wu MD 2010 Hydrothermal route for cutting graphene sheets into blue-luminescent graphene quantum dots *Adv. Mater.* **22** 734-738
- [8] Luo ZT, Vora PM, Mele EJ, Johnson ATC and Kikkawa JM 2009 Photoluminescence and band gap modulation in graphene oxide *Appl. Phys. Lett.* **94** 111909
- [9] Eda G, Lin YY, Mattevi C, Yamaguchi H, Chen HA, Chen IS, Chen CW and Chhowalla M 2010 Blue photoluminescence from chemically derived graphene oxide *Adv. Mater.* **22** 505-509
- [10] Mei QS and Zhang ZP 2012 Photoluminescent graphene oxide ink to print sensors onto microporous membranes for versatile visualization bioassays *Angew. Chem. Int. Ed.* **51** 5602-5606
- [11] Mei QS, Zhang K, Guan GJ, Liu BH, Wang SH and Zhang ZP 2010 Highly efficient photoluminescent graphene oxide with tunable surface properties *Chem. Commun.* **46** 7319-7321
- [12] Subrahmanyam KS, Vivekchand SRC, Govindaraj A and Rao CNR 2008 A study of graphenes prepared by different methods: characterization, properties and solubilization *J. Mater. Chem.* **18** 1517-1523
- [13] Pimenta MA, Dresselhaus G, Dresselhaus MS, Cancado LG, Jorio A and Saito R 2007 Studying disorder in graphite-based systems by Raman spectroscopy *Phys. Chem. Chem. Phys.* **9** 1276-1290
- [14] Girtan M and Folcher G 2003 Structural and optical properties of indium oxide thin films prepared by an ultrasonic spray CVD process *Surf. Coat. Technol.* **172** 242-250
- [15] Zhu YW, Murali S, Cai WW, Li XS, Suk JW, Potts JR, and Ruoff RS 2010 Graphene and graphene oxide: synthesis, properties and applications *Adv. Mater.* **22** 3906-3924