

Effect of Reaction Temperature on Structural and Optical Properties of Reduced Graphene Oxide

Prerna Bansal, A. S. Panwar, and D. Bahadur

Abstract—Present study is aimed to see the influence of reaction temperature on the structural and optical properties of reduced graphene oxide powder samples. In the present work, aqueous solutions of graphite oxide (GO) were reduced at two different temperatures (80 and 95 °C) using hydrazine hydrate. XRD and Raman studies showed that sample reduced at higher temperature has lesser defects. UV-visible spectral studies showed a blue shift in the absorption peak of GO after reduction due to the increased structural ordering because of restoration of sp^2 carbon with temperature. More shift is observed for the sample reduced at higher temperature. Our study establishes a correlation between structural and optical properties of reduced graphene oxide powder samples with temperature.

Index Term—Graphite oxide (GO), reduced graphene oxide (RGO), photoluminescence (PL).

I. INTRODUCTION

Graphene, a single layer sheet of carbon atoms, has attracted great interest in recent years for its extraordinary mechanical, electrical, thermal and optical properties [1]-[3]. There are various approaches used for graphene synthesis. These approaches include micro-mechanical exfoliation of graphite, epitaxial growth, chemical vapor deposition (CVD) and chemical approaches like graphite oxidation and reduction and intercalation techniques [4]-[7]. Although first three methods can produce graphene with lesser defects and with better physical properties but chemical oxidation and reduction methods are advantageous in terms of high yield, solutions based processability, low cost and ease of implementation. We have synthesized graphite oxide (GO) from graphite powder using a recently proposed improved Hummer's method [8]. As synthesized graphite oxide (GO) is further reduced using hydrazine hydrate at two different reaction temperatures (80 and 95 °C). Our experimental results suggest that higher reaction temperature leads to better reduction of GO giving reduced graphene oxide (RGO) with lesser defects.

II. EXPERIMENTAL SECTION

A. Synthesis of Graphite Oxide (GO)

An improved method [8] for the preparation of graphite

oxide (GO) is used to oxidize pure Graphite (Sigma-Aldrich, 45 μ m, 99.99%) for preparation of graphite oxide (GO) using Conc.H₂SO₄, Conc.H₃PO₄ and KMnO₄ as oxidizing agent.

For the improved method, a 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (60:6.66ml) was added to a mixture of graphite flakes (500mg, 1 wt equiv.) and KMnO₄ (3.0 g, 6 wt equiv), producing a slight exotherm to 45-50 °C. The reaction was then heated to 55 °C and stirred for 12 hours. The reaction was cooled to room temperature and then kept in an ice bath with 30% H₂O₂ (0.5mL). Further, it was filtered using Nylon filter paper with 0.2 μ m pore size in a vacuum filtration assembly. Remaining solid material was washed multiple times with water, 30%HCl, and ethanol through centrifugation (7000 rpm for 15min. at 12 °C) and the supernatant was decanted away every time. The remaining material was coagulated with 35ml of diethyl ether and the resulting suspension was filtered again. The solid obtained on the filter paper was vacuum-dried overnight at 50 °C.

B. Reduction of Graphene Oxide Using N₂H₄ at Two Different Reaction Temperatures (80 and 95 °C)

As-synthesized graphite oxide (GO) (20mg) was dispersed in water (100ml) to create a 0.2 wt% dispersion [7]. Exfoliation of graphite oxide (GO) to graphene oxide was achieved by ultra-sonication of the dispersion in a bath sonicator for 1 hour. The obtained brown dispersion was kept for centrifugation (7000 r.p.m. at 12 °C) for 30 minutes to remove any unexfoliated graphite oxide. The resulting homogeneous GO dispersion was mixed with 8 μ l of hydrazine solution (80% pure) and kept for stirring in a flat bottom flask on a magnetic stirrer at 80 °C for 6 Hours. Upon heating the brown dispersion turned into black precipitate. It was then filtered and resulting filtrate was dried overnight in a vacuum oven at 50 °C giving RGO powder. To see the effect of temperature on the reduction of graphite oxide, same reduction protocol was repeated at 95 °C.

III. RESULT ANALYSIS AND DISCUSSION

A. XRD Results

X-ray diffraction (XRD) patterns for graphite oxide (GO) and reduced graphene oxide (RGO) powder samples are shown in Fig. 1. XRD study confirmed the reduction of graphite oxide with a shift of sharp diffraction peak of GO (2 θ ~9.56 °) to broad diffraction peak of reduced graphene oxide (RGO) at 2 θ ~23 °. It is observed that sample reduced at 95 °C is more crystalline than the sample reduced at 80 °C, with the evolution of [100] peak.

From table I, it is observed that Peak position of [002] peak shifts towards higher '2 θ ' values and 'd' spacing value was found to decrease with temperature.

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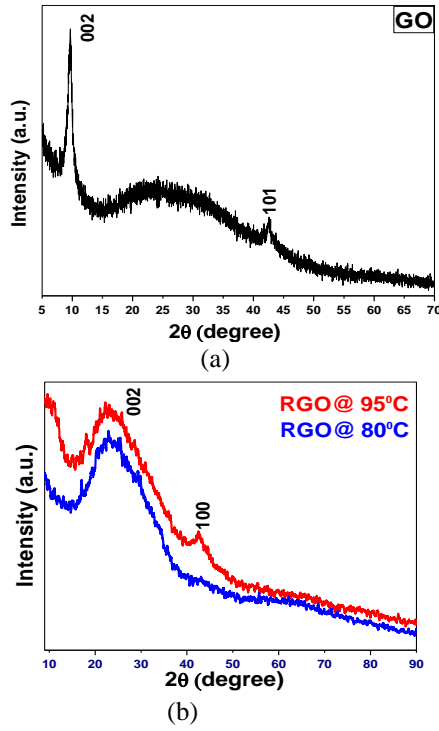


Fig. 1. XRD pattern of (a) GO and (b) RGO powder samples.

TABLE I EFFECT OF REACTION TEMPERATURE FOR [002] PEAK OF RGO

Reaction Temperature (°C)	2θ (°)	FWHM (°)	Plane spacing d (Å)	Crystallite size (nm)
80	22.14	0.40	4.01	20.16
95	22.28	0.53	3.98	15.12

B. Raman Spectra Analysis

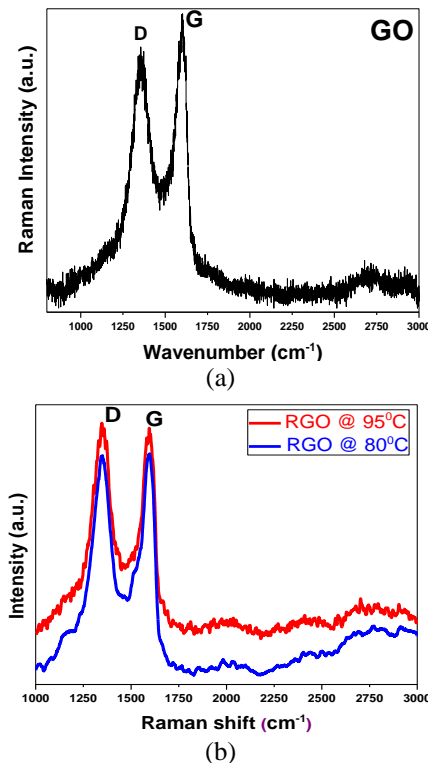


Fig. 2. Raman spectra of (a) GO and (b) RGO powder samples.

It is known that a Raman spectrum of pure graphite shows a strong G peak at 1570 cm^{-1} due to the first order scattering of E_{2g} modes. A broadened D peak is seen at 1350 cm^{-1} due to the reduction in size of in-plane sp^2 domains in graphite induced by the creation of defects and distortions of the sp^2 domains [7]. Fig. 2a shows the Raman spectra of GO with 'D' peak at 1349 cm^{-1} and 'G' peak at 1581 cm^{-1} . Ratio of the 'D' peak intensity to the 'G' peak intensity (I_D/I_G) for GO is ~ 0.84 . Fig. 2b shows Raman spectra of RGO prepared at 80°C and at 95°C . I_D/I_G ratio for RGO reduced at 95°C (~ 1.32) is smaller than the RGO reduced at 80°C (~ 1.41), indicating that the sp^2 domain size increases at higher reaction temperatures.

C. FTIR Results

Fourier-transform infrared spectroscopy (FTIR) spectra is recorded for GO and RGO powder samples with KBr as reference. Fig. 3 presents the FTIR spectra of GO and RGO samples reduced at 80°C and 95°C .

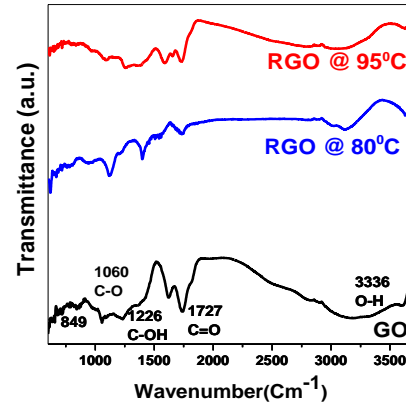


Fig. 3. FTIR spectra of GO and RGO powder samples.

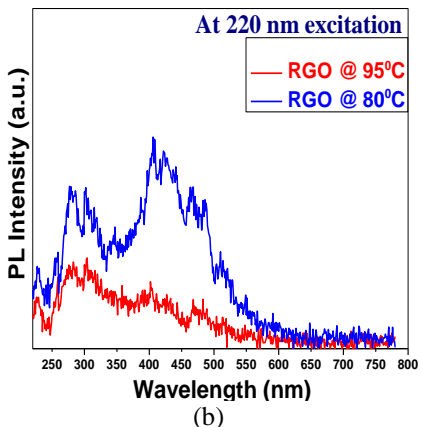
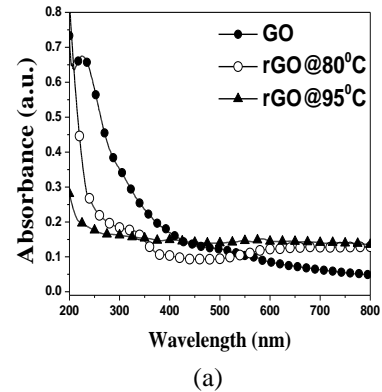


Fig. 4. (a) UV-vis absorption spectra and (b) PL spectra of GO and RGO.

Fourier-transform infrared (FTIR) spectra of GO confirms the presence of sharp broad peak of intercalated free H₂O molecules at nearly 3300 cm⁻¹. Peaks corresponding to -COOH(carboxyl), -OH(hydroxyl), and >O(epoxide) groups are observed at ~1740, ~1233, and ~1030 cm⁻¹ respectively. FTIR spectra indicate the vaporization of intercalated free water molecules with temperature, as shown by the decrease of intensity of peaks correspond to -OH functional groups with temperature.

D. Optical Studies

Fig. 4 (a) shows the UV-visible spectra of the GO, showing a sharp absorption peak at 220 nm, which is attributed to the π - π^* transitions of the C-C aromatic rings [8]. After the reduction of GO, the absorption peak was blue shifted for both the RGO samples. Fig. 4(b) presents the room temperature photoluminescence (PL) spectra, which shows that the defect peak is suppressed in the sample reduced at higher temperature. Our UV study reveals that sample reduced at higher temperature has smaller optical gap. The significant blue shift is due to the increased structural ordering due to restoration of sp² domains with temperature.

IV. CONCLUSIONS

We have reduced aqueous solutions of GO at two different reaction temperatures (80 and 95 °C) using hydrazine hydrate. XRD and Raman results were found in agreement with each other showing that higher reaction temperature leads to more crystalline nature of RGO sample with lesser defects. Optical studies suggest that due to the increased structural ordering with temperature, there is a blue-shift in the absorption spectra of RGO. Our study shows that crystalline nature, defects and optical properties of RGO depends on its reduction temperature.

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