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Reduced Graphene Oxide Film Based Highly Responsive Infrared Detector

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ABSTRACT: Due to the unique optical properties, graphene can effectively be used for the detection of infrared light. In this regard, reduced graphene oxide (RGO) has drawn considerable attention in scientific society because of simplicity of preparation and tunable properties. Here, we report the synthesis of RGO by solvothermal reduction of graphene oxide (GO) in ethanol and the detection of infrared light (1064 and 1550 nm) with metal - RGO - metal configuration. We have observed that photocurrent, responsivity as well as the external quantum efficiency increase with C/O ratio. The responsivity value in near-infrared region can be as high as 1.34 A.W⁻¹ and the external quantum efficiency is more than 100%. Response times of these devices are in the order of few seconds. Overall, the responsivity of our device is found to be better than many of the already reported values where graphene or reduced graphene oxide is the only active material. The high value of quantum efficiency is due to strong light absorption and the presence of mid-gap state in RGOs.

KEYWORDS: reduced graphene oxide, infrared detector, mid-gap state, temperature sensor

1. INTRODUCTION

Now-a-days, infrared detectors are being used in many applications such as rail safety, gas leak detection, flame detection, night flying, night surveillance, night vision goggles and also space operations.[1] Graphene is a zero band gap material so it absorbs a broad spectrum of light. This property has made graphene a highly potential material for infrared detector. Unfortunately, a single layer graphene absorbs only $\sim 2.3\%$ of incident white light,[2] and photo-generated electrons and holes in graphene recombine within few picoseconds.[3-5] Lower absorption and faster carrier recombination lead to low photo-response.[6-8] In order to use graphene as an effective photodetector, absorption as well as life time of photo-excited electrons and holes should be increased. Built-in electric field near metal – carbon nanotube junction can separate photogenerated electron and holes, preventing quick recombination.[9] But this kind of effects are limited at the junctions. Introduction of defects in graphene sheets leads to creation of band gap and also limits the recombination of charge carriers.[6, 7, 10] Though plasmonic nanostructures, micro-cavities have been used to enhance the absorption efficiency of graphene,[11-14] responsivity still remains in few tens of mA.W^{-1} . The light absorption efficiency can also be increased by simply increasing the number of layers in graphene.[15] Therefore, few layers graphene with considerable amount of defects on the sheets is a potential material for highly responsive infrared photo-detector.[16, 17] Few layers structure and ease preparation makes reduced graphene oxide (RGO) a very important candidate of the graphene family. Properties of RGO can be tuned by tuning the amount of reduction [18-22] and also it can be reduced by many different reducing agents.[23-26] We have prepared RGO without using any extremely harmful chemicals like hydrazine and also the method of preparation is simple. We have used ethanol as reducing agent.[27] It effectively reduces graphene oxide. We also

report the detection of infrared light. The devices consisting of “metal - RGO - metal” configuration show high responsivity even at very low bias. The responsivity in NIR region can be as high as 1.34 A.W^{-1} and the external quantum efficiency $>100\%$ has been achieved. Response times of these devices are in the order of few seconds. To our knowledge, the responsivity is much better than most of devices based on graphene or RGO as the only active material.

2. EXPERIMENTAL SECTION

2.1 Materials and Method. Graphite flakes were purchased from Sigma Aldrich. Potassium permanganate (KMnO_4) and sulfuric acid (H_2SO_4) were purchased from Fisher Scientific. Sodium nitrate and hydrochloric acid were purchased from SDFCL. Ethanol was purchased from local supplier. All the chemicals were at least more than 99% pure and used without further purification.

Graphitic oxide (GO) is prepared according to Hummers method. Details of the method are reported elsewhere.[28] Reduction of GO is achieved by solvothermal method with ethanol as solvent. First, 80 mg of GO is added to 40 ml of ethanol. Then these mixtures are sonicated for 200 min. in a 30 kHz TELSONIC ULTRASONICS bath sonicator. After sonication, GO dispersion is transferred into a 50 ml teflon lined autoclave and kept in a muffle furnace at 180°C for 3, 6, 12, 24 and 36 h. After solvothermal reduction, the furnace is allowed to cool naturally. After that the product mixtures are centrifuged at 5000 rpm and washed with ethanol. Then the products are dried in vacuum overnight. The RGOs are named as RGO1, RGO2, RGO3, RGO4, and RGO5 for 3, 6, 12, 24, and 36h of reduction respectively.

2.2 Characterizations. X-ray diffraction (XRD) studies have been carried out using RigakuSmartLab X-ray diffractometer with Cu K α as X-ray source. Raman spectra have been acquired using LabRAM HR system with 532 nm excitation source. Absorption and infrared (IR) spectra have been recorded using PerkinElmer UV/VIS/NIR Lambda 750 spectrometer and Bruker FTIR instrument, respectively. X-ray photoelectron spectroscopy (XPS) measurements have been done using KRATOS ANALYTICAL's AXIS Ultra photoelectron spectrometer with Al K α as X-ray source. Scanning electron microscopy (SEM) images are taken with ZEISS's GEMINI ULTRA 55 FE-SEM, while transmission electron microscopy (TEM) images are taken with FEI Tecnai F30 S-TWIN TEM.

2.3 Device Fabrication and Opto-electrical Measurement. Silver electrodes with 200 nm thickness and a gap of 95 μ m are deposited on cleaned quartz substrates by thermal evaporation (Figure S1). To fabricate the devices, 4.8 mg of RGO is dispersed in 150 μ L toluene by sonication and drop-casted in between the electrodes with a micro pipette. The devices are dried at $\sim 40^\circ\text{C}$ on a hotplate for ~ 45 min. and cooled to the room temperature. A CNI's MDL-III 1550 nm laser (with an optical coupler of ~ 2 mm radius) and MIL-III 1064 nm (with a beam radius 2.5 mm) have been used as the IR source. Optical chopper SR540 has been used for chopping measurements. Tektronix Keithley 2400 source measure instrument is used for electrical studies.

3. RESULTS AND DISCUSSION

SEM images [Figure S2(a) and (b)] reveal some amount of agglomeration in RGO. TEM images [Figure S2(c) and (d)] reveal the layered nature of RGO. Inter-layer spacing is ~ 3.5 Å. SAED pattern [Figure S2(d) inset] reveals hexagonal symmetry with inner most diffraction spots corresponding to (1100) planes and diffraction spots next to that are from (2110) planes. (1100)

planes correspond to a d-spacing of ~ 0.19 nm and (2110) planes correspond to a d-spacing of ~ 0.11 nm. XRD pattern (Figure S3) of GO shows a peak at around $11.86^\circ 2\theta$. Oxygen functionalities incorporation in between the (002) planes lead to larger interplanar distances.[29] After reduction, diffraction peak restores around graphitic peak ($26.51^\circ 2\theta$) at $25.46^\circ 2\theta$. Very broad nature of the peaks is due to few layers structure and presence of defects in RGO. Absorption spectrum of GO and RGOs have been taken in N-Methyl-2-pyrrolidone (NMP). As the reduction increases, the absorption increases in visible and infrared spectrum (Figure 1 a). Infrared spectra of GO and RGO (Figure S4) also indicate restoration of aromaticity after reduction. Alkane C-H stretching and C-H rocking absorption intensity also decreases. On the other hand C-C aromatic stretching absorption and C-H in plane bending absorption increases. EDS and XPS survey spectra of GO and RGO (Figure S5) show vivid difference of carbon and oxygen contain before and after reduction of graphitic oxide. Figure 1b shows the XPS C1s spectrum of GO which can be deconvoluted to four peaks. These peaks are arising from C-C/C=C (~ 284.5 eV), C-O (~ 286.5 eV), C=O (~ 288.3 eV) and CO(OH) (~ 290.2 eV).[30] The very nature of C1s peak of GO indicates oxygen incorporation on the layers of graphite flakes and the C/O ratio is ~ 1.96 . XPS C1s spectrum (Figure 1c) show that oxygen functionalities are mostly removed during reduction process. The C/O ratio for different RGOs has been evaluated from the XPS spectra and produced in table 1. Raman spectra of GO, RGO3 (Figure 1d) show four major peaks. The strong peak at ~ 1590 cm^{-1} corresponds to G peak.[31] Raman peaks at 1345 and 2695 cm^{-1} are called as D peak and 2D (or G') peak and the peak around 2935 cm^{-1} is known as D+G peak.[31, 32] For perfectly crystalline graphene D – band remains absent because the corresponding A_{1g} mode does change the overall polarizability.[33] It requires defect or disorder in the crystal to get activated.[33, 34] D peak only appears when size of the graphene sheets

decreases or defects gets incorporated on graphene sheets and can be used to quantify amount of defects in graphene. Though, the ratio of I_D/I_G is the measure of defects in graphene, [31, 33-35] the ratio obtained for GO and RGO is inconclusive as the value is very much position-dependent. Non-uniform size, presence of heteroatom in GO and RGO leads to position dependent I_D/I_G value.

Figure 1. (a) Absorption spectra of RGO samples, (b and c) XPS C1s spectra of GO and RGO3 respectively, (d) Raman spectra of GO and RGO.

Table 1. Atomic percentage of carbon and oxygen in RGO as obtained from XPS analysis.

Sample	C %	O%	C/O
GO	66.27	33.73	1.96
RGO 1	85.73	14.27	6.00
RGO 2	86.29	13.71	6.29
RGO 3	86.97	13.03	6.67
RGO 4	87.19	12.81	6.80
RGO 5	87.41	12.59	6.94

Photocurrent measurements of the devices are carried out with 1550 and 1064 nm laser irradiation. Figure 2a shows the temporal response curves for RGO3 with 1550 nm excitation with a bias of 0.3 V. As soon as IR radiation falls on the device, photocurrent quickly increases and reaches its saturation level and the saturated photocurrent increases with increasing IR radiation intensity. Increase in intensity of IR radiation generates higher number of excited electrons and holes that leads to higher photocurrent. To determine the relation between photocurrent (I_{PC} = current after illumination – dark current) and intensity of radiation (I_L) we have plotted I_{PC} vs. I_L at a constant bias of 0.3 V and fitted with the equation,

$$I_{PC} = \alpha * I_L^\beta,$$

where α and β are constants. β is 1.14, 1.27, 1.45, 1.28 and 1.28 for RGO1, RGO2, RGO3, RGO4, and RGO5, respectively with 1550 nm irradiation (Figure 2b). Temporal responses of RGO3 at different intensities of 1064 nm excitation (at a constant voltage of 0.3 V) are shown in figure 2(c). β is found to be 1.64, 1.58, 1.57, 1.64 and 1.55 for RGO1, RGO2, RGO3, RGO4 and RGO5, respectively [Figure 2(d)]. The non-unity of β values is indicative of complex processes

of electron-hole generation, trapping of electrons and recombination.[6, 36, 37] In this context, it is worthy to note that photocurrent is linear with bias voltage as shown in figure S6.

Figure 2. Photoresponse of RGO3 to (a) 1550 nm and (c) 1064 radiation with different radiation intensity at constant bias of 0.3V. (b and d) variation of photocurrent with intensity.

Bolometric temperature rise of RGO can also lead to generation of photocurrent.[38, 39] In order to shed light on this, we studied the effect of temperature on electrical properties of the devices

and measured the temperature rise by irradiation (Figure S7 and Table S1). No appreciable rise in temperature (< 0.1 degree) could be detected (with a resistance temperature detector, resolution of 0.1 K) for ~ 50 s exposure of infrared radiation ($\sim 80 \text{ mW.cm}^{-2}$). We have also carried out photocurrent studies using a chopper [Figure S8]. It is well known that bolometric temperature rise (ΔT_B) depends on chopper frequency and the bolometric effect is dominant at lower frequency. This indicates that bolometric effect can be avoided at higher frequency. However, we observed no change in photocurrent with the variation of chopper frequency [Figure S8 (b) and (c)]. The initial decrease in photocurrent during chopping is due to reduction of laser exposure time to half of its initial value. These two measurements suggest photocurrent is due photovoltaic effect and not bolometric effect.

Figure 3(a) and (b) display the temporal photoresponse of RGOs with 1550 and 1064 nm radiation of 80 mW.cm^{-2} at 0.5 V. Irrespective of the excitation wavelength, it is interesting to note that photocurrent increases with C/O ratio as shown in Figure 3(c). As the C/O ratio increases, the band gap of RGO decreases.[21, 40, 41] As the band gap decreases, the absorption cross section increases that causes the generation of more electron-hole pair and produces higher photocurrent.

Responsivity (R) of a photodetector indicates the efficiency of photocurrent generation per unit incident radiation per unit area. Responsivity of a photodetector is calculated as,

$$R = I_{PC}/(I_L * A),$$

where I_{PC} is the photocurrent, I_L is the light intensity and A is the effective area.[7, 42, 43] The external quantum efficiency (EQE) is the ratio of the number charge carrier collected by the

device to the number of photons irradiated on the effective area (A) of the device and can be estimated using the relation,

$$EQE = hcR/e\lambda,$$

where h is the Plank's constant, c is the velocity of light, e is the charge of an electron and λ is the wavelength of incident radiation.[7, 44]

Figure 3. Temporal response of different RGOs for (a) 1550 nm and (b) 1064 nm radiation ($I_L = 80 (\pm 0.6)$ mW.cm⁻² and $V_{S-D} = 0.5$ V). (c) Photocurrent and (d) EQE vs. C/O ratio of RGOs ($I_L = 80 (\pm 0.6)$ mW.cm⁻² and $V_{S-D} = 0.5$ V).

Table 2. Responsivity and EQE of RGOs at $I_L = 80 (\pm 0.6) \text{ mW.cm}^{-2}$ and $V_{S-D} = 0.5 \text{ V}$.

Sample	R (A/W)		EQE(%)	
	$\lambda(1550 \text{ nm})$	$\lambda(1064 \text{ nm})$	$\lambda(1550 \text{ nm})$	$\lambda(1064 \text{ nm})$
RGO 1	0.55	0.42	44	49
RGO 2	0.72	0.61	58	72
RGO 3	1.09	0.91	87	106
RGO 4	1.23	1.11	98	129
RGO 5	1.34	1.21	107	141

Responsivity and EQE values for 1550 nm and 1064 nm excitation are listed in table 2. Variation of EQE values with the C/O ratio in RGO for both 1064 nm and 1550 nm infrared irradiation have been shown in figure 3(d). Data points are well fitted with the equation,

$$EQE = \kappa * x^\gamma,$$

where x = C/O ratio and κ and γ are constants. γ for 1550 and 1064 nm radiation is ~ 6.2 and ~ 7.2 , respectively indicates faster increase of EQE for 1064 nm excitation as compared to 1550 nm.

I-V characteristic shows Coulomb blockade effect specially at low temperature (Figure S9 a). Transport of charge carriers through RGO sheets occurs via hopping mechanism (Figure S9 b). As discussed earlier, the band gap decreases with increase of C/O ratio that leads to increase of photocurrent as well as the EQE. Higher absorption at 1064 nm is believed to be the underlying reason for higher γ value for 1064 nm radiation as compared to 1550 nm. In this context, the role

of mid-gap state band (MGB) needs to be discussed. Although RGOs are highly reduced, still they contain ~14.3% to 12.6% oxygen (atomic percentage). The reduction of sheet size, incorporation of defects during sonication, high temperature reduction and presence of oxygen functionalities are believed to create MGB in RGOs.[6, 45-47] MGB can trap photoexcited electrons.[6, 48] During the lifetime of trapped electrons corresponding holes recirculate through the circuit generating a gain in photocurrent (Schematic 1).[6, 48-53] Thus, combined effects of higher absorption and presence of MGB in RGO lead to high responsivity and EQE values of our RGO based photodetectors. EQE exceeds 100% for both 1550 and 1064 nm irradiation for highly reduced graphene oxide based devices.

Schematic 1: Electron trapping in mid-gap state and hole hopping.

Temperature dependent measurement shows that photocurrent decrease with increase in temperature (Figure 4). Trapping in mid-gap state band is efficient at low temperature. As the

temperature increases, trapping becomes less effective that leads to lower photocurrent. Plot of photocurrent vs. temperature indicates almost linear variation of photocurrent with temperature (Figure 4b). Thus the prepared RGO shows potential as a temperature sensor.

Figure 4. (a) Temporal photoresponse of RGO 4 at different temperature ($\lambda=632$ nm), (b) Variation of photocurrent with temperature.

In most cases, the responsivity of graphene or RGO is in range of few mA.W^{-1} or less.[13, 14, 42, 54-62] Due to poor absorption and fast carrier recombination, EQE is very low for monolayer or very few layer graphene based photodetector. The responsivity and EQE values of our RGOs are comparable with the graphene nano-ribbon as an active material.[44] Using RGO or graphene as the only active material, the responsivity of prepared RGO is found to be better than many of the reported literature.

Both rise (figure 5a) and decay (figure 5b) of photocurrent are fitted with the following exponential relation,

$$I_t = I_f + A_1 * \exp(-t/\tau_1) + A_2 * \exp(-t/\tau_2),$$

where I_t is photocurrent at any time t and I_f is the final photocurrent, A_1 and A_2 are constants (depends on incident light intensity), and τ_1 and τ_2 are time constants.[7, 44, 48] Rise and decay of photocurrent for 1064 nm excitation have been shown in figure S10 (a) and (b). Values of time constants are evaluated for RGOs and provided in table 3 (1550 nm excitation) and table S2 (1064 nm excitation). All the cases, τ values indicate a faster growth (or decay) followed by a slower saturation. These results are in accordance with the previous reports.[7, 44] The values of time constants indicate that the responses of our RGO based photodetectors are faster than many other reported values.

Figure 5. (a) Rise and (b) decay of photocurrent (1550 nm excitation) of different RGOs ($V_{S-D} = 0.3V$, $I_L = 80 (\pm 0.6) \text{ mW.cm}^{-2}$).

Reproducibility of photocurrent is checked over 20 cycles (Figure S11). A brief summary of results from previous works on graphene and RGO based photodetector have been listed in table

S3.It may be noted that in most of the graphene (or RGO) based photodetector, the responsivity value is much lower and time constant values are much higher compared to our photodetectors.

Table 3. Time constants, response and recovery time of photodetectors for 1550 nm infrared irradiation ($V_{S-D} = 0.3V$, $I_L = 80 (\pm 0.6) \text{ mW.cm}^{-2}$).

Active Material	Rise(s)		Decay (s)	
	τ_1	τ_2	τ_1	τ_2
RGO 1	0.25	8.78	0.32	4.27
RGO 2	0.07	4.30	0.34	4.22
RGO 3	0.17	5.12	0.35	5.19
RGO 4	0.25	6.10	0.12	3.66
RGO 5	0.20	7.20	2.03	10.49

4. CONCLUSIONS

We have prepared highly reduced RGO by solvothermal reduction in ethanol. Devices have been fabricated by drop casting RGO on silver electrodes. Infrared photoresponse studies of the devices have been carried out with 1550 and 1064 nm laser source and the photocurrent is found to be photovoltaic in nature. Interestingly, EQE increases with C/O ratio and higher than 100% is obtained for RGO with higher C/O ratio which is believed to be due to the combined effects of strong absorption and mid-gap states assisted gain. Highest responsivity obtained in our experiment is 1.34 and 1.21 for 1550 nm and 1064 nm infrared irradiation, respectively. The responsivity and response time of our photodetectors is much better than many of those values which are already reported for RGO based photodetector and comparable with commercial ones.

In addition, our RGO based photodetectors exhibit stable and reproducible photocurrent over many cycles. Another interesting observation is that the photocurrent decreases almost linearly with temperature which can be exploited as temperature sensor as well.

Conflicts of Interest: The authors declare that they have no conflict of interest.

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