Thermoluminescence properties of graphene–nano ZnS composite

Geeta Sharma*, S.W. Gosavi
Department of Physics, University of Pune, Pune 07, India

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This work describes the thermoluminescence (TL) of graphene oxide (GO), reduced graphene oxide (RGO) and graphene–nano ZnS composite. Graphene oxide was synthesized using Hummer’s method and then reduced to graphene by hydrazine hydrate. G–ZnS was synthesized via in-situ reduction of graphene oxide (GO) and zinc nitrate ([Zn(NO₃)₂] by sodium sulfide (Na₂S). The structures of samples were characterized by X-ray diffraction (XRD) and transmission electron microscope (TEM). XRD pattern confirmed the formation of graphene oxide, reduced graphene oxide and G–ZnS lattice. The p-XRD spectrum of G–ZnS shows peaks of ZnS superimposed on those of graphene and the particle size of ZnS in the complex is less than 10 nm. Ultra thin graphene and graphene oxide sheets with size ranging between tens to several hundreds of square nanometers are observed in TEM images. The TEM micrographs of G–ZnS show that ZnS particles are embedded in graphene sheets and the average particle size of ZnS particles in the composite is less than 10 nm. Samples of RGO, GO and G–ZnS were exposed to different doses of γ-rays in the range of 1 Gy to 50 kGy. The reduced graphene oxide (RGO) did not show any thermoluminescence emission. The thermoluminescence glow curve of GO has a single broad peak whose peak position varied between 500 and 550 K with an absorbed dose increasing from 1 Gy to 5000 Gy. GO shows most intense TL peak, positioned at 523.6 K for a dose of 10 kGy. The reduced graphene oxide and G–ZnS lattice did not show any thermoluminescence emission. The thermoluminescence glow curve of GO shows a linear response curve of G–ZnS is found to be linear over a larger dose range from 1 Gy to 50 kGy whereas the response curve of GO shows linearity only at low doses up to 100 Gy.

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1. Introduction

Semiconductor nanoparticles are an important topic of interest because of their unique optical and electronic properties owing to quantum confinement effect and large surface area. These nanoparticles have increased band gap as compared to their bulk counterparts leading to blue shift in the absorption and emission spectra. The bandgap of these nanoparticles can be tuned by controlling the size of the particles hence can be tailored for various applications [1–4]. ZnS is one of the II–VI compound semiconductors and is well known for its applications in the field of optoelectronic devices such as, light emitting diodes and flat panel displays [5] owing to its broad band luminescence from the near ultraviolet to near infrared region. Because of its direct energy bandgap (∼3.7 eV) it is suitable to be used as host matrix for variety of dopants.

The properties of semiconductors can be tailored by doping suitable dopants and by changing the particle size which in turn change their bandgap. Another method for altering the properties of semiconductors is to make their hybrids with different materials such as ferrites and carbon based materials. Reports are available regarding the filling of carbon nanotubes with metals and metal oxides [6,7]. With the advent of graphene, researchers all over the world are involved in studying and altering the properties of graphene for technological applications [12]. Large scale research is being carried out to harness its use in nano-mechanical and nano-electronic devices [13]. Graphene, a single layer of carbon atoms is booming in material science these days because of its unique electronic, thermal and mechanical properties [8–11]. Hence an attempt is made to synthesize and study the thermoluminescence (TL) properties of ZnS–graphene composite.

For studying the defect structure of the insulators and semiconductors thermoluminescence method is generally used. Many synthetic materials have been developed and characterized to evaluate their feasibility as thermoluminescence dosimeters (TLD) from low doses (i.e., 1 kGy) to high doses (i.e., 10 kGy) [4,5]. The TL properties of pure and doped ZnS below room temperature have been extensively studied over the last 60 years [6–11] whereas, the work done on the TL properties of ZnS, either in bulk or thin film forms; above room temperature up to now is very scanty [8–10]. Moreover, there are no reports till date regarding the thermoluminescence study of
graphene complex with nano ZnS. However, there are few reports related to TL studies of graphene using different irradiation sources. Electron or ion irradiation produces lattice disorder, which alters physical properties of graphite and carbon nanotubes. This motivated us to carry out the present study where synthesis of graphene oxide, reduced graphene oxide and graphene–ZnS (G–ZnS) complex have been carried out and their thermoluminescence properties have been studied for different doses of gamma radiation for investigating their potential for dosimetric applications.

2. Experimental

2.1. Synthesis of graphene oxide, reduced graphene oxide and graphene–ZnS composite

First the graphene oxide was synthesized after oxidizing graphite with KMnO4 in the presence of sulfuric acid using Hummer’s method [14]. The solid product was separated by centrifugation, washed repeatedly with acetone and dried at 65 °C for 12 h.

Next, graphene quantum sheets were synthesized by reducing graphene oxide (GO) using hydrazine (H2N2O). The larger particles and partially unused graphite were removed by centrifuging (in de-ionized water) at 4500 rpm for 10 min at room temperature, and the product so formed was suitable for further synthetic procedures. The solution was again diluted with de-ionized water and sonicated in an ultrasonic bath for 30 min. Hydrazine was added and sonication continued for a further 210 min to get pure graphene suspension. The total synthesis time was 4 h and the sample is designated as reduced graphene oxide (RGO). The light weight black product floating on the solution was washed thoroughly with distilled water and alcohol and dried under vacuum at 370 °C for 2 h to get graphene powder.

To synthesize graphene–ZnS, about 250 mg of graphene oxide was dispersed in 50 ml of 0.035 M solution of Zn(NO3)2 by sonication for half an hour. The Na2S solution was added to this dispersion and solution was stirred for 30 min. The suspensions were checked for completion of precipitation. The resulting black solids were washed several times with water followed by acetone and dried in air at 65 °C. These were then heated at 100 °C in N2 atmosphere for 6 h to further reduce the partially reduced graphene oxide sheets. These samples are hereafter referred to as graphene–ZnS (G–ZnS).

2.2. Characterizations

To confirm the formation of GO, RGO and G–ZnS; X-ray diffraction pattern was recorded at room temperature by using Cu-target (Cu-Kα line at 1.54 Å) on Bruker AXS D8 Advance X-ray diffractometer. TEM images were obtained on Transmission Electron Microscope, “TECHNAI G2 20U-TWIN (FEI, Netherlands)”, operated at 200 kV. For taking images, 1 mg powder sample was put in 4 ml of ethanol and ultrasonicated for 10 min to form a suspension. A drop of this suspension was then put on a carbon coated copper grid (200 mesh) and dried in air for half an hour. The grid was viewed under the TEM and images were taken. For recording thermoluminescence, 5 mg of powder samples were exposed to Co60 gamma rays for different doses. The TL glow curves were recorded using a computerized TL Reader [Model TL 1009], Nucleonix Systems. The glow curves were recorded by heating the samples at a uniform rate of 5 K s−1 with the help of a temperature controller, and the luminescence emission was detected by a photo-multiplier (PM) tube. The photo-current from the PMT tube was amplified by a DC amplifier interfaced to a personal computer for recording the TL output. At least three glow curves were recorded for each sample to confirm the consistency in the measurements.

3. Results and discussion

3.1. X-ray diffraction and transmission electron microscopy

Fig. 1(a), (b), and (c) show the XRD pattern of RGO (reduced graphene oxide), GO (graphene oxide) and G–ZnS (graphene–ZnS) respectively. The graphene oxide was synthesized from raw graphite via its oxidation. The basal spacing of GO calculated from the 001 reflection is 0.739 nm which is in agreement with the values reported in literature [15]. The reduction of graphene oxide leads to the formation of graphene which is indicated by the appearance of peak at 25.8° (0.34 nm) and a second peak at 43.1° (0.209 nm) in Fig. 1(a). Reduction of parent GO with hydrazine, lead to change in the XRD pattern with a basal spacing of 0.34 nm rather than 0.73 nm in parent GO [16]. The difference in XRD pattern of GO and RGO confirms the conversion of graphene oxide to graphene.

Further, graphene oxide was used to make graphene nanocrystalline zinc sulfide composite (G–ZnS). Fig. 1(c) shows the XRD pattern of G–ZnS. The p-XRD spectrum of G–ZnS shows peaks of ZnS superimposed on those of graphene. The ZnS peaks are observed at 28.8°, 48.2° and 56.7° corresponding to (1 1 1), (2 2 0) and (3 1 1) planes of cubic crystalline ZnS respectively and is in agreement with the standard data available at (JCPDS PDF-80-0020). It is revealed that the particles exhibit a zinc-blende crystal structure. The graphene peaks are overshadowed by ZnS peaks, however weak signature of graphene planes are visible at 43.1°.

Hence, the graphite oxide has been reduced to graphene in G–ZnS complex. The particle size of ZnS in G–ZnS is calculated using Debye-Scherrer formula and found to be less than 10 nm.

Fig. 2(a), (b) and (c) show the TEM image of GO, RGO and G–ZnS respectively. Ultra thin graphene oxide sheets with size ranging between tens to several hundreds of square nanometers are visible in Fig. 2(a). SAED pattern is also shown in the inset of Fig. 2(a). Fig. 2(b) shows the TEM image of reduced graphene oxide. Folded thin layers of graphene resembling crumpled silk veil waves with approximately size of few hundred square nanometers are clearly visible in the image. These sheets are transparent and very stable under electron beam. In addition, the right hand side in Fig. 2(b) is the HRTEM image of RGO where lattice planes are clearly visible. SAED pattern of RGO shows the sixfold ring pattern (shown in the inset of Fig. 2(b)). On comparing the SAED pattern of GO and RGO we have found that there is...
difference in the crystallinity of both the samples. The GO sample is modestly crystalline as indicated by its diffused diffraction pattern, while the RGO formed is highly crystalline as it shows sharp diffraction patterns, suggesting that latter has a more regular carbon framework than former. On the other hand, the image of G–ZnS shows that ZnS particles are embedded in graphene sheets. The SAED pattern of G–ZnS shows the six fold pattern arising due to graphene in addition to ring pattern from ZnS particles, indicating the formation of graphene–ZnS complex. The size of the particles is very small (less than 10 nm) as visible from Fig. 2(c) and is in agreement with the XRD result.

3.2. Thermoluminescence (TL)

Thermoluminescence of GO, RGO and G–ZnS was recorded for the dose varying from 1 Gy to 5 kGy. Graphene oxide shows thermally stimulated emission (TSE) during heating above the room temperature. Graphene oxide samples, with dose of 1 Gy, 10 Gy, 100 Gy and 5000 Gy show a single peak at 518 K, 514 K, 510 K and 515 K respectively. The peak may be due to relaxation of some kind of defects created by gamma irradiation, as unirradiated GO, did not show any emission. The irradiation with gamma may be producing lattice defects or disorders, such as vacancies, interstitial atoms, Frenkel defects etc. The energy deposited by the ionization energy in the lattice may be released by defect transformation, into lower energy configuration. The defect transformation may need different activation energies which is obtained when the sample is stimulated by thermal energy during TSE. It is also observed from Fig. 3(i) that there is increase in peak intensity with increasing gamma dose and it is mainly due to the generation of more number of defects in the lattice.

Fig. 3(ii) shows the TL glow curves of GO for the dose varying from 10 kGy to 50 kGy. All the glow curves, up to 10 kGy have similar shape, while for higher doses i.e., at 20 kGy and 50 kGy respectively, the shape of the glow curves distorts with fall in intensity. Specifically, the sample exposed to a dose of 10 kGy shows most intense TL peak, positioned at 523.6 K but the sample exposed to a dose of 20 kGy shows drastically fall in TL intensity and the peak is positioned at 508.7 K with shoulder on higher temperature side at 530.65 K and one more peak appeared at 586 K. These additional peaks may be due to creation of additional defects. With further increase in gamma dose, the TL intensity further reduces and shape is also altered, indicating the lattice structure is disrupted by the higher doses of gamma irradiation. Due to gamma irradiation, the GO nano-sheets may get broken up caused due to evaporation of the oxygen and hydrogen containing functional groups [17]. Moreover, there is variation in the peak position with variation of the gamma dose may be due to disorganization of the initial C–C structure of graphene oxide.

The glow curve for 10 kGy dose is found to be the most intense and simple, hence it is opted for further analysis (Fig. 4). The analysis of the glow curve is being done by Chen’s peak shape method. It is one of the most popular and acceptable methods and is also called as Chen’s half width method [18]. It is applicable for the experimental glow curves which are very simple. In this method, three points on the peak are used: the temperature of maximum intensity, $T_m$ and the low and high half intensity temperatures $T_1$ and $T_2$. Chen found that $E$, $s$ and $b$ could be

![Fig. 2.](image-url) (a) TEM image of graphene oxide and inset shows its SAED pattern. (b) TEM image of reduced graphene oxide and inset shows it’s SAED pattern. (c) TEM image of G–ZnS and inset shows it’s SAED pattern.

![Fig. 3.](image-url) TL emission spectrum of graphene oxide irradiated with different gamma radiation doses from (i) 1 Gy to 5000 Gy and (ii) 10 kGy to 50 kGy.
evaluated by using three parameters,
\[ \omega = T_2 - T_1, \quad \tau = T_m - T_1 \quad \text{and} \quad \delta = T_2 - T_m \] (1)
The kinetic order \( b \) is a monotonic function of the ratio \( \mu_g = \delta / \omega \), where \( \mu_g \) is called the geometrical factor or form factor, which has been defined by Halperin and Briner [19].

Theoretically, the form factor which ranges from 0.37 and 0.56 is close to 0.42 for first order kinetics and 0.52 for second order kinetics [20]. In first order kinetics it is assumed that there is no retrapping of charges, whereas in second order kinetics retrapping of charges occurs. The form factor is independent of the activation energy, \( E \) and strongly depends upon the order of kinetics. The activation energy \( E \) can be calculated using the empirical formulae given by Chen [21] and Chen and Kirsh [22].

\[ E = c_\alpha \left( \frac{kT^2}{\alpha} \right) - b_{\omega \alpha} (2kT_m) \] (2)

with
\[ \alpha = \tau, \delta, \omega, \]
\[ \tau = T_m - T_1, \quad \delta = T_2 - T_m, \quad \omega = T_2 - T_1, \]
\[ c_\tau = 1.51 + 3.0(\mu_g - 0.42), \quad c_\delta = 0.976 + 7.3(\mu_g - 0.42), \]
\[ c_\omega = 2.52 + 10.2(\mu_g - 0.42), \quad b_\omega = 1.58 + 4.2(\mu_g - 0.42), \]
\[ b_\delta = 0, \quad b_\omega = 1 \]

where \( k \) the Boltzmann constant and its value is \( 8.6 \times 10^{-5} \) eV K\(^{-1}\).

The calculated value of \( \mu_g \) for GO was found to be 0.50, which indicates second order kinetics involved in it and the activation energy \( (E_\tau, E_\delta, E_\omega) \) was found to be 2.87 eV, 2.70 eV and 2.82 eV.

3.2.2. Graphene–ZnS

Fig. 5 shows the TL glow curves of G–ZnS irradiated at different doses of gamma radiation from 1 Gy to 50 kGy. The glow curves over the entire range of gamma irradiation have a single peak. With increasing gamma dose, the intensity of the glow curve increases with variation in the peak position. The peak is found to be shifted towards lower temperature side i.e., at 527 K, 515 K, 508 K, 492 K and 497 K with increasing dose from 1 Gy to 50 kGy. Earlier coworkers have found that ZnS has single glow curve. Yazici et al. have studied the thermoluminescence properties of ZnS thin films and showed that the samples have a single glow curve around 393 K [23]. It is found that, complexing ZnS with graphene has shifted the TL peak to higher temperature between 497 K and 527 K which is one of the important requirements for a material to be used as a dosimeter.

The glow curves observed in G–ZnS may be due to defects present in ZnS. Since many authors have found that the defect levels responsible for the thermoluminescence of a material belongs to the host lattice and dopants only modify these levels [24–26]. It has been found by earlier coworkers [27] that the four types of point defects may be present in pure ZnS. The defects may be associated with Zn or S vacancies. The vacancies of sulfur and zinc are equivalent to localized donor and acceptor states respectively. The interstitial Zn atoms lead to donor states and sulfur atoms to acceptor states. The interstitial atoms may cause additional deformation in the lattice owing to strain caused by it. This may lead to rearrangement of the nearest neighbors. As the sulfur ions are larger than the Zn ions, the interstitial sulfur induces more strain to the lattice. These defects capture free electrons generated due to gamma irradiation and act as electron traps. However, the sample synthesized is a complex between graphene and ZnS. The reduced graphene oxide in our study is found to have shown no TL signal when exposed to gamma radiations. The graphene in G–ZnS complex is affecting the defects of ZnS. The variation in the peak position with increasing dose may be firstly due to the disorganization of energy levels of ZnS due to gamma irradiation and secondly due to the influence of graphene defects on that of ZnS lattice [28,29].

G–ZnS has found to have enhanced intensity of TL emission than GO, may be due to large number of defects in former. The glow curve for 50 kGy (shown in Fig. 6(a)) was chosen for the analysis as it is the most intense and simple one. The value of form factor, \( \mu_g \) is found to be 0.46 which indicate first order kinetics in it. The glow curve is having a single but very broad peak hence there can be superimposition of some glow peaks in it. For analysis of TL glow curve, it was deconvoluted using Glow fit deconvolution software which is based on the First Order Kinetic model [30,31] and the glow curve fitting is done using an iterative Levenberg Marquardt algorithm [32]. The first order kinetic equation is given by

\[ l(T) = I_0 \exp \left[ 1 + \left( \frac{E}{kT} \right) \frac{T - T_m}{T_m} \right] \left( \frac{T^2}{T_m^2} \right) \exp \left( \left( \frac{E}{kT} \right) \frac{T - T_m}{T_m} \right) \right] \left( 1 - \Delta - \Delta_m \right) \] (3)

where \( \Delta = 2kT/\Delta, \Delta_m = 2kT/m/\Delta \).

Fig. 6(b) shows the experimental glow curve for of G–ZnS for a dose of 50 kGy, deconvoluted into three peaks. The trapping parameters obtained from the deconvoluted glow peaks are shown in Table 1. The goodness of fit is obtained by figure of merit (FOM) which is 0.03 indicating a good fit between

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Fig. 4. Highly intense and stable TL glow curve of GO irradiated at a gamma dose of 10 kGy used for the calculations of trapping parameters.

Fig. 5. TL glow curves of G–ZnS irradiated at different doses of gamma radiation from 1 Gy to 50 kGy.
experimental and theoretical fitted peak, which also indicates it to be of first order.

From the values of $\mu_g$ of GO and G–ZnS, it can be inferred that there is retrapping of charge carriers in GO, while retrapping does not occur in G–ZnS.

3.2.3. TL Response

Fig. 7 shows the TL response curve of G–ZnS and GO for the gamma irradiation dose from 1 Gy to 50 kGy. For a phosphor to be used for the dosimetric purposes, its dose response should be linear. G–ZnS shows a linear behavior from 1 Gy to 50 kGy and further no saturation is observed. However, GO shows a linear behavior only for low doses i.e., upto 100 Gy. With further increase in the gamma dose, the response rises nonlinearly till 10 kGy and then falls abruptly from 10 kGy to 50 kGy. The linear behavior over low doses may be due to generation of number of defects and disorders proportional to the gamma dose. At doses higher than 100 Gy there is a large generation of defect sites and disorders responsible for TL signal, leading to rapid rise in the TL response till 10 kGy. At doses higher than 10 kGy the lattice structure is disrupted due to gamma irradiation resulting in fall of TL response curve.

CaSO$_4$:Dy is a well known standard TLD material. Salah et al. has studied in detail the TL behavior of CaSO$_4$:Dy (microcrystalline and nanocrystalline) and has found that nanocrystalline CaSO$_4$:Dy shows a linear behavior upto 10 kGy of gamma exposure while the microcrystalline CaSO$_4$:Dy has a linear behavior only upto 1 kGy of the gamma exposure [33]. G–ZnS has a linear behavior over a larger dose range than standard CaSO$_4$:Dy (nanocrystalline and microcrystalline). Therefore, in all, G–ZnS complex is observed to be an ideal phosphor to be explored for the dosimetric applications since it can effectively been used for measurement of high gamma dose, whereas GO may be explored to be used for low dose measurement i.e., upto 100 Gy.

4. Conclusions

Graphene oxide was synthesized using Hummer’s method and then reduced to graphene by hydrazine hydrate. G–ZnS sample was successfully synthesized via in-situ reduction of graphene oxide and zinc nitrate. XRD confirms the formation of graphene oxide, reduced graphene oxide and graphene–ZnS. TEM micrographs also shows ZnS nanoparticles embedded in the graphene sheets. The thermoluminescence properties of GO, RGO and G–ZnS were studied using gamma as the excitation source. RGO did not show any TL emission. Among the three systems (GO, RGO and G–ZnS) G–ZnS shows a good linear response for the gamma dose from 1 Gy to 50 kGy and can be used effectively for the low and highdose dosimetric applications, whereas, GO system can be used for the measurement of low dose up to 100 Gy.

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