Synthesis and luminescence of graphene-nano calcium sulphide composite

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HIGHLIGHTS

- G-CaS was synthesized using in situ reduction of calcium salt and graphene oxide.
- Samples were characterized by XRD, TEM, PL, FTIR, XPS, Raman Spectroscopy.
- TEM of G-CaS show CaS particles having size less than 50 nm are embedded in graphene.
- G-CaS shows PL emission at 440 nm when excited with 350 nm.
- PL emission intensity in case of G-CaS is lower than CaS but it is luminescent.

ABSTRACT

Graphene-nanocrystalline calcium sulphide has been synthesized using in-situ reduction of calcium salt and graphene oxide. Graphene oxide was prepared using Hummer’s method. Surface morphology and crystal structure of samples were observed by transmission electron microscopy (TEM) and X-Ray diffraction (XRD). 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-CaS show that CaS particles are embedded in graphene sheets and the average particle size of CaS particles in the composite is less than 50 nm. The reduction in the intensity of various functional groups in FTIR spectrum also confirms the formation of graphene. The UV-Visible spectra of CaS shows absorption peak at 220 nm with a small shoulder at 250 nm whereas in G-CaS 220 nm absorption peak has reduced intensity and the shoulder at 250 nm has now shifted to 270 nm due to modification in the defect structure of CaS by graphene. CaS and G-CaS shows photoluminescence emission at 470 nm (λexc = 375 nm) and 440 nm (λexc = 350 nm) respectively, however emission intensity of G-CaS is relatively lower than CaS. Although the emission intensity is found to be lower than CaS, addition of CaS to graphene in G-CaS complex has made graphene luminescent. XPS spectra also indicate reduction of various oxygen containing functional groups in highly reduced graphene oxide and G-CaS.

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1. Introduction

Graphene, a 2D layer of carbon atoms has drawn a lot of attention in material science these days owing to its unique electronic, thermal and mechanical properties [1–4]. It’s unique properties have lead to new research areas in material science for it’s use in nano-mechanical and nano-electronic devices. Kang et al. have demonstrated high performance, flexible, transparent heaters etc based on large scale graphene films synthesized by chemical vapour deposition on Cu foils [5]. Tien et al. have produced graphene nanosheets decorated with metal nanoparticles and investigated the electro catalytic activities [6]. Besides graphene, its oxide (graphene oxide) is another derivative of carbon which is explored on large scale for bio-sensing, high performance ultra capacitors, fuel cells and electro catalysts [7–11].

In comparison to graphene, which is zero bandgap material, graphene oxide exhibit insulating properties and is fluorescent because of defect related optical bandgap. Luo et al. have studied and demonstrated the photoluminescence and bandgap modulation in...
graphene oxide (GO) and have reported PL emission of GO at 752 nm when excited at 500 nm [12]. Moreover attempts are made to make G and GO fluorescent by doping variety of ions in it. Reports are available in literature regarding N doping in graphene and graphene oxide which show visible luminescence between 400 and 550 nm [13]. B.K. Gupta et al. have synthesized Eu – graphene complex by doping Eu2O3 in graphene oxide and then carrying out its thermal decomposition and found it to be luminescent (614 nm and 618 nm) [14].

Presently, the semiconductor nanoparticles is becoming 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 an 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 and material of the particles and therefore can be tailored for specific application [15–18]. Further the properties of these materials (non linear optical properties, absorption etc.) can be tailored by complexing it with carbon based materials [30]. Reports are available regarding filling of carbon nanotubes with metal and metal oxides [15,20]. However there are very less reports available regarding the synthesis and complexing of alkaline earth sulphides with graphene. To the best of our knowledge there are no reports regarding the synthesis and characterization of nano CaS: graphene composite and it’s fluorescent study. Here in for the first time synthesized and characterized the nano CaS-graphene composite. In the present paper various properties of the synthesized nanocomposite are studied using X-ray Diffraction, Transmission Electron Microscopy, Photoluminescence, UV-Visible Spectroscopy, FTIR, XPS and Raman Spectroscopy. The samples was done using X-ray Diffraction, Transmission Electron Microscopy, Photoluminescence, UV-Visible Spectroscopy, FTIR, XPS and Raman Spectroscopy. The XRD spectra of a) GO, b) HRG, c) GCaS and d) CaS.

2. Experimental

2.1. Synthesis of graphene oxide and highly reduced graphene

Analytical grade graphite, potassium permanganate (Kmno4), sulphuric acid (H2SO4), hydrazine hydrate (H2N2O), calcium chloride (CaCl2·2H2O) and sodium sulphide (Na2S) were used as starting materials. Ethanol and distilled water were used as the solvents.

First, the graphene oxide was synthesized after oxidizing graphite with KmnO4 in presence of sulphuric acid using Hummer’s method [21]. 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) which has been found to be the best reducing agent in producing very thin graphene sheets [22,23]. 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 highly reduced graphene (HRG). The light weight black product floating on the solution, was washed thoroughly with distilled water and alcohol and subsequently dried under vacuum at 370 °C for 2 h to get graphene powder. This highly reduced graphene was used for comparison in latter experimentation.

2.2. Synthesis of graphene nano-CaS composite

About 250 mg of GO was dispersed in 50 ml of 0.035 M solution of CaCl2·2H2O in ethanol and sonicated for 30 min in N2 atmosphere to prevent oxidation. The Na2S solution was added to this dispersion and was stirred for 30 min till the precipitation was observed. The resulting black solid (G-CaS) was washed several times with de-ionized water followed by acetone washing and dried at 65 °C. This powder was then heated at 100 °C in N2 atmosphere for 6 h for further complete reduction of any residual GO and to obtain pure HRG-nano CaS composite. These samples are hereafter referred to as G–CaS. Here for the first time we have synthesized G-CaS nanocomposite with this method.

The above procedure was repeated in the absence of GO to obtain free CaS nanoparticles as control. The characterization of all the samples was done using X-ray Diffraction, Transmission Electron Microscopy, Photoluminescence, UV-Visible Spectroscopy, FTIR, XPS and Raman Spectroscopy.

![Fig. 2. IR spectrum of GO, HRG and GCaS.](image-url)
Fig. 3. (a) TEM images and SAED pattern of graphene oxide, (b) High resolution TEM images and inset shows the SAED pattern of highly reduced graphene. (c) TEM micrograph of CaS and G-CaS with their respective SAED patterns in the inset.
3. Results and discussion

3.1. XRD

To confirm the formation of compounds, p-XRD of various samples was done. Fig. 1 shows XRD pattern of GO, HRG, CaS and G-CaS composite. The d’ value of GO calculated from the 001 reflection is 0.739 nm which is in agreement with the values reported in literature [24]. Reduction of graphene oxide leads to the formation of highly reduced graphene which is indicated by appearance of peak at 25.8° (0.34 nm) and a weak peak at 43.1° (0.209 nm). Thus reduction of parent GO with hydrazine, lead to reduction in the d’ value to 0.34 nm [22]. In the present study, graphite powder was oxidized using a mixture of sulphuric acid and KMnO₄ in water based solutions. During this process various oxygen containing functional groups such as hydroxyl, carbonyl, epoxy and peroxy etc get bonded to the basal planes of the graphite structure due to which GO posses larger interlayer spacing than graphene. Change in XRD pattern between GO and HRG confirm removal of the oxygen containing functional groups from graphene oxide.

XRD pattern of G-CaS in Fig. 1 shows the peaks only due to CaS nanoparticles and no peaks due to GO or graphite which indicates complete exfoliation of graphene oxide in the composite. The pattern of G-CaS and CaS matches perfectly with the standard data available in JCPDS card no 77-111. The particle size of free CaS nanoparticles was found to be ~30 nm using Debye Scherrer formula. More importantly, the XRD pattern of G-CaS also gives same pattern and particle sizes as for free CaS (but no GO peak and very low intensity peaks of HRG) probably this indicates separate presence of nano CaS in G-CaS composite.

3.2. FTIR

FTIR has been used to check the reduction of GO sheets. Fig. 2 shows the FTIR spectra of GO, HRG and G-CaS. The stretching vibrations of C=–C and carbonyl groups (C=O) on the edges of the layers or conjugate carbonyl groups are observed at 1536 cm⁻¹ and 1720 cm⁻¹ respectively [21]. While the band at 1059 cm⁻¹ can be assigned to the stretching vibrations of C=O. The peak at 1650 cm⁻¹ is attributed to COOH [31]. The characteristic peak at 1248 cm⁻¹ may be due to epoxy C=O. The stretching vibration of hydroxyl group can be seen in form of broad band around 3626 cm⁻¹.

The intensity of 3626 cm⁻¹, 1720 cm⁻¹, 1650 cm⁻¹, 1536 cm⁻¹, 1059 cm⁻¹ bands have reduced, and the 1720 cm⁻¹ peak has almost disappeared in the IR spectrum of HRG. While the stretching vibrations observed in the FTIR spectra of GO is not observed in G-CaS indicating reduction of GO sheets to graphene sheets and effective exfoliation of GO by Na2S.

3.3. HRTEM

Morphological structures of samples were observed by TEM analysis. Fig. 3 shows TEM images of GO, HRG, CaS and G-CaS. Fig. 3(a) shows the ultra thin graphene oxide sheets with size ranging between tens to several hundreds of square nanometers; however these sheets appear to be fragmented. SAED pattern is also shown in Fig. 3(a). Closed ring pattern is visible in the electron diffraction pattern. Fig. 3(b) (left) shows the images of HRG. Folded thin layers of graphene resembling crumpled silk veil waves with approximate size of few hundred square nanometers are clearly visible in the images. These sheets are transparent and very stable under electron beam. HRTEM image (right) of HRG in Fig. 3(b) clearly shows the lattice planes.

SAED pattern of HRG shows the six fold ring pattern. On comparing the SAED pattern of GO and HRG 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 HRG formed is highly crystalline as it shows sharp diffraction patterns, suggesting that HRG has a more regular carbon framework than GO.

TEM images of free CaS and G-CaS complex is shown in . The particle size of free CaS and G-CaS complex is less than 50 nm which is in close agreement with XRD results. Globular morphology is revealed in these images. The images of G-CaS show that CaS particles are embedded in graphene sheets. It appears that graphene sheets get folded on CaS particles. The SAED pattern of G-CaS shows the six fold pattern arising due to graphene in addition to ring pattern from CaS, indicating the formation of G-CaS complex.

3.4. UV-Visible and photoluminescence

The reduction of GO to G-CaS has been monitored by UV-Visible absorption spectroscopy (Fig. 4). The UV-Visible spectra of all materials were recorded in powder form. Pure CaS shows a strong peak around 220 nm with a small shoulder at 250 nm. Two weak peaks are also visible at 330 nm and 380 nm. GO and HRG shows similar absorption behaviour, peaks at 221 nm and at 265 nm are visible which can be due to partial restoration of π-conjugation within the graphene plane [30]. In case of G-CaS absorption is observed at 220 nm and a shoulder is formed at 270 nm.

The absorption edge at 275 nm in CaS is due to band to band transition from valence band to conduction band. The weak peaks at 330 nm and 380 nm may be due to escalation of electrons from an impurity centre to the conduction band [32]. The impurity centres may be associated with S²⁻ vacancies. These vacancies introduce localized acceptor states. The interstitial atoms may cause additional deformation in the lattice owing to strain caused by it, leading to rearrangement of the nearest neighbors. These defects may act as electron traps [33]. However the absorption in G-CaS is affected largely by graphene in G-CaS. The 220 nm absorption peak has reduced intensity as compared to CaS and the shoulder at 250 nm in CaS has now shifted to 270 nm with increased absorption indicating modification in the defect structure of CaS due to graphene. It should be noted that absorption of GO, G-CaS and HRG is greater than CaS at wavelengths higher than 400 nm may be due to dark colour of the samples as CaS prepared was of white colour and GO, G-CaS and HRG were having grey to black colour. The
differences in the UV-Visible spectra of pure CaS, GO, HRG and G-CaS may be attributed to the introduction of carbon species, which can absorb light and modify the surface of nano-particles [34].

In Fig. 5(a) spectrum (a) is PL excitation spectrum of CaS ($\lambda_{\text{emission}} = 458$ nm); (b) is PL emission spectrum of CaS monitored at excitation wavelength of 265 nm and (c) is the emission spectrum of CaS at an excitation wavelength of 375 nm. There are two excitation peaks of CaS at 265 nm and 375 nm which may be attributed to inter band excitation of CaS nanocrystallites [35].

Excitation at 265 nm gives a very weak emission peak at 365 nm and a broad emission at 470 nm. While excitation with 375 nm wavelength gives a broad peak at 470 nm and peak at 365 nm is however not visible in spectrum (c). The emission at 365 nm may be assigned to the presence of trace levels of oxygen present in the lattice [32] while emission at 470 nm may be due to the transition between defect levels lying between conduction and valence bands. The CaS shows complex energy absorption and emission with excitation energies less than the bandgap. These excitation

![Graph showing PL spectra](image)

Fig. 5. (a) PL (i) excitation spectrum of CaS monitored at emission wavelength of 458 nm (b) emission spectrum of CaS at an excitation wavelength of 265 nm; (c) emission of CaS at an excitation wavelength of 375 nm. (b): PL (a) excitation spectrum of G-CaS monitored at emission wavelength of 440 nm; (b) emission spectrum of G-CaS at an excitation wavelength of 260 nm; (c) emission spectrum of G-CaS at an excitation wavelength of 260 nm. (c) PL emission spectrum of (a) CaS at excitation wavelength of 265 nm (b) G-CaS at excitation wavelength of 260 nm; (ii) PL emission spectrum of (a) CaS at excitation wavelength of 440 nm (b) G-CaS at emission wavelength of 350 nm; (iii) PL excitation spectrum of (a) CaS at emission wavelength of 458 nm (b) G-CaS at emission wavelength of 440 nm. (d) EDX spectrum of GCaS, (e) PL emission spectra of GO and HRG.
energies may be from valence band to localized defect energy level which are associated to $S^2-$ vacancy [33].

CaS and SrS prepared by Wang et al. using solvothermal route also shows two excitation peaks at 330 nm and 399 nm and a broad emission peak at 550 nm [35]. Blue shift in the emission and the excitation in the present case as compared to Wang et al. may be due to nanosize effect since particle size reported by them is $\sim$100 nm whereas it is 30 nm in the present case.

Fig. 5(b) shows the PL emission and excitation spectra of G-CaS. G-CaS shows the excitation peaks at 352 nm monitored at $\lambda_{\text{emission}} = 440$ nm. The emission peaks are observed to be shifted to 440 nm when excited at 350 nm contrary to CaS emission at 470 nm. G-CaS was also excited at 260 nm and the emission peaks earlier observed at 440 nm has now shifted at 427 nm. Emission and excitation peaks are found at different positions in G-CaS and CaS may be due to interaction of graphene with calcium sulphide lattice which lead to the modification of defect structure of host since carbon species can absorb light and modify the surface of nano-particles [34]. The fluorescent intensity is found to be decreased for G-CaS. This may be due to quenching of surface related emission due to the interactions of the surface of CaS with graphene or conversion of excitation energy to phonons through non-radiative transitions. Fall in intensity may be attributed to the transfer of some of the emitted energy from CaS nanoparticles to graphene. To make a clear comparison of PL emission and excitation spectra of G-CaS and CaS all them were merged in Fig. 5(c).

In order to find out how much CaS was loaded onto the graphene sheets we have recorded the EDX spectrum of G-CaS sample. Fig. 5(d) shows the EDX of G-CaS, and it is clear from EDX that approximately 28 mass % of CaS was loaded on 34 mass % of graphene. It is found that mass of CaS is less than that of graphene in the complex which may be one of the reasons for fall in luminescence intensity. The PL emission from G-CaS is encouraging for technological applications, making it a useful photonic material for solid state devices.

GO and HRG both showed very weak emission at 630 nm when excited at 500 nm and neither them showed any emission with excitation of 250 nm. Fig. 5(e) shows the PL emission spectra of GO and HRG. Although graphene is intrinsically a zero gap semimetal [12], but it may be oxidized in a manner that produces photoluminescence. Oxidation of graphene sheet modified it and can

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**Fig. 6.** Raman spectra of GO, G-CaS and HRG.

**Fig. 7.** (a) High resolution C1s XPS spectra of GO, (b) High resolution C1s XPS spectra of HRG, (c) High resolution C1s XPS spectra of G-CaS.
introduce direct band gap behaviour [25]. The disruption of π network due to the formation of oxygen containing functional groups in GO can give rise to finite electronic band gap. Extremely weak and broad PL from GO may be originating from the carbon sp² domain/clusters [25–27]. However it does not show any emission when irradiated with UV light (emission might be very weak to be observable to the naked eye).

3.5. Raman spectroscopy

Raman spectroscopy is a powerful technique to study the carbon based materials as it can probe ordered and disordered crystal structure of carbon. The spectra were recorded using a 632.81 nm laser as the excitation source. Fig. 6 shows the spectra of GO, G-CaS and HRG. HRG shows the D and G band at 1315 cm⁻¹ and 1596 cm⁻¹ respectively. The G band is characteristic of three coordinate planar (sp² hybridized) carbon. And the broad and intense D band at 1315 cm⁻¹, is due to the disorder induced in the sp² hybridized carbon lattice. The Raman spectrum of G-CaS shows similar D and G bands, though the D band is observed at the same position, the G band is slightly shifted towards lower wave number side and is observed at 1580 cm⁻¹. The results indicate small size of the in plane sp² domains of graphene [28]. GO shows the D and G bands at 1325 cm⁻¹ and 1598 cm⁻¹. It is found that I_D/I_G for GO samples is 1.02. After reduction the I_D/I_G has been slightly increased to 1.10 in HRG and 1.09 in G-CaS. This can be attributed to the significant decrease in size of the in plane sp² domains in HRG and G-CaS [28,36].

3.6. XPS

Fig. 7(a), (b) and (c) shows the high resolution Cls, XPS spectra of GO, G-CaS and HRG. The Cls peak of graphene oxide consists of C–C (sp² carbon in the basal plane, 284.4 eV), C–O (286.1 eV) and O–C=O (288.7 eV) [29]. As seen from Fig. 7(a), the C–O contribution is particularly high. After hydrazine reduction CO ratio has notably reduced in HRG and the bonds are observed at 284.5 eV (C–C), 286.1 eV (C–O) and 287.9 eV (C=O). The bond at 288.7 eV was not observed in HRG, however a new bond is observed at 287.9 eV due to C=O. The intensity of all the oxygen containing functional groups has been reduced in HRG as observed in Fig. 7(a) and (b).

The spectrum of Cls of G-CaS is shown in Fig. 7(c). The peaks are observed at 284.4 eV (C–C), 286.3 eV (C–O), 288.6 eV (O–C=O) and 290.7 eV. The peak at 290.7 eV may be due to the C=CH group present, since the samples were finally washed with ethanol. The peaks similar to GO are observed in G-CaS, but at reduced intensity. Moreover a peak at 290.7 eV is observed in G-CaS which is not found in GO for the above said reason. XPS spectra indicate the reduction of various oxygen containing functional groups in G-CaS. Fig. 8 shows the XPS spectrum of O1s of GO and G-CaS. It can be inferred from this figure that various oxygen containing functional groups attached to GO has now reduced in G-CaS.

4. Conclusions

Hybrid of graphene and alkaline earth sulphide was synthesized using calcium sulphide, as confirmed by the structural characterization of the prepared samples using XRD, FTIR, Raman Spectroscopy, XPS and transmission electron microscopy. XRD, FTIR, Raman Spectroscopy and XPS indicate the reduction of graphene oxide to graphene in the G-CaS complex. An attempt is made to make graphene luminescent. Pure graphene oxide and highly reduced graphene shows negligible PL emission at 630 nm when excited at 500 nm. While the complex of graphene and calcium sulphide (G-CaS) shows PL emission at 440 nm when excited with 350 nm. Though the PL emission intensity observed in case of G-CaS is lower than CaS but it is luminescent, encouraging its usage in technological applications, making it useful photonic material for solid state devices.

References


