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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 GCaS 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.

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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 ($\lambda_{exc.} = 375$ nm) and 440 nm ($\lambda_{exc.} = 350$ 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.

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

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graphene oxide (GO) and have reported PL emission of GO at752 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 Eu_2O_3 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 [19,20]. 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, for its possible applications in novel optical devices, using a very simple method for synthesis. Other composite nano materials such as Cu_2S, PbS etc. with graphene can also be synthesized with this method and can further be explored for tunable fluorescence applications in graphene technology. Graphene oxide (GO) and highly reduced graphene (HRG) has also been synthesized and characterized for comparing their properties with that of nano CaS: graphene composite.

2. Experimental

2.1. Synthesis of graphene oxide and highly reduced graphene

Analytical grade graphite, potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4), hydrazine hydrate (H_6N_2O), calcium chloride ($CaCl_2 \cdot 2H_2O$) and sodium sulphide (Na_2S) were used as starting materials. Ethanol and distilled water were used as the solvents.

First, the graphene oxide was synthesized after oxidizing graphite with $KMnO_4$ 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 (H_6N_2O) 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.

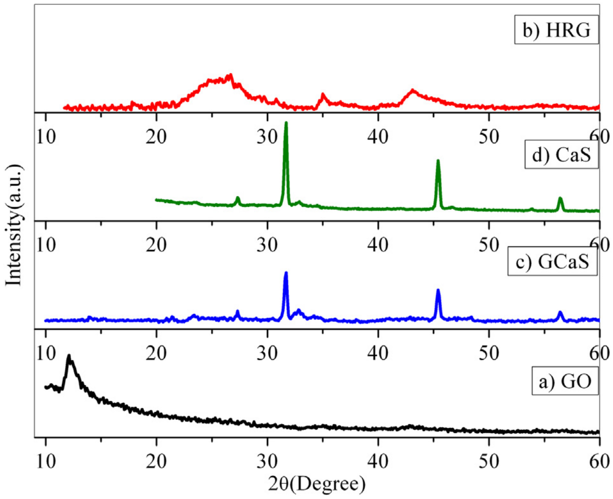

Fig. 1. The XRD spectra of a) GO, b) HRG, c) GCaS and d) CaS.

2.2. Synthesis of graphene nano-CaS composite

About 250 mg of GO was dispersed in 50 ml of 0.035 M solution of $CaCl_2 \cdot 2H_2O$ in ethanol and sonicated for 30 min in N_2 atmosphere to prevent oxidation. The Na_2S 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 N_2 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.

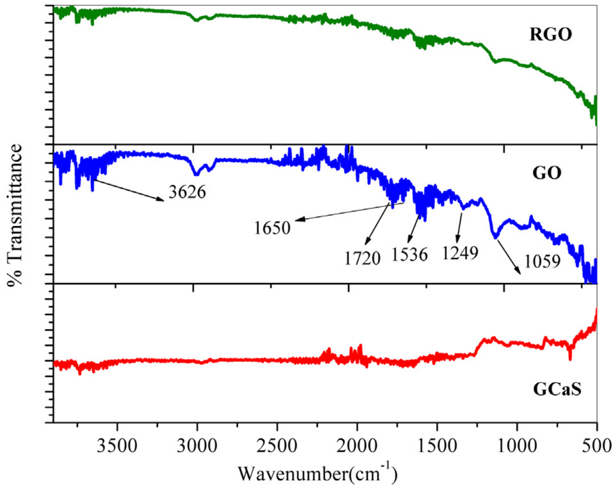

Fig. 2. IR spectrum of GO, HRG and GCaS.