

Synthesis, characterization and spectroscopy of composites of graphene with CdSe and CdS nanoparticles

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Nanocomposites of few-layer graphene with nanoparticles of CdSe and CdS have been synthesized by two different methods, one involving ultrasonication of a mixture of graphene and the chalcogenide nanoparticles, and another involving assembly at the organic-aqueous interface. The nanocomposites have been examined by electron microscopy, electronic absorption and photoluminescence spectroscopies as well as Raman spectroscopy. Electron microscopy reveals that the nanoparticles are dispersed on the graphene surface. Raman spectra show the presence of definitive electronic interaction between the nanoparticles and graphene depending on the capping agent. Photoluminescence spectra are markedly influenced by the interaction of the nanoparticles with the graphene surface, depending on the capping agent.

Keywords: Nanocomposites, Graphene, Chalcogenide nanoparticles, Liquid-liquid interface, Raman spectroscopy

Graphene-semiconductor nanoparticle composites are of much interest due to their potential applications in different fields¹. The theoretical surface area of single-layer graphene is $\sim 2600 \text{ m}^2/\text{g}$, while few-layer graphenes of $1000\text{-}1500 \text{ m}^2/\text{g}$ have been generated². Graphenes are thus desirable 2-D supports for many purposes. As a result of its high specific surface area and good conductivity, graphene is a promising electron acceptor in photovoltaic devices³ where a major challenge is the effective separation of the photogenerated electron-hole pairs and the transfer of electrons to the electrode. Carbon nanotubes decorated with semiconductor nanoparticles have been found to possess desirable properties for use in such devices⁴⁻⁷. Graphene would be expected to be equally good or even better because of its high surface area. Furthermore, graphene can be produced at low cost. There are some reports on the synthesis of semiconductor-based graphene nanocomposites. CdSe nanoparticles can be attached to reduced graphene oxide (RGO) by adding RGO to the reaction solution during the process of synthesizing CdSe nanoparticles⁸. Kim *et al.*⁹ have electrochemically deposited CdSe nanocrystal thin films over graphene. Low-temperature refluxing is found to yield CdS-graphene nanocomposites by using graphene oxide as

the starting material¹⁰. A dispersion of graphite oxide in an aqueous solution of $\text{Cd}^{2+}/\text{Zn}^{2+}$ on treatment with H_2S gas results in the deposition of metal sulphide nanoparticles over graphene sheets^{11,12}. Fluorescent graphene-CdSe composites can be prepared by interaction of graphene with CdSe nanoparticles in the presence of long chain surfactants¹³. In spite of these efforts, there is need to explore simpler and better methods of generating nanocomposites of CdS and CdSe nanoparticles with graphene and related materials, wherein the nanoparticles properly bind to the graphene surface.

In this article, we report the synthesis and characterization of nanocomposites of graphene with CdSe and CdS nanoparticles capped with different capping agents. The capping agents were expected to provide better binding of the nanoparticles to the graphene surface. We have prepared the nanocomposites by two methods. In one method, graphene was sonicated with CdSe or CdS nanoparticles capped with appropriate capping agents in toluene medium. In the second method, CdSe nanoparticles were deposited on the surface of large-area graphene self-assembled at the liquid-liquid interface¹⁴. We have also prepared water soluble nanocomposites with RGO using mercaptopropionic

acid-capped CdSe nanoparticles. We have examined the nanocomposites by Raman spectroscopy and other techniques.

Materials and Methods

Synthesis of graphene samples

Six-layer graphene (EG) was prepared by thermal exfoliation of graphite oxide. Another sample of graphene, HG, was prepared by carrying out arc discharge of graphite in the presence of H₂ (200 Torr) and He (500 Torr). HG contains 2–3 layers of graphene¹⁵. RGO was obtained by the hydrazine reduction of single-layer graphene oxide (SGO) in *N,N*-dimethylformamide (DMF)/water solution¹⁶.

Synthesis of nanocomposites with CdSe and CdS nanoparticles capped with pyridine (py-CdSe and py-CdS) or alkane-thiols (thiol-CdSe)

We have employed the solvothermal reaction between cadmium stearate [Cd(st)₂] and Se or S powder, in the presence of trioctylphosphine oxide (TOPO) in toluene and a catalytic amount of tetralin to prepare the CdSe and CdS nanoparticles^{17,18}. The resulting TOPO-capped CdSe and CdS quantum dots were dissolved and kept in hexane. The TOPO ligand was exchanged with pyridine¹⁹ by refluxing the particles (60 mg) in anhydrous pyridine (15 mL) at 118 °C under argon for 24 h. The average diameters of the py-capped CdSe and CdS nanoparticles were 3.5 and 6 nm respectively.

Solvothermal reaction was carried out between cadmium stearate [Cd(st)₂] and Se powder, in the presence of dodecanethiol in toluene and a catalytic amount of tetralin¹⁷ to obtain the thiol-capped CdSe nanoparticles. The average diameter of these CdSe nanoparticles was 5 nm.

Nanocomposites of graphene with nanoparticles were prepared as follows: 1 mg of graphene (EG or HG) along with 1 mg of py-CdSe, py-CdS or thiol-CdSe nanoparticles were dispersed in toluene medium by subjecting the mixture to ultrasonication for 15 min. The resulting suspensions were washed with toluene to remove excess CdSe nanoparticles.

Synthesis of nanocomposites at the liquid-liquid interface

The liquid-liquid interface, known to be an excellent medium to generate nanocrystalline films of inorganic materials²⁰, was employed to prepare large-area graphene-CdSe nanoparticle composites. Cadmium cupferronate was used as the cadmium source and 1,1-dimethylselenourea as the selenium source for the preparation of CdSe. Stock solutions of

cadmium cupferronate and 1,1-dimethylselenourea were prepared by taking 1 mg of each in 100 ml of toluene and 100 ml of water respectively (1 µg/ml). A few drops of *n*-octylamine were added to the cadmium cupferronate stock solution to make it completely homogeneous. Then 2 mg of few-layer graphene was added to the cadmium cupferronate solution and subjected to sonication for 1 h at four intervals of 15 min each. For the synthesis of EG-CdSe nanocomposite, the solution containing cadmium cupferronate and EG was added slowly to 20 ml of 1,1-dimethylselenourea stock solution taken in 100 ml glass beaker. The reaction mixture was left undisturbed for 24 h. After 24 h, a thin black coloured film formed by self-assembly at the toluene-water interface. The toluene in the upper layer was gently removed by syringe without disturbing the film. The film was lifted onto a desirable solid substrate for characterization purposes. This method was employed for the preparation of other nanocomposites as well.

Water soluble composites with mercaptopropanoic acid-capped CdSe nanoparticles (MPA-CdSe)

A solution containing 0.24 mmol of Cd(OAc)₂·2H₂O and 0.58 mmol of 3-MPA in 48 ml of distilled water was prepared and the pH adjusted to 9.3 with 1 M NaOH solution. The solution was taken in a three-necked flask fitted with a septum and valves and de-aerated by bubbling N₂ for 1 h. Sodium selenosulphate was injected into the solution under vigorous stirring. The solution was then refluxed²¹ at 100 °C for 10 h. The resulting solution contained MPA-capped CdSe nanoparticles with an average diameter of 4 nm. 1 mg of RGO along with 1 mg of MPA-CdSe nanoparticles was ultrasonicated in water for 15 min to give the RGO-MPA-CdSe nanocomposite. Resulting suspensions were washed several times with water to remove excess amount of CdSe nanoparticles.

Characterization

The morphology of the CdSe nanostructures in EG-CdSe composites was studied by field emission electron microscopy (FESEM) with FEI Nova-Nano SEM-600 instrument. Transmission electron microscope (TEM) images were recorded with TECHNAI instrument operated at an accelerating voltage of 200 kV. UV spectra of the films and dispersions were recorded with a Perkin-Elmer Lambda 900 UV/vis spectrophotometer. Photoluminescent spectra were recorded with a Perkin-Elmer (model LS 55) spectrophotometer.

Raman spectra were recorded with a LabRAM HR high resolution Raman spectrometer (Horiba-Jobin Yvon) using a He-Ne laser (633 nm).

Results and Discussion

Pyridine-capped CdSe (py-CdSe) nanoparticles with an average diameter of 3.5 nm were sonicated with the graphene sample EG to obtain nanocomposites. In Fig. 1(a), we show FESEM image of the composite of py-CdSe with EG. EDX analysis confirms the presence of Cd and Se in the composite (see inset in Fig. 1a). The composite of py-CdSe nanoparticles with HG was prepared in a similar fashion and a FESEM image of this composite is shown as an inset in Fig. 1(a). TEM images confirm relatively uniform coverage of the CdSe nanoparticles over the graphene surface. A typical TEM image of the composite of py-CdSe with EG is shown in Fig. 1(b). XRD patterns of these composites show that the CdSe nanoparticles exist in the wurtzite structure.

Nanocomposites of thiol-CdSe nanoparticles with the two graphene samples, EG and HG, were prepared by ultrasonication in toluene medium. In Fig. 2(a) & (b), we show FESEM images of the composites of thiol-CdSe nanoparticles with EG and HG respectively. The CdSe nanoparticles nicely decorate the graphene samples. In Fig. 2(c) & (d), we show low and high magnification TEM images of the composite of thiol-CdSe with EG. The average particle size of thiol-CdSe particles is around 5 nm. The inset in Fig. 2(c) gives the electron diffraction pattern of the particles. The individual particles seem to be single crystalline as revealed by the presence of lattice fringes.

We have prepared composites of EG and HG samples with py-CdS nanoparticles with an average diameter of 6 nm by ultrasonication. Typical FESEM images of the nanocomposites of py-CdS nanoparticles with EG and HG respectively are shown in Fig. 3(a) & (b). The py-CdS nanoparticles are uniformly coated over the graphene surfaces. EDX analysis confirms the presence of Cd and S as can be seen from the inset in Fig. 3(a). EG+py-CdS and HG+py-CdS composites absorb at 480 nm and show negligible emission.

Raman spectroscopy is known to be extremely useful to characterize graphene, in particular to understand the interaction of graphene with nanoparticles of semiconducting materials^{22,23}. Thus, the shifts in the Raman G band are useful in understanding the nature of interaction of graphene with the interacting species^{23,24}. For example, this technique has been used to characterize the nature of electronic interaction in composites of graphene with inorganic nanoparticles²³. We have studied the Raman spectra of EG, HG and CdSe nanoparticles along with those of the nanocomposites. In Fig. 4(a), we show the Raman spectra of EG and of the EG+py-CdSe nanocomposite. Raman spectra of HG and the HG+py-CdSe nanocomposite are shown in Fig. 4(b). We readily see that the G-band of graphene hardens (blue-shift) on interaction with the CdSe nanoparticles. The D-band does not show any significant change. Shifts in the 2D-band are observed on interaction of EG with thiol-CdSe and py-CdSe nanoparticles. HG shows a similar behaviour on interaction with thiol-CdSe and py-CdSe nanoparticles. Similar shifts are observed in the case of py-CdS-graphene nanocomposites. In

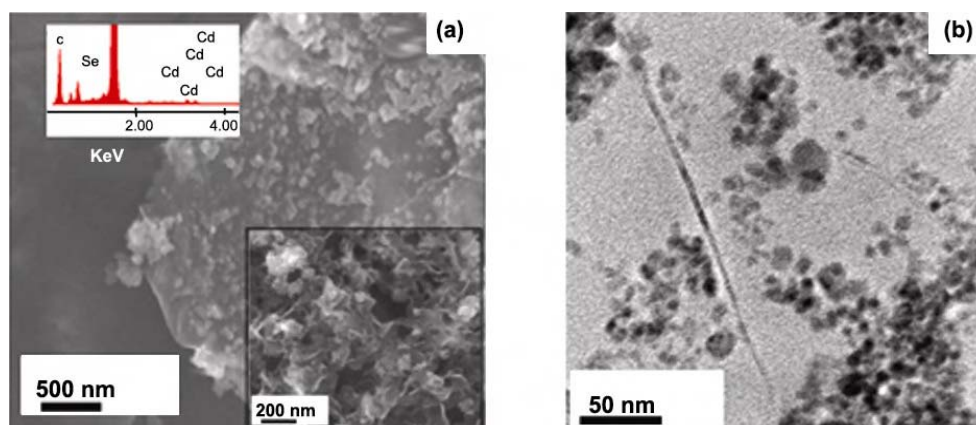


Fig. 1 — (a) FESEM images of EG decorated by py-CdSe. Top inset in (a) shows EDX analysis and bottom inset shows a FESEM image of HG decorated by py-CdSe. (b) TEM image of EG decorated by py-CdSe.

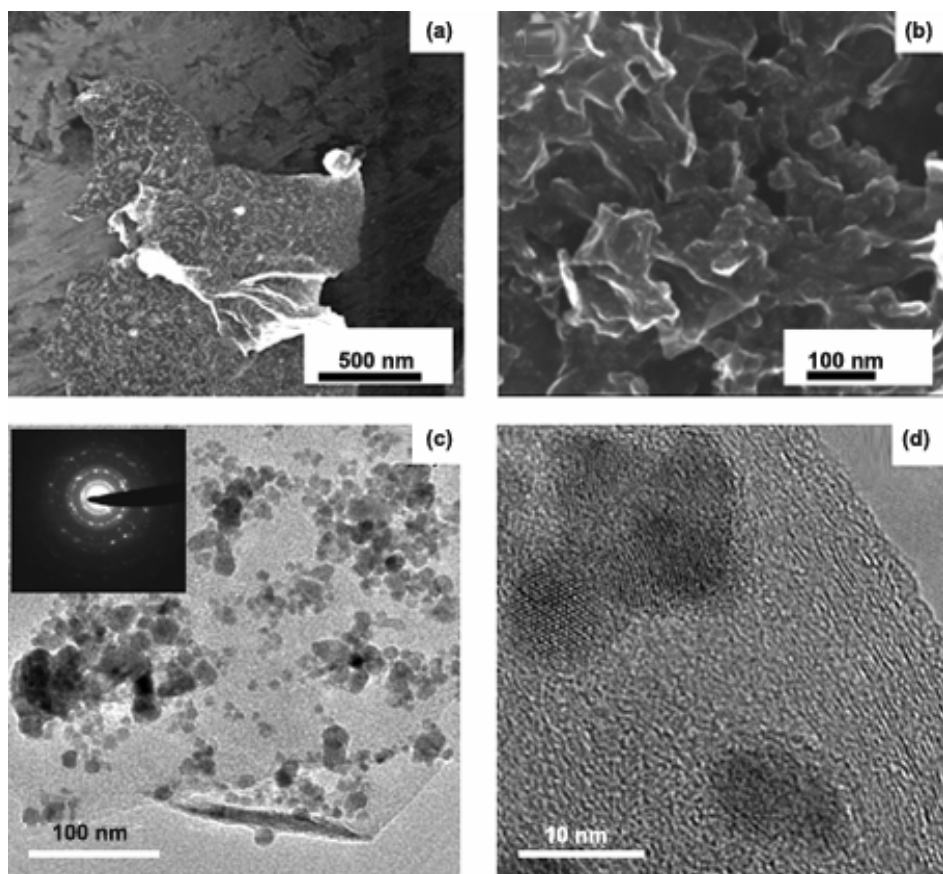


Fig. 2 — FESEM images of thiol-CdSe decorated (a) EG and (b) HG. Low and high magnification TEM images of thiol-CdSe decorated EG are shown in (c) and (d) respectively. Inset in (c) shows the electron diffraction pattern.

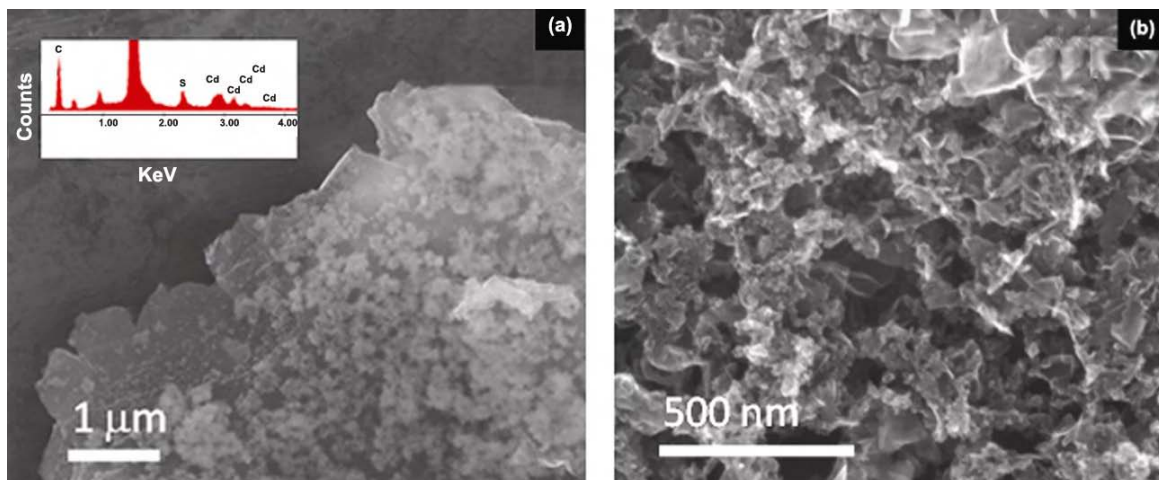


Fig. 3 — FESEM images of nanocomposites of py-CdS with (a) EG and (b) HG. Inset in (a) shows the EDX analysis.

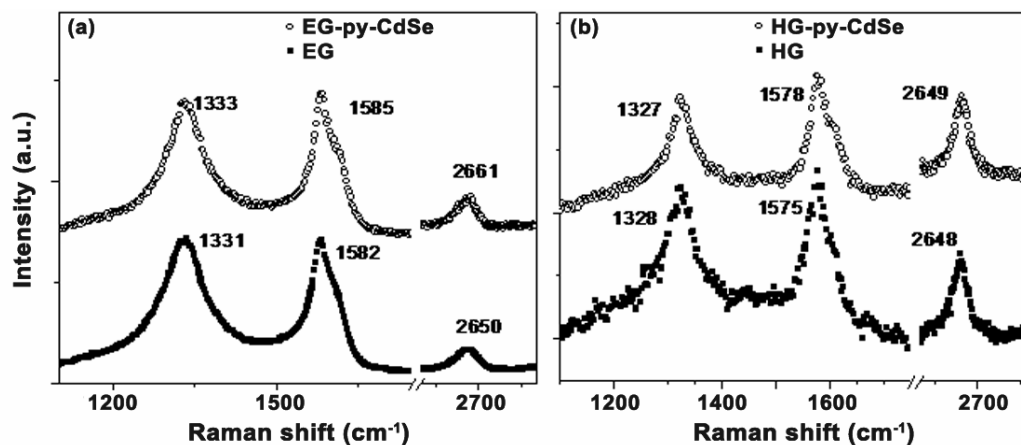


Fig. 4 — Raman spectra of pristine and py-CdSe decorated (a) EG and (b) HG.

Table 1, we have listed the Raman frequencies and the ratios of intensities of the D and G bands (I_D/I_G) as well as of the 2D and G bands (I_{2D}/I_G). The I_{2D}/I_G decreases in the case of EG+thiol-CdSe. Interestingly, the I_D/I_G ratio in EG-py-CdSe remains around the same as in EG, but the I_{2D}/I_G ratio becomes larger. The I_D/I_G also increases in EG-py-CdS. In the case of HG, I_{2D}/I_G becomes large in HG-py-CdSe and HG-py-CdS, unlike HG-thiol-CdSe, which is less than in HG. It is difficult to fully interpret these results at the present stage, except to say that these changes result from the electronic interaction between the nanoparticles and graphene. It should be noted that unlike HG whose surface is clean, EG would have some oxygen functionalities on the surface. Furthermore, pyridine-capped nanoparticles show distinct differences in the Raman spectra compared to the thiol-capped nanoparticles.

Kim *et al.*⁹ report that CdSe quantum dots (average size ~ 10 nm) induce red shifts in G and 2D bands of graphene. The observed red-shifts are attributed to quantum dot induced electron injection into graphene. The mechanism of n-doping by CdSe quantum dots is intriguing. Because the work function of graphite (4.6–5.0 eV)²⁵ is located in the HOMO–LUMO gap of CdSe²⁶, it is possible that electrons from the conduction band of CdSe quantum dots flow into graphene. In the case of single-walled carbon nanotubes (SWNTs), Li *et al.*¹⁹ have shown that the G-band of SWNTs blue shifts on interacting with py-CdSe nanoparticles. We have used a 632 nm laser in our Raman experiments and the CdSe and CdS nanoparticles absorb light below 632 nm. These quantum dots, therefore, cannot inject electrons into graphene. The observed shifts in our experiments

Table 1 — Raman band positions and intensity ratios of graphene and graphene nanocomposites

	Raman band positions (cm ⁻¹)			Intensity ratios	
	D-band	G-band	2D-band	I_D/I_G	I_{2D}/I_G
EG	1331	1582	2650	2.21	0.31
EG-thiol-CdSe	1330	1588	2655	1.12	0.20
EG-Py-CdSe	1333	1585	2661	2.10	0.44
EG-Py-CdS	1330	1585	2648	2.9	0.18
HG	1328	1575	2648	1.68	0.75
HG-thiol-CdSe	1330	1583	2660	1.39	0.51
HG-Py-CdSe	1327	1578	2649	1.17	0.91
HG-Py-CdS	1328	1577	2650	1.05	0.82

cannot be explained by the above mechanism. The G band position is known to be sensitive to electron or hole doping in graphene^{23,27}. Blue shifts have been generally found when there is electron withdrawal from graphene by molecules such as TCNE.

We have studied the electronic absorption spectra as well as photoluminescence spectra of the CdSe-graphene nanocomposites. The CdSe nanoparticles and the composites absorb around the same region. EG-thiol-CdSe and HG-thiol-CdSe composites show a broad absorption band around 450 nm and an intense band around 540 nm. EG-py-CdSe and HG-py-CdSe composites absorb at 490 nm. The PL spectra of the nanocomposites show characteristic emission of the CdSe nanoparticles. Typical PL spectra of EG-thiol-CdSe and EG-py-CdSe composites are shown in Fig. 5(a) and (b) respectively. The EG-thiol-CdSe composite shows the PL band centered at 565 nm whereas the EG-py-CdSe composite shows a low intensity PL band around 580 nm. Graphene is known to quench the emission of CdSe nanoparticles. Furthermore, electronic interaction between CdSe nanoparticles and graphene

would also depend on the nature of the capping agent. The low intensity PL band in the case of graphene-py-CdSe compared to graphene-thiol-CdSe arises from these considerations. The observed differences between EG-py-CdSe and EG-thiol-CdSe in their photoluminescence and absorption spectra are also reflected in the Raman spectra as mentioned earlier.

The liquid-liquid interface^{14,20} has been employed by us to prepare large area graphene-nanoparticle composites. A FESEM image of EG-CdSe composite film formed at the organic-aqueous interface after 24 h of reaction is shown in Fig. 6(a). The film extends over several micrometers. The FESEM image reveals decoration of CdSe nanoparticles over the graphene surfaces. Such extended decoration was possible because of the use of the liquid-liquid interface. Adsorption of cadmium cupferronate on the

few-layer graphene helps in more effective reaction of 1,1-dimethyl selenourea. Figure 6(b) shows a HREM image of a EG-CdSe composite film. The image shows the presence of lattice fringes in the CdSe nanoparticles of 4-5 nm diameter. Figure 7 shows electronic absorption and PL spectra of a EG-CdSe composite film. The absorption spectrum²⁸ shows an intense band around 480 nm and a broad band around 530 nm. The particle size of CdSe nanoparticles calculated from the absorption spectrum is in close agreement with that from TEM. The PL spectrum shows an intense signal at around 670 nm. It should be noted that the CdSe particles in the composites prepared at the liquid-liquid interface are not capped by strongly binding reagents. Accordingly, the Raman G-bands show negligible shifts in the nanocomposites prepared by this method.

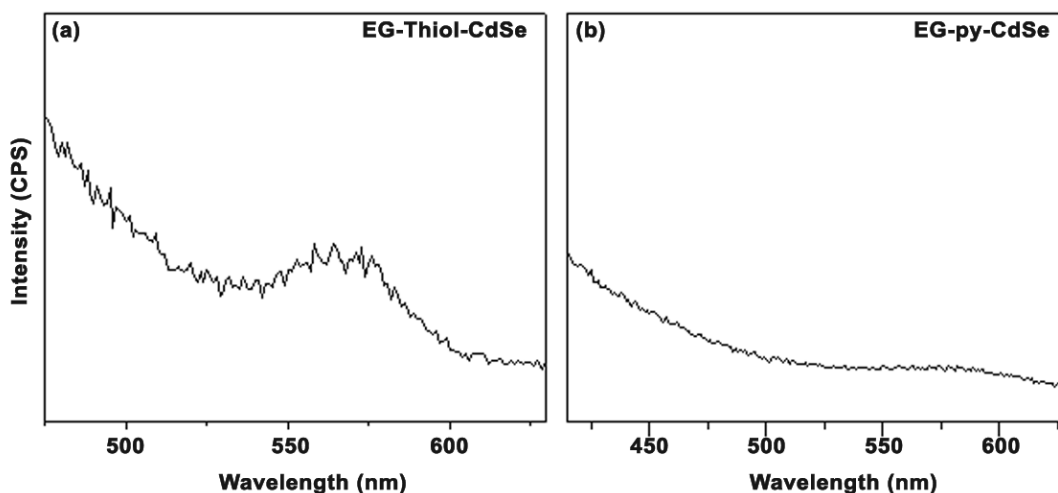


Fig. 5 — PL spectra of nanocomposites of (a) thiol-CdSe with EG and (b) py-CdSe with EG.

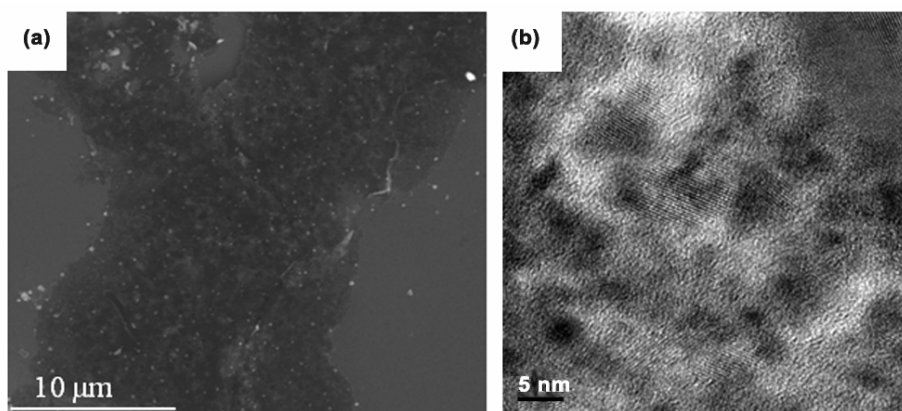


Fig. 6 — (a) FESEM and (b) TEM images of EG-CdSe prepared at the liquid-liquid interface.

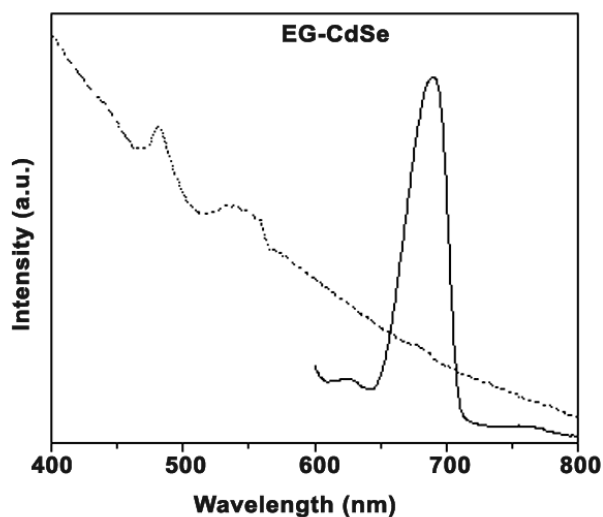


Fig. 7 — UV and PL spectra of EG-CdSe prepared at the liquid-liquid interface.

We have studied the interaction of CdSe nanoparticles with RGO as well. We have prepared water soluble CdSe nanoparticles by capping them with mercaptopropionic acid (MPA) by ultrasonication. The size of the MPA-CdSe nanoparticles as found by the TEM images in Fig. 8(a) is 4 nm. In Fig. 8(b), we show a FESEM image of the RGO + MPA-CdSe composite. From the figure we see that the entire RGO flake is covered with MPA-CdSe nanoparticles. The PL spectrum of the MPA-CdSe nanoparticles in Fig. 9(a) shows a band at 425 nm and another centered at 570 nm corresponding to band edge and defect emission respectively. There is complete quenching of the PL bands of the MPA-CdSe nanoparticles on interaction with RGO (Fig. 9b). This is considered to be due to excited electron transfer between CdSe nanoparticles and RGO⁹. On interaction of RGO with MPA-CdSe,

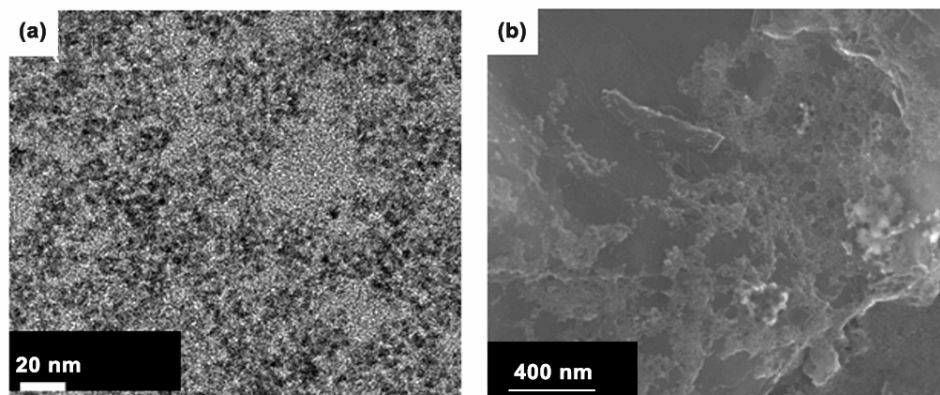


Fig. 8 — (a) TEM image of MPA-CdSe nanoparticles and (b) FESEM image of MPA-CdSe decorated RGO.

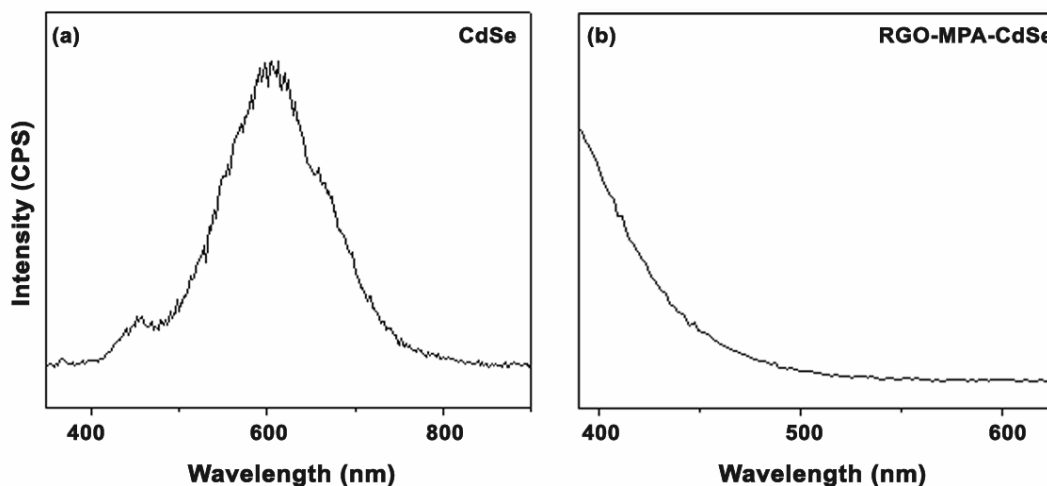


Fig. 9 — PL spectra of (a) MPA-CdSe and (b) MPA-CdSe decorated RGO.

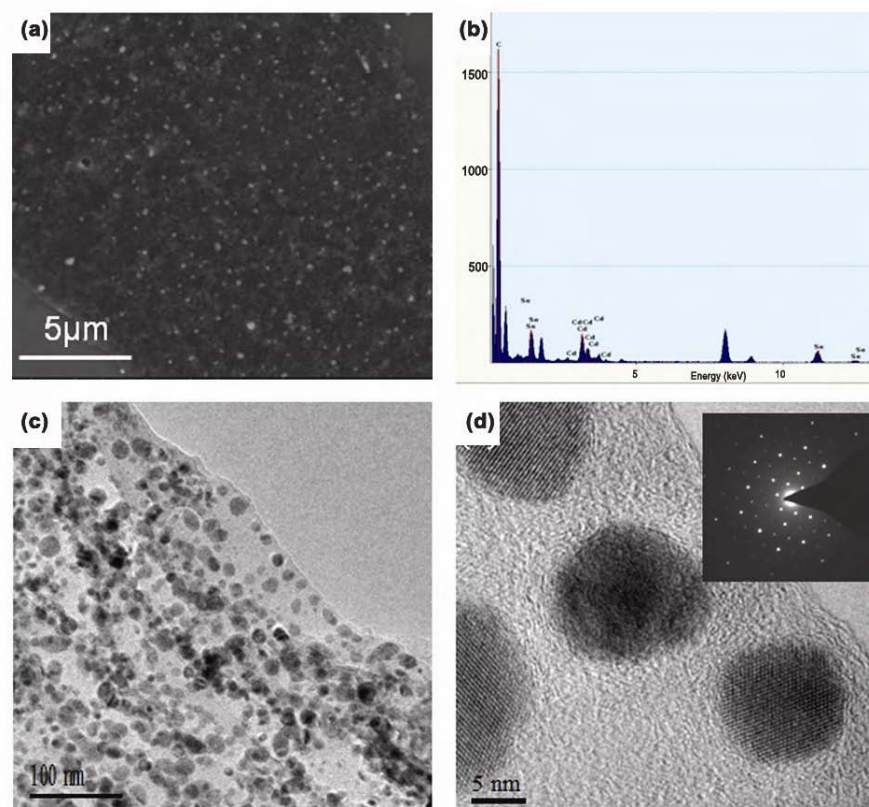


Fig. 10 — (a) FESEM image and (b) EDX pattern of RGO-CdSe prepared at the liquid-liquid interface. (c) Low and (d) high magnification TEM images of RGO-CdSe.

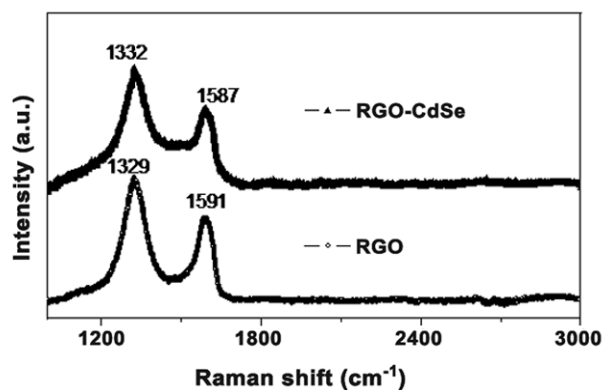


Fig. 11 — Raman spectra of RGO-CdSe and pure RGO prepared at liquid-liquid interface.

the Raman G-band of RGO shifts from 1596 to 1602 cm^{-1} and there is negligible shift in D-band frequency.

We have also employed the liquid-liquid interface to prepare the RGO-CdSe nanocomposite. Figure 10(a) shows a FESEM image of a RGO-CdSe composite film extending over several micrometers. The image shows that CdSe nanoparticles nicely

decorate over reduced graphene oxide. Figure 10(b) gives the EDX analysis corresponding to the FESEM image in Fig. 10(a). Figure 10(c) & (d) shows the TEM and HREM images of the RGO-CdSe composite films. The HREM image indicates the presence of lattice fringes of the CdSe nanoparticles. The inset in Fig. 10(d) shows the electron diffraction pattern of the RGO-CdSe composite, which confirms the single crystalline nature of CdSe nanoparticles over RGO.

The Raman spectra of RGO-CdSe and RGO are shown in Fig. 11. RGO shows the G-band at 1591 cm^{-1} whereas the composite of RGO and CdSe shows the band at 1587 cm^{-1} , exhibiting softening of G-band. This result suggests the occurrence of charge transfer interaction between RGO and CdSe nanoparticles, similar to that found between graphene and electron donor molecules like aniline²³.

Conclusions

In conclusion, two simple procedures have been employed to synthesize nanocomposites of few-layer graphenes with nanoparticles of CdSe and CdS. The evidence of electronic interaction between

nanoparticles and graphene is provided by Raman spectroscopy. Photoluminescence of the nanoparticles shows the dependence of the spectra on the capping agent used on nanoparticles. Thus, the PL bands of py-CdSe are quenched more effectively compared to thiol-CdSe by graphene. The PL bands of MPA-capped CdSe nanoparticles are quenched completely by RGO.

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