Surface charge doping induced carrier type reversal in spin coated CdS/rGO layered nanohybrid films

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Abstract

The growth of reduced graphene oxide (rGO) based semiconductor nanohybrids through simple, scalable, additive-free and cost-effective route has fascinated significant attention of researchers for both fundamental research areas and its commercial applications. In the present work, cadmium sulphide/reduced graphene oxide (CdS/rGO) films were sequentially or layer-by-layer (LBL) deposited by spin coating method. The samples were characterized by using x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV-visible spectroscopy, Raman spectra and Hall measurements. The cubic phase of the CdS and formation of rGO was confirmed by XRD measurements. The FESEM micrographs elucidate a change in morphological features with rGO content in CdS/rGO nanohybrid films. The Raman spectra indicate the characteristic features for nanostructured CdS and rGO in these samples. Optical transmission is found to increase along with a decrease in optical gap with rGO content. Hall measurements showed the change in the majority carrier concentration with rGO content or the observation of surface charge transfer doping (SCTD) in these nanocomposites. The change in dispersion of refractive index with rGO content for CdS/rGO nanocomposites in terahertz (THz) spectral region has been observed. These results are very important for the development of new functionality of nanohybrid materials for emerging technologies.

1. Introduction

Researchers strive hard to find an environment friendly alternative energy source for fossil fuel and utilize the renewable sustainable energy efficiently for the global energy crisis. The development of solar cells, super capacitors, photocatalytic degradation, photocatalytic water splitting, photolysis, photo electrochemical cell, dye degradation and sensors etc are the solutions to ease the energy demand. All these properties have strong dependence on the charge generation-recombination phenomena for the semiconducting materials or their hybrid counterparts. The discovery of Graphene in 2004 by Novoselov and Geim, the carbon atoms are arranged in sp2 hybridized honeycomb lattice has minimum thickness of 0.32 Å, high surface area (theoretically 2630 m2 g−1), ambipolar transistor behaviour and high intrinsic carrier mobility of 5000 to 20,000 cm2 V−1s−1 for flat-bed transistors [1,2]. Recently, the reliable production of graphene derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) offers a new way to synthesize graphene based composites. rGO is considered as physical analogue of graphene and cost effective substitute of the same which can be produced by reducing the oxygen functional groups (epoxy, carboxyl, alcohol) present on the edge and basal plane of graphene oxide (GO) [3–5].

On the other hand, the wide band gap (II-VI) semiconductors have found exceptional electrical and optoelectronic properties, making them as a potential candidate in various fields like field emission transistors (FET), light emitting diodes (LED), photodetectors, biosensors and so on. Most of them exhibit...
unipolar electrical conductivity, that is, n-type conductivity for ZnS, ZnSe, CdS, and CdSe and p-type conductivity for ZnTe and CdTe [6]. Among these, cadmium sulfide (CdS) is n-type semiconductor with direct band gap (2.42 eV) have promising candidate for efficient light harvesting media and excellent charge separation properties for their applications in photocatalytic degradation, sensor, bio imaging, solar cell, water splitting, photochemical catalysts and luminescence devices etc [7, 8].

CdS/rGO nanocomposites are very useful in enhancement of photocatalytic performance [9, 10], biosensors [10], solar cells [11], photovoltaic devices [12] and selective organic transformations [13], pollutants degradation [14]. These composites can be synthesized by solvothermal method [15], microwave-assisted method [16], electrostatic assembly process [17], hydrothermal method [18], reflux condensation [19], chemical precipitation method [20], ionic-liquid method [21], solvothermal method [22], radiation assisted method [23] etc and very recently by the layer-by-layer (LBL) self-assembly fabrication technology [24]. However, the synergetic effect possessed by these nanohybrid materials can be potentially utilized for the development of optoelectronic devices if the structure-property relationship is completely understood for these materials.

This work reports the synthesis of CdS/rGO nanohybrid films by simple spin coating technique with different weight percentage of rGO. Since CdS is electron donor and rGO is electron acceptor, therefore, the surface charge transfer doping (SCTD) can be achieved in these nanohybrid films. The synthesized samples were characterized by x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV-Vis spectroscopy, Raman spectroscopy and Hall measurements. The refractive index in THz spectral region (0.2–2.0 THz) has also been reported.

2. Experimental

2.1. Materials and characterization techniques
The precursor chemicals such as graphite flakes (98%, LOBA CHEMIE), KMnO₄, H₂SO₄, H₃PO₄ (98%, RANKEM), 30% H₂O₂ (MOLYCHEM), 30% HCl, ethanol (RANKEM), distilled water (LOBA CHEMIE), cadmium acetate dehydrate, thiourea (99%, Sigma Aldrich), 2-methoxymethanol, diethanolamine (HN(CH₂CH₂OH)₂) (CDH) are used for synthesis. All chemicals were used without further purification.

2.2. Preparation of glass substrates
The glass substrates were cleaned gently using detergent, dipped in freshly made aqua regia (H₂SO₄:HNO₃=3:1) for 3 h, sonicated for 1 h in distilled water. After this treatment, these samples were successively washed with acetone and water for three times and finally they were dried at 80 °C in oven. The glass slides are then cut into (1.5 × 1.5) cm² for spin coating.

2.3. Deposition of CdS films
CdS films were deposited on very well cleaned glass substrates by sol-gel spin coating method [7]. Firstly, the CdS solution was prepared for spin coating by dissolving 1.0 M cadmium acetate (CH₃COO)₂Cd.2H₂O and 1.0 M thiourea (NH₂CSNH₂) in 2-methoxymethanol separately and kept them under constant stirring for 1 h. Then, both the solutions were mixed and stirred magnetically for half an hour at 70 °C. Then, diethanolamine was added to adjust pH of the solution to 9. The solution was aged for 12 h for the completion of the gelation process. This solution was then spin coated on well cleaned glass substrates at 3000 rpm for 30 s. This process was repeated for 15 times to increase the film thickness and finally post-annealed at 200 °C for 2 h in hot oven.

2.4. Growth of GO and rGO films
The solution of 0.2 mg ml⁻¹ of freshly synthesized GO was prepared in 100 ml of water and then ultrasonicated for 1 h duration for their exfoliation in solution form. This solution was spin coated on glass substrates at 3000 rpm for 30 s and dried at 150 °C. This step was repeated ten times for getting these films and finally annealed at 200 °C for 2 h in hot oven.

2.5. Growth of CdS/rGO films
Graphene oxide was synthesized by using Improved Hummer’s method [5, 25]. The freshly synthesized GO was dissolved and then ultrasonicated (1 h) for exfoliation in their solutions. The freshly prepared CdS solution and GO solution were sequentially spin coated on glass substrates at 3000 rpm for 30 s using layer-by-layer (LBL) deposition method. Each time the coated films were dried at 150 °C in oven and 10 layers of each and finally CdS layer was deposited on CdS/rGO for getting nanohybrid films. These samples were annealed at 200 °C for 2 h in hot oven. The different samples for 0.00, 0.04, 0.12 and 0.20 mg ml⁻¹ rGO in water was used for the synthesis of different samples i.e CdS/rGO-0, CdS/rGO-1, CdS/rGO-3 and CdS/rGO-5 respectively.
2.6. Characterization

The crystalline phases were identified by using an x-ray diffraction (X’Pert Pro, Panalytical Instruments) equipped with Cu Kα (λ = 1.54056 Å) radiation. The morphology of the films was determined using field emission scanning electron microscopy (SUPRA 55, Carl Zeiss). The optical properties were recorded using a UV-visible spectrophotometer (UV-1800, SHIMADZU). Raman spectra was recorded with unpolarized light in backscattering configuration using Renishaw-in-Via Raman system equipped with Ar laser (wavelength 514.5 nm) and suitable filters. Electrical property was studied in van der Pauw’s geometry by employing a Hall measurement system (Ecopia HMS 3000, Bridge technology) under magnetic field. Measurements on both positive and negative magnetic field directions were carried out to minimize the magneto-resistance contributions as well as the voltage probe misalignment effects. The carrier concentration (n) was calculated from \( R_{\text{H}} = \frac{1}{ne} \), and the mobility (\( \mu_{\text{H}} \)) from \( \mu_{\text{H}} = \frac{\sigma}{ne} \), where e is the electron charge. The refractive index in THz spectral region was studied using indigenously built THz oscillator (available at Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad, India) and schematic arrangement of different components are described elsewhere [26].

3. Results and discussion

3.1. Structure analysis

Figure 1 shows the x-ray diffractogram for CdS/rGO nanohybrid films. The broad diffraction peak for cubic phase of CdS was observed at ∼26.68° (JCPDS No: 42-1411), indicating the growth of nanoparticle [7, 8]. The formation of shoulder at lower diffraction angle (24.5° peak can be assigned to rGO) than CdS phase confirm the incorporation of rGO in CdS/rGO composites [9–12]. No typical diffraction peaks for the carbon species are observed in the composites, because the relatively low diffraction intensity of the expected rGO peak at ∼24.5° is most likely shielded by the main cubical CdS peak at 26.6°.

Figure 2(a) shows the Raman spectra for the as synthesized GO and rGO films. The D and G bands are observed at 1360 cm⁻¹ and 1600 cm⁻¹ respectively. It has been observed that the intensity ratio (I_D/I_G) changes from 0.78 for GO to 1.23 for rGO for depicting the increase in defectiveness upon thermal annealing or conversion of GO to rGO. Figure 2(b) illustrates the Raman spectra for CdS/rGO nanohybrid films. It has been observed that characteristic Raman peaks for both rGO and CdS existed in the spectra of composite films. The intense and broad peaks at 310, 612, 915 and 1215 cm⁻¹ can be assigned to fundamental optical phonon mode (LO), the first over tone mode (2LO), the second overtone (3LO) and the third overtone (4LO) of CdS, respectively [8]. The other two peaks characteristic of carbon materials, i.e. rGO in present case are observed at 1384 and 1590 cm⁻¹, which are referred as D band (breathing mode of κ-point phonons of A1g symmetry) and G band (E2g phonon of sp² bonds of carbon atoms) respectively. The ratio peak intensity for D and G band (I_D/I_G)
Figure 2. (a) Raman spectra of spin coated GO and rGO films, and (b) Raman spectra, (c) Deconvoluted Raman spectra for CdS/rGO nanohybrid films.
and conduction bands, $\alpha$ where in ID $rGO$ content in nanohybrid indicate the degree of defectiveness of $rGO$. The intensity of D and G peaks are enhanced with the increase in the variation of change in Raman spectra signifies the incorporation of CdS with $rGO$ in the literature [12, 19].

Figure 2(c) shows the deconvoluted characteristic CdS Raman peak (Lorentzian components) for CdS/$rGO$ nanohybrid films. The first-order and second-order optical phonon modes can be considered as the superposition of several components i.e., surface optical (SO) and longitudinal optical (LO) modes [8] and tabulated in table 1. Here, the SO phonon modes were blue shifted and broadened with particle size for CdS/$rGO$ – 1 samples and the increase in SO phonon frequency, which is assumed to be Fröhlich mode, caused by the phonon dispersion and lattice contraction [27]. The broadening of surface phonons can be the result of boundary relaxation process at the interface between CdS and $rGO$ nanoparticles. For CdS/$rGO-3$ and CdS/$rGO-5$ samples, the collision of SO phonon with electrons lead to increase in inelastic scattering and correspondingly the SO phonon frequency gets red shifted. However, the increase in phonon dispersion and lattice contraction due to collision, the inelastic scattering of electron with phonon increases to favour decrease in electron mobility. The influence of SO phonons on carrier scattering and its electronic transport properties was explained by using full-band ensemble Monte Carlo method [28]. Due to enhanced electron-phonon scattering, the electron mobility decreases while the holes concentration and mobility increases with $rGO$. Ultimately, the polarity of CdS can be tuned into p-type by surface charge transfer doping [6]. The role of SO mode and surface change doping with $rGO$ incorporation in CdS are discussed in section 3.3.

Figures 3(a)–(d) shows the microscopic image of CdS/$rGO$ samples. This agglomerated or interconnected granular morphology with narrow size distribution has been observed for pure CdS or CdS/$rGO-0$ films. The incorporation of $rGO$ lead to change in morphological features i.e. the formation of cauliflower like structures for CdS/$rGO-1$ films along with the observation of transparent ultrathin $rGO$ layer beneath these structures (the decreased clarity for central crater among nanostructures). Further increase in $rGO$ content, lead to the formation of continuous network of interconnected grains with disappearance of spherical or cauliflower like structures to favour smooth morphology CdS structures formed above $rGO$ layers. For CdS/$rGO-5$ nanohybrid, the formation of closely packed continuous network resulting in coral branches-like shape due to the excellent hybridization of the $rGO$ and CdS nanoparticles. The $rGO$ sheets may act as bridges for the connection between different CdS nanoparticles in CdS/$rGO$ nanohybrid films [12, 29, 30].

### Table 1. Frequency ($\nu$) and full width half maximum ($\beta$) for the surface optical and longitudinal optical phonon modes for CdS/$rGO$ nanohybrid films.

| S. no. | Sample codes | First-Order $\nu$($\beta$) [cm$^{-1}$] | Second-Order $\nu$($\beta$) [cm$^{-1}$] |
|--------|--------------|----------------------------------------|----------------------------------------|
|        |              | SO mode | LO mode | SO mode | LO mode |
| 1.     | CdS/$rGO-0$  | 273(75) | 315(28) | 568(32) | 615(48) |
| 2.     | CdS/$rGO-1$  | 289(110)| 312(36) | 566(24) | 609(45) |
| 3.     | CdS/$rGO-3$  | 262(20) | 303(25) | 537(6)  | 603(48) |
| 4.     | CdS/$rGO-5$  | 263(19) | 303(24) | 529(110)| 603(78) |

3.2. Optical properties

3.2.1. UV-vis-NIR spectra

Figure 4(a) shows the transmission spectra for CdS/$rGO$ nanohybrid films. It has been easily seen from the figure that the remarkable increase in transmittance in visible region for CdS/$rGO$ films. It can be ascribed to the incorporation of highly transparent $rGO$ (transmittance ~97.7%) in these composites [31]. The band gap is calculated by using Tauc’s relation [32]:

$$(\alpha h\nu)^n = B(\nu - E_g)$$

where $\alpha$ is absorption coefficient, $B$ is a parameter that is related to the effective masses associated with valence and conduction bands, $n = 2$ for direct transition, $h\nu$ is photon energy and $E_g$ is optical gap. Figure 4(b) shows the variation of $(\alpha h\nu)^2$ versus $h\nu$ for CdS/$rGO$ nanohybrid films. The value of optical gap is 2.21 eV for CdS films [7, 8] and the values as 1.97 eV, 2.12 eV and 1.78 eV for the increasing $rGO$ (1, 3 and 5 wt.%) contents in CdS/$rGO$ films [19, 21]. The small content of $rGO$, the increase in nanoparticle size can be related to decrease in optical gap due to agglomeration of CdS nanoparticles or the $rGO$ act as structure directing units. Further increase in $rGO$ content causes the decrease in particle size of CdS nanoparticles to favour increase of optical gap for CdS/$rGO-3$ samples. But, the contributions of inelastic scattering of electron-phonons may be increased (for highest content of $rGO$) to favour the decrease in optical gap for CdS/$rGO-5$ samples. This can be ascribed to its
enhanced ability to absorb the visible light making them a promising photocatalyst for the solar driven application [13, 14].

3.3. Electrical properties
The electrical properties of CdS/rGO nanohybrid films were measured by Hall measurements. The carrier concentration was determined by using the formula $n = -B_z I / t V_H Q$, where $B_z$ denotes the magnetic field, $I$ the DC electric current, $t$ the sample thickness, $V_H$ the Hall voltage, and $Q$ the electronic charge. The values of charge mobility, resistivity, carrier concentration and Hall coefficient for CdS/rGO nanohybrid films are listed in table 2. Here, the Hall coefficient varies from negative to positive value ($-0.019$ to $0.544$), i.e. the change in dominant carrier concentration from n-type (CdS) to p-type (CdS/rGO) with the incorporation of rGO. The addition of rGO in CdS, favour slight decrease in electron density, and can be credited to passivation of defect sites of CdS in the presence of rGO. As the ratio of rGO in CdS/rGO increases, the charge mobility and carrier concentration decreases. Since, the rGO and CdS form p-n heterojunction structure or efficient charge carrier compensation for nanohybrid films and finally, the carrier type reversal for CdS/rGO films with sufficient rGO content. This carrier type reversal have been accompanied with increase in resistivity and change in Hall coefficient from negative to positive [3]. As discussed earlier, the size dependent broadening of SO mode was mainly attributed to boundary relaxation at the interface between quantum dot and its host material. While the change in SO phonon frequency implies the change in disorder and dispersion of nanostructure which results in electron coupling by SO phonons. This affects the electron mobility and change in Fermi level of the composite thin films by Rode’s Iterative method [33] and Drude model of dielectric function [34]. As surface optical phonon scatters the electron, the electron mobility gets decreased. The Hall measurements proved that the polarity of CdS changed from n-type to p-type by the addition of rGO by surface charge transfer doping from rGO to CdS in CdS/rGO films.

3.4. Optical constant in THz region
Figure 5 contains plots of the average refractive indices of CdS/rGO nanocomposites thin films with different weight percentage of rGO in 0.1–2.0 THz frequency. We found that the index of refraction decreases with frequency for pure CdS and CdS/rGO-1, whereas the index of refraction increases with frequency for CdS/rGO nanocomposites thin films CdS/rGO-3 and CdS/rGO-5. Maximum ($n = 5.5$) and minimum ($n = 2.7$) values.

Figure 3. FESEM images for CdS/rGO nanohybrid samples.
were observed at 0.1 and 1.45 THz for CdS/rGO-0, but the average value \( n \) is 3.3. Maximum \( n = 2.8 \) and minimum \( n = 2.6 \) values were observed at 0.1 and 1.45 THz for CdS/rGO-1, but the average value \( n \) is 2.7. Maximum \( n = 1.3 \) and minimum \( n = 0.6 \) values were observed at 2.0 and 0.1 THz for CdS/rGO-3, but the average value \( n \) is 1.2. Maximum \( n = 1.9 \) and minimum \( n = 1.8 \) values were observed at 0.1 and 2.0 THz for CdS/rGO-5, but the average value \( n \) is 1.85. Between 1.0 to 1.5 THz regions the shoulder shape proves that there is an excellent hybridization between CdS and rGO nanoparticles and the density of nanomaterials increases. In CdS/rGO-0, the refractive index decreases with increase of frequency and it proves the nanoparticles density decreases. The variation of refractive index with respect to frequency change in CdS/rGO-
1 decreases, increases in CdS/rGO-3, stabilizes in CdS/rGO-5 and it proves the variation of nanoparticles density and hybridization level between CdS and rGO nanoparticles.

4. Conclusion

The surface charge transfer doping in nanohybrids of CdS (n-type) with rGO (p-type) have been successfully synthesized by layer-by-layer assembly using the spin coating technique. The broad diffraction peak near 26.6° indicates the synthesis of CdS nanoparticles while the formation of shoulder at 24.5° related to the rGO or the formation of CdS/rGO nanohybrid films. The ratio of $I_D/I_G$ reveals the reduction of GO into rGO. The observation of fundamental, first, second and third order optical phonon modes for CdS have been found in Raman measurements. The change in position and full width at half maximum for the surface optical and longitudinal optical phonon modes are correlated with electron phonon interaction or decreased electron mobility for CdS/rGO nanohybrids. The electrical measurements also indicate the surface change transfer doping induced carrier type reversal in CdS/rGO nanohybrids. The change in transmission and optical gap also suggest the formation of CdS/rGO nanohybrid films. The dispersion of refractive index in THz spectral region also found to change for CdS/rGO nanohybrid films. These results are very useful for the development of novel functionality for the hybrid materials.

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Figure 5. Spectral variation of refractive index ($n$) in THz frequency region for CdS/rGO nanohybrid films.
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