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Synthesis and Physical Characterization of Magnetron Sputtered Graphene-CdS bilayer

3.1 Introduction

Chalcogenides, especially of cadmium have provided their potential as efficient absorber of electromagnetic radiation. The CdS is an II-VI group semiconductor. In recent years, there has been huge interest focused on the CdS due to its potential applications in optoelectronics technology such as solar cell. Semiconductor nanocrystals have received great interest in basic research and industrial development due to their special electronic and physical properties [180, 181]. Due to their remarkable characteristics, several organic and inorganic broadband semiconductor materials such as ZnS, ZnO, TiO₂, GaN, CdS, graphene quantum dots, and their compounds have been explored in different electronic device applications. [182-187] II-VI semiconductor-multilayer nanostructures, in particular, have received a lot of attention as being appropriate for a variety of device applications. [110] Due to its wide energy bandgap of 2.422 eV, emission tunability, good transparency, n-type conductivity, excessive stability, excellent extinction coefficient, and high dipole moment, cadmium sulphide (CdS) (AII-BVI compounds) shows excellent applicability in diverse fields (photovoltaic devices, light-emitting diodes, thin-film transistors, and photocatalysts). [188-191] However, the drawbacks associated with cadmium-based semiconductors are poor surface area and high charge recombination rate of charge carrier generated throughout photo excitation method. [192-197] Coating of environment-friendly electron-transport materials, such as conductive polymer thin films, carbon nanotubes (CNTs), and graphene, is a simple and effective approach to minimize fast recombination. [195, 198-201]

Among others, for example, has attracted attention due to its outstanding physicochemical properties. [202-205] Because of various beneficial characteristics, Graphene is the most suitable support for developing a hybrid material with improved features. [206-208] It was

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reported earlier that graphene played an important role in device application due to close conduction distance and extensive transmission efficiency excessive transmission performance. [209-211] A review of literature revealed that different deposition techniques for CdS thin films have been developed, among which pulsed laser deposition (PLD) [212], Chemical bath deposition [213, 214], Molecular beam epitaxy (MBE) [215, 216], Spray Pyrolysis [119, 217], Sputtering [82, 218, 219] and Thermal evaporation [220, 221]. Herein, a series of CdS/Graphene hybrids were synthesized using an RF sputtering technique in order to achieve the best experimental conditions for improving the physical attributes. The RF sputtering method is a helpful technique for CdS thin film deposition because it allows for greater control of film consistency, shape, contamination-free environment, and thickness across broad areas than other methods. [222-224] In RF sputtering, thin film growth is determined by the kinetic energy of the atoms generated and their substrate interactions. Sputtering factors such as deposition pressure, time, sputtering strength, and substrate temperature influence the kinetics of atoms impacted on the substrate, which then alter the growth process, increasing the overall performance of CdS thin films.

However, in terms of the electric current, optimization of CdS for exceptional amounts of Graphene has not been reported. Systematic strategy and performance tests, as well as execution tests, were used to characterize the synthesized thin film. A detailed study of the physical properties of CdS/Si, Graphene/Si, and CdS/Graphene/Si thin films is also being carried out in order to optimize structural, electrical, and surface topographical properties for CdS thin films for various device applications, such as as an absorber layer in solar cells. CdS nanocomposite thin films were deposited and examined deposition process in this chapter. The hybrid has a lot of potential in a variety of electronic devices because of its

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overall performance, which includes high sensitivity, maximum quantum efficiency, and fast response time. Finally, we provide our findings and conclusions. The hybrid exhibit great potential in various field of electronic devices having an overall performance having large sensitivity, maximum quantum efficiency, and good response speed.

3.2 Methods and characterization

3.2.1 Fabrication of film

CdS/Graphene hybrid material thin film was deposited via RF magnetron sputtering under controlled growth conditions with RF power 150W on n-type (422) single crystal silicon wafers substrates at room temperature under high vacuum (2×10^{-6} Torr). The resistivity and thickness of silicon wafers were ($300 \pm 20 \text{ } \mu\text{m}$) and (3000 to 6000 Ωm), respectively. Graphene nanoplates were dispersed in ethanol by sonication for 20 min to give graphene ink with an approximate ratio of 5 mg L^{-1} as shown in Figure 3.1.

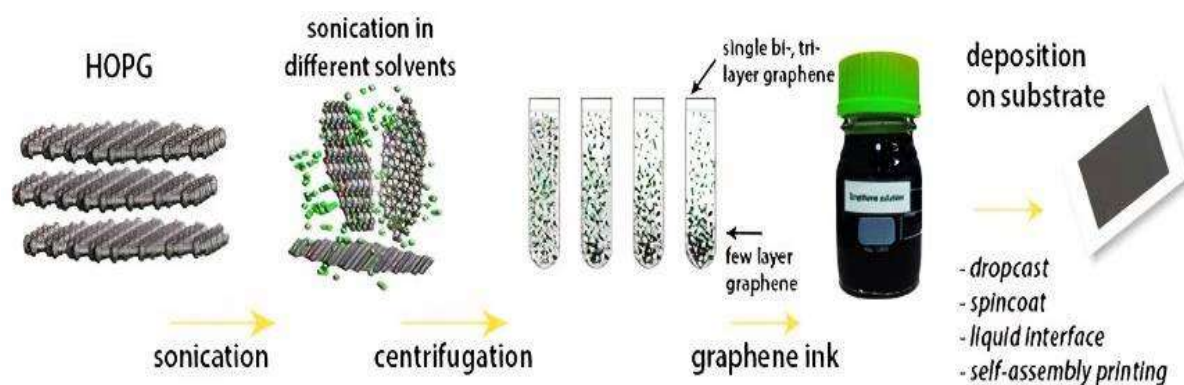


Figure 3.1. Graphene dispersion stages on the substrate

Graphene Nanoplates with 99.5wt% purity and volume resistivity $4 \times 10^{-4} \text{ } \Omega\text{.cm}$ used as a growing layer on silicon. We used a solid compact plate of CdS target. The dimension of silicon substrates was $1\text{cm} \times 1\text{cm}$. Substrates were ultrasonically cleaned first using alcohol for 5 min then acetone for 10 min. The substrates have been organized with a

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standard cleaning technique utilizing natural organic solvents earlier that being etched in HCl for 30 s [225], rinsed for 10 min with de-ionized water, dried with nitrogen fuel to cast off surface contamination, and fixed on the substrate holder. The CdS-nanoparticles decorated graphene Nanosheets (CdS/Graphene on the silicon wafer) and on the silicon substrate were prepared by a Magnetron Sputtering with the RF power of 150W as shown in Figure 3.2.



Figure 3.2. Address layer of cadmium sulfide sample grown on graphene

Parameters	Test conditions
Graphene Density	5 mg/ml
Solvents	Ethanol (Merck)
Sonication Time	20 min
Substrate temp.	°40+5°C

Table 3.1. The table of experiment conditions and parameters.

The basic parameters like base pressure and deposition pressure have been set as 10^{-6} Torr and 2×10^{-2} Torr, respectively. The separation between the target and the substrate was ~ 7 cm. for synthesizing uniform consistent thin films, substrates had been kept rotating all through the sputtering process. And the deposition time was set to 20 min.

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3.2.2 Characterization

The sample was characterized by several techniques like UV-VIS FTIR, Raman spectra, and I-V characteristics. The morphology of Graphene/Si, CdS/Si, and CdS/Graphene/Si, and films were investigated under a Field emission scanning electron microscope using a HITACHI S-4160. Structural analysis of Graphene/Si, CdS/Si, and CdS/Graphene/Si thin films were carried out which were equipped focused by X-ray diffraction (Philips Xpert, with Cu-K α radiation ($\lambda = 0.15418$ nm)). Further, a dual-beam UV-Vis spectrophotometer (Cary 500 UV/VIS/NIR spectrophotometer) was used utilized to investigate the absorption properties and transparency over the spectral region of 200-800 nm. FTIR spectroscopy was used to investigate with an accuracy of 0.1 nm in the range of UV/VIS and 0.4 nm in the range of NIR and wavelength ranging from 175 to 3300 nm using Thermo Nicolet Nexus 870 spectrometer. Current-Voltage (I-V) measurements were also performed on different samples. The voltage applied to the specimen from the stabilized DC power supply was increased from -1V to +1V. The voltage connected to the sample and the current flowing through it was measured using electrometers of type (Keithley-2361). Synthesized samples have been recorded using Thermo/Nicolet FT-Raman 960, having a spectral range of 400 cm^{-1} to 4000 cm^{-1} with a He/Ne laser (excitation wavelength of 633 nm). The electrical resistivity measurements on samples were determined by the four-point probe.

3.3 Results and discussion

3.3.1. Surface morphology

Figure 3.3 demonstrates the FESEM micrographs of Graphene/Si and CdS/Graphene/Si hybrid material. As seen in Figure. 3.3a₁ and 3.3a₂ graphene show a 2D sheet-like surface, which plays an important role as a supporting material in CdS growth. As seen in Figure.

3.3b₁ and 3.3b₂ hybrid show that CdS particle randomly stacked together had a uniform distribution over graphene sheets. Hybrid indicates an appropriate interfacial interaction between CdS particle and graphene sheets. The as-deposited thin films exhibit irregular grains and bubbles exhibit on the surface because of their crystalline structure. Sheets of Graphene are curled and grooved and the surface morphology of CdS particles shows spherical morphology with less aggregation and a smaller diameter, which offers a large surface area that, benefits various electronic device applications. [226]

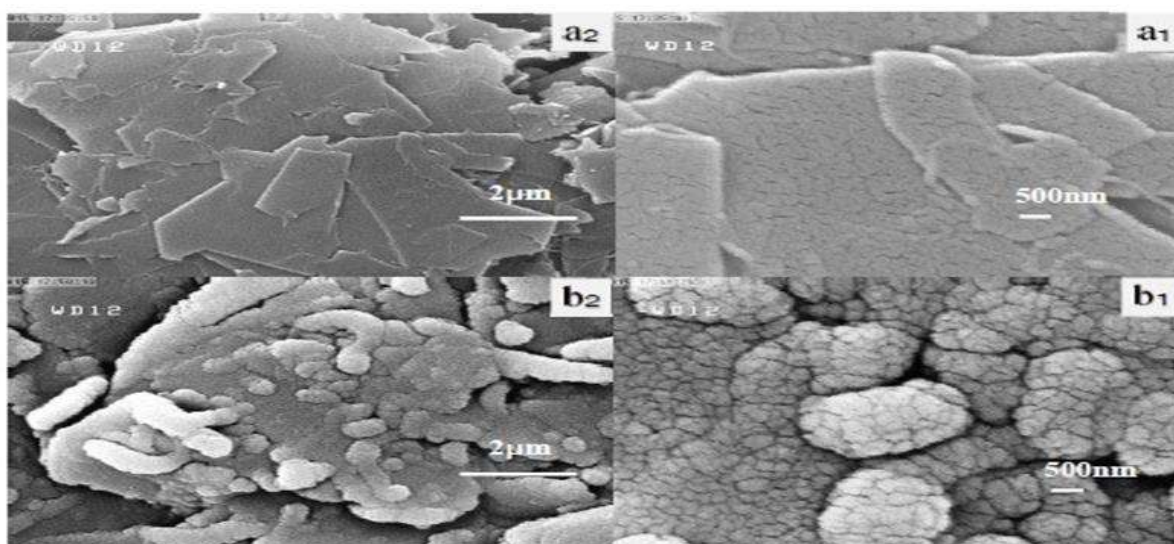


Figure 3.3 FESEM images of (a₂,a₁) Graphene/Si, (b₂,b₁) Graphene/CdS/Si

3.3.2 X-ray diffraction analysis

To study various phases and crystallinity of synthesized material, XRD was performed using Philips Xpert, with Cu-Kα radiation ($\lambda = 0.15418$ nm). Figure 3.4 indicates the XRD pattern of the graphene, pure CdS, and CdS/Graphene hybrid. The diffraction peaks of the graphene sheet at $2\theta \sim 26^\circ$ and 54° matched properly with the hexagonal crystal structure of graphene and were indexed as (002) and (004) facets, respectively. [227,

228] The peaks at 2θ values of 26.51, 38.51, 43.71, 47.81, and 54.81 can be ascribed to the (002), (220), (110), (103) and (004) crystal planes of hexagonal CdS, respectively. [229] Additionally, all the XRD peaks of the pure CdS coordinate similar to CdS with the hexagonal crystal structure and were identified as the (002), (220), (110), (103), and (004) planes of the hexagonal structure [44].

The X-Ray diffraction pattern sample of the CdS/Graphene hybrid appears to be a simple mixture of the reflection pattern of Graphene and natural CdS, where no significant modifications were observed in the relative intensity of every peak. The strongest peak, at $2\theta \sim 26^\circ$, is believed to correspond to each carbon (002) on graphene and CdS (002), which shows almost equal to identical positions. Synthesized hybrid material indicates decrease intensities than those for natural CdS. This would be due to the graphene wrapped across the surface of the CdS particles. Hybrid material exhibits comparable diffraction peaks with pure CdS particles, while no diffraction peak of graphene was examined because the regular stack of graphene sheets is destroyed by the intercalation of CdS particles [230]. This indicates out the formation of a new phase throughout the hybrid formation.

3.3.3 UV-Vis spectra

The UV-Vis of CdS, Graphene, and CdS/Graphene hybrid is demonstrated in Figure 3.5. Figure 5(a) indicates UV light absorption at different wavelengths and Figure 3.5(b) shows UV-Vis diffuse reflectance spectra (DRS) of pure CdS and CdS/Graphene hybrid. the absorption spectra of pure CdS at 500 nm which correspond to the bandgap of 2.48 eV using the formula (Bandgap = $1240/\lambda_{\text{nm}}$) [231]

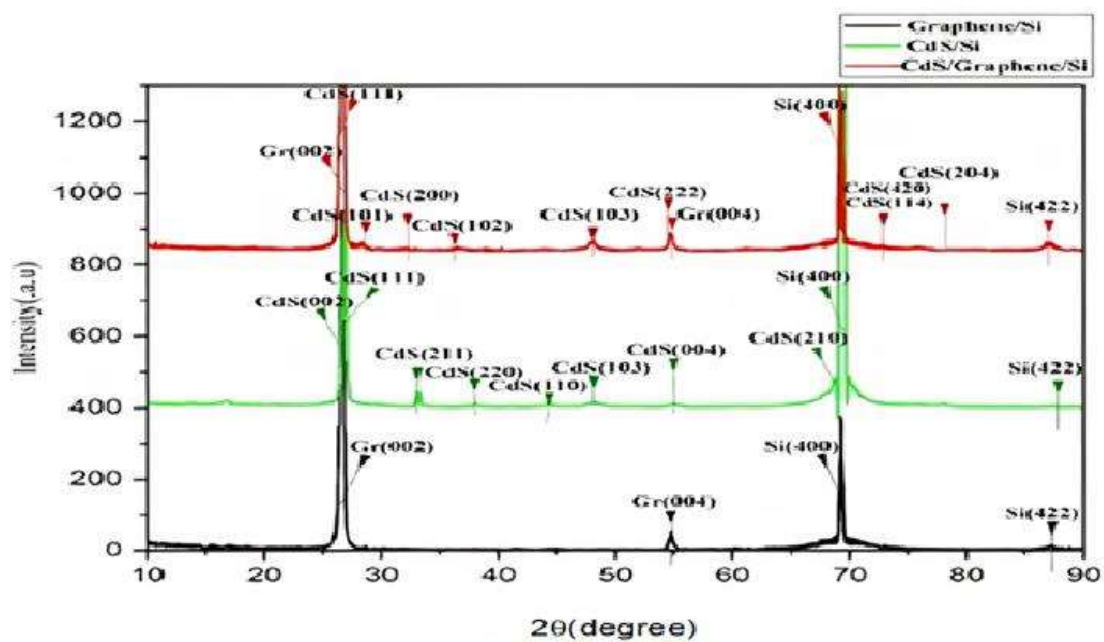


Figure 3.4 XRD results of pristine graphene, CdS/Graphene nanocomposite, and pure CdS

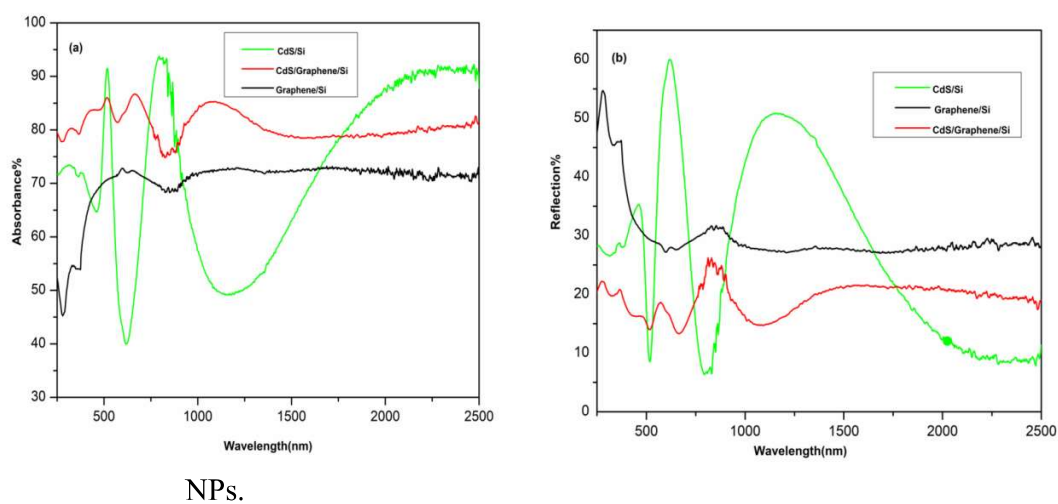


Figure 3.5 (a) UV-VIS spectra **(b)** UV-Vis reflectance spectra graphene/Si, CdS/Si, CdS/graphene/Si hybrid

After the introduction of graphene, CdS (CdS/graphene) undergo a redshift and enhanced absorption both in the ultraviolet region and visible region. Furthermore, CdS/Graphene hybrid has a continuous absorbance band is shown in CdS/Graphene hybrid matched properly with pure CdS in the visible range from 500-900 nm compared, graphene can improve the surface electrical charge of CdS [232]. Hence, CdS/Graphene hybrid is more efficient to utilize visible light.

3.3.4 Raman spectral analysis

Raman spectroscopy is a viable and non-destructive experimental method that is widely used to study structural information of carbon-based materials [233]. Figure 3.6, appears the Raman spectra for graphene and CdS/Graphene hybrid, respectively. The results showed the existence of G-band besides the imperfections D-band in both the samples. The G-band is ascribed in-plane vibrations of sp^2 hybridized carbon atoms. The Raman spectra of graphene sheets show D and G bands allotted to the κ -point phonons of the A_{1g} symmetry and E_{2g} phonon of the sp^2 carbon at 1353 and 1593 cm^{-1} , respectively which shifts to lower wavelength 1340 and 1577 cm^{-1} after reduction due to the formation of the CdS/Graphene hybrid. Further, the two peaks at 300 and 600 cm^{-1} have been related to the longitudinal optical (LO) phonon modes of CdS/Graphene hybrid.

Three extra characteristic peaks positioned at 1345, 1573, and 2711 cm^{-1} were discovered, which compare to D, G, and 2d peaks of graphene, respectively. 2D band appears at around 2711 cm^{-1} shows the multilayer graphene structure, which was also moreover compared by other groups [234, 235]. The 2D band is originated due to a twofold resonance transition which brought because of the generation of two phonons with inverse energy. [236] Moreover, D peak having lower intensity shows lower disorder in graphene structure. [237,

238] However, the fundamental longitudinal optical phonon mode (LO) and the first-order (1LO) phonon modes peaks of the CdS/Graphene hybrid have been decreased due to the decreasing CdS concentration in comparison to pure CdS. This also confirms the formation of the CdS/Graphene hybrid. Because cadmium sulphide has been deposited on a single-layer graphene structure, the D band intensity has increased relative to the G band, and both bands shifted to higher wavenumbers [239].

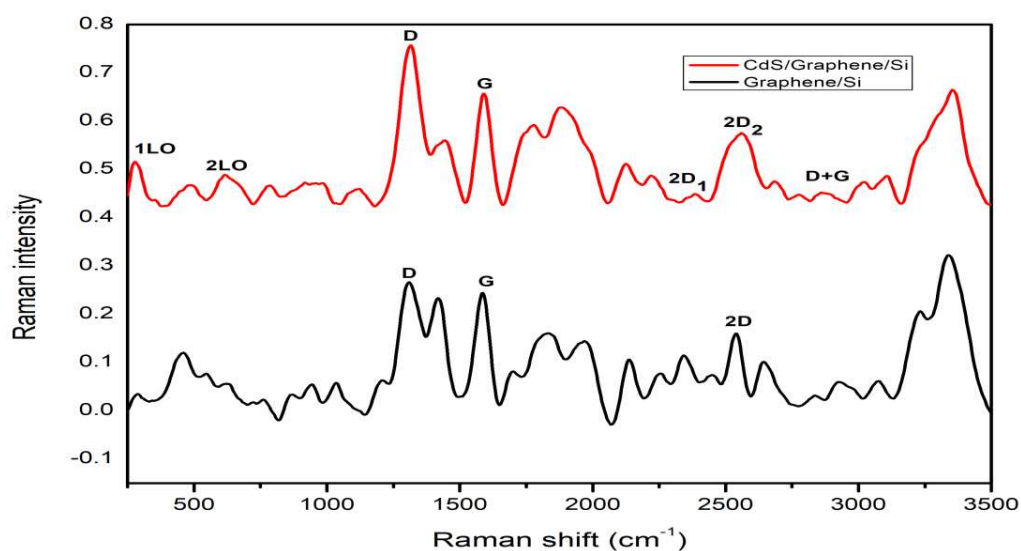


Figure 3.6. Raman spectra of (a) graphene and (b) CdS/Graphene hybrid material.

3.3.5 FTIR study

To understand the presence of functional groups and chemical interactions involved between different graphene and CdS functional groups, FTIR was performed using Thermo Nicolet Nexus 870 spectrometer. The FTIR spectra of (a) graphene (b) CdS/graphene hybrid materials are represented in Figure 3.7. At 2935 cm^{-1} and 2880 cm^{-1} , The existence of two absorption band doublet is shown by pure graphene spectra corresponding to

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symmetric and antisymmetric stretching vibrations of the $-\text{CH}_2$ group, respectively [240]. Additionally, the peak appears appeared peaks at $1730, 1626, 1230, 1080$, and 790 cm^{-1} , respectively that confirms the presence of $\text{C}=\text{O}$ stretching, vibration from carbonyl groups, $\text{C}=\text{C}$ vibration from aromatic carbon, $\text{C}-\text{OH}$ stretching vibrations, $\text{C}-\text{O}$ vibrations from epoxy groups, and $\text{C}-\text{O}$ vibration from alkoxy group in graphene [241-243]. Existence of $\text{C}=\text{O}$ stretching, vibration from carbonyl groups, $\text{C}=\text{C}$ vibration from aromatic carbon, $\text{C}-\text{OH}$ stretching vibrations, $\text{C}-\text{O}$ vibrations from epoxy groups, and $\text{C}-\text{O}$ vibration from alkoxy group in graphene [241-243]. The spectrum of synthesized hybrid materials ($\text{CdS}/\text{Graphene}$) indicates the existence presence of $\text{C}=\text{C}$ having moderate bonding at 1600 cm^{-1} , $\text{C}=\text{C}$ bond having strong bond at 750 cm^{-1} , $\text{C}-\text{OH}$ bond at 1350 cm^{-1} , $\text{C}-\text{O}-\text{C}$ bond at 1230 cm^{-1} . Thus, the appearance of new peaks and shifting of peaks show the confirmation of the existence of interaction between graphene and CdS .

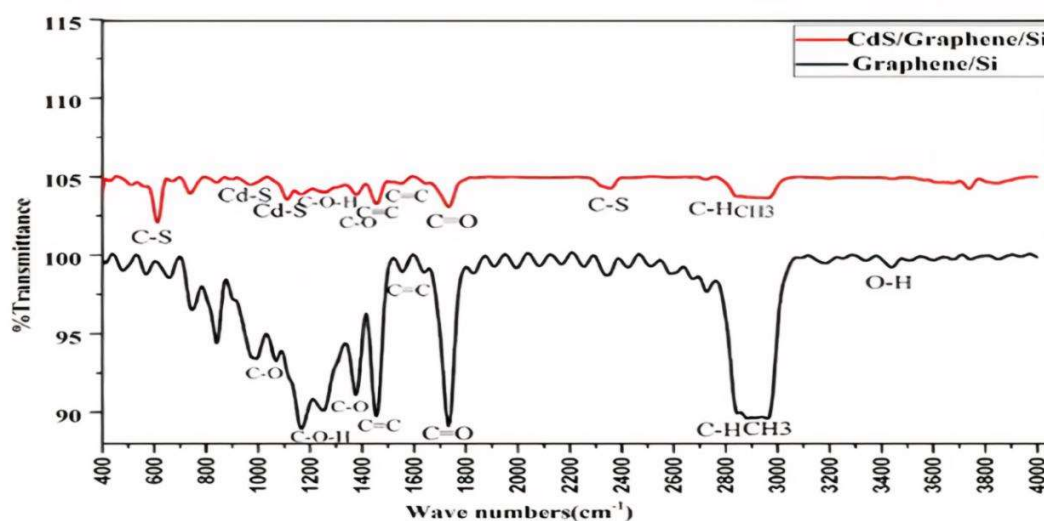


Figure 3.7 FTIR spectra of graphene/Si and $\text{CdS}/\text{Graphene}/\text{Si}$

3.3.6 Electrical analysis

For electrical analysis, the 4-point probe conductivity measurements of as-prepared films with graphene, CdS/Graphene hybrid were performed using Current-Voltage (I-V) measurements (Figure 3.8). The current-voltage (I-V) characteristics of the CdS/Graphene hybrid showed a semiconducting behavior. The voltage across the sample and the current flowing through it were measured using electrometers of type (Keithley-2361). Transverse current-voltage measurement was also performed employing a high-precision source meter. Figure 3.8 and Table 3.2 indicate that the current is increased in presence of graphene due to an increment in grain size which further reveals an improvement in crystallinity.

In comparison with CdS, the enhancement in the current of CdS/Graphene hybrid has been observed that confirms the generation of photo induced charge carriers, which can be explained in Figure 3.8. Therefore, electrical conductivity is observed to increase due to the variance of charge carrier density and mobility as well as the crystallization of grains.

The electrical resistivity of CdS/Si, Graphene/Si, and CdS/Graphene/Si Thin films measured using the DC four-point probe technique. The resistivity follows the relation-

$$\rho = \frac{\pi}{\ln(2)} \times \left(\frac{V}{I}\right) = 4.532 \times \left(\frac{V}{I}\right)$$

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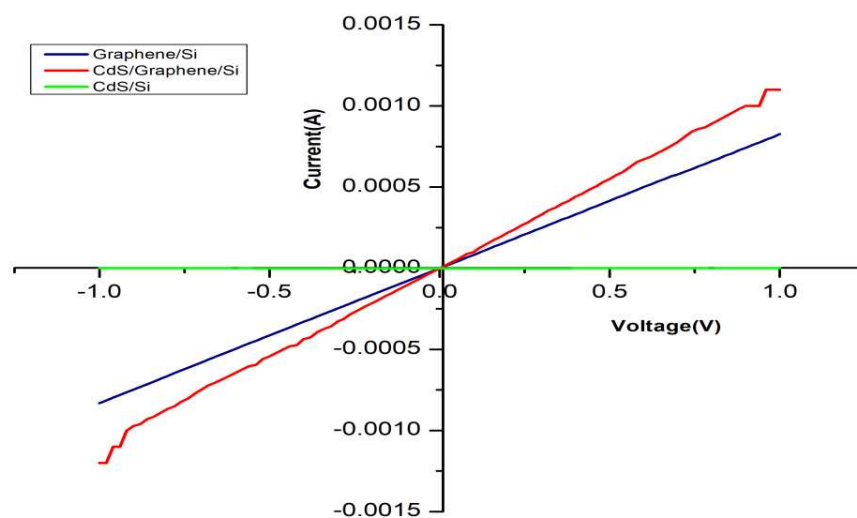


Figure 3.8 Current-voltage (I-V) characteristics of CdS/Si, graphene/Si and CdS/graphene/Si.

Samples	CdS/Si	Graphene/Si	CdS/Graphene/Si
Sheet resistivity	350	6.5	3.4

Table 3.2: Variation of sheet Resistivity of CdS/Si, Graphene/Si, and CdS/Graphene/Si thin films

3.3.7. MECHANISM/ THEOREM SECTION

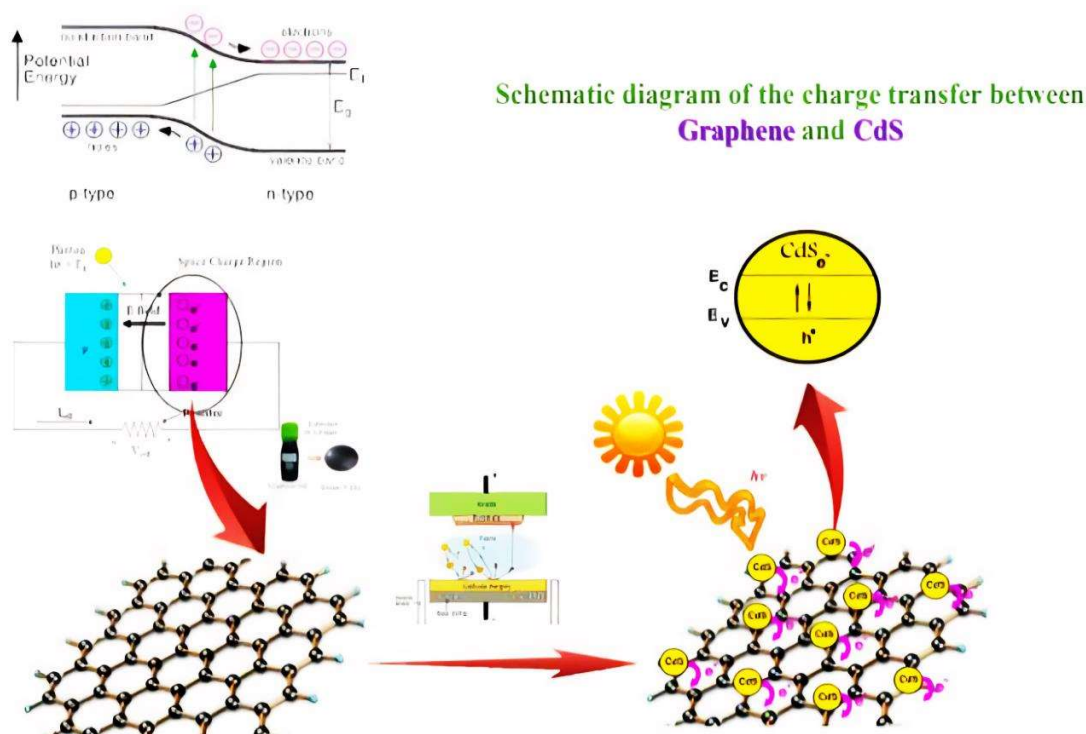
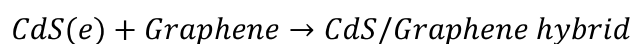
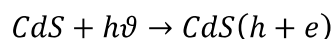


Figure 3.9. Schematic diagram of the charge separation and transfer in the Graphene–cadmium sulfide (Gr–CdS) system under visible light

The above analysis is based on the excitation mechanism of charge transfer. The physical and chemical properties of Cadmium sulfide (CdS) (II-VI semiconductor) are well known. [244] which has a suitable band gap that could accelerate photo-induced electron transfer and electron-hole pair separation. A similar mechanism has been reported previously for TiO_2 -graphene and ZnO -graphene composites.[245, 246] The schematic diagram of the charge transfer mechanism is shown briefly in Figure 3.9. When CdS is exposed to visible light, it absorbed visible light considerably. Generation of photo-induced electron-hole has been taken place, which causes the appreciable enhancement of local EM-Field near the

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rough surface of CdS by photo-excited “electrons” and “holes”. It was previously reported that the electrons stored properties in CdS and charge transfer mechanism are readily scavenged by carbon nanomaterials such as graphene, fullerenes, and carbon nanotubes.[247-249] Additionally, because of physical and chemical properties i.e. high conductivity Graphene could promote charge separation and impede the electron-hole pair generation. The energy barrier between CdS and Graphene is about 1eV. Therefore, Graphene acts as an electron acceptor in our system which was reported in previous studies.[250, 251]



In this chapter, Graphene interacts with CdS undergo visible irradiation. The slow addition of Graphene with Cd²⁺ ion and S²⁻ ion provides uniform solubility, better adhesion, and maximum substitution of ion on the surface of Graphene sheets. Graphene has an excellent capability in capturing, storing the charge carriers and offers them to provide more opportunities to contact with a reactant in various photo-catalytic activities. Therefore, Graphene tends to enhance the availability and lifetime of charge carriers. Thus improve the photo catalytic and optoelectronic properties of CdS. Therefore, Graphene largely enhances the availability and lifetime of charge carriers, and thus improves the physical properties of CdS.

3.4. Conclusion

To increase current, we proposed a simple and effective method for hybridising CdS nanospheres with graphene nanosheets. Using an RF sputtering technique, a hybrid

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CdS/Graphene was fabricated. The electron transfer from functionalized CdS nanoparticles to graphene reduces the resistivity of graphene nanostructures thin film significantly.

In this chapter, the synthesized hybrid exhibited excellent optoelectronic characteristics, with graphene supporting in charge carrier promotion, separation, and transfer, which is responsible for CdS aggregation and overgrowth, as well as enhances current and providing better photo stability. The current-voltage properties of hybrid nanocomposites appear to be straight linear, and the resistivity was found to be lower. As a result, the synthesised hybrid is light source selective and can be used in a variety of device applications, such as solar cells and biosensors like photo detectors.