To study the photoluminescence properties of CdS/PVK Nanocomposites

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Abstract: In optoelectronic applications Cadmium Sulfide have very good substance. Which creates interest to describe its optical studies in nanoscale range? Presently photoluminescence of CdS/PVK nanocomposites have been reported. Chemical method is used to prepare the composites and characterized them XRD, UV-Visible absorption and study their photoluminescence. The study of XRD indicates CdS nanocrystals formation having cubic zinc blend crystal structure, with three peaks of planes are respectively 111, 220, and 311. Size of particle is calculated using DebyScherrer's technique. It has obtained within 3 to 12 nm. Results from XRD shows that when CdS concentration is increases in PVK the particle size also increases. The optical absorption spectra of the nanocomposites show blue shifted absorption edge which show increased band gap because of quantum confinement effect. Absorption side is shifted on larger wave length shows reducing the band gap with increasing CdS concentration, which indicates increase in particle size. The wavelength of 400 nm is incident on PVK, photoluminescence (PL) exhibit single peak on 451 nanometer and covers spectral range from 400 to 600 nm. The CdS nanocrystals give single peak at 530 nm when excited separately by 400 nm. In CdS/PVK nanocomposites two PL peaks are obtained, first peak due to PVK near 450 nm and second peak due to CdS near 530 nm.PL intensity decreases with increasing concentration of CdS in PVK.

Keywords:

1. Introduction

The Nanocomposites of organic also inorganic polymers compound reveal its electrical, thermal, mechanical, magnetic and optical properties, which are superior as compared to these, discrete constituents [1-4]. This effect shows the network interaction with the bonding faces and synthesizing. The hybrid hole transfer semiconducting compound of organic polymer such as poly N-vinyl carbazole or PVK is widely used in so many applications [4]. Cadmium sulfide or CdS was excellent semiconducting materials for optoelectronics, inorganic and electronic uses [5-10]. Nanoclusters Hybrids of cadmium sulfide and polymer both shows its excellent charge generation and charge transfer capacity, effect of mobility and processibility of inorganic and organic compounds [11-14]. Whereas the clusters of CdS nanoparticles are distributed in the polymer matrix of PVK it has been observed that its photoconductivity is also increases. These indicate the carrier transporting medium and the photo charge generation of CdS nanoclusters and PVK matrix of polymer [11]. Already, CdS and PVK nano composite prepared the mixing of their precursors. The result from precursor particles or the semiconducting compound of synthesized nanoparticles distribution is very difficult in polymer matrix. The preparation of CdS/PVK nanocomposites Wang [15-17] has also proposed. Khanna [18] also reported the nanoparticles of CdS prepared with DMF. It has metallic surface which shows constant light emission. In polymer the nano particles of CdS have synthesized and thin film spread neatly, thus escaping the packing of multistage particles. Polymers are long time stability and flexible reprocess ability material [19].In nanomaterials the optical and electrical properties are controlling its particle size. Hence it attracts curiosity of their basic applied features. In present we have synthesized CdS/PVK nanocomposite and characterize by XRD, studies their property such as absorption spectra, photoluminescence spectra.

2. Experimental

The nanocomposite of CdS/PVK thin films was synthesized, to take the 400mg of PVK polymer and 10 ml DMF. Both are dissolved with at 80ºC temperature and constant stirring. Cadmium acetate was mix at the fix amount of CdS in PVK. The amount of CdS was 10, 20, 30 40 and 50% of polymer, than the loading of CdS in polymer is same amount. The final solvent stirred at half hours. By applying nitrogen and H_2S gases for few second to refluxed the solution. Colour of solution changed to turnip yellow. After stirring following chemical reaction was occured:

$$PVK + Cd(CH_3COO)_2 + H_2S \rightarrow CdS/PVK + 2CH_3COOH$$

The resultant solutions were spread on plan glass plates and dried in an oven for several hours. To obtain the nanocomposite thin film of CdS/PVK. Study their optical properties such as photoluminescence, absorption spectra, and characterized by XRD

3. Results and Discussion

Analysis of XRD or X-Ray Diffraction: To describe the XRD studies of CdS/PVK nanocompounds. It shows the very good diffraction pattern matching from literature [20]. Figure (1) shows the XRD for different CdS loading in PVK. XRD shows broadening patterns of diffraction peaks for different CdS/PVK nanocomposite. The broad nature of diffraction peaks shows the nanocrystallites formation. These diffraction broadening peaks were obtained and the value of two theta nearly 18^0, 26^0, 44^0 and 52^0. From Fig. (1), PVK diffraction peak at 2θ is obtain 18^0 and CdS peaks are 26^0, 44^0 and 52^0, matching the crystalline planes (111), (2 2 0) (311) of cubic CdS formation [21]. The broadening nature of XRD peaks indicated the formation of CdS nano particles. The particles size and space lattice are evaluated from the Bragg's law and Debye Scherrer formula [22].

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ --------(1)}$$

Where the symbols (K, λ , β, θ) have their usual meanings. Equation (1) is use calculated the size of CdS nano crystal and it is obtained within 3 to 12 nm. The computed space lattice is 5.8 Å which is very close to its standard value 5.83 Å.

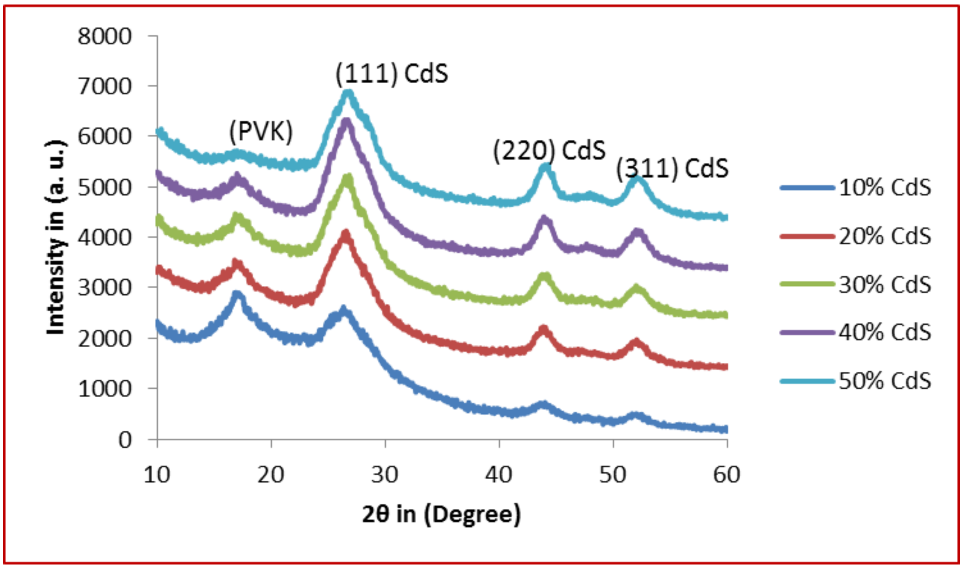


Fig. (1) The XRD pattern for CdS/PVK Nanocomposites

Analysis of UV/Visible Absorption Spectrum:

Fig. (2) Indicate the optical absorption spectra of CdS/PVK nanocomposites. The absorption spectra of UV/Visible light are obtained within 200-700 nm in CdS/PVK nanocomposites with 0, 10%, 20%, 30%, 40%, 50% concentration of CdS in PVK. It is found that there is minor absorption within 500-700 nm for all samples. Suddenly absorption increases giving on absorption edge at lower wavelength. The absorption side shifted in lower wavelength for lower CdS loading. The onset absorption was obtained at 300, 340, 380, 420, 440 and 490 nm of CdS loading in PVK are 0, 10, 20, 30, 40 and 50% serially. In optical absorption the energy band gap of nanocomposite calculated from its absorption edge by applying the following equation

$$Eg = \frac{hc}{\lambda} \quad \text{------------} \quad (2)$$

Where the parameters, c velocity of light, h Planck's constant, λ absorption wavelength. It is seen from the Fig. (2) that pure PVK does not show any absorption at wavelength above 340 nm. Nanoparticle of CdS is increases then absorption edge shifts towards the higher wavelengths. The photon energies corresponding to onset of absorption gives effective band gap. The values of effective Eg are obtained as 4.13, 3.64, 3.26, 2.95, 2.82 and 2.53eV respectively for 0, 10%, 20%, 30%, 40%, 50% concentration of CdS in PVK.

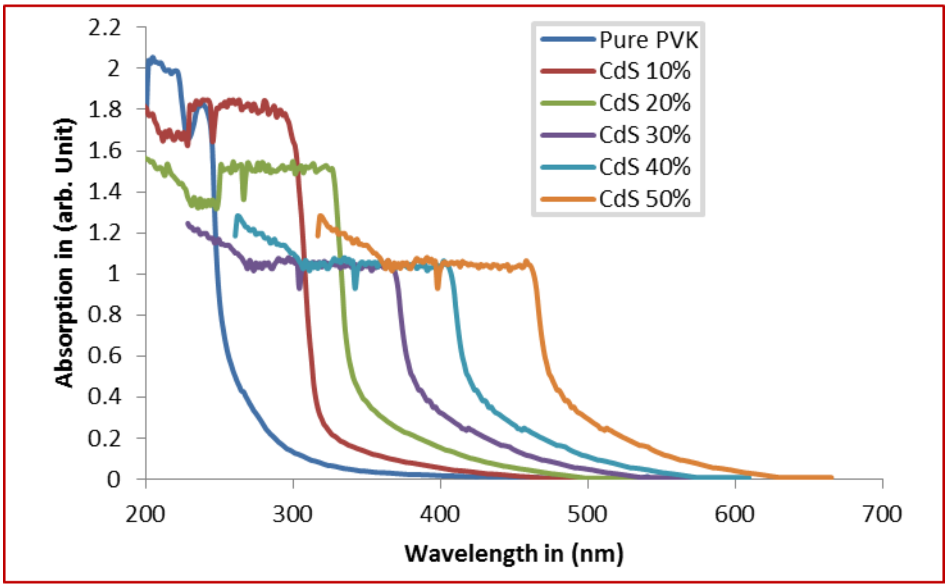


Fig (2) Optical Absorption Spectra of CdS/PVK Nanocomposites

The particle size of nanocrystals has been calculated by effective mass approximation model [23] and the hyperbolic band model [24] using equation (3) and (4). Therefore, the expression for the radius of nanoparticle is obtained as

$$r^2 = \frac{h^2}{8\,(E'g - E_g)}\left(\frac{1}{m_e{}^*} + \frac{1}{m_h^*}\right) \quad \text{-----------------} \quad (3)$$

$$r^2 = \frac{h^2 Eg}{2m_e{}^*(Eg'^2 - Eg^2)} \quad \text{-------------------} \quad (4)$$

Where Eg = 2.42 eV is band gap of bulk CdS, Eg is calculated band gap, h = 6.66×10^{-34} J-sec, $m_e{}^* = 0.2\times9.1\times10^{-31}$ kg and $m_h{}^* = 0.7\times 9.1\times10^{-31}$ kg are effective masses of electron and hole

The particle size was estimated using the equation (3) (4) and (1) and it is given in Table (1)

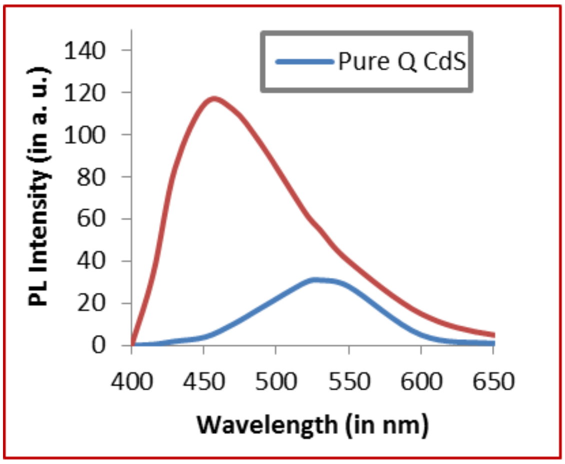
Table (1) Particle size are calculated through XRD and absorption edge

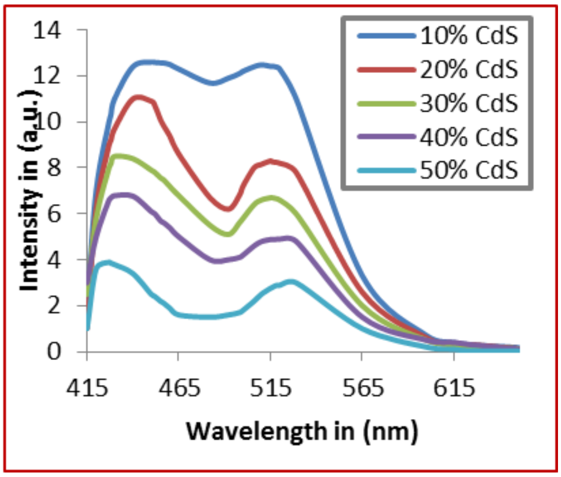
Sample name	CdSconcentration in PVK In (%)	Absorption edge wavelength	Energy band gap Eg(eV)	Diameter of particles by		
				EMA (in nm)	HBM (in nm)	XRD (in nm)
CdS/PVK - I	10%	340	3.64	2.94	3.21	3
CdS/PVK – II	20%	380	3.26	3.49	4.10	3.5
CdS/PVK– III	30%	420	2.95	4.39	5.10	3.9
CdS/PVK– IV	40%	440	2.82	5.01	5.87	5.7
CdS/PVK – V	50%	490	2.53	9.62	11.0	8.5

From table (1), shows the particle size in increasing order by increasing the CdS concentration. Particle size is obtained from energy band gap (Eg) , effective mass approximation model, hyperbolic band model and XRD. Results from all studies are agree to each other.

Photoluminescence Spectra: The photoluminescence spectrum of pure PVK and quantum dots CdS (Q-CdS) are shown in fig(3) . Pure PVK gives peak at 451 nm and Q-CdS give single peak at 530 nm when excited separately by 400 nm.

Fig (4) gives the photoluminescence spectrum for CdS/PVK) samples with different CdS concentration in polymer. It is excited through 400 nm light. It can be seen from PL spectra that two PL peaks are obtained. The first peak at 450 nm due to PVK and second peak occurs at near 530 nm which may be attributed to defects related transitions in CdS. The PL intensity of both peaks is decreased with higher loading of CdS on PVK polymer.





.**Fig (3)** Photoluminescence Spectrum of Pure PVK andQ-CdS, The excitation wavelength is 400 nm.

Fig.(4): PL spectra for CdS/PVK nanocomposites at various concentrations

The wavelength of photon energy and PL intensity for various samples, it is given in Table (2). From table the PL intensity reduced with increasing CdS concentration in PVK.

TABLE (2) PL (Emission Wavelength and Intensity) for CdS/PVK Nanocomposites

Sample name	**CdSconcentration in PVK (%)**	**PL Emission Peak excited by 400 nm**		**Intensity**
		Wavelength (in nm)	**Photon Energy**	
CdS/PVK - I	10%	510	2.43eV	12.4
CdS/PVK – II	20%	515	2.41eV	8.4
CdS/PVK – III	30%	516	2.4eV	6.7
CdS/PVK –IV	40%	520	2.38eV	4.9
CdS/PVK – V	50%	529	2.34eV	3.0

Explanation for Luminescence Mechanism in CdS/PVK Nanocomposite: - The PL intensity decreases by higher loading of CdS on PVK. The transition in defects states of CdS and carbazole moieties of PVK shows the photoluminescence of CdS/PVK. In PL the absence of CdS emission band gap is found. Due to with quenching interfacial charge transfer of CdS and PVK which reduced the PL intensity. The closed contact in carbazole moiety of PVK and CdS surface of nanoparticles quenching phenomena of nanocomposite was occurred. This close contact easily transfers the electron and hole charge carrier of interface with PVK and CdS. Carbazole groups of PVK the electrons were excited into the lowest unoccupied molecular orbital (LUMO) and holes were left in the highest occupied molecular orbital (HOMO) then photons are absorbed. The excited electrons from pure PVK will return back from LUMO to HOMO with the process of radiative transition and light emitting at 450 nm. In the nanocomposites, of PVK/CdS, the excited electrons are migrating from PVK to CdS due to lower energy level. This situation of interfacial charge-transfer from LUMO to HOMO reduced PL intensity [25-32].

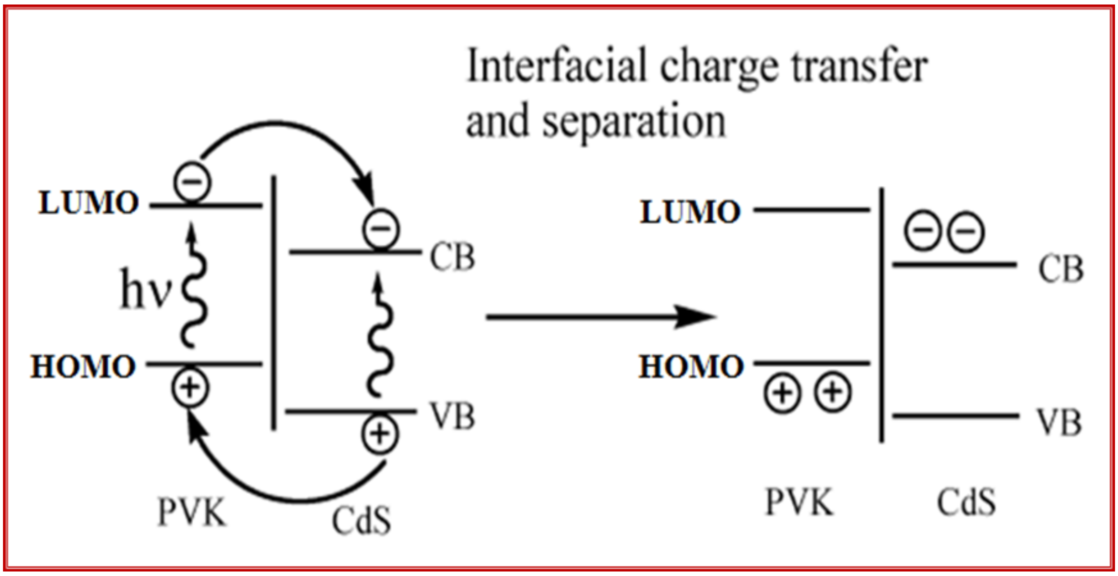


Fig.(5): A schematic presentation of the interfacial charge generation, transfer, and separation between Q-CdS and PVK in CdS/PVK composites**.**

In case of CdS/PVK nanocomposites the 400 nm photons may excite electron from Cd^{2+} level to conduction band which decay non radiatively to S^{2-} level subsequent transition from S^{2-} to Cd^{2+} levels and gives light emission at about 530 nm. Slight variation in the energy levels may occur due to quantum confinement in nano crystals. By increasing CdS concentration the electron from PVK migrate favorably to CdS and fills holes at Cd^{2+} levels. This reduces the probability of electron transition from S^{2-} to Cd^{2+} levels reducing the luminescence intensity. Fig. (6) Shows the energy level diagram of CdS/PVK.

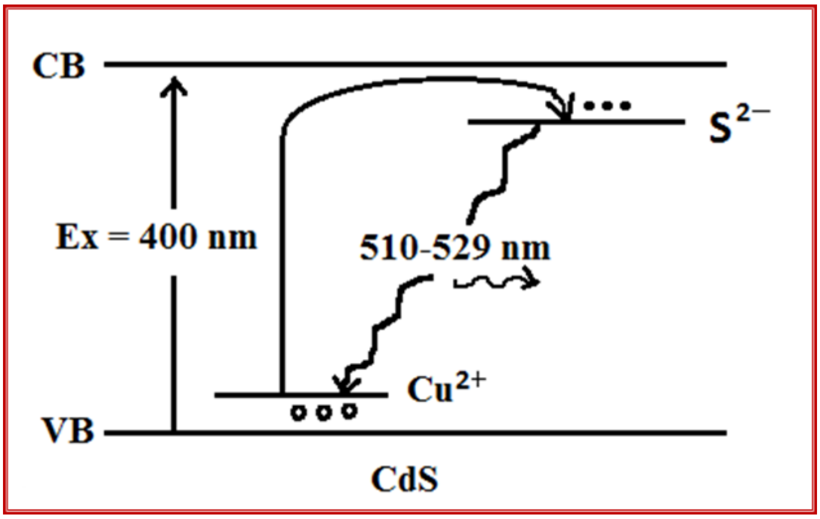


Fig. (6) Schematic Energy level diagram for different concentration of CdS in PVK**.**

4. Conclusions:

Chemical methods are used to prepare the CdS/PVK nanocomposites with different concentration of CdS in polymer. To studies their optical properties and characterized by XRD. The size of the nanoparticle is increases with higher loading of CdS in PVK. The XRD studies reveal the formation of cubic zinc blende CdS crystals structure. Using Scherer's formula through XRD the crystal size obtained within 3 to 12 nm and increases with increasing CdS concentration. In CdS/PVK nanocomposite the absorption is obtain within 300-500 nm. With increasing CdS concentration in PVK the absorption edge was red shifted. This is due to effect of quantum confinement for larger particle, higher the CdS loading. The size of particle is computed from energy band gap by effective mass approximation and hyperbolic band model satisfy with result from XRD also.Pure PVK gives peak at 451 nm and Q-CdS give single peak at 530 nm. It excited separately by 400 nm. The PL spectra of pure PVK gives peak at 451 nm and Q-CdS give single peak at 530 nm when excited separately by 400 nm. In CdS/PVK nanocomposites two PL peaks are obtained, first peak due to PVK near 450 nm and second peak due to Q-CdS near 530 nm.PL intensity decreases with higher loading of CdS in polymer. This may be with interfacial charge transfer between at CdS-PVK interface and separating of electrons and holes.

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