Research Journal of Pharmaceutical, Biological and Chemical Sciences

Spectroscopic inquest of CdS, PbS and ZnS Doped PVP composite: A Density Functional Theory Approach.

AM Abdelghany[1], MS Meikhail[2], EM Abdelrazek[2], and MM Aboud[2]

[1]Spectroscopy Department, Physics Division, National Research Center, Dokki, 12311, Cairo, Egypt.
[2]Physics department, Faculty of Science, Mansoura University, 35516, Mansoura, Egypt.

ABSTRACT

Nano-crystals of CdS, PbS and ZnS were successfully in-situ prepared and used as a dopant in polyvinyl pyrrolidone (PVP) polymeric matrix via simple casting technique. Prepared samples examined theoretically using density functional theory (DFT) and experimentally through combined Fourier transform infrared (FTIR) and (UV/Vis) spectroscopy. DFT calculations and FTIR experimental results shows the persistence of the characteristic bands of polymer network in their positions while pyrrolidinone ring adsorbed CdS, PbS and ZnS surfaces preferably via the non-bonding electrons of the carbonyl group. UV/Vis experimental data was employed to calculate the optical energy gap of virgin and doped polymeric matrix. Optical band gap and particle size were calculated and is in agreement with the results obtained from Transmission electron microscopy (TEM). The prepared spherical Nano-crystals were found to be uniformly distributed within PVP matrix.

Keywords: PVP; CdS, PbS and ZnS nanoparticles; DFT; band structure; FTIR; UV/Vis.

INTRODUCTION

The field of nanotechnology has a wide utilization in numerous applications, for instance an enormous advancement of utilizing semiconductors of II-VI group in union of opto-electronics and in emitting diodes gadgets because of their huge direct band gap which make them great in synthesis. Nano-sized semiconductors have same good properties as nanoparticles which are strongly depend on their size [1]. Nano-sized semiconductors show a good chemical reactivity because of their high surface to volume ratio results in high chemical reactivity. The decrease of their size also leads to an increase of the band-gap energy that is known as a quantum size effect. most of the physical and chemical properties of prepared nanoparticles depend on their crystallite size, prepared nanocrystals tend to making clusters and so they must be stabilized using various polymers and surfactants [2].

Polyvinylpyrrolidone (PVP) used for capping nanocrystals and prevent them from agglomeration. PVP was used to improve the complexation or interaction between PVP and semiconductors of II-VI group [3]. A computational method has studied the interaction of semiconductors of II-VI group with PVP based on Density Functional theory by observing the interaction of pyrrolidinone and N-methyl-2-pyrrolidinone (monomers of PVP) with filled materials [4]. Combination between Fourier transform infrared spectroscopy (FTIR) and density functional theory (DFT) used to clarify the mechanism of interaction of metal sulfide with PVP polymeric matrix and understanding the mechanism of adsorption of pyrrolidinone on the surface of nano-crystals of CdS, PbS and ZnS.

The aim of the present study is to introduce a semi-experimental method for investigation of the interaction in molecular level between polymeric matrix of PVP and different dopant semiconducting sulfides namely (CdS, PbS and ZnS) nano-crystallites. Moreover, to shade a light on the mechanism of interaction between those dopants and polymeric matric using theoretical approach (density functional theory).

MATERIALS AND METHOD

Three films of PVP filled individually with inorganic metal sulfides namely (CdS, ZnS and PbS) were prepared via in-situ wet chemical precipitation method. Polymeric matrix dissolved in double distilled water while metal sulfide originally prepared in situ using analytical grade reagent with specific ratio: 2:1 (Thiuorea: Cadmium Acetate or Zinc acetate or Lead Acetate) for obtaining their composites with polymeric matrix PVP/XS where (X= Cd, Zn and Pb) as shown in table (1), Thiuorea added drop by drop (one drop/second) using a burette with the vigorous stirring to the metal acetate aqueous solution in the presence of the virgin polymeric matrix at 40 °C. A nano-crystallite of metal sulfide of the cross ponding acetate salt was formed and indicated by the change in color of the whole composite after two hours. The obtained solutions containing desired metal sulfide were casted to a glass dish and dried in oven at T = 60 °C for 3 days to remove any remind solvent traces. Films of thickness ranging from 0.5 to 0.2 mm were peeled from dishes and stored in dry place until use.

Table 1: Nominal composition of polymeric matrix PVP and metal sulfide filler.

Filler type	CdS	ZnS	PbS
PVP (wt. %)	95	95	95
Filler (wt. %)	5	5	5

X-ray diffraction scans were obtained at Bragg's angle (2θ) ranging from (5-60°) using PANalytical X'Pert PRO XRD operating at 30kV with Cu K_α radiation (where, λ = 1.540 Å). UV/Vis absorption spectra were measured and recorded in the wavelength region of (190 – 900 nm) using spectrophotometer (UNICAM UV/Vis Spectrometer, England). FTIR vibrational absorption spectra carried out using the single beam Fourier transform-infrared spectrometer (Nicolet *i*S10, USA) in the spectral range of   (4000–400cm^{-1}). Transmission electron microscope (TEM), (JEOL-JEM-2100, Japan) was used to study the size, shape and distribution of the nanoparticles within the polymeric matrix during preparation process.

DFT calculations and models

Density functional theory (DFT) calculations was performed in the framework of Gaussian 03 programs [5]. Recently, a reasonable agreement between the theoretical and experimental data obtained in amorphous materials using DFT approach was observed by several authors [6, 7]. In this study the interaction between PVP and nanocrystals of II-VI group were optimized using the Becke's three parameter hybrid functional [8] with the Lee et al [9]. An electron core potential basis set (3-21G) for CdS and (lanl2mb) for (PbS, ZnS) combined with (B3LYP) correlation functional employed for the minimization and optimization of the electronic structure.

RESULTS AND DISCUSSION

Experimental Fourier transform infrared analysis

Fig.1. shows FTIR absorbance spectra of pure PVP with PVP/CdS, PVP/PbS and PVP/ZnS nanocrystals films respectively in the region (4000–400 cm^{-1}). The characteristic bands of vibrations formed in the prepared films were listed in Table 2.

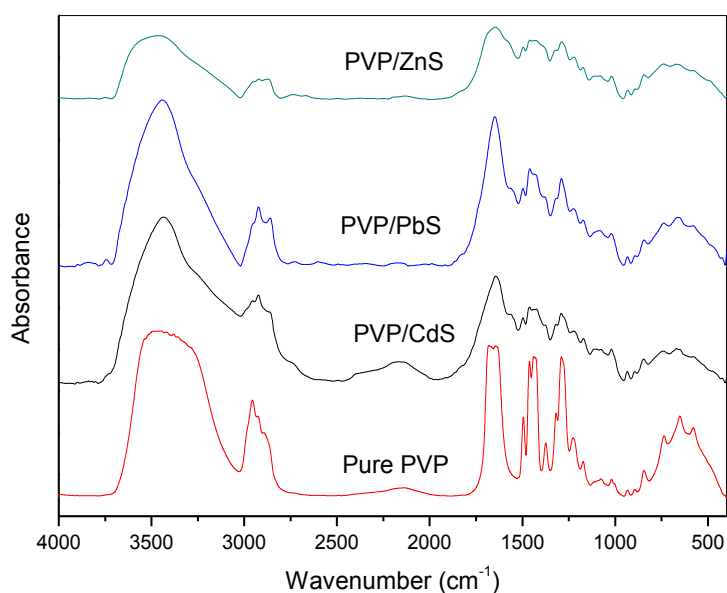**Figure 1: FTIR absorption spectra of pure and doped PVP films.**

Table 2: FTIR band assignment of different vibrational modes for prepared samples

Wavenumber (cm^{-1})	Band Assignments	Ref
1280	C-N stretching or C-O stretching	[10]
1437	CH_2 scissoring	[11]
1660	C = O, C= C	[12-15]
2945	CH_2 asymmetric stretching	[16]
3425	O-H stretching	[17]

Theoretical Fourier transform infrared analysis

Density functional theory was used for studying complex interaction between pyrrolidinone and N-methyl-2-pyrrolidinone (monomers of PVP) and nanocrystals of CdS, PbS and ZnS. As shown in Fig.2 the possible probabilities of interaction between PVP with nanocrystals of CdS, PbS and ZnS. PVP may interact with filled materials via adsorption of pyrrolidone ring on the surface of filled materials by means of;

- Nonbonding electrons of carbonyl group.
- Adsorption of pyrrolidone via Nitrogen atom.
- Adsorption via both carbonyl group and Nitrogen atom.
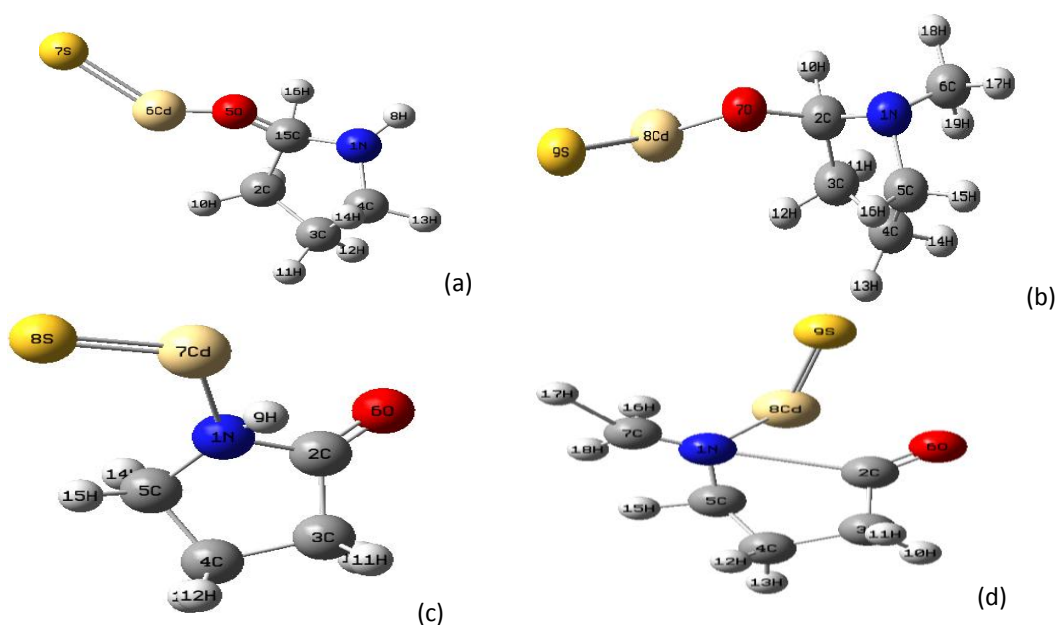

M= CdS,PbS and ZnS
R= H,CH₃
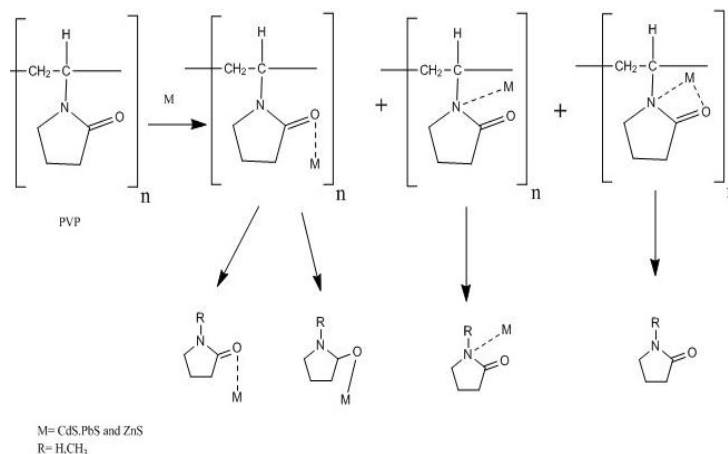
**Figure 2: Possible modes of interaction between PVP and Silver and Gold nanoparticles at room temperature**

Figs. 3, 4 show optimized structure of four possible modes of interaction between PVP/CdS, PVP/PbS with obtained theoretical and experimental FTIR, while Fig.5 show optimized structure of three possible of interaction between PVP/ZnS with the obtained experimental and theoretical FTIR obtained from optimized structure of possible modes of interaction respectively, the fourth possible mode of interaction between PVP/Zns is rejected to be optimized and so there is no theoretical FTIR for it.

A combination between theoretical calculation and experimental FTIR show that nano-crystals of cadmium sulfides, Lead Sulfide and Zinc sulfide were stabilized by chemical interaction with oxygen atom of pyrrolidone ring, while other theoretical modes of interactions show low agreement with experimental data.

X-Ray Diffraction Analysis (XRD)

X-ray diffraction pattern of pure PVP shows two broad bands at about $2\theta=10.9°$ and $20.4°$ represent the semi-crystalline nature of PVP. X-ray patterns of pure PVP and samples filled with CdS, PbS and ZnS shown in Fig.6a, b and c respectively.

(a)

(b)

(c)

(d)
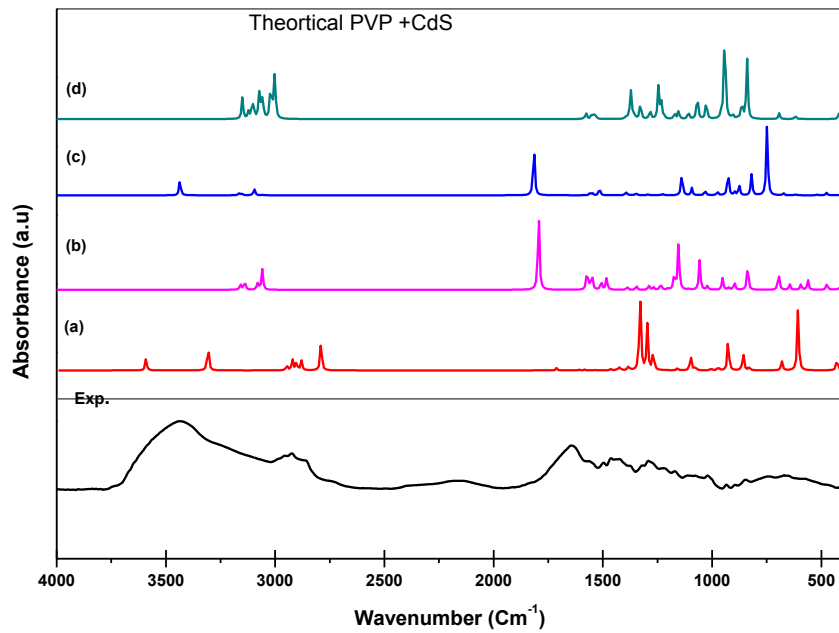
Figure3: Optimized structure of four possible interaction modes of PVP/CdS with experimental and theoretical FTIR absorption spectra.

There was a noticeable change in the intensity of XRD peaks after doping CdS, PbS and ZnS nanocrystals. The intensity of peaks at $2\theta=10.9°$ and $2\theta=20.4°$ observed to decrease after adding CdS, PbS nanocrystals while the band at $2\theta = 20.4$ was found to be increased in case of PVP sample filled with ZnS nanocrystals. There is no characteristic peaks appear for CdS, PbS and ZnS nanoparticles which refer to complete interaction between PVP and CdS, PbS and ZnS nanocrystals,
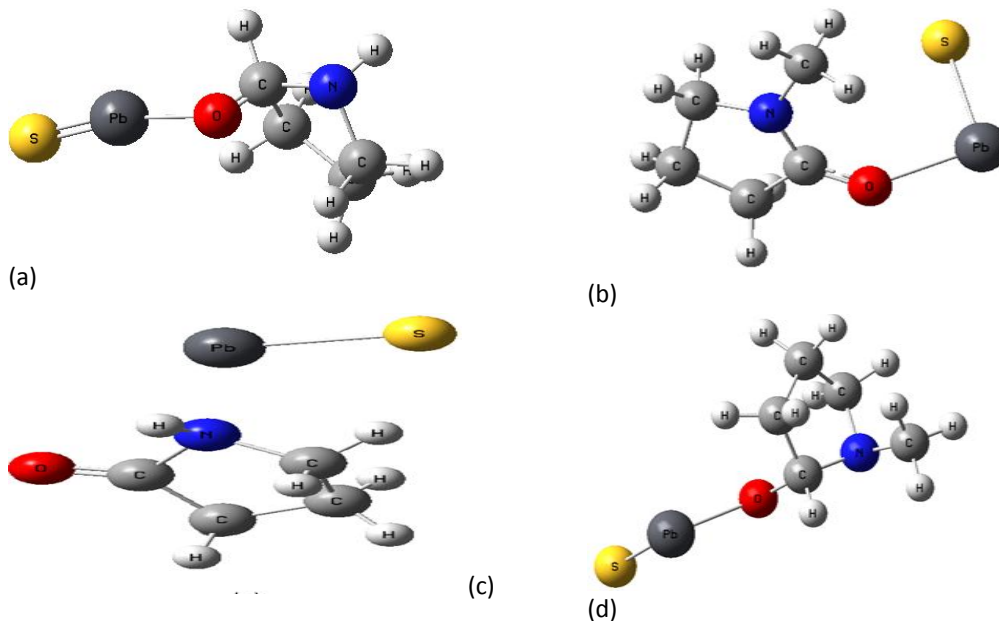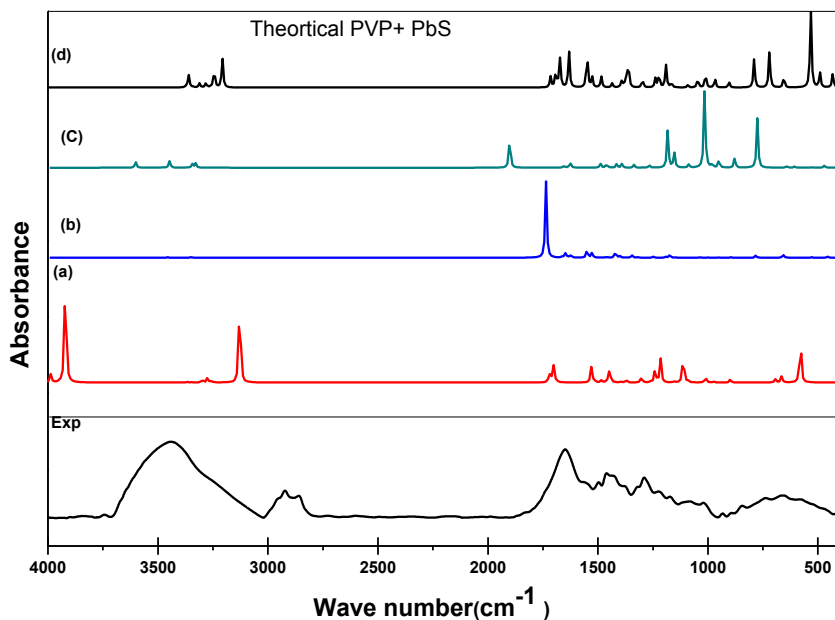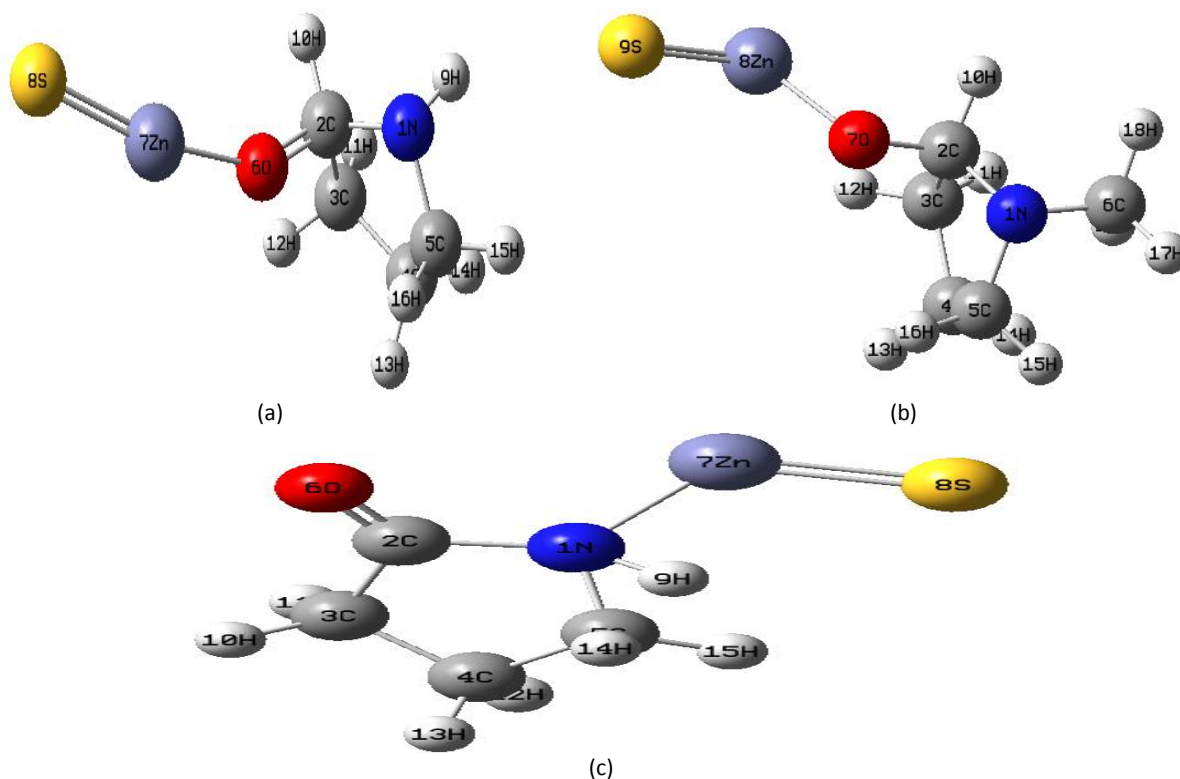
Figure 4: Optimized structure of four possible interaction modes of PVP/PbS with experimental and theoretical FTIR absorption spectra.
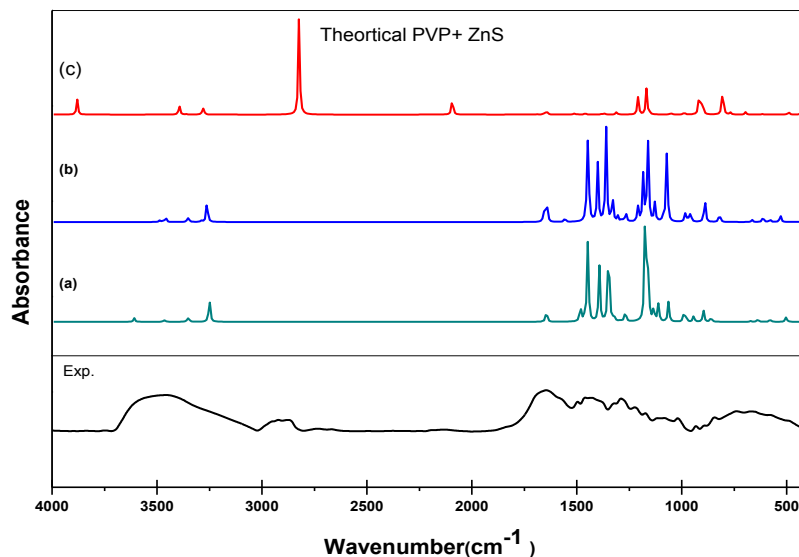

(a)

(b)

(c)

Figure 5: Optimized structure of four possible interaction modes of PVP/ZnS with experimental and theoretical FTIR absorption spectra.

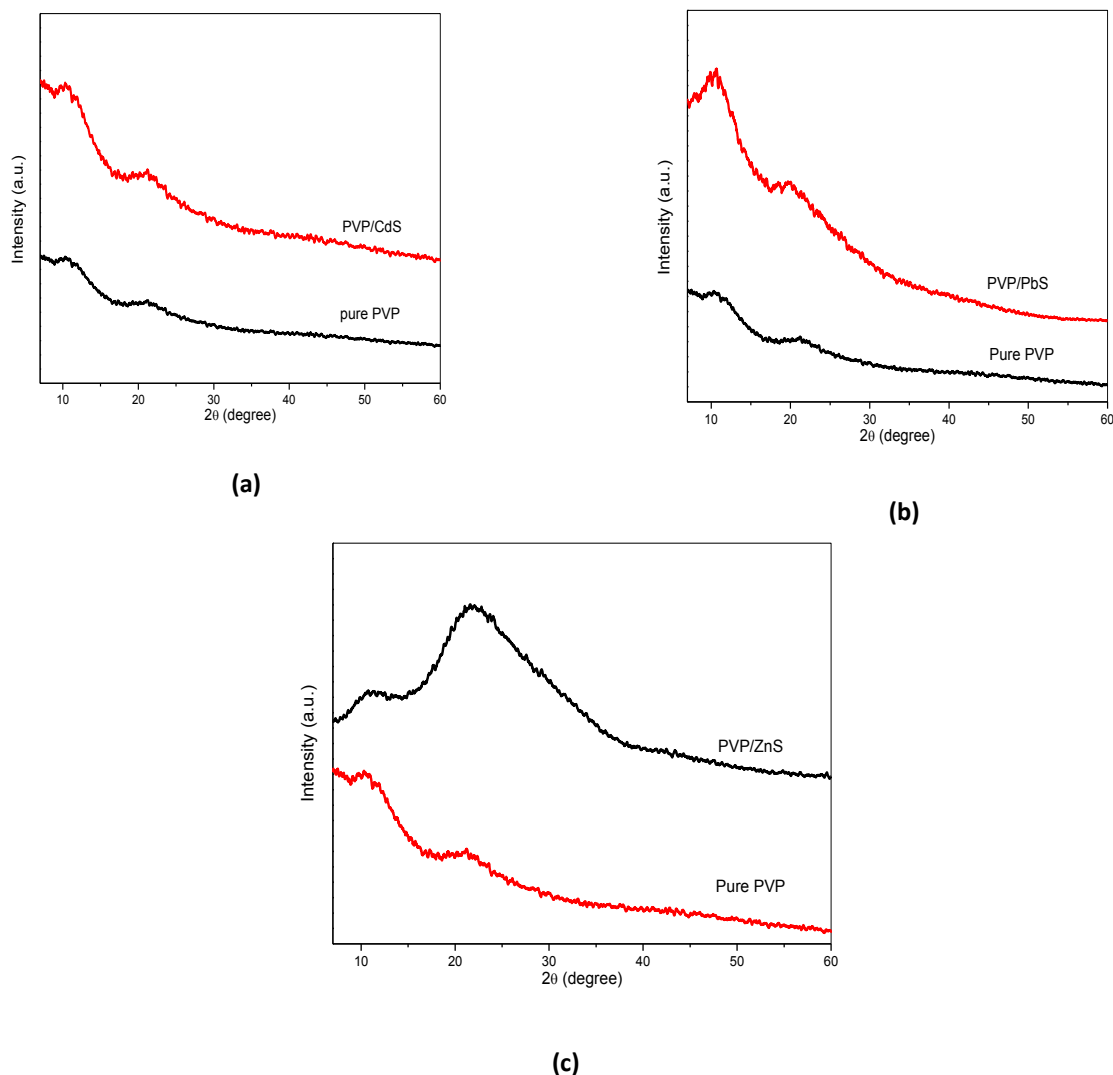
(a)

(b)

(c)

Fig.6 X-ray diffraction pattern of pure PVP and samples that filled with (a)Cadmium Sulfide (b) Lead Sulfide (c) Zinc sulfide nanocrystals

UV-Vis absorption and optical properties calculations

Figure 7 reveals the UV/Vis absorption spectra of pure PVP and PVP filled with metal sulfides (CdS, PbS and ZnS). It is noticed that absorption band around 234 nm corresponds to (π→π*) transition associated with the presence of carbonyl groups (C=O) of PVP backbone [18] which appears in experimental and theoretical FTIR vibrational band at about 1660 cm $^{-1}$.

The direct method for calculating optical band gap of materials was mulled over its absorption spectra. The essential absorption demonstrates a sudden ascent in absorption, known as absorption edge, which can be used to determine the optical band gap ($E_g = hc/\lambda$) where h is Planck's constant. Absorption is expressed in terms of a coefficient α (absorption coefficient), where α = 2.303 A/d and d is the sample thickness. Absorption coefficient α for amorphous materials related to the energy of the incident photon as follows [19]:

$$\alpha h\upsilon = \beta\left(h\upsilon - E_g\right)^r \qquad \text{For } h\upsilon > E_g$$
$$\alpha h\upsilon = 0 \qquad \text{For } h\upsilon < E_g$$

Where $h\upsilon$ is the energy of incident photon E_g is the optical energy gap, β is a constant and r = 1, 2, 3, 1/2 and 3/2, depending on the nature of the electron transitions responsible for the optical absorption.

(a)

(b)

(c)
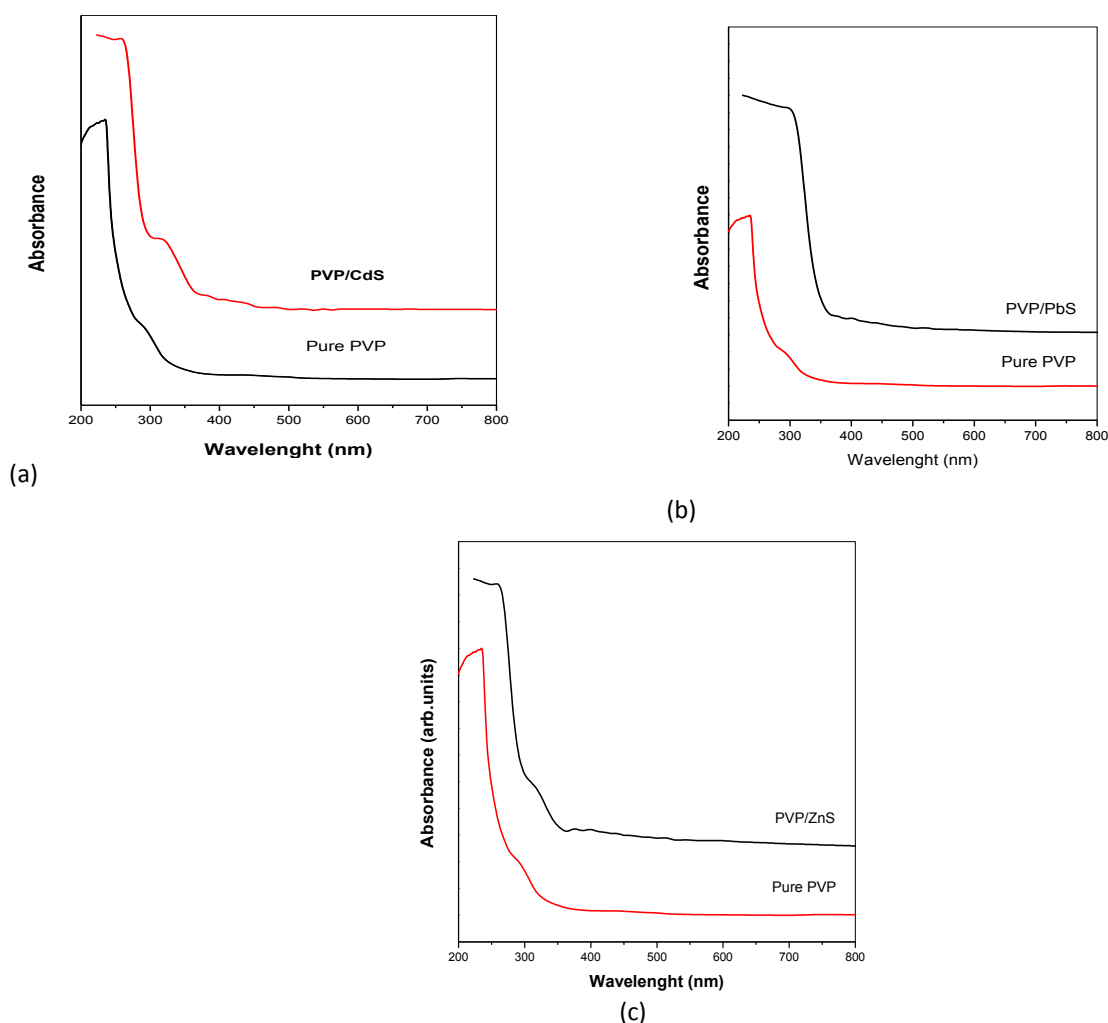
**Figure 7: UV/Vis absorption spectra of Pure PVP and samples that filled with
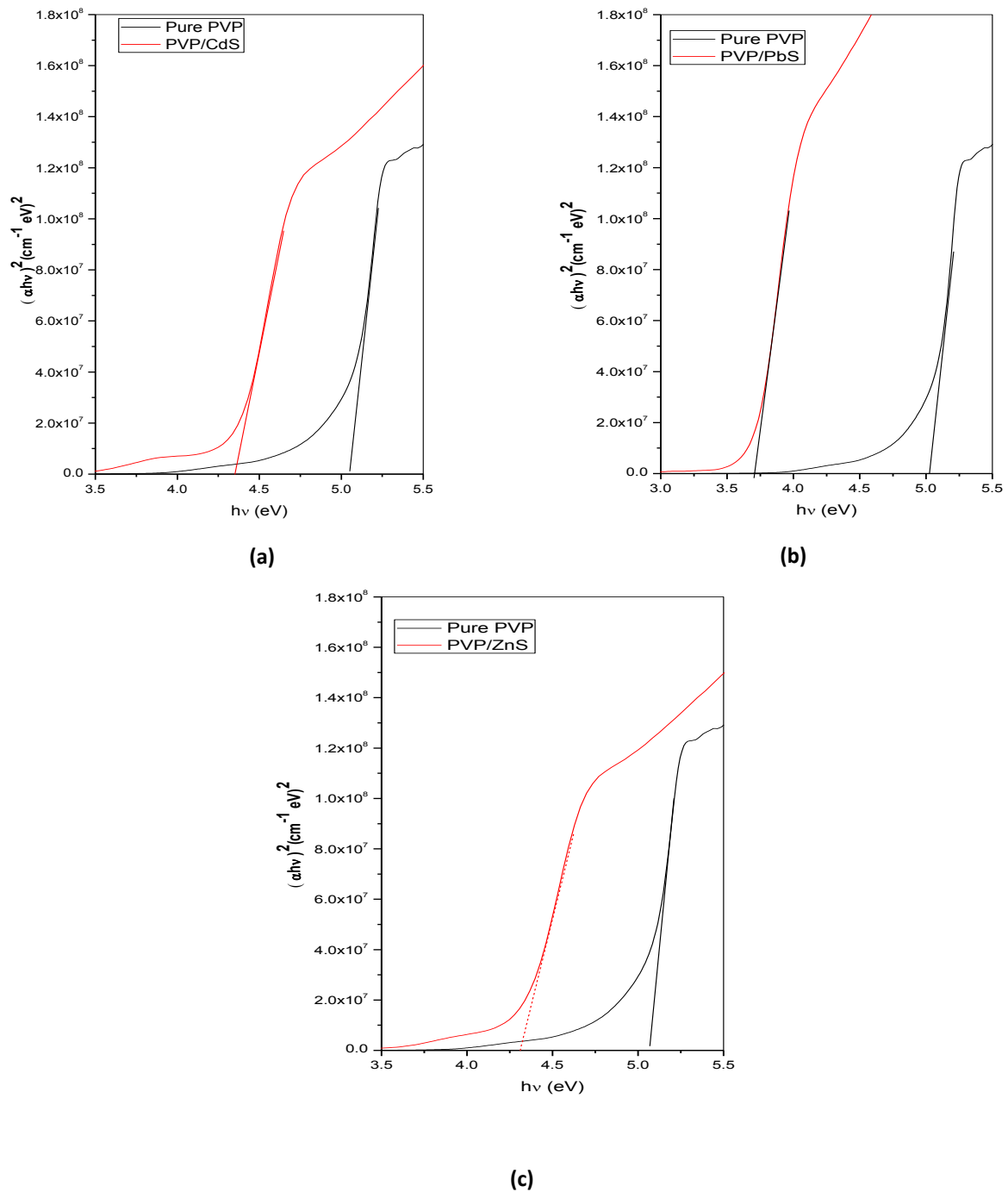(a)Cadmium Sulfide (b) Lead Sulfide
(c) Zinc sulfide nanocrystals**

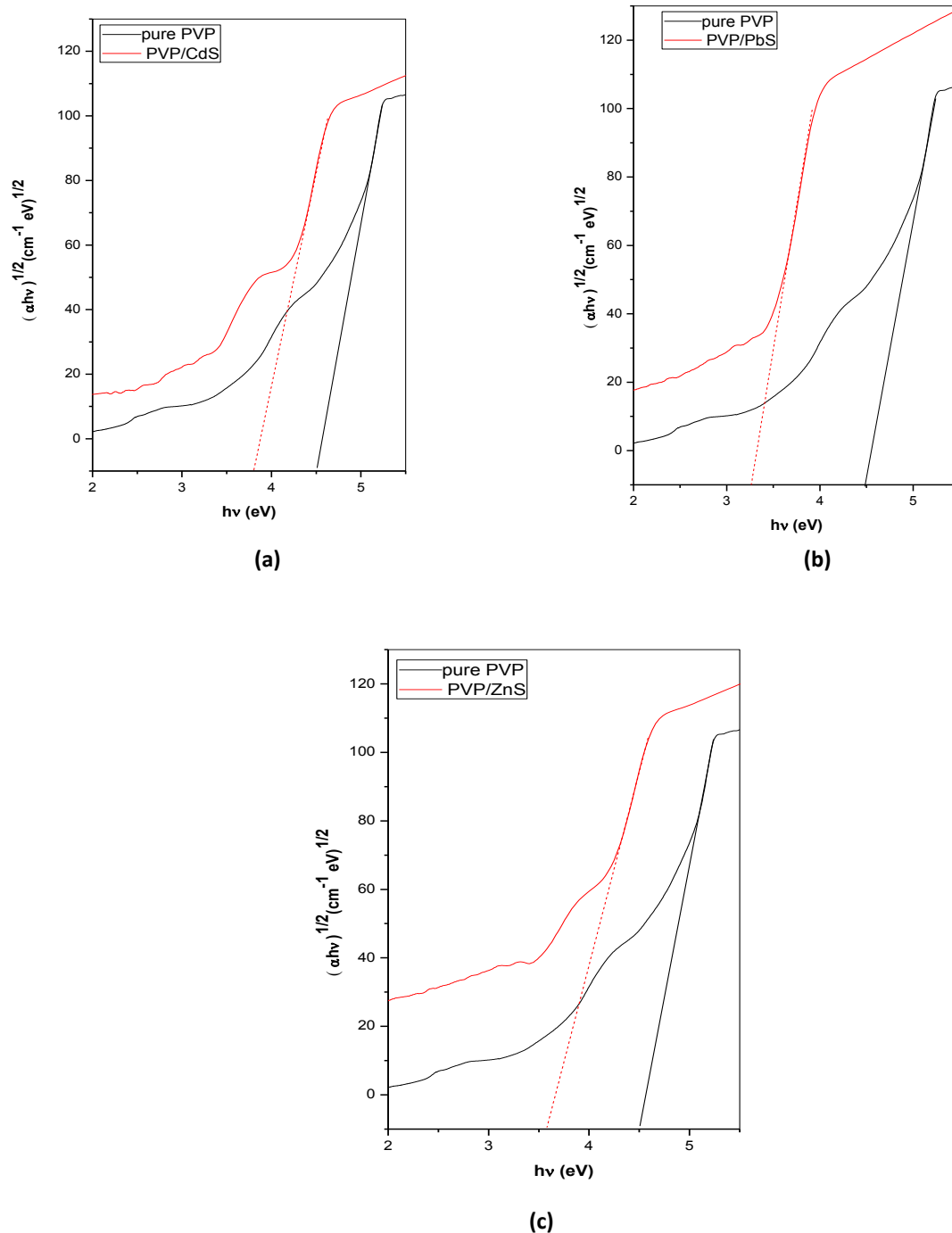(a)

(b)

(c)

Figure 8: Davis and Mott plot of the $(\alpha h\upsilon)^2$ a function of photon energy $(h\upsilon)$ for pure PVP and samples that filled with
(a)Cadmium Sulfide   (b) Lead Sulfide
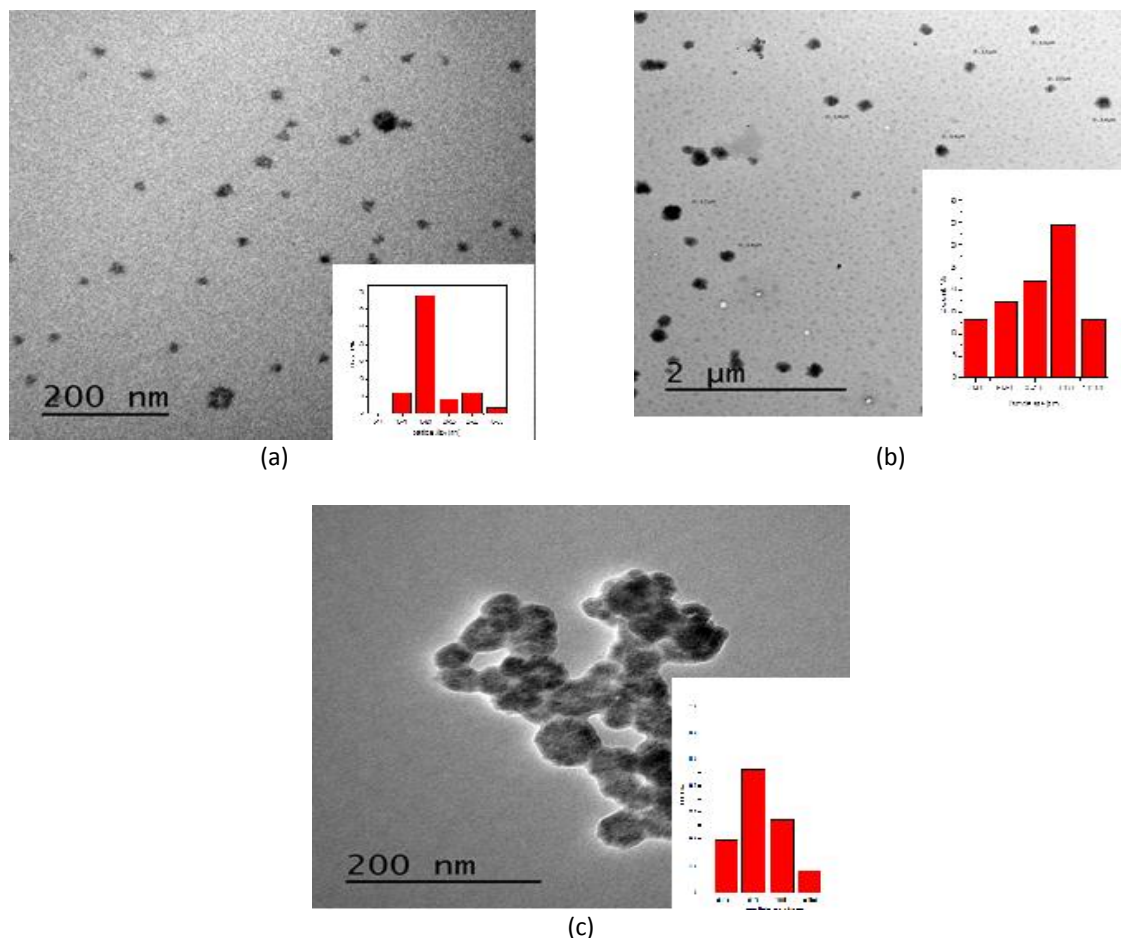(c) Zinc sulfide nanocrystals

(a)

(b)

(c)

Figure 9: Davis and Mott plot of the $(\alpha h\upsilon)^{1/2}$ a function of photon energy $(h\upsilon)$ for pure PVP and samples that filled with
(a)Cadmium Sulfide (b) Lead Sulfide
(c) Zinc sulfide nanocrystals

The exponent r = 1/2 in case of direct electronic transition and r = 2 in case of indirect electronic transition. Davis and Mott[20, 21] reported that near fundamental band edge, both direct and indirect transitions occurs and can be observed by plotting $(\alpha h\upsilon)^{2}$ and $(\alpha h\upsilon)^{1/2}$ versus photon energy $(h\upsilon)$.

Fig.8 shows the Davis and Mott plot of the $(\alpha h\upsilon)^{2}$ as a function of photon energy $(h\upsilon)$ for pure PVP and samples filled with CdS, PbS and ZnS nanocrystals. the optical band gap of pure PVP, PVP/CdS, PVP/PbS and PVP/ZnS, while Fig.9 shows the Davis and Mott plot of the $(\alpha h\upsilon)^{1/2}$ as a function of photon energy $(h\upsilon)$ for pure PVP and samples filled with CdS, PbS and ZnS nanocrystals.

Transmission electron microscopy (TEM)

Fig.10 Show TEM images of the appropriation and the morphology with the molecule size histogram of Cadmium Sulfide, Lead Sulfide and Zinc sulfide nanocrystals inside PVP polymer individually. It is clear that from the histogram, nanocrystals show a uniform circular shape and uniform conveyance.

(a)

(b)

(c)

Fig.10: TEM image of the distribution and the morphology with the particle size histogram of for pure PVP and samples that filled with
(a)Cadmium Sulfide   (b) Lead Sulfide
(c) Zinc sulfide nanocrystals

CONCLUSION

Polyvinyl pyrrolidone (PVP) polymeric matrix doped with nano-crystals of CdS, PbS and ZnS were successfully in-situ prepared via simple casting technique. Combined DFT – FTIR data were used to investigate the type of interaction in the molecular level. Both DFT calculations and FTIR experimental results show the persistence of the characteristic vibrational bands of polymeric network in their positions and with minor change in its intensities. Theoretical calculation obtained from DFT suggests that pyrrolidinone interact with metal sulfides, namely (CdS, PbS and ZnS) nanocrystals surfaces preferably via the non-bonding electrons of the carbonyl group. Optical band gap and particle size obtained from (TEM) was found to be in agreement with that calculated from UV/Vis absorbance spectra. Transmission electron microscopy (TEM) shows also, that CdS, PbS and ZnS nanocrystals were uniform dispersed within the polymeric matrix.

REFERENCES

[1] Praus P, Dvorsky R, Kozak O, Koci K. Zinc Sulphide Nanoparticles for Photochemical Reactions: Reduction of Carbon Dioxide and Oxidation of Phenol. Nanocon, Czech Republic. 2011.
[2] Kozák O, Praus P, Kočí K, Klementová M. J Coll Interf Sci 2010;352(2):244-51.
[3] Gupta B, Anjum S, Ikram S. J Appl Polym Sci 2013;129(2):815-21.
[4] Mdluli PS, Sosibo NM, Revaprasadu N, Karamanis P, Leszczynski J. J Mol Str 2009;935(1):32-8.
[5] Gaussian09 RA. 1, MJ Frisch, GW Trucks, HB Schlegel, GE Scuseria, MA Robb, JR Cheeseman, G. Scalmani, V. Barone, B. Mennucci, GA Petersson et al., Gaussian. Inc, Wallingford CT. 2009.
[6] Chiş V, Venter MM, Leopold N, Cozar O. Vibrational Spectroscopy 2008;48(2):210-4.
[7] Muniz-Miranda M, Cardini G, Pagliai M, Schettino V. Chem Phys Lett 2007;436(1):179-83.
[8] Wong MW. Chem Phys Lett 1996;256(4):391-9.
[9] Miehlich B, Savin A, Stoll H, Preuss H. Chem Phys Lett 1989;157(3):200-6.
[10] Tawansi A, El-Khodary A, Abdelnaby M. A study of the physical properties of FeCl 3 filled PVA. Curr App Phy 2005;5(6):572-8.
[11] Li X-G, Kresse I, Springer J, Nissen J, Yang Y-L. Polymer 2001;42(16):6859-69.
[12] Abdelaziz M, Abdelrazek E. Physica B: Condensed Matter 2007;390(1):1-9.
[13] Abdelrazek E, Elashmawi I, El-Khodary A, Yassin A. Curr App Phy 2010;10(2):607-13.
[14] Jin WJ, Lee HK, Jeong EH, Park WH, Youk JH. Macromol Rapid Commun 2005;26(24):1903-7.
[15] Laot CM, Marand E, Oyama HT. Polymer 1999;40(5):1095-108.
[16] 16. Abdelghany A, Abdelrazek E, Rashad D. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2014;130:302-8.
[17] Borodko Y, Habas SE, Koebel M, Yang P, Frei H, Somorjai GA. The J Phys Chem B 2006;110(46):23052-9.
[18] Reddy CVS, Sharma A, Rao VN. Polymer 2006;47(4):1318-23.
[19] Thutupalli G, Tomlin S. J Physics D App Phy 1976;9(11):1639.
[20] Camassel J, Auvergne D, Mathieu H, Triboulet R, Marfaing Y. Solid State Commun 1973;13(1):63-8.
[21] ElBatal F, Ibrahim S, Abdelghany A. J Mol Str 2012;1030:107-12.