



Optical and structural characteristics of polyvinyl chloride doped with cadmium

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ABSTRACT: Pristine samples of polyvinyl chloride (PVC) in addition to other samples containing different dopant levels of the synthesized cadmium selenide quantum dots (CdSe QD's) were successfully prepared using the traditional liquid casting route. X-ray diffraction (XRD), Fourier transform Infrared (FT-IR), and Ultraviolet/Visible (UV/Vis.) spectroscopic measurements were employed to retrace structural variations in the structure associated with increasing dopant levels of CdSe QD's. X-ray diffraction pattern of synthesized CdSe QD's reveals the hexagonal crystalline structure belongs to Wurtzite and in agreement with that of the Joint Committee on Powder Diffraction Standards (JCPDS). The amorphous nature of studied samples points out the interstitial position taken by the dopant CdSe Qd's. Fourier transform infrared shows repetitive spectral data indicating physical interaction between dopant and polymeric matrix and supporting XRD findings. UV/Vis. Electronic spectra reveal a quiet change in the optical energy gap resulting from the increasing level of dopant within the polymeric matrices.

Keywords: PVC; FT-IR; UV/Vis.; CdSeQD's

1. Introduction

Polymer nanocomposite is a unique class of materials with unique and modified physical characteristics as well as a wide range of industrial uses. Several pieces of research on polymer nanocomposites have been published. These include various polymer matrices such as polyimide, polypropylene, polyurethane, etc [1-3]. Poly-vinyl chlorides (PVC) is a polymer commonly used by the variants of polymers. It was incorporated in many reports of nano-composite production. The PVC polymer is a thermoplastic material that consists of both chlorine and carbon that represent 57 and 43% respectively. It is also a brittle one secure and insoluble in alcohol but more soluble in tetrahydrofuran [4]. This type of thermoplastic polymer is used to make a variety of goods, including sanitary equipment, furniture, toys, clothing, and electrical wire insulation. PVC may be utilized in a variety of sectors, including medical applications, because of its extended service life, high transparency, flexibility, and low cost [5-7].

Ekimov and Onushenko were the first to identify quantum dots (QDs) as tiny semi-

conductor crystals. The first use of biological imaging was reported in 1998, using a glass matrix with the first, back in 1981. The field of QDs has since been growing steadily and now includes solar cells, photovoltaic applications devices, manufacturing of light-emitting diodes (LED), photodetectors, computers, biomedicine imaging, and so on. The Near-Infrared (NIR) (650 nm) is not available for most conventional organic label colors possibility of emissions; this region is highly sought after for biomedical imaging because of its low light dispersion and low tissue absorption are the reasons why QDs with their adjustable optical properties gained considerable interest [8-10]. These semiconductors provide nanometric optical characteristics that are distinctive and intriguing, such as high quantity yield, size-adjustable light emission, and excellent photo and chemical stability. QDs range in size from 2 to 10 nm and are made of mostly elements from classes II-VI, III-IV (such as Cd, Pb, and Hg). IV-VI in the periodic table. The researchers have established ternaries more recently II, III, VI QDs (where I = Cu and Ag, III = Ga and In, VI = S or Se).

Different types of the same light wavelength, QDs, and their narrow emission bands can be excited about multiple assays, they can be detected simultaneously.

The structure, size, and thickness of the QD shells determine the fluorescence bands. If the particle size is smaller, the energy levels take on atom-like characteristics and are distinct from the energy spectrum seen in bulk materials; in other words, these unique qualities come from the physical decrease of the confinement of the states of the load carriers nanoparticles size. [11]. To use QDs in system Conditions, they must be active or passive, as of their high surface and reactivity. When picking The stabilizer, the absorption must be taken into account and the profile of the luminescence spectra; the quantum yield, as well as the Lifetime, depends on the composition of the environment.

There is a growing interest in improving the nano-theranostic simultaneous sensing systems, Photo, and therapy. QDs offer a wide range of possible uses, including sensors, medication administration, and biomedical imaging, among others. Photovoltaic cells, laser, and thin-film transistors, Diode-emitting light, and other nanoscale devices are all possible uses for CdSe-polymer nanocomposites [12,13]. Numerous methods to synthesize CdSe have been developed in a thin-film form comprising chemical bath deposition (CBD) [14] evaporation by vacuum [15], electrodeposition [16], Pyrolysis spray [17], and adsorption of successive ionic layers and (SILAR) Reaction [18]. CBD method is used for the polymer-capped production of CdSe thin films with nanocomposite because it is simple to handle, cost-effective, and appropriate for large-scale deposition [16,17]. Recently, several studies have focused on the production and characterization of cadmium selenide (CdSe) QDs in polymeric matrices using a synthetic wet chemical method [19,20]. CdSe QDs successfully prepared by Borkovsk et al. embedded in a polymer matrix, and the annealing effects. The temperature was investigated regarding the luminescent properties of nanostructures [21]. The CdSe NPs covered with PVC were synthesized by Shah et al. via a simple chemical route and they studied the influence of concentration of

precursors, aging, and the temperature of reaction on the as-synthesized size of the CdSe NPs and their optical properties [22]. Kushwaha et al reported synthesis and photoluminescence characteristics of CdSe/PVA polymer nanocomposites containing different mass fractions of filler [23]. Ma et al. established the production of CdSe nanoparticles distributed through a one-step PVA matrix at ambient temperature. The method of solution growth and the investigation of its optical and structural properties [24].

The present work aims to synthesis a new composite material comprising an organic polymer with inorganic CdSe QDs as a filler in the dopant level and to study their optical and structural role.

2. Experimental details

2.1. Material used

Polyvinyl Chloride in the form of a white solid powder was purchased from Sigma Aldrich Company of chemicals and has a chemical formula $(-\text{CH}_2-\text{CHCl}-)_n$ with high molecular weight. Synthesis of CdSe quantum dots (QD's) was previously discussed elsewhere [25]. Tetrahydrofuran (THF) $\text{C}_4\text{H}_8\text{O}$ with M.W. 72.11 was obtained from Alpha Chemika and used as a common solvent.

2.2. Sample Preparation

2.2.1. Preparation of polyvinyl chloride (PVC)

120 ml of the solution of (THF) was used to dissolve the pre-calculated amount of PVC powder. The polymeric powder was vigorously stirred at room temperature to get a clear bubble-free and transparent solution. The obtained solution was cast at 50°C in glass Petri dishes. The prepared samples were peeled from the dishes and placed in a desiccator until use.

2.2.2. Preparation of Quantum Dots (QDs) Suspension

50 ml of (THF) was used to dissolve the pre-calculated amount of QDs powder and then put in a sonicator for mixing which produced the clear solution.

2.2.3. Preparation of Composite Samples

120 ml of a solution of (THF) was used to dissolve the pre-calculated amount of PVC

powder, 120 ml of mixed (PVC) and (THF) divided into 6 beakers. Added different amounts QDs (0.5, 1, 2, 4 and 8 ml) into 6 beakers. The obtained solution was cast at 50°C in glass Petri dishes. The prepared samples were peeled from the dishes and placed in a desiccator until use. Sample abbreviation and their composition were listed in the table (1).

Table 1: Name abbreviations and their composition

	CdSe QD ml Added	PVC (gm)
PVC0	0.0	1
PVC1	0.5	1
PVC2	1.0	1
PVC3	2.0	1
PVC4	4.0	1
PVC5	8.0	1

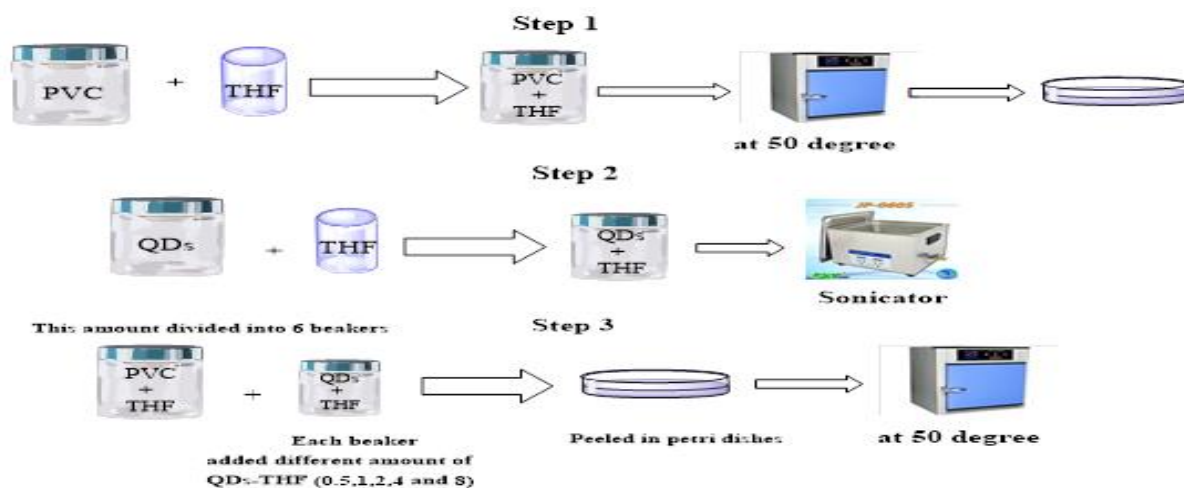


Fig. 1: Schematic representation of preparation technique

3. Results and discussion

3.1. Characterization of dopant CdSe QD's

Fig. 2 describes the UV/Vis. spectral data of the studied CdSe QD's in correlation with their transmission electron micrograph and electron diffraction. UV spectrum shows a presence of two characteristic peaks originally located at 255 and 418 nm as previously discussed by several authors [25-27]. In addition, TEM images point to the formation of 3-5 nm CdSe QD's with hexagonal patterns supporting the findings of the XRD pattern.

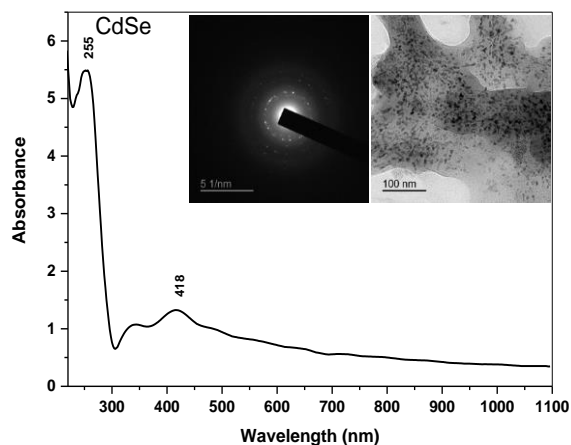


Fig. 2: UV/Vis. spectrum, TEM and electron diffraction of the studied CdSe QD's

3.2. X-ray diffraction analysis

Fig. 3 discloses the X-ray diffraction (XRD) pattern of the studied CdSe QD's. The obtained pattern reveals the presence of sharp diffraction peaks located at 2θ angles 23.9, 25.3, 27.0, 42.0, 45.8, and 49.8 corresponding to (100), (002), (101), (110), (103), and (112) planes of hexagonal structure with ($a = 4.299 \text{ \AA}$ and $c = 7.010 \text{ \AA}$) and in agreement with that of (JCPDS) CAS No. 08-0459 [28].

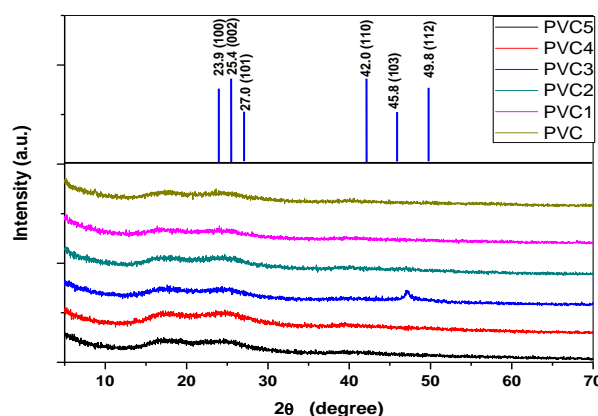


Fig. 3: XRD patterns of synthesized crystalline CdSe QD's, PVC, and samples of PVC doped with CdSe QD's.

XRD of doped samples reveals the absence of any sharp peaks which can be interpreted in

terms of low-level doping (ppm) level and/or the interstitial position taken by QD's within the polymeric chains and supporting the idea of physical interaction and the weak possibility of chemical interaction resulting from the strong covalent bonding within PVC.

3.3. FT-IR absorption spectra

FT-IR absorption data represents a powerful tool that supplies a huge amount of information about the structure of the material at the subatomic level. Besides, it can determine the type of functional groups present in the studied samples. FT-IR absorption spectra are shown in Fig. 4 indicated that pristine (PVC) polymer characterized through a specific vibrational band located at nearly 2974, 2912 cm^{-1} and in agreement with that reported by Subban and Arof [29] and attributed for C-H group of CHCl and C-H of CH_2 asymmetric stretching vibrations, respectively. Three successive sharp intense bands in the fingerprint region located at 1435 cm^{-1} (wagging CH_2), 1330, and 1253 cm^{-1} were assigned to, $\delta_{\text{C-H}}$ of CHCl. A medium band at 1068 cm^{-1} related to C-C vibration. Two weak peaks at 966 were assigned to the rocking vibration of CH_2 , 698, 616 cm^{-1} due to stretching vibrations of C-Cl. All reported speaks with their assignments were recorded and tabulated as shown in Table (2).

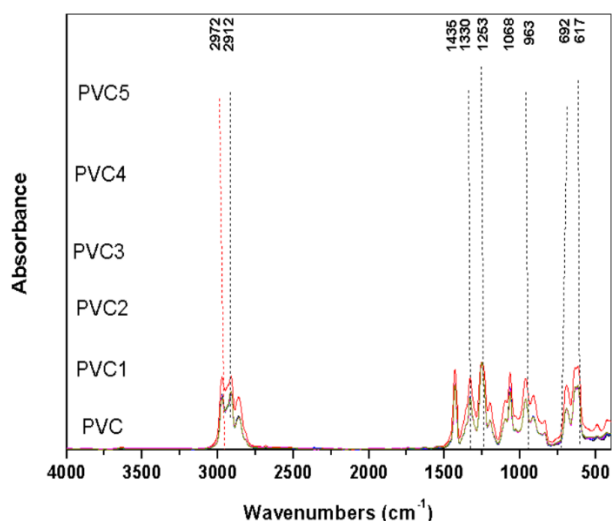


Fig. 4: FT-IR optical absorption spectra of studied samples

Spectra of PVC modified of different doping levels of CdSe quantum dots did not indicate the existence of any interaction or complexation between different compartments that may result in the appearance of a new peak or shift in the polymer cage peak frequencies.

Table 2: FT-IR band position and attribution

Wavenumber (cm^{-1})	Assignment	Ref.
2974	C-H group of CHCl	29, 30
2912	C-H of CH_2 asymmetric stretching vibrations	30, 31
1435	CH_2 Wagging	29-31
1330, 1253	$\delta_{\text{C-H}}$ of CHCl	29
1068	C-C vibration	29
966	rocking vibration of CH_2	31
698, 616	stretching vibrations of C-Cl	31

3.4. UV/Vis. optical Absorption spectra

The electronic transition of the studied base shown in Fig. 5 shows the major bands of studied polyvinyl chloride (PVC) previously studied by several authors [31]. PVC spectrum consists of an intense sharp band located at about 210 nm attributed to $n \rightarrow \pi^*$ and a less intense peak at about 280 nm attributed to the $\pi \rightarrow \pi^*$. Samples that comprising polymer doped with QD's show nearly parallel behavior with higher intensities and without any absorption peaks till the end of measurements indicating the presence of physical interaction between dopant and polymeric matrix resulting from the strong covalent bond constituting the polymer matrix. Such observations agree with that obtained from XRD suggesting that CdSe QD's in the dopant level takes an interstitial position between the atoms of the parent network increasing their randomness and amorphous nature.

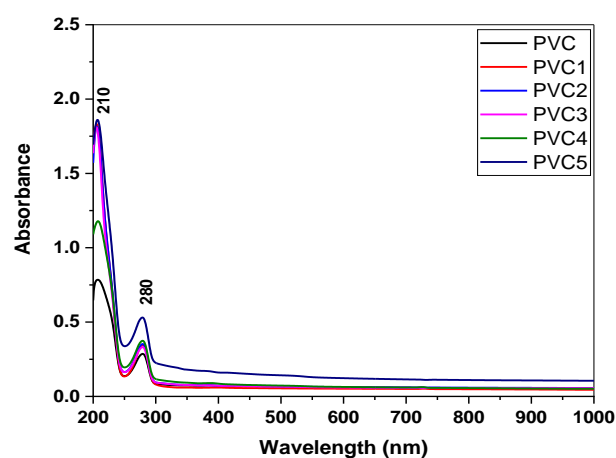


Fig. 5: UV/Vis. optical absorption spectra of the studied samples

Values of optical energy gap (E_{gap}) were calculated from the UV/Vis. spectral data using

Mott and Davis formula [32] describing the photon energy ($h\nu$) in terms of absorption coefficient α and constants m and B :

$$(\alpha h\nu)^m = B(h\nu - E_{\text{gap}})$$

The values of HUMO, and LUMO energy were also calculated for the optimized structures and compared with that obtained from energy gap calculations Table (3) and represented in Fig. 6.

Table 3: Absorption edge and calculated energy gaps of studied samples

Sample	λ_{edge}	E_{opt}	$(\alpha h\nu)^{1/2}$ [cm ⁻¹ eV] ^{1/2}	$(\alpha h\nu)^2$ [cm ⁻¹ eV] ²
PVC	271	4.57	4.5	5.52
PVC1	329	3.76	5.1	4.24
PVC2	339	3.65	4.47	5.52
PVC3	366	3.88	4.46	5.57
PVC4	476	2.60	4.12	4.08
PVC5	493	2.82	4.1	5.38

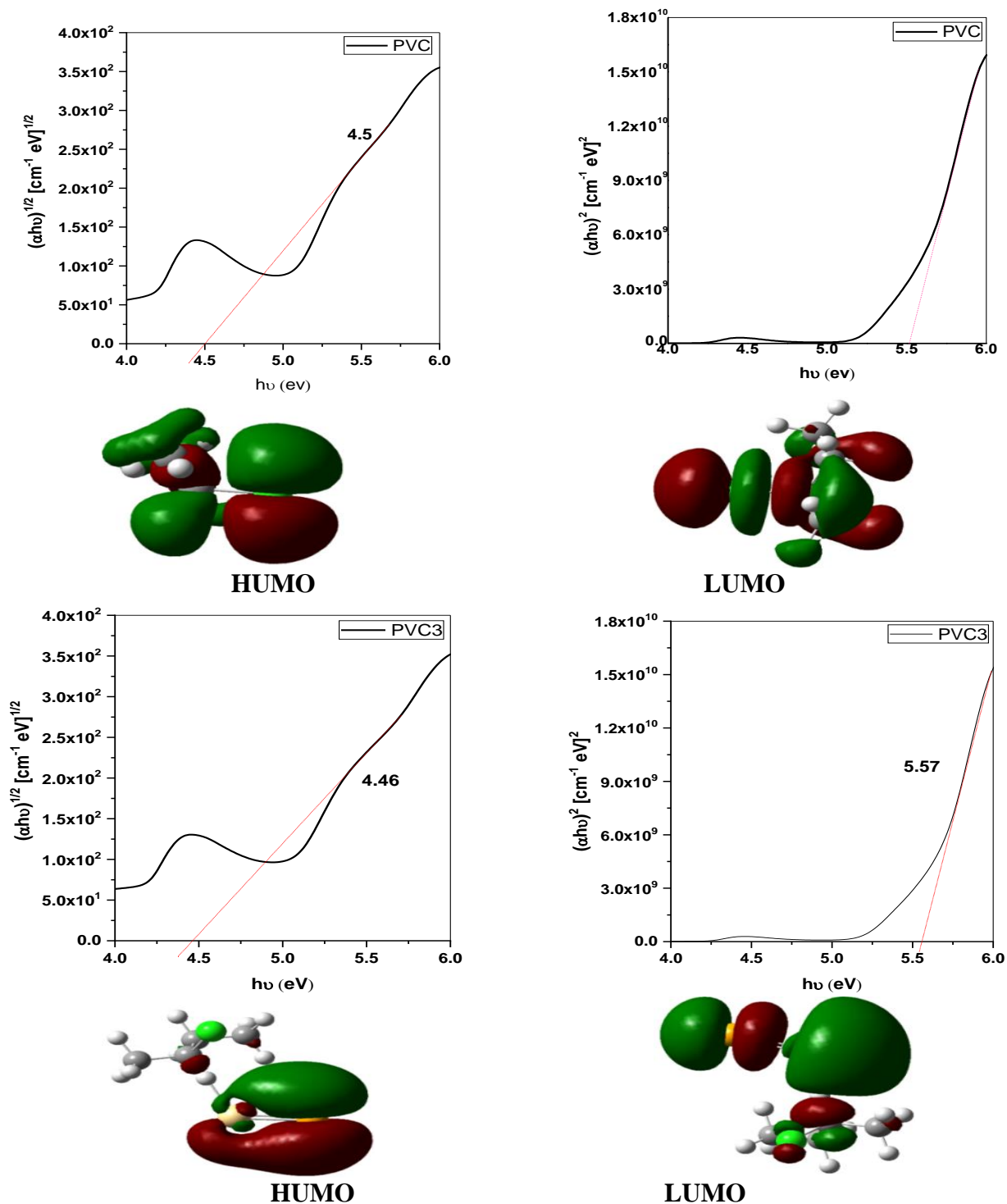


Fig. 6: Tauc Plots, HUMO, and LUMO analysis for exemplified samples.

4. Conclusions

Pristine PVC sample in addition to other samples containing different dopant levels of cadmium selenide quantum dots was successfully synthesized using the traditional liquid casting route. X-ray diffraction pattern of the synthesized CdSe QD's reveals the formation of hexagonal crystalline phase of Wurtzite whose in agreement with that of JCPDS card no(08-0459). The amorphous nature of studied samples points out the interstitial position taken by the dopant CdSe Qd's. FTIR shows repetitive spectral data indicating physical interaction between dopant and polymeric matrix and supporting XRD findings. UV/Vis. Electronic spectra reveal a quiet change in the optical energy gap resulting from the increasing level of dopant within the polymeric matrices.

5. References

1. Abdelghany, A.M., Abdelrazek, E.M., Rashad, D.S. (2014). Impact of in situ preparation of CdS filled PVP nanocomposite. *Spectrochimica Acta Part A: Mol. Biomol. Spectr.*, **130**, 302-308.
2. Sun, X., Huang, C., Wang, L., Liang, L., Cheng, Y., Fei, W., & Li, Y. (2021). Recent progress in graphene/polymer nanocomposites. *Adv. Mater.*, **33(6)**, 2001105.
3. Abdelghany, A.M., Youssif, M.I., Abdelrazek, E.M., Rashad, D.S. (2021). ICMMS-2: Computational DFT Study of Gold Containing PVP/PEO/Gold Organometallic Polymer Nanocomposites. *Egypt. J. Chem.*, **64(3)**, 7-8.
4. Hollande, S., Laurent, J.L. (1997). Study of discolouring change in PVC, plasticizer and plasticized PVC films. *Polym. Degrad. Stabil.*, **55(2)**, 141-145.
5. Hakkarainen, M. (2003). New PVC materials for medical applications—the release profile of PVC/polycaprolactone–polycarbonate aged in aqueous environments. *Polym. Degrad. Stabil.*, **80(3)**, 451-458.
6. Coldur, F.A., Andac, M., Isildak, I., Saka, T. (2009). A micro-sized PVC membrane Li⁺-selective electrode without internal filling solution and its medical applications. *J. Electroanal. Chem.*, **626(1-2)**, 30-35.
7. Velu, R., Jayashankar, D.K., & Subburaj, K. (2021). Additive processing of biopolymers for medical applications. In *Add. Manufactur.* (pp. 635-659). Elsevier.
8. Kim, S.H., Man, M.T., Lee, J.W., Park, K.D., Lee, H.S. (2020). Influence of size and shape anisotropy on optical properties of CdSe quantum dots. *Nanomater.*, **10(8)**, 1589.
9. Moreno- Serna, V., Méndez- López, M., Vásquez- Espinal, A., Saldías, C., Leiva, Á. (2020). Chitosan/P3HT biohybrid films as polymer matrices for the in- situ synthesis of CdSe quantum dots. Experimental and theoretical studies. *J. Appl. Polym. Sci.*, **137(36)**, 49075.
10. Yingming, S., Pan, H., Chu, H., Mamat, M., Abudurexiti, A., Li, D. (2021). Core-shell CdSe/ZnS quantum dots polymer composite as the saturable absorber at 1.3 μm: Influence of the doping concentration. *Physics Letters A*, **400**, 127307.
11. Jiang, H., & Ju, H. (2007). Electrochemiluminescence sensors for scavengers of hydroxyl radical based on its annihilation in CdSe quantum dots film/peroxide system. *Anal. Chem.*, **79(17)**, 6690-6696.
12. Jiang, W., Singhal, A., Zheng, J., Wang, C., Chan, W.C. (2006). Optimizing the Synthesis of Red-to Near-IR-Emitting CdS-Capped CdTe_xSe_{1-x} Alloyed Quantum Dots for Biomedical Imaging. *Chem. Mater.*, **18(20)**, 4845-4854.
13. Abolghasemi, R., Rasuli, R., & Alizadeh, M. (2020). Microwave-assisted growth of high-quality CdSe quantum dots and its application as a sensitizer in photovoltaic cells. *Mater. Today Commun.*, **22**, 100827.
14. Chang, C.H., Lee, Y.L. (2007). Chemical bath deposition of CdS quantum dots onto mesoscopic TiO₂ films for application in quantum-dot-sensitized solar cells. *Appl. Phys. Lett.*, **91(5)**, 053503.
15. Cingarapu, S., Yang, Z., Sorensen, C.M., Klabunde, K.J. (2009). Synthesis of CdSe quantum dots by evaporation of bulk CdSe using SMAD and digestive ripening processes. *Chem. Mater.*, **21(7)**, 1248-1252.

16. Ikram, A., Sahai, S., Rai, S., Dass, S., Shrivastav, R., & Satsangi, V. R. (2014). Synergistic effect of CdSe quantum dots on photoelectrochemical response of electro-deposited α -Fe₂O₃ films. *J. Power Sources*, **267**, 664-672.
17. Riad, K.B., Hoa, S.V., Wood-Adams, P.M. (2021). Metal Oxide Quantum Dots Embedded in Silica Matrices Made by Flame Spray Pyrolysis. *ACS Omega*, **6(17)**, 11411-11417.
18. Jin, B.B., Kong, S.Y., Zhang, G.Q., Chen, X.Q., Ni, H.S., Zhang, F. Zeng, J.H. (2021). Voltage-assisted SILAR deposition of CdSe quantum dots to construct a high performance of ZnS/CdSe/ZnS quantum dot-sensitized solar cells. *J. Colloid Interf. Sci.*, **586**, 640-646.
19. Sabah, A., Tasleem, S., Murtaza, M., Nazir, M., Rashid, F. (2020). Effect of polymer capping on photonic multi-core-shell quantum dots CdSe/CdS/ZnS: impact of sunlight and antibacterial activity. *J. Phys. Chem. C*, **124(16)**, 9009-9020.
20. Gajendiran, J., Vijayakumar, V., Senthil, V.P., Reddy, C.P., Ramya, J.R., Gokulraj, S. (2020). Ionic liquid assisted wet chemical synthesis CdS quantum dots and their structural, morphological, optical, electrochemical, photocatalytic, antibacterial and hemocompatibility characterization. *Optik*, **213**, 164638.
21. Borkovska, L.V., Korsunska, N.E., Kryshtab, T.G., Germash, L.P., Pecherska, E.Y., Ostapenko, S., Chornokur, G. (2009). Effect of conjugation with biomolecules on photoluminescence and structural characteristics of CdSe/ZnS quantum dots. *Semiconductors*, **43(6)**, 775-781.
22. Shah, H., Xin, Q., Jia, X., Gong, J.R. (2019). Single precursor-based luminescent nitrogen-doped carbon dots and their application for iron (III) sensing. *Arabian J. Chem.*, **12(7)**, 1083-1091.
23. Kushwaha, K., Gautam, N., Singh, P., Ramrakhaini, M. (2012, May). Synthesis and photoluminescence of CdSe/PVA nanocomposites. In *J. Phys.: Conf. Series* **Vol. 365(1)**, p. 012014. IOP Publishing.
24. Ma, X.D., Qian, X.F., Yin, J., Xi, H.A., Zhu, Z.K. (2002). Preparation and characterization of polyvinyl alcohol capped CdSe nanoparticles at room temperature. *J. Coll. Interf. Sci.*, **252(1)**, 77-81.
25. Meikhail, M.S., Abdelghany, A.M., Awad, W.M. (2018). Role of CdSe quantum dots in the structure and antibacterial activity of chitosan/poly ϵ -caprolactone thin films. *Egypt. J Basic Appl. Sci.*, **5(2)**, 138-144.
26. Amiri, G.R., Fatahian, S., Mahmoudi, S. (2013). Preparation and optical properties assessment of CdSe quantum dots. *Mater. Sci. Appl.*, **4**, 134-137 (doi.org/10.4236/msa.2013.42015)
27. Carrillo-Carrión, C., Cárdenas, S., Simonet, B. M., & Valcárcel, M. (2009). Quantum dots luminescence enhancement due to illumination with UV/Vis light. *Chem. Commun.*, **35**, 5214-5226.
28. Bang, J.U., Lee, S.J., Jang, J.S., Choi, W., Song, H. (2012). Geometric effect of single or double metal-tipped CdSe nanorods on photocatalytic H₂ generation. *J. Phys. Chem. Lett.*, **3(24)**, 3781-3785.
29. Subban, R.H.Y., Arof, A.K. (2004). Plasticiser interactions with polymer and salt in PVC-LiCF₃SO₃-DMF electrolytes. *Europ. Polym. J.*, **40(8)**, 1841-1847.
30. Ramesh, S., Leen, K.H., Kumutha, K., Arof, A.K. (2007). FTIR studies of PVC/PMMA blend based polymer electrolytes. *Spectrochim. Acta Part A: Mol. Biomol. Spectr.*, **66(4-5)**, 1237-1242.
31. Abdelghany, A.M., Meikhail, M.S., Asker, N. (2019). Synthesis and structural-biological correlation of PVC/PVAc polymer blends. *J. Mater. Res. Technol.*, **8(5)**, 3908-3916.
32. Mott, N.F., Davis, E.A. (2012). Electronic processes in non-crystalline materials. Oxford university press. International series of monographs on physics.