BEÜ Fen Bilimleri Dergisi
6(1), 61-68, 2017

BEU Journal of Science
6(1), 61-68, 2017

*Araştırma Makalesi / Research Article*

# Characterization and Photovoltaic Studies of Capped ZnS, CdS and $Cd_{1-x}Zn_xS$ (x=0.025) Nanoparticles

Sabit HOROZ[1*], M. Sait İZGİ[2], Ömer ŞAHİN[2]
[1]*Siirt University, Faculty of Art and Sciences, Department of Physics, 56100, Siirt, Turkey*
[2]*Siirt University, Faculty of Engineering and Architecture, Department of Chemical Engineering, 56100, Siirt, Turkey*

**Abstract**

Capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS nanoparticles (NPs) were prepared by co-precipitation method using mercaptoethanol as capping agent. X-ray diffraction (XRD), photoluminescence (PL) and optical absorption measurements were performed to characterize their structural and optical properties. The lattice constants and average crystallite size of cubic phase of capped ZnS, $Cd_{1-x}Zn_xS$ and CdS NPs calculated from the XRD measurement. The quantum confinement effect on the NPs has been observed in the optical analysis. In addition, it is seen that the luminescence band of $Cd_{1-x}Zn_xS$ NPs enhances with the presence of Zn content. The incident photon to electron conversion efficiency (IPCE) and current density (J) - voltage (V) measurements exhibited that Capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs coated on the $TiO_2$ NWs has better performance compare to capped ZnS and CdS NPs on the $TiO_2$ NWs. Capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs can be promising material to improve the solar cell performance.

**Keywords:** Co-precipitation Method, Capped ZnS, $Cd_{1-x}Zn_xS$ and CdS Nanoparticles, Structural and Optical Properties, Solar Cells.

## 1. Introduction

In recent time, there has been great drive in the synthesis and characterization of mono dispersed nano particles of II - IV compounds. The reason is that the optical, electronic and thermodynamic properties of the particles in the nanometer range are different from the optical, electronic and thermodynamic properties of the bulk materials, usually due to the quantum confinement. These unique properties can cause interesting linear and nonlinear optical properties such as optoelectronic probes for irregular DNA structures, fluorescence probes in peptides, which have great potential in technological applications [1-5].

The control of the crystallite size can be used to prepare materials with unique properties to meet these needs. However, there is a problem with the crystallite size growing over time. One way to overcome this problem is to develop nanoparticle-polymer composite materials [6]. Such an approach is to incorporate particles into a suitable host to form nano composites [7]. Hence, the particle can be directly grown in a host with the desired properties. The use of polymers as the main material is very attractive due to the stabilization of the nanoparticles (NPs) and the prevention of permanent aggregation and their long-term stability and ease of reprocessing [8]. These inorganic-organic NPs with physical properties have potential application in the fields of molecular and electronic and photovoltaic devices, catalysis, molecular diagnostics and interface electron transfer [9-10].

NPs can be synthesized by several well-known methods [11-13]. The co-precipitation method which is a simple and inexpensive method is considered as one of the most appropriate method. In comparison other methods which require long time and extreme laboratory conditions, the NPs can be synthesized with simple laboratory equipments and within a few hours using the co-precipitation method [14-15].

---

[*] Sorumlu yazar: sabithoroz@siirt.edu.tr

*Geliş Tarihi: 02/03/2017 Kabul Tarihi: 06/06/2017*

In our present study, we report the synthesis of ZnS, CdS and $Cd_{1-x}Zn_xS$ (x=0.025) NPs. Samples were prepared by co-precipitation using mercaptoethanol as a capping agent at room temperature. We have studied their structural, optical and photovoltaic properties.

## 2. Materials and Method

Commercial $Cd(CH_3COO)_2.2H_2O$ as Cd source, Zn $(CH_3COO).2H_2O$ as Zn source and $Na_2S$ as S source, were of analytical grade and were used without further purification to synthesize capped ZnS, CdS and $Cd_{1-x}Zn_xS$ nanoparticles (NPs) at room temperature using co-precipitation method.

For synthesis of ZnS;

In typical co-precipitation method, 0.1 M of aqueous solutions of cation source, Zn $(CH_3COO)_2$. $2H_2O$ and anion source, $Na_2S$, were separately prepared into two different beakers. These two solutions were transferred into another beaker and then stirred at certain time to get homogeneous mixture at room temperature. Two milliliters (ml) of mercaptoethanol was added onto the mixture when the stirring process was continued. The precipitated sample was separated by filter paper and the resultant particles were washed in water and ethanol to get rid of unwanted compounds inside the particles. The final solution was calcinated in oven at the certain temperature. Then, the obtained white powders were grinded using a mortar to get ZnS NPs.

For synthesis of CdS;

In typical co-precipitation method, 0.1 M of aqueous solutions of cation source, Cd $(CH_3COO)_2$. $2H_2O$ and anion source, $Na_2S$, were separately prepared into two different beakers. These two solutions were transferred into another beaker and then stirred at certain time to get homogeneous mixture at room temperature. Two milliliters (ml) of mercaptoethanol was added onto the mixture when the stirring process was continued. The precipitated sample was separated by filter paper and the resultant particles were washed in water and ethanol to get rid of unwanted compounds inside the particles. The final solution was calcinated in oven at the certain temperature. Then, the obtained white powders were grinded using a mortar to get CdS NPs.

For synthesis of $Cd_{1-x}Zn_xS$;

0.025M of aqueous solutions of Zn $(CH_3COO)$. $2H_2O$ was added to 0.1 M of aqueous solutions of Cd $(CH_3COO)_2$. $2H_2O$ and then followed the same procedure mentioned above for ZnS and CdS NPs.

The structural properties were studied by x-ray diffraction (XRD) on a Rigaku x-ray diffractometer with Cu $K_\alpha$ ($\lambda$= 154.059 pm) radiation. UV-Vis absorption spectra were recorded using a Perkin- Elmer Lambda 2 spectrometer. Photoluminescence (PL) measurement was carried out with a Perkin-Elmer LS 50B at room temperature, using 310 nm as the excitation wavelength. Incident photon to electron conversion efficiency (IPCE) and current density (J) versus voltage (V) measurements were performed by using PCE-S20 with a monochromatic light source consisting of a 150-W Xe lamp and a monochromator. For IPCE and J-V measurements, fluorine doped tin oxide (FTO, $13\Omega.sq^{-2}$) conductive glass substrates were used as the photo electrodes. The $TiO_2$ nanowires (NWs) were coated on the FTO substrates using the doctor blade method, and then sintered at 450 $^0C$ for 45 minutes. A suspension of ZnS, CdS and $Cd_{1-x}Zn_xS$ (x=0.025) NPs were dropped on the FTO substrates with the $TiO_2$ NWs. The substrates were dried with $N_2$ gas and secured against $Cu_2S$ counter electrodes containing polysulfide electrolytes.

## 3. Results and Discussions

XRD patterns for capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs prepared by co-precipitation method at room temperature, are shown in Figure 1 (a, b, c). All peaks of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and

CdS NPs can be identified as those of zinc blende crystal structure of ZnS ((JCPD No: 65-0309) and CdS (JCPD No: 65-2887), which correspond to the (111), (220) and (311) planes.

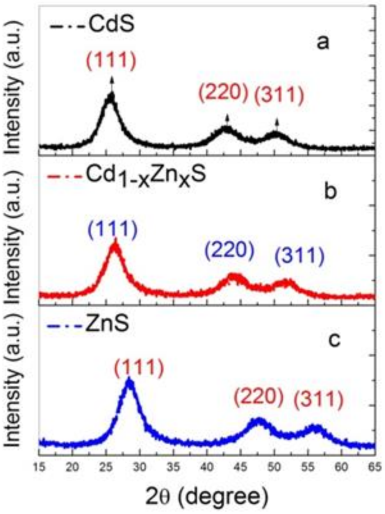

**Figure 1.** XRD patterns of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs synthesized at room temperature.

Lattice constant of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs was calculated from the position of the peak (111) using formulas as given equation 1 [16].

$$a = \frac{\lambda}{2\,sin\,\theta}\sqrt{h^2 + k^2 + l^2} \tag{1}$$

where $a$ lattice is constant, $\theta$ is the Bragg's diffraction angle, $\lambda$ is the wavelength of x-ray and *(hkl)* are Miller indices.
Lattice constant values for capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs, are given in Table 1.

**Table 1.** $a$ values for capped ZnS, $Cd_{1-x}Zn_xS$ and CdS NPs.

| Samples | Lattice constant values for (111)(Å) |
|---|---|
| Capped ZnS NPs | 5.37 |
| Capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs | 5.83 |
| Capped CdS NPs | 5.92 |

The obtained $a$ values for capped ZnS and CdS NPs match with the earlier results reported by Parvaneh et al. [17] and Rodrgues et al. [18], respectively. It can be clearly seen that the lattice constant for capped $Cd_{1-x}Zn_xS$ (x=0.025) gradually decreases in the presence of Zn content. It causes a shift on the peaks towards ZnS. This trend is consistent with Vegard's law [19], indicating a homogenous alloy structure. All broad peaks of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs represents that the sizes of the samples become smaller. Debye- Scherer's formula (3) as given in Equation 2 was used to calculated the average crystallite sizes of the NPs from the peak widths of the relatively strong (111) diffraction.

$$t = \frac{0.9\lambda}{\beta cos\theta} \tag{2}$$

where $t$ is the mean size of the NPs, $\lambda$ is the wavelength of x-ray, $\beta$ is the broadening measured as the full width at half maximum (FWHM) in radians and $\theta$ is Bragg's diffraction angle. The size of capped ZnS and CdS NPs obtained from the XRD peak widths is around 2.66 nm which is consistent with studies carried out by Sabit et al. [11] and Kumar et al. [20], respectively while it is found 2.28 nm for capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs. This result shows that the decrease in crystallite size is clearly from the increase the $\beta$ of the XRD peaks of the NPs due to the size effect.

For UV-Vis measurements, the certain amounts of the capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs were successfully dispersed in ethanol. Figure 2 shows the optical absorption spectra of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs prepared using the co-precipitation method at room temperature.

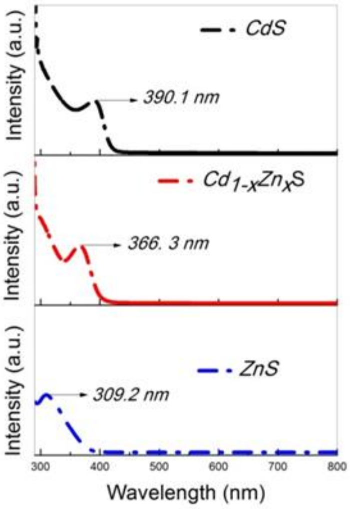

**Figure 2.** The UV-Vis absorption spectra of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs synthesized at room temperature.

The absorption peak shown in Fig. 2 was at 309.2 nm for capped ZnS NPS and at 390.1 nm for capped CdS NPs. It can be clearly seen that the absorption peaks for capped ZnS and CdS NPs are blue shifted unlike the UV of spectrum of bulk ZnS and CdS. Using these peak positions, the energy band gap ($E_g$) values for capped ZnS and CdS NPs were found as 4.01 eV and 3.18 eV. These results are consistent with quantum confinement effect on the energy band gap of bulk ZnS (3.7 eV) [21] and CdS (2.4 eV) [22]. It was observed that the absorption for capped $Cd_{1-x}Zn_xS$ (x=0.025) (366.3 nm, 3.3 eV) is shifted to shorter wavelength with the presence of Zn content compare to capped CdS NPs. The reason behind this shifting can be explained by formation alloy CdZnS by the formation of alloyed CdZnS NCs via intermixing of wider band gap ZnS with narrower-band gap CdS. It is important to note that Zn content plays a very significant role in the band gap of CdS [23].

Figure 3 represents room temperature photoluminescence (PL) spectrum under 310 nm excitation wavelengths for capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs to investigate luminescence properties.

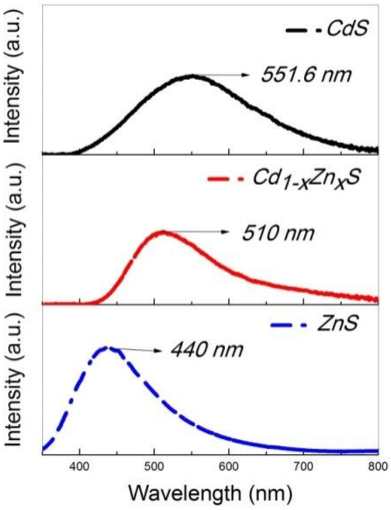

**Figure 3.** Photoluminescence (PL) spectra at room temperature, excited with a wavelength of 310 nm for capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs synthesized at room temperature.

It is seen that the capped ZnS NPs has only one blue emission band centered at 440 nm, which is related to radiative recombination involving defect states in the ZnS NPs whereas the emission band, which is attributed to radiative transition of surface defect states, are located at 551.6 nm for capped CdS NPs. In the presence of Zn content, the center emission peak of capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs shifts to 510 nm. This blue shifted is in good agreement with the absorption spectra are indicated in Fig. 2. The reason of the shift was explained by P. Yang et al. [24]. They described that the luminescence mechanism of the $Cd_{1-x}Zn_xS$ (x=0.025) NPs in the presence of Zn. When CdS NPs absorb photons; the electrons are excited from valence band to the conduction band and are trapped by defects. Presence of Zn leads the recombination of the defects and excitation states which provide modified surface trap states which enhances and shifts the luminescence band.

The incident photon to electron conversion efficiency (IPCE) measurements can be used to define as the number of photogenerated charge carriers contributing to the current per incident photon. The IPCE spectra of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs coated on the $TiO_2$ NWs are demonstrated in Fig. 4.

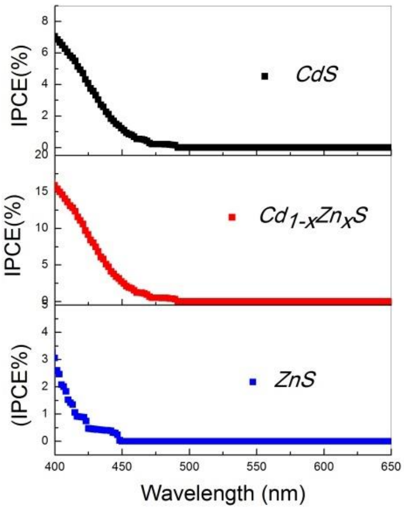

**Figure 4.** The IPCE spectra of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs coated on the $TiO_2$ NWs The band gap value and IPCE efficiency for capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs are shown in Table 2.

**Table 2.** Compare to The band gap values and IPCE efficiencies for capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs

| Samples | Band gap value (eV) | IPCE efficiency (%) |
|---|---|---|
| Capped ZnS NPs | 3.91 | 3.1 |
| Capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs | 3.38 | 16 |
| Capped CdS NPs | 3.18 | 7.1 |

The presence of Zn in capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs contributes to a significant enhancement in the IPCE efficiency. The main reason beyond this is that the spectral response of capped CdS NPs is improved by Zn content. The similar result was observed in $Zn_{1-x}Mn_xS$ NPs (11).

It is an important note that a substantial improvement was observed in the performance of the capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs is shown in Fig. 5. The reason of this enhancement could be due to fact that Zn content in capped CdS NPs inhibits the charge recombination between CdS NPs and $TiO_2$ surface.

This causes an increase of current density ($J_{SC}$) [25]. The power efficiencies indicated in Table 3, were found 0.6%, 2.84% and 1.24 % for capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs, respectively.

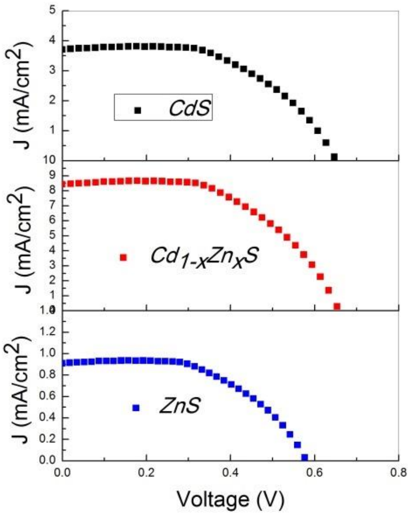

**Figure 5.** J-V plots of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs coated on the $TiO_2$ NWs

**Table 3.** Comparison of $V_{OC}$, $J_{SC}$ and η of capped ZnS, $Cd_{1-x}Zn_xS$ and CdS NPs coated on the $TiO_2$ NWs

| Samples | Open Circuit Voltage, $V_{OC}$, (V) | Short Circuit Current Density, $J_{SC}$, (mA/cm$^2$) | Power conversion efficiency (η %) |
|---|---|---|---|
| Capped ZnS NPs | 0.58 | 0.90 | 0.60 |
| Capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs | 0.65 | 8.40 | 2.84 |
| Capped CdS NPs | 0.65 | 3.70 | 1.24 |

## 4. Conclusions

In this study, the structural, optical and photovoltaic properties of capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs synthesized by co-precipitation method using mercaptoethanol as capping agent, are investigated. Capped ZnS, $Cd_{1-x}Zn_xS$ (x=0.025) and CdS NPs possess cubic zinc blende structure which is confirmed by x-ray diffraction (XRD) pattern. The quantum confinement effect on the NPs has been observed in the optical analysis. In addition, it is seen that the luminescence band of $Cd_{1-x}Zn_xS$ (x=0.025) NPs enhances with the presence of Zn content. IPCE measurements indicate that Zn content results in improvement in the solar cell efficiency. Capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs (η=2.84) coated on the $TiO_2$ NWs exhibit better performance as compared capped ZnS (η=0.60) and CdS (η=1.24) NPs coated on the $TiO_2$ NWs. Factors such as the reduction of electron recombination and the enhancement of electron transport in $TiO_2$ can be ascribed to an improvement in photovoltaic performance due to Zn content. Hence, capped $Cd_{1-x}Zn_xS$ (x=0.025) NPs can be promising material to improve the device performance.

## References

1. Akturk A., Tas H., Koksal K., Sahin M. 2016. The Electronic and Optical Properties of a Triexciton in CdSe/ZnS Core/Shell Quantum dot Nanocrystals, Philosophical Magazine, 96 (6): 584-595.
2. Koc F., Koksal K., Sahin M. 2017. Effect of a Buffer Layer between the Shell and Ligand on the Optical Properties of an Exciton and Biexciton in type-II Quantum dot Nanocrystals, Philosophical Magazine, 97 (3): 201-211.
3. Horoz S., Lu L., Dai Q., Chen J., Yakami B., Pikal J.M., Wang W., Tang J. 2012. CdSe Quantum dots Synthesized by Laser Ablation in Water and Their Photovoltaic Applications, Applied Physics Letters, 101: 223902.
4. Tilley R.D. 2008. Synthesis and Applications of Nanoparticles and Quantum Dots, Chemistry in New Zealand, 146-150.
5. Xu X., Hu L., Gao H., liu S., Wageh S., Al-Ghamdi A.A., Alshahrie A., Fang X. 2015. Controlled Growth from ZnS Nanoparticles to ZnS–CdS Nanoparticle Hybrids with Enhanced Photoactivity, Advanced Functional Materials, 25 (3): 445-454.
6. Goodwin J.W., Hearn J., Ho C.C., Ottewill R.H. 1974. Studies on the Preparation and Characterisation of Monodisperse Polystyrene Laticee, Colloid and Polymer Science, 252:464-471.
7. Murray C.B., Norris D.J., Bawendi M.G. 1993. Synthesis and Characterization of Nearly Monodisperse CdE (E = S, Se, Te) Semiconductor Nanocrystallites, Journal of the American Chemical Society, 115: 8706.
8. Potter B.G., Simmons J.H. 1988. Quantum Size Effects in Optical Properties of CdS-glass Composites, Physical Review B, 37: 10838.
9. Liu J., Sheina E., Kolawlewski T., Mccullough R.D. 2002. Angewandte Chemie International Edition, Tuning the Electrical Conductivity and Self-assembly of Regioregular Polythiophene by Block Copolymerization: Nanowire Morphologies in New Di- and Triblock Copolymers, 41: 3259.
10. Watson K.J., Zhu J., Nguyen S.T., Mirkin C.A. 2000. Redox-Active Polymer-Nanoparticle, Hybrid Materials Pure and Applied Chemistry, 72: 67-72.
11. Horoz S., Dai Q., Maloney F.S., Yakami B., Pikal J.M., Zhang X., Wang J., Wang W., Tang J. 2015. Absorption Induced by Mn Doping of ZnS for Improved Sensitized Quantum-Dot Solar Cells, Phys. Rev. Applied, 3: 024011.
12. So W.-W., Jang J.-S., Rhee Y.-W., Kim K.-J., Moon S.-J. 2001. Preparation of Nanosized Crystalline CdS Particles by the Hydrothermal Treatment, Journal of Colloid and Interface Science, 237: 136.
13. Bhattacharjee B., Ganguli D., Iakoubovskii K., Stesmans A., Chaudhuri S. 2002. Synthesis and Characterization of sol-gel Derived ZnS: $Mn^{2+}$ Nanocrystallites Embedded in a Silica Matrix, Bulletin of Materials Science, 25: 175-180.
14. Kripal R., Gupta A.K., Mishta S.K., Srivastava K., Pandey A.C., Prakash S.G. 2010. Photoluminescence and Photoconductivity of ZnS:Mn(2+) Nanoparticles Synthesized via Co-Precipitation Method, Spectrochimica Acta Part A, 76: 523.
15. Thambidurai M., Muthukumarasamary N., Agilan S., Sabari N., Murugan N., Balasundaraprabhu R. 2011. Structural and Optical Characterization of Ni-doped CdS Quantum dots, Journal of Material Science, 46: 3200-3206.
16. Taylor A., Sinclair H. 1945. On the Determination of Lattice Parameters by the Debye- Scherer Method, Proceedings of the Physical Society, 57: 126.
17. Parvaneh I., Samira S., Mohsen N. 2015. Characterization of ZnS Nanoparticles Synthesized by Co-precipitation Method, Chinese Physics B, 24(4): 046104.

18. Rodriguez P., Muñoz-Aguirre N., San-Martín Martinez E., González de la Cruz G., Tomas S.A., Zelaya Angel O. 2008. Synthesis and Spectral Properties of Starch Capped CdS Nanoparticles in Aqueous Solution, Journal of Crystal Growth, 310: 160-164.
19. Furdyna J.K.J. 1988. Diluted Magnetic Semiconductors, Appl. Phys., 64: R29.
20. Kumar S., Kumar S., Jain S., Verma N.K. 2012. Magnetic and Structural Characterization of Transition Metal Co-doped CdS Nanoparticles, Applied Nanoscience, 2: 127-131.
21. Khamala B., Franklin L. Malozovsky Y., Stewart A., Saleem H., Bagayoko D. 2016. Calculated Electronic, Transport and Bulk Properties of Zinc Blende Zinc Sulphide (zb-ZnS), Computational Condensed Matter., 6: 18-23.
22. Elilarassi R., Maheshwari S., Chandrasekaran G. 2010. Structural and Optical Characterization of CdS Nanoparticles Synthesized using a Simple Chemical Reaction Route, Rapid Communications, 4: 309-312.
23. Zhong X., Feng Y., Knoll W., Han M. 2003. Alloyed $Zn_xCd_{1-x}S$ Nanocrystals with Highly Narrow Luminescence Spectral Width, J. Am. Chem. Soc., 125: 13559-13563.
24. Yang P., Lu M. K., Song C. F., Liu S. W., Chu D., Yuan D. R., Cheng X. F. 2003. Preparation and Tunable Photoluminescence Characteristic of $Ni^{2+}$: $SrAl_2O_4$, Optical Materials., 24: 575.
25. Kim H.J., Kim J.H., Durga I.K., Punnoose D., Kundakarla N., Reddy A.E., Rao S.S. 2016. Densely Packed Zinc Sulfide Nanoparticles on $TiO_2$ for hindering Electron Recombination in dye Sensitized Solar Cells, New Journal of Chemistry, 40: 9176-9180.