Research Article

One-Step Thermolysis Synthesis of Divalent Transition Metal Ions Monodoped and Tridoped CdS and ZnS Luminescent Nanomaterials

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Mn^{2+} , Co^{2+} , or Ni^{2+} monodoped CdS (or ZnS) and Mn^{2+} - Co^{2+} - Ni^{2+} tridoped CdS (or ZnS) have been successfully synthesized by novel one-step thermolysis method using thiourea as a sulphur source. The synthesized nanomaterials were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). It is found that the average diameter and morphology of the synthesized samples varied with the nature of dopant ion. The successful doping of Mn^{2+} - Co^{2+} - Ni^{2+} tridoped ions into the host CdS (or ZnS) was proved by the EDX spectra. The luminescence of CdS is only enhanced when monodoped with Mn^{2+} whereas it is enhanced when ZnS is either monodoped with Mn^{2+} , Co^{2+} , or Ni^{2+} or tridoped with Mn^{2+} - Co^{2+} - Ni^{2+} . The synthesized samples could therefore offer opportunities for further fundamental research and technological applications.

1. Introduction

In recent years, II–VI semiconductors have been attracting increasing attention due to their excellent prospective use as optoelectronic devices [1], solar cells [2], light-emitting diodes [3], quantum dots [4], photocatalyst [5], drug delivery [6, 7], and multicolor fluorescent markers in biological systems [8], in magnetic functionality [9, 10]. Among these semiconductors, CdS and ZnS have wide band gap energy of 2.42 and 3.68 eV, respectively [11, 12].

Zinc sulfide is chemically stable and characterized by low toxicity and large band gap compared with other chalcogenides such as ZnSe and ZnO [13, 14]. ZnS has been used widely as an important phosphor for photoluminescence (PL), electroluminescence (EL), and cathodoluminescence (CL) devices [15].

CdS powder is of potential applications in the production of light sources emitting in the green region, in the technology of solar cells and photocells [16] as well as laser screen materials, projection color TVs, and nuclear radiation detectors [17–19].

In addition, CdS and ZnS are suitable for use as host materials for a variety of dopants because of their wide band gap. The doping of metal ions in CdS or ZnS has led to unique optical, electrical, chemical, and mechanical properties, which cannot be found in the undoped materials [20]. Transition metal ions are the most interesting impurities as they introduce deep levels in the gap region, which can influence not only the optical characteristics but also the electrical and magnetic properties, influencing their practical applications [21].

SCHEME 1: Proposed mechanism for metal ion doped CdS formation where M^* is Ni, Co, or Mn ions and Y is the number of water molecules.

Doping of CdS or ZnS nanoparticles by transition metal ions, for example, Mn^{2+} [22], Co^{2+} [23], and Ni^{2+} [24, 25], has been successfully done by techniques such as thermal evaporation, sol-gel processing, coprecipitation, and microemulsions. Most of these techniques have several steps and are not cost effective [26–35].

The simultaneous presence of two kinds of defects known as codoping can lead to remarkable change of the semiconductor properties such as photoluminescence properties [36] and magnetic properties [37–39].

There are limited studies on synthesis and luminescence of codoped CdS [25, 40] and codoped ZnS [36, 41–45]. Moreover, there are some studies reported on tridoped ZnO [46] and tridoped TiO_2 [47–49].

To the best of our knowledge, there are no reported studies on synthesis and luminescence of tridoped CdS or tridoped ZnS. This prompted us to tackle the problem of one-step synthesis of tridoped CdS and ZnS and their characteristic luminescence for possible exploitation as tagging materials.

2. Experimental

2.1. Materials. Zinc (II) nitrate hexahydrate, cadmium (II) acetate dehydrate, manganese (II) tetrahydrate, cobalt (II) nitrate hexahydrate, and nickel (II) nitrate hexahydrate were obtained from Sigma-Aldrich. Ethyl alcohol was laboratory grade chemical. All the reagents were used without further purification.

2.2. Methods. Nanometal ions doped CdS was prepared by cadmium-thiourea complex thermolysis route at 200°C (see Scheme 1).

To prepare Mn^{2+} 10% CdS nanomaterials, the stoichiometric ratio of cadmium (II) acetate dehydrate, manganese (II) nitrate tetrahydrate, and thiourea were taken as 1:0.1:2. In this method, the powder solid materials of 0.01 mol cadmium (II) acetate dihydrate, 0.001 manganese (II) nitrate tetrahydrate, and 0.02 mol thiourea were mixed in a crucible and transferred into oven at 200°C for 2 hours. The product was collected and washed with distilled water and then ethanol. Finally it dried at 80°C for 1 hour.

Other metal ions (Ni^{2+} or Co^{2+}) monodoped CdS was prepared according to the above procedure.

Mn^{2+} - Co^{2+} - Ni^{2+} tridoped CdS was prepared according to the above procedure by mixing 0.01 mol cadmium (II) acetate dehydrate, 0.001 mol of manganese (II) nitrate tetrahydrate, cobalt (II) nitrate hexahydrate, nickel nitrate (II) hexahydrate, and 0.02 mol thiourea and transferred into oven according to the above procedure.

SCHEME 2: Proposed mechanism for metal ion doped ZnS formation.

Pure CdS was also prepared in the same way.

Transition metal ions doped ZnS, Mn^{2+} - Co^{2+} - Ni^{2+} tridoped ZnS, and pure ZnS were prepared by zinc-thiourea complex thermolysis route at 200°C . The synthetic procedure is identical to that of CdS by using zinc (II) nitrate hexahydrate instead of cadmium (II) acetate dehydrate (see Scheme 2).

2.3. Instrumentation. Identification of the crystal phases was conducted by X-ray diffraction analysis. The X-ray diffraction (XRD) patterns were obtained by using a Bruker-AXS D8 Advance, with Ni filtered $\text{Cu K}\alpha$ radiation in the range of 2θ from 4° – 60° . The reference data for the interpretation of the XRD patterns were obtained from the Joint Committee on Powder Diffraction Standards (JCPDS) files.

The grain size was determined from the X-ray diffraction patterns using the Scherrer formula ($G = \lambda/D \cos \theta$), where G is the grain size, λ is the wavelength of the X-rays (1.5418), D is the width of the peak at half maximum, and θ is the angle of incidence of X-ray beam.

Electron microscopy studies were undertaken using transmission electron microscopy (TEM) (JEOL JEM-1230, with an accelerating voltage of 40–120 KV) and scanning electron microscopy (SEM) (JEOL JXA-840A Electron Probe Microanalyzer, using an accelerating voltage of 30 KV) with an attached energy dispersive X-ray spectrometer (EDX). EDX measurements were acquired at a number of points in the samples. SEM samples were prepared on an appropriate disk and coated with gold to make the samples conductive to electrons.

Luminescence spectra were measured in the range 254–800 nm using a Perkin Elmer LS 55. Perkin Elmer LS 55-PC Spectrofluorophotometer (with 3 nm excitation and emission slit width).

3. Results and Discussion

3.1. Structure Morphology. Figure 1 shows the XRD data of CdS and metal ions doped CdS. All the diffraction peaks of metal ions doped CdS are consistent with the values of the standard (JCPDS card number 41-1049) and can be indexed to pure hexagonal CdS structure (Figure 1).

In addition, no secondary phase is detected in the XRD patterns which illustrates that the obtained products arrays are highly pure and single phase crystal. Peaks at $2\theta \approx 24.8^\circ$, 26.4° , 28.1° , 36.6° , 43.6° , 47.8° , and 51.8° are attributed to (100), (002), (101), (102), (110), (103), and (112) CdS planes, respectively.

As shown in Figure 1, XRD peak broadening indicates the small size of the obtained CdS and metal ions doped CdS

FIGURE 1: XRD of (a) CdS, (b) Co^{2+} doped CdS, (c) Ni^{2+} doped CdS, (d) Mn^{2+} doped CdS, and (e) Mn^{2+} - Co^{2+} - Ni^{2+} tridoped CdS.

FIGURE 2: XRD of (a) ZnS, (b) Co^{2+} doped ZnS, (c) Ni^{2+} doped ZnS, (d) Mn^{2+} doped ZnS, and (e) Mn^{2+} - Co^{2+} - Ni^{2+} tridoped ZnS.

nanocrystals. XRD patterns show the very broad and wide peaks of pure CdS (Figure 1-(a)). In case of dopant metal ion, it could be observed that XRD peaks get sharper (Figure 1-(b), Figure 1-(e)) indicating that nanocrystal size is larger when grown in the presence of dopant ions [50].

The XRD pattern of Figure 2 shows three strong diffraction peaks with $2\theta \approx$ values of 28.71° , 48.19° , and 56.78° which appear due to reflection from the (008), (110), and (118) planes of hexagonal zinc sulphide. All the diffraction peaks of metal ions doped ZnS are consistent with the values of the standard (JCPDS card number 39-1363) and can be indexed to pure hexagonal ZnS structure.

We also observed the typical broadening of the peaks indicating very small size of the synthesized ZnS and metal ions doped ZnS particles [51].

From XRD patterns, it can be found that the positions of diffraction peaks slightly shift with metal ion doped CdS or ZnS, reflecting the d values changes due to ionic radii difference between the dopant ion and the host (cadmium or zinc) ion. The ionic radii of Cd^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , and Ni^{2+} are 0.095, 0.074, 0.083, 0.069, and 0.065 nm, respectively [52]. All of the dopant ions are smaller than the host Cd^{2+} or Zn^{2+} ions except Mn^{2+} relative to Zn^{2+} , suggesting that, at this slightly large doping ratio (10%), the dopant metal ion

Full scale 2076 cts cursor: 0.013 (17217 cts)

FIGURE 3: EDX spectrum for 10% Mn^{2+} - Co^{2+} - Ni^{2+} tridoped CdS nanoparticles.

Full scale 2076 cts cursor: 0.013 (17331 cts)

FIGURE 4: EDX spectrum of the synthesized 10% Mn^{2+} - Co^{2+} - Ni^{2+} tridoped ZnS nanoparticles.

enters to the lattice substitutionary interstitially leading to increasing the interplaner spacing (d) values (see Tables 1 and 2) [53]. Mn^{2+} dopant ion is larger than Zn^{2+} , so manganese replaced some of the zinc atoms leading to increasing d values [44].

The possible chemical reaction that takes place on the heated substances to produce CdS could be as follows [53, 54]. Thiourea dissociates and releases S^{2-} ; the cadmium acetate or zinc nitrate was believed to be interlinked by sulfide atom. In consecutive step, the C-S bond of sulfide source molecule breaking and the simultaneous formation of Cd-S or Zn-S bond, resulting in the growth of CdS or ZnS nanomaterials [55, 56].

The successful doping of Mn^{2+} - Co^{2+} - Ni^{2+} tridoped ions into the host (CdS or ZnS) can be proved by energy dispersive X-ray spectrometer (EDX) spectra.

As shown in Figures 3 and 4 as well as Tables 3 and 4, EDX spectra indicate that the finger print signals for (cadmium or zinc), sulfur, manganese, cobalt, and nickel elements were observed.

As shown in Tables 3 and 4, the elements atomic % of cadmium, sulfur, manganese, cobalt, and nickel are 37.98, 53.17, 0.3, 4.34, and 4.2, respectively. The elemental atomic % of zinc, sulfur, manganese, cobalt, and nickel are 38.72, 58.41, 0.29, 1.39, and 1.19, respectively. It should be noted that the dopant manganese atomic ratio in tridoped CdS or tridoped ZnS is very small compared with that of nickel and cobalt.

For Mn^{2+} - Co^{2+} - Ni^{2+} tridoped CdS or tridoped ZnS the dopant ions are assumed to substitute the host (Zn or Cd) ions or to be inserted as interstitial ions. The solubility of MnS

CdS				Co ²⁺ doped CdS				Ni ²⁺ doped CdS				Mn ²⁺ -Co ²⁺ -Ni ²⁺ tridoped CdS			
2θ (degree)	d Value (Å)	Grain size G (nm)	2θ (degree)	d value (Å)	Grain size G (nm)	2θ (degree)	d value (Å)	Grain size G (nm)	2θ (degree)	d value (Å)	Grain size G (nm)	2θ (degree)	d value (Å)	Grain size G (nm)	
—	—	—	24.85	3.57	3	24.99	3.56	53.5	24.92	3.57	6.6	24.72	3.59	3	
26.74	3.33	3	26.54	3.36	32.4	26.51	3.35	28.3	26.57	3.35	30	26.58	3.35	43.4	
—	—	—	28.36	3.14	5.6	28.09	3.17	7.6	28.16	3.16	13.1	28.20	3.16	15.6	
44.37	2.04	4.5	43.71	2.07	10.7	43.70	2.06	14.3	43.70	2.07	17.1	43.80	2.06	19.9	
47.84	1.89	6.8	47.88	1.90	5	47.95	1.89	9.1	47.95	1.90	12.3	48.00	1.89	16.1	
52.21	1.75	13.7	52.07	1.75	8.2	51.83	1.76	7.2	51.94	1.78	8.1	52.07	1.75	8.3	

CdS			Co ²⁺ doped CdS			Ni ²⁺ doped CdS			Mn ²⁺ -Co ²⁺ -Ni ²⁺ tridoped CdS		
2θ (degree)	d Value (Å)	Grain size G (nm)	2θ (degree)	d value (Å)	Grain size G (nm)	2θ (degree)	d value (Å)	Grain size G (nm)	2θ (degree)	d value (Å)	Grain size G (nm)
—	—	—	24.85	3.57	3	24.99	3.56	53.5	24.92	3.57	6.6
26.74	3.33	3	26.54	3.36	32.4	26.51	3.35	28.3	26.57	3.35	30
—	—	—	28.36	3.14	5.6	28.09	3.17	7.6	28.16	3.16	13.1
44.37	2.04	4.5	43.71	2.07	10.7	43.70	2.06	14.3	43.70	2.07	17.1
47.84	1.89	6.8	47.88	1.90	5	47.95	1.89	9.1	47.95	1.90	12.3
52.21	1.75	13.7	52.07	1.75	8.2	51.83	1.76	7.2	51.94	1.78	8.1

TABLE 2: The computed *d* value (Angstrom), angle (2-Theta °), and grain size of 10% metal doped ZnS.

ZnS			Co ²⁺ doped ZnS			Ni ²⁺ doped ZnS			Mn ²⁺ doped ZnS			Mn ²⁺ -Co ²⁺ -Ni ²⁺ tri-doped ZnS		
2θ (degree)	<i>d</i> Value (Å)	Grain Size <i>G</i> (nm)	2θ (degree)	<i>d</i> value (Å)	Grain size <i>G</i> (nm)	2θ (degree)	<i>d</i> value (Å)	Grain size <i>G</i> (nm)	2θ (degree)	<i>d</i> Value (Å)	Grain size <i>G</i> (nm)	2θ (degree)	<i>d</i> value (Å)	Grain size <i>G</i> (nm)
28.72	3.106	3.9	28.66	3.11	37.9	28.40	3.32	3	28.51	3.12	3	28.57	3.12	3
48.19	1.887	3.7	47.58	1.90	9.6	47.81	1.90	3	47.42	1.91	3	47.62	1.91	3
56.78	1.619	3.9	56.48	1.63	7.8	56.38	1.63	3	56.30	1.63	3.1	56.64	1.62	3

TABLE 3: Elements ratio calculated from EDX results of the synthesized 10% Mn-Ni-Co-doped CdS nanoparticles.

Element	Weight%	Atomic%
S K	26.26	53.17
Mn K	0.26	0.30
Co K	3.94	4.34
Ni K	3.80	4.20
Cd L	65.75	37.98
Totals	100.00	100.00

TABLE 4: Elements ratio calculated from EDX results of the synthesized 10% Mn-Ni-Co-doped ZnS nanoparticles.

Element	Weight%	Atomic%
S K	40.96	58.41
Mn K	0.35	0.29
Co K	1.80	1.39
Ni K	1.53	1.19
Zn K	55.36	38.72
Totals	100.00	100.00

FIGURE 5: TEM picture of pure undoped CdS at a magnification of 300 KX.

($k_{SP} \sim 10^{-10}$) is far higher than that of NiS ($k_{SP} \sim 10^{-19}$), CoS ($k_{SP} \sim 10^{-21}$), ZnS ($k_{SP} \sim 10^{-22}$), and CdS ($k_{SP} \sim 10^{-27}$) [57]. Species having higher solubility in water precipitate more difficultly and so Co^{2+} and Ni^{2+} ions can easily displace Cd^{2+} or Zn^{2+} of the host lattice. MnS is far more higher soluble than CdS or ZnS. Thus, Mn^{2+} is much less efficient at displacing Cd^{2+} or Zn^{2+} of the host lattice.

The ionic radii of Cd^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , and Ni^{2+} are 0.095 nm, 0.074 nm, 0.083 nm, 0.069 nm, and 0.065 nm, respectively [52]. The Co and Ni dopant ions are smaller than that of Mn. This results in ease substitution of Zn ions by Co and Ni ions or to be inserted as interstitial ions.

As can be seen from figure 5, pure CdS nanoparticles have an average diameter of 6 nm. On the other hand, in the presence of dopant ions, the particle size of the samples increases (Figures 5, 6, 7, 8, 9, 10, 11, 12 and 13) (see Tables 1

FIGURE 6: TEM picture of Co^{2+} doped CdS at a magnification of 400 KX.

FIGURE 7: TEM picture of pure Co^{2+} doped CdS at a magnification of 600 KX.

and 2), which is corroborated with the XRD results. Because the dopant metal ions are small, they can easily occupy the substitutional sites as well as the interstitial sites of the host lattice. The interstitially entrance of dopants leads to the expansion of host lattice and hence particle size increasing. The ion radius of Mn^{2+} is larger than that of Co^{2+} and Ni^{2+} and so it leads to the more expansion of the host lattice and hence Mn^{2+} doped CdS gave the largest particle size. Mn^{2+} - Co^{2+} - Ni^{2+} tridoped CdS also gave small particle size than Mn doped CdS. The small ionic radii of Co^{2+} and Ni^{2+} in comparison to that of Mn^{2+} , explains the easiest interstitial doping for Co^{2+}/Ni^{2+} . The doped CdS forms heterogeneous nano-spheres, which are uniform in morphology and particle size (Figures 6 to 13). As shown in Figures 5 to 13, pure CdS nanoparticles show tendency to disperse as they settle on the carbon coated copper grid (Figure 5). On the other hand, in the presence of dopant metal ions, the samples show tendency to agglomerate as they settle on the carbon coated copper grid (Figures 6 to 13). Aggregation of the doped CdS nanocrystals may be due to the high surface energy of the doped CdS nanocrystals [58]. Metal ions dopants form spherical shape due to the redeposition of ions from {001} to the other facets to make an equilibrium spherical shape [6].

FIGURE 8: TEM picture of Ni^{2+} doped CdS at a magnification of 300 KX.

FIGURE 10: TEM picture of Mn^{2+} doped CdS at a magnification of 150 KX.

FIGURE 9: TEM picture of Ni^{2+} doped CdS at a magnification of 600 KX.

FIGURE 11: TEM picture of Mn^{2+} doped CdS at a magnification of 300 KX.

As shown in Figures 14, 15, 16, 17, and 18, the ZnS nanostructured materials with the size of 50–100 nanometers in diameter are obtained. The contrast variations within the image suggest that the spheres are composed of nanocrystallites.

From the TEM micrographs, it is clear that the nanoparticles obtained without doping are quantum dots (Figure 14). On the other hand, in the presence of a dopant ion, the particle size of the samples increased, which is corroborated with the XRD results.

3.2. Photoluminescence Spectroscopy. Figure 19 shows photoluminescence (PL) spectra of doped and undoped CdS. These spectra were recorded in spectral range of 370–650 nm with an excitation wavelength of 360 nm. The PL spectra of pure CdS quantum dots have emission peak as shown in Figure 19-(a), the corresponding luminescence peaks centered at about 485 nm originated from the band edge and the broad emission centered at around 530 nm arises from trap-related recombination from surface defects sites. This emission results from radiative recombination of electrons and holes via the surface defect states present in the nanocrystals [59]. The electrons and holes, after excitation across the band edge,

trickle down nonradiatively to the surface states lying in the band gap region. Radiative deexcitation across the surface states in CdS nanocrystals gives rise to bright yellow-green fluorescence observed at around 500 nm [60].

Luminescence properties of manganese, cadmium, and nickel doped CdS nanocrystals have been mainly studied. The PL intensity increased in case of Mn^{2+} and decreased in case of Co^{2+} and Ni^{2+} . This is due to the fact that the doped Mn^{2+} ions provide good traps for the excited electrons [60]. The ion radius of Cd^{2+} , Mn^{2+} , Co^{2+} , and Ni^{2+} are 0.095 nm, 0.083 nm, 0.069 nm, and 0.065 nm, respectively [52]. Mn, Ni, or Co ions may be in CdS sites as substitutional or as interstitial ions of CdS nanoparticles. When these ions are doped into the CdS nanoparticles, cadmium ions (0.095 nm) will be replaced by the smaller Ni or Co ions in the host lattice and hence Ni or Co deep centers are formed, which can inhibit more electrons (holes) to be excited and can lead to the enhancement of nonradiative recombination processes. As a result, Ni and Co dopant ions emission intensities become weaker than that of pure CdS nanoparticles [61]. Also Ni doped CdS shows (Figure 19-(d)) weaker luminescence than that of codoped CdS because Ni ionic radius is smaller than that of Co and so

FIGURE 12: TEM picture of Mn^{2+} - Co^{2+} - Ni^{2+} tridoped CdS at a magnification of 200 KX.

FIGURE 13: TEM picture of Mn^{2+} - Co^{2+} - Ni^{2+} tridoped CdS at a magnification of 500 KX.

FIGURE 14: TEM picture of pure ZnS 400 KX.

FIGURE 15: TEM picture of Mn^{2+} doped ZnS 60 KX.

FIGURE 16: TEM picture of Co^{2+} doped ZnS 400 KX.

FIGURE 17: TEM picture of Ni^{2+} doped ZnS 250 KX.

FIGURE 18: TEM picture of Mn^{2+} - Co^{2+} - Ni^{2+} tridoped ZnS at a magnification of 250 KX.

FIGURE 19: PL emission spectra of undoped CdS and 10% metal ion doped CdS excited at 360 nm.

FIGURE 20: PL emission spectra of undoped ZnS and 10% metal ion doped ZnS excited at 254 nm.

can easily replace Cd ion. Furthermore, CdS luminescence is quenched in the case of Mn²⁺-Co²⁺-Ni²⁺ tridoped CdS. This is due to the replacement of cadmium ion in the host lattice by Ni and Co ions.

Figure 20 shows PL emission spectra of undoped ZnS and 10% metal ions doped ZnS. The photoluminescence emission peak for the synthesized undoped ZnS nanoparticles (Figure 20-(a)) is observed at ~376 nm which could be ascribed to a recombination of electrons at the sulfur vacancy donor level with holes trapped at the zinc vacancy acceptor level [62]. Co²⁺ and Ni²⁺ dopant ions show sharp peaks at 379 and 377 nm, respectively (Figure 20-(b) and Figure 20-(c)). Whereas Mn²⁺ and tridopant ions show broad peaks at 374 and 370 nm, respectively (Figure 20-(d) and Figure 20-(e)), they also gave new peaks at 396 and 400 nm, respectively. This observed change in the PL is due to the change in the band gap of the semiconductor on the addition of certain impurity element referred to as “bowing” effect [43].

The luminescence mechanism of ZnS nanoparticles doped with Mn²⁺, Ni²⁺, or Co²⁺ can be described as follows: the nanosized ZnS matrix absorbs ultraviolet photons; the electrons are excited from the valence band to the conduction band and are trapped by defects. Light emission is observed due to the recombination of the defects and the excitation states induced by the composite center of the dopant ion. When Mn²⁺, Ni²⁺, or Co²⁺ as activation ions are doped in ZnS nanoparticles, more electrons are easily excited. And the radiative recombination of luminescence processes is enhanced. Thus, the relative photoluminescence intensity of samples is dramatically increased [41]. In doped nanoparticles large number of dopant centers are concentrated near the surface of the nanoparticles, leading to give better emission efficiencies compared to that of pure ZnS [13].

The ion radii of Zn²⁺, Mn²⁺, Co²⁺, and Ni²⁺ are 0.074 nm, 0.083 nm, 0.069 nm, and 0.065 nm, respectively [52]. MnS

is far more soluble than that of ZnS; furthermore, Mn²⁺ could not easily displace Zn²⁺ ion of the host lattice because Mn²⁺ ionic radius is larger than that of Zn²⁺. The new peak at 396 and 400 nm for Mn²⁺ doped ZnS and Mn²⁺-Co²⁺-Ni²⁺ tridoped ZnS, respectively, may be due to mixed face formation. Also Mn²⁺ and Mn²⁺-Co²⁺-Ni²⁺ tridoped create point defects, which may result in the observation of new emission peaks.

In case of Ni and Co dopant, not much change in the PL peaks position is observed comparing with that of pure CdS (Figure 20-(b) and Figure 20-(c)) but the intensity increased in all of the doped ZnS samples. The PL intensity of the tri, Mn, Co, or Ni doped sample is about three, five, fifty, or seventy times, respectively, that of pure ZnS nanoparticles. Increasing in the PL intensity is observed because more electrons can be excited with using of Mn, Co, or Ni ions. Moreover, they induce defects and excited states to the ZnS, which result in the PL in the visible region [41]. The enhancement of luminescence intensity is one of the phenomena ascribed to the size effect that luminescence intensity increases with decrease of particle size [63].

The weaker PL intensity of Mn²⁺-Co²⁺-Ni²⁺ tridoped ZnS (Figure 20-(e)) compared with that of Mn ion monodoped ZnS (Figure 20-(b) to Figure 20-(d)) could be attributed to the very high doping concentration (10%) inducing concentration quenching effect [64].

4. Conclusion

This work reports on a facile one-step preparation of Mn²⁺, Co²⁺, or Ni²⁺ monodoped or tridoped CdS or ZnS.

The successful doping of Mn²⁺-Co²⁺-Ni²⁺ tridoped ions into the host CdS (or ZnS) was proved by the EDX spectra.

Transmission electron microscopy investigations of the synthesized samples revealed different morphologies.

Photoluminescence of CdS is quenched with Co²⁺ or Ni²⁺-mono-doped ions and with tridoped Mn²⁺-Co²⁺-Ni²⁺ ions, whereas Mn²⁺ doped CdS showed luminescence enhancement.

Photoluminescence of ZnS enhanced with doping, especially when monodoped with Ni²⁺ or Co²⁺. These compounds, therefore, offer opportunities for further technological applications; such as in electroluminescence devices, phosphors, light emitting displays, and optical sensors.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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