Research Article

The Effect of Polyvinylpyrrolidone on the Optical Properties of the Ni-Doped ZnS Nanocrystalline Thin Films Synthesized by Chemical Method

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We report the optical properties of polyvinyl-pyrrolidone (PVP) and the influence of PVP concentration on the photoluminescence spectra of the PVP (PL) coated ZnS:Ni nanocrystalline thin films synthesized by the wet chemical method and spin-coating. PL spectra of samples were clearly showed that the 520 nm luminescence peak position of samples remains unchanged, but their peak intensity changes with PVP concentration. The PVP polymer is emissive with peak maximum at 394 nm with the exciting wavelength of 325 nm. The photoluminescence exciting (PLE) spectrum of PVP recorded at 394 nm emission shows peak maximum at 332 nm. This excitation band is attributed to the electronic transitions in PVP molecular orbitals. The absorption edges of the PVP-coated ZnS:Ni0.3% samples that were shifted towards shorter wavelength with increasing of PVP concentration can be explained by the absorption of PVP in range of 350 nm to 400 nm. While the PVP coating does not affect the microstructure of ZnS:Ni nanomaterial, the analyzed results of the PL, PLE, and time-resolved PL spectra and luminescence decay curves of the PVP and PVP-coated ZnS:Ni samples allow to explain the energy transition process from surface PVP molecules to the Ni²⁺ centers that occurs via hot ZnS.

1. Introduction

Despite intensive research on conductivity, local domain orientation, and molecular order in organic semiconductor thin films [1], the relationship between morphology, chain structure and conductivity of the polymer is still poorly understood. Recently, researchers all over the world have worked on the improvement of electrical conductivity investigated the charge transport and the energy band of a variety of polymers (polyazomethine, aliphatic-aromatic copolyimides). All determined parameters of the electrical conductivity and the energy band have been found to be related to the influence of the polymer chain structure [2–4].

During the last few years there have been extensive experimental and theoretical studies of luminescence, nonlinear optical and electrical properties of a variety of polymers

(novel conducting copolymer based on dithienylpyrrole, azobenzene, and EDOT units) in the direction of material science as electronic devices and displays [2, 3, 5–8]. New progress has been made in the area of thermoelectric (TE) applications of conducting polymers and related organic-inorganic composites [9, 10]. Other research efforts aimed to identify the role of additives in optimizing the morphology of organic solar cells and discussed the role of bimolecular recombination in limiting the efficiency of solar cells based on a small optical gap polymer [11, 12].

Recently, methods have been developed to cap the surfaces of the nanoparticles with organic or inorganic groups so that the nanoparticles are stable against agglomeration. Among the inorganic semiconductor nanoparticles, zinc sulfide ZnS is an important II-VI semiconductor, which has been studied extensively because of its broad spectrum of

potential applications, such as in catalysis and electronic and optoelectronic nanodevices. Furthermore, luminescent properties of ZnS can be controlled using various dopants such as Ni, Fe, Mn, and Cu [13–19]. They not only give luminescence in various spectral regions but also enhance the excellent properties of ZnS. In order to cap the ZnS nanoparticles, some particular passivators of ZnS have been used, such as polyvinyl alcohol (PVA) [20] and polyvinylpyrrolidone (PVP) [21–25]. Understanding the effect of capping on nanoparticles is one of the most important topics nowadays. The influence of surface passivation on luminescence quantum efficiency of ZnS:Mn²⁺ and ZnS:Cu²⁺ nanoparticles has been discussed when using sodium hexametaphosphate (SHMP), PVP and PVA as coating agents [26–28]. However, till now, there are only a few papers focused on investigation of the optical properties of PVP-coated ZnS nanocomposite materials and the process of energy transfer from organic surface adsorbate of PVP to the dopant ions (Cu²⁺, Mn²⁺). Furthermore, there are not any papers completely investigating the optical properties of PVP-coated ZnS: Ni nanocomposite materials.

Thus, in this paper we report the optical properties of PVP (polyvinyl-pyrrolidone) and the influence of PVP concentration on the PL spectra of the PVP-coated ZnS: Ni nanocrystalline thin films synthesized by the wet chemical method and spin-coating. Further, the influences of PVP concentration on the general features of the PL spectra and the process of energy transfer from the PVP to the Ni²⁺ luminescent centers in doped ZnS as well as the optical band gap variation are also discussed.

2. Experiments

2.1. Preparation of ZnS: Ni Nanopowders. The polymer polyvinyl-pyrrolidone and initial chemical substances with high purity (99.9%) (Merck chemicals) were prepared as follows:

Solution I: 0.1 M Zn(CH₃COO)₂ in water,

Solution II: 0.1 M NiSO₄ in water,

Solution III: 0.1 M Na₂S in water,

Solution IV: CH₃OH: H₂O (1: 1).

Firstly, ZnS: Ni nanoparticles were synthesized by the wet chemical method. Solutions I, II, and III were mixed at an optimal pH = 4.5 and in an appropriate ratio in order to create Ni-doped ZnS powder materials with different molar ratios of Ni²⁺ and Zn²⁺ as follows: 0.0%, 0.2%, 0.3%, 0.6%, and 1%. The precipitated ZnS nad NiS nanoparticles were formed by stirring of the mixed solutions at 80°C for 30 minutes following the chemical reactions

These precipitated ZnS and NiS nanoparticles were filtered by filtering system and then washed in distilled water and ethanol several times. Finally, they were dried under nitrogen gas for 6 h at 60°C. These powder samples were named ZnS, ZnS: Ni0.2%, ZnS: Ni0.3%, ZnS: Ni0.6%, and ZnS: Ni1%, corresponding to different molar ratios of 0.0%, 0.2%, 0.3%, 0.6%, and 1% of Ni²⁺ and Zn²⁺.

2.2. Preparation of Thin Films and Powders from PVP-Capped ZnS: Ni Nanocrystals. In order to study the role and the effect of PVP on the optical properties of ZnS: Ni, the PVP coated ZnS: Ni nanoparticles were synthesized by keeping a constant nominal Ni concentration of 0.3%, but variation of polymer concentrations.

2.2.1. Preparation of Thin Films from PVP Capped ZnS: Ni Nanocrystals. After washing, 0.1 g formed ZnS: Ni0.3% precipitates were dispersed into 10 mL of CH₃OH: H₂O (1: 1) solvent. This mixture was called solution IV. Similarly, 0.1 g of PVP was dissolved in 10 mL of CH₃OH: H₂O (1: 1) solvent and was called solution V. After that these two solutions IV and V were mixed with each other at various volume ratios of (5: 0), (5: 1), (5: 2), (5: 3), (5: 4), and (5: 7) under continuous stirring for 1 h at speed of 3000 rpm.

The thin films M-PVP(5: 0), M-PVP(5: 1), M-PVP(5: 2), M-PVP(5: 3), and M-PVP(5: 4) were produced by the spin-coating method on glass substrate using the rotation speed of 1500 rpm with the same drop-by-drop method and dried at 60°C for all samples.

2.2.2. Preparation of Powders from PVP-Capped ZnS: Ni Nanocrystals. In order to receive the PVP coated ZnS: Ni0.3% nanopowders with different PVP concentrations, the mixed solutions of IV and V were centrifuged at speed 3000 rpm. Then, the received PVP-coated ZnS: Ni0.3% nanoparticles were dried at 80°C. These PVP coated ZnS: Ni0.3% nanopowders are named B(5: 0), B(5: 1), B(5: 2), B(5: 3), B(5: 4) and B(5: 7).

2.3. Research Methods. The microstructure of these samples was investigated by X-ray diffraction (XRD) using XD8 Advance Bruker Diffractometer with CuK_α radiation of $\lambda = 1.5406 \text{ \AA}$ and high-resolution transmission electron microscope (HR-TEM). Photoluminescence (PL) spectra, photoluminescence exciting (PLE) spectra, and the absorption spectra of these samples at room temperature were recorded by Fluorolog FL3-22, HP340-LP370 Fluorescence Spectrophotometer with an excitation wavelength of 325 nm, 337 nm, xenon lamp XFOR-450, and JASCO-V670 spectrophotometer, respectively. The time-resolved PL spectra of samples were measured by GDM-100 spectrophotometer using Boxca technique.

3. Results and Discussion

3.1. Analysis of Microstructure by XRD Patterns, Atomic Absorption Spectroscopy, and TEM. Figure 1 shows X-ray diffraction spectra of the pure ZnS nanopowders (inset), ZnS: Ni0.3% with different PVP concentration, B(5: 0), B(5: 1), B(5: 4), corresponding to curves a, b, and c. The analyzed results show that all samples have a sphalerite structure. The three diffraction peaks of $2\theta = 28.8^\circ$, 48.1° , and 56.5° with strong intensity correspond to the (111), (220), and (311) planes. It is shown that the PVP polymer does not affect the microstructure of ZnS: Ni nanomaterials. Thus, one can point out that the PVP coating on the surface

FIGURE 1: The X-ray diffraction spectra of samples B(5:0); B(5:1); B(5:4)—curves a, b, c, and respectively—and pure ZnS nanopowders (inset).

TABLE 1: The band gap of PVP, B(5:0), B(5:1), B(5:2), B(5:3), B(5:4), and B(5:7) samples with different PVP concentrations.

No.	Sample	E_g (eV)	Grain size (nm)
1	B(5:0)	3.11	2,4
2	B(5:1)	3.19	2,4
3	B(5:2)	3.24	
4	B(5:3)	3.28	
5	B(5:4)	3.29	2,5
6	B(5:7)	3.43	
7	PVP	4.19	

of ZnS:Ni nanoparticles possesses the same structure as the amorphous shells (in Figure 2(a)). From the diffraction peaks of 2θ and the standard Bragg relation, the interplanar distance $d = 3.12 \text{ \AA}$ and then the lattice constant $a = 5.4 \text{ \AA}$ for the cubic phase were calculated by the following equations:

$$2d \sin \theta = n\lambda, \quad \frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}, \quad (2)$$

where d is the interplanar distance and h, k , and l denote the lattice planes.

The average size of the Ni-doped ZnS grains is about 2–3 nm, was calculated by which the Scherrer formula (in Table 1).

Figure 2(b) gives the molecular structure and formula of polyvinyl-pyrrolidone (PVP) with both N and C=O groups. In PVP, nitrogen is conjugated with adjacent carbonyl groups. Thus, the role of PVP consists of (a) forming passivating layers around the ZnS:Ni core due to coordination bond formation between the nitrogen atom of PVP and Zn^{2+} and (b) preventing agglomeration of the particles by the repulsive force acting among the polyvinyl groups [23].

Figure 3(a) presents the HR-TEM image of B(5:3) sample. Figure 3(b) demonstrates the distributions of the adjacent interplanar distances of (111) planes corresponding

to Figure 3(a) (inset). From Figure 3(b) the adjacent interplanar distance of (111) planes is about $3.13 \text{ \AA}$. This result is suitable for the XRD patterns and proves that the crystalline is obtained in the as-synthesized samples ZnS:Ni-PVP.

3.2. Photoluminescence Spectra Measurements. Figure 4 shows the photoluminescence PL spectra with the exciting wavelength of 325 nm of the ZnS:Ni0.2%, ZnS:Ni0.3% ZnS:Ni0.6%, ZnS:Ni1.0%, and ZnS powder samples, corresponding to curves a, b, c, d, and e. The peak maximum of ZnS is about 450 nm, meanwhile the PL spectra of ZnS:Ni0.2%, ZnS:Ni0.3% ZnS:Ni0.6%, and ZnS:Ni1.0% samples show peak maximum at 520 nm. In order to study the influence of Ni concentration on photoluminescence of samples, all measured parameters (such as temperature, sample volume, and exciting wavelength intensity) were kept constant for every measurement of samples. This clearly shows that the luminescence peak maximum positions of ZnS:Ni samples are unchanged, but their intensities change rather strongly with increasing of PVP concentration. One of these samples with the large luminescence intensity is ZnS:Ni0.3% sample. The relative luminescence intensity of this sample is also about double of that of the pure ZnS sample. In comparison with other results, this result also agrees with previous works [13, 15], in which the samples were synthesized from initial chemicals: $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, NiSO_4 , and TAA ($\text{C}_2\text{H}_5\text{NS}$). The blue emission band of pure ZnS sample is attributable to the intrinsic emission of defects, vacancy, and an incorporation of trapped electron by defects at donor level under conduction range when the dopant-Ni was added into the hot ZnS semiconductor. Moreover, due to the energy levels of $\text{Ni}^{2+}(\text{d}^8)$ in ZnS semiconductor materials, the lowest multiplex term ^3F of the free Ni^{2+} ion is split into $^3\text{T}_1$, $^3\text{T}_2$, and $^3\text{A}_2$ through the anisotropic hybridization [13, 15]. Thus, the green luminescence of about 520 nm is attributed to the d-d optical transitions of Ni^{2+} , and the luminescent center of Ni^{2+} is formed in ZnS.

In order to observe the influence of PVP concentration on optical properties of samples, the M-PVP(5:0), M-PVP(5:1), M-PVP(5:2), M-PVP(5:3), and M-PVP(5:4) thin films were measured by the photoluminescence PL spectra using the exciting wavelength of 325 nm (in Figure 5). It is clearly shown that these luminescence peak positions of samples remain unchanged but their peak intensities increase with increasing of PVP concentration from (5:0) to (5:4).

These results show that PVP does not affect the microstructure of ZnS:Ni but plays an important role to improve the optical properties of ZnS:Ni nanoparticles.

3.3. Absorption Spectra and Photoluminescence Excitation (PLE) Spectra. The absorption spectra of PVP sample and the B(5:0), B(5:1), B(5:2), B(5:3), B(5:4), and B(5:7) samples (PVP-coated ZnS:Ni0.3% samples with different PVP concentrations) are shown in Figure 6.

It is known that the light transition through the environment can be demonstrated by the Beer-Lambert law:

$$I(\nu) = I_0(\nu) \cdot e^{-\alpha(\nu)d}, \quad (3)$$

FIGURE 2: (a) HR-TEM image of B(5:3) sample. (b) The structure and formula of polyvinyl-pyrrolidone (C_6H_9NO)_n.

FIGURE 3: (a) HR-TEM image of B(5:3) sample. (b) The interplanar distances of (111) planes.

where $I_0(\nu)$ and $I(\nu)$ are intensities of light in front of and behind the environment, $\alpha(\nu)$ is absorption coefficient of this environment relative to photon with energy $h\nu$, and d is the thickness of the film.

Formula (3) can be rewritten in logarithmic form:

$$\alpha(\nu) \cdot d = \ln \frac{I_0(\nu)}{I(\nu)} = \ln 10 \cdot \lg \frac{I_0(\nu)}{I(\nu)} = 2.3 \cdot A \quad \text{or} \quad \alpha = \frac{2.3A}{d}, \quad (4)$$

with $A = \lg(I_0(\nu)/I(\nu))$ being the absorption.

The relation between absorption coefficient α and energy of photon was represented by the following equation [22]:

$$\alpha = \frac{K(h\nu - E_g)^{n/2}}{h\nu}, \quad (5)$$

where K is a constant, E_g is the band gap of material, the exponent n is dependent on the type of transition (here, $n = 1$ for the direct transition of ZnS:Ni semiconductor).

From (4) and (5), it can be written as

$$(Ah\nu)^2 = B(h\nu - E_g), \quad \text{where } B \text{ is constant.} \quad (6)$$

By (6), the absorption spectra of samples are converted into the plots of $(Ah\nu)^2$ versus $h\nu$ (Figure 6 inset). The values of the band gap E_g were determined by extrapolating the straight line portion of the $(Ah\nu)^2$ versus $h\nu$ graphs to the $h\nu$ -axis (Figure 6 inset). Table 1 gives the band gap values of PVP and the B(5:0), B(5:1), B(5:2), B(5:3), B(5:4), and B(5:7) samples, calculated from these absorption spectra. It is clear that the band gap of the B(5:0) sample (ZnS:Ni0.3% sample) is smaller in comparison with that of pure ZnS (3.68 eV). This decreasing is possibly attributed to the band-edge tail constitution of state density in band gap, by the s-d exchange interaction between 3d⁸ electrons of Ni²⁺ and s conduction electrons in ZnS crystal [29, 30]. On the contrary to this issue of ZnS:Ni (in comparison with that of pure ZnS), the band gap of the PVP-coated ZnS:Ni samples increases from 3.11 eV to 3.43 eV with the increasing of PVP concentration (the absorption spectra shifted toward shorter wavelength).

Because ZnS:Ni nanoparticles were formed in preparation process before they dispersed into PVP matrix, therefore, PVP do not effect to size of nanoparticles. However, the PVP play an important role as the protective layer, against agglomeration ZnS:Ni nanoparticles and contribute to

FIGURE 4: PL spectra of powder samples.

FIGURE 5: PL spectra of thin films.

FIGURE 6: The absorption spectra of PVP, B(5:0), B(5:1), B(5:2), B(5:3), B(5:4), and B(5:7) samples. The plots of $(A\hbar\nu)^2$ versus $\hbar\nu$ (inset).

FIGURE 7: PL spectra and PL excitation (PLE) spectra of PVP (inset).

FIGURE 8: The PLE band of B(5:3) monitored at 520 nm.

increase optical properties of ZnS:Ni nanoparticles. The absorption edge and right shoulder of PVP in the range from 230 nm to 400 nm and the absorption edges and right shoulders of PVP-coated ZnS:Ni0.3% samples in range from 350 nm to 400 nm showed clearly the shift toward to short wavelength with increasing of PVP concentration. Due to the PVP absorption the photons in wavelength range from 230 nm to 400 nm, and thus the blue shift of the absorption edge in the range from 350 nm to 400 nm can be explained by increasing of PVP concentration of the PVP-coated ZnS:Ni0.3% samples.

In order to examine the process of energy transfer in the PVP-coated ZnS:Ni nanoparticles, the PVP and B(5:3) samples were measured by the PL, the PLE spectra as in Figures 7 and 8, respectively. It is interesting to see that the PVP is emissive with peak maximum at 394 nm with the exciting wavelength of 325 nm. Simultaneously, the PLE spectrum recorded at 394 nm emission of PVP shows peak maximum at 332 nm in Figure 7 (inset). This excitation

FIGURE 9: The time-resolved PL spectra of PVP at 300 K excited by pulse N_2 laser with 337 nm wavelength, pulse width of 7 ns, and frequency of 10 Hz. The delay times after the excitation pulse are 33 ns, 37 ns, 40 ns, 44 ns, and 50 ns, respectively.

band is attributed to the electronic transitions in PVP molecular orbitals. Alternatively, the blue emission band of PVP at 394 nm is attributed to the radiative relaxation of electrons from the lowest energy unoccupied molecular orbital (LUMO) to the highest energy occupied molecular orbital (HOMO) levels in PVP [31]. As seen in Figure 7 (inset), the PLE band of PVP monitored at 394 nm has a peak maximum at 332 nm, while the PLE band of B(5:3) monitored at 520 nm (Figure 8) shows a peak maximum at 395 nm. These results show that the PL peak of 394 nm of PVP sample coincided exactly with the PLE peak of B(5:3) sample. Thus, the exciting wavelength of 325 nm is becoming the luminescent emission at 520 nm of the PVP-coated ZnS:Ni samples. From above analysed results of PLE spectra of PVP, B(5:3) samples and the PL spectra of the sample systems (Figures 4 and 5) with the exciting wavelength of 325 nm, it is reasonable to suppose that (i) the high energy band in the PLE spectrum of ZnS:Ni-PVP arises from the surface PVP molecules, (ii) the energy transfer occurs between the energy levels of surface PVP molecular orbitals and the luminescence centers of ZnS:Ni, and (iii) the energy transition from surface PVP molecules to the Ni^{2+} centers occurs via hot ZnS.

3.4. Time-Resolved PL Spectra and Luminescence Decay Curves. The investigation of the kinetic decay process of electrons in energy bands is very important to the study of luminescence. It can provide a scientific basis for the improvement of the luminescence efficiency of optical materials. Figure 8 shows the time-resolved PL spectra of PVP at 300 K excited by pulse N_2 laser with 337 nm wavelength, pulse width of 7 ns, and frequency of 10 Hz. These peaks of these spectra are shifted toward longer wavelength from 428 nm to 437 nm with increasing of the delay time from 33 ns to 50 ns. It shows clearly that these peaks belong to the right shoulder in range of 390–470 nm of PL spectrum

FIGURE 10: The PL decay curve of PVP.

of PVP excited by laser wavelength of 325 nm (in Figure 7). Beside that, Figure 9 also shows that the PL peak intensity decreases while the spectral width of the PL band (full-width at half-maximum) decrease with increasing of the delay time. These PL properties are attributed to electron transition from LUMO to HOMO levels in PVP molecules.

Figure 10 shows the PL decay curve of PVP at 428 nm when using exciting wavelengths 337 nm. The decay curve shows that the number of free photoelectrons in exciting energy bands (corresponding to 428 nm wavelength) is decreased by exponential attenuation and is given by $n \propto e^{-t/\tau}$, where τ is the lifetime of electrons in exciting energy band. From this PL decay curve, the lifetime of free photoelectrons is calculated as $\tau = 15.5$ ns for PVP at 428 nm. The lifetime τ is shorter than that in ZnS:Mn, Cu samples sintered at high temperatures [32]. On the other hand, the lifetime τ is very short, thus it is characteristic of the radiative relaxation of electrons from the lowest energy unoccupied molecular orbital (LUMO) to the highest energy occupied molecular orbital (HOMO) levels in PVP. From the above analyzed results of PVP, the blue luminescence of PVP may be attributed to the radiative relaxation of electrons from LUMO to HOMO levels as in Figure 12.

3.5. On the Energy Transfer from Surface PVP Molecules to the Ni^{2+} Centers. The PVP is a conjugated polymer with both N and C=O groups. So with the ZnS:Ni-PVP samples, it is believed that the bond between metal ions and PVP can give rise to overlapping of molecular orbitals of PVP with atomic orbitals of metal ions in surface regions [23, 31]. Thus, from the above results, we believe that the PVP passivating layers around the ZnS:Ni core described in Figure 11 are formed by coordination bond between the nitrogen atom of PVP and Zn^{2+} [31]. Figure 11 shows the incomplete coverage with low concentration of PVP (Figure 11(a)) and the complete coverage with higher concentration of PVP (Figure 11(b)).

FIGURE 11: The PVP coverage of ZnS : Ni grains.

FIGURE 12: Schematic illustration of various electronic transition and energy transfer processes in ZnS : Ni-PVP.

It is clear from these above analyzed results of the PL spectra, PLE spectra, time-resolved PL spectra, and luminescence decay curves of PVP and PVP-coated ZnS : Ni samples that the energy transition process from surface PVP molecules to the Ni^{2+} centers occurs via hot ZnS illustrated as in Figures 12(a) and 12(b).

4. Conclusion

From the above experimental results, the influence of surface passivation on the luminescence intensity of ZnS : Ni nanoparticles has been observed due to efficient energy transfer from the surface PVP molecules to the Ni^{2+} centers in ZnS : Ni nanoparticles. With increasing the PVP concentration, the absorption edge of the PVP-coated ZnS : Ni nanoparticles shows the blue shift, which is explained due to the influence of PVP concentration on the shift of the absorption spectra.

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