Comparative study of photoluminescence properties of various lead sulfide morphologies

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ABSTRACT:
Photoluminescence analysis is a useful method to study the optical properties of semiconductor nanostructures. Distinct processes take place to result in the light emission from the nanostructure. Various deposition methods and morphologies changed the emission band in semiconductor nanostructures. Three different morphology of Lead Sulfide structures such as nonospheres, star-shaped and dendrite nanostructures have been analyzed and the Photoluminescence results were compared. In three cases, band emissions are in visible region and it was observed that the incidence of quantum limits in resulting of increasing surface to volume ratio is impressive to optical properties.

KEYWORDS: Nanostructures; Quantum confinement ; Lead sulfide; Optical applications; Photoluminescence; Morphology; Emission band; Full width at half maximum; Recombination; Transition.

1. INTRODUCTION

During the two past decades, much investigation has been done on nanostructures. These investigations are outcome of the transition from micro-particles phase to nano-particles phase and exhibit various properties from nanostructure. For this reason the nanostructures have attracted the attention of many researchers. In nano-phase with by increasing the surface to volume ratio, quantum confinement appears. Therefore recognition and controlling of them is very important.

Among these, compound semiconductor nanostructures are important. Lead Sulfide (PbS) is one of these compound semiconductors with narrow band gap (0.41ev) [1], that have important optical applications such as solar cells and infrared detectors [2], solar control coatings [3] optical fibers and broadband optical amplifiers [4]. So far various forms of PbS nanostructures such as nanowires [5], nanorods [6] and nanoclusters [7] have been reported.

It has been demonstrated that Photoluminescence (PL) spectroscopy is a fast and nondestructive tool for appreciating optical properties of nanostructures. In fact PL spectroscopy gives us emission bands and so we can understand that what wavelengths will be emitted. This emission bands can also give us information about the impurities in the sample. Of course only impurities become identified in this way that will participate in emission recombination. Three distinct processes take place to result in the light emission from the nanostructures: (1) absorption of exciting light that is production cause of electron-hole pairs, (2) partial radiative recombination of these electron-hole pairs and (3) escape of this radiation from the system. Existence of emission band in PL spectrum caused by this processes. In this paper optical properties of three different morphology of PbS nanostructure were investigated by PL spectra analysis. Emission bands have been studied and tried to be a comparison between them. For all PL spectra were measured using a Perkin-Elmer LS55 luminescence spectrometer.

2. PBS NANOSPHERES

These nanostructures grown by Mozafari *et al* [8]. Their growth method has been chemical deposition (CD). Fig. 1 presents transmission electron microscopy (TEM) images of these PbS nanocrystals (NCs).
The morphology of the PbS sample in Fig.1 is uniform sphere-shaped particles. According to this image, diameters of the particles are 80-150 nm. X-ray diffraction (XRD) analysis confirmed the formation of

PbS nanoparticles. Also in this work, effects of heat treatment on physical, microstructural and optical characteristics of PbS NCs were investigated. Fig. 2 shows the PL spectra of deposited PbS NCs.

PL spectra were recorded at the excitation wavelengths of 328 nm. A strong and narrow band with high intensity centered at 657 nm (1.89 eV and red region from visible wave spectrum) which come from the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes [8].

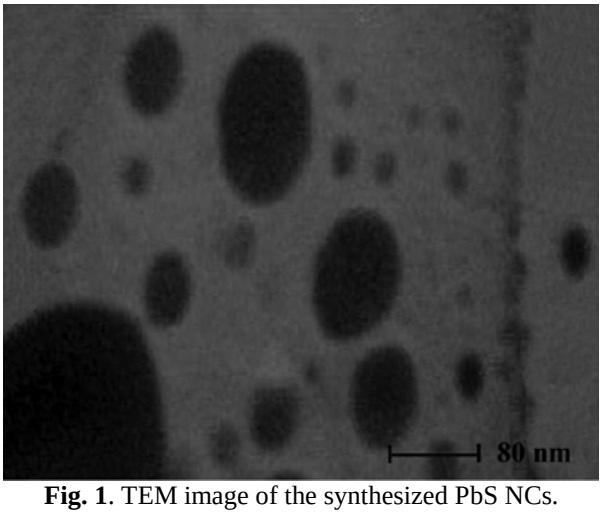

Fig. 1. TEM image of the synthesized PbS NCs.

Full width at half maximum (FWHM) for this band is about 11.44 nm. PL result shows that with increasing temperature Followed heat-treatment, the bands were shifted toward the larger wavelength that is a red shifting. The red shifting of emission band can be explained by the thermal expansion phenomenon. It has been reported that this kind of band edge luminescence arises from the recombination of excitons and/or shallowly trapped electron-hole pairs. The apparent red-shift and the strong peak are also indicative of the size quantization attributed to quantum confinement of charge carriers in the restricted volume of the nanoparticles [1]. Also peak intensity was increased. This relative increase of the PL intensity with the increase in the heat-treatment temperature, suggested the depletion of the grains which plays a major role in increasing defect densities. In other words, this gradual increase of PL emission intensities revealed a significant reduction in the surface/volume ratio of heat-treated samples [8].

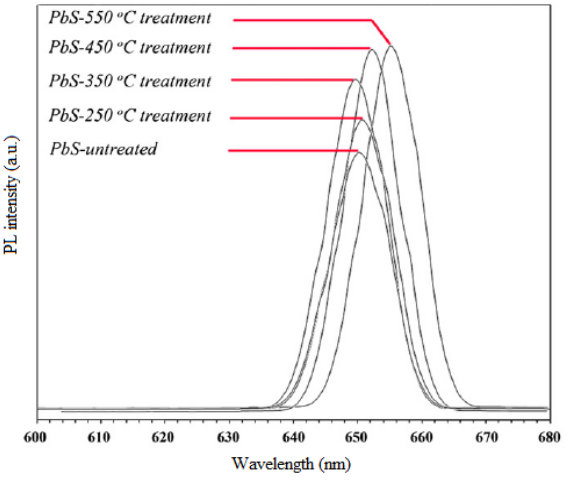

Fig. 2. PL spectra of different samples before and after heat treatment.

With increase in the heat-treatment temperature, the FWHM also was decreased, which indicates better crystallinity of the PbS NCs heated at 550 ^{0}C, because heat-treatment improved the texture of the NCs and decreasing the crystal defects [9].

3. PBS STAR-SHAPED NANOSTRUCTURES

These nanoparticles grown by Yousefi *et al* [10]. Their growth method has been hydrothermal method. Fig. 3 (a, b) presents Scanning Electron Microscopy (SEM) images of this PbS nanoparticles. This metal sulfide was then added to the ABS copolymer in order to increase its thermal stability. The morphology of them is star-shaped. According to these images, the length and diameter of the trunks are 2-3 µm and 400–600 nm, respectively.

Fig. 2c shows the SEM image of ABS/PbS nanocomposite that proved that the nanostructures were dispersed in the ABS matrix regularly. Fig. 2d is a cross sectional SEM image of the ABS/PbS nanocomposite, that confirms the presence of PbS in the copolymer. XRD analysis confirmed the formation a pure face-centered-cubic PbS structure with a lattice constant a = 5.941 Å, in agreement with the literature value (JCPDS card No. 77–0244).

Fig. 4 shows the Room temperature PL spectra of star-like and ABS/PbS PbS structures. PL spectra (4a) for star-like PbS were measured at the excitation wavelengths of 353 nm and other (4b) for ABS/PbS PbS structures were measured at the excitation wavelengths of 340 nm. The PL spectrum for star-like PbS nanostructure consists of one strong peak

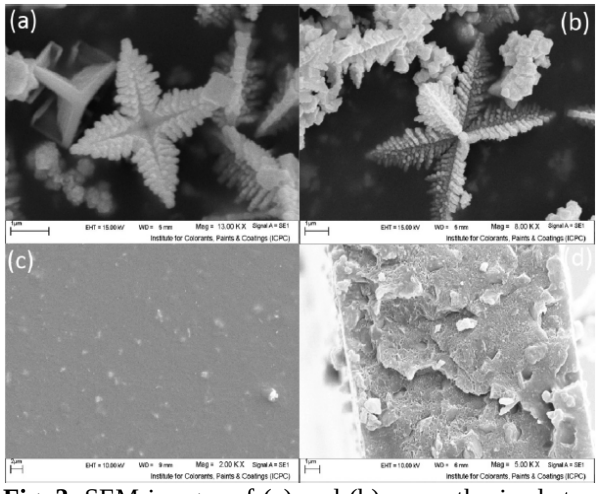

Fig. 3. SEM images of (a) and (b) as synthesized star-shaped PbS nanocrystals, (c) ABS/PbS nanocomposite and (d) cross sectional SEM image of ABS/PbS nanocomposite.

(3.08 eV and visible region), that can be ascribed to a high level transition in PbS semiconductor crystallites. FWHM for this emission band is about 8 nm. The PL spectrum for ABS/PbS PbS structures consists of one strong peak at 407 nm (3.05 eV and visible region). This kind of band edge luminescence arises from the recombination of excitons and/or shallowly trapped electron-hole pairs [10]. FWHM for this emission band is 12 nm. With decrease of the excitation wavelengths, band emission in PL spectra has the red shift.

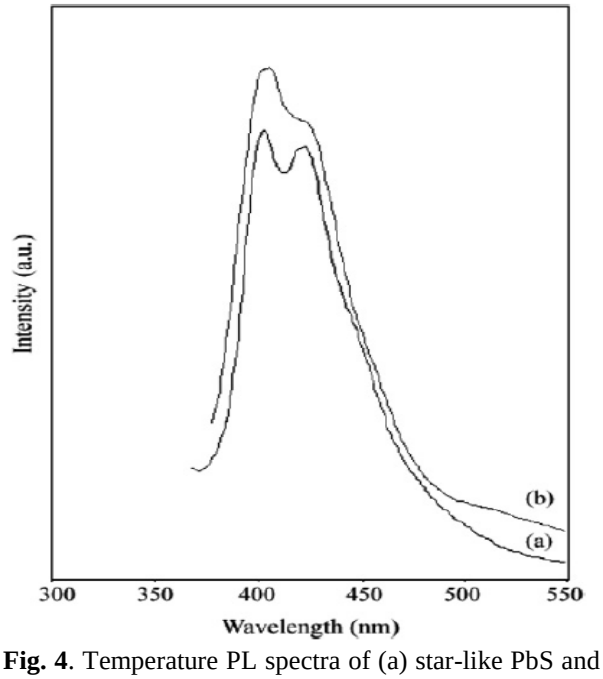

Fig. 4. Temperature PL spectra of (a) star-like PbS and (b) ABS/PbS nanocomposite.

4. PBS DENDRITE NANOPARTICLES

These nanoparticles grown by Xiong *et al* [11]. Their growth method has been solvothermal method in a mixed solution made of ethylenediamine (en) and distilled water. Fig. 5 (a, b and c) presents field emission scanning electron microscopy (FESEM) images of this PbS nanoparticles. The morphology of them is dendrite. The diameters of the branches are 650–680 nm.

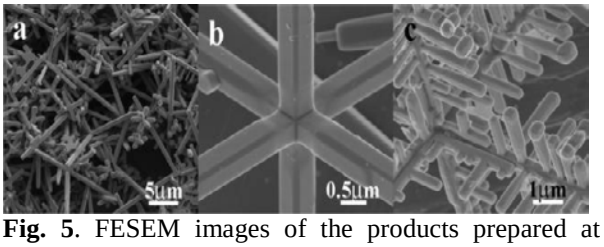

Fig. 5. FESEM images of the products prepared at reaction for 48 h at 220 °C.

Of course in this work by varying the experimental conditions such as the reagent ratios, the volume ratio of ethylenediamine and water, and the reaction temperature, PbS nanoparticles with controllable morphologies were conveniently obtained using our proposed method. XRD analysis confirmed the formation of PbS. The reflection peaks of the different products can be indexed as face-centered-cubic (fcc) rock-salt-structured PbS with a lattice constant of a = 5.926 Å, which is in good agreement with the literature values (JCPDS Card No. 05-592, a = 5.936 Å).

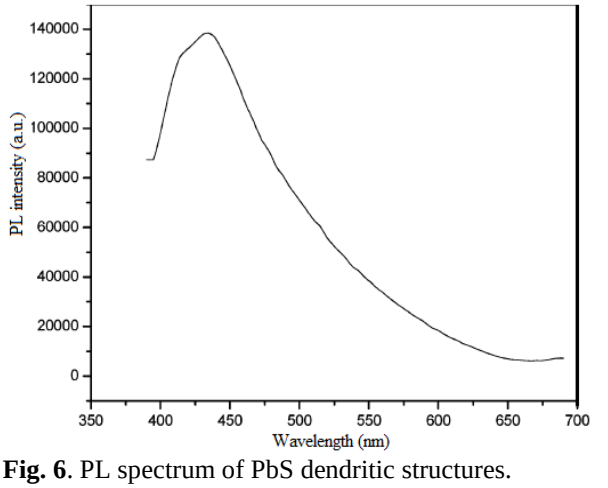

Fig. 6. PL spectrum of PbS dendritic structures.

Fig. 6 shows the Room-temperature PL spectra of deposited PbS dendritic structures. PL spectra were measured at the excitation wavelengths of 360 nm. A sharp and strong peak at 433 nm (2.86 eV and violet region from visible wave spectrum) is observed. Emission bands at 433 nm are usually related to the transition of electrons from the conduction band edge to holes, trapped at interstitial Pb^{2+} sites. FWHM for

this emission band is about 53 nm [11].

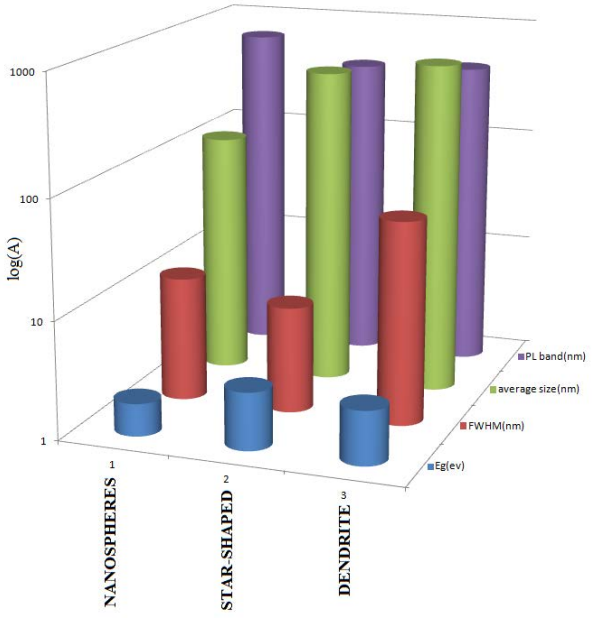

Fig. 7. Comparison of the desired parameters of nanostructures.

5. CONCLUSION

Various morphology of nanostructures PbS that were deposited by various methods and were found to be polycrystalline in nature with cubic phase structure, have been studied by PL analysis and their potentials towards for optical applications were evaluated. Band emissions in three morphology are in visible region, despite various wavelengths excitation. In all case, existence of sharp and intense peaks indicating the privileged crystalline and optical properties of nanostructures than other structures.

It can be said that with increase the particles size, FWHM also increases that represents decreased in crystalline and optical properties. Also band gap energy increases and PL emission have a shift to the lower wavelength. This is shown in Figure. 7.

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