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SYNTHESIS OF Mo-DOPED ZnS NANOPARTICLES AND INVESTIGATION OF THEIR STRUCTURAL, OPTICAL AND PHOTOVOLTAIC PROPERTIES

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ZnS and molybdenum (Mo) doped ZnS nanoparticles were synthesized at room temperature by co-precipitation method without any capping agent. The crystal structures of the synthesized ZnS and Mo-doped ZnS nanoparticles were determined to be zinc blend by x-ray powder diffraction (XRD). The calculated average crystal sizes are 2.70 and 2.68 nm for ZnS and Mo-doped ZnS nanoparticles, respectively. As a result of optical absorption measurements, it was observed that Mo dopant affects the energy band gap value of ZnS nanoparticles. The band gap value for ZnS and Mo-doped ZnS nanoparticles was determined as 4.07 and 4.17 eV, respectively. EDX measurement indicated that elemental percentages of Zn, S and Mo in the Mo-doped ZnS nanoparticles are 48.91, 50.25 and 0.84, respectively. The photovoltaic properties of Mo-doped ZnS nanoparticles were investigated for the first time in this study. The photon-to-current conversion (IPCE) measurements were carried out for ZnS and Mo-doped ZnS nanoparticles to compare their IPCE (%) values. The obtained result provides a new way to improve performance of ZnS-based solar cell structure.

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1. Introduction

Nanotechnology is the design, characterization, and application of nanomaterials. As a function of nanoparticles, these nanomaterials have been found to be versatile materials because they are used in optoelectronic devices depending on various band gaps [1]. Synthesis and characterization of zinc sulfide (ZnS) nanoparticles have been studied in different technological areas due to their quantum confinement effect on surface-volume ratio and small size of nanoparticles [2-4]. They are widely used in a wide range of applications such as UV-diodes, phosphors on flat panel displays [1], and photocatalysis [5], sensors [6] and bio-devices [7].

The bulk ZnS has a wide band gap energy of 3,68 eV [8]. The band gap is the energy required for electrons to enter the excited state. Theoretically, small size particles show a larger band gap than similar stacks and the energy equal to or higher than their band gap energy is required to enter an excited state [9-11]. ZnS, which is a semiconductor material with wide band gap and because of its energy band characteristic, becomes a good host material [12].

The doping, which is an approach to adjust the energy level surface states of ZnS, is an effective method. Different types of doping have been used at different concentrations to develop the characterization and optical properties of ZnS nanoparticles [13-16]. There are limited studies about the photovoltaic characteristics of doped ZnS nanoparticles whereas un-doped and doped nanoparticles have been widely driven as sensitizers in devices [17-19]. In our previous studies,

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we reported that Mn, Eu and Fe-doped ZnS semiconductor materials plays a noteworthy role to enhance incident photon to current efficiency value [20-22].

In our current study, ZnS and Mo-doped ZnS nanoparticles were synthesized at room temperature using the co-precipitation method. The photovoltaic properties of Mo-doped ZnS nanoparticles were investigated for the first time in this study. The photon-to-current conversion (IPCE) measurements were carried out for ZnS and Mo-doped ZnS nanoparticles to compare their IPCE (%) values. Moreover, the structural, optical and elemental properties were characterized using x-ray diffraction (XRD), optical absorption and energy dispersive x-ray (EDX) measurements, respectively.

Our study suggests a new way to improve performance of ZnS- based solar cell structure.

2. Materials, method and characterizations

Zinc acetate dehydrate (Zn (CH_3COO).$2H_2O$), sodium sulfide (Na_2S) and ammonium molybdenum tetrahydrate ($(NH_4)_6Mo_7O_{24}$) were used as the sources to synthesize ZnS and Mo-doped ZnS nanoparticles.

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. 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 heated in oven 80 ^{0}C. Then, the obtained white powders were grinded using a mortar to get ZnS nanoparticles.

For preparing Mo-doped ZnS nanoparticles; a certain amount of $(NH_4)_6Mo_7O_{24}$ was added onto aqueous solution of Zn (CH_3COO). $2H_2O$ and then followed the same procedure mentioned above.

Incident photon to electron conversion efficiency (IPCE) measurement was performed by using PCE-S20 with a monochromatic light source consisting of a 150-W Xe lamp and a monochromator. Structural properties of nanoparticles were characterized by x-ray diffraction on a Rigaku x-ray diffractometer with Cu K_α (λ= 154,059 pm) radiation. Optical characterization was performed by ultraviolet-visible on a Perkin-Elmer Lambda 2. The elemental analysis was studied by energy dispersive x-ray measurement (JEOL JSM 5800).

3. Results and discussions

Fig. 1 (a-b) indicates the recorded XRD patterns for ZnS and Mo-doped ZnS nanoparticles. The observed three broad diffraction patterns correspond to the (111), (220) and (311) planes of zinc blende structure of ZnS. The obtained result is consistent with standard data (JCPD No: 65-9585). It was not observed any diffraction patterns in XRD patterns of Mo-doped ZnS nanoparticles corresponding to Mo compounds or oxides.

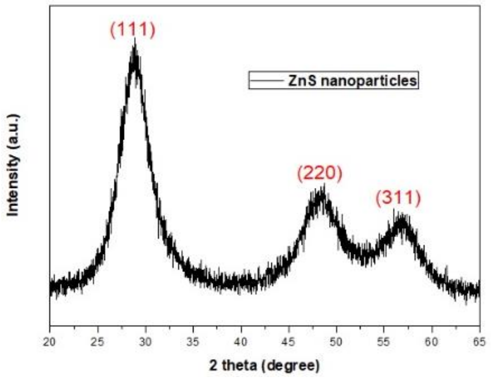


Fig. 1a. The recorded XRD patterns for ZnS nanoparticles

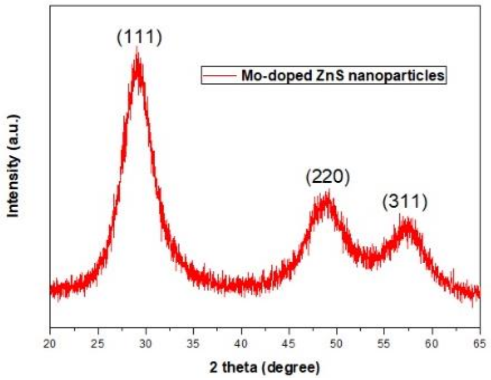


Fig. 1b. The recorded XRD patterns for Mo-doped ZnS nanoparticles

The average particle sizes of ZnS and Mo-doped ZnS nanoparticles, calculated from the full width at half height of diffraction peaks using Debye-Scherrer's relation given in Equation 1, are 2.70 and 2.68 nm, respectively.

$$d = 0.9 \lambda / (\beta \cos\theta) \tag{1}$$

where d is the mean size of quantum dots, λ is the wavelength of x-ray, β is the broadening measured as the full width at half maximum (FWHM) in radians, and θ is Bragg's diffraction angle.

The recorded room temperature optical absorption spectra for ZnS and Mo-doped ZnS nanoparticles are shown in Fig. 2 (a-b).

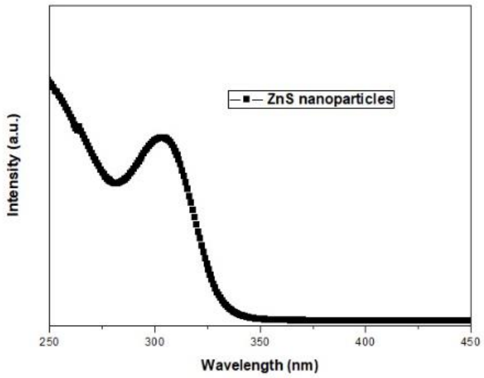


Fig. 2a. The recorded room temperature optical absorption spectra for ZnS Nanoparticles

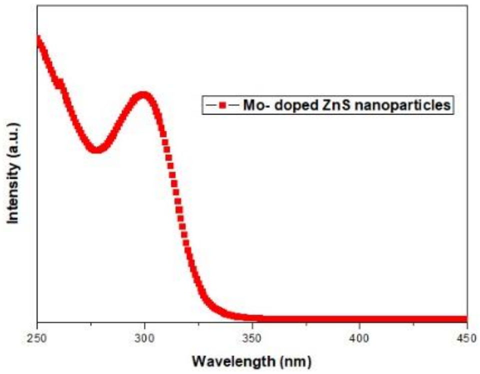


Fig. 2b. The recorded room temperature optical absorption spectra for Mo-doped ZnS nanoparticles

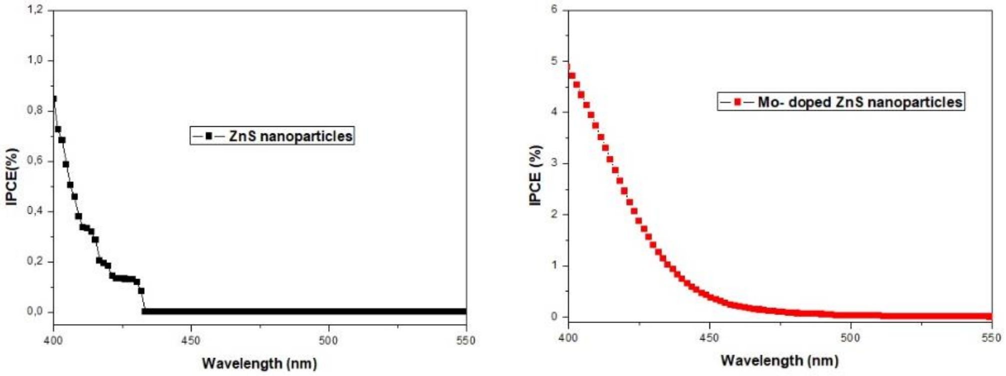
It can be clearly seen that the absorption peak of ZnS nanoparticles due to band-edge absorption is located at around 304 nm (4.07 eV). The obtained band dap value for ZnS nanoparticles is higher than the band gap value of bulk ZnS (3.68 eV). Thus, it can be said that there is the quantum confinement effect on the band gap of nanoparticles. Similar absorption spectrum was observed for Mo-doped ZnS nanoparticles but the absorption band is located at 297 nm (4.17 eV) is slightly shifting to shorter wavelengths (blue-shift). The ionic radius of (60 pm) Mo^{6+} ions are lower than ionic radius of (75 pm) of Zn^{2+} ions. This situation can be reason behind the blue shift in optical absorption spectrum of Mo-doped ZnS nanoparticles. Moreover, it confirms the replacement of Zn ions with doped Mo ions in the ZnS lattice.

The energy dispersive x-ray (EDX) spectrum was used to confirm the elemental compositions of ZnS and Mo-doped ZnS nanoparticles. The elemental percentages for both samples obtained from EDX patterns are given in Table 1.

Table 1. The elemental percentages for ZnS and Mo-doped ZnS nanoparticles

Elements	Elemental percentages for ZnS nanoparticles	Elemental percentages for Mo doped ZnS nanoparticles
Zn	48.18	48.91
S	51.52	50.25
Mo	-	0.84

Incident photon to electron conversion efficiency (IPCE) can evaluate the charge generation and collection of the solar cell. Fig. 3(a-b) display the IPCE(%) spectra for ZnS and Mo-doped ZnS nanoparticles.



a) *b)*

Fig. 3. The recorded IPCE spectra for a) ZnS and b) Mo-doped ZnS nanoparticles

There are two observations should be noted. One of is that nanoparticles with smaller particle size have better incident photon to electron conversion efficiency. The obtained IPCE (%) values at 400 nm for Mo-doped ZnS and ZnS nanoparticles are 4.71 % and 0.90%, respectively. The second is that the spectral response range of Mo-doped ZnS wider than ZnS nanoparticles. The introduction of impurities of dopant enhances the spectral response of the nanoparticles [23]. So that more electrons transferred to the external circuit and the generation of dark current is also suppressed.

Furthermore, the increment in the IPCE (%) value may base on the mid-gap states created by Mo doping which reduces the recombination of photo-excited carriers, blocks the interfacial recombination of the injected transfer from TiO_2 to polysulfide electrolytes and enhances the capture for electrons. Thus, our result suggests that Mo additive material plays important role to improve the efficiency of ZnS based solar cells.

4. Conclusions

ZnS and Mo- doped ZnS nanoparticles were synthesized at room temperature by co-precipitation method without any capping agent. The crystal structures of the synthesized ZnS and Mo-doped ZnS nanoparticles were determined to be zinc blend by XRD measurement. The calculated average crystal sizes are 2.70 and 2.68 nm for ZnS and Mo-doped ZnS nanoparticles, respectively. As a result of optical absorption measurements, it was observed that Mo dopant affects the energy band gap value of ZnS nanoparticles. The band gap value for ZnS and Mo-doped ZnS nanoparticles was determined as 4.07 and 4.17 eV, respectively.

EDX measurement indicated that elemental percentages of Zn, S and Mo in the Mo-doped ZnS nanoparticles are 48.91, 50.25 and 0.84, respectively. The photovoltaic properties of Mo-doped ZnS nanoparticles were investigated for the first time in this study. The obtained IPCE (%) values for ZnS and Mo- doped ZnS nanoparticles are 0.9 and 4.71, respectively. Consequently, our study suggests a new way to improve performance of ZnS- based solar cell structure.

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