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SYNTHESIS OF COBALT-ALLOYED ZnS QUANTUM DOTS AND INVESTIGATION OF THEIR CHARACTERISTICS

SINTEZA S KOBALTOM LEGIRANIH ZnS KVANTNIH PIK IN RAZISKAVA NJIHOVIH ZNAČILNOSTI

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Co-alloyed ZnS quantum dots were synthesized with the coprecipitation technique at 300 K. The measurements of current density versus voltage and incident photon to electron-conversion efficiency showed that Co-alloyed ZnS quantum dots could be utilized as the materials to boost the performance of devices. Furthermore, the magnetic, optical and structural characteristics of Co-alloyed ZnS quantum dots were investigated. It was determined that Co-alloyed ZnS quantum dots have a cubic structure and their size is 2.71 nm, which is smaller than the size of pure ZnS quantum dots (2.72 nm). Optical studies revealed that the absorption and emission of Co-alloyed ZnS quantum dots are blue shifted compared to pure ZnS quantum dots. The magnetization versus magnetic field measurement indicated that Co-alloyed ZnS quantum dots show ferromagnetic behavior at 300 K. As a conclusion, this study proposes that Co-alloyed ZnS quantum dots could be convenient for optical and magnetic applications.

Keywords: ferromagnetism, quantum dots, photovoltaic characteristics, semiconductor

Avtorji prispevka so sintetizirali s Co legirane kvantne pike (točke oz. tvorbe nanometrske velikosti) s koprecipitacijsko tehniko pri 300 K. Meritve odvisnost gostote toka od napetosti in učinkovitosti zamenjave vpadnega fotona napram elektronu so avtorjem pokazale, da bi lahko s Co legirane ZnS kvantne pike koristno uporabili kot materiale, ki izboljšajo (ojačajo) delovanje naprav. Nadalje so avtorji raziskovali magnetne, optične in strukturne lastnosti s Co legiranih ZnS kvantnih pik. Ugotovili so, da imajo le-te kubično strukturo in da je njihova velikost 2,71 nm, kar je manj kot je velikost čistih (nelegiranih) ZnS pik (2,72 nm). Optične študije so pokazale, da je absorpcija in emisija s Co legiranih ZnS kvantnih pik premaknjena v modro v primerjavi z nelegiranimi ZnS kvantnimi pikami. Meritve magnetizacije v odvisnosti od jakosti magnetnega polja pa so pokazale, da se pri 300 K s Co legirane ZnS kvantne pike obnašajo kot feromagnetiki. V zaključku avtorji pričujoče študije ugotavljajo, da bi lahko bile s Co legirane ZnS kvantne pike primeren material v napravah za optične in magnetne aplikacije.

Ključne besede: feromagnetizem, kvantne pike (točke), fotovoltaične karakteristike, polprevodnik

1 INTRODUCTION

During the past decades, the progression of the preparation and characterization of quantum dots revealed new dimensions of physics and provided possibilities for the production of new materials.[1,2] ZnS is an omnipresent semi-conductor that is commonly studied as a vigorous material for optoelectronics and energy applications because of its better chemical stability and environmental friendliness compared to the other chalcogenides.[3,4] At the same time, the wide band range of ZnS quantum dots limits their use in devices as sensitizers.

Alloyed quantum dots, diluted magnetic semiconductors, are a new class of luminescent materials for the applications of nanocomposite materials with new opportunities for research.[5,6] ZnS quantum dots alloyed with Mn (manganese), Cu (copper), Ni (nickel) and Co (cobalt) have been synthesized and their characteristics have been widely investigated.[6–9] Recently, Co has been used as a doping material in ZnS quantum dots. P. Yang et al.[10] examined the optical characteristics of Co-alloyed ZnS quantum dots. They reported that Co^{2+} and Co^{3+} alloyed ZnS quantum dots emit visible light. P. Yang et al.[10] observed that Co- and Cu-alloyed ZnS quantum dots indicate a boost in the photoluminescence emission.

In addition, diluted magnetic semiconductors can result in covetable material characteristics used for magnetic applications.[11] J. M. D. Coey et al.[12] stated that in diluted magnetic semiconductors, acting as usual semiconductors, the magnetization might be induced by the exchange interactions facilitated by free carriers. The nature of dopants and the synthesis techniques cause ferromagnetism in diluted magnetic semiconductors.[13,14] There are only few articles on the magnetic characteristics of Co-alloyed ZnS. S. Kumar et al.,[15] S. Sambaviaam et al.[13] and M. Lu et al.[16] stated that ZnS alloyed with Co^{2+} ions show ferromagnetic behavior. M. Lu et al.[16] also observed that ferromagnetism increases in Co-alloyed ZnS as the Co concentration is increased.

There are few published papers about the photovoltaic characteristics of alloyed ZnS quantum dots while pure and doped quantum dots have been widely used as sensitizers in devices.[17–19] It was reported that Mn, Eu and Fe alloyed ZnS quantum dots play a noteworthy role

in enhancing incident photon to the current efficiency value.[6,20,21]

In this study, the synthesis and characterization of Co-alloyed ZnS quantum dots are reported. The photovoltaic characteristics of Co-alloyed ZnS quantum dots were investigated for the first time.

2 EXPERIMENTAL PART

The technique used in the previous study was used to synthesize ZnS quantum dots.[6] With a typical wet chemical method, 0.1-M Zn $(CH_3COO).2H_2O$ was dissolved in 40-ml dimethylsulfoxide (DMSO); then 0.5 mL of 1-thioglycerol was added dropwise into the mixture at 300 K. Then a 10-mL aqueous solution of Na_2S was injected into the above solution. The solution was stirred at 300 K for several hours to obtain a homogeneous mixture of ZnS. ZnS quantum dots were separated from the solution by adding non-solvent acetone; then they were centrifuged and rinsed several times to get rid of any un-reacted ions remaining outside the clusters.

For the preparation of Co-alloyed ZnS quantum dots, a 0.003-M aqueous solution of Co $(CH_3COO)_2.4H_2O$ was added to the solution of Zn $(CH_3COO).2H_2O$ and then treated in a similar way.

Magnetic, optical and structural characteristics of Co-alloyed ZnS quantum dots were characterized with the instruments described in our previous study.[22]

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

$$d = 0.9\,\lambda / (\beta\cos\theta) \quad (2)$$

3 RESULTS

Table 1: a for ZnS and Co-alloyed ZnS quantum dots

Samples (quantum dots)	Plane	Pattern site (degree)	a (nm)
ZnS	(111)	28.88	0.536
Co-alloyed ZnS	(111)	29.03	0.532

Table 2: Values of V_{OC}, J_{SC}, *FF* and η % for ZnS and Co-alloyed ZnS quantum dots

Samples (quantum dots)	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF*	η %
ZnS	0.57	1.39	0.48	0.92
Co-alloyed ZnS	0.59	3.21	0.50	1.83

4 DISCUSSION

X-ray diffraction patterns for ZnS and Co-alloyed ZnS quantum dots are presented in **Figure 1**. The obtained three patterns show that the samples have a cubic phase of ZnS (JCPD no: 65-9585). It was observed that the structure of ZnS quantum dots remains same after the Co-doping. This situation reveals that the cubic structure of ZnS quantum dots is not changed due to the introduction of Co into the ZnS lattice.

The lattice constant for the samples, a, was calculated using Equation (1).

The pattern site and lattice constant for the (111) plane for the samples are shown in **Table 1**.

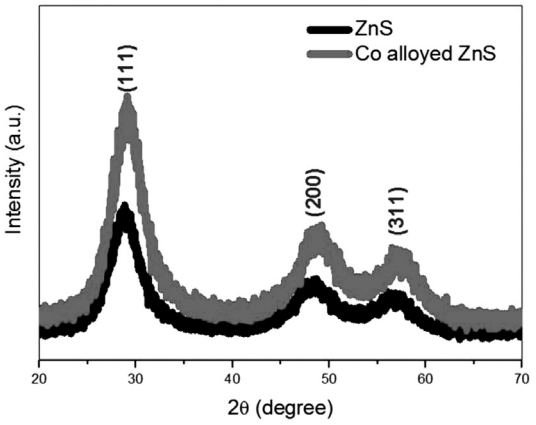

Figure 1: X-ray diffraction patterns for ZnS and Co-alloyed ZnS quantum dots

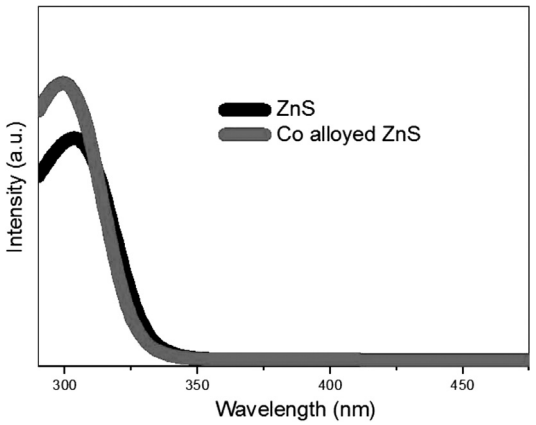

Figure 2: Absorption spectra for ZnS and Co-alloyed ZnS quantum dots

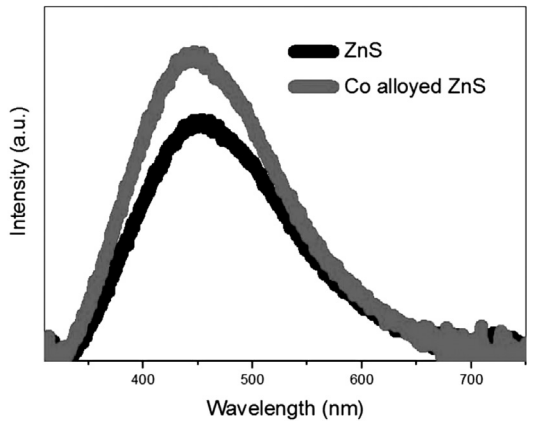

Figure 3: Photoluminescence spectra for ZnS and Co-alloyed ZnS quantum dots

As can be seen from **Table 1**, the diffraction peak corresponds to the (111) plane of Co-alloyed ZnS quantum dots, shifted a little toward the high angle compared with that of ZnS quantum dots. This feature suggests that the Co^{2+} ions substitute the Zn^{2+} ions, resulting in a reduced lattice constant. All the patterns of ZnS and Co-alloyed ZnS quantum dots show that the size of the pure ZnS and Co-alloyed ZnS quantum dots becomes smaller. The average particle size of quantum dots was calculated from the pattern widths using the relation given as Equation (2).

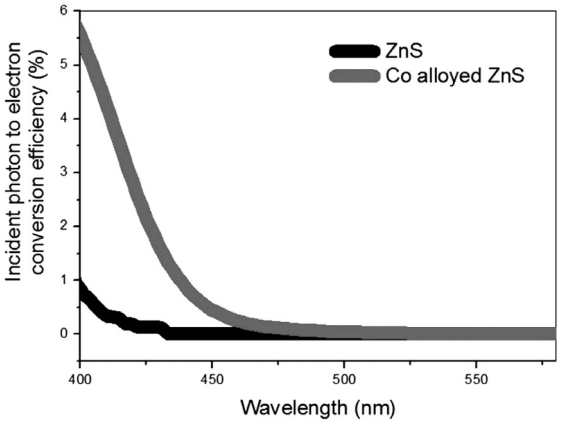

Figure 4: Incident photon to current efficiency spectra for ZnS and Co-alloyed ZnS quantum dots

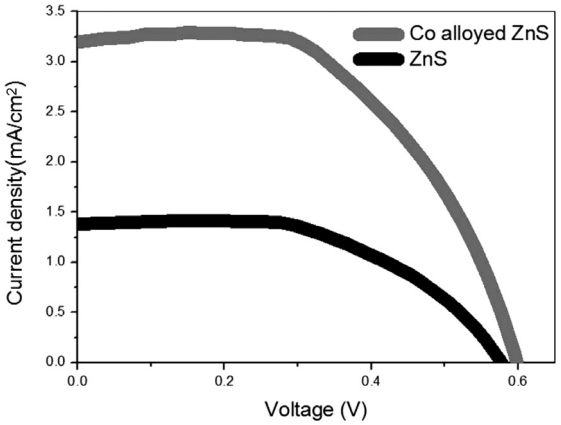

Figure 5: Current density/voltage plot for ZnS and Co-alloyed ZnS quantum dots

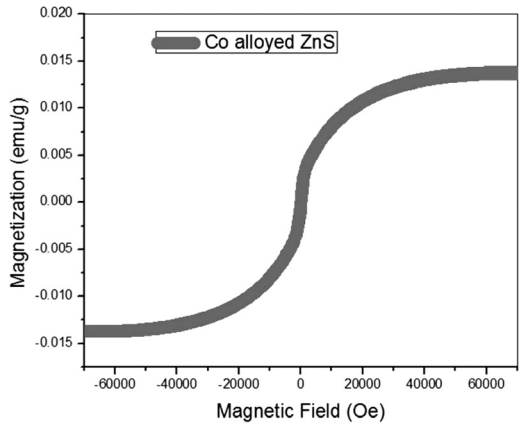

Figure 6: Magnetic hysteresis of Co-alloyed ZnS quantum dots at 300 K

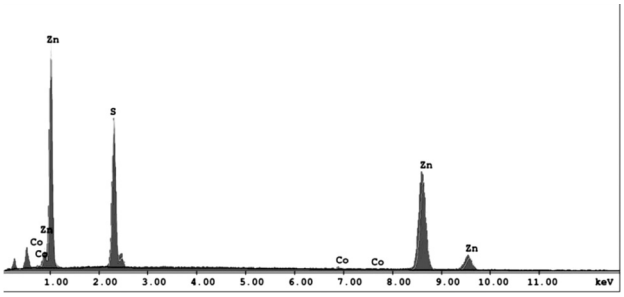

Figure 7: Energy-dispersive x-ray spectrum for Co-alloyed ZnS quantum dots

The size of ZnS and Co-alloyed ZnS quantum dots found from the pattern width is 2.72 nm and 2.71 nm, respectively. This result, which is in good agreement with the investigation of S. Kumar et al.,[23] indicates that the reduction in the particle size is clearly caused by the rise in the full width at half maximum of the quantum-dot patterns due to the size effect.

The optical-absorption spectra for ZnS and Co-alloyed ZnS quantum dots are shown in **Figure 2**. It can be seen that the absorption peak for ZnS quantum dots, owing to the band-edge absorption, is located at around 304 nm (4.07 eV), as it is of a higher energy than the band gap of bulk ZnS (3.68 eV) and consistent with the quantum-confinement effect on the band gap of quantum dots. The peak position for Co-alloyed ZnS was found to be 299 nm (4.15 eV).

The reason for the blue shift was explained by Kumar et al.[23] They reported that the blue shift in Co-alloyed ZnS quantum dots could be due to the fact that Co^{2+} ions (70 pm) have a smaller radius than the substituted Zn^{2+} (74 pm). It can be said that different energy stages are formed in the energy band of Co-alloyed ZnS quantum dots. This confirms the substitution of Zn ions with alloyed Co ions in the ZnS matrix.

Photoluminescence gives us information about the energy states of impurities and defects and helps us explore the optical characteristics of quantum dots. **Figure 3** indicates photoluminescence spectra for ZnS and Co-alloyed ZnS quantum dots obtained at a 310-nm excitation wavelength.

A broad emission peak located at 452.5 nm was observed for ZnS quantum dots. This peak is related to the radiative recombination involving defect states in ZnS owing to the absence of Zn^{2+} or S^{2-} ions in the ZnS lattice. Similar results were obtained by S. Sapara et al.,[24] N. Karar et al.[25] and W. Chen et al.[26] They reported that the photoluminescence emission peak of ZnS could be attributed to native impurities, the de-excitation of defect states and donor-acceptor pairs in ZnS.

A photoluminescence-emission peak was observed at 444.8 nm for the Co-alloyed ZnS. It is blue shifted compared to ZnS. The reduction in size, as a result of the quantum-confinement effect, could be the reason for this shifting. It should be noted that the Co-dopant plays an important role in enhancing the fluorescence efficiency of ZnS. This result is consistent with the result reported by Yang et al.[10]

Plotting incident photon to electron conversion efficiency can help us evaluate the charge generation and collection of solar cells. **Figure 4** indicates the incident photon to electron conversion efficiency spectra for ZnS and Co-alloyed ZnS quantum dots.

Two observations should be noted. One of them is the fact that quantum dots with a smaller particle size have a better incident photon to electron conversion efficiency. The values obtained at 400 nm for Co-alloyed ZnS and ZnS quantum dots are 5.5 % and 1 %, respectively. The second observation is the fact that the spectral response range of the Co-alloyed ZnS is wider than that of the pure ZnS. T. Li et al.[27] reported that the introduction of impurities of the dopant enhances the spectral response of quantum dots. Thus, more electrons are transferred to the external circuit and the generation of dark current is also suppressed.

Figure 5 demonstrates the current density/voltage characteristic of ZnS and Co-alloyed ZnS quantum dots.

It is clear that Co-alloyed ZnS shows a significant improvement in the efficiency. The open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and power-conversion efficiency (η %) correspond to the parameters of solar cells (see **Table 2**).

As shown in **Table 2**, the calculated values of η % for ZnS and Co-alloyed ZnS quantum dots are 0.92 and 1.83, respectively. The increment in η % may be based on the mid-gap states created by Co-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 the Co-dopant plays an important role in improving the efficiency of ZnS-based solar cells.

Figure 6 demonstrates the magnetization (M)/magnetic field (H) curve for the Co-alloyed ZnS quantum dots measured at 300 K.

As seen, the M-H curve for the Co-alloyed ZnS quantum dots indicates ferromagnetic behavior. The reasons of the ferromagnetism could be the intrinsic coupling between the doped Co-atoms and aggregated Co-atoms in the ZnS lattice or the sulfur vacancies and zinc interstitials.[28,29] Other reasons could be ruled out because no secondary phases were observed during the X-ray diffraction analysis.

The energy-dispersive X-ray spectrum was used to confirm the elemental compositions of Co-alloyed ZnS quantum dots. The peaks obtained from the energy-dispersive X-ray spectrum for Co-alloyed ZnS quantum dots are shown in **Figure 7**, and they are associated with Zn, S and Co. The obtained energy-dispersive x-ray results proved that the Co content was successfully alloyed with the ZnS quantum dots.

5 CONCLUSIONS

The magnetic, optical, structural and photovoltaic characteristics of ZnS and Co-alloyed ZnS quantum dots were investigated. ZnS and Co-alloyed ZnS quantum dots have a cubic structure and the particle size of the Co-alloyed ZnS quantum dots (2.71 nm) is smaller than that of the ZnS quantum dots (2.72 nm). Optical-absorption spectra revealed that the absorbance of Co-alloyed ZnS quantum dots is blue shifted compared to ZnS quantum dots. It was also observed that the enhancement of the photoluminescence intensity may be ascribed to the creation of new radiation centers or the size reduction caused by the Co-alloying in the ZnS matrix. The measurements of the incident photon to electron conversion efficiency and current density versus voltage showed that Co-alloyed ZnS quantum dots could be used as sensitizers to boost the performance of devices. The power-conversion efficiency (η %) obtained was 0.91 and 1.83 for ZnS and Co-alloyed ZnS quantum dots, respectively. Another important observation on the photovoltaic characteristics of Co-alloyed ZnS quantum dots is the fact that their spectral-response range is wider than that of ZnS quantum dots. The M-H measurements indicated that Co-alloyed ZnS quantum dots show ferromagnetic behavior at 300 K. The ferromagnetism observed for Co-alloyed ZnS quantum dots could be ascribed to the intrinsic coupling between the doped Co-atoms or the sulfur vacancies and zinc interstitials.

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