Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2026, т. 24, № 2, сс. 469–475
https://doi.org/10.15407/nnn.24.02.0469

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Надруковано в Україні.

PACS numbers: 61.05.cp, 61.82.Rx, 68.37.Og, 78.40.Fy, 78.67.Hc, 81.07.Ta, 82.35.Np

Effect of Swift Heavy-Ion Irradiation on ZnS Quantum Dots

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The effect of high-energy ion beams (swift heavy ions) on ZnS quantum dots embedded in a polyvinylpyrrolidone (PVP) matrix is studied. A 100 MeV oxygen-ion beam is chosen for the irradiation experiment with doses of $2{\cdot}10^{11}$ and $4{\cdot}10^{11}$ ions/cm^2. As the ion dose increases, the optical absorption edge of the irradiated quantum dots shows a slight red shift compared to the unirradiated (virgin) samples. This shift suggests a minor change in the particle size due to ion irradiation, which is further confirmed by high-resolution transmission electron microscopy images.

Досліджено вплив високоенергетичних йонних жмутів (швидких важких йонів) на квантові точки ZnS, вбудовані у матрицю полівінілпіролідону (PVP). Для експерименту з опроміненням обрано жмут йонів Оксиґену з енергією у 100 МеВ із дозами у $2{\cdot}10^{11}$ та $4{\cdot}10^{11}$ йонів/см^2. Зі збільшенням дози йонів край оптичного вбирання опромінених квантових точок демонструє незначний червоний зсув порівняно з неопроміненими (чистими) зразками. Цей зсув свідчить про незначну зміну розміру частинок внаслідок йонного опромінення, що додатково підтверджується зображеннями високої роздільчої здатности, одержаними за допомогою просвітлювальної електронної мікроскопії.

Key words: ZnS, quantum dots, swift heavy ions, irradiation, nanotechnology.

Ключові слова: ZnS, квантові точки, швидкі важкі йони, опромінення, нанотехнології.

(Received 17 February, 2025)

1. INTRODUCTION

Swift heavy ion (SHI) irradiation is recognized as an effective technique for modifying the optical and electronic properties of quantum dots [1]. SHI typically causes ion implantation in crystalline structures, generating additional electronic states in the quantum-dots' band gap. This, in turn, impacts charge separation and recombination dynamics. ZnS thin films, an *n*-type semiconductor in the II–VI group, have a wide direct band gap of $E_g = 3.65$ eV (bulk). In this study, ZnS quantum dots are synthesized and irradiated with a 100 MeV oxygen-ion beam at two doses: $2{\cdot}10^{11}$, $4{\cdot}10^{11}$ [ions/cm^2]. Characterization of both irradiated and unirradiated samples is performed using optical absorption spectroscopy and XRD analysis. TEM results indicate that the particle size does not significantly change. The PVP capping layer prevents excessive growth of the quantum dots during synthesis but does not participate in the chemical reactions [2].

Furthermore, PVP and trace by-products from the reaction are water-soluble, allowing them to be removed by washing with distilled water and filtering the precipitate. The ZnS quantum dots are also irradiated with a 100 MeV Ni-ion beam at doses of $2{\cdot}10^{11}$, $4{\cdot}10^{11}$ ions/cm^2. The fluence rate, defined by the exposure time to high-energy radiation, is detailed in Table 1. Higher ion-irradiation doses are avoided, as SHI produces heat, potentially melting the sample and making it unsuitable for further study.

2. EXPERIMENTAL

Preparation of ZnS Sol. To prepare the ZnS sol, 3 grams of $ZnCl_2$ are dissolved in 100 mL of double-distilled water and heated for 4 hours at a temperature between 70°C and 80°C. The solution is degassed by bubbling nitrogen gas through it for 3 hours. Afterward, a few drops of HNO_3 are added, followed by moderate stirring. Simultaneously, an aqueous solution of Na_2S is prepared by dissolving 3 grams of Na_2S pellets in 100 mL of double-distilled water. This Na_2S solution is then slowly added to the $ZnCl_2$ solution using a

TABLE 1. SHI irradiation dosage with respect to time of exposure.

Ion dose, ions/cm^2	Fluence in terms of time, sec.
0	0
$2{\cdot}10^{11}$	32
$4{\cdot}10^{11}$	64

dropper until the mixture becomes milky white. The solution is left in a dark chamber at room temperature for 12 hours to stabilize. This results in a white solution containing ZnS quantum dots.

Preparation of PVP Matrix. A 4-gram amount of powdered polyvinylpyrrolidone (PVP) is dissolved in 100 mL of double-distilled water. The solution is stirred with a magnetic stirrer for 4 hours at 80°C until it becomes transparent, then, kept in a dark chamber for 2 hours for stabilization.

Synthesis of ZnS Quantum Dots in PVP Matrix. 20 mL of the PVP matrix is mixed with 10 mL of the prepared ZnS solution. The mixture is heated and stirred for 2 hours at a stirring rate of 200 rpm. Afterward, it is kept in a dark chamber for 12 hours to ensure complete reaction. This one results in the synthesis of ZnS quantum dots embedded in the PVP matrix. The liquid mixture is then cast onto a laboratory glass substrate to form a thin film, which is dried in an oven [3].

Irradiation of Samples. Thin films of ZnS quantum dots, with dimensions of 1×1 cm^2, are prepared for irradiation. One sample is reserved as an unirradiated (virgin) specimen. The irradiation is carried out on two identical samples, mounted on a vacuum-shielded vertical ladder. These samples are irradiated under high vacuum ($4.6\cdot10^{-6}$ Torr) in the material sciences chamber, using a 100 MeV oxygen-ion beam with a beam current of approximately 1.0 pnA (particle nanoampere), provided by the 15UD tandem pelletron accelerator at IUAC, New Delhi, India. The ion fluence (dose) is varied between $2\cdot10^{11}$ and $4\cdot10^{11}$ ions/cm^2 [4].

Characterization of Synthesized Samples. The synthesized samples are characterized using UV/Vis spectrophotometry, x-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM). The ion beam-induced effects are analyzed based on the absorption edge, measured using a Perkin Elmer Lambda 35 UV-VIS spectrophotometer in the range of 190–900 nm. X-ray diffraction patterns are obtained using a Bruker AXS x-ray source (CuK_α), and HRTEM analysis is conducted using a JEM 1000 C XII microscope.

3. RESULTS AND DISCUSSIONS

The absorption spectra of the synthesized ZnS quantum dots are presented in Fig. 1. From the figure, it can be seen that the undoped ZnS exhibits a prominent absorption edge at 225 nm, which is identified by drawing a tangent from the point, where there is a sudden increase in absorption (as shown in Fig. 2) until it intersects the x-axis.

The spectra of the irradiated samples show a slight shift in the strong absorption edges compared to the virgin sample. This sug-

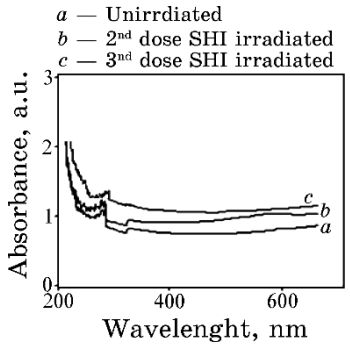

Fig. 1. UV–Visible absorption spectroscopy of (*a*) pristine ZnS and ZnS quantum dots irradiated with (*b*) 1st dose and (*c*) 2nd dose.

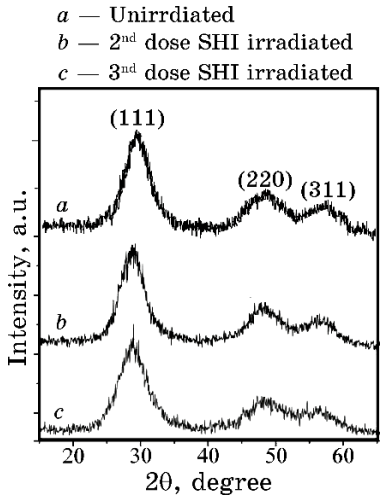

Fig. 2. XRD spectra of ZnS specimen; *a*, *b*, *c* correspond to virgin sample and samples irradiated by 1st and 2nd dose of oxygen SHI, respectively.

gests a minor agglomeration of particles in the specimen following ion irradiation. The nanoband gap of the quantum dots (E_{gn}) is determined from the absorption edge using the formula $E_{gn} = hc/\lambda$, where $hc = 1.12$ eV and λ represents the absorption edge value [5]. The particle size is estimated from the absorption edge using the Hyperbolic Band Model (HBM) [6]:

$$R = \sqrt{\frac{2\pi^2 h^2 E_{gb}}{m^* \left(E_{gn}^2 - E_{gb}^2\right)}}, \tag{1}$$

where R is radius of quantum dot, E_{gb} is bulk band gap, E_{gn} is quan-

tum-dot band gap, h is Planck's constant, m^* is effective mass of specimen (for ZnS, $3.64 \cdot 10^{-31}$ kg). This model yields the average particle sizes (virgin and irradiated samples) at around 10 nm.

The XRD characteristics of synthesized ZnS quantum-dot samples are shown in Fig. 2. The approximate (average) size of the particle is calculated by using the 'Debye–Scherrer formula' [7]:

$$D = \frac{0.9\lambda}{W \cos\theta}. \quad (2)$$

The equation involves λ, the wavelength of the x-ray (0.1541 nm), and θ, the glancing angle. W and D represent the full width at half maximum ($FWHM$) and the particle diameter (crystallite size), respectively.

The crystalline planes associated with the first, second, and third XRD peaks correspond to (111), (220), and (311), respectively [9]. The average particle size of the synthesized quantum dots, as estimated from the XRD spectra and diffractogram peaks, falls within the range from 9.61 nm to 11.2 nm. Additionally, by comparing the obtained XRD peaks with the standard data from the International Center for Diffraction Data (ICDD) card number JCPDS 00.001.0792, it is confirmed that the peaks match those of standard ZnS. This indicates that the quantum dots possess a Wurtzite crystalline structure [8]. Quantum-dots' formation and sizes are confirmed by taking the high-resolution transmission electron microscope (HRTEM) images of the prepared samples. It can be observed in Fig. 3 that the size of synthesized ZnS quantum dots is of around 10 nm, which is in close agreement with that of the estimated sizes obtained from absorption spectroscopy and XRD.

Table 2 presents the absorption edge, particle size estimated by the Hyperbolic Band Model, Scherrer formula, and HRTEM for different samples of ZnS quantum dots (both virgin and irradiated). The estimated values are in close agreement to the original size as determined from the HRTEM images. Below, it is the data from Table 2, analyzed from the results.

4. CONCLUSIONS

The study successfully investigates the effect of swift heavy ion (SHI) irradiation on ZnS quantum dots embedded in a polyvinylpyrrolidone (PVP) matrix. The synthesis of ZnS quantum dots and their subsequent irradiation with 100 MeV oxygen-ion beams at two different doses (of $2 \cdot 10^{11}$ and $4 \cdot 10^{11}$ ions/cm^2) have demonstrated notable changes in their optical properties.

The absorption spectra of irradiated quantum dots exhibit a

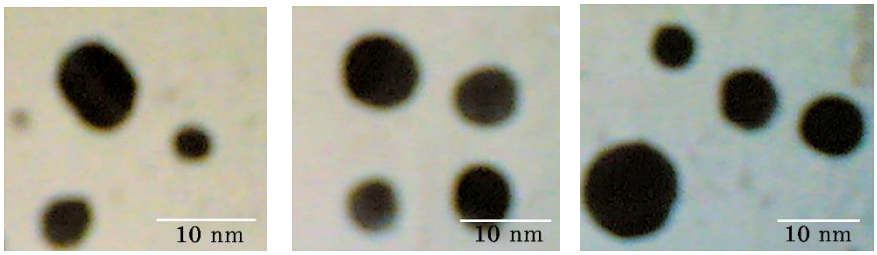

Fig. 3. HRTEM images of ZnS specimen *a*, *b*, *c* correspond to virgin sample and samples irradiated by 1st and 2ndose of oxygen SHI, respectively.

TABLE 2. The absorption edge, particle size estimated by the Hyperbolic Band Model (HBM), Scherrer formula, and HRTEM for different samples of ZnS quantum dots (both virgin and irradiated).

Sample	Ion dose ions/cm^2	Absorption edge, nm	E_{gn}, eV	Size from HBM = 2R, nm	Size from Scherrer formula, nm	Size from HRTEM, nm
ZnS	0	225	5.4	7	8.2	10
SHI irradiated ZnS	$2{\cdot}10^{11}$	250	4.48	7.8	9.4	12
SHI irradiated ZnS	$4{\cdot}10^{11}$	340	3.29	9.5	13.5	16

slight red shift in the absorption edge compared to the unirradiated samples, indicating a change in particle size due to ion irradiation. This red shift is further confirmed by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) results, which suggest the formation of quantum dots with a size range from 9.6 to 11.2 nm, consistent with the values derived from the absorption edge.

The XRD analysis confirmed that the quantum dots retain a Wurtzite crystalline structure after irradiation, with peaks matching the standard ZnS data. The increase in particle size with increasing irradiation dose suggests slight agglomeration of the quantum dots. Moreover, the calculated nanoband gap values further support these findings, indicating that ion irradiation has an influence on the electronic structure of the quantum dots.

The results of this study offer valuable insights into the effects of SHI irradiation on the properties of ZnS quantum dots, which can be utilized to tailor the properties of quantum dots for specific applications in optoelectronics, sensors, and photovoltaics. Further research is needed to explore the long-term effects of higher irradiation doses and the potential for modifying quantum-dot properties through different ion-beam parameters.

ACKNOWLEDGMENT

The authors would like to thank Central Instrument Lab (CIL), Assam University, Assam, India for providing the instrumental set up for the experiment.

REFERENCES

1. S. S. Nath, D. Chakdar, and G. Gope, AZojomo *Journal of Materials Online*, https://doi.org/10.2240/azojono0128
2. A. Ganguly, S. S. Nath, and V. M. Srivastava, *Chalcogenide Lett.*, **17**, No. 10: 487 (2020); https://doi.org/10.15251/CL.2020.1710.487
3. Bharati Debnath, Ganga Halder, and Sayan Bhattacharyya, *Sci. Adv. Mat.*, **6**, No. 6: 1160 (2014); https://doi.org/10.1166/sam.2014.1881
4. Soumee Chakraborty, S. Dhara, T. R. Ravindran, S. Sarkar Pal, M. Kamruddin, and A. K. Tyagi, *AIP Advances*, **1**: 032135 (2011); https://doi.org/10.1063/1.3628347
5. Pralay K. Santra and Prashant V. Kamat, *J. Am. Chem. Soc.*, **134**, Iss. 5: 2508 (2012); https://doi.org/10.1021/ja211224s
6. Houcine Labiadh and Slah Hidouri, *J. King Saud Univ.-Sci.*, **29**, No. 4: 444 (2017); https://doi.org/10.1016/j.jksus.2016.12.001
7. K. R. Nemade and S. A. Waghuley, *Results in Physics*, **3**: 52 (2013); https://doi.org/10.1016/j.rinp.2013.03.001
8. Abhigyan Ganguly, Saradindu Panda, Siddhartha Sankar Nath, and Gautam Gope, *Nanosistemi, Nanomateriali, Nanotehnologii*, **22**, Iss. 1: 85 (2024); https://doi.org/10.15407/nnn.22.01.085