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# ENHANCED EFFICIENCY IN SWIFT 100 MeV Ni ION IRRADIATED ZnS QUANTUM DOT SENSITIZED SOLAR CELL

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The influence of high energy ion beam (swift heavy ion) on ZnS quantum dots used as a sensitizer in a solar cell, is studied in this article. 100MeV Nickel ($Ni^{7+}$) ion beam is utilized for the irradiation experiment with two doses of $1\times10^{11}$ ions/cm$^2$ and $2\times10^{11}$ ions/cm$^2$. The irradiated quantum dots are deposited as a sensitizing layer on a ZnO photoelectrode solar cell, and Current-density v/s Voltage characteristics is measured under illuminated condition. A higher value of current density is obtained for irradiated samples at a lower dose, while at a higher dose, the current density decreases. In addition, the other solar cell performance parameters are also reported for unirradiated, as well as irradiated quantum dot sensitized solar cells.

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*Keywords:* ZnS quantum dots, Ion irradiation, QDSSC.

## 1. Introduction

Quantum dot sensitized solar cells (QDSSCs) have recently emerged as a field of interest among researcher because of their impressive ability to harvest a wider range of sunlight and the multiple exciton generation from single-photon absorption, low-cost, simple fabrication, and size-dependent band gap tenability over a wide range [1]. In addition, their optical properties can be tailored by controlling the size of nanoparticles for maximizing solar absorption [2]. In most commonly used sensitized solar cells, organic dyes are used as sensitizers, which generally have strong absorbance in the range of 350–700 nm but only weak absorption in the IR region [3]. Also, organic dyes are costly and unstable towards water and oxygen. But in quantum dots (QDs) the size-dependent bandgap enables the harvest of the solar spectrum in both the visible and infrared regions [4]. Hence, semiconductor quantum dots are considered a suitable alternative to organic dyes as sensitizers in solar cell structures [5]. Fig. 1 shows the general structure and working of a typical QDSSC.

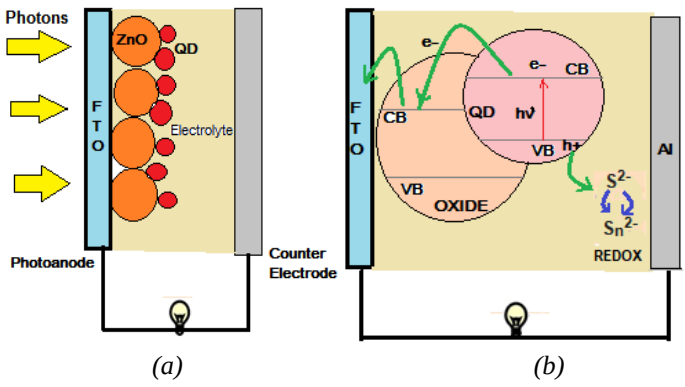


*Fig. 1. (a) General structure of a QDSSC, (b) Operation of a typical QDSSC.*

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The photovoltaic researchers are constantly looking for better and more efficient techniques to alter the quantum dot's electronic properties to harness a more efficient solar spectra utilization for solar cell applications. Swift Heavy Ion (SHI) irradiation is considered one of the most efficient methods of altering quantum dots' optical and electronic properties [6,7]. The SHI often results in ion implantation in crystal structures that lead to the creation of extra electronic states in the bandgap region of quantum dots, which affects the charge separation and recombination dynamics in the quantum dot sensitized solar cells (QDSSCs) [8]. It may also introduce crystal defects and intermediate energy states in the forbidden energy gap region that alters quantum dots' optical properties. The method of ion irradiation is highly controlled and the ion implantation amount is highly specific. Unlike chemical doping, which is generally carried out in quantum dots, the ion irradiation process is much more controlled. Hence, it is expected to give better results in terms of doping effects in quantum dots.

In the present report, the effect of swift heavy ion (SHI) irradiation of ZnS quantum dot with $Ni^{7+}$ ion beam is investigated as a solar cell sensitizer in a ZnO/ZnS based QDSSC. ZnS thin film is an n-type semiconductor in the II-IV group, characterized by wide direct bandgap energy of Eg = 3.65 eV (bulk). Chalcogenides are generally used in developing optoelectronic device structures because of their easy fabrication and optical absorption and emission properties. The effect of SHI irradiation of ZnS quantum dots as a sensitizing layer in solar cells has not been studied previously. In the present work, a simple chemical method is adopted for the synthesis of ZnS quantum dots on the polyvinylpyrrolidone (PVP) matrix. PVP capping layer restricts the growth of QDs during the synthesis process while it does not participate in the chemical reaction [9]. ZnS quantum dots are irradiated with 100 MeV Ni-ion beam of two doses of $1\times10^{11}$ ions/cm$^2$ and $2\times10^{11}$ ions/cm$^2$. A simple sol gel-based chemical bath deposition technique has been utilized for QDSSC fabrication. An improved current density- voltage characteristic is obtained for high voltage $Ni^{7+}$ ion irradiated quantum dot sensitizing layer, and thereby highly improved efficiency is reported in this article.

## 2. Experimental

The 6 gms of powdered PVP is dissolved in 100 ml of double-distilled water and stirred by a magnetic stirrer for 3 hrs at $80^0$C until a transparent viscous PVP solution is obtained. To prepare the ZnS solution, 4 gms of $ZnCl_2$ is dissolved in 100 ml of double-distilled water and heated at temperature 80 $^0$C for 3 hours. A few drops of $HNO_3$ are added following by moderated stirring to maintain the solution's pH value. $Na_2S$ solution is prepared on dissolving 3 gms of $Na_2S$ pallet in 100 ml of double-distilled water. This aqueous solution of $Na_2S$ is added dropwise to the solution of $ZnCl_2$ until the whole solution turns milky white. Finally, 20 ml of the previously prepared PVP sample is mixed with 10 ml of the ZnS solution. The mixture is heated and stirred for 2 hrs at the stirring rate of 200 rmp. Then the samples are separated into three separate portions. The irradiation experiment is carried out on two identical samples, while the third is kept unirradiated (pristine). Samples are irradiated (exposed) in the Material Sciences chamber under a high vacuum ($4.6 \times 10^{-6}$torr) by using the 100 MeV $Ni^{7+}$ ion beam with an approximate beam current of 1.0 pnA (particle Nano ampere). The ion doses used are $1 \times 10^{11}$ ions/cm$^2$ as the first dose and the second dose of $2 \times 10^{11}$ ions/cm$^2$.

To prepare the QDSSCs, ZnicAccetate ($ZnC_2H_3O_2$) and Sodium Hydroxide (NaOH) are mixed in ethanol to obtain ZnO. The ZnO is then deposited on three separates conductive FTO coated glass (resistivity <10 ohms/sq.) using tape template method and doctor's blade technique and are heated at $80^0$C for 1 hour and air annealed at 450 $^0$C. Thereafter, the three ZnO coated glass plate is dip-coated by immersing it in the previously prepared ZnS quantum dot solutions (pristine and irradiated), for around 60 seconds each to form ZnS QD layer on the oxide by chemical bath deposition (CBD). Few drops of polysulphide electrolyte solution (2M of $Na_2S$ and 3M S) [9] are then added on the ZnO-CdS deposited FTO glass plates sandwiched with a thin aluminum plate. Thin glass coverslips are used as spacers in between to prevent any short between the FTO and the aluminum counter electrode. The aluminum plate is held together with the FTO

photo-electrode by using scotch tapes and clips. Two metal crocodile probes were connected, one to the FTO plate and another to the aluminum plate.

The synthesized samples are tested by UV/VIS spectrophotometer, X-ray diffraction spectrometer, Atomic Force Microscopy (AFM), and High-Resolution Transmission Microscope (HRTEM). UV-vis light absorption spectra are obtained using Perkin Elmer Perkin Elmer Lamda 35 Ultraviolet-Visible (UV-vis) spectrophotometer and AFM using Nano scope 111a. X-ray diffraction (XRD) patterns are obtained from Bruker AXS with X-ray source: Cu Ka and HRTEM. Current-voltage relations of the fabricated solar cells are studied by using a multimeter (Keithley 2001). The photocurrent is measured under the illumination of a 500 W Xenon lamp (100 $mWcm^{-2}$) with an illumination area of 0.3 $cm^{-2}$.

## 3. Results and discussion

Optical absorption spectra of SHI irradiated and the pristine ZnS quantum dot samples, are shown in Fig. 2. It is clear that the spectra of irradiated samples exhibit a redshift in their absorption edges with respect to that of the pristine sample. This indicates small particle agglomeration in the specimen after ion irradiation, which increases the size of quantum dots. Also, from the absorption spectra, average particle sizes have been assessed theoretically by using the hyperbolic band model [10]:

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

where R is the quantum dot radius, $E_{gb}$ and $E_{gn}$ are the bulk bandgap and the quantum dot bandgap, respectively, m* is the effective mass of the specimen, h is Planck's constant (h-bar is reduced plank constant i.e h/2π). Here, the bulk bandgap ($E_{gb}$) for ZnS is 3.65eV, and electron effective mass at room temperature is 3.64 x $10^{-31}$ Kg [14]. The quantum dot band gaps ($E_{gn}$) of the prepared samples is determined as the bandgap corresponding to the absorption edge.

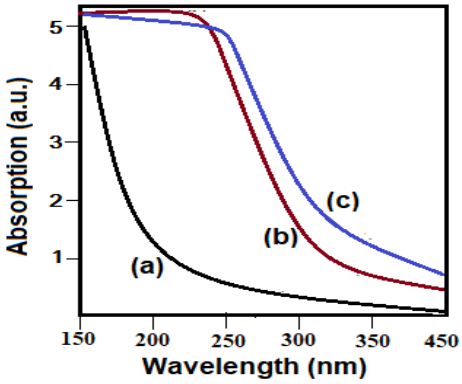



*Fig. 2. UV-Visible absorption spectroscopy of (a) pristine ZnS and ZnS quantum dots irradiated with (b) 1st dose and (c) 2nd dose.*

Similarly, from the X-ray diffraction study in Fig. 3, the average particle size (crystallite size) is calculated by using the Debye-Scherrer formula [11]:

$$D = \frac{0.9\lambda}{W\cos\theta} \tag{2}$$

'λ' is the wavelength of X-ray (0.1541 nm), 'W' is FWHM (full width at half maxima), 'θ' (theta) is the glancing angle, and 'D' is particle diameter (crystallite size). The crystalline planes corresponding to the XRD peaks are (111), (220), and (311). Considering all the peaks (2θ in degree) in the X-ray diffractogram, the average crystallite (quantum dot) size has been estimated to be 7.5 nm - 8.3 nm. By further analyzing the XRD with the help of ICDD (International Center Diffraction Data), it can be concluded that ZnS quantum dots are "wurtzite" in structure. HRTEM and AFM images of ZnS quantum dots are shown in Fig 4 and Fig. 5, respectively. It is evident in the HRTEM image (Fig. 4) that ZnS crystals (quantum dots) are circular with sizes varying from around 9 nm-20 nm. The AFM image shows an increase of roughness in surface morphology with increase in ion irradiation dosage.

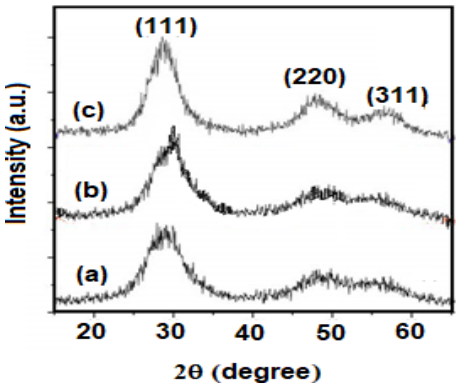
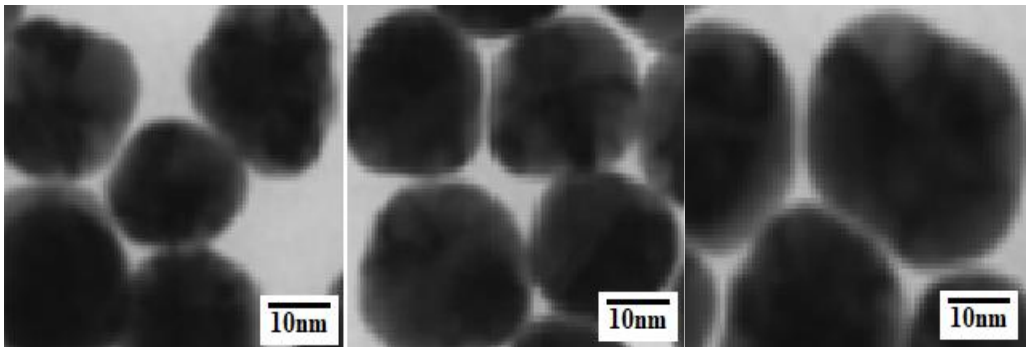



*Fig. 3. X-ray diffraction spectra of (a) pristine ZnS and ZnS quantum dots irradiated with (b) 1st dose and (c) 2nd dose.*

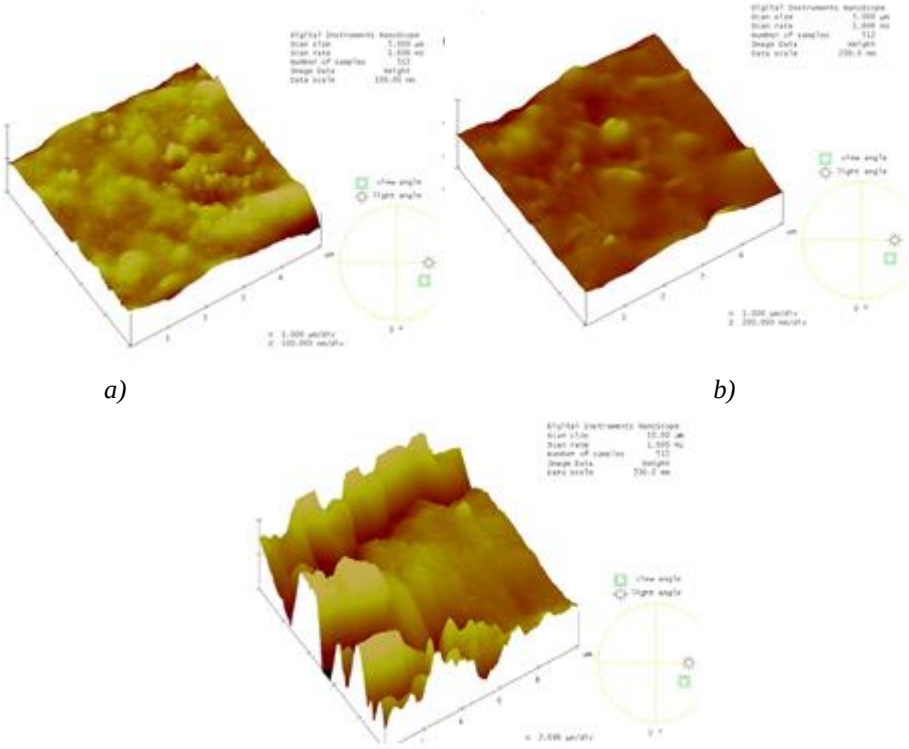
*Table 1. Data from optical absorption, XRD, and HRTEM for ZnS quantum dots.*

| Sample | Ion dose (ions/cm$^2$) | Fluence (sec.) | Absorption edge (nm) | Size from HBM (nm) | Size from Scherrer Formula (nm) | Size from HRTEM (nm) |
|---|---|---|---|---|---|---|
| ZnS | 0 | 0 | 206 | 11 | 10.1 | 10 |
| SHI irradiated ZnS | $1\times 10^{11}$ | 16 | 325 | 17.6 | 16.7 | 16 |
| SHI irradiated ZnS | $2\times 10^{11}$ | 32 | 338 | 20.8 | 19.6 | 22 |




*a)* *b)* *c)*

*Fig. 4. HRTEM image of (a) pristine ZnS and ZnS quantum dots irradiated with (b) 1st dose and (c) 2nd dose.*



*a)* *b)*

*c)*

*Fig. 5. AFM image of (a) pristine ZnS and ZnS quantum dots irradiated with (b) 1st dose and (c) 2nd dose.*

Fig. 6 shows the current density–voltage (*J–V*) characteristics for pristine ZnS and two dosages SHI of nickel ion irradiated quantum dot sensitized ZnO thin film based solar cells under white light illumination condition. It can be readily observed that there is a notable improvement in current density for 1st dosage (1 x $10^{11}$ ions/$cm^2$) of irradiation. This increase in current density may be attributed to the fact that due exposure to SHI, Ni ions get implanted into the ZnS quantum dots lattice contributing to the significant increase in current density value due to its transient electronic behavior [12, 13]. Nickel has a unique electronic configuration, [Ar]$3d^8 4s^2$, which results in electronic behavior contradictory to that predicted from the periodic table. In neutral atoms, the *n*s and *(n -1)d* orbitals are very close in energy with *n*s orbitals having slightly lower energy. Hence, Ni loses s electron before the d- electron. But in the case of ionic Ni, the energy of the *(n -1)d* orbitals is significantly less than that of the *n*s electrons. Therefore, the *n*s electron are removed first, leaving behind unpaired *d* electrons. The presence of unpaired d electron results in *d-d* transition in nickel ion when excited by a photon [8,14]. This *d-d* transition contributes to an enhancement in electron conduction resulting in an improved current density ($J_{sc}$) in Ni ion-implanted ZnS quantum dot sensitized solar cell [15]. But at higher ion irradiation dose (2 x $10^{11}$ ions/$cm^2$), crystal defects, ion penetration, and agglomeration of closely spaced quantum dots occur introducing crystal defects, which results in a decrease in the current density [14, 16].

The short circuit current density ($J_{sc}$) and open-circuit voltage ($V_{oc}$) is obtained from J–V curves obtained under white light illumination. Fill Factor (FF) and power conversion efficiency ($\eta$) is calculated by using the Eq. (3) and Eq. (4), respectively [17, 18]. Efficiency as high as 2.6% is obtained by irradiation of quantum dots, which is higher than that of the pristine ZnS QDSSCs and those previously reported ZnS-QD/ZnO based QDSSCs [19, 20]. The effect of Ni transition metal ion irradiation on ZnS quantum dots sensitized solar cells is studied for the first time in this

article and much higher efficiency operation has been obtained. The other solar cell parameters for pristine ZnS and the two irradiated ZnS QDSSCs are shown in Table 2.

$$FF = \frac{J\max . V\max}{Jsc.Voc} \tag{3}$$

$$\eta = \frac{Voc \times Jsc \times FF}{Pin} \tag{4}$$

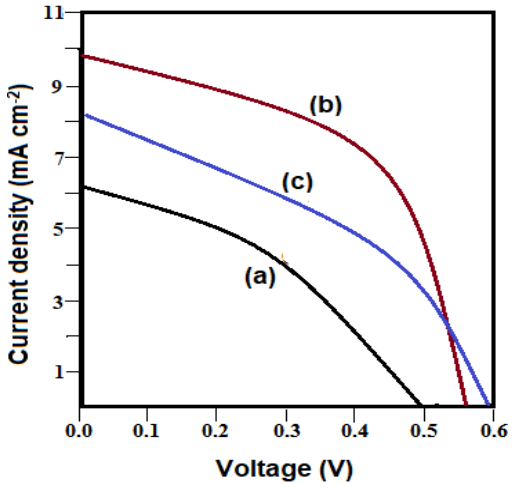



*Fig. 6. Current density- voltage characteristics of ZnO based QDSSC with (a) pristine CdS, and CdS quantum dots irradiated with (b) 1st dose and (c) 2nd dose, as a sensitizer.*

*Table 2. Photovoltaic parameters of pure ZnS and swift heavy ion of $Ni^{7+}$ irradiated ZnS quantum dot sensitized ZnO solar cells.*

| Samples | Ion dose (ions/cm$^2$) | Voc (V) | Jsc (mA cm$^{-2}$) | Fill Factor | η % |
|---|---|---|---|---|---|
| ZnS | 0 | 0.48 | 6.2 | 0.51 | 1.52 |
| ZnS:Ni 1st dosage | $1\times 10^{11}$ | 0.56 | 9.7 | 0.48 | 2.61 |
| ZnS:Ni 2nd dosage | $2\times 10^{11}$ | 0.6 | 8.3 | 0.38 | 1.9 |

## 4. Conclusions

ZnS quantum dots in the PVP capping matrix is synthesized via sol-gel chemical method. The quantum dots are irradiated with two different dosages of 100MeV swift heavy ion beam of Nickel ($Ni^{7+}$). The pristine and the SHI irradiated quantum dots are characterized by using UV-Visible absorption spectroscopy, XRD pattern, HRTEM, and AFM to reveal the effect of ion irradiation on the structural and optical properties of the samples.

The synthesized quantum dots are introduced on a ZnO thin film solar cell to act as a sensitizer. The solar cell parameters are obtained for the pristine ZnS as well as for the irradiated ZnS QD sensitized devices, under white light illuminated condition. The current-voltage characteristics show an enhancement in current density and efficiency at lower dosage of swift heavy ion irradiation. For a higher dosage, the photo-conversion efficiency of the device deteriorates.

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