

Swift heavy ion irradiated SnO₂ quantum dots based nano light emitting device

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SnO₂ quantum dots are synthesized via chemical method and exposed to 100 MeV high energy Nickel ion beam (swift heavy ion). The prepared quantum dot samples have been examined in a fabricated ZnO/QD based nano light emitting device by studying the variation of electroluminescence with variation of supply voltage at room temperature. Higher value of light emission and almost linear variation of EL intensity with voltage is obtained for irradiated quantum dots compared to that of pristine ones. Thus swift heavy ion irradiated SnO₂ quantum dots are better suited as high intensity light emitting device at room temperature.

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1. Introduction

Semiconductor quantum dots (QDs) finds its applications in various fields of research such as sensors, optoelectronic devices, solar cells, etc. [1,2]. Quantum dots are zero dimensional semiconductors that are spatially confined in all three dimensions due to which they exhibits very unique set of optical and electrical properties such as larger absorption coefficient, size tunable band structure, and large extinction coefficient [3]. One of such useful tunable properties of quantum dots is electroluminescence, i.e. emission of light on application of voltage [4]. In the present article this property of 100 MeV swift heavy ion (SHI) irradiated quantum dots is explored to fabricate a nano light emitting device (LED).

In the present investigation, colloidal SnO₂ quantum dots are prepared on polyvinylpyrrolidone (PVP) matrix via quenching method [5]. PVP polymer matrix restricts the growth of quantum dots, while itself remaining inert to the chemical reaction. The sample is then exposed to 100 MeV Ni⁺² high energy swift heavy ion. The prepared samples have been examined by different characterizing methods to reveal the effect of SHI on quantum dots. Next, the synthesized irradiated as well as the pristine SnO₂ QD samples are tested by fabricating a ZnO/QDs based device on transparent conducting glass (TCO) substrate. The schematic diagram of the fabricated voltage sensing LED is shown in Fig. 1. Electroluminescence study is carried out on the device at room temperature. The study reveals that quantum dots exposed to ion irradiation gives considerably higher electroluminescence at room temperature compared to that of the pristine ones.

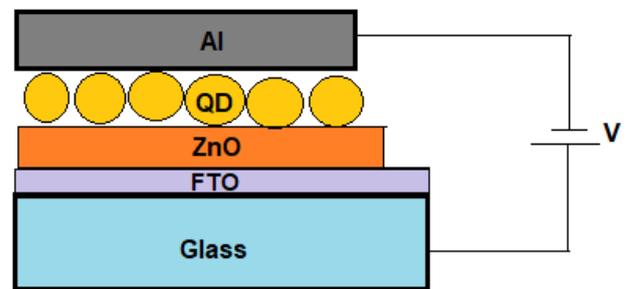


Fig. 1. Schematic diagram of the ZnO/SnO₂-QD based light emitting device (color online)

2. Experimental

To synthesize SnO₂ quantum dots by quenching method, 5 gms of SnO₂ powder is heated at 1000°C for 8 hours and then quenched into 5 wt% aqueous solution of polyvinylpyrrolidone (PVP) matrix kept at ice cold temperature followed by its moderate stirring (200 rpm). The film is developed on the laboratory glass slides by placing a few drops of SnO₂ quantum dot solution (embedded in PVP) on a clean slide and stretching over it by another clean slide, for characterization [5]. The samples are separated into two separate portions. The irradiation experiment is carried out on one of the sample while the other one is kept unirradiated (pristine). Sample is irradiated (exposed) in the Material Sciences chamber under high vacuum (4.6×10^{-6} torr) by using the 100 MeV Ni²⁺ ion beam with an approximate beam current of 1.0 pA (particle Nano ampere) for 16 seconds.

For fabrication of the LED, Zinc Acetate and Sodium Hydroxide (NaOH) was mixed in ethanol to obtain ZnO which is then deposited uniformly on conductive FTO coated glass (resistivity <10 ohm/sq.) by using tape

template method and doctor's blade technique. Then they are heated at 100 °C and air annealed at 400 °C to solidify the thin film and to planarize the surface of ITO which is known to contain small particles causing electrical shorts. Next the ZnO coated glass plate is dip-coated by immersing it in the previously prepared SnO₂ quantum dot solutions, for around 1 min. each to form SnO₂ QD layer on the oxide layer. Then they are sandwiched with a thin aluminium plate, held together with the FTO plate with scotch tapes and clips. Two metal crocodile probes were connected one to the FTO plate and another to the aluminium plate to serve as the voltage supply contacts [6].

The samples have been characterized by Optical absorption spectroscopy (using Perkin Elmer Lambda 35 1.24), X-ray diffraction (XRD) (Bruker AXS, X-ray source: Cu Ka), High Resolution Transmission Electron Microscopy (using JEM 1000 C XII), and Electroluminescence spectroscopy (using HITACHI-F-2005).

3. Results and discussions

Optical absorption spectroscopy shows red shifted absorption edge of the prepared SHI irradiated samples with respect to the pristine ones (Fig. 2). Absorption spectra show strong absorption edge of 260 nm for pristine and 310 nm for irradiated samples. The little red shift signifies small amount of crystal defect or particle agglomeration in the SHI exposed samples [7, 10]. As particles agglomerate, the radius of quantum dot increases, as a result of which it absorb higher wavelength. This phenomenon can be observed in the absorption spectra, as the irradiated spectra is shifted towards higher wavelength, i.e. red shifted. By considering absorption edge of SnO₂ samples, average crystallite (particle) size is estimated and found to be around 10-12 nm by using the following hyperbolic band model [8].

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

where R is quantum dot radius (2R is the diameter and hence the particle size), E_{gb} is the bulk band gap, E_{gn} is quantum dot band gap (calculated from the sharp absorption edge from Fig. 2), h is Planck's constant, m^* is effective mass.

Similarly, from X-ray diffraction study in Fig. 3, average particle size (crystallite size) is calculated by using Debye-Scherrer formula [9]:

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

where, ' 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). Considering all the peaks (2 θ in degree) in the X-ray

diffraction, the average crystallite size of the synthesized samples are estimated to be in and around 10-12 nm. The XRD shows peak at (110), (101), and (211), which corresponds to that of JCPDS card number 41-1445.

As there is no significant change in the XRD patterns of pristine and the irradiated samples hence it is evident that there is no change in crystal structure of the quantum dots. The data from the Absorption and XRD spectra for the synthesized quantum dots are shown in Table 1. The size of the synthesized quantum dots are confirmed to be in the range of 10-12 nm (pristine and irradiated) by TEM images as shown in Fig. 4. Note that there is a slight increase in size of irradiated quantum dots due to agglomeration of particles on SHI irradiation [9]. The HRTEM image confirms the formation of nanoparticles. The size estimated from the Absorption spectra and XRD spectra are approximate values, and are found to be close to that of the original particle diameter as can be observed from the HRTEM image.

Fig. 5 shows the Energy Dispersive X-Ray (EDX) spectra of the synthesized SnO₂ quantum dots. Specific peaks of Sn and O can be observed in both Fig. 5(a) and 5(b). But in Fig. 5(b) an additional peak corresponding to Ni is clearly visible in case of Ni SHI irradiated sample. This presence of the Ni peak in the irradiated sample's EDX spectra indicates that Ni ion has been incorporated into the crystal of SnO₂ quantum dots. This proves that there have been slight alterations in the crystal structure of the samples. The ion irradiation results in creation of ionic vacancies in the crystalline structure of the irradiated sample [12,14].

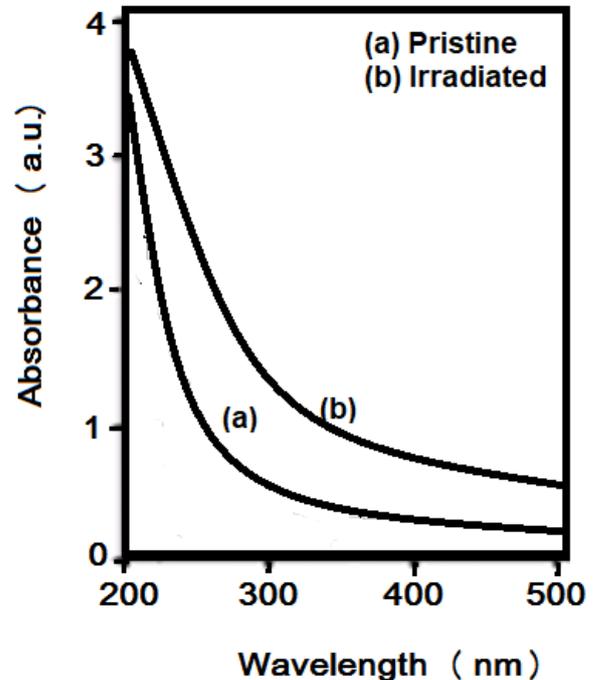


Fig. 2. UV-Vis Absorption spectra of synthesized (a) unirradiated and (b) irradiated SnO₂ quantum dots

Table 1. Absorption and XRD data for pristine and irradiated SnO₂ quantum dots

Sample	Abs. Edge (nm)	Size from UV-Vis (nm)	XRD peaks	Size from XRD (nm)
SnO ₂	293	10.2	110 (26.3) 101 (31.2) 211 (47.8)	9.7
SnO ₂ : Ni irradiated	312	12.1	110 (27.1) 101 (31.8) 211 (47.3)	10.4

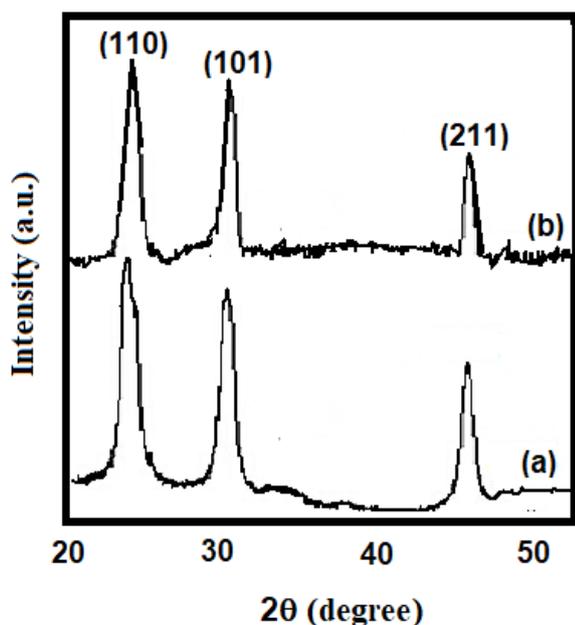


Fig. 3. XRD pattern of synthesized (a) unirradiated and (b) irradiated SnO₂ quantum dots

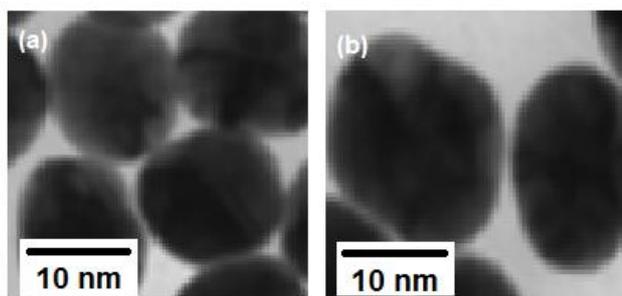


Fig. 4. TEM image synthesized (a) unirradiated and (b) irradiated SnO₂ quantum dots PVP matrix

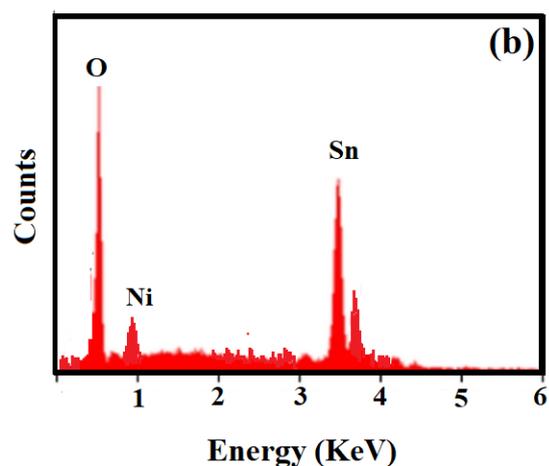
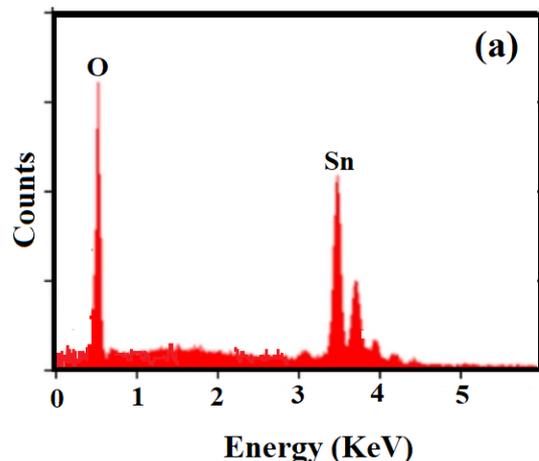


Fig. 5. EDX spectra of synthesized (a) unirradiated and (b) irradiated SnO₂ quantum dots PVP matrix

To test the working of SnO₂ quantum dots as Nano Light emitting device, Electroluminescence (EL) of the device is studied at room temperature (Fig. 6) [10]. It is observed that SnO₂ quantum dots shows appreciable electroluminescence at around 590 nm at room temperature. The intensity of emission increases significantly in case of SHI irradiated samples. The possible reason behind the enhanced emission is the increase in number of ionic vacancies created within the crystal on being exposed to high energy ions [12]. The luminescence intensity is tested for higher bias voltage and it is observed that the emission intensity increases with increase in applied voltage in both cases almost linearly [13]. High bias voltage causes damage to the sample if operated for long time hence it can be stated that SHI irradiated samples are better suited for LED applications compared to that of pristine ones. The irradiated samples shows higher EL intensity at lower bias voltage compared to that of the un- irradiated device operated at same applied voltage [14]. Also as an added advantage, the devices have a very fast response speed in the order of 10⁻⁹ sec [14,15]. Variation of EL intensity with bias voltage is plotted in Fig. 7 and is presented in tabular form in Table 2.

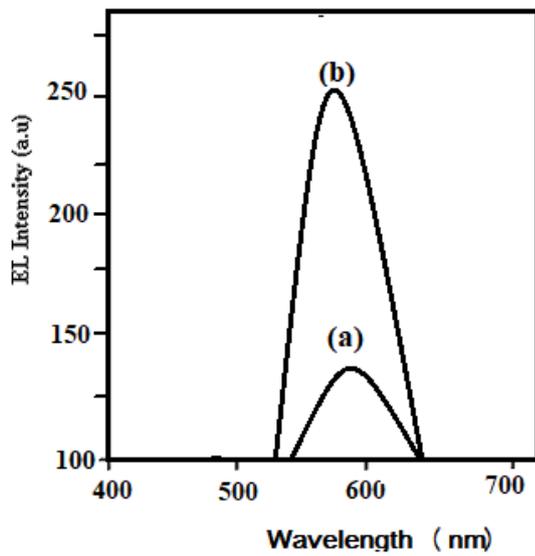


Fig. 6. Electroluminescence (EL) of (a) unirradiated and (b) irradiated SnO₂ quantum dots at applied voltage of 5V at room temp. 300 K

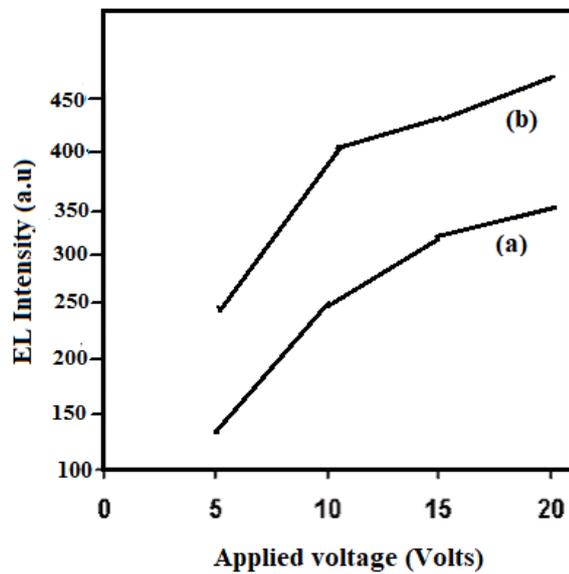


Fig. 7. EL intensity Vs applied voltage for (a) unirradiated and (b) irradiated SnO₂ quantum dots at applied voltage of 5V at room temp. 300 K

Table 2. Electroluminescence (EL) data unirradiated and irradiated SnO₂ quantum dots at applied voltage of 5V at room temp. 300 K

Applied voltage (V)	EL intensity (a.u.) pristine	EL intensity (a.u.) Irradiated	Response time
5	130	250	Of the order of 10 ⁻⁹ sec
10	250	380	
15	300	405	
20	345	450	

4. Conclusions

SnO₂ quantum dots are synthesized on PVP matrix polymer via. quenching method and are exposed to 100 MeV swift heavy ions of nickel metal. The fabricated quantum dots are characterized by using standard characterizing methods such as UV-Vis spectroscopy, XRD, and TEM imaging to confirm the structural and optical characteristics of the fabricated nano-dimensional particles. The quantum dots are tested for a fabricated ITO/ZnO/QD structured nano light emitting device, using electroluminescence study for a range of applied voltage. SnO₂ shows appreciable electroluminescence at room temperature, for a low range of applied voltage, with very fast response. It was also observed that the EL intensity is significantly higher for irradiated SnO₂ based device at same values of applied voltage values. Thus Ni SHI irradiation of SnO₂ quantum dots, greatly enhances the light emitting intensity in a quantum-dot based LED device.

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