

Enhancing electroluminescence in CdS quantum dots by swift heavy ion irradiation

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Quantum dots of CdS, embedded in Poly-Vinyl-Alcohol (PVA) capping layer is prepared using simple chemical method and swift heavy ions (SHI) of Cu are used to irradiate the samples. The SHI irradiation dosages used are of 1×10^{11} and 3×10^{11} ions/cm². The unirradiated as well as the irradiated samples of CdS quantum dots are then characterized and tested for Electroluminescence at room temperature, using a ZnO/CdS-QD device fabricated on FTO coated glass plate and aluminum as the other electrode. The applied voltage is increased and the intensity of the electroluminescence is measured and plotted for each device. For an applied voltage range from 2.5- 20V, the Electroluminescence increased from 220 a.u. to 600 a.u. for first dose, and from 260 a.u. to 755 a.u. for 2nd dose of ion irradiation. Significant increase in electroluminescence was observed due to irradiation of CdS quantum dots, and for a certain range of applied voltage the intensity plot is almost linear.

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1. Introduction

Among many unique properties of quantum dots (QDs), electroluminescence is one of the property that makes quantum dots extremely useful in Light Emitting Devices (LEDs) applications [1]. Electroluminescence (EL) is the phenomenon by which some materials emit lights of specific wavelengths under the influence of applied voltage. The color that is the wavelength of light emitted by the quantum dot depends on the type of material and the particle size of quantum dots. Another feature of EL in nano particles is that the intensity of emission can be controlled by altering the applied voltage [2].

In the present work Cadmium Sulphide (CdS) quantum dots are synthesized to study the phenomenon of electroluminescence. Simple chemical process is used for synthesizing the quantum dots, and Poly Vinyl Alcohol (PVP) is used as capping layer to control the size of the particles during synthesis. The effect of irradiating the quantum dots to swift heavy ions (SHI) on electroluminescence is also explored to improve the EL intensity [3]. For the irradiation purpose 100 MeV swift heavy ion beams of Cu are used two doses of 1×10^{11} and 3×10^{11} ions/cm². The ion – dose basically signifies the time for which the quantum dot samples are exposed to the SHI beams. Table 1 demonstrated the dosage level and their corresponding time of exposure.

Table 1. Ion doses and corresponding exposure time

Dosage (Ions/ cm ²)	Fluence in terms of counts (sec)
1×10^{11}	16
3×10^{11}	48

For testing the effect of voltage change and ion irradiation on the EL intensity of the quantum dots, an optoelectronic device having a FTO/ZnO/CdS-QD/Al type structure is fabricated as shown in Fig. 1. Voltage is applied across the FTO glass and Al, which acts as the electrodes and the EL intensity if noted and plotted against the applied voltage, at room temperature. It was observed that irradiated samples of CdS quantum dots demonstrates significantly higher EL intensity for a particular applied voltage compared to that of pristine ones. This increase in electroluminescence on exposure high energy ion beams, may be attributed to the fact that on high energy beam irradiation, crystal defects are introduced in the quantum dots. Also, for a lower range of applied voltages the EL intensity plot is almost linear, which is one of the condition for Light Emitting Device (LED) applications.

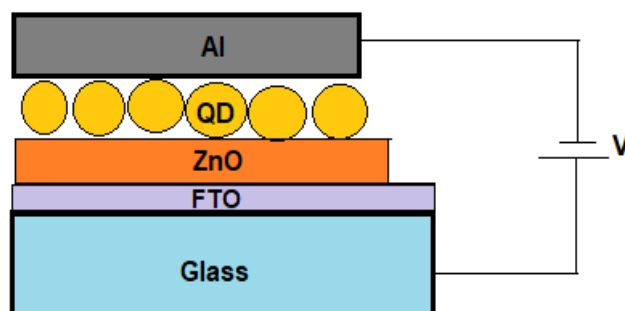


Fig. 1. Schematic diagram of the ZnO/CdS-QD based light-emitting device (colour online)

2. Experimental

The capping layer is prepared chemically by dissolving 0.43 grams of poly-vinyl alcohol (PVA) in 100 milliliters of double-distilled water to create a 0.1M solution at room temperature. A translucent, viscous PVA solution is produced after three hours of continuous stirring of the mixture at 200 rpm with a magnetic stirrer set at 800 °C. 0.1M CdCl₂ solution is made by dissolving 5.03 grams of CdCl₂ in 25 milliliters of double-distilled water and mixed into the PVA solution. 0.2 grams. To form 0.1M of an aqueous solution of Na₂S, 25ml of distilled water is added to Na₂S pellets. Na₂S solution is then is put into the mixer slowly by means of a dropper until the whole solution turns yellow. After four hours of mixing the two, a little amount of HNO₃ is added to the mixture of PVA and CdCl₂ solutions for pH balance. After stabilizing for ten hours at room temperature in a dark laboratory, the solution is filtered to remove the desired CdS precipitate and then washed three times with deionized water. Three equal portions are taken from the precipitate. One portion is kept unirradiated pristine while the other two portions are used in the irradiation experiment [4]. All chemicals used in the synthesis were obtained from Sigma- Aldrich, with 99% purity.

In the Material Sciences chamber, the two samples are exposed to radiation at a high vacuum of 4.6×10^6 Torr utilizing a 100 MeV Cu²⁺ ion beam with a beam current of about 1.0 pA (particle nano ampere). The initial dose of ions utilized one one sample was of 1×10^{11} ions/cm², and that on the second portion was of 3×10^{11} ions/cm².

For the next part, that is, for fabricating the Light Emitting Device, ZnO is prepared in-situ on a FTO glass plate (Technistro, resistivity <10 Ω/sq. meter), by mixing equal proportions of Zinc Acetate (ZnC₄H₆O₄) and Sodium Hydroxide (NaOH). The central area of the FTO glass plate was used by using tape template method, and the deposited ZnO layer was made uniform using doctor's blade technique. To solidify the oxide coating on the surface of the transparent conducting oxide (TCO) glass plate, it is first heated to 80 °C and then air annealed at 450 °C. Subsequently, the TCO glass plate coated with ZnO is submerged in the previously prepared CdS nanoparticle solution for around sixty seconds to create a layer of quantum dots on the oxide. The extra solution is wiped off from the sides and the thin aluminum plate is placed on the device to act as the other non-transparent electrode. As a result, the produced LED device features a TCO/ZnO/CdS-QD/Al layered structure that is secured using paper clips and scotch tape. The voltage is then applied across the FTO glass and the aluminum electrodes.

A transmission microscope (TEM), an X-ray diffraction spectrometer, an energy disruptive X-ray (EDX) examination, and a UV/VIS spectrophotometer are used to test the CdS nano dots. The Perkin Elmer Lambda 35 ultraviolet visible (UV-vis) spectrophotometer is used to obtain UV-vis light absorption spectra. Cu-Kα is the X-ray source utilized to obtain X-ray diffraction (XRD) patterns from Bruker AXS, and the JEM 1000 C XII high resolution transmission electron microscope (TEM) is

employed. The device of the HITACHI-F-2005 series is used to obtain the room temperature EL spectra.

3. Results and discussions

The optical absorption spectra as obtained for the Swift heavy ion irradiated and pristine CdS quantum dots are presented in Fig. 2. It is clear that the spectra of the irradiated samples show a slight shift of the strong absorption edges compared to the spectra of the untouched sample. This indicates a small agglomeration and formation of crystal defects in the quantum dot crystal due to exposure to high energy ion beams of Cu. Also, based on strong absorption edges of each absorption spectra curves, average particle sizes can be theoretically estimated with the effective mass model [5]:

$$E_{gn} - E_{gb} = \hbar^2 \pi^2 / 2mR^2 \quad (1)$$

In the above formula, the left hand side is the difference between are the nano-material (E_{gn}) and the bulk band gap (E_{gb}) of the particle. As the band gap in nano-materials increases with decrease in size, hence the nano-band gap is always greater than the original band gap of the bulk material. The bulk band gap of CdS is 2.84 eV [6], while the value of nano-band gap is estimated by drawing tangent at the absorption edge of the absorption spectra. The corresponding point at which the tangent cuts the x-axis (λ in nm) is used to determine the value of E_{gn} by using the formula $E_{gn} = hc / \lambda$. "h" is the plank's constant and "h bar" is reduced plank constant i.e $\hbar = h/2\pi$, and the electron effective mass (m^*) is the effective mass of CdS at room temperature is $0.21m_0$ for CdS [4,6]. Here "R" is the radius of the particle to be calculated by using the formula. The data from the absorption spectra is presented in Table 2.

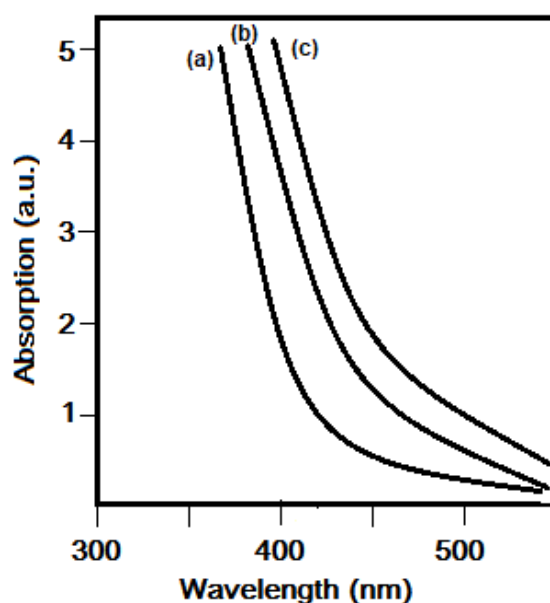


Fig. 2. UV-Visible absorption spectroscopy of (a) pristine CdS and CdS quantum dots irradiated with (b) 1st dose and (c) 2nd dose

Table 2. UV-Vis absorption data for Cu SHI irradiated CdS quantum dots

QD sample	Absorption edge (nm)	Band gap (eV)	Size (nm) from EMA
CdS	410	3.02	6.2
CdS: Cu 1 st dose Irradiated	450	2.75	6.5
CdS: Cu 2 nd dose Irradiated	460	2.70	6.6

The results from the XRD study for the pristine as well as the irradiated CdS QDs samples is shown Fig. 3. The XRD peaks are observed to be at (111), (220) and

(311) planes, which matches with that of CdS (JCPDS card number 002-0454) [4]. As all the three XRD plots looks similar, and not much change has occurred in the spectra on SHI irradiation, it can be confirmed that no significant damage has been done to the CdS crystal due to ion irradiation. Again, the particle size can be estimated from the XRD peaks with the help of Scherrer Formula [7]:

$$D = 0.9\lambda / W \cos\theta, \quad (2)$$

In the above relation, D is the diameter of the particle to be determined. ' λ ' is the wavelength of X-ray (0.1541 nm) which is a constant, The value of FWHM (full width at half maxima, W) and glancing angle (θ) are both determined from the obtained XRD peaks.

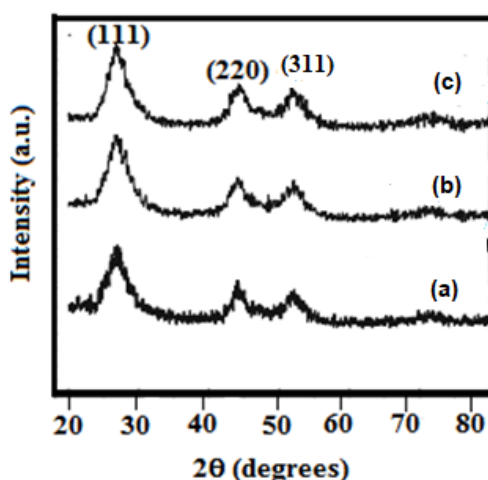


Fig. 3. XRD spectra of (a) pristine CdS and CdS quantum dots irradiated with (b) 1st dose and (c) 2nd dose

Table 3. XRD data for Cu SHI irradiated CdS quantum dots

QD sample	2θ	Avg. Size (nm) from Scherrer formula
CdS	13 (111) 28 (220) 31 (311)	6.03
CdS: Cu 1 st dose Irradiated	13.20 (111) 28.10 (220) 31.10 (311)	6.24
CdS: Cu 2 nd dose Irradiated	13.28 (111) 28.14 (220) 31.20 (311)	6.33

High resolution TEM images of the prepared CdS quantum dots are shown in Fig. 4. Little increase in QD size on increasing the ion irradiation dose can be observed in the HRTEM images in Fig. 4(b) and 4(c), indicating creation of defects in the QDs on irradiation with swift heavy ions of Cu.

To confirm the presence of Cu ion defects in the CdS quantum dot samples, the energy dispersive X-ray (EDX) spectrum of pristine CdS, as well as the two doses of Cu²⁺ irradiated CdS quantum dots are taken for comparison. As can be observed in Fig. 5, peaks for Cd and S are common in all the three spectra. But in case of Fig. 5(b) and 5(c) one can observe the presence of additional peaks for Cu. This confirms the presence of Cu ion defects within the crystal structure of the CdS quantum dots.

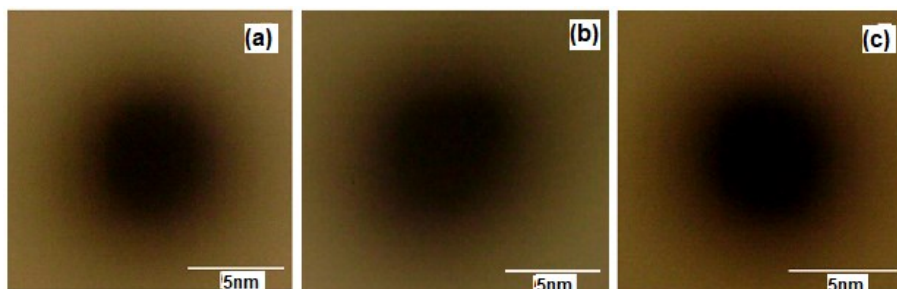


Fig. 4. HRTEM images of (a) pristine CdS and CdS quantum dots irradiated with (b) 1st dose and (c) 2nd dose (colour online)

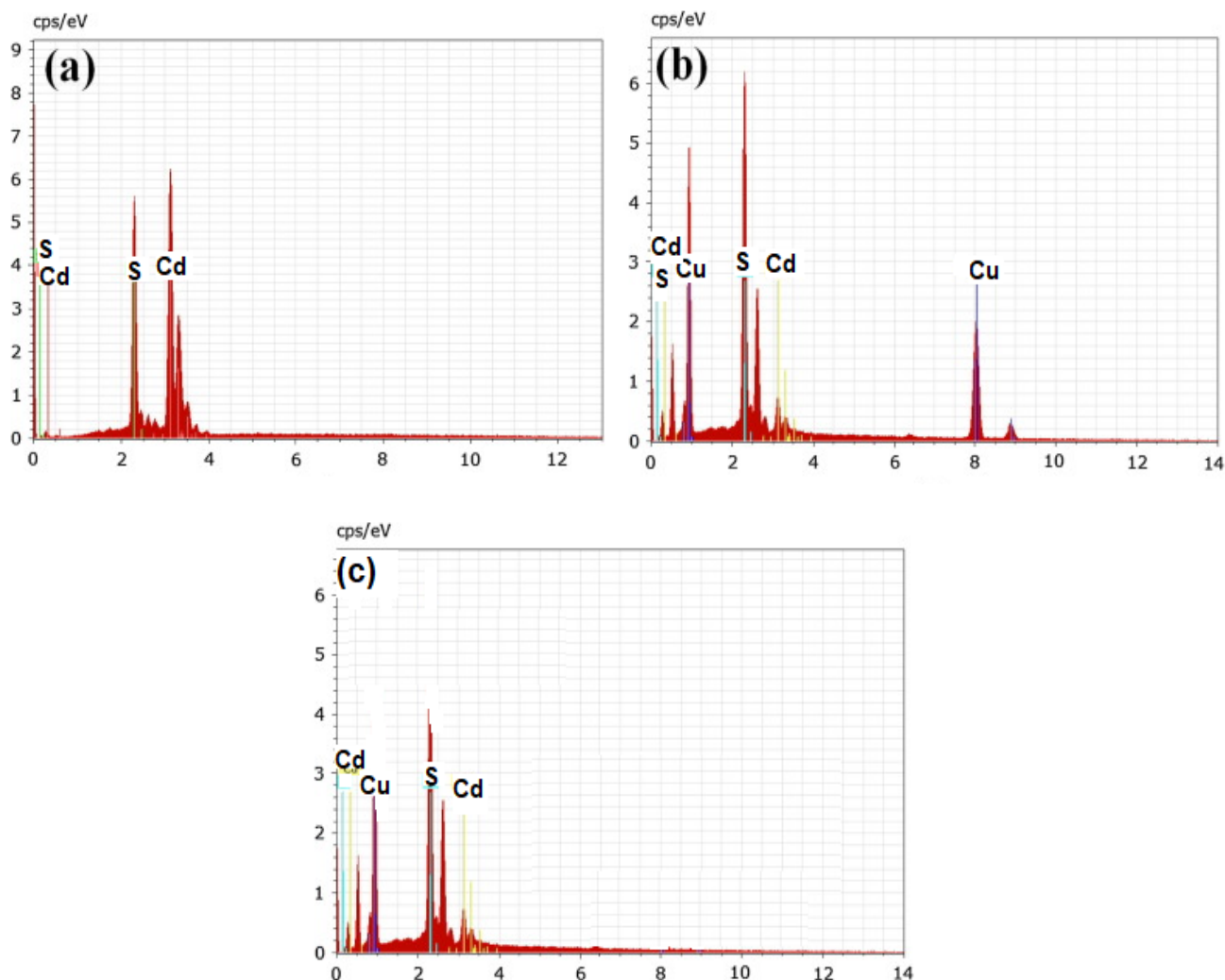


Fig. 5. EDX spectra of (a) pristine CdS and CdS quantum dots irradiated with (b) 1st dose and (c) 2nd dose (colour online)

The synthesized CdS quantum dots are then used to fabricate FTO/ZnO/QD/Al type nano light emitting devices (LEDs) and are tested for electroluminescence (EL) phenomenon at room temperature. Voltage is applied across the FTO and Al terminals and is varied from 2.5V to 20V range. It was observed that, at room temperature (300 K), the EL peak for CdS quantum dots is obtained in and around 540 nm wavelength. The EL spectra for all the tested samples are presented in Fig. 6. EL phenomenon in case of CdS quantum can be attributed to the presence of Cd^{+2} vacancies within the crystal structure of CdS [8]. Significant increase in EL intensity can be observed for a particular applied voltage on irradiating the CdS nanoparticles with Cu ions. As explained previously, the creation of ionic vacancies and defects within the CdS quantum dot crystal on exposure to high energy ions is the primary reason for enhanced electroluminescence in irradiated samples [9]. The data obtained from EL spectra is presented in tabulated form in Table 4. Also, the EL emission in case of CdS nano-dots starts almost instantaneously, which is an added advantage in case of

LED application [9]. The EL intensity for pristine as well as the irradiated CdS nano-dot samples are presented in Fig. 7. It can be observed that the plots are mostly linear for lower values of applied voltages.

It may be noted that although EL intensity increases with higher dosage of SHI emission, but exposure of quantum dots to high energy ions in irradiation chamber creates heat. Prolong exposure of quantum dot samples to SHI irradiation, tends to melts and agglomerate, forming larger particles and on further irradiation it produces enough heat to vaporize the samples [11]. Hence only low dosage of Cu SHI irradiation, that is 1×10^{11} and 3×10^{11} ions/cm², are considered in the present study. Also, it is inevitable from the EL spectra that for higher applied voltages the EL intensity increases. But, as can be seen in Fig. 7, the linearity is maintained only for lower values of applied voltages. For voltages above 20V, the EL intensity plots remains no more linear. Thus for light emitting device applications, CdS QD based devices are suitable for lower ranges of applied voltages.

Table 4. Electroluminescence (EL) pristine CdS QDs and Cu SHI irradiated CdS QDs at room temp. 300 K

Applied Voltage (V)	EL intensity (a.u) at 300 K		
	pristine CdS QDs	1 st dose Cu SHI Irradiated CdS QDs	2 nd dose Cu SHI Irradiated CdS QDs
2.5	170	220	260
5	240	275	355
10	355	410	455
15	390	500	690
20	440	615	755

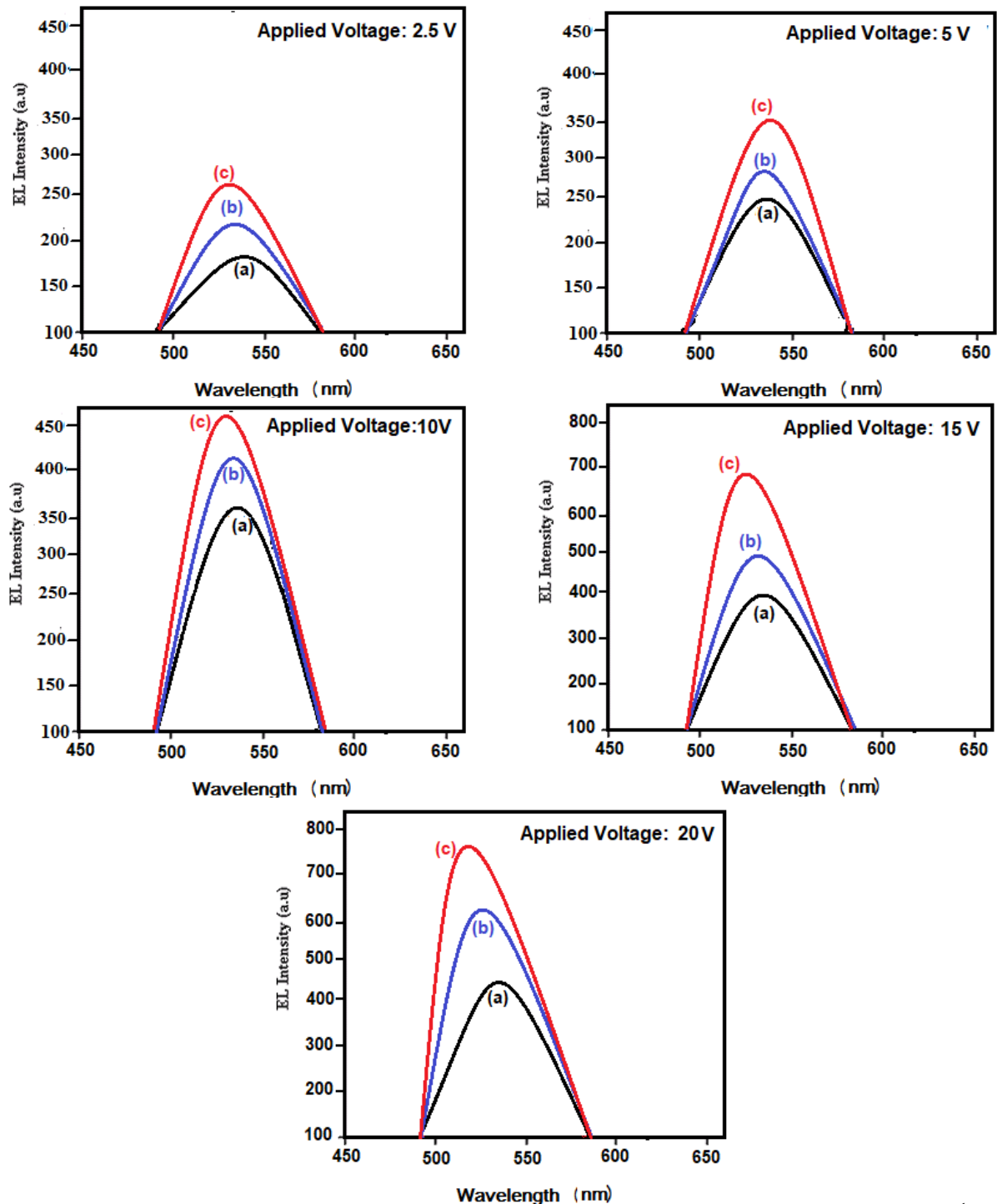


Fig. 6. Electroluminescence (EL) for (a) pristine CdS and CdS quantum dots irradiated with (b) 1st dose and (c) 2nd dose for different applied voltages at room temp. 300 K (colour online)

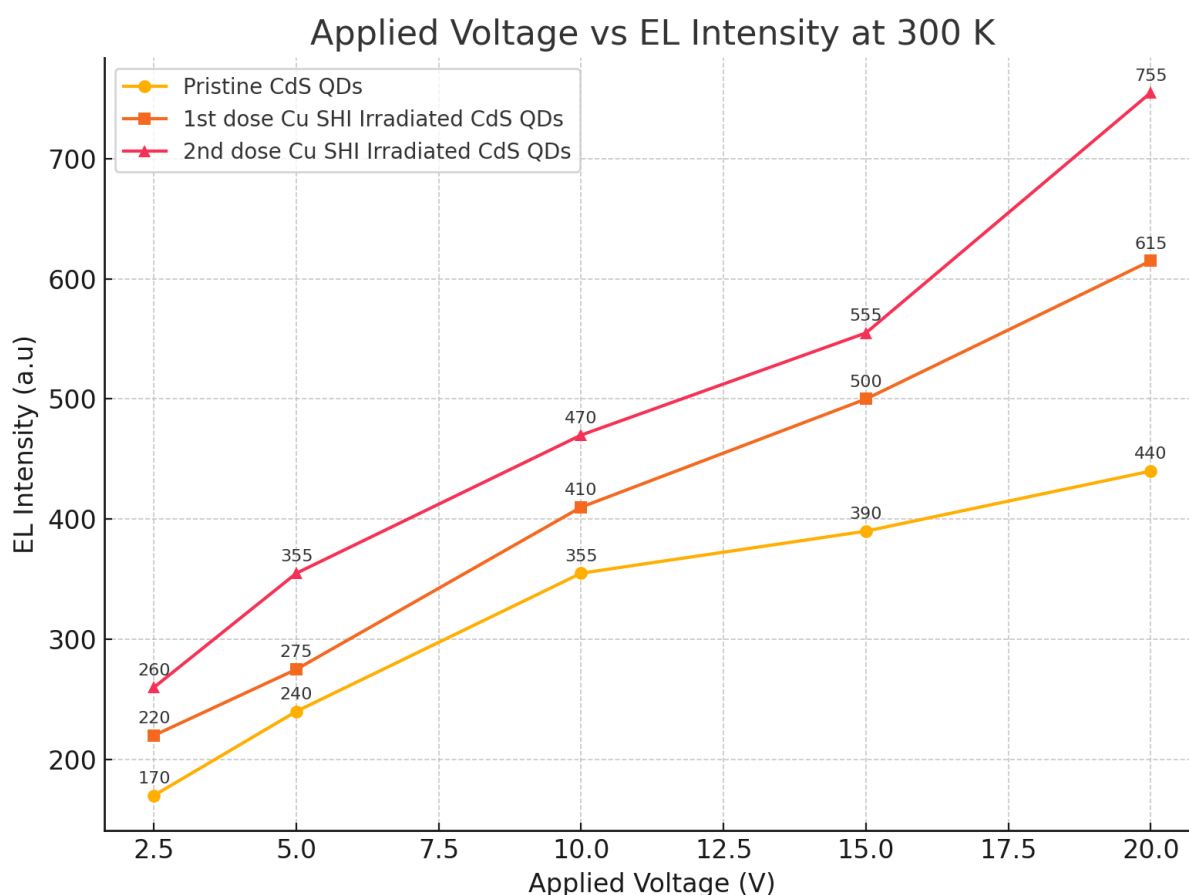


Fig. 7. The EL intensity Vs. applied voltage for (a) pristine CdS and CdS quantum dots irradiated with (b) 1st dose and (c) 2nd dose at room temp. 300 K (colour online)

4. Conclusions

CdS quantum dots are prepared on PVA polymer capping layer using simple chemical synthesis method. The samples are irradiated using high energy swift heavy ions of copper, to introduce defects within crystals. The pristine and irradiated CdS quantum dots are characterized using standard instruments such as absorption spectrometer, XRD spectrometer, HRTEM, and EDX to study their optical and crystalline properties. Next these quantum dots are used to test for electroluminescence, by fabricating a QD on ZnO device, with FTO and aluminum as the two terminals for applying voltage.

All observations were taken at room temperature, and it was observed that the EL intensity in case of irradiated samples are higher than that of unirradiated CdS quantum dot samples. The intensity increases for higher dosage of ion irradiation for a particular applied voltage. Also, the EL intensity plot shows linear variation with applied voltage for a lower range of applied voltage.

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