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Green Luminescence of Copper doped ZnTe Quantum Dots

L. Baruah[1,2], B. I. Sharma[2] & S. S. Nath[3,*]

[1]Deptt. of Physics, Biswanath College, Assam, India.
[2]Deptt. of Physics, Assam University, Silchar, Assam, India.
[3]Central Instrumentation Laboratory, Assam University, Silchar, India.

Abstract

Here we report luminescence study of copper doped ZnTe quantum dots prepared through a simple chemical route. XRD investigation shows the cubic structure ZnTe:Cu nanoparticles. UV-Visible is used to study the optical absorption and it is observed that band gap energy increases by 1.91 eV for the nanostructure. The size measurement gives an approximate size of less than 15 nm quantum dots by effective mass approximation method. Intense luminescence peaks are observed in green region. Enhanced luminescence peak are responsible for the incorporation of Cu^{2+} ion in all quantum dots.

Keywords: Chemical route, Copper doped, Green luminescence, Electroluminescence.

INTRODUCTION

Semiconductor nanoparticles have attracted considerable interest because of their tunable effective band gaps as well as wide applicability including microelectronics, nonlinear optics and solar energy conversion (1-6). In general, inorganic nanocomposites are low cost in terms of both materials and processing techniques compared to expensive materials of the conventional semiconductor processing industry. This enables easy production of large area devices like solar cells from inorganic nanocomposites (7-10). The group II-VI nanocrystals such as CdSe, CdTe,

CdS ZnS and ZnSe (11-23), have been studied extensively, and QDs with a CdSe core and a ZnS shell are currently commercially available. ZnTe is important for development of various semiconductor devices, including blue LEDs, laser diodes, solar cells, and components of microwave generators. Many methods have been developed to synthesize II-VI nanocrystals. Synthesis of highly monodisperse quantum dots (QDs) over a range of chemical composition is still a challenge in material science. Several manufacturing techniques that usually employ molecular processing in vacuum or liquid medium are in use (14). Most of the techniques are expensive, as well as inefficient in materials and energy use. Hence, there is an ever-growing need to develop cheap and nontoxic synthesis procedures. But only few reports are available about the preparation of ZnTe QDs. Dwivedi et al. (15) prepared ZnTe nanoparticles of 2.6 nm based on the chemical replacement reaction among the chemical compounds. Deng et al. (16) have prepared colloidal core shell ZnTe/ZnSe quantum dots having size less than 4 nm.

This study concerns the preparation of Copper doped zinc teluride (ZnTe) quantum dots through chemical route, where we have adopted a completely new approach. Synthesis by chemical route has many advantages over other methods. Two main advantages are chemical stability and slow agglomeration rate, which make the study more authentic and reliable (17). XRD, EDAX, HRTEM and SEM micrograph are used to investigate the structural properties of the prepared ZnTe:Cu QDs. UV-Vis absorption spectroscopy and FL spectroscopy have been used to observe the optical behavior. Electroluminescence studied has reveals sharp intense luminescence peak. This indicates that ZnTe:Cu QDs can be used as nano light emitting devices.

EXPERIMENTAL

To prepare Copper doped ZnTe QDs, hydrazine hydrate, ethylene glycol and de-ionised water are mixed in the volume ratio of 1:3:6 respectively. Then, 0.6 g zinc acetate and 0.638 g tellurium powder are poured into the conical flask. The solution is refluxed under vigorous stirring at 300 ^{0}C and Copper Chloride is poured with the solution and stirred for 6 h. When the reaction is over the greenish brown precipitate is collected and washed with anhydrous ethanol and hot distilled water for several times. Then it dried in vacuum at 50 ^{0}C for 6 h. We have prepared ZnTe QDs with different doping concentration of copper. Sample ‘A’, ‘B’, ‘C’ and ‘D’ are three different samples with doping concentration 0%, 1%, 2% and 3% respectively.

The prepared samples are characterized by XRD study (Bruker, wavelength 0.1541 nm) and EDAX to explore the basic geometry and average size of the QDs. UV–visible absorption spectra are recorded using a Perkin Elmer Lambda-35 UV–visible spectrophotometer. HRTEM observations are performed by using a Jeol JEM-2100 transmission electron microscope, operating at 200 kV accelerating voltage, with an

interpretable resolution limit of 0.16 nm. For TEM experiments of ZnTe:Cu samples, a small drop has dropped onto a carbon coated copper grid, allowing the alcohol to evaporate. High resolution TEM image are obtained in order to evaluate the particle shape, structure and diameter distribution. Fluorescence (FL) spectra of the samples are recorded with Perkin Elmer LS-45 Fluorescence spectrometer. Optical measurements are carried out at room temperature under ambient condition.

RESULTS AND DISCUSSION

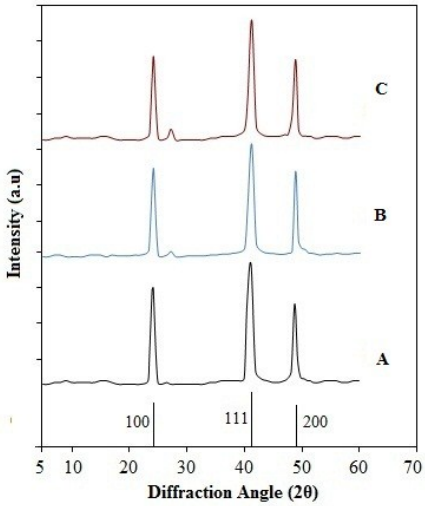

Fig. 1 X-ray diffraction (XRD) patterns of ZnTe:Cu samples.

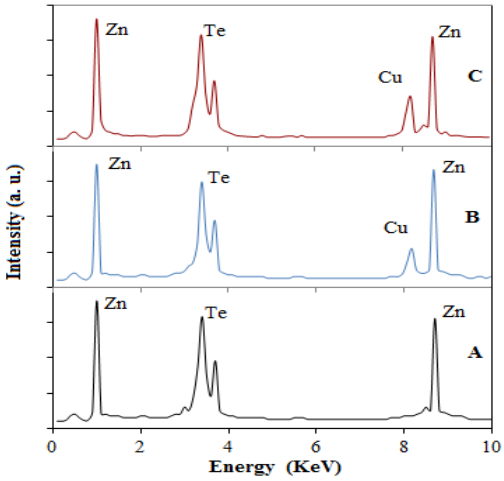

Fig. 2 EDAX patterns of and ZnTe:Cu samples.

In Fig. 1, typical X-ray diffraction (XRD) spectra of samples A, B and C with doping concentration 0%, 1% and 2% are shown respectively. The diffraction peaks for lattice planes <100>, <111>, and <200> are found at 2Θ values of 24.2°, 41.2°, and 48.8° respectively for all doped and undoped samples. A low intense peak observed at 27.18^0 for the Cu doped ZnTe samples which is differ from the undoped sample. EDAX analysis (Fig. 2) of the samples reaveals the presence of copper in doped samples. The diffractograms agree with the bulk zinc blende structure. The particles sizes (d= diameter) are determined using the Debye-Scherrer formula (18); $d = (0.9\lambda/\omega \cos \Theta)$, where λ is the wavelength of the X-ray and ω is the full width at half-maximum (fwhm) of the diffraction peak at angle Θ. The average particle size 'd'(19) is found to be 8.6 nm , 8.8 nm and 9.4 nm for samples A, B and C respectively. The size of the particles of highly doped samples C is slightly larger than samples B and A.

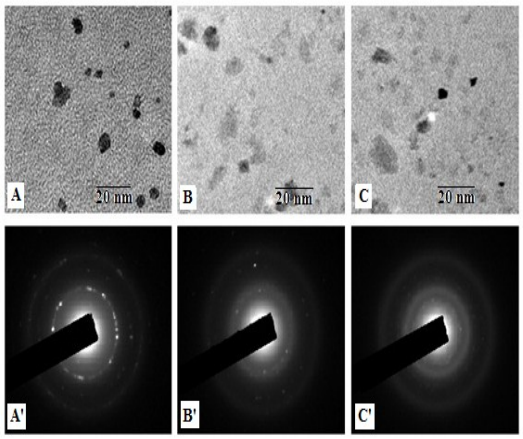

Fig. 3 High-resolution (HR) TEM images, SAED patterns of ZnTe:Cu QDs.

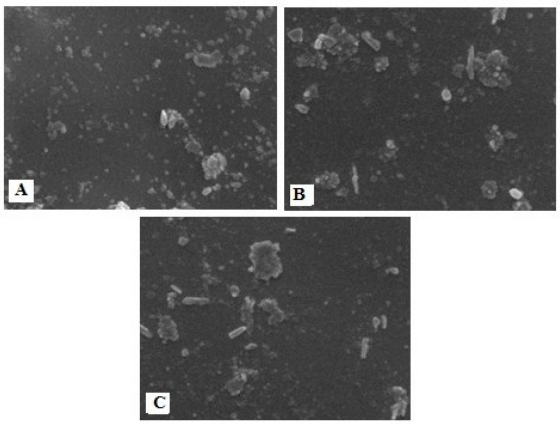

Fig. 4 SEM images of undoped and doped ZnTe and QDs.

The Morphology of the ZnTe:Cu QDs are observed by TEM and SEM as shown in fig. 3 and fig. 4. It is evident from the TEM (HR) micrographs that the average size of particles as directly measured from the ruler of the image is 2-14 nm. The selected area electron diffraction (SAED) patterns (Fig. 3A', B', C') show the good diffraction rings which indicates the lattice planes <100>, <111> and <200>. The intensity of the diffraction rings for sample A and C indicates that the particles c rystallized with good crystalline nature. The high resolution TEM micrograph shown in Fig. 3(a), clearly endorses the formation of well-separated and crystalline nanoparticles of ZnTe:Cu. The SEM images indicates rough surfaces of ZnTe:Cu QDs.

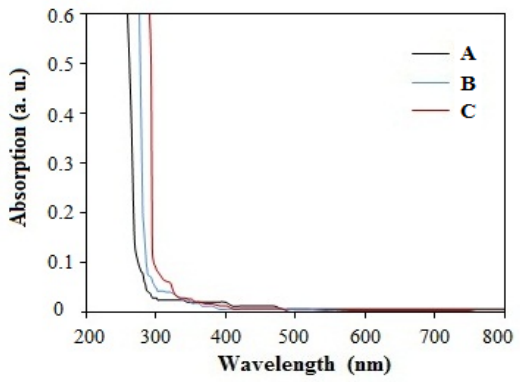

Fig. 5 Optical absorption spectra of ZnTe:Cu QDs.

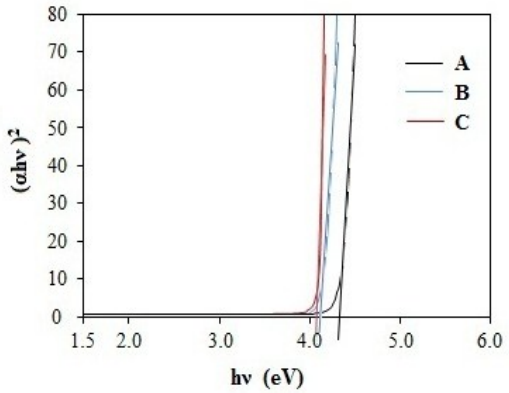

Fig. 6 Band gap energy spectra of ZnTe:Cu

Fig. 5 compares the optical absorption spectra of ZnTe QDs with ZnTe:Cu QDs using different doping concentration. The absorption spectra have been observed at room temperature. Blue shifted absorption edges are observed for all the three samples compared to bulk counterpart, which may be caused due to the quantum confinement (18). The absorption edges are appeared at 283 nm, 298 nm and 301 nm for the samples A, B and C respectively. The sharp absorption peaks reveals that the size of the ZnTe QDs could be close to monodisperse (17). Energy band gap of the particles have been determined from the fig. 5 using the Tauqe model (20). A graph has been plotted $(\alpha h\nu)^2$ vs $h\nu$, where α is the absorption coefficient, and $h\nu$ is the energy in eV. For the samples A, B and C, the values of band gaps are 4.39 eV (19), 4.15 eV and 4.14 eV respectively; where the band gap energy for bulk ZnTe is 2.23 eV. The band gap increases by an amount 1.91 eV for the doped samples. From the band gap information, the sizes of the ZnTe:Cu QDs are calculated using the effective mass approximation (EMA) method (21). The values of the particle sizes are calculated to be 11.72 nm, 12.44 nm and 12.5nm for A, B and C respectively.

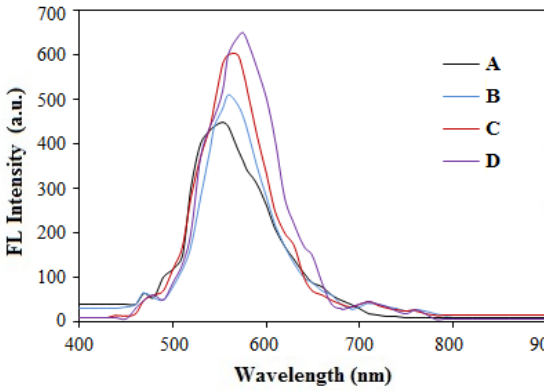

Fig. 7 Fluoroscence spectra of the ZnTe:Cu QDs.

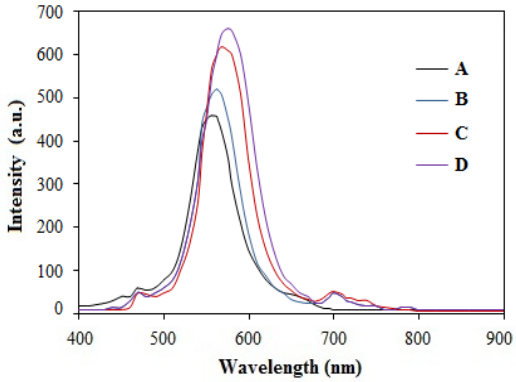

Fig. 8 Electroluminescence spectra of the ZnTe:Cu QDs.

Fig. 7 displays fluorescence spectra recorded at room temperature for all the prepared samples. It has been observed that for an excitation wavelength at 350 nm, a luminescent peak appears at 554 nm, 562 nm and at 569 nm and 576 nm for samples A, B, C and D respectively. Electroluminescence spectra (Fig. 8) of the samples follow the FL spectra in the same wave length range. The luminescence peaks of samples are observed in the green region. The luminescence peaks are attributed the intermediate surface states of the QDs (22). Peak intensity gradually increase with the increase of doping concentration of Copper and becomes tend to saturate at higher concentration. The increased luminescence intensity of ZnTe:Cu is probably due to involvement of Cu^{2+} ions in all doped samples (23). Additionally, the emission peak

is slightly shifted to the higher wavelength side with the increase of doping concentration and the peak width become wide, which may be due to the increase in the size of the ZnTe:Cu QDs (24). But the EL peaks are narrow and sharper than FL peaks. Consequently, ZnTe:Cu QDs are applicable for producing Light Emitting devices (LEDs) in green region.

CONCLUSIONS

Here, copper doped ZnTe quantum dots have synthesized of sizes <15 nm by adopting a simple chemical route. The XRD patterns exhibited the cubic structure for all the samples and no other crystalline phase is detected. Due to the quantum confinement effect, the absorption edges of all samples are blue shifted and consequently the band gap of the nanoparticles is increased compared with bulk material by an amount 1.91 eV. The luminescence peak is observed within 554 nm – 575 nm. The luminescence peak can be attributed to intermediate surface states in ZnTe:Cu QDs. The emission peak is slightly shifted to longer wavelength with the increase of doping concentration. The present advancement of ZnTe:Cu QDs open up the possibility of developing nano LEDs in green region.

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