



Photoluminescence studies of Silver doped CdTe Semiconducting QDs

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Abstract: This paper presents study of silver doped CdTe (Ag: CdTe) Semi conducting quantum dots (SQDs). The microwave (MW) assisted method of synthesis employed in this study, is found to be an effective doping method for SQDs. EDX and FTIR studies confirm the doping. A hump observed in pure CdTe absorption spectra near 400 nm is a characteristic feature of all the II-VI compounds, representing presence of traps in the band gap region; diminishes after Ag doping. This observation leads to an interesting doping mechanism proposed in this paper based on the UV-VIS optical absorption studies. XRD results, show better crystallinity and bigger size of the Ag:CdTe SQDs as compared to bare CdTe. PL emission spectra show enhancement in intensity along with a huge red shift in the peak obtained for Ag:CdTe SQDs as compared to that observed in bare CdTe SQDs, which can be attributed to the bigger size of SQDs after silver doping.

Key Words: Semiconducting SQDs (SQDs), EDX, FTIR, Uv-Vis, XRD, PL.

1. Introduction

Synthesis of luminescent doped nanocrystals, introducing impurities or dopants is a powerful method to control and introduce new functions to solid materials, including tailoring the optical, magnetic or electrical properties. Doped semiconducting quantum dots (SQD) are used for various technological applications [1-2], especially, optoelectronic, magnetic, biological and spintronic applications. Among the II–VI inorganic semiconducting nanostructures, CdTe is toxic but chemically more stable with direct band-gap energy of (1.45 eV). Hence, it is suitable for short wavelength optoelectronic applications. Further, CdTe can be easily doped to reasonably high concentrations of both p-Type and n-Type charge carriers [3]. This property of CdTe is helpful in making homo and heterojunction devices. Doping of transition metal ions in SQDs has potential application as luminescent labels for bio-imaging or for white light LEDs. [4].

There are various reported methods of synthesis of doped and un-doped CdTe SQDs [5]. In this study

we are reporting MW assisted method to synthesize Metal doped SQDs at moderate temperature, enabling homogenous nucleation and a better control over particle size [6-8]. The metal chosen for this study as dopant is silver (Ag) which may be incorporated as an acceptor in the II–VI compounds, since it influences the electrical conductivity as well as optical properties of this material [9]. The EDX, FTIR, UV-VIS optical absorption and Photoluminescence studies verify the conformal doping and enhanced optical properties of as prepared Ag: CdTe SQDs.

2. Experimental

The precursor solution of Cd²⁺ was prepared using 0.01M solution of CdCl₂·2.5H₂O, 0.1M GSH, mixed in 40 ml of Toluene solvent. Borax buffer solution was used to adjust the pH 10. The mixture was kept in ultra-sonicator for vigorous stirring for 30 min. After that 0.25 mol K₂TeO₃ was quickly injected. The mixture was stirred again for another 20 min.

The as obtained mixture was kept in a MW oven for 1 min at 300W power. The mixture was cooled

down to $\sim 50^{\circ}\text{C}$. The as prepared CdTe SQDs solution was concentrated to $\frac{1}{4}$ th of the original volume, finally precipitated using 2-propanol and collected via centrifugation. CdTe SQDs dispersion was prepared by re-dissolving this colloid precipitate in 3ml DD water. For synthesizing silver doped SQDs, 1ml solution of Ag NPs were included in the precursor solution.

3 Results and Discussion

3.1 EDX and FTIR study

Fig. 1 shows the EDX spectra of Ag: CdTe SQDs, showing atomic percentage of constituents and functional groups present in the as prepared material respectively. The EDX data compiled in Table 1 confirms the doping percentage of Ag.

Table 1. EDX Analysis of Ag Doped SQDs

Elements	Ag	
	Wt%	At%
C K	34.91	33.56
Na K	1.99	1.25
S K	20.43	18.92
Cl K	32.82	14.18
K K	0.48	2.18
Ag K	2.16	2.30
Cd L	4.58	1.61
Te L	2.58	1.32

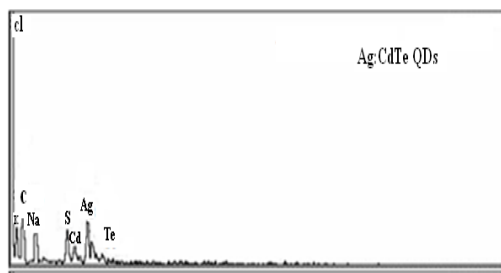


Fig 1 EDX analysis of Metal doped CdTe SQDs

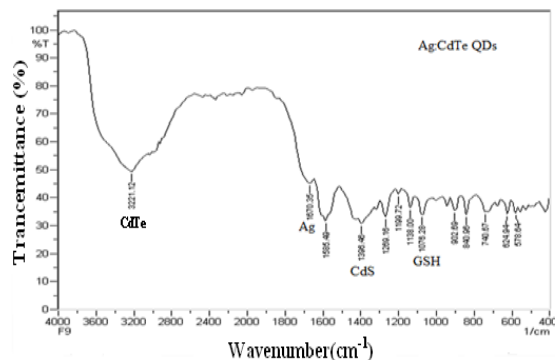


Fig. 2 FTIR Spectra of Ag: CdTe SQDs

Fig. 2 shows the FTIR peaks corresponding to various constituents of the as prepared SQDs. Presence of Ag in this figure show successful doping of silver ions in the CdTe matrix.

3.2 Morphological and Structural Studies

The SEM micrograph (JEOL EO JSM 5600) in Fig.3 indicates presence of spherical agglomerates consisting of individual nanoparticles approximately in the size - range of 25-56 nm. The XRD pattern matches with the JCPDS file (JCDS card no.65-1046) of CdTe and was carried out to confirm the crystalline nature of the particles, which scans over the 2 theta (θ) range of 20–80°. The XRD pattern was obtained both for pure CdTe SQDs and Ag: CdTe SQDs, shown in Fig.4. XRD pattern of the CdTe SQDs exhibits three peaks at around 25°, 39° and 47°, which are attributed to (111), (220) and (311) planes of the cubic (zinc-blende) phase of CdTe. The XRD pattern of Ag: CdTe SQDs is similar with that of CdTe SQDs, which means the crystal structure of CdTe is well preserved. However, the diffraction peaks are slightly shifted, with sharper peaks indicating enhanced crystalline nature and bigger size of doped SQDs. These changes can be attributed to the doping of Ag impurities in CdTe SQDs.

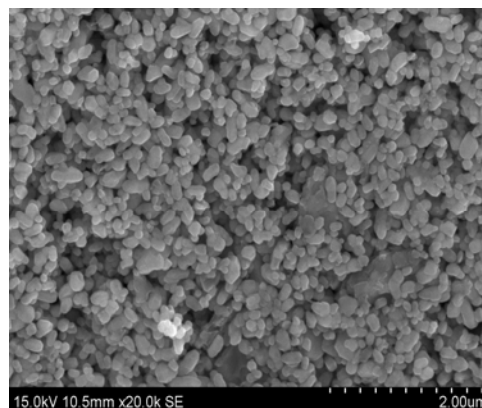


Fig.3 SEM Micrograph of Ag: CdTe SQDs

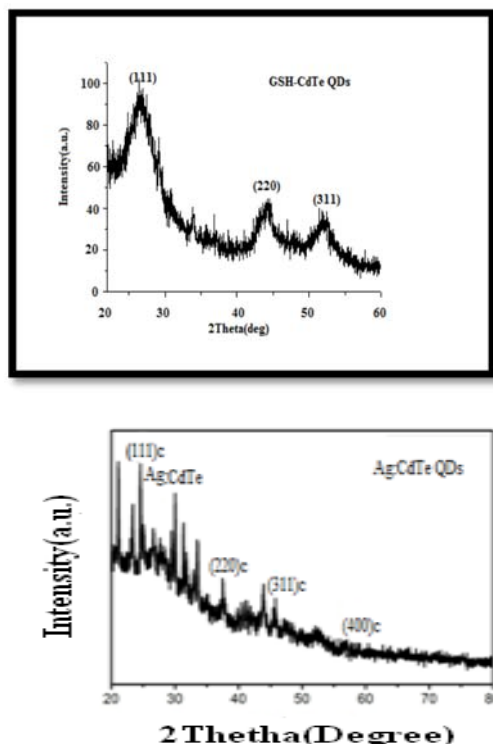


Fig. 4 XRD Spectra of Bare CdTe SQDs and Ag: CdTe SQDs

3.3 Optical Studies

Fig. 5 shows the UV - Vis optical absorption spectra of Ag:CdTe SQDs, the absorption edge of Ag:CdTe are considerably red-shifted as compared to that of undoped CdTe. This absorption shift is due to the quantum size effect, representing a change in band gap along with excitonic features. The effect of the quantum confinement on doping depends upon the size of the host crystal [10]. As the size of the host crystal decreases, the degree of confinement and its effect increases [11]. The atomic radii of Ag are bigger than that of Cd, so we expect to see enhanced quantum confinement effect. The band gap energy of the nanocrystals was calculated from a simple energy wave equation and the determined values are 3.54eV for undoped SQDs. This shows an increase in the band gap of bare CdTe from 1.72 eV for bulk to 3.75 eV in present case, due to the quantum confinement effect. However, after silver doping the band gap decreases slightly from 3.54 eV for bare CdTe to 2.75 eV for Ag:CdTe SQDs. In Ag:CdTe SQDs Ag replaces Cd ions in the lattice, and due to its bigger atomic radii, a decrease in band gap is observed in this case. A clear red shift in the band gap energy

after silver doping confirms the XRD results showing bigger crystalline size after doping.

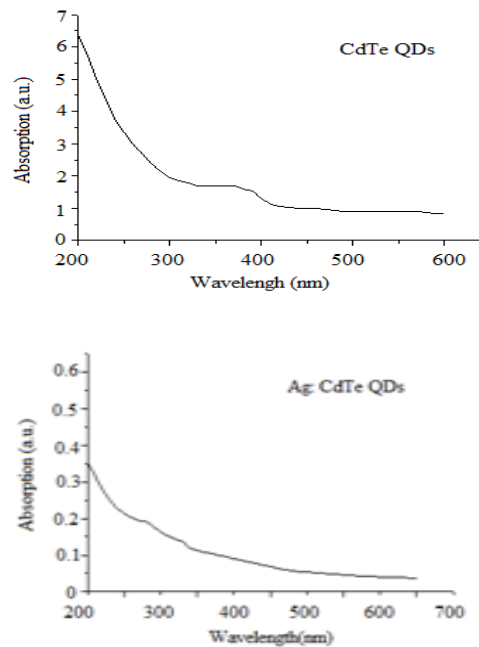


Fig.5.Absorption Spectra of Undoped CdTe and Ag doped CdTe SQDs

Further, this study reveals the Ag doping mechanism in CdTe. The hump observed in pure CdTe SQDs absorption spectra near 400nm in fig. 5; is a characteristic feature of all the II-VI compounds, representing presence of traps in the band gap region. This hump is smoothed out in Ag:CdTe. This clearly shows that the trap levels are filled and the band gap was modified after Ag doping.

3.4 PL Studies

As shown in in Fig.6, the emission peaks of Ag:CdTe SQDs is centered around 690 nm characterized by high intensity good symmetry and relatively narrow spectral width. Bare SQDs of CdTe show PL peak around 500 nm. This red shift attributed to bigger grain size and better crystallinity confirms the results observed in XRD and UV-VIS optical absorption studies.

The most striking evidence for the doping is the enhancement in the emission intensity of the Ag doped CdTe in relation to the pure CdTe NPs. It is obvious that Ag is acting as a sensitizing agent enhancing the radiative recombination processes. Thus, the photoluminescence efficiencies of Ag: CdTe samples are higher than those of pure CdTe SQDs. Similar red-shift is also observed in the Ag:CdTe SQDs. Such absorption shift is ascribed

to the increase of the particle size as a consequence of the quantum confinement [12].

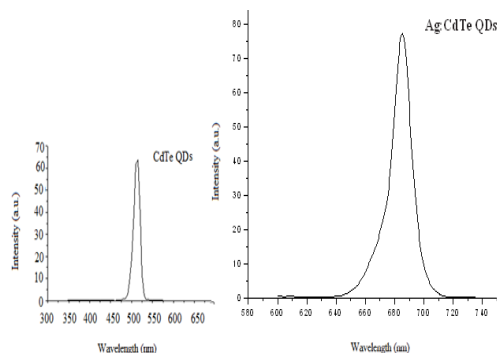


Fig. 6 PL emission Spectra of Undoped and Ag Doped CdTe SQDs

Several possible mechanisms have been proposed to explain the fluorescence enhancements of the Ag-doped CdSe SQDs [13-14]. To discuss the fluorescence enhancement mechanism in the Ag doped CdTe SQDs in this work, the energy levels for the excitation, relaxation and radiative emission of the excitons in the CdTe and Ag:CdTe SQDs are illustrated in Fig. 7.

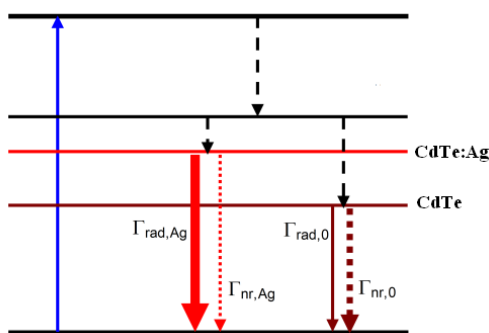


Fig. 7. Illustration of the excitation, relaxation and radiative emission of the excitons in bare CdTe and Ag:CdTe SQDs.

The dopant Ag induces slight increase of absorption with absorption band edge almost unchanged, prominent decrease of the fluorescence, large enhancement of the radiative rate ($\Gamma_{rad, Ag}$) and efficient suppression of the nonradiative rate (Γ_{nr}). Therefore, the dominating mechanism of fluorescence enhancement is attributed to an extra carrier as well as a positive charged center induced by the doped Ag impurity. These extra carriers could fill the trap states of the SQDs, the electrostatic field produced by the remaining charged impurity center could also enhance the fluorescence [14-15].

4 Conclusions

The MW assisted method employed in the present study, is found to be an effective doping method for SQDs. Conformal doping is observed in the sample. EDX and FTIR studies confirm the doping. Experimental studies like PL, UV-Vis absorption confirms the effect of doping in SQDs. This study successfully paves way to synthesize doped SQDs through a greener synthesis process. A simple doping mechanism for silver ions is reported in the paper. The PL study shows an enhanced intensity of the Ag:CdTe SQDs as compared to bare CdTe, with a huge red shift in the PL peak, corresponding to bigger grain size of SQDs obtained after doping.

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