

# Optical properties and NIR Photoluminescence of Dy<sup>3+</sup> doped CdS Q-dots dispersed in borosilicate glass for biophotonics applications.

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**Abstract:** We synthesised CdS Q-dots and Dy<sup>3+</sup> doped CdS Q-dots dispersed in borosilicate glasses and evaluated their optical and NIR photoluminescence properties. When excited with an 800nm source, new strong photoluminescence emissions from 850 to 1150 nm were observed in the NIR are reported. These new find states may be attributed to NIR virtual or trap states of the CdS S-Qdot. The strong photoluminescence emission spectrum observed from 850 to 950 nm corresponds to electron-hole recombination for as-prepared CdS-Q-dot glasses. However, this photoluminescence emission disappeared upon heat treatment due to photoluminescence emission from defect states.

## 1 Introduction

Over the last few decades, materials with broadband near-infrared (NIR-I&II) region photoluminescence light sources have attracted significant attention owing to their potential applications in biological imaging, high-capacity telecommunication, and energy harvesting<sup>1</sup>. The quantum dots (Q-dots) of II-VI binary chalcogenide semiconductors (e.g., CdS) dispersed in a glass matrix tend to crystallise in the 2-10 nm regime. Due to the quantum confinement effect, the RE-ion (e.g. Dy<sup>3+</sup>) co-doped CdS offers unique access to the NIR spectral region, which otherwise is not possible by doping with Dy<sup>3+</sup>-ion alone<sup>2-3</sup>. The crystallisation-dependent absorption and photoluminescence properties of Q-dots with RE-ions may be tuned by controlling heat treatment temperature and time below the glass transition temperature after melting and quenching the glass. These two heat treatment parameters also control the phonon vibrational, absorption edge or optical band gap, and stoke shift of the photoluminescence spectra. By incorporating the Q-dots in a silicate matrix, the sub-nanometer scale materials also resist photo- and environmental degradation. Tuning the Q-dots particle size during synthesis can lead to meaningful changes in optical absorption, exciton energies or trap states, electron-hole pair recombination, and photoluminescence properties<sup>3</sup>. The spectroscopic changes observed are attributed to the overlap of dichalcogenide (e.g. CdS states) with the RE<sup>3+</sup> electronic transitions 4f-4f or 5d-4f, which may allow efficient energy transfer from Q-dots to RE<sup>3+</sup> ion's well-defined electronic transitions. For instance, various RE<sup>3+</sup> ions doped Q-dots.<sup>2-3</sup> Shim et al.<sup>4</sup> fabricated Er<sup>3+</sup> doped PbS Q-dots dispersed in borosilicate glass, exhibiting a blue shift in the absorption and photoluminescence, which was attributed to the decrease in the size of PbS Q-dots with increasing Er<sup>3+</sup> ion concentration. The results cited here show the potential of utilising CdS Q-dots and Dy<sup>3+</sup>-ion-doped CdS Q-dots dispersed borosilicate-based glasses for fabricating waveguides for near-IR applications.

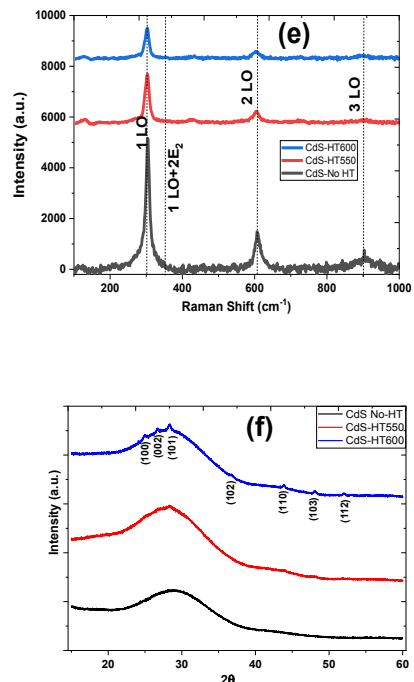
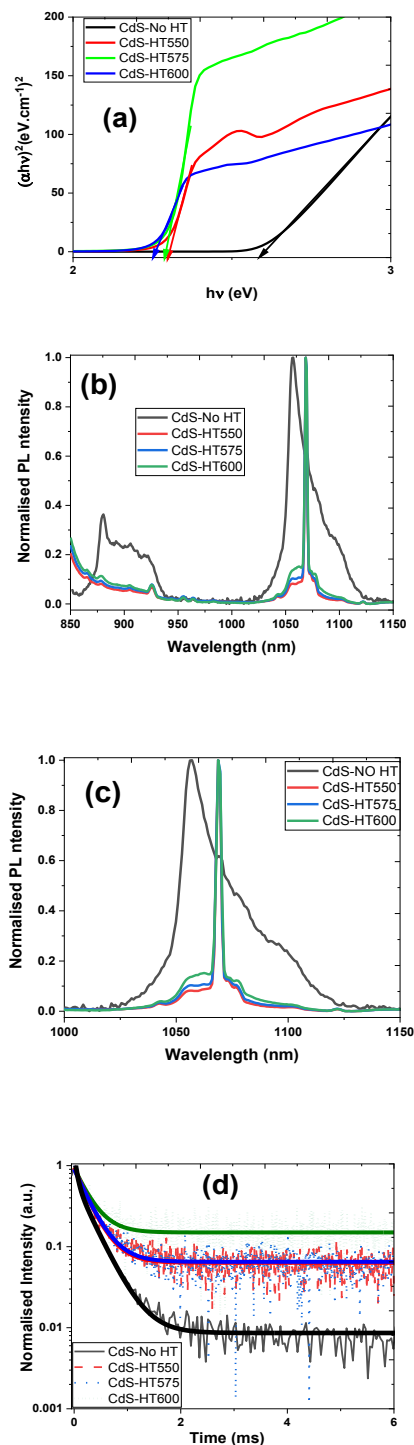
**2. Experimental details:** We prepared CdS Q-dots and Dy<sup>3+</sup>-ion-doped CdS Q-dots dispersed borosilicate-based glass matrices using conventional melting and quenching techniques. The precursor borosilicate glasses

were prepared with composition (in wt%): 50SiO<sub>2</sub>-10Na<sub>2</sub>O-6MgO-12K<sub>2</sub>O-10ZnO-6B<sub>2</sub>O<sub>3</sub>-4TiO<sub>2</sub>-(2-x) CdS-xDy<sub>2</sub>O<sub>3</sub>, [where x=0, 0.25 and 0.50 wt% of Dy<sup>3+</sup>]. Two batches of 50g of starting borosilicate glass, with dopant compositions CdS and CdS-Dy<sup>3+</sup>-doped Q-dots, were melted in an alumina crucible between 900°C and 1250°C for 4 hours in the air. Subsequently, the homogenised molten borosilicate liquid was cast into a preheated brass mould at 550°C and annealed for an hour. The furnace was switched off, so the annealed glass cooled slowly to room temperature. The annealed samples were polished, cut, and heat treated at 550°, 575° and 600°C for 6 hours to investigate the effect of the growth behaviour of CdS- and CdS-Dy<sup>3+</sup>-ion doped Q-dots on the spectroscopic properties.

**3. Results and discussions:** The absorption spectra of as-prepared and heat-treated samples were collected using a UV-visible spectrophotometer in the wavelength range of 250–2500 nm for characterising the bandgap edge and optical transitions in CdS- and CdS-doped with Dy<sup>3+</sup>-ion glass samples. The characterised optical band gap energies for the as-prepared CdS Q-dots and heat-treated samples are compared in Figure 1 (a). The red shift in optical band gap energy from 2.584 eV to 2.251 eV with respect to bulk (E<sub>g</sub> =2.42 eV) indicates an increase in the CdS Q-dot size. A similar trend was also observed in the Dy<sup>3+</sup>-doped CdS Q-dot in glasses and heat-treated samples. Furthermore, the optical absorption spectra were simulated using Mie scattered and effective-medium theory to deduce Q-dots size and distribution from the shape of the optical absorption edge. We observed that the particle size increases with increasing heat-treat temperature in all three samples prepared. The visible and near-infrared photoluminescence (PL) of the various CdS Q-dots and Dy<sup>3+</sup> doped CdS Q-dots-borosilicate glasses were analysed using 450 nm and 800 nm excitation sources and compared with the heat-treated samples. Figure 1(b-c) compares the NIR PL emission spectra of as-prepared and heat-treated CdS Q-dots glass samples at 550, 575 and 600°C for 6 hrs when excited with an 800nm diode laser with 0.45 W power. The PL emission of as-prepared CdS Q-dots reveals three broad emission bands occurring at 870 nm, 1049 nm and 1068 nm, as illustrated in Figure 1(b). Upon heat treatment, several weak intensity peaks were observed between 850 nm and 975 nm (Figure 1(b)), whereas a high-intensity sharp

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peak was observed at 1068 nm, as shown in Figure 1(b), demonstrating the potential of using CdS Q-dots in the glass matrix for NIR lasers suitable for tissue characterisation in 1020-1120nm window for biophotonic applications. The PL decay dynamics for non-heat-treated and heat-treated samples are shown in Figure 1(d), which are fitted with a single exponential decay function. The results indicate the lifetime decreases from 300.6  $\mu$ s to 263.2  $\mu$ s as the heat-treated temperature increases.



**Fig. 1:** As-prepared CdS Q-dots borosilicate glass and heat-treat at 550, 575, 600  $^{\circ}$ C, (a)Optical band gap energy, (b) and (c) PL emission under 800 nm excitation, (d) PL decay curve at 1068 nm, (e) Raman spectral and (f) XRD patterns.

Furthermore, we will present Raman spectroscopy and X-ray diffraction characteristics obtained from the semiconductor Q-dots grown in the glass matrix shown in Figure 1(e) and (f) <sup>5</sup>.

## References

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