



Electron Irradiation Effects on MPA capped CdTe Quantum Dots

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Abstract

Water-soluble fluorescent CdTe quantum dots (QDs) were synthesized using Na_2TeO_3 and CdCl_2 as precursors, and Mercapto Propionic Acid (MPA) as surface stabilizer. Thus grown MPA capped CdTe QDs were irradiated using 8 MeV electrons. Steady-state, time-resolved emission spectroscopy, and UV-visible absorption spectroscopy were performed before and after irradiation. The photoemission wavelength, intensity and lifetimes were found to vary with electron dose. The intensity and wavelength were found increasing at lower doses where as they were decreasing at higher electron doses. Moreover, a blue shift in emission wavelength was also observed. These changes in optical properties suggest that the irradiation assisted oxidation and corrosion of surface of CdTe QDs..

Keywords: Irradiation, Quantum Dots.

1. Introduction

Quantum dot (QD) is a semiconducting nanoparticle whose size is less than or equal to Bohr exciton radius. These luminescent semiconductor quantum dots including II-IV and III-V semiconducting nanocrystals, have attracted worldwide research because of their excellent optical properties, such as size tunable fluorescence and narrow as well as symmetric emission profile with a broad excitation range [1- 9]. These unique optical properties of QDs were exploited for applications, such as fluorescent markers in molecular and cellular labeling, imaging, sensing and diagnostics. In all such applications radiation directly interacts with QDs. In addition, different characterization techniques such as TEM, SEM, and XRD, primarily used for imaging of nanostructure, are based on the interaction of electrons with nano material under test. Such interactions can cause changes in its physical and chemical properties. Therefore it is essential to know the way radiation interacts with such nanostructure and the changes it can impart to them. Furthermore, Ionizing radiation has also been employed for synthesis and modification in the properties of QDs [10-15]. Most of irradiation changes (such as size and shape) in QDs are due to restructuring or modification of surface of the quantum dots. For instance, after prolonged exposure of UV radiation on thioglycolic acid (TGA) capped water solvable CdTe QDs, a shell of CdS was formed on CdTe core [13] and similar studies using electrons was reported by the author with all details [12]. In contrast, when QD surface is modified with different capping agents such as mercaptoethane sulfonic acid (MES), 2- mercaptoacetic acid, and 3-mercapto propionic acid (MPA), it was observed that instead of formation of CdS shell on QD core, it's bare surface was directly exposed to aqueous media leading to photo oxidation [k16-k18]. However, most of the irradiation studies reported so far have been focused on the use of UV photons for surface modification where as the studies using electrons to control the surface properties of colloidal QDs are very sparse. The

electron irradiation studies can not only ascertain reported photo degradation mechanism of UV irradiation, it can also give an understanding of the necessary precautions needed to ensure proper testing of samples using electron microscopy .

Semiconductor QDs are emerging as a new class of fluorescent labels for chemical analysis, cell imaging, and biomedical diagnostics [19-21]. Many researchers have used fluorescent water soluble CdTe QDs for such purposes. However its application is limited due to presence of Cd²⁺ ion, which is toxic [22-28]. Furthermore, radiation as probe in bio imaging can enhance release of Cd²⁺ ion which renders QDs as radiation sensitizing agent [29]. For in vivo and clinical imaging, the potential toxicity of QDs remains a major concern. Therefore, the study on cytotoxicity of CdTe QDs in presence and absence of radiation is useful. In order to get insight of its practical applications in clinical imaging as well as radiation protector or sensitizer.

In the present study, colloidal MPA capped CdTe QDs were grown using hydrothermal method and irradiated by 8 MeV electrons. Various optical characterization techniques such as steady state and time resolved photo luminescence (PL) and UV-Visible absorption spectroscopy were used to find the changes before and after irradiation on QDs properties. .

2. Experimental Details

2.1 Materials and methods

Na₂TeO₃ and CdCl₂ as precursors and Mercapto Propionic Acid (MPA) as surface stabilizer are procured from Sigma Aldrich and the yeast cell type *Saccharomyces cerevisiae* X2180 was acquired from BARC, Mumbai, India.

2.2. Preparation of MPA capped CdTe QDs

A simple efficient hydrothermal method was used for the synthesis of Mercapto Propionic Acid (MPA) capped CdTe QDs. Trisodium Citrate Dehydrate (100 mg), Sodium Tellurite (0.01 mol/L, 4 mL), and Sodium Borohydride (50 mg) were successively added to 4 mL of Cadmium Chloride solution (CdCl₂, 0.04 mol/L) and diluted by adding 32 mL ultra-pure water. To the prepared solution, MPA was added to obtain the growth solution for MPA capped CdTe QDs. The solution was autoclaved in stainless steel autoclave with Teflon liner at 180 °C for 45 min. then, the grown QDs were washed twice with IPA to remove unwanted Cadmium and Tellurium ions and stored at 4 °C in dark place.

CdTe colloidal QDs were irradiated with electron doses ranging from 0.2 kGy – 2.6 kGy using 8 MeV Microtron Accelerator available at Mangalore University, India. The samples were taken in microtubes and exposed to 8 MeV electrons at a distance of 30 cm from the beam exit port of the Microtron accelerator. The details of the facility are reported elsewhere [30]. Samples were characterised for changes before and after irradiation. Absorption spectra were recorded using Shimadzu UV - 3101PC double beam spectrophotometer. TCSPC studies were carried out using Chronos BH and Edinburgh FLS 920. Picoseconds LEDs (excitation wavelength of 320 nm – 450 nm, pulse width 750 ps and 1MHz rep rate) were used as excitation source in the present study.

3. Results and Discussion

3.1. Electron irradiation effect of MPA capped CdTe QDs.

In order to investigate the effect of electron irradiation on optical properties of QDs, samples were characterized using, UV–visible spectrophotometry, photoluminescence spectrometry and time resolved emission spectroscopy before and after 8 MeV electron irradiation. The emission spectrum was obtained for an excitation wavelength corresponding to the wavelength of the absorption peak. Luminescence decay was studied using time-correlated single photon counting technique.

3.1.1. Steady State Photoluminescence Spectroscopy

The analysis of PL properties provides sufficient indication of dose level required for an efficient passivation of QD surface for improved PL properties.

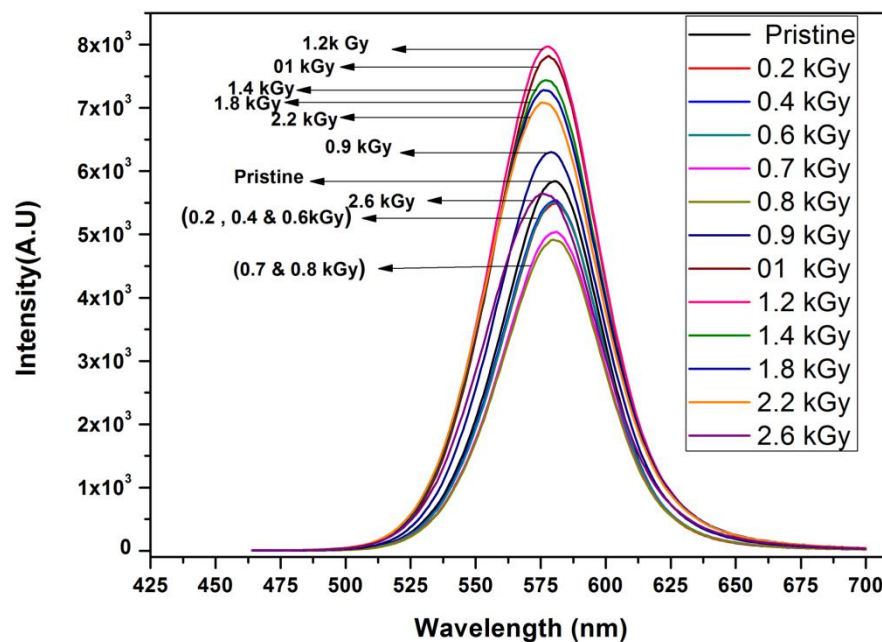


Figure 1. PL spectra of pristine and irradiated MPA capped CdTe QDs.

The most prominent effects of electron irradiation on MPA capped CdTe QDs can be observed in steady state PL spectra (figure 1). Three types of changes in luminescence spectra were observed with changes in irradiation dose as shown in figure 2. Initially, there is a slight decrease in intensity for doses up to 0.8 kGy, subsequent 35 % increase in intensity for doses up to 1.2 kGy and steady decrease in intensity for dose higher than 1.2 kGy. Besides, blue shift in emission wavelength for dose greater than 0.8 kGy was observed (figure 2). Cordero et al. [31] observed similar changes in CdSe quantum dot and attributed increased luminescence to adsorption of water molecules on the surface of the quantum dot which passivates surface traps. In addition, adsorbed water molecules act to oxidize the surface of the quantum dots, which results in the blue shift of the exciton emission peak [32–36]. With this background knowledge, a similar explanation is proposed. Irradiation assisted degradation (above 0.8 kGy) of MPA produces disulfide molecules, which are water soluble, readily removed from the QD surface and dissolve into the aqueous solution [37]. As a result,

bare surface of the QDs were exposed to aqueous environment. Adsorption of water or surfactant molecules to this exposed surface could passivate surface defects resulting in enhancement of QD exciton emission [36]. Further, adsorbed water molecule effectively reduces size of QD surface by oxidation of surface, and hence, blue shift in emission spectra for increased irradiation dose. Therefore, it is the competition between surface passivation by water molecule and photo oxidation processes, which is responsible for the nature of luminescence observed [32]. The decrease in emission for doses greater than 1.2 kGy may be due to photo corrosion of oxide layer thus formed.

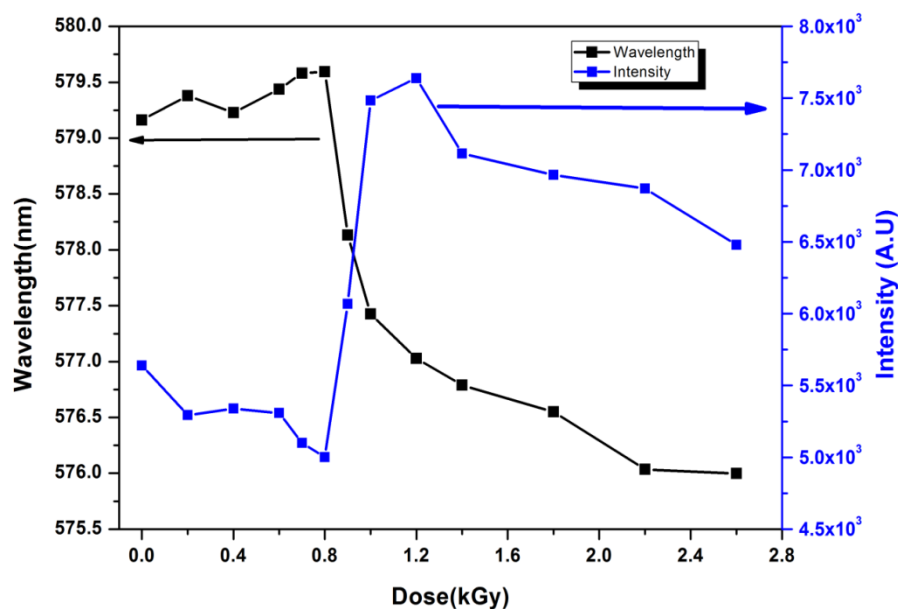


Figure 2. Changes in emission intensity and emission wavelength of MPA capped CdTe quantum dots for various radiation doses.

In order to confirm oxidation of CdTe core as explained earlier, Histidine was added while irradiating QD. Histidine is a well-known oxygen scavenger [38] and must prevent oxidation of surface of quantum dots.

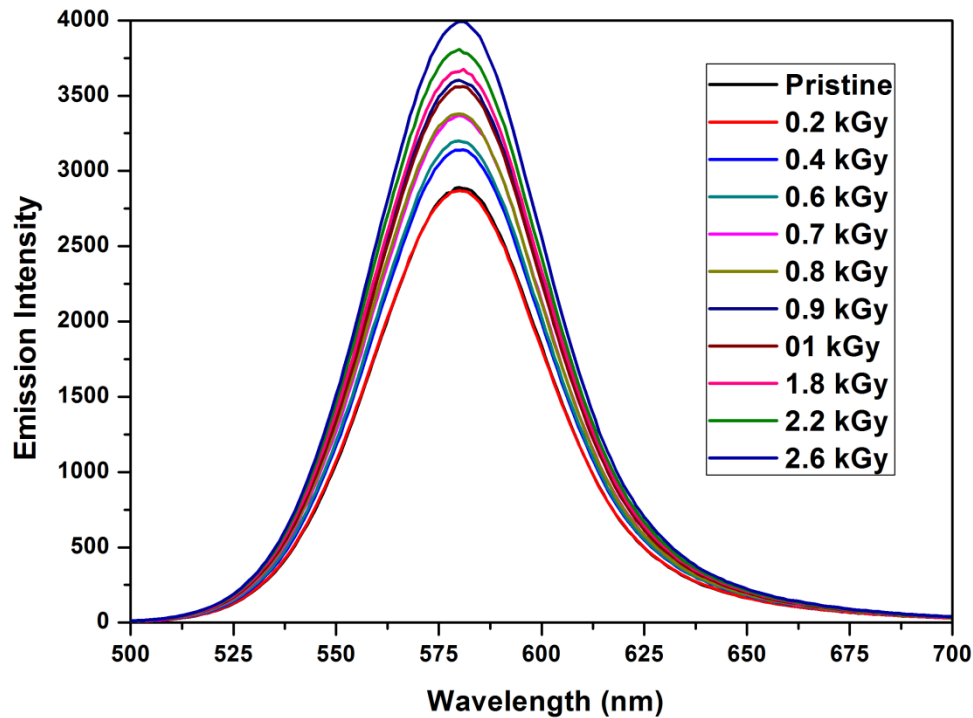


Figure 3. PL spectra of pristine and irradiated MPA capped CdTe Quantum dots after addition of Histidine.

PL spectra of irradiated CdTe quantum dots to different doses after addition of Histidine are shown in figure 3. Blue shift in PL spectra as observed in figure 1 was not observed after addition of Histidine. This reduction in Blue shift after addition of Histidine indicates reduction in photo oxidation [38] due to scavenging of reactive oxygen species created during irradiation.

3.1.2. Time Resolved Emission Spectroscopy

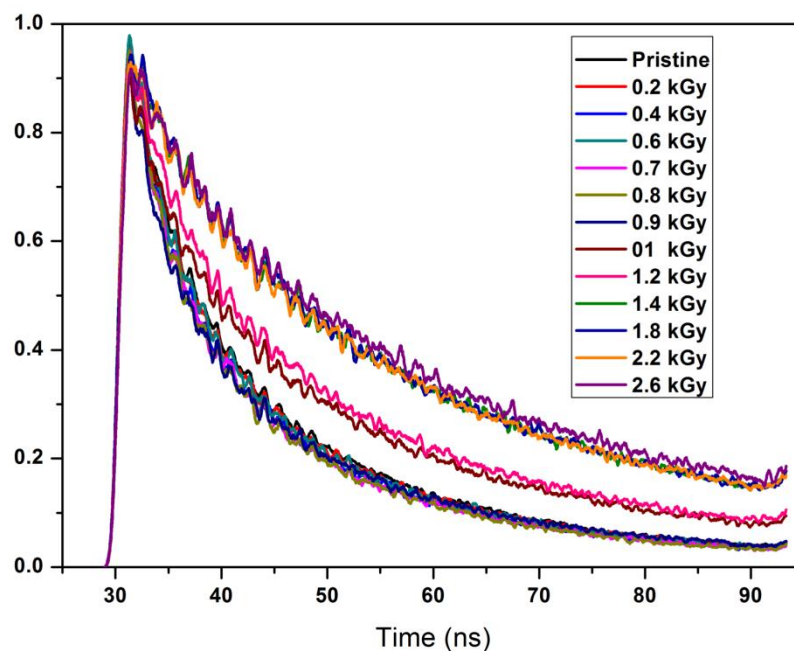


Figure 4. Time resolved emission spectra of CdTe quantum dots for various radiation doses.

In order to support the oxidation of surface of QD as explained earlier, time resolved emission spectroscopy was carried out. Fluorescence decay profile of pristine and irradiated MPA capped quantum dot is shown in figure 4. The decay curves were fitted (as determined from the residuals and χ^2 values) to a triple exponential decay function and Average PL lifetime was calculated (table 1). Increase in average lifetime (τ_{avg}) with increase in dose from 0.8 kGy to 1.4 kGy was observed. Such increase in lifetime can be attributed to passivation of surface by water molecules thereby formation of radiative relaxation pathways [39]. Further decrease in average life time for doses greater than 1.4 kGy can be attributed to formation of new surface defects due to photo corrosion and photo oxidation. τ_1 , τ_2 , τ_3 and α_1 , α_2 , α_3 are pre-exponential factors and decay times respectively, corresponding to different relaxation pathways [40]. The τ_3 component arises from electron-hole recombination at the core with little contribution from the surface states. The long lifetime component, τ_2 can be attributed to the involvement of the surface states. The τ_1 (life time is of 7 to 9 ns) component can be considered as arising from the involvement of the shallow trap states [41, 42]. Therefore, an increase in life time of τ_2 component for doses ranging from 0.8 kGy to 1.4 kGy can be attributed to passivation of surface states by water molecules thereby aiding radiative recombination. No systematic changes were observed for τ_1 and τ_2 component.

Table 1. Decay parameters for irradiated and unirradiated samples. Where α_1 , α_2 , α_3 and τ_1 , τ_2 , τ_3 , τ_{avg} are decay amplitude and decay time respectively.

Dose (kGy)	τ_1 ns	τ_2 ns	τ_3 ns	α_1	α_2	α_3	$\langle T_{avg} \rangle$ ns
Pristine	7.51	26.2	1.26	3.9	2.59	2.4	11.26783
0.2	9.09	29.5	1.45	4.06	1.99	2.95	11.09866
0.4	6.9	24.4	1.33	3.94	2.83	2.76	10.48361
0.6	7.28	25.1	1.22	4.05	2.67	2.93	10.37053
0.7	7.15	25.5	1.22	4.22	2.58	3.26	9.93441
0.8	5.75	22.9	0.715	4.38	3.16	3.64	8.9581
0.9	7.49	27.1	1.23	3.69	2.53	3.15	10.68043
01	8.13	32.9	0.809	2.23	2.43	2.08	14.80113
1.2	8.55	34.3	0.746	2.28	2.3	2.11	14.94141
1.4	9.14	39.6	0.469	1.11	2.25	1.44	20.81683
1.8	13	44.1	1.56	1.3	1.86	0.626	26.38736
2.2	9.91	40.4	0.747	1.09	2.19	1.09	22.90438
2.6	7.41	39.4	0.0636	1.02	2.01	1.0	21.5684

3.1.3. UV-Vis Spectroscopy

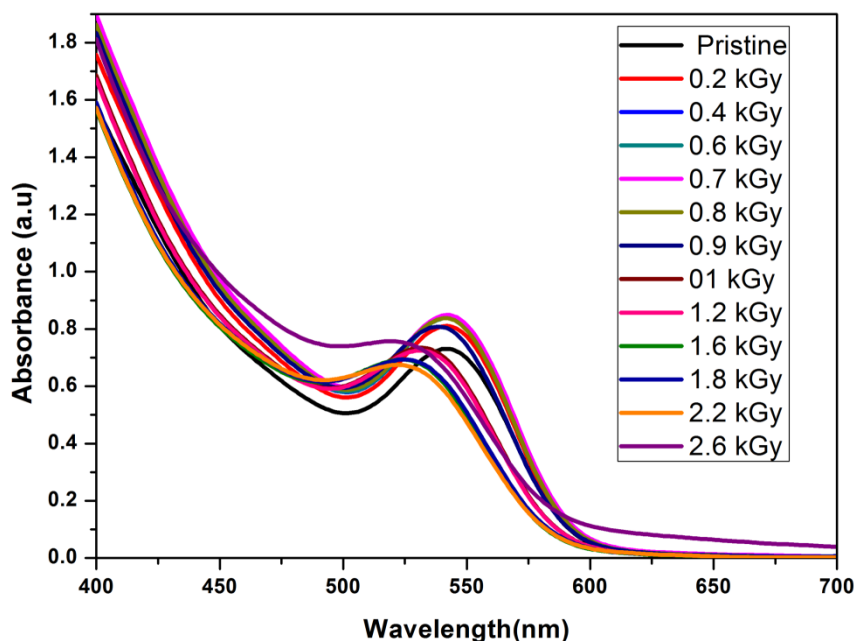


Figure 5. UV-Visible absorption spectra of irradiated and pristine MPA capped CdTe quantum dots for various doses

The irradiation assisted oxidation of MPA capped CdTe QDs can be readily monitored by recording UV-Vis spectra of the samples irradiated for different doses (figure 5). Blue-shift (about 20 nm for dose from 0.8 kGy to 2.6 kGy) in resonance absorbance with increase in dose was observed for doses greater than 0.8 kGy. This is due to decrease in size of CdTe QDs for doses more than 0.8 kGy which can be attributed to formation of cadmium oxide on surface of CdTe quantum dot at the expense of CdTe core. In addition to this, formation of higher band gap Cadmium oxide may contribute to blue shift in resonance absorbance.

4. CONCLUSIONS

Water-soluble fluorescent CdTe QDs have been synthesized using hydrothermal technique and irradiated with 8 MeV electrons using Microtron Accelerator. Steady-state & time-resolved emission spectroscopy, and UV-visible absorption spectroscopy were performed before & after irradiation. Increase in emission intensity & blue shift in emission wavelength due to dissociation of MPA and adsorption of water molecule upon irradiation were primary mechanisms in case of electron irradiation of MPA capped CdTe QDs. Blue shift in emission wavelength was minimized upon addition of oxygen scavenger such as Histidine which helps in quenching of photo oxidation.

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