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Gamma irradiation effects on optical properties of CdTe quantum dots

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Gamma radiation assisted changes in stability and optical properties of CdTe colloidal quantum dots (QD) capped with 3-mercaptopropionic acid (MPA) molecules have been reported in this article. Synthesized QDs in water, using hydrothermal method, have been exposed to different gamma doses to see the changes in their light absorption and emission properties of QDs. Colour of light absorption and emissions are blue shifted for lower pH conditions followed by precipitation (after few days) of the whole dissolved materials as a response to irradiation due to photo-oxidation. Surprisingly, redshift has been observed for the same gamma doses when pH of QDs solution raised to higher number which also results in improved stability of QDs to with stand against irradiation (compared to acidic pH environment). Therefore, the solution of QDs with higher pH value is stable for future useful modifications of QD structures using radiation. These modifications may include the growth of single or multishells over core QDs by using this irradiation method to enhance their stability and optical properties.

Keywords: Quantum dots, Gamma irradiation, Fluorescence, Optical stability, Hydrothermal method

1 Introduction

Nanomaterials with their unique properties are being used for variety of applications in different areas of science and technology. Among various types of nanoparticles, quantum dots (QD) are semiconducting nano-crystals with excellent opto-electronic properties. Exhibition of such properties from QDs is mainly due to their bandgap which can be tuned by growing it into different sizes. In all the collections of QDs made out of different materials, CdTe is a binary semiconducting nano single crystal with its band gap tenability lies in the optical region. Therefore, CdTe QDs are used in LEDs[1], solar cells[2], bio imaging and tagging[3] applications. These CdTe QDs are fluorescence colloidal materials which are easily processable through solution at the time of devising. Passivation of QDs with capping agent leads to boost in their properties in solution (or colloidal) form. This also helps in having intense radioactive decay of absorbed light by QDs when these cappers passivate dangling bonds on their surface. This would also contribute in avoiding agglomeration problems. Therefore, these are like eliminators of surface defects to boost their fluorescent and colloidal properties. Moreover, capping agents are important to show quality performances by QDs. It is also one among the other parameters used to vary QDs band gap. It also provides stability and tagging possibility of different biological systems in application level. QDs are more advantageous over traditionally used dyes in number of ways for opto-electronic as well as bio related applications. Some issues with dyes, which made to look for QDs as replacing materials, are mainly due to their instability when tagged to biological systems. These issues arise from aging and repeated characterization using light (ordinary light or UV through microscope). QDs are more stable than these dyes[3] in such situations. They can also change in their color of light emission where it is not so easy in the case of dyes.

In view of all the above, QDs in solution form are very important. Studies on irradiation effects on these QDs in solution form yield useful informations to modify them aiming to enhance their properties. Such informations help to use irradiation as a method itself for synthesizing and modifying (like growth of shells over core) of these QDs. This chemical free method would avoid bringing contaminations to QDs while synthesizing them. This would also not rise temperature of the solution. Therefore, this method is highly competitors for practiced methods available so far due to such reasons; no chemicals, no elevated

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temperature and no complicated procedures. Gamma is one such ionising irradiation among many other, available. With proper practical knowledge and control over all other parameters make this gamma irradiation as an effective and efficient method as explained above. Therefore, this study is aimed to see irradiation effects on MPA capped CdTe QDs in colloidal form. The pH of the solution was varied to find out the stable condition for QDs to withstand in different gamma doses.

2 Materials and Methods

All chemicals used in the present study were analytical grade. Cadmium chloride (99%) and sodium tellurite (99% pure), respectively, were purchased from FLUKA and ALDRICH companies. Other chemicals such as 3-mercaptopropionic acid (MPA), sodium borohydrate, and tri-sodium citrate dehydrate were procured from MERCK chemicals. Double distilled water was used throughout the study.

Initially, QDs were synthesised using hydrothermal method. As prepared QDs were characterized using UVS, PLS and XRD. These QDs in colloidal form were taken in different polypropylene tubes and exposed to different gamma doses.

Shimadzu UV - 1800 – Spectrophotometer was used for UV-Vis spectroscopy (UVS). X-ray diffraction (XRD) analysis was conducted from Rigaku Miniflex 300 X-ray diffractometer with CuKα 1.5406 Å instrument. Perkin Emler, LS 55 instrument was used for photo-luminescence studies (PLS).

Hydrothermal method was used for synthesizing MPA capped colloidal CdTe QDs in water. The ratio of precursors used is Cd:Te:MPA::1:0.25:8 to carry out synthesis experiments of CdTe QDs. Stock solutions were prepared for cadmium and tellurium sources using cadmium chloride (99%) and sodium tellurite, respectively. MPA was used as capping agent with the ration of 8:1 with cadmium. Tri-sodium citrate dehydrate was used as buffering agent. Total volume of the water medium was fixed to 40 mL. Sodium borohydrate as the catalyzer was introduced to reduce tellurium from its complex to make the reaction carried out. Procedure of synthesis was followed as reported in literature[4] with little modifications. As-prepared reaction mixture was poured into autoclave of Teflon housing with stainless steel. This is the reaction chamber for the hydrothermal method. The solution in this setup was kept in hot air oven with fixed temperature 180 °C. Hot air oven with continuous rotating fan facilitates uniform air circulation during the experiment. The reaction was allowed for 11 min with intension of achieving particular size of QDs. The heating was stopped after the stipulated duration and the temperature of the reaction container was allowed to cool down naturally to avoid formation of defects. The sealed autoclave was opened when it was reached room temperature. The QDs containing collide was taken out and washed with isopropanol alcohol as anti-solvent to remove unused precursors. The colloid was stored in refrigerator for the further experiments.

As prepared QDs using hydrothermal method emitting red in color to naked eyes in water was taken in different polypropylene small vials. These vials were directly exposed to gamma radiation by placing them in its rotating sample holder. Then these vials were taken out and used for optical studies such as UVS and PLS.

Irradiation chamber consists of Cobolt 60 pencils as continuous source of gamma radiation (Fig. 1). These source pencils are joined together to make a cylinder where the sample holder is rotated in the middle of these cylinder to delivery clean and uniform gamma radiations. The specification of the gamma chamber – 5000 is given in Table 1.

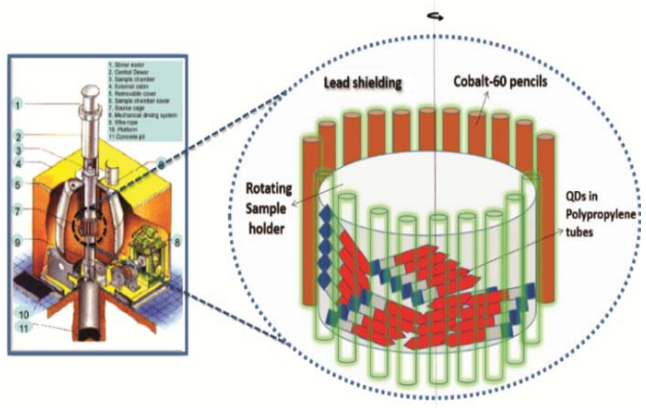

Fig. 1 — Gamma irradiation chamber - 5000.

Table 1 — Specification of gamma irradiation chamber – 5000

Specifications of the Unit	
Co_{60} source capacity (Max)	13455 Ci (497.8TBq at the time of irradiation)
Dose rate at maximum capacity	9.5 kGr/hr
Dose rate uniformity	Radial +25% or better, Axial -25% or better
Irradiation volume	sample chamber-5liters
Size of sample chamber	17.2 cm (dia)×20.5 cm (h)
Shielding material	lead & stainless steel
Size of unit	125 cm (l)×106.5 cm (w) × 150 cm (ht)
Timer range	6 s onwards

3 Results and Discussion

Figure 2 shows UVS, PLS and XRD graphs of as synthesized MPA capped CdTe QDs using hydrothermal method. The nature of curves in all these graphs confirms the successful growth of QDs. The wavelength (stock) shift between absorption (UVS) and emission (PLS) curves (with being symmetric) of light (which is 55 nm) indicates the growth of quality CdTe QDs capped with MPA. XRD pattern shown in the bottom row of Fig. 2 confirms the crystal structures of QDs (which retained its bulk structural properties of CdTe crystals). The obtained broad peaks which are situated in different 2θ positions as 24.85°, 41.975° and 49.4125°, respectively, for (111), (220) and (311) planes[5].

In order to see the systematic irradiation effects on these QDs, solution pH and gamma doses were varied. Therefore, the solution was taken in different vials for different pH number to treat them for different gamma doses. The selection of pH number was based on stability of emission of light by QDs without any precipitation for variation in pH number to be observed from naked eyes. Because, when there is no stability of QDs in solution, effects of irradiation on QDs cannot be seen.

QDs solution in vial of pH 5 (and below) were precipitated. Therefore, 6 and 7 (as synthesized) were selected for acidic domain of pH number. Furthermore, pH 10 and 12 were selected and varied in solutions for basic domain limits. Variation of pH below 7 was carried out by adding few drops of HCl whereas NaOH was used to increase the pH number to 10 and 12. These vials were exposed to gamma doses from 300 Gy to 20 kGy.

Figure 3 shows the UVS spectra of all the QDs with varied pH number. These UVS curves of QDs were blue shifted for 6 and 7 pH conditions whereas red shifted for 10 and 12 conditions. Blues shift is the indication of reduction of size which followed by increase in the quantum confinement effect. This size reduction is due to photo-oxidation of CdTe QDs at lower pH values for varied gamma irradiation doses. Contrarily, higher pH values turn the shifting towards to red region of electromagnetic spectra which shows that the QDs are correcting its boundary using available precursors by increasing their size, slightly. Furthermore, PLS spectra were taken for detailed analysis. Figure 4 shows that the PLS spectra of the same gamma irradiated samples. For pH 6 and 7, curves were sudden flattened for 300 and 600 Gy gamma doses.

This is the indication of lowering in intensity of fluorescence emission which is due to increase of

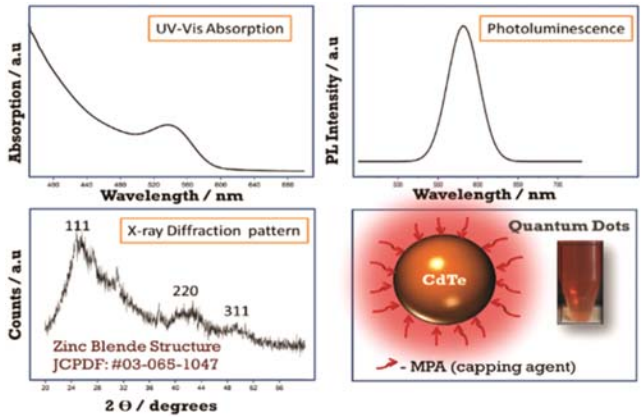

Fig. 2 — UVS spectra and PLS spectra (first row). XRD spectra and vial capture of CdTe QDs (second row).

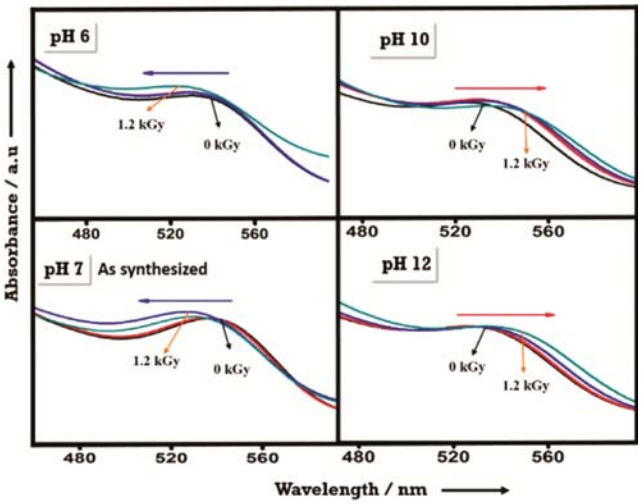

Fig. 3 — UVS spectra for pH number 6 and 7 (as synthesized) and pH 10 and 12.

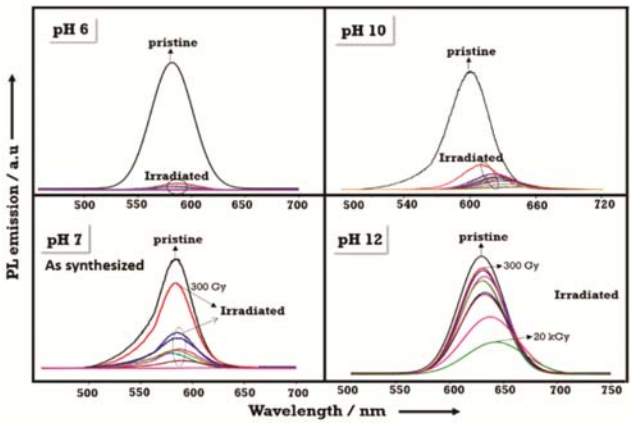

Fig. 4 — PLS spectra for pH number 6 and 7 (as synthesized) and pH 10 and 12.

surface defects as a response to irradiation. These surface defects lead to increase of non-radiative decay pathways. This depicts that QDs were PL quenched by gamma irradiation at acidic conditions due to photo-oxidation and finally to be precipitated. Contrarily, for basic conditions PLS curves started to stay long lived. For pH 12 QDs, PLS curves were not completely grounded even the gamma doses were increased up to 20 kGy. Therefore, basic conditions are suitable for QDs for any further modifications without much damaging their initial optical properties. Such modifications may include formation of shells over core QDs.

4 Conclusions

This study concludes that the optical properties of CdTe QDs capped with MPA were stable for varied gamma doses when their pH number of the solution was raised to higher basic region.

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