

One Pot Room Temperature Synthesis of CTAB Capped Highly Luminescent CdTe Quantum Dots in an Aqueous Medium and their Free Radical Scavenging Activity

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In the present paper, we have reported room temperature synthesis of CTAB capped CdTe quantum dots in an aqueous medium for free radical scavenging assay choosing BHA as the reference free radical. The formation of CdTe QDs required relatively shorter reaction time with quantum yield up to 40 %. Their optical properties, surface morphology and structural characterizations were employed through UV-Visible absorption spectroscopy, Photoluminescence, FE-SEM, Powder-XRD, Raman spectroscopy and DSC-TGA techniques. These QDs showed maximum absorption at 551 nm and their shape was spherical with average particle size of about 3-4 nm as noted by surface morphology. The results showed that the synthesized CdTe QDs have an excellent antioxidant activity. This type of semiconductor quantum dot is a promising material for the upcoming generation in high speed optics and biomedical fields.

Keywords: CTAB, CdTe QDs, Radical scavenging activity.

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1. INTRODUCTION

Metal chalcogenide based systems have drawn great attention in utilizing semiconductor Quantum dots for biological activities. Semiconductor quantum dots (QDs) are the nano-scale inorganic crystals with typical dimensions in the range of 1-10 nm [1-3]. Due to their quantum confinement of charge carriers in tiny space, QDs show some unique and fascinating optical properties [4-6]. Fluorescent semiconductor QDs has been evolved from electronic to biological applications over the past few years [3]. The colloidal synthesis of QD is well suited for the biological tagging materials. Size dependence of their optical and electronic properties is a unique feature of chiral quantum dots [7-9]. Fast moving and the most exciting interface of the present nanotechnology is mainly by the use of quantum dots (QDs). In particular, when these quantum dots are made water-soluble, they can be utilized for bio-labels, energy transfer, and storage devices [10-11]. The water-solubility of these QDs can be achieved by capping organic layer called CTAB, which can make it highly fluorescent. Luminescent quantum dots play an important role in the biological and chemical sensing in cellular environments [12-13]. Despite the recent progress, much work needs to be still done in order to study the electrical behavior of quantum dots [14-15]. It has been generally agreed that metal chalcogenide nanoparticles are essentially inert and non-toxic to the living cells. Quantum dots are semiconductor inorganic nanoparticles that are emerging as alternative tools to the organic fluorescent dyes used in bio imaging [13-16]. Reported CdTe QDs or fluorescent nanoparticles have been given high priority in many potential applications. But, there is a possibility of release of highly toxic free cadmium ions in case of such cadmium based nanoparticles.

Present work emphasizes synthesis of highly luminescent, water-soluble CTAB capped CdTe QDs by chemical reduction method at room temperature. The

synthesis process utilizes Cd and Te precursors in very dilute form and allows single step preparation of quantum dots. Further study includes the FESEM, UV-visible spectroscopy, Photoluminescence, Powder XRD, DSC, TGA, which results in the morphology, absorption property, luminescence property, structure and thermal property of the CdTe QDs respectively, with satisfactory results. These quantum dots showed excellent antioxidant activity against Butylated Hydroxy Anisole (BHA) which was used as reference standard for the free radical scavenging activity.

2. MATERIALS AND METHODS

2.1 Materials

All chemicals were of the highest Purity and were used without further purification. They were namely, Cadmium chloride ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$), Sodium Tellurite (Na_2TeO_3), Sodium borohydride (NaBH_4), Cetyl Trimethyl Ammonium Bromide- CTAB ($\text{C}_{19}\text{H}_{42}\text{NBBr}$) (purchased from Himedia), Dimethyl sulfoxide (DMSO), Methanol, 1,1-diphenyl-2-picryl hydrazyl (DPPH: Sigma Aldrich), and Butylated Hydroxy Anisole (BHA). In addition to these chemicals, doubly distilled water was used throughout the experiment.

2.2 Synthesis of CdTe Quantum Dots

The water-dispersed CTAB capped CdTe QDs were synthesized at room temperature with a typical molar ratio of 1:1 with doubly distilled water. Sodium borohydride was made to react with sodium telluride powder to give sodium hydrogen telluride (NaHTe). It was then added to the binary mixture of C-TAB and CdCl_2 and kept at room temperature for further reaction.

After some time the black color precipitate was obtained which indicated the formation of CdTe QDs Fig. 1. The solution was washed with doubly distilled water and centrifuged at 5000 rpm for about an hour

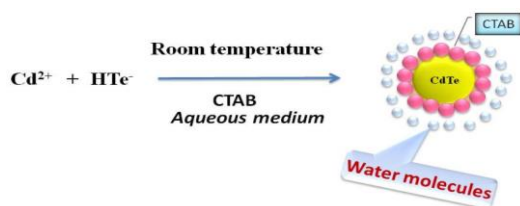


Fig. 1 – Mechanism involved in the formation of CdTe quantum dots in aqueous medium

and the same procedure was followed for several times (7 times) to remove residual reagents from the sample and to get the purely luminescent CdTe solution. Finally, obtained solution was dried under lamp for certain time to get its powder form and was utilized for antioxidant activity.

2.3 Characterization of Chemically Synthesized CdTe QDs

UV Vis spectroscopy is a technique used to quantify the light that is absorbed and scattered by a sample. Nano-particles have optical properties that are sensitive to size, morphology, agglomeration state and concentration near the nanoparticle surface, which makes UV Vis spectroscopy a valuable tool for identifying, characterizing and studying these materials. Nanoparticles made from certain metals strongly interact with specific wavelength of light which is its unique optical property. Hence, in the present report, UV-Visible spectroscopic studies (UV-Vis spectrophotometer Hitachi U-3310 Japan) were carried out using quartz cuvette with de-ionized water as a reference solvent. Also, Photoluminescence spectra were recorded on fluorescence spectrophotometer (model: Hitachi F-7000, Japan) wherein, light gets emitted from the sample when it is excited by the photons. To determine crystal structure, phase and dimension of material, X-ray powder diffraction technique was used. The structural parameter of synthesized material was performed using Rigaku pro analytical X-ray diffractometer with wavelength at 1.514×10^{-10} m for 2θ 0° to 80° [3, 17]. In order to study the morphology of QDs, SEM analysis was performed using JEOL Model JSM-6390LV and to identify some organic functional group of the compound, FT-IR measurement was carried out on a FT-IR spectrophotometer (Nicolet 6700) in the range of 400 to 4000 cm^{-1} using dry KBr pellet as a reference standard [18-17]. Moreover, Raman spectroscopy technique was used to observe vibrational, rotational and other low-frequency modes. The Raman spectral measurements were made on a NXR 6700 FT-Raman spectrometer where a diode pumped air-cooled continuous wave Nd:YVO₄ laser with an excitation line at 1064 nm provided a power of $\sim 500 \text{ mW}$ [19-20]. Thermal analysis by differential scanning calorimetry (DSC) (Quanta-20, USA) and thermo gravimetric analysis (TGA) (SDT Q-600 TA instruments, USA).

3. RESULTS AND DISCUSSION

The synthesis of non-cytotoxic QDs is critically important for their widespread applications, which largely rely on the understanding of their cytotoxicity [21-22]. The cytotoxicity of CdTe QDs was believed to be associ-

ated with the liberation of cadmium ions from the surface of the crystal lattice. The formation of CdTe QDs was confirmed by UV-Visible absorption, which was observed at 551 nm as shown in the Fig. 2.

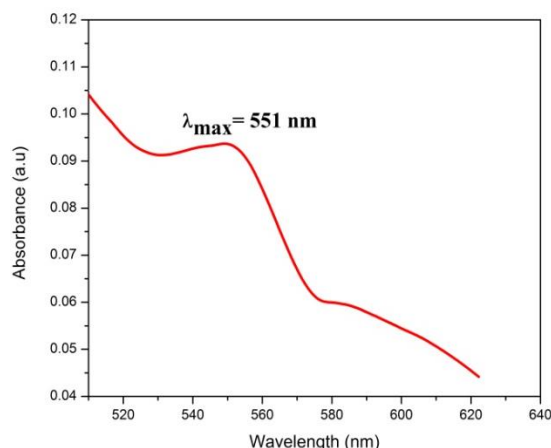


Fig. 2 – UV-Visible absorption spectra of CdTe QDs

Fig. 3 describes the photoluminescence of CdTe QDs at 630 nm . Fluorescence spectra and absorption spectra are important tools for the confirmation of quantum-confined property of metal QDs and also for the characterization of C-TAB capped CdTe QDs. To identify the presence of different functional group in CdTe QDs, they were subjected to FT-IR measurement and Fig. 4 depicts their resulting FT-IR spectra. The broad peak observed for the CdTe QDs at 3428 cm^{-1} corresponds to hydroxyl group with H-bonded OH stretching. The peak at 2919 cm^{-1} and 2851 cm^{-1} shows methylene C-H asymmetric and methylene C-H symmetric stretching respectively, representing saturated aliphatic group. Olefinic group of alkenyl C=C stretch is seen at 1636 cm^{-1} . The intense peaks at 1444 cm^{-1} and 1380 cm^{-1} show the presence of carbonate and carboxylate ions respectively, due to inorganic ions, and carboxylic acid in the compound whereas, 906 cm^{-1} and 856 cm^{-1} account for aromatic phosphates present in the synthesized material [23-25].

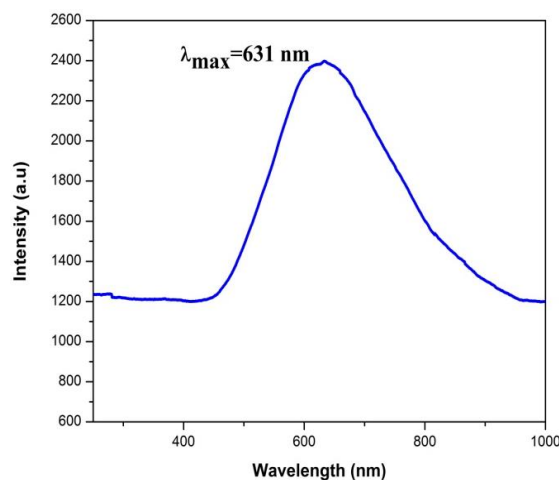


Fig. 3 – Photoluminescence spectra of CdTe QDs

Powder X-ray diffraction is a technique for deriving crystalline size and structure of nanomaterial. Fig. 5

shows the diffraction pattern obtained for CTAB capped CdTe QDs powder precipitated from aqueous solution. Analysis of XRD results for different 2θ values (16, 29, 43) and miller indices (010, 001, 101) show their orthorhombic structure (by JCPDS Data 65.6662) [23, 26]. As shown, the diffraction peaks are broader, which implies that the size of the QDs is smaller and the result can be explained by the Debye- Scherrer formula.

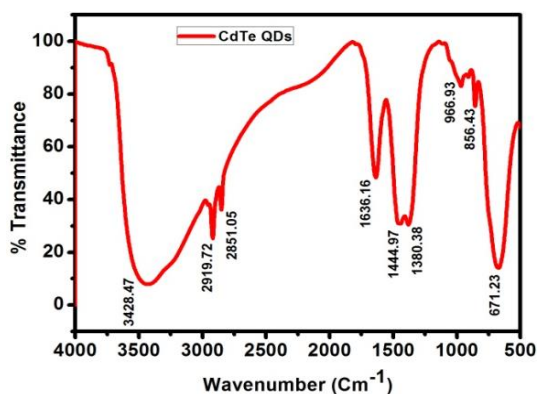


Fig. 4 – The FT-IR spectra of CTAB capped CdTe QDs

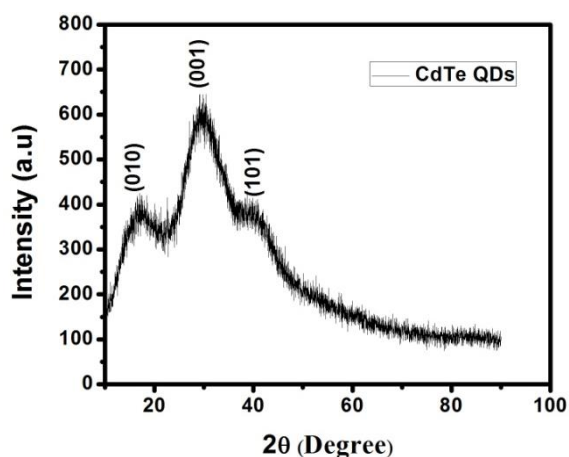


Fig. 5 – X-ray diffraction pattern of CTAB capped CdTe QDs

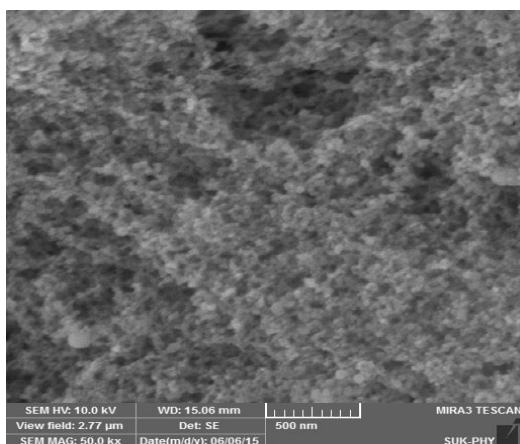


Fig. 6 – SEM image for CTAB capped CdTe QDs

The surface morphology and size of the synthesized CTAB capped CdTe QDs were investigated using SEM analysis. From FE-SEM image it was observed that the

particles are uniformly distributed and are in spherical shape as shown in Fig. 6. The particles are tightly bounded without agglomeration of the CdTe QDs. The size of the synthesized CdTe QDs was measured using pixel ruler and it was found to be 3 nm.

Raman spectroscopy is one of the vibrational spectroscopic techniques used to provide information about molecular vibrations and crystal structures. It is a good tool to study the interaction of protein and nanoparticles with respect to gain and to get a deeper insight into the mechanism of surface modification. The Raman spectrum is sensitive to some molecular bonds, and is used to measure the ligand binding on nanoparticles. In the present report, the CTAB capped CdTe QDs solution was incubated in a U-type glass capillary for Raman measurement. The spectrum showed the highest peak at around 162.17 cm^{-1} which could be assigned for the fundamental longitudinal optical phonon mode of CdTe QDs Fig. 7 [27].

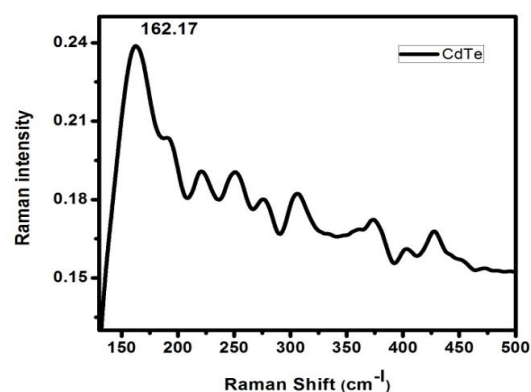


Fig. 7 – Experimental Raman spectra of CdTe quantum dots

3.1 DSC and TGA Analysis of CdTe QDs

The technique that permits the continuous weighing of a sample as a function of temperature and measure heat absorbed or liberated during heating. The typical DSC & TGA curves of the CdTe QDs measured under N_2 atmosphere during heating Fig. 8.

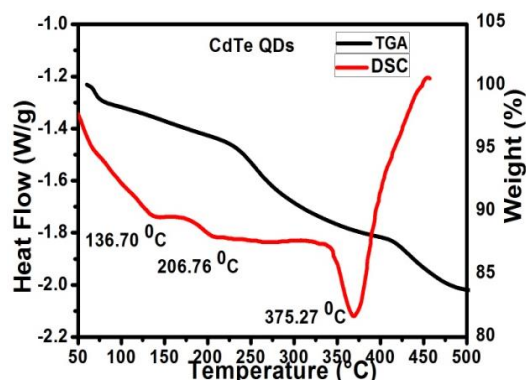


Fig. 8 – DSC and TGA curve of CTAB capped CdTe quantum dots

In order to know the melting temperature of CdTe QDs as well as to evaluate the processing conditions for ligand removal, DSC and TGA studies were acquired. The DSC of the CdTe quantum dots shows a sharp exothermic peak at 375.27 °C and smaller peaks at

136.70 °C, 206.76 °C.

These thermal loss events are consistent with loss with organic ligands. On the other hand, in the case of CTAB capped CdTe QDs the TGA curve exhibits two weight loss steps. The weight loss of 5 % is onset temperature 213 °C and 7.3 % at 420 °C temperature remains almost constant [28-29]. The weight loss is due to removal of ligand from the surface of nanoparticles.

3.2 Free Radical Scavenging Assay

The effect of synthesized quantum dots on DPPH radical was studied using standard method [30]. 1 mg of sample was added 1 ml of water and sonicated at 140 Hz for 2 mins. Upper layer of the sonicated solution was used for further study. Different concentrations (10 µg, 50 µg and 100 µg) of the sample in dimethyl sulfoxide (DMSO) were taken in a series of test tubes. The volume was adjusted to 500 µl by adding methanol. 5 ml of a 0.1 mM methanolic solution of 1,1-diphenyl-2-picryl hydrazyl (DPPH; from Sigma Aldrich) was added to these tubes and shaken vigorously. A control without the test compound, but with an equivalent amount of methanol was maintained. The tubes were allowed to stand at room temperature for about 20 mins. The absorbance of the samples was measured at 517 nm and Butylated hydroxy anisole (BHA) was used as reference standard. Percentage free radical scavenging activity of samples in comparison with BHA. The free radical scavenging activity was calculated using the formula:

$$\% \text{ Radical Scavenging Activity} = \frac{\text{Control Absorbance} - \text{Sample Absorbance}}{\text{Control Absorbance}} \times 100$$

Capped QDs were found to be potent free radical scavenger when compared to standard ascorbic acid. Free radical scavenging activity of CdTe QDs at higher concentration (100 µg/ml) is comparable to standard ascorbic acid as shown in Table 1. An antioxidant works in stopping the oxidation by neutralizing the free

Table 1 – Antioxidant activity of CdTe QDs with standard ascorbic acid

Concentration	% free radical scavenging	
	CdTe QDs	BHA
10 µg	– 0.35	7.80
50 µg	3.90	39.72
100 µg	40.60	83.51

radicals produced here. In order to neutralize the free radicals, the antioxidant itself undergoes oxidation during the process. Chemically synthesized CTAB capped CdTe QDs showed excellent antioxidant activity.

4. CONCLUSION

We have successfully demonstrated the synthesis of highly luminescent CTAB capped CdTe QDs prepared in aqueous medium and linked to antioxidant activities. We have also studied the size (3 to 4 nm) and shape (orthorhombic) dependence of the CdTe Quantum Dots. Thermal stability and weight loss of the ligands were studied with respect to temperature under nitrogen atmosphere. Compared to the used QDs prepared in organic phase, QDs prepared in water phase are of low cost and easily linked with biomolecules. Our preliminary results illustrate that CdTe QDs prepared in aqueous medium will probably become an attractive and an alternative probe in bio-targeting. The study provides potential applications in medical and biological fields too.

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