Synthesis of Magnetic Ions-Doped QDs Synthesized via a Facial Aqueous Solution Method for Optical/MR Dual-Modality Imaging Applications

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Abstract

This research reports the preparation and examination of Cadmium Telluride (CdTe) Quantum Dots and doping CdTe QDs with Europium (Eu), Gadolinium (Gd), and Manganese (Mn) prepared in aqueous solution using TGA as a capping agent. Magnetic QDs (MQDs) are important agents for fluorescence (FL) /magnetic resonance (MR) dual-modal imaging due to their excellent optical and magnetic properties. Herein, the chemical bonds, structural, fluorescence, and magnetized properties of CdTe QDs and effect of Mn, Eu, and Gd ions doping on their properties were examined by X-ray powder diffraction (XRD), high-resolution transmission electron microscopy (HRTM), Energy-dispersive X-ray spectroscopy (EDX), Fourier-transform infrared spectroscopy (FTIR), photoluminescence spectroscopy (PL), Ultraviolet-visible spectroscopy (UV-Vis), and vibrating sample magnetometer measurements (VSM). Almost similar X-Ray patterns with the absence/presence of ions for all samples with cubic crystal structures were obtained which indicates that the introduction of ions into CdTe QDs could not alteration the cubic primary structure of CdTe. Monodisperse size distribution with seemingly-spherical shapes, and also, the estimated mean diameters about 3 and less than 3 nm of QDs Were obtained. The effect of X ions injection on the fluorescence and UV-Vis properties of the QDs were also investigated. Optical studies showed the decreases in bandgap with the heating time increases during synthesis, and they undergo red-shift. The CdTe nanocrystals with high PL quantum yields were achieved in more than 6 h of heating. Also, investigations have shown the quenching of fluorescence by the existence of ions in the CdTe QDs. And Also, all the ions doped QDs exhibited ferromagnetic behavior at room temperature by a vibrating sample magnetometer which confirmed the success of the presentation of ions into CdTe cubic crystal structure. They can have been employed as a suitable contrast agent successfully for biological applications such as FL/MR dual-modal imaging.

1. Introduction

II–VI quantum dots (QDs) demonstrate one of the most significant types of nanomaterials [1,2]. Quantum dots show unique optical properties such as broad absorption [3], narrow, sharp and symmetric emission [3-5], high fluorescence quantum yield (QY) [6,7], high photo-stability [8], significant Stokes shift [9], supreme water solubility [9,10], and particle size-dependent band gaps and fluorescence (FL) [9], which is determined by broad excitation ranges and excellent robustness against photo-bleaching [5,11]. Because of their advantages, QDs have been extensively introduced great prospects in optronics [12,13], photovoltaics [13,14], thermal or light-emitting diodes [15,16], and especially in fluorescence technique [17-21] that can afford high sensitivity, high spatial resolution, target specificity, and real-time imaging at the cellular level for disease diagnosis [22,23], and other applications such as the biotracking of medicine molecules [24,25], biosensing [26], illness detection [27], photodynamic therapy (PDT) [28], antimicrobial prevention [29], bioimaging [30] and molecular-biology [31].

The optical properties of quantum dots such as fluorescence, can be managed by doping through designing the combination [32-37]. Hence, the possibility of control over the incorporation of doping elements into QDs lattices actions a significant role in a large number of applications. In this decade, rare-

earth-doped QDs have been fascinating major interest because of unique photoluminescence and electroluminescence properties that this doping is the main route to adjust their physical behaviors [38-40]. These QDs doped with rare earth elements have presented a high luminescence yield [41]. Rare-earth ions-doped quantum dots, because of both optical and magnetic potential in a single unit is of specific importance in the field of bioimaging [42-48]. Since the paramagnetic ions including, Gd^{+3} , Eu^{+3} , and Mn^{+2} are effective T1 contrast agents for magnetic resonance imaging, these ions doped quantum dots can behave effectively as fluorescence-magnetic resonance imaging bimodal agents [49]. So, synthesis methods have already been developed for getting X-doped ZnS, ZnSe, CdSe, and CdS QDs [32-38]. Several works explain the capabilities of Zn^{+2} -doped CdTe QDs synthesis [50,51]. In general, many factors contribute in quality and crystallinity of the final outcome of synthesis procedure [52], such as temperature, pH, pressure, time of reaction, and stirring conditions. There are also a number of works such as optical-magnetic bi-functional paramagnetic ions-doped quantum dots (MDQDs) based on CdSe [42,43], CdTe [44,45], ZnO [46] and Si [47,48] QDs that have been designed and researched. Matching to the papers, there are only a few reports on the optical properties [53-55] and the magnetic properties of rare-earth-doped CdTe such as Gd^{+3} , Eu^{+3} , and Mn^{+2} -doped CdTe in any form.

In the present study, CdTe and CdTe doped QDs with Eu, Gd, Mn elements, and coated with ligand TGA were grown in aqueous solution through a hot injection method. The size of QDs was controlled by changing the refluxing time in a wide range of 1-8 h. Then their chemical, structural, luminescence, magnetic properties via FTIR, XRD, HRTEM, EDX, PL, UV-Vis, and VSM spectroscopy were studied.

2. Experimental Section

2.1 Materials:

We obtained Tellurium powder (Te, 99.99%), Thioglycolic acid (TGA, 99%), sodium borohydride ($NaBH_4$, 98%), Cadmium sulfate ($CdSO_4 \cdot 8H_2O$, 98%), sodium hydroxide (NaOH, 97%), Gadolinium chloride ($GdCl_3 \cdot 6H_2O$, 99.99%), Europium nitrate ($Eu(NO_3)_3 \cdot 5H_2O$, 99.99%), Manganese nitrate ($Mn(NO_3)_2 \cdot 4H_2O$, 99.5%), deionized water and acetone (CH_3COCH_3 , 99.5%) from Merck, Germany and used without purification.

2.2 Preparation of CdTe QDs with TGA capping

The preparation of aqueous CdTe QDs with TGA capping was similar to a procedure reported formerly using NaHTe, CdSO₄, and Thioglycolic acid (TGA) [56]. Briefly, into a flask containing 0.11 g Te powder and 7 mL deionized water under argon (Ar) atmosphere added 0.276 g reducing factor ($NaBH_4$) and stirred for 3 h. Then, into a flask containing 150 mL deionized water added 0.36 g Thioglycolic acid as the stabilizer and 0.612 g CdSO₄. Using NaOH solution, the pH of the solution was adjusted to 10.0. The mixture was degassed for 30 min by Ar bubbling. In this stage, a fresh NaHTe solution in 43 mL deionized water was injected into the resultant solution under stirring and then heated to 100 °C for 5 h under an Ar atmosphere. The synthesized QDs solution was precipitated with acetone, separated by centrifugation,

and finally dispersed in ultrapure water. The TGA-CdTe QDs were fabricated by a temperature strategy with Solution (1) and (2) as illustrated in Fig.1.

2.3 Preparation of CdTe-X (X=Gd, Eu, and Mn) QDs:

The CdTe-Gd were also prepared with the same method used for TGA-CdTe QDs with the difference that 0.1% molar mass of gadolinium chloride powder was added to the second solution before injecting the tellurium section. The final solution was grown for 5 hours at 100°C. The prepared CdTe-Gd QDs solution was precipitated using acetone and separated by centrifugation, and finally dispersed in DI water. The CdTe-Eu and CdTe-Mn were also prepared with the same method used for CdTe-Gd QDs. The CdTe-X (X=Mn, Eu and Gd) QDs were fabricated by a temperature strategy with Solution (1) and (3) as illustrated in Fig.1.

2.4 Characterization

Characterizations of the synthesized QDs were carried out using XR-D, UV-Vis, FT-IR, HRTEM, PL, EDX, and VSM analysis. The crystal structures of QDs were determined utilizing X-ray diffraction (XRD, Philip X'Pert Pro MPD X-ray diffractometer with Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$). Infrared spectra in area 200–4000 cm^{-1} were recorded on the Perkin-Elmer, Spectrum RX FTIR, USA instrument using KBr pellets. Electronic absorption spectra were recorded in region 200–900 nm by using Perkin Elmer UV-Vis spectrophotometer. The PL spectra were measured with G9800A Agilent, under ambient conditions. The high-resolution transmission electron microscopy (TEM) image of the QDs was acquired on a JEOL, JEM-2100F, 200KV electron source. Also, the energy-dispersive X-ray spectroscopy (EDX) pattern of the QDs was recorded on RONTec EDS. The magnetic properties were determined by using Magnetic daghigh kavar, MDKB's fully integrated vibrating sample magnetometers (VSM) at room temperature.

3. Results And Discussion

In our paper, the CdTe-X QDs are synthesized in aqueous solution by 5 h of heating at 100°C. The high-resolution transmission electron microscopy (HRTEM) images and Energy-Dispersive X-ray spectroscopy of the CdTe-X (X= Gd, Eu, and Mn) QDs shown in fig.2 (a-f) revealed the formation of seemingly -spherical shapes with an almost monodisperse size distribution. The estimated mean diameters of the CdTe-X (X= Gd, Eu, and Mn) QDs were 3 and less than 3 nm. Energy dispersive X-ray analysis (EDXA) revealed that the CdTe-X (X= Gd, Eu, and Mn) QDs were composed of Cd, Te, and X (X= Gd, Eu, and Mn) elements, and the X content was approximately 6.73, 3.64 and 1.24 wt%, respectively (Figure 1b, d, and f of the table). Also, figures are clear that the strong signals of Cd, Te, and X indicate that the nanoparticles were made of CdTe-X (X= Gd, Eu, and Mn) QDs. The presence of X (X= Gd, Eu, and Mn) ions with no other impurity ion confirms the purity of synthesized QDs.

The synthesized CdTe and CdTe-X (X= Gd, Eu, and Mn) QDs in aqueous solution by 5 h of heating at 100°C were characterized by FTIR and XRD determine their conjugation and structure. Fig. 3(A) shows the FTIR spectra of TGA, TGA-caped QDs, and CdTe-X in the range of 200–4000 cm^{-1} . The characteristic

peaks of CdTe and CdTe-X bands at 2563 cm^{-1} can be attributed to the Vibration band of S–H that is observed in the free TGA molecules disappeared on the coordination of these molecules with colloidal CdTe and CdTe-X [57,58]. This is evidence of the formation of the S–Cd bond between TGA ligand molecule and QDs. We observed TGA peaks ascribed to the asymmetric and symmetric stretch vibrations of carboxyl groups shifted after being connected to QDs, confirming the formation of TGA-capped QDs [58]. The crystal structures determined by X-ray diffraction are shown in Fig.3 (B). Data were collected at room temperature in 2θ range of $10-75^\circ$. The diffraction peaks were indexed by CdTe and CdTe-X (X= Gd, Eu, and Mn) QDs (JCPDS No. 65-1046) [59]. The XRD results showed reflection planes at (111), (220) and, (311) for CdTe and CdTe-X. We obtained almost similar patterns for all samples indicating similar cubic crystal structures for CdTe, and CdTe-X [57]. The mean crystalline size of CdTe and CdTe-X were determined according to FWHM of diffraction peak based on the Scherer's equation 3nm , which is consistent with the results of the HRTEM. No other impurity peaks were established, which demonstrates that the presence of X (X = Gd, Eu, and Mn) into CdTe QDs could not alter the cubic crystal structure of CdTe. Also, the intensity of the peaks decreased with X ions (X = Gd, Eu, and Mn), which could be due to the lattice disorder caused by the presence of dopant atoms in the CdTe host lattice [60].

Fig. 4 presents the room temperature photoluminescence (PL) spectra of CdTe and CdTe-X (X = Gd, Eu, and Mn) QDs prepared during the 1-8 h of heating and recorded with an excitation wavelength of 405 nm . For all Four samples in the Figures a-d, with the increase in the reaction time, the emission peak wavelengths red-shifted accompanying with the broadening of peaks that mainly due to the inhomogeneity in particle size and the growth of QDs and. The emission peak wavelengths were 572 , 572 , 573 , and 567 nm for the CdTe, CdTe-Gd, CdTe-Eu, and CdTe-Mn QDs, respectively, after 8h reaction. With the presence of X (X = Gd, Eu, and Mn) ions, the emission intensity Drastically reduced under the same reaction time. The surface effects of the doped QDs were increased because of the doping of X (X = Gd, Eu, and Mn) ions whose ionic radius is differing from Cd^{2+} [45] and this leading to the suppressing of the fluorescence of the doped CdTe QDs.

CdTe QDs show an increase in FWHM with a time increase to 3 h , then a decreasing trend (5h), and as the heating time increases, FWHM remains constant. Samples of CdTe-Gd and CdTe-Mn QDs show FWHM changes in similar growth times, sometimes increasing and decreasing, but the overall trend is rising. But the FWHM of CdTe doped with Eu ions, although increasing, is higher than CdTe, CdTe-Gd, and CdTe-Mn QDs. After 8h of growth time, CdTe QDs have the least and CdTe-Eu QDs have the most FWHM. But FWHM of CdTe-Mn QDs in the first 4 hours is less than CdTe QDs, but has increased in later times. In other words, particle size distribution with the presence of Gd, Eu, and Mn ions has expanded the peak of the fluorescence.

Fig. 5 shows the temporal evaluation of the PL emission peaks and PL Intensity of CdTe and CdTe-X (X = Gd, Eu, and Mn) QDs prepared during the 1-8 h of heating. The emission peak position is displaced and increased from 1 h to 8 h of heating time that the amount of displacement was 30.2 , 33.2 , 35.2 , and 36.19 nm for the CdTe, CdTe-Gd, CdTe-Eu, and CdTe-Mn QDs, respectively. This difference in displacement may be due to the presence of X (X = Gd, Eu, and Mn) ions and the effect on growth rate or

changes in the electronic structure of quantum dots. Also, PL peak intensity for CdTe is increased by a specific time and then decreased. In the samples of Mn-CdTe QDs, the behavior of the intensity changes is similar to that of CdTe and CdTe-Gd QDs, but these changes occur at a lower slope. In the Eu-CdTe QDs pattern, the overall trend of change in the intensity of the intensity is increasing. This indicates that the increase in heating time has caused the QDs to become higher PL efficiency. Presumably, the presence of Europium ions has reduced surface traps by increasing the heating time on the surface of the quantum dots. In general, the PL intensity of CdTe QDs doped with Gd, Eu, and Mn is less than that of CdTe QDs, which may be due to the placement of Gd, Eu, and Mn ions in the structure of QDs that due to the difference in the radius of these ions, it is with the radius of the Cd ions that it causes structural defects and as a result a decrease in intensity. CdTe and CdTe-Eu QDs have the highest and lowest fluorescent intensities, respectively.

Photographs of the four samples (CdTe, CdTe-X (X= Gd, Eu, and Mn)) in reaction time from 1 to 8 h were taken under visible light and 360 nm UV light, respectively (fig.6). Figures 6 a, c, e, and g indicates that the prepared CdTe and CdTe-X (X= Gd, Eu, and Mn) QDs solutions are transparent under visible light and large particles are not observed in them, which suggests that these QDs are well-dispersed in the aqueous phase without further treatment. Under UV irradiation, the as-prepared CdTe and CdTe-X (X= Gd, Eu, and Mn) QDs solutions emit bright as shown in Figure 6 b, d, f, and h. The colors of these CdTe and CdTe-X (X= Gd, Eu, and Mn) QDs are consistent with the corresponding PL spectra in Figure 4. In all solutions containing QDs, the trend of light emission changes is observed over time. Their emission has changed from green light emitted at an early time to yellow and orange light emitted, and the rate of these changes varies in different samples.

Figure 7 shows the absorption spectra and bandgap changes of CdTe and CdTe-X (X= Gd, Eu, and Mn) QDs during the 1-8 h of heating in aqueous solution. For CdTe QDs in the Figure 7a, with the increase in the reaction time, the absorption peak wavelengths red-shifted and accompanying with the broadening of peaks. This is owing to the weakening effect of Quantum Confinement with increasing size. The absorption spectrum in the longer wavelengths is almost zero. This indicates that the solution of the QDs is uniform and the light scattering of particles does not occur in the colloidal solution. The absorption peak position of the QDs has been red-shifted during growth time (displacement for CdTe QDs: 32.358 nm). The exciton peak positions red-shifted from the aqueous solutions of CdTe and CdTe-X (X= Gd, Eu, and Mn) QDs (Fig7 b, c, and d), with displacement rates of 40.32, 39.66, and 43.26, respectively, and this can indicate the growth of quantum dots [61,62]. Comparing the position of the 4 sample peaks, the rate of changes in the peak position of CdTe QDs doped with Gd, Eu, and Mn is greater than of CdTe QDs, so the presence of foreign ions has affected the growth rate of quantum dots. The optical band gap (E_g) of QDs, was computed from the $(\alpha h\nu)^2$ vs $h\nu$ ($E - E_g$) curves from the transmittance data, where α is the optical absorption coefficient in cm^{-1} , h is Planck's constant, and $h\nu$ is the photon energy in eV [63]. Figure7 (e) shows the bandgap changes of CdTe and CdTe-X (X= Gd, Eu, and Mn) QDs during the 1-8 h of heating in aqueous solution. The obtained values of E_g for 4 samples during the heating showed in all QDs, the energy gap decreases as the heating time increases, which could be related to the growth of the

particle size [61,62]. The slope of the energy gap changes in all quantum dots is almost the same. This decrease in E_g correlates with corresponding red shift in the absorption spectra, this shift may be due to the introduction of new shallow energy levels in between the band gap on addition of dopant ions in host CdTe QDs [45].

To study the magnetic properties of the CdTe-X (X= Gd, Eu, and Mn), magnetization hysteresis measurements were done using vibrating sample magnetometer (VSM). Fig. 8 shows the M-H curves of the CdTe-X (X= Gd, Eu, and Mn) QDs and The inset curve is shown enlarged view around -140 to 140 Oe applied magnetic field. The un-doped CdTe exhibited a diamagnetic, whereas all the CdTe QDs doped with X ions (X= Gd, Eu, and Mn) showed clear magnetization hysteresis, indicating ferromagnetic behavior at environment temperature. The diamagnetic behavior of the un-doped CdTe QDs was ascribed due to the lack of unpaired electrons in its d orbital [64,65].

The saturation magnetism calculated is 0.072, 0.006, 0.223, and 0.121 emu/g for CdTe-Gd, CdTe-Eu, and CdTe-Mn respectively. From this figure, there was a notable enhancement in the saturation magnetization with adding X ions and the amount of saturation magnetization CdTe- Eu QDs higher than CdTe-Gd and CdTe-Mn QDs. This denotes that Eu ions higher than Gd and Mn ions were magnetically ordered with respect to the applied magnetic field (H). CdTe-X (X= Gd, Eu, and Mn) QDs, ferromagnetism is considered to originate from the exchange interaction between free delocalized carriers and the localized d, f spins on the Gd, Eu and Mn ions (electrons and holes). The values of magnetization (M_s), coercivity (H_c),

retentivity (M_r), $S(\frac{M_r}{M_s})$, μ_{rs} , and χ are shown in Table 1. The observed environment-temperature ferromagnetism of the CdTe-X (X= Gd, Eu, and Mn) QDs may be due to the substitution of X ions in place of Cd^{2+} in the CdTe lattice without changing their structure [66,67].

Table. 1 Magnetization (M_s), coercivity (H_c), retentivity (M_r), μ_{rs} , χ , and S values of CdTe-Gd, CdTe-Eu and CdTe-Mn QDs.

Sample's	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	μ_{rs}	χ	$S=M_r/M_s$
CdTe-Gd	0.072	0.0046	77.36	1.00093	0.00093	0.063
CdTe-Eu	0.223	0.0058	34.88	1.006	0.006	0.026
CdTe-Mn	0.121	0.0076	134.5	1.00089	0.00089	0.062

4. Conclusions

CdTe and CdTe-X (X= Gd, Eu, and Mn) nanoparticles coated with ligand TGA were synthesized by an aqueous method. Then, synthesized QDs were characterized by FTIR, XRD, EDX, HRTEM, VSM, and optical spectroscopy. Doping of X ions did not change the cubic crystal structure, but caused more QDs to grow. EDX spectra revealed the existence of X ions in CdTe-X QDs powders. The effect of the X (X= Gd, Eu, and Mn) dopant on the optical properties of Prepared QDs was investigated in detail. The PL and UV-Vis spectra of all the samples showed broad emission peaks and decreased fluorescence intensity. The

magnetization measurements clearly showed room temperature ferromagnetism in X ions doped CdTe powders. The cause of the observed magnetism is X ions interactions.

Declarations

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Figures

Figure 1

Schematic of the formation of TGA-capped CdTe and CdTe-X (X=Gd, Eu, and Mn) QDs.

Figure 2

HRTM images and EDX spectra of prepared a,b) CdTe-Gd, c,d) CdTe-Eu, and e,f) CdTe-Mn QDs.

Figure 3

(A) FTIR spectra and (B) X-ray diffraction pattern analysis of TGA-capped a) CdTe, b) Gd-CdTe, c) Eu-CdTe and d) Mn-CdTe QDs.

Figure 4

Fluorescence spectra of (a) CdTe, b) CdTe-Gd, c) CdTe-Eu, and d) CdTe-Mn QDs (reaction time, 1–8 h; λ_{ex} = 405 nm).

Figure 5

Trend of changes in the corresponding PL Peak Position (a) and PL Intensity (b) during the heating.

Figure 6

Photographs of QDs under visible light and UV light (a,b) CdTe QDs, (c,d) CdTe-Gd QDs, (e,f) CdTe-Eu QDs and (g,h) CdTe-Mn QDs (reaction time, 1-8h; from left to right).

Figure 7

Absorption spectra of (a) CdTe, (b) CdTe-Gd, (c) CdTe-Eu, and (d) CdTe-Mn QDs, and Trend of changes in the bandgap of $\alpha \rightarrow b$ during the heating process. (reaction time, 1–8 h).

Figure 8

Magnetization versus magnetic field hysteresis loop for a) CdTe-Gd, b) CdTe-Eu, and c) CdTe-Mn QDs. The inset shows enlarged view around -140 to 140 Oe applied magnetic field.