Effects of growth time on the material properties of CdTe/CdSe core/shell nanoparticles prepared by a facile wet chemical route

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Abstract

This study presents a facile synthetic approach used to prepare CdTe/CdSe core/shell nanoparticles (NPs). The effects of reaction time on the material properties of the CdTe/CdSe NPs are reported. It was realized that the reaction time has significant impact on the CdSe shell growth on the CdTe core. Various techniques were used to characterize the as-prepared CdTe/CdSe NPs. The x-ray diffraction (XRD) was used to study the crystal structure and the possible growth of the CdSe shell on the CdTe core. The results obtained indicated the formation of zinc blende crystal structure which was transformed from a polycrystalline to single crystalline structure. The XRD pattern displayed features that are intermediate between the CdTe and CdSe, a sign of shell formation and not two separate compounds formed. This was also supported by high resolution transmission electron microscope images obtained. The crystallite sizes estimated using Scherrer formula were all less than 3 nm showing that the NPs are in quantum confinement regime. Scanning electron microscope was used to determine the surface topography while the energy x-ray dispersive spectrometer displayed the elemental composition of the as-prepared NPs. SEM and HRTEM images showed uniformly distributed spherical NPs with some agglomerations observed at longer duration of synthesis. The optical properties (photoluminescence (PL) and absorbance) investigated at different reaction times (20, 40, 60 and 80 min) presented novel features which show the formation of a thin CdSe shell on the CdTe core NPs. The PL emission wavelength was dramatically red shifted upon the growth of the CdSe shell on the CdTe core (from 541–615 nm). Other unique features of the as-grown CdTe/CdSe NPs are discussed in detail. The obtained results displayed good material properties of the CdTe/CdSe NPs suitable for use in biomaging applications.

1. Introduction

The group of semiconductor nanoparticles (NPs) usually classified as core/shell NPs or otherwise known as core/shell quantum dots (QDs), are a category of strained NPs which have drawn considerable interest due to their interesting unique structural, electronic and optical features. The lattice mismatch between the shell and the core of these materials are known to greatly impact on the fluorescence efficiency of these materials [1, 2]. Quantum dot is a semiconductor NP with zero dimensions and has smaller radius as compared to the bulk Bohr exciton radius. The material properties of such nanocrystals display different properties from the bulk material due to the effects of quantum sizes. These QDs show a greater band gap than the bulk value which decreases as the size of the QDs increase. The effects of quantum incarceration cause the nanomaterial to possess tunable optoelectronic properties.

Additionally, QDs have a sharp density of states making them to possess good optical and transport properties. The applications of these core/shell NPs are dependent on their size and shape. These include LEDs, LASERs, display devices, photovoltaic and biomedical imaging which have been made possible due to the narrow emission and wide absorption bands of the QDs [3, 4]. Various morphologies of Cd-based materials are also used in various applications such as solar cell, supercapacitor and gas sensors [5, 6]. The broad absorption
spectra displayed by these QDs also make it possible to produce more efficient solar cell devices. For NPs to be used as light emitters, they need to emit a stable light against photo and chemical degradations. In order to achieve this, the NPs surfaces are coated with inorganic materials which are known to possess a wider band gap to cover the energy band gap of the core NP [7, 8]. This is done to enhance the photoluminescence (PL) quantum yields through surface passivation of non-radiative recombination sites. It is reported that NPs coated with inorganic shell material are stronger and have greater efficiency to undergo the processes required to build solid state structures than the organically passivated counterparts [1, 9–12].

Heterostructure NPs display unique material properties due to the spatial separation of charge carriers. These core/shell heterostructures are classified into two categories: type-I which has bestriding band configuration and type-II whose band orientation is staggered [13]. There has been an increasing interest on the type-II core/shell heterostructure, for instance, the CdTe/CdS NPs. This is because of the long decay lifetime caused by spatial separation of holes and electrons between the shell and the core [13–15]. Furthermore, the photoexcitation of type-II NPs heterostructures have staggered band offsets which are accompanied by charge transfer across the boundary between the two materials. The PL emission energy from these type-II NPs is lower than the PL from either of the constituent NP, thus paving ways of obtaining near-infrared emission [16, 17]. The core–shell structures are prepared in such a way that they passivate the surface traps, and thus increase the quantum efficiencies of the QDs. Various type-I core–shell structures like the, CdSe/ZnS, CdSe/CdS, CdS/ZnS and InP/ZnS [13, 18–20] have been studied widely and were found to represent extremely stimulating options of representing the common organic dye molecules in applications such as labelling processes especially bio-labelling where the in vitro or in vivo labelling of a bio molecule is conducted and it is detected using the PL of the QD [21]. In addition, various core–shell nanostructures including CdS/HgS/CdS/ZnSe/ZnS CdSe/CdS/ZnS were extensively studied and reported by Dirks et al [22]. These studies presented various concepts and preparation techniques used. However, most of the techniques and methodologies used require sophisticated equipment which are also expensive as compared to our current study.

Also, core/shell NPs are extremely useful nanocrystals with engineered material features. The features of either the core or shell material are to a certain extent different. These features can be changed by modifying the starting precursors or the ratio of core to shell [23]. This is because the properties of the core NP such as thermal stability and reactivity can be enhanced by coating the material with a desired shell. The manipulation of the surface functions is done in order to meet the requirements needed for various specific applications [24, 25]. The choice of the material used as the coating/shell depends strongly on the purpose in which the NPs are intended for.

There are various approaches of preparing high-quality core/shell NPs reported. These include epitaxial growth, aqueous synthesis, and the organometallic routes among others [26–28]. In most of the methods reported, evolution of the shell on the core NP was found to be an effective method to remove the bonds hanging on the surface and to enhance the spectral characteristics of the NPs [29]. In comparison to the organometallic route, aqueous synthesis of NPs is inexpensive, mimicable and less venomous. The aqueous synthetic approach of preparing CdTe/CdSe core/shell QDs reported include; illumination, selective photochemical etching, microwave irradiation and ultrasound [30–32]. However, these techniques even if they are effective, are relatively intricate and need extra expensive apparatus to use. Sol-gel technique of preparing CdTe/CdSe core/shell NPs has least been studied to the best of our knowledge.

In this investigation, a sol-gel method of preparation by a simple wet chemical route was used to study the effects of reaction time on the shell growth and the material properties of CdTe/CdSe NPs. The ability to concoct the band gap of CdTe/CdSe core/shell NPs opens great doors to various choices of NP material for desired applications. Control of the NP size, size distribution and optimization of NP structure by tuning of the band gap are known to be beneficial to both electron transfer and collection. Band gap engineering can be achieved by spraying small coating on the NPs within the quantum confinement regime which would cause lattice strain thus modifying the band gap of the NPs grown. The as-grown CdTe/CdSe NPs characterised by various techniques were found to have good structural and optical properties suitable for use in biological applications.

2. Experimental procedure

2.1. Chemicals

Analytical grade of the chemicals used for this study were purchased from Sigma Aldrich and used without any form of purification done. They include: potassium tellurite (K₂TeO₃) (>90%), anhydrous cadmium chloride (>99%), selenium powder (>99%), L-cysteine (>98%), sodium borohydride, acetone (>99%) and sodium sulphite (>98%).
Reduction of selenium was done using the procedure described in the text. Molar ratios of Cd: Cyst: Te: NaBH4 were controlled at 1:1:0.4:10. The CdTe NPs were removed from the hot sodium borohydride precursor solutions. The mixture was stirred continuously for 5 min followed by an addition of excess amount of tellurite (adjusted to 11 by dropwise addition of 1M NaOH. A second mixture containing a 0.04 mmol of potassium mixed in a beaker. The cadium to L-cysteine molar ratio was controlled at 1:1. The pH of the solution was then prepared as follows; Under stirring for 5 min, equal molar solutions of cadmium chloride and L-cysteine were prepared in 100 ml deionised water. This formed sodiumselenosulphate which became the source of the Se ions used in the growth of CdSe shell. Secondly, 0.2 mmol of cadmium chloride and 0.2 mmol of L-cysteine were dissolved in DI (50 ml). The Se was then added to 11 by dropwise addition of 1M NaOH. The preformed CdTe NPs were added into the solution under stirring for 5 min followed by addition of 3 ml of the reduced Se. The mixture was poured into a 3-necked flask containing the cadmium and L-cysteine precursor solutions. The mixture was stirred continuously for 5 min followed by an addition of excess amount of sodium borohydride (0.8 mmol). The final solution was then refluxed at 100 °C in open air for 30 min. The molar ratios of Cd: Cyst: Te: NaBH4 were controlled at 1:1:0.4:10. The CdTe NPs were removed from the hot plate, cooled down to room temperature, washed three times by addition of excess acetone (approximately 30 ml per wash) and then dried to await the coating of the CdSe shell on it. Aliquot of the sample was taken to study its optical properties.

2.2. Synthesis of CdTe core
Syntheses of the CdTe core NPs were carried out using a method described in [33]. The CdTe core NPs were prepared as follows; Under stirring for 5 min, equal molar solutions of cadmium chloride and L-cysteine were mixed in a beaker. The cadmium to L-cysteine molar ratio was controlled at 1:1. The pH of the solution was then adjusted to 11 by dropwise addition of 1M NaOH. A second mixture containing a 0.04 mmol of potassium mixed in a beaker. The cadium to L-cysteine molar ratio was controlled at 1:1. The pH of the solution was then prepared as follows; Under stirring for 5 min, equal molar solutions of cadmium chloride and L-cysteine were prepared in 100 ml deionised water. This formed sodiumselenosulphate which became the source of the Se ions used in the growth of CdSe shell. Secondly, 0.2 mmol of cadmium chloride and 0.2 mmol of L-cysteine were dissolved in DI (50 ml). The pH was then adjusted to 11 by dropwise addition of 1M NaOH. The preformed CdTe NPs were added into the solution under stirring for 5 min followed by addition of 3 ml of the reduced Se. The mixture was poured into a 3-necked flask and reacted at 100 °C under reflux in open air condition. The CdSe shell NPs were left to grow for various reaction times (CdTe-0 min, Q1–20 min, Q2–40 min, Q3–60 min and Q4–80 min). Small amount of the NP solution in each sample was taken out and cooled down to room temperature in order to monitor the optical properties of the CdTe/CdSe NPs. The as-prepared CdTe/CdSe NPs were cleaned by precipitation using acetone and dried for further characterization.

It’s important to understand the CdTe/CdSe core/shell formation mechanism. Basically, in our previous work [33,35] the formation mechanism of CdTe and CdSe NPs were discussed in detail, and a lot has been borrowed from that work. However, for the formation of CdSe shell on the CdTe core is as shown in the scheme 1.

After the formation of CdTe core (i), upon introduction of reduced Se into the precursor solution, the Se reacts with excess Cd \(^{2+}\) to form a thin shell of CdSe on the CdTe core freely (scheme I(ii)). As the growth time increases, the shell thickness increases systematically (as seen in scheme 1, (iii and iv)) until a point of saturation and distortion where the CdTe/CdSe core/shell become agglomerated and no longer crystalline.

2.3. Synthesis of CdTe/CdSe core/shell NPs
Reduction of selenium was done using the procedure described in [34]. Selenium (0.31 g) was reduced using sodium sulphite (1 g) in 100 ml deionised water (DI) and refluxed for 6 h at 80 °C. This formed sodiumselenosulphate which became the source of the Se ions used in the growth of CdSe shell. Secondly, 0.2 mmol of cadmium chloride and 0.2 mmol of L-cysteine were dissolved in DI (50 ml). The pH was then adjusted to 11 by dropwise addition of 1M NaOH. The preformed CdTe NPs were added into the solution under stirring for 5 min followed by addition of 3 ml of the reduced Se. The mixture was poured into a 3-necked flask and reacted at 100 °C under reflux in open air condition. The CdSe shell NPs were left to grow for various reaction times (CdTe-0 min, Q1–20 min, Q2–40 min, Q3–60 min and Q4–80 min). Small amount of the NP solution in each sample was taken out and cooled down to room temperature in order to monitor the optical properties of the CdTe/CdSe NPs. The as-prepared CdTe/CdSe NPs were cleaned by precipitation using acetone and dried for further characterization.

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2.4. Characterization of the CdTe/CdSe core/shell NPs
The morphological and composition analyses were carried out using a JEOL JSM-7800F model of scanning electron microscope (SEM) which has an Oxford Aztec Energy-dispersive x-ray spectroscope (EDS) in it and a high-resolution transmission electron microscope (HRTEM) was used to also confirm the formation of CdTe/CdSe core/shell NPs. The crystal structure was characterized by means of an Advance Bruker D8 model of x-ray diffractometer (XRD) (Philips) from Germany which uses a Cu Anode x-ray tube. The wavelength of the K\(\alpha\) radiation is approximately 1.5406 Å. Shimadzu evolution 100 was utilized to measure the absorbance of the as-prepared NPs in the 200–800 nm range. The obtained spectra were then used to estimate the energy band gaps for all the samples. PL spectroscopy was executed on a Cary Eclipse fluorescence spectrophotometer; model LS-55 with an in-built 150W xenon flash lamp as the excitation source to measure the emission and excitation energies of the as-prepared samples. Suitable excitation wavelength was selected by means of filter (grating).
3. Results and discussion

3.1. XRD analysis

The structural characteristics of the as-grown CdTe/CdSe NPs were studied using x-ray diffractometer. These studies were carried out in order to determine the formation of CdSe shell on the CdTe core NPs. The crystal structures of the as-prepared samples were obtained by comparing the corresponding XRD pattern with the standard diffraction file. Figure 1(a) show the XRD patterns for the CdTe core and the CdTe/CdSe NPs with the corresponding JCPDS files plotted on top (CdSe) and bottom (CdTe) of the plot. At zero minute of shell growth, is CdTe core NPs. The CdTe and CdTe/CdSe at 20 min display three broad diffraction peaks which are well indexed to the 111, 220 and 311 diffraction planes of the CdTe NPs. As the reaction time increased, the structure was transformed from being polycrystalline to single crystalline. The XRD patterns of the as-obtained CdTe/CdSe NPs were observed to posses features which are intermediate between the CdTe and CdSe semiconductor materials. No separate peaks were observed as they match well with the zinc blende cubic crystal structure of both CdTe and CdSe (JCPDS file no. 75–2086 for CdTe and 19–0191 for CdSe). The observed results indicate the clear formation of heterostructure. The broad peaks presented by the XRD patterns are due to the small particle sizes in the nano range.

There was an obvious shift of the XRD peaks to higher diffraction angle with an increase in reaction time as depicted in figure 1(b). Difference in the relative peak intensities is also observed (inset in figure 1(b)). A great enhancement of the reflection peak intensities is realised when the CdSe coating was introduced into the CdTe core. The shift in the diffraction angles to higher 2theta could be due to the formation of the CdSe shell on the CdTe core NPs while the increase in the relative peak reflections of the CdTe/CdSe NPs is attributed to the improved crystal quality of the NPs. In order to estimate the shell thickness, the crystallite sizes of the CdTe/CdSe NPs obtained were calculated by means of Debye–Scherrer equation (equation (1)) [36];
where $D$ is the crystallite size, $\lambda$ is the wavelength of CuK$_\alpha$ radiation (1.5406 Å), $\theta$ is the Bragg’s diffraction angle, and $\beta$ is the full width at half maximum (FWHM) broadening. Crystallite sizes found from the XRD results increased with an increase in the reaction time. The growth observed was very small indicating the formation of thin shell on the CdTe NPs.

The shell thickness is seen to increase as the reaction progressed to longer duration of synthesis. The estimated size of the obtained crystals were; 2.31, 2.34, 2.40, 2.42 and 2.43 nm for CdTe-0 min, Q1–20 min, Q2–40 min, Q3–60 min and Q4–80 min respectively. From these results, the shell thickness was simply predicted by subtracting the size of the CdTe NPs from the size of the CdTe/CdSe core/shell NPs. The shell thickness was found to be 0.03, 0.9, 0.11 and 0.12 nm for Q1–20 min, Q2–40 min, Q3–60 min and Q4–80 min, respectively.

During the calculation of the shell thickness, it was assumed that the shell is coated onto the CdTe layer by layer as a coherent structure. In this case the CdTe just like thin films acts as a substrate to which the shell will be coated to form the heterostructure. This is supported by the fact that most of the calculated lattice parameters show a slight deviation from the standard values of CdTe. Although Smith et al. [37] reported that the ideal method of calculating the shell deposition is to find the exact number of uncapped orbitals of the surface atoms on the NPs after which the specific number of the elemental precursors is then added to the NPs to form a monolayer of the shell. They acknowledge that getting the exact values is not yet possible and therefore correlation with the theoretically calculated values was done.

In the reported method, careful control of the CdTe core NPs was conducted to minimize the errors that could occur in the size of the core. At the initial stage of growth, the shell is believed to assume the lattice constants of the core material. As the reaction progresses this behavior declines as the shell thickness become thick enough to be able to compress the core. This explains why the obtained lattice constants were more inclined to the CdTe than the CdSe standard values.

Table 1. Structural parameters showing comparison of the CdTe core and the CdTe/CdSe NPs prepared at various reaction times.

| Sample | d-spacing (nm) | Lattice parameter, $a$ (Å) | Strain, $\varepsilon$ | Dislocation density, $\delta$ |
|--------|----------------|-----------------------------|---------------------|-----------------------------|
| CdTe   | 0.3726         | 6.454                       | 0.1823              | 0.1872                      |
| Q1     | 0.3618         | 6.283                       | 0.1769              | 0.1833                      |
| Q2     | 0.3638         | 6.301                       | 0.1778              | 0.1736                      |
| Q3     | 0.3634         | 6.294                       | 0.1776              | 0.1708                      |
| Q4     | 0.3655         | 6.331                       | 0.1787              | 0.1694                      |

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Figure 1(c) depicts the variations in the crystallite sizes and XRD FWHM of the as-prepared CdTe/CdSe NPs for various reaction times. It was found that the XRD FWHM is inversely related to the crystallite sizes. Calculation of the lattice parameters was also done in order to determine the dimensions of the unit cell. The dimensions of a cubic crystal structure are equal ($a = b = c$). The standard lattice constant for CdTe is 6.410 Å while for CdSe 5.937 Å as obtained from the JCPDS files 75–2086 and 19–0191 for CdTe and CdSe respectively. The calculated values of the d-spacing and lattice constant, are presented in table 1. It is observed that the lattice parameters deviate from the CdTe and CdSe standard values. This deviation could be due to the fact that the CdSe shell is trying to adopt the lattice constant of the CdTe core during growth which leads to substantial deformation of the core when a thick shell has been formed on the CdTe core. Also, the presence of strain in the NPs could contribute to the deviation of the lattice parameters from the standard values.

The microstrain ($\varepsilon$) values of the as-prepared CdTe/CdSe NPs were therefore estimated using the following equation (2) [38]:

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$  \hspace{1cm} (2)

where $\theta$ is the diffraction angle and $\beta$ is the full width at half maximum.

On the other hand, the length of the dislocation lines per unit volume commonly known as the dislocation density ($\delta$) was calculated by means of Williamson and Smallman equation (3) [39, 40]:

$$\delta = \frac{\beta}{4 \tan \theta}$$  \hspace{1cm} (3)
where $D$ is the crystallite size obtained from the XRD results. The estimated values of the strain and dislocation density were tabulated in Table 1 and presented in graph as shown in Figure 1(d). The strain and dislocation density in the as-prepared CdTe/CdSe NPs were found to generally decrease with increase in the reaction time.

### 3.2. SEM and HRTEM analysis

The surface topography and particle density of the as-prepared CdTe and CdTe/CdSe core/shell NPs were studied and presented in Figure 2(a). The investigation on the effects of reaction time on the shell growth on the CdTe NPs was carried out for various reaction times. The CdTe core and CdTe/CdSe core/shell presented a compactly filled and homogeneously spread spherical particles over the whole surface. When coated with CdSe shell and reaction time varied, the shell is believed to grow in thickness thus causing the whole particles to grow in sizes, hence, the observed variation in the particle sizes for different reaction time. At longer growth time, Q4 (80 min) show large spherical and rod-like particles with some agglomerations. This indicates that longer reaction time does not favour the evolution of uniform shell on the CdTe core which could be due to the fact that at longer reaction time, the capping ligands are depleted from the precursor solution thus causing the observed agglomeration in the particles. Figure 2(b) is the EDS spectra which show the presence of expected elements in the samples prepared.

Figure 2(c) is a representative HRTEM image of CdTe/CdSe core/shell NPs prepared at 20 min of growth time. The images presented were taken at different magnifications and positions of the sample. It is evident from

$$
\delta = \frac{1}{D^2}
$$

(3)
the HRTEM images that there is formation of a thin shell of CdSe NPs on the CdTe NPs core as displayed in figure 2(c) iii and iv. There is also observation of clear lattice fringes which is an indication of highly crystalline material obtained. Figure 2(d) shows analysis on the particle size obtained from the HRTEM images. The Analysis was carried out using ImageJ software and the approximate values of the diameters, which are equivalent to the particle sizes were represented in a histogram as shown in figure 2(d).

The average particle size was found to be approximately 4.73 nm for the Q1–20 min sample. This value is slightly larger than the value obtained from the XRD analysis. This discrepancy observed could be due to agglomeration of the particles which causes more than one particle to combine hence affecting the approximation using the software.

3.3. Photoluminescence (PL) analysis
The PL analyses of the as-prepared CdTe/CdSe NPs were carried out in order to study the behavior of the CdTe when CdSe shell coating is introduced to it. The obtained PL spectra are presented in figure 3(a). The observed PL spectra displayed Gaussian shapes with narrow FWHM. One emission peak was observed from the spectra for all the samples indicating formation of one particle of CdTe/CdSe and not separate particles of CdTe and CdSe NPs. The PL emission was shifted to longer wavelength when the CdSe coating was introduced to the preformed CdTe NPs. The red shift is attributed to the possible growth of the CdSe shell on the CdTe NPs. Variation in the PL relative intensity was also observed.

For the type II CdTe/CdSe NPs, Milliron et al [41] observed that it is either CdTe or the CdSe NPs or the transitional states that occur at the junction between the two materials that can absorb the photons. When either of these occur, formation of electro-hole pairs are formed and these encourages partial separation of charges into
electrons and holes in the boundary of CdTe to act as donor and CdSe to act as the acceptor causing electrons to locate at the CdSe region and holes at CdTe region [42].

According to the theoretical model of electronic structure in type-II NPs suggested by Ivanov et al [13], the hole is confined in the CdTe core, but the electron depending on the shell thickness is delocalized over the entire CdTe/CdSe volume for thin shell or the electron is confined at the CdSe if there is a thick shell. Figure 3(b) depicts PL analyses on the changes in the PL emission peaks and the relative intensity of the as-obtained CdTe/CdSe NPs. The emission peaks were red shifted upon addition of CdSe coating and continuously shifted to longer wavelengths as the reaction time increased to 80 min. The additional coating in this model causes a
reduction in the quantum confinement effects thus leading to the red shift in PL emission in the as-prepared CdTe/CdSe NPs even though the size of CdTe core was kept constant. The presence of strain in the CdTe/CdSe NPs interface as observed from the XRD results can also cause the PL emission to be shifted to longer wavelengths [43].

The PL relative intensity of the absorbed photons was significantly increased when the coating was introduced. It was observed that after the growth of CdSe on the pre-prepared CdTe core by addition of the reduced Se into the growth solution, the PL intensity of CdTe was greatly enhanced due to improved crystallinity. When the reaction time progressed, PL quenching was observed. This quenching could be due to dislocation of the electrons and holes caused by the type II band gap offset [42, 44–48].

The values of the PL FWHM obtained from the spectra were fitted in the graph shown in figure 3(c). There is a sharp decrease in the FWHM value when the CdSe shell was introduced to the CdTe core and grown for 20 min. The decrease in this FWHM is due to uniform and narrow size distribution of the particles. An increase in this value observed when reaction time was increased could be due to formation of randomly and non-uniform particles as also observed in the SEM images.

Commission International de l’Eclairage (CIE) was employed to calculate the x and y chromatic coordinates used to determine the colour coordinates of the emitted light. These coordinates tells of the region around which the emitted colour measured NPs is located. From the emission spectra, the chromaticity image was obtained and displayed in figure 3(d). All the samples show emission colours in the orange/red region of the CIE diagram. The shift in the emission colour to the red region is displayed by the CIE image thus confirming the obtained results from the PL measurement analyses.

3.4. UV–vis analysis

The evolution of the optical properties of the as-prepared CdTe/CdSe NPs were monitored using aliquots taken from the freshly prepared samples by means of evolution 100 UV–vis spectrophotometer. The data were collected for different samples, plotted and presented in figure 4(a). The optical properties of particles in the
nano scale are affected by the growth of a shell around a core NP. There is a clear difference in the absorbance properties of the core–shell particles when compared to the bare CdTe NPs as shown in figure 4(a). The spectra show a sharp band edge which is red shifted upon addition of Se into the growth solution and increase in the reaction time (0–80 min) as shown in table 2. The observed red shift when Se was introduced is an indication of the formation of the core–shell structure in the prepared samples. The red shifts in the absorbance spectra of the core–shell (Q1, Q2, Q3 and Q4) NPs relative to the parent material can be said to be due to the relaxation of quantum confinement caused by the additional coating. Well-resolved absorption maxima is observed for the bare CdTe and Q1 (20 min) at around 590 nm which is said to be due to the higher energy transition of the NPs. These absorption maxima are replaced by featureless absorption tails for CdTe/CdSe coated structure at longer duration of growth. This is due to the behavior of indirect semiconductors near the band edges [13]. Additionally, the coated NPs (Q1–20 min, Q2–40 min, Q3–60 min and Q4–80 min) show higher absorbance than the CdTe core in the blue region of the spectra This is attributed to the higher effective density of states in terms of their larger sizes [15, 49].

The red shift of the absorption edges evidently seen in figure 4(a) could be due to the growth of the shell on the CdTe core as reaction time was increased from 0–80 min. The electronic structure of a material is defined by its band gap energy. Tauc relation (equation (4)) [50] was used to predict the energy band gap of the as-obtained CdTe/CdSe NPs.

\[
\alpha h\nu = A(\nu - E_g)^n
\]

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the incident photon energy, \(A\) is a constant and \(E_g\) is the electronic band gap of the semiconductor material.

The values of the energy band gaps of the as-prepared CdTe/CdSe NPs were approximated by drawing a tangent of \((\alpha h\nu)^2\) on Tauc’s plot and extrapolating to the \((\alpha h\nu)^2 = 0\) axis as shown in figure 4(b). From the Tauc plot, the obtained band gap energies of CdTe/CdSe NPs were 4.32, 3.87, 3.26, 3.15 and 3.08 eV for various reaction times (CdTe-0 min, Q1–20 min, Q2–40 min, Q3–60 min and Q4–80 min). With an increase in the
reaction time, the band gap energies display an inverse behaviour. The inverse relationship between the reaction time and the energy band gaps of the as-prepared NPs is possibly due to the growth of the CdTe/CdSe NPs as a result of shell growth. The bulk band gap energy of CdTe is 1.5 eV [50] while for CdSe is 1.74 eV [51]. The obtained values display greater values compared to the bulk values for both CdTe and CdSe (table 2). The observed discrepancies could be due to the reduction of the degrees of freedom as a result of quantum confinement effects [52].

Furthermore, the observed results support the formation of the shell on the preformed CdTe NPs. This is because the obtained band gap energies neither belong to CdTe nor CdSe but for the CdTe/CdSe core–shell nanomaterial formed.

4. Conclusion

CdTe/CdSe NPs were successfully prepared by sol-gel technique via a simple wet chemical process using L-cysteine as the complexing agent. L-cysteine capped CdTe NPs acted as the core for growing various CdSe shell sizes by varying the reaction time. The as-prepared CdTe/CdSe NPs were characterized using various techniques to obtain the structural and optical properties of these NPs. Morphological studies conducted showed the formation of spherical NPs with some agglomerations at longer reaction time. The XRD results revealed the formation of polycrystalline and single crystalline zinc blende crystal structure at various reaction times. All the calculated crystallite sizes were under 3 nm. Variation in the reflection peak intensities were observed, which reached maximum at 20 min of growth (Q2 sample). This improvement of the crystal quality was also observed from the most intense PL emission peak and supported by the clear lattice fringes observed from the HRTEM images. In comparison to CdTe core, the CdTe/CdSe NPs showed a noticeable shift in the PL emission to longer wavelengths with the possible colour-tune to the near-infrared wavelength due to the introduction of CdSe coating. Band gap energies which are higher than the bulk band gaps of both CdTe and CdSe were obtained which is as a result of small NPs in the quantum confinement regime. As the reaction time increased, the band gap values of as-prepared CdTe/CdSe NPs decreased from 4.32–3.08 eV for various reaction times (0–80 min). Q2 sample possessed good structural and optical properties which can be applied in various bioimaging applications.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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