Synthesis and characterisation of CdSe QDs by using a chemical solution route

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An efficient synthesis process approach based on a chemical solution route is developed for the cadmium selenide quantum dots (CdSe QDs) that utilise photonic and optoelectronic device manufacturing. The developed route consists of dissolving the cadmium chloride ($CdCl_2.H_2O$), 2-mercaptoethanol and sodium selenide anhydrous (Na_2SeO_3). The different characterisation parameters such as ultraviolet (UV) absorbance, x-ray diffraction (XRD), scanning electron microscopy, energy dispersive x-ray and transmission electron microscopy (TEM) were employed in order to develop the CdSe QDs. When the sample was analysed from the UV–visible studies, the bandgap was about 2.16 eV, whereas the bulk CdSe bandgap was about 1.78 eV. The developed CdSe QDs possessed a cubic crystal structure with crystalline dimensions of about 4.86 nm. Its surface morphology and structure showed the smooth appearance of the surface. The result indicated agglomerated spheres. Ultimately, according to XRD and TEM results, the crystalline dimension was determined in good agreements.

1. Introduction: The cadmium selenide (CdSe) is the II–VI semiconductor material that has attained great research focus due to its crystalline dimensions in the nanometer scale [1]. Semiconductor nanocrystals, also called quantum dots (QDs), are fluorescent inorganic particles having typical diameters ranging between 1 and 10 nm. In optoelectronic devices, manufacturing purpose of the CdSe QDs is to perform a wide range of applications such as fluorescent nanomarkers, light-emitting diodes, lasers and solar cells [2–5]. The QDs have obtained a great exploration due to their convenience of optical and electrical characterisations. The CdSe nanoparticle semiconductor material is known as QDs when the crystalline dimension is between 2 and 10 nm [6]. The electronic characterisation of the crystals depends on the crystalline dimension and shape. When the crystalline dimension causing the energy gap between the higher valence band and the lower conduction band is very low, more energy is required for exciting the dots. Its conductive properties are determined by controlling the size of the crystal, which is the principal advantage of QDs. Moreover, the QDs show excellent optical and electrical properties on account of their small sizes. Their valence electron that is excited to a certain energy level emits energy in the form of photons. The excited electron returns to the ground state and associating with the hole, then, the fluorescence of the QDs is generated. Due to quantum confinement effects, the energy of the emitted photon is determined by the crystalline dimension of the QDs [7].

By using various methods or employed Cd and Se precursors, many researchers have attempted to synthesise the CdSe QDs. The CdSe QDs preparation has been recently attempted via colloidal reaction method [8], one-pot hydrothermal synthesis [9], liquid paraffin with a mixture [10], microwave and electron beam irradiation [11, 12] and aqueous solution [13–15]. When comparing with these routes, the synthesis procedures by using an aqueous solution is exhibiting good water solubility that is simple, green and highly reproducible. In this report, a cost-effective chemical solution process is applied to produce the device quality CdSe QDs for photovoltaic applications. According to some of our earlier reports [16–20], this process is suitable for nanostructure material production when compared with thin films.

2. Material and methods

2.1. Synthesis of CdSe QDs: In present work, CdSe QDs were synthesised by using a cost-effective chemical solution route. QDs synthesis mechanism can be simply prepared by changing only the reaction with each other in a chemical solution process. It is based on the manipulation of the atoms and molecules to assemble materials by the bottom-up approach. The formation of the precipitate can occur from an identical liquid form because of substantial conversion and chemical solution. Furthermore, careful controlling of the pH value of the precipitation can result in mono-disperse nano-sized particles. Moreover, low toxicity and cost-effectiveness is maintained with ecological behaviour by using this process.

There are three solutions of $CdCl_2.H_2O$, 2-mercaptoethanol (ME) and sodium selenide anhydrous (Na_2SeO_3), which were prepared in the de-ionised water with magnetic stirring for this purpose. First, $CdCl_2$ solution was poured into a spout balloon container and meanwhile, ME solution was added to the same balloon. Finally, Na_2SeO_3 solution was added to the balloon under atmosphere control condition passing through the nitrogen (N_2) gas. The resulting solution was washed several times by using de-ionised water and then was centrifuged in order to remove any impurity. Thereafter, the precipitated sample was dried at room temperature. All processes were done at room temperature environment. In our previous reports [21–25], we have proposed the developing and implementation of this procedure in details to synthesise some nanostructure materials.

2.2. Experimental technique: The ultraviolet (UV) absorption was measured by using a UV-1800 spectrophotometer (double-beam UV–visible spectrophotometer) recording in the photon wavelength range between 400 and 800 nm. The x-ray diffraction (XRD) patterns were recorded by using a X'Pert high score PANalytical diffractometer with Cu-Kα radiation, operated at 45 kV and 40 mA, with angular range $10° \leq 2\theta \geq 80°$. Additionally, the morphology and atomic compositions (elemental) of the sample were also consummated with a scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) of LEO 1430 VP system. Eventually, the transmission electron microscopy (TEM) measurement was performed for understanding the changes in the morphology of the synthesised CdSe QDs, with field emission TEM, using JEOL JEM 2100F HRTEM Microscope operated at 200 kV.

3. Results and discussion: Different materials are used to make the QDs and they are capped with various metal cations. The chemical

solution route has opened up unique opportunities for CdSe QDs that cannot be provided by any other synthesis process. Owing to their size-tunable emission covering the whole visible spectrum, there are many reasons to believe that the low-dimensional CdSe QDs synthesised by the chemical solution route will be extremely useful for bio-imaging in the recent year. It is also reasonable to believe that the route presented here could be used for large-scale fabrication of QDs. The electronic state can be described in terms of valence and conduction bands that are essential properties. However, as the fragment becomes smaller, the wavelength of the electrons is near to the range of the crystalline dimension and the laws of classical physics have to be replaced by the quantum confinement effect.

Fig. 1 indicates the absorption spectrum of CdSe QDs. The absorption peak of the obtained CdSe QDs achieved by UV–visible spectrophotometer is 573 nm. From the absorption curve bandgap energy, E_g was calculated by using the following formula:

$$E_g = hc/\lambda$$
$$E_g = 1240/\lambda\,\text{eV} \quad (1)$$
$$E_g = 2.16\,\text{eV}$$

Due to the UV–visible spectrum for CdSe QDs in aqueous solution, the absorption peak was 573 nm (2.16 eV), relative to the blue shift of the bandgap of bulk cubic CdSe was 698 nm (1.78 eV). According to the other researcher reports, the absorption peak of CdSe QDs in the same solution was 543 nm that corresponds to $E_g = 2.28$ eV [26, 27]. Herein, the experimental result was similar that in quite well agreement with other researcher reports. Therefore, the bandgap energy of CdSe QDs was larger than bulk and thin-film materials.

To determine the bandgap energy of the fluorescent light, it has opened up the potential applications for many new materials. The CdSe QDs can be easily used in optoelectronic device manufacturing. It is a more stable semiconductor and shows photoluminescence and electro-photoluminescence property within the visible spectrum because of higher bandgap energy.

According to the standard JCPDS Card No. 19–019, Fig. 2 shows the XRD spectrum that indicates the cubic crystal structure. The XRD spectrum shows the diffraction planes (111), (220) and (311) corresponding to the diffraction peaks that appeared at $2\theta = 25.20°$, 41.90° and 49.70°, respectively. The result was in good agreement with the works reported earlier [28, 29]. Furthermore, the diffraction peaks revealed that the ultrafine particles were synthesised with poor crystallisation form. The peak broadening in the XRD pattern was developed due to a low crystalline dimension of nanostructure materials. The average crystalline dimension D can be calculated for the CdSe QDs by using the full width at half maximum (FWHM) of the (111) diffraction peak according to Debye–Scherrer's [30] formula

$$D = (0.9\lambda)/\beta\cos\theta \quad (2)$$

where the wavelength of the incident x-ray is λ, the FWHM of the (111) peak is β in radians and the Bragg diffraction angle is θ. The calculated average crystalline dimension of the CdSe QDs was 4.86 ± 0.02 nm.

The main theme in nanotechnology, only several nanometres in size indicates the QD is a very small semiconductor particle. The QDs are useful applications in bio-imaging and physico-chemical stability in order to prevent the leakage of toxic ions. The particle sizes <10 nm exhibit a property known as quantum confinement effect of CdSe. The quantum confinement effect in materials is confined to the electrons to a very small volume. The properties of CdSe QDs are tunable based on their size. A smaller QD has the required energy to excite an electron between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). This quantum confinement effect can be observed as a blue shift in absorbance spectra. The decrease of the QD size causes the absorbance peak shift to short wavelengths (blue shift). This means an energy gap increase. This is the primary indication to obtain the quantum confinement effect. CdSe QDs have been implemented in a wide range of applications. CdSe-based materials also have potential uses in biomedical applications by injecting appropriately prepared CdSe nanoparticles.

Fig. 3 shows both the SEM image and EDX spectrum of the CdSe QDs. The SEM was used to explore the surface morphology and the structure of the studied sample. The experimental result showed the smooth appearance of the surface indicating the agglomerated spheres [31]. The surface of agglomerates being grain in size had formed. In addition, the SEM image demonstrated that the CdSe QDs had a spherical morphology and the grain size could be estimated in low dimensions. It was clear that the grain size at high concentration of CdSe QDs took a definite shape and the CdSe were dispersed well in chemical solution route. That meant that the morphology of CdSe QDs biocomposites was critically affected by using this route. This revealed good crystallinity, which was highly separated from each other indicates the formation of QDs. The appearance of lattice plane of CdSe in the image results from the effective role of the chemical solution process. EDX spectroscopy was employed to examine the elemental composition that the CdSe QD_S was composed of Cd and Se. There were peaks

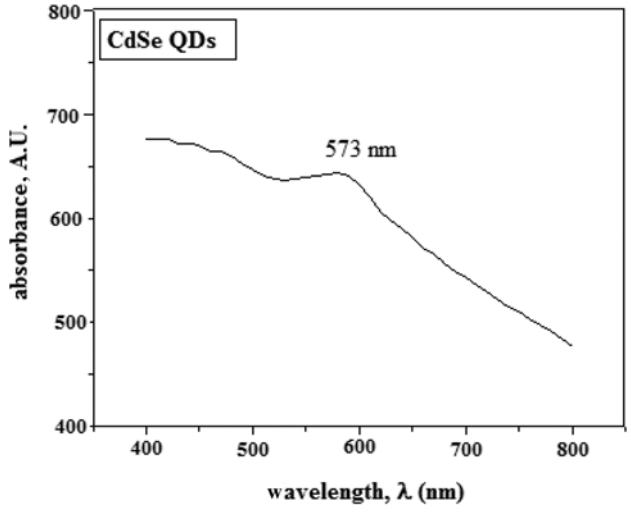

Fig. 1 *UV–visible absorption spectrum of CdSe QDs*

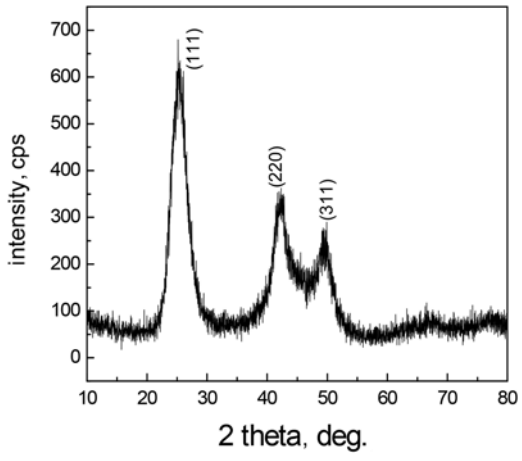

Fig. 2 *XRD spectrum of CdSe QDs*

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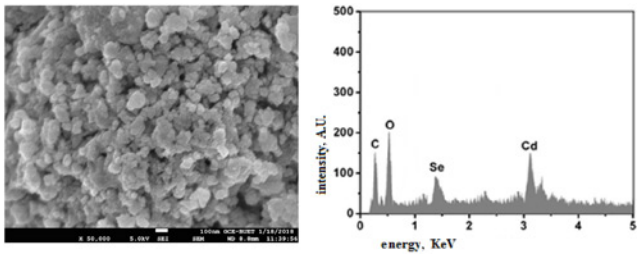

Fig. 3 *SEM image and EDX spectrum of CdSe QDs*

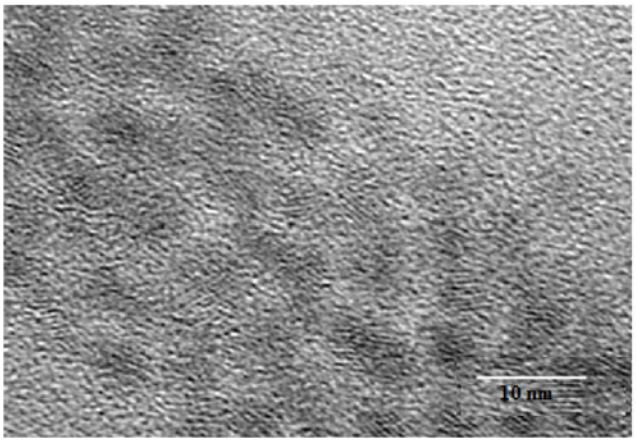

Fig. 4 *TEM image of CdSe QDs*

respectively associated with element Cd and Se displayed by the host material of CdSe QDs as shown in Fig. 3. The existences of other peaks are attributed to carbon (C) and oxygen (O). The surface layer may be strongly oxidised and this may take into account the presence of O. The presence of C may be due to the casting pot which may have been C or the whole of C. Another reason for the presence of C and O in EDX analysis is the predator's remnants of previous studies, which were also observed in this diagram. The result was similar to other researcher reports [29, 32, 33].

Fig. 4 shows the TEM image with slightly non-uniform contrast and background of the CdSe QDs. In some places, the non-touching QDs could be seen distributed separately from one another while at other regions; they formed agglomeration to form mosaics phenomena. This accumulation of particles was due to the non-uniform precipitation of CdSe QDs. To verify the morphology and crystalline dimension of the CdSe QDs, it could be estimated by observing the TEM image. Fig. 4 revealed a cluster of nanoparticles which were almost spherical that had very low dimensions. The crystalline dimension indicated the low dimension which was in good agreement with that found from XRD results [34–36].

4. Conclusion: The CdSe QDs were properly synthesised in room environment and were having quite consistent size. From the UV–visible studies, the bandgap of CdSe QDs was about 2.16 eV. The XRD result showed the broadening of peaks indicating the cubic crystal structure which was the low crystalline dimension. Moreover, the SEM image demonstrated that the QDs were a spherical morphology. In addition, the grain size could be estimated in low dimensions. The results were confirmed to be in good agreement by means of the TEM investigation. The ability of CdSe QDs means that they have effective applications in solar cells, light-emitting diode and biological imaging. Consequently, it will have a greater consequence of the nanotechnology in the near future.

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