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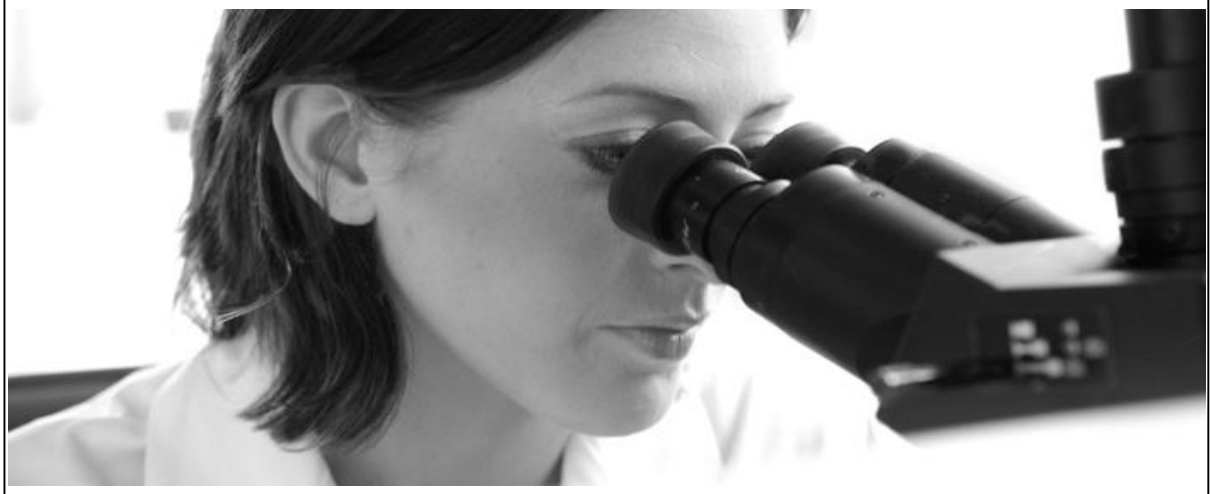

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RESEARCH ARTICLE

SYNTHESIS AND OPTICAL CHARACTERIZATION OF CdS, CdSe QUANTUM DOTS AND $CH_3NH_3SnCl_3$ PEROVSKITE SENSITIZERS USED IN SOLAR CELL APPLICATIONS

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ABSTRACT

The present work deals with the synthesis and optical characterization of sensitizers CdS, CdSe quantum dots (QDs) and metal halide perovskite $CH_3NH_3SnCl_3$, which were successfully fabricated by adopting solution chemistry route. Subsequent characterization studies were carried out on the synthesized samples using UV-Visible spectroscopy and photoluminescence spectroscopy. The optical band gaps were calculated as 2.75 eV (450 nm), 2.69 eV (460 nm) and 2.60 eV (476 nm) for CdS, CdSe QDs and $CH_3NH_3SnCl_3$ respectively. The photoluminescence (PL) properties of the QDs nanocrystal represent a series of best sensitizers that are highly efficient for solar cell applications, highly pure in emission colour, stable and tunable by simply varying the size of the nanocrystals. The experimental results suggested that the existence of the PL bright point observed at 560nm, 540nm and 780nm for CdS, CdSe QDs and perovskite $CH_3NH_3SnCl_3$ respectively.

INTRODUCTION

Nanomaterials can exist in three dimensional (3-D) colloids, two dimensional (2-D) quantum well; one dimensional (1-D) structures (nanowires, nanorods, etc.) and even zero dimension (0-D) quantum dots. Quantum dots have diameter approximately between two to ten nanometers, which put them in a special size range that retains some properties of bulk materials as well as some properties of individual atoms and molecules that constitute them [1,2]. A great deal of interest has been dawning on the colloidal chemistry based semiconductor nanocrystallites, also known as quantum dots. Since the size of the dots is much less than the exciton Bohr radius, the electron-hole pair in a quantum dot is tightly confined in all three dimensions, known as quantum confinement, which produces a number of pronounced modifications in the optical properties of the semiconductor. Because of the strong quantum confinement, quantum dots have unique size-dependent optical properties, which are much more superior to the conventional organic fluorescence materials. There electronic characteristics are closely related to the size and shape of the individual crystal. If the size of the crystal is small, then band gap between the higher valence band and the lowest conduction band becomes higher and more energy is required for exciting the dot and consequently, more energy is released when the crystal returns to its resting state.

A principal advantage with quantum dots is that by controlling the size of crystals, the conductive properties of the material are controlled. Because of their small size, QDs display unique optical and electrical properties. Size-dependent optical properties of QDs [3], broad excitation spectra, narrow, tunable and symmetric emission spectra [4], easily tunable band gap with size [5] can be exploited in optoelectronics devices including LEDs [6], Solar Cells [7], Lasers [8] etc. Quantum dots are quickly replacing the dyes, found to be superior to traditional organic dyes on several counts viz. brightness, stability (allowing much less photo bleaching) [9]. It has been estimated that quantum dots are 20 times brighter and 100 times more stable than traditional fluorescent dyes [10]. It was found that modulation of band gap through size offers new ways to control photo response and photo conversion efficiency of the solar cell. In the solar cell, sunlight excites the electron from the valence band to the conduction band and creates an electron-hole pair. Flows of electrons takes place across the p-n junction, hence constitute electricity. Photons of sunlight having energy, lower than the band gap are not absorbed, photons of greater energy are absorbed, but excess energy is

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dissipated as heat which lowers the efficiency of solar cells. Since quantum dots have a tunable optical band gap, so the use of QDs in the solar cells create an intermediate band gap and hence increases their efficiency. Three major ways to utilize quantum dots in solar cell include (i) metal-semiconductor or Schottky junction photovoltaic cell (ii) polymer-semiconductor hybrid solar cell, and (iii) quantum dot sensitized solar cell [6].

QDs can be synthesized by a number of techniques with the starting material existing either in vapour, liquid, or solid state. Up to now, numerous methods have been reported for the preparation of CdS and CdSe nanoparticles. They are molecular beam epitaxy [11], metal organic vapour chemical deposition [12], solvothermal [13] and hydrothermal method [14]. In the case of solar cell application, semiconductor nanomaterials can be used as a light absorbing material (photosensitizer) in either a solid-state p-n junction structure or a photo electrochemical junction type [15]. Dispersion of semiconductor nanocrystal on a high surface area n-type or p-type support is an effective method to utilize it as a photosensitizer. For this reason, semiconductor (or quantum dot)-sensitized solar cell has recently attracted a lot of interest [16, 17]. Organic-inorganic hybrid $CH_3NH_3PbX_3$ (X = Br, I) perovskites have been introduced by Kojima *et al*. [18] in 2009 as a new class of DSSC sensitizing materials. Recently, a power conversion efficiency of 6.54% at one sun was reported based on perovskite semiconductor $(CH_3NH_3)PbI_3$ [19]. Fig.1 shows the crystal structure of the metal halide $CH_3NH_3SnX_3$ (X = Cl, Br, I) perovskite.

In this work, an attempt has been made to synthesis quantum dots and perovskite sensitizers via solution chemistry routes, which are most popular sensitizers in solar cell applications. Subsequent characterization studies were carried out on the synthesized samples using UV-Visible spectroscopy and photoluminescence spectroscopy.

MATERIALS AND METHODS

Synthesis of CdS QD

Cadmium sulphide QD was synthesized by using the solution chemistry route. The starting materials for the synthesis of CdS nanoparticles were cadmium nitrate as cadmium source, sodium sulphide as sulphur source and ethanol as solvent. All chemicals were of analytical grade Merck products and used without further purification. The reaction matrix employed in this study consisted of $CdNO_3$ and Na_2S in the molar ratio of 20mM : 20mM. The reaction matrix was prepared in two parts. Typical synthesis, cadmium nitrate and sodium sulphate were mixed in 50 ml of ethanol. The solution stirred until the cadmium nitrate was completely dissolved and a light yellow homogeneous solution was obtained [20].

Synthesis of CdSe QD

CdSe nanocrystals were synthesized by solution chemistry route. At first, 0.5M $CdNO_3$ was dissolved in 50 ml of methanol, and at the meanwhile, 0.5M sodium selenosulphate $(Na_2SeSO_3 \cdot 5H_2O)$ solution, stirring at 70 ◦C for 10 min, was added to the first solution and then stirred to form an orange red solution [21].

Synthesis of Metal Halide $CH_3NH_3SnCl_3$ perovskite Sensitizer

Preparation of CH_3NH_3Cl

CH_3NH_3Cl was synthesized by reacting 30 mL of methylamine (40% in methanol) and 32.3 mL of hydrochloric acid (57 wt% in water) in a 250 mL round-bottom flask at 0 °C for 2 h with stirring. The precipitate was recovered by putting the solution on a rotary evaporator and carefully removing the solvents at 50 °C. The yellowish raw product methyl ammonium chloride (CH_3NH_3Cl) was washed with diethyl ether by stirring the solution for 30 min, a step which was repeated three times, and then finally recrystallized from a mixed solvent of diethyl ether and ethanol [22].

Preparation of $CH_3NH_3SnCl_3$

To prepare $CH_3NH_3SnCl_3$, readily synthesized CH_3NH_3Cl (0.395g) and $SnCl_2$ (1.157g), were mixed in 10ml of DMF at 60 °C for overnight with stirring. The small beaker is immediately sealed and kept in dark at room temperature. Aluminium foil is used over the lid of the sample beaker to prevent reaction with sun light [23].

Characterization

The UV-Visible absorption spectrum of the samples was recorded in the range of 200-800 nm, employing a UV–Vis–NIR spectrophotometer (Varian-5000). The photoluminescence (PL) emission spectra of the samples were recorded with a Spectrofluorometer
(Jobin Yvon, FLUOROLOG–FL3-11).

RESULTS AND DISCUSSION

UV-Visible Analysis

The UV-Visible spectroscopy has become an effective tool in determining the particle size and optical properties of materials. The samples were administered for optical investigation to obtain the diameter of the nanocrystals and optical band gap energy.

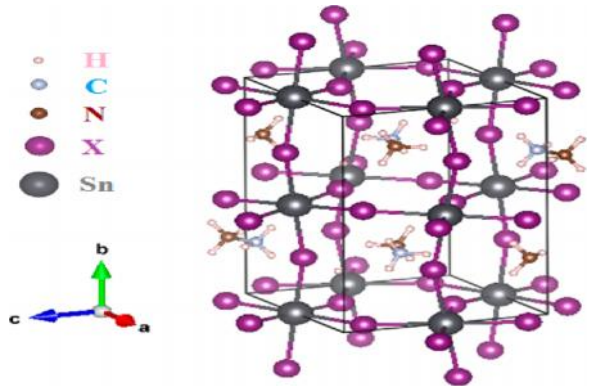

Figure.1 Crystal structure of orthorhombic $CH_3NH_3SnX_3$ (X = Cl, Br, I) perovskite

The UV-Visible spectra of the CdS and CdSe quntumdots are shown in Fig. 2. The maximum absorption peak value for CdS and CdSe QDs are observed at 450 and 460 nm respectively.

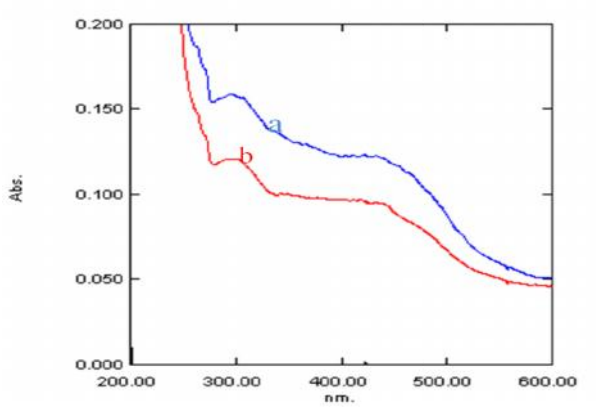

Figure. 2 UV- Visible absorption spectrum of CdS (a) and CdSe(b) quantumdots

Fig. 3. shows the UV-Visible spectra of the $CH_3NH_3SnCl_3$ perovskite. It exhibits the maximum absorption peak at 476 nm. The band gap energy of the samples was calculated from the following relation using absorption wavelength.

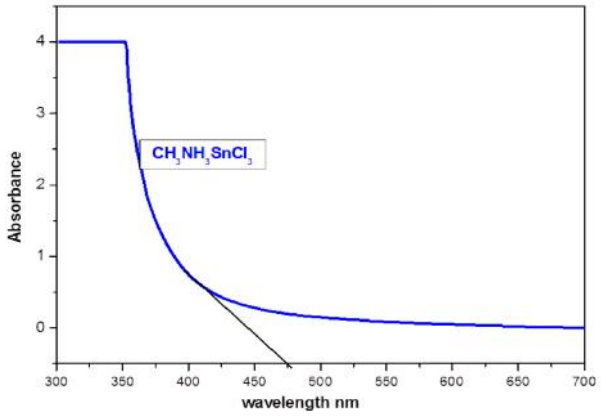

Figure. 3 UV-Visible absorption spectra of $CH_3NH_3SnCl_3$ perovskite

$$E_g = \frac{hc}{\lambda_{max}} eV$$

Where E_g is band gap energy of the nanoparticles. From the excitonic absorption peak, h is the Planck's constant (6.626 x10^{-34} J s), c is the velocity of light (3 x 10^8 m/s) and λ_{max} is the maximum absorption wavelength of the sample. The calculated band gap energy values of the sensitizers CdS, CdSe QDs and $CH_3NH_3SnCl_3$ perovskite are 2.75 eV, 2.69 eV and 2.60 eV respectively. The particle size of the quantum dots can be accessed from the absorption wavelength of the UV-Visible spectra by using Hyperbolic band model [24]

$$R = \sqrt{\frac{2\pi^2 h^2 E_{gb}}{m^*(E_{gn}^2 - E_{gb}^2)}}$$

Where, R = quantum dot radius (2R is the diameter and hence, indicates particle size)

E_{gb}= bulk band gap (2.42 eV for CdS, 1.74 eV for CdSe and 2.8eV for perovskite)

E_{gn}=quantum dot band gap (calculated from the absorption peak)

h = Planck's constant (6.626 x10^{-34} J s)

m* = effective mass of specimen (1.82 x 10^{-31} kg for CdS, 1.18 x 10^{-31} kg for CdSe and 1.94 x 10^{-31} kg for ($CH_3NH_3SnCl_3$ perovskite)[25, 26].

The calculated particle sizes of the samples are 2.59 nm, 1.74 nm and 1.27 nm for CdS, CdSe QDs and metal halide $CH_3NH_3SnCl_3$ perovskite respectively. The prepared QDs and $CH_3NH_3SnCl_3$ perovskite are shown in Fig.4.

Figure 4 The as prepared QDs and $CH_3NH_3SnCl_3$ perovskite

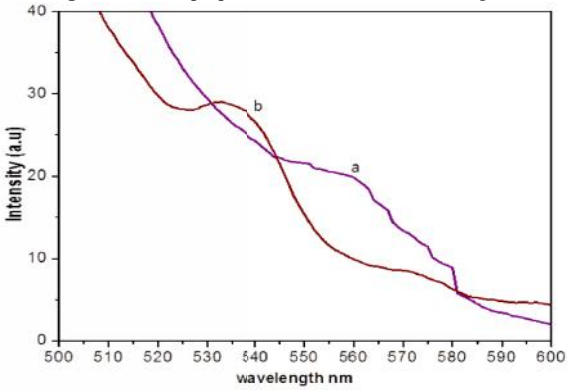

Figure.5 PL spectrum of CdS(a) and CdSe(b) QDs

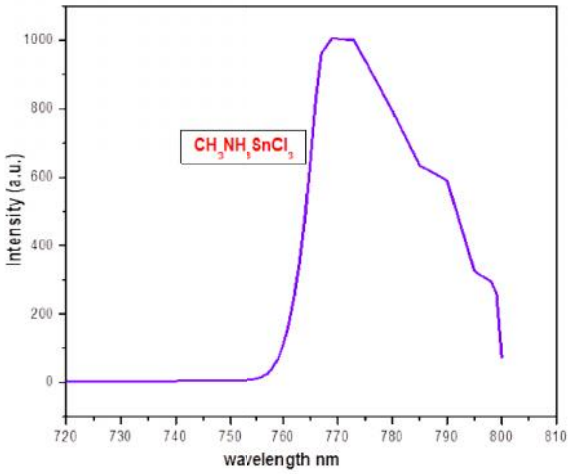

Figure. 6. PL spectrum of metalhalide $CH_3NH_3SnCl_3$ perovskite

Photoluminescence Study

The emission properties of semiconductor nanocrystals can be characterized by four fundamental parameters; they are brightness, emission colour, colour purity, and stability of the emission. In the present work, because of quantum size effect, the band gap of nanocrystals increases as their size decreases. As a result, the emission colour of the band-edge PL of the nanocrystals shifts continuously from red (centered at 650 nm) to blue (centered at 450 nm) as the size of the nanocrystals decreases. In view of the fact that the emission colour of semiconductor nanocrystals is strongly dependent on size [27] and shape, [28] the colour purity of the emission becomes dependent on the size and shape distribution of a nanocrystal. Fig.5. show the PL spectra of CdS and CdSe nanoparticles at room temperature, which exhibited a broad band edge emission from 504 nm to 560 nm for 450 nm excitation. The best PL quantum yield reported for the as-prepared nanocrystals are around 20% in the wavelength range between 520 and 600 nm. The stability and the reproducibility of the PL quantum yield are both not predictable [29]. Fig. 6. shows the PL spectra for metal halide $CH_3NH_3SnCl_3$ perovskite sample. It exhibits the broad band emission at 750 to 800 nm for 470 nm excitation.

CONCLUSION

In conclusion, CdS, CdSe quantum dots and metal halide $CH_3NH_3SnCl_3$ perovskite samples were successfully synthesized by using the solution chemistry route. The synthesized samples were characterized by UV-visible and photoluminescence studies. The calculated optical band gap energy values of the sensitizers CdS, CdSe QDs and $CH_3NH_3SnCl_3$ perovskite are 2.75 eV, 2.69 eV and 2.60 eV respectively. The calculated particle sizes of the samples CdS, CdSe QDs and $CH_3NH_3SnCl_3$ perovskite are 2.59 nm, 1.74 nm and 1.27 nm respectively. These prepared QDs nanocrystals represent a best emitters that are highly efficient, highly pure in emission colour, stable and continuously tunable.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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