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A simple synthesis route of low temperature CdSe-CdS core-shell quantum dots and its application in solar cell

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ABSTRACT

Synthesis of colloidal semiconductor quantum dots (QDs) has become a major research area in the field of material science. Over the last two decades QDs have been employed successfully in sensitizing the mesoporous semiconductors like TiO_2, ZnO etc. in various configurations thus giving birth to a new branch of low cost solar cells known as quantum dot sensitized solar cells (QDSSCs). In this paper we report low temperature synthesis of core-shell CdSe-CdS quantum dots (QDs) using wet chemical technique. A quantum dot solar cell (QDSC) was also prepared with the core-shell QDs as working electrode and a well explored solid polymer electrolyte. The QDSC was characterized and its stability was monitored for a period of two months in laboratory conditions.

1. Introduction

The semiconducting structures having dimensions smaller than their exciton Bohr radius forces the motion of excitons to be confined in space. The confinement of excitons in all three directions gives rise to quantum dots. The quantum confinement results in appearance of discrete energy levels leading to existence of multiple exciton generation (MEG), tunable band gap and size dependent photoluminescence in quantum dots (QDs). The II-VI group semiconductor nanocrystals and their QDs have been explored extensively over the past few decades owing to their exceptional optical, electronic and chemical properties thus unlocking new domains of research in optoelectronics, photonics and bio-labeling [1–6].

Over the last two decades QDs have been employed successfully in sensitizing the mesoporous semiconductors like TiO_2, ZnO etc. in various configurations thus giving birth to a new branch of low cost solar cells known as quantum dot solar cells (QDSC) [7–13]. Recently in a review we reported a new QD solar cell without the use of mesoporous semiconductor exhibiting a Voc of over 1 V [14]. Continuing with the efforts, in this paper we report low temperature synthesis of core-shell CdSe-CdS QDs using wet chemical technique and its application in QDSCs.

2. Materials used

Selenium metal powder (Se), cadmium acetate dehydrate Cd $(CH_3COO)_2{\cdot}2H_2O$, 2-mercaptoethanol ($HOCH_2CH_2SH$) also known as βME and potassium iodide (KI), were purchased from Qualikems Fine Chemical Pvt. Ltd., India. Sodium sulfite (Na_2SO_3), polyethylene oxide (PEO) (Mw = 5,00,000) and polyethylene glycol (PEG) (Mw = 200) were purchased from Sigma-Aldrich. N,N-Dimethylformamide (DMF), chloroplatinic acid (H_2PtCl_6), Ti (IV) bis (ethyl -aceto -acetato)-diisopropoxide solution (2wt% in 1- butanol) also known as blocking layer, sodium sulphide (Na_2S) fused flakes and acetonitrile were purchased from Fisher Scientific while polyvinylidene fluoride (PVDF) (Mw = 1,00,000) was purchased from Alfa Aesar. FTO glasses of sheet resistance 8Ω/sq were purchased from Sigma-Aldrich. All the chemicals were of analytical grade and were used without further purification. Double distilled (DD) water was used wherever required.

3. Experimental section

For synthesis of core-shell structured QDs, the process followed was similar to that reported for CdSe (alone) in our previous work [15]. In a typical process, 0.063 gm of Se and 0.304 gm of Na_2SO_3 were mixed in a two-neck flask with 40 ml double distilled (DD) water under vigorous stirring for the formation of Na_2SeSO_3 and refluxed until the solution seemed transparent. 0.1066 gm of $Cd(CH_3COO)_2{\cdot}2H_2O$ were dissolved separately in 50 ml of DD water in two beakers at 40 °C under continuous stirring. In two sample bottles 0.078 gm of Na_2S was dissolved in DD water at room temperature. After an hour of stirring, 20 ml of the Na_2SeSO_3 was injected into the two cadmium solutions followed by addition of equal volume of Na_2S solution within seconds. The colour started changing immediately from milky to orange. In one beaker

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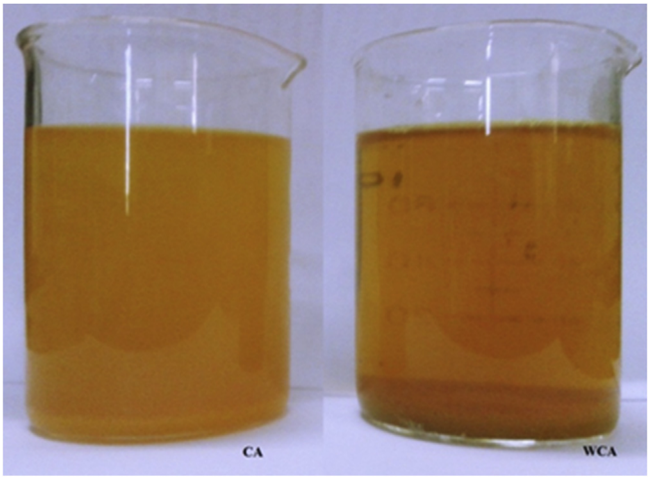

Fig. 1. The prepared core-shell QD solutions; CA and WCA.

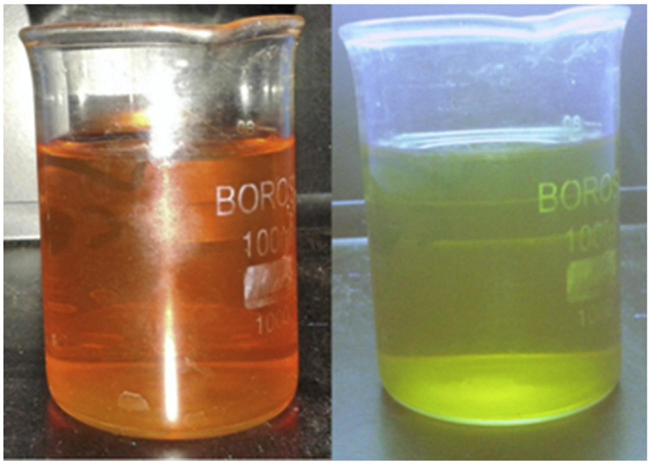

Fig. 2. Left - CA solution under daylight. Right – CA solution under short range UV light.

0.3 ml of 2-mercaptoethanol (βME) was added drop-wise, thus one solution prepared with capping agent and other without, marked as CA and WCA respectively. The final temperature was 50 °C. Both samples as seen after preparation are shown in Fig. 1. It can be clearly seen that the particles have settled down in the WCA solution whereas no such precipitation of particles is seen in the CA solution signifying the essence of capping on the core-shell structure. Also the colour of WCA seems darker compared to CA thus suggesting the presence of bigger particles in WCA.

The CA solution was seen in a ultra-violet fluorescence cabinet using daylight and short range UV light (wavelength 250 nm). The CA solution exhibited fluorescence in the UV light as shown in Fig. 2.

Further both solutions were centrifuged at 15,000 rpm for 8 min followed by washing with DD water and toluene before leaving it overnight in vacuum at room temperature for drying. The obtained powder was crushed properly and stored in Eppendorf tubes for further characterization.

4. Results and discussions

UV–Vis absorption was carried out using UV-1800 Shimadzu spectrophotometer in the wavelength range of 700–250 nm. Miniscule amount of the powdered samples of CA and WCA were ultra-sonicated in DD water for proper dispersion before pouring them in quartz cuvette for analysis. The absorption curves of CA and WCA are shown in Fig. 3. As can be seen from Fig. 3, the CA solution starts absorbing at 545 nm and reaches the absorption maxima at 410 nm while the WCA solution starts absorbing at 600 nm having multiple absorption maxima with the prominent λ_{max} at 448 nm. The multiple slope changes in the absorption spectra of WCA signify presence of particles of wide size range thus confirming the effect of βME in controlling the particle size of the CdSe-CdS core-shell structure.

The energy gap of the core-shell structure was analysed using Tauc's equation as shown below.

$$(\alpha h\nu) = B(h\nu - Eg)^r \tag{1}$$

where B is a constant, α is the absorption coefficient, hν is the photon energy, Eg is the optical band gap and r is an index which depends on the nature of electronic transition responsible for optical absorption. The value of r is ½ for direct allowed transition and 2 for indirect allowed transition. CdSe and CdS both are known to have direct band gap structure. As direct transition happens in case of cadmium QDs a plot between $(\alpha h\nu)^2$ and wavelength (nm) is shown in Fig. 4. The calculated energy-gap of CA was 2.57eV and that of WCA was 2.23eV. Also the WCA energy-gap curve shows irregularity in slope suggesting presence of QD particles of varying sizes. Hence further analyses were not carried

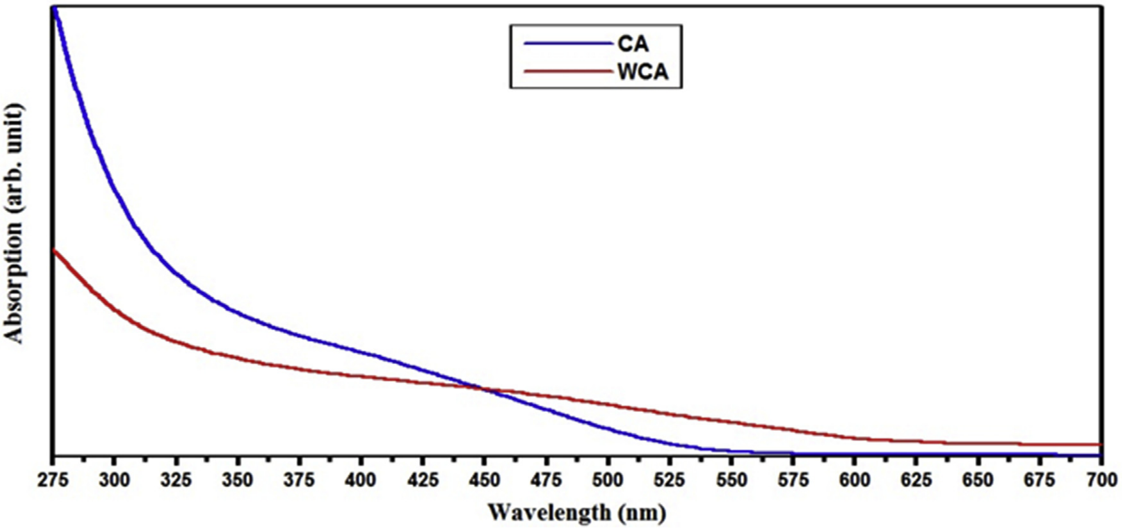

Fig. 3. UV–Vis absorption spectra of the as prepared core-shell QDs.