Stimulus Effect of Solvents on Cadmium Sulfide Quantum Dots Prepared for Solar Cell Application

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Abstract

Cadmium Sulfide quantum dots were prepared in three solvents such as distilled water, ethanol, and isopropyl alcohol respectively. Solvent dependence of cadmium sulfide quantum dots was investigated under XRD, TEM, UV, PL, and J–V characteristics. The results showed CdS quantum dots with sizes ranging from 7.5, 8.2, to 9 nm which enabled the control of the optical properties and consequently the solar cell performance. The optical absorption spectrum was observed near the ultra-violet region. Absorbance spectra reveal that there is a blue shift in the absorbance as the quantum dot size decreases due to the quantum confinement effect. For photoluminescence spectra, the emission peaks were observed at 430 nm, 468 nm, and 470 nm respectively. Among the solvents, cadmium sulfide quantum dots prepared with ethanol has the highest power conversion efficiency of 0.68%.

Keywords

Cadmium sulfide · Quantum dots · Quantum dot sensitized solar cells · Electrical properties

1 Introduction

Quantum dots (QDs) are semiconducting materials. It has perfect crystallinity and is defined by particle size. It has a unique optoelectronic property and it can be controlled by the growth process [1]. Quantum dots also have properties combined between bulk semiconductors and atoms. Quantum dot-sensitized solar cells (QDSSCs) are observed as the most promising applicant for the development of next-generation solar cells because QDSSCs can be fabricated by low-cost and simple techniques [2]. Cadmium Sulfide (CdS) quantum dots have good physical properties and could be used in a wide range of applications including energy, biomedical research, and environmental treatment [3] and it is reported as the most promising material to be used as a quantum dot sensitizer to show better performance in solar applications [4, 5]. In quantum dot sensitized solar cells, an electrode of titanium dioxide was used to achieve an efficiency of around 10–11% which is economically applicable to silicon-based solar cells [6, 7]. In solar cell applications, semiconductor materials are used for light absorption [8–10]. One of the most essential ways of using a quantum dot as light absorber material in photovoltaic devices is due to their ability to inject charge carriers between titanium dioxide (i.e., introducing electrons) and electrolyte (i.e., introducing holes) to understand the significance of energy level arrangements [11]. II–VI semiconductor quantum dots have received great interest due to their remarkable optical qualities such as low half peak width, high brightness, tunable emission, and broad absorption properties [12]. Researchers used II–VI semiconductors for optoelectronic applications for the reason that their emission spectrum and absorption spectrum can be modified in the visible region and near-infrared region based on the composition and size of the materials [13]. Comparatively less attention was provided to inorganic semiconductor materials like quantum dots (e.g., CdS) [14, 15] because the deposition of quantum dots on the surface of mesoporous titanium dioxide (m-TiO₂) is very less so it is necessary to increase the deposition of quantum dots and it can be done by self-assembly binding method [16, 17]. There are different types of methods to create QDs. Some of the known methods are the Hot-injection method [18], Hummer’s method, SILAR (Successive Ionic Layer Adsorption and Reaction) method [19], Hydrothermal method [20], and Co-Precipitation method. In this article, QDs are synthesized by a Top-down method (i.e.) the Co-precipitation method. In the Co-precipitation method,
normally soluble compounds are precipitated. The purpose of the synthesis procedure is to control the nucleation and development of particles in a solution of a chemical precursor including cation and anion sources [21]. QDs are excellent photovoltaic absorbing materials and are identified as effective sensitizers for quantum dot-sensitized solar cell applications [22]. Apart from that, QDs are used in multiple applications such as LEDs, flat panel displays, memory elements, photodetectors, lasers, and also in biological research.

2 Experimental Section

2.1 Materials

Cadmium nitrate, sodium sulfide flakes, polyvinylpyrrolidone k90, isopropyl alcohol, and ethanol were purchased from Sigma-Aldrich servings as precursors for the synthesis of cadmium sulfide (CdS) quantum dots. Titanium dioxide, fluorene-doped tin oxide (FTO) substrate, potassium iodide, iodine, and acetonitrile were used for the device fabrication. All aqueous solutions were prepared with double-distilled water.

2.2 Characterization Details

The third generation Empyrean, Malvern Panalytical multipurpose diffractometer with MultiCore Optics X-Ray sources: Cu Kα (λ = 1.54 Å) and was utilized to find out the PXRD analysis. UV–Vis spectrophotometer Shimadzu UV-1800 was used to study the light absorption properties of prepared samples, and photoluminescence spectra of cadmium sulfide quantum dots were taken by the excitation with Shimadzu RF-5301. The electrical properties were monitored by using a simulator (ABET technologies, model 10500) with an ozone-free DC xenon arc lamp at one sun (AM 1.5G or 100mW/cm²). The transmission electron microscope studies were taken by JEOL JEM 2100 (200 kV) analytical electron microscope.

2.3 Synthesis Process of CdS

The experiment was done to know how the different types of solvents help to promote the efficiencies of the quantum dots for solar cell applications. In the Co-precipitation method, the reagents involved in the synthesis of QDs are cadmium nitrate (Cd(NO₃)₂) as cadmium source, sodium sulfide (Na₂S) as a sulfide source, here Na₂S which is used as a reducing agent, and polyvinylpyrrolidone (PVP) is used as a capping agent. Here the capping agent is used to avoid coalescence and to achieve stability in the synthesis of CdS quantum dots. The synthesis process was performed at room temperature [23]. 0.0162 M of Cd(NO₃)₂, 0.0256 M of Na₂S, and 20 percentage weight of PVP were individually made in 50 ml of deionized water (DI water). To achieve a clear solution, Cd(NO₃)₂ was added to the PVP solution and stirred for 30 min. After that, while stirring gradually added Na₂S to the above-mentioned solution and continuously stirred for one hour to obtain a clear solution. During this process, the colorless solution turns yellow, then orange. The solution was then placed in a dust-free environment. To obtain a cadmium sulfide quantum dot solution, it was filtered and washed with double distilled water, ethanol, and acetone to remove the capping agent and contaminants. At 60 °C, the precipitate was dried in a hot air oven. Finally, the dried precipitate was crushed and grained, and weighed (1.95 g). Thus, the quantum yield of cadmium sulfide was 83%. Then, 50 mg of CdS QDs was added to 10 ml of three different solvents namely distilled water (DW), ethanol (EtOH), and isopropyl alcohol (ISO) and it was sonicated for many hours as shown in Fig. 1a and b. This was done to

![Fig. 1](https://example.com/figure1.png)

Photograph of prepared CdS quantum dots (a) under normal light (b) under UV light

![Fig. 1](https://example.com/figure1.png)

(a)

(b)
know how the solvent medium influences the optical properties of cadmium sulfide quantum dots and to enhance the efficiency.

2.4 Device Fabrication

By using the Doctor-blade method, TiO₂ semiconductor paste was deposited on FTO coated glass substrate. Then, TiO₂-coated FTO films were immersed into the compound solutions (CdS quantum dots prepared with three different solvents namely distilled water, ethanol, and Isopropyl alcohol) for 24 h. It was used as a photoanode and the graphene was coated on the FTO substrate by using a pencil used as a counter electrode. Therefore, photoanode and counter electrodes were assembled into a sandwich-type cell. An electrolyte was prepared by using potassium iodide (KI), iodine (I), acetonitrile, and it was injected between the cells. The active area of the cell is 0.5 cm².

3 Results and Discussion

3.1 Powder XRD Analysis

X-ray diffraction pattern of cadmium sulfide quantum dots dissolved with three solvents which are shown in Fig. 2. Several well-defined peaks are observed in the XRD pattern. For distilled water, the peaks located at 2θ angles of 26.4°, 43.95°, and 51.81° belong to the (111), (220), and (311) crystalline planes of the cubic structure of CdS quantum dots which matched with the PCPDF file no (80-0019). For ethanol, the peaks are located at 2θ angles of 24.82°, 27.55°, and 35.42° belong to the (101), (102), and (200) crystalline planes of the hexagonal structure of CdS QDs which matched with PPDF file no (89-2944). For isopropyl alcohol, the peaks located at 2θ angles of 24.82°, 27.57°, and 35.43° belong to the (101), (102), (111), and (200) crystalline planes of the hexagonal structure of CdS QDs which matched with PPDF file no (89-2944). The strong and sharp diffraction peaks indicate the formation of a well-crystalline sample. It can be seen that the major peak (111) and (101) is strongly dominating the other peaks.

Debye–Scherrer’s formula (1) was used to determine the average crystallographic size for all of these peaks of different solvents,

\[
(D) = \frac{0.9\lambda}{\beta \cos \theta}
\]

where D is the crystal size, λ is the X-ray wavelength, θ is the Bragg angle in radians, and β is the full width at half maximum of the peak in radians. The crystallite size of various solvents, as obtained by extending the relevant X-ray peaks using the Debye–Scherrer equation is 9.29 nm for distilled water, 7.43 nm for ethanol, and 8.25 nm for isopropyl alcohol, respectively. The particle size reported by TEM is similar to the average crystallite size obtained by XRD patterns and it is represented in Table 1.

3.2 Transmission Electron Microscope (TEM) Studies

The morphological and size distribution histogram analysis of synthesized CdS QDs was undertaken by using a transmission electron microscope. TEM images of CdS quantum dots dissolved with three types of solvents are depicted in Fig. 3a–c. From TEM measurements, the size of CdS quantum dots was calculated, as shown in Table 1. The size of CdS quantum dots for distilled water, ethanol, and isopropyl alcohol are 9 nm, 7.5 nm, and 8.2 nm. The Selected Area Electron Diffraction (SAED) pattern of CdS quantum dots images was shown in Fig. 3a(ii), b(ii), c(ii) and it is very well matched with the XRD results. From the TEM image, the d spacing values have been calculated for distilled water is 0.16 Å, ethanol is 0.13 Å and isopropyl alcohol is 0.15 Å, respectively.

| Sample | Crystallite size obtained by XRD (nm) | Particle size obtained by TEM (nm) |
|--------|--------------------------------------|-----------------------------------|
| DW     | 9.29                                 | 9                                 |
| EtOH   | 7.43                                 | 7.5                               |
| ISO    | 8.25                                 | 8.2                               |
3.3 UV–Visible Spectra Analysis

The optical absorption spectrum of cadmium sulfide quantum dots dissolved with three types of solvents is shown in Fig. 4. The optical absorption spectrum was observed for the solvent’s isopropyl alcohol between (315–520), distilled water between (440–530), and ethanol between (310–500) respectively. The absorbance spectra of quantum dots are strongly nearby the ultraviolet region then absorbance is decreased with wavelength and became almost constant nearby the infrared region. It also has a higher thickness which may be ascribed to the occurrence of band-to-band transition that revealed the dependency of absorbance spectra on quantum dots.

Fig. 3 a (i), b (i), c (i) are TEM images of CdS QDs, a (ii), b (ii), c (ii) the images of SAED patterns, a (iii), b (iii), c (iii) are the images of d-spacing values and a (iv), b (iv), c (iv) are the images of size distribution histogram, in the order of a Distilled water, b Ethanol and c Isopropyl alcohol
As a result, the blue-shifted absorption peaks could be due to a reduction in the particle size of cadmium sulfide quantum dots [24]. The direct bandgap was determined by extrapolating the straight line of the Tauc plot for zero values of absorbance coefficient where the linear nature of the plot revealed the presence of direct optical transition. The optical band gap energy was calculated by using Tauc’s Eq. (2), in which the absorption coefficient obtained in UV–Vis spectroscopy can be related to the optical band gap energy,

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

where \( \alpha \) is the absorption coefficient, \( h \) is Planck’s constant, \( \nu \) is the frequency of incident photons, \( C \) is a constant, and \( E_g \) is the bandgap of CdS quantum dots with three different solvents and \( n = 1/2 \) for direct transition [25]. The optical bandgap energy values for CdS QDs with different solvents such as distilled water, ethanol, and isopropyl alcohol are found to be 2.03 eV, 2.51 eV, and 2.49 eV, respectively, and plotted graphs are shown in Fig. 5. A reduction in direct bandgap is observed due to a decrease in grain size and bandgap narrowness.

### 3.4 Photoluminescence Spectra Analysis

Photoluminescence (PL) analysis was utilized for investigating the material’s energy level. PL spectra of cadmium sulfide quantum dots dissolved with three types of solvents as shown in Fig. 6. For distilled water, the PL emission peak was observed at 468 nm (blue emission), the emission peak for ethanol was observed at 470 nm and it has blue emission, and for isopropyl alcohol, the emission peak was observed at 430 nm and it has violet emission, respectively. This analysis renders that the intensity of the PL emission peak of the photoanode is significantly higher than that of other samples. The increased PL emission shows that the addition of the ion in CdS quantum dots can cover an emission window similar to that of the current workhorse of intrinsic QDs emitters and generates electronic states in the mid-gap region of the quantum dot recombination and charge separation. The rise of photoluminescence improves the emission quantum yield of quantum dots, which is more beneficial for the production of further excitons (electrons and holes). In the generic photoluminescence testing, a light source with photon energy upper than the bandgap energy of the quantum dot is applied.
to excite the quantum dot. Then the photons are absorbed and the QDs are excited and the final electron–hole pair is formed with finite momenta existence in the valance band and conduction respectively. So, the PL emission peak is achieved from the recombination of the electrons and holes. In addition, in the QDs sensitized solar cells, the electrons are often transferred to electrodes, less recombination happens with holes, and high PL intensity would cause high charge density in the cell.

### 3.5 J–V characterization of Solar Cell

Figure 7 shows the J–V curve of the prepared CdS quantum dots solar cells, the CdS quantum dots are dissolved with three different solvents. When exposed to light cadmium sulfide quantum dots generate photoexcited electrons and holes, electrons travel from the conduction band of cadmium sulfide quantum dots to the step-structure of the photoanode. The electrostatic interaction between an intrinsic charge of metal cation (Cd2+) and the induced charge of TiO2 surface, which is formed by the degree of solution pH over the point of zero charges of TiO2 is the most important parameter for determining the extent of CdS adsorption [26]. Table 2 represents the parameters of CdS quantum dots solar cells. The fill factor (FF) is calculated by utilizing the formula (3)

\[
FF = \frac{J_m \times V_m}{J_{sc} \times V_{oc}}
\]

where \(J_m\) represents the maximum current density, \(J_{sc}\) denotes the short-circuit current density, \(V_m\) indicates the maximum voltage and \(V_{oc}\) represents the open-circuit voltage, respectively. Power conversion efficiency (PCE) is calculated by using the formula (4)

\[
\eta\% = \frac{FF \times J_{sc} \times V_{oc}}{Input\ Power} \times 100\%
\]

The above results in Table 2 clearly show that the solvent ethanol has the highest efficiency compared to distilled water and isopropyl alcohol. From the plotted graph (Fig. 7), the PCE of distilled water was found to be 0.2290\% (\(J_{sc} = 2.2429\) mAcm\(^{-2}\), \(V_{oc} = 0.3363\) V and FF = 0.3036), the PCE of ethanol was 0.6810\% (\(J_{sc} = 3.9574\) mAcm\(^{-2}\), \(V_{oc} = 0.4834\) V and FF = 0.3560) and the PCE of isopropyl alcohol was 0.3193\% (\(J_{sc} = 6.2968\) mAcm\(^{-2}\), \(V_{oc} = 0.2003\) V and FF = 0.2532). The efficiency of ethanol was increased due to the formation of an anti-reflection film to reduce the incident light reflected from the surface of the cell. This was due to the fact that an increase in grain size thereby reduces the number of grain boundaries and results in the formation of a more ordered structure of the quantum dot at a higher deposition substrate temperature. It is well known that the electrical transport properties of QDs are markedly different from those of single crystals due to the presence of grain boundaries. And
also, the anti-solvent effect of alcohol can help to increase CdS quantum dot adsorption or allow better penetration into a deep pore of a mesoporous film when a mixture of water and the alcoholic solvent is used [26].

4 Conclusion

Cadmium sulfide quantum dots solar cells have been prepared well and dissolved with three types of solvents and then it is utilized for QDSSC device fabrication. UV–Visible spectra analysis shows the absorption peak in the ultraviolet region. PL spectra study results the CdS quantum dots were found to be the emission peaks were observed at 468 nm for distilled water, 470 nm for ethanol, and 430 nm for isopropyl alcohol. PXRD result confirms that distilled water has a cubic structure, ethanol, and isopropyl alcohol have a hexagonal structure. The size of the particles was calculated from TEM analysis for distilled water is found to be 9 nm, ethanol is 7.5 nm and isopropyl alcohol is 8.2 nm. TEM study proves that the prepared CdS quantum dots sizes are less than 10 nm in range. The J–V characteristics results prove that the CdS quantum dots dissolved with ethanol have the highest efficiency of 0.6810% compared to the other solvents such as distilled water (0.2290%) and isopropyl alcohol (0.3193%). By observing these three solvents ethanol has the highest power conversion efficiency (PCE) of 0.68%. The observed results in the present article prove that the solvent ethanol is a promising material and it can be suggested for solar cell application.

Fig. 7 J–V Characteristics of CdS QDs dissolved with different solvents, a Distilled water (DW), b Ethanol (EtOH), and c Isopropyl alcohol (ISO)
Table 2 Parameters of the CdS quantum dots solar cells

| CdS QDs dissolved with solvents | Open-circuit voltage ($V_{oc}$) V | Short-circuit current density ($J_{sc}$) mA/cm² | Fill factor (FF) | Efficiency $\eta$ (%) |
|--------------------------------|---------------------------------|---------------------------------|-----------------|---------------------|
| DW                             | 0.3363                          | 2.2429                          | 0.3036          | 0.2290             |
| Ethanol                        | 0.4834                          | 3.9574                          | 0.3560          | 0.6810             |
| Isopropyl alcohol              | 0.2003                          | 6.2968                          | 0.2532          | 0.3193             |

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Declarations

Competing interest All the authors declare that there are no competing interests.

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