The Influence of Dopant Concentration on Optical-Electrical Features of Quantum Dot-Sensitized Solar Cell

Dang Huu Phuc 1,2, Ha Thanh Tung 3,*, Van-Cuong Nguyen 4 and My Hanh Nguyen Thi 5

Abstract: In this study, TiO2/CdS/Cd0.8−xMnx−xSe, TiO2/CdS/Cd0.8−xMnxCux−xSe, and TiO2/CdS/Cd0.8−xAg2xSe thin films were synthesized by chemical bath deposition for the fabrication of photoanode in quantum-dot-sensitized solar cells. As a result, the structural properties of the thin films have been studied by X-ray diffraction, which confirmed the zinc Blende structure in the samples. The optical films were researched by their experimental absorption spectra with different doping concentrations. Those results were combined with the Tauc correlation to estimate the absorption density, the band gap energy, valence band and conduction band positions, steepness parameter, and electron–phonon interaction. Furthermore, the electrical features, electrochemical impedance spectrum and photocurrent density curves were carried out. The result was used to explain the enhancing performance efficiency.

Keywords: dopant concentration; quantum dots; cadmium selenite; cadmium sulfur

1. Introduction

In recent years, nanocrystals have attracted attention from scientists globally due to their advanced features, such as high absorptivity, durable material composition, and efficient ruling of energies [1] Because of these properties, these semiconductors can be used in various fields, for example, as photoelectronics, photodetectors, quantum-dot-sensitized solar cell (QDSSCs), and other types of photoelectronic [2].

In recent decades, quantum dots (QDs) have attracted attention from scientists globally because of their unique properties, such as: high adsorption coefficient, stable chemical composition, and efficient control of the band gap (\(E_g\)) [3,4]. Because of these properties, these semiconductors can be used in various fields, such as: photoelectronics, photodetectors, quantum-dot-sensitized solar cells, and other types of solar cells [5–7]. Over the years, CdSe QDs have been extensively investigated by scientists worldwide. They were applied to the photoanodes in the QDSSCs owing to their low cost, easy fabrication, and high stable chemical composition. However, the resistance of the CdSe films is significantly larger, and the energies of these films are smaller than those of bulk CdSe. Therefore, the amount of excited electrons generated in the conduction band (CB) of CdSe QDs to be transferred to the CB of TiO2 semiconductor was considerably low. Recently, a new technique has been applied to improve the current density and energy conversion of QDSSCs using CdSe QDs doped with transition metals such as Mg [5], and Co [8]. The exchange interaction between the transition metal and the electronic states of the CdSe QDs is fundamental for the study of optical and electrical properties of the QDSSCs. Generally, because of the doping of the transition metals in nano semiconductors, \(E_g\) and high-absorbing photons are generated in different regions. As a result, the photocurrent density, which is due to the
movement of the excited electrons in the circuit, increases [9,10]. Moreover, after doping, the recombination and dynamic resistance of TiO$_2$/QDs and diffusion resistance of TiO$_2$ film ($R_{cd}$), and counter electrode/electrolyte ($R_{ct}$) decrease significantly [11].

In previous articles, TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se (as $0\% \leq x \leq 5\%$, at%), TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se (as $0\% \leq x \leq 40\%$, at%), and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se $0\% \leq x \leq 40\%$, at% thin films have investigated and optimized characterizations of the materials as morphological analysis through FE-SEM, TEM; structure through XRD, Raman, EDX; optical properties as UV-Vis; lifetimes of excited electrons for fabricating photoanode in QDSSCs. In this research, we focus on the optical-electrical properties by their experimental absorption spectra with different doping concentrations and combination with the Tauc correlation to estimate the absorption density, the band gap energy, valence band and conduction band positions, steepness parameter, and electron–phonon interaction in the samples.

2. Results and Discussion

2.1. Structural Characterization

The structural TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se QDSSCs have been performed by X-ray diffraction. The obtained X-ray diffraction patterns are shown in Figure 1. For all thin films, the chart lists various parameters calculated from the diffraction peaks at 43.2° and 50.1° corresponding to the (220) and (311) crystal planes, respectively, of CdS, and CdSe zinc blende structure (JCPDS No. 88-2346 and JCPDS No. 41-1019) [12]. The peaks at 25.4°, 37.6°, 47.5° and 54.5° correspond to the (101), (004), (200), and (211) planes of the TiO$_2$ Anatase structure [13]. In addition, the peak at 25 °C for TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se films conducted from the FTO, because all films were coated on the FTO [13].

![Figure 1. The X-ray diffraction of the TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se QDSSCs.](image)

2.2. Optical Characterization

In photovoltaic cells, both the optical and electrical features of component materials must be investigated extensively. In this study, the absorption spectra, transmission, and reflection spectra of QDSSCs were recorded using UV-Vis. From the absorption spectra, we can determine various optical parameters, such as the absorption coefficient, $E_g$ of materials to control further band tail and study the defect states inside materials. TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se films recorded approximately 11.7 µm, 12.675 µm, and 13.013 µm of thickness from Figure 2, respectively.
In Figure 3a, the absorbance density of the TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se thin films significantly increased by approximately 17%, when compared with undoped film with that of TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se photoanode. Moreover, the absorption density of the TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se thin films decreased by approximately 11%, when compared with TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se thin films. Furthermore, the absorption density of TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se photoanodes shifted towards a longer wavelength (from 507 nm for undoped films to 605 nm for doped films). This is attributed to the replacement of the Cd atoms by the metal atoms in the films and a proper crystallization of the films corresponding to a suitable doping-concentration-reducing effect state [14]. The 605 nm absorption peak of the TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se film was attributed to the transition of the VB of Se to d-state of Cu dopant in the $E_g$ of pure CdSe QDs [15].

From the UV-Vis spectra, using the Tauc relation in Equation (1), we variously determined the $E_g$ of the TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se films with dopants [16]

$$a h\nu = a \nu (h\nu - E_g)^n$$

where $a$ is noted as a coefficient of light coming adsorption, $h\nu$ is noted as a light coming energy, $a$ is not the change factor, CdSe QDs has the direct band gap, and $n = 0.5$. After plotting Equation (1) in Figure 3b, $E_g$ of the films was estimated and recorded (shown in Table 1).

Figure 3b,c illustrates the valuable $E_g$ for CdSe-doped photoanodes varying from 1.87 eV to 1.78 eV, which is smaller than that without doped photoanode (2.08 eV). Furthermore, by observation, the $E_g$ values of CdSe-doped photoanodes depended significantly on the change in dopants. Here, the reduced $E_g$ of the doped films resulted from two factors: an increase in particle size after doping [17], and a change in force density on account of the presence of Cu-Se, Mn-Se, and Ag-Se pairs in the extended lattice at the expense of Cd-Se in the host lattice [18]. Therefore, the dopant energy levels, called transition energies, are presented in the $E_g$ of pure CdSe QDs. Subsequently, these photons obtain energy below $E_g$ of pure CdSe nano semiconductor, which can be absorbed at dopant energy levels before they are transferred to the CB of pure CdSe semiconductor. Therefore, $J_{SC}$ was significantly increased on account of a large number of absorbed photons and, consequently, the absorption peak shifted towards a longer wavelength. Furthermore, both the conduction band and valence band positions of the TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se films were estimated by the Tauc formula and listed in Table 1. Obtained CB values of $-3.98$, $-3.7$, and $-4.1$ eV corresponding to the TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se films, respectively, are higher than the CB value of $-4.105$ eV of pure CdSe QDs. Therefore, the presence of doping metals, which has increased the CB value in the doped films.
pared to that in the undoped CdSe QDs, aids in the transition of excited electrons from the CdSe QDs to TiO2.

Table 1. $E_g$, CB, and VB were estimated by Tauc equation and the band tail, $\sigma$, $E_{cb}$ were obtained from the absorption spectra.

| Atom%            | $E_g$ (eV) | $X$ (eV) | $E_{CB}$ (eV) | $E_{VB}$ (eV) | $E_U$ (eV) | $\sigma$ (eV) | $E_{cb}$ (eV) |
|------------------|-----------|----------|---------------|---------------|------------|--------------|---------------|
| CdSe film        | 2.08      | 5.145    | −4.105        | −6.2          | 0.786      | 0.033        | 20.25         |
| Cd$_x$Cu$_{1-x}$Se film | 1.87      | 4.91     | −3.98         | −5.85         | 2.11       | 0.012        | 54.5          |
| Cd$_x$Mn$_{1-x}$Se film | 1.79      | 4.62     | −3.7          | −5.5          | 2.33       | 0.011        | 59.97         |
| Cd$_x$Ag$_{2-2x}$Se film | 1.78      | 4.99     | −4.1          | −5.88         | 1.26       | 0.0205       | 32.6          |

Figure 3. Variation in (a) the absorption spectra and (b) $(ahv)^2$ plots with the changing Ag ratio and the dependence of $E_g$ and (d) the absorption coefficient on the compositional TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-2x}$Se thin films.

Due to the band structure and transition energies of materials in the absorption process, the absorption coefficient is estimated using an equation correlation [19], as follows

$$\alpha = \frac{2.3026.A}{d}$$  

where $A$ and $d$ are the absorption density and the thickness of the film, respectively.

As can be seen in Figure 3d, $\alpha$ significantly increases after doping, and a shift in the absorption peak for CdSe doping metals compared to that without dopant occurs. This
result, obtained from the replacement of Cd atoms by the metal dopants in the doped films, which induces the d-state electrons of dopant atoms, appeared in $E_g$ of CdSe QDs to introduce the energy levels of dopant in the $E_g$ of CdSe QDs. Therefore, the absorption coefficient of the doped films was enhanced significantly because the appearance of the transition energy levels ensured that a large number of photons was absorbed in different regions [20,21].

To correlate the localized states with the $E_g$ of the films, the Urbach energy ($E_u$) of the films was determined as follows [22]

$$\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)$$  \quad (3)

The Urbach plots between ln($\alpha$) and $h\nu$ and $E_u$ (which are estimated from the slope of the curves between ln($\alpha$) and $h\nu$) are shown in Figure 4. As is evident, the valuable $E_u$ depends on the type of doping metal. There was a minor decrease in its $E_u$, from 0.786 eV (undoped film) to 2.33 eV (doped films), due to the reduced defect states in the TiO$_2$/CdS/Cd$_{1−x}$Cu$_{1−x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1−x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2−2x}$Se films [23]. The $E_u$ value of 2.33 eV was achieved for Cu doping, and was approximately two times higher than the band tail energy values for Mn and Ag doping (shown in Table 1). This implies that the large defect states in the films are a result of the unsatisfied bond, and the center of those defect states in $E_g$ of the TiO$_2$/CdS/Cd$_{1−x}$Cu$_{1−x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1−x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2−2x}$Se films. Depending on the dopant, the defect state center can appear in the middle of $E_g$, near the VB, or near the CB [24].

![Figure 4](image_url)

**Figure 4.** The dependence of (a) the ln($\alpha$) of the films and (b) the Band tail energy on the compositional TiO$_2$/CdS/Cd$_x$Cu$_{1−x}$Se and TiO$_2$/CdS/Cd$_x$Mn$_{1−x}$Se and TiO$_2$/CdS/Cd$_x$Ag$_{2−2x}$Se thin films.

The absorption spectrum of the photovoltaic cells depends on several factors, such as the type of doping material, doping concentration, photoconductivity, thickness of the film, and especially, photon absorption in film. The steepness parameter, $\sigma$, is considered to result from the electron–phonon interaction ($E_{ep}$). $\sigma$ is correlated with $E_{ep}$ via the following correlation: $E_{ep} = 3/2\sigma$. Figure 5 and Table 1 show the variations in $\sigma$ and $E_{ep}$, respectively. As can be seen in Figure 4a, $\sigma$ shows a downward trend as the concentration of the doping metal reduced to a minimum of 3% (0.011 eV), which implies a stronger electron–phonon interaction energy corresponding to the TiO$_2$/CdS/Cd$_x$Cu$_{1−x}$Se film as a result, confirming that the bond energy is as a parameter of film composition [24]. Furthermore, the $E_{ep}$ value for the TiO$_2$/CdS/Cd$_x$Cu$_{1−x}$Se film (59.97 eV) is significantly higher than for the TiO$_2$/CdS/Cd$_x$Ag$_{2−2x}$Se film (32.6 eV) or the CdSe film (20.25 eV), and $\sigma$ increases considerably. Evidently, the compositional variations in ternary TiO$_2$/CdS/Cd$_x$Cu$_{1−x}$Se,
TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-2x}$Se thin films caused variations in the optical parameters [24].

![Graph](image1)

**Figure 5.** The dependence of (a) $\sigma$ and (b) $E_{e-p}$ in metal addition in films.

### 2.3. Electrical Properties

In this section, we study the current–voltage (J-V) characteristics of QDSSCs and, subsequently, the estimated primary physical parameters using one illuminated J-V curve. The photovoltaic device significantly depends on the four resistances in a photovoltaic cell: an external resistance ($R_D$), internal resistance ($R_d$), series resistance ($R_s$), and a shunt resistance ($R_{SH}$) (Figure 6). Ideally, $R_s$ should be zero, and $R_{SH}$ should be infinite. As a result of the dynamic parameters, significant power losses caused by the dynamic resistances due to various factors, such as manufacturing defects, technological processes, and natural materials, are estimated.

![Diagram](image2)

**Figure 6.** The circuit of a photovoltaic cell [25].

In [26], we conducted the equations for dynamic parameters as follows

$$R_D = \frac{V_1 - V_2}{I_2 - I_1} \quad \text{(4)}$$

$$R_d = \frac{1}{\alpha(I_2 - I_1)} \ln \left( \frac{I_{ph} + I_o - I_1}{I_{ph} + I_o - I_2} \right) \quad \text{(5)}$$

$$R_s = R_D - R_d \quad \text{(6)}$$

$$R_{SH} = \frac{V_{OC}}{I_{ph} - I_o(e^{\alpha V_{OC}} - 1)} \quad \text{(7)}$$

$$\alpha = \frac{q}{n k_B T} \quad \text{(8)}$$
where $q$ and $k_B$ are the electronic charge and Boltzmann constant, respectively, $T$ is the room temperature, $I_{ph}$ is the incident light intensity, and $I_0$ is the diode saturation current. The obtained physical parameters are listed in Table 2.

Table 2. The values of the performance efficiency (efficiency, short-circuit current, open-circuit voltage, fill factor) and $R_D$, $R_d$, $R_{SH}$, $R_s$ were estimated from J-V curves and $R_{ct1}$, $R_{ct2}$ were obtained from the EIS experiment.

| Atom%          | $J_{SC}$ (mA/cm²) | FF  | $V_{OC}$ (V) | $\eta$ (%) | $R_D$ (Ω) | $R_d$ (Ω) | $R_{SH}$ (kΩ) | $R_s$ (Ω) | $R_{ct1}$ (Ω) | $R_{ct2}$ (Ω) |
|----------------|-------------------|-----|--------------|------------|-----------|-----------|---------------|-----------|----------------|----------------|
| CdSe film      | 12.4              | 0.379 | 0.42        | 1.97 ± 0.01 | 33.75  | 96.5  | 12.4         | 62.8        | 629            | 193            |
| Cd$_x$Cu$_{1-x}$Se film | 19.89              | 0.419 | 0.505      | 4.24 ± 0.003 | 25.31  | 61     | 19.9         | 35.7        | 255            | 21             |
| Cd$_x$Mn$_{1-x}$Se film | 18.99              | 0.381 | 0.52       | 3.9 ± 0.005  | 27.51  | 64.1  | 18.99        | 36.6        | 205            | 25             |
| Cd$_x$Ag$_{2-x}$Se film | 11                 | 0.53  | 0.47       | 2.75 ± 0.008 | 41.81  | 108    | 10.92        | 66.2        | 256            | 23             |

In this experiment, samples of photovoltaic cells fabricated using the TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se, TiO$_2$/CdS/Cd$_x$Mn$_{1-x}$Se, and TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se photoanodes were recorded by a Keithley 2400 source meter under identical illumination condition. Figure 7a,b show the graphical representation of the measurement results. The performance efficiency of the photovoltaic cells is sensitive to the concentration of the metal dopants (Figure 6). For example, the energy conversion value increased significantly from 1.97% (undoped film) to 4.24% (TiO$_2$/CdS/Cd$_x$Cu$_{1-x}$Se film), and the highest efficiency was obtained for Cu doping. Furthermore, the efficiency dropped to 2.75% (for TiO$_2$/CdS/Cd$_x$Ag$_{2-x}$Se film).

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![Figure 7](image-url)  
**Figure 7.** (a) Variation of photocurrent density–voltage curves and (b) dependence of the performance efficiency on metal addition in films.
cell, practically, there is an upper limit of 20 kΩ for $R_{SH}$. According to Table 2, the $R_{SH}$ values for doped films are higher without dopant, and the highest, 19.9 kΩ, is obtained from the TiO$_2$/CdS/Cd$_{x}$Cu$_{1-x}$Se film. Evidently, $R_{SH}$ is sensitive to the doping metal; while, for C doping, $R_{SH}$ reaches a maximum value of 19.9 kΩ for Ag doping, $R_{SH}$ value decreased to 10.92 kΩ for TiO$_2$/CdS/Cd$_{x}$Ag$_{2-x}$Se film. This result was also proven as the UV-Vis peak moves to a longer wavelength owing to the reduced $E_g$ and enhanced $E_{e-p}$ discussed in Section 3.2. Furthermore, our result also agrees with reference [26].

Conventionally, electrochemical impedance spectroscopy (EIS) was found by Mosa–Sero [27] to determine the occurring processes through contacts, TiO$_2$ film and polysulfide electrolyte. These investigation and analysis processes included several steps, such as the pumping of excited charges from the CB of QDs to the CB of TiO$_2$, diffusive charges inside the TiO$_2$ film before moving to the external circuit, the transfer of electrons to the counter electrode/polysulfide. In this case, an equivalent circuit was extracted from the EIS fitting using the Nova software. As far as the EIS fitting is concerned, the equivalent circuits for simulation were chosen for a consistent match between the EIS experiment and EIS fitting. Subsequently, $R_{ct1}$ and $R_{ct2}$ were obtained from EIS fitting. Those values are listed in Table 2.

Figure 9a–c shows the EIS curves of the photovoltaic cells based on the metal dopants, and dynamic resistance curves in the counter electrode/polysulfide electrolyte surface, and in the redox process of electrolysis, $R_{ct1}$, and the recombination resistance at TiO$_2$/QDs surface, and in TiO$_2$ film, $R_{ct2}$. In the same way, the recombination resistances, which
are listed in Table 2, depend significantly on the doping concentration of the metal dopants. A downward trend was observed $R_{ct1}$ value from 629 $\Omega$ (undoped film) to 205 $\Omega$ ($\text{TiO}_2/\text{CdS}/\text{Cd}_{x}\text{Mn}_{1-x}\text{Se}$ film) or to 255 $\Omega$ ($\text{TiO}_2/\text{CdS}/\text{Cd}_x\text{Cu}_{1-x}\text{Se}$ film). The value of $R_{ct1}$ was the lowest (205 $\Omega$) for the $\text{TiO}_2/\text{CdS}/\text{Cd}_{x}\text{Mn}_{1-x}\text{Se}$ film, and it increased to a maximum value of 256$\Omega$ for the $\text{TiO}_2/\text{CdS}/\text{Cd}_x\text{Ag}_{2-2x}\text{Se}$ film. This implies that a decrease in the recombination resistance at the counter electrode/polysulfide electrolyte surface and in the redox process of the electrolyte resulted in the enhanced current density (19.89 mA/cm$^2$) and energy conversion (4.24%) compared to those for the undoped film (12.4 mA/cm$^2$ and 1.97%, respectively) [28]. Furthermore, as mentioned above, the correlation with $R_{ct2}$ caused the recombination resistance in the photovoltaic cells, which indicates that the recombination processes at $\text{TiO}_2$/QDs surface, inside QDs, and the diffusion of charges in $\text{TiO}_2$ film were correlated to the $\text{TiO}_2/\text{CdS}/\text{Cd}_{x}\text{Cu}_{1-x}\text{Se}$ film, $\text{TiO}_2/\text{CdS}/\text{Cd}_{x}\text{Mn}_{1-x}\text{Se}$ film, and $\text{TiO}_2/\text{CdS}/\text{Cd}_x\text{Ag}_{2-2x}\text{Se}$ film. Therefore, $R_{ct2}$ is pivotal in explaining the enhanced current density and performance efficiency after the proposed metal doping. Correspondingly, the values of the $R_{ct2}$ decreased from 193 $\Omega$ (undoped film) to 21 $\Omega$ (Cu doping). The value of $R_{ct2}$ was the lowest for Cu doping (21$\Omega$), and increased to a maximum of 23 $\Omega$ for Ag doping. This result is consistent with the results from the photocurrent density curve, absorption spectra, and the band tail energy. Because of the reduced recombination resistance, a large number of charges accumulated, further reducing the recombination process of the excited electrons with the surface states of QDs, resulting in the fast pumping of excited charges between CdS, CdSe and TiO$_2$ [29].

![Figure 9](image-url)

**Figure 9.** (a) Variation of the Electrochemical Impedance Spectra and (b) dependence of the recombination resistances: (b) polyelectrolyte and polyelectrolyte/counter electrode contact ($R_{ct1}$) and (c) TiO$_2$/QDs contact and diffusion resistance in TiO$_2$ films ($R_{ct2}$).
3. Experiment

3.1. Materials

TEC7 Glass Plates 3.2 mm (2.2 mm of thickness, 1.2 \times 2 \text{ cm} = 0.196 \text{ cm}^2 \text{ of area}) was purchased from Sigma in Frankfurter, German. Titania paste, Sodium Selenite (Na\text{2}Se\text{O}_3), Cd(NO\text{3})\text{2}, 2H\text{2}O, Na\text{2}S.9H\text{2}O, Cu(NO\text{3})\text{2}, 3H\text{2}O, Mn(CH\text{3}COO)\text{2}, 4H\text{2}O, AgNO\text{3}, Na\text{2}SO\text{3}, NaOH, Se powder, KCl, Na\text{2}S, S were bought from Sigma in Frankfurter, German. All chemicals were used directly without further purification.

3.2. Preparation Processes

TiO\text{2} film was coated on the Fluorine-doped tin oxide (FTO) followed by annealing in air at 500 °C.

Fabrication of CdS film: The FTO/TiO\text{2} film was dipped in Cd\text{2}+-solution (2.665 g Cd(NO\text{3})\text{2}.2H\text{2}O dissolved in a 20 mL mixture of ethanol and pure water in 1:1 ratio) for 5 min, and then washed with ethanol. Furthermore, it was dipped in S\text{2}2− solution (12 g of Na\text{2}S.9H\text{2}O, dissolved in 100 mL mixture of methanol and pure water in 1:1 ratio) for 5 min and then washed with methanol. This two-step process formed a single layer of the CdS film. Two layers of the CdS film were coated by repeating the two-step process.

Fabrication of Cu\text{2}+ Doped, Mn\text{2}+ Doped, and Ag\text{2}+ Doped CdSe Films

For Cu\text{2}+ doping, Cd\text{2}+- and Cu\text{2}+-solution (0.1 M Cd(NO\text{3})\text{2}.2H\text{2}O and 0.1 M Cu(NO\text{3})\text{2}.3H\text{2}O dissolved in a 30 mL mixture of ethanol and pure water in 1:1 ratio) was kept for 5 min, and then washed with ethanol.

For Mn\text{2}+ doping, Cd\text{2}+ and Mn\text{2}+-solution (0.1 M Cd(NO\text{3})\text{2}. 2H\text{2}O and 0.1 M Mn(CH\text{3}COO)\text{2}. 4H\text{2}O dissolved in 30 mL mixture of methanol and pure water in 1:1 ratio) was kept for 5 min, and then washed with methanol.

For Ag\text{2}+ doping, Cd\text{2}+ and Ag\text{2}+-solution (0.1 M Cd(NO\text{3})\text{2}.2H\text{2}O and 0.1 M AgNO\text{3} dissolved in a 30 mL mixture of ethanol and pure water in 1:1 ratio) was kept for 5 min, and then washed with methanol.

Furthermore, for the fabrication of Cu\text{2}+, Mn\text{2}+, and Ag\text{2}+ doped films, the previously synthesized FTO/TiO\text{2}/CdS were, respectively, separately dipped into the solutions mentioned above. Subsequently, the films were dipped in Se\text{2}2−-solution (2.27 g Se powder and 0.6 M Na\text{2}SO\text{3} were dissolved in 100 mL of water and then added to 5 mL of 1 M NaOH. Furthermore, the solution was stored at 70 °C in 7 h) for 15 min at 50 °C, and then washed with pure water to form a single layer of the CdSe film desired doping material. Three layers of the CdSe film with the desired doping material were coated by repeating the above process. Finally, the films were annealed in the range from 120 °C to 300 °C as in vacuum for 30 min.

The polysulfide electrolyte was prepared by mixing 0.5 M Na\text{2}S, 0.2 M S, and 0.2 M KCl in pure water in 7:3 ratio.

The photoanodes have been synthesized and characterized using XRD (Philips, PANalytical X’Pert, CuKα radiation). The absorption spectra were recorded using a UV-Vis JASCO V-670. The completed photovoltaic cells were characterized using a Keithley 2400 source meter developed by SOLARENA, Sweden. The obtained J-V curves are supported to estimate the valuable electrical range of devices. The scanning speed voltage of the equipment was set at 5 mV/s in the range from V\text{OC} to 0. The electrochemical impedance spectroscopy was performed using an impedance analyzer (ZAHNER CIMPS).

4. Conclusions

TiO\text{2}/CdS/Cd\text{x}Cu\text{1−x}Se, TiO\text{2}/CdS/Cd\text{x}Mn\text{1−x}Se, and TiO\text{2}/CdS/Cd\text{x}Ag\text{2}2\text{x}Se thin films were successfully synthesized on FTO glass as photoanodes in solar cells, which were sensitive to Cu\text{2}+ counter electrode. The QDSSCs using the TiO\text{2}/CdS/Cd\text{x}Cu\text{1−x}Se photoanode exhibits the highest performance: J\text{SC} = 19.89 mA/cm\text{2}, V\text{OC} = 0.505 V, FF = 0.379, and \eta = 4.24% as a result of enhancing electrocatalytic activity, charge transfer and charge collection, reducing recombination, and the longer excited electron lifetime. The optical
parameters also are sensitive to dopant. This implies that large defect states in the films are a result of the unsatisfied bond and the center of those defect states in $E_g$ of Cd$_x$Cu$_{1-x}$Se films. They can be seen in the middle of $E_g$, near the $V_B$, or near the $C_B$. Furthermore, the electrical properties of the Cd$_x$Cu$_{1-x}$Se were also investigated through the $R_s$, $R_{SH}$ dynamic resistance, recombination resistance, diffusion resistance in TiO$_2$ layer, and TiO$_2$/QDs, $R_{ct1}$, $R_{ct2}$. As a result, the recombination and dynamic resistance of TiO$_2$/QDs and diffusion in TiO$_2$ ($R_{ct2}$) films, and the diffusion at the counter electrode/electrolyte ($R_{ct1}$), decreased significantly.

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