### Accepted Manuscript

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PII:	\$1010-6030(17)31686-6
DOI:	https://doi.org/10.1016/j.jphotochem.2018.05.029
Reference:	JPC 11299
To appear in:	Journal of Photochemistry and Photobiology A: Chemistry
Received date:	15-11-2017
Revised date:	15-5-2018
Accepted date:	21-5-2018

Please cite this article as: Jayaweera EN, Kumara GRA, Kumarage C, Ranasinghe SK, Rajapakse RMG, Bandara HMN, Ileperuma OA, Dassanayake BS, CdS nanosheet-sensitized Solar Cells Based on SnO2/MgO Composite Films, *Journal of Photochemistry and Photobiology, A: Chemistry* (2018), https://doi.org/10.1016/j.jphotochem.2018.05.029

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### CdS nanosheet-sensitized Solar Cells Based on SnO<sub>2</sub>/MgO Composite Films

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Title: CdS nanosheet-sensitized Solar Cells Based on SnO<sub>2</sub>/MgO Composite Films

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- 1. CdS nanosheets were used to sensitize the SnO<sub>2</sub>/MgO-based solar cells.
- 2. A ZnS layer was also deposited on the CdS nanosheets, which acts as a capping layer to passivate the surface states of CdS nanosheets as well as a barrier to suppress the recombination of photo-generated electrons with the electrolyte.
- 3. A power conversion efficiency of 1.33% could be obtained in this regard which is comparable with those obtained by other systems sensitized by CdS.

### Highlights

- CdS nanosheets were used to sensitize the SnO<sub>2</sub>/MgO-based solar cells.
- A ZnS layer was also deposited on the CdS nanosheets, which acts as a capping layer to passivate the surface states of CdS nanosheets as well as a barrier to suppress the recombination of photo-generated electrons with the electrolyte.
- A power conversion efficiency of 1.33% could be obtained in this regard which is comparable with those obtained by other systems sensitized by CdS.

#### Abstract

We report CdS nanosheet-sensitized solar cells based on SnO<sub>2</sub>/MgO composite films for the first time. Though, TiO<sub>2</sub> and SnO<sub>2</sub> have been used for semiconductor-sensitized solar cells (SSCs), composite films based on SnO<sub>2</sub>, have not yet been used to fabricate SSCs. In this work, CdS nanosheets were used to sensitize the SnO<sub>2</sub>/MgO-based solar cells. A thin film of CdS nanostructures was deposited on the mesoporous, SnO<sub>2</sub>/MgO film by chemical bath deposition (CBD) method at different bath temperatures. A ZnS layer was also deposited on the as-prepared CdS nanosheets, which acts as a capping layer to passivate the surface states of CdS nanosheets as

well as a barrier to suppress the recombination of photo-generated electrons with the electrolyte. A power conversion efficiency of 1.33% could be obtained in this regard which is comparable with those obtained by other systems sensitized by CdS.

Keywords: CdS nanosheets, semiconductor-sensitized solar cells, SnO<sub>2</sub>/MgO composite films, chemical bath deposition

#### 1. Introduction

Inorganic semiconductor nanoparticles have received considerable attention as promising sensitizers for photovoltaic devices due to their intriguing optical and electrochemical properties including, high extinction coefficient, easily tunable band gap and multiple exciton generation [1-4]. Among the possible materials, group II-VI semiconductor materials such as CdS, CdSe and PbS have proven to be the most promising sensitizers [1, 5-10]. These semiconductors have been deposited either as QDs or as a thin layer on the mesoporous TiO<sub>2</sub> films [5-10].

Relatively lower conversion efficiencies have been reported for the semiconductorsensitized solar cells (SSCs) due to several reasons. Mainly, the higher recombination rate of photo-generated electrons with the surface states of the sensitizer nanoparticles results in lower conversion efficiencies of SSCs. Unlike the dyes used in dye-sensitized solar cells (DSCs), these narrow-band gap semiconductor nanoparticles act as recombination centers themselves [11]. Therefore, surface modification methods of nanoparticles have been adopted to effectively reduce the recombination rate to give relatively higher conversion efficiencies for the solar cells sensitized with the narrow-band gap semiconductors [8, 12].

CdS with a band gap of 2.42 eV, possesses the ideal optical and electrochemical properties to be utilized in photovoltaic applications [5, 6]. The highest power conversion efficiency reported so far, for any CdS-sensitized solar cell is 4.88%, which is for boron and nitrogen co-doped TiO<sub>2</sub>based solar cell [7]. Though there are a number of reports on solar cells utilizing CdS thin films or QDs as light absorber, there are no any reports on solar cells employing CdS nanosheets. In this study, for the first time, we report the CdS nanosheet-sensitized solar cells based on SnO<sub>2</sub> composite films. Though, TiO<sub>2</sub> and SnO<sub>2</sub> have been used for SSCs, composite films based on SnO<sub>2</sub>, have not yet been used to fabricate SSCs. The lower effective electron mass of SnO<sub>2</sub> (0.17 $m_e$ ) compared to that of TiO<sub>2</sub> (10 $m_e$ ) results in higher electron mobilities than that of TiO<sub>2</sub> [13]. In this regards, it has been expected for SnO<sub>2</sub> to outperform TiO<sub>2</sub>. On the contrary, the efficiencies

reported for SnO<sub>2</sub>-based DSCs have been very low due to the high rate of recombination of the photo-generated electrons with I<sub>3</sub><sup>-</sup> ions in the electrolyte or the oxidized dye [14, 15]. This high rate of recombination attributes to the high electron mobilities. In order to reduce the recombination losses, utilization of the core shell configuration has been introduced by Tennakone *et al.* [15]. The idea is to coat the surface of the semiconductor nanoparticles with a wide band-gap semiconductor or an insulator such as MgO, Al<sub>2</sub>O<sub>3</sub> and CaCO<sub>3</sub> etc. [14-17]. Similarly, here, SnO<sub>2</sub>/MgO film was used to improve the performance of the solar cell by effectively suppressing the electron recombination at SnO<sub>2</sub>/sensitizer interface. In this work, CdS was used to sensitize the SnO<sub>2</sub>/MgO film by chemical bath deposition (CBD) method at different bath temperatures. Moreover, a ZnS layer was also deposited on the as-prepared CdS particles, which acts as a capping layer to passivate the surface states of CdS nanosheets as well as a barrier to suppress the recombination of photo-generated electrons with the electrolyte.

#### 2. Experimental

#### 2.1 Preparation of SnO<sub>2</sub>/MgO Composite Films

SnO<sub>2</sub> colloidal suspension in water (Wako Chemicals, Japan) (3.0 ml), acetic acid (Wako Chemicals, Japan, 99.7%) (10 drops) and MgO (Breckland Scientific, UK, 98%) (0.018 g) were ground in a motar. Then Triton X-100 (Sigma, USA, 99.5%) (5 drops) and ethanol (Hayman, England, 99.9%) (40.0 ml) were added to the mixture and the resulting suspension was sonicated for 15 min and sprayed onto cleaned FTO glass plates, kept on a hot plate, at 150 °C [17]. Then, the as prepared SnO<sub>2</sub>/MgO composite films were sintered at 500 °C for 30 min and allowed to cool down.

### 2.2 Deposition of CdS

In order to obtain CdS thin films, a reaction solution of 100 ml was used which consisted of 0.01 M CdSO<sub>4</sub> (Sigma-Aldrich, 99%), 1.1 ml NH<sub>3</sub>(aq) solution (Surechem, England, 35% w/w) and de-ionized water. The SnO<sub>2</sub>/MgO composite film-deposited FTO plates were fixed to an axel, vertically, and were rotated at a speed of 180 rpm. Deposition of CdS was carried out for 1 hr by

adding 0.2 M CS(NH<sub>3</sub>)<sub>2</sub> (Sigma-Aldrich, USA, 99%) drop wise throughout the experiment. The experimental setup used to deposit CdS on SnO<sub>2</sub>/MgO composite films is shown in fig. 1.

The optimum thickness of the SnO<sub>2</sub>/MgO film was determined by varying the thickness and measuring the corresponding photovoltaic parameters where, CdS deposition was carried out at a bath temperature of 50 °C. In order to investigate the optimum bath temperature for the deposition of CdS, the bath temperature was varied from 30 °C to 80 °C. Fig. 2 depicts the CdSsensitized SnO<sub>2</sub>/MgO films prepared at 40 °C (yellow colour) and 80 °C (orange-yellow colour). Then samples were cleaned with running deionized water for 5 min to remove loosely adhered CdS. Samples were then dried in a N<sub>2</sub> gas flow and were annealed at 200 °C for 1 hr in air.



Fig. 1. Experimental setup used to deposit CdS on SnO<sub>2</sub>/MgO composite films.





Fig. 2. CdS-sensitized  $SnO_2/MgO$  films where CdS deposition was carried out at bath temperatures of (a) 40 °C (yellow colour) and (b) 80 °C (orange-yellow colour).

#### 2.3 Deposition of ZnS Capping Layer

The ZnS coating was deposited by successive ionic layer adsorption reaction (SILAR) method (2 cycles). Here, the CdS-deposited electrode was dipped in 0.5 M Zn(CH<sub>3</sub>COO)<sub>2</sub> (Prolabo, Belgium, 99.8%) and 0.5 M Na<sub>2</sub>S (Analytical Regent, India, 35%) aqueous solutions for 1 min, washing thoroughly with deionized water prior to each immersion to remove excess ions [12].

#### **2.4 Construction of SSCs**

The fabricated working electrodes were sandwiched with a Cr-coated, lightly platinized FTO counter electrode and the intervening space was filled with the liquid electrolyte (0.1 M LiI, 0.05 M I<sub>2</sub>, 0.6 M dimethylpropylimidazolium iodide, 4-*tert*-butylpyridine in acetonitrile).

#### 2.5 Characterizations

UV-vis spectroscopic studies were carried out using a Shimadzu UV-1800 spectrophotometer to confirm the formation of CdS on the SnO<sub>2</sub>/MgO films. In order to study the crystal structures of as deposited CdS, X-ray diffraction (XRD) patterns of CdS-deposited SnO<sub>2</sub>/MgO films were obtained using Siemens D5000 and Rigaku (RINT-TTR III) X-ray diffractometer (Cu K $\alpha$ 1,  $\lambda$ -1.54056 Å). The scanning electron microscopic (SEM) images of the CdS deposited films were obtained using a Hitachi S4700 scanning electron microscope. Then, the *J*-*V* characteristics of the SSCs were obtained under AM 1.5 illumination using a solar simulator (PECcell-L01) coupled to a digital source meter (Keithley, 2400 model). Then the impedance spectra were obtained for ZnS-treated and non-treated SnO<sub>2</sub>/MgO/CdS elecctrodes, in the dark, under forward bias conditions (– 0.55 V), using a potentiostat (Autolab PGSTAT12) equipped with a frequency response analyzer. Impedance spectroscopic (IS) studies were carried out in the frequency range of 100 kHz-0.01 Hz by applying a 10 mV sinusoidal signal.

### 3. Results and discussion

#### 3.1 Optimization of the SnO<sub>2</sub>/MgO Film Thickness

The SEM images of the SnO<sub>2</sub>/MgO composite films depicting their surface morphologies are shown in fig. 3(a). The porous nature of these films is clearly visible in the SEM images. The

XRD pattern of SnO<sub>2</sub>/MgO composite film is depicted in fig. 3(b). However, in the XRD pattern, only the peaks corresponding to the tetragonal crystal structure of rutile SnO<sub>2</sub> (JCPDS card no.: 41-1445) are discernible. The relevant crystal planes of (110), (101), (200), (211) and (220) are denoted in fig 3 (b). Absence of the peaks corresponding to MgO in the XRD patterns could be explained presumably by the ultrathin nature of this coating material. Apparently, the very small layer thickness of MgO is not adequate enough to give rise to observable peaks in the XRD pattern.



Fig. 3. (a) SEM image of  $SnO_2/MgO$  composite film and (b) XRD pattern of  $SnO_2/MgO$  composite film where the peaks corresponding to the  $SnO_2$  are marked with filled circles.

The *J-V* characteristics obtained for the ZnS-treated CdS-sensitized solar cells by varying the thickness of mesoporous SnO<sub>2</sub>/MgO are depicted in fig. 4. Here, CdS was deposited at a bath temperature of 50 °C. Table 1 summarizes the corresponding photovoltaic parameters. In DSCs, thickness of the mesoporous semiconductor oxide film determines the amount of dye loading. Similarly, thickness of the mesoporous film is decisive for the semiconductor-sensitized solar cells (SSCs), as the degree of CdS growth and therefore the efficiency of SSCs depends on the former. On the other hand, increasing the thickness would adversely affect the electron transport through the mesoporous film, consequently increasing the recombination of photogenerated electrons. The diffusion length which is characteristic of the semiconductor, constrains the optimum thickness of the mesoporous layer. The optimum thickness of the mesoporous film with respect to a given sensitizer is therefore determined by compromising between the aforementioned factors. However, in SSCs, determination of the optimum thickness of the mesoporous film needs some additional facts to be taken into consideration.

The efficiency of these CdS-sensitized solar cells depends significantly on the thickness of the SnO<sub>2</sub>/MgO film. Accordingly, the highest efficiency of 0.96% is obtained for the cell

corresponding to a SnO<sub>2</sub>/MgO film thickness of 6  $\mu$ m. The current density and similarly the efficiency increases as the thickness of SnO<sub>2</sub>/MgO film increases from 4  $\mu$ m to 6  $\mu$ m and a significant decrease in the current density as well as in the efficiency is observed as the thickness increases beyond 6  $\mu$ m. The initial increase in the current density from 2.26 mA cm<sup>-2</sup> to 2.90 mA cm<sup>-2</sup> is ascribed to the increase in the effective area of CdS film. Decrease in the current density afterward could be due to blocking of pore mouths of the thick SnO<sub>2</sub>/MgO films as the CdS grows near the surface of the former, concomitantly hindering the further growth of CdS inside the pores at the inner regions of the film as well due to the increases. Moreover, *FF* decreases as the thickness of the SnO<sub>2</sub>/MgO film has not produced the expected result, yet has negatively impacted the performance of the SSCs. The optimum thickness of the SnO<sub>2</sub>/MgO measoporous film which corresponds to the best photovoltaic performance is thus predominantly determined by the process of CdS deposition.

Thickness/ μm	Jsc /mA cm <sup>-2</sup>	Voc /V	FF	η(%)
4	2.26	0.514	0.696	0.81
6	2.90	0.529	0.628	0.96
9	2.80	0.521	0.602	0.87
13	1.84	0.517	0.619	0.59
15	1.36	0.489	0.592	0.40

Table 1. Photovoltaic parameters of the SnO<sub>2</sub>/MgO/CdS/ZnS-based SSCs corresponding to different thicknesses of the SnO<sub>2</sub>/MgO film



Fig. 4. J-V characteristics of  $SnO_2/MgO/CdS/ZnS$  solar cells corresponding to different thicknesses of the  $SnO_2/MgO$  mesoporous film.

### 3.2 Effect of Bath Temperature on CdS Deposition

The corresponding *J-V* characteristics of the ZnS-treated, SnO<sub>2</sub>/MgO-based CdSsensitized solar cells, which were fabricated at different CdS bath temperatures, are shown in fig. 5. Also, table 2 summarizes the photovoltaic parameters of these SSCs prepared at different CdS bath temperatures. The highest power conversion efficiency,  $\eta$ , of 1.33% is obtained for the SnO<sub>2</sub>/MgO/CdS/ZnS-based solar cell where CdS is deposited at a bath temperature of 40 °C. On the contrary, the lowest efficiency is obtained for the SSC corresponding to a CdS bath temperature of 80 °C. Therefore, in order to study the correlation between the efficiency of SSCs and the CdS bath temperature, SEM images of the CdS deposited at these two temperatures of 40 °C and 80 °C were obtained (fig. 5).



Fig. 5. J-V characteristics of  $SnO_2/MgO/CdS/ZnS$ -based SSCs fabricated at different CdS bath temperatures.

Table 2. Photovoltaic parameters of SnO<sub>2</sub>/MgO/CdS/ZnS-based SSCs fabricated at different bath temperatures

Bath to	emperature / °C	$J_{SC}/mA\;cm^{-2}$	$V_{OC}  / V$	FF	η(%)
	30	2.26	0.507	0.646	0.74
	40	3.60	0.523	0.706	1.33
	50	3.12	0.530	0.629	1.04
	60	2.12	0.517	0.687	0.75
	70	1.63	0.511	0.622	0.52
	80	1.18	0.473	0.606	0.34



Fig. 6. SEM images of the CdS nanostructures grown at (a) 40 °C and (b) 80 °C.

As evident from the SEM images (fig. 6(a)) interconnected CdS nanosheets have grown on the SnO<sub>2</sub>/MgO film. A homogeneous coverage of CdS nanosheets can be observed on the SnO<sub>2</sub>/MgO film where the CdS deposition was carried out at a bath temperature of 40 °C. However, CdS deposition at carried out at a bath temperature of 80 °C has resulted in two different structures: CdS nanosheets and large particles (fig. 6(b)). The different morphologies of CdS obtained in these two bath temperatures should undoubtedly be attributed to the CdS growth process dominant at each temperature. Also, in contrast to the glass or FTO substrates, the rough surface of the mesoporous SnO<sub>2</sub>/MgO film must have acted as a template for the growth of CdS nanosheets. As reported in the literature, chemical bath deposition (CBD) of CdS on bare FTO has

resulted in CdS thin films, whereas utilizing polymer templates has resulted in the growth of CdS nanoflowers [18-20].

From the mechanistic viewpoint, basically two processes namely ion-by ion and clusterby-cluster are responsible for the growth of CBD CdS on a substrate [18-20]. The corresponding reactions can be written as follows. Further, a schematic diagram explaining the ion-by-ion and cluster–by-cluster mechanisms is shown in fig. 7 [18, 19].

- (a) ion by ion process:  $Cd^{2+} + S^{2-} \rightarrow CdS$
- (b) cluster by cluster process :  $nCd^{2+} + 2n(OH)^{-} \rightarrow [Cd(OH)_2]n$  $[Cd(OH)_2]_n + nS^{2-} \rightarrow nCdS + 2nOH^{-}$

It has been reported that at temperatures above 60 °C, cluster-by-cluster mechanism is prominent in the growth process of CdS. Then at lower temperatures than that, ion-by-ion mechanism, the less thermally activated process, is favoured [21]. Moreover, latter is known to result in larger crystallite size of the CdS compared to the former. On the contrary, in this study, the SEM images reveal that the deposition of CdS carried out at 40 °C where ion-by-ion mechanism is prominent results in homogeneous coverage of CdS nanosheets while at 80 °C where cluster-by cluster mechanism is prominent, non-uniform coverage of comparatively larger aggregated particles and nanosheets is obtained.



Fig. 7. The CdS growth mechanisms (a) ion-by-ion and (b) cluster-by-cluster [14].

Then a satisfactory explanation for the efficiencies obtained the SSCs can be provided by considering the morphology of as deposited CdS. As the bath temperature decreases from 40 °C to 30 °C, not only  $J_{SC}$  but also  $V_{OC}$  and FF, and consequently the efficiency decrease. This could be attributed to the poor kinetics at lower bath temperatures below 40 °C, which might have resulted in non-uniform coverage of CdS. The highest  $J_{SC}$  of 3.60 mA cm<sup>-2</sup>, obtained for the SSC where CdS was deposited at 40 °C, confirms that this very temperature provides the optimum conditions for the uniform growth of CdS nanosheets on the SnO<sub>2</sub>/MgO mesoporous film. As the CdS bath temperature increases above 40 °C, the corresponding power conversion efficiency of the fabricated SSCs tends to decrease, mainly owing to the decrease in the  $J_{SC}$ . A significant decrease in  $J_{SC}$  from 3.60 mA cm<sup>-2</sup> to 1.18 mA cm<sup>-2</sup> is observed as the bath temperature increases from 40 °C to 80 °C. Moreover, as the bath temperature is increased to 60 °C decrease in the  $J_{SC}$  becomes more pronounced, resulting in quite low  $J_{SC}$ s in the temperature range of 60 °C – 80 °C, compared to that of 30 °C – 50 °C. This could be attributed to the two different mechanisms operative in the two different temperature ranges resulting in different morphologies of CdS. The low current densities observed for the SSCs where CdS deposition was carried out at higher bath temperatures

can be mainly due to two reasons; non-uniform coverage of CdS on the mesoporous  $SnO_2/MgO$  film and the formation of larger particles and aggregates of CdS that are too large to fill in the pores of the interconnected  $SnO_2/MgO$  layer. Consequently,  $V_{OC}$  and the power conversion efficiencies tend to decrease as the bath temperature increases.

#### 3.3 Structural Characterization of CdS-sensitized SnO<sub>2</sub>/MgO Films

#### 3.3.1 UV-Visible Spectroscopic Studies

The UV-visible absorption spectra of bare SnO<sub>2</sub>/MgO and SnO<sub>2</sub>/MgO/CdS electrodes, where CdS was deposited at 40 °C are shown in fig. 8. The absorption onsets of bare SnO<sub>2</sub>/MgO and SnO<sub>2</sub>/MgO/CdS electrodes are 353 nm 489 nm, respectively. The observed red shift in the absorption, for SnO<sub>2</sub>/MgO/CdS electrode compared to SnO<sub>2</sub>/MgO electrode, confirms the formation of CdS nanosheets on SnO<sub>2</sub>/MgO composite film. The optical bandgap of the CdS nanosheets grown on the SnO<sub>2</sub>/MgO is calculated using the Tauc plot [21]. The corresponding bandgap is calculated to be 2.4 eV, which is the same as for the bulk CdS. This implies that though the thicknesses of the CdS nanosheets are in order of nanometers the other dimensions being relatively large, could have given rise to this bandgap value. This is expected since in order to observe the quantum confinement effect, the dimensions of the prepared CdS nanosheets should be less than the Bhor radius, which is 8 nm for CdS [22, 23].



Fig. 8. UV-visible absorption spectra of SnO<sub>2</sub>/MgO and SnO<sub>2</sub>/MgO/CdS electrodes.

#### 3.3.2 XRD Analysis

The XRD pattern obtained for the CdS-sensitized  $SnO_2/MgO$  film, where CdS was deposited at 40 °C, is shown in fig. 9. The observed peaks at  $2\theta$  values of  $24.8^{\circ}$ ,  $26.5^{\circ}$ ,  $27.9^{\circ}$ ,  $43.7^{\circ}$ ,  $47.8^{\circ}$  and  $52.7^{\circ}$  can be indexed to (100), (002), (101), (110), (103) and (104) of crystallographic planes of hexagonal CdS (JCPDS card no.: 75-1545). The predominant peak observed at  $26.5^{\circ}$  can be attributed to the preferential orientation of CdS nanosheets.



Fig. 9. XRD pattern of CdS nanosheets grown  $SnO_2/MgO$  film. Peaks corresponding to CdS and  $SnO_2$  are denoted by  $\blacktriangle$  and  $\bullet$  respectively

### 3.4 Effect of ZnS Passivation Layer

Apparently, the only difference between DSCs and SSCs is that the dye is being replaced by a semiconductor. However, inherent recombination processes of sensitizing semiconductor, regardless of their morphology, impart a fundamental difference between them and the dyes. While the carefully designed chemical structures of the dyes in DSCs serve to minimize the recombination of photogenerated electrons, these semiconductor sensitizers act as recombination centers themselves. Therefore, a ZnS passivation layer has been widely employed to significantly enhance the performance of quantum dot-sensitized solar cells (QDSCs) [11,12,24,25]. In this

regard one should distinguish between the different recombination pathways in SSCs in order to understand the role of ZnS in suppressing the recombination losses.

Basically, as the electron/hole pairs are generated in the sensitizing semiconductor (SS) upon illumination, beside the electron injection to the hosting semiconductor, trapping and quenching of electrons by radiative and non-radiative recombination also take place [11,12]. Moreover, the photo-generated electrons in the SS can be captured by the accepter species in the electrolyte [11, 12]. These electrons injected into the CB of the host semiconductor can then recombine with the holes or the accepting surface states in SS. These trapped electrons in the surface states in SS are consequently quenched by internal recombination or with the acceptor species in the electrolyte. These trap state-mediated recombination pathways can be effectively hindered by utilizing the ZnS passivation layer [12]. It has been proven that as ZnS passivates the surface states of SS, electron trapping and consequently the internal non-radiative recombination as well as recombination with the electrolyte are appreciably being suppressed [12]. Furthermore, this ZnS layer can act as not only a physical barrier but also a potential barrier owing to the large bandgap of ZnS. Hence, the aforementioned recombination pathway of direct electron transfer from the SS to the electrolyte can also be hindered.

In order to study the effect of ZnS coating on the enhancement of the power conversion efficiency of SSCs, *J-V* characteristics were obtained for the SSCs with and without the ZnS coating, where CdS was deposited at 40 °C (fig. 10). A significant improvement in the power conversion efficiency from 0.51% to 1.33% is observed for the ZnS-treated solar cell. A detailed comparison of photovoltaic parameters of these samples is given in table 3. The ZnS treatment results in a conspicuous increase in the *J<sub>SC</sub>*, *V<sub>OC</sub>* and FF of the respective solar cell. This striking enhancement is undoubtedly ascribed to the passivation of the surface states of CdS nanosheets by ZnS and ZnS acting as a potential barrier to block the electron leakage from CdS nanosheets to the electrolyte. Either way, recombination of photogenerated electrons is substantially reduced, the electron injection from CdS nanosheets to SnO<sub>2</sub> increases. Therefore, upon ZnS treatment current density has increased from 2.20 mA cm<sup>-2</sup> to 3.60 mA cm<sup>-2</sup>. As a result, density of conduction band electrons in SnO<sub>2</sub> increases and the quasi-Fermi level shifts to higher energies thereby giving rise to higher *V<sub>OC</sub>s*. With the introduction of ZnS coating, *V<sub>OC</sub>* increases from 0.501 V to 0.523 V. Also,

it is noteworthy that the ZnS layer acts as a protective shell for the CdS nanosheets to improve stability of the latter in the presence of corrosive  $I^{-}/I_{3}^{-}$  redox couple.



Fig. 10. *J-V* Characteristics of ZnS-treated and untreated SnO<sub>2</sub>/MgO/CdS-based SSCs where, CdS nanosheets were grown at 40 °C.

Table 3. Photovoltaic parameters of ZnS-treated and untreated SnO<sub>2</sub>/MgO/CdS-based SSCs where CdS nanosheets were grown at 40 °C.

Electrode	Jsc/mA/cm <sup>-2</sup>	Voc/V	FF	η(%)
SnO <sub>2</sub> /MgO/CdS	2.20	0.501	0.464	0.51
SnO <sub>2</sub> /MgO/CdS/ZnS	3.60	0.523	0.706	1.33

### 3.5 Impedance Spectroscopic Analysis of ZnS-treated and Untreated SnO<sub>2</sub>/MgO/CdSbased SSCs

Compared to DSCs, several additional recombination pathways are present in SSCs under normal operational conditions [11]. However, in the dark under forward bias conditions, some recombination pathways diminish, since no electron/hole pairs are generated in the absorbing material i.e. CdS nanosheets. Thus, the recombination mechanisms simplify to that dictated in fig. 11 (a). Therefore, impedance spectroscopic measurements can be now utilized to reveal how effective the ZnS layer is in suppressing these two trap-mediated recombination pathways,  $r_1$  and  $r_2$ . However, as a number of interfaces are present in the SSCs, in practice, it is difficult to precisely

differentiate between chemical capacitance of different elements and electron recombination reactions taking place at each interface. Hence, a simplified model (fig. 11 (b)) was used to determine the charge transfer resistances at interfaces and the chemical capacitance  $(C_{\mu})$ , considering the SnO<sub>2</sub>/MgO/CdS/ZnS as a single entity, where  $R_t$ ,  $R_r$  and  $Z_d$  are the charge transport resistances, charge transfer resistance at the interfaces, and the diffusion impedance of the electrolyte, respectively. The impedance spectra obtained for the SSCs based on ZnS-treated and non-treated  $SnO_2/MgO/CdS$  electrodes, under a bias voltage of -0.550 V, are depicted in fig. 12. The calculated  $R_r$  and  $C_{\mu}$  for each SSC are summarized in table 4. A recombination resistance,  $R_r$ , of 3.69 k $\Omega$  is obtained for the SSC based on SnO<sub>2</sub>/MgO/CdS electrode. On the other hand, in the presence of the ZnS passivation layer,  $R_r$  increases to 9.96 k $\Omega$ . Therefore, it is clearly evident that, when ZnS is coated around the CdS nanosheets, it effectively reduces the density of surface states in the latter thus suppressing the recombination losses. Though the ultra-thin MgO layer-coated around SnO<sub>2</sub> might have had suppressed the recombination denoted by  $r_1$  in fig. 11(a), the relatively higher  $R_r$  values obtained in the presence of ZnS layer prove that the major contribution to the recombination losses comes from the second pathway  $(r_2)$ . Interestingly, the significant decrease observed in  $C_{\mu}$  as the ZnS layer is introduced can be ascribed to the passivation of surface states by the latter.



Fig. 11. (a) Recombination pathways present in SnO<sub>2</sub>/MgO/CdS/ZnS-based SSCs in the dark under forward bias conditions, where  $r_1$  and  $r_2$  are recombinations occurring via CdS surface states and (b) The equivalent circuit used to fit IS data, where  $C_{\mu}$ ,  $R_t$ ,  $R_r$  and  $Z_d$  are the chemical

capacitance, charge transport resistance, charge transfer resistance at the interfaces, and the diffusion impedance of the electrolyte, respectively.



Fig 12. Impedance spectra of SSCs based on bare and ZnS-treated  $SnO_2/MgO/CdS$  electrodes obtained in the dark under a bias voltage of -0.550 V

Table 4. Calculated  $R_r$  and  $C_{\mu}$  for SSCs based on SnO<sub>2</sub>/MgO/CdS and SnO<sub>2</sub>/MgO/CdS/ZnS electrodes

Electrode	$R_r / k\Omega$	$C_{\mu}  x 10^{-6} / F$
SnO <sub>2</sub> /MgO/CdS	3.69	757
SnO <sub>2</sub> /MgO/CdS/ZnS	9.96	89

### 4. Conclusion

The chemical bath deposition method (CBD) was used to successfully grow CdS nanosheets on the measoporous SnO<sub>2</sub>/MgO film. The optimum thickness of the SnO<sub>2</sub>/MgO film for CdSsensitized solar cells was found to be 6 µm and the optimum bath temperature was found to be 40 °C at which the ion-by-ion mechanism is responsible for the growth of CdS nanosheets. The red shift observed in the UV-Vis absorption spectrum confirmed the formation of CdS nanostructures on the SnO<sub>2</sub>/MgO film. Further, the XRD analysis confirmed that the as deposited CdS had the hexagonal crystal structure. A significant improvement in the power conversion efficiency of SSCs, from 0.51% to 1.33%, was obtained by introducing a ZnS capping layer over the CdS

nanosheets, where CdS was deposited at a bath temperature of 40 °C. The effect of the ZnS capping layer was further investigated by the impedance analysis. In this context, the  $R_r$  values of ZnS treated and untreated CdS were calculated to be 9.96 k $\Omega$ , 3.69 k $\Omega$  respectively.

#### Acknowledgement

This work was supported by the National Science Foundation of Sri Lanka (NSF/Fellow/2011/02).

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