Efficient CdS/CdSe/ZnS quantum dot sensitized solar cells prepared by ZnS treatment from methanol solvent

M Samadpour^{1*}

¹Department of Physics, K. N. Toosi University of Technology, PO Box 15418-49611, Tehran, Iran

*Corresponding authors: samadpour@kntu.ac.ir

Abstract

Here a systematic study is performed on the effect of ZnS treatment on quantum dot (QD) sensitized photoanodes from alcoholic precursors. We show that the efficiency of quantum dot sensitized solar cells (QDSCs) can simply improve by replacing convenient aqueous precursors with methanolic ones during ZnS deposition using the successive ionic layer adsorption and reaction (SILAR) method. The open circuit voltage of the cells was increased more than 60 mV and their efficiency was improved more than 70% by a simple ZnS treatment of the CdS/CdSe sensitized photoanodes. We explain that ZnS methanolic precursors, compared to aqueous ones, can diffuse deeper into the mesoporous CdS/CdSe sensitized TiO₂ anode. The efficiency of CdS/CdSe sensitized cells was increased from 2.43% ($V_{oc}=544$ mV, $J_{sc}=10.5$ mA/cm², FF=0.42) to 4.23% ($V_{oc}=612$ mV, $J_{sc}=13.3$ mA/cm², FF=0.52) by a simple ZnS treatment. A comprehensive study is carried out on the effect of the ZnS treatment on QDSCs performance by diffuse reflectance spectroscopy (DRS), impedance spectroscopy (IS), and applied bias voltage decay (ABVD) methods. Our results confirm that enhancing the recombination resistance is clearly one of the most important roles of the ZnS treatment. We show that, in spite of the enhanced open circuit voltage, the TiO₂ conduction band is not shifted by the ZnS treatment.

The results also demonstrate that ZnS deposition from low surface tension solutions can be systematically applied to enhance the performance of QDSCs.

Key words: solar cell, quantum dot, ZnS, SILAR, efficiency, EIS

1. INTRODUCTION

Recently, third generation photovoltaics have received tremendous attention among researchers, as they achieve efficiencies greater than the Shockley-Queisser limit [1]. A review of the literature indicates that one of the most promising contributions to this breakthrough is to make QDSCs with high efficiency and economically reasonable prices.

In QDSCs, incident light is absorbed by semiconductor QDs, injecting the photogenerated electrons into a mesoporous wide band gap semiconductor layer (i.e. TiO₂), which subsequently transports the photogenerated electrons through the external load [2, 3]. The oxidized QD is then restored by a redox electrolyte that acts as a hole transporting media. In QDSCs, the

optoelectronic properties of semiconductor materials can be tailored by controlling their size and shape, due to the quantum size effects [4-8]. Semiconductor QDs represent unique properties such as large extinction coefficient, intrinsic dipole moments, suitable photostability, and generation of multiple excitons by a single photon illumination [9-12].

During the last decade, QDSCs efficiency has been noticeably improved; however, the typical energy conversion efficiencies of QDSCs are still lower than those of silicon or thin film solar cells. This reveals the need for greater modification on current structures to achieve higher performance. In the past few years, various promising approaches have been introduced for efficiency enhancement in QDSCs. These approaches include making nanocomposite structures of the photoanode [13, 14] or doping the photoanode [15, 16]; new routes for sensitizing the photoanode by QDs like cosensitizing or sensitizing by core/shell structures [17-18]; introducing new counter electrodes [19, 20]; optimizing the electrolyte composition and modifying the photoanode by post treatments like TiCl_4 [21], O_2 plasma [22], mercaptopropionic acid [23] and fluorine treatment [24], annealing the photoanode in air/Ar atmosphere [25], and deposition ZnS on QD sensitizers [26-28]. Among these modification methods, ZnS treatment is the most popular one which has been generally used in all QDSCs after pioneering report of Yang et al. [26] and its modification by Toyoda et al. in 2008 [27]. Reviewing the literature also indicates that considerable enhancement in QDSCs efficiency is constantly obtained by the ZnS treatment. Recently, Guijarro et al. studied the effect of the ZnS treatment on the performance of QDSCs [28]. They showed that the ZnS treatment not only enhance the rate of electron transfer in the photoanode, but also decreases the electron recombination from photoanode with the redox electrolyte. Currently, the ZnS treatment is conventionally carried out by SILAR deposition of Zn^{2+} and S^{2-} precursors from aqueous solutions over QD (CdS, PbS, CdSe, etc.) sensitized TiO_2 electrodes [27-34].

Here, we show that solvents like methanol with a low surface tension have better permeability into mesoporous TiO_2 structures than typically used aqueous solutions. Consequently more efficient ZnS deposition takes place for methanolic precursors.. Here, ZnS was deposited on CdS/CdSe sensitized photoanodes from both aqueous and methanolic solvents by the SILAR method. We have observed that the ZnS treatment from methanolic solvents, compared to convenient aqueous solutions, leads to the greater efficiency enhancement in QDSCs. The cells prepared without and with different ZnS treatments were systematically analyzed in order to investigate the origin of the beneficial effect of the ZnS treatment. We clearly verify in this study that one of the main effects of ZnS coating is to increase the electron recombination resistance at the photoanode/electrolyte interface. We show that the lower surface tension of methanol solvent than that of aqueous one leads to the more effective diffusion of Zn^{+2} precursors into the mesoporous structure of the photoanode. Therefore, more effective ZnS deposition takes place on the CdS/CdSe sensitized photoanodes. This consequently decreases

the electron recombination and dark current in the cells. As a result, 4.23% efficiency ($V_{oc}=612$ mV, $J_{sc}=13.3$ mA/cm², FF=0.52) is obtained by our modified ZnS treatment which is near 75% improvement in comparison to the cells with no treatment.

2. EXPERIMENTAL METHODS

2.1. Electrode preparation

The photoanodes have a double-layer of TiO₂ made by a transparent and an opaque thin film of TiO₂ paste with nanoparticles of different sizes. TiO₂ layers are deposited on the fluorine doped tin oxide (FTO) glass substrates by the doctor blade method. Transparent layers are prepared via a TiO₂ paste with 20 nm nanoparticles (18NR-AO, Dyesol). The opaque layer is formed by 20-400 nm TiO₂ particles (WER4-O Dyesol) and has superior light scattering properties than the transparent layer. In order to improve the electrical properties, photoelectrodes were sintered at 450 °C for 30 min before being sensitized by QDs.

2.2. Electrode sensitization

CdS and CdSe semiconductors were grown in situ on TiO₂ nanostructured electrode using SILAR and CBD methods, respectively. The SILAR method is performed following the recently described method [29]. Briefly, for the deposition of CdS, Cd²⁺ ions are deposited from a methanolic 0.05 M solution of Cd(NO₃)₂ × 4H₂O. Here a 0.05 M solution of Na₂S × 9 H₂O in methanol/water (50/50 V/V) is selected as a S²⁻ source. A single SILAR cycle for CdS deposition is consisted of 1 minute dip-coating of the TiO₂ electrode into the Cd²⁺ precursor and subsequently into the S²⁻ solution, during 1 min too. After each precursor bath, the photoanode is rinsed by the corresponding solvent to remove the chemical residuals from the surface and then dried with a N₂ gun. For CBD deposition, Na₂SeSO₃ solution was prepared by refluxing Se and Na₂SO₃ in Milli-Q water at 70 °C for 4 hours while N₂ was purging. A chemical bath solution was prepared by mixing 80 mM of CdSO₄ solution and 80 mM of Na₂SeSO₃ solution with 120 mM of nitriloacetic acid. The CdS sensitized TiO₂ electrodes were immersed in the chemical bath solution at 10 °C for 12 h and then washed with Milli-Q water and dried by a N₂ gun [30].

2.3. ZnS treatment

In this study two different kinds of ZnS treatment were performed on CdS/CdSe sensitized electrodes. In the first convenient method, CdS/CdSe sensitized electrodes were alternately dipped into 0.1M Zn(CH₃COO)₂ and 0.1M Na₂S aqueous solutions for 1 min/dip, being rinsed with Milli-Q ultrapure water between dips [27-34]. In this method two-six SILAR cycles were used for ZnS deposition. In the second method, 0.1M Zn(CH₃COO)₂ and 0.1M Na₂S were prepared in methanol solution and methanol/water (75/25 V/V), respectively. In this method,

CdS/CdSe sensitized electrodes were alternately dipped into 0.1M $\text{Zn}(\text{CH}_3\text{COO})_2$ and 0.1M Na_2S methanolic solutions for 1 min/dip, while being rinsed with methanol between dips. Here also various SILAR cycles were used for ZnS deposition.

2.4. QDSC preparation

The cells were prepared by clamping the sensitized photoanode and Cu_2S counter electrode by means of a scotch spacer (thickness 50 μm) and filling with a droplet of polysulfide electrolyte. The polysulfide electrolyte contained 1 M Na_2S , 1 M S, and 0.1 M NaOH solution in Milli-Q ultrapure water. The Cu_2S counter electrodes were prepared by dipping brass in HCl solution at 70°C for 5 min and then dipping it into polysulfide solution for 5 min, resulting in a porous Cu_2S electrode. The area of the cells was 0.3 cm^2 .

2.5. Solar Cell Characterization

J-V curves were measured at AM1.5 G, where the light intensity was adjusted to one sun intensity (100 mW/cm^2). Impedance spectroscopy (IS) and applied bias voltage decay (ABVD) measurements [35] were carried out with a FRA equipped PGSTAT302N from Autolab Company. For IS, a 20 mV AC signal was scanned in a frequency range between 400 KHz and 0.1 Hz, while different forward biases were applied to the cells at the dark condition. Morphology and chemical composition of photoanodes were investigated by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM).

3. RESULTS AND DISCUSSION

Here two types of TiO_2 paste were deposited on the substrates as explained in the experimental section. The first was deposited as a transparent layer and the second as a scattering layer. SEM micrograph from the transparent TiO_2 layer on the FTO substrate is presented in Figure 1a.

Figure 1

Transparent TiO_2 films were sensitized by CdS/CdSe QDs, and then scratched from the FTO substrate and investigated by TEM (Figure 1b). According to Figures 1a and 1b, TiO_2 nanoparticles have sizes in the range 10-30 nm in the transparent layer which leads to enough surface area for the deposition of CdS/CdSe light harvesting QDs. Figure 2a indicates the SEM micrograph from the scattering layer.

Figure 2

This layer was sensitized by CdS/CdSe QDs and then scratched from the FTO substrate to be investigated by TEM. According to Figures 2a, b it is observed that the second layer consists of TiO_2 nanoparticles with 20-450 nm particle size distributions. This size distribution not only prepares enough surface area for the deposition of QD sensitizers, but also enhances the light

scattering and consequently light harvesting in the cells. The detailed structure of CdS/CdSe sensitized TiO_2 structures was investigated by a higher magnification TEM image (Figure 3). According to this figure, the CdS nanostructures deposited by the SILAR method have a clear spherical morphology while CdSe nanostructures are deposited as a continuous thin layer and nocore-shell structures are observed here. As explained before, CdSe nanostructures were deposited by CBD method and this could explain their different morphology compared to CdS nanostructures.

Figure 3

The structure scheme of the cells is represented in Figure 4. As can be seen in Figure 4, photoanodes are sensitized with CdS/CdSe QDs and ZnS is deposited on the QDs. Moreover various QDSCs have been prepared to determine the effect of different ZnS treatments. Here ZnS was deposited on CdS/CdSe sensitized cells from a methanolic Zn^{+2} precursor with 2, 3 and 4 SILAR cycles.

In addition, ZnS was deposited on CdS/CdSe sensitized cells using conventional method (from aqueous precursors) for the purpose of comparison [27-34]: ZnS was deposited by 2 SILAR cycles from an aqueous Zn^{+2} precursor. Current-voltage properties of CdS/CdSe sensitized cells with various ZnS treatments: deposition from aqueous and methanolic precursor is presented in Figure 5.

Figure 4

Figure 5

In order to have more accurate comparison of photovoltaic parameters of QDSCs, solar cell parameters containing open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and conversion efficiency are shown in Table 1.

Table 1: Photovoltaic parameters of the QDSCs prepared and analyzed: photocurrent j_{sc} , open circuit voltage V_{oc} , fill factor FF , and efficiency, as a function of the type of the Zn^{+2} and S^{-2} precursor for ZnS deposition tested under standard conditions (100 mW/cm² AM 1.5G).

Type of the Zn^{+2} and S^{-2} precursor	SILAR cycles	V_{oc} (mv)	J_{sc} (mA/cm ²)	FF(%)	Efficiency
Without treatment	0	544	10.5	42	2.39
aqueous	2	555	12.2	46	3.11
methanolic	2	556	12.5	51	3.54
methanolic	3	560	13.0	51	3.71

methanolic	4	603	13.6	52	4.26
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According to Table 1, a general beneficial effect is observed after ZnS treatments, in any case that we deposit ZnS from aqueous or methanolic precursors. The results indicate that ZnS deposition from aqueous precursor has enhanced open circuit voltage, current density and fill factor. Consequently these enhancements leads to efficiency improvement (3.11 %) in comparison to the cells prepared without any treatment (2.39 %). According to this table, substituting aqueous precursor with methanolic one and using same SILAR cycles for ZnS deposition have enhanced the efficiency to 3.54 % in comparison to 3.11 %. This result indicates the superior properties of methanolic precursor, as compared to aqueous precursor. Regarding the enhanced efficiency of the cells after ZnS deposition from methanolic precursors, more SILAR cycles were performed in order to optimize the efficiency. Here the number of SILAR cycles was increased from 2 to 4.

We also deposited ZnS with 5 SILAR cycles. The efficiencies of cells with 5 SILAR cycles were enhanced to 4.57% (V_{oc} =623 mV, J_{sc} =14.4 mA/cm², FF=0.51), but their performance was not stable. Here the efficiency of the cells decreased to less than their initial value (3.46 %) after about 30 min and thus, they were excluded.

We also attempted to increase SILAR cycles even more; however, it led to partial detachment of the deposited layers from the sample.

Comparison between the efficiencies of the cells with 2 (3.54%), 3 (3.71%) and 4 (4.26%) SILAR cycles of ZnS deposition, represented the superior properties of the methanolic precursor and enhancement of the performance by increasing the number of SILAR cycles. Here the open circuit voltage is boosted from 544 mV to 603 mV and the efficiency is improved from 2.39 % to 4.26 % mV by simple deposition of ZnS from alcoholic precursor (Table 1). This result indicates the crucial role of the precursor type in the performance of QDSCs.

It is noticeable that normally high open circuit voltages are expected after the ZnS treatment. However, the typical open circuit values in QDSCs (generally less than 600 mV) are lower than those in dye sensitized solar cells (normally more than 750 mV). This is mainly related to the large interface area that exists between QD sensitizers while we have only a monolayer of dye molecules in dye sensitized solar cells (DSCs) [36, 37]. Charge transport through QD sensitizers enhances the recombination in comparison with DSCs. In addition, some part of recombination is originated from the surface trap density of states, which in this case the ZnS treatment could decrease the recombination noticeably. Literature review indicates that the record V_{oc} values are obtained by modifying the structure of TiO₂ photoanode and not only by the ZnS treatment which indicates that more effective parameters like TiO₂ structure should be optimized in order to have even more efficiencies [38]. Here we have also more open circuit voltages in the cells

with the ZnS treatment, and in spite of moderate enhancement in the V_{oc} values, an expected increasing behavior from 555 mV up to 603 mV is obtained (Table 1). It is important to note that here various optimizations are performed on $TiO_2/CdS/CdSe$ photoanodes (before the ZnS treatment) regarding our previous researches [24, 30]. Consequently the performance of the cells is considerable even before the ZnS treatment. Besides enhancing the recombination resistance, one of the main effects of the ZnS treatment is enhancing the charge transfer efficiency in the cells. This enhancement is originated from suitable electronic band structure of ZnS relative to the TiO_2 conduction band (CB) which pronounces charge injection from QDs into the TiO_2 , resulting in more current densities to be obtained [36, 37](Table 1). According to Table 1, the current densities are increased from 10.5 mAcm^{-2} to 13.6 mAcm^{-2} after the ZnS treatment.

According to Table 1, the fill factor of the cells without the ZnS treatment is 0.42 which is almost near the typical values for optimized QDSCs [24, 30]. It is also important to note that, the fill factor of the cells without the ZnS treatment (0.42) is improved after the ZnS treatment from aqueous (0.46) and methanolic (0.51) solvents according to the results in Table 1. This improvement indicates that the ZnS treatment could improve the charge transport properties of the photoanode and consequently, enhance the fill factor.

According to Table 1, the fill factors of the cells with 2, 3 and 4 SILAR cycles of the ZnS treatment from methanolic solvent are very similar (0.51-0.52). This behavior indicates that increasing the number of ZnS deposited layers to more than two cycles has no beneficial effect on the fill factor. This result indicates that the photoanode performance is not the only parameter that affects the fill factor. Reviewing the literature indicates that restricted charge transfer at the CE/Electrolyte interface is the main parameter that affects the fill factor. Restricted charge transfer at the CE/Electrolyte interface accumulates space charges and therefore, creates s-shaped deformations in the current voltage characteristics of the cells [39, 40]. As a result, performance of the cells decreases by diminishing the fill factor considerably. This results show that, higher number of fill factors and consequently, better efficiencies could be obtained by modifying counter electrodes as we also explained before [20].

We also examined J-V characteristics of the cells for 3, 4, 5 and 6 cycles of ZnS deposition from the aqueous solvent in order to compare the results with the cells prepared by the same SILAR cycles of ZnS deposition from the methanolic solvents (Figure 6).

Figure 6

Table 2 indicates the photovoltaic properties of the cells which are prepared by 2-6 cycles of ZnS deposition from the aqueous solvent.

Table 2: Photovoltaic parameters of the QDSCs prepared and analyzed: j_{sc} , V_{oc} , FF , and $Efficiency$, as a function of the number of SILAR cycles that is utilized for ZnS deposition from aqueous solvent, tested under standard conditions (100 mW/cm² AM 1.5G).

Precursor type	SILAR cycles	V_{oc} (mv)	J_{sc} (mA/cm ²)	FF(%)	Efficiency
Aqueous	3	547	11.9	47	3.05
Aqueous	4	498	9.23	45	2.06
Aqueous	5	391	8.86	46	1.59
Aqueous	6	375	8.13	43	1.31

According to the results in Table 2, efficiency and especially, open circuit voltage has been reduced by increasing the amount of ZnS deposition. Here it seems that by increasing the number of SILAR cycles and due to insufficient permeability of the aqueous precursors through the photoanode structure, ZnS deposition occurs on the exterior surface of the photoanode which can disturb the effective electrolyte diffusion within the mesoporous structure of the photoanode. Consequently, electron recombination is enhanced which potentially could reduce the open circuit voltage and efficiency (Table 2). It is important to note that, unlike the ZnS treatment from the methanolic precursors by more than 5 SILAR cycles (explained before), no detachment of the ZnS layer was observed by increasing the number of SILAR cycles in the case of aqueous precursor. This may be related to the better solubility of Zn (CH₃COO)₂ and especially, Na₂S × 9 H₂O in the aqueous solvents in comparison to methanolic ones.

To analyze the effect of ZnS precursors on the cells performance, systematic characterizations were carried out on QDSCs with and without the ZnS treatment so that the origin of the observed improvement could be recognized.

Figure 7 indicates the diffuse reflectance of the bare TiO₂, and TiO₂/CdS/CdSe/ZnS (from the aqueous solution) and TiO₂/CdS/CdSe/ZnS (from the methanolic solution).

Figure 7

Here a blue shift in the diffuse reflectance is observed in the bare TiO₂ as compared to the TiO₂/CdS/CdSe/ZnS (from the aqueous or methanolic solution) which is originated by the visible light absorption by CdS and CdSe QDs. Also the diffuse reflectance properties of TiO₂/CdS/CdSe/ZnS structures are very similar for the ZnS treatment from aqueous or methanolic precursors (Figure 7). This result indicates that, the superior properties of the ZnS treatment from methanolic precursors are not originated from the improvement in the light scattering properties.

Moreover, IS and ABVD measurements were carried out on QDSCs. Figure 8a indicates the Nyquist diagram of the cells without the ZnS treatment, and also with the ZnS treatment from aqueous and methanolic precursors at 0.36 volt bias voltage under dark condition. Also the fitting results obtained by Zview software are plotted in Figure 8a. Experimental results were

fitted by the model, as explained before [34, 41], and are presented in Figure 8b. Here R_s , R_{tr} , R_{re} , $R_{cathode}$, C_μ and $C_{cathode}$ are the series resistance, electron transport resistance in the photoanode, electron recombination resistance at the photoanode/electrolyte interface, charge transfer resistance at the cathode/electrolyte interface, chemical capacitance of the photoanode and the cathode chemical capacitance, respectively.

Figure 8

According to Figure 8a, the diameter of the second arc (corresponding to the recombination resistance at the photoanode/electrolyte interface (R_{re})) has the maximum value for the ZnS treatment from methanolic precursors. Such diagrams were obtained in various applied biases (0, 0.06, 0.12, 0.18, 0.24, 0.30, 0.36, 0.42, 0.48 and 0.54 volt) for the cells made by no ZnS treatment and different ZnS treatments from aqueous or methanolic precursors (all diagrams are not shown here but the fitting result is presented in the following). The chemical capacitance, C_μ , and recombination resistance, R_{rec} , of the cells were obtained by the model explained in Figure 8b and are presented in Figures 9a and 9b, respectively.

Figure 9

C_μ is plotted against the voltage in the sensitized electrode, V_F , eliminating the voltage drop of series resistance, V_{series} , (contacts, counter electrode, electrolyte diffusion) by $V_F = V_{app} - V_{series}$. Here V_{app} is the applied direct potential to the cell in the IS measurements. Furthermore, R_{rec} is plotted (Figure 9a) vs the voltage drop in a common equivalent conduction band (CB), V_{ecb} , where the effect of different TiO_2 CBs between samples is removed [34, 40, 41]. The chemical capacitance in Figure 9a displays an exponential behavior with V_F , which indicates that trap states have an exponential distribution near the conduction band edge [40, 41]. According to Figure 9a, all the samples show very similar slopes for C_μ , specifying a similar density of states [40]. However, C_μ is not shifted, indicating that ZnS deposition does not affect the relative position of the TiO_2 CB. As is clear from Figure 9a, the chemical capacitances of the samples made by the ZnS treatment from aqueous and methanolic precursors overlapped and are not shifted relative to each other. This overlap confirms that the TiO_2 conduction band position is not affected by the ZnS treatment from aqueous or methanolic solvents. Consequently, the enhanced open circuit voltage after ZnS deposition could not be originated from the upwards displacement of the TiO_2 CB. On the other hand, the open circuit voltages of the cells prepared from methanolic precursors are enhanced in comparison to the cells made by the ZnS treatment from aqueous precursors (Table 1). Open circuit voltage (V_{oc}) is the difference between the TiO_2 Fermi level energy and the energy level of the redox electrolyte ($V_{oc} = V_f - E_{redox}$). Here electrolyte is fixed for all the samples and consequently, E_{redox} is same for all the samples. Regarding the higher V_{oc} in the cells with methanolic precursors than in those with the aqueous precursors (Table 1), the TiO_2 Fermi level would have an upward shift when we change the solvent from aqueous to methanolic. Figure 9b indicates that the ZnS treated samples have a

higher recombination resistance (lower recombination) than the untreated samples. Consequently, greater open circuit photovoltage are obtained for ZnS treated cells in comparison to untreated ones (see Table 1). This finding points out the role of recombination on the QDSC performance. These results indicate that a similar mechanism is used for efficiency enhancement regardless of ZnS deposition from methanolic or aqueous precursors. However, higher recombination resistance is observed by the IS measurements while using methanolic based deposition of ZnS (Figure 9b) which will be discussed in the following.

The lower recombination observed by the IS measurements in ZnS deposited cells was confirmed by comparing the electron lifetime, τ_n , of the ZnS treated and untreated samples (Figure 10a).

Figure 10

Moreover τ_n was measured by ABVD method under dark conditions as the IS measurements. Regarding the ZnS treated cells, higher lifetimes are obtained, as expected from the higher recombination resistance previously mentioned. Figure 10b indicates the current voltage characteristic of the cells in the dark condition. According to this figure lower dark currents are obtained for the cells with ZnS treatment which are in good agreement with the enhanced recombination resistance (Figure 9b) and the greater electron life time (Figure 10a) in these cells. In order to understand the reason for superior properties of methanolic precursors compared to aqueous ones, $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$ photoanodes were investigated by the EDX analysis. Here we investigated the chemical composition of the deposited layers at the surface and also 7 microns below the surface in order to measure the degree of precursors' diffusion into the mesoporous structure of the photoanode. To this end, the samples were cut from the middle and the cross section of the layers was investigated by the EDX analysis. Figure 11a indicates the cross section of the samples.

Figure 11

The EDX analysis was also carried out in the line scan mode from the two indicated dashed lines, as shown in Figure 11a, one of which is near the surface (line A) and the other is 7 microns deep into the sample (line B). Figure 11b shows the results of the typical line scan, which clearly indicate the Ti, O, Cd, S, Se and Zn elements in the sample. It should be noted that such an analysis was performed on all the cells, the results of which are indicated in Table 3.

Table 3: Atomic percent of Zn at the anode surface and at the 7 microns below the anode surface for various samples with aqueous and methanolic ZnS treatments.

Type of the Zn^{+2} and S^{-2} precursor	SILAR cycles	Zn at the anode surface (atomic %)	Zn at the 7 microns below the anode surface (atomic %)
aqueous	2	0.78	0.58
methanolic	2	0.91	0.74

methanolic	3	1.6	0.9
methanolic	4	2.99	1.52

From this table, it can be seen that the amount of Zn element has been reduced through moving deep into the sample for both aqueous and methanolic precursors. This indicates that we have gradient of ZnS concentration in the photoanodes. However, it is observed that the amount of Zn element is enhanced after replacing aqueous precursors with methanolic ones for the same SILAR cycles. It seems that lower surface tension of methanol solvents than that of aqueous solvents, has led to the more effective diffusion of Zn^{+2} precursors into the mesoporous structure of the photoanode. According to this table, samples with 4 SILAR cycles of ZnS deposition from methanolic precursors have the highest ZnS deposition on CdS/CdSe QDs which have led to their best performance. This result indicates that even greater efficiencies could be obtained by finding methods with capability of homogeneous deposition of ZnS QDs on the mesoporous TiO_2 /CdS/CdSe structures.

4. CONCLUSIONS

We showed in this study that ZnS treatment has a general beneficial effect on QDSCs efficiency with both aqueous and methanolic precursors. Efficiency enhancement after ZnS treatment is originated from the decrease of recombination at the photoanode /electrolyte interface. , as was observed by the IS and ABVD measurements. Moreover, we demonstrated that the lower surface tension of methanol solvents than that of aqueous solvents, leads to the more effective diffusion of Zn^{+2} precursors into the mesoporous structure of the samples. As a result, QDSCs with efficiencies as high as 4.24% have been prepared for CdS/CdSe sensitized cells, using the ZnS treatment from alcoholic precursors. This study leads to an important conclusion that even higher efficiencies could be obtained by precise adjustment of the deposition parameters in simple wet chemical deposition methods like SILAR or CBD.

Acknowledgements:

This work was financially supported by Iran National Science Foundations. We also acknowledge the support from Institute for Nanoscience and Nanotechnology of Sharif University of Technology (Tehran, Iran) for letting us to use their FRA equipped PGSTAT302N (from Autolab Company) instrument. Also we would like to thanks Ms. Parisa Parand for preparing SEM and TEM micrographs of the samples.

Figure and Table Captions:

Figure 1: SEM micrograph from the TiO_2 transparent layer (a), TEM image of the $\text{TiO}_2/\text{CdS}/\text{CdSe}$ QDs, scale bar is 200 nm in figure 1a and 100 nm in figure 1b.

Figure 2: SEM micrograph from the TiO_2 Scattering layer (a), TEM image of the $\text{TiO}_2/\text{CdS}/\text{CdSe}$ QDs in the scattering layer (two typical large nanoparticles are indicated by arrows in the inset of this figure), scale bar is 1 micron in figure 2a and 200 nm in figure 2b.

Figure 3: High magnification TEM image of the CdS/CdSe sensitized TiO_2 structures. CdS quantum dots are indicated by the dotted circular lines and CdSe nanostructures are indicated by dashed parallel lines. Scale bar is 5 nm.

Figure 4: Schematic structure of the cells, photoanode is sensitized by $\text{CdS}/\text{CdSe}/\text{ZnS}$ QDs

Figure 5: Current-voltage properties of CdS/CdSe sensitized cells with various aqueous (aq) and methanolic (Meth) ZnS treatments with different number “#” of SILAR cycles (#S).

Figure 6: Current-voltage properties of CdS/CdSe sensitized cells with aqueous (aq) ZnS treatment with different number “#” of SILAR cycles (#S).

Figure 7: Diffuse reflectance of the bare TiO_2 , $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$ (from the aqueous solution) and $\text{TiO}_2/\text{CdS}/\text{CdSe}/\text{ZnS}$ (from the methanolic solution). Here “aq” in the figure means aqueous solvent and “meth” means methanolic solvent.

Figure 8: a) Nyquist diagram and the fitting results of the cells without ZnS treatment, ZnS treatment from aqueous and methanolic precursors at 0.36 volt bias voltage under dark condition. Here “E” in the figure means the experimental data, “F” means the fitting results, “aq” means aqueous solvent, “meth” means methanolic solvent and the number (#) of SILAR cycles is indicated by “#S”. b) The equivalent circuit model that was used for fitting the experimental results [34, 41]. Here R_s , R_{tr} , R_{re} , $R_{cathode}$, C_μ and $C_{cathode}$ are the series resistance, electron transport resistance in the photoanode, electron recombination resistance at the photoanode/electrolyte interface, charge transfer resistance at the cathode/electrolyte interface, chemical capacitance of the photoanode and the cathode chemical capacitance respectively.

Figure 9: (a) Chemical capacitance, C_μ , is plotted against the voltage drop in the sensitized electrode. (b) Recombination resistance, R_{rec} , is plotted against the voltage drop in a common equivalent conduction band (CB), V_{ecb} . Here “aq” in the figure means aqueous solvent, “meth” means methanolic solvent and number (#) of SILAR cycles is indicated by “#S”.

Figure 10: a) electron lifetime, τ_n , of ZnS treated and untreated samples, τ_n has been measured by ABVD under dark conditions. b) Current voltage characteristic of the cells in the dark condition. Here “aq” in the figure means aqueous solvent, “meth” means methanolic solvent and number (#) of SILAR cycles is indicated by “#S”.

Figure 11: a) samples' cross section. EDX analysis is performed in the line scan mode from the two indicated dashed lines in the figure, one is near the surface and the other is 7 microns deep into to sample. b) typical line scan results which clearly indicate the Ti, O, Cd, S, Se and Zn chemical elements in the sample.

Table 1: Photovoltaic parameters of the QDSCs prepared and analyzed: photocurrent j_{sc} , open circuit voltage V_{oc} , fill factor FF , and efficiency, as a function of the type of the Zn^{+2} and S^{-2} precursor for ZnS deposition tested under standard conditions (100 mW/cm² AM 1.5G).

Table 2: Photovoltaic parameters of the QDSCs prepared and analyzed: j_{sc} , V_{oc} , FF , and *Efficiency*, as a function of the number of SILAR cycles that is utilized for ZnS deposition from aqueous solvent, tested under standard conditions (100 mW/cm² AM 1.5G).

Table 3: Atomic percent of Zn at the anode surface and at the 7 microns below the anode surface for various samples with aqueous and methanolic ZnS treatments.

References

- [1] Shockley W, Queisser H J 1961 *Journal of applied physics* **32(3)** 510-9
- [2] O'Regan B and Grätzel M 1991 *Nature* **353** 737-40
- [3] Mathew S, Yella A, Gao P, Humphry-Baker R, Curchod B F E, Ashari-Astani N, Tavernelli I, Rothlisberger U, Nazeeruddin M K and Gratzel M 2014 *Nat. Chem* **6** 242-7
- [4] Jun H K, Careem M A and Arof A K 2013 *Renewable and Sustainable Energy Reviews* **22** 148-67
- [5] Choi H, Nahm C, Kim J, Kim C, Kang S, Hwang T and Park B 2013 *Current Applied Physics* **13** S2-S13
- [6] Samadpour M, Ghane Z, Ghazyani N, Tajabadi F and Taghavinia N 2013 *Journal of Physics D: Applied Physics* **46** 485101
- [7] Samadpour M, Irajizad A and Molaei M 2014 *Chinese Physics B* **23 (4)** 047302
- [8] Rühle S, Shalom M and Zaban A 2010 *ChemPhysChem* **11** 2290-304
- [9] Yu W, Qu L H, Guo W Z and Peng X G 2003 *Chem. Mater* **15** 2854-60
- [10] Alivisatos A P *Science* 1996 **271** 933-7

- [11] Ellingson R J, Beard M C, Johnson J C, Yu P, Micic O I, Nozik A J, Shabaev A and Efros A L 2005 *Nano Lett* **5** 865–71
- [12] Schaller R D, Klimov V I 2004 *Phys. Rev. Lett* **92** 186601
- [13] Chen J, Li C, Zhao D W, Lei W, Zhang Y, Cole M T, Chu D P, Wang B P, Cui Y P, Sun X W and Milne W I 2010 *Electrochemistry Communications* **12(10)** 1432-5
- [14] Zhu G, Xu T, Lv T, Pan L, Zhao Q and Sun Z 2011 *Journal of Electroanalytical Chemistry* **650 (2)** 248-51
- [15] Samadpour M, Rezanejade-Bardajee G, Ghiasvand-Gheysare S and Shafagh P 2015 *Journal of Physics D: Applied Physics* **48(9)** 095101
- [16] Santra P K and Kamat P V 2012 *Journal of the American Chemical Society* **134(5)** 2508-11
- [17] Lee Y L and Lo Y S 2009 *Advanced Functional Materials* **19(4)** 604-9
- [18] Ning Z, Tian H, Yuan C, Fu Y, Qin H, Sun L and Agren H 2011 *Chemical Communications* **47(5)** 1536-8
- [19] Parand P, Samadpour M, Esfandiar A and Iraj-Zad A 2014 *ACS Photonics* **1** 323-30
- [20] Arabzade S, Samadpour M and Taghavinia N 2015 *RSC Advances* **5(57)** 45592-8
- [21] Kim J, Choi H, Nahm C, Kim C, Nam S, Kang S, Jung D R, Kim J I, Kang J and Park B 2012 *J. Power Sources* **220** 108-13
- [22] Leschkies K S, Divakar R, Basu J, Enache-Pommer E, Boercker J E, Carter C B, Kortshagen U R, Norris D J and Aydil E S 2007 *Nano Lett* **7(6)** 1793-8
- [23] Pan Z, Zhao K, Wang J, Zhang H, Feng Y and Zhong X 2013 *ACS nano* **7** 5215-22
- [24] Samadpour M, Boix P P, Giménez S, Iraj-Zad A, Taghavinia N, Mora-Seró I and Bisquert J 2011 *The Journal of Physical Chemistry C* **115** 14400-7
- [25] Chong L W, Chien H T and Lee Y L 2010 *Journal of Power Sources* **195(15)** 5109-13
- [26] Yang S M, Huang C H, Zhai J, Wang Z S and Jiang L 2002 *Journal of Materials Chemistry* **12(5)** 1459-64
- [27] Shen Q, Kobayashi J, Diguna L J and Toyoda T 2008 *Journal of Applied Physics* **103** 084304
- [28] Guijarro N, Campiña J M, Shen Q, Toyoda T, Lana-Villarreal T and Gómez R 2011 *Physical Chemistry Chemical Physics* **13(25)** 12024-32
- [29] Braga A, Gimenez S, Concina I, Vomiero A and Mora-Sero I 2011 *J. Phys. Chem. Lett* **2** 454–60
- [30] Samadpour M, Giménez S, Boix P P, Shen Q, Calvo M E, Taghavinia N, Iraj-Zad A, Toyoda T, Míguez H and Mora-Seró I 2012 *Electrochimica Acta* **75** 139-47
- [31] Lee Y L, Huang B M and Chien H T 2008 *Chemistry of Materials* **20(22)** 6903-5
- [32] Giménez S, Mora-Seró I, Macor L, Guijarro N, Lana-Villarreal T, Gómez R, Diguna L J, Shen Q, Toyoda T and Bisquert J 2009 *Nanotechnology* **20** 295204
- [33] Barea E M, Shalom M, Giménez S, Hod I, Mora-Seró I, Zaban A and Bisquert J 2010

Journal of the American Chemical Society **132(19)** 6834-9

- [34] González-Pedro V, Xu X, Mora-Seró I and Bisquert J 2010 *ACS Nano* **4** 5783-90
- [35] Bisquert J, F A, Greenshtein M and Mora-Sero I 2004 *J. Am. Chem. Soc* **126** 13550–9
- [36] Hodes G 2008 *The Journal of Physical Chemistry C* **112(46)** 17778-87
- [37] Hod I, González-Pedro V, Tachan Z, Fabregat-Santiago F, Mora-Seró I, Bisquert J and Zaban A 2011 *The Journal of Physical Chemistry Letters* 2011 **2(24)** 3032-5
- [38] Sudhagar P, Song T, Lee D H, Mora-Seró I, Bisquert J, Laudenslager M, Sigmund W M, Park W I, Paik U and Kang Y S 2011 *The Journal of Physical Chemistry Letters* **2(16)** 1984-90
- [39] Wagenpfahl A, Rauh D, Binder M, Deibel C and Dyakonov V 2010 *Phys. Rev. B* **82** 115306
- [40] Julian B, Brault V, Ahmad S, Breau L, Nazeeruddin M K, Marsan B, Zakeeruddin S M and Grätzel M 2012 *Energy & Environmental Science* **5** 6089-6097
- [41] Fabregat-Santiago F, Bisquert J, Garcia-Belmonte G, Boschloo G and Hagfeldt A 2005 *Sol. Energy Mater. Sol. Cells* **87** 117–31
- [42] Fabregat-Santiago F, Garcia-Belmonte G, Mora-Seró I and Bisquert J 2011 *Physical Chemistry Chemical Physics* **13** 9083-118

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

a)

Figure 8

Figure 9

Figure 10

Figure 11