The electrochemical property of the CdS/CdSe co-sensitized with TiO_2 electrodes

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ABSTRACT.

In this work, we have studied the electrochemical of the different electrodes through the Electrochemical impedance spectra (EIS). The experimental results indicated an increasing recombination in the photoanodes because more CdS QDs were loaded more on the TiO_2/CdS/CdSe/ZnS. The results indicate that the photogenerated electrons were captured by the defect states in the QDs. Therefore, the electron transfer was more diffusively hindered, which increased the charge recombination and back transport reaction.

Keyword*: passivation, solar cells, quantum dots.*

INTRODUCTION

Recently, the scientists in the world have interested in the quantum dots solar cells (QDSSCs) based on the TiO_2 subtrate. The QDSSCs based on the QDs have more advantages than the Dye sensitized solar cells (DSSCs) based on the molecules for some reasons: (1) the molecules only absorb the light in visible, (2) and are unstable in the air enviromental. Beside the disadvantages of the moleccules, the QDs has some advantages such as quantum confinement effect, the higher coefficients than the dyes, the generation of multiple electron – hole pairs by a single incident photon [1-2]. Moreover, the tunable adsorption band of the QDs can be perform by the changed their size for the light harvesters in QDSSCs [3].

For those reasons, the QDSSCs were promised to become the candidate for the high efficiency. Firstly, Vogel and colleagues prepared the QDSSCs based on CdS QDs and obtained the low efficiency [4]. In 2008, many scientists only studied the single QDs as CdS, CdSe, PbS… for the application in the QDSSCs. Therefore, the results obtained the low efficiency. For the next years, the series articles focus on the improving efficiency of the QDSSCs with the subject such as: to improve the adsorption of the photoanodes [5], [6]; to use the different methods such as chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR)... [7]; to apply the core – shell QDs to reduce the surface states in the QDs [8]. However, the efficiency of the QDSSCs was still lower than the efficiency of the DSSCs at the present due to the high surface states at the TiO_2/QDs contact and the large diffusion resistance in the TiO_2 film.

In this work, we have studied the electrochemical of the different electrodes through the Electrochemical impedance spectra (EIS). The experimental results indicated an increasing recombination in the photoanodes because more CdS QDs were loaded more on the TiO_2/CdS/CdSe/ZnS. The results indicate that the photogenerated electrons were captured by the defect states in the QDs. Therefore, the electron transfer was more diffusively hindered, which increased the charge recombination and back transport reaction.

EXPERIMENT

The films were coated with TiO_2 layers by silk-screen printing, and were then annealed at 500°C for 30 minutes. Their sizes ranged from 10 nm to 30 nm. The thickness of the TiO_2 films was approximately 4 µm, as measured by a stylus. Then, the films were dipped in 40 mmol $TiCl_4$ solution for 30 minutes at 70°C and sintered at 500°C for 30 minutes.

TiO_2/CdS/CdSe/ZnS films were synthesized using the SILAR and colloidal synthesis methods. First, the TiO_2 film was dipped in 0.5 M Cd^{2+}-ethanol solution for 1 minute and rinsed with ethanol. Then, the film was dipped for 1 minute in 0.5 M S^{2-}-methanol solution and rinsed with methanol after being dried in air (a SILAR cycle). The number of CdS QDs increased by repeating the assembly cycles with three cycles. Second, the TiO_2/CdS assembly was immersed in CdSe solution (size ~3 nm) for 20 hours before being dried at room temperature. For the ZnS passivation layers, TiO_2/CdS/CdSe photoanodes were dipped into 0.1 M Zn^{2+} and 0.1 M S^{2-}-solutions for 1 minute and rinsed with pure water between the two dips (a total of two cycles). Finally, the films were annealed in a vacuum environment at 300°C to prevent oxidation. The TiO_2/CdS/CdSe/ZnS thickness was measured using a stylus. The average thickness of CdS (3 cycles), CdSe (20 hours), and ZnS (2 cycles) were 351.9 nm, 80 nm and 257.8 nm respectively.

Fabrication of QDSSCs

The structure of the QDSSCs was designed using a Surlyn between the photoanodes and counter electrodes at 170°C. The electrolyte was filled from a hole made on the counter electrode. The active area of the QDSSCs was 0.38 cm^2. The polysulfide electrolyte consisted of 0.5 M Na_2S, 0.2 M S and 0.2 M KCl in Milli-Q ultrapure water/methanol (7:3 by volume).

Characterization

The morphologies of the samples were investigated using transmission electron microscopy (TEM). The crystal structure was analyzed using an X-ray diffractometer (Philips, PANalytical X'Pert, CuKα radiation). The absorption properties of the samples were investigated using a diffuse reflectance UV–vis spectrometer (JASCO V-670). Photocurrent – voltage measurements were performed on a Keithley 2400 source meter using a simulated AM 1.5 sunlight with an output power of 100 mW/cm^2 produced by a solar simulator (Solarena, Sweden).

RESULTS AND DISCUSSIONS

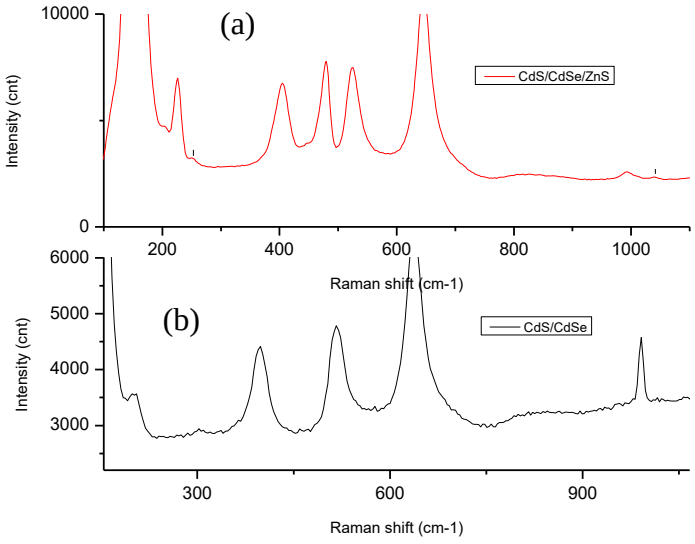

Figure 1. The Raman of the TiO_2/CdS/CdSe photoanode (a) with ZnS layers and (b) without ZnS coated.

To investigate the change of the tructural electrodes after annealing, the Raman analysis was performed. Figure 1 shows the raman of different photoanodes such as: without ZnS layers and with ZnS coated. The peaks at 145cm^{-1}, 395cm^{-1}, 518cm^{-1}, 639cm^{-1} is the oscillation modes correspond to the TiO_2 anatase and the oscillation modes 1LO (205 cm^{-1}), and 2LO (410cm^{-1}) the CdS, CdSe cubic. So, from results of the raman, we noted that the CdS, CdSe QDs loaded on the TiO_2 film.

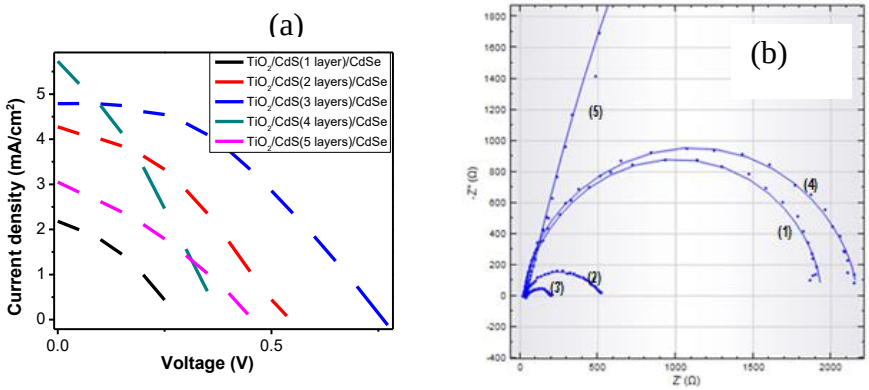

Figure 2. (a) The I-V curves and (b) the Electrochemical impedance spectra (EIS) of the QDSSCs

Table 1. The parameters photovoltaic of the QDSSCs

Cells	Thickness (µm)	J_{SC} (mA/cm^2)	V_{OC}(V)	Fill factor FF	Efficiency η(%)
TiO_2/CdS(1)/CdSe(3)/ZnS(2)	6.0	2.18	0.29	0.35	0.22
TiO_2/CdS(2)/CdSe(3)/ZnS(2)	6.4	4.28	0.54	0.37	0.86
TiO_2/CdS(3)/CdSe(3)/ZnS(2)	6.8	4.79	0.76	0.41	1.52
TiO_2/CdS(4)/CdSe(3)/ZnS(2)	7.2	5.73	0.39	0.31	0.68
TiO_2/CdS(5)/CdSe(3)/ZnS(2)	7.6	3.05	0.45	0.32	0.45

Table 2. The parameters of the QDSSCs obtained to the EIS

QDSSCs	R_r (Ω)	C(µF)
TiO_2/CdS(1)/CdSe/ZnS	351	46.4
TiO_2/CdS(2)/CdSe/ZnS	333	44.9
TiO_2/CdS(3)/CdSe/ZnS	92.7	1040
TiO_2/CdS(4)/CdSe/ZnS	1930	600
TiO_2/CdS(5)/CdSe/ZnS	16100	35.4

R_r was noted the recombination resistance.

For determined the effect of the CdS thickness on the performance efficiency, we investigated to the I-V curves of the QDSSCs based on the different photoanodes. The Figure 2(a) shows the I-V curves of the QDSSCs with CdS layers. The QDSSCs based on the TiO_2/CdS(3 layers)/CdSe/ZnS photoanode were determined to open circuit (V_{OC}) of 0.44 V, short current (J_{SC}) of 13.97 mA/cm^2, fill factor of 0.41 and efficiency (**η**) of 2.07 % (Table 1). The result agree well with the UV-Viss. The obtained performance efficiency were low when the numbers SILAR were below 3 layers. To explane for the reason, we noted that the CdS nanocrystall were little loaded on the TiO_2 films. The performance efficiency decreased. Similarly, The obtained performance efficiency were low when the numbers SILAR were over 3 layers because the CdS nanocrytall interwinded.

To further investigate the dynamic resistance of the QDSSCs, the EIS spectra under illuminated conditions for QDSSCs with different CdS SILAR cycles were obtained out to investigate the charge transfer process. Figs 2b present the Nyquist plots of the TiO_2/CdS/CdSe when the SILAR cycles of CdS changed from one to five. The EIS results show two semicircles at high frequency and low frequency. The small semicircle was due to the resistance movement of charge at the Pt/electrolyte (R_{ct1}) and FTO/TiO_2 interfaces, and the large semicircle was due to the resistance against the electron diffusion in the TiO_2 and the charge recombination resistance at the TiO_2/QDs/electrolyte interface (R_{ct2}) and against the inner diffusion in the electrolyte (Z_w). Using Fit & Simulator software, we fitted the EIS results for of all of the samples, and the values of R_s, R_{ct1}, R_{ct2} are listed in Tables 2. R_s is the set of resistance to the charge transfer at the Ag/FTO/TiO_2 front contact and the Ag/FTO/Pt back contact; R_s values of approximately 38.1 Ω were obtained for the best photoanodes. This result demonstrates that the applied technique is significant.

Figure 2b shows that the radius of the semicircles increased when the SILAR cycles of CdS QDs were under 3 layers or over 3 layers, respectively. Compared with the other photoanodes, the TiO_2/CdS(3)/CdSe(3)/ZnS(2) photoanode displayed smaller R_{ct1} and R_{ct2} values (9.21 Ω and 83.5 Ω, respectively) and a larger lifetime (3.2 ms) (shown in Table 2). Additionally, a fast electron transfer at the TiO_2/QDs/electrolyte interface and reduction in recombination are observed because the ZnS coating protected the CdS/CdSe QDs. Upon increasing the SILAR cycles of CdS QDs over 3 layers, the dynamic resistance was enhanced. The experimental results indicated an increasing recombination in the photoanodes because more CdS QDs were loaded more on the TiO_2/CdS/CdSe/ZnS. The results indicate that the photogenerated electrons were captured by the defect states in the QDs. Therefore, the electron transfer was more diffusively hindered, which increased the charge recombination and back transport reaction.

CONCLUSIONS

The QDSSCs based on the TiO_2/CdSe photoanodes with the different $TiCl_4$ treatment times. The result shows that this nanoscale coating enhances the power

conversion efficiency of 0.575 % compared with power conversion efficiency of 0.02 % of TiO_2 photoanodes without $TiCl_4$ solar cells.

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