

PHOTOVOLTAIC AND IMPEDANCE CHARACTERISTICS OF MODIFIED SILAR GROWN CDS QUANTUM DOT SENSITIZED SOLAR CELL

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Abstract

Cadmium Sulphide (CdS) quantum dots (QDs) were deposited on nanostructured TiO₂ film using a modified Successive Ionic Layer Adsorption and Reaction (SILAR) method. Nanostructured TiO₂ on FTO glass and Platinum on FTO are used as photoelectrode and Counter electrode respectively. High resolution Transmission Electron Microscopy (HRTEM) image revealed CdS QDs adsorbed on nanostructured TiO₂. The photovoltaic characteristics and impedance spectroscopy properties of CdS quantum dot sensitized solar cell (QDSSC) were analyzed under air mass 1.5 illuminations. At the SILAR adsorption time of 2 min (10 cycles), the QDSSC measured a short circuit current density of 2 mA/cm² and an open circuit voltage of 0.45 V under air mass 1.5. In a widespread frequency range, the capacitance –voltage, the conductance –voltage, the series resistance-voltage measurements were carried out for the QDSSC applications. A conduct of positive to negative capacitance was observed from the measured characteristics of capacitance- voltage which is attributed to the injection of electrons from FTO electrode into TiO₂.

Key words: Nanostructured TiO₂, CdS QDSSC, SILAR method, photovoltaic measurements, impedance characteristics.

1. INTRODUCTION

The promising candidates for photovoltaic devices are Quantum dot-sensitized solar cells (QDSSCs) which are considered to be the next generation renewable energy source. QDSSCs have the capability to control the theoretical maximum efficiency limit of silicon solar cells called 'Shockley-Queisser limit' (~ 33%) (Shockley & Queisser 1961). This is based on large extinction coefficient, large intrinsic dipole moments, multiple exciton generation effect and their tunable band gap (Guijarro 2010, Underwood et al. 2001, Nozik 2002, Schaller et al. 2006, Klimov 2006, Nozik 2008). A widely used variety of quantum dot (QD) sensitizers in the QDSSCs are Cadmium sulfide, cadmium selenide, lead sulfide and lead selenide (Kumar et al 2013, Chate et al 2012, Jung et al 2011, Lee et al. 2009, Senthamilselvi et al. 2012, Biswas et al. 2008). The most commonly used among them is CdS having good optical properties, long lifetime and a suitable band gap. There are generally two methods for the synthesis of QDs adsorbed on nanostructured wide band gap semiconductors known as successive ionic layer adsorption and reaction (SILAR) and chemical bath deposition (CBD) (Ruhle et al. 2010). In CBD method, the anionic and cationic precursors react under the gradual value of atmospheric condition or with a rapid heating process in a single reactor (Amanullah et al.2005) Due to its simplicity this method is suitable for the development of large scale photovoltaic devices. Hence, it is very difficult to precisely control size distribution and the optical properties of the QDs while in SILAR method the process consists of anionic and cationic precursors placed in two reactors distinctly and semiconductor films are immersed one by one in the two reactors. The SILAR method is better than the CBD method due to it results in near stoichiometry formation. Moreover it leads to a uniform QD distribution, high IPCE values and high QD coverage degree attained in QDSSCs.

It is observed in SILAR method that QDs characteristics can be monitored by varying the number of cycles, the molar concentration of precursors and the adsorption time (Jeong et al. 2014). The reported studies of different researchers on QDSSCs studies have shown different SILAR cycles. There are a very few reported studies showing the photovoltaic characteristics of QDSSCs and the optical properties of QDs using different SILAR

adsorption times (Bang et al. 2009, Nozik 2002, Nozik 2008, Lee et al. 2009). Impedance spectroscopy has been demonstrated as an excellent technique for the characterization of different types of solar cells.

In the present work, CdS quantum dots were adsorbed on a three layered semiconducting titanium dioxide (TiO₂) film by a modified SILAR method with low adsorption time (2 min), long duration of heating (10 min) and cooling (RT) and drying with nitrogen in between each cycle. HRTEM was studied to analyze the surface morphology of the CdS QDs. I-V characteristics and impedance measurements were carried out to study the photovoltaic properties as well as impedance characterization of the CdS QDSSCs.

2. EXPERIMENTAL

2.1 Preparation of TiO₂ photo electrodes, Quantum dots and counter electrodes

Photo electrodes with an active area of 0.283 cm² are prepared on FTO coated glass with three layers, titanium isopropoxide with spin coating, TiO₂ nano-crystalline paste using doctor-blade technique, and a thin layer of titanium chloride with spin coating. The quantum dots are deposited on this film by SILAR technique. This film was dipped into a 0.5 M Cadmium Nitrate [Cd (NO₃)₂] ethanol solution (Cadmium cationic precursor) for 2 min, rinsed with ethanol, heated for 10 min, cooled to room temperature and then dipped for another 2 min into a 0.5 M Sodium Sulfide [Na₂S] water solution (Sulphur anionic precursor) and rinsed again with water, heated for 10 min, cooled to room temperature. The CdS adsorbed TiO₂ film is dried with N₂ air stream. The two-step dipping procedure is called 1 SILAR cycle and the process continued to 10 cycles. Counter electrodes are prepared with sputtering on FTO.

2.1. Preparation of electrolyte solution

Polysulfide electrolytes were prepared by mixing suitable quantities of 0.5M Na₂S, 2M S, and 0.2M KCl powders in water/ methanol solution taken in the ratio 3/7.

2.2 Fabrication of QDSSC

The QD-adsorbed TiO₂ film was used as the working electrode and platinum coated FTO glass as counter electrode. The electrodes were assembled into a sealed cell with a cello tape spacer and binder clips, with an active area equal to the area of the TiO₂ film. A suitable electrolyte solution was introduced to this sealed cell. The electrolyte was injected from the edges into the open cell, and the cell was tested immediately with I-V characteristics for photovoltaic properties and C-V, G-V and R_s- V measurements for impedance spectroscopy characterization.

2.3 Measurements

Keithley 4200 semiconductor characterization system was used for I-V, C-V, G-V and R_s- V characteristics. The photovoltaic measurements were made using a small area class- BBA solar simulator and TM-206 solar power meter was used for measuring the intensity. Surface morphology of CdS QDs on TiO₂ was observed using TEM (JEOL-2100F). All the measurements were done at room temperature.

3. RESULTS AND DISCUSSION

3.1 TEM studies of CdS quantum dots

The surface morphology of the synthesized CdS studied by the high resolution transmission electron microscopy (HRTEM) is shown in Figure 1. The presence of lattice planes is noticeable in the HRTEM image which suggests the crystallinity in CdS quantum dots (Dhyani, H, et al). The TEM image exhibits the substantial dispersion of CdS QDs and most of the dots are observed to have the elliptical shape with diameter ranging from 5 to 8 nm. The HRTEM image of a single quantum dot with well-defined lattice planes is highlighted.

3.2 Photovoltaic Characteristics of CdS QDSSC

Variation of V_{oc} with J_{sc} obeys the following relation:

$$V_{OC} \equiv \frac{nkT}{q} \ln \left(\frac{J_{sc}}{J_o} + 1 \right) \quad (1)$$

where n is the diode ideality factor, k is the Boltzmann's constant, q is the electric charge, and J_o is the reverse saturation current density. Current - Voltage characteristics of CdS QDSSC is shown in Fig. 2. It can be seen from the figure 2 that the photocurrent and photovoltage values show an increasing trend with increasing illumination intensities (Hagfeldt A, et al., 1994).

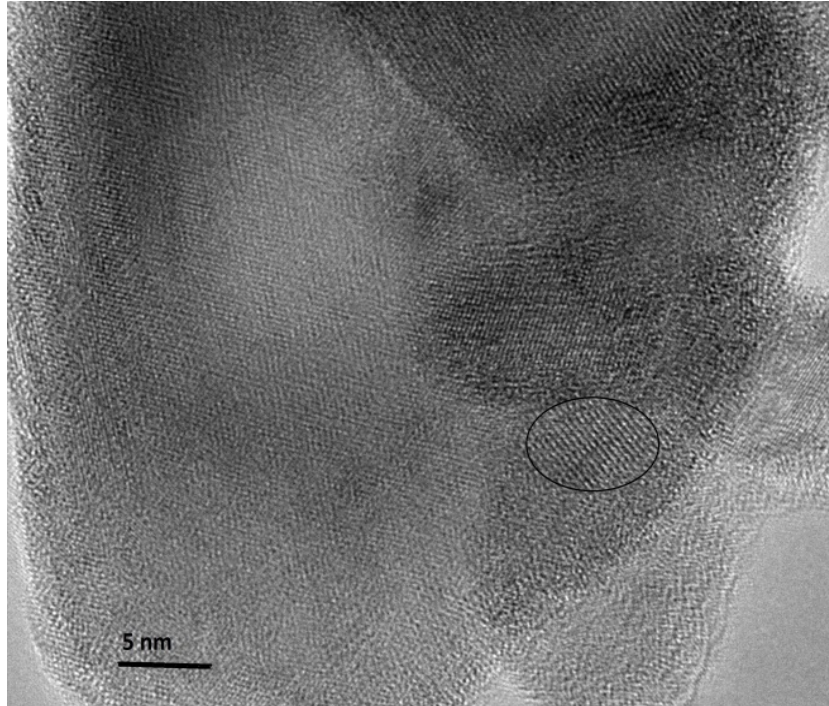


Fig. 1. HRTEM image of CdS adsorbed on TiO₂

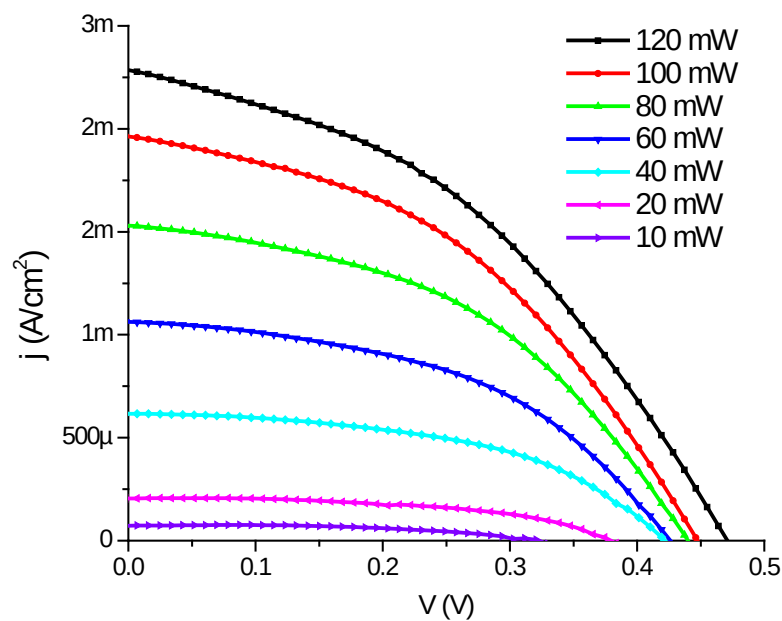


Fig. 2. Current – Voltage characteristics of CdS QDSSC

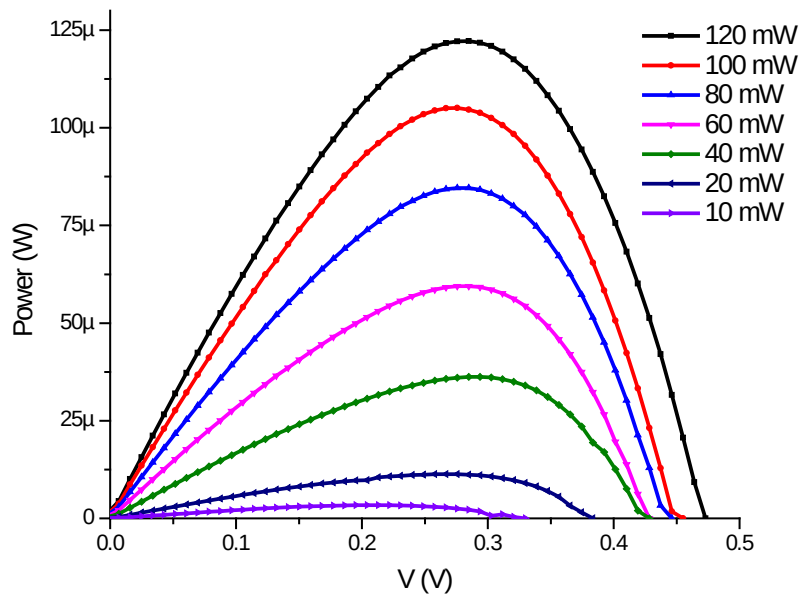


Fig. 3. Power – Voltage characteristics of CdS QDSSC

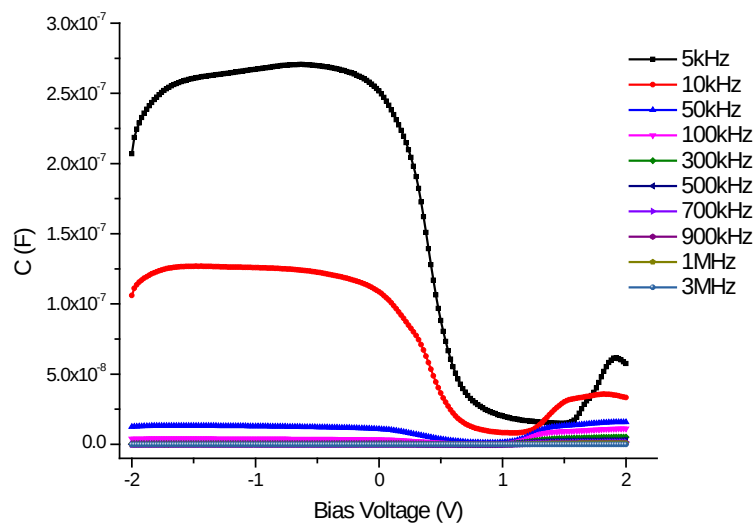


Fig. 4. Capacitance – Voltage characteristics of CdS QDSSC

The photovoltaic performance parameters include output power, open circuit voltage and short circuit current. Power – Voltage characteristics of CdS QDSSC is shown in Fig.3. The maximum power is given by:

$$P_{max} = I_m \times V_m, \quad (2)$$

where I_m is the maximum current and V_m is the maximum voltage at each illumination intensity. The results show an increasing behavior of electric power with the increasing bias voltage which touches its maximum power and then starts decreasing until touches zero values if we further increase the applied voltage. Maximum power indicates how much maximum power of the QDSSC can be delivered to its external load. The recorded

results show that maximum power peak is moved to lower voltages if we increase incident light as follows: 0.32 V, 5 μW at 20 mW/cm^2 and 0.28 V, 0.106 mW at 100 mW/cm^2 .

3.3 Impedance characteristics (C-V, G-V and R_s -V measurements) of CdS QDSSC

Fig. 4 shows the capacitance-voltage characteristics at different frequencies for CdS QDSSC. It can be seen that with the increase of the bias voltage from -2.0 V to +2.0 V, the capacitance also exhibits an increasing behavior slowly and thereafter it reaches its maximum followed by a decrease in its values leading towards saturation and showing an increasing trend for 5 and 10 kHz frequencies after 1.5 V and 1.25 bias voltages. However, by increasing the frequency from 50 kHz to 3 MHz the device capacitance represents a decreasing trend towards zero and even switching to negative capacitance after 300 kHz frequency which is believed to be the injection of electrons from FTO electrode into TiO_2 . Similar observations were reported by Kron et. al (2002) and attributed the origin of negative capacitance (i.e., inductive) in DSSC in general is the injection of electrons from light facing electrode ITO into TiO_2 . Similar observations were emphasized by yahia et.al (2011) and concluded the theory of decrease in resistance within the pores due to role of electrons to modulate the number of holes in the hole conductor. The time gap between electron injection and the modulation of the hole concentration leads to the observed inductive behavior. Our work requires more measurements and analysis to substantiate the similar interpretation of positive to negative switching of capacitance in CdS QDSSC is due to injection of electrons from FTO into TiO_2 .

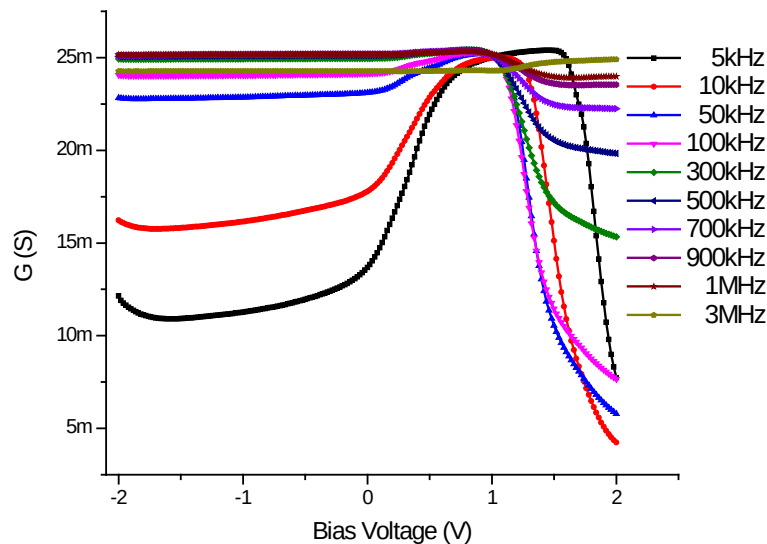


Fig. 5. Conductance – Voltage characteristics of CdS QDSSC

Room temperature measured plots of conductance versus the bias voltage from -2V to +2V at different frequencies are shown in Fig. 5. This method is established on the losses of conductance due the exchange of majority carriers between the interface states and majority carrier band of the semiconductor when a small ac signal is applied (20 mV in the present study) to the semiconductor devices (Nicollan, E.H & Goetzberger, A 1965). It can be seen from the figure 5 that the conductance increases, reaches a maximum at 1 mV bias voltage and a decreasing trend is noticed upto the bias voltage 2V. Also, the conductance is increased with the increase of the applied frequency up to 100 kHz followed by a decrease in its values and the trend is slowed down with the further increase of the frequency due to the change of the capacitance from the positive values to the negative values.

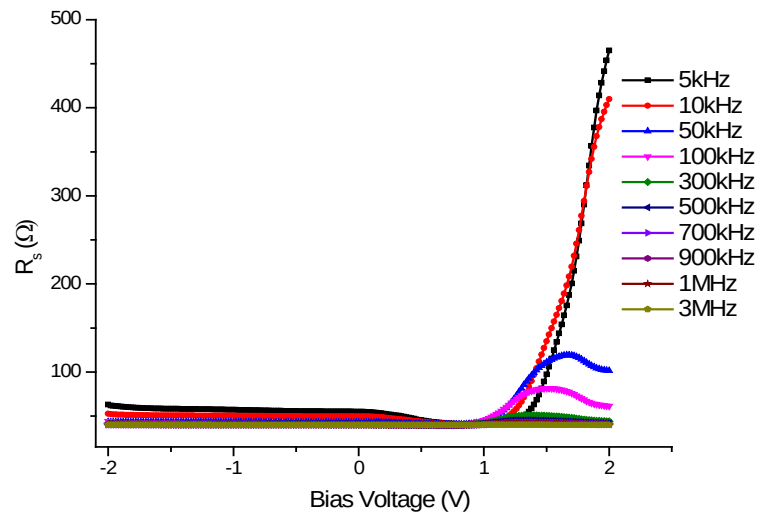


Fig. 6. Resistance– Voltage characteristics of CdS QDSSC

Fig. 6 shows the series resistance dependence of voltage and frequency. The admittance Y_{MA} for the solar cells is expressed by the following relation:

$$Y_{MA} = G_{MA} + j\omega C_{MA}, \quad (3)$$

The series resistance was evaluated from the admittance at different frequencies by the following formula:

$$R_s = \left(\frac{G_M}{G_{MA}^2 + \omega^2 C_{MA}^2} \right) \quad (4)$$

where R_s the series resistance is the real part of the impedance. The series resistance values were determined using the measured cell capacitance C_M and conductance G_M at various frequencies from 5 kHz to 3 MHz. It is observed from the Fig. 6 that the decrease in series resistance is gradual with the increasing frequency from -2V upto a biasing voltage 1.0 V at lower frequencies. Thereafter, there is a sharp increase in resistance followed by a slowed down trend in increase of resistance for frequencies upto 100 kHz. However, there is as marginal increase in resistance for the applied higher frequencies in the biasing range -2V to +2V. This behavior is almost similar in QDSSC as compared to DSSC. It may be due to the fact (Akkal, B et. al 2000) that at higher frequencies, the interface states cannot track the ac signal and hence its capacitance to the total capacitance is very small. The increase of resistance value though marginal with the increase of frequency beyond 100 kHz is attributed to the capacitance switching from positive to negative values.

4. CONCLUSION

HRTEM image supports the adsorption of CdS QD on TiO_2 whose diameter is 5 nm with well-defined crystalline planes. At the SILAR adsorption time of 2 min (10 cycles), the CdS QDSSC measured a short circuit current density of 2 mA/cm^2 and an open circuit voltage of 0.45 V under air mass 1.5. The CdS QDSSC recorded results show that the maximum power peak is moved to lower voltages with the increase of incident light as follows: 0.32 V, $5 \mu\text{W}$ at 20 mW/cm^2 and 0.28 V, 0.106 mW at 100 mW/cm^2 . An important inference from C-V measurements is that the cell exhibits a behavior of positive to negative capacitance above 500 kHz frequency in the voltage range -2 V to +2 V. This behavior is attributed to the injection of electrons from FTO electrode into TiO_2 . Impedance spectroscopy analysis of the cell corroborated with the C-V measurements.

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