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BaTiO$_3$ Photoelectrodes for CdS Quantum Dot Sensitized Solar Cells

Ke Meng, Praveen K. Surolia and K. Ravindranathan Thampi$^*$

For the first time, layers of nano-sized perovskite BaTiO$_3$ particles were successfully applied as photoelectrodes for making CdS quantum dot sensitized solar cells (QDSSC). The optical and electrochemical properties of BaTiO$_3$ on FTO glass substrates were studied. The performance of cells was maximized by controlling the growth cycles of CdS and surface passivation of BaTiO$_3$ films. The encouraging power conversion efficiency (PCE) of 1.51\% achieved points to the potential of using perovskites for sensitization and co-sensitization applications in third generation solar cells. It augers well with the recent trend of finding more compatible and stable perovskites for applications in mesoscopic sensitized solar cells.

Introduction

The third generation PV comprising of advanced thin films and newer PV concepts promise potentially higher energy conversion efficiencies and lower costs, among which dye- and Q-dot- sensitized solar cells (DSSC and QDSSC) are particularly promising. QDSSCs have a particular advantage due to the beneficial optoelectronic properties of QDs. It includes tuneable bandgaps, high molar extinction coefficients, large intrinsic dipole moments and scope for multiple charge carrier generation capabilities. Semiconductor QDs of Cd-chalcogenides and PbS have been successfully applied as sensitizers in solar cells.

In a typical QDSSC, QDs are deposited on a wide band gap mesoporous semiconductor electrode film and typically TiO$_2$ is the most used electrode material. ZnO, SnO$_2$, Nb$_2$O$_5$ and Zn$_2$SnO$_4$ have also been studied as wide band gap semiconductor materials for Q-dot sensitization. Chen et al. applied single- and multi-layer porous ZnO nanosheets to make CdS QDSSC, which showed a maximum power conversion efficiency (PCE) of 1.16\%. SnO$_2$ was used as the wide band gap semiconductor material for CdS QDSSC by Zhou et al. while their cells resulted in a PCE of only 0.22\%. Zhang et al. used a highly crystalline Nb$_2$O$_5$F nanostructured photoelectrode in CdS QDSSC and achieved a PCE of 1.68\%. Zn$_2$SnO$_4$ nanorod arrays were introduced in CdS QDSSC by Bora et al. leading to a PCE of 1.24\%. Although the energy conversion performance of solar cells applying these wide band gap materials remain lower than that of cells applying TiO$_2$ nanostructures, various groups have investigated the effect of the wide band gap materials' optical and electrochemical properties on the photovoltaic performance of the solar cells on the hope that better QDSSC could be developed in the near future using some of these highly stable wide bandgap oxides. Our report is a positive development in this direction.

Recently perovskite materials are intensively being studied in the realm of efficient third generation photovoltaic cells. Perovskite like CH$_3$NH$_3$PbI$_3$ materials were employed as sensitizers in heterojunction solar cells providing power conversion efficiencies of over 15\%\textsuperscript{19, 20}. (CH$_3$NH$_3$)$_2$PbI$_3$ nanocrystals were also introduced as co-sensitizers in QDSSC yielding a power conversion efficiency of 6.5\%\textsuperscript{21}. There is also a study reporting perovskite materials as redox mediators from our group itself\textsuperscript{22}. This recent trend to find replacements for traditional materials assumes significant importance for producing stable and reliable PV technologies even if the initial power conversion efficiencies are not record breaking. An all perovskite based stable solar cell is becoming a distinct possibility for which stable perovskites with good energy conversion efficiencies are required. Traditional perovskites of ABO$_3$ type are very stable and requires a revisit, especially where wide bandgap materials are suited for sensitization. BaTiO$_3$ is a perovskite ferroelectric semiconductor with a band gap of 3.2 - 3.5 eV\textsuperscript{23}. It was applied in the past as a wide band gap semiconductor for sensitization in DSSC; however, it was described as ‘inert’ due to its poor performance and the inability to bind dyes to the surface\textsuperscript{24}. A thin BaTiO$_3$ layer was tested in QDSSC as a passivation layer for TiO$_2$ films in order to improve the cell performance by preventing charge recombination\textsuperscript{25}. To the best of our knowledge, however, BaTiO$_3$ has not yet been successfully applied in QDSSC.

In this study, BaTiO$_3$ was introduced in QDSSC as a wide band gap semiconductor material for the first time. BaTiO$_3$ nanoparticles with diameters of tens of nanometres were synthesized first, followed by depositing it as meso-porous...
layers on FTO substrates via screen-printing. The obtained BaTiO$_3$ film was characterized to evaluate its electrical and optical properties. The BaTiO$_3$ films were then sensitized by CdS QDs to fabricate QDSSCs. The cells’ performance was maximized by controlling the QDs growth cycles. Further cell performance improvement was obtained by passivating the BaTiO$_3$ films with ZnO coating layers. An overall power conversion efficiency of 1.51% was obtained with $V_{oc}$=673 mV, $J_{sc}$=4.78 mA/cm$^2$ and FF=47.69% from our best cells. These results demonstrate that perovskite BaTiO$_3$ can be a promising photoelectrode material for QDSSCs and perhaps also for constructing an all perovskite stable novel PV cell allowing 15-20% PCE in the near future$^{26}$.

Experimental Section

Synthesis of BaTiO$_3$ nanoparticles: BaTiO$_3$ nanoparticles were synthesized through a hydrothermal method reacting TiCl$_4$ with BaCl$_2$ in a basic medium$^{27}$. Typically, 5 ml of TiCl$_4$ (Aldrich) was added to 70 ml of chilled deionized (DI) water with stirring. 18 g of BaCl$_2$·2H$_2$O (Sigma) was then added to this solution while stirring. 150 ml of 2 M NaOH was further added to provide a basic pH. The final mixture was kept at 100°C for 8 hours in a round bottom flask equipped with a condenser for facilitating the BaTiO$_3$ crystal growth. The resulting precipitate was filtered and washed with DI water several times and dried in a furnace at 60°C.

Preparation of BaTiO$_3$ Photoelectrodes: The BaTiO$_3$ paste was prepared by following a standard procedure used to prepare TiO$_2$ paste$^{28}$. Photoelectrodes were manufactured using the screen-printing method based on a layer-by-layer printing of BaTiO$_3$ paste on fluorine doped tin oxide (FTO) conducting transparent glass sheets. By controlling the number of prints, BaTiO$_3$ films with accurate thicknesses were fabricated. After this, the electrodes were sintered at 325°C, 375°C, 450°C and 500°C for 5 mins, 5 mins, 15 mins and 30 mins, respectively. The cell active area was 0.28 cm$^2$. A ZnO passivation layer on the BaTiO$_3$ films was manufactured by simply immersing the photoelectrode in 0.5 mM Zn(NO$_3$)$_2$ ethanol solution followed by air drying and sintering at 400°C for 30 min$^{29}$, when required. A TiO$_2$ passivation layer on the BaTiO$_3$ films was formed by dipping the photoelectrode in 50 mM TiCl$_4$ solution for 30 mins at 70°C, followed by rinsing and sintering at 500°C for 30 mins$^{30}$. A BaTiO$_3$ passivation layer was deposited on the BaTiO$_3$ films by immersing the photoelectrode in 50 mM BaCl$_2$ and 50 mM TiCl$_4$ mixed solution for 10 mins, followed by 30 mins sintering at 400°C.

Sensitization of BaTiO$_3$ Films: The BaTiO$_3$ films were sensitized with CdS quantum dots using successive ionic absorption and reaction (SILAR) method. Briefly, 0.5 M Cd(NO$_3$)$_2$ ethanol solution and 0.5 M Na$_2$S methanol/DI water (1:1v) solution were prepared as the starting solutions for the SILAR process. The bare electrodes with BaTiO$_3$ layers were immersed into Cd(NO$_3$)$_2$ solution for 1 min at first, followed by 1 min rinsing by ethanol and 1 min drying by argon flow. The electrodes were then dipped into Na$_2$S solution for 1 min followed by further rinsing with methanol for 1 min and drying. Each series of the two dipping processes was called ‘one SILAR cycle’. A ZnS passivation layer was always deposited on the CdS quantum dots by dipping the CdS sensitized electrodes alternately into 0.2 M Zn (NO$_3$)$_2$ in ethanol and 0.2 M Na$_2$S in methanol/DI water for 1 min/dip$^9$. The electrodes were rinsed and dried with argon after each dipping.

Fabrication of QDSSC: A water based polysulfide electrolyte and Cu$_2$S counter electrodes were applied for fabricating cells. The electrolyte contains 1 M Na$_2$S, 1 M S and 0.1 M NaOH in DI water. The counter electrodes were fabricated following the procedure described in our earlier report$^{31}$. Briefly, a Cu film with hundreds of nanometres thickness was firstly electrodeposited on FTO glass electrodes in a three-electrode system involving Ag/AgCl reference electrode, platinum wire counter electrode and an electrolyte of 5 mM CuSO$_4$, 1 M Na$_2$SO$_4$ and 0.5 M H$_3$BO$_3$ in deionized water. The Cu plated FTO glass piece was then immersed in a polysulfide solution containing 1 M Na$_2$S and 1 M S in DI water for 1 min, followed by DI water rinsing and drying under argon flow. The working electrode and counter electrode were sandwiched together using a hot melt Bynel™ polymer gasket (50 micron thick). Electrolyte was filled into the space between the two electrodes through a hole in the counter electrode using vacuum back filling method. The back hole was finally sealed with a piece (0.1 mm thick) of glass heat sealed with Bynel™ polymer.

Characterization: Absorption and transmission spectra were recorded using a SPECORD 210 PLUS Double Beam UV-VIS spectrophotometer. XRD was measured using a Siemens D5000 diffractionmeter. SEM images were recorded with a Hitachi TM-1000 Scanning Electron Microscope (SEM) (Hitachi High Technologies Ltd). EDX was carried out using an APOLLO XV Silicon Drift Detector and a Kratos Axis ULTRA was used to record the XPS spectra. Photoelectrochemical measurements including current density /voltage (J-V) curve, open circuit voltage ($V_{oc}$), short circuit current density ($J_{sc}$) and fill factor (FF) were measured using a Newport 91195A-1000 solar simulator and Newport 69920 Arc Lamp Power Supply. A Newport 8108A Air Mass Filter was placed before the output of the solar simulator to simulate the AM 1.5 spectrum with irradiance powers of 1000 W/m$^2$. J-V, electrochemical impedance spectroscopy (EIS) and open circuit voltage decay (OCVD) measurements were recorded with a GAMRY Instruments Potentiostat. Incident photon to current conversion efficiency (IPCE) was measured and recorded using a Gilden Photonics IPCE system and software.

Results and Discussion

The crystal structure and the nature of the as-prepared BaTiO$_3$ nanoparticles, BaTiO$_3$ films on FTO substrates and the CdS sensitized BaTiO$_3$ films on FTO substrates were characterized using X-ray diffractometry. Figure 1 (a) presents the XRD pattern of the as prepared BaTiO$_3$ powders. All the characteristic peaks were well indexed to the cubic phase of BaTiO$_3$ (JCPDS file No. 74-1968). The sharp peaks indicated the formation of well-crystallized, single phase BaTiO$_3$ crystal grains. Figure 1 (b) presents the XRD pattern of the BaTiO$_3$ films on FTO substrates. The newly emerged peaks were indexed to the FTO substrate (JCPDS file No. 77-0447). No separate peaks were observed after the CdS sensitization of the BaTiO$_3$ films coated FTO substrates as displayed in Figure 1 (c). The peaks of CdS are superimposed by both the BaTiO$_3$ and FTO peaks. However, the enhanced CdS coupled with BaTiO$_3$ or FTO peaks and weakened remaining peaks indicate the formation of CdS QDs, though with possible nano-sizes and lower crystallinity$^{31}$.
Scanning electron microscopy allowed investigation of the morphology of the BaTiO$_3$ nanoparticles and its films. Surface SEM image of BaTiO$_3$ nanoparticles shown in Figure 2 (a) and the particle-size distribution histograms seen in Figure 2 (b) indicate a narrow size distribution of the nanoparticles with an average diameter of around 34 nm, while the BaTiO$_3$ powders having an agglomerated shape and an aggregate size of 125-350 nm. Figure 2 (c) and (d) present surface and cross-section SEM. The cross-section image (Figure 2 (d)) shows the porous structure of the BaTiO$_3$ film; while it also shows the resulting film is 26 µm in thickness. Figure 2 (e) and (f) show the surface and cross-section SEM of the CdS quantum dots sensitized BaTiO$_3$ films. Due to the small sizes of the QDs, no obvious difference was observed after the sensitization, however the remaining micro-size pores even after the CdS deposition allow an intimate contact between the electrolyte and the Q-dots, which enhances the regeneration of the QDs after electron injection and suppresses the charge recombination rate, thus improving the overall cell performance. The uniform coating of CdS QDs on BaTiO$_3$ film can be concluded from the EDX mapping on the cross-section of the CdS sensitized BaTiO$_3$ films as shown in Figure 2 (g).

Light scattering ability of the wide band gap material in QDSSC is important for improving the light harvesting and thus the incident photon to current conversion efficiency (IPCE) of the cell$^{32}$. UV-visible absorption and transmission spectroscopy was employed to characterize the light scattering ability of the BaTiO$_3$ films. According to Figure 3, the transmission of the BaTiO$_3$ films is only slightly higher than 20% in the visible range. The results indicate strongly the significant light scattering ability of the BaTiO$_3$ films. The scattering of light by spherical particles highly depends on the particle size and incident light wavelengths.$^{33}$ The BaTiO$_3$ nanoparticle aggregates with sizes of hundreds of nanometres have comparable size with the wavelength of visible light resulting in an enhanced light scattering. The multi-reflection between the BaTiO$_3$ particles can effectively enhance the optical pathway of incident light.

![Figure 1: XRD patterns of the (a) BaTiO$_3$ nanoparticles (b) BaTiO$_3$ films on FTO substrates and (c) CdS sensitized BaTiO$_3$ films on FTO substrates](image1)

![Figure 2: (a) Surface SEM image of BaTiO$_3$ nanoparticles (b) BaTiO$_3$ particle-size distribution histograms (c) Surface SEM image of BaTiO$_3$ films on FTO (d) Cross-section SEM image of BaTiO$_3$ films on FTO (e) Surface SEM image of CdS sensitized BaTiO$_3$ films (f) Cross-section SEM image of CdS sensitized BaTiO$_3$ films on FTO (g) EDX mapping for the area shown by (f)](image2)

![Figure 3: UV-visible absorption and transmission spectra of the BaTiO$_3$ films on FTO (BaTiO$_3$ film thickness 26 µm)](image3)
The energy level alignment between the wide band gap material and the sensitizer plays a vital role to construct efficient photovoltaics. UV-vis absorption spectroscopy and X-ray photoelectron valance-band spectroscopy (XPS) determined the band edges of the BaTiO$_3$ nanoparticles. According to the UV-vis absorption spectrum of the BaTiO$_3$ films as shown in Figure 3, a band gap of 3.26 eV can be estimated for the BaTiO$_3$ nanoparticles. The XPS spectrum in Figure 4 (a) indicates the maximum valence band edge value is ca. 1.4 eV for the BaTiO$_3$ nanoparticles. According to the energy diagram in Figure 4 (b), with similar band gap positions as TiO$_2$, the BaTiO$_3$ nanoparticles should be a promising wide band gap material for CdS QDSSC due to the well matched band edges between CdS QDs and BaTiO$_3$ nanoparticles.

![Figure 4: (a) XPS spectrum of the BaTiO$_3$ films (b) Energy alignment diagram of CdS-BaTiO$_3$ system](image)

With the enhanced light scattering property and good band gap match, the BaTiO$_3$ nanoparticles could be considered as good wide band gap material for QDSSC. CdS quantum dots were deposited on BaTiO$_3$ films as sensitizers via SILAR method. 3-11 SILAR cycles of CdS were deposited on 26 µm BaTiO$_3$ films printed on FTO glass. The CdS quantum dots were always passivated with a ZnS thin layer. The J-V characteristics of solar cells are presented in Figure 5 and the cell parameters obtained from the J-V curves are listed in Table 1. The results show that with the increase of SILAR cycles from 3 to 9, the $J_{sc}$ gradually increases from 1.04 to 3.79 mA/cm$^2$, which can be ascribed to additional SILAR cycles enhancing the deposition of bigger sizes and larger numbers of CdS quantum dots on BaTiO$_3$ films providing enhanced light absorption; while the $V_{oc}$ increased from 491 to 608 mV and FF increased from 45.51 to 55.41%, which is due to the better coverage of CdS quantum dots on BaTiO$_3$ films. This reduces the charge recombination at the BaTiO$_3$/electrolyte interface. Further increase of CdS SILAR cycles to 11 leads to decreased $J_{sc}$ of 3.36 mA/cm$^2$ and FF of 49.82%. This can be reasoned by the fact that after optimum deposition of CdS, too many SILAR cycles lead to more surface defects on the QDs, which increase the chances for charge recombination. Moreover, the overloaded CdS QDs may lead to pore blocking, which hinders the holes scavenging process. Thus, the optimized number of CdS SILAR cycles on 26 µm BaTiO$_3$ films is obtained at 9 cycles with a power conversion efficiency (PCE) of 1.26%. The thickness of BaTiO$_3$ films was also varied by controlling the number of BaTiO$_3$ layers on FTO substrate to maximize the cell performance. Solar cells with 3, 5, 7 and 9 layers of BaTiO$_3$ sensitized by 9 cycles of CdS were fabricated and cells with 7 layers of BaTiO$_3$ showed the best performance. The 7 layers BaTiO$_3$ film has a thickness of 26 µm and it is taken for all other film characterizations.

As discussed in the introduction part, an earlier study, which used BaTiO$_3$ nanoparticles based photoelectrodes for DSSC applications, have described this material as ‘inert’ when interacted with dyes. However, in cells where they decorated the 50 nm diameter BaTiO$_3$ particles with 5 nm TiO$_2$ nanoparticles, a promising overall power conversion efficiency of more than 5% was measured. They attributed the low performance of the BaTiO$_3$/dye system to the poor affinity of dye on BaTiO$_3$ particles, and by introducing a network of TiO$_2$ particles the dye adsorption was greatly enhanced. This resulted in enhanced photocurrents and higher photo conversion efficiencies. Indeed, the interaction between dye and TiO$_2$ is mainly attributed to the affinity between the carboxylic anchoring-group of the dye and the Ti$^{4+}$ ions on the TiO$_2$ (101) plane. When Ba$^{2+}$ ions are introduced through the crystalline BaTiO$_3$ into such a semiconductor system, the bonding affinity and electronic coupling between the dye and the titanium ions in the BaTiO$_3$ could be weakened. However, in the BaTiO$_3$/CdS QD case, the CdS quantum dots are crystalized and grown directly on the BaTiO$_3$ particles without any anchoring –COOH group. The situation with respect to its affinity to BaTiO$_3$ and its electron injection ability are considerably different. Thus the promising performance of CdS quantum dot sensitized BaTiO$_3$ solar cells is made possible.
photoelectrodes were recorded to evaluate the sizes and passivation layers on BaTiO$_3$. The absorbance increases with increasing SILAR cycles indicating the increased amount of CdS QDs deposition, while the growth of the CdS QD size is suggested by the red shift of the absorbance shoulder and onset position. Figure 6 (a) shows the incident photon to current conversion efficiency (IPCE) of cells fabricated with 9 cycles of CdS deposition on BaTiO$_3$ films. A maximum IPCE of 30% was obtained at 400 nm. The IPCE values were integrated with the incident photon flux of standard AM1.5 to get the calculated $J_{sc}$ which is 2.83 mA/cm$^2$. The measured $J_{sc}$ value of 3.74 mA/cm$^2$ as shown in Table 1 is slightly higher than the calculated value, which is due to fact that charge separation and collections are more efficient under a much higher illumination intensity (J-V measurement) than that used for the IPCE measurement.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>491</td>
<td>1.04</td>
<td>45.51</td>
<td>0.24</td>
</tr>
<tr>
<td>5</td>
<td>508</td>
<td>1.79</td>
<td>54.32</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>543</td>
<td>3.07</td>
<td>53.64</td>
<td>0.89</td>
</tr>
<tr>
<td>9</td>
<td>608</td>
<td>3.74</td>
<td>55.41</td>
<td>1.26</td>
</tr>
<tr>
<td>11</td>
<td>606</td>
<td>3.36</td>
<td>49.82</td>
<td>1.00</td>
</tr>
</tbody>
</table>

UV-vis absorption spectra of the CdS QDs sensitized BaTiO$_3$ photoelectrodes were recorded to evaluate the sizes and numbers of the incorporated CdS QDs and are presented in Figure 6 (a). The absorbance increases with increasing SILAR cycles indicating the increased amount of CdS QDs deposition, while the growth of the CdS QD size is suggested by the red shift of the absorbance shoulder and onset position. Figure 6 (b) shows the incident photon to current conversion efficiency (IPCE) of cells fabricated with 9 cycles of CdS deposition on BaTiO$_3$ films. A maximum IPCE of 30% was obtained at 400 nm. The IPCE values were integrated with the incident photon flux of standard AM1.5 to get the calculated $J_{sc}$ which is 2.83 mA/cm$^2$. The measured $J_{sc}$ value of 3.74 mA/cm$^2$ as shown in Table 1 is slightly higher than the calculated value, which is due to fact that charge separation and collections are more efficient under a much higher illumination intensity (J-V measurement) than that used for the IPCE measurement.

<table>
<thead>
<tr>
<th>Coating layers</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare BaTiO$_3$</td>
<td>608</td>
<td>3.74</td>
<td>56.18</td>
<td>1.26</td>
</tr>
<tr>
<td>Bare ZnO</td>
<td>473</td>
<td>5.25</td>
<td>23.03</td>
<td>0.57</td>
</tr>
<tr>
<td>ZnO</td>
<td>673</td>
<td>4.78</td>
<td>47.69</td>
<td>1.51</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>550</td>
<td>4.20</td>
<td>60.09</td>
<td>1.39</td>
</tr>
<tr>
<td>Double TiO$_2$layer</td>
<td>465</td>
<td>3.35</td>
<td>44.71</td>
<td>0.70</td>
</tr>
<tr>
<td>TiO$_2$+ZnO</td>
<td>539</td>
<td>4.09</td>
<td>55.87</td>
<td>1.23</td>
</tr>
<tr>
<td>BaTiO$_3$ layer</td>
<td>630</td>
<td>3.02</td>
<td>45.50</td>
<td>0.87</td>
</tr>
</tbody>
</table>

The J-V characteristics and cells parameters with and without the ZnO passivation layers on BaTiO$_3$ films are shown in Figure 7 and Table 2, respectively. With introduction of the ZnO passivation layer, the $V_{oc}$ of the cells have increased significantly from 608 mV to 673 mV. $V_{oc}$ is determined by the difference between the quasi-Fermi level of the photoelectrode and the redox potential of the electrolyte; it is also dependent on the rate of the electron recombination at the semiconductor-electrolyte interface. The introduction of ZnO with its high conduction band edge helps to increases the quasi-Fermi level of the photoelectrode while the compact ZnO layer itself operates as an energy barrier to the back electron transfer from BaTiO$_3$ nanoparticles to the electrolyte. Both of these contribute to the higher $V_{oc}$. The $J_{sc}$ of the cells applying ZnO passivation layer also increases by 1 mA/cm$^2$, which further suggests the suppression of electron recombination occurring at the BaTiO$_3$-electrolyte interface. Overall, the cells with ZnO passivation layer show a promising power conversion efficiency of 1.51%, which is 20% higher than cells with bare BaTiO$_3$ films sensitized by CdS QDs.
Electrochemical impedance spectroscopy (EIS) was introduced to investigate the impact of the ZnO passivation layer on the cell performance. Figure 8 (a) shows typical Nyquist plots of the cells with and without the ZnO coating layer. A typical EIS spectrum of DSSC consists of three semicircles responding to the high-frequency, middle-frequency and low-frequency regions when the cells are biased at its $V_{oc}$; while the responses are attributed to the charge transfer at the counter electrode-electrolyte interface, the carrier transport at the photoanode-electrolyte interface and the ions diffusion process in the electrolyte, correspondingly. This characteristic is also applicable to QDSSC except that for a relatively low-performing QDSSC, a double-semicircle spectrum is always observed where the feature of the diffusion process is not presented. In this study, we focus on the charge transfer and recombination at the BaTiO$_3$/electrolyte interface in the middle-frequency region. Nyquist plots of both cells indicate the ZnO layer reduces the charge transfer resistance, which is mainly due to the suppression of charge recombination at the BaTiO$_3$/electrolyte interface. The Bode-phase plots of the cells obtained from EIS measurement (Figure 8 (b)) were introduced to investigate the electron life time ($\tau_n$) in the CdS sensitized BaTiO$_3$ nanostructure using the equation $\tau_n = 1/(2\pi f_{max})$ where $f_{max}$ is the maximum frequency of the middle-frequency peak. The $f_{max}$ values for cells with and without ZnO layer are 30 Hz and 63 Hz, respectively. Correspondingly, the electron lifetime is calculated to be 5.3 ms and 2.5 ms for the cells assembled by BaTiO$_3$ films with ZnO coating layer and bare BaTiO$_3$ films, respectively. The longer electron lifetime by introduction of the ZnO layer demonstrates the retardation of charge recombination at the BaTiO$_3$/electrolyte interface.

Open circuit voltage decay measurements (OCVD) helped to further analyse the excited electron lifetimes. The results in Figure 9 indicate that the $V_{oc}$ decay of cells with ZnO coating layer is much slower than cells with bare BaTiO$_3$. Lower $V_{oc}$ decay leads to increase in the electron life time. This further indicates the ZnO layer’s ability to suppress electron recombination at the BaTiO$_3$/electrolyte interface. The results obtained from OCVD are consistent with the results acquired from the EIS measurements. We conclude that ZnO coating on BaTiO$_3$ films can therefore effectively suppress electron leakage and thus enhance the overall cell performance.

Figure 10 is a schematic illustration of the effect of ZnO passivation layer on BaTiO$_3$ films. The electron recombination is suppressed by the coating of the ZnO layer. As per the proposed mechanism, excited electrons in the conduction band of CdS can effectively inject into the conduction band of BaTiO$_3$ through the ZnO intermediate energy level; however, the ZnO layer works as an energy barrier prohibiting the back electron transfer from the conduction band of BaTiO$_3$ into the electrolyte. As a result, the number of electrons injected to the FTO substrate increases leading to a higher $J_{sc}$, while the electron accumulation in the BaTiO$_3$ is also enhanced resulting in a high $V_{oc}$, thereby the overall power conversion efficiency is improved.
Conclusions

BaTiO$_3$ nanoparticles were synthesized and characterized to investigate their optical and electrical properties. The nanoparticles were further introduced successfully as a wide band gap material in QDSSC, which to the best of our knowledge, is for the first time. Sensitized by CdS QDs via SILAR method, the QDSSC applying the BaTiO$_3$ films showed maximum power conversion efficiencies at 9 SILAR cycles. A ZnO coating layer was then applied on BaTiO$_3$ films and a PCE of 1.51% was obtained which is 20% higher than cells with bare BaTiO$_3$ films. The enhancement of cell performance is attributed to the suppression of back electron transfer at the BaTiO$_3$-electrolyte interface by the ZnO passivation layer, which was ascertained by EIS and OCVD measurements. The results indicate that the perovskite type BaTiO$_3$ material is indeed a promising wide band gap material for third generation solar cells such as QDSSC. This is to be seen in the light of the recent advancements made in solar cells using perovskites.

Acknowledgements

Ke Meng acknowledges the funding support received from China Scholarship Council. Praveen K. Surolia received support from European Commission’s FP7 SMARTOP project under the Grant Agreement number 265769. K.R. Thampi acknowledges the funding support received from Keilman Foundation and the China Scholarship Council. Praveen K. Surolia received funding support from the Royal Society of Chemistry, UK.

Notes and references

22. J. R. Kantor, 1924.
For the first time, perovskite BaTiO$_3$ nanoparticles were applied as a photoelectrode material for quantum dot sensitization in solar cells, yielding a promising power conversion efficiency of 1.51%.