Solar Energy Conversion by the Regular Array of TiO$_2$ Nanotubes Anchored with ZnS/CdSSe/CdS Quantum Dots Formed by Sequential Ionic Bath Deposition

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The photoanode electrode of TiO$_2$ nanotubes (NTs) anchored with ZnS/CdSSe/CdS quantum dots (QDs) was prepared by anodization of Ti metal and successive ionic layer adsorption and reaction (SILAR) procedure. The tuning of the band gap of CdSSe was done with controlled composition of Cd, S, or Se during the SILAR. A ladder-like energy structure suitable for carrier transfer was attained with the photoanode electrode. The power conversion efficiency (PCE) of our solar cell fabricated with the regular array of TiO$_2$ NTs anchored with CdSSe/CdS or CdSe/CdS QDs [i.e., (CdSSe/CdS/TiO$_2$NTs) or (CdSe/CdS/TiO$_2$NTs)] was PCE = 3.49% and 2.81% under the illumination at 100 mW/cm$^2$, respectively. To protect the photocorrosion of our solar cell from the electrolyte and to suppress carrier recombination, ZnS was introduced onto CdSSe/CdS. The PCE of our solar cell with the structure of a photoanode electrode, (ZnS/CdSSe/CdS/TiO$_2$ NTs/Ti) was 4.67% under illumination at 100 mW/cm$^2$.

Key Words: TiO$_2$ nanotubes, Quantum dots, SILAR, Solar cell

Introduction

Recently, semiconductor sensitized solar cells are selected as one of the most promising alternative energy sources and attracted great attention as a third-generation photovoltaic device. The formation of anodic TiO$_2$ nanotubes has been widely investigated because of a wide range of applications such as photocatalysis, photoanode electrodes, supercapacitors, hydrogen generators, and solar cells.\(^1,2\) For the application of TiO$_2$ for the solar cell, however, TiO$_2$ itself is less efficient because it (band gap $E = \sim 3.2 \text{ eV}$) captures only the UV portion of sunlight (4% of the whole solar emission).\(^3\) Therefore, to enhance the solar energy conversion efficiency, we need to extend the solar energy absorption as much as possible through the visible to IR region. To improve the solar energy conversion efficiency is to capture as much sunlight as possible. And thus, firstly, the creation of impurity states near the valence band edge (O 2p character) or/and the conduction band edge (Ti 3d(t$_{2g}$) character) of TiO$_2$ by doping it with non-metal anions such as C,\(^4\) N,\(^5\) and S\(^6\) or with transition metal cations such as Fe\(^{3+}\), V\(^{4+}\), Mn\(^{2+}\), Ni\(^{2+}\), and Cr\(^{3+}\),\(^8\) respectively, can extend the absorption to longer wavelengths (i.e. to the visible region: ~50% of the whole solar emission). Secondly, semiconductor QDs with band gaps lying in the visible or IR spectral range such as CdS,\(^9\) CdSe,\(^10\) CdTe,\(^11\) and PbS,\(^12\) are attached to the channel wall of the regular array of TiO$_2$ nanotubes in order to extend the solar energy absorption to the visible or IR.\(^13\) Previously, Yuh-Lang Lee and other researchers reported that they achieved a maximum solar energy conversion efficiency of 4.22% with the CdSe/CdS/TiO$_2$ photoanode electrode.\(^14\) Specially, with ternary CdSSe alloy composition modulated, we can adjust the absorption wavelength of CdSSe from red to blue in the visible region.\(^15-18\) There are also two well-known methods to deposit the colloidal QDs layer on mesoporous metal oxides such as TiO$_2$. One approach is to presynthesize the colloidal QDs surface-passivated with ligands and then to join them with metal oxide surfaces through linker molecules or electrostatic interaction.\(^19,21\) The other is the direct growth of QD layers on metal oxide surfaces in situ through chemical bath deposition (CBD)\(^22\) or successive ionic layer adsorption and reaction (SILAR).\(^23-25\) However, at most, 14% of surface of nanoporous TiO$_2$ film was anchored with QDs through linkers or was directly adsorbed with presynthesized colloidal QDs.\(^26\) In the SILAR method with Na$_2$SeO$_3$, Se\(^2-\) is slowly released in the presence of Cd\(^{2+}\) and is poorly controlled.\(^27\) The SILAR with SeO$_2$ instead of Na$_2$SeO$_3$ is carried out for the better deposition of metal selenides.\(^24\) In the SILAR method, cationic and anionic precursors are dissolved in separate vessels. For one deposition cycle, the photoanode electrode with the regular array of TiO$_2$ nanotubes is dipped into the precursor solution containing the metal cation. After rinsing excess precursors and drying them off, the photoanode electrode is dipped into the second precursor solution containing the anion and then the second rinsing-off step completes the deposition cycle. The average QD size deposited onto the photoanode electrode with the regular array of TiO$_2$ nanotubes can be controlled by the number of deposition cycles.

In this study, the photoanode electrode fabricated with the regular array of TiO$_2$ nanotubes (NTs) anchored with ZnS (outer)/CdSSe/CdS (closer to TiO$_2$ NTs) quantum dots was prepared by the following steps: 1) the formation of the regular array of TiO$_2$ nanotubes on a Ti metal sheet, 2) the surface treatment of the TiO$_2$ nanotubes with TiCl$_4$ for the
removal of surface defect sites on NTs, 3) the sequential deposition of CdS, CdSSe, and ZnS, in situ, onto the channel walls of TiO$_2$ nanotubes by the successive ionic layer adsorption and reaction (SILAR) procedure. A ladder-like energy structure suitable for carrier transfer was attained from ZnS/CdSSe/CdS through TiO$_2$ nanotubes to a Ti metal sheet. The more photoinduced charge carriers were generated and transferred from the anchored quantum dots to the TiO$_2$ nanotubes and thus, the solar energy conversion efficiency was enhanced.

The general experimental scheme we take to produce the photoanode electrode made with the regular array of TiO$_2$ nanotubes anchored with ZnS/CdSSe/CdS quantum dot layers is given in Figure 1. The energy structure associated with the materials used is also shown in Figure 1.

The power conversion efficiency (PCE) of our solar cell fabricated with the regular array of TiO$_2$ nanotubes anchored with CdS/CdSSe or CdSe/CdS QDs was PCE = 3.49% and 2.81% under the illumination at 100 mW/cm$^2$, respectively. To protect the photocorrosion of our solar cell from the electrolyte and to prevent the carrier recombination, ZnS was introduced onto CdSSe/CdS. The power conversion efficiency (PCE) of our solar cell with the structure of a photoanode electrode, (ZnS/CdS/CdSSe/TiO$_2$ NTs/Ti metal sheet) was 4.67% under the illumination at 100 mW/cm$^2$.

**Experimental**

**Materials.** Titanium foil (0.25 mm thickness, 99.6% purity, Goodfellow, England), ammonium fluoride (NH$_4$F, Junsei Chemical Co., 97.0%), ethylene glycol (Samchun Chemical Co., 99.5%), cadmium nitrate tetrahydrate (Cd(NO$_3$)$_2$·4H$_2$O, Junsei Chemical Co., 98.0%), sodium sulfide pentahydrate (Na$_2$S·5H$_2$O, Yakuri pure, 98.0%), sodium sulfide (Na$_2$S, Sigma-Aldrich, 98.0%), selenium dioxide (SeO$_2$, Sigma-Aldrich, 98.0%), zinc sulfate heptahydrate (ZnSO$_4$·7H$_2$O, Daejung chemical Co., 99.0%), ethyl alcohol (C$_2$H$_5$OH, Dusan Chemical Co., 99.9%), titanium(IV) chloride solution (TiCl$_4$, Sigma-Aldrich), 4-mercaptobenzoic acid (C$_7$H$_5$O$_2$S, Sigma-Aldrich, 99.0%), and sodium sulfite heptahydrate (Na$_2$SO$_3$·7H$_2$O, Junsei Chemical Co., 95.0%) are used as received.

**Fabrication of an Array of TiO$_2$ Nanotubes on a Flat Ti Sheet.** The growth of TiO$_2$ nanotubes was done in ethylene glycol containing 0.7 wt % NH$_4$F and 2 vol % H$_2$O electrolyte at 25 °C by anodizing Ti foil (0.25 mm thickness, 99.6% purity, Goodfellow, England) with the application of 60V DC (N5753A model, Agilent) for 2 h. Ti foil was prepared as follows: washed with ethanol and acetone, followed by conventional oven-dry at 50 °C. The vertically aligned array of TiO$_2$ nanotubes as-grown was annealed at 450 °C for 1 h under ambient air condition to improve their crystallinity.\textsuperscript{31}

**TiCl$_4$ Treatment on the TiO$_2$ Nanotubes.** To improve the structural quality and to remove surface defect sites of the grown TiO$_2$ nanotubes, we dipped as-grown anatase TiO$_2$ nanotubes in 30 mL of 5 mM TiCl$_4$ aqueous solution and then took it out and kept it in an oven for 150 min at 50 °C. We took it out from the oven and then washed it with deionized (DI) water and dried it in an oven at 90 °C for 30 min. We finally annealed it at 450 °C for 1 h under ambient air condition. The digital images of TiO$_2$ nanotubes untreated and treated with TiCl$_4$, were shown in Figure 2.

**SILAR Procedure for the Growth of CdS, CdSSe, CdSe, and ZnS Layers.** The optimized regular array of TiO$_2$ nanotubes surface-treated with TiCl$_4$ was alternatively soaked in two different solutions to deposit CdS: in 0.50 M Cd(NO$_3$)$_2$·4H$_2$O dissolved in DI water for 3 min and then in 0.50 M Na$_2$S·5H$_2$O dissolved in DI water. It was rinsed in DI water and acetone for 1 min to remove excess precursors. This kind of cycle was repeated 20 times (denoted with “CdS20”). The average QD size deposited onto the regular array of TiO$_2$ nanotubes was controlled by the number of deposition cycles.

To deposit CdSSe ternary alloy subsequently next to CdS layer, the SILAR cycle was performed with 0.60 M Cd(NO$_3$)$_2$·4H$_2$O dissolved in ethanol, 0.20 M Na$_2$S dissolved in methanol/ethanol (7:3 v:v), and 0.30 M SeO$_2$ dissolved in ethanol: dipped in each solution for 3 min. We repeated the SILAR cycle 3 times (denoted with “CdSSe3”). For the deposition of CdS subsequently next to CdS layer, 0.40 M Cd(NO$_3$)$_2$·4H$_2$O dissolved in ethanol and 0.40 M SeO$_2$ dissolved in ethanol were prepared under inert N$_2$ atmosphere. The photoanode electrode of TiO$_2$ nanotubes deposited with CdS was dipped into 0.40 M SeO$_2$ dissolved in ethanol and 0.40 M Cd(NO$_3$)$_2$·4H$_2$O dissolved in ethanol for 3 min, respectively. Then it was washed and dried. We repeated it 10 times (denoted with “CdSe10”). For the protection of our solar cell photoanode electrode from the photocorrosion and the prevention of carrier recombination, ZnS capping layer finally was deposited. 0.50 M ZnSO$_4$·7H$_2$O dissolved in ethanol and 0.50 M Na$_2$S·5H$_2$O dissolved in ethanol were prepared. We dipped the photoanode electrode.
of TiO₂ nanotubes deposited with CdSSe/CdS (i.e., CdSSe/CdS/ TiO₂ NTs photoanode electrode) into each solution prepared for 2 min. All of the samples prepared were put into a quartz tube with a diameter of 3.15 cm and then located in the center of a horizontal tube furnace. We heated it for 1 h at 450 °C and then let it cooled down naturally to room temperature. Finally, ZnS/CdS/CdS/TiO₂ NTs/a Ti metal sheet photoanode electrode was obtained.

**Electrolyte Solution.** Photocurrent-electrochemical process was carried out in a solution containing 0.35 M Na₂SO₃ and 0.24 M Na₂S in DI water where the polysulfide electrolyte was used. We used a three-electrode configuration consisting of the as-prepared sample photoanode electrode as a working electrode (active area, 0.13 cm²), a platinum mesh as a counter electrode, and a saturated Ag/AgCl electrode as a reference electrode.

**Characterization and Measurement of the Materials.** The anodization current with time was automatically monitored using a digital multimeter (34401A, HP) interfaced with a notebook computer. The surface morphologies of the samples were characterized by a field-emission scanning electron microscope (Carl Zeiss, SUPRA 55VP). The top and side view measurements to observe the crystallinity of the sample were made at a 300 kV high-resolution transmission electron microscope (JEOL, JEM-3000F). Analytical TEM (FEI, Tecnai F20) operated at 200 kV was used to observe the arrangement of TiO₂ nanotubes. The absorption spectra were obtained by a diffuse reflectance UV-Vis spectrophotometer (cary 5000, varian). The crystal structure patterns were obtained using a monochromatic Cu Kα radiation (λ = 1.54 Å) in the 2θ angle range of 20° to 80° with X-ray diffractometer (D8-Advance, Bruker). The J-V curves were obtained with a solar simulator (Oriel 91160) at intensity of 100 mW/cm² (equivalent to one sun at AM1.5 filter) and a potentiostat (Potentiostat/Galvanostat, EG&G 2634A). The prepared electrodes were anodically polarized from 1.0 V to −1.0 V at a scan rate of 5 mV/s.

**Results and Discussion**

**Morphology of the Regular Array of TiO₂ Nanotubes Surface-treated with TiCl₄ at Various Concentrations.** The regular array of TiO₂ nanotubes with a high crystallinity and free of surface defects are desirable as the photoanode electrode for the solar energy conversion. The surface treatment of the regular array of TiO₂ nanotubes with TiCl₄ was known to induce new TiO₂ growth on the preexisting metal oxide so that surface defective oxide tubes were cured. The surfaces of TiO₂ nanotubes were treated with TiCl₄ and then thermally annealed.

As shown in Figure 2(a) and (b), the channel walls of TiO₂ nanotubes treated with TiCl₄ were smoother and more crystalline than those untreated. The optimal length of TiO₂ nanotubes for solar energy conversion is known to be 20µm with the consideration of efficient collection of electrons without any absorption loss. Thus, we grew TiO₂ nanotubes of about 20 µm in length. The HR-TEM images of TiO₂ nanotubes untreated with TiCl₄ or treated with TiCl₄ together with SEAD (selected area electron diffraction) patterns are shown in Figure 2(c) and (d), respectively. X-ray diffraction patterns of as-prepared TiO₂ nanotubes and TiO₂ nanotubes treated with 5 mM TiCl₄ were given in Figure 2(e). Some particulates on the surface of TiO₂ nanotubes treated with TiCl₄ were noticeable. Some TiO₂ particles were grown onto it. With these data we identified that it was anatase phase (JCPDS Card no. 21-1272; a = 3.785 Å, c = 9.514 Å). From the SEAD patterns, we knew a lot of newly grown polycrystalline TiO₂ particles on the surface of pre-existing TiO₂ nanotubes. The structural defects and cracks in TiO₂ nanotubes which disrupt the flow of electrons are removed by the surface passivation with TiCl₄. The newly grown polycrystalline TiO₂ through surface passivation with TiCl₄ were formed next to the preexisting TiO₂ nanotubes as shown in Figure 2.
coupling TiO$_2$ nanotubes with a low band gap semiconductor material such as CdS, CdSSe was made. The photoactivity of TiO$_2$ NTs sensitized with CdS has been reported to be enhanced.\(^{36}\) Adjusting the composition variable $x$ in ternary Cd$_x$S$_{1-x}$Se$_1$ alloy semiconductor, we tune its band gap to the desirable value with the reference to Vegard's law.\(^{39,41}\) We varied the composition (i.e., $x$ value) in Cd$_x$S$_{1-x}$Se$_1$ alloy (0 $\leq$ $x$ $\leq$ 1) in terms of the molar S/Se ratio of the precursors and we obtained ternary CdSSe QDs of a desired band gap.\(^{15,40,41}\) Another good property with CdS and ternary CdSSe alloy was of roughly identical onset potential $\approx$ 0.67 V vs Ag/AgCl. We prepared 6 different ternary Cd (Y)S (X)Se alloy [(Y, X): (0.2 M, 0.1 M), (0.2 M, 0.2 M), (0.2 M, 0.3 M), (0.1 M, 0.2 M), (0.2 M, 0.2 M), (0.3 M, 0.2 M)] anchored on the channel wall of TiO$_2$ nanotubes (length, L = $\approx$ 20 $\mu$m) grown on a flat Ti sheet by controlling the molar S/Se ratio of precursors. The results with 6 different ternary Cd (Y)S (X)Se alloy were given in Figure 3 and Figure 5.

In order to produce Cd (Y)S (X)Se/TiO$_2$ NTs, we dipped TiO$_2$ NTs treated with TiCl$_4$ into each solution containing each precursor ion for the 3 minutes of reaction time and repeated 3 SILAR cycles. The UV-Vis absorption diffused reflectance spectra of CdS/TiO$_2$ NTs, CdSe/TiO$_2$ NTs, and Cd (Y)S (X)Se/TiO$_2$ NTs photoanode electrodes were given in Figure 3. The absorption edges of CdS/TiO$_2$ NTs and CdSe/TiO$_2$ NTs photoanode electrodes appear at 2.48 eV (500 nm) and 1.72 eV (718 nm), respectively. Those of Cd (Y)S (X)Se/TiO$_2$ NTs photoanode electrodes with Y = 0.2 M, X = 0.1, 0.2, 0.3 M are 1.98 eV (626 nm), 1.92 eV (645 nm), and 1.88 eV (658 nm), respectively.

With Se-richer than S in ternary CdSSe alloy as in Cd (0.2 M)S (0.3 M)Se, its absorption edge gets more red-shifted. So we were able to tune the band gap via composition variation in the unit of molar concentration (M).\(^{42}\) The TEM images in Figure 4 reveal the rough surface morphology of CdSSe/TiO$_2$ NTs photoelectrode (length = $\approx$ 20 $\mu$m) on a flat Ti sheet. The ternary CdSSe alloy was overcoated all over the TiO$_2$ NTs and was not evenly distributed over the surface. The CdSSe QDs on TiO$_2$ NTs were crystallized and had similar structures of the bulk CdS and CdSe (JCPDS Card no. 41-1049; $a$ = 4.141 Å, $c$ = 6.720 Å; JCPDS Card no. 75-5681; $a$ = 4.298 Å, $c$ = 7.008 Å, respectively). The elemental mapping profile across the Cd (Y = 0.2 M)S (X = 0.3 M)Se/TiO$_2$ NTs photoanode electrode confirms that the photoanode electrode indeed consists of CdSSe QDs on TiO$_2$ NTs. The element analysis for multi-elements Ti, O, Cd, S, and Se was shown in Figure 4(c) to (h). Ti and O elements were located over the whole part of the TiO$_2$ nanotubes whereas Cd, S, and Se elements were located randomly on the nanotubes and existed in much lower quantities.

To find the optimized ternary composition, we measured current-voltage characteristics of Cd (Y)S (X)Se/TiO$_2$ NTs treated with TiCl$_4$ photoanode electrode with various compositions. Figure 5(a) and (b) are current-voltage characteristics of Cd (Y = 0.1, 0.2, 0.3 M)S (X = 0.2 M)Se/TiO$_2$ NTs treated with TiCl$_4$ photoanode electrode and Cd (Y = 0.2 M)S (X = 0.1, 0.2, 0.3 M)Se/TiO$_2$ NTs treated with TiCl$_4$ photoanode electrode, respectively. Table 1 lists electrochemical parameters of the photoanode with ternary Cd (Y)S (X)Se/TiO$_2$ NTs.

Figure 3. (a) UV-Vis absorption diffuse reflectance spectra of CdS, Cd (0.2 M)S (X = 0.1, 0.2, and 0.3 M), or CdSe sensitized TiO$_2$ NTs photoanode electrode, (b) Estimated band gap using Vegard's law at different composition (X).

Figure 4. (a) TEM images of QDs-TiO$_2$ NTs (b) HR-TEM image and SAED patterns of CdSSe QD on TiO$_2$ NTs photoanode electrode, and (c)-(h) The elemental mapping of CdSSe QDs on TiO$_2$ NTs photoanode electrode by STEM image scan.
alloy deposited on the TiO$_2$ nanotubes. It turned out that the Cd (Y = 0.2 M)S (X = 0.3 M)Se/TiO$_2$ NTs photoanode electrode was found to show the highest efficiency among them. Thus the optimized composition of ternary Cd (Y)S (X)Se alloy was found to be Cd (0.2 M)S (0.3 M)Se. In Figure 5(a) and (b), applied potential was measured with respect to an Ag/AgCl reference electrode.

Several groups examined the co-sensitization of CdS and CdSe or CdTe nanocrystals on TiO$_2$ or ZnO nanorods. The stacked layers of CdS and CdSe were made on the TiO$_2$ or ZnO nanorods by chemical evaporation method. In order to achieve efficient QD-sensitized TiO$_2$ NTs photoanode electrode, the band arrangement of QDs-TiO$_2$ NTs should be a ladder-like energy structure suitable for carrier transfer in the electrolyte solution. With the optimal Cd (0.2 M)S (0.3 M)Se alloy composition, we fabricated the photoanode electrode in which Cd (0.2 M)S (0.3 M)Se layer was located between CdS and ZnS layers. As shown in Figure 5(b), as Se content increases in Cd (Y)S (X)Se (Y = 0.2 M; X = 0.1, 0.2, 0.3 M; Y = 0.1, 0.2, 0.3 M, X = 0.2 M) alloy deposited on the channel wall of TiO$_2$ nanotubes under light illumination.

Table 1. Electrochemical parameters of ternary Cd (Y)S (X)Se (Y = 0.2 M; X = 0.1, 0.2, 0.3 M; Y = 0.1, 0.2, 0.3 M, X = 0.2 M) alloy deposited on the channel wall of TiO$_2$ nanotubes under light illumination.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd (0.2 M)S (0.1 M)Se</td>
<td>0.643</td>
<td>9.24</td>
<td>0.385</td>
<td>2.29</td>
</tr>
<tr>
<td>Cd (0.2 M)S (0.2 M)Se</td>
<td>0.594</td>
<td>11.5</td>
<td>0.378</td>
<td>2.59</td>
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<tr>
<td>Cd (0.2 M)S (0.3 M)Se</td>
<td>0.671</td>
<td>16.5</td>
<td>0.360</td>
<td>3.98</td>
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<tr>
<td>Cd (0.1 M)S (0.2 M)Se</td>
<td>0.624</td>
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<td>0.412</td>
<td>3.53</td>
</tr>
<tr>
<td>Cd (0.2 M)S (0.2 M)Se</td>
<td>0.594</td>
<td>11.5</td>
<td>0.378</td>
<td>2.59</td>
</tr>
<tr>
<td>Cd (0.2 M)S (0.3 M)Se</td>
<td>0.643</td>
<td>9.24</td>
<td>0.385</td>
<td>2.29</td>
</tr>
<tr>
<td>Cd (0.3 M)S (0.2 M)Se</td>
<td>0.661</td>
<td>12.6</td>
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<td>3.43</td>
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Figure 5. Current-Voltage characteristics of Cd (Y)S (X)Se/(TiO$_2$ NTs treated with TiCl$_4$) photoelectrode, (a) Cd (Y = 0.1, 0.2, 0.3 M)S (X = 0.2 M)Se/(TiO$_2$ NTs treated with TiCl$_4$) photoelectrode. (b) Cd (Y = 0.2 M)S (X = 0.1, 0.2, 0.3 M)Se/(TiO$_2$ NTs treated with TiCl$_4$) photoanode electrode.

Figure 6. Current-Voltage characteristics (Top.) FESEM images (Bottom) of the CdS/CdSSe/CdSe sensitized TiO$_2$ NTs photoanode electrode, here, the deposition sequence of QDs on TiO$_2$ NTs is CdS, CdSSe, CdSe(n)) with CdSe layer made through the # of SILAR cycles (n): (a) CdS/CdSSe/CdSe3 (n = 3), (b) CdS/CdSSe/CdSe5 (n = 5), and (c) CdS/CdSSe/CdSe8 (n = 8).
of QD layers on the TiO$_2$ NTs were performed and their I-V characteristics were measured to find out the best solar energy conversion photoanode electrodes.

As shown in Figure 7, a CdSSe/CdS sensitized TiO$_2$ NTs photoanode electrode was more effective than CdSe/CdS sensitized TiO$_2$ NTs photoanode electrode. Furthermore, the final deposition of ZnS as a photocorrosion protecting layer on CdSSe/CdS/TiO$_2$ NTs photoanode electrode (the deposition sequence was from the right to the left) was beneficial. The results altogether from Figures 5 to 7 indicate that Cd (0.2 M)S (0.3 M)Se is an optimal composition for a ternary CdSSe alloy and that ZnS/CdSSe/CdS (The deposition sequence on TiO$_2$ NTs was from the right to the left.) was appropriate QD layers. As summarized in Table 2, the PCE of the ZnS/CdSSe/CdS (CdS or CdSe/CdS quantum dots was PCE = 3.49% and 2.81% under the illumination at 100 mW/cm$^2$, respectively. To protect the photocorrosion of our solar cell fabricated with the regular array of TiO$_2$ nanotubes anchored with ZnS/CdSSe/CdS quantum dots was prepared by the following steps: 1) the formation of the regular array of TiO$_2$ nanotubes on a Ti metal sheet, 2) the surface treatment of the TiO$_2$ nanotubes with TiCl$_4$ for the removal of surface defect sites on NTs, 3) the sequential deposition of CdS, CdSSe, and ZnS, in situ, onto the channel walls of TiO$_2$ nanotubes by the successive ionic layer adsorption and reaction (SILAR) procedure. The tuning of the band gap of CdS was done in terms of controlling the composition of Cd, S, or Se during the SILAR procedure. In this way, a ladder-like energy structure suitable for carrier transfer was attained from ZnS/CdSSe/CdS through TiO$_2$ nanotubes to a Ti metal sheet. The more photoinduced charge carriers were generated and transferred from the anchored quantum dots to the TiO$_2$ nanotubes and thus, the solar energy conversion efficiency was enhanced. The power conversion efficiency (PCE) of our solar cell fabricated with the regular array of TiO$_2$ nanotubes anchored with CdSSe/CdS or CdSe/CdS quantum dots was PCE = 3.49% and 2.81% under the illumination at 100 mW/cm$^2$, respectively. To protect the photocorrosion of our solar cell photoanode electrode from the electrolyte and to suppress the carrier recombination, ZnS was introduced onto CdSSe/CdS. The power conversion efficiency (PCE) of our solar cell with the structure of a photoanode electrode, (ZnS/CdSSe/CdS/TiO$_2$ NTs/Ti metal sheet) was 4.67% under the illumination at 100 mW/cm$^2$.

Table 2. Electrochemical parameters of CdS, CdSe, CdS/CdSe, CdS/CdSSe, and CdS/CdSSe/ZnS sensitized TiO$_2$ NTs photoanode electrodes under light illumination. Here the deposition sequence of CdS/CdSe, CdSe, and CdS/CdSSe/ZnS on TiO$_2$ NTs/Ti photoanode electrodes are (CdS→CdSe), (CdS→CdSe), and (CdS→CdSSe→ZnS), respectively.

<table>
<thead>
<tr>
<th>Photoanode electrode</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
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<td>0.456</td>
<td>1.96</td>
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<tr>
<td>CdSe</td>
<td>0.547</td>
<td>14.6</td>
<td>0.286</td>
<td>2.28</td>
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<tr>
<td>CdS/CdSe</td>
<td>0.586</td>
<td>16.2</td>
<td>0.295</td>
<td>2.81</td>
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<tr>
<td>CdS/CdSSe</td>
<td>0.606</td>
<td>17.3</td>
<td>0.333</td>
<td>3.49</td>
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<tr>
<td>CdS/CdSSe/ZnS</td>
<td>0.707</td>
<td>16.0</td>
<td>0.413</td>
<td>4.67</td>
</tr>
</tbody>
</table>

Figure 7. Current-Voltage characteristics of CdS, CdSe, CdS/CdSe, CdS/CdSSe, and CdS/CdSSe/ZnS on TiO$_2$ NTs/Ti photoanode electrodes under light illumination. Here the deposition sequence of QDs on NTs is CdS, CdS/CdSe, CdS/CdSSe, and CdS/CdSSe/ZnS (here, the deposition sequence of QDs on NTs is CdS, CdS/CdSe, and ZnS.) sensitized TiO$_2$ NTs photoanode electrodes.

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