Photoelectric performance of TiO₂ nanotube array photoelectrodes sensitized with CdS_{0.54}Se_{0.46} quantum dots

Ruchi Gakhar^a, York R. Smith^b, Mano Misra^b and Dev Chidambaram^{a*}

^aMaterials Science and Engineering, University of Nevada, Reno, NV, USA

^bDepartment of Metallurgical Engineering, University of Utah, Salt Lake City, UT, USA

Abstract

The photoelectrochemical performance of CdSSe quantum dots tethered to a framework of vertically oriented titania (TiO₂) nanotubes was studied. The TiO₂/CdSSe framework demonstrated improved charge transfer due to its unique band edge structure, thus validating the higher photocurrent generation. The composite film led to an 11-fold enhancement in comparison to the control TiO₂ film, implying that the ternary quantum dots and the nanotubular structure of TiO₂ work in tandem to promote charge separation and favorably impact photoelectrochemical performance. Further, the results also suggest that structural and optoelectronic properties of TiO₂ films are significantly affected by the thicknesses of the CdSSe layer.

Keywords: CdS_xSe_{1-x} quantum dots, TiO₂ nanotubes, anodization, SILAR, photoelectrochemical

Introduction

Semiconductor Quantum Dots (QDs) with tunable band gaps offer a solution to the problems associated with the use of conventional organic dyes in solar devices by harvesting a wider portion of the solar spectrum [1, 2]. Quantum dots show high emission quantum yield, narrow and symmetric emission peaks, and tunable, size-dependent band gaps [3]. In addition, the high photostability and chemical stability of QDs compared to organic dyes enables their use in the design of photovoltaic devices that require long exposure times. It has been demonstrated that quantum confinement greatly affects the width of the optical band gap and associated spectral features in semiconductor nanocrystals. Spatial confinement results in multi-exciton generation (MEG), also referred as Inverse Auger effect, which largely affects the power conversion efficiency of quantum dots-sensitized solar cells (QDSSCs) [4, 5]. [ENREF 3](#) However, the performance of QDSSCs is still lower than that of their dye-sensitized solar cells (DSSCs) counterpart [3], inspite of the fact that the theoretical maximum conversion efficiency of QDSSCs (44%) is considerably higher than that of DSSCs (31%) [6]. Therefore, attempts are being made to improve the efficiency of QDSSCs.

The most widely studied photoanode materials are oxide semiconductors, particularly TiO_2 , since it is stable under visible light illumination. Until recently, the sensitization of TiO_2 with semiconductor QDs has been investigated mainly with titania nanoparticulate films. Such films, however, suffer from structural disorders due to grain boundaries, which impede the charge separation efficiency and charge transport through the material. These drawbacks render TiO_2 particulate films less efficient as photoanodes while, TiO_2 nanotubes arrays (NTA), with their unique properties, offer improved charge transfer characteristics. Titania nanotube arrays have advantages over particulate films such as cheap and facile fabrication technique, high

surface area to volume ratio, tunable dimensions (pore size and tube length), and the 1D architecture furnishes less impeded pathways for electron transfer and transport [7, 8].

As sensitizers, cadmium chalcogenide (CdX , $\text{X} = \text{S, Se or Te}$) QDs have attracted considerable attention in QDSSC research over the last few years [9-20]. It has been noted that CdX absorb photons efficiently because these have a bulk material band gap above 1.3 eV; band gaps for CdS , CdSe and CdTe are 2.25 eV, 1.73 eV, and 1.49 eV, respectively. By altering the size of the QDs, the band gap can be tuned further to match a desired band gap range. While considerable studies have been conducted on co-sensitization of TiO_2 with CdS and CdSe [20-30] [ENREF 9](#), only few studies can be found on CdSSe/TiO_2 NTA heterostructure [31-33]. Chong *et al.* studied CdSSe quantum dots attached to TiO_2 nanobelts synthesized by hydrothermal route and found remarkable enhancement in photocurrent with good reproducibility for sensitized samples [31]. Luo *et al.* synthesized photoelectrodes with nanorods of CdS , CdSe , and CdSeS deposited onto TiO_2 nanorod arrays and found that the $\text{TiO}_2/\text{CdSeS}$ heterostructure was the most stable [32]. Park *et al.* demonstrated the fabrication of regular arrays of TiO_2 nanotubes anchored with ZnS/CdSSe/CdS quantum dots by the SILAR method, which exhibited a power conversion efficiency of 4.67% in a QDSSC configuration [33].

The current study presents a simple, yet efficient, route for the synthesis of TiO_2 NTA heterostructure in conjunction with quantum sized CdSSe clusters. A balance between energetics and kinetics of the system has been realized by means of alignment of the conduction band edges, where, the conduction band (CB) of CdSSe lies above the CB of TiO_2 . The morphology and crystallinity of the CdSSe layer was characterized and correlated with photoelectrochemical activity.

Experimental

Self-organized TiO₂ nanotube arrays were synthesized by anodic oxidation of an ultrasonically cleaned Ti foil. The anodization was carried out in an organic electrolyte containing 0.5 wt.% NH₄F at 40 V (DC) for 1 hour. The details of the experiment can be found elsewhere [34, 35]. [ENREF 1](#) After anodization, the films were rinsed with isopropyl alcohol to remove any particulates on top of the film. The film was then annealed in air at 450 °C for 2 hours.

CdSSe nanocrystals were deposited on TiO₂ NTAs using the Successive Ionic Layer Adsorption and Reaction (SILAR) technique. The solvent used for precursor solution was 50/50 vol.% ethanol/H₂O and deposition time was 1 minute. The deposition was carried out under ambient temperature and pressure conditions. The samples were prepared with 5, 7 and 9 cycles of deposition, where one SILAR cycle comprised of immersion of annealed TiO₂ NTA film in 0.02M Cd(CH₃CO₂)₂ solution for one minute, followed by rinsing in ethanol/H₂O solvent and subsequent immersion in 0.02 M Na₂S solution, and finally in a Na₂Se solution (generated *in-situ* by the reduction of Se metal with 0.04 M NaBH₄). The films were then annealed at various temperatures under N₂ atmosphere for 1 hour to analyze the variation in photoelectrochemical properties of TiO₂ NTA with post-synthesis annealing temperature.

Structural and Optical Characterization

UV-visible absorption spectra of prepared photoelectrodes were obtained with a Shimadzu UV-2401PC UV-Vis diffuse reflectance spectrophotometer. BaSO₄ was used as the reflectance standard in the wavelength range of 200-800 nm. The surface morphologies of TiO₂ NTAs and CdSSe-deposited TiO₂ NTA films were examined by a Hitachi S-4800 scanning electron microscope equipped with an energy dispersive spectrometer (Oxford EDS system).

Transmission electron micrographs were recorded using a JEOL analytical field emission transmission electron microscope (TEM) model JEM 2100F equipped with Oxford energy dispersive spectrometer (EDS). The acceleration voltage set to 200 kV during analysis. The crystalline phases were investigated by X-ray diffraction (XRD) carried out using a Rigaku Miniflex XRD (CuK = 1.54059 Å) from $2\theta = 20$ to 80 degrees with a step size of 0.01 degrees and dwell time of 0.5 degrees/min. The XRD data was analyzed using Rigaku PDXL2 analysis software and indexed to standard pdf cards. Surface speciation was studied using a PHI 5600 model X-ray photoelectron spectrometer (XPS) with a monochromatic AlK (1486.6 eV) excitation source. The spectrometer was calibrated to the Ag 3d_{5/2} line at 368.27±0.05 eV. The XPS spectra were recorded at 14kV and 300W, with an analysis area of 800µm². The survey spectra were acquired at pass energy of 29.35 eV and narrow scans at 23.95 eV. Charging effects were corrected using the adventitious C 1s line at 284.6 eV. After 5 point smoothing of data, the peaks were fitted using SDP v4.6 Gaussian fitting software from XPS International. The photoelectrochemical (PEC) responses of the samples were measured in a conventional three-electrode system with CdSSe-deposited TiO₂ NTAs with surface area of 2.5 cm² as the working electrodes, coiled platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode in aqueous solution containing 0.35 M Na₂SO₃ and 0.25 M Na₂S. The measurements were conducted under ambient conditions in a custom-made quartz window cell with a Gamry® Reference 600 potentiostat. A 300 W Xe lamp solar simulator supplied by Newport served as incident light source. The visible light intensity through standard AM 1.5G filter was tuned to 100 mW/cm² measured using a Newport Thermopile Sensor 919P-003-10. Mott-Schottky (M-S) analysis were conducted using photoanodes sensitized with 9 cycles of deposition (unannealed film and films annealed at 300°C and 400°C) under dark conditions in the

aqueous electrolyte of 0.25 M Na₂S and 0.35 M Na₂SO₃. Analysis was carried out by polarizing from -0.8 V to -1.2 V (vs. Ag/AgCl) at 1000 Hz and 10 mV AC potential.

Results and Discussion

Optical absorption Study

The UV-visible light absorbance properties of TiO₂ NTA/CdSSe(*n*) photoanodes are depicted in Fig. 1. The effect of the number of deposition layers (*n* =5, 7 and 9 cycles) and post-synthesis annealing temperature (200°C, 300°C and 400°C) on the optical performance of the modified electrodes was studied and compared with unsensitized TiO₂ NTAs (Fig. 1). Plain TiO₂ NTA film shows an absorption edge at 380 nm, corresponding to the bandgap of the anatase phase of titania [36, 37]. An additional feature (broad peak) appearing around ~480 nm, is mainly due to trapped charge carriers within nanotubes [38, 39]. [ENREF 25](#) Transient absorption studies showed that the trapped holes absorb at wavelengths of 430 nm or shorter while trapped electrons show a prominent absorption peak around 650 nm. Superposition of spectra from trapped electrons and holes may be responsible for absorption at wavelengths around 480 nm [39]. After coupling with CdSSe QDs, the high absorption of CdSSe nanoclusters in the visible region overlaps the response due to TiO₂ and instead a broad response with absorption onset around 650 nm (for 5 cycles of deposition) was observed. With increasing deposition cycles (to 7 and 9 cycles), the absorption onset was observed to red-shift due to the size quantization effect. Annealing under N₂ atmosphere also tends to affect the optical performance of films. With annealing at 300°C, the absorption intensity increased and absorption edge experienced red-shift. Moreover, with annealing at higher temperatures (400°C), the absorption onset further shifted to longer wavelengths in all cases, but the absorption intensity decreased for films with 9 deposition

cycles, possibly due to the aggregation of nanocrystals. This improved visible light absorption of the composite films might be attributed to the band gap range of CdSSe QDs (1.6 to 2.2 eV), and demonstrates the possibility of improved photoactivity of the TiO₂ NTA/CdSSe hybrid photoanode.

Phase Analysis

The XRD profiles (Fig. 2) display the morphology of TiO₂NTA/CdSSe (9) film before and after thermal annealing (at 400 °C) under N₂ atmosphere. The XRD diffraction profile of as-deposited TiO₂ NTA/CdSSe(9) electrode reveals the diffraction patterns similar to the anodized film and peaks can be indexed for underlying Ti metal (JCPDS file no.: 01-089-5009) and TiO₂ anatase phase (JCPDS file no.: 01-073-1764) layer grown on the top. These peaks are labeled as '1' and '2' for Ti substrate and anatase TiO₂, respectively. However, after thermal annealing under N₂, the film shows the presence of additional diffraction peaks, which can be attributed to CdS_{0.54}Se_{0.46} phase (JCPDS file no.: 01-089-3682), labeled as '3', shifted to a lower angle (lower 2θ value). According to Bragg's law, such downshift of peak position indicates an increase in lattice parameter [40, 41]. These results demonstrate the formation of CdS_xSe_{1-x} alloy with a particular stoichiometry of x= 0.54. Another interesting observation is that the alloy formed only after annealing, since there are no peaks corresponding to CdSSe phase in unannealed films. This indicates that the species are only physically adsorbed during SILAR deposition and they tend to form a crystalline phase during thermal annealing.

Microscopic Analysis

Figs. 3 and 4 depict the surface and cross-sectional images to highlight the morphological change of the TiO₂ nanotube array films before and after CdSSe deposition. Fig. 3a shows the formation

of regularly arranged nanotubes grown perpendicular to the Ti foil substrate. From the SEM images, the wall thickness and mean inner pore diameter were estimated to be approximately 20nm and 70nm, respectively. The open structure of the nanotubes provides superior access for sensitizer material as well as promotes unidirectional charge transport due to the one-dimensional feature of the nanotubes. After QD deposition, the walls of NTs became rougher due to being decorated with QDs Figs. 3 (b-d) and 4b). The top view images of CdSSe-sensitized NTs with varying number of deposition cycles are shown in Figs. 3b-d. The images clearly indicate the increased QD loading on the NTs with increasing deposition cycles. With annealing, the QDs aggregate to form nanocrystals and small clusters. It can be seen from Fig. 4b that the QDs cover both the outer and inner surfaces of NT arrays, owing to the decreased resistance to mass transfer offered by the inner surface. TEM images of sensitized TiO₂ NTA/CdSSe film at two different magnifications are shown in Fig. 5. The images clearly depict the formation of randomly distributed spherical quantum dots, with average diameter size of 5 nm on the surface of the sensitized film.

XPS Analysis

The core-level scans of Cd 3d, Se 3d, Se 3p and S 2p regions are provided in Fig. 6. The peak fitting parameters are provided in Table I. The sharp doublet at binding energies of 404.9 and 411.6 eV (Fig. 6a) can be attributed to Cd 3d_{5/2} and Cd 3d_{3/2} peaks, respectively [42]. A spin-orbit doublet (Fig. 6b) with components at 53.5 eV and 54.2 eV indicates the presence of Se²⁻ species. The observed peaks may be ascribed to Se 3d_{5/2} (main and second contribution) and are highly sensitive to the chemical preparation techniques [43]. The broad XPS peak around 160 eV (Fig. 6c) comprises of S 2p and Se 3p peaks. Peak fitting of the peak showed the presence of four signals at 160.3, 166.4, 161.5 and 162.7 eV. The first two components correspond to Se 3p (Se

3p_{3/2} and Se 3p_{1/2}, respectively) and other two components correspond to S 2p (S 2p_{3/2} and S 2p_{1/2}, respectively). These peaks are in accordance with earlier studies reported for CdSSe and thus, evidently support the formation of CdSSe alloy [44].

Photoelectrochemical measurements

Photoexcitation of the TiO₂ NTA-CdSSe photoanode with subsequent charge transport mechanism can be summarized by the following reactions [45] :

where, equations 1 and 2 are the photoexcitation and recombination events, equation 3 is the electron transfer from CdSSe to TiO₂, and equation 4 is the hole transfer from CdSSe to the redox couple (Red) resulting in oxidized products (Ox). The electrons transferred to titania via equation 3 are collected and result in the generation of anodic current. Scavenging of accumulated holes in the valance band of CdSSe is important to maintain stability of the absorber layer (eqn. 4). If there is extensive accumulation of holes, CdSSe will begin to oxidize and result in diminishing photoelectrochemical performance over time. Sacrificial electrolytes such as sulfides are used to help stabilize chalcogenide sensitizers as they have suitable redox potentials. In this study, the electrolyte used consists of Na₂S and Na₂SO₃. The Na₂S acts as a hole scavenger and is oxidized to prevent the corrosion (eqn. 4). Hole scavenging can also occur by eqns. 5, 6, and 8. To ensure hydrogen production at the cathode, Na₂SO₃ is added to help reduce disulfides back to sulfides, which has been demonstrated to be beneficial to improve

photocurrent density and hydrogen production in previous studies [46, 47]. Also, the SO_3^{2-} ions mainly yield thiosulfate ions [48]:

In order to investigate the potential application of the CdSSe-sensitized TiO_2 NTA photoelectrodes, the photoelectrochemical performance of $\text{TiO}_2\text{NTA}/\text{CdSSe}$ photoelectrodes under AM 1.5G visible light irradiation was obtained and results are illustrated in Fig. 7. For comparison, photoresponse of unmodified TiO_2 NTA photoelectrode has also been shown along with the composite photoelectrodes. As observed, unmodified TiO_2 NTA showed a photocurrent density of $\sim 1.4 \text{ mA}/\text{cm}^2$ at 0.4 V Vs SCE. Sensitization with CdSSe was found to led to a considerable increase in photoactivity in all cases (Table II). For the film with 5 cycles of deposition, a photocurrent density of $2.41 \text{ mA}/\text{cm}^2$ at 0.4 V Vs SCE ($\sim 72\%$ increase compared to unmodified TiO_2 NTA film) was observed. Post deposition annealing also led to a profound change in the photocurrent density. Films with 5 cycles of deposition annealed at 300°C , resulted in $4.62 \text{ mA}/\text{cm}^2$ (at 0.4 V Vs SCE) of photocurrent density. Annealing the films at 400°C was found to result in an even higher photocurrent density of $5.43 \text{ mA}/\text{cm}^2$ (at 0.4 V Vs SCE). This increase can be correlated with the increase in crystalline nature, as inferred from XRD, that results in improved current transport and light harvesting ability [49].

The composite films with more deposition cycles (7 and 9 cycles) was found to improve photocurrent density due to increased QD loading, as observed in the SEM images. The enhancement of photocurrent density with more QD loading can be associated with the increase in absorption as observed in Fig. 1. Similar results have been reported earlier [34, 35, 50]. The maximum current obtained in this study was recorded for film sensitized with 9 cycles of deposition and annealed at 400°C; this film produced a photocurrent density of 15.58 mA/cm² (at 0.4 V Vs SCE), which was ~11-fold increase compared to unmodified TiO₂ NTA film. Further increase in the number of SILAR cycles (greater than nine) resulted in a decrease in the photocurrent, which can be attributed to the aggregated nanocrystals that act as recombination centers for photoinduced charge carriers [37, 51, 52]. [ENREF_12](#) These results clearly indicate that CdSSe QDs contribute significantly to the improvement in charge transfer and photoactivity of TiO₂ based electrodes. The photocurrent density achieved in the current study is higher than the values obtained for CdS/CdSe-sensitized TiO₂ based systems studied previously [31, 32, 49, 50, 53-57].

The transient photocurrent responses of TiO₂, and CdSSe/TiO₂ NTA photoelectrodes were recorded under chopped light illumination and are shown in Fig. 8. The initial photocurrent spike upon illumination signifies the separation of plasmon-induced electron-hole pairs at the semiconductor-electrolyte interface. Followed by the spike, photocurrent decreases until it attains a stable value. This decay in photocurrent density can be attributed to recombination processes [58]. The small dark current for CdSSe/TiO₂ photoelectrodes observed from the i-t curves of the films indicates that CdSSe/TiO₂ films possess a superior interfacial structure that inhibits the recombination of the injected electrons from TiO₂ to the electrolyte at the interface, and therefore, higher conversion efficiency can be achieved. The results demonstrate that in addition

to improved light absorption, the CdSSe-TiO₂ heterojunction facilitates charge separation at the interface.

Mott-Schottky (M-S) analysis [59] is a useful technique to examine electrode/electrolyte interfacial electronic properties. Fig. 9 shows the M-S data obtained for the photoanodes sensitized with 9 cycles of deposition (unannealed film and films annealed at 300°C and 400°C) under dark conditions in the aqueous electrolyte of 0.25 M Na₂S and 0.35 M Na₂SO₃.

Based on the well-documented theory of semiconductor/electrolyte interfacial capacitance, the electronic properties in terms of charge carrier density (N_A) and flat-band potential (E_{FB}) can be obtained from the Mott-Schottky equation [60]:

$$\frac{1}{C^2} = \frac{2}{e\epsilon\epsilon_0 N_A} \left(-\Delta\phi - \frac{k_B T}{e} \right) \quad (11)$$

$$-\Delta\phi = E - E_{FB} \quad (12)$$

where, C is the capacitance, e is the elementary electronic charge (1.6×10^{-19} C), ϵ_0 is the permittivity in vacuum (8.85×10^{-14} F/cm), ϵ is the dielectric constant, k_B is the Boltzmann constant, T is the temperature (298 K), and E is the applied bias. The linear portion of the $1/C^2$ vs E plots is fit within the potential domain in which the samples behave as capacitors. From this slope (m), N_A can be determined by,

$$N_A = \frac{2}{e\epsilon\epsilon_0 m} \quad (13)$$

and the intercept of the line yields E_{FB} .

The bulk dielectric constant of CdSe is 8~9 [61]. It has been recognized that the dielectric constant for nanomaterials is less than the bulk dielectric constant due to lower

screening of confined electrons [62, 63]. Li and Li [64] developed a model to describe the effect of size, shape, and alloy composition of semiconductor nanocrystals. Dielectric constant values in the range of 4~7 were reported, depending upon size, shape, and alloy composition for $\text{CdS}_x\text{Se}_{1-x}$ and were within 5% agreement of experimental values. However, it should be noted that these values are for single particles and not agglomerates of particles, which is often the case. Agglomerates of nanoparticles can contain a large amount of defects, including vacancies and dangling bonds [65]. These defects have an effect on the space-charge distribution at the interface of the particles by giving either a positive or negative charge. When polarized these charges migrate within the field, causing a large number of dipole moments to become trapped in the defects and results in a much larger dielectric constant [65]. A value of 70 was used for titania [66], while a value of ~10,000 was used for CdSSe [65, 67] and a weighted average of the two dielectric values was used based on the EDS analysis. This led a value of ~1000, which was subsequently used for M-S analysis. The charge carrier densities for samples that underwent 9 cycle of deposition were calculated from eqns. (11)-(13) to be $1.88 \times 10^{21} \text{ cm}^{-3}$ (UA), $1.05 \times 10^{21} \text{ cm}^{-3}$ (300°C), and $1.36 \times 10^{21} \text{ cm}^{-3}$ (400°C). The respective flat band potentials were -1.054 V, -1.002 V, and -1.055 V vs. Ag/AgCl. The relative band edge positions obtained from the M-S analysis and absorbance studies are shown in Fig. 10.

In a recent work by Chen and Wang [68], the thermodynamic redox potentials of semiconductors in aqueous solution was surveyed. Although the values obtained experimentally differ from theoretical values, it should be noted that M-S analysis typically works best for highly crystalline electrodes and discrepancies between reported E_{FB} values typically arise due to imperfections and defects in the electrode. There was also an observed frequency dependence on obtaining E_{FB} values, implying the presence of surface states.

From the M-S analysis, it was also observed that the charge carrier density decreased with annealing. Significantly larger carrier concentrations have been reported to result in thinner depletion layer leading to lower quantum efficiencies [69]. For semiconductor/liquid interfaces, photogenerated electron-hole pairs are separated by an internal electric field (i.e. band bending). Transport of holes in regions that are not depleted of majority carriers can result in significant recombination and reduced photocurrent responses. The depletion layer thickness (d_{SC}) can be estimated by the following relationship and has been plotted vs. $E - E_{FB}$ in Fig. 11 for the various samples that underwent 9 cycles of deposition:

$$d_{SC} = \sqrt{\frac{2\epsilon\epsilon_0(E - E_{FB})}{eN_A}} \quad (14)$$

We observe that the annealed samples have increased depletion width compared to the unannealed samples. To compare the depletion width, we consider half the size of the CdSSe nanocrystals (~10 nm diameter) plus half the width of the nanotube wall (~5 nm). Hence, a full depletion (~10 nm) is observed for samples annealed at 300°C, and 400°C at approximately $E - E_{FB}$ ~0.94 V and 1.2 V, respectively, whereas for the unannealed sample, a $E - E_{FB}$ ~1.7 V is required. It is interesting to note that although the 400°C sample demonstrates the highest photoelectrochemical activity, the depletion width compared to the 300°C annealed sample is not as wide and requires a larger applied potential for full depletion to occur. Moreover, the 400°C sample has a more negative E_{FB} and higher charge carrier density. The more negative E_{FB} , or higher energy conduction band position, for the 400°C annealed film is one of the possible reasons for the improved photoelectrochemical activity over other photoelectrodes in this study. Such negative potential shift of the conduction band provides the increased driving force for charge transfer from sensitizer to TiO₂ [25, 70, 71]. Similar results have been reported earlier [25, 34, 70, 71]. As discussed earlier, another contributing factor for improved PEC activity is

the higher crystallinity of CdSSe observed after annealing at 400°C (as observed from XRD results). Higher crystallinity leads to a reduction in recombination centers and therefore improve light-harvesting ability and efficient charge transport [49].

Conclusions

The CdSSe-sensitized TiO₂ photoelectrodes were synthesized using a convenient SILAR process. The influence of the thickness of the CdSSe and the annealing temperature on photoelectrochemical response was studied. Photovoltaic characteristic of TNTAs exhibit substantial improvement upon sensitization and again with the increase in CdSSe layer thickness. For film with 9 cycles of sensitization and annealed at 400°C, sensitization was found to result in a 11-fold enhancement in photocurrent. The markedly enhanced photoresponse of sensitized electrodes is a direct outcome of synergetic effects of highly ordered nanotubular TiO₂ matrix and uniformly dispersed CdSSe QDs. The crystalline nature of TiO₂ together with its nanotubular geometry provided a large surface area for fast and efficient transfer of photogenerated electrons.

Acknowledgements

The authors sincerely thank Dr. Wen-Ming Chien for technical assistance regarding XRD measurements and Kodi Summers for assistance with preparation of samples. We also thank Dr. Mojtaba Ahmadiantehrani for obtaining the TEM images. This work was funded by Department of Energy under contracts DE-FC36-06-GO86066 and DE-EE0003158.

References

- [1] L. Brus, Electronic wave functions in semiconductor clusters: experiment and theory, *J. Phys. Chem.*, 90 (1986) 2555-2560.
- [2] A.P. Alivisatos, Perspectives on the physical chemistry of semiconductor nanocrystals., *J. Phys. Chem.*, 100 (1996) 13226-13239.
- [3] H.K. Jun, M.A. Careem, A.K. Arof, Quantum dot-sensitized solar cells—perspective and recent developments: A review of Cd chalcogenide quantum dots as sensitizers, *Renewable and Sustainable Energy Reviews*, 22 (2013) 148-167.
- [4] R.D. Schaller, V.I. Klimov, High efficiency carrier multiplication in PbSe nanocrystals: implications for solar energy conversion, *Physical review letters*, 92 (2004) 186601.
- [5] A.J. Nozik, Multiple exciton generation in semiconductor quantum dots, *Chemical Physics Letters*, 457 (2008) 3-11.
- [6] H.J.Q. W. Shockley, *J. Appl. Phys*, 32 (1961) 510-519.
- [7] Z. Liu, X. Zhang, S. Nishimoto, M. Jin, D.A. Tryk, T. Murakami, A. Fujishima, Highly Ordered TiO₂ Nanotube Arrays with Controllable Length for Photoelectrocatalytic Degradation of Phenol, *The Journal of Physical Chemistry C*, 112 (2007) 253-259.
- [8] Z. Zhou, S. Yuan, J. Fan, Z. Hou, W. Zhou, Z. Du, S. Wu, CuInS₂ quantum dot-sensitized TiO₂ nanorod array photoelectrodes: synthesis and performance optimization, *Nanoscale research letters*, 7 (2012) 1-8.
- [9] D. Liu, P.V. Kamat, Photoelectrochemical behavior of thin cadmium selenide and coupled titania/cadmium selenide semiconductor films, *The Journal of Physical Chemistry*, 97 (1993) 10769-10773.
- [10] J. Chen, D. Zhao, J. Song, X. Sun, W. Deng, X. Liu, W. Lei, Directly assembled CdSe quantum dots on TiO₂ in aqueous solution by adjusting pH value for quantum dot sensitized solar cells, *Electrochemistry Communications*, 11 (2009) 2265-2267.
- [11] P. Sudhagar, J.H. Jung, S. Park, Y.-G. Lee, R. Sathyamoorthy, Y.S. Kang, H. Ahn, The performance of coupled (CdS: CdSe) quantum dot-sensitized TiO₂ nanofibrous solar cells, *Electrochemistry Communications*, 11 (2009) 2220-2224.
- [12] X.-Y. Yu, B.-X. Lei, D.-B. Kuang, C.-Y. Su, High performance and reduced charge recombination of CdSe/CdS quantum dot-sensitized solar cells, *Journal of Materials Chemistry*, 22 (2012) 12058-12063.
- [13] S. Sun, L. Gao, Y. Liu, J. Sun, Assembly of CdSe nanoparticles on graphene for low-temperature fabrication of quantum dot sensitized solar cell, *Applied Physics Letters*, 98 (2011) 093112.
- [14] Y. Lai, Z. Lin, D. Zheng, L. Chi, R. Du, C. Lin, CdSe/CdS quantum dots co-sensitized TiO₂ nanotube array photoelectrode for highly efficient solar cells, *Electrochimica Acta*, 79 (2012) 175-181.

- [15] J. Chen, W. Lei, C. Li, Y. Zhang, Y. Cui, B. Wang, W. Deng, Flexible quantum dot sensitized solar cell by electrophoretic deposition of CdSe quantum dots on ZnO nanorods, *Phys. Chem. Chem. Phys.*, 13 (2011) 13182-13184.
- [16] C.J. Raj, S. Karthick, S. Park, K. Hemalatha, S.-K. Kim, K. Prabakar, H.-J. Kim, Improved photovoltaic performance of CdSe/CdS/PbS quantum dot sensitized ZnO nanorod array solar cell, *Journal of Power Sources*, 248 (2014) 439-446.
- [17] G.-Y. Lan, Z. Yang, Y.-W. Lin, Z.-H. Lin, H.-Y. Liao, H.-T. Chang, A simple strategy for improving the energy conversion of multilayered CdTe quantum dot-sensitized solar cells, *Journal of Materials Chemistry*, 19 (2009) 2349-2355.
- [18] Y. Zhu, R. Wang, W. Zhang, H. Ge, L. Li, CdS and PbS nanoparticles co-sensitized TiO₂ nanotube arrays and their enhanced photoelectrochemical property, *Applied Surface Science*, 315 (2014) 149-153.
- [19] L. Yu, Z. Li, Y. Liu, F. Cheng, S. Sun, Enhanced photoelectrochemical performance of CdSe/Mn-CdS/TiO₂ nanorod arrays solar cell, *Applied Surface Science*, 309 (2014) 255-262.
- [20] Z. Li, L. Yu, Y. Liu, S. Sun, CdS/CdSe Quantum dots Co-sensitized TiO₂ Nanowire/Nanotube Solar Cells with Enhanced Efficiency, *Electrochimica Acta*, 129 (2014) 379-388.
- [21] G. Zhu, L. Pan, T. Xu, Z. Sun, CdS/CdSe-cosensitized TiO₂ photoanode for quantum-dot-sensitized solar cells by a microwave-assisted chemical bath deposition method, *ACS applied materials & interfaces*, 3 (2011) 3146-3151.
- [22] Y.L. Lee, Y.S. Lo, Highly Efficient Quantum-Dot-Sensitized Solar Cell Based on Co-Sensitization of CdS/CdSe, *Advanced Functional Materials*, 19 (2009) 604-609.
- [23] C.-F. Chi, S.-Y. Liao, Y.-L. Lee, The heat annealing effect on the performance of CdS/CdSe-sensitized TiO₂ photoelectrodes in photochemical hydrogen generation, *Nanotechnology*, 21 (2010) 025202.
- [24] Y.-L. Lee, C.-F. Chi, S.-Y. Liao, CdS/CdSe Co-Sensitized TiO₂ Photoelectrode for Efficient Hydrogen Generation in a Photoelectrochemical Cell[†], *Chemistry of materials*, 22 (2009) 922-927.
- [25] X.-F. Gao, W.-T. Sun, G. Ai, L.-M. Peng, Photoelectric performance of TiO₂ nanotube array photoelectrodes cosensitized with CdS/CdSe quantum dots, *Applied Physics Letters*, 96 (2010) 153104.
- [26] Q. Zhang, X. Guo, X. Huang, S. Huang, D. Li, Y. Luo, Q. Shen, T. Toyoda, Q. Meng, Highly efficient CdS/CdSe-sensitized solar cells controlled by the structural properties of compact porous TiO₂ photoelectrodes, *Physical Chemistry Chemical Physics*, 13 (2011) 4659-4667.
- [27] T. Zewdu, J.N. Clifford, J.P. Hernández, E. Palomares, Photo-induced charge transfer dynamics in efficient TiO₂/CdS/CdSe sensitized solar cells, *Energy & Environmental Science*, 4 (2011) 4633-4638.

- [28] C.-F. Chi, H.-W. Cho, H. Teng, C.-Y. Chuang, Y.-M. Chang, Y.-J. Hsu, Y.-L. Lee, Energy level alignment, electron injection, and charge recombination characteristics in CdS/CdSe cosensitized TiO₂ photoelectrode, *Applied Physics Letters*, 98 (2011) 012101.
- [29] S. Huang, Q. Zhang, X. Huang, X. Guo, M. Deng, D. Li, Y. Luo, Q. Shen, T. Toyoda, Q. Meng, Fibrous CdS/CdSe quantum dot co-sensitized solar cells based on ordered TiO₂ nanotube arrays, *Nanotechnology*, 21 (2010) 375201.
- [30] H.J. Lee, J. Bang, J. Park, S. Kim, S.-M. Park, Multilayered semiconductor (CdS/CdSe/ZnS)-sensitized TiO₂ mesoporous solar cells: all prepared by successive ionic layer adsorption and reaction processes, *Chemistry of Materials*, 22 (2010) 5636-5643.
- [31] S.V. Chong, N. Suresh, J. Xia, N. Al-Salim, H. Idriss, TiO₂ Nanobelts/CdSSe Quantum Dots Nanocomposite, *The Journal of Physical Chemistry C*, 111 (2007) 10389-10393.
- [32] J. Luo, L. Ma, T. He, C.F. Ng, S. Wang, H. Sun, H.J. Fan, TiO₂/(CdS, CdSe, CdSeS) Nanorod Heterostructures and Photoelectrochemical Properties, *The Journal of Physical Chemistry C*, 116 (2012) 11956-11963.
- [33] S. Park, Y. Seo, M.S. Kim, S. Lee, Solar energy conversion by the regular array of TiO₂ nanotubes anchored with ZnS/CdSSe/CdS quantum dots formed by sequential ionic bath deposition, *Bull. Korean Chem. Soc.*, 34 (2013) 856-862.
- [34] R. Gakhar, A. Merwin, K. Summers, S.K. Pilli, D. Chidambaram, Application of Zn_xCd_{1-x}Se-sensitized TiO₂ nanotube arrays as photoanodes for solar cells, *Journal of Materials Chemistry A*, 2 (2014) 10116–10125.
- [35] R. Gakhar, K. Summers, R. Palaniappan, S.K. Pilli, D. Chidambaram, On the sensitization of TiO₂ nanotube array photoelectrodes with Mn_xCd_ySe, *RSC Advances*, 4 (2014) 49729-49736.
- [36] W.-J. Yin, H. Tang, S.-H. Wei, M.M. Al-Jassim, J. Turner, Y. Yan, Band structure engineering of semiconductors for enhanced photoelectrochemical water splitting: The case of TiO₂, *Physical Review B*, 82 (2010) 045106.
- [37] X.-F. Gao, H.-B. Li, W.-T. Sun, Q. Chen, F.-Q. Tang, L.-M. Peng, CdTe Quantum Dots-Sensitized TiO₂ Nanotube Array Photoelectrodes, *The Journal of Physical Chemistry C*, 113 (2009) 7531-7535.
- [38] Y. Lai, L. Sun, C. Chen, C. Nie, J. Zuo, C. Lin, Optical and electrical characterization of TiO₂ nanotube arrays on titanium substrate, *Applied surface science*, 252 (2005) 1101-1106.
- [39] D.W. Bahnemann, R. Dillert, P.K.J. Robertson, *Chemical Physics of Nanostructured Semiconductors*, edited by A.I. Kokorin and D.W. Bahnemann, (VSP BV), Eindhoven, The Netherlands, 2003), Chap. 7. (2003).
- [40] Z. Li, L. Yu, Y. Liu, S. Sun, Efficient quantum dot-sensitized solar cell based on CdS_xSe_{1-x}/Mn-CdS/TiO₂ nanotube array electrode, *Electrochimica Acta*, 153 (2015) 200-209.
- [41] J. Pan, M.I.B. Utama, Q. Zhang, X. Liu, B. Peng, L.M. Wong, T.C. Sum, S. Wang, Q. Xiong, Composition-Tunable Vertically Aligned CdS_xSe_{1-x} Nanowire Arrays via van der Waals Epitaxy: Investigation of Optical Properties and Photocatalytic Behavior, *Advanced Materials*, 24 (2012) 4151-4156.

- [42] K.R. Murali, A. Austine, B. Jayasutha, D.C. Trivedi, Photoelectrochemical cells based on CdSe films brush plated on high-temperature substrates, *Solar Energy Materials and Solar Cells*, 90 (2006) 753-759.
- [43] B. Canava, J. Vigneron, A. Etcheberry, J.F. Guillemoles, D. Lincot, High resolution XPS studies of Se chemistry of a Cu(In,Ga)Se₂ surface, *Applied Surface Science*, 202 (2002) 8-14.
- [44] I. Rufus, V. Ramakrishnan, B. Viswanathan, J. Kuriacose, Surface characterization of CdS_{0.62}Se_{0.38} by X-ray photoelectron spectroscopy, *Journal of materials science letters*, 11 (1992) 252-254.
- [45] Y.R. Smith, R. Gakhar, A. Merwin, S.K. Mohanty, D. Chidambaram, M. Misra, Anodic Titania Nanotube Arrays Sensitized with Mn- or Co-Doped CdS Nanocrystals, *Electrochimica Acta*, 135 (2014) 503-512.
- [46] S. Banerjee, S.K. Mohapatra, P.P. Das, M. Misra, Synthesis of coupled semiconductor by filling 1D TiO₂ nanotubes with CdS, *Chemistry of materials*, 20 (2008) 6784-6791.
- [47] C.-F. Chi, Y.-L. Lee, H.-S. Weng, A CdS-modified TiO₂ nanocrystalline photoanode for efficient hydrogen generation by visible light, *Nanotechnology*, 19 (2008) 125704.
- [48] P. Gomathisankar, K. Hachisuka, H. Katsumata, T. Suzuki, K. Funasaka, S. Kaneco, Photocatalytic hydrogen production with CuS/ZnO from aqueous Na₂S + Na₂SO₃ solution, *International Journal of Hydrogen Energy*, 38 (2013) 8625-8630.
- [49] A. Tubtimtae, M.-W. Lee, Effects of passivation treatment on performance of CdS/CdSe quantum-dot co-sensitized solar cells, *Thin Solid Films*, 526 (2012) 225-230.
- [50] D.R. Baker, P.V. Kamat, Photosensitization of TiO₂ Nanostructures with CdS Quantum Dots: Particulate versus Tubular Support Architectures, *Advanced Functional Materials*, 19 (2009) 805-811.
- [51] J. Xue, Q. Shen, W. Liang, X. Liu, F. Yang, Photosensitization of TiO₂ nanotube arrays with CdSe nanoparticles and their photoelectrochemical performance under visible light, *Electrochimica Acta*, 97 (2013) 10-16.
- [52] H. Feng, L. Zhou, J. Li, T.T.T. Tran, N. Wang, L. Yuan, Z. Yan, Q. Cai, A photoelectrochemical immunosensor for tris(2,3-dibromopropyl) isocyanurate detection with a multiple hybrid CdTe/Au-TiO₂ nanotube arrays, *Analyst (Cambridge, U. K.)*, 138 (2013) 5726-5733.
- [53] G. Ai, W. Sun, X. Gao, Y. Zhang, L.-M. Peng, Hybrid CdSe/TiO₂ nanowire photoelectrodes: Fabrication and photoelectric performance, *Journal of Materials Chemistry*, 21 (2011) 8749-8755.
- [54] L.-W. Chong, H.-T. Chien, Y.-L. Lee, Assembly of CdSe onto mesoporous TiO₂ films induced by a self-assembled monolayer for quantum dot-sensitized solar cell applications, *Journal of Power Sources*, 195 (2010) 5109-5113.
- [55] Y.-L. Lee, B.-M. Huang, H.-T. Chien, Highly Efficient CdSe-Sensitized TiO₂ Photoelectrode for Quantum-Dot-Sensitized Solar Cell Applications, *Chemistry of Materials*, 20 (2008) 6903-6905.

- [56] Y.-L. Lee, Y.-S. Lo, Highly Efficient Quantum-Dot-Sensitized Solar Cell Based on Co-Sensitization of CdS/CdSe, *Advanced Functional Materials*, 19 (2009) 604-609.
- [57] H. Yang, W. Fan, A. Vaneski, A.S. Sussha, W.Y. Teoh, A.L. Rogach, Heterojunction Engineering of CdTe and CdSe Quantum Dots on TiO₂ Nanotube Arrays: Intricate Effects of Size-Dependency and Interfacial Contact on Photoconversion Efficiencies, *Advanced Functional Materials*, 22 (2012) 2821-2829.
- [58] J. Yu, G. Dai, B. Huang, Fabrication and Characterization of Visible-Light-Driven Plasmonic Photocatalyst Ag/AgCl/TiO₂ Nanotube Arrays, *The Journal of Physical Chemistry C*, 113 (2009) 16394-16401.
- [59] M. Dolata, P. Kedzierzawski, J. Augustynski, Comparative impedance spectroscopy study of rutile and anatase TiO₂ film electrodes., *Electrochimica Acta*, 41 (1996) 1287-1293.
- [60] A.J. Bard, L.R. Faulhner, *Electrochemical Methods: Fundamentals and Applications*. 2nd ed.; John Wiley & Sons: New Delhi, (2004) p751-754.
- [61] R. Geick, C. Perry, S. Mitra, Lattice Vibrational Properties of Hexagonal CdSe, *Journal of Applied Physics*, 37 (1966) 1994-1997.
- [62] C. Delerue, M. Lannoo, G. Allan, Concept of dielectric constant for nanosized systems, *Physical Review B*, 68 (2003) 115411.
- [63] L.-W. Wang, A. Zunger, Pseudopotential calculations of nanoscale CdSe quantum dots, *Physical Review B*, 53 (1996) 9579.
- [64] M. Li, H. Li, Modeling Dielectric Constant of Semiconductor Nanocrystals, *Nanotechnology*, *IEEE Transactions on*, 11 (2012) 1004-1008.
- [65] S. Suresh, C. Arunseshan, Dielectric Properties of Cadmium Selenide (CdSe) Nanoparticles synthesized by solvothermal method, *Applied Nanoscience*, 4 (2014) 179-184.
- [66] C. Richter, C.A. Schmuttenmaer, Exciton-like trap states limit electron mobility in TiO₂ nanotubes, *Nature nanotechnology*, 5 (2010) 769-772.
- [67] M. Ahmad, M. Rafiq, M. Hasan, Transport characteristics and colossal dielectric response of cadmium sulfide nanoparticles, *Journal of Applied Physics*, 114 (2013) 133702.
- [68] S. Chen, L.-W. Wang, Thermodynamic Oxidation and Reduction Potentials of Photocatalytic Semiconductors in Aqueous Solution, *Chemistry of Materials*, 24 (2012) 3659-3666.
- [69] M. Butler, Photoelectrolysis and physical properties of the semiconducting electrode WO₃, *Journal of Applied Physics*, 48 (1977) 1914-1920.
- [70] J. Chen, J. Wu, W. Lei, J.L. Song, W.Q. Deng, X.W. Sun, Co-sensitized quantum dot solar cell based on ZnO nanowire, *Applied Surface Science*, 256 (2010) 7438-7441.
- [71] L. Yang, R. Zhou, J. Lan, Q. Zhang, G. Cao, J. Zhu, Efficient band alignment for Zn_xCd_{1-x}Se QD-sensitized TiO₂ solar cells, *Journal of Materials Chemistry A*, 2 (2014) 3669-3676.

Figures and Table Captions

Table I. Peak-fitting parameters for core-level scans of Cd 3d, Se 3d, Se 3p and S 2p peaks.

Table II. Summarized photocurrent values from i-V analysis of TiO₂ NTA/CdSSe films synthesized with varied number of deposition cycles and annealing temperature.

Fig. 1. Absorption spectra of pure nanocrystalline TiO₂ NTA film, and the films sensitized with (a) TiO₂ NTA/CdSSe(5); (b) TiO₂ NTA/CdSSe(7); (c) TiO₂ NTA/CdSSe(9); at annealing temperatures of 300°C and 400°C, respectively. Absorption edge was found to undergo red shift with increase in number of deposition cycles.

Fig. 2. Stacked XRD patterns of (a) TiO₂ NTA/CdSSe(9) unannealed sample, and (b) sample annealed at 400°C. The patterns reveal that CdS_{0.54}Se_{0.46} phase appears after annealing.

Fig. 3. Scanning electron microscopy images (top view) of (a) Unsensitized TiO₂ NTA (b) TiO₂ NTA/CdSSe (7)-400°C, (c) TiO₂ NTA/CdSSe(9)-UA, and (d) TiO₂ NTA/CdSSe(9)-400°C. The images depict that the CdSSe nanocrystals are uniformly attached to surface of TiO₂ NTAs.

Fig. 4. Cross-sectional view of (a) unsensitized TiO₂ NTAs and (b) sensitized TiO₂ NTA/CdSSe (9) film. The sensitized sample was subjected to thermal treatment under nitrogen atmosphere at 400°C for 1 hour. CdSSe deposits are clearly visible on the walls of nanotubes.

Fig. 5 (a and b). Transmission electron micrographs of sensitized TiO₂ NTA/CdSSe film at two different magnifications.

Fig. 6. X-ray photoelectron spectra for TiO₂ NTA/CdSSe composite film showing (a) Cd 3d peak (b) Se 3d peak and (c) S2p and Se3p peak. The compositional analysis confirms the adherence of CdSSe nanocrystals on the surface of sensitized film.

Fig. 7. i-V characteristics of sensitized films as working electrodes measured under 100 mW/cm² intensity (AM 1.5 global filter) (a) TiO₂ NTA/CdSSe(5) (b) TiO₂ NTA/CdSSe (7), (c) TiO₂ NTA/CdSSe(9).

Fig. 8. i-t characteristics of sensitized films as working electrodes (a) TiO₂ NTA/CdSSe(5) (b) TiO₂ NTA/CdSSe (7), (c) TiO₂ NTA/CdSSe(9) measured under 100 mW/cm² intensity (AM 1.5 global filter). The figure shows that the current density increases instantaneously upon illumination confirming stability of photoanodes.

Fig. 9. Mott-Schottky plot of the photoanodes under dark conditions in 0.25 M Na₂S + 0.35 M Na₂SO₃. Analysis was carried out by polarizing from -0.8 V to -1.2 V (vs. Ag/AgCl) at 1000 Hz and 10 mV AC potential.

Fig. 10. Band edge diagram constructed using Mott-Schottky and absorption data.

Fig. 11. Depletion width as a function of applied potential using Equation 14.

Figures and Tables

	Label	Species	BE (eV)	FWHM
	A	Se 3p _{3/2}	159.4	1.56
	B	Se 3p _{1/2}	165.3	2.08
S2p and Se3p	C	S 2p _{3/2}	160.7	1.53
	D	S2p _{1/2}	162.1	1.09

	Label		BE (eV)	FWHM
	A	Se (-II) main contribution	53.35	0.95
Se3d	B	Se (-II) second contribution	54.23	0.97

	Label		BE (eV)	FWHM
	A	3d _{5/2}	404.9	1.03
Cd3d	B	3d _{3/2}	411.63	1.02

Table I. Peak-fitting parameters for core-level scans of Cd 3d, Se 3d, Se 3p and S 2p peaks.

Electrode	Annealing Temperature	Photocurrent density (mA/cm ²)		
		No. of deposition cycles		
TiO ₂ NTA/CdSSe		5 cycles	7 cycles	9 cycles
	UA	2.41	6.42	6.22
	300°C	4.62	10.16	12.41
	400°C	5.43	14.57	15.58

Table II. Summarized photocurrent values from i-V analysis of TiO₂ NTA/CdSSe films synthesized with varied number of deposition cycles and annealing temperature.

Fig. 1. Absorption spectra of pure nanocrystalline TiO_2 NTA film, and the films sensitized with (a) TiO_2 NTA/CdSSe(5); (b) TiO_2 NTA/CdSSe(7); (c) TiO_2 NTA/CdSSe(9); at annealing temperatures of 300°C and 400°C , respectively. Absorption edge was found to undergo red shift with increase in number of deposition cycles.

Fig. 2. Stacked XRD patterns of (a) TiO_2 NTA/CdSSe(9) unannealed sample, and (b) sample annealed at 400°C. The patterns reveal that $\text{CdS}_{0.54}\text{Se}_{0.46}$ phase appears after annealing.

Fig. 3. Scanning electron microscopy images (top view) of (a) Unsensitized TiO_2 NTA (b) TiO_2 NTA/CdSSe (7)-400°C, (c) TiO_2 NTA/CdSSe(9)-UA, and (d) TiO_2 NTA/CdSSe(9)-400°C. The images depict that the CdSSe nanocrystals are uniformly attached to surface of TiO_2 NTAs.

Fig. 4. Cross-sectional view of (a) unsensitized TiO₂ NTAs and (b) sensitized TiO₂ NTA/CdSSe (9) film. The sensitized sample was subjected to thermal treatment under nitrogen atmosphere at 400°C for 1 hour. CdSSe deposits are clearly visible on the walls of nanotubes.

Fig. 5 (a and b). Transmission electron micrographs of sensitized TiO₂ NTA/CdSSe film at two different magnifications.

Fig. 6. X-ray photoelectron spectra for TiO_2 NTA/CdSSe composite film showing (a) Cd 3d peak (b) Se 3d peak and (c) S2p and Se3p peak. The compositional analysis confirms the adherence of CdSSe nanocrystals on the surface of sensitized film.

Fig. 7. i-V characteristics of sensitized films as working electrodes measured under 100 mW/cm² intensity (AM 1.5 global filter) (a) TiO₂ NTA/CdSSe(5) (b) TiO₂ NTA/CdSSe (7), (c) TiO₂ NTA/CdSSe(9).

Fig. 8. i-t characteristics of sensitized films as working electrodes at 0 V Vs SCE (a) TiO_2 NTA/CdSSe(5) (b) TiO_2 NTA/CdSSe (7), (c) TiO_2 NTA/CdSSe(9) measured under 100 mW/cm^2 intensity (AM 1.5 global filter). The figure shows that the current density increases instantaneously upon illumination confirming stability of photoanodes.

Fig. 9. Mott-Schottky plot of the photoanodes under dark conditions in 0.25 M Na_2S + 0.35 M Na_2SO_3 . Analysis was carried out by polarizing from -0.8 V to -1.2 V (vs. Ag/AgCl) at 1000 Hz and 10 mV AC potential.

Fig. 10. Band edge diagram constructed using Mott-Schottky and absorption data.

Fig. 11. Depletion width as a function of applied potential using equation 14.