Increased efficiency of dye-sensitized solar cells by addition of rare earth oxide microparticles into a titania acceptor

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ABSTRACT

The addition of 400 micron scale rare-earth metal oxide particles to the TiO_2 nanoparticle acceptor layer of a dye-sensitized solar cell (DSSC) dramatically increases the efficiency of the solar cell by 10-30%. Oxidized neodymium powder, Nd_2O_3 , combined with TiO_2 nanoparticles forms a composite photoanode containing a wide range of Nd_2O_3 particle sizes. Based on absorbance measurements, the dye-uptake on the $\text{Nd}_2\text{O}_3/\text{TiO}_2$ anode increases substantially compared to both a standard anode and to one made from a mixture of large and small TiO_2 particles. Electrochemical impedance spectroscopy (EIS) shows a similar electron lifetime, but increased electron transport diffusion coefficient through the $\text{Nd}_2\text{O}_3/\text{TiO}_2$ composite as compared to TiO_2 only. This shows that the $\text{Nd}_2\text{O}_3/\text{TiO}_2$ composite has a lower internal resistance for charge transport. This decrease in resistance, possibly due to the filling of trap states by the Nd_2O_3 valence or f-states, and increased dye uptake results in improved efficiency by simple incorporation of Nd_2O_3 powder.

Keywords: Rare earth oxide, hybrid solar cell, dye sensitized, photovoltaic, titanium dioxide

1. Introduction

Since first described by Grätzel and co-workers, dye-sensitized solar cells (DSSCs) have been extensively investigated as a possible alternative to traditional semiconductor photovoltaic cells. DSSCs offer relatively high photo-conversion efficiencies while providing potential savings in fabrication costs compared to crystalline semiconductor photovoltaics [1-3]. In the DSSC, a photoanode consisting of dye-coated TiO_2 nanoparticles is combined through an electrolyte redox couple to a counter electrode. The dye absorbs sunlight, and transfers photo-excited electrons to the conduction band of the TiO_2 , where the charge then diffuses to reach the electrode contact. Interfacial engineering [4] and surface modification of the oxide material are major strategies used to improve the efficiency of DSSCs [5]. This includes depositing a scattering layer of large size TiO_2 particles on top of the active layer [6], controlling the haze of the film by incorporating larger TiO_2 nanoparticles into the film [7, 8], chemically modifying the surface of the active layer with molecular linkers [9-11], coating the active layer with another metal oxide to form core/shell structures [12, 13], and doping the photoanodes with metal ions [14], metal nanoparticles [15, 16] or other dopants [17] or metal oxides [18].

Rare earth metals and oxides, well known for optical materials applications, show much promise as dopants to improve TiO_2 for photovoltaic applications [19-21]. Rare earth doping has been observed to reduce the band-gap of TiO_2 particles and increase the surface area of TiO_2 nanoparticle films [22]. Rare earth doping improves TiO_2 photocatalytic activity and photoelectrochemical response of a TiO_2 anode [23]. A hybrid organic/inorganic solar cell was demonstrated in which the TiO_2 was completely replaced by rare earth oxide [24]. In DSSCs, a

number of studies have shown that incorporation of a rare earth dopant in the photoanode can improve the cell efficiency [21, 25-32]. The rare earth material is usually incorporated from the rare earth salt precursor into the TiO₂ nanostructures during synthesis [25, 28, 30, 31, 33], sometimes as a core/shell structure [31], but has also been incorporated by soaking a prepared TiO₂ photoanode into a rare earth salt solution followed by calcination [29] or by mixing rare earth nanoparticles with TiO₂ nanoparticles followed by film preparation and calcination [27]. Improvements are often not well understood, but have been attributed to increased dye coverage [19, 34], improved electron injection [28, 30, 35], decreased recombination [19, 28, 34], reduction of trap states [35, 36], or increased electron diffusion [19, 28, 34, 35]. There is considerable variation in results. For example, Y and Nd have been shown to both enhance [35, 37] and decrease [19, 36] the efficiency in different reports. Another type of material involves upconverting [38-44], downconverting [25, 40, 45-50], or dual-mode [51] luminescent rare earth nanostructures, which allow improved light collection efficiency when incorporated into the TiO₂ photoanode in DSSCs. They can also help improve efficiency through light scattering [39, 43, 50, 52], altering the energy level of the TiO₂ [43, 48, 53], or by reducing recombination processes [47, 54, 55] at the TiO₂/electrolyte interface. Overall, the maximum efficiencies are in the 9-10% range for dye-sensitized TiO₂ photoanodes doped with rare earth materials [29, 44, 55]. Qin *et al.* recently reported 11.2% efficiency with a perovskite-based solar cell by incorporating 0.5% Y into the TiO₂ layer [56].

While the results of rare earth doping are certainly promising, the incorporation procedures have been limited, the improvements vary significantly and are the reasons for the improvement are not very well understood. A more systematic approach is needed for further, reproducible improvement through optimization of the rare earth doping element, the concentration, and

incorporation method. A better fundamental understanding of the material properties and enhancement mechanism is also needed to make significant advancements in this area. In this article, we add to this knowledge base by reporting on a dramatically different method for incorporating rare earth materials into a traditional TiO_2 photoanode of a DSSC. Here, 400 micron scale Nd_2O_3 “mesoscale” particles (powder) are mixed directly with the TiO_2 nanometer scale colloids to form the photoanode. The film created in this manner is highly non-uniform and contains a large range of particle sizes. Despite this simple and crude method of rare earth doping, absorbance measurements show that the $\text{Nd}_2\text{O}_3/\text{TiO}_2$ composite film takes-up 28% more dye than the standard TiO_2 film and that the efficiency of DSSCs made with the composite anodes improves substantially by 10 to 30%. Decreasing the dye coverage of the composite electrode to match that of the standard electrode still results in a substantial increase in efficiency, suggesting that improved transport properties contribute significantly to the improved efficiency. Importantly, this work lays the groundwork for future studies exploring other strategies of incorporating rare earth elements into TiO_2 in the solid phase, which may lead to improvements in enhancement, greater device reproducibility, and a better understanding of the enhancement mechanism.

2. Experimental

2.1. Photoanode Preparation

Fluorine doped tin oxide (FTO) coated glass slides were solvent cleaned, and then soaked in 40 mM TiCl_4 solution at 70 °C for 30 min. The slides were masked with adhesive tape to create a 0.25 cm² window. Dyesol TiO_2 paste (DSL 18 NR-T or 30NRD) was then deposited using the

doctor blade method, and this process was repeated to obtain a film thickness of approximately 8.8 μm . In the highest efficiency cells, an additional 3-4 μm thick scattering layer of 200-400 nm TiO_2 particles (WER-2) was also deposited. The paste was sintered at 500 $^{\circ}\text{C}$ for 1 h, post treated with TiCl_4 and then sintered again at 500 $^{\circ}\text{C}$ for 1h. For the composite electrodes, 40 mesh oxidized Nd powder (Alfa Aesar) was ground finely with the TiO_2 paste in a chosen weight ratio and then deposited on the FTO slides in the first layer using the procedure described above. The second layer was performed with the Dyesol TiO_2 paste only as described above. The percentage of Nd reported in the main text refers to the percent Nd in the first layer only. Sensitization of the FTO/ TiO_2 and FTO/ TiO_2 - Nd_2O_3 electrodes was achieved by immersing the electrodes into a 0.3 mM solution of Dyesol N719 dye in a 1:1 mixture of acetonitrile and *t*-butanol. Counter electrodes with holes made by 0.8 mm diamond tip drilling bit (UKAM, USA) were created by coating a cleaned FTO slide with a drop of Platisol and heating to 500 $^{\circ}\text{C}$ for 20 min. Both electrodes were painted by hot melted indium chunk from the contact to the edges to produce good electrical contact. Sandwich cells were prepared by inserting plastic ionomer (Surlyn) between the working electrode and counter electrode; heating at 118 $^{\circ}\text{C}$ for one minute in a thermal press (model number, MPRESS912, HeatPress Nation, USA). For more improvement in hermetical sealing of devices, epoxy was placed all around the contact joining the photoanode and the counter electrode. A drop of electrolyte was placed on the top of hole made in the counter electrode. If sealing was good, the drop would not go into the device because of the air pressure produced by the trapped air in between the counter electrode and photoanode. The whole device was kept in a small vacuum box, and air was pumped out for 15s. When air was pumped in, the electrolyte filled the vacuum space or the porous part of the dye-coated photoanode. The drilled hole was then filled with liquid Surlyn sealant again, and on the

top of it, a drop of melted Crystalbond adhesive wax (Ted Pella, USA) was applied to seal the hole. Epoxy was placed on top of the cooled wax

2.2. Photoelectrochemical Measurements

For photoelectrochemical measurements, the cells were illuminated with simulated 1.5 AM solar light (Newport Oriel) with an intensity of 100 mW/cm^2 (1 Sun). The intensity of the light was set based on the voltage response of a commercially purchased, calibrated 1 cm^2 reference silicon solar cell from Abet Technologies, Inc., USA with in-built KG5 filter (uncertainty = 8%). The light source was set to 1 Sun by adjusting the light intensity until the reference silicon solar cell gave a reading of 100 mV as measured by a voltmeter. A homemade optical sample holder was used to mount the reference silicon solar cell. After setting the light intensity, the reference silicon solar cell was replaced with the fabricated dye-sensitized solar cell (DSSC) under study in the same location at the same distance from the light source as dictated by the optical holder. The devices were masked by sticky black paper tape with an open window area of 0.16 cm^2 prepared by a laser printer. Black electrical tape was used to seal all edges of the DSSC devices in order to prevent light piping. Current-voltage curves were obtained with a Model 273A EG & G Princeton Applied Research Potentiostat by scanning the voltage from 0.2 V to -1.0 V at a scan rate of 20 mV/s to the cells and measuring the current. The same device measured at least 5 times per day over a 7 day period gave the same results with less than 4% relative standard deviation, showing very good reproducibility of the measurement system.

2.3. Other Characterization

Absorbance spectra of the real photoanodes were measured with a Varian Cary 50 Win UV-VIS spectrophotometer and diffuse reflectance spectroscopic (DRS) measurements were performed using a Lambda 950 PerkinElmer DRS Instrument. Electrochemical Impedance Spectroscopic (EIS) measurements were performed using a CHI 660a electrochemical workstation. A 10 mV AC perturbation at open circuit voltage was applied between the photoanode and the platinum counter electrode with a frequency range of 1000 kHz to 5 mHz. The photoanodes were maintained at the open circuit voltage by illuminating with white light (35 mW/cm^2) produced from an optical fiber (Fiber Optic Illuminator Model 190, Dolan-Jenner).

3. Results and discussion

Figure 1 compares images of traditional TiO_2 nanoparticle films (A, C, and E) and those created by combining 5% oxidized 40 mesh Nd powder with the TiO_2 nanoparticles (B, D, and F). Figure 1(A) and (B) show optical images, while the others show electron microscope images at increasing magnification. The Nd_2O_3 particles are clearly visible as large protrusions within the TiO_2 nanoparticle film. Grinding of the mixture produces a distribution of Nd_2O_3 particles from 100s of nm up to 100 microns. Increased magnification reveals that cracks have formed near the Nd_2O_3 particles during sintering. Fig. 1(D) and (F) show that the nanoscale TiO_2 particles fill the cracks, along with the region on top of the Nd_2O_3 mesoparticles. Optical reflectance measurements of the TiO_2 and composite electrodes (Supplementary Data, Figure S1) show that the TiO_2 band edge is not affected by the Nd_2O_3 particles, however, additional features due to Nd_2O_3 optical transitions are observed [57].

Six batches of photoanodes were fabricated and characterized. Each batch contains both standard TiO_2 photoanodes, and photoanodes mixed with 5% (by weight) oxidized 40 mesh Nd

powder. Following measurements, results from multiple (from 2 to 4) devices of the same type in a single batch are averaged together. Figures 2A and 2B show the current density versus bias for the Nd_2O_3 modified devices and unmodified devices, respectively. Each color corresponds to a different batch (the results from batch 2 are left out for clarity). The voltage axis is reversed between the two plots to allow for easier comparison of the data. There is considerable variation in the current-voltage characteristics between different batches of solar cells. However, for each batch, the short circuit current is substantially higher for the samples containing the Nd_2O_3 than for the standard DSSCs. Figures 2C-F are box plots summarizing the photoelectrochemical parameters measured for the Nd_2O_3 -modified (solid boxes) and unmodified (hashed boxes) photoanodes for all six batches. As shown in Fig. 2C (and described above) the short circuit current density is higher for the Nd_2O_3 modified samples than for the unmodified samples in each batch. This produces the observed efficiency increase shown in Fig. 2D; the improvement in efficiency due to Nd_2O_3 modification ranges from about 10 to 30%. Changes in the fill factor (Fig. 2E) and open circuit voltage (Fig. 2F) are small and inconsistent among the different batches, suggesting that the Nd_2O_3 has little impact on these parameters. Table S1 in the supporting information summarizes the photoelectrochemical measurements and dark current onset voltage for all of the batches of Nd_2O_3 modified and unmodified devices. The dark current onset voltage fluctuates in a similar manner between the modified and unmodified samples, suggesting that the recombination kinetics are similar in both types of photoanodes. Further experiments show that the Nd_2O_3 modification does not negatively impact the device stability as long as it is sealed properly. Well-sealed Nd_2O_3 modified samples exhibit little change in the short circuit current and efficiency for up to 40 days (See Figure S2 of supplementary data).

Photoelectrochemical measurements show that the efficiency of DSSCs with photoanodes modified with Nd_2O_3 is strongly dependent on the concentration of Nd_2O_3 by weight relative to the TiO_2 . In Figure 3, the current density versus bias is plotted for samples containing varying weight concentrations of Nd_2O_3 under 1.5 AM solar light. Both 5% and 20% Nd_2O_3 concentration samples have higher efficiency than the TiO_2 only sample, while above 20% the efficiency is reduced. The inset shows a plot of the efficiency as a function of the weight percentage of Nd_2O_3 mesh particles, indicating that the maximum efficiency occurs at ~5% by weight. This set of data was obtained from a separate batch of samples from those shown in Figure 2.

To better understand the improved efficiency, optical absorbance measurements were performed on the composite and standard anode materials after soaking in dye for 24 hours. Figure 4A shows the resulting absorbance spectra. Both TiO_2 and TiO_2 -5% Nd_2O_3 samples show similar absorbance peaks due to the dye. The metal-to-ligand charge transfer (MLCT) band of the N719 dye appears at 538 nm in the pure TiO_2 sample and at 544 nm in the sample with 5% Nd_2O_3 , a small red shift. The main influence of the Nd_2O_3 incorporation is to increase the magnitude of the dye absorbance by approximately 28%, indicating that the 5% $\text{Nd}_2\text{O}_3/\text{TiO}_2$ hybrid film is able to uptake appreciably more dye than the standard sample. As shown in Figure S3 of supporting information, the increase in absorbance is maximized for 5% Nd_2O_3 concentration, similar to the dependence on efficiency shown in Figure 3. Figure 4B shows the magnitude of absorbance of the MLCT band as a function of dye soaking time for both 5% Nd_2O_3 and pure TiO_2 . The absorption for the 5% Nd_2O_3 sample rapidly increases above the pure TiO_2 sample, reaching a maximum after approximately 5 hours of soaking. The same behavior occurred reproducibly for 3 samples of 5% Nd_2O_3 and 3 samples of pure TiO_2 . Experiments

involving the removal of dye from the 5% Nd_2O_3 and pure TiO_2 photoanodes followed by analysis of the dye quantity in solution agreed well with the transmission measurements from Figure 4A and 4B.

As shown in Figure 1, the composite anodes have a distribution of Nd_2O_3 particle sizes with the formation of cracks nearby, where the Nd_2O_3 and cracks are coated with smaller TiO_2 nanoparticles following sintering. It is possible that the cracked surface of the photoanode results in a larger surface area, and is able to adsorb a larger quantity of dye than a more uniform surface. To test this hypothesis, anodes were made that contained 400 micron scale TiO_2 particles mixed with the TiO_2 nanoparticles. As shown in supplementary data Figure S4, the surface of the all TiO_2 composite electrode appears very similar to the surface of the 5% Nd_2O_3 – TiO_2 electrode, with cracks also forming around the larger particles. However, there is an insignificant increase in the MLCT band absorbance of the TiO_2 composite electrode compared with the TiO_2 nanoparticle electrode (Figure S4-C) and the efficiency of DSSCs made from the TiO_2 composite electrodes is virtually identical to those made from the TiO_2 nanoparticle electrodes (Figure S4-D). This shows that the ability to adsorb large amounts of dye is specific to rare earth oxide incorporation. It also shows that the mesoscale particles of TiO_2 intermixed in the cathode do not function as an effective scattering layer [6] or improve the efficiency based on increased haze [7, 8] in our case, making these explanations for the improved efficiency in the Nd_2O_3 composite samples unlikely. Others have reported improved efficiency when mixing larger particles or powders of TiO_2 of various shapes and sizes with nanoscale TiO_2 nanoparticles [58-60], which has been attributed to increased dye loading, improved light collection, and improved electron transport, but we did not observe significant improvements for the addition of 5% microscale TiO_2 under our experimental conditions.

To determine whether the efficiency increase observed is mainly due to increased dye uptake, solar cells were prepared with TiO_2 only and TiO_2 -5% Nd_2O_3 photoanodes that had the same dye coverage. Using the dye adsorption kinetics data in Figure 4B as a guide, 5% Nd_2O_3 anodes were soaked in dye for 2 hours, while pure TiO_2 anodes were soaked for 2.5 hours. The resulting absorbance spectra for the two anodes are shown in Figure 4C. In this case, the MLCT band absorbance for the dye is virtually identical for the two different anodes, indicating that the dye coverage is also the same. Figure 4D shows the plots of current density versus bias in light for the two photoanodes with the same dye coverage. In both cases, the efficiency is appreciably lower than that observed for these photoanodes with full dye coverage using a 24 hour soak (Figure 2). However, the 5% Nd_2O_3 anode still produced a significantly higher efficiency (5.39%) than the pure TiO_2 anode (3.65%), even though the dye coverage was the same. This shows that dye coverage is not the only reason, and probably not the main reason, for the improved efficiency of the TiO_2 -5% Nd_2O_3 photoanodes compared to TiO_2 only.

Figure 4 shows that the Nd_2O_3 mesoparticles incorporated into TiO_2 not only increase dye uptake, but also somehow improve charge collection and transport through the photoanode. To further investigate the charge transport within the cell, we used electrochemical impedance spectroscopy (EIS). Figure 5A shows the EIS Nyquist plots for the same photoanodes whose J-V plots are shown in Figure 3 and Figure 5B shows the corresponding Bode plots. In the Nyquist plots there are three distinct semi-circles. The left semi-circle denotes the high frequency window (100 kHz – 500 Hz) and measures charge transfer from the counter electrode to the electrolyte. The middle semi-circle corresponds to the medium frequency window (100 Hz – 1 Hz), and measures the TiO_2 /Dye/electrolyte or TiO_2 - Nd_2O_3 /Dye/electrolyte interface. The right semicircle corresponds to the low frequency window (1 Hz – 5 mHz) and is normally

considered to measure diffusion of the electrolyte/redox couple [61, 62]. There are three key features of the middle semi-circle region of the Nyquist plot [62]. First, the recombination kinetics can be estimated by the peak frequency from this central arc [62]. A low peak frequency is desired for slow recombination kinetics and long electron lifetimes. This enhances the collection efficiency of injected electrons. Second, the diameter of the semi-circle is indicative of the electron recombination resistance. Third, the shape of the arc is indicative of the ratio of electron recombination resistance to the resistance of electron diffusion through the TiO_2 or $\text{Nd}_2\text{O}_3/\text{TiO}_2$ film. A clear circular shape indicates that the former is much larger than the latter, which is desired for high efficiency cells [62]. As shown in Figure 5A, the smallest diameter semi-circle is observed for 5% Nd_2O_3 followed by 0% Nd_2O_3 , 50% Nd_2O_3 , and finally 75% Nd_2O_3 . This could indicate that electron recombination resistance is the lowest in the 5% Nd_2O_3 films, which is not desirable. However, the Bode plots in Figure 5B show that the peak frequency for the 5% and 0% Nd_2O_3 are very similar (14 and 12 Hz, respectively), indicating similar electron recombination kinetics for those two films. The peak frequency of the 50% Nd_2O_3 and 75% Nd_2O_3 films are clearly large, indicative of faster recombination kinetics and shorter electron lifetimes, which explains why those films exhibit lower efficiencies. Considering that the recombination kinetics are similar for the 5% and 0% Nd_2O_3 photoanodes, it is more desirable to have a smaller semi-circle (lower impedance) in the middle frequency region. This feature (smaller semi-circle in middle frequency) in EIS has been demonstrated previously for DSSCs as a function of increasing dye coverage [63] and increasing TiO_2 thickness [62, 64, 65], as long as the thickness does not exceed the electron diffusion length. Increased dye coverage can lead to a lower impedance in this region when going from very low coverage to full monolayer [63], which has been attributed to recombination occurring through

the dye molecule, but the V_{OC} also increases. However, with almost full initial monolayer coverage, a further improvement in coverage by a cycling procedure led to higher impedance in this region due to a more passivating dye layer, which improved efficiency by blocking recombination [66]. In both cases, increased dye coverage accompanied an increase in open circuit voltage, which we did not observe in our case.

The open circuit voltage is not significantly different and the dark current data and Bode plots both reveal that the recombination kinetics are very similar when comparing TiO_2 and 5%- Nd_2O_3/TiO_2 photoanodes. Accordingly, we attribute the lower impedance in the middle frequency regime to lower resistance to electron diffusion through the 5%- Nd_2O_3/TiO_2 photoanode as compared to TiO_2 only, leading to a larger electron diffusion length. A lower impedance in this regime, but similar frequency in a Bode plot and similar open circuit voltage was also observed previously as the thickness of a TiO_2 film increased [62], which also resulted in a larger effective electron diffusion coefficient. The lower resistance to electron diffusion through the mesoporous film indicates that the presence of Nd_2O_3 either reduces trapping kinetics, increases detrapping kinetics, or decreases the number of trap states in TiO_2 . Since a decrease in the number of trap states should increase the electron lifetime, which did not occur in our case, our data is most consistent with the Nd_2O_3 favorably altering the trapping and detrapping kinetics [64]. This would instead lead to a larger electron diffusion coefficient and longer diffusion length as observed.

To understand how the Nd_2O_3 might alter the trapping and detrapping kinetics, consider the simple energy diagram of the Dye/ TiO_2/Nd_2O_3 system in the inset to Figure 5A. The Nd_2O_3 valence band edge (filled f and spd states) has been calculated to lie well within the TiO_2 band gap, while the conduction band (spd states), and empty f-band lie above the band edge of the dye

LUMO level [67-69]. It is unlikely that the Nd_2O_3 would provide an additional transport path for the photo excited electrons from the dye since the conduction band energy is too high, and the f-states, while available, are localized states with high transport resistance. However, it is known that TiO_2 contains mid-gap surface trapping states that capture injected charge from the dye and lower the efficiency. It is possible that the Nd_2O_3 acts to occupy these states (not eliminate) through charge transfer from photoexcited states corresponding to the transitions shown in Figure S1, or from the Nd_2O_3 valence band. Injected electrons from the photo excited dye can then transfer through the TiO_2 without being trapped [70]. This mechanism is highly speculative at this time and more work is needed to definitively rule out possible effects of dye coverage, improved light scattering, or other mechanisms. We also note that Nd likely occupies a larger volume of the film than that shown by the location of the large microscale Nd_2O_3 particles in the images, since Nd may diffuse into the TiO_2 particles during the grinding and sintering process. Spatial elemental characterization of the films and incorporation of nanoscale Nd particles into the photoanodes will allow us to better quantify and control the extent of Nd incorporation into TiO_2 in future studies.

4. Conclusions

In conclusion, a dramatically improved efficiency has been observed in a DSSC incorporating a composite working electrode composed of a simple mixture of TiO_2 nanoparticles and Nd_2O_3 mesoscale particles (Nd powder). The addition of the large rare earth oxide particles greatly increases the dye uptake of the film and reduces the electron diffusion resistance through the TiO_2 film to the FTO contact. It is shown that the incorporation of rare earth oxides into photoanodes is a promising approach to improve the efficiency of DSSCs, and

through variation in material, incorporation method, and particle size it is anticipated that further improvements are possible.

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Supplementary Data:

The reflectivity of the photoanodes, a summary table of results from all devices, results of a stability test on a well-sealed device, and characterization of TiO₂ meso/nano samples is included in the supplementary data.

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FIGURE CAPTIONS

Figure 1. Images of the surface of TiO_2 (A, C, and E) and 5% $\text{Nd}_2\text{O}_3/\text{TiO}_2$ (B, D and F) photoanodes. A-B show optical microscope images while C-F show scanning electron microscope images.

Figure 2. Current-density versus bias for A) Nd_2O_3 modified and B) unmodified photoanodes measured under 1.5 AM illumination. Different batches are shown as different colored lines: Batch 1(yellow), 2 (not shown), 3 (black), 4(blue), 5(green) and 6(red). (C-F) Box plots show C) short circuit current D) efficiency E) fill factor and F) open circuit voltage for each of the six batches. Solid blocks show Nd_2O_3 modified samples, hashed blocks show traditional unmodified samples.

Figure 3. Current-voltage characteristics of DSSCs made with anodes containing varying percent weight concentrations of Nd_2O_3 . Inset: Efficiency as a function of Nd_2O_3 percent weight concentration.

Figure 4. A) UV-vis absorbance spectra for anodes made with 5% $\text{Nd}_2\text{O}_3/\text{TiO}_2$ composite anodes (green solid line) and traditional unmodified TiO_2 anodes (red dashed line) soaked for 24 h. B) Absorbance as a function of dye soaking time. C) Absorbance after reduced dye soaking time of 2 h for 5% $\text{Nd}_2\text{O}_3/\text{TiO}_2$ and 2.5 h for TiO_2 . D) Current density-voltage characteristics in light for the dye coverage corresponding to C).

Figure 5. A) Electrochemical impedance spectra for photoanodes containing different concentrations of Nd_2O_3 . Inset: Band diagram showing trap filling in TiO_2 due to Nd_2O_3 charge states. B) Bode plots corresponding to the impedance spectra in A)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5 revised