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# Rationally Designed, Three-Dimensional Carbon Nanotube Back-Contacts for Efficient Solar Devices

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Devices designed to convert sunlight into usable sources of energy have become the focus of increased attention in the past decade due to the diminishing nature of fossil fuel resources.<sup>[1]</sup> As a result, recent research efforts have focused on improving solar device performance and cost using novel processes, materials and device technologies.<sup>[2,3]</sup> One example includes the use of three-dimensional (3-D) architectures to enhance the carrier collection efficiency and photon management of the devices.<sup>[4-6]</sup> In such a device concept, the efficiency of thin film solar devices can be enhanced by orthogonalizing the light absorption and carrier collection processes, especially for the material systems that exhibit low minority carrier lifetimes.<sup>[7]</sup> In addition, surface reflectance is reduced and the absorption is enhanced, thus improving the overall conversion efficiency. One route for fabricating 3-D solar devices involves the use of textured substrates and/or back-contacts followed by the conformal deposition of thin films of the absorber material.<sup>[8]</sup> In this regard, exploring scalable and tunable nanotexturing processes with high-aspect ratio features is required.

Here, we demonstrate the fabrication of textured carbon nanofiber (CNF) arrays for the back-contact of solar devices with improved photon capture properties. Using a scalable,

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#### DOI: 10.1002/aenm.201100436

solution-phase condensation process,[9-11] conductive and chemically robust CNF scaffolds with tunable pitch and feature shape/size are obtained. To explore the utility of the proposed approach, the nanotextured CNF electrodes are coated with conformal thin films of TiO<sub>2</sub> absorber layer for water oxidation.<sup>[12-17]</sup> Unlike the use of other reported TiO<sub>2</sub>/CNF architectures, or nanotubes and nanowires made of TiO<sub>2</sub>,<sup>[18-23]</sup> this morphology allows us to design antireflective absorbing layers to decouple and optimize absorption and carrier collection. Based upon this, we demonstrate an enhancement of up to 3 times in the short circuit current density  $(I_{SC})$  for the 3-D CNF/TiO<sub>2</sub> photoelectrochemical (PEC) device as compared to its planar counterpart. Antireflection is particularly important as it is not feasible to use conventional antireflective coatings in PEC cells since the effective junction is formed at the semiconductor-liquid interface.<sup>[24]</sup> Such a coating would inhibit the injection of photo-generated minority carriers into the solution.

Figure 1 demonstrates the general fabrication approach for textured CNF back-contacts. First, vertically aligned CNF arrays (Figure 1a,c) are grown in a plasma-enhanced chemical vapor deposition system on Si/SiO2 substrates using Ni catalyst thin films (thickness, 30 nm), supported on conductive Cu/Ti bilayers (thickness, 200/30 nm).<sup>[25]</sup> The fabricated CNF array is electrically addressable by the substrate and exhibits an average vertical height of ~10 µm and CNF diameters between 10-120 nm, as measured by SEM. Following the growth process, the vertically aligned CNF arrays are textured using a scalable solution-phase condensation process (Figure 1b,d).<sup>[9-11]</sup> Here, CNFs are exposed to a 20  $\mu$ L drop of acetone (~0.6 × 0.6 cm<sup>2</sup> sample size) which is then dried under ambient conditions. Upon drying, capillary forces cause reorganization of the vertically aligned carbon nanofiber morphology, which is inherently dependent on the surface tension of the liquid.<sup>[9]</sup> Solvents with different surface tensions were found to yield variable structures upon drying, with acetone yielding the highest density of compact pillar structures with a base diameter of 4–5  $\mu m$ (Figure 1d) that resulted in the most optimal device performance. The use of other solvents and drying conditions resulted in either larger pillars with smaller out-of-plane angles or else ridge-like pillars that formed cellular, interconnected structures. Therefore, acetone condensation was utilized throughout experiments described here.

Atomic layer deposition (ALD) at 250 °C was utilized to coat  $TiO_2$  thin films with varied thicknesses ( $T_{TiO2} = 80-400$  nm) on the surface of the texturized CNF templates as the light-absorbing material. As demonstrated in SEM images shown in



**Figure 1.** (a,b) Scheme of process depicting the capillary-force drying and texturizing of the as-grown carbon nanofiber arrays, (c) SEM image of as-grown carbon nanofiber array, and (d) SEM image of a texturized carbon nanofiber array. Scale bar in (c) and (d) is 3  $\mu$ m.

Figure 2a–d, this TiO<sub>2</sub> coating is highly conformal. The TiO<sub>2</sub> thicknesses were confirmed for these structures by utilizing destructive SEM imaging (Figures 2c,d) where the pillars were intentionally broken to expose the conformal TiO<sub>2</sub> layer and the CNFs within. In order to determine the crystal structure of the TiO<sub>2</sub>, x-ray diffraction (XRD) and Raman spectroscopy measurements were performed as shown in Figures 2e and 2f, respectively. From the XRD spectrum, the peaks labeled with "A" correspond to those of an ordered anatase phase of TiO<sub>2</sub> (body-centered cubic, I41/amd (141) JCPDS Card No. 108976). In addition, Raman spectroscopy depicts low frequency modes at ~147, 401, 520, and 639 cm<sup>-1</sup> correlating well to the known modes of anatase TiO<sub>2</sub>, also independently verifying the presence of anatase TiO<sub>2</sub>.<sup>[26]</sup> It should be noted that anatase TiO<sub>2</sub> has a slightly higher band gap energy (3.2 eV) than other crystalline phases of TiO<sub>2</sub>, but has also been suggested to be a more effective water oxidation photocatalyst.<sup>[27]</sup> Also, evident from the Raman spectrum are the broad and overlapping D and G bands centered around 1380 and 1600 cm<sup>-1</sup>, respectively arising from the sp<sup>3</sup> hybridized graphitic structure of CNFs, similar to multiwalled nanotubes<sup>[28]</sup> (Figure 2(d)).

Figure 3b shows the current-potential curves for TiO<sub>2</sub>/CNF structures with various  $T_{\text{TiO2}}$  utilizing an aqueous 1 M NaOH electrolyte solution. The measurements were taken under AM 1.5 G (1 sun) solar radiation using a three-electrode setup equipped with a Pt counter electrode and an Ag/AgCl reference electrode. AM 1.5 G illumination was utilized as a standard to compare the effect of electrode structure on the photocurrent generated by the TiO<sub>2</sub> absorber. As expected, the overall measured photocurrent is found to increase with increasing thickness for  $T_{\text{TiO2}} < 300$  nm due to enhanced absorption, with the greatest margin of increase in the thickness range of 80–220 nm. This range corresponds to 1-3 times the previously reported minority carrier diffusion length in TiO<sub>2</sub> ( $L_D$ ~70–100 nm).<sup>[29,30]</sup> Beyond  $T_{\text{TiO2}}$ ~300 nm (i.e.,  $T_{\text{TiO2}} > ~3 L_D$ ), further increase in the thickness does not result in photocurrent enhancement

since the generated carriers are mostly lost to recombination prior to reaching the surface.

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In order to directly demonstrate the performance benefits of 3-D device architecture, we compare the measured JSC of TiO2/CNF structures to those of planar TiO2/graphite devices. Here,  $J_{SC}$  for the three-electrode measurement is defined at the thermodynamic threshold voltage where the three-electrode cell has a net gain of free energy under illumination (0.216 V) based on the Nernst equation. The planar devices were made by the ALD of TiO2 on a pressed graphite surface polished with 900 grit sandpaper and cleaned prior to coating. Shown in Figure 3c are the  $I_{SC}$  values for both the planar graphite and CNF templates as a function of  $T_{\text{TiO2}}$ . The 3-D TiO<sub>2</sub>/CNF architecture consistently exhibits 2-3x enhancement in JSC as compared to the planar devices with the same TiO<sub>2</sub> physical thickness.

We now consider factors that could contribute to the observed enhancement. These include reduced surface reflectance, (ii) enhanced optical (i) path length for the same TiO2 physical thickness, and (iii) improved carrier collection efficiency. The reflectance of planar and 3-D textured samples can be directly assessed. Shown in Figure 4a is the percent reflectivity, R, as measured for the planar TiO<sub>2</sub>/graphite substrate, and the coated texturized CNF templates. For both samples,  $T_{\rm TiO2} \sim 60{-}80$  nm. The reflectivity of the CNF templates is  $R_{3.D} = 0.5-0.7\%$  in the ultraviolet and visible regimes, whereas the reflectivity of the planar graphite is  $R_{\text{planar}} = 14-22\%$ . Here, the effect of diffused light is ignored which can affect the absolute reflectance measured, but will not change the observed trend. The drastic low surface reflectance observed for 3D TiO<sub>2</sub> structures arises from the subwavelength tip-diameter, minimizing the interaction of light with the surface. An enhancement factor,  $\gamma$ , can be defined as  $\gamma = (100 - R_{3-D})/(100 - R_{planar})$ , which yields a suggested 1.2–1.3 times increase in device performance for the 3-D architecture based on minimized reflections. Given that conventional antireflective coating cannot be utilized in PEC devices, the use of a structural anti-reflective approach explored here is particularly important. Yet, reflectance alone does not explain the 2-3x enhancement in  $J_{SC}$  that is experimentally observed.

Next, we examine the effect of increased optical path<sup>[4,31–33]</sup> in textured CNF structures. The probability of a photogenerated carrier to diffuse to the semiconductor-electrolyte interface scales as  $P \propto \exp\left(\frac{T_{\text{TiO2}}}{L_{\text{D}}}\right)$ , suggesting that only the carriers generated within  $\sim 3L_{\text{D}}$  of the surface contribute to  $J_{\text{SC}}$  with the rest mostly being lost to recombination processes. For TiO<sub>2</sub>, given the previously reported  $L_{\text{D}} = 70-100 \text{ nm},^{[29,30]}$  the maximum active thickness within which the carrier can be collected is hence only ~300nm. However, the optical characteristic length (~90% of all above-gap photons are absorbed) is on the order of 1  $\mu$ m.<sup>[34]</sup> This suggests that structures that decouple the optical and carrier collection path lengths would result in enhanced device efficiencies. In this regard, CNF/TiO<sub>2</sub>

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**Figure 2.** (a,b) SEM images of texturized carbon nanofiber arrays coated with (a) 80 nm TiO<sub>2</sub>, and (b) 400 nm TiO<sub>2</sub>. Inset in both images are higher magnification views. (c,d) Top-view SEM image of a broken TiO<sub>2</sub>/CNF pillar with (c) 80 nm and (d) 400 nm TiO<sub>2</sub> coating. Characterization of TiO<sub>2</sub>/CNF architectures using (e) XRD and (f) Raman spectroscopy to confirm the presence of anatase TiO<sub>2</sub> and the wall quality of the CNFs, respectively.

architecture explored here presents an advantage. A scheme depicting this mechanism is shown in Figure 4b. In this case, the high aspect-ratio structure inherent in the textured CNF electrodes results in the formation of a semiconductor absorber with a normal vector (along the direction of the thickness) oriented with some angle >60° relative to the average angle of incident radiation. This means that the effective thickness of the semiconductor is significantly greater than the actual physical thickness meaning that many more photons will be absorbed closer to a point where they can be collected.

The average out-of-plane angle of the textured CNFs (1–2 µm structure base radius, 10 µm height) explored here is  $\theta$  = 75°–85° on average based on SEM characterization (Figure S1). For ideal normal incident radiation, geometrical considerations suggest a structure with  $\theta \sim 80^{\circ}$  to yield ~ 6x enhancement in the optical path length as compared to the physical material thickness. This means for  $T_{\text{TiO2}}$  = 300 nm ~ 3 $L_{\text{D}}$ , an optical path length of ~1.8 µm can be achieved for the normal incident light. In actuality, this simple geometric consideration considerably overestimates the enhancement factor since it assumes only an

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**Figure 3.** (a) Scheme depicting the three-electrode setup utilizing  $TiO_2$  deposited on conductive CNF back contacts as the absorber of AM 1.5 G solar irradiation, and the reference (AgCl/Ag) and counterelectrode (Pt) configuration. (b) Current-potential curves of  $TiO_2$  coated carbon nanofiber arrays with different  $TiO_2$  thicknesses using a simulated AM 1.5 G solar spectrum in 1 M NaOH (dark current: 150 nm  $TiO_2/CNF$ ) and (c) Short circuit current density ( $I_{SC}$ ), defined at E = 0.216 V based on the three-electrode configuration, as a function of  $TiO_2$  thickness for both  $TiO_2$  coated, texturized CNFs and  $TiO_2$  coated planar graphite.



**Figure 4.** (a) Percent reflectance as a function of wavelength for both planar graphite and coated, texturized CNF arrays demonstrating the anti-reflective nature of the CNF arrays (60 and 80 nm TiO<sub>2</sub> coating, respectively). (b) Scheme depicting antireflective nature of highly 3-D structure, and visually demonstrating other possible means by which a 3-D structure can enhance behavior of a solar device.

ideal normal irradiation. Therefore, it should be used simply as a guideline rather than a strict calculation.

Experimental results in support of this geometric analysis are discussed in the supporting information (Figure S3), where similarly antireflective TiO2/CNFs with a significantly lower pillar density (and lower out-of-plane angle) yield only a 2x enhancement to device performance in comparison to flat TiO<sub>2</sub>/graphite. Although this does not decouple the physics of the absorption and collection processes that lead to these enhancements, it does demonstrate that electrode structure is a principle component of enhanced device performance from 3-D semiconductor scaffolds. Therefore, this suggests that the textured CNF electrodes as a back-contact for a thin semiconducting absorbing layer offers a rational approach for obtaining devices with a balance between the effective thickness for maximized absorption, and the actual thickness, which could ideally be tuned to  $L_{\rm D}$ . In this particular case of TiO<sub>2</sub>, this yields high efficiency since most absorbed photons have energies near the semiconductor band-gap energy. We further conclude that rational design of semiconductor architecture, in addition to chemical features of the semiconductor material (i.e. band





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gap) are important in designing efficient solar devices. This is particularly true for metal-oxides, where poor minority carrier lifetimes can be compensated by tuning the structure of the electrode–perhaps yielding a route toward high efficiency devices from cheap and readily available materials.

In summary, we develop here a technique to fabricate scalable, 3D back-contact architectures for solar devices utilizing a solution-textured CNF array template. Utilizing TiO<sub>2</sub> as an example absorber layer for PEC, a ~3x enhancement of measured *J*SC was observed compared to planar substrates. We explain the enhancement as being due to a combination of reduced reflectance, enhanced absorption due to increased effective optical path length, and enhanced carrier collection efficiency. The CNF back-contacts reported here present a generic route for enhancing the performance of conventional thin-film solar devices, including PVs, especially for materials with small  $L_D$ , less than the characteristic absorption length. Graphitic CNFs are particularly attractive for such back-contact applications due to their high conductance, lack of surface native oxide layers, and high chemical robustness.

#### **Experimental Section**

Aligned Carbon Nanofiber Growth: Vertically aligned carbon nanofiber (CNF) arrays were grown in a plasma-enhanced chemical vapor deposition system utilizing  $C_2H_2$ ,  $H_2$ , and NH<sub>3</sub> precursors using a general approach described in more detail elsewhere.<sup>[25]</sup> The as-grown samples had CNF vertical heights of ~10  $\mu$ m based on SEM imaging. Catalyst growth substrates were deposited utilizing electron-beam evaporation using a 200 nm thick Cu layer, a 30 nm thick Ti layer, and a 30 nm thick Ni layer on a *p*-Si substrate with 50 nm SiO<sub>2</sub>. The Ti layer acts as an interdiffusion barrier for the Ni catalyst while still allowing the substrate to remain conductive following growth. Following growth, the CNFs were exposed to liquid treatment using a drop of solvent, dried, and then coated using ALD.

Atomic Layer Deposition: ALD coating was performed using a Picosun Sunale system with intermittent 0.1 sec pulses of titanium tetrakis isopropoxide and water vapor between 5 second N<sub>2</sub> purges. The deposition temperature was 250 °C. This condition results in a deposition rate of ~0.2–0.3 Å/cycle.

AM 1.5 G Photocurrent Measurements: Photocurrent measurements were performed utilizing a Newport solar simulator (50–500 W, model 67005), which was tuned to 100 mW/cm<sup>2</sup> using a broadband power meter. The photocell in which measurements were performed was custom-made (Adams & Chittenden) with a 40 mm quartz window for sample illumination. Prior to filling the photocell with 1 M NaOH electrolyte, the incident light intensity was calibrated to 1 sun at the exact position where the TiO<sub>2</sub> absorbing material is illuminated. To compare the effect of electrode structure or TiO<sub>2</sub> thickness on measured photocurrents, current-potential curves are taken for different samples in the same configuration. To prepare electrodes for measurements, Ag paint is utilized to contact the Cu layer on which the 3-D carbon nanofibers are grown, and Dow Corning 3140 RTV waterproof adhesive is utilized to isolate all surfaces of the sample except the active TiO<sub>2</sub> coated CNFs.

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

#### Acknowledgements

This work was partially funded by Berkeley Sensor and Actuator Center, and Mohr Davidow Ventures. The synthesis part of this work was supported by a LDRD from Lawrence Berkeley National Laboratory (LBNL). Reflectance measurements were performed using facilities in the Electronic Materials Program, LBNL, which is supported by supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. A.J. acknowledges a Sloan Fellowship and support from the World Class University program at Sunchon National University.

Received: July 31, 2011

Revised: September 28, 2011

Published online: October 26, 2011

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## Supporting Information

for Adv. Energy Mater., DOI: 10.1002/aenm.201100436

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Figure S1. Zoomed-in SEM image showing textured CNF pillars following acetone condensation. In this case, the base of the pillar has a radius of ~ 1.4  $\mu$ m with  $\Theta$  ~ 81°. It should be noted that this undershoots the pillar height due to out-of-plane parallax during imaging. On average, most pillars are found to have widths at the base of structure near or below 2  $\mu$ m, which validates the estimation of 75° <  $\Theta$  < 85° in the main text.





**Figure S2.** Simple geometrical argument relating the effective thickness of a semiconductor coated on a three-dimensional nanostructure  $(t_{eff})$  to the actual coated thickness (t) as a function of the tilt angle of the nanostructure. In correspondence with Figure 4, the effect of a three-dimensional structure can be envisioned to be most apparent when the tilt angle is between 60°-85°, yielding a ratio of  $t_{eff}/t > 2$ . For light incident or nearly incident on the semiconductor, this yields a significantly enhanced effective optical path length that can yield enhanced absorption near the charge collection point. Such an effect is analogous, but yet more tailorable, than the enhancement that occurs due to surface-bound scattering nanoparticles.



**Figure S3.** (a) Short circuit current density ( $J_{SC}$ ) as a function of ALD coated TiO<sub>2</sub> thickness for coated texturized carbon nanofibers processed to have a significantly lower density of "pillars" compared to results described in Figs. 1 and 3, overlaid with data from Fig. 3. Similar to that shown in Fig. 3c, this result is compared to the values of  $J_{SC}$  obtained from TiO<sub>2</sub> coated onto smooth pressed graphite substrates. (b) SEM image of the lower density texturized carbon nanofiber substrates, emphasizing the significantly enhanced pillar pitch as compared to that discussed in Figure 1. Although such coated CNF structures are similarly anti-reflective, the enhancement of  $J_{SC}$  is only ~ 2 times that obtained from TiO<sub>2</sub>/planar graphite – smaller than the factor of ~ 3 obtained with the higher density texturized structure. This demonstrates that the structure of the texturized CNFs in Figs. 1 and 2 utilized in this study plays a key role in the enhanced photoelectrochemical performance, beyond that which can be explained by only anti-reflectivity. This suggests that enhanced carrier collection due to reduction of band-to-band recombination (Fig. S4, Fig. 4) and enhanced carrier collection are key features in the enhanced current density and efficiency measured in these threedimensional architectures.