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### Recommended Citation

Uddin, MJ, Grissom, G, Leal, M, Galvez, V, Trad, T, Touhami, A, Islam, N, Parsons, J, & Moore, HJ. "Self-Aligned Carbon Nanotube Yarns for Multifunctional Optoelectronic Applications." Proceedings of the ASME 2016 International Mechanical Engineering Congress and Exposition. Volume 10: Micro- and Nano-Systems Engineering and Packaging. Phoenix, Arizona, USA. November 11–17, 2016. V010T13A032. ASME. <https://doi.org/10.1115/IMECE2016-67441>

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## SELF-ALIGNED CARBON NANOTUBE YARNS FOR MULTIFUNCTIONAL OPTOELECTRONIC APPLICATIONS

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### ABSTRACT

In this work, the morphology and electrocatalytic features of carbon nanotube yarns at the structural level allow for enhanced photoconversion efficiency. The energy conversion of electron-hole pairs within the carbon nanotube yarn (CNY) due to the functionalization with nanostructured photoactive TiO<sub>2</sub> phases is remarkable. A well oriented anatase TiO<sub>2</sub> thin layer (approximately 100 nm) forms at the interfaces of CNY and TiO<sub>2</sub> mesoporous film when the sample is precoated and annealed at 350°C. Field Emission Scanning Electron Microscopy (FESEM) images show the integrity and homogeneity of the TiO<sub>2</sub> surface, which is indicative of the overall durability of the CNY-based dye sensitized solar cell (DSSC); Coating TiO<sub>2</sub> on self-aligned carbon nanotube yarns provides several benefits from their high chemical stability, excellent functionality, nontoxicity and relatively low cost. The maximum photon to current conversion efficiency ( $\eta_{AM1.5}$ ) achieved with prolonged-time stability was 3.1%.

### INTRODUCTION

Over the last three decades, we have witnessed significant developments in the use of carbon nanotubes (CNTs) in solar cells, sensors, and structural materials. CNT based photovoltaic cells have shown increased efficiencies in solar energy harvesting. CNY based devices have the potential to provide energy in remote locations without the demand in care and handling of the current and more fragile PV energy sources. This added durability opens up new possibilities to modernize undeveloped infrastructures in remote areas of the world.

CNTs bundled into highly aligned yarns for use in CNY based wires provide a new support for sensitizer-loaded semiconductor nanophase, consequently acting as a base for flexible, easily weavable, or even wearable photovoltaic cells. DSSC's will play an important role in the future of flexible

smart surfaces, which have the ability to provide feedback in real time of the support's current status, location, environmental conditions, as well as providing energy for communication devices [1, 2]. DSSC's using fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO) glass have recently surpassed energy conversion efficiencies of 12%, however, the incorporation of these conventional flat cells may yet prove a challenge to engineering structures due to their rigid substrate and unavoidable thickness [3]. Using flexible wire shaped DSSCs has proven a viable alternative to these solid substrates. DSSCs with incorporated polymerized liquid electrolytes have demonstrated promising cell performance nearly comparable to FTO and ITO solid-state cells [4-6]. Several research efforts [2, 4, 7, 8] on flexible DSSC's are distinctively carried out on polymer supported transparent conductive oxides (TCO) electrodes. Ito et al.[6] and Yamaguchi et al. [9] reported that the photoenergy conversion efficiency with flexible 2D DSSC's using titanium or plastic supported ITO flexible sheets reached up to 7.6%. Our current study focuses on the development of photovoltaic cells based on functionalized CNYs. Herein, we describe the design and use of highly inter-aligned and ultra-strong CNY-based photovoltaic cells as an alternative and innovative base for solar cells, which up until now have generally been built around rigid substrates such as FTO and ITO glass [2]. These fiber-based solar cells have power conversion efficiencies independent of light source location and they are generally referred to as three dimensional cells.

### MATERIALS AND METHODS

CNY was soaked in acetone under minor agitation for three hours to dissolve the polymer coating. The CNY was then rinsed with acetone for approximately one minute with light, intermittent sonication, and then air dried at room temperature. The CNY was rinsed with Milli-Q water for one minute and sonicated as stated above. All sonication's were done carefully as expansion of the CNY during sonication is clearly evident and could lead to degradation of the mechanical integrity of the CNY if excessive sonication were to take place. After baking, the CNY was rinsed for one minute each in Milli-Q water, acetone, 2-propanol, sonicated as stated above, and air-dried at room temperature. The CNY was functionalized by placing in nitric acid (70 wt %) for 12 hours in a shaker at 60 RPM. The CNY was removed from the nitric acid and rinsed three times with Milli-Q water, acetone, 2-propanol, and then sonicated as stated above to facilitate removal of any remaining polymer ash followed by air drying at room temperature. The working electrode was treated by submerging the working electrode in enough Triton X to cover for five minutes and sonicated as stated above. Approximately 2 mL of ethanol was added to the Triton-X solution in order to thin the solution, followed by further sonication. The solution was further thinned with ethanol until the Triton-X was easily poured off. The working electrode was prepared by twisting five individual yarns together allowing the mechanical properties of the twisted yarns to twist back upon them in order to make a thread as you might make a yarn or a rope out of hemp or wool. This method creates a working electrode that is approximately 75  $\mu\text{m}$  wide as each individual carbon nanoyarn is approximately 25  $\mu\text{m}$  wide. A thin film of nano-TiO<sub>2</sub> was grown as a base for the micro-TiO<sub>2</sub> film on the working electrode (WE). The preparation of the sol was reported elsewhere[2].

The TiO<sub>2</sub> nano-sol was prepared by using the same titanium precursor in 2-propanol. The final volume of the nano solution was approximately 100 mL. The sol is mixed under vigorous stirring in 50 mL of two propanol, 1 mL of glacial acetic acid, and 5.9 mL of titanium isopropoxide. The WE was submerged in the titanium dioxide nano sol for one minute and calcined at 100°C for 10 minutes and the process was repeated a total of three times [10]. The WE was then placed in the macro – sol for 5 to 7 seconds and dried at room temperature. Each WE was then calcined at 300°C for five minutes. This coating and calcining process was repeated a total of three times, with the final calcine lasting 30 minutes at 300°C. A 0.05M TiCl<sub>4</sub> solution was prepared and the WE's were placed in the solution for a period of 12 hours. Without further cooling, the TiO<sub>2</sub> wires were submerged in N719.

The WE's were now ready for the chemical bath deposition process. Sources of selenium, cadmium, and sulfur were prepared as follows. The selenium source was prepared by reflux for seven hours at 70°C using a 0.7 molar solution in Millie Q H<sub>2</sub>O of sodium selenite. After refluxing, the solution was held at 50°C in preparation for the quantum dot bath. The source of cadmium was prepared as a 0.5 molar cadmium nitrate/ethanol solution. This process was also repeated a total

of three times. The WE's were then placed in the sodium selenite solution and held at 50° for one hour, then removed and dried at room temperature. A poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) quantum dot solution was prepared using 0.003 wt% at 1:1. The P<sub>3</sub>HT solution is 50 mg in 10 mL of chloroform. The PCBM is 50 mg in 10 mL of chlorobenzene. These two solutions were mixed separately and stirred for two minutes; the solutions were then mixed together thoroughly. The WE's were placed into the P<sub>3</sub>HT/PCBM solution for 12 hours. A N719 dye sensitizer solution was then prepared by mixing 20 mL of N719 solution in *tert*-butanol/acetonitrile solution at a 1:1 ratio. The acetonitrile was added to a beaker while the N-719 was stirring. *tert*-Butanol is then added to the solution encouraging the N-719 to dissolve and facilitate the recrystallization of the N-719 on the WE. Since the solution is light sensitive, these operations must take place under dark conditions. The CNY WE's were immersed in the capital and N-719 dye sensitizer for 24 hours at room temperature and then they are removed and dried at room temperature. This completed the functionalization of the working electrode. The preparation of the counter electrode (CE) was initiated by washing in 1.5 M sulfuric acid and 0.5M nitric acid for three minutes and then dried at room temperature. The CE was then washed with mili-Q H<sub>2</sub>O for three minutes and dried at room temperature, soaked in Triton–X for five minutes, and air dried at room temperature. The CE was washed thoroughly in Millie Q H<sub>2</sub>O for five minutes under light agitation. A process of thin-film deposition was used to platinize the counter electrode by using a sputtering target at 1.5 KV and 8.0 mA for 40 seconds. Finally, WE's were wound with the CE's with the thread pitch of approximately 1 mm in preparation for cell assembly.

## RESULTS AND DISCUSSION

Figure 1a-d shows the SEM images of the CNT based CE and WE of the three dimensional optoelectronic rods. Figure 1a-b shows the detailed structural feature of the CE, which is composed of enormous numbers of individual carbon nanotubes. The individual carbon nanotubes were approximately 80% interaligned with approximately 20% composed of entangled nanotubes. The entangle tubes of the electrode materials ensure fast electron collection from the device interior and transportation toward the external circuit board. Energy dispersive spectroscopy (EDS) provides the elemental composition of the electrode materials, which clearly infer that the electrode is made of CNT and they contain a certain amount of surface functional groups Figure 1c-d shows the surface morphology of the TiO<sub>2</sub> nanophase deposited over the electrode surface. It is clearly evident that the TiO<sub>2</sub> nanophase was coated on the entire working electrode surface. The nanostructured photoactive TiO<sub>2</sub> phase with nanoporous nature is clearly evident in Figure 1d. Structural phase and grafted layer thickness of the TiO<sub>2</sub> nano and macro films is critically important to the proper working performance of the photovoltaic cells. The donor-accepter characteristics of

electron transfer within bulk heterojunction are critically important to make efficient PV devices.

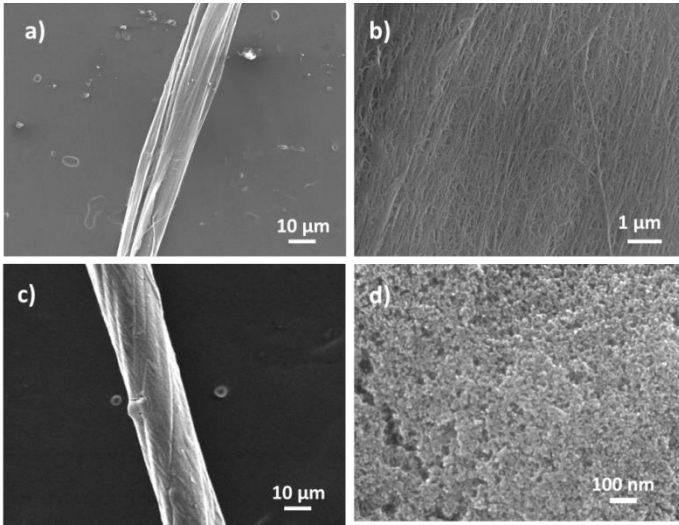


Figure 1. a) FESEM images of a) CNT yarn as CE, b) selected small area of CE which shows it consists of enormous number of CNTs, b) TiO<sub>2</sub> film coated CNT yarn (WE), and c) selected small area of TiO<sub>2</sub> film deposited on the WE.

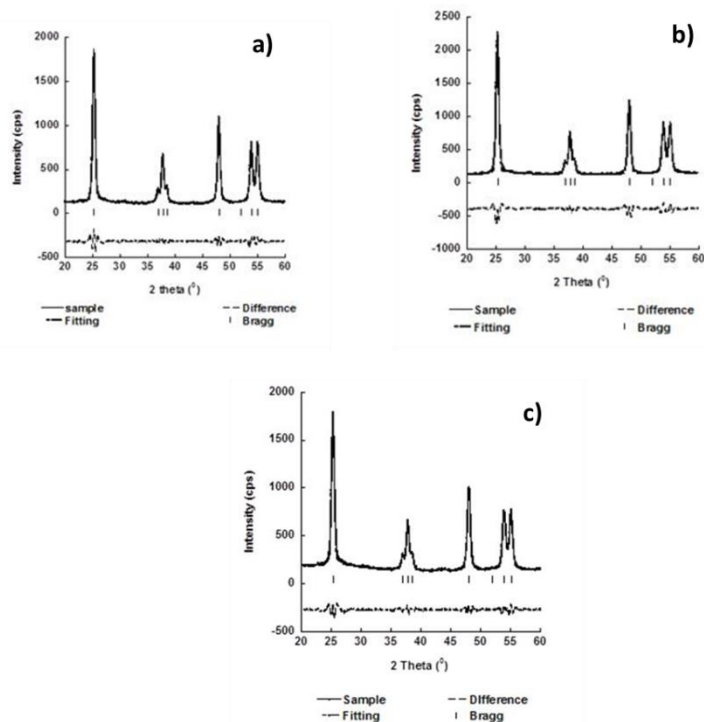
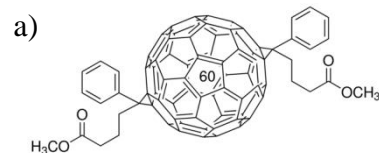


Figure 2: XRD pattern of CdSe-TiO<sub>2</sub>, CdS-TiO<sub>2</sub> and CdSe-CdS-TiO<sub>2</sub> deposited on the CNY based cells.

SEM images that show the integrity and homogeneity of the TiO<sub>2</sub> surface indicate the overall durability of the Dye

Sensitized Photovoltaic CNY (DSP-CNY) for its use in flexible materials. EDS analysis provides data indicating the penetration and distribution of the various functionalization resulting from the chemical bath deposition process and incorporation in the polymer to the CNY by thin film deposition. The pore-filling characteristic features of the TiO<sub>2</sub> macro and nano coats, penetration of TiCl<sub>4</sub>, and cadmium sulfide (CdS) and cadmium selenide (CdSe) quantum dots were determined by EDS and FESEM. These techniques clearly indicate the structural integrity of the 3D PV cell and surface composition prior to and during functionalization. EDS data suggests that no solvent remains from the initial preparation sequence, which would be detrimental to cell function (*Figures not shown for the sake of brevity*).

The XRD patterns of the CdS-TiO<sub>2</sub>, CdSe-TiO<sub>2</sub> and of CdSCdSe-TiO<sub>2</sub> samples are illustrated in Figure 2 a-c. These broader peaks at  $2\theta = 25.32$  (101), 36.98 (103), 37.84 (004), 38.59 (11 2), 48.06 ( 200), 51.99 (202), 53.94 (105) and 55.09 (211) are indicative of anatase phase. The remarkable widths of these peaks are a direct indication that the particles sizes of the deposited photocatalyst are quite small. From the full width at half maximum (FWHM) of the peaks, by using the Scherrer's equation  $L_c = K\lambda/(\beta\cos\theta)$  [11] (where  $\lambda$  is the X-ray wavelength,  $\beta$  is the FWHM of the diffraction line,  $\theta$  is the diffraction angle, and  $K$  is a constant, which has been assumed to be 0.9), an average diameter of the TiO<sub>2</sub> particles is estimated about several nanometers. An additional peak on the pattern, which would correspond to the CdSe and CdS particles on the TiO<sub>2</sub> film, are absent due to their trace amount. Polymer, Bis(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6.6]C62 (mixture of isomers), Bis[60] PCBM (PCBM 62) and Poly(3-hexylthiophene-2,5-diyl) (P3HT) (Figure 3 a-b), sensitizer based photovoltaic cells facilitate a high efficiency rate in photon to electron conversion. Carrier conversion efficiency ( $\eta_c$ ) and energy conversion efficiency ( $\eta$ ) of carbon nano-yarn (CNY) based photovoltaic devices are improved when semiconducting polymers incorporating C62 or its functionalized derivatives are used in conjunction with CdS and CdSe. Composite films and quantum dot functionalization of the CNY takes place by chemical bath deposition. Use of the organic sensitizers such as fullerenes shows approximately a 29 percent increase in use of electrons per photon and a 2.9 percent increase in efficiency[12]. CNY based photovoltaic cells show enhanced photoconversion efficiency with enhanced electron-hole pair stability. This improvement is due to functionalization of the CNT with nano and macro coats of TiO<sub>2</sub> and semiconducting polymers incorporating C60 or its functionalized derivatives.



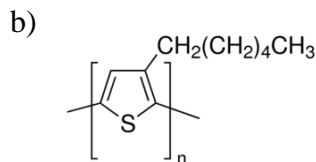


Figure 3: a) Bis(1-[3-(methoxycarbonyl)propyl]-1-phenyl)-[6,6]C62 (mixture of isomers), Bis[60]PCBM (PCBM 62) and b) Poly(3-hexylthiophene-2,5-diyl) (P3HT).

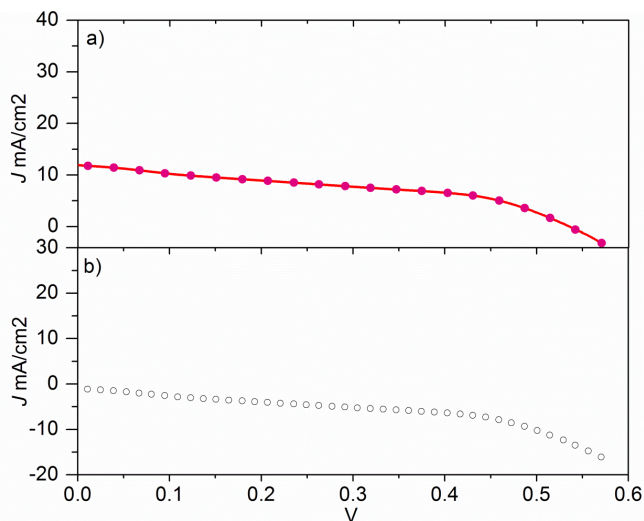


Figure 4.  $J$ - $V$  curve of CNT-CNT yarn cells. This  $J$ - $V$  curve was recorded under solar irradiation (AM 1.5G). The gray curve represents the dark current output by the cells.

Figure 4 shows the  $J$ - $V$  curve of a synthesized 3D PV cell under simulated solar irradiation source. The intertwined of five CNT yarns potentially creates an efficient  $\text{TiO}_2$ -CNT interface through increasing the cell diameter. This combination both in WE and CE generate of  $J_{sc}$  and  $V_{oc}$  of  $12 \text{ mAcm}^{-2}$  and  $0.55 \text{ V}$ , respectively. Though this system shows a  $\sim 0.55 \text{ V}$  open circuit voltage, it improved the short circuit current to  $12 \text{ mAcm}^{-2}$ , which is much greater than that of the photovoltaic system consisting of lower numbers of CNT yarns. The maximum fill factor of the cell found approximately 0.45 during optimization of the WEs' diameter. However, this highly flexible cell generates a remarkable power output with photon to photocurrent generation efficiency of  $\sim 3.1\%$ , which is many folds larger than that of previously reported solid state wire-shaped flexible DSSC [13, 14]. The CNT yarns as CE show better performance than Pt wire as CE in photogenerated electron collection during cell operation, [2] which suggest that the electrocatalytic performance of CNT yarn as CE in comparison with metallic wire under same irradiation condition exhibit notably higher catalytic performance to solid electrolyte

redox pair. The CNT-CNT 3D photovoltaic cells, which do not contain any of costly transparent conductive oxides, is highly flexible and uses an all solid state electrolyte confirms the cell's surface adaptability, transportation feasibility and expanded operational capability.

## CONCLUSION

A CNT-CNT yarn based photovoltaic flexible cells have been synthesized by grafting  $\text{TiO}_2$  films using layer-by-layer deposition method on CNT yarns. A surface engineered and independent CNT yarn was twisted around  $\text{TiO}_2$ /CNT-yarn as a CE. The number of CNT yarns of the WE that intertwined together influence the energy conversion efficiency of flexible 3D cells. A CNT yarn as a WE with solid-state electrolyte produced an enhanced photon to current conversion efficiency (3.1%) using simulated solar light (AM 1.5,  $100 \text{ mWcm}^{-2}$ ). These 3D cells have excellent intrinsic light sensing and conversion capabilities making them potentially applicable in the development of a multifunctional composite fabric or large civil and aerospace structures by weaving or imprinting these photovoltaic fibers.

## ACKNOWLEDGMENTS

This research work was generously supported by a Welch Foundation Departmental Grant (BX-0048).

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