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Three-dimensional carbon nanotube yarn based solid state solar cells with multiple sensitizers exhibit high energy conversion efficiency

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ABSTRACT

Fiber-type dye sensitized solar cells that are non-metallic, flexible, and thread-like in structure have many potential military and functional textile applications. With the use of quantum dots (QD), exciton transfer facilitators (Phenyl-C61-butyric acid methyl ester-PCBM) and Poly(3-hexylthiophene-2,5-diyl-P3HT), and careful preparation of the TiO_2 oxide layer deposited on the carbon fiber working electrode, an optimized efficiency of 7.6% was obtained. Carbon nanotube yarn (CNTY) was used to prepare both the working and counter electrodes of the fabricated cells. $TiCl_4$ annealing of the TiO_2 layer was carried out and the resulting oxide layer morphology was found to be very uniform. The quantum dots, cadmium sulfide (CdS) and cadmium selenide (CdSe), were deposited directly onto the surface of the nanoporous oxide layer using chemical bath deposition (CBD). Also, the P3HT and PCBM were applied and deposited via CBD on the working electrode as a bulk heterojunction material. Potentiometric characterization of the prepared cells performed at different cell lengths and showed that the maximum efficiency was obtained for cells approximately 3.5 cm in length. Photovoltaic performance of these solid state three dimensional cells was also carried out for different cell configurations.

1. Introduction

Dye sensitized solar cells (DSSCs) were originally developed in the late 1960s after it was discovered that organic dyes in conjunction with an oxide electrode can produce electricity (Gerischer et al., 1968). Since then, the comparatively low cost of DSSCs to other solar cell technologies and their ability to be manufactured out of flexible and three dimensionally structured materials has prompted significant research into increasing the power conversion efficiency of DSSCs (Fan et al., 2008).

The principle component of DSSCs is the dye/metal oxide layer interface (the two innermost components visible in the abstract graphic) where electron-hole pairs (Frenkel excitons) are generated when energetic photons excite the dye molecules adsorbed on the metal oxide surface (Thavasi et al., 2009). If the nanostructured metal oxide layer is only 10 μm thick, an individual photo-generated electron will visit 10^6 nanoparticles before reaching the cell's cathode (Hu et al., 2007). Thus, when preparing the TiO_2 (metal oxide) surface it is very important to minimize surface defects which can act as hole traps and lower overall cell efficiency. To this end, many methods have been used to improve the characteristics of the oxide layer either during deposition on the underlying substrate (Domtau et al., 2016; Samsuri et al., 2017) or post deposition (Li et al., 2016). $TiCl_4$ treatment of the TiO_2 surface acts to remove surface irregularities by effectively depositing a nanoporous TiO_2 layer over the microporous TiO_2 layer, which fills in any gaps in the TiO_2 thin film. $TiCl_4$ treatment alone has been reported in the past to increase cell efficiency by up to 1.3 fold (Lee et al., 2012). Furthermore, the TiO_2 layer produced by the sol–gel process used in this work is thick enough to promote light scattering according to Mie theory (Fu and Sun, 2001).

Decoration of the TiO_2 surface with both CdS (bandgap of 2.42 eV) and CdSe (bandgap of 1.84 eV) quantum dots (hemispheres visible in the abstract graphic) can further improve cell performance by allowing for efficient conversion of photons over a wider energy range than is possible with the N719 dye/TiO_2 layer alone (Lin et al., 2007; Sabet and Salavati-Niasari, 2014). Quantum dots also have an advantage in that their optical properties and band gaps are tunable by adjusting the size of the quantum dots (Zou and Sun, 2014), which potentially allows for

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tuning of cell characteristics to maximize efficiency as well as mixing of quantum dots of multiple sizes to easily prepare multijunction solar cells (Lei et al., 2017). Additionally, quantum dots can generate multiple excitons if absorbing a photon with sufficient energy (Kundu et al., 2017), and any multiexciton generation will improve the observed power conversion efficiency. CdS quantum dots, with their relatively large bandgap are able to absorb incident high energy photons that would otherwise be absorbed less efficiently by the dye layer, and CdSe quantum dots with their lower bandgap is able to convert lower energy photons than CdS. The somewhat broad size distribution of the QDs also contributes to a more inclusive photon adsorption range. Finally, the lowest energy photons can be converted by the extensively studied dye N719 (Koops et al., 2009), which itself begins electron injection at ~775 nm and thus has an effective bandgap of 1.60 eV (Bisquert, 2011). A potential hurdle is that degradation of the quantum dots via photo corrosion may occur if direct contact is made between the electrolyte and the quantum dots, so it is vital that they be well-protected from the electrolyte.

Materials with high electron affinities (electron transporters) and others with low ionization potentials (hole transporters) have been employed in DSSCs to aid in electron-hole pair dissociation. Hole transport materials are readily ionizable and help to transport holes away from the photoactive dye/oxide layer interface, thus improving charge separation and overall cell efficiency (Abrusci et al., 2011; Chevrier et al., 2017; Kroon et al., 2008). Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a conductive/fully conjugated thiophene polymer that can aid in hole transport away from the photoactive surface (Chevrier et al., 2017), and has been well studied in DSSC applications (Zhao et al., 2010). Electron transport materials have high electron affinities and transfer electrons away from the dye/metal oxide interface, and like hole transport materials, help to improve overall cell efficiency by lowering the incidence of charge recombination (Pham et al., 2017; Zhou et al., 2010). Phenyl-C61-butyric acid methyl ester (PCBM) is a fullerene compound that readily accepts electrons due to its large conjugated network, and thus is well suited for use in DSSCs as an electron acceptor/transport layer (Zhou et al., 2010). Because exciton diffusion in both PCBM and P3HT is limited, deposition of these materials separately as homogenous layers can impair cell efficiency, thus deposition of a P3HT/PCBM matrix (bulk heterojunction) is preferable to avoid diffusion-limited electron/hole transfer (Kroon et al., 2008).

DSSCs that are flexible and possess cell geometries that differ from the traditional flat two-dimensional panel type have been the topic of a fair amount of research due to their inherent advantages over rigid flat panels. Specifically, flexible cells have the ability to absorb light from any incident angle and may be deployed in applications requiring flexibility, such as incorporation into fabric (Fu et al., 2013). The degree of flexibility exhibited by previously prepared flexible cells (Fan et al., 2008) is somewhat limited by the use of a metallic working electrode. Carbon nanofiber is an inexpensive, strong, flexible, conductive, and chemically inert substrate that is potentially ideal for use in DSSCs, as both the working and counter electrodes (Arbab et al., 2016; Jaksik et al., 2017). Carbon nanofibers for use as DSSC electrodes must be well aligned in the direction of the fiber to maximize conductivity which can be accomplished via extrusion during the manufacturing process (Kim et al., 2017). Furthermore, TiO_2/CNT hybrid nanostructured have been shown to natively exhibit better energy conversion efficiencies due to the intricate nanostructure of the CNT material enhancing charge separation efficiency compared to relatively smooth metallic electrodes (Dembele et al., 2013).

Herein, we present the preparation of novel, flexible, three dimensionally structured dye sensitized solar cells utilizing carbon nanofiber working and counter electrodes, a $TiCl_4$ treated TiO_2 photoelectrode, a P3HT hole transport layer/PCBM electron transport layer, and CdS/CdSe QD photosensitizers. The structure of the photovoltaic cells resembles that of twisted wires with a central counter electrode surrounded by five working electrodes as shown in the abstract graphic. The cells consist of a wound carbon nanofiber working electrode coated with TiO_2, then layered with CdS and CdSe quantum dots, a homogenous PCBM/P3HT bulk heterojunction layer, N719 dye, and finally wrapped with a carbon nanotube yarn counter electrode and wetted with a semi solid-state iodine redox-couple based electrolyte.

2. Methods

The working and counter electrodes were prepared from carbon nanotube yarn (CNTY), which was purchased from Nancomp Technologies Incorporated (USA). For preparation of the working electrode, the polymer coating applied to the CNTY upon manufacturing was removed via calcining in air and successive sonication in acetone, Milli-Q water, and a mixture of Milli-Q water, acetone, and 2-propanol for approximately 1 min each using low intensity pulses. The yarn was then air dried at room temperature before being rinsed with each of the solvents once more and then functionalized by treating with 70% nitric acid for a period of twelve hours in a shaker at 60 RPM. After functionalization, the yarn was subjected to similar washing and drying processes to ensure that the polymer coating was removed. The working electrode was composed of six CNTYs twisted together and the average CNTY diameter was 25 μm, thus giving the overall average cell diameter as ~69.6 μm due to pentagonal, rather than perfect hexagonal packing, around the center electrode.

Deposition of the microporous TiO_2 layer was performed using a nano-sol solution composed of 5.9 ml of titanium isopropoxide and 1 ml glacial acetic acid in 50 ml of isopropanol. The working electrode was submerged in this solution for one minute followed by calcination at 100 °C for 10 min. This process was repeated three times with the final calcination lasting 30 min at 300 °C in atmospheric condition.

One solution using 30 ml of deionized water, 2 ml of glacial acetic acid, 0.5 ml of TEA, and a few ml of TiP were mixed in a beaker for 5 min under vigorous stirring. Another solution of 30 ml of deionized water with nitric acid (70 wt%) was stirred for several min. The two solutions were mixed together, stirred for 30 min, and hydrothermally treated in an autoclave for overnight. Thereafter, 5.2 g of polyethylene glycol was added to the sol and 50% by volume of the solvent evaporated under vigorous stirring at 100 °C. The TiO_2 film anchored onto the yarn using chemical bath deposition process and was then calcined at 300 °C for 5 min. The coating process was repeated 5 times to ensure a TiO_2 film thickness of 15–20 μm covered the yarn. The deposition of nanoporous TiO_2 was completed by soaking the prepared working electrodes in 0.05 M $TiCl_4$ for twelve hours (Uddin et al., 2014).

CdS and CdSe quantum dots were assembled on the TiO_2 film using a chemical bath deposition method. CdS quantum dots were deposited by submerging the electrode in a dilute ethanolic solution of $Cd(NO_3)_2$ for 5 min followed by dipping into a methanolic solution of Na_2S for 5 min. The selenium source was prepared by refluxing Se (0.3 M) for 8 h at 70 °C using a dilute aqueous solution of Na_2SO_3. CdSe was deposited on the film by dipping the yarn into an ethanolic solution of $Cd(NO_3)_2$ for 5 min followed by rinsing with ethanol for 1 min. The working electrode was then dipped into the Na_2SeSO_3 solution for one hour at 50 °C.

After being air dried at room temperature, the working electrodes were placed into the PCBM/P3HT solution for twelve hours. A solution of P3HT in chloroform (5 mg/mL) and PCBM in chlorobenzene (5 mg/mL) were prepared separately and stirred for 2 min prior to being mixed in a 1:1 proportion. Finally, the WE was submerged in a 0.003 wt% solution of the dye sensitizer N719 (Di-tetrabutylammonium *cis*-bis (isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II)) in 1:1 *tert*-butanol/acetonitrile for 24 h under darkness. The N719 solution was prepared by mixing 20 ml of N719 in *tert*-butanol/acetonitrile solution at a 1:1 ratio. The acetonitrile was added to the N719 under stirring and then *tert*-butanol was added to encourage dissolution of the N719 and recrystallization on the working electrode.

The counter electrode was prepared by washing the CNTY in 1.5 M