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Influence of functional derivatives of an amino-coumarin/MWCNT composite organic hetero-junction on the photovoltaic characteristics

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ABSTRACT

A layer of a coumarin derivative\multiwall carbon nanotube (MWCNT) composite was sandwiched between an indium tin oxide (ITO) layer and a top metal electrode. This layer acted as the active hetero-junction (middle hetero-junction) in a triple hetero-junction organic solar cell. The composition of the organic material in the middle hetero-junction component, second from the ITO layer, was varied, keeping the weight percentage of the MWCNTs constant, to investigate the photovoltaic properties of the cell. The choice of amino-coumarin and its derivatives were dictated by the need for a high efficiency organic up-converter. Amino-coumarin is a two photon absorbing organic donor whereas CNTs are acceptors and ballistic charge transport media. For those reasons, amino-coumarin-CNT composite materials were selected as a photo active layer to will absorb the sub-band photons effectively. Additionally, the radial self-assembling of the CNTs inside the organic matrix (during synthesis) enhances the photovoltaic characteristics of the material. The photo induced charge transport mechanism between the MWCNTs and organics was analyzed using photo luminescence (PL) measurements. By the use of 15 wt% of CNTs with the organics, more than 90% of the PL signal was quenched, indicating an ultrafast transport mechanism between the donor and acceptor materials.

1. Introduction

Photovoltaics made from polymers are low cost and environmentally friendly but their major problems include their narrow spectral absorption range, low charge mobility and short diffusion length [1,2]. Increased efficiency demands absorption of photons in a broader range. However, the low efficiency persists because of the lesser participation of the sub band gap photons [3]. The participation of the sub band gap photons can be effectively increased by the use of an organic up-converter [4]. The organic up-converter is the material which absorbs two photons of same energy simultaneously and generates an electron–hole pair. Therefore, studies regarding efficient organic up-converters are of considerable interest.

Nanomaterials added to the polymer have been able to solve the problems of charge mobility and carrier diffusion length [5] to some extent. However, some issues in processing and efficient materials selection in preparing high efficiency and commercially viable solar cells remain unresolved. To improve the solar cell efficiency by increasing the number density of photo-exciton dissociation and carrier transport, various nanostructures like nanorods, nanowires (NWs) and nanoparticles, combined with conjugated polymers have been utilized in solar cells [6–10].

Application of carbon materials, specifically carbon nanotubes (CNTs), in organic photovoltaic devices is of

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considerable interest [11–14]. It has been demonstrated that CNTs along with conjugated polymers favor charge transport and exciton dissociation [15–17]. It has also been reported that CNTs provide efficient hole transportation in a blend of conjugated polymers and enhances carrier mobility [18].

Usually, the photo-responsive organic/CNT layer is prepared by the self-assembly of CNTs and the organic component within an aqueous solution. But the problem is in obtaining ordered self-assembling on an electrode. The regularity is hindered because of poor dispersion of the CNTs in the organic component which reduces the device power conversion efficiency characteristics [19]. The device characteristics not only depend upon the property of the organic component and the 1-D nanostructured material but also on their arrangement in the device [20]. The greater the ordered assembling of the 1-D nanostructure inside the organic matrix, the higher will the charge transfer percolation path be and hence, higher the efficiency. Different approaches have been taken by different groups to modify the CNTs chemically and physically in order to increase their dispersion [15,21]. Here, we report an increased ordering in the assembly of the CNTs in the organic component based on the structural designing of the organic molecule.

In this work, one two photon absorbing organic donor with a 1-dimensional nanomaterial as a photonic up-converter has been studied. An amino-coumarin (–NH_2-coumarin) and the amino-coumarin functionalized in the seventh position of the coumarin moiety (amino-coumarin with β-napthoxy acetic acid functional group (–NH_2-coumarin-NOAA) and amino-coumarin with 2,4 dichlorophenoxy acetic acid functional group(–NH_2-coumarin-2,4D)) were chosen as the donor materials [22]. As amino-coumarin and its derivatives show two-photon absorption and undergo reversible photodimerization [23], it is expected that the incorporation of the coumarin complex with CNTs will produce a photovoltaic response. However, this organic derivative and CNT composite active layer also remains transparent to visible light. So, the composite layer can be used as a second layer next to the indium tin oxide (ITO) transparent electrode in layered photovoltaics which can effectively absorb the sub-band photons and produce additional electron–hole pairs. The fabrication and operation of organic/CNT bulk hetero junction single layer photovoltaic structures based on coumarin derivatives has been described. The effects of changing the molecular functionalised group to the base coumarin and dispersing it with the CNTs and the corresponding change in their photovoltaic characteristics were also investigated.

2. Material and methods

2.1. Synthesis of coumarin derivatives

Several different coumarin derivatives were synthesized and this work has been reported previously [24]. The molecular structures of the as-synthesized organic compounds of the amino-coumarin and its functional derivatives are shown in Fig. 1. Amino-coumarin (–NH_2-coumarin), amino-coumarin with β-napthoxy acetic acid functional group (–NH_2-coumarin-NOAA) and amino-coumarin with 2,4dichlorophenoxy acetic acid functional group (–NH_2-coumarin-2,4D organic complexes were used for the preparation of the photovoltaic cells.

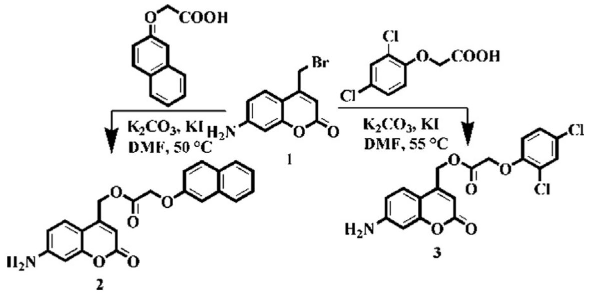

Fig. 1. Molecular structures of the as-synthesized organic compounds of the amino-coumarin and its functional derivatives.

2.2. Growth of CNTs

The CNTs were grown using nickel as the catalyst upon the Si(1 0 0) substrate by atmospheric chemical vapor deposition (APCVD). The detail of the synthesis of CNTs has been reported elsewhere [25]. To remove the metal catalyst particles and amorphous carbon particles, the as-grown CNTs were refluxed in 2.6 M HNO_3 in 140 °C for 8 h. The residue was then washed with distilled water until the pH became neutral. After that, the solution was centrifuged for 15 min and the product was separated out. Lastly, the separated product was dried at 100 °C for 12 h to yield purified CNTs.

2.3. Preparation of the device

The photovoltaic devices were fabricated on patterned indium tin oxide (ITO) coated glass substrates. The sheet resistance of the ITO anode was 10 Ω/□.

Prior to organic layer deposition, ITO substrates were cleaned thoroughly in acetone, isopropyl alcohol and de-ionized water in sequence by an ultrasonic cleaner followed by drying with nitrogen gas for 30 s. For developing the film, 5 wt% of the coumarin derivative was dissolved in aceto-nitrile. A 100 nm thick coumarin/CNTs layer was spin coated on the ITO anodes from a solution containing 15 wt% CNTs and 5 wt% of coumarin derivative in aceto-nitrile. Spin coated coumarin/CNT substrates were annealed at around 80 °C for 15 min to remove the solvent completely. Finally, a 120 nm thick aluminium top electrode strip was deposited by thermal evaporation through a shadow mask to define a square shaped active area of 4 mm^2. Aluminium was used as the top electrode to fabricate the complete cell structure as ITO/coumarin: CNT/Al (shown in Fig. 2).

2.4. Characterization of the samples

The thickness of different layers was monitored by a stylus profilometer (Veeco Dektak3). Atomic force microscopy (AFM) Nanonics™ 2000 in intermittent contact mode was used to study the surface morphology of the photoactive layer.