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Mathematical Modeling and Analysis of Carbon Nanotube Photovoltaic Systems ⋆

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Abstract: This article considers first-principles predictive modeling of carbon nanotube photovoltaic (PV) devices, with the objective being to increase predictive capabilities to the point that systems engineering approaches can be applied. After covering some background, the state of the art in first-principles modeling is reviewed and extended to include the construction of realistic spatial placements of carbon nanotubes within the device during manufacturing and the effects of exciton hopping between carbon nanotubes. Challenges in the construction of improved first-principles models and some promising future directions are discussed.

Keywords: Solar energy, solar cells, mathematical models, distributed models, nonlinear models, physical models, state-space models

1. INTRODUCTION

Photovoltaic (PV) devices directly convert sunlight into electricity. Widespread use of PVs has been hampered by high cost of generating electricity from the commercially available silicon-based solar cells (Umeyama and Imahori, 2008). Developing lower cost PVs that exhibit high cell performance is of great practical importance for increasing the use of solar energy. PV devices of commercial/scientific interest can be grouped into three generations (Bagnall and Boreland, 2008). Third-generation devices have an advantage in terms of maximum possible efficiency at the thermodynamic limit compared to that of first- and second-generation devices. Because sunlight contains photons with a wide range of energies from approximately 0.5 to 3.5 V, only about 1/3 of the total energy can be utilized from first- or second-generation PV devices (Conibeer, 2007). This limit is a result of photons with a lower energy than the optical bandgap frequently not being absorbed and the fact that the excess kinetic energy of "hot" carriers (i.e., photons with higher energy than the bandgap) is often lost as heat through various scattering processes. On the other hand, third-generation PVs can potentially reduce the energy losses associated with the cooling of hot carriers while rendering the absorption of sub-bandgap photons possible through multi-exciton generation (where two or more excitons are produced from a hot exciton created by absorption of high-energy photons), increasing the theoretical efficiency limit (Wang et al., 2013).

Cost and performance requirements make semiconducting single-walled carbon nanotubes (SWCNTs) attractive photo-absorbers for near-infrared PV applications. SWCNTs are potentially very cheap to manufacture due to their solution process-ability, naturally abundant source materials (carbon), and continuously reducing cost of scalable fabrication and purification (Bernardi et al., 2012). SWCNTs have widely tunable properties. For example, selective or broadbrand absorption of light spanning from the ultraviolet to the near-infrared can be enabled by combining different types of SWCNTs. This versatility can improve the light absorption efficiency (Arnold et al., 2013). SWCNTs have one-dimensional (1D) nanowire-like structures that are closely associated with ideal electron and hole transport in organic solar cells (Bernardi et al., 2012). Experimentally, SWCNTs demonstrate superior exciton and free carrier diffusivity and mobility, have exceptionally large absorption cross-sections, and are resistant to oxidation by water and oxygen (i.e., relatively stable) compared to other promising organic and inorganic PV materials (Bernardi et al., 2012). SWCNTs can be combined with other materials and nanostructures to produce unique heterostructures with beneficial and potentially unexpected properties (Wang et al., 2013).

Single-walled nanotube (SWNT) PVs with 0.01–1.7% external quantum efficiency have been reported using single (Jain et al., 2012), mixed semiconducting (Bernardi et al., 2012), and mixed semiconducting and metal chiralities (Arnold et al., 2013) in a variety of configurations including bulk (Bernardi et al., 2012) and planar heterojunctions (Jain et al., 2012). Polymers (Ren et al., 2011) and fullerenes (Jain et al., 2012) have been used to enable exciton dissociation and/or co-photoabsorption. Despite this progress, the observed device efficiencies are lower than that of their silicon counterparts and far below the theoretical limit. Moreover, even basic questions of suitable/optimal device properties and configurations, such as nanotube chirality, density, orientation, and film thickness, remain unanswered due to the complex system dynamics.

This article considers first-principles modeling of carbon nanotube PV devices suitable for the analysis of performance and in determining optimal device configurations and properties, and points out needs that can be addressed

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by the process systems community. Section 2 describes the devices and the physical processes that must be captured in the model. The modeling of carbon nanotube PV devices is reviewed in Section 3. Extensions to include the effects of three-dimensional carbon nanotube placement on operating efficiency within a PV device, as well as challenges and ideas for future directions, are described in Section 4.

2. PROCESS DESCRIPTION

In organic PV devices, the three major processes associated with converting sunlight to electrical power are (1) **Light absorption:** Absorption of sunlight photons in an photoactive layer to form excitons, (2) **Exciton transport:** Migration, and subsequent dissociation, of excitons at an interface (e.g., donor-acceptor heterojunction or charge-collecting electrode) to form free electrons and holes, and (3) **Free carrier transport:** Movement of free electron and holes toward their respective electrode to yield a photocurrent in an external circuit.

These processes behave according to the system and device geometry under consideration. The interest in this work is in carbon nanotube PVs with geometries similar to that shown in Fig. 1, which represents a network of intersecting (virtually 1D) SWCNTs. These tubes can be in contact with a variety of conduction and valence band charge-collecting electrode configurations including those where an electrode acts as a co-photoabsorber (e.g., fullerenes). As such, the overall device description can be broken down into four connected blocks. First, the geometry and properties of the device must be specified *a priori* (termed the **geometry** problem). Next, system inputs (e.g., sunlight power entering the device) must be specified and, finally, these inputs pass through the **light**, **exciton**, and **free carrier** processes (described above) producing some outputs of interest (e.g., current, external quantum efficiency).

The relevant physics, known to date, within these blocks are described below. The **light**, **exciton**, and **free carrier** processes depend on each another and cannot be solved independently unless certain phenomena are neglected.

2.1 Geometry of the Three-dimensional Nanotube Network

The geometry problem defines the space on which the various physical phenomena occur, and consists of all relevant configurational and material information decided upon by the maker of the device. A large network of interconnected nanotubes on the device scale can be complex to describe mathematically, which is further complicated by the fact that SWNT commonly bundle together, resulting in an arrangement that has different properties than the individual tubes. Even unbundled SWNT can have significantly heterogeneous films with large variation in film density at the micron scale (Bellisario et al., 2014).

2.2 Light Absorption

The conditions of the sunlight (e.g., intensity, orientation) are inputs to the system and can only be manipulated via the geometry and location of the device. As such, the

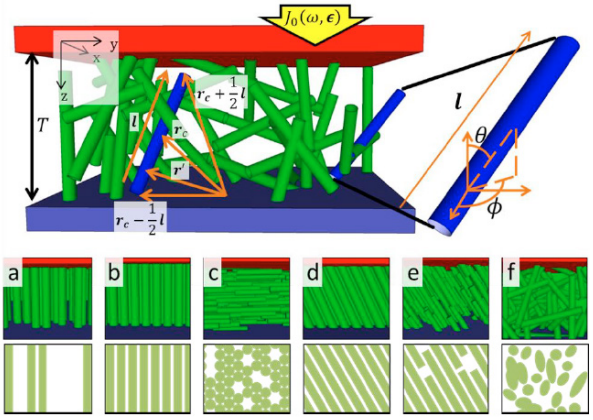

Fig. 1. Model geometry showing center relative to the origin $\mathbf{r}_c$, orientation $\hat{\boldsymbol{l}} \triangleq (\theta, \phi)$, and length l of a nanotube. The thickness of the device is denoted T and the light enters perpendicular to the x-y direction with irradiance $J_0(\omega, \boldsymbol{\epsilon})$. The top image is a schematic of the side view of the device and (a–f) are examples of different film geometries along the cross-section of the device: (a) sparse vertically aligned film, (b) close-packed vertically aligned film, (c) horizontally aligned film with density above the percolation threshold, (d) single-layer deposited aligned film at some arbitrary angle, (e) multi-layer deposited aligned film at some arbitrary angle, (f) isotropic film. Reproduced from Bellisario et al. (2014).

concern is how the sunlight is affected after entering the PV device. The ways in which light can be transformed inside a nanotube-based PV device are
(1) **Photon absorption:** Photons can be absorbed by the nanotubes (dependent on their absorption cross-section) or by any co-absorber to generate excitons.
(2) **Photon emission:** Excitons at the nanotube bandgap can relax by radiative decay and emit a photon through fluorescence/photoluminescence. The photon will have energy equal to that of the bandgap and will be emitted in a direction perpendicular to the nanotube, which affects both the wavelength and propagation direction of the light.
(3) **Scattering:** The nanotubes can deflect light without absorption, causing the light to deviate from a straight path within the device. Rayleigh scattering, which is elastic light scattering by particulate matter much smaller than the wavelength of light, is likely the main scattering source by SWNTs.

2.3 Exciton Transport

The absorption of light produces excitons, which are locally bound electron-hole pairs held together by the electrostatic Coulomb force (electrically neutral quasiparticle). The processes that can occur to an exciton inside a nanotube PV are
(1) **Generation:** Excitons are generated by absorbed light. The energy of a created exciton is at the energy of the photon that was destroyed, which can lead to "hot" excitons at energies above the bandgap. These hot excitons nonradiatively decay to the bandgap with exponential probability and a time constant on the order of 10 fs.
(2) **Diffusion:** Excitons are capable of "diffusing" along