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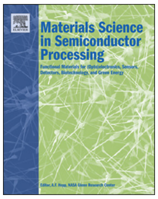

Carbon nanotubes for organic/inorganic hybrid solar cells

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ABSTRACT

This article describes the material properties and thin film forming strategies for carbon nanotubes. It summarizes the developments and the challenges related to doping and reviews the highlights over the past decade about organic/inorganic hybrid solar cells using carbon nanotubes (CNTs) CNTs. Replacing the indium tin oxide electrode by CNT spiderwebs have displayed solar cell efficiencies of about 3–4% for organic bulk heterojunction devices, enabling a cost effective fabrication of organic solar cells by roll-to-roll process. Investigations on SWNT/Si hybrid solar cells with efficiency of 17% demonstrate the possibility of wide range applications of SWNTs in organic/inorganic hybrid solar cells.

Contents

1. Introduction

Transparent conducting films (TCF) exhibit transparancy to the visible light and at the same time possess good electrical conductivity. Such films have found applications in many electrical devices such as solar cells, sensors, electrodes for displays of TVs, touch screens, etc [1,2]. The most widely used TCF is the indium tin oxide (ITO). However, the material contains indium, which is a rare metal typically found in limited geographical locations. Materials cost, importance of indium resources, and the demand in using ITO is soaring, so that in the near future ITO can become one of the strategic materials that cannot satisfy the increasing demand. These drawbacks have led to increasing the research attention to searching the indium-free TCF. Recently, graphene [3–6] and CNTs (CNT) [7,8] have emerged as promising In-free candidates to be used as transparent and conducting materials [9]. Studies and applications of graphene as a TCF in photovoltaic technology [10–14], e.g. in Si based solar cells [15–18], are in an early phase. Considering the short history of graphene, several

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fundamental questions are yet to be answered in relation to its preparation and implementation in devices. CNTs might be also good candidate for replacement of ITOs. This issue specially is important in organic solar cells, enabling to form highly flexibel solar cells by roll-to-roll processing.

In the past few years, the role of CNTs in solar cells has been extended from the effective hole transporting materials for organic solar cells to photo active materials for Si-based cells. Hybrid solar cells were fabricated by depositing intrinsic *p*-type SWNT thin-films on *n*-type Si wafers without involving any high-temperature process for $p-n$ junction formation. The hybrid solar cells showed a high power-conversion-efficiency of 17% [19]. These results together with the advanced properties of CNTs such as low reflectance, high mechanical stability and chemical resistance to air are the strong motivations for the further development of this topic. Optimizing chemical properties of CNTs could also serve as a platform for next-generation solar cells such as, e.g., hybrid CNT/classical inorganic (CIGS, CdTe etc.), CNT/polymer, and all carbon solar cells.

This review will focus on developments and challenges related to CNTs and on highlights over the past decade about its applications in organic and hybrid solar cells. At first, some basic information on different types of CNT structures, their opto-electronic properties and characterization tools will be briefly adressed. CNTs syntesized and purified using different methods have diverse physical and chemical properties, which will yield films with distinct performance. Therefore, the chemical methods of preparation of CNTs for photovoltaic applications will be analyzed in Section 2. One of the major advantages in using CNTs is their ability to be deposited to substrates from solution. One of the primary research areas for making transparent conductive films is to process the CNT material into printable inks. The Section 3 will outline major approaches to disperse CNTs and focus on the most important details with regards to processing CNT thin films from solution. In Section 4.1, a variety of doping techniques for making transparent conductive CNT films will be presented and the post-treatment effects will be evaluated. The latest progress on CNT transparent conductive films and their applications in organic bulk heterojunction solar cells using a P3HT/PCBM blends will be summarized in Section 4.2. In Section 4.3, the role of CNTs in the photo active layer is briefly discussed and very recent developments on *p*-CNT/*n*-Si hybrid solar cells are summarized.

2. CNT structures and opto/electronic properties

CNTs are cylinder-shaped molecules with large aspect ratios. Radius of a CNT can be as small as a few nanometers. The length of CNTs can be in the range from 100 nm to 20 cm depending on the synthesis conditions. The walls of the tubes are made up of a hexagonal lattice of carbon atoms analogous to the atomic planes of graphite. At their ends, they are capped by one half of a fullerene-like molecule. It is well known that the properties of CNTs are related to their structures. In the most general case, a CNT is composed of a concentric arrangement of many cylinders. Diameter of such multi-walled nanotubes (MWNTs) can reach up to 100 nm. Single-walled nanotubes (SWNTs) possess the simplest geometry and have been observed with diameters ranging from 0.4 nm to 3.0 nm. The formation of a SWNT can be visualized through the rolling of a graphene sheet.

MWNTs behave independent of their structural parameters as a metal, whereas the electrical characteristics of SWNTs depends on its chirality. The structural characterization of SWNTs is based on the orientation of the tube axis with respect to the hexagonal lattice given by its chiral vector, which is denoted by its chiral indices (*n* and *m*). SWNTs with chiral indices $n-m=\ 3j$ for $j=0$ are metallic (*m*-SWNTs) and all the others have non-zero band gap. SWNTs with $n-m=3j$ for $j>0$ have a very small band gap of $E_g<kT$ referred to as "semi metals" and SWNTs with $n-m=3j\ +/-\ 1$ (with $j\ >0$) have larger band gap (around 1 eV) refered to as "semiconducting" SWNTs (*s*-SWNTs). Here *k* is the Boltzman constant and *T* is the temperature. Semiconducting behavior of the SWNTs can be inverted to metallic behavior by chemical doping as discussed in Section 3.

A disadvantage of SWNTs is that the synthesis in most cases results in a mixture of the metallic and semiconducting SWNTs. Therefore, developing the strategies to separate metallic and semiconducting SWNTs is an actual target with great importance for solar cell applications of CNTs. Absorbance [20] and Raman [21] measurements are the characterization tools, which allows to distinguish whether the SWNT is a metallic or semiconducting. If the SWNTs are in the mixed state state consisting of metallic and the semiconducting types, the samples possess the black color [22], because the absorption bands caused by the metallic and the semiconducting nanotubes cover almost the entire range of the visible region. Absorbance spectra of SWNTs will be shifted to higher energies with decreasing the nanotube diameter [23]. Non-functionalized SWNTs shows photovoltaic response [24,25]. The general consensus in the literature is that photocurrent generation is caused by electronic transitions between van Hove singularities in SWNTs which upon illumination leads to creation of excitons [26,27].

Raman spectroscopy has been a very powerful tool to study electronic and vibrational properties as well as to analyze purity of CNTs [28,29]. The two important Raman modes for SWNTs are the radial breathing mode (RBM) appearing at low frequencies and the tangential (*G* band) multi-feature coming up at higher frequencies. The disorder-induced (*D*) band gives information about the amount of amorphous carbon and related inpurities. Raman spectra of MWNTs is similar to those of SWNTs. The primary differences are the lack of RBM modes and a much more prominent *D* band in MWCTs [30]. The more prominent *D* band in MWNTs is to be expected to a certain extend given by the multilayer configuration and indicates more disorder in the structure. The RBM features correspond to the coherent vibration of the C atoms in the radial direction, as if the tube were "breathing". These features are unique for SWNTs and occur with frequencies ω_{RBM} between 120 and 350 cm^{-1}. The location of the RBM peak depends on the nanotube diameter ($0.7\ \mathrm{nm}<d<2\ \mathrm{nm}$) following the rule $\omega_{\mathrm{RBM}}\sim 1/d$. The *G*-bands are associated with sp^2 bonding in carbon systems and occur at frequencies between 1500 $\mathrm{cm}^{-1}$and 1650 cm^{-1}. The central frequency of the *G*-band can be used for estimation of diameter of SWNTs. Furthermore, it allows to distinguish the metallic and semiconducting SWNTs each from other. The strong differences in *G*-band between the metallic and semiconducting SWNTs can be detected by in Raman measurements.

Like the other sp^2-hybridized carbons, SWNTs also display *D*-band at 1250–1450 cm^{-1}. The intensity and shape of the *D*-band depends on concentration of carbon impurities and of surface defects. The *D*-band of the crude material with a peak at 1350 cm^{-1} is commonly quite broad with a full-width-at-half-maximum (FWHM) at about ~50 cm^{-1}. A sharp *D*-band with a FWHM at ~20 at 1350 cm^{-1} indicates to lower concentration of impurities and high crystallinity. On the other hand, if during purification acidic treatment will be used, then the *D* band can be broadened when side walls of the CNTs are partly oxidized.

3. Synthesis and purification strategies

CNTs can be synthesized from a variety of different materials and several catalysators will be used. Below we describe the three methods often used in synthesis of CNTs: electric arc-discharge, catalytic decomposition of gaseous hydrocarbons, and laser ablation. Electric arc-discharge technique uses two electrodes. At least one of the electrodes is made of graphite. Carbon atoms are