Performance evaluation of photovoltaic cells using functionalized carbon nanotube and polyaniline film

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Abstract
The use of polyaniline (PANI) and carbon nanotubes (CNTs) as photovoltaic materials has been presented in this paper. The promising properties of PANI and CNTs have encouraged utilizing them in photovoltaic devices and studying their performance. The photovoltaic performance of PANI has been studied with and without CNTs. We found that there is a considerable increase in the short circuit current density from 3.49 to 8.86 mA cm$^{-2}$ with the use of CNTs in the device and also an increase in power conversion efficiency. The incorporation of CNTs film had led to an efficient transport of photo-generated holes to the anode and suppressed the recombination of free charges generated, thus increasing the efficiency of the device. The performance of the device shows that the PANI and CNTs can be effectively utilized as photovoltaic materials in a photovoltaic cell.

Keywords: carbon nanotubes, chemical vapor deposition, photovoltaic cell, polyaniline, thin film

Classification numbers: 5.14

1. Introduction
The development of photovoltaic (PV) cell based on conjugated polymer is of great interest and has a wide research area. Organic photovoltaic cells (OPV) have advantages over inorganic cells due to their ease of fabrication, low cost and low weight [1], low temperature process [2] and potential to be fabricated onto a large area on flexible substrates [3]. The main challenge in the photovoltaic cell is to increase the photocurrent either by material or by changing the material [4]. A huge amount of research is in progress for the development of novel materials for use in a photovoltaic cell. Organic materials are promising materials to cut down the cost of photovoltaic cell due to its ease of fabrication using simple techniques such as spin-coating, ink-jet printing and spray pyrolysis techniques [5]. The basic requirement for photovoltaic materials is to generate free charge carriers produced by the photo-excitation process. Subsequently, these carriers are transported through the device to the electrodes without recombining with oppositely charged carriers [6]. Organic semiconductors based on conjugated polymers and small molecular organic materials are creating potential interest in an ongoing effort to lower the cost of solar cells [1]. To improve the performance of OPVs, carbon nanotubes (CNTs) have been introduced recently to OPV devices. CNTs are the potential materials for solar cell application because of their high charge mobility, chemical stability, effective mechanical strength [7, 8] and a wide range of band gap coinciding with the solar spectrum, thus reducing the carrier scattering and improving the absorption of light [9].

Among the many available conducting polymers, PANI is one of the promising polymers in photovoltaic cell due to its tunable electrical properties, environmental stability and its ease of synthesis [10–12]. Due to these excellent properties, ongoing research enables its application in sensors [13, 14], lithium batteries [15], light emitting diodes and solar cell. PANI is the potential candidate for the photovoltaic cell to cut down its cost with its ease of processing into solution [16]. It has been understood from the literature that PANI can be used as a hole transport layer [17], charge generator and charge...
collector in an organic photovoltaic cell (OPV), p-n heterojunction cell and Schottky junction solar cell, respectively [18].

To date, according to our knowledge, only few works have been done to prepare the solar cell with the use of PANI and CNTs. The main aim of this paper is to understand the performance of this simple solar cell with the use of easy processable materials, so that they can be easily integrated in complex structures in the future for better performance and reduce the cost of photovoltaic cell by avoiding the use of expensive polymers.

2. Experimentation

2.1. Synthesis of functionalized carbon nanotube (f-CNT)

The carbon nanotube (CNT) was prepared using an iron catalyst supported on aluminum oxide of 129 μm size at 550 °C and ethanol as a carbon source. The CNTs are purified and functionalized by sonication in the mixture of H2SO4 and HNO3 (3:1) followed by filtration and washing repeatedly with deionized water. The purified CNTs were dispersed in dichloroethane in the sonication bath for 12 h. After sonication, the solution was left for impurities to settle down. The resultant solution was centrifuged at 12 000 rpm and the supernatant was retained for film formation.

2.2. Synthesis of polyaniline

PANI was synthesized by chemical oxidative polymerization method using ammonium peroxidisulfate as an oxidizing agent in the presence of HCl as a catalyst. 2 ml of aniline was added to 1 M HCl on constant stirring in a beaker. 4.99 g of ammonium peroxidisulfate in 1 M HCl was added to the above solution slowly. The temperature at 0 °C was maintained for 7 h to complete the polymerization process. The resultant residual after the polymerization reaction was filtered and washed with HCl until the filtrate turned colorless to obtain the emeraldine salt form. The emeraldine salt form was dedoped with ammonia solution which was soluble in an organic solvent such as m-cresol. The dedoped PANI was then washed with methanol and dried at 60 °C for 20 h to get a dried PANI powder. For film formation, the PANI was dissolved in m-cresol and stirred for 10 h and the solution was filtered with Whatmann filter paper [19].

2.3. Preparation of photovoltaic cell

The schematic device structure is shown in figure 1. The glass/indium tin oxide (ITO) substrate was cleaned in an ultrasonic bath with water and acetone repeatedly. The cleaned ITO was dried using N2 gas for 10 min. A thin intermediate layer of PANI was spin-coated over the cleaned and dried ITO substrate at 3000 rpm for 30 s. The glass/ITO/PANI layer was subsequently dried for 15 min at 373 K. The CNTs film was spin-coated at 2000 rpm on the dried PANI film. The deposited CNTs layer was dried and annealed at 353 K in an ambient thermal condition in the furnace for 10 min to remove any traces of the solvent. Finally, the fabrication of photovoltaic devices was completed by depositing a thin cathode layer (Al electrode) by thermal deposition of pure Al metal over the CNTs layer and thus making a complete device structure glass/ITO/PANI/CNTs/Al.

Scanning electron microscopy (SEM, JOEL JSM-6390) was used to identify the diameter of the synthesized CNTs under an accelerating voltage of 20 kV. Fourier transform infrared (FTIR) spectroscopy was employed to determine the structure of synthesized PANI. The PANI powder was mixed with KBr and ground in a mortar and pestle and the transmission was measured between 4000 and 400 cm\(^{-1}\). The performance of the device was measured with an AM 1.5, 100 mW cm\(^{-2}\) solar simulator under an illuminated condition. The I–V measurements were performed using a Keithley 2400 source meter.

3. Results and discussions

3.1. Electron microscope

An SEM micrograph is shown in figure 2 for the synthesized CNT product. The image reveals that the produced carbon nanotubes (CNTs) have the diameter varying from 20 to 30 nm and are web-like, entangled and catalyst is encapsulated at few locations.
### 3.2. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of PANI were recorded in the range of 4000–400 cm\(^{-1}\) as shown in figure 3. The formation of PANI was confirmed by the absorption bands at 3460, 1626, 1129 and 830 cm\(^{-1}\), which were attributed to the vibration of N-H, C-C, Ph-NH-Ph and C-N in the aniline unit. The bands at 1717 cm\(^{-1}\) and 1626 cm\(^{-1}\) are attributed to the c-c stretching mode of the benzene rings and vibration of quinone rings [13]. The absorption band at 1368 cm\(^{-1}\) is due to the C-H stretch and C-H bends of the polymer [20]. The peaks at 1129 and 1226 cm\(^{-1}\) are due to C-C stretching and C-C twisting of the alkyl chain, respectively [21].

### 3.3. Current–voltage characterization

The PV cell was tested for I–V response, as shown in figure 4, under irradiated conditions of AM1.0 using solar simulator Model 94023A, Oriel make.

The power conversion efficiency (PCE) \(\eta\) was calculated according to the standard relationship:

\[
\eta = \frac{V_{oc} I_{sc}}{P_{in}} FF, \quad (1)
\]

where \(V_{oc}\), \(I_{sc}\), \(P_{in}\) and \(FF\) are the open-circuit voltage, the short-circuit current, the incident light power and the fill factor \((FF)\), respectively.

The \(FF\) is obtained using the relationship

\[
FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}}. \quad (2)
\]

The \(FF\) measures the quality of solar cell as a source of power and is defined as the ratio between the maximum power delivered to an external circuit and the potential power. \(V_{max}\) and \(I_{max}\) are, respectively, the values of the voltage and current densities for maximizing the product of I–V when the device operates as an electrical power source.

The parameters of the photovoltaic cell, open circuit voltage \((V_{oc})\), short circuit current density \((I_{sc})\), fill factor \((FF)\) and power conversion efficiency \((\eta)\) are tabulated in table 1. Device B shows higher current density and efficiency compared to device A. When the photovoltaic cells are illuminated at the ITO/PANI heterojunction, the photo-excited charge carriers dissociate into free holes and electrons. The electrons are transported from ITO to the cathode and the holes are transported to the anode from CNTs collected from PANI film. The two driving forces in developing the solar cells are PANI for creating a uniform homogenous layer on ITO substrate and the excellent property of CNTs for collecting and transporting the charge. The high open circuit voltage of device A is due to the formation of uniform homogenous layer of PANI on ITO substrate with a minimum loss of incoming light in the visible region of the spectrum. Poor charge transportation of PANI decreases the \(FF\). On the other hand, by incorporating CNTs film in photovoltaic cell, the short circuit current density increases from 3.49 to 8.86 mA cm\(^{-2}\) in comparison with device B. Since, the CNT film acts a semitransparent conducting material where the charges are collected and transported to the anode efficiently, the enhancement in the \(I_{sc}\), \(FF\) and power conversion efficiency was probably due to more efficient electron transport through the nanotube percolation paths. The nanotubes layer provides additional paths for the electrons to disperse, suppressing charge recombination and enhancing charge transportation.

### Table 1. Performance parameters of PV devices.

| Device structure               | \(V_{oc}\) (V) | \(I_{sc}\) (mA cm\(^{-2}\)) | \(FF\) | PCE (\(\eta\)) |
|-------------------------------|----------------|-----------------------------|-------|----------------|
| Device A (ITO/PANI/Al)        | 0.4            | 3.49                        | 0.153 | 0.21           |
| Device B (ITO/PANI/CNTs/Al)   | 0.32           | 8.86                        | 0.1917| 0.53           |

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Figure 3. FTIR spectrum of PANI.

Figure 4. I–V characteristics of PV devices.

Table 1. Performance parameters of PV devices.
4. Conclusions

The performance of PV cell is influenced by various factors of charge generation, charge diffusion, recombination processes etc, at the heterojunction. The incorporation of CNTs enhances the photovoltaic efficiency with its effective charge collection and transporation properties. The performance of this photovoltaic cell can be enhanced by optimizing the PANI and CNTs thickness and concentration.

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