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Functionalization of multi-walled carbon nanotubes (MWCNTs) with nitrogen plasma for photovoltaic device application

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Abstract

Multi-walled carbon nanotubes (MWCNTs) placed under nitrogen (N_2) and argon (Ar) microwave plasma in order to functionalize covalently their side walls with nitrogen containing groups. X-ray photoelectron spectroscopy (XPS) study shows surface modification of the MWCNTs with imine, amine, nitride and amide groups grafted on the side walls. Due to the functional groups, homogenous distribution of MWCNTs in solvent could be obtained. For photovoltaic device fabrication MWCNTs film was casted over n-Si wafer and poly(3-octylthiophene) solution was infiltered. Devices with functionalized MWCNTs show short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (η) as 1.8 mA/cm^2, 0.20 V, 24% and 0.086%, respectively. In the composite film functionalized MWCNTs facilitate photo induced charge separation and efficient holes transportation, suppressing recombination of photo generated charges.

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Keywords: Functionalization of CNTs; Microwave plasma; Photovoltaic device

1. Introduction

Composite materials of carbon nanotubes with polymer have been investigated and exploited for fabrication of photovoltaic devices [1–3]. Carbon nanotubes (CNTs) along with conjugated polymers have been demonstrated to favor hole transportation and excitons dissociation [4]. CNTs can improve exciton dissociation by providing field at the polymer nanotubes interface. The blend of CNTs with conducting polymers allows formation of devices with high interfacial area, which can lead to a large pair dissociation region. This will create a potential difference, which can be benefited by the enhanced potential gradient at CNTs terminals [5–8]. These properties of CNTs with conjugated polymer have generated a great interest in developing photovoltaic devices. More over potential application of CNTs for hole-collecting electrodes in photovoltaic devices were also demonstrated [9,10]. Substitution of Tin-doped indium oxide electrode by carbon nanotubes electrode has been demonstrated in organic photovoltaic device and light emitting diode [11,12]. However, application of carbon nanotubes in photovoltaic device was hindered due to their poor solubility and hence restricting homogenous thin film formation.

Functionalization of CNTs sidewalls represent a solution in order to improve the interactions between CNTs and solvent or polymer matrix and thus increase there dispersion ability [13]. There are mainly two different approaches for surface modification of CNTs. One is the

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non covalent functionalization which has been carried out by several processes such as ultra-sonication, addition of surfactants, polymer wrapping, etc. [14–19]. The other approach relies on the covalent grafting of functional groups on the side walls of CNTs [20]. Covalent bonding between CNTs and polymer allows optimal interfacial strength and thus there can be perfect load transfer to the CNTs can be achieved. Covalent functionalization of CNTs generally achieved by solvent processing or by ball milling [21–24]. By these processes only very small fraction of CNTs get functionalized. Recently, microwave generated N_2 plasma has been used for surface functionalization of CNTs with nitrogen containing functional groups [25,26].

In this paper, we report one step process surface wave microwave (SW-MW) plasma functionalization of MWCNTs modified with nitrogen containing functional groups. XPS analysis of CNTs shows presence of amine, amide and nitride functional groups. With the functionalization of MWCNTs good dispersion in organic solvent and homogenous film formation can be achieved. Functionalized MWCNTs were incorporated in poly(3-octylthiophene) (chemical formula $(C_{12}H_{22}S)_n$) and n-Si heterojunction photovoltaic device. There are considerable improvements of photovoltaic device performance with modified CNTs incorporation. Details study of functionalization of CNTs by atomic nitrogen and incorporation in photovoltaic device were discussed.

2. Experimental

MWCNTs were synthesized as described previously [27] using plant based precursor turpentine oil by spray pyrolysis at 800 °C. Transition metal particles (Co, Fe) supported on silica gel was used as catalyst for CNTs synthesis. Synthesized CNTs were initially heated at 450 °C for 30 min in the atmospheric air to remove the amorphous carbon. Preheated CNTs were treated with 6 M NaOH and 6 M HCl and washed with copious amount of water. Finally CNTs were again heated at 450 °C for 30 min. Purified CNTs were placed in SW-MW plasma chamber under N_2 and Ar flow. $N_2 + Ar$ microwave plasma was introduced in the chamber via a surface guide supplied by 2.45 GHz microwave generator. Flow rate of N_2 and Ar was kept constant as 50 sccm and 50 sccm, respectively. Gas flow to the chamber was regulated by mass flow controller. Plasma treatment was performed at microwave power 100 W and at gas composition pressure 54 Pa. The time of plasma treatment was kept fixed for 25 min. Microwave plasma treated CNTs were analyzed by XPS and Raman study and used for photovoltaic device fabrication. CNTs were dispersed in chloroform solvent with 0.5 mg/ml concentration by sonicating the solution. For device fabrication highly doped n-Si (resistivity 0.1 Ω cm, thickness 500 μm) substrates were cleaned with acetone and methanol and treated with HF to remove the pre-coated SiO_2 layer. Functionalized MWCNTs solution is spin coated over n-Si at 600 rpm so as to form porous thin film. This CNTs film is infiltered with P3OT solution by spin coating at 600 rpm. Finally semi transparent gold electrode (10–15 nm) was deposited by sputtering gold target, so as to make the device structure complete.

XPS measurement of as synthesized CNTs and SW-MW plasma treated CNTs were carried out on SSX-100 photoelectron spectrometer and quantitative analysis of XPS spectra was done from the area of the peak normalized with quantification factor of the element. Visible Raman spectroscopy of the CNTs was carried out on NRS-1500 W Laser Raman. Optical transmission and absorption studies of P3OT and P3OT–MWCNTs films deposited on quartz substrates were done by UV–VIS–NIR spectroscopy on a JASCO V-570 UV–VIS–NIR spectrophotometer. Current density–voltage (I–V) characteristics were measured at room temperature (25 °C) using JASCO SS-200 W solar simulator in the dark and under AM 1.5 simulated solar radiation. Top gold electrode was deposited by sputtering of gold target in E-1030 ION SPUTTER. Transmission electron microscopy (TEM) measurements of MWCNTs were carried out by using an FE-TEM, JEOL-2100F. Scanning electron micrograph (SEM) studies were done using a field emission scanning electron microscope, FESEM, Hitachi S-4300 equipped with an EDAX analyzer Horiba.

3. Results and discussion

Before SW-MW plasma treatment, purified CNTs were analyzed by XPS study. XPS measurement of MWCNTs shows presence of carbon and oxygen peak centered at 284 eV and 534 eV, respectively. Quantitative analysis shows presence of 1.8% (atomic percentage) oxygen atoms along with carbon atoms, which is generally observed in as synthesized CNTs. XPS study of the $N_2 + Ar$ plasma treated CNTs shows presence of carbon (peak centered at 284 eV), oxygen (peak centered at 534 eV) and also nitrogen atoms (peak centered at 400 eV). XPS spectrum of

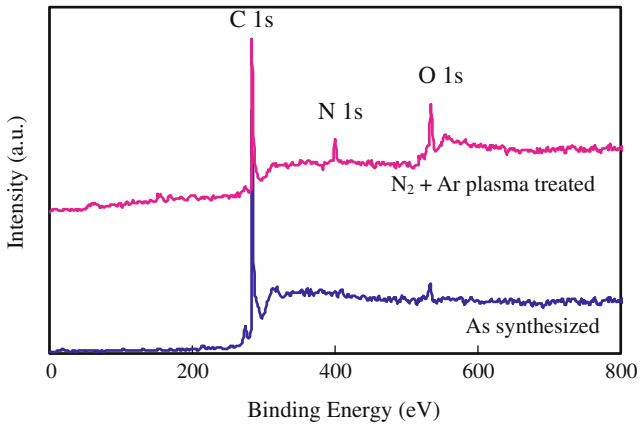

Fig. 1. XPS spectra of as synthesized MWCNTs and MWCNTs treated with $N_2 + Ar$ microwave plasma.