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Facile Synthesis of Polyaniline-Single Wall Carbon Nanotube Nanocomposite as Hole Transport Material and Zinc Oxide Nanorodes as Metal Oxide to Integration Solid-State Dye-sensitized Solar Cells

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Abstract

Novel low-cost Polyaniline (PANI)-single wall carbon nanotubes (SWNT or SWCNT) nanocomposite - based hole transport materials (HTMs) as substitutes to the expensive HTM Spiro-OMeTAD have been synthesized and designed for the applications in solid-state dye-sensitized solar cell (DSSCs). The HTMs were prepared through a facile steps reaction from cheap starting material. These HTMs exhibit good solubility and charge-transport ability. The DSSCs based on PANI-SWNTs achieved power conversion efficiency (PCE) of 1.55% under air conditions, that is comparable to the cells employing the normally used Spiro-OMeTAD (1.827%). For DSSCs, we found that the solar cells synthesized based on vertical ZnO nanowire arrays by using a mixture paste of PMII, LiI and solid iodine as electrolyte SWNT enable better photovoltaic performance than that of pure PANI. These results show that easily synthesized PANI-SWNTs- HTMs have great prospect to replace the expensive Spiro-OMeTAD for DSSCs.

Keywords: Nanocomposite, SWNT, PANI, Solid State Dye Sensitized Solar Cells.

HILIGHT

- An efficiency of 1.55 % can be achieved with nanocomposite (PANI/SWNTS)
- Using photoanode ZnONW as a base semiconductor increases the efficiency of DSSCs.
- (PANI/SWCNTs) as alternatives to the expensive Spiro-OMeTAD.
- Easy synthesized nanocomposite semiconductor of SWCNTs - PANI as HTM

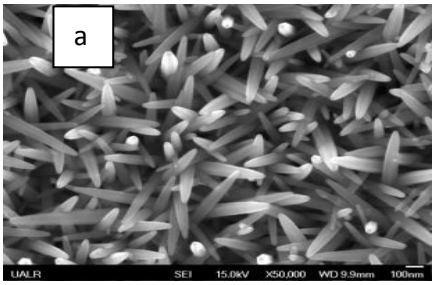
I. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have arisen as an alternative promising material to conventional silicon-based solar cells owing to possibly low production costs, easy-synthesis process and high conversion efficiencies [1–6]. After two decades of researches and development, liquid state electrolyte-based DSSCs have achieved power conversion efficiency (PCE) of over 14.3% based on organic dyes [7]. However, these liquid-based DSSCs suffer from the risk of electrolyte leakage and corrosion problems due to using electrolyte consists of tri-iodide/iodide (I_3^-/I^-) redox couple, which may limit the long-term stability of solar cells devices. Significant efforts devoted to alternative liquid electrolytes have resulted in the development of solid-state dye-sensitized solar cells (DSSCs), paying solid state organic or inorganic hole transport materials (HTMs). Organic electronics or conductive polymer have recently applied as hole transport materials (HTMs) in (DSSCs) [7]. Among various organic semiconductor, polyaniline (PANI) is very interesting material because of its simple preparing, availability, and its cost [8,9], and it can be easily applied as an organic hole transport material (HTM). However, it has a problem of having low mobility due to charge transfer resistance which is the essential balk toward its wide applications [10]. Yanagida's group firstly photoelectrically deposited PANI on ruthenium dye (N3) that affixed TiO_2 surface as HTM [11]. Different challenging issues should be facile to use ZnO nanorode instead of TiO2 for increasing the interfacial area by traveling to the Nano scale levels of this technology to improve the efficiency of (DSSCs) [12]. DSSCs technology is recommended to resolve problem of electrolyte

leakage. In this work, we synthesized and designed high-efficiency solid state dye-sensitized solar cells based vertical ZnO nanowire arrays. This has been done by employing a mixture paste of PMII, LiI, and solid iodine as electrolyte. Polyaniline-single wall carbon nanotube, PANI-SWNT, composites were fabricated on FTO glass-substrate by *in situ*-polymerization, and then used as counter electrode to replace the conventionally used expensive Pt electrode. A power conversion efficiency of 1.55% from the device with PANI-SWNT nanocomposite coated on FTO glass as counter electrode was obtained from the primary results.

II. EXPERIMENTAL DETAILS

Growth of ZnO nanowires (NW): the ZnO NW arrays that vertically aligned have been fabricating on glass substrates (FTO) by electrochemical method at low temperatures. A layer of ZnO thin films were firstly grown on the FTO substrates by using 0.05M zinc nitrate (Alpha Aessar) that was melted in a blend of methanol and de-ionized water (50v:50v). The time and temperature of the growth were 5min and 70°C, respectively. A voltage of -2.5V was applied with two Au electrodes, that were used as working electrode which connected to the FTO glass substrate and as a counter electrode. ZnO NW arrays were then grown in the next step on the top of the ZnO thin film using an electrolyte, that consists of 0.01M zinc nitrate and 0.01M hexamethylenetetramine in de-ionized water. The temperature of this growth was kept at 95°C under a -2.6V of applied potential between working and counter electrodes as mentioned in our previous manuscripts [13]. The fabricated ZnO nanowires, that are aligned vertically on the substrate and have an average diameter of 100-200 nm, can be shown in Fig. 1a.



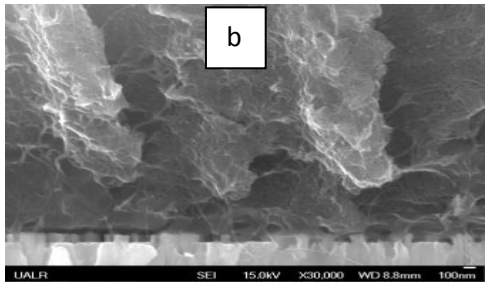


Figure (1): SEM images of ZnO nanowire arrays (a), Nanocomposite materials PANI-SWNTS (b), the scale is 100 nm each 2mm.

Electrochemical polymerization of PANI: In this step, the aniline monomer was used after filtering twice under reduced pressure and melting into a 1M sulfuric acid to prepare a 0.1M solution. Then, the polyaniline was fabricated using a galvanostatic step method under a 3V of applied voltage. FTO glass with a surface area of 1.5cm^2 and a paper clip were used as a working electrode and as a counter electrode, respectively. The estimation of the electro deposited polyaniline amount was done by weighing the working electrode before and after the electrodeposition.

Fabrication of PANI-SWNT composite thin-film: In this work, cheap SWNTs were used that have a purity of more than 99 wt%. The dimensions of these tubes are 1-2nm, 0.8-1.6nm, and 3-30µm for the outer diameter, the inner diameter and the length, respectively. (0.1mg) of SWNTs were first melted in 1ml DMF under sonication for 3h, and then air-brushed onto FTO glass. After that, PANI was precipitated on top of SWNT/FTO glass, and filled the tiny spaces and voids in the network of SWNT. The produced PANI-SWNTs nanocomposite film, that seems to have its two components distributed and mixed uniformly with each other, is shown in the cross section image in Fig.1b

Solar cell fabrication: After preparing FTO glass/ZnO NW structure, ethanol solution (N719) was immersed on it and let to dried. Then, the surfaces of both FTO/PANI-SWNT and FTO/ZnO NW/N719 structures were exposed to a mixture [0.6M 1-methyl-3 propoylimidazolium iodide (PMII) + 0.1M LiI + 2g I] electrolyte. The final solar cells' structure was carried out by sandwiching the FTO glass/ZnO NW/ N719/PMII and PANI-SWNT/FTO glasses as it can be seen in Fig. 2.

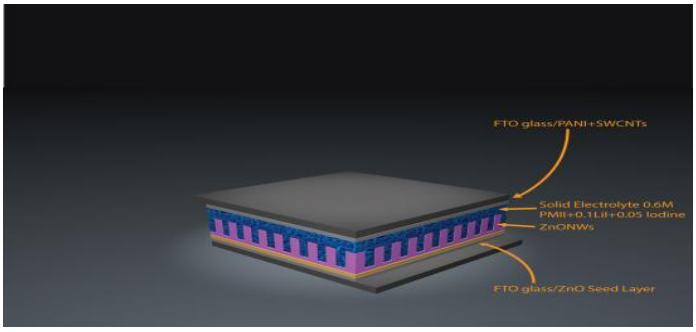
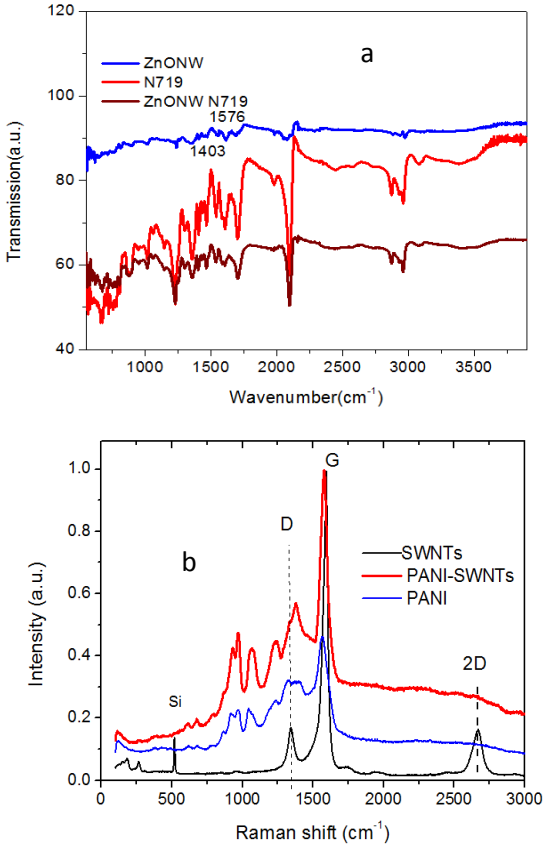


Figure (2): illustration of the ZnO nanowires/N719 dye/ PANI-SWNT nanocomposite solid state dye sensitized solar cells' structure.

III. RESULTS AND DISCUSSION



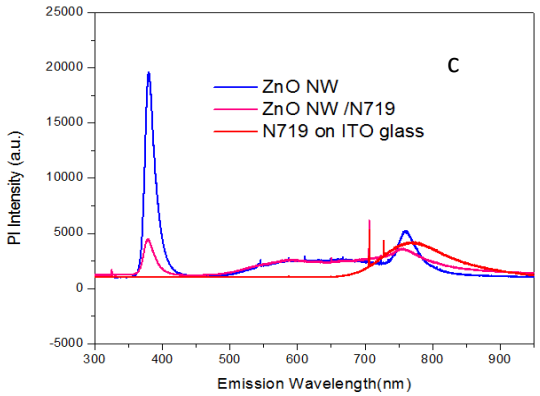


Figure (3): FTIR spectra (a) ,The Raman scattering spectra (b) and PL spectra (c) of SWNT, PANI-SWNT

The FTIR spectrum of the ZnO NW fabricated by electrochemical method, that was obtained in the range 400-4000 cm^{-1} correlated to metal oxide bond (ZnO), is shown Fig. 3a. It can be detected that for both ZnO NW and ZnO NW treated by N719 Dye, the peaks in the range of 1400-1500 cm^{-1} refer to C=O bonds .Also, the O-H bending vibration can be found in the existence of the adsorbed band located at 1626 cm^{-1}. The FTIR spectra of the dye modified ZnO NW was used to investigate the binding between the dye molecules (N719) and the surface of ZnO NW. The solar cells efficiency is highly depended on charge injection process and on bonding configuration of the dye molecules on the ZnO NW. Further, electrostatic and chemical interaction between ZnO NW surface and the adsorbed dye molecules strongly affect the electron transfer in Solid state dye sensitive solar cells. Thus, the absorption appeared at 2105 cm^{-1} of N719 dye is assigned to the SCN stretch model of N-bounded SCN ligand [14]. Moreover, the IR spectrum that observed at 1370 cm^{-1} and 1610 cm^{-1} are consistent with the bidentate coordinate .The same results were reported previously and stated that the coordination of N719 dye on ZnO NW occurs mainly by contribution of unidentate and partially by bidentate linkage [13].

Fig. 3b illustrates Raman Spectra analysis of the pure PANI, SWNT and the PANI-SWNT composite synthesized films. It can be detected that Raman scattering peaks of single-cylinder nanotubes shown at the low

frequency (< 400 cm^{-1}) are assigned to radial breathing mode. Also, the peak located at 1591 cm^{-1} of pure SWNT is referred to E_{2g} mode of graphite wall [15]. The band that is located at 1334 cm^{-1} is attributed to slightly disturbed graphite [16]. The peak at 1581 cm^{-1} in the spectrum of PANI is referred to the C=C backbone stretching of PANI, while the peaks located at 1052 cm^{-1} and 1083 cm^{-1} are both attributed to the C–H in plane deformation [17]. Further, peak located at 1330 cm^{-1} and 1370 cm^{-1} is assigned to the PANI ring-stretching mode [18], while bands located at 940 cm^{-1} and 990 cm^{-1} are referred to the ring deformation related to dication (bipolaron), and radical cation (polaron), respectively [19,20]. Moreover, the intensity of peak that is located at 1334 cm^{-1} increases with the increment of the feeding mass ratio of SWNT to aniline, refereeing to the increment of SWNT existence in the composite film.

Fig. 3c shows the photoluminescence spectra of ZnO NW (blue line) ,and N719 grafted ZnO NW (Red line) in methanol that excited at 325 nm at the same optical density. This Fig. indicates that the photoluminescence was quenched in both UV and visible regions when the N719 grafted to the ZnO nanowires to be sensitized. One can conclude the possibility of the dye N719 resonance energy transfer which causes the static quenching due to dye aggregation on to the ZnO NW surface. Thus, these attribute to the efficient photo-induced electron transfer from the dye N719 to the ZnO NW.

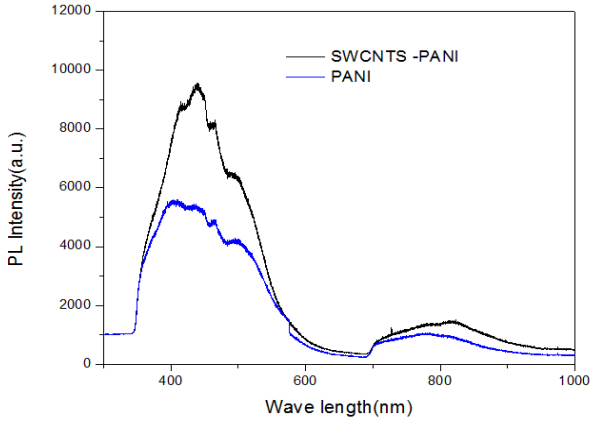


Figure (4): Photoluminescence of PANI-SWNTs nanocomposite and pristine PANI.

PANI returns to the conductive polymers' group with non-degenerate ground state, which significantly affects its electrical and optical properties [21]. The essential charge carriers in these polymers are polarons, and after effective amount of doping, bipolarons instead of solitons [22]. Typical Band gap value of pristine PANI is about 400 nm, and it depends mainly on conditions of fabrication [23]. Also, PANI exhibits high absorption of sub-band gap, that can be understood as a result of the transitions between valence band, polaron, and bipolaron states [24]. PANI offers only very low photoluminescence (PL) quantum yield although its strong broad-band absorption in comparison with other polymers with non-degenerate ground state [25]. However, strong PL is detected only on PANI nanocomposite and PANI scattered in certain organic solvents [26]. For PANI films, two broad PL bands that have maximum values of 410 nm and 800 nm is appeared as it is shown in Fig. 4, and the explanation of its existence is still controversial. Also, the original PL spectrum for electro-chemical PANI shows high-frequency broad-band of low intensity. In the PANI-SWNT composites, the intensity of the peak located at 520 nm is notably low because of the interaction between its two components.

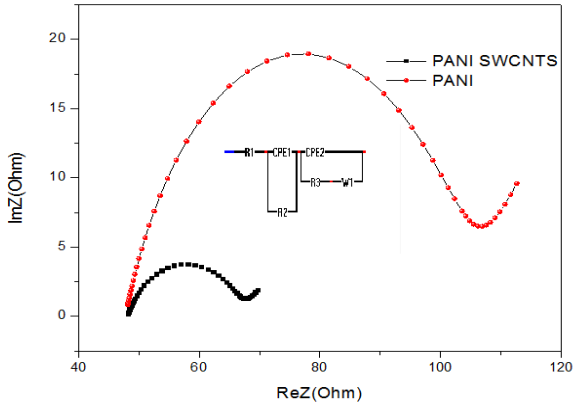


Figure (5): Electro-chemical impedance spectroscopic curves of PANI and PANI-SWNTs that coated counter electrode under dark and illumination.

TABLE I:

Illustrate the parameters that were used to fit the measured data in the equivalent circuit

Sample	$R_1(\Omega)$	$R_2(\Omega)$	$R_3(\Omega)$	$CPE_1(F)$
PANI	658	846	76	$1.08x10^{-5}$ F
	654	817	45	$1.5x10^{-5}$ F
PANI-SWNT	45.6	160	65.7	$5x10^{-5}$F
	43	95	49.8	$1.5x10^{-54}$F

Electrochemical impedance spectroscopic (EIS) spectra of the solar cell structures with and without SWNTs have been carried out to study the impact of SWNTs on the performance of the solar cell. The EIS analysis is considered to measure the charge-transfer resistance that related to the electrolyte paste reduction, and also to give a valuable information about the capability of charge collection in the solar cells. Applied voltage of 0.3 V with a 0.005 to 1 MHz frequency range were used to carry out the measurements. As shown In Fig. 5, a semi-circle curve was shown from Pristine PANI spectrum while double semi-circle characteristics were exhibited from the one with nanocomposite. It can be found that the EIS have been changed as a result of increment in charge transfer through the composite in case of using SWNTS in the solar cells. Fitting experimental data with an equivalent circuit provides useful information shown in Table 1, that consists of the series resistance (R_1), charge transfer resistance (R_2) and (R_3), and space charge capacitance (CPE1). The charge transfer resistance is well known effective parameter that provides considerable information about the charge collection and injection in solar cells [26]. From this data, it can be seen that, while (R_3) has not been changed significantly, (R_2) under illumination for nanocomposite film (95

Ω) is much smaller than for the one with the pristine PANI (845 Ω). Therefore, this indicates that the present of SWNTs enhances the charge transfer in the nanocomposite materials.

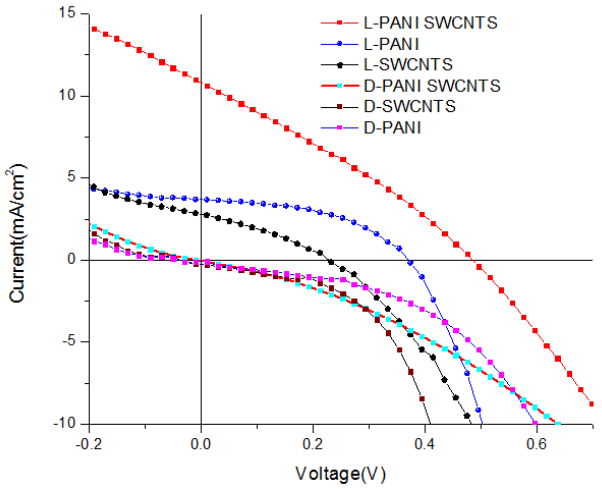


Figure (6): Characteristics of Photocurrent – Voltage curve of DSSCs with PANI and PANI-SWNTs carried out under typical 100 mA/cm^2 light irradiation.

From Fig. 6, it can be seen that there is a significant improvement in the performance of the DSSCs when using PANI-SWNTs as HTM. The cell with SWNTs produces higher values in all solar cell parameters overall. It has higher output current then the one with pristine PANI. Also, its short-circuit current density J_{SC} is enhanced from 4.5 to 11 mA/cm^2, and its open-circuit voltage V_{OC} is increased from 0.38 to 0.56 mV. Moreover, the fill factor FF is improved from 20% to 30%, and the conversion efficiency is enhanced from 0.64 to 1.55% by using SWNTs. These results demonstrate that using SWNTS plays an important role in solar cell performance, and would increase its conversion efficiency from 3 to 5 times. This improvement can be understood from the impact of the increment of contact area between the PANI-SWNT (HTM) and the paste, that provides efficient charge transportation in DSSCs.

IV. CONCLUSSION

In short, we have fabricated in this study polyaniline-single wall carbon nanotube (PANI-SWNT) composites on FTO glass using in situ electro-chemical polymerization in order to introduce new type of counter electrode to replace the expensive Pt electrode used in dye sensitized solar cells (DSSCs). ZnO nanowire arrays were deposited vertically on ZnO buffered FTO glass and applied as a 3D photoanode. High efficiency DSSCs were designed by sandwiching the FTO glass/ZnO NW/ N719/PMII and PANI-SWNT/FTO glasses. Our study stated that 1.55% power conversion efficiency of DSSCs was obtained from the device with PANI-SWNT composite coated on FTO glass as counter electrode, that is considerably higher than that built with only PANI. This light conversion enhancement is due to effective improvements in charge transport in the PANI-SWNT composites, and enhanced photon absorption due to the ZnO array's vertical structure.

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