Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/materialsA

Journal of Materials Chemistry A

RSC publishing

COMMUNICATION

A durable SWCNT/PET polymer foil based metal free counter electrode for flexible dye-sensitized solar cells

Cite this: DOI: 10.1039/xoxx00000x

Syed Ghufran Hashmi^a, Thomas Moehl^b, Janne Halme^a, Ying Ma^a, Tapio Saukkonen^c, Aswani Yella^b, Fabrizio Giordano^b, Jean David Decoppet^b, Shaik. M. Zakeeruddin^b, Peter Lund^a, Michael Grätzel^b.

Received ooth January 2012, Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Abstract. An ITO free, highly conductive PET foil is fabricated by depositing aqueous single-walled carbon nanotube (SWCNT) ink that exhibits remarkable durability when exposed to severe mechanical stability tests. Excellent adhesion of the SWCNT film on PET was obtained by aging the ink overnight at 50 °C before deposition. A counter electrode for dye-sensitized solar cell was fabricated by electro-polymerizing PEDOT polymer over the SWCNT film which gave 7% solar cell efficiency and low (0.4 Ω cm²) charge transfer resistance.

Dye-sensitized solar cells (DSSCs) have been intensively studied as prospective alternative to conventional p-n junction solar cells, because of the potential for their fabrication at low cost ^[1]. The advantage of DSSCs over silicon-based solar cells is the possibility for the roll-to-roll mass production when lightweight polymer (usually indium doped tin oxide-polyethylene terephthalate (ITO-PET) and indium doped tin oxide polyethylene naphthalate (ITO-PEN)) is used as flexible substrate ^[2-4]. Flexible solar panels offer many advantages over classic rigid solar panels: i) they can be installed easily on buildings with any shape of surfaces due to flexible nature; ii) their light weight could enable them as a mobile power source for various portable electronic devices; iii) the cost of solar cells would be significantly reduced by using plastic substrate instead of the transparent conductive oxide (TCO) glass substrates, since the current production of TCO glass involves expensive vacuum processes. Therefore, the development of flexible DSSCs has attracted extensive research interest in recent year. To promote the flexible DSSCs in the competitive photovoltaic market, the foremost prerequisite is the durability of these types of flexible solar

cell, thus robust fabrication of materials on the polymer sheets associated with photo electrode (PE) and counter electrode (CE) is necessary. Unfortunately, as plastic substrates limit the thermal treatment to around 150 °C, most of the conventional mature techniques for PE and CE films fabrication on glass substrate, e.g. screen-printing followed by sintering for TiO₂ film ^[5], or thermal platinization for Pt CE ^[2], ⁶ can no longer be utilized. To overcome this problem, some low-temperature deposition processes for both PE and CE need to be explored that could give same robustness of the materials over the polymer sheets like on glass. Lately, some studies have been carried out on fabrication of efficient photo anode for flexible DSSCs, typically TiO₂ film either on ITO-PET or ITO-PEN substrates ^[7-11]. For instance, Weerasinghe and co-workers reported the fabrication of well-adhered TiO₂ electrodes using binder-free TiO_2 slurry obtained by ball-milling and acidic treatments ^[4, 8]. The deposited layer was further treated with cold iso-static pressing (CIP) to improve the mechanical stability of TiO₂ nano particles over ITO-PEN ^[4] which resulted a conversion efficiency of 6.3%. Moreover, Miyasaka and co-workers showed high adhesion of low temperature TiO₂ binder free film on ITO-PEN which exhibited ~ 6% efficient flexible DSSC^[12].

However, the trend is not same for the counter electrode (CE) and the mechanical stabilities of its associated materials over polymer substrates are either rarely reported or were found problematic. For instance the carbonaceous materials in their various forms such as activated carbon ^[13-15], carbon black ^[16, 17], graphene ^[18, 19] have widely been tested in DSSCs both on rigid fluorine doped tin oxide (FTO) coated glass and flexible ITO-PET or ITO-PEN polymer substrates as potentially inexpensive alternative catalyst material to replace the

COMMUNICATION

Page 2 of 8 Journal Name

traditional expensive platinum catalyst layer. Nevertheless all the above-mentioned reports do not speak about the mechanical stabilities of the deposited material. Also in our earlier experiments, the replacement of ITO with single walled carbon nanotubes (SWCNTs) over the PET polymer was demonstrated by utilizing a dry transfer process and a metal free counter electrode was fabricated which exhibited 4% efficiency when used in the DSSC ^[20]. However the adhesion of this conductive SWCNT film was also not satisfactory. Additionally the detachment of carbon composite's nanoparticles and flaking off the carbon composites catalyst film over polymer sheets was clearly evident in another of our studies ^[2] which affected mainly the fill factor (*FF*) of the *IV* curves and reduced the overall efficiency ^[2].

As a remedy to these adhesion problems, a water-based SWCNT ink was recently developed that can be simply spread on the substrate and dried at 100-120 ° C for 5 min to create ca. 8-10 µm thick SWCNT network films with sheet resistance of ca. 22 $\Omega/sq^{[21]}$. Notable for this ink was its excellent adhesion to PVC: the SWCNT films deposited on PVC sheets withstood both repetitive bending at least down to 2.5 cm radius of curvature and repetitive tape adhesions tests with only a few percent increase in sheet resistance. When the films were further spin-coated with a thin layer of PEDOT-TsO conducting polymer that functioned as an electrocatalyst, the PVC/SWCNT/PEDOT films could be used as well performing Pt- and ITO-free counter electrode in DSSC^[21]. Nevertheless, in that work satisfactory adhesion of the SWCNT was observed only on PVC, presumably due to preferential wettability properties of PVC compared to other polymers.

Here we report that with the above-mentioned ink, excellent adhesion of the SWCNT films can be reached also to PET substrates, provided that the ink is let to age overnight at elevated temperature before deposition. We thus repeated the earlier study (ref. [21]), with small modifications to the ink and sample preparation, and communicate the results here.

The main difference to ref. [21] was an overnight aging of the ink at 50 °C, which further increased the viscosity of the ink and therefore its wetting properties, presumably by completing the micelle formation of the surfactant (dodecyl benzene sulfonic acid sodium salt, SDBS) over SWCNT. It was observed that similar viscosity increase occurs also at room temperature but takes longer time (several days).

The deposition scheme is shown in Figure 1 (a-d) where the conductive patterns of SWCNT were obtained by first masking the substrate with tape (Figure 1a) followed by spreading the aqueous SWCNT ink over active areas with a commonly available disposable pipette (Figure 1b). Then the substrate was placed on a preheated hotplate at 120 °C. Upon solvent drying in less than 5 minutes (Figure 1c), the nonconductive PET polymer foil was rapidly transformed into a highly conductive substrate (Figure 1d).



Figure 1 (a-d): Demonstration of the process a) tape mask was framed to obtain the patterns. b) Ink spread through commonly available pipette. c) Solvent drying at 120 °C. d) SWCNT conductive patterns of various widths.

The mechanical stability of the deposited SWCNT was examined with bending and tape adhesion tests as in ref. [21], but with the difference that also a stronger adhering tape (3M Magic) was used and the samples were bent even down to 1 cm radius of curvature. The tests confirmed excellent adhesion of the SWCNT to PET.

Figure 2 represents the results of a SWCNT loaded PET foil stripe (*L*=5 cm and *W*=1 cm) which was consecutively bent (10 times) over different bending radii (ranged from 2.5 cm to 1 cm) and relaxed and its sheet resistance ($R_{\rm SH}$) was regularly measured. This conductive PET foil exhibited remarkable elasticity and its $R_{\rm SH}$ was almost remained unchanged (~ 25 Ω /Sq) when sequentially bent over 2.5 cm, 2 cm and 1.5 cm bending radii (Figure 2 a-c). The marginal change in $R_{\rm SH}$ (< 5%) was observed when the stripe was further bent over a severely small (1cm) bending radius. Hence the overall change in the $R_{\rm SH}$ from the very first relax mode value (~ 25 Ω /Sq) of 2.5 cm bending radius till the last relaxed value of 1cm (~ 25.7 Ω /Sq) was only 2.8% showing the excellent elasticity of the deposited SWCNT.



Figure 2: Bending test of SWCNT coated PET foil over a) 2.5 cm bending radius b) 2 cm bending radius c) 1.5 cm bending radius d) 1 cm bending radius.

The further strength of deposited SWCNT over PET polymer foil was also examined with a surface adhesion test with two different types of pressure sensitive tapes (3M Removable and 3M Magic). The SWCNT loaded PET polymer substrate (W = 2 cm, L = 2.1 cm) was rolled down with a 2 kg metallic roller disk under the pressure sensitive tapes and the tapes were pulled out at 90° as shown in Figure 3 (a-d). The effect of 'pressing' was seen when the tested substrate experienced the heavy rolling under tape A (3M Removable, Figure 3 a-b) which may have initially increased the contact adhesion between the SWCNT network and resulted an initial decrement (2.4%) in overall $R_{\rm SH}$ of the substrate with the first two tape adhesions (Figure 3b). This decrement was maintained with the further three more consecutive tape adhesions and pulling and no significant changes were observed (Figure 3b).

To confirm the extreme strength, the adhesion of SWCNT/PET substrate was further tested under more sticky tape (3M Magic) which was again consecutively rolled down with the 2 kg metallic roller disk and pulled at 90° (five times) and its $R_{\rm SH}$ was measured (Figure 3 c-d). This introduced a gradual but marginal increase (2%) in the $R_{\rm SH}$ values (Figure 3 d). However the net effect in the change in $R_{\rm SH}$ after 10 times heavy rolling and tape pulling was < 1% which means almost no change from the initial $R_{\rm SH}$ value. These results certified the superb adhesion of the deposited SWCNT over PET polymer.



Figure 3: Tape adhesion test a) Tape pulling (3M Removable) at 90° b) $R_{\rm SH}$ versus number of tape pulling (3M Removable). c) Tape pulling (3M Magic) at 90° d) $R_{\rm SH}$ versus number of tape pulling (3M Magic).

The mechanism of this remarkable adhesion of SWCNT has already been explained in our earlier report ^[21] i.e. the good wetting of the exposed surface (PET polymer here) which can be obtained by reducing the surface tension of the ink formulation and increasing the interaction forces between the substrate and the ink ^[21]. The added surfactant sodium dodecyl benzene sulfonic acid sodium salt (SDBS) plays a key role in many ways; it increases the solubility of dispersed SWCNTs in deionized water (DIW), separates the individual SWCNTs ^[22] and reduces the surface tension of the ink rheology ^[21, 22].

Therefore, inspired by these fascinating mechanical stability results, this highly conductive substrate was tested as a counter electrode in dye-sensitized solar cell where the conductivity/sheet resistance requirement of the substrates typically ranges from 5 Ω /Sq to 60 Ω /Sq ^[23]. However, the SWCNTs alone were not found catalytic enough in our earlier experiments ^[20, 21], therefore the electro-polymerization step over SWCNTs ^[20] was performed (See experimental section) to improve the catalytic properties of SWCNTs.

The scanning electron microscope (SEM) images of the deposited SWCNT over PET foil and electro-polymerized SWCNT layer are shown in Figure 4 (a-b). Figure 4 a reveals a highly porous but random network of SWCNT bundles homogenously distributed over PET. No visible agglomeration was detected in the SWCNT suggesting a stable dispersion of nanotubes in the solvent. The typical length of individual nanotube seems to be in the range 1-2 μ m (Figure 4 a). Moreover, some of the surfactant particles (50-150 nm) which were added to promote the solubility as well as separation of the individual nanotubes settled in the voids (< 100 nm) of the porous nanotubes network (Figure 4 a). On

with

standard

photoelectrodes.

between

based

low

Page 4 of 8

the other hand, polymerization step gave very thin coverage of PEDOT polymer over SWCNT which also penetrated into the voids of the nanotube network (Figure 4 b).



Figure 4: SEM images of a) single walled carbon nanotubes network with surfactant particles (b) PEDOT coverage over SWCNT network.

Finally, to verify the applicability of the PET/SWCNT/PEDOT films as DSSC counter electrode, test solar cells were prepared and their photovoltaic performance was measured. The results are presented in Figure 5 and Table 1.

Note that rigid FTO-glass was used instead of flexible plastic since the objective of the experiment was not to realize a fully flexible DSSC, but to characterize the performance of the SWCNT/PEDOT CE in a DSSC prepared otherwise from well performing and well known materials. Glass substrates facilitated also reliable filling and sealing of the electrolyte, and the high photocurrent densities generated by standard FTO-glass based PEs allowed for challenging the charge transfer capability of the CEs at conditions relevant for high efficiency cells. In a hypothetical but plausible manufacturing scenario, these flexible plastic CEs foils, thanks to their high mechanical durability, could be manufactured with fast and



cost-effective roll-to-roll techniques and laminated together

manufacturing costs and high energy conversion efficiency.

performance FTO-glass

compromise

high

as

а

Figure 5: IV curve of the TPCE and PET/SWCNT/PEDOT CE based DSSC and measured under one sun equivalent light intensity. TPCE = thermally platinized counter electrode. PET/SWCNT/PEDOT CE = polyethylene terephthalate / single walled carbon nanotube/PEDOT counter electrode.

Table 1: *IV* and EIS parameters of each type of DSSC measured under one sun equivalent light intensity. The short circuit current density J_{SC} was calculated based on the photoelectrode area of 0.16 cm². Series and counter electrode resistance (R_{S} and R_{CE}) are measured by EIS. Total cell resistance (R_{CELL}) is determined by the slope of IV curves at V_{OC} .

Cell type*	J _{SC} (mA/cm²)	V _{OC} (mV)	FF (%)	η (%)	R _{CELL} (Ω)	<i>R</i> _S (Ω)	R _{CT} (Ωcm²)
TPCE	14.9	738	76	8.5	27	9	0.5
PET/SWCNT/ PEDOT CE	14.4	702	70	7.0	58	30	0.4
*TPCE = Thermally platinized counter electrode							

PET/SWCNT/PEDOT CE = Polyethylene terephthalate single walled carbon nanotube - PEDOT counter electrode.

The fabricated flexible PET/SWCNT/PEDOT counter electrode based DSSC exhibited excellent photovoltaic characteristics such as high fill factor (\sim 70%), high short

Journal Name

circuit current density ($J_{SC} = 14.4 \text{ mA/cm}^2$) and open circuit voltage ($V_{\rm OC}$ = 702 mV) and efficiency (7%) that are reasonably close to the photovoltaic parameters of the 8.5% efficient thermally platinized counter electrode (TPCE) based DSSC prepared with same procedures (Figure 5, Table 1). (We mention here that in this study, these procedures differed from the typical preparation of optimized ca. 11 % efficient TPCE DSSCs ²⁴, as described in the experimental section, and thus a lower efficiency was expected). Nevertheless, higher cell resistance ($R_{CELL} = 58 \Omega$, corresponding to the slope of the IV curve at $V_{\rm OC}$) was observed in PET/SWCNT/PEDOT CE based DSSC compared to the R_{CELL} (27 Ω) of the TPCE DSSC (Table 1) which is an expected result primarily due to the four times lower $R_{\rm SH}$ (7 $\Omega/{\rm Sq}$) of FTO coated glass compared to $R_{\rm SH}$ (25-35 $\Omega/{\rm Sq}$) of SWCNTs. The lower $R_{\rm SH}$ of FTO Glass/thermally platinized counter electrode (TPCE) is in line with the higher FF (76%, Figure 5, Table 1) compared to PET/SWCNT/PEDOT.

Also the total ohmic series resistance $R_{\rm S}$, measured with electrochemical impedance spectroscopy (EIS) at V_{OC} under illumination (data not shown), was higher in the PET/SWCNT/PEDOT cells (30 Ω , Table 1) than in the TPCE cells (9 Ω , Table 1). On the other hand, the charge transfer resistance at the counter electrode R_{CT} was similar in both cases: 0.4 Ω cm² with PET/SWCNT/PEDOT and 0.5 Ω cm² with TPCE (data not shown). This indicates that both CE materials had similar electro-catalytic performance for the triiodide reduction reaction. The low charge transfer resistance of PEDOT catalyst layer has been already reported in the literature ²⁵. The result also confirms that the FF was lower in the PET/SWCNT/PEDOT cells mainly due to the higher R_{SH} as anticipated based on the direct $R_{\rm SH}$ measurements discussed above, and not due to catalytic performance limitations.

This study also confirms the results of our previous report ^[21] where similar characteristics such as high adhesion and good $R_{\rm SH}$ of the deposited SWCNT were achieved on PVC substrate ^[21]. Also there, lower *FF* was seen due to slightly higher $R_{\rm SH}$ compared to DSSC with TPCE. In the future, the objective of the research will be to decrease $R_{\rm SH}$ by adjusting the concentration of the surfactant sodium dodecyl benzene sulfonic acid sodium salt (SDBS) particles without compromising the adhesion characteristics of SWCNTs. Increasing the SWCNT film thickness from the present ca. 5 $-10 \,\mu\text{m}$ should in principle decrease R_{SH} and optimization of the amount of PEDOT could potentially decrease $R_{\rm CT}$. Future studies should also address the adhesion of the PEDOT or alternative catalyst material on the SWCNT film, although we do not expect it to be as problematic and critical as achieving good adhesion of the much thicker SWCNT film on the substrate.

Hence this highly conductive SWCNT coated PET foil in combination with PEDOT unveils amazing characteristics in terms of very high elasticity, flexibility, durability and remarkable potential when tested as counter electrode in DSSC. In the future development, a rolling or pressing step could perhaps also be used to further reduce the overall sheet resistance of the substrate as by the results from the tape adhesion test.

In summary, we demonstrated rapid transformation of a commonly available PET polymer foil into highly conducting ITO free substrate through an easy and quick deposition technique of an aqueous SWCNT ink. This metal free SWCNT coated flexible PET foil exhibited marginal (2.8%) change in the sheet resistance when subjected to severe repetitive bending tests down to 1 cm bending radius. The strong mechanical stability was also confirmed with repetitive tape adhesion tests that showed marginal net change in the sheet resistance. This substrate was then tested for counter electrode application in dye-sensitized solar cell yielding high efficiency (7%) and high catalytic activity in terms of very low charge transfer resistance ($R_{\rm CT} = 0.4 \ \Omega {\rm cm}^2$).

In conclusion, thanks to an additional aging step in the ink preparation, the SWCNT films prepared from a water-based SWCNT ink adhere well not only to PVC but also to PET polymer foil that is a more commonly used substrate material in flexible solar cells and printed electronics. The combination of good adhesion and low sheet resistance makes these SWCNT films an interesting electrode candidate for various electrochemical devices besides the dye-sensitized solar cells demonstrated here.

Experimental setup

Materials

Single walled carbon nanotubes (purity > 90%, bundle length 1-5 μ m, diameter 4-5 nm) were purchased from Carbon Solutions. Surfactant sodium dodecyl benzene sulfonic acid sodium salt was purchased from Fluka Chemica. Monomer 3, 4-ethylenedioxythiophene (EDOT), Lithium perchlorate (LiClO₄). Chloroplatinic acid hydrate (H₂PtCL₄.6H₂O) and all the solvents were obtained from Sigma Aldrich. C101 dye was synthesized as reported earlier ²⁴.

Counter electrodes (CE)

Thermal platinization

Thermal platinization on FTO coated glass (TEC 7) was performed by drop casting (1 drop) 10mM Chloroplatinic acid hydrate (H₂PtCl₄. 6H₂O) solution (2 Propanol) followed by sintering the substrates at 410 °C for 20 minutes. The substrates were then cooled down to room temperature and were sealed in a plastic box before use.

CNT ink formulation

0.05 g of single walled carbon nanotubes were first added with 0.1 g of surfactant sodium dodecyl benzene sulfonic acid sodium salt in 10 ml of deionized water (DIW). The solution was then sonicated with a tip sonicator (Branson model 450D, pulse on 1sec, pulse off 2 sec) for 30 minutes and a well dispersed ink was obtained at the end of process. The ink was additionally aged overnight at 50 °C to increase the viscosity of the solution. Except for the aging, this ink formulation followed ref. [21] and was not optimized further.

<u>Dip coating of polyethylene terephthalate (PET) polymer</u> substrates in SWCNT ink

Highly conductive SWCNT layers over PET foil were obtained by directly dipping the PET polymer substrates into the SWCNT ink. The substrates were then taken out from the SWCNT ink contained and dried at 120 °C on a preheated hotplate for 5 minutes. Upon solvent evaporation in 5 minutes, highly adhesive SWCNT patterns (5 μ m) were obtained. The thickness of the SWCNT film was determined through a cross sectional SEM image. This ink deposition procedure and obtained film thickness was similar to ref. [21] and were not optimized further.

Electro-polymerization of SWCNT coated PET substrates

Monomer 3, 4-ethylenedioxythiophene (EDOT)) was electropolymerized at +1 volt (as described in our earlier work ^[20]) over SWCNT loaded PET substrate via chronocoulometry in an aqueous solution contained 0.3 M LiClO₄ and 0.3 mM EDOT. The deposition rate and charge was kept constant for 60 sec and around 70 mC/cm² respectively. Note that in ref. [21] the PEDOT deposition was done by spin coating with essentially similar results.

Photoelectrodes (PE)

The photo electrodes for this experiment were prepared as described before ²⁶. In short the FTO coated glass substrates (Sheet resistance 15 Ω /Sq, Pilkington) were first cleaned with mild detergent and then were sequentially sonicated in acetone and ethanol solutions (15 mins each) and the dried with compressed air. Further cleaning of the substrate was performed for 25 minutes in UV-O₃ cleaner (UVO-Cleaner, Model 256-220, Jelight Company Inc, USA) and then the substrate were directly immersed in 40 mM TiCl₄ solution and heated in a preheated oven at 70 °C for 30 minutes in a closed container. Then all the substrates were sequentially rinsed with deionized water and ethanol solutions and were dried with compressed air. 8 um and 5 um thick layer of nano crystalline TiO₂ particles (20 nm) and scattering particles (400 nm) respectively were sequentially deposited via screen printing on the TiCl₄ treated substrates and heated at 110 °C for 5 minutes. The deposited layers were then sintered at 500 °C for 30 minutes and were cooled down to room temperature. After that the TiCl₄ treatment step was repeated as described above and the substrates were then sintered again at 500 °C for 30 minutes and were cooled down to room temperature to complete the sequence. Then the photo electrodes were sensitized with dye C 101. The active area of the photoelectrode was (0.16 cm^2) . The photoelectrodes we not the focus of the work, but were employed as a standard

component in the test cells that we prepared to characterize the performance of the PET/SWCNT/PEDOT CEs in DSSC.

2.3 Cell assembly

The PE and CE were separated with a thick (35-70 µm) Bynel frame foil that also defines the cell channel. A quick drying epoxy (Magic Epoxy - Pakistan) was also employed at the border of cells with flexible counter electrode based DSSC to avoid any possible leakage of liquid electrolyte. Then the electrolyte (Z960 i.e. 1 M DMII, 0.03M I₂, 0.05 M LiI, 0.5M tBPy, 0.1M GuSCN in Acetonitrile: Valeronitrile = 85:15) was injected through the drilled hole at PE side. The cells were then sealed with 15 µm thick Surlyn foil and a thin glass cover. The silver contacts were then fabricated with ultrasonic soldering system (MBR electronics, Model USS-9200) on both FTO glass based PE and CE whereas low temperature silver ink (Plano GmbH) was coated on non-active area of SWCNT/PEDOT deposited PET polymer based counter electrodes. We indicate here that the preparation procedure of the DSSCs for this study were somewhat different from that of optimized TPCE DSSCs²⁴ as follows: 1) A less conductive and less transparent FTO-glass was used (TEC-15 instead of NSG-10), 2) the drilling of the electrolyte filling holes and their sealing were done for the both cell types on the photoelectrode side instead of the counter electrode side, and 3) no antireflection coatings or films were used at the photoelectrode side. Note that the test cell preparation, except for the CEs, was somewhat different than in ref. [21], and hence, comparison of the present results with ref. [21] can be made only with respect to the adhesion characteristics and sheet resistance of the PET/SWCNT films. The higher cell efficiency obtained here (7% vs. 5% in ref. [21]) is mainly due to different PE preparation, smaller active area, and less viscous electrolyte, which gave higher efficiency also for the TPCE cell (8.5% vs. 5.2% in ref. [21]).

2.4 Measurements

The photovoltaic (IV curves) measurement was performed in an artificial solar simulator under 1000 W/m² light intensity equivalent to 1 Sun by applying external potential bias and at the same time the current was recorded via digital source meter (Keithley, Model 2400). A 450 W Xenon lamp (Oriel) was used as light source which was loaded with a sunlight filter (Schott K113) to minimize mismatch between the spectrum of light source and the AM 1.5G. The light was incident on the cell from the photoelectrode side. Due to the high absorbance of the PEs and low reflectance of both type of studied CEs, the effect of back-reflection of light from the CEs is assumed to have negligible effect on the short-circuit current density of these cells, as has been shown experimentally for similar materials in the Supporting Information of ref. [20]. The impedance spectra of the cells were measured with the electrochemical impedance spectrum analyzer (Zahner-Elektrik IM6 potentiostat) whereas Zview2 software was used to fit the measured data with our earlier reported equivalent circuit. Scanning electron microscopes Zeiss Ultra 55 FEG-SEM and JEOL JSM-7500FA were used to record the images of the samples.

Mechanical durability test

Bending test

SWCNT pattern was coated on PET foil (L=5 cm, W=1 cm, thickness ~ 5-10 µm) and then was consecutively bended and relaxed for 10 times over different bending radii (ranged from 2.5 cm to 1 cm and the resistance (R) of the SWCNT film was measured. The sheet resistance was calculated by using the formula i.e. $R_{\text{SH}} = (R^*W)/L$ where W and L are the width and length of the film respectively between the electrical contacts.

Tape adhesion test

Two different types of pressure sensitive tapes (3M Removable and 3M Magic denoted as tape A and B respectively) were first applied (five times for each tape) over the SWCNT coated PET foil (L=2.1 cm and W=2 cm). The sticking was assured by rolling over the tape with a 2 kg metallic disk multiple times and then the tape was pulled at 90° angle. The resistance of the substrate was measured after each tape pulling. The sheet resistance was then calculated by using the same formula as mentioned in the bending test section.

Acknowledgement

This work was funded from National Consortium for Low Cost Photovoltaic from the Academy of Finland (Grant number 13135143). Ghufran Hashmi thanks Tekniikan edistämissäätiö (Finnish Foundation for Technology Promotion) for the travel grant and Mr Janne Patakangas for the help in the bending test. MG thanks the ECR Advanced Grant Agreement no. 247404 under the CE-Mesolight project and Swiss National Science Foundation for partial financial support.

Corresponding authors:

janne.halme@aalto.fi, michael.graetzel@epfl.ch

^a New Energy Technologies Group, Department of Applied Physics, Aalto University School of Science, P.O Box 15100, FI-00076 Aalto Finland.

^b Laboratory of Photonics and Interfaces, Ecole Polytechnique Federale de Lausanne (EPFL), CH G1 551, Station 6, CH-1015 Lausanne – Switzerland.

^c Engineering Materials Group, Department of Engineering Design and Production, Aalto University School of Science, FIN-00076 Aalto, Finland.

References

[1] G. Hashmi, K. Miettunen, T. Peltola, J. Halme, I. Asghar, K. Aitola, M. Toivola, P. Lund, *Renew Sust Energ Rev*, 2011, **15**, 3717-3732.

[2] S. G. Hashmi, J. Halme, T. Saukkonen, E. Rautama, P. Lund, *Phys Chem Chem Phys*, 2013, **15**, 17689-17695.

[3] T. Miyasaka, Y. Kijitori, *J Electrochem Soc* 2004, **151**, A1767-A1773.

[4] H. C. Weerasinghe, P. M. Sirimanne, G. P. Simon and Y. B. Cheng, *Prog Photovolt: Res Appl* 2012, **20**, 321–332.

[5] S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy, M. Grätzel, *Prog Photovoltaics*, 2007, **15**, 603-612.

[6] N. Papageorgiou, W. F. Maier, M. Grätzel, *J Electrochem Soc*, 1997, **144**, 876-884.

[7] T. Yamaguchi, N. Tobe, D. Matsumoto, H. Arakawa, *Chem Commun* 2007, 4767.

[8] H. C. Weerasinghe, P. M. Sirimanne, G. P. Simon, Y. B. Cheng, *Journal of Photochemistry and Photobiology A: Chemistry* 2009, **206**, 64.

[9] H. Lee, D. Hwang, S. M. Jo, D. Kim, Y. Seo, D. Y. Kim, *ACS Applied Materials & Interfaces* 2012, **4**, 3308.

[10] Y. Han, J. M. Pringle, Y. Cheng, *RSC Advances* 2014, 4, 1393.

[11] H. C. Weerasinghe, F. Huang, Y. B. Cheng, *Nano Energy*, 2013, **2**, 174–189.

[12] T. Miyasaka, M. Ikegami, Y. Kijitori, *J Electrochem Soc*, 2007, **154**, A455-A461.

[13] J. Chen, B. Li, J. Zheng, J. Zhao, H. Jing, Z. Zhu, *Electrochim Acta*, 2011, **56**, 4624.

[14] J. Chen, K. Li, Y. Luo, X. Guo, D. Li, M. Deng, S. Huang, Q. Meng, Carbon, 2009, **47**, 2704.

[15] G. Veerappan, K. Bojan, S. Rhee, Renew Energ 2012, **41**, 383.

[16] J. M. Kim, S. W. Rhee, Electrochimica Acta, 2012, 83, 264–270.

[17] W. Huang, X. Zhang, F. Huang, Z. Zhang, J. He, Y. Cheng, *J. Nanoparticle Research*, 2012, **14**, 838.

[18] L. Wan, S. Wang, X. Wang, B. Dong, Z. Xu, X. Zhang,
B. Yang, S. Peng, J. Wang, C. Xu, *Solid State Sci*, 2011, 13, 468.

[19] J. D. Roy-Mayhew, D. J. Bozym, C. Punckt, I. A. Aksay, *ACS Nano*, 2010, **4**, 6203.

[20] K. Aitola, M. Borghei, A. Kaskela, E. Kemppainen, A. G. Nasibulin, E. I. Kauppinen, P. D. Lund, V. Ruiz, J. Halme, *J Electroanal Chem*, 2012, **683**, 70.

[21] S. G. Hashmi, J. Halme, Y. Ma, T. Saukkonen, P. Lund, (2013), A Single-Walled Carbon Nanotube Coated Flexible PVC Counter Electrode for Dye-Sensitized Solar Cells. Advanced Materials Interfaces. doi: 10.1002/admi.201300055

[22] M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson and A. G. Yodh, *Nano Lett*, 2003, **3**, 269.

[23] G. Hashmi, K. Miettunen, J. Halme, I. Asghar, H. Vahlman, T. Saukkonen, Z. Huaijin, P. Lund, *J. Electrochem. Soc*, 2012, **159**, H656-H661.

[24] F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing, R. H. Baker, P. Wang, S. M. Zakeeruddin, M. Gratzel, *J. Am. Chem. Soc.* 2008, **130**, 10720–10728.

[25] S. Ahmad, J. Yum, Z. Xianxi, M. Gratzel, H. Butt, M. K. Nazeeruddin, *J Mater Chem*, 2010, **20**, 1654–8.

[26] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Gratzel, Thin Solid Films, 2008, **516**, 4613–4619.