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# Enhanced efficiency in dye sensitized solar cells with nanostructured Pt decorated multiwalled carbon nanotube based counter electrode

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# ABSTRACT

Nanostructured Pt decorated functionalized multiwalled carbon nanotubes (Pt/f-MWNTs) cast on fluorine doped tin oxide coated glass (FTO) is demonstrated as a novel counter electrode (CE) for dye sensitized solar cells (DSSCs). Pt particles (20 wt.%, size <5 nm) are uniformly decorated on f-MWNTs using a facile microwave assisted polyol reduction method. The DSSC fabricated with Pt/f-MWNTs CE (effective Pt loading ~10  $\mu$ g cm<sup>-2</sup>) exhibits an enhanced efficiency of ~5.4% (under an illumination of AM 1.5 G, 100 mW cm<sup>-2</sup>), compared to ~2.3% and 4.5% for f-MWNTs and Pt CE based reference DSSCs. The CEs are fabricated without using conventional binders using a simple doctor blade method. A new equivalent circuit is proposed to model the electrochemical impedance behavior of porous f-MWNTs based CE. On the other hand, the behavior Pt/f-MWNTs based electrode is similar to that of Pt nanoparticles but with higher catalytic activity. Cyclic voltammetry studies reveal that Pt/f-MWNTs counter electrode offers greater catalytic surface area and facilitates faster reaction at its surface.

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## 1. Introduction

The counter electrodes in dye sensitized solar cells (DSSCs) [1] usually consist of a thin layer of Pt deposited on fluorine doped tin oxide (FTO) coated glass substrates. Pt is chosen due to its excellent catalytic activity toward tri-iodide reduction, a mechanism essential for the continuous operation of a DSSC. The Pt counter electrode is also chemically stable in the highly corrosive iodide electrolyte used in DSSCs [2–4]. Generally, these films have a Pt loading of ~10–100  $\mu$ g cm<sup>-2</sup>, a thickness of ~10 nm and a charge transfer resistance ( $R_{ct}$ ) of ~1–2  $\Omega$  cm<sup>2</sup> [2–6]. The low  $R_{ct}$  observed in Pt films results in a fast rate of tri-iodide reduction at the counter electrode, thereby limiting the recombination reaction occurring at the TiO<sub>2</sub>-electrolyte interface to a considerable extent [7]. The resulting decrease in the dark current leads to an overall increase in power conversion efficiency. Therefore, at present, the highly efficient DSSCs employ Pt as counter electrodes [8–10].

Although several low cost counter electrode materials such as CoS, Cu<sub>2</sub>S, Au, carbon in its various forms and conducting polymers [11–15] have been developed, a suitable replacement for Pt counter electrode has not yet been found. Pt being inevitable, high performance at low costs can only be obtained by better utilization of the surface area of Pt, thereby, facilitating lesser material usage. Use of Pt nanoparticles instead of a film can, in principle, offer higher

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0013-4686/\$ - see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.electacta.2012.04.013 surface area and therefore increased catalytic activity. However, unless the Pt particles are strongly adhered to the substrate, they can leach out and eventually deposit on the TiO<sub>2</sub> surface, causing short-circuit by catalyzing the recombination reaction [7]. In addition, unsupported Pt nanoparticles tend to oxidize easily. To avoid these, Pt nanoparticles can be dispersed on suitable catalyst support materials. Reports indicate the use of NiO [16], SnO<sub>2</sub> [17], acetylene black [18], carbon black [19], etc. as support materials for Pt. Even with the above counter electrode materials, the performances of DSSCs rarely exceed those of Pt based cells.

In this context, multiwalled carbon nanotubes (MWNTs) can be an interesting choice as catalyst support material for DSSCs. MWNTs are coaxial cylinders of graphitic carbon, discovered by Sumio Iijima in 1991 [20]. They possess excellent properties such as large surface area, high electrical conductivity, good thermal and chemical stability [21]. Most importantly, they can be tailored through functionalization and metal decoration to suit specific application. As a result, they have been used directly or as catalyst support material in different fields such as gas sensors, biosensors, gas adsorption and storage and nanofluids [22-26]. Also, defect rich species of MWNTs have shown excellent catalytic activity toward tri-iodide reduction in DSSC [27]. Furthermore, in comparison to other one-dimensional carbon nanostructures such as single walled carbon nanotubes, carbon fibres, coils or helices, high purity MWNTs can be prepared in large quantities. Hence, in this paper, we demonstrate the use of Pt decorated functionalized MWNTs (f-MWNTs) as a novel counter electrode material for DSSCs. Fine particles of Pt could be uniformly deposited on f-MWNTs by a

simple and rapid method. The DSSC with Pt/f-MWNTs based counter electrode shows much higher power conversion efficiency than the Pt or f-MWNTs based reference DSSCs. Detailed electrochemical impedance spectroscopy and cyclic voltammetry measurements are carried out to investigate this high performance.

# 2. Experimental

#### 2.1. Materials

P25 TiO<sub>2</sub> was a generous gift from Degussa, Germany. FTO conducting plates (TEC 22-7, TEC 22-15), SX1170-25 spacer, Pt catalyst Plastisol, and Ruthenium 535 bis-TBA (N719) dye were purchased from Solaronix, Switzerland. LiI was purchased from Merck. All other reagents used were purchased from Sigma–Aldrich or Alfa Aesar. High purity de-ionized (DI) water was used for all experiments. The FTO plates were cut into 1.75 cm × 1.25 cm and rinsed with soap water and DI water, followed by successive ultrasonication in DI water, acetone and ethanol. The electrolyte used in DSSC consists of 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.6 M DMPII (1,2-dimethyl-3-propylimidazolium iodide) and 0.5 M TBP (tert-butyl pyridine) in acetonitrile. The dye solution was prepared by dissolving N719 in acetonitrile and tert-butanol (1:1) at a concentration of 0.5 mM.

#### 2.2. Synthesis of MWNTs, f-MWNTs and Pt/f-MWNTs

MWNTs were prepared by catalytic chemical vapor deposition of acetylene over alloy hydride catalysts at  $\sim$ 700 °C in the presence of Ar. Details are given elsewhere [28]. As-synthesized MWNTs were purified by air oxidation and acid treatment methods to remove the amorphous carbon and metallic impurities. The acid treatment for purification was carried out by refluxing with concentrated HNO<sub>3</sub> for 24 h. For further functionalization, purified MWNTs were ultrasonicated in concentrated H<sub>2</sub>SO<sub>4</sub>:HNO<sub>3</sub> (3:1) for 3 h. The sample was washed with DI water, filtered using a nitrocellulose membrane and dried in vacuum to obtain fine powder of f-MWNTs. To decorate Pt, 80 mg f-MWNTs were dispersed in ethylene glycol:water (2:1) solution (30 mL) by ultrasonication. Calculated amount (5.3 mL) of 1 wt.% aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O was added dropwise to the f-MWNTs dispersion and the resulting solution was stirred 12 h. pH of solution was adjusted to 12.5 by adding 1 M aqueous NaOH solution. The solution was placed in a microwave oven and exposed to microwave (800W, pulses of 2 min) to reduce Pt precursor to Pt metal [29,30]. The sample was washed with DI water, filtered and dried to obtain Pt/f-MWNTs. Assuming complete reduction of Pt precursor, 20 mg Pt can be obtained from 5.3 mL. Thus, the loading of Pt in Pt/f-MWNTs is expected to be 20 wt.%.

# 2.3. Fabrication of DSSCs

The photoanode and the counter electrode were fabricated on pre-cleaned and cut FTO substrates. The counter electrodes were fabricated as follows. f-MWNTs and Pt/f-MWNTs were dispersed in ethanol:Nafion solution (10:1 by volume) by ultrasonication for 1 h to give a concentration of 5 mg mL<sup>-1</sup>. The slurry was spread on masked FTO plates (TEC 22-7) using a glass rod. Two parallel layers of Scotch 3 M tape served as the mask. The layer was allowed to air dry for a few minutes. The deposition was repeated to get ~10  $\mu$ g cm<sup>-2</sup> of Pt (i.e. 50  $\mu$ g cm<sup>-2</sup> of Pt/f-MWNTs catalyst). The films were sintered finally at 200 °C on a hot plate. The final area of counter electrode was reduced used to 0.5 cm<sup>2</sup>. The Pt counter electrode was fabricated using commercially available Platisol solution. The solution was brush coated on masked FTO plates and dried on a hot plate. The final sintering was done in a muffle furnace at 400 °C for 30 min. For the photoanode, a TiO<sub>2</sub> paste formulation was made

based on that developed by Nazeeruddin et al. [31]. The resultant paste was spread on FTO plates (TEC 22-15) using a glass rod. Again, the dimensions and thickness were controlled using a framework of Scotch 3M tape. The coatings were finally sintered at 450 °C in a furnace for 1 h. The active areas of the photo anode were ~0.25 cm<sup>2</sup>. No other treatments (such as TiCl<sub>4</sub> pre- and post-treatments) are carried out. The TiO<sub>2</sub> films were immersed in N719 dye solution for ~12 h for complete dye uptake. The TiO<sub>2</sub> photoelectrode and the carbon based counter electrodes were clamped with a SX 1170-25 film as spacer, cut into appropriate size and shape. The space between the electrodes was filled with the iodide electrolyte.

# 2.4. Characterization

X-ray diffraction was carried out using a PANalytical X'PERT Pro X-ray diffractometer with nickel-filtered Cu K $\alpha$  radiation as the X-ray source. The pattern was recorded in the  $2\theta$  range of 10–90° with a step size of 0.016°. Identification and characterization of functional groups were carried out using Perkin Elmer FT-IR spectrometer in the range of 400–4000 cm<sup>-1</sup>. The morphology of the sample was characterized by field emission scanning electron microscopy (FESEM, FEI QUANTA 3D). Elemental analysis was carried out by EDX analyzer in the FESEM system. High resolution transmission electron microscopy (HRTEM) was carried out using a TECNAI F 20 (S-Twin) microscope. For HRTEM measurements, the sample was dispersed in absolute ethanol using mild ultrasonication and casted onto carbon coated Cu grids (SPI supplies). The I-V characteristics of the fabricated solar cells were measured under AM 1.5 G solar radiation using a Newport 150 W Class A Solar Simulator attached with Keithlev 2420 source meter. The intensity was calibrated to give an output of 1 Sun (100 mW cm<sup>-2</sup>) using a thermopile detector and also using a NREL calibrated Si reference cell. Cyclic voltammetry measurements were carried out in three electrode system consisting of Pt wire as counter electrode, Ag/AgCl as reference electrode and the catalyst coated FTO substrate as the working electrode. The electrolyte consisted of 5 mM LiI, 0.5 mM I<sub>2</sub> and 0.1 M LiClO<sub>4</sub> in acetonitrile. Electrochemical impedance measurements were carried out using sandwiched symmetric cell configuration in the frequency range of 100 kHz-0.1 Hz using Solartron 1400 and 1470E Cell Test System. Under this condition, two identical electrodes are prepared from the same catalyst. They are clamped together with a spacer in between. The space is filled by the same electrolyte that is used in the fabricated DSSCs. An ac signal of 10 mV was applied over at 0V dc bias to obtain the data. The geometric area of the films was maintained at  $0.5 \,\mathrm{cm}^2$ . The obtained data were fit with appropriate equivalent circuits using ZSimp 3.1 software.

# 3. Results and discussion

#### 3.1. Decoration of Pt nanoparticles

Pt decoration on f-MWNTs was carried out by microwave assisted polyol reduction method instead of the conventional refluxing method. The schematic of the same is shown in Fig. 1. The purified MWNTs were treated with concentrated acids to produce surface functional groups such as carboxyl, hydroxyl and carbonyl. Generally these functional groups have a site ratio of 4 (-OH):2 (-COOH):1 (-C=O) [32]. The -OH groups make f-MWNTs highly hydrophilic [33], and therefore dispersible in aqueous solvents such as ethylene glycol:water (2:1) used here. The -COOH and -CO groups, on the other hand, affect the decoration of metal nanoparticles [34] by acting as anchoring sites. The metal precursor, H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O when added to the solution dissociates to give Pt ions. These ions get attached to the negatively charged functional



**Fig. 1.** Metal decoration. Schematic depicting the attachment of functional groups on the surface of MWNTs (f-MWNTs) and decoration of Pt nanoparticles on functionalized MWNTs (Pt/f-MWNTs).

groups such as carboxyl and carbonyl via ion exchange or coordination mechanism [35]. This is the nucleation step. Upon microwave heating, the polyol ethylene glycol decomposes into formaldehyde which acts as a reducing agent. Consequently, the surface Pt ions get reduced to well-dispersed Pt nanoparticles [36]. This bond is generally, strong enough to withstand even ultrasonication process. Therefore, the Pt particles are held strongly on the nanotube surface. pH of the solution plays an important role in determining the particle size and distribution. At pH higher than 10, Pt nanoparticles with a narrow size distribution can be obtained. The detailed mechanism on the effect of pH can be found in the work of Lee et al. [36] Li et al. [37] and Yang et al. [38] Hence, in the present work, a pH > 12 was maintained. In addition, the microwave procedure used here assists is uniform and rapid decoration of metal nanoparticles.

#### 3.2. Spectroscopic analysis

The FT-IR spectra presented in Fig. 2 further supports this argument. MWNTs show minimal amount of functional groups as can be seen from the figure (dotted curve). The lack of functional groups makes them hydrophobic in nature. The small amount of functional groups present is due to the purification procedure which



**Fig.2.** Functional groups. FT-IR spectra of (a) MWNTs (red dotted line), (b) f-MWNTs (green dashed line), and (c) Pt/f-MWNTs (blue solid line) showing the presence of various functional groups such as hydroxyl, carboxyl, carbonyl, etc. on the surface of the nanotubes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Formation of composite. Powder X-ray diffraction patterns of (a) f-MWNTs and (b) Pt/f-MWNTs confirming the formation of the composite.

involves treatment with acids. On further functionalization (dashed curve), various functional groups get attached to the surface, making them hydrophilic. The vibrations that are present in f-MWNTs are –OH stretching at  $\sim$ 3430 cm<sup>-1</sup>, –CH<sub>x</sub> antisymmetric and symmetric stretching at 2920 cm<sup>-1</sup> and 2850 cm<sup>-1</sup>, –OH bending at 1620 cm<sup>-1</sup>, C=O at 1720 cm<sup>-1</sup>, C=O at 1250 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> [22,23]. From this we can deduce that the functional groups that are mainly present are hydroxyl, carboxyl, and carbonyl. On Pt decoration (solid curve), the intensities of the functional groups such as –COOH and –CO reduce significantly, suggesting that metal decoration occurs preferentially at these sites. –OH groups are present to a lesser extent than in f-MWNTs, as indicated by peak intensity.

# 3.3. Structural analysis by X-ray diffraction

X-ray diffraction (XRD) patterns of f-MWNTs and Pt/f-MWNTs are presented in Fig. 3. f-MWNTs exhibit the crystalline peaks of graphite and have been indexed according to JCPDS file no. 89-8487. The most intense peak occurs at a  $2\theta$  of ~26.5°. This corresponds to (002) plane of hexagonal graphite and has a *d*-spacing of 0.34 nm. In the case of f-MWNTs, this d-spacing corresponds to the distance between the walls. Peaks corresponding to (100) and (101) planes can be seen at 42.9° and 44.5°, respectively. The other graphitic peaks are negligible in intensity. After metal decoration, peaks corresponding to f.c.c. Pt can be seen along with the peaks of MWNTs. The diffraction profile of Pt was indexed according to the JCPDS file no. 87-0646. The peaks at  $2\theta \sim 40.1^{\circ}$ ,  $46.4^{\circ}$ ,  $67.9^{\circ}$  and  $81.5^{\circ}$  correspond to (111), (200), (220) and (311) planes, respectively. The crystallite size of Pt was determined from the (220) peak using the Scherrer equation to be  $\sim$ 3.7 nm. This peak was chosen over the highly intense (111) peak as this peak suffered no overlap with neighboring peaks of either MWNTs or Pt. It is to be noted here that no peaks corresponding to either platinum oxide or platinum carbide were observed. As mentioned earlier, unsupported Pt nanoparticles get oxidized immediately. Therefore, absence of any oxide peaks suggests that Pt particles are bonded to MWNTs. Absence of carbide peaks suggests that Pt does not form regular bonds with MWNTs, suggesting that the interaction is electrostatic.

# 3.4. Electron microscopy

High resolution electron microscopy studies were carried out to analyze the morphology of the samples. Fig. 4 shows the FESEM and EDX images of f-MWNTs and Pt/f-MWNTs. f-MWNTs and



Fig. 4. Microscopy and elemental analysis. FESEM images of (a) f-MWNTS and (b) Pt/f-MWNTs. (c) EDX spectrum of Pt/f-MWNTs showing the presence of ~20 wt.% Pt on f-MWNTs.

Pt/f-MWNTs (Fig. 4a and b) show a densely packed morphology consisting of randomly oriented MWNTs of nearly uniform diameters. Extremely small particles of Pt decorated on the nanotubes can be seen in the FESEM image of Pt/f-MWNTs. The loading of Pt on f-MWNTs is expected to be ~20 wt.%, based on the amount used during synthesis. To confirm the metal loading, EDX analysis was carried out (Fig. 4c). The peaks corresponding to C and Pt can be seen. The weight percentage of Pt was found to be ~19.2 wt.%,

close to the expected value. This value was determined by taking the average of the values obtained at several spots.

The TEM and HRTEM images of the samples are shown in Fig. 5. Fig. 5a shows clearly the hollow nature and thick walls of MWNTs. MWNTs were found to have outer diameters in the range 20–30 nm and inner diameters of  $\sim$ 10 nm. This was also confirmed from the HRTEM image of f-MWNTs in Fig. 5b and  $\sim$ 26 walls could be counted. The interlayer separation was calculated to be 0.34 nm.



Fig. 5. Particle size and decoration: (a) TEM and (b) HRTEM images of f-MWNTs showing their hollow and multiwalled nature. (c) Dark field TEM, and (d) HRTEM images of Pt/f-MWNTs depicting the uniform decoration of Pt nanoparticles on f-MWNTs.



**Fig. 6.** *I–V* characteristics. Current voltage characteristics of DSSCs with f-MWNTs (green circles), Pt (red squares) and Pt/f-MWNTs (20 wt.% Pt – blue triangles; 40 wt.% Pt – purple diamonds) based counter electrodes, measured under AM 1.5 simulated solar radiation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Also the outer few tubes were found to be damaged due to the harsh oxidation treatment given. Pt/f-MWNTs (Fig. 5c) exhibit morphology similar to that of MWNTs but in addition consist of Pt nanoparticles attached to MWNTs. Even at a scale of 100 nm (magnification ~60,000) the particles were not visible clearly in normal bright field imaging in TEM. Hence, a dark field TEM image of Pt/f-MWNTs is presented. The image shows uniform coating of f-MWNTs with Pt nanoparticles, which appear as shiny dots on f-MWNT surface. The HRTEM image of Pt/f-MWNTs presented in Fig. 5d shows Pt particles of very small size attached on the surface of MWNTs. Majority of the particles had a size of ~2 nm. Some larger particles of ~4 nm in size were also observed. Since, larger crystallites generally dominate in XRD patterns, the Scherrer formula gave a crystallite size of ~3.7 nm, instead of 2 nm.

#### 3.5. I-V characteristics of fabricated solar cells

To evaluate the *I*–*V* characteristics of solar cells prepared with different counter electrodes, DSSCs were fabricated with similar photoanodes, dye and electrolyte. Keeping all other parameters constant, it is possible to evaluate the performance of counter electrode alone. Three types of counter electrodes were prepared namely, f-MWNTs, Pt, and Pt/f-MWNTs. 5 cells were fabricated for each counter electrode type and the *I*-*V* characteristic were measured under 1 Sun AM 1.5 simulated solar illumination. The I-V curves are plotted in Fig. 6 and average values are summarized in Table 1. It can be seen that Pt counter electrode based DSSC has a short circuit current density  $(J_{sc})$  of ~9.3 mA cm<sup>-2</sup> and a fill factor (FF) of ~0.66, resulting in a high efficiency of 4.5%. With f-MWNTs as counter electrode, the FF reduces to 0.32 and  $J_{sc}$  to 8.9 mA cm<sup>-2</sup>. This suggests that undecorated f-MWNTs based counter electrode has a poor catalytic activity toward tri-iodide reduction. In the case of Pt/f-MWNTs (20 wt.% Pt) counter electrode based DSSC, the Jsc

#### Table 1

Solar cell parameters. The characteristic parameters of the fabricated DSSCs such as open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), fill factor (FF) and efficiency ( $\eta$ ).

Material	$V_{\rm oc}$ (V)	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	FF	η (%)
Pt	0.74	9.3	0.66	4.5
f-MWNTs	0.69	8.9	0.33	2.1
Pt/f-MWNTs (20 wt.%)	0.70	12.2	0.64	5.4
Pt/f-MWNTs (40 wt.%)	0.71	9.96	0.63	4.7

#### Table 2

Equivalent circuit parameters. Charge transfer resistance and other parameters obtained for the various counter electrodes measured in symmetric sandwich cell configuration.

Material	$R_{\rm s}(\Omega)$	$R_{\rm ct}$ ( $\Omega  {\rm cm}^2$ )	$Q:Y_{o}(S)$	Q:n	$R_{\rm pore}  (\Omega  {\rm cm}^2)$
Pt	19.1	1.8	$1.7  imes 10^{-5}$	0.93	_
f-MWNTs	15.4	360	$5.2 imes10^{-4}$	0.95	10.9
Pt/f-MWNTs	16.2	0.4	$4.4\times10^{-5}$	0.90	-

increases by ~15% and 32% with respect to that of f-MWNTs and Pt based cells. The FF increases from 0.3 in f-MWNTs based cells to 0.64 in Pt/f-MWNTs based cells, which is comparable to that of Pt. As a consequence of these changes, the power conversion efficiency ( $\eta$ ) of Pt/f-MWNTs based cells is ~5.4%, which is greater than that of f-MWNTs based cells by ~170% and Pt based cells by 20%.

This remarkable improvement in the efficiency of Pt/f-MWNTs based DSSC is clearly due to an increase in the Jsc, though it has a slightly lower FF. This behavior is also seen in f-MWNTs based cells wherein, though the FF is too less,  $J_{sc}$  comparable to that of Pt is obtained. In recent reports on similar systems [39,40], enhanced efficiency was also obtained due to increase in Jsc, although the FFs were lower than those of their Pt based reference DSSCs. The increase in Isc was attributed mainly to increased surface roughness and catalytic activity. However, the lower FFs observed in these systems have not been addressed. Generally, an increase in  $J_{\rm sc}$  is accompanied by an increase in FF. While this is true for planar electrodes such as Pt, the same need not be true for rough electrodes. Therefore, the increase in  $J_{sc}$  could indeed be due to increased surface area, improved catalytic activity, or conductivity effects in these rough systems. The lower FF, on the other hand, could be due to porosity in the electrodes. Note that the porosity being referred to is not that of the material but of the electrode. We propose that in carbon based counter electrodes fabricated without binders (or removed due to sintering), significant amount of pores could be present. Consequently, the electrolyte can slowly percolate through the pores and interact with the FTO electrode. Hence, a combined effect of FTO and carbon material would be observed, resulting in low FF. Other carbon nanostructures such as graphene also exhibit comparable or increased current densities at low FF [41]. However, if the pure carbon nanostructures are modified by metal decoration, etc., the behavior can become complex. Surface area and catalytic effects arise due to the nanostructuring of Pt. To verify this, DSSCs were fabricated with Pt/f-MWNTs counter electrode containing 40 wt.% Pt ( $20 \mu g cm^{-2}$ ). This cell showed a lower efficiency due to the decrease in Isc. In this sample, the Pt nanoparticles agglomerate due to the high loading, resulting in an increase in crystallite size. Consequently, surface area and catalytic activity reduce which decrease the current density. Interestingly, the FF improved by a small extent. To further understand this behavior, electrochemical studies were carried out.

## 3.6. Electrochemical impedance spectroscopy

To determine the catalytic activity of the electrodes toward triiodide reduction, electrochemical impedance spectroscopy (EIS) was carried out. Fig. 7a shows the impedance spectra for Pt, f-MWNTs and Pt/f-MWNTs electrodes measured in a symmetric sandwich cell configuration. Z' and Z'' are real and imaginary parts of impedance, following IUPAC convention. The inset, Fig. 7b and c shows the magnified view of the spectra. Fig. 7d and e gives the equivalent circuits which are used to model the impedance behavior in these electrodes. The values have been summarized in Table 2. The Pt counter electrode shows a large semicircle in the high



**Fig. 7.** Catalytic activity. (a) Electrochemical impedance spectra of Pt (red squares), f-MWNTs (green circles) and Pt/f-MWNTs (blue triangles) in a symmetric sandwich cell configuration. (b) and (c) are the magnified data of (a). (d) and (e) are the equivalent circuits used to model the impedance spectra of Pt, Pt/f-MWNTs and f-MWNTs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

frequency region corresponding to the Pt/electrolyte interface and a small semicircle in the low frequency region corresponding to the diffusion of ionic moieties. This kind of behavior is modeled according to Randles type equivalent circuit with minor modifications as shown in Fig. 7d. The ideal capacitance  $C_{dl}$  is replaced by a constant phase element, Q which represents the capacitance at rough surfaces. The admittance in this case is represented by  $Y_0 = Y_{00}(i\omega)^n$ , where  $Y_{OO}$  and *n* are frequency-independent parameters ( $0 \le n \le 1$ ; for n = 1,  $Q = C_{dl}$  [41,42]. In the case of Pt counter electrode, n = 0.93. The slight deviation from the ideal capacitance is probably due to the roughness introduced by brush coating method used for Pt deposition and hence the use of Q instead of  $C_{dl}$ . The charge transfer resistance ( $R_{ct}$ ) was determined to be 1.8  $\Omega$  cm<sup>2</sup>. As we do not expect any surface area effects in pure Pt based films, we conclude that the low R<sub>ct</sub> of Pt is solely due to its catalytic activity toward triiodide reduction. This catalytic activity is responsible for the high FF, generally observed in Pt electrodes. For modeling the diffusion of ionic species, the diffusion parameter O is used. This is different from Warburg impedance and appears at finite length conditions. Its admittance is given as  $Y_0 = Y_{00}(i\omega)^{1/2} \operatorname{coth}[B(i\omega)^{1/2}]$ , where  $Y_{00}$  is related to conductance and B is inversely related to time constant of the regeneration of diffusion process [42]. This bounded diffusion is responsible for second semicircle in the impedance spectrum. If the infinite Warburg term (W) is used, a 45° line is obtained instead of a semicircle.

In the case of the present f-MWNTs based electrodes, the traditional equivalent circuit could not satisfactorily explain the observed behavior. It was recently reported by Roy-Mayhew et al. [41] that in porous carbon based electrodes, an additional diffusion impedance term arises in the high frequency region due to the diffusion through the electrode pores. However, in the present case it was found that a simple Opore did not satisfactorily fit the high frequency semicircle. The traditional circuit shown in Fig. 7d, also does not simulate the observed spectrum. The equivalent circuit shown in Fig. 7e fits the obtained impedance spectra more accurately. Further modeling/experiments may be required to understand the interaction at porous electrodes. Nevertheless, the first semicircle does not represent the charge transfer resistance of the electrode, as can be confirmed from the poor performance of our f-MWNTs based DSSC. The second larger semicircle now represents the charge transfer resistance and the constant phase element. The  $R_{ct}$  for f-MWNTs was found to be 360  $\Omega$  cm<sup>2</sup>, which is reason for its poor catalytic activity and hence lower FF.

The Pt/f-MWNTs counter electrode behaves similar to Pt, as can be seen from Fig. 7c. The first semicircle represents the electrode electrolyte interface and the second semicircle represents the diffusion of ionic species between the two electrodes. Hence the same equivalent circuit was used to fit the impedance spectrum (Fig. 7d). Pt/f-MWNTs electrode has a very low  $R_{ct}$  of 0.4  $\Omega$  cm<sup>2</sup>. This very low  $R_{\rm ct}$  is responsible for the high catalytic activity and therefore high current density of Pt/f-MWNTs based counter electrode. Interestingly, the FF of Pt/f-MWNTs based DSSC is lower than that of Pt, even though it has a lower  $R_{ct}$ . This kind of behavior is also observed in recent reports on similar systems [39,40,43]. The reason for this is not yet clear. Jeon et al. have attributed this to surface resistivity of the electrode. Similarly, we determined the bulk electrical conductivity of the samples by linear four probe method. While purified f-MWNTs have a conductivity of  $60 \,\mathrm{Sm^{-1}}$ , Pt/f-MWNTs have  $3.2 \times 10^3$  S m<sup>-1</sup>. Pure Pt has been reported to have a conductivity of  $17.1 \times 10^3$  S m<sup>-1</sup> [40]. Thus, Pt has a higher FF than other counter electrodes. The porosity effects described in the case of f-MWNTs is not significant in the case of Pt/f-MWNTs. The presence of Pt nanoparticles alters the kinetics of tri-iodide reduction considerably. Moreover, the uniform distribution of Pt on MWNTs ensures that there are a large number of catalytic sites available for reduction which is not the case with f-MWNTs.

It can be noted that the series resistance of f-MWNTs is lower than that of Pt/f-MWNTs and Pt. The trend is in fact, opposite to the changes in bulk electrical conductivity. Therefore, this behavior can be explained only in terms of contact/adhesion between the material and the FTO counter electrode. The f-MWNTs make better contact due to their hydrophilic nature. After Pt decoration, only some functional groups remain free making them less hydrophilic. This results in poorer contact with the FTO substrate and hence the  $R_s$  is higher. However, it is not clear if these changes affect the DSSC behavior since dominant role is generally played by  $R_{ct}$  or the total series resistance ( $R_s + R_{ct}$ ) [44].

#### 3.7. Cyclic voltammetry studies

Cyclic voltammetry (CV) studies were carried out to further understand the catalytic activity of the electrode materials. Fig. 8 shows the CV curves for f-MWNTs, Pt and Pt/f-MWNTs in the potential window of -0.4 to 1.2 V vs. Ag/AgCl taken at scan rate of 50 mV s<sup>-1</sup>. Two pairs of redox waves are expected, according to literature [41,45]. A pair of anodic and cathodic currents corresponding to the oxidation ( $A_{ox}$ ) and reduction ( $A_{red}$ ) of I<sub>2</sub>/I<sub>3</sub><sup>-</sup>, as



**Fig. 8.** Catalytic surface area. Cyclic voltammograms for f-MWNTs (green dotted line), Pt (red dashed line) and Pt/f-MWNTs (blue solid line) electrodes, obtained at scan rate of  $50 \text{ mV s}^{-1}$ . The counter electrode was a Pt wire and the reference electrode was Ag/AgCl. The electrolyte consisted of 5 mM Li, 0.5 mM l<sub>2</sub> and 0.1 M LiClO<sub>4</sub> in acetonitrile. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

given by Eq. (1), is expected at higher potentials. Another pair,  $B_{\text{ox}}$  and  $B_{\text{red}}$ , corresponding to the oxidation and reduction of  $I^-/I_3^-$  couple (Eq. (2)) is expected at lower potentials.

$$3I_2 + 2e^- \leftrightarrow 2I_3^- \tag{1}$$

$$I_3^- + 2e^- \leftrightarrow 3I^- \tag{2}$$

From Fig. 8, it can be seen that Pt and Pt/f-MWNTs exhibit both the redox waves whereas f-MWNTs do not display any peak other than  $B_{0x}$  (the current is too low to be resolved from the background for the other peaks). This directly suggests that f-MWNTs based electrode has very low catalytic activity. Furthermore, the peak anodic and cathodic currents in Pt/f-MWNTs are higher than in Pt. This suggests that Pt/f-MWNTs is more catalytic than Pt. However, since f-MWNTs do not show any catalytic activity, the higher activity of Pt/f-MWNTs is mainly due to the presence of nanostructured Pt. It is known that the peak separation between the anodic and cathodic peaks,  $E_{pp}$ , varies inversely as the rate of a reaction [41]. From Fig. 8, it can be seen that Pt and Pt/f-MWNTs have  $E_{pp}$  of ~470 and 380 mV, respectively. This immediately suggests that tri-iodide reduction happens rapidly at Pt/f-MWNTs surface rather than on pure Pt which can be again attributed to the presence of large number of highly catalytic nanosized Pt clusters. This increased catalytic activity is responsible for higher exchange current density in Pt/f-MWNTs based electrodes. The Bred peak in Pt/f-MWNTs is shifted towards positive potential compared to that of Pt which suggests that there are lower overpotential losses in Pt/f-MWNTs. The total series resistance values of the electrodes, Pt/f-MWNTs  $\sim$ 16.6  $\Omega$  and Pt  $\sim$ 20.9  $\Omega$  reaffirm that there is lower overpotential loss in Pt/f-MWNTs.

Further cyclic voltammetric experiments were carried out by changing the scan rates. Fig. 9a and b depicts the variation of  $E_{\rm pp}$ and  $I_{\rm p}$  (peak cathodic,  $I_{\rm pc}$  and peak anodic,  $I_{\rm pa}$  currents) vs. square root of the scan rate (v). It can be seen from Fig. 9a that, as the scan rate is reduced,  $E_{\rm pp}$  decreases. As the scan rate is reduced the oxidized species have sufficient time to diffuse from the bulk of the solution toward the electrode and interact with the catalyst leading to an increase in the catalytic activity. The decrease in  $E_{\rm pp}$  with scan rate is steeper for Pt than for Pt/f-MWNTs, which could be understood on the basis of the following argument. The particle size of Pt loaded on MWNTs is very less compared to that of the bulk film. As a result, the Pt nanoparticles have a higher catalytic activity than in



**Fig. 9.** Rapid electron transfer. (a) Variation of  $E_{pp}$  with square root of scan rate and (b) variation of peak cathodic ( $I_{pc}$ ) and anodic ( $I_{pa}$ ) currents with square root of scan rate for Pt (red squares) and Pt/f-MWNTs (blue triangles) suggesting rapid electron transfer kinetics at Pt/f-MWNTs surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the pure film form. Therefore, even at high scan rates Pt/f-MWNTs can reduce all the tri-iodide species present near the electrode. In other words, Pt/f-MWNTs based electrode has rapid electron transfer kinetics due to the surface area effect ensuing from the nanoparticle distribution. From Fig. 9b, we see that  $I_p$  versus  $v^{0.5}$  is nearly linear in the case of Pt/f-MWNTs whereas some deviation can be observed in the case of Pt. Further, from the inset in Fig. 9b we can see that  $I_{pa}/I_{pc}$  is nearly constant and closer to 1 in the case of Pt/f-MWNTs whereas significant deviation from reversibility ( $I_{pa}/I_{pc} = 1$ ) can be observed in the case of pure Pt electrode. Deviation from reversibility suggests slower electron transfer kinetics in the case of Pt. Pt/f-MWNTs based electrode allows rapid electron transfer kinetics and is therefore reversible. Thus, Pt/f-MWNTs is a better electrode for the reduction of tri-iodide in DSSCs due to the presence of Pt nanoparticles.

#### 4. Conclusions

Nanostructured Pt particles were successfully and uniformly decorated on f-MWNTs by a rapid and facile method. The DSSC fabricated with Pt/f-MWNTs as counter electrodes with a Pt loading of  $\sim 10 \,\mu g \, cm^{-2}$  showed an efficiency of 5.4%, an improvement by 20% and 135% over the conventional Pt and f-MWNTs

counter electrodes based DSSCs. Based on cyclic voltammetric and electrochemical impedance measurements, the superior performance of Pt/f-MWNTs could be attributed to higher catalytic activity and large accessible surface area of nanosized Pt.

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