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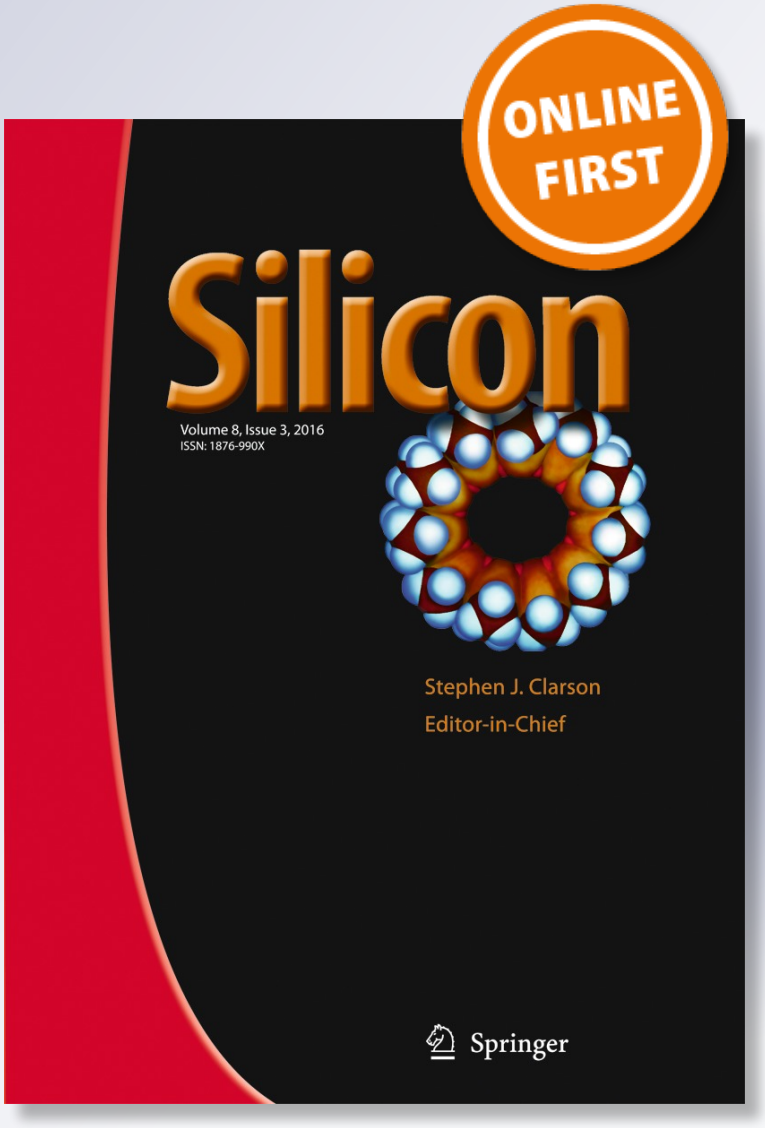

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ORIGINAL PAPER

Botanical Hydrocarbon Sources based MWCNTs Synthesized by Spray Pyrolysis Method for DSSC Applications

S. Kalaiselvan[1] · K. Balachandran[2] · S. Karthikeyan[3] · R. Venckatesh[4]

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Abstract The present study aims to synthesize corrosion free counter electrodes for DSSC and evaluate their efficiency in comparison with carbon electrodes. We compare the PCE (Power Conversion Efficiency) of a MWCNT counter electrode DSSC with a carbon coated counter electrode DSSC. MWCNTs are prepared by a spray pyrolysis method and TiO_2 nanoparticles are prepared by a WCT (Wet Chemical Technique). XRD analysis for TiO_2 $2\theta = 25.3$ shows the presence of anatase phase and $2\theta = 25.9$ shows the hexagonal graphite structure of MWCNTs. SEM images of TiO_2 nanoparticles show irregular morphology and for MWCNTs, the SEM image shows the formation of MWCNTS. The exact grain size of MWCNTs and TiO_2 nanoparticles are studied by TEM analysis. In the DSSC application, MWCNTs coated the DSSC show higher efficiency (2.5 %) than carbon coated DSSC (1.9 %).

Keywords TiO_2 · MWCNTs · Spray pyrolysis · DSSC

✉ K. Balachandran
balananostar@gmail.com

[1] Department of Chemistry, Hindusthan College of Engineering and Technology, Coimbatore, Tamil Nadu, India

[2] Department of Chemistry, Vivekanandha College of Engineering for Women, Namakkal, Tamil Nadu, India

[3] Department of Chemistry, Chikkanna Government Arts College, Tirupur, Tamil Nadu, India

[4] Department of Chemistry, Government Arts College, Udumalpet, Tamil Nadu, India

1 Introduction

In recent years dye sensitized solar cells (DSSC) gained much attention because of their properties such as low fabrication cost, robust nature, environmental compatibility and simplicity of the process [1–3]. DSSC consist of dye modified photo-anode, electrolytic solution and counter cathodes.

Recently, dye modified nanosized TiO_2 powders have been used as a working electrode for dye sensitized solar cells, due to the higher efficiency than any other metal oxide semiconductor. However as reported the best TiO_2 solar efficiency could hardly reach 11.5 % [4]. Additionally TiO_2 has proven to be the most suitable for widespread solar energy conversion and environmental applications due to its biological and chemical inertness, strong oxidizing power, cost effectiveness, long term stability against photo-corrosion and chemical corrosion [5].

A number of methods have been used to synthesize TiO_2 nanoparticles, including e-beam evaporation, chemical vapour deposition, flame hydrolysis, spray pyrolysis and sol-gel. The interest in the use of sol-gel methods is due to several advantages: good homogeneity, ease of composition control, low processing temperature, ability to fabricate large area coatings and low equipment cost [5–7].

In DSSC the counter electrode plays a major role to improve the electron transportation. Although platinum coated FTO (fluorine doped tin oxide plates) as the counter electrode is usual, it is expensive and it could be corroded in triiodide containing solutions to generate platinum iodides such as PtI_4 [8, 9]. As a result, many types of carbonaceous materials such as carbon nanotubes (CNTs) [10] carbon black [11] and graphite [12] are used as counter electrodes.

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Among all these CNTs have some special features. CNTs are unique nanoscale objects with the combined advantages of large surface area, high electrical conductivity, chemical stability [13], good mechanical property, thermal conductivity [14], corrosion resistance towards iodine, high reactivity for triiodide reduction and low cost [15, 16].

In general, CNTs are synthesized by arc discharge, laser ablation, CVD and spray pyrolysis method. Among these methods spray pyrolysis is regarded as a promising method to synthesize carbon nanotubes (CNTs), because of its benefits to achieve a high yield of CNTs that can be easily scaled up for the production of CNTs at a relatively low cost. Moreover it provides an easy way for the controlled insertion of liquid additives into the reactor.

To date there have been numerous purified petroleum products such as methane, ethylene, acetylene, benzene, and xylene that are in practice used for synthesizing CNTs. Considering the environmental effects and depleting fossil fuels such as petroleum product sources, the cost of these petroleum based products is expected to increase in the near future. Therefore, it is inevitable to look for alternative eco-friendly carbon precursors. The advantages of a plant derived eco-friendly carbon precursor are that it is very cheap, renewable biomaterial, green, abundantly available and, owing to these factors, it has a huge potential to be used as the carbon source for the synthesis of CNTs. There are a few reports on the synthesis of CNTs from natural precursors such as camphor [17], pine oil [18], Jactropha curcas oil [19] Cymbopogen flexuosus oil [20], Helianthus annuus oil [21], Madhuca Longifolia Oil [22], Glycine Max Oil [23] and Brassica Juncea oil [24].

In our previous work [25], we have shown that the power conversion efficiency (PCE) of DSSC has been enhanced by doping SiO_2 in TiO_2 photo-anodes using carbon coated counter electrodes. In this present work we study the PCE comparison between corrosion free CNTs and carbon coated counter electrodes using N3 cis-Bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato ruthenium (II)) dye sensitized TiO_2 photo-anodes. The TiO_2 nanoparticles were synthesized by a wet chemical technique and CNTs by a spray pyrolysis method using the renewable precursor Oryza Sativa oil and they were characterized by XRD, SEM and TEM analysis.

2 Materials and Methods

2.1 Materials

All reagents used were of analytical grade purity and were procured from Merck Chemical Reagent Co., Ltd., India and the FTO plates were procured from Sigma-Aldrich Co, India.

2.2 Synthesis of TiO_2 Nanoparticles

In the synthesis of TiO_2 nanoparticles, titanium tetraisopropoxide (TTIP) was used as a precursor, Hydrochloric acid (HCl) as peptizing agent and ethanol were used as the solvent medium. HCl was mixed with ethanol and it was stirred for a few minutes. To this solution TTIP was added. The ratio of HCl, C_2H_5OH and TTIP was 1:4:2 respectively. The stirring was continued for 1 h at room temperature. Then 50 ml of distilled water was added, the temperature was raised to 50 °C and stirred for 3 hr until the solution changed into a colorless gel. The highly viscous gel was dried at room temperature for 15 days to get amorphous TiO_2 powder. Finally the amorphous TiO_2 was calcined at 400 °C for 1 hr to get crystalline TiO_2.

2.3 Synthesis of Carbon Nanotubes

2.3.1 Preparation of Mixture of Catalysts

The Fe-Mo catalyst supported on silica was prepared by a wet impregnation method. Metal salts i.e. 10 g of $Fe(NO_3)_3.6H_2O$ and 1 g of $(NH_4)Mo_7O_{24}.4H_2O$ were dissolved in 100 mL methanol and mixed thoroughly with 4 g of silica. The solvent was then evaporated and the resultant cake was heated at 100 °C for 3 hours in a muffle furnace and ground in an agate mortar. The fine powders were calcined for 1 hour at 450 °C.

2.3.2 Synthesis and Purification of Multi Walled Carbon Nanotubes (MWCNTs)

The as prepared catalyst was placed on the quartz boat and then it was placed in the heating furnace in a nitrogen atmosphere. At 750 °C, the methyl ester of Oryza Sativa oil was introduced into the quartz boat through a spray nozzle and the flow was maintained using a saline tube at the rate of 0.5 ml/min and the deposition time lasted for 45 min. Then the reactor was allowed to cool to room temperature. About 5 g of MWCNTs were stirred with 20 mL of 1N HCL at 60°C, to this mixture 20 mL of H_2O_2 was added, and the stirring was continued for 30 min. Finally, all the MWCNTs were washed with deionised water and dried at 120 °C in a hot air oven for 2 hours.

2.4 Characterization of Synthesized TiO_2 and CNTs

The crystalline structure of synthesized TiO_2 nanoparticles and CNTs were analysed with a D8 Advance X-ray diffraction meter (Bruker AXS, Germany) at room temperature, operating at 30 kV and 30 mA, using Cu Ka radiation (k = 0.15406 nm) and grain size was calculated

by Scherrer's formula. Surface morphologies of synthesized TiO_2 nanoparticles and CNTs were characterized with a scanning electron microscope (SEM) (Model JSM 6390LV, JOEL, USA). The nanoparticles and CNTs were viewed through a transmission electron microscope (TEM) (JEOL-TEM 2100) at high magnification and exact particle size was determined.

2.5 Surface Area Measurements

The surface area, pore size and pore volume of the nanomaterials were analyzed using a BET analyser model Micromeritics Gemini 2375, Surface Area Analyser (Micromeritics Inc., Norcross, GA). The BET specific surface areas of the samples were 65, 75 and 95 m^2/g for TiO_2, carbon and MWCNTs.

2.6 Fabrication of DSSC

2.6.1 Preparation of TiO_2 Electrode and Treatment with Dye

Thin nano-structured photo-anode film was fabricated using synthesized TiO_2 nanoparticles by employing a doctor blade technique. 1 g of TiO_2 nanoparticles were ground in a mortar and pestle with addition of an appropriate amount of distilled water and methanol. After making a viscous paste, it was further diluted with distilled water and then 10 mL of Triton X-100 was added for better adhesion of the paste on the conducting substrate. The paste was spread on the conducting substrate with a glass rod using adhesive tape as spacers. After drying in air, the film was sintered for 30 minutes at 400 °C in a muffle furnace. After sintering, the TiO_2 films were sensitized in 0.5 mM of N3 (cis-Bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato ruthenium(II)) containing acetonitrile dye solution for 12 hours. The dye-sensitized electrodes were rinsed with acetonitrile to remove excess unanchored dye molecules on the surface.

2.6.2 Preparation of Counter Electrodes

Preparation of carbon coated counter electrodes followed the method described in our previous paper [25]. The CNT coated counter electrode was prepared by the following method. About 1 g of CNTs was placed in a mortar, 5 mL of Triton X 100 solution was added and it was ground for 10 min, then the paste was spread on the conducting substrate with a glass rod using adhesive tape as spacers. After drying in air, the film was dried for 30 minutes at 400 °C in a hot air oven for the complete combustion of the Triton X 100 solution.

2.6.3 Electrolyte Preparation

The electrolyte solution was composed of 0.5 M LiI/0.05 M I/0.5 M TBP (4-tert-butylpyridine), it was prepared by 0.63 g of iodine (Mol. Wt.=126.9), 6.7 g of lithium iodide (LiI) (Mol.Wt.=133.8) and 9.5 g of TBP (Mol.Wt=191.3) dissolved in 100 mL of acetonitrile solution.

2.6.4 Film Thickness Measurement

The thickness of samples was measured using an Alpha-Step-D-600 Stylus Profiler. A thin nano-structured photo-anode film was fabricated using synthesized TiO_2 nanoparticles and its film thickness was 230 nm.

2.6.5 Assembly of TiO_2 and CNTs based DSSC

The DSSC was fabricated using standard two-electrode configurations (photo-anode and counter electrode), comprising dye sensitized TiO_2/FTO (with an active surface area of 0.25 cm^2) as photo-anode and CNTs coated FTO as a counter electrode. For two-electrode measurement, the liquid electrolyte I^-/I_3^- (iodide and triiodide) was injected between the photo-anode and counter cathode, pressing firmly. A thin layer of parafilm was used as a spacer to avoid short-circuiting between the two electrodes. A binder clip was fixed externally to maintain the mechanical grip of the cell without any further sealing, which finalized the assembly of the DSSC. The V- I characteristics of current were measured by a Keithley electrometer under the light radiation source of 1000 mW/cm^2.

The same procedure was followed for the carbon coated counter electrode based DSSC. The following cell configurations were used to record I–V plots:

$FTO/TiO_2/N3/I^-/I_3^-/CNT/FTO$

$FTO/TiO_2/N3/I^-/I_3^-/C/FTO$

3 Results and Discussion

3.1 Characterizations of TiO_2 Nanoparticles and MWCNTs

Figure 1a shows XRD patterns of TiO_2 nanoparticles. The crystallite type of the TiO_2 was pure anatase. The TiO_2 particles show Bragg's reflections at about $2\theta = 25.3°$, 37.8°, 48.3° and 54.3° corresponding to (101), (004), (200) and (211) planes referred to as tetragonal crystal planes of anatase phase TiO_2 [26]. The most intense reflection at $2\theta = 25.3°$ is assigned to anatase (d101). The powders show the crystalline pattern and the observed d-lines

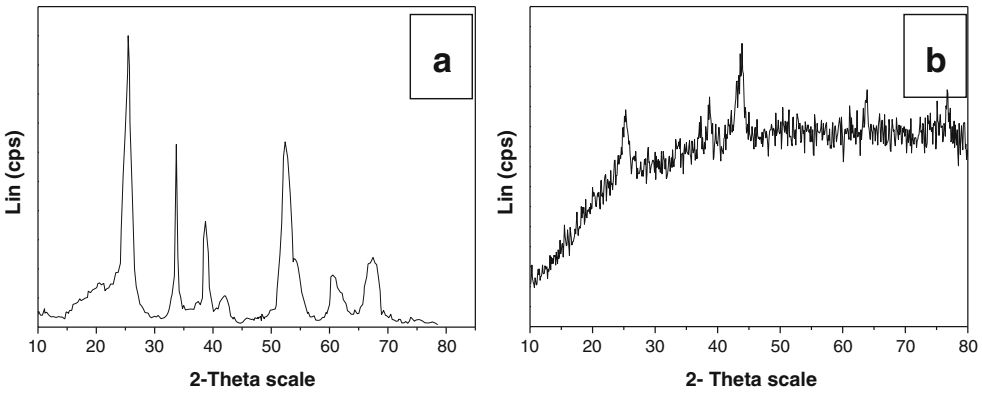

Fig. 1 XRD patterns of **a**) TiO_2 nanoparticles, **b**)MWCNTs

match the reported values for the anatase phase. The average crystallite size was determined from a slow scan of the powders in the range 24–27 with a step of 0.01- min^{-1} from Scherrer's equation using the (101) reflections of the anatase phase assuming spherical particles. An estimate of the grain size (G) from the broadening of the main (101) anatase peak can be made by using Scherrer formula. The nanocrystallite sizes were found to be 15 nm for TiO_2. A typical XRD pattern of the as synthesized MWCNTs is shown in Fig. 1b. The presence of peaks at angles $2\theta = 25.9°$ and 44.3° indicates that the synthesized nanomaterials to be CNTs. The peaks are indexed to be the [002] and [101] reflections of hexagonal graphite. The presence of the [002] peak in the XRD spectra of CNTs indicates the concentric cylindrical nature of graphene sheets (d002 = 2.03 nmnm) nested together, and that the nanotubes are multi-walled in nature [27].

Figure 2a shows SEM images of TiO_2 nanoparticles. The TiO_2 particles exhibited irregular morphology due to the agglomeration of primary particles with an average diameter of 15–20 nm. Figure 2b shows the SEM image of the as-synthesized nanostructures over Fe-Mo bimetallic catalyst, impregnated in silica at 750 °C under the flow of nitrogen by the spray pyrolysis method. The carbon nanostructures are found to be irregularly shaped with diameter in the range of 50-80 nm. The reason for the observation may be attributed to insufficient precursor concentration at the reaction zone to generate carbon through pyrolysis.

In order to obtain more detailed structural information TEM analysis was performed. The TEM images of as prepared TiO_2 particles are shown in Fig. 3.a. The TEM analysis of TiO_2 particles revealed a highly clustered nature. TEM analysis strongly supported the nanophase formation of TiO_2 particles. The average particle size measured from TEM was found to be in the range of 10-20 nm, which slightly varied from the particle size obtained from XRD analysis. It was assumed that the crystallites were formed without any local strain. The selected area electron diffraction analysis (SAED) shows continuous ring patterns which originate from the polycrystalline state or by more crystallites attached to the surface of the single particles. The bright ring pattern shows a high density of crystallites present in the composites.Fig. 3.b shows the TEM images of MWCNTs. The HRTEM image clearly shows well-graphitized layers of MWCNTs with inner and outer diameter in the range of 20-40 nm, grown from catalytic decomposition of the methyl ester of Oryza Sativa oil at 750 °C. Amorphous carbon and catalyst particles are rarely seen in the HRTEM image of the sample. The SAED pattern exhibited a pair of small but strong arcs for (002), together with a weak ring for (100) diffractions. The appearance of

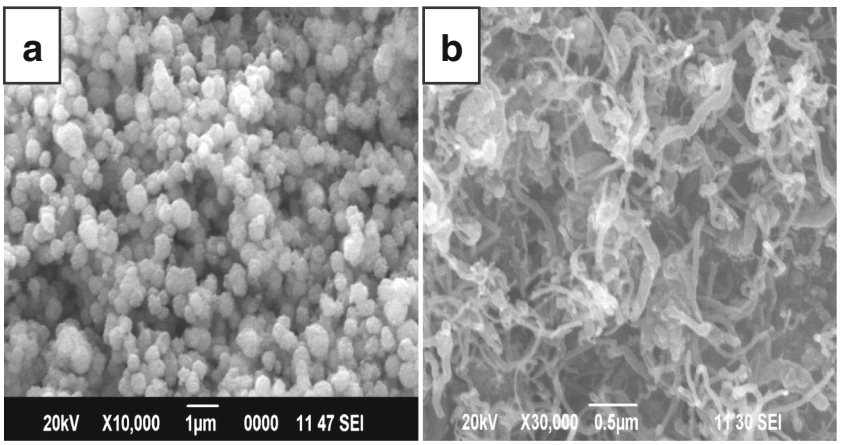

Fig. 2 SEM images of **a**) TiO_2 nanoparticles, **b**)MWCNTs

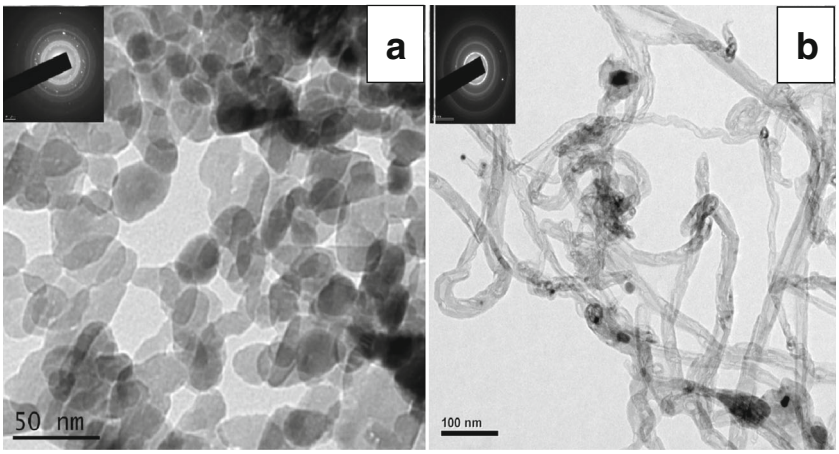

Fig. 3 TEM images of **a**) TiO_2 nanoparticles, **b**)MWCNTs

(002) diffractions as a pair of arcs indicates some orientation of the (002) planes in the CNTs. The sharp rings are evidence of polynanocrystalline material representing diffraction from a few crystals. A diffuse pattern would be obtained from amorphous substances. The single bright spots are reflections from certain individual crystals.

Figure 4 shows the UV-Visible spectra of TiO_2 nanoparticles. In the current measurement the onset of the absorption peak of maximum absorbance occurred at 372 nm for TiO_2. The optical band gap of the material was calculated by effective mass approximation and it was found to be 3.3eV for TiO_2.

Mechanism of formation of MWCNTs Adsorption and decomposition of the precursor occurs on the surface of the catalyst nanoparticles dispersed on the support surface. Subsequently, the carbon atoms dissolve and diffuse into the nanoparticle interior to form a metal–carbon solid solution. Nanotube growth occurs when supersaturation leads to carbon precipitation into a crystalline tubular form.

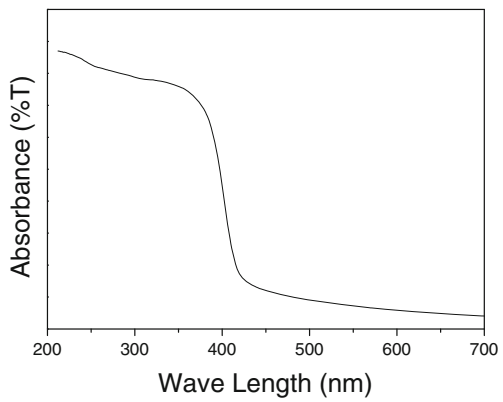

Fig. 4 UV-Visible spectra of TiO_2 nanoparticles

3.2 Photovoltaic performances of Dye Sensitized Solar Cells

The current - voltage (I-V) characteristics of a DSSC constructed by using TiO_2 particles sensitized with N3 under illumination condition (1000 W cm^{-2}) are shown in Fig. 5. The fill factor and conversion efficiency of the fabricated TiO_2 DSSC are calculated as follows

$$FF = \frac{Vmax * J\,max}{Voc * Jsc}$$

$$\eta = \frac{FF * Voc * Jsc}{Pin}$$

Where,

V_{oc} = open circuit voltage, Jsc = short circuit current density, Vmax= maximum voltage,

J_{max} = maximum current density, P_{in} = power input (1000 W/ cm^2).

The short-circuit current densities (JSC) were found to be 6.2 and 7.5 (mA/cm^2), fill factors were 0.425 and 0.444 and conversion efficiencies 1.9 and 2.5 for carbon coated and CNTs coated counter electrode respectively. Nam et al.,

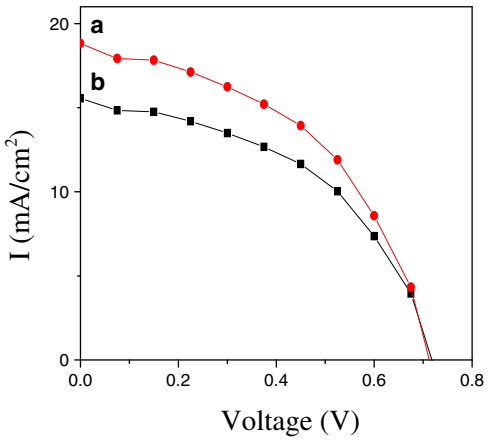

Fig. 5 I-V characteristics of **a**) MWCNTs coated FTO, **b**) carbon coated FTO

achieved 8.03 % PCE [28] and Lee et al., achieved 6.75 % PCE [29] using a MWCNT counter electrode and N719 (Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)) as sensitizer.

The PCE of the CNT coated counter electrode is higher when compared with the carbon coated counter electrode DSSC. The reason for the increase in the PCE of the CNT coated DSSC is high electrical conductivity by the distribution the that CNT facilitates in the charge transfer reaction by easy electron transfer. The distribution of the CNT in the counter electrode activates the charge transfer by promoting the I^{3-}/I^{-} redox reaction rate by easily taking up liquid electrolyte into numerous nanostructures. Using CNTs in that counter electrode increases the the contact area between the electrolyte and counter electrode and gives a good I^{3-}/I redox reaction. High electrical conductivity and excellent catalytic activity of the CNT lead to higher PCE. Similarly the BET analysis shows the carbon coated FTO has a low surface area when compared with the CNT coated FTO. The low surface area reduces the redox reaction, so the carbon coated CNT gives lower efficiency.

4 Conclusion

TiO_2 nanoparticles were synthesized by WCT and MWCNTs were synthesized by the spray pyrolysis method. The synthesized nanostructures were characterized by XRD, SEM and TEM analysis. TEM images exhibit the nanophase formation of TiO_2 and MWCNTs. In DSSC the CNT coated counter electrode gives a high PCE when compare the carbon coated counter electrode because of the high electrical conductivity and excellent catalytic activity of MWCNTs giving higher efficiency than the carbon coated counter electrode.

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