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Effect of Platinum loaded Multi Walled Carbon Nanotube Counter Electrode on Dye Sensitized Solar Cell

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Abstract—Dye Sensitized solar cells were the Photovoltaic cell that converts visible light energy into electrical energy. DSSC can be used to produce electrical energy in a wide range of light conditions. They can be used indoor as well as outdoor. DSSC convert both artificial and natural light into energy that can be used in electronic devices. Dye Sensitized solar cells are able to provide energy with a more affordable cost of fabrication and the production than solar cells that are made from crystalline silicon. Counter electrode also known as Auxiliary electrode. It is made from fluorine-doped tin oxide (FTO) glass which is coated with Catalyst layer to increase electron transfer rate. In order to obtained enhanced energy conversion rate of DSSC, Multi-Walled carbon nanotubes (MWCNTs) were used in counter electrode. Platinum counter electrode and Platinum-Multi-Walled CNT counter electrode were fabricated. All these counter electrodes were fabricated on FTO glasses. The performance of solar cell was measured with the help of solar light simulator. The Structure of counter electrodes were studied by Scanning Electron Microscopy images. Results shows that enhanced efficiency was obtained by using the Pt-MWCNT Counter Electrode.
Keywords—DSSC, Counter Electrode, Pt, MWCNT, Efficiency

I. Introduction

The energy demands were increasing day by day ,as well the oil prices too and increasing global warming results in the rise of research in the field of eco-friendly sources of energy. Solar energy is one of the alternative source of energy to overcome these problems. Solar energy can be used in the form of electrical energy by using Photovoltaic cell (Solar cell). Solar energy is present in abundant amount and the conversion process is not harmful to the environment, thus it is a eco-friedly process of generation of electrical energy.

The principle of conversion of sunlight into electrical energy is found by Chapin and Fuller in 1960s. Initially the solar cells were fabricated by silicon, thus known as silicon (Si) solar cell. This solar cell was the " first generation Solar cell ". Due to the increasing price of the raw materials of Silicon solar cell, it is necessary to evolved the "second generation solar cell". The second generation cell is made by a thin layer of a-Si, CdTe, CuInSe2 (CIS). Along with the development of technology the solar cell that utilizes the abundant natural raw materials, which is non-toxic and able to produce high conversion efficiency is fabricated. This is the “Third generation solar cell” known as Dye sensitized solar cell.

The Third generation solar cells were able to provide energy with a more affordable cost of production and fabrication than crystalline silicon solar cells. Dye-sensitized solar cell based on dye-sensitized nanocrystalline titanium dioxide and [Ru(4,40-dicarboxylic acid 2,20-bipyridine)2(NCS)2] have been reported by Regan and Gratzel in 1991 [1] .In 1991 the sensitized electrochemical photovoltaic device with a conversion efficiency at that time of 7.1%under solar illumination was made. The evolution has continued progressively since then ,with efficiency now 10%. DSSC has been attracting considerable attention, as they are the alternative to conventional silicon solar cell. Easy handling and relatively high photon-to-current conversion efficiency are the advantages of DSSC over Si-solar cell. Generally, Platinum coated electrode is used as the counter electrode in DSSC. It is because of the fact that platinum have high electrochemical activity. Platinum counter electrode is costly thus, a low cost electrode with high electrochemical activity is an important requirement to enhance the practical utility of DSSC.

Practically, the conversion efficiency of DSSC is lower than silicon solar cells. Many studies have been conducted in order to obtain enhanced efficiency of Dye Sensitized Solar Cell. Different methods like doping metal ions into TiO2 electrode, increasing porosity and crystallizing of TiO2 electrode, use of alternative electrolyte or use of different counter electrode were used in order to obtained enhanced efficiency of DSSC.

Carbon nanotubes (CNTs) have properties like very high mechanical strength, very good thermal stability, high thermal and electrical conductivity .Also CNT shows good Catalytic activity for the reduction of tri-iodide . These make CNTs very useful in fields of Electronics and cells. Sung Uk Lee et al[2] used Single wall and multi wall carbon nanotubes (SWCNT and MWCNT) for the fabrication of counter electrodes in dye-sensitized solar cells.They fabricated the counter electrode by repeated deposition and drying of carbon nanotubes and Platinum over an FTO glass. Among two electrodes he fabricated, the highest efficiency of solar cells (4.36%) was achieved by using MWCNT and lower efficiency solar cells (4.03%) was fabricated by addition of SWCNT. Thus, MWCNT-CE is used in DSSC.

II. Principle of Dye Sensitized Solar Cells

The standard Dye Sensitized Solar Cell consists of two sandwiched glass layered with transparent conducting oxide. One electrode is of porous titanium dioxide (TiO2) layer on which dye molecules were stained. This electrode is known as Photo-electrode. The other electrode is the counter-electrode .It is coated with catalyst layer. Electrolyte layer of redox species (I^- and I^{3-}) exists between the working electrode and counter electrode. The general structure of a DSSC is illustrated in fig.1.

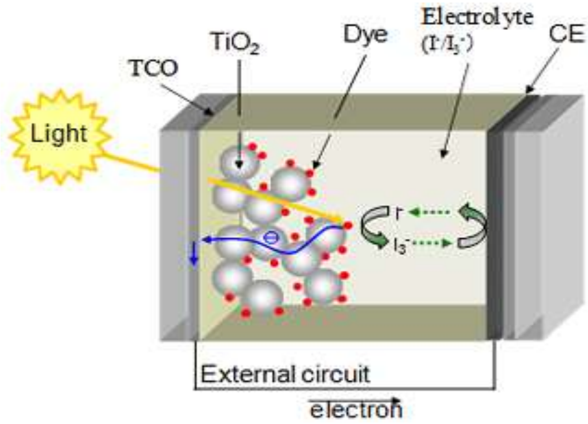


Figure 1. Working of DSSC

The working principle of a DSSC is completely based on the kinetics electron transfer reactions. The mechanisms which occur during electron transfer in the DSSC is as follows:

Light falls on the dye, Dye molecules absorbs the photons that were incident on it. Thus, by the absorption of photons dye molecule gets excited. Due to which electron from highest occupied molecular orbital is excited into lowest unoccupied molecular orbital as shown by equation (1).

The free electron is injected into the conduction band of TiO_2 and then through transparent conducting oxide towards the external circuit. Electron eventually reach the catalyst layer (Pt or MWCNT) and then gets recombine with holes within the electrolyte, in form of tri iodide I^{3-}, to produce iodide ion I^- through redox reactions. This reaction was shown by Eq. (3). The negative charge of I^- diffuses back into the dye and reacts with the oxidized molecule D^+ and a full electrical cycle is therefore completed (see Equation (4)). The reaction were showed below[3].

$$D + h\upsilon \rightarrow D^* \quad (1)$$
$$D^* \rightarrow D+ + e- \quad (2)$$
$$I3- + 2\ e- \rightarrow 3I- \quad (3)$$
$$3I- + 2D+ \rightarrow I3- + 2D \quad (4)$$

III. Fabrication Procedure of Counter electrodes

For fabrication of DSSC, TiO2 paste , N719 dye , Iodine electrolyte, H_2PtCl_6 (Chloroplatinic acid), multi walled carbon nanotubes (purity : >95%, diameter: 10-20 nm and length: 20 μm),TiCl4 and de-ionized water were used as raw materials. Titanium tetrachloride used in this study was diluted at 0 °C by water to make 2 M stock solution. This solution was kept in a freezer and freshly diluted to 40 mM for each TiCl4 (Titanium tetrachloride) treatment.

To prepare the counter electrodes that were used in DSSC, holes were drilled in the FTO glasses, then the perforated glasses were washed with H_2O and 0.1 M HCl-ethanol solution and cleaned by ultrasound in an acetone bath for around 10 min. In order to removed residual organic contaminants from it, it is heated in air for around 12 to 15 min at 400 °C.

For preparing platinum counter electrode ,the Pt catalyst were deposited on the FTO glasses by dipping perforated glass in the 0.2 wt.% H_2PtCl_6 solution and heat treatment at 400 °C for around 13 min. This counter electrode is called "platinum counter electrodes" (Pt-CE)[4]

Pt-loaded MWCNT solution was prepared by mixing acid treated Carbon Nanotube powder (0.2 wt. %) with 0.2 wt.% H_2PtCl_6 solution. The dye-covered TiO2 electrode and different counter electrode were assembled into a sandwich type cell, filled by electrolyte and sealed [4] as shown in fig 1.

The microstructure and the thickness of the (TiO2) working electrode and counter electrodes were measured by scanning electron microscopy (SEM) (cam scan MV2300). The catalytic properties of counter electrodes were measured by the cyclic voltammetry. The performance of the dye-sensitized solar cell was examined by using the solar simulator (Model No.81172, Oriel Co.) at an intensity of 1000 w/cm^2 [4]

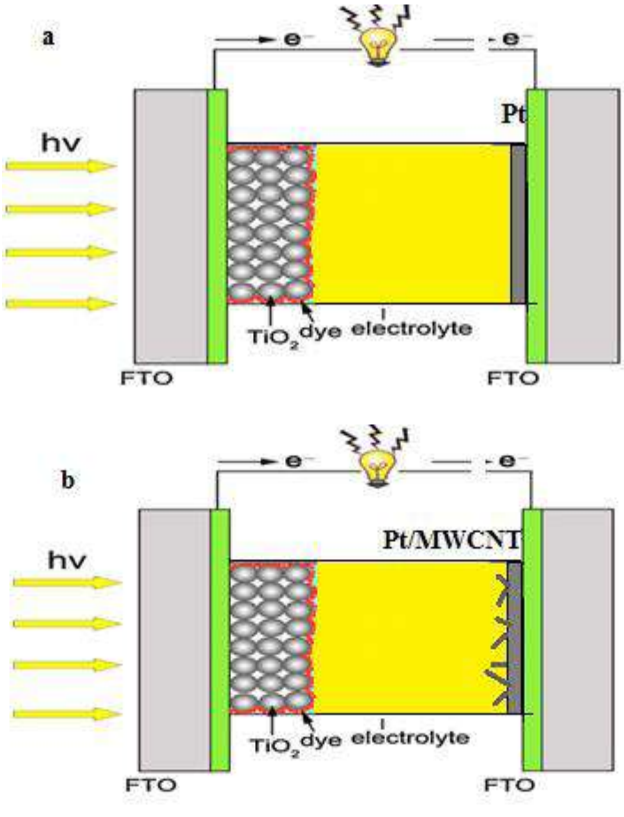


Figure 2. Schematic figure of the DSSC fabricated by(a)Pt-CE (b)MWCNT-Pt CE

The conversion efficiency of the DSSC was characterized by short- circuit photocurrent density, the open-circuit voltage, the fill factor of the cell and the intensity of the incident light. The efficiency of the DSSC is given by

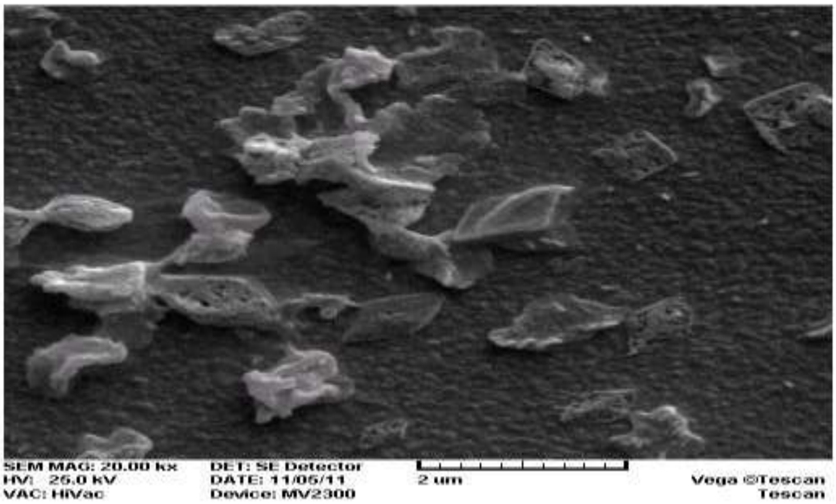
$$\eta = (Jm\ Vm)/Pin = FF(Voc\ Jsc)/Pin \qquad (1)$$

$$FF = (Jm\ Vm)/(Jsc\ Voc) \qquad (2)$$

In Eq. (1), η is the the conversion efficiency of the cell, Jm is the maximum current density, Vm is the maximum voltage , Pin the intensity of the incident light, and in Eq. (2), FF is the fill factor , Voc is the open-circuit voltage and Jsc is the short- circuit photocurrent density.

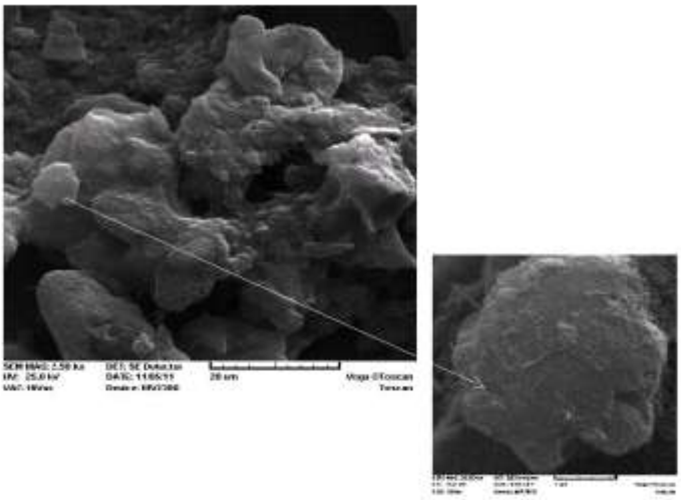
IV. Result And Discussion

The Scanning electron microscopy images of different counter electrodes are shown in Fig.3. The SEM image of Pt- counter electrode clearly shows that the Platinum film is not compact on Surface of electrode (FTO) glass and also, the platinum film is not completely coated on electrode surface. Many Large pores were also seen on surface of Counter electrode. This may decrease catalytic properties of Pt-counter electrode (Fig3.a).



(a)

Figure 3(a).The Scanning Electron Microscopy images of Pt-counter electrodes



(b)

Figure 3(b).The Scanning Electron Microscopy images of Pt-MWCNT counter electrodes

By addition the of CNTs in the Pt film of counter electrode, the carbon nanotube particles acquires every little scape on counter electrode surface and inside the poros film of Platinum layer. This will result in increasing of the effective surface area of the Platinum film on counter electrode. Thus catalytic properties of counter electrode may improves. Refer Fig 3b.

The cyclic voltammograms of all counter electrodes in iodide electrolyte were shown in Fig. 4. Based on this, the electrochemical properties of Pt-MWCNT-Counter Electrode were found to be better than the Platinum-Counter Electrode. Also, Pt-MWCNT counter electrode showed a highest current density at the reduction reaction peak (0.25 V) than Pt-Counter electrode. This indicates that the rate of the redox reaction of Pt-MWCNT-Counter Electrode is higher than that of Pt-counter electrode[4].

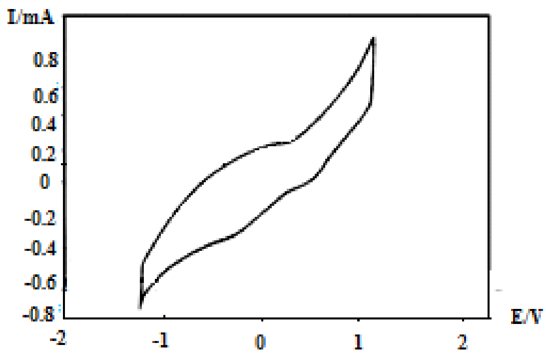


Figure 4(a). Capacitance-Voltage curve for DSSC with Pt-MWCNT-CE

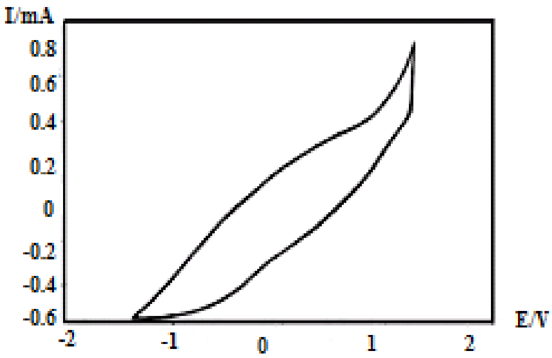


Figure 4(b). Capacitance-Voltage curve for DSSC with Pt-CE

The increase in the effective area of catalysis improves the current density. The surface area of MWCNT-Pt counter electrodes is much larger than that of the Pt and CNT counter electrodes. These results in regeneration of iodide ions thus a high conversion efficiency of DSSC is achieved.

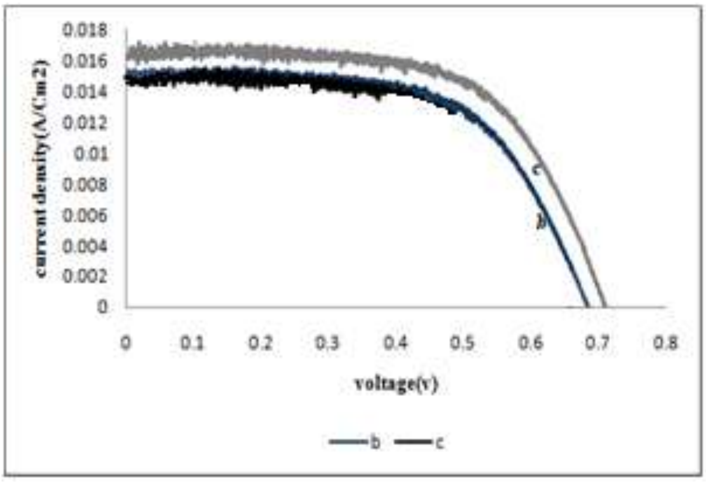


Figure 5. I–V curve for Dye Sensitized Solar Cell with different counter electrodes ,(c)-Pt-loaded CNT,(b)-Pt electrode

The I-V curve characteristics [4] of DSSC were shown in fig.5. From I-V characteristic curve, it is seen that the relatively high voltage and current density were obtained by DSSC with Pt-MWCNT-CE. And relatively low voltage and current density were obtained by using Pt CE. Studies shows this immerges from high metallic nature or their extraordinary high electrical conductivity or large surface area of counter electrodes.

By spraying CNT particles on counter electrode, the particle of CNT can be deposited on the surface of Pt and also into the porous space and thus the surface area of the Pt is increased. Pt acts as a light reflector and thus by increasing effective area the light absorption by the surface can be improved [5] .These facts were the main reason for the increase in efficiency of the solar cell when the Pt- MWCNT film is used as a counter electrode.

Table I. J–V parameters of cells with different counter electrode

Number	Counter electrode	Short circuit Current (Jsc) (mA/cm2)	Open circuit voltage (Voc) (V)	Fill factor	conversion efficiency (η) (%)
1	Pt	15.3	0.670	0.70	7.2
2	Pt-MWCNT	17.2	0.690	0.71	8.6

V. Conclusion

By using MWCNT doped platinum counter electrode the current density and voltage of 17.2 mA/cm^2, 0.690 V were obtained respectively. The conversion efficiency of 8.6% was also obtained by using Pt-MWCNT CE. As showm in Table 1. The Pt-MWCNT-CE DSSC showed highest photovoltaic performances. Carbon Nanotubes behaved as catalysts in the redox reaction,thus increases rate of reaction.

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