Improve Efficiency in Dye-Sensitized Solar Cell by Surface modification of TiO_2 Photoelectrode by Spray Pyrolysis

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Research Article

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Abstract

Pure TiO_2 and surface-modified TiO_2 (SMT) films from zinc acetate solution have been developed with fluorine-blended SnO_2 (FTO) auxiliaries. support material using spray pyrolysis for use into dye-sensitation solar cells (DSCs). Powder X-ray diffraction (PXRD) profiles indicate that pure TiO_2 and SMT exhibit the same crystal structure. Optical absorption studies do not indicate a significant absorption difference between SMT and pure TiO_2. Impedance measurements reveal that ZnO covered on TiO_2 nanoparticles increase particular exterior imepedance also suppress about reverse transmission from photo-induced electron emmiting with SMT to the electrolyzer. Surface morphology and surface fundamental study were performed using FE-SEM, field emission scanning electron microscopy and EDX, energy dissipation X-ray spectroscopy. The photo electrochemical (J-V curves) values of DSCs for pure SMT and TiO_2 thin films have been relatively investigated. Outstanding results display such that about bypassed photo electric current (J_{SC}) of pure TiO_2 increased from 16.73 $mAcm^{-2}$ to 18.09 $mAcm^{-2}$ additionally through open-loop voltage (V_{OC}) for DSCs containing SMT thin films changed between 0.71 V to 0.75 V. This indicates that the ZnO layer on TiO_2 nanoparticles contributes to the surface resistance, which impedes the flow of back scattered electrons to the electrolyte significantly. Cell power transformation productivity has been increased about 8.25 to 9.3%.

Highlights

- XRD profiles of the pure TiO_2 and the SMT films. Both the pure TiO_2 and the SMT films consist of anatase phase.
- ZnO/TiO_2 energy boundary which prevents the recombination processes in most of TiO_2 nanoparticles present at the top surface of the photoanode.
- light-induced electrons exist extracted further effictively from the photoelectrode, also therefore causing an growth in V_{OC} and J_{SC}
- The red as well as green colors indicated the existance of Ti and Zn elements.
- The electron transformation in the nanosized TiO_2 photoelectrode is caused by the micrographs of the layer.

1. Introduction

From a report by O'Regan and Grätzel, low-cost dye sensitized solar cells (DSSCs) are considered amongest best optimistic competitors for solar energy conversion rather than expensive silicon solar cells [1]. The nanoporousphoto-electrode has high effective surface, which exactly allowes capable anti particle infusion and brightness collecting in DSSCs. However, the impermeable cathode allows the reclassification of charge carriers with electrode arrangement interconnection as a result of the insufficiency attributed to intensity obstruction level during the period alter [2, 3]. For above mentioned past two decades, various methods have been reported on reducing that assault combination during

electrolyte and electrode interface [4–6]. Majority of the reports were based on the modification of TiO_2 via chemical routes. Surface-modified TiO_2nano materials exhibit the enhancement of photo current generation activity due to surface-adsorption properties as well as good stability [7]. The modified TiO_2 films by poly ethylene oxide (PEO), Polyvinyl achohol (PVA) polymers were evaluated on the level of crystallinity, optical transmission along with maximum major point on the photocatalytic action from thin-films. Previous report indicated that polymer-modified films showed seven times higher efficiency than the unmodified ones [8]. Theformation of carbonaceous polymeric deposit was observed on the titania surface due to Benzene activation. These surface-modified photoelectrode materials exhibit the enhancement of photo-activityprocess by the degradation of phenolic compounds exspecially in visible region [9]. In the previous reports [10, 20] the use of ZnO or MgO coating on TiO_2 surface was found to reduce the recombination process. Growth techniques for example the doctor blade procedure [11], protect printout technique [12], anodization method [13] sol-gel approach [20] have became utilized in favour of the development of TiO_2 thin films for application in DSCs. Kim et al.[14] reported on flexible and fabricated solar cells as dye-sensitized through ZnO-modified TiO_2 nano-crystal photoelectrodes developed by spraying ethanol solution mixed with $ZnCl_2$solution. Roh et al. [5] enhanced an photoconversion capability nearby means of ZnO-coated TiO_2 electrodes produced through RF magnetron sputtering. The effect about O_2 plasma process plus ZnO film on SEM and assimilation features, production from DSCs, as well as interfaced electrochemistry characteristics were investigated. Among these methods, spray pyrolysis technique has drawn considerable attention due to the advantages such as low processing temperature, ease of control over compositional homogeneity and thin film formation over relatively large area at low-cost. In order for improve the photo-energy transition performance of a solar cell, several methods to enhance that characteristics on this TiO_2 electrodes [15–16] have been reported. The use a bilayer system [17–18] is one such popular method. In the bilayer system preparation, second metal oxide is coated on first metal oxide electrode.The interface between the metal oxides enables effective dimensional seperation of light–induced charge, and also reduced the recombined value about photo-infusion electrons. Particular charge combination toward an interconnection for this electrical conduction could also perform a significant function across device operation. Hence better sophisticated device architectures are required in the fabrication for the improvement of capability and permanent constancy. An interesting method of suppressing charge combination corresponds for covering that TiO_2 photograph through broad energy gap metal oxide compounds such as Al_2O_3, ZnO, MgO, SnO_2, and Nb_2O_5. [19–21]. The TiO_2 nanoparticles are used widely to enhance the dye uptake that provides exterior states with that nanoparticles of TiO_2. These provides less pathways for easy recombination through the cations from that redox electrolyte as a result of the narrowness with in the energy energy gap. Hence the photo-injected electrons can be excited not at all unique to the conduction group to TiO_2, however additionally to the surface states which are distributed below the conduction band. Photo-injected electrons could experience thousands of trapping/detrapping events before they attain the obvious conductive oxide based film. The electron emitting within capture siteseasily get combined accord redox reaction ion previously the occurance of a detract occrrence as the detrapping value comes to more slowly with that capture speed [22]. Hence the structure of an intrinsic

energy obstacle corresponds to essential at the electrode/anion interacted in favour of greater that material patition for the introduce electrons after the cations of the redox electrolyte reaction. The coating connected with wide band gap material as a surface modifier or a layer decreasing the rate of back scattering of electrons is shown in Fig. 3. In the current research, pure TiO_2 film and surface-modified TiO_2 (SMT) film were prepared by zinc acetate using the spray pyrolysis technique. The prepared samples were characterized using XRD, optical absorption, FE-SEM, EDX, impedance and photoelectrochemical measurements.

2. Experimental

2.1 Development of dye sensitized solar cells:

TiO_2 photoanode

Fluorine-doped SnO_2 conduction glass (FTO 10–15 /Asahi Glass, Japan) is used as a surface for the evidance of TiO_2 photographic film. Anatomical TiO_2 friction solution (~ 3-6nm) prepared using the conventional method [23]. Firstly, TiO_2 films around 17–25 μm thickness have been provided through spray pyrolysis approach. In this procedure, 0.25 to 0.3g p 25 (grain size ~ 25nm TiO_2 powder/Nihon Aerosol, Japan) was combined with 5-6ml of acetic acid to prevent agglomeration.

Moreover 20ml colloidal mixture (average particle size ~ 3–6 nm/ TKC-302, Tayca, Japan) was mixed and sonicated for homogenous mixing. Secondly, ZnO(particle size ~ 20nm) is dissolved in acetic acid and then subjected to ultrasonic treatment for about 30 minutes to get fine zinc acetate homogeneous solution. Finally, certain amount (10ml) of ethanol was added before spraying. This zinc acetate solution around 4–5 ml was sprayed around exterior of TiO_2 film. Pure TiO_2 in addition SMT films were sintered at 500^oC for 3 hours. Finally, the films has been absorbed in N719 dye solvent for absorption after 10h.

Liquidcathode

Compositions of 2-dimethyl-3-*n*-propylimidazolium, 0.1MLiI, 0.05MI_2, 0.6M1, 0.5M4-*tert* butylpyridine and finally 0.1M GuSCN in acetonitrile were used as electrolyte.

Counter cathode

Sputtered Pt electrode was employed as a counter cathode.

DSSC fabrication

TheTiO_2-coated side of the photoanode plate was positioned vertically against and parallel to the platinum-coated side of the another glass plate maintaining some separation with the aid of clamps. Liquid electrolyte is placed between between TiO_2 anode and platinum catalyst.Subsequently,the photoanode and the catalyst plates were connected by using clips for electrical connection.

3. Sample Characterization

XRD samples are measured using the RINT Ultima-3 (Riga, Japan) in the 2θ angle range from (10^0 -70^0) degrees. The optical absorption spectra was recorded in the of 800 – 200 nm wavelength range using UV-Visible-near-infrared spectrophotometer, V-630 (JASCO, Japan).The surface morphology observation and elemental analysis of SMT electrodes were done by using FE-SEM, JSM-7001F (JEOL, Japan) EDS (Bruker, Japan). The J-V Characteristics were measured by using Solar Simulator, XCS-150 (JASCO, Japan) with a xenon lamp power supply under a intensity of light 100 $mWcm^{-2}$. The vital region of cells used to be made as 0.25 cm^2. Impedance magnitude being made through a computer moderate Frequency reaction Analyzer, FRA 5022 and HZ-5000 (nF) automated polarization technique (Hokuto Denko, Japan). The frequency extent is 0.01 to 100 kHz, and the magnitude of the modulation signal is 10 mV.

3.1 Results and Discussion

3.2 X-ray diffraction study

Figure 1 illustrates the XRD profiles of the pure TiO_2 and the SMT films.Both the pure TiO_2 and the SMT films consist of anatase phase (JCPDS # 01-075-2545). Diffraction peaks of the SMT film are about identical as long as the pure TiO_2 film without for a slight reduction in the peak intensity. No diflection peaks originated from ZnO, certain a small amount of sprayedzinc acetate on surface does not change the structure of anataseTiO_2. In the figure (1), (2),(3) and (4) represent the (110), (101), (211) and (301) diffraction peaks of SnO_2 (JCPDS # 00-046-1088)respectively withthe films deposited on the FTO glass substrates.

4. Optical Absorption Study

To investigate the physical source for the improvement of solar cells, SMTand measured the color absorption effect on pure TiO_2 films. Hence both films were kept in dye solution over night for adsorption. In order to estimate the adsorption of dye atoms with that both photoelectrodes, desorption through saturated particular photoelectrodes within 3ml NaOH solvent in two different bottles. These desorbed solutions were used for optical absorption studies. We did not find significant difference in the absorption of pureTiO_2 and SMT films. Kao et al. [24] information that this amount for dye adsorbent in pure TiO_2 as well as SMT films was almost the same and the values of J_{SC} for these two samples were significantly different. They explained that the improvement of $J_{SC}$and $V_{OC}$was due in favor of the removal about interfacial charge combination through that coating out of ZnO film. This corresponds to owing to the partition for photogenerated negatively and positively charge carriers through the ZnO/TiO_2 energy boundary which prevents the recombination processes in most of TiO_2 nanoparticles present at the top surface of the photoanode.

5. Electrochemical Impedance Study

Figure 2 Illustrates the electrochemistry resistance range (EIS) of that pure TiO_2 and SMT electrodes, were ReZand –ImZ correspond toward that actual as well as imaginary section on that electrochemical resistance spectrum, respectively. Solar cell designed state from the solar cellfor the resistance calculation is the similar such as that for the J-Vmeasurement. It was found that the characteristic frequency of (ω_3) of the DSSCs prepared from SMT electrode better lower about such that for the DSSCs produced from plain TiO_2 cathode. The reciprocal for particular typical distribution ω_3 gives the recombination life time of the free electron with in the current carrying group for TiO_2 [25–26]. Therefore, that decrease inside particular characteristic frequency ω_3 means that the photo-injected electrons inTiO_2 conduction band have a longer life-time in the SMTphotoelectrode. In this process, the cell made of SMT electrode comes to collected from a porous arrangement also fourelectrical resistant that configure the path: (i) the resistivity for anion solvents, (ii) charge transmission impedance toward through electrolyte/TiO_2 be in contact in addition through TiO_2/FTO interconnection, along with (iii) resistance of this electrons in that TiO_2 film.Increase in ω_3 shows such that the ZnO-coating increased the outside impedance for TiO_2 photoelectrodes including prevent the reverse shift of photogenerated pair of electrons with SMT nanoparticles get the electrolyte into the TiO_2/dye/electrolyte interacted. Thus this light-induced electrons exist extracted further effictively from the photoelectrode, also therefore causing an growth in V_{OC} and J_{SC}. Dong et al. observed similar behaviour in the Perovskite solar cells [27]. Genearlly, low photovoltage should be due to low charge-transfer rate. Therefore, the improvement of boundary speed used to be affirmed through the basic shift at the level of the effective area of the anodic TiO_2 electrode over zinc acetate coating. The recovery of the interfacial charge was confirmed by chemical change in the surface area of the anodic TiO_2 electrode with zinc acetate coating. The thin ZnO covering influence the electronic transsport inside the anodic TiO_2 / electrolyte interface by increasing the electron forever. This is achieved by preventing the back-reaction of electrons taken out with the photo electrode during the operation of the solar cell. Moreover, the back-reaction improves in the cell due to the retardation of the photocurrent. Further electrons are gathered with the driving basic material as the loss of photoelected electrons at the capture locations. Therefore, the improvement in the conversion efficiency of the anodic TiO_2 electrode spread with zinc acetate is appropriate to the below factors:

1. The presence of a thin ZnO covering on one TiO_2 photonode exterior causes an enhance in V_{OC} due to a negatively change in the local Fermi level. The coating generates an inherent energy barrier that retards the charge recombination in the TiO_2/electrolyte interacted.

2. Particular improvement ofJ_{sc} can be assigned to this transport of more electrons with in that TiO_2 anode. This back transfer for electrons reduced because of barrier effect of thin ZnO film formed as illustrated Fig. 3. Zinc acetate spraying on the surface of TiO_2nanoparticles forms exterior condition or trap areas over this surface. The electrons with in certain plot band potential (V_{FB}) derived with the charge transfer using the surface trap conditions in to bandgap of TiO_2. Surface states of Ti^{3+} influence the

electron lifetime of the photo-injected electrons in the interfacial region.In our case,zinc acetate sprayed on TiO_2nanoparticles formed a surface layer that minimized direct recombination of back scattering electrons to the electrolyte.The improved electrical conduction isdue to presence for a ZnO coating on the surface infavour of TiO_2 nanoparticles. The coating also enabled good electrical connectivity between the particles.

6. Fe-sem And Edx Study

Fig. 4 depicts the FE-SEM micrographs for the SMT thin films. It is found that there is no change on the morphologyof film after deposition and sintering. The red as well as green colors indicated the existance of Ti and Zn elements only. We found that Zinc acetate uniformly sprayed throughout the surface of TiO_2.The electron dispersive X-ray (EDX) spectrum reveals that the existence of Zn, Ti and O_2 components in the SMT film displayed in Fig. 5.

7. Ipce & J-v Characterstics Study

The photovoltaic data of the DScs invented trough pure TiO_2 as well as SMTnanoporous electrodes are summarized in Table I. By this open circuit current density and potential enhanced about the spraying of Zinc acetate on this appear of TiO_2 anode. Particularly, the greateer V_{OC} is because of motion of the TiO_2conduction gap to the cathode direction, which is connected to the creation of a thin potential film on that TiO_2 surface [28]. Additionally, the creation for thin ZnO barrier is lowering the electron rcombination process among the photoinjected electrons of TiO_2 and the triiodide ions of the redox electrolyte. This raise the V_{OC} from that cell. According to a previous research [29], the development in photoconductivity used to be aassigned to the lagging the particle dtaparture under the charge transmission toward the interconnection about the anodic TiO_2 electrolyte /electrode. The betterment of photocurrent does not related to the amount of dye adsorbed as no significant difference in adsorption was observed. This intensity be associated to electron transmission of the photoinjected electrons. Kang et al. [10] explained by using XPS analysis that depth of 10 nm from the surface, the presence of Ti^{3+}trap sites can be considered as surface states. The decrease in the concentration of Ti^{3+} defect states by 10% retards the charge recombination. Hence the photoinjected electron loss via Ti^{3+} trap states enhance the V_{oc} for the solar cell. The photo transformation performance greater by ∼12.9% when 4–5 ml zinc acetatewas sprayed as revealed in Fig. 6. The enhancement of transformation efficiency with zinc acetate spray may be explained through two factors: (i) electronn combination in the electrolyte/electrode interface and (ii) electron transfer in the nano-sized TiO_2 cathode. Electron combination in the electrolyte/ electrode interact produce a loss of electron group through the TiO_2 film. The formation of layer ZnO barrier can delayed the charge combination process. The electron transformation in the nanosized TiO_2 photoelectrode is caused by the micrographs of the layer. Therefore, the improvement of IPCE can be assigned to the removal of electron combination with the thin ZnO layer on TiO_2 nanoparticles. A thin ZnO layer blocks the flow of electrons in the backward direction (trioxides of redox electrolyte and cations

of dye), which enhances Wokoff solar cells [30]. The limitation of charge recombination at the TiO_2/dye/electrolyteint is also interaction comes to one of the major elements for the advance of V_{OC} and FF of DSCs [30, 31]. The generated electrons generally move towards the FTO surface from the TiO_2 porous electrode. But, some of the generated electrons eventually get back scattered towards the electrolyte without any obstacles between TiO_2 and electrolyte. ZnO coating also resistsback scattered electrons to the electrolyte and enhances electronic conduction in TiO_2 nanoparticles to the conducting substrate. The dark current measurement gives the information about the interface charge recombination. The dark current is significantly reduced by spraying zinc acetate on the TiO_2 particles as shown in the inset of Fig. 7. This observation in the reduction of charge recombination is constant about the earlier review [32]. Zhouet al. [10] praposed the reduction in charge recombination on the SMT samplein the dark state. The large magnitude of dark current show that the expansion of charge recombination method among the photoinjected electrons from the excited dye molecule arranged in the LUMO, and the I_3^- ions in the electrolyte. The low-charge recombination process during the photoexcited electrons in the TiO_2 film and die cations increses the kinetic dynamics in the order from μs to ns.

The apperance of the dark current on the SMT specimen were moved to a negative importance, that confirms the constraint of charge recombination process due to surface modification.

Conclusions

As prepared pure TiO_2 and SMT working electrodes were studied for the performances of DSSCs. The bypass current density $J_{SC}$and the open-loop voltageV_{OC} for single pure TiO_2 films are 16.73 $mAcm^{-2}$ plus 0.71 V. These values improvedupto 18.09 $mAcm^{-2}$ and 0.75 V, for the DSCs by spraying zinc acetateas a surface modifier throughout the film. The solar power transformation efficiencyof DSCs can even exist better layer coating zinc acetate on the surface of TiO_2 nanoparticles. It is closed that the spraying of zinc acetate on TiO_2 film provides the surface resistance that suppresses back transfer electrons to the electrolyte and improves J_{SC} and V_{OC}. Hence the energy conversion efficiency increases compared to the DSSCs fabricated with pure TiO_2 film.

Declarations

Acknowledgement

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Tables

Table I. Thephoto electrochemical parameters of DSSCs using pure TiO_2 and SMTnanoporous electrodes.

Sample	V_{oc} (V)	J_{sc} ($mAcm^{-2}$)	FF	(η)
Pure TiO_2 (24μm)	0.71	16.73	0.69	8.25
Pure TiO_2 (24μm)	0.71	17.19	0.68	8.25
ZnO (~4-5 ml) sprayed TiO_2 (24μm)	0.75	18.09	0.69	9.32
ZnO (~4-5 ml) sprayedTiO_2 (24μm)	0.74	17.95	0.69	9.24
ZnO (~10 ml) sprayed TiO_2 (25μm)	0.78	10.74	0.68	5.76

Figures

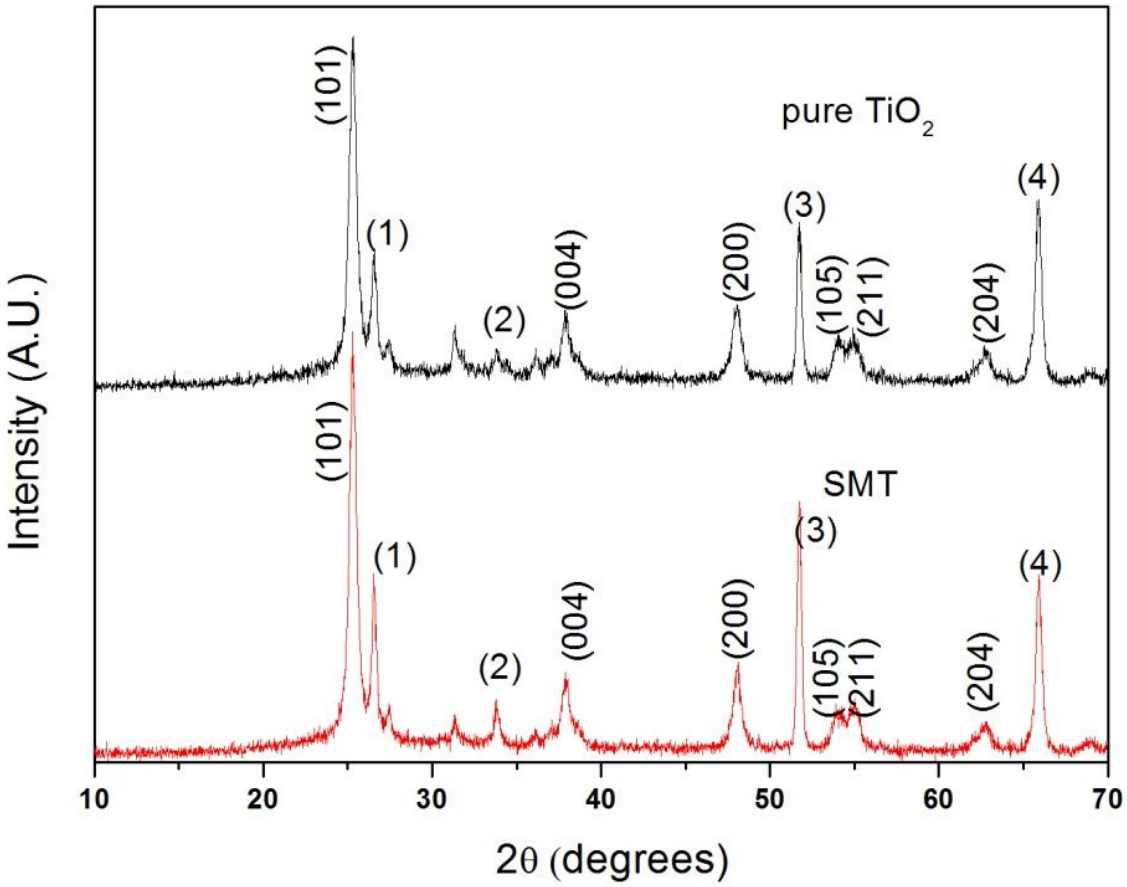

Figure 1

XRD profiles of pure TiO2 and SMT films.

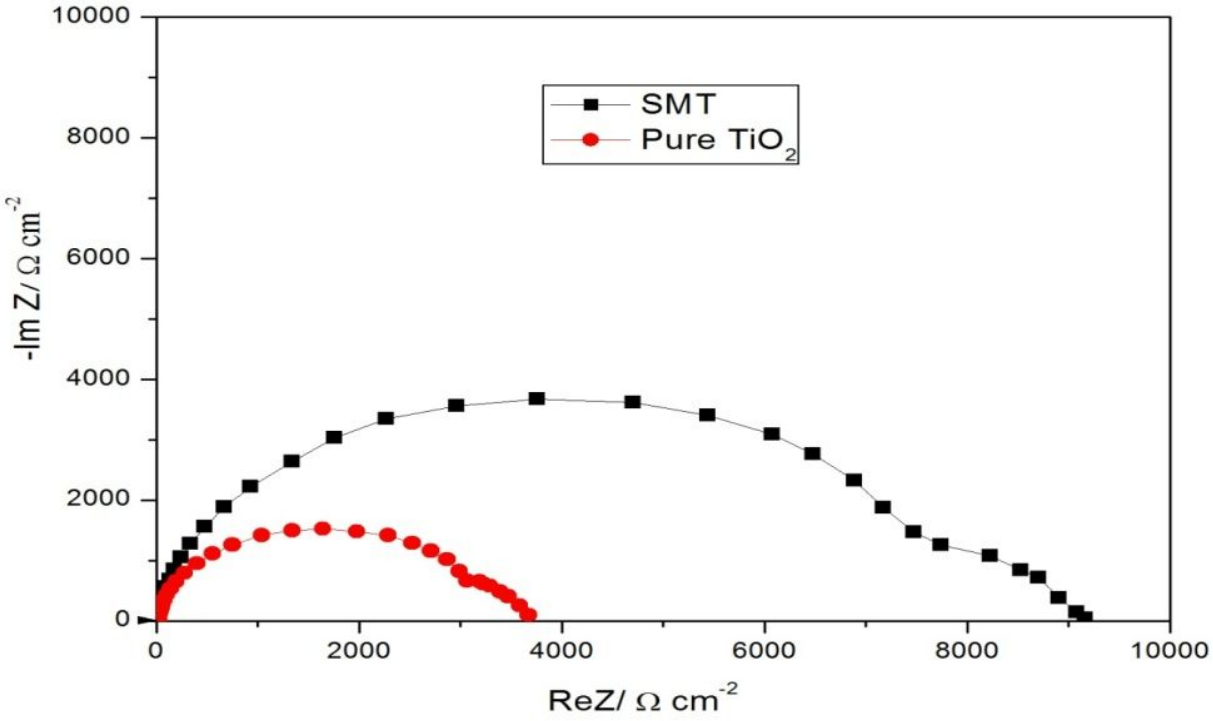

Figure 2

Impedance spectras of pure TiO2 and SMT cells.

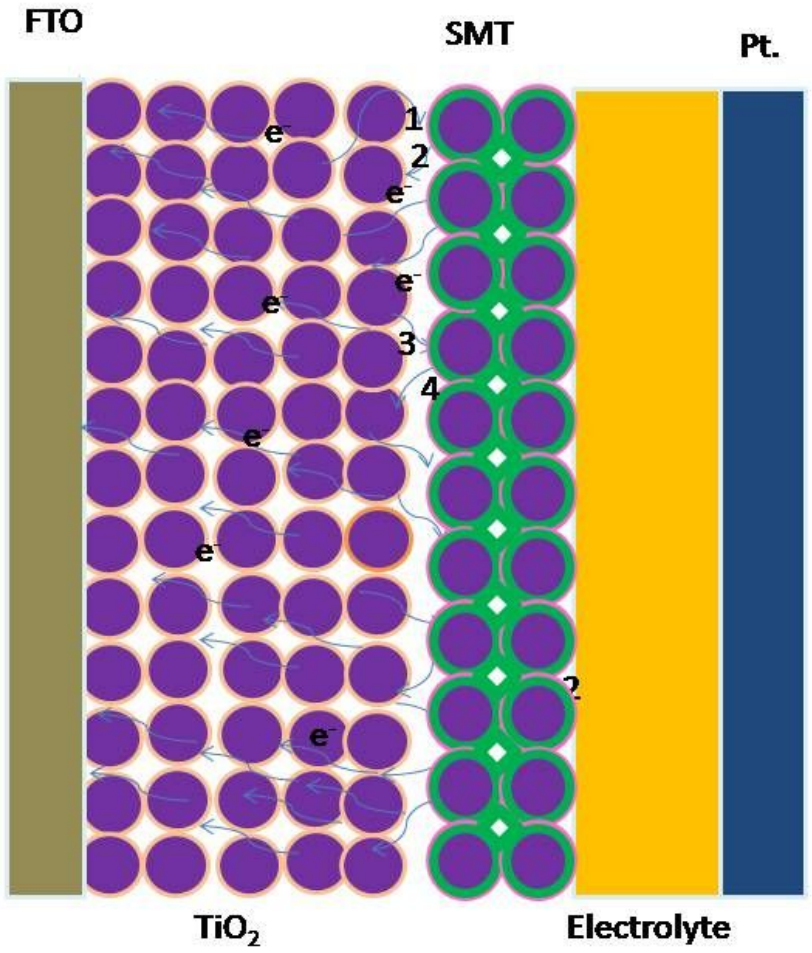

Figure 3

The working principle of solar cell based on SMT working electrode.

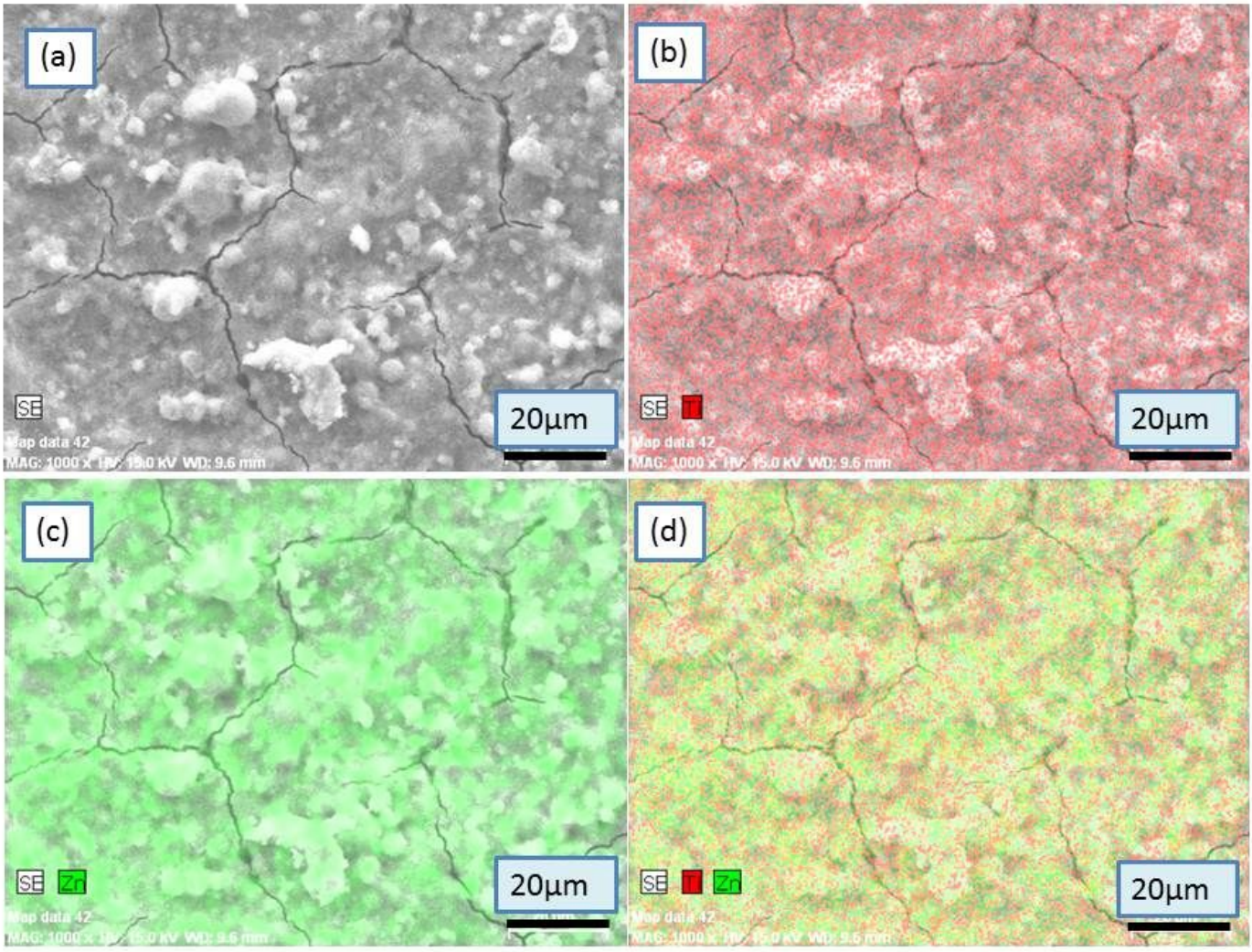

Figure 4

FE-SEM images of SMT film. Green and Red colours indicate the presence of Zn and Ti respectively. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

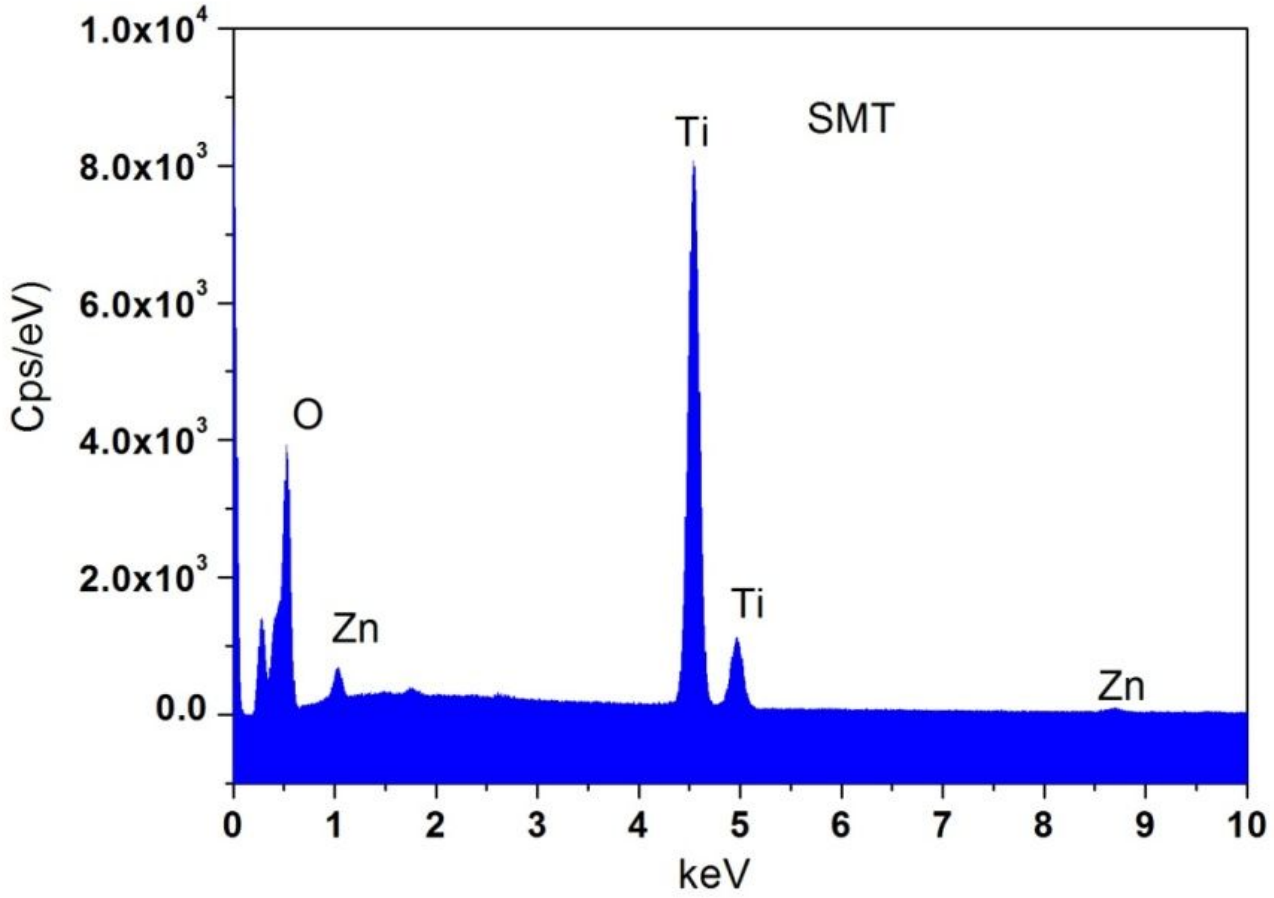

Figure 5

The EDS analysis of SMT film.

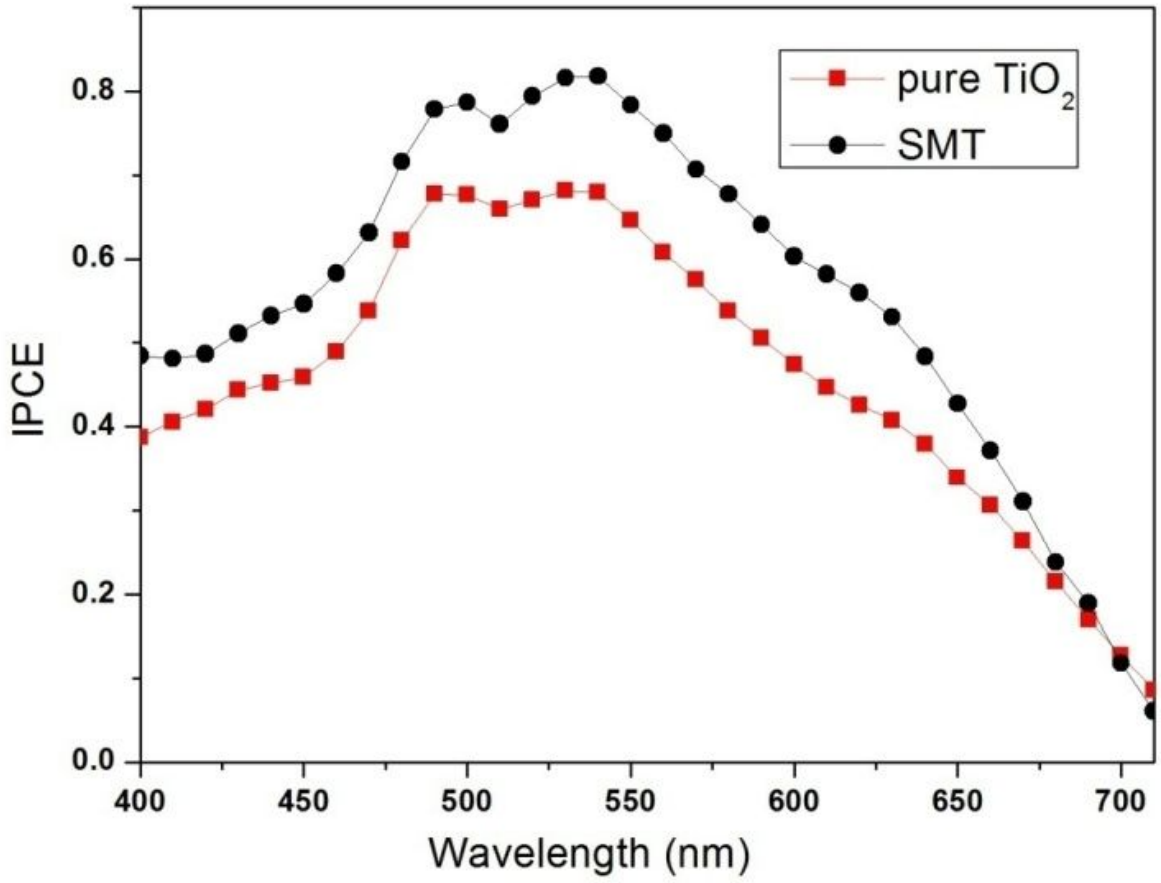

Figure 6

IPCE curves of pure TiO2 and SMT based DSSCs.

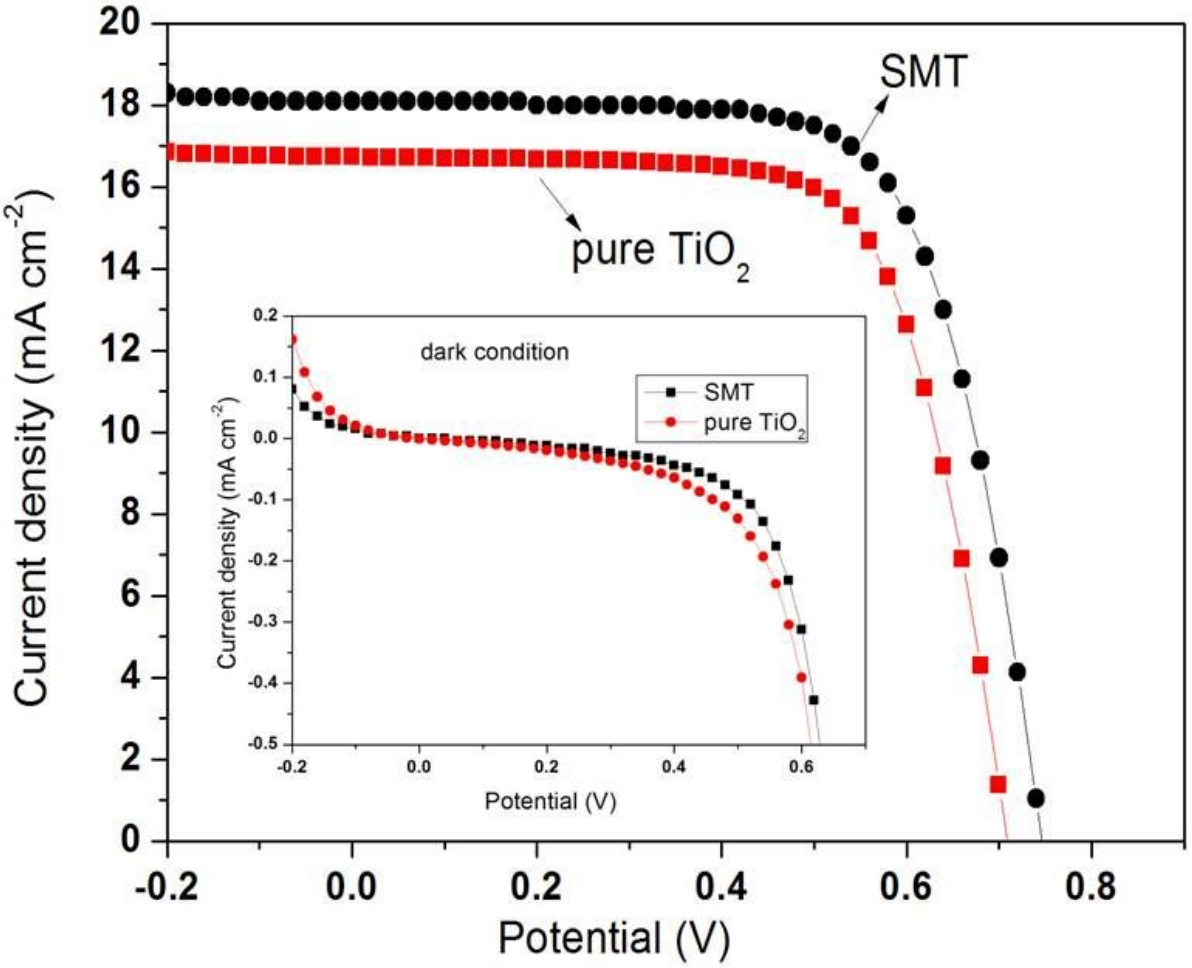

Figure 7

J-V characteristics of DSSCs based on pure TiO2 and SMT electrodes.