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Effect of Photoanodes on the Performance of Dye-Sensitized Solar Cells

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Abstract:
Dye sensitized Solar cell (DSSC) is a photo-electrochemical system which converts solar energy into electrical energy. In the present era DSSCs takes so much attention because of their considerably high efficiencies at a comparably low production cost. The nanostructured electrode plays a vital role in device properties. Originally, the nanostructured TiO_2 were widely used as DSSC electrodes. Further, nanostructured ZnO has shown a great deal of research interest as the electrode material in DSSCs due to some of its fascinating properties. Compared to other semiconductors, it has unique properties such as large exciton binding energy, wide band gap, high breakdown strength, cohesion and exciton stability. In this paper, the construction and electron transport mechanism of DSSCs devices are described and a comparison of performances of DSSCs fabricated with ZnO or TiO_2 photo electrodes was made in terms of its device parameters. This is further correlated with the band structure & density of states (DOS) of ZnO and TiO_2 using Density functional theory (DFT) and finally the photovoltaic performance of ZnO and TiO_2 based DSSCs was discussed to elucidate the differences.

Keywords: Dye-Sensitized Solar Cells, Titania Nanopowders, Zinc Oxide Nanorods, Photovoltaic Properties, Band Structure, Density of States, Density Functional Theory

1 Introduction

The end of fossil fuels is a matter of anxiety for our civilization because our daily life just can't be imagined without it. Again, according to web data total existing coals till now will give us energy to take us as far as 2088. So, scientists will give their attention to the renewable energy and the nuclear energy more and more for the last few decades to save our mankind [1]. And we all know that Solar energy is major renewable energy which has the potential to overcome all the difficulties [2]. According to web data sunlight received by Earth for only one hour is sufficient to fulfil the annual energy required for all the people worldwide [3]. But the problem is that we can't use properly the solar energy till now for the reason that many of the solar energy systems are very much expensive than our conventional systems. So, if we have become the solar energy devices very much familiar so that can be reached door to door worldwide and all mankind understand its benefits and then this will become the most remarkable achievement for the existence of our civilization.

Now the most leading technology in the commercial market of solar cells is Inorganic silicon wafer-based solar cells by cause of their high efficiency [4]. But due to their high manufacturing costs, scientists have encouraged to develop low cost and environmentally friendly solar cells [5]. In this connection, dye-sensitized solar cells (DSSCs) have been introduced as cheaper substitute than silicon solar cells [6].

This is the reason why people give so much attention to DSSCs as this is a transparent and flexible system which directly converts solar light energy to electrical energy at low fabrication cost [7]. Herewith DSSCs can be used as cost-effective power generating system in urban areas and there may be a chance of producing power generating windows using DSSCs [8]. In this paper, we will describe how a DSSCs operate and how its efficiency can be increased by using ZnO or TiO_2 type materials as photo anode and which is more relevant for this purpose [9].

One of the most important components of DSSC is photo-anode which determines the conversion efficiency as it supports the dye molecules and plays an important role in transferring electrons from dye molecules to the transparent back contact. For this purpose, we have tried to make a comparison between TiO_2 and ZnO photo-electrodes on the basis of band structure analysis and DOS, then by describing Current-voltage curves of DSSCs based on ZnO and TiO_2 and also by scanning electron microscope (SEM) images, X-ray Diffraction (XRD) pattern and finally by solar cell parameters. In this study we have used WIEN 2K software for analyzing band structure and Density of States (DOS) calculation. The software operates in python programming and using Density Functional Theory (ATK-DFT in software) for band structure analysis and DOS calculation.

Many scientists are trying to develop efficiency of DSSC [10] by using different types of dyes or different types of semiconductor electrodes or combination of two electrodes etc. They found many things till now which gradually increases many fields of this industry and many things yet to be discovered which may tremendously change our thinking about it and we reconstruct it more easily and more effectively. By analyzing Band structure and Density of states of TiO_2 and ZnO, we found that these two materials have shown very similar nature to DSSC as a wide band gap semiconductor electrode. ZnO has very interesting features which bring it to be used in DSSC instead of TiO_2. Observing DOS, we have already found that ZnO is more efficient as photoanode but it is also be noted that it has lower energy conversion efficiency than TiO_2 so as a result we can say that though TiO_2 is more relevant as DSSC electrode but ZnO has a power to improve DSSC efficiency. It is obtained from the experiment that efficiency of DSSC can be increased by a suitable amount with the use of TiO_2 and ZnO mixture (80:20) rather than using only pure TiO_2.

The density functional theory (DFT) and time-dependent DFT (TD-DFT) can provide a deeper understanding of the relationship between the molecular structure and properties of compounds. Thus, theoretical calculations are important to design new and efficient electrodes for DSSCs.

2 Experimental Details

2.1 *Materials and Methods for Assembling DSSC*

In DSSC, On the top there is a transparent anode which is an ITO (Indium tin Oxide) coated glass plate. TiO_2 was placed on ITO coated glass by doctor blading technique and placed it on hot plate for sintering at 450°C for 30 minutes. Now the plate is dipped in a solution for next 24 hours. After soaking this in the dye, a covalent bond is produced between the thin layer of dye to the surface of TiO_2/ ZnO film [11]. Now another plate is made with thin layer of redox electrolyte spread on a conductive plate (e.g. Platinum metal). At last the two plates are attached and sealed for prevent the electrolyte from leaking.

2.2 *Fabrication ZnO or TiO_2*

Nano crystalline particles of ZnO/TiO_2, approx. equal size (~15 nm) are used to prepare mesoporous electrodes for DSSCs which are interconnected and allow for electronic conduction to occur [12]. Usually this nanoparticles pasting is done by screen printing or scraper on a conducting glass plate coated with transparent conducting metal oxide layer. The porosity of this mesoporous film is varying from 20 to 80% for this type of sintering. The pores create an interconnected network which is filled by electrolyte or some kind of charge transfer material or amorphous type of transmitter. As a result of this an electronic junction of extremely large contact area is formed showing interesting and useful opto-electric properties.

2.3 *Operation*

Sunlight enters to DSSC through the transparent ITO layer and then the incident photon strikes to the dye molecules and is absorbed by complex dye photosensitizers adsorbed on theTiO_2/ZnO surface. As a result, photosensitizers are excited from the ground state (S) to the excited state (s*), Excited electrons are injected into the conduction band of the TiO_2/ZnO and oxidation of photosensitizer (S+) happens. Passing through the nanoparticles of TiO_2 finally electrons reach the counter electrode as shown in the diagram.

The oxidized photosensitizer(s+) collects electrons from the redox medium and reduced to the ground state (S) and the redox medium oxidized. Now the redox mediator diffuses to the counter electrode and reduced to previous ionic state.

Chemical Processes with Schematic energy level diagram

I. $S + h\nu \rightarrow S^*$ (photon absorption and excitation)
II. $S^* \rightarrow S^+ + e^-$ (TiO_2) (Oxidation of photosensitizer)
III. $S^+ + e^- \rightarrow S$ (Reduction of photosensitizer)
IV. $I3^- + 2e^- \rightarrow 3I^-$ (Reduction of redox mediator)

3 Computational Details

3.1 *Reason of using ZnO or TiO_2 type crystalline materials*

The choice of oxide materials depends on various properties such as material content, chemical composition, structure and surface morphology etc. From the analysis of material content and surface morphology it has been found that two crystalline forms of TiO_2 are important, Anatase and Rutile. Of which Anatase is the stable form in low temperature and gives transparent and colorless mesoporous films. Due to this in almost all type of DSSCs, Anatase form of TiO_2 is used. TiO_2 and ZnO fulfil all properties which is appropriate for DSSCs study and gives suitable output that is why they dominant over all other oxide materials.

3.2 Reason of using ZnO or TiO_2 type crystalline materials

The crystal structure of ZnO and TiO_2 were taken as given in the following table.

Table 1: Geometry of ZnO and TiO_2

ZnO	TiO_2
Hexagonal	Body Centered Tetragonal
a=3.2495 Å, c=5.2069 Å α=β=90°, γ=120°	a=3.7842 Å, c=9.5146 Å α=β=γ=90°

3.3 Band Structure and Density of states analysis

The above diagrams of band structure and density of states of titanium oxide (Anatase) and Zinc oxide (Zincite) analyzed using WIEN 2K. All Calculation was done by Density Functional Theory for energy calculations.

The Band gap was obtained as 3.26 eV for TiO_2 and 3.24 eV For ZnO Which is very close to the Observable Band gap of TiO_2 and ZnO (~3.2 eV). Below, let us discuss about the Process or calculator settings of ATK-DFT and the output calculated from the software.

3.4 ATK-DFT Brillouin Zone scan

The band program automatically scans over the high symmetry k-points which forms the Brillouin Zone boundary. The list of allowed k-points for this study are TiO_2 BCC Gamma, m, n, p, x (K-points) ZnO Hexagonal Gamma, a, h, k, l, m (k-points).

3.5 Density of States

In condensed matter physics we described the density of states (DOS) of a system is described as the number of states per unit interval of energy at each energy level available to be occupied. High DOS at a specific energy level indicates that there is a huge no of states available for occupation of electrons whereas in DOS graph a DOS of zero means that there are no states to occupy. For the case of atoms or molecules in a system (unlike isolated systems) we did not obtained a discrete density distribution but we get a continuous spectrum of density of states as mentioned in above pictures. So, it is very important to study the density of states of a material for knowing its features and characteristics and the type of the material.

Here for TiO_2 and ZnO, it is noticed that though the band gap of both are nearly equal but there is some discrepancy observed in their DOS calculation. Therefore, by analyzing DOS we can roughly give an idea about the efficiency of using both the material in DSSCs.

Finally, we can conclude that because Zincite has much more DOS value in the valence band region than TiO_2 as shown in the DOS-Energy plot which indicates that there are more state available for electrons in the valence band of ZnO film that means more possibility of transition to the conduction band and more efficient for using as a photoanode in DSSC and thus we obtained more photocurrent for ZnO than TiO_2 in IV characteristics.

3.6 Energy Conversion Efficiency of TiO_2 and ZnO

TiO_2 is the most commonly or extensively studied oxides used in DSSCs because of its fascinating optoelectrical properties. But Now Zinc Oxide (ZnO) has been introduced as an alternative of titanium Oxide (TiO_2) to the latest researches. Scientists found that use of ZnO as semiconductor electrode in DSSC's gives great potential and improve the cell performance.

3.7 The Band gap of ZnO and TiO_2

The Band gap of ZnO is similar to that for TiO_2 at 3.2Ev. Electron carrier mobility of ZnO is 115-155 cm^2/Vs^2 which is much higher than that of TiO_2 which has been noted to be ~10-5 cm^2/Vs^2 and also it can be doped with both n-type and p-type. Therefore, it is expected that Nanostructured ZnO can be used as a good electron acceptor and transparent material in the study of dye sensitized solar cells. It is also found that ZnO has been used for the application in blue/Ultraviolet (UV) opto-electric devices and in Piezoelectric devices.

This are the main Reasons for choosing ZnO. But there are some limitations of using ZnO Such that, though it shows flexibility in synthesis and morphologies more than TiO_2. But the chemical stability of ZnO is much less than that of TiO_2 therefore Dye adsorption nature is very much poor for ZnO.

ZnO shows chemical stability for normal dye concentration but after prolonged immersion in high dye concentration it's film quality and structure get affected though TiO_2 film electrodes remains invariant for both cases.

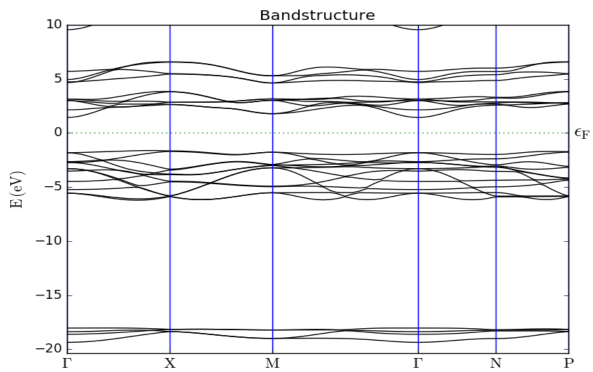

Figure 1(a): Band structure of TiO_2

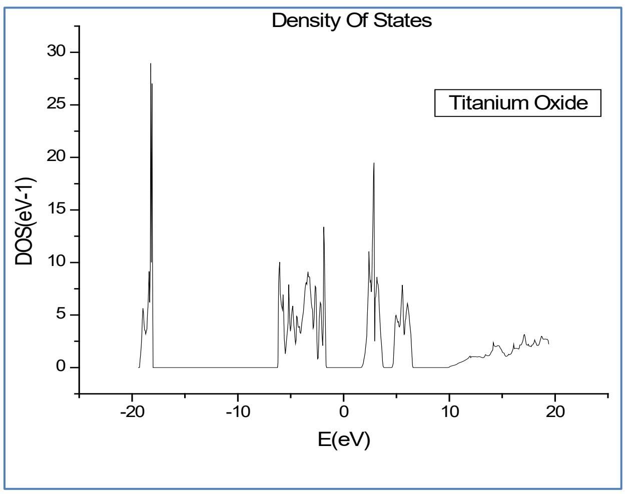

Figure 1(b): DOS of TiO_2 from DFT calculation

Also, it was found that electron transport times and dependence of light intensity to be similar for both ZnO and TiO_2 But Electron lifetime has been obtained significantly higher in ZnO than that in TiO_2. Although recombination rate for ZnO is much lower than that for TiO_2.Therefore it is very tough to compare between TiO_2 and ZnO, which one is best?? Because at some point ZnO dominates over TiO_2 whereas similarly for other some cases we obtained the opposite side i.e. TiO_2 is much efficient than ZnO. So, at last by analyzing all of the above we can finally conclude that TiO_2 is more relevant than ZnO for light energy conversion.

4 Result and Discussion

The sensitizing dye must have the following properties in order to achieve high conversion efficiency. The dye should absorb light at wavelengths up to the largest wavelength in the sun light spectrum. The exited state of

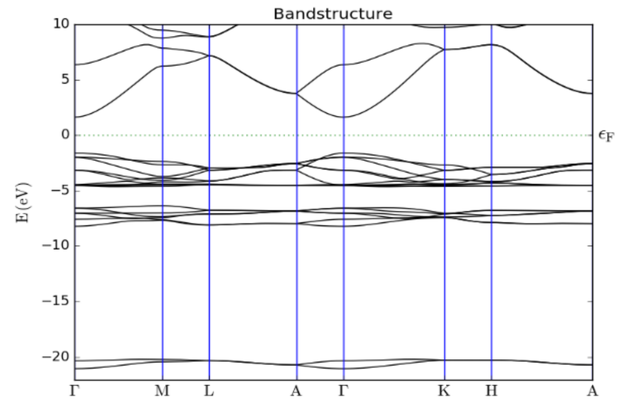

Figure 2(a): Band structure of ZnO

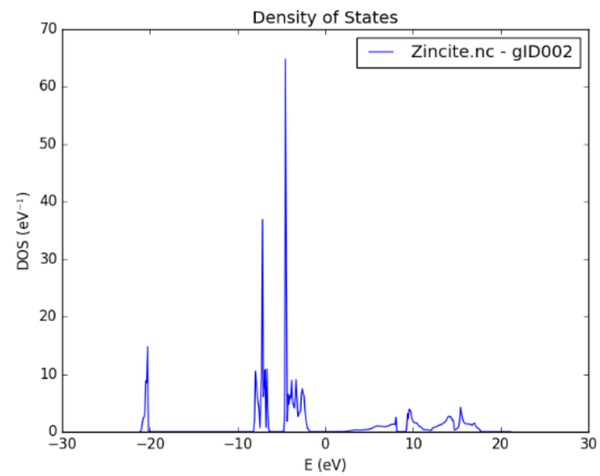

Figure 2(b): DOS of ZnO from DFT calculation

the adsorbed dye molecule should be higher enough than the conduction band edge of the ZnO to present an energetic driving force for the electron injection process. The adsorbed dye molecule should be stable enough in the working environment (at the semiconductor-electrolyte interface) to sustain long time of operation at exposure to natural daylight. Good adsorption to the semiconductor surface. High solubility to the solvent used in the dye impregnation.

4.1 Selection of the Dye:

The peaks of the absorption spectra of the dyes are in tune with HOMO-LUMO energy difference of the dye [13]. Since no single dye can perform efficiently in the entire visible spectrum, the present work is focused on the performance study of I-V curve of DSSCs with dyes having broadband absorption in the visible spectrum for efficient harvesting of light by DSSCs [14]. Based on our previous studies [15], Rose Bengal dye was identified for further investigation. The Rose Bengal dye absorbs a larger fraction of the solar spectrum in the visible region

460–650 nm. And this dye has been used further to sensitize different types of ZnO electrodes of the DSSCs.

For measurement of Photovoltaic Properties, I-V characteristics of DSSCs based on nanoporous ZnO fabricated from Nano Powders and ZnO nanorods fabricated through Sol-gel technique, using Rose Bengal dye was recorded [16]. Figure 3(b) shows the photocurrent resistance characteristics for ZnO-nanorod DSSC. In general, the energy conversion efficiency of ZnO DSSCs is lower than that of TiO_2 DSSCs. Note that the efficiency of ZnO-nanorod-based DSSCs with natural dyes is typically 1-2%.

4.2 Performance of the DSSC:

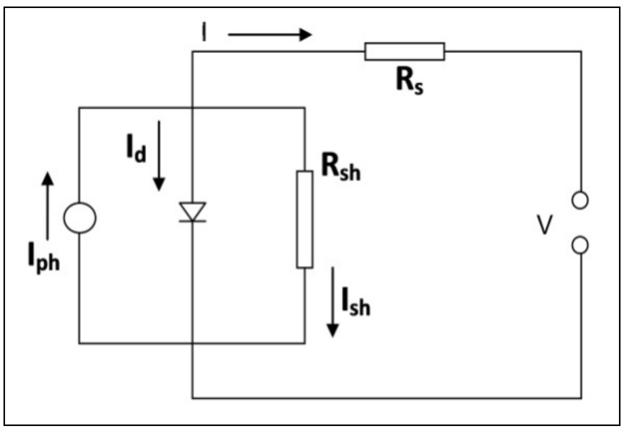

Figure 3(a): Equivalent circuit of a DSSC cell

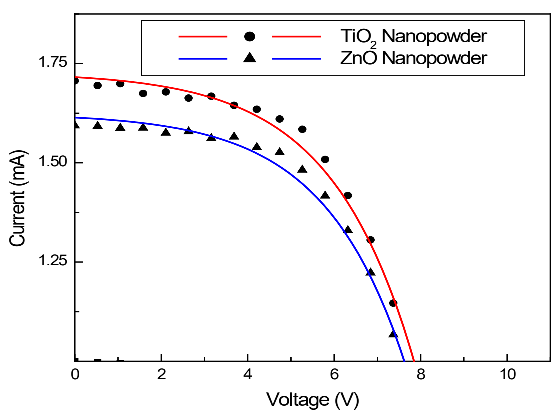

Figure 3(b): Current-voltage curves of DSSC's based on ZnO and TiO_2 Nanopowder

The I-V characteristics were recorded for DSSCs based on ZnO nanorods and ZnO nanopowders, with varying external resistances under illumination. The ZnO nanorods and ZnO nanopowders has more or less same open circuit voltage. This is expected as the open circuit voltage is determined mainly by the ZnO and the redox couple in the electrolyte, It can be seen from Figure 1 that the ZnO nanopowders has got almost same value of the direct band gap as that of the ZnO nanotubes and we are using the same electrolyte for the two systems.

4.3 Photovoltaic Properties:

The open-circuit voltage (V_{oc}), short circuit current (I_{sc}), maximum voltage (Vmax), maximum current (Imax), values of DSSC cells with ZnO nano-rods and nanopowders were calculated from Figure 3(b) and fitted with the Eqn. 4 for one diode equivalent circuit model (Figure 3(a) by Newton-Raphson's method). Results of Curve fitting are given in Table 2.

The parasitic resistances (series and shunt) of DSSCs are important parameters that affect its efficiency. The resulting parasitic resistances, series (Rs) and shunt resistance (Rsh) were evaluated from these results. ZnO Nanopowder Based DSSC has high series resistance, whereas using ZnO Nanorod based DSSC we get subsequent reduction in series resistance, which results in substantial difference in cell performance. Form the data of Table 1, it was confirmed that for all kinds of cells, higher the shunt resistance, the efficiency is lowered and efficiency raises with lower series resistances. The fill factor (FF) for all the cells using two different type of photoanodes are also evaluated from the I-V characteristics using equation (1) and finally the energy conversion efficiency (η) is calculated using equation (2). All these results are presented in Table 2.

Table 2: Solar cell parameters of the two DSSCs

Photoanode	ZnO	TiO_2
V_{oc} (V)	0.61	0.56
I_{sc} (mA)	2.1	1.18
I_s (μA)	13.26	9.88
R_s (Ω)	0.00308	0.00489
R_{sh} (Ω)	3461	5011
A	4.55	4.57
FF	0.49	0.56
η (%)	1.56	1.01

All cell parameters like Ideality Factor (A), Fill factor (FF) and Energy conversion efficiency (η) [17] of ZnO based DSSCs with two different type of photo-anodes were calculated and also presented in Table 1, where values are calculated from current voltage curves of DSSC cells fabricated with two photo-anodes.

The ZnO Nanorods shows highest efficiency and lowest fill factor, whereas Nano-powder shows lowest efficiency and highest fill factor. This improvement in efficiency for the Nanorods is due to the improvement in open circuit current achieved through higher density of electron states near the conduction band edge for Nanorods. The improvement of efficiency can also be due to lower thickness of the ZnO nanolayer achieved through the sol-gel fabrication causing lower diffusion length for the electrons.

It was noted that the Nanorods lower series and shunt resistances. Ideality factor (A) indicates perfectness of the diode in the equivalent circuit, and it is 1.0 for a perfect diode. In our observation, an improvement in ideality factor of 4.55 for ZnO Nanorods was observed, compared with 4.57 of ZnO Nano powders. Due to same reason, the fill factor of Nanorods is also lower.

5 Conclusion

DSSCs structures were fabricated over an ITO coated glass substrate with two different photoanodes, ZnO and TiO2. The efficiencies of cells using these two photoanodes were discussed. The efficiency of DSSCs using ZnO photoanode was found to be greater than that of the TiO_2 photoanodes. The DSSC structure with ZnO nanorods yields a higher open circuit voltage than DSSCs with TiO_2 nanopowders deposited on ITO glass. Studies of parasitic resistances parameters (Rs and Rsh) of DSSCs from I-V curve using the equivalent circuit one-diode model are also compared. In general, a ZnO nanopowder based DSSC has got superior qualities than the DSSC's based on DSSC with TiO_2 nanopowders grown by the sol-gel method.

The band structure and density of states of TiO_2 and ZnO photoanodes and simulated using DFT/ATK-DFT. The variation in the values of cell parameters in two types of DSSC's were discussed in the light of the band structure and density of states of the two types of photo anodes.

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