



## A REVIEW ON TITANIUM DIOXIDE FOR DYE SENSITIZED SOLAR CELLS APPLICATION

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### ABSTRACT

The past two decades Titanium Dioxide (TiO<sub>2</sub>) based Dye sensitized solar cells (DSSC) has received more and more attentions from academia and industry because it is widely studied material for the safe and reliable energy supply due to its low fabrication cost, eco-friendly production and competitive efficiency. The present review deals with recent advances made through the semiconductor nanoparticles sensitization on well aligned DSSC, which is combining to form a photo conversion device, are the conducting substrate, dye, photo anode, catalyst and electrolyte. Among this various component photo anode is probably the main component which determines the energy conversion efficiency and TiO<sub>2</sub> is widely recognized component for photo anode from the researchers. This review also deals with the efficient fabricate methods for TiO<sub>2</sub> preparation and characterization to improve the efficiency of TiO<sub>2</sub> photo anode for DSSC. Here reviewed photoelectric conversion efficiency of DSSC has exceeded 11% for cell using TiO<sub>2</sub> but still it is two times lower than silicon cell technology. To overcome this limitation, the vast research studies developed highly efficient DSSCs by the material break through and have a current record of 15% efficiency.

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### INTRODUCTION

Thin film technologies are one of the important technologies to fabricate solar cell because it is required minimum active materials. The two panes of glass substrate use to make sandwiched thin film solar cells and it is more flexible and low cost to compare silicon fabricated solar cell due to their low efficiency and large area consumption [1-2]. The liquid electrolyte were fabricated by using titanium dioxide it is provide electron to transport charge in Dye-sensitized solar cell and inorganic semiconductors are most efficient solar cells [3-7] However, the liquid electrolyte present in such cells creates both short-term and long-term sealing problems and this has activated the search for alternative hole transporting systems such as gelled molten salt electrolytes, polymer electrolytes etc, but still using the inorganic I<sup>3</sup> <sup>-</sup>/I<sup>-</sup> as hole transport medium [8-10].

Major advances were made in this direction. The use of conjugated p-type polymers instead of the electrolyte as charge transport medium was also reported in the literature. We have shown that the efficient class of hole transport compounds with a triarylamine structural unit which is well-known for its high hole transport mobility could be used instead of the liquid electrolyte to obtain a solid state dye-sensitized cell [11-12]. This type of solid state cell was later further optimized in the

Grätzel group by using a low molecular weight spiro-compound as hole conductor and using additional additives such as lithium salt and dopants to increase the conductivity of such a cell to obtain higher power conversion efficiencies [13-15]. One of the major differences between the electrolyte cell and p-type semiconductor cell lies in the nature of charge transport: ionic transport controlled by diffusion prevails in the former whereas electronic transport influenced by conductivity and charge transport mobility plays the deciding role in the latter. Dye-sensitized Solar Cell (DSSC) that the principle works is a blend of the optical, electrical and chemical. This type of solar cell is believed to be able to provide alternative energy concept with a more affordable cost of production and the fabrication technology that is simpler than its predecessors solar cells are made from crystalline silicon. Although until now the energy conversion efficiency of DSSC was produced by a lower than silicon solar cells, but the type of DSSC solar cells is still the potential to produce a much higher efficiency in the future, given the current efficiency is still far from the efficiency that can be achievable in theory [16-18]

#### Structure and Principle of TiO<sub>2</sub> and DSSC

The fundamental properties of TiO<sub>2</sub> crystal phases remains very important properly due to their important role to effectively utilize solar energy. For instance, photocatalytic splitting of water into H<sub>2</sub> and O<sub>2</sub>, 3 photovoltaic generation of electricity, 4 degradation of environmentally hazard materials, 5,6 and reduction of CO<sub>2</sub> into hydrocarbon fuels. 7 The gap between valence and conduction bands and the optical

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absorption property are vital to all these applications. the transformation of rutile and anatase directly to columbite-structured TiO<sub>2</sub> has been observed. The physical structure of a standard DSSC consists of two sandwiched glass layered with transparent conducting oxide (TCO). One electrode features a porous titanium dioxide nano particles (Nano TiO<sub>2</sub>) layer stained with dye molecules-named as photo-electrode, while the other is the counter-electrode in which carbonano tube (CNT) (or other catalysts) is deposited upon it. Electrolyte layer of redox species (I<sup>-</sup> and I<sub>3</sub><sup>-</sup>) exists between the two electrodes after they are being sandwiched together. The general structure of a DSSC is illustrated in Fig.1 and 2.

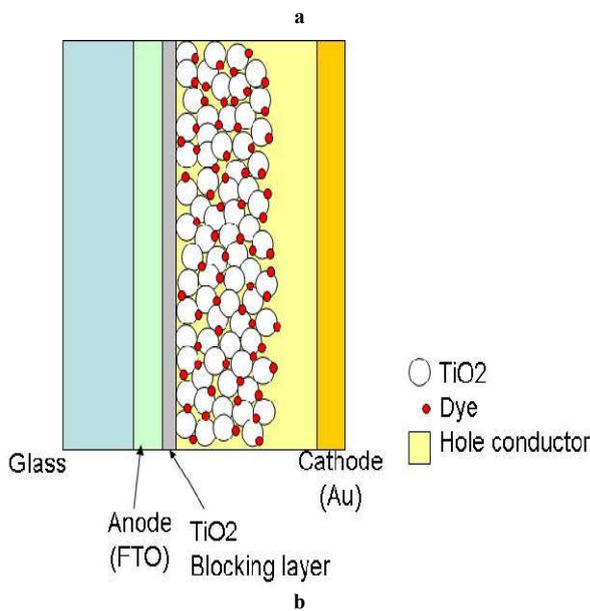
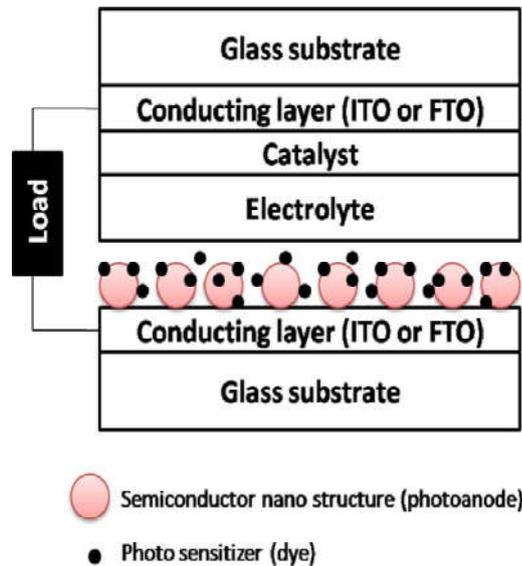


Figure 1 (a) Schematic Diagram of Dye Sensitized Solar Cell (b) Electron Transfer to Cathode

Structure of the CNT based DSSC. The working principle of a DSSC is based on the kinetics of the electron transfer reactions. The photoelectrochemistry mechanisms which occur during electron transfer within the DSSC are as follows: a dye molecule is excited upon photon (hν) absorption whereas electron is excited from highest occupied molecular orbital (HOMO – D) into lowest unoccupied molecular orbital (LUMO – D\*) as shown by equation (1). The electron transfer phenomenon is shown in figure 1 b. b The free electron is subsequently injected into the conduction band of Nano TiO<sub>2</sub>

and transparent conducting oxide (TCO) towards the external circuit and left the oxidized dye molecule D<sup>+</sup> ((Eq. (2)). Electron reach the catalyst layer (Pt or C) and then recombine with holes within the electrolyte, in form of tri iodide (I<sub>3</sub><sup>-</sup>), to produce iodide ion (I<sup>-</sup>) through redox reactions.[19-21] This reaction was shown by Eq. (3). The negative charge of I<sup>-</sup> diffuses back into the dye and reacts with the oxidized molecule D<sup>+</sup> and a full electrical cycle is therefore completed

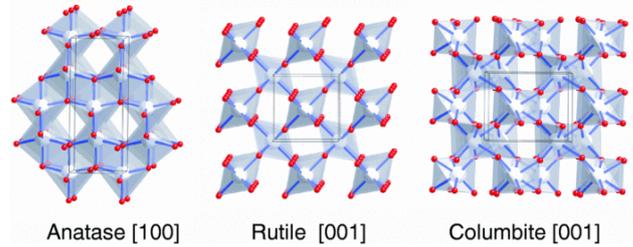


Figure 2 Crystal Structure of TiO<sub>2</sub>

Table 1 TiO<sub>2</sub> Experimental Data

TiO <sub>2</sub> Structure	Space group	Structure parameters	Wyckoff positions
Rutile	P42/mnm	a=b=4.641, 4.587a, 4.593b, 4.594c c=2.968, 2.954a, 2.959b, 2.958c	Ti 2a (0, 0, 0) O 4f (0.305, 0.305,
Anatase	I41/amd	a=b=3.797, 3.782a, 3.785b, d c=9.720, 9.502a, 9.512b, 9.514d	Ti 4a (0, 0, 0) O 8e (0, 0, 0.206)
Columbite	Pbca	a=9.263, 9.184e b=5.510, 5.447e c=5.167, 5.145e	Ti 8c (0.129, 0.089, 0.862) O1 8c (0.010, 0.148, 0.182)

The electrons of the DSSC emit and transfer arrange in the sequence as follows:

- The dye (D) is excited (D\*) by the absorption of photon energy (hν).  
 $D + h\nu \rightarrow D^*$
- The electrons of excited dye jump to the conducting band (CB) of the Nano TiO<sub>2</sub> at the same time.  
 $D^* \rightarrow D + e^- \text{ (CB)}$
- The dye with emitted electrons (D<sup>+</sup>) could react with the iodide ion (I<sup>-</sup>) or receive the electrons from the conducting band of the Nano TiO<sub>2</sub> and returns to the dye (D) again.  
 $3I^- + 2D^+ \rightarrow I_3^- + 2D$   
 $D^+ + e^- \rightarrow D$
- The iodide ion (I<sup>-</sup>) further receives the electrons from the counter electrode and returns to the iodide ion (I<sup>-</sup>) again. the reaction is shown in figure 1(b).  
 $I^- + 2e^- \rightarrow 3 I^-$

**Performance Affecting factor of DSSC**

**Light scattering capability**

TiO<sub>2</sub> nanoparticles due to very small size demonstrate high transparency in solar spectrum and most of the incident photons are transmitted from the device without any work done. It is therefore necessary to improve the light absorption and scattering capability of photoanode so that the sensitizer within the semiconductor architecture could pickup energy efficiently. New photoanode architecture introducing another layer of relatively large particles over the nanoparticle layer of TiO<sub>2</sub> has been suggested. This over-layer increased the light scattering and consequently improved absorption/scattering ability of photoanode. In early days, many studies have been

focused on light scattering effect based on Mie theory, the Monte Carlo Model and many flux theory. Since then, the light scattering concept has been widely used to improve the performance of DSSC and many architectural and compositional strategies have been evaluated which will be discussed in detail in rest of the sections. Improving the light scattering ability by employing multifunctional scattering layers such as use of thermoelectric materials should be preferred rather than using single function scattering layer [22-25]

### **Recombination of Charge**

The key energy conversion process in DSSC is a photo induced charge separation at the metal oxide/dye/electrolyte interface. It is essential that the electron move through semiconductor network to the transparent conducting oxide layer before dye relaxation and the electron pickup by the electrolyte failing to do this will help recombination reactions to take place resulting in lower photo conversion efficiency of the device. Typically incident photons excite the electrons in dye molecule (which is trapped inside the semiconductor network) and this electron is picked up by the semiconductor. This system is called donor-bridge-acceptor unit having a chromophore (electron donor) anchored on the semiconductor nanoparticle (electron acceptor) surface with the help of any molecular spacer and functional group Charge recombination reaction between dye and photo injected electrons occurs over micro – mili seconds time scale. The wide range of time scales is usually defined as the trapping of electrons by localized states of TiO<sub>2</sub> surfaces. Standard electron kinetics as shown in Table 1 seems favourable to electron injection but nanoparticle comes with various defects (i.e. TiO<sub>2</sub>/electrolyte interface defects, grain boundaries and/or bulk defects) and surface states (the energy states generated below the conduction band) which impede the electron transportation and promote recombination reactions [26-28]

### **Contact Interfacial**

The interface of conducting substrate layer and semiconductor layer is vital in transporting electrons in the external circuit. Two competitive reactions i.e. electron transfer from semiconductor to conducting substrate layer and electrolyte regeneration reaction on this layer can occur To impede the back reaction of electrons it is important to make a good contact between conducting substrate layer and semiconductor layer and reduce substrate exposure to electrolyte. One approach is to form a thin compact layer on the conducting substrate before deposition of semiconductor oxide layer. This layer not only improves electron collection but also decrease recombination reactions. Treatment of conducting substrate with titanium chloride (TiCl<sub>4</sub>) is a successful technique which decreases recombination reaction by reducing direct contact of electrolyte with conducting substrate [29-30]. Tin oxide (SnO<sub>2</sub>) thin films have also been investigated between the conducting substrate and TiO<sub>2</sub> layer and almost 15% improvement in electron transfer to external circuit has been reported compared to bare interface without changing the transmittance Another important interface is the semiconductor layer/dye/electrolyte interface. Good surface treatment of semiconductor layer improves the dye uploading and reduces electron recombination reactions. One strategy is the surface coating of semiconductor layer with insulating thin films. The TiCl<sub>4</sub> post treatment of the semiconductor TiO<sub>2</sub> proved

successful in reducing electron recombination, an increase of photocurrent by 10–30% has been reported depending on the quality of the deposited layer [31].

### **Dye pickup**

Dye pickup by the semiconductor layer is one of the most important efficiency improvement parameter which defines the amount of electron production. The more the dye molecules pickup more will be the excited electrons and subsequently more will be the electron/current density. Many semiconductor structures such as nanorods, nano forest, nanotubes, aerogels, three dimensional nanostructures, mesoporous powder and beads and other nano-architectures have been employed and examined for efficient dye uploading (shapes will be discussed in morphology section). Surface functionalization (using co-adsorbents [32] of semiconductor oxide architecture with carboxylic groups and/or other functional groups have been investigated to facilitate proper wetting of semiconductor layer with dye to improve the performance of the device. It is important to understand the role of oxygen vacancies towards the loading capacity of photoanode. And cost effective methods should be investigated to effectively improve the dye pick up property of photoanode.

### **Dye/electrolyte sealing**

Another engineering problem to manufacture reliable solar device is the leakage of liquid dye and electrolyte. This leakage decreases the lifetime of DSSC making it undependable for commercialization. One solution to this problem is the use of semi-solids /quasi-solids polymeric electrolytes. Quasi-solid electrolytes containing polysulfide and hybrid organic-inorganic material in ZnO/CdS/CdSe DSSCs have been employed. These electrolytes not only solved the sealing problems but also improved the conversion efficiency from 1.2% to 4.5%. The recent development is the room temperature ionic liquid electrolyte (RTILs). It's a group of organic salts containing cation and anion from pseudo-helid family. It is likely that RTILs could minimize the problem of sealing and enhance the stability by virtue of their inherent properties i.e. good chemical and high temperature stability, minimal vapor pressure, minimal response to flame and high ionic conductivity [33-35]

### **Fabrication methods**

Choosing an optimum fabrication method for DSSC depends on various factors such as production volume, size, shape complexity, capital investment, production flexibility, energy demand, human factor etc. there exists triangular closed loop relationship among materials, properties and fabrication as described elsewhere. The properties of any product strongly depend upon the manufacturing method selected. A comparative study of spin coating and doctor blade technique have been made and concluded that doctor blade technique is superior than spin coating technique due to its low capital investment, easy operation, less material wastage and its fast production rate. Despite its advantages over spin coating it also has some limitations which include low particle concentration and low evaporation rate. Design and selection of fabrication method is always a trade-off between properties and cost, so it very important to have good knowledge of multiple classes of processes [36].

## CONCLUSION

The status of solar energy as a major source of our energy demand is expected to change as the demand for clean energy increases. During the last two decades significant advances have been made in developing nanostructure architectures and other new composite materials. Many of the newly synthesized nanomaterials hold the promise of being able to meet the global challenge of supplying clean energy. DSSC technology in this regard has been extensively studied due to its promising potential for high efficiency, low production cost and eco-friendly nature. The basic limitations of DSSC technology is the interfacial contact & reactions, light scattering and absorption ability and the choice of optimum manufacturing route. In this review, an attempt has been made to introduce evolution of TiO<sub>2</sub> photoanode for dye sensitized solar cells such as doping with other elemental ions, development of nanocomposites and synthesis of new nano-architectures to enhance the performance of DSSCs. An attempt to introduce fabrication methods has also been made to provide knowledge about the current fabrication methods. Commercial viability of DSSC technology is possible by choice of optimum manufacturing route and choice of raw materials. New and cost effective photoanode materials other than TiO<sub>2</sub> needs to be explored which possess high electron mobility, high oxygen vacancies to improve the dye pick up, good light absorption ability as TiO<sub>2</sub> can absorb only UV portion of sun-light and possess excellent corrosion resistance As the photoanode materials being used to date such as TiO<sub>2</sub> and others require high temperature annealing to improve efficiency of DSSCs which is not suitable for flexible printed photoanodes as TiO<sub>2</sub> cannot be annealed at 540–500 °C with plastic sheet substrate. New ways such as thermal spray technique has to be trialled to deposit TiO<sub>2</sub> maybe with water flow on the backside of substrate to avoid melting

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