

Performance of the Dye-sensitized Solid-state Photovoltaic Solar Cell Depending on the Cluster Size of TiO₂ Electrode

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Abstract

A fully dye-sensitized solid-state photovoltaic nanoporous n-TiO₂/dye/p-CuI was constructed by depositing p-CuI onto a nano-porous film of n-TiO₂ coated with dye. Tannin and cyanidin were used as the dyes coated on the TiO₂ electrode. The photovoltage and the photocurrent of the cell mainly depended on the cluster size of the TiO₂ film. And, the TiO₂ electrode with two layers of different particle sizes also affected on the photovoltage and photocurrent of this cell.

Keywords: Dye-sensitizations; Photovoltaics; Nano-porous films; Cyanidin; Tannin

Introduction

The biggest problem faced by the whole world is the shortage of energy because conventional sources of energy are being rapidly depleted while the energy demand increase gradually with the increase in the human population. Photovoltaic conversion of solar energy appears to be one of the solution for this energy demands of the future. In terms of human history, the life of the sun is effectively infinite and its energy is being radiated to the earth whether it is directly used or not. And also the use of photovoltage for direct conversion of solar energy introduces no contaminants to the environment.

The development of photovoltaic cells can be traced back at least by 16 decades to the discovery by Becquerel (1839) that a photovoltage resulted from the action of light on an electrode in an electrolytic solution [1]. In the modern era (1954), silicon single crystal cell [2] is the most popular solar cell and with improved technology, its efficiency under terrestrial sunlight had reached 14% by 1958. Although the efficiency of the silicon solar cell is quite high as compared with other solar cells that had been invented in that period, the large scale use of this devices for electricity generation is prohibitively expensive mainly due to its production cost. It appears that thin-film technology is essential for the development of low-cost solar cells. In the thin-film approach, reduction of cost can be achieved by using small amounts of material and inexpensive processing techniques. Dye-sensitized solid state photovoltaic solar cell is one type of such thin-film solar cell.

In this n-type/dye/p-type semiconductor device, the photo excited dye molecules sandwiched between the two semiconductors inject electrons into the n-type material and holes into the p-type material (Fig. 1), that is

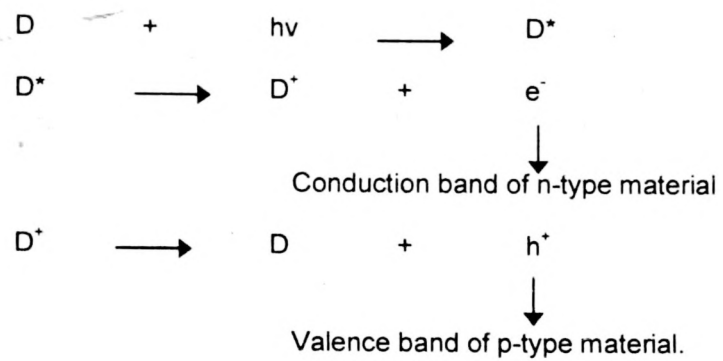


Fig 2 depicts the relevant band position of such n-type/dye/p-type dye-sensitized solid-state photovoltaic solar cell.

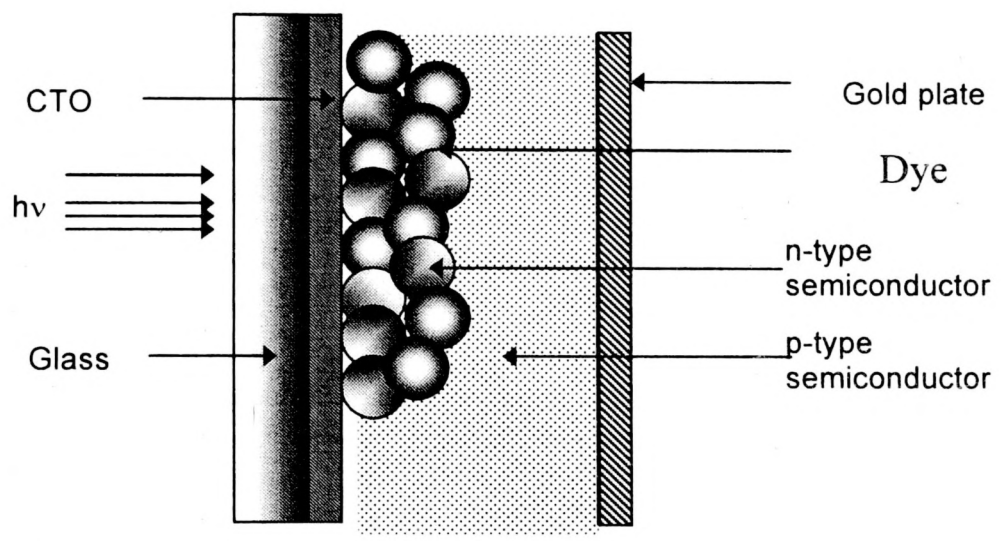


Fig 1. The construction of the nano-porous n-type / dye / p-type photovoltaic solar cell.

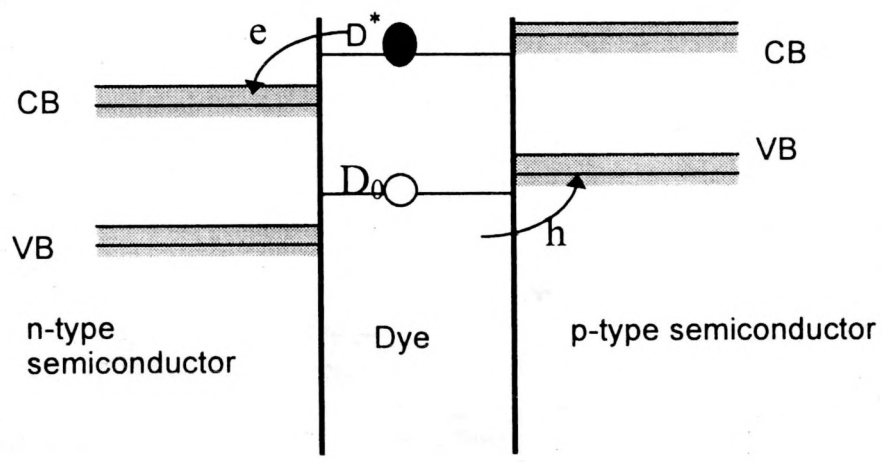


Fig 2. A schematic energy level diagram illustrating the relative band positions of semiconductors and the energy levels of the dye in dye-sensitized solid-state photovoltaic solar cell.

in this cell. nano-porous film of TiO_2 has been used, because such a film can have an effective surface area that can be enhanced 1000-fold compared to the projected geometric area [3-5]. The cluster size of the TiO_2 film can affect the effective surface area. Therefore, the photovoltage and the photocurrent of the cell seem to be mainly depending on the cluster size of the TiO_2 film. This work describes the performance of this dye-sensitized solid-state photovoltaic cell based on the above parameter.

Experimental

Glacial acetic acid (by 1ml from 2ml to 8ml) was added to the mixture of Titanium isopropoxide (5 ml) and isoproponol (20 ml, 99.9%) and then 5ml of water was added drop wise while stirring the mixture. Hydrolysis of titanium isopropoxide produced fine crystallites of Titanium dioxide (TiO_2) and the above procedure prevented their agglomeration.

Nano-porous layers of TiO_2 were coated on fluorine doped conducting tin oxide glass plates (1.5 x 2 cm sheet resistance $\sim 10 \Omega/\square$) by the following method. The CTO glass plate was placed on the surface of a hot plate (surface temperature $\sim 150^\circ\text{C}$) and colloidal TiO_2 prepared earlier was spread evenly on the surface and allowed to dry. The plate was then sintered at 450°C for 4 minutes and the loose crust on the sintered surface was removed. The above coating process (i.e. drying and sintering) was repeated for a number of times until the thickness of the film TiO_2 deposited on CTO glass was approximately 3 μm .

The TiO_2 coated CTO glass plates were cleaned by boiling in acetone and subsequently the plates were dried in a stream of hot air. The dried plates were boiled in the dye solutions for a few minutes and the plates were allowed to cool in the dye solution for one hour. The dyed plates were then rinsed with ethanol and dried in a nitrogen atmosphere.

Cuprous iodide (CuI) polycrystalline powder was prepared by mixing aqueous solution of potassium iodide (KI) and copper sulphate (CuSO_4) (copper sulphate in slight excess) in the presence of sulphurous acid [6]. Sulphurous acid removes iodine liberated in the reaction and excess copper sulphate prevents dissolution of CuI in water in the presence of I^- ions. The precipitate of CuI was washed with hot water, followed by acetone and dried in vacuum at $\sim 80^\circ\text{C}$ for one hour to remove any remaining iodine.

A solution of CuI was prepared by dissolving 0.6 g of CuI powder and 0.001g of CuBr_2 in 50 ml of moisture free acetonitrile (Aldrich 98%). CuI was deposited on the dye coated porous TiO_2 film by the procedure described below. The dye coated TiO_2 plate was dipped into the CuI solution and then dried in a current of hot air. This process was repeated until all the pores of the TiO_2 film were filled with CuI . For efficient functioning of the cell, it is essential that the CuI layer extends above the TiO_2 film. This was successfully achieved by spraying the CuI solution onto the surface of the plate, heated to 150°C . Spraying was repeated until the surface resistance of CuI is reduced to $50\text{-}60 \Omega/\square$. At this point the estimated thickness of CuI layer above the nano-porous TiO_2 film is $\sim 6.0 \mu\text{m}$. Incorporation of CuBr_2 gave better quality films, the reason is not fully understood.

The electrical contact on the CuI surface was made by pressing a gold or graphite coated CTO glass onto the CuI surface and then the cell was sealed using epoxy resin.

Results and discussion

In this experiment, TiO₂ and CuI were used as n-type and p-type semiconductors, respectively. Experimental observation showed that the photovoltage and the photocurrent of the cell mainly depend on the cluster size of the TiO₂ film and its optimum value of above parameters is not strongly dependent on the type of the dye used. Therefore, tannin [7] and cyanidin [8] were used as the dyes coated on the TiO₂ electrode.

Dependence of the photo voltage and photo current on the particle size of the TiO₂ colloids

The particle size of TiO₂ in the colloidal solution can be changed by varying the pH value of the mixture. The pH value of the colloidal solution can be changed directly by varying the amount of acetic acid added in the preparation process of the TiO₂ colloidal solution. Figure 3 shows the particle size distribution of the TiO₂ colloids prepared with different amounts of acetic acid measured by particle size analyzer. The average particle size in between 1.0μm and 0.05μm of these distributions were taken and tabulated in table 1. It can be seen that the average particle size decrease with the addition of higher amounts of acetic acid.

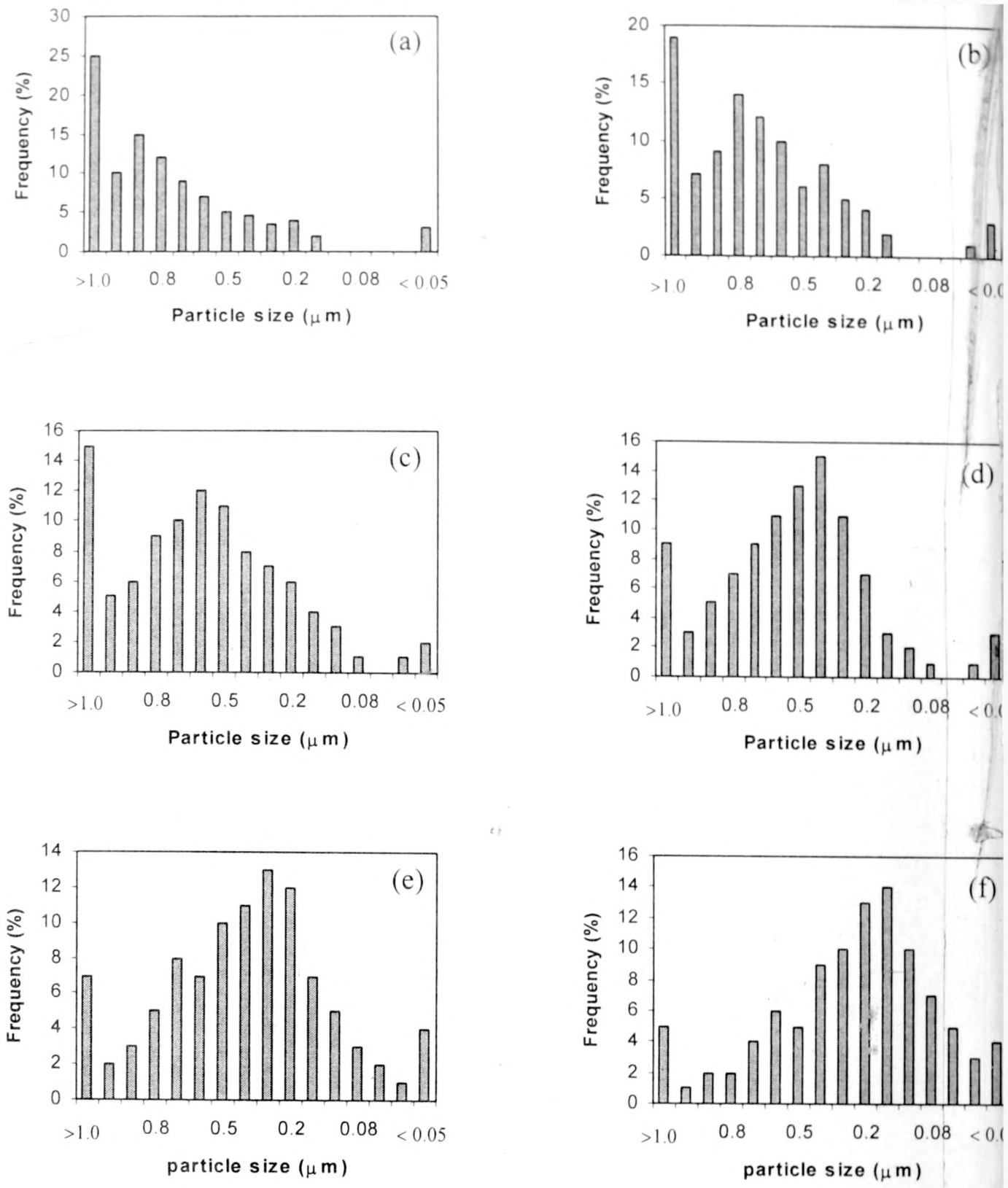


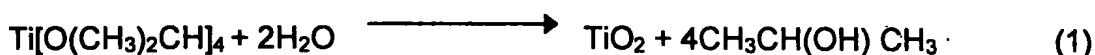
Figure 3. Particle size distribution of TiO_2 colloids prepared with acetic acid
 (a) 3ml (b) 4ml (c) 5ml (d) 6ml (e) 7ml and (f) 8ml .

Amount of acetic acid added (ml)	pH value of the solution	Highest frequency of the size of TiO ₂ particles (μm)	
3ml		5.81	0.9
4ml		3.09	0.8
5ml		2.08	0.6
6ml		1.16	0.4
7ml		0.75	0.3
8ml		0.43	0.1

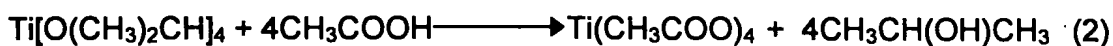
Table 1: Highest frequency of TiO₂ particles in between 1.0μm and 0.05μm prepared with different amounts of acetic acid.

This mechanism can be well understood by observing following reactions.

Titaniumisopropoxide undergoes the following reaction with water,



It reacts with acetic acid and hydrolyzes as follows,



The slow rate of hydrolyzation produces quantum size particles in the colloidal mixture. With the increase of the rate of hydrolyzation, particles become larger.

Amount of acetic Acid used (ml)	pH value of TiO ₂ colloidal Solution	Dyes			
		Tannin		cyanidin	
		I _{sc} (mA/cm ²)	V _{oc} (mV)	I _{sc} (mA/cm ²)	V _{oc} (mV)
4.0	3.09	1.7	400	2.2	400
5.0	2.08	1.7	450	2.2	450
5.5	1.57	1.7	480	2.2	480
6.0	1.16	1.6	480	2.0	480
7.0	0.75	1.5	480	2.0	480
8.0	0.43	1.3	480	1.8	480

Table 2: Variation of the short-circuit photocurrent (I_{sc}) and the open-circuit photo voltage (V_{oc}) of the solid state photovoltaic cell with the pH value of the TiO₂ colloidal solution.

The table 2 shows the variation of the open-circuit photovoltage (V_{oc}) and the short-circuit photocurrent (I_{sc}) of the cell with the pH value of the TiO_2 colloidal solution, which is used to deposit TiO_2 films on the conducting tin oxide glass plates. From the observation of the results shown in table 1, it become clear that the optimum value for both photovoltage and photocurrent is obtained when $pH \sim 1.57$, which results with the addition of 5.5 ml of acetic acid to the colloidal mixture. The increase of pH value (ie decrease in H^+ concentration) has lead to low photovoltage. The particle size of TiO_2 is influenced by the H^+ concentration in the TiO_2 colloidal solution. Low concentration of H^+ leads to large TiO_2 particles. Therefore CuI (p-type semiconductor) is in direct contact with the CTO glass plate, making a short circuit path, thereby resulting in a low photovoltage.

The decrease in pH value (ie increase in H^+ concentration) has lead to a low photo current. High concentration of H^+ produces small TiO_2 particles. Therefore, these particles are packed very closely to each other in the TiO_2 film. The resistance of such a film is very high (in $M\Omega$ range). Therefore, the rate of charge transfer inside the TiO_2 film is very slow which results in a low photocurrent.

TiO_2 electrode prepared with two different particle sizes

In this study it was observed that two layers of TiO_2 having different particle sizes could be used to enhance the photovoltage and the photocurrent of a dye-sensitized solid-state cell. The first layer of the electrode was coated with a colloidal solution having particles of small sizes (colloidal solution with $pH \sim 0.75$) and the second layer with a colloidal solution having particles of relatively larger size ($pH \sim 1.57$). In the preparation of the second type of TiO_2 electrode, we had to interchange the order of these two particle sizes. That is, in the latter electrode larger colloidal particles were in contact with the material while smaller particles were on top. The observed open-circuit photovoltage (V_{oc}), short-circuit photocurrent (I_{sc}), fill factor (FF) and efficiency (η) for the two methods with cyanidin as the dye are listed in table 3. Fig 4 shows the I-V curves of these two solar cells.

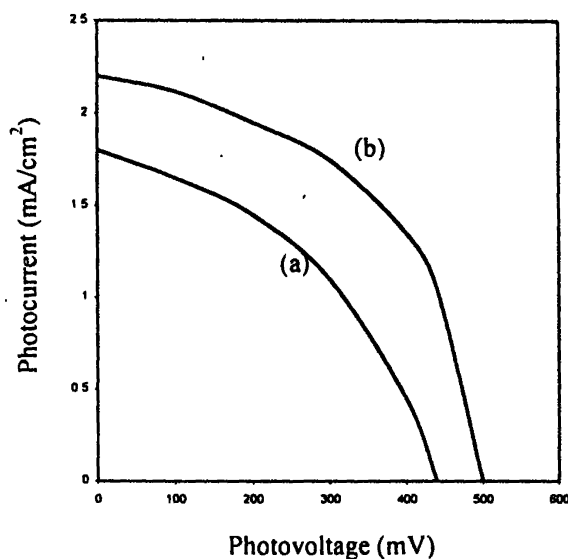


Fig 4. I-V curves of n- TiO_2 / Cyanidine / p-CuI with TiO_2 electrode having (a) large particles on top (b) small particles on top.

PH value of first layer of the TiO ₂ solution	PH value of second layer of the TiO ₂ solution	V _{oc} (mV)	I _{sc} (mA/cm ²)	FF	η%
0.75	1.57	440	1.8	0.42	0.33
1.57	0.75	500	2.2	0.49	0.54

Table 3: Open-circuit photovoltages (V_{oc}) and short-circuit photocurrents (I_{sc}) of the cell n-TiO₂ / cyanidin/ p-CuI, with the TiO₂ electrode coated with two layers of different particle sizes.

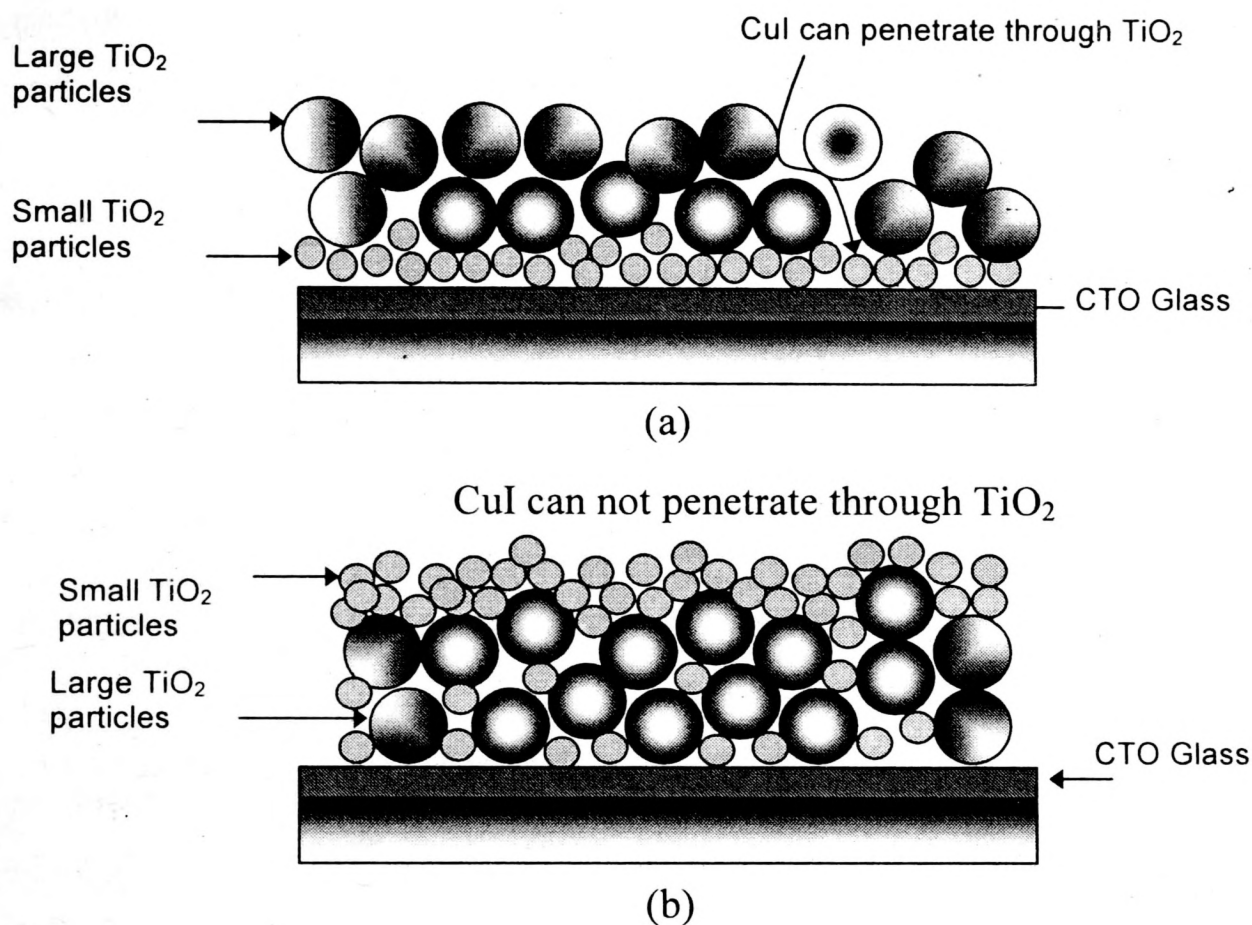


Fig 5: Schematic cross-section of TiO₂ electrode with two layers of different particle sizes (a) large particles on top (b) small particles on top.

When the electrode is coated such that the large particles lie on top, the CuI can penetrate via the holes of the loosely packed large TiO₂ particles and come in contact with the CTO glass across the thin layer of TiO₂ particles. Hence the photovoltage becomes low.

When the electrode is coated such that small particles are on top, the small particles block the holes of the loosely packed large particles of TiO₂. Then it avoids short

circuiting and thereby increase the photovoltage. As well as, it increases the effective surface area resulting in an enhanced photo current.

Conclusion

An attempt has been made to improve the dye-sensitized solid-state photovoltaic cell based on TiO₂ film and the following observations were made.

- Photovoltage and photocurrent of the cell are highly affected by the particle size of TiO₂. Large and small particle sizes of TiO₂ lead to low photovoltages and low photocurrents respectively. The pH value of the TiO₂ colloidal solution prepared to make the TiO₂ electrode determine the particle size of TiO₂ and the optimum output is achieved corresponding to the pH value 1.57 (addition of 5.5ml of acetic acid to the mixture).
- A TiO₂ electrode with two layers of different particle sizes has also been examined. Electrodes prepared with a coating of small particles on top of a layer comprising relatively large TiO₂ particles produced the highest photovoltages and photocurrents.

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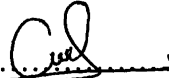
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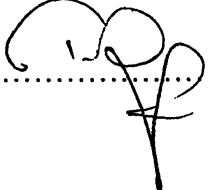
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