

## Optimal Effect of TiO<sub>2</sub> Particles Size on the Current – Potential Behaviour of Dye Sensitized TiO<sub>2</sub> Solar Cells

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The goal of this experimental work is to investigate the effect of the size distribution of TiO<sub>2</sub> nanoparticles on the efficiency of a dye sensitized solar cell. The concerned TiO<sub>2</sub> nanoparticles were produced by a sol gel process. A TTIP precipitation in a nitric acid aqueous solution was performed in order to obtain a particles suspension, then a maturation and stabilization step gave rise to a stable colloidal material. Different size nanocolloids were produced and analyzed.

Dye sensitized TiO<sub>2</sub> solar cells were built up by coating transparent conductive oxide (TCO) slide with the produced nanocolloid. The titania layer was the anode of the solar cell, whose cathode consisted of a Pt wire counter electrode. Moreover, TCO slides coated with TiO<sub>2</sub> were treated with TiCl<sub>4</sub> in order to increase the solar cell efficiency. The best results were obtained by producing slide surfaces with a mixture of particles 10 and 50 nm in size and treated with TiCl<sub>4</sub>.

### 1. Introduction

The amount of solar energy that strikes the earth's surface in only one hour approximately equals the amount of fossil flues consumed globally in one year. In order to use the solar energy for human profit, technology is focused on the improvement of methods for converting sunlight into energy. Photo electrochemical cells can convert light into either electricity, chemical flues, or both. It consists of two electrodes : a semiconductor working electrode and a metal counter electrode in a solution containing a redox couple. The counter electrode performs the reverse reaction of the semiconductor electrode and electricity is produced with no chemical changes. (Kilsa et al., 2002)

Semiconductors with band gap energies between 1,1 – 1,7 eV are ideally suited for efficient conversion of solar energy. Unfortunately, semiconductors with such a small band gaps are easily corroded in aqueous solution. Hence, stable photo electrochemical cells based on small band gap semiconductors can only be obtained in non - aqueous solutions. An alternative is to use wide band gap semiconductors, such as TiO<sub>2</sub>, which is present in nature in form of ilmenite or leucocene ores and as rutile beach sand, and alternatively may be produced by means of chemical synthesis, usually accomplished

by the sol- gel process ( Hintz et al., 2004). However, such materials only absorb UV light and have a poor overlap with the solar spectrum. A strategy to overcome this problem is to use a dye that can absorb visible light . Once the sun light photons reach the dye, the electrons are injected from the photo excited dye molecules in the valence band to the conduction band of  $\text{TiO}_2$  and their transport dynamics determines the charge collection efficiency. Essentially, this kind of device needs to fulfil only two functions: photo generation of the carriers (electrons and holes) in a light absorbing material and transfer of the charged carried to a conductive contact that will transmit the electricity.

Since the first DSSC was created by Michael Gratzel, an increasing number of researchers have contributed to improve its energy efficiency, which has a maximum value around 10 %. (Gratzel,1999.)

In the standard preparation method, the nanostructured  $\text{TiO}_2$  coated electrode is formed by deposition of a paste containing  $\text{TiO}_2$  nanoparticles of desired size. Barbé et al. (1997) studied the influence of the characteristics of  $\text{TiO}_2$  on the solar cell efficiency. In particular he emphasized the importance of the pore-size distribution of the nanostructured material, which depends also on the original nanoparticle size distribution. In this work, the effect of the titania particle size on the cell efficiency was investigated by using home made titanium nanoparticles of different dimensions, moreover, a coating with  $\text{TiCl}_4$  on the titania surface was applied and the efficiency improvement evaluated.

## 2. Experimental

$\text{TiO}_2$  colloid solutions were prepared by hydrolysis of titanium isopropoxide,  $\text{Ti}(\text{OCH}_2(\text{CH}_3)_2)_4$  (Aldrich), by using deionized water acidified with  $\text{HNO}_3$  65% b.w. under vigorous stirring. During the hydrolysis agglomerated nanostructured particles, up to a few microns in size were formed. In order to restore the original nanometric particles, the produced particles were maintained in a nitric acid aqueous solutions under high stirring for 24 h. The final crystal size depends on the nitric acid concentration: the lowest particles dimension was obtained by adopting a 0.1 M solution as was verified by a previous study (Stoller et al., 2007) . Then, the mixture was hotly stirred and progressively concentrated. A white stable colloidal sol resulted from this procedure. This colloid was heated in an autoclave to improve the stabilization. The produced nanocolloid was cooling down to room temperature, then polyethylene Glycol PGE 35K 35000 was added and the mixture was maintained under stirring for 24 hours . The conductive glass,  $\text{SnO}_2:\text{F}$  (Pilkington TEC 15) was coated by the gel and the thickness of the  $\text{TiO}_2$  film was measured by a profilometer ( DEKTAR 3030). The electrode was air-dried and then heated in an oven at temperature scale from  $80^\circ\text{C}$  until  $450^\circ\text{C}$  to change the titania crystal phase from rutile to anatase. Finally, in order to increase the cell efficiency, the electrode was firstly treated by depositing overnight over its surface three drops of 0,2M  $\text{TiCl}_4(\text{aq})$ , then it was rinsed with water and with ethanol, and dried with flowing nitrogen. The electrolyte used to perform the DSSC was a specifically made laboratory product, consisting of  $\text{LiI}$ ,  $\text{I}_2$ , pyridine and pyridinium triflate (Pomykal, 1999).Once the electrodes were cooled down to about  $120^\circ\text{C}$ , they were immersed in an ethanolic dye solution.

To realize the cell and measure the cell voltage, the electrode was placed on a photochemical measurement standard support. The current density – potential curve was recorded using a three – electrode potentiostatic set up with Pt wire reference and Pt counter electrode. The distance between the working and counter electrodes was approximately 2 mm and the cell was filled with electrolyte by using a syringe. The working electrode was lighted through the conducting glass, whose lighted surface was 0.25 cm<sup>2</sup>.

The current density- potential curve measurements were preformed with electrodes coated with the produced colloid as well as with Solaronix paste and Aeroxide colloid for comparison. The colloid, here named Aeroxide, was produced by adding water, ethanol, triton and acetyl acetone to Aeroxide particles until a homogeneous slug was obtained. Each colloid surface was morphologically analyzed, and the colloid stability as well as the particles size was measured. The SEM images of the TiO<sub>2</sub> layer allowed a careful morphological analysis. The TiO<sub>2</sub> layer deposited over the conductive slide, the layer thickness was measured by means of a profilometer, whereas the particles size distribution and the Z-potential of the colloidal solution were determined by means of a Nanosizer 90 Plus supplied by Brookhaven.

The performance of a photo electrochemical cell is characterized by three quantities: (i)the short circuit current density ( $I_{sc}$ ) which is the maximum current density that can flows between the two electrodes, (ii) the Open-Circuit Voltage ( $V_{oc}$ ) which is a measure of the maximum Gibbs free energy that can be obtained in the cell , (iii) The values of voltage and current, respectively VMPP and IMPP, yielding maximum power with reference to the current-voltage curve of the specific solar cell (Kilsa et al.,2002). Usually the maximum power is expressed by a variable, named Fill Factor ( $ff$ ), which is defined as:

$$ff = \frac{V_{MPP}I_{MPP}}{V_{OC}I_{SC}} \quad (1)$$

Accordingly, the total maximum obtainable power is:

$$P_{MAX} = V_{OC}I_{SC}.ff \quad (2)$$

Finally, the energy conversion efficiency of the solar cell is defined as the power produced by the cell ( $P_{MAX}$ ) divided by the power incident on the representative area of the cell ( $P_{light}$ ):

$$\eta = \frac{P_{MAX}}{P_{light}} \quad (3)$$

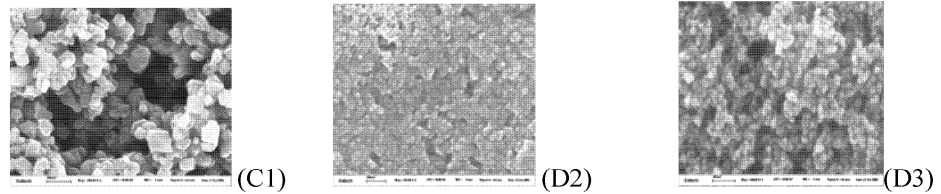
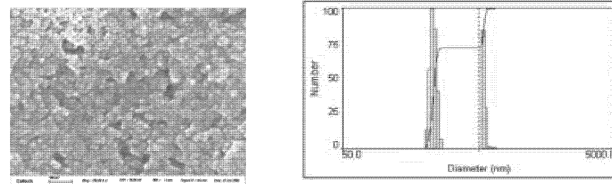
To determine the cell efficiency firstly the current-voltage curve was determined by putting the cell under a calibrated light source, 1000 W/m<sup>2</sup> in power, then the Fill Factor was evaluated by eq. (1) and finally eq. (3) was applied.

### 3. Results

During the colloid preparation, two different HNO<sub>3</sub> concentrations were adopted in order to investigate the acid charge effect on the particles de-agglomeration process (0,1M- I D:D and 0.25M- ID:C). Moreover, the thermal treatment in autoclave (maturation)was performed at different temperatures(210°C-ID:1 and 190°C-ID:2). Cells were also prepared by using Solaronics and Aeroxide slugs, as reference materials.

**Table 1:** Characteristics and performances of the produced cell

ID	Size (nm)	Layer thickness, ( $\mu\text{m}$ )	TiCl <sub>4</sub> treatment	Efficiency%
C1	50-100	9	No	0.53
C1	50-100	9	Yes	0.76
C2	5-15	8	No	0.99
C2	5-15	8	Yes	1.49
C3	100	10	No	0.49
C3	100	10	Yes	0.62
D1	10	8	No	1.12
D1	10	8	Yes	1.98
D2	5	7	No	0.98
D2	5	7	Yes	1.65
D3	10-20	8	No	1.29
D3	10-20	8	Yes	1.98
MIX	10/50-100	9	No	1.36
MIX	10/50-100	9	Yes	2.08
Com_1	5/40		No	1.08
Com_1	5/40		Yes	1.81
Com_2	17		No	0.69
Com_2	17		Yes	0.85

**Figure 1.** SEM images of samples by using a single class of TiO<sub>2</sub> colloids**Figure 2.** SEM image and CSD of TiO<sub>2</sub> mixture colloidal material (MIX in Table 1).

It is interesting to observe that the MIX material exhibits in Fig. 2 a well distinguished bimodal size distribution, as expected. Table 2 shows Z – potential of the final nanocolloids samples.

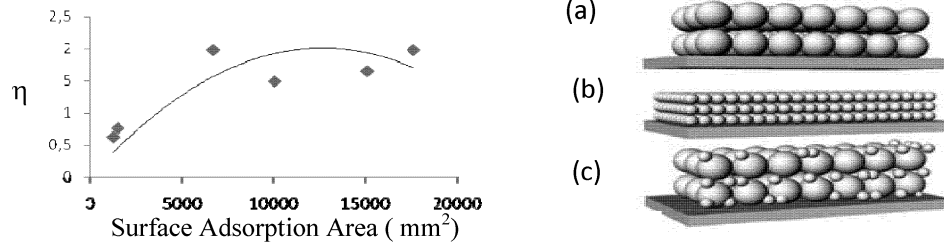
**Table 2 – Z- Potential measured for each coating**

Colloid ID	C1	C2	C3	D1	D2	D3	MIX
Z-Potential (mV)	46.2	45.1	32.2	62.3	54.2	46.8	38.0

An important characteristic, related to the cell efficiency, is the so called surface adsorption, defined as the TiO<sub>2</sub> free area where the dye can be absorbed. When the assumption of constancy of the size particles is done, the surface adsorption is given by:

$$S_{AA} = \left(\frac{\alpha}{r}\right) * \left(\frac{A_i}{r^3}\right) * 4\pi r^2 \tag{6}$$

where  $\alpha$  is the layer thickness,  $A_i$  is slide incident area and  $r$  the particle equivalent radius.



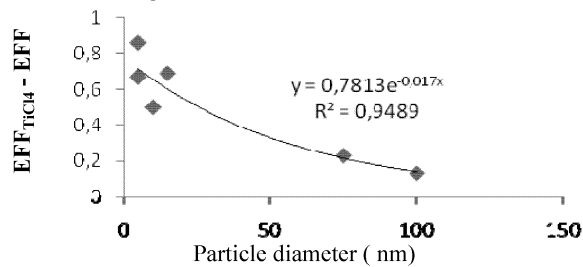
**Figure 3.** Efficiency of the solar cell vs. surface absorption

**Figure 4.** Conductive glass slide coated with (a) 50/100 nm nanoparticles resulting in a 9 μm layer, (b) 5/10nm nanoparticles resulting in a 7 μm layer and (c) with a MIX colloid resulting in a 9 μm layer

From the above figure, it is possible to observe a direct relationship between the efficiency and the absorption surface area as expected. The efficiency curve exhibits a maximum at a surface absorption around 1300 mm<sup>2</sup>.

During the coating process done by means of colloids with very small nanoparticles (< 20 nm) to thin layers were obtained, therefore a multilayer coating was implemented, which unfortunately entails cracking phenomena. On the contrary, the coating with bigger particles colloids leads to a thick layer, but in this case the surface area is smaller and the dye absorption rate is lower. A way to overcome such difficulties was to use a coating with a colloids mixture containing both nanoparticles of small size, i.e. 5 nm, and relatively large size, i.e. 50-100 nm. In such a way a thick layer with an high coating surface area can be obtained and the DSSC efficiency is optimized.

The TiCl<sub>4</sub> pos treatment showed to be very important for the cell efficiency. This latter, in fact, exhibited a percentage increase from 10% to 70%, after the treatment, depending on the coating surface characteristics.



**Figure 5:** Efficiency of the solar cell vs. surface absorption

Thinner particles layers led to higher efficiency increase, as shown in Fig. 4, where the difference between the cell efficiency before and after the treatment, i.e.  $EFF_{TiCl_4} - EFF$ , is reported as function of the colloid particles diameter. The best fitting of the obtained results, it given by an exponential curve. When the  $TiO_2$  colloid particles size exceed 150 nm the efficiency increase becomes negligible

It has be to be noticed that the obtained values of efficiency are not satisfactory and well lower than expected values, this was because the adopted die and polyelectrolyte materials were not optimized. However, the scope of this work was just to compare cell performances with respect to the photo electrochemical layer.

#### 4. Conclusions

The crystal size distribution of titania nanoparticles in the paste used for the positive electrode of a die sensitized solar cell is an important factor, which significantly affects the cell efficiency. In this work it was found that the best choice is a bimodal crystal size distribution consisting of two classes of crystals 5 and 50-100 nm in size, respectively. By assuming just one class of nanoparticles, efficiency increases as much as the particles size decreases. The  $TiCl_4$  treatment the  $TiO_2$  coated slides is very beneficial for the cell efficiency, by entailing more important improvements in case of colloids with smaller particles size.

#### 5. Bibliography

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