Original Article

Dye sensitized solar cells based on titanium dioxide nanoparticles synthesized by flame spray pyrolysis and hydrothermal sol-gel methods: a comparative study on photovoltaic performances

Abdelkhalq Aboulouard a,*, Burak Gultekin b, Mustafa Can c, Mustafa Erol d, Ahmed Jouaiti a, Benachir Elhadadi a, Ceylan Zafer b, Serafettin Demic e

a Laboratory of Sustainable Development, Sultan Moulay Slimane University, Faculty of Sciences and Technologies, B.P.523, 23000 Beni Mellal, Morocco
b Solar Energy Institute, Ege University, TR-35100 Izmir, Turkey
c Izmir Katip Celebi University, Department of Engineering Sciences, 35620 Izmir, Turkey
d Dokuz Eylul University, Department of Metallurgical and Materials Engineering, Buca, Izmir 35160, Turkey
e Izmir Katip Celebi University, Department of Material Science and Engineering, 35620 Izmir, Turkey

A R T I C L E  I N F O

Article history:
Received 8 April 2019
Accepted 27 November 2019
Available online 9 December 2019

Keywords:
Flame spray pyrolysis
Sol gel
Hydrothermal method
Dye sensitized solar cells.

A B S T R A C T

Synthesis methods, shape and size of the nanocrystalline titanium dioxide (TiO_{2}) are very crucial parameters for the power conversion efficiency of dye sensitized solar cells. In this article, nanoparticles of TiO_{2} powders have been synthesized via flame spray pyrolysis and hydrothermal sol-gel methods. These powders have been characterized by X-ray diffraction and scanning electron microscopy. In particular, the photovoltaic performances of the dye sensitized solar cells based on TiO_{2} synthesized by flame spray pyrolysis and hydrothermal sol-gel method have been compared. A commercial dye, N719 and a platinum doped counter electrode have been used for fabricating cells. Furthermore, a standard dye sensitized solar cell device has been fabricated by using a commercial Titania electrode in order to use as a reference cell. As a result, power conversion efficiencies of solar cells (under standard conditions, AM 1.5 G, 100 mW cm^{-2}) have been calculated as 2.44, 3.94, and 7.67 % with TiO_{2} synthesized via flame spray pyrolysis method, hydrothermal sol-gel method and reference Titania electrode, respectively.

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1. Introduction

The technology of solar energy is a promising solution that has, recently, been more and more needed and used to satisfy our energy needs as coal and natural reserves are being consumed at swifter rates [1,2]. Solar cells based on silicon are
most extensively utilized, however their manufacturing cost are very high [3,4]. The next challenge is to manufacture solar cells based on inexpensive materials with simple manufacturing processes. This type is dye-sensitized solar cells (DSSCs) invented by O'Regan and Gratzel in 1991 [5–10]. In DSSCs, dye which is synthetic or extracted from natural resources, is used as “the sensitizer”. The sensitizer dye generates electrons and holes under illuminations. The generated electrons are transfer to the conduction band of the acceptor semiconductor metal oxide, while holes are transfer to the electrolyte.

Many efforts have been dedicated by the scientific community to develop more effective dyes such as ruthenium complexes [11], porphyrin [12,13], carbazole [14,15], metal-free organic dyes [16–18] and natural dyes that are extracted from fruits and leaves [19–22]. Recently, quantum-dot dyes have been proposed as sensitizer to enhance the spectral response and stability of the DSSC into visible region [23–25].

The most efficient DSSC uses liquid electrolyte such as iodide/triiodide (I−/I3−), which is one of the main components of the cell. The volatility and leakage have been the major problems faced with the electrolyte. Cobalt complexes have exhibited promising results as an alternative to I−/I3− redox couple, within their lower visible light absorption and higher redox potential [26–30]. Another component improving the efficiency is a suitable photoelectrode, which should have a high transparency, large surface area, high electron injection and collection rates. TiO2 and ZnO have been proposed as the promising semiconductors materials in DSSCs applications [31]. Different types of nanostructures of these semiconductor materials have been fabricated, including nanoparticles, nanofibers, nanotubes, nanowires and nanorods [31–36]. In addition to this, other materials have been used as photoanodes such as graphene within its high mobility, high transparency and SnO2 within its high mobility and wide band gap [31,34,35,37–39].

The last component in DSSC, which acts as catalyst and collects electron from the external circuit is a counter electrode. Platinum is widely used due to its high catalytic properties and electrical conductivity. The major disadvantage of the platinum is its high cost. Currently, the carbon materials are preferable to replace the platinum because of their low cost, high catalytic properties, high chemical stability, and corrosion resistance [40–45].

Many factors affect the conversion efficiency of DSSCs, including the methods of production of TiO2 powder. This concerns chemical vapor deposition (CVD), magnetron sputtering, hydrothermal method, sol-gel method, flame spray pyrolysis (FSP) [46–51], and the preparation of TiO2 film on transparent conductive oxide (TCO) [52–60]. In particular, the thickness, morphology of the TiO2 film [52,61,62], the counter electrode [63], the conductivity and transmittance of the conducting glass, the electrolyte and the type of dye [64] are among other factors.

From this point of view, the aim of this work is to contribute to these activities by presenting a first study dealing with the photovoltaic performances of DSSCs based on TiO2 made by hydrothermal sol-gel (HT) and flame spray pyrolysis (FSP) methods in the same conditions. A close search in the literature exhibits that TiO2 powder produced by hydrothermal sol-gel and flame spray pyrolysis in DSSCs has already been proposed [49,65–69]. In particular, nanoparticles of TiO2 powders have been synthesized via HT and FSP methods. The amount of TiO2 powder and chemical solvents are fixed to elaborate nanocrystalline film. Moreover, the active areas of the solar cells and the thickness of TiO2 film on FTO are fixed. The powders have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photovoltaic performances of the DSSCs based on TiO2 nanoparticles synthesized by FSP and HT have precisely been compared. A reference DSSC (REF) has been prepared by using a commercial Titania electrode (Solaronix S.A) exploited in the comparison of photovoltaic performances with the cells made by FSP and HT powders. A commercial dye N719 has been used in all cells as the standard sensitizer.

The outline of this paper is as follows. The experimental work is presented in the second section, where our materials and measurements used in the experiments are described. To prepare the TiO2 nanoparticles by HT and FSP methods, the operating mode is reported. In the end of this section, the DSSCs are prepared and characterized. In the third section, the results from XRD patterns of TiO2 powders, SEM images, and the photovoltaic performances are discussed. The last section is devoted to conclusion.

2. Materials and methods

2.1. Materials and measurements

All chemicals and solvents used in the present work were received from SIGMA Aldrich. The standard dye N719 was received from SOLARONIX. Its chemical structure is illustrated in Fig. 1.

The sealing material, obtained from DuPont Co., is the thermoplastic polymer Surlyn®1702 showing a thickness of 50 μm.

To characterize the current-voltage characteristics under standard conditions, simulated sunlight (AM 1.5 filter, 100 mW/cm²), a source meter (the KEITHLEY 2400) and a data acquisition software (Labview) were used. The incident photon to current conversion efficiencies (IPCE) were measured by using an Enlitech QE-R system.
X-ray diffraction pattern was carried with a X-ray diffractometer (Rigaku Ultima IV X-Ray Diffractometer, powder mode, CuKα radiation). Scanning electron microscopy (SEM) image was achieved using a Zeiss/Supra 55 FE-SEM.

The films were coated on the fluorine doped tin oxide glass (FTO) with a conductivity of 13–15 Ω/sq by doctor blade technique and their thicknesses were measured by Ambios XP Stylus Profiler.

The repetitive method was used to determine the experimental error on efficiency.

2.2. Preparation of TiO₂ nanoparticles

2.2.1. Hydrothermal sol-gel (HT)

Into 12 g glacial acetic acid, 58.6 g titanium tetraisopropoxide Ti(OPr)i₄ were injected under vigorous stirring. The resulting solution was then added dropwise into 290 ml cooled deionized water. To adjust the pH 1–2, we added 5.4 ml nitric acid (65 % HNO₃) to the colloidal suspension. In the oven, under 78 °C for 75 min, the sol was peptized. The latter was completed to 370 ml by adding water and transferred to the Teflon baker equipped autoclave. For hydrothermal growth of the particles, the autoclave was placed at 235 °C for 12 h in the oven. To the autoclaved suspension, 2.4 ml nitric acid (65 % HNO₃) were added and the final mixture was concentrated to 16.5 % (w/w) TiO₂.

It was observed that 40 % (w/w) of TiO₂ paste was obtained after centrifuging the remaining water with ethanol. 79 g anhydrous α-terpineol and 4.5 % ethyl cellulose in ethanol were added. Then, the paste was sonicated for 10 min by ultrasonic horn at 200 W [70]. In order to remove all ethanol, a rotary evaporator was used. The resulting paste was placed in the oven for 1 h at 530 °C to obtain TiO₂ powder.

2.2.2. Flame spray pyrolysis (FSP)

The TiO₂ solution was prepared from titanium (IV) isopropoxide (Ti[OCH(CH₃)]₃) precursor and dissolved in xylene. The concentration of solution is 0.68 M. For FSP (Np10, Tethis, Italy), the liquid precursor solution is fed by a syringe pump into the center of methane/oxygen with a flow rate of 5 mL/min and dispersed by oxygen. By adjusting the orifice gap area, the pressure drop at the capillary tip was fixed at 2 bars. A smaller flame ring issuing from an annular gap was used to ignite the spray flame. The flame supporting a constant premixed methane/oxygen with a flow rate of 5 L/min and a ratio of ½ is fixed. To provide any additional oxygen sheath flow, a sintered metal plate ring is surrounding the supporting flame. A vacuum pump with a cellulose filter was used to collect the produced powder [71].

2.3. Preparation and characterization of DSSCs

DSSCs were fabricated in sandwich geometry. Initially, two pastes were prepared from the powders produced by HT and FSP, separately. For this purpose, 0.44 g of the TiO₂ powder was ground in a mortar. Then 0.3 mL of acetic acid and 0.044 g of polyethylene glycol (PEG) were added in a mortar. A few drops (7.7 μL) of Triton X100 were implemented to facilitate the separation of colloid.

The FTO glass substrates were cleaned for 10 min with distilled water, ethanol and acetone in ultrasonic bath, respectively, and dried with nitrogen. By using doctor blade technique, the TiO₂ colloid were coated on the FTO glass substrates and sintered at 450 °C for 30 min. The active electrodes areas were 1 cm². Ambios XP stylus profiler was used to measure the thickness, which was found equal to 4 μm for each film associated with a constant thickness.
The dye N719 (5 mM) was prepared in 25 mL of absolute ethanol. The electrodes coated by the TiO₂ colloid prepared by FSP and HT powders. In addition to that, the reference titania was immersed into the dye for 16 h. Then, the electrodes dipped into acetonitrile for 15 min.

The electrolyte was composed of 0.5 M LiI, 0.05 M I₂ and 0.5 M 4-TBP in the acetonitrile-valeronitrile (1:1). The platinum counter electrodes (Solaronix S.A) were dried at 450 °C for 15 min. Finally, DSSCs were assembled in sandwich geometry. The electrolyte was injected in small holes of the counter electrodes. These holes were sealed by Surlyn, as illustrated in Fig. 2.

3. Results and discussion

To determine the anatase and rutile phases, the powders produced by HT and FSP were characterized by XRD. The patterns are plotted in Fig. 3.

It follows that, for FSP process, the five high intensity peaks at 2θ = 25.3, 37.77, 48.08, 54.02, 55.08°, indexed as (101), (004), (200), (105), (211) indicate the nanocrystalline anatase structure. The crystal peaks at 2θ = 27.44, 36.11°, indexed as (110), (101) show the nanocrystalline rutile structure. By using the reference intensity ratio (RIR), the percentage of anatase is 92 %, while for the rutile is 7.8 %. According to the Debye-Sherrer equation, the size of particles is around 16 nm. For HT process, the five high intensity peaks at 2θ = 25.24, 37.73, 47.99, 53.81, 55.22°, indexed as (101), (103), (200), (105), (211) respond to the nanocrystalline anatase structure. The crystal peaks at 2θ = 27.49, 53.81°, indexed as (110), (211) correspond to the nanocrystalline rutile. The RIR shows that the percentage of anatase is 95 % and for the rutile is 5.3 %. By using Debye-Sherrer equation, the size of particle is approximately 13.25 nm. The observed peaks matched with the reference spectrum (JCPDS no. 21-1272 and 21-1276).

To investigate the morphology of such structures, the SEM images of TiO₂ powders produced by FSP and HT were recorded, and these images are presented in Fig. 4.

These SEM images indicate the agglomeration of nanoparticles. However, the FSP sample showed higher agglomeration. Furthermore, the size of nanoparticles produced by FSP is larger than that produced by HT. The agglomeration of nanoparticles can be explained as non-ordered and porous nanoparticles.

Under standard global AM 1.5 solar irradiation, the photovoltaic performances of DSSCs, made by FSP, HT, and reference cell are shown in Fig. 5. The results of these performances are summarized in Table 1.

The average efficiencies were calculated from Table 1 in order to determine the experimental error.

For FSP: average = \( \frac{(\text{FSP1} + \text{FSP2} + \text{FSP3})}{3} \) = 2.349%
For HT: average = \( \frac{(HT1 + HT2 + HT3)}{3} \) = 3.894%

For REF: average = \( \frac{(REF1 + REF2 + REF3)}{3} \) = 7.323%

The efficiencies errors were calculated using the formula below:

Error = sup |average value – cell value|

Where cell value represents conversion efficiency of each cells.
- For FSP: error = 0.125%
- For HT: error = 0.045%
- For REF: error = 0.349%

It can be observed that the variations in the performance of DSSCs measured in the case of different cells are minimal. The maximum efficiency corresponding to a maximum value of current density, which agrees with the results found by Fazli et al. [72]. We note that high values of fill factor correspond to maximum efficiencies due to low series resistance [43].

In the rest of this work, we used solar cells with maximum performance values (current density, fill factor and efficiency) to find out why HT cells perform well (Table 2, Fig. 6).

At the same conditions, the sensitized solar cell made by FSP gave a short-circuit current density \( J_{SC} \) of 5.25 (mA cm\(^{-2}\)), open circuit voltage \( V_{OC} \) of 720 (mV) and a fill factor of 0.64 as well as a conversion efficiency \( \eta \) of 2.44 %. The sensitized solar cell made by HT generated a \( J_{SC} \) of 13.46 (mA cm\(^{-2}\)), \( V_{OC} \) of 660 (mV), FF: 0.44, \( \eta \): 3.94 %. Both cells were compared with the reference cell giving \( J_{SC} \): 19.56 (mA cm\(^{-2}\)), \( V_{OC} \): 720 (mV), FF: 0.54, \( \eta \): 7.67 %.

From Table 2, it can be noticed that the short-circuit density of HT cell is higher than the short-circuit density of FSP cell. This difference is due to the aggregation and particles size according to XRD and SEM analyses. Jeng et al. [73] demonstrated that small nanoparticles size of TiO\(_2\) with good morphology lead to a large contact surface and low resistance. This allows a good injection of electrons into the electrode, which means a higher current density and good efficiency.

### Table 1 – DSSCs performances parameters of cells under standard conditions.

<table>
<thead>
<tr>
<th>Cells</th>
<th>( J_{SC} ) (mA cm(^{-2}))</th>
<th>( V_{OC} ) (mV)</th>
<th>FF</th>
<th>( J_{MPP} ) (mA cm(^{-2}))</th>
<th>( V_{MPP} ) (mV)</th>
<th>Efficiency(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSP1</td>
<td>5.254</td>
<td>720</td>
<td>0.645</td>
<td>4.518</td>
<td>540</td>
<td>2.439</td>
</tr>
<tr>
<td>FSP2</td>
<td>5.194</td>
<td>720</td>
<td>0.637</td>
<td>4.415</td>
<td>540</td>
<td>2.384</td>
</tr>
<tr>
<td>FSP3</td>
<td>5.173</td>
<td>680</td>
<td>0.632</td>
<td>4.448</td>
<td>500</td>
<td>2.224</td>
</tr>
<tr>
<td>HT1</td>
<td>12.922</td>
<td>640</td>
<td>0.443</td>
<td>10.229</td>
<td>380</td>
<td>3.887</td>
</tr>
<tr>
<td>HT2</td>
<td>13.459</td>
<td>660</td>
<td>0.44</td>
<td>10.368</td>
<td>380</td>
<td>3.939</td>
</tr>
<tr>
<td>HT3</td>
<td>13.230</td>
<td>660</td>
<td>0.442</td>
<td>10.154</td>
<td>380</td>
<td>3.858</td>
</tr>
<tr>
<td>REF1</td>
<td>18.556</td>
<td>700</td>
<td>0.511</td>
<td>15.913</td>
<td>440</td>
<td>7.002</td>
</tr>
<tr>
<td>REF2</td>
<td>19.223</td>
<td>700</td>
<td>0.515</td>
<td>16.585</td>
<td>440</td>
<td>7.297</td>
</tr>
<tr>
<td>REF3</td>
<td>19.566</td>
<td>720</td>
<td>0.545</td>
<td>16.679</td>
<td>460</td>
<td>7.672</td>
</tr>
</tbody>
</table>

For Fig. 6 – \( J-V \) curves of FSP, HT, and REF cells which have maximal values of performance (under standard global AM 1.5 solar irradiation and dark).
Table 2 – DSSCs which have maximal values of performance.

<table>
<thead>
<tr>
<th>Cells</th>
<th>Jsc (mA cm⁻²)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>M.Power (mW cm⁻²)</th>
<th>Jmpp (mA cm⁻²)</th>
<th>Vmpp (mV)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSP</td>
<td>5.25</td>
<td>720</td>
<td>0.64</td>
<td>2.44</td>
<td>4.52</td>
<td>540</td>
<td>2.44 ± 0.125</td>
</tr>
<tr>
<td>HT</td>
<td>13.46</td>
<td>660</td>
<td>0.44</td>
<td>3.94</td>
<td>10.37</td>
<td>380</td>
<td>3.94 ± 0.045</td>
</tr>
<tr>
<td>REF</td>
<td>19.56</td>
<td>720</td>
<td>0.54</td>
<td>7.67</td>
<td>16.68</td>
<td>460</td>
<td>7.67 ± 0.349</td>
</tr>
</tbody>
</table>

**Fig. 7** – IPCE spectra of FSP, HT, and REF cells which have maximal values of performance.

Fig. 7 shows the results of incident to current conversion efficiencies (IPCE) for FSP, HT, and REF cells. It is observed that 520 nm is the maximum value of IPCE spectra for FSP and REF cells as well as 530 nm for the HT cell. The efficiencies of FSP, HT, and REF cells are about 17.3, 46 and 59.8 %, respectively.

The IPCE spectrum of HT cell is larger than that of the FSP cell, signifying that the charge recombination is reduced. The charge injection is greater with HT cell.

These results agree with the photovoltaic data cited in the previous paragraph.

### 4. Conclusion

In this paper, photovoltaic performances of DSSCs based on TiO₂ prepared by HT and FSP processes at the same conditions have been compared. In particular, nanoparticles of TiO₂ powders using a flame spray pyrolysis and hydrothermal sol-gel agents and solvents have been optimized to prepare nanocrystalline film. Synthesized powders have been characterized by XRD and SEM. Concretely, we have compared the photovoltaic performances of DSSCs based on TiO₂ nanoparticles synthesized by FSP and HT. We have found that η=2.44, 3.94 and 7.67 % with FSP powder, HT powder, REF Titania electrode, respectively under standard conditions, AM 1.5G, 100 mW cm⁻².

This work comes up with many open questions. The interesting one is associated with the improvement of the photovoltaic performance of cells.

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Acknowledgements**

The authors gratefully acknowledge the financial funding of the Mevlana fellowship program. The authors appreciate the support of Izmir Katip Celebi University, Turkey and Solar Energy Institute, Ege University, Turkey. The authors are grateful to Dr. Metin Yurdmuşal from Dokuz Eylül University, Turkey for his invaluable supports on materials supply.

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