Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 8 (2010) 28–32

Physics Procedia

www.elsevier.com/locate/procedia

VI Encuentro Franco-Español de Química y Física del Estado Sólido
VI^{ème} Rencontre Franco.Espagnole sur la Chinie et la Physique de l'État Solide

Effect of testing conditions on the photovoltaic performance of ZnO-based dye sensitized solar cells

Irene Gonzalez-Valls, Mónica Lira-Cantu*

Centre d'Investigació en Nanociència i Nanotecnologia (CSIC-ICN), Campus UAB edifici Q, 2nd floor. Bellaterra, Barcelona (Spain)E-08193

Abstract

Dye-sensitized solar cells based on vertically-aligned ZnO nanorod, were analyzed at different conditions. Stability tests showed an improvement on solar conversion efficiency between ~20% (1000 W/m^2) and ~50% (1800 W/m^2). This behavior was ascribed to the physisorption/chemisorption of the N-719 dye on the ZnO due to UV light. Studies at different temperatures proved that the performance of the cells can double when decreasing temperature from 72ºC to room temperature. An increase on the efficiency and decrease in FF was observed when light intensity is increased. IPCE analyses were used to monitor the stability of the solar cells with time.

Keywords: Dye-sensitized solar cells; vertycally-aligned ZnO nanorods; stability tests; UV-light irradiation; excitonic solar cells, ZnO.

1. Introduction

The application of ZnO in Excitonic Solar Cells, XSCs, (organic, dye sensitized and hybrid) has been rising over the last few years due to its similarities with the most studied semiconductor oxide, TiO_2[1]. ZnO presents comparable bandgap values and conduction band position as well as higher electron mobility than TiO_2[2]. It can be synthesized in a wide variety of nanoforms applying straightforward and scalable synthesis methodologies [3,4]. Specially, the application of vertically-aligned ZnO nanostructures it is thought to improve contact between the donor and acceptor material in organic solar cells (OSC), or improve electron injection in Dye sensitized solar cells (DSCs) [5]. Up to date, DSCs based on ZnO have already achieved promising power conversion efficiency values of about 6-7% [6]. In this work we analyzed the effect of different testing parameters on the photovoltaic performance of DSC based on ZnO, especially the effect temperature and light irradiation intensity on power conversion efficiency and the effect of UV light on solar cell lifetime.

---

* Corresponding author. Tel.: +34-93580185 3; fax: +34-93580185 3.
E-mail address: monica.lira@cin2.es.

doi:10.1016/j.phpro.2010.10.007

2. Experimental

All chemicals were commercial and used without further purification. ZnO electrodes were prepared on ITO (indium-tin oxide) slides (Solems). First, A ZnO sol-gel solution, prepared from zinc acetate and diethanol amine (DEA) [8], was deposited by spin-coating at 1500 rpm on top of clean ITO slides. Then the substrates were sintered at 450ºC/2h. ZnO nanoparticles (NPs) synthesized by Pacholski *et. al.* Method [9] were spin-coated 3 times at 1000 rpm on the ZnO buffer layer prepared before, between layers the slides were dried at 150ºC for 10 min. The growth of ZnO nanorods (NRs) was carried out in a equimolar aqueous solution of 25 mM zinc nitrate hexahydrate and HMT at 96ºC between 1h and 6h [7]. The aqueous solution was changed every 4 hours. After, the substrates were rinsed with deionized water, dried under N_2 and sintered at 450ºC/30 min. Characterization was carried out in a scanning electron microscopy (SEM, HITACHI-S-570), transmission electron microscopy (TEM, 120 KV- JEOL 1210 equipped with EDS analyzer LINK QX 2000 X). X-ray powder diffraction analyses between 5 and 120 degrees in a XRD, RIGAKU Rotaflex RU200 B instrument, using CuKα_1 radiation. UV-Visible analyses of solutions and thin films were made in a Shimadzu 1800 spectrophotometer.

Dye-sensitized solar cells (DSCs) preparation: first, ZnO electrodes were sensitized in a 0.5 mM solution of N719 dye (Solaronix) at different times. After, a counter electrode of FTO platinized (Pt-Catalyst T/SP, Solaronix) was bounded thermally with the ZnO electrode using a hot melt foil (SX1170, Solaronix) and the liquid electrolyte filled the internal space. For long-term measurements, DSC were hermetically sealed with the same hot melt sealing foil applying vacuum to introduce the liquid electrolyte by capillary forces. Temperature analyses were fulfilled with a handmade glass chamber where the temperature was measured constantly with a digital thermohygrometer (HD2301/01, Afora) introduced in the chamber and a Hueber instrument heated the system. A UV-filter (<400 nm) from Thorlabs was used. The solar simulation was carried out with a Steuernagel Solarkonstant KHS1200. Light intensity was adjusted at 1000W/m^2 with a bolometric Zipp & Konen CM-4 pyranometer. Calibration of the sun simulator was made by several means applying a calibrated S1227-1010BQ photodiode from Hamamatsu and a minispectrophotometer from Ava-Spec 4200. The AM1.5G reference spectrum was according to ASTM G173 standard. IV-curves were measured using a Keithley 2601 multimeter connected to a computer and software. IPCE analyses were carried out with a QE/IPCE measurement System from Oriel at 10 nm intervals between 300 and 700 nm. The results were not corrected for intensity losses due to light absorption and reflection by the glass support.

3. Results and discussion

Figure 1 shows the ZnO NRs length and diameter measured by SEM at different growth times. Longer growth times resulted in longer NRs and also 2 types of diameters appeared. Most of the NRs had a diameter around 40 nm but some had bigger diameters and when the growth time increased, increased as well the number of NRs with bigger diameters. Cross-section and top view SEM images of a 6h ZnO NR electrode are also showed in Figure 1.

X-ray diffraction analyses on the ZnO NRs electrodes show wurtzite phase of ZnO and a preferential orientation along the [002] peak due to vertical growth of the NRs on the ITO substrate. Good crystallinity of the ZnO NRs was observed by TEM (not shown).

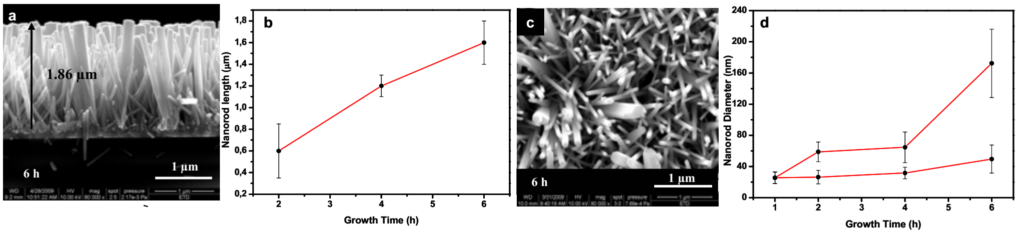

Figure 1. FE-SEM images of a 6h growth time ZnO NRs electrode a) Cross-section and c) top view. Dimensions of ZnO NRs with growth time b) length and d) diameter.

DSCs of ZnO NRs at different growth times were analyzed and the average values obtained of the 5 best cells (up to 12) are indicated in table 1. As it was expected, longer NRs resulted in higher performances. Devices were analyzed at 1000 W/m^2 (A.M. 1.5) at 72ºC and the active are was ~0.2 cm^2.

Table 1. Photovoltaic values of ZnO NRs DSCs obtained at different growth times.

Growth Time (h)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Efficiency (%)	Temperature (ºC)
2	0.361 ± 0.030	1.52 ± 0.20	37 ± 2	0.21 ± 0.05	72
4	0.406 ± 0.025	2.19 ± 0.71	36 ± 2	0.33 ± 0.12	72
6	0.466 ± 0.046	3.20 ± 0.22	35 ± 2	0.53 ± 0.04	72

Stability analyses of sealed DSCs were fulfilled to know the durability of the cells. One DSC was irradiated at 1000 W/m^2 using a UV-filter (cut the light < 400 nm) (cell 1), another cell was measured at the same light intensity but without UV-filter (cell 2) and the last was irradiated at 1800 W/m^2 (cell 3). The three cells were kept in the dark at room temperature between measurements (during the measurements the temperature was 72ºC). Figure 2a shows the efficiency variation of the cells with time. We observed that cell 2 and 3, irradiated with UV-light, improved their performances during the first hours of analyses (~20% efficiency increase for cell 2 and ~50% for cell 3) while efficiency of cell 1 remained unchanged. UV-light irradiation showed to have a positive effect on the DSCs performances. In principle, we could argue that the efficiency improvement is due to the higher amount of light reaching the cell. Nevertheless, it has been attributed to the physisorption/chemisorption assistance between the dye N719 and the ZnO NRs reported by others and by our previous work [7]. The interaction between dye-ZnO NRs has been explained as the result of 3 steps: dye diffusion, dye chemisorption and [Dye^{2+} -ZnO] complex formation [7]. IV curves of the best results obtained for the 3 cells are showed in figure 2b. Maximum values for cell 1 (1000 W/m^2, UV-filter) were: 0.514 V, 1.23 mA/cm^2, 0.42 FF and 0.27% efficiency; Cell 2 (1000 W/m^2): 0.535 V, 2.34 mA/cm^2, 0.39 FF and 0.49% efficiency and cell 3 (1800 W/m^2): 0.612 V, 3.22 mA/cm^2, 0.38 FF and 0.75% efficiency. IPCE spectra (measured at room temperature) had 2 peaks, one at ~370 nm and the other at ~520 nm (Figure 2c). Peak ~370 nm slightly increases with time while the peak ~520 nm decreases. No correlation between IPCE and power conversion efficiency was found, probably to the balance between the two IPCE peaks.

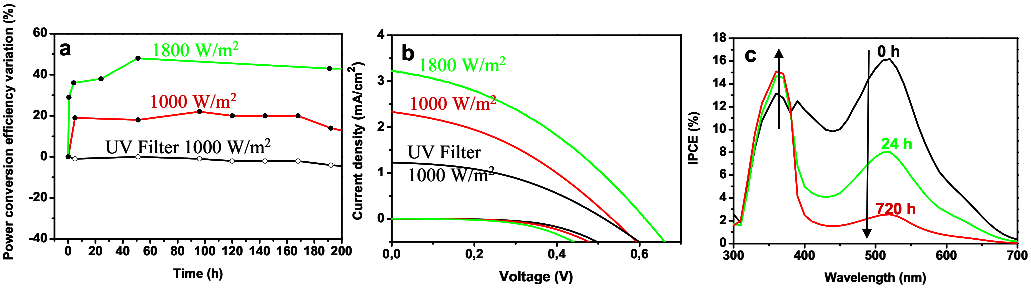

Figure 2. Sealed DSCs of 6h ZnO NRs (~1.8 μm) and sensitized for 2h in N719 dye solution. Samples were analyzed without UV-filter (at 1000 and 1800 W/m^2) and with UV-filter (at 1000 W/m^2). a) Power conversion efficiency variation (%) observed with time, b) IV-curves obtained for each device at maximum efficiency during lifetime studies and c) IPCE spectra for different DSC analyzed at different periods of time: freshly prepared (0h), after efficiency increased (24h) and once the solar cell was completely degraded (720h).

To study the effect of temperature and light irradiation we were carried out test at temperatures between 25 to 75º C and incident power light from 800 to 1500 W/m^2. In addition, measures were also carried out with and without the application of an UV-light filter (< 400 nm) for each experiment. Figure 3a shows the variation of the power efficiency for different temperatures. In general, we observed that higher temperatures results in lower power conversion efficiencies and the higher the light intensity the higher the power conversion efficiency. The V_{oc} (not shown here) is strongly affected by temperature changes, while J_{sc} (not shown) shows only slight or null variation up to temperature of 55ºC, after which J_{sc} decreases. The latter effect of J_{sc} with temperature has been observed by other groups in TiO_2-based DSCs [10,11]. In the case of the FF (not shown), it also decreases when temperature is increased due to the decrease in V_{oc} and J_{sc} and slight decreases when light irradiation is increased due to an increase of series resistances (R_s, calculated using the definition R_s=dV/dI$_{(I=O)}$), the R_s increases from 89.9 $\Omega\cdot cm^2$ at 25ºC to 95.2 $\Omega\cdot cm^2$ at 75ºC). Series resistances for TiO_2 DSCs with temperature were observed to have the opposite behavior [10]. Figure 3b shows the efficiency variation depending on light intensity for measurements with and without UV-light filter (< 400 nm). Solar cells measured with UV-light filter show lower power conversion efficiencies, as expected when filters are applied (less light reaching the cell). Nevertheless, lifetime for solar cells with or without UV-filter was shown to be almost the same: up to 200 h for all systems.

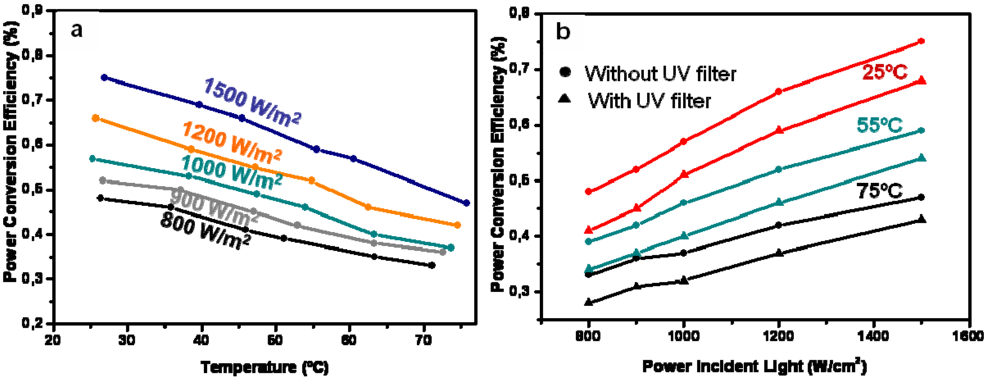

Figure 3. Sealed DSCs of 6h ZnO NRs (~1.8 µm) and sensitized for 2h in N719 dye solution. a) Power conversion efficiency with temperature at different light intensities and b) Power conversion efficiency with Power incident light at 25ºC, 55ºC and 75ºC measured with and without UV-light filter (< 400 nm).

4. Conclusions

In this work we report the effect of different testing conditions on the power conversion efficiency of vertically-aligned ZnO dye sensitized solar cells. Increase of solar cell efficiency between 20% and 50% was observed due to the effect of UV-light irradiation. The interaction between the N719 Dye and the ZnO nanorods seem to take place in 3 well-defined steps: dye diffusion, dye chemisorption and [Dye^{+2}-ZnO] formation. We report a direct correlation of these processes to the lifetime of the DSC and IPCE analyses. We have also observed that these processes occur regardless of the application or not of an UV filter or if the device is stored in the dark. The only difference is the time at which each process takes place, being the sample irradiated with UV light the one showing faster degradation. Effect of different temperatures and incident light intensities were also studied on DSCs. Efficiencies of the cells decreased when the temperature increased and for higher light intensities, efficiencies increased.

Acknowledgements

The authors want to acknowledge the projects ENE2008-04373 and PIE-200860I134 and the Ph.D. scholarship awarded to I.G-V (BES-2009-028996) from the Spanish Ministry of Science and Innovation, MICINN. To the Consolider NANOSELECT project CSD2007-00041. To the Xarxa de Referència en Materials Avançats per a l'Energia, XaRMAE (Network on Advanced Materials for Energy) of the Catalonia Government.

References

[1] M. Gratzel, *Nature,* **414**, 338-344 (2001).

[2] M. Quintana, T. Edvinsson, A. Hagfeldt, G. Boschloo, *J.Phys. Chem. C*, **111**, 1035-1041 (2007).

[3] Z. L. Wang, *Mater. Today*, **7**, 26-33 (2004).

[4] Q. F. Zhang, C. S. Dandeneau, X. Y. Zhou, G. Z. Cao, *Adv. Mater.*, **21**, 4087-4108 (2009).

[5] I. Gonzalez-Valls, M. Lira-Cantu, *Energy Environ. Sci.,* **2**, 19-34 (2009).

[6] T. Yoshida, *23rd European Photovoltaic Solar Energy Conference and Exhibition,* Valencia, Spain (2008).

[7] I. Gonzalez-Valls, M Lira-Cantu, *Energy Environ. Sci.,* **3**, 789-795 (2010).

[8] M. Lira-Cantu, F. C. Krebs, *Sol. Energy Mater. Sol. Cells,* **90**, 2076-2086 (2006).

[9] C. Pacholki, A. Kornowski, H. Weller, *Angew. Chem. Int. Ed.,* **41**, 1188-1191 (2002).

[10] M. Berginc, U. Opara, M. Jankovec, M. Topic, *Sol. Energy Mater. Sol. Cells,* **91**, 821-828 (2007).

[11] M. Toivola, L. Peltokorpi, J. Halme, P. Lund, *Sol. Energy Mater. Sol. Cells,* **91**, 1733-1742 (2007).