

TiO₂ thin films (1 μm) with ordered porosity used as high performance photoelectrode in DSSC

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Abstract

Mesoporous anatase thin films are very promising materials to act as electrode in dye-sensitized solar cells. Randomly oriented nanocrystalline TiO₂ particles are usually used to prepare photoelectrodes with a thickness of 10-15 μm. Templated-assisted dip-coating techniques are used to obtain thin films with ordered porosity. The use of different templates influences the film porosity in terms of long-range order, percentage of porosity, pore size and pores connectivity. The photovoltaic performances of the samples have been evaluated. Such mesostructured films are compared in terms of photovoltaic performance with TiO₂ nanoparticles films, generally used in DSSC.

Results and discussion

Film mesostructure

As displayed in **Figure 1**, TEM analysis shows that a higher relative humidity (RH) leads to a better organization of the mesostructure.^{1,2} The samples deposited under 25% RH and directly stabilized at 300°C present a "wormlike" structure (figures 1-a and 1-b). Films deposited under 25% RH and aged at 75% RH before stabilization present a "gridlike" mesostructure (figures 1-c and 1-d).

Film porosity and surface area

Percentages of porosity, surface area values and pore size distribution can be extracted from atmospheric poroellipsometry (AEP) adsorption-desorption curves. To perform atmospheric poroellipsometric measurements, an ellipsometer was coupled with an ellipsometric porosimetry device. This device consists in a chamber containing the film to analyze in which the environment is modulated by a pulsed air flow with controlled partial pressure of water (**Figure 2**). The record of the adsorption-desorption hysteresis of the water into the film porosity, shown in **Figure 3**, allows the determination of the percentage of porosity and the surface area. A pore size distribution (PSD) can be calculated from the AEP data (**Figure 3** insert).

Percentages of porosity and total surface areas, calculated for each 1 μm-film, are listed in **table 1**. The total surface area of the commercial film (nanoparticles, 3 μm, Dyesol) could not be determined by AEP and an indicative value was found in the literature to be 100-150 m²/cm².³ For the mesostructured films, the total surface area follows the same evolution as the percentage of porosity: the higher porosity, the higher surface area. However, this should be modulated by the pore size distribution.

Microporosity can significantly contribute to the total surface area while being not accessible for dye molecules and electrolyte species. Therefore, values of surface area calculated for pores with a diameter higher than 4 nm⁽³⁾ are also presented in **table 1**. As expected from the pore size distribution curves (not shown here), the gridlike films show a much lower "accessible" surface area, standing for a substantial contribution of microporosity (< 4nm). On the contrary, the wormlike films show virtually no difference between total and accessible surface area. Their porosity is then considered as higher than 4 nm diameter and totally accessible for pore filling in DSSC application.

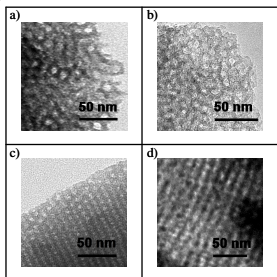


Figure 1: TEM micrographs of a) F127 wormlike film, b) P123 wormlike film, c) F127 gridlike film, d) P123 gridlike film

Photovoltaic performances

1 μm thick mesoporous films were compared in terms of photovoltaic behavior with a 3 μm commercial film of TiO₂ nanoparticles purchased from Dyesol. Results are reported in **table 1**.

It can be seen that the film organization affects the conversion percentage: wormlike films are more efficient than their gridlike counterpart. Besides, P123 cells always show better performances than F127 cells, most probably due to their higher porosity, leading to a better dye loading. However, while the F127 gridlike film presents a roughly similar accessible surface area (pores > 4nm) as the F127 wormlike sample, its conversion efficiency is weaker. Pores must be misaligned, affecting the pores connectivity and thus the dye loading. Indeed, a typical gridlike mesostructure is characterized by several gridlike domains of a few hundreds of nanometers, randomly oriented (**Figure 4**). Such misalignment of channel-like pores can significantly hinder dye and electrolyte filling and limit the photoactive interface.

As also listed in **table 1**, the four samples present approximately the same open circuit voltage (V_{oc}) and the same fill factor (FF). V_{oc} values reflect the electron density in the conduction band of the TiO₂. The high V_{oc} values observed can be attributed to low recombination losses between the TiO₂ and the electrolyte or the dye.⁴ The relatively low values of the fill factor are attributed to high resistance of the conducting glass substrates used in this study (66 Ω/sq). When conducting glass with a resistance of 15 Ω/sq are used, the fill factor values reach 70 %.

The observed conversion efficiencies are mainly affected by the current density in short circuit conditions (J_{sc}). This parameter is known to be largely determined by the dye loading and thus the surface area and the pores connectivity.

In mesoporous TiO₂ films, the high values of accessible porosity, combined with a regular pores organization, could lead to a very high dye loading during the soaking step (measurements in process). The large number of dye molecules adsorbed on the anatase surface leads to an efficient light harvesting and subsequent high photoelectron production. The well-ordered porosity is expected to promote a complete and homogeneous penetration of electrolyte into the pores, making possible an efficient regeneration of oxidized dye molecules. Additionally, the small thickness of the films allows a quick transport of photogenerated electrons towards the collecting electrode. Those parameters will help to avoid recombination losses under illumination.

In comparison with 3μm Dyesol device, mesoporous electrodes seem to be competitive in term of photovoltaic activity. The best mesostructured device with a 1 μm thick photoactive layer already provides 2.29 % conversion efficiency whereas commercial nanocrystalline film (3μm) only provides 2.42 % conversion efficiency. This superiority is mainly attributed to the higher accessible surface area in mesostructured films, along with a better control on the pore diameter and pores connectivity, leading to a better dye loading and electrolyte impregnation.

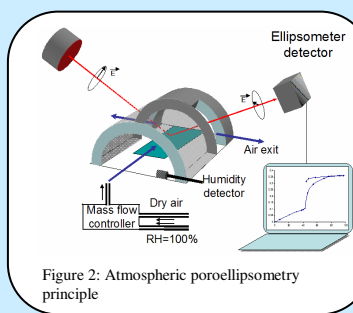


Figure 2: Atmospheric poroellipsometry principle

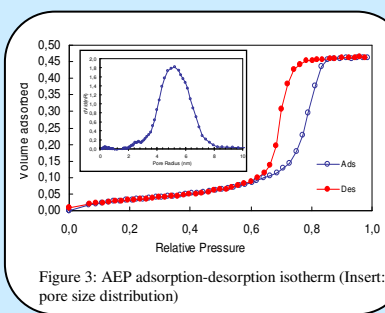


Figure 3: AEP adsorption-desorption isotherm (Insert: pore size distribution)

Table 1: Properties of 1 μm thick mesostructured films: porosity, surface area and photovoltaic performances

Device	AEP porosity (%)	Total surface area (m ² /cm ²)	Surface area (m ² /cm ²) ∅ pores > 4nm	V _{oc} (V)	J _{sc} (mA/cm ²)	P _{max} (mW/cm ²)	FF (%)	η (%)
F127 wormlike 1 μm	31.5	163	161	0.750	3.35	1.19	55.6	1.39
P123 wormlike 1 μm	38	225	225	0.724	5.52	1.95	57.3	2.29
F127 gridlike 1 μm	35.5	199	148	0.767	2.49	0.91	56.5	1.08
P123 gridlike 1 μm	44	288	176	0.732	4.68	1.59	54.7	1.87
Dyesol Nanocryst., 3 μm	/	100-150 ³	/	0.776	5.32	2.05	58.6	2.42

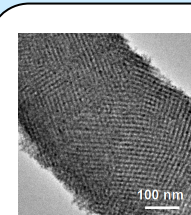


Figure 4: TEM micrograph of multioriented gridlike domains

Conclusion

Mesoporous films have been assembled in photovoltaic devices and compared with a commercial nanocrystalline film. The accessible surface area and the film organization seem to be the most influent parameters on the photovoltaic behavior. Indeed, the surface area and the film organization, influencing the pore connectivity, affect the dye loading.

When compared to commercial nanocrystalline thin films, better performances can be obtained with thinner films when the sample is mesostructured. Such noteworthy characteristic could be exploited in the field of all solid-state DSSC in which the solid electrolyte can not penetrate deep inside the TiO₂ film.⁵

In the future, it will be interesting to increase the thickness of the mesoporous films up to 5 μm and study the influence on the conversion efficiency. However, it will be necessary to perfectly tune the thermal treatment applied during the multi-deposition process.

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