

High Performance dye sensitized solar cells based on multilayered structure of P90 and P25 titania nanoparticles

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1. Introduction

Since the pioneering work of Grätzel and coworkers in 1991, the dye sensitized solar cells (DSSCs) have attracted remarkable attention due to their promise for low-cost photovoltaics [1]. It has often been documented that one of the most critical elements in DSSCs is a compact thin film of mesoporous TiO₂ nanoparticles on a conducting substrate [2]. The light harvesting efficiency of DSSCs depends crucially on the crystalline phase, particle size, and surface area of TiO₂ nanoparticles. Moreover, morphology and porosity of TiO₂ films have a direct influence on the efficiency. Herein, we systematically studied the multilayered TiO₂ electrodes made of P90 and P25 nanoparticles, commercially available from Tegsa Inc. Manipulating the structure of the TiO₂ films have led to an appreciable improvement in the DSSC performance.

2. Experiment

Anatase phase Titania powders of two types, AEROXIDE® TiO₂ P25 and VP TiO₂ P90 were provided from Japan Aerosil Inc. Fluoprine-doped SnO₂ glass (FTO, 15 Ω/square) and Pt paste (Pt catalyst T/SP) were purchased from Solaronix SA. Paste containing P25 and P90 was prepared by a bead-mill method from TiO₂ powder, citric acid, ethylene glycol, α-Terpineol, ethanol and distilled water. The P25 and P90 paste was opaque or semi-transparent, respectively. The TiO₂ paste was coated onto FTO substrates by doctor-blading method, and then sintered at 500 °C for 30 min. In order to ensure the good light reflection effect, coating the P90 paste as the bottom layer was followed by deposition of the P25 nanoparticles as the middle layer, and by that of the submicroparticles ~ 400 nm in diameter as the top layers. The mesoporous TiO₂ photoelectrodes were preheated at 120 °C for 30 min; after cooling down, the electrodes were washed with ethanol to remove the remaining small glass fragments. Afterwards, they were immersed in a 0.35 mM N-719 solution in acetonitrile and t-butyl alcohol for 24 h at room temperature to allow complete dye adsorption. After taking them out, the excess of dye molecules on the electrodes were washed away by acetonitrile for several times, and then the electrodes were dried with a hair dryer. A Surlyn film 25 μm thick was applied between the photoelectrode and a counter electrode (a platinum-sputtered FTO glass). The cell was sealed by heating at 125 °C. The electrolyte solution was composed of 0.1 M LiI, 0.05 M I₂, 0.5 M 1-propyl-3-methylimidazolium iodide, 0.1 M GNCS, and 0.3 M 4-tert-butylpyridine in acetonitrile.

The active area of cells is 0.25 cm². The photocurrent-voltage (I-V) characteristic curves were measured by Keithley 2420 under AM1.5G illumination. The morphology of TiO₂ film was observed by using a field emission scanning electron microscope (FESEM; JEOL Ltd, JSM-6700F).

3. Results and discussion

Large nanoparticles in a bottom region close to the FTO surface would bring about an unwanted back scattering of light and thus prevents the light from penetrating to dye molecules in a middle and top regions. To minimize light loss due to such a back scattering, smaller nanoparticles should be placed in the bottom region near the FTO surface. Layer of the larger particles were then loaded onto that of the smaller nanoparticles. The FESEM images of the top and cross sectional views of the layers of TiO₂ nanoparticles were shown in Figs. 1(a)–(d). It is apparent from these images that average particle size of P90 is smaller than that of P25.

With the same film thickness the photovoltaic performance of DSSCs is better for P90 than for P25. This is because smaller nanoparticles having higher specific surface area can adsorb greater amount of dye molecules leading to higher photocurrent and higher external quantum yield.

Therefore, the P90 TiO₂ layer in the bottom region absorbs more incident light and produce

higher photocurrent. And also there is negligible back scattering effect at the P90 film. The remaining light that have escaped from photoabsorption by dye molecules is transmitted to the upper layers without any loss owing to light scattering or reflection at the boundaries of the nanoparticles. This facilitates effective light absorption of dye molecules in the middle and top region. On the other hand, smaller particles size of P90 makes it easy to recapture the reflected or back scattering light from the top scattering layer [3]. The hierarchical structure of the three different type of TiO₂ made the best use of the incident light to realize high energy conversion efficiency.

We found that the DSSCs with high energy conversion efficiency can be achieved by stacking the smallest P90 particles at the bottom and the largest 400-nm particles at the top. The photovoltaic parameters of the DSSCs

fabricated in such a manner are summarized in Table 1. DSSCs with 400-nm particles at the top layer above P25 have shown the highest efficiency. In summary, setting smaller particle size P90 in the bottom layer followed by a bit larger nanoparticle P25, together with the top layer of light-reflection 400-nm particles, has turned out to be the best arrangement for achieving higher solar efficiency.

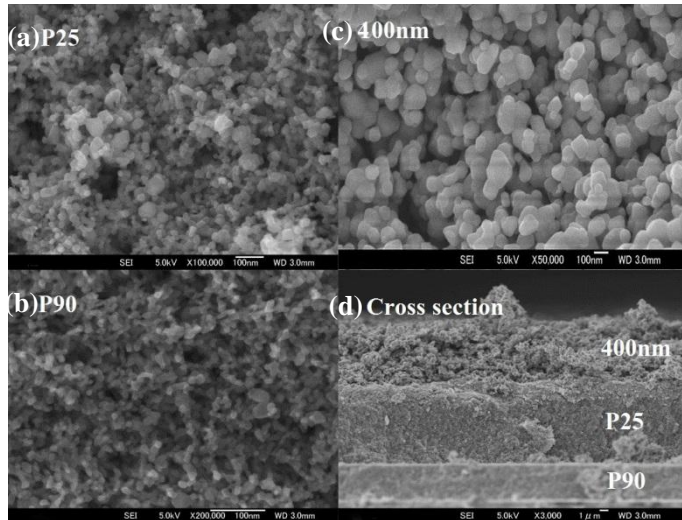


Figure 1. Images of FESEM. The top views of single-layered TiO₂ films prepared with (a) P25 and (b) P90 nanoparticles. (c) Top view of the light reflection layer made of 400-nm submicroparticles. (d) The cross sectional view of the triple-layered structure of TiO₂ piled on an FTO electrode.

Table 1. Summary of the results of photovoltaic measurements of DSSCs with multi-layered structures: P90 in the bottom, P25 in the middle, and 400-nm particles at the top as the light reflection layer (LRL).

TiO ₂ Particles	J_{sc} (mA/cm ²)	V_{oc} (V)	Fill factor	Efficiency (%)
P90	11.8	0.74	0.72	6.40
P25	12.4	0.67	0.70	5.85
P90+P25	17.21	0.71	0.70	8.55
P90+400nm	18.32	0.73	0.71	9.50

References

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