

Role of the polymer thermal stability on the efficiency of compact layer-by-layer TiO₂ films as blocking layers in dye-sensitized solar cells

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Abstract – Charge recombination at the conductor substrate/electrolyte interface has been prevented by using efficient blocking layers of TiO₂ compact films in dye-sensitized solar cell photoanodes. Compact blocking layers have been deposited before the mesoporous TiO₂ film by the layer-by-layer technique using titania nanoparticles as cations and different polymers as polyanions. The efficiency of the TiO₂ blocking layers is dependent on the morphology of the film that is related to the polymer thermal stability. For instance, the application TiO₂/sulfonated polystyrene blocking layer leads to a 28% increase in the cell's overall conversion efficiency, from 5.7% to 7.3%.

Dye-sensitized solar cells, DSCs, have been recognized for their high efficiency on converting light into electricity by using readily available and environmentally friendly materials [1], however an understanding of the limiting factors in the DSC performance is crucial to develop systems with higher efficiencies, stability and lifetime. Charge recombination is a common process in DSCs that limits their performance[2,3]. It takes place mainly at the TiO₂/sensitizer and FTO/TiO₂ interfaces. At the FTO/TiO₂ interface, charge recombination occurs due to the physical contact between the electrolyte and the FTO surface. A way to prevent that consists in applying a compact oxide layer on the FTO before the semiconductor mesoporous layer. In this work, we describe the role of the polymer thermal stability on the efficiency of layer-by-layer titania films as compact blocking layers. The blocking layers are deposited before the mesoporous TiO₂ film using 5-7 nm TiO₂ nanoparticles as cations and different polyelectrolytes. Compact films using sodium sulfonated polystyrene (PSS), sulfonated lignin (SL) or polyacrylic acid (PAA) as polyanions have been characterized in terms of their morphologies and composition before and after the sintering step. SEM and AFM micrographs reveal that after sinterization the TiO₂/PSS films are compact with plates of nanoparticles aggregates and very low porosity. In an opposite way, the TiO₂/PAA films become more porous. The changes in the morphology are associated to the thermal stability of the polymer as evaluated by thermogravimetric analysis and X-ray photoelectron microscopy. XPS. The TiO₂/SL films have an intermediary behavior between the PSS and PAA-based films with some changes after the sintering step. As shown in the Table 1, the efficiency of the 30 TiO₂/PSS bilayers as blocking layers in DSCs is higher than the TiO₂/PAA films. The results indicate that the maintenance of the compact morphology is a key aspect for the effectiveness of the blocking layers.

Table 1: Photoelectrochemical parameters of DSCs with different photoanodes (AM 1.5 solar radiation; P_{irr} = 100 mW cm⁻²)

sample	V _{oc} / V	J _{sc} / mA cm ⁻²	Ff	η /%	increase / %
Control	0.66 ± 0.02	13.0 ± 0.8	0.66 ± 0.01	5.6 ± 0.5	-
TiO ₂ /PSS	0.70 ± 0.01	15.8 ± 0.3	0.67 ± 0.01	7.3 ± 0.1	29
TiO ₂ /SL	0.68 ± 0.01	15.0 ± 0.5	0.69 ± 0.01	6.9 ± 0.3	23
TiO ₂ /PAA	0.69 ± 0.01	11.8 ± 0.3	0.72 ± 0.04	5.8 ± 0.3	3.5

References

- [1] A.S. Polo, M.K. Itokazu, N.Y. Murakami Iha, Coord. Chem. Rev., 248 (2004) 1343-1361.
 [2] P.J. Cameron, L.M. Peter, S. Hore, J. Phys. Chem. B, 109 (2005) 930-936.
 [3] A.O.T. Patrocínio, L.G. Paterno, N.Y. Murakami Iha, J. Photochem. Photobiol. A: Chem. 205 (2009) 23-27.