



Tuning bimodal porosity in TiO₂ photoanodes towards efficient solid-state dye-sensitized solar cells comprising polysiloxane-based polymer electrolyte

Anil Kumar Bharwal^{a,b}, Laura Manceri^b, Fannie Alloin^{a,**}, Cristina Iojoiu^a, Jennifer Dewalque^b, Thierry Toupance^c, Catherine Henrist^{b,*}

^a Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP (Institute of Engineering Univ. Grenoble Alpes), LEPMI, 38000, Grenoble, France

^b University of Liège, CESAM-GREENMAT, Allée du Six-Aout 13, 4000, Liège (Sart Tilman), Belgium

^c Université de Bordeaux, Institut des Sciences Moléculaires, ISM UMR 5255 CNRS, 351 Cours de la Libération, F-33405, Talence, Cédex, France

ARTICLE INFO

Keywords:

Thin films
Templating
Bimodal porosity
TiO₂
DSSCs
Polymer electrolytes

ABSTRACT

This article describes a cell architecture that achieves enhanced light harvesting with less dye quantity while simultaneously improving the performance of the polysiloxane-based solid-state dye-sensitized solar cells (DSSCs). We report the synthesis of bimodal mesoporous anatase TiO₂ films by a dual templating approach, combining a block-copolymer template (Pluronic P123) and polystyrene nanospheres (PS) as soft and hard templates, respectively. The AFM and TEM analysis of TiO₂ films revealed a mixture of mesoporous and macroporous morphology in which dual porosity is generated by combustion of soft and hard templates. The size of the macropores was varied by employing PS beads with different diameters (62, 130 and 250 nm). The influence of the macropore size on the dye loading and pore infiltration is the main purpose of this article. The bimodal porosity leads to increased light scattering due to enhanced optical path length, and better pore infiltration of the polysiloxane electrolyte is achieved. The amount of dye uptake by the dual films is lower than that of soft films because the large pore size reduces the total surface area. The optimum bimodal structure was obtained when combining P123 surfactant and the 130 nm PS beads leading to the lowest charge transfer resistance and a high efficiency for DSSCs is reported with both liquid and polymer electrolytes. Even if the dye uptake was lower, the photovoltaic performance has been maintained and improved in some devices. The open circuit voltage and fill factor were improved, owing to a successful joining of different effects i.e. increased light harvesting, facile electrolyte penetration and reduced charge recombination.

1. Introduction

There is an increasing demand in developing economical and efficient technologies for the direct exploitation of the solar energy for generating electricity, water splitting, and sustaining applications like photodegradation [1–6]. Over the past few years, porous materials have attracted increasing interest due to their potential applications in the fields of catalysis, photovoltaic, adsorption and separation processes [7]. Tremendous efforts have been made in the synthesis of ordered micro-, meso-, and macroporosity coexisting together [8–10]. Hierarchically ordered materials with both mesoporous and macroporous structures are truly useful for a wide range of dye-sensitized solar cells (DSSCs). The ordered mesopores provide high surface area for dye adsorption while interconnected macropores can act as channels for viscous electrolytes infiltration. Titanium dioxide (TiO₂) is a widely

studied material, because of its low cost, high chemical stability, outstanding electronic and optical properties associated with some polymorphs as anatase phase [11–13]. Thus, anatase thin films have attracted considerable attention in past years, being mostly used in applications such as photovoltaic and photocatalysis due to their higher photoactivity compared to the rutile or brookite phase [12,14,15].

Nano-structured anatase TiO₂ is often used because of its high surface area and mesoporosity which are mainly governed by the grains size, shape, and 3D packing [14]. The mesoporous TiO₂ based photoanodes have been successfully employed in obtaining highly efficient DSSCs [16,17]. Hence, controlling the morphology, crystal growth and porosity of nano-structured TiO₂ has been widely explored in DSSCs applications [18,19]. Although power conversion efficiencies over 13% were reached, long-term stability and leakage of the liquid electrolyte still remain a critical issue [20,21]. To circumvent this limitation, a

* Corresponding author.

** Corresponding author.

E-mail addresses: fannie.alloin@lepmi.grenoble-inp.fr (F. Alloin), catherine.henrist@uliege.be (C. Henrist).

promising approach for making cost effective photovoltaic cells consists in filling mesoporous TiO₂ films with organic semiconductors or polymer electrolytes [22–25]. Polymer electrolytes based on polysiloxane have gained worldwide attention owing to their high stability, low glass transition temperature (T_g) and highly flexible backbone [26]. Recently, we demonstrated that polysiloxane-based conducting poly(ionic liquid) (PILs) can be employed in photoelectrochemical cells [27].

However, porosity strongly influences the dye adsorption and the polymer electrolyte penetration, which are critical parameters in DSSC functioning [28]. The most commonly used surfactant to tune the textural properties of TiO₂ layers is the P123 Pluronic ((PEO₂₀–PPO₇₀–PEO₂₀) triblock copolymer [29,30]. However, the use of P123 as a template only generates small pore size (less than 10 nm) arising from its micelle diameter which hampers an easy pore infiltration of solid electrolytes. The polystyrene beads approach is a simple and effective alternative method of preparing multiscale porous TiO₂ structures [9,31] but besides facile electrolyte penetration, a meaningful loss of specific surface is obtained. Assemblies of both mesoporous TiO₂ particles (with diameters of several hundred nanometers) and nanostructured TiO₂ fibers have been applied in the view of obtaining bimodal structures [32,33]. Materials with dual porosity are thought to be advantageous over individual macroporous or mesoporous counterparts since they combine high surface area, better pore infiltration, favorable light scattering effects, faster electron transfer and lower charge recombination [32,34,35].

Yang et al. have first synthesized bimodal porous silica using the P123 and F127 surfactants and colloidal crystals as templates in various patterned micromolds [36]. Until now, a very limited number of bimodal porous TiO₂ has been reported in photocatalysis and photovoltaic applications [37,38]. Fu et al. first attempted to synthesize bimodal porous TiO₂ film with Ti(OBu)₄ as Ti⁴⁺ source and P123 and colloidal crystals as dual templates. However, only ordered macropores with 205 nm in size were obtained [39]. Recently, our group attained dual structures comprising macropores and mesopores of around 150 and 10 nm, respectively, which were prepared using polystyrene beads (PS) as hard templates and P123 surfactant as soft template [40]. Ahn et al. successfully employed PIL such as poly(1-(4-ethenylphenyl)methyl)-3-butyl-imidazolium iodide inside TiO₂ thin films with dual porosity and assembled DSSC showing higher performance than the one with conventional TiO₂ nanoparticles films (based on Dyesol commercial pastes) [41]. To the best of our knowledge, there have been no reports on bimodal TiO₂ electrodes tested in DSSC including polysiloxane based electrolytes.

Inspired by this, we herein report on the preparation of a series of dually structured TiO₂ by using PS beads of various sizes, while keeping the P123 soft template. The films obtained by spin-coating were then used in DSSCs comprising polysiloxane-based polymer electrolytes and their performances were compared to those of DSSCs fabricated with a conventional liquid electrolyte. The impact of such hierarchical structure on dye loading, light scattering and subsequent power conversion efficiency is thoroughly discussed. The study reveals that a specific design of the TiO₂ structure is required to exploit the advantages of using a viscous but more stable electrolyte as PILs.

2. Experimental section

2.1. Materials and chemicals

P123 Pluronic ((PEO₂₀–PPO₇₀–PEO₂₀) surfactant (molecular weight = 5800 g mol⁻¹), titanium tetraisopropoxide (TTIP) and butan-1-ol were purchased from Sigma Aldrich. Hydrochloric acid was purchased from Acros Organic. FTO glass substrates (15 Ω/sq) were purchased from Dyesol. Polystyrene nanospheres (Ø = 62, 130 and 250 nm) dispersed in water at 10 wt % were purchased from Bang Laboratories, USA. N-719 dye and polymer spacer SX-1170-25 (25 μm

thick) were purchased from Solaronix. Acetonitrile was purchased from ABCR GmbH and Co. The 3-methoxypropionitrile, 1-butyl-3-methylimidazolium iodide, iodine, guanidine thiocyanate, 4-*tert*-butylpyridine, valeronitrile were purchased from Sigma-Aldrich.

2.2. Mesoporous thin film synthesis (SOFT TiO₂ films)

Mesoporous thin films were prepared by using the Pluronic surfactant P123 as soft template [42] and by adapting the procedure from Henrist et al. in order to increase the film thickness and homogeneity obtained by spin-coating [40]. The TiO₂ precursor solution was prepared by mixing a solution of P123 (1.005 g) in 1-butanol (11.2 ml) with a solution of TTIP (3.96 g) in concentrated HCl (2.07 mL) and stirring for 2 h. For a single coating, 150 μL of the resulting mixed precursor solution was deposited by spin coating on the substrate for 2 s at 1930 rpm, 2 s at 2500 rpm and finally 30 s at 6900 rpm. Between the different layers deposited, the stabilization was performed by heating the fresh film during 30 min on a hot plate pre-heated at 300 °C. The partial condensation of the inorganic network and structure stabilization (partial contraction of the film and pores merging) occurred during this step, which prevents the film dissolution during the next spin coating step. When the desired number of layers was reached, the film was then calcined during 30 min at 500 °C with a heating rate of 1 °C min⁻¹. The calcination step was required to fully condense the inorganic network, crystallize anatase and burn out all the organic residues, leading to a porous structure. The corresponding films are hereafter named “SOFT” and “mesoporous” for photoanodes synthesized by soft templating only (single pore size).

2.3. Bimodal thin film synthesis (DUAL TiO₂ films)

To avoid uncontrolled hydrolysis of the TTIP, water from the commercial PS nanosphere (62, 130 and 250 nm) suspensions was first evaporated by using freeze-drying. Anhydrous PS beads were then redispersed in butan-1-ol under ultrasonication to obtain a 10 wt% PS beads suspension. Dried PS beads do retain their original structure after the freeze drying process (Fig. S1). The PS suspension was then mixed to the previously synthesized TiO₂ precursor (section 2.2) in a 1.5:1 vol ratio and stirred for 1 h prior to deposition. For a single coating, 150 μL of the precursor solution was dropped on the FTO glass and spin-coated for 2 s at 1930 rpm, 2 s at 2500 rpm and finally 30 s at 6900 rpm. In the case of dual templating, stabilization was achieved by heating the fresh film during 30 min on a hot plate pre-heated at 150. When the desired number of layers was reached, the film was calcined during 30 min at 500 °C with a heating rate of 1 °C min⁻¹. Labels DUAL-62, DUAL-130 and DUAL-250 were used for the films synthesized with PS beads of 62, 130 and 250 nm, respectively. The terms “DUAL” and “bimodal” refer to samples containing the two populations of pores resulting from the dual templating route.

2.4. Preparation of polymer electrolyte

Polysiloxane based polymer electrolyte was synthesized by functionalization and quaternization of the poly(methylhydrosiloxane)-*co*-methylhydrosiloxane copolymer (with Si-H functionality of 15%–18%) according to a recently reported procedure [27]. The polymer and 0.05 M iodine were dissolved in a very small amount of 3-methoxypropionitrile/valeronitrile (1/1, v/v). For the sake of comparison, a reference liquid electrolyte solution was prepared with the following composition: 0.6 M 1-butyl-3-methylimidazolium iodide, 0.03 M iodine, 0.1 M guanidine thiocyanate and 0.5 M 4-*tert*-butylpyridine in acetonitrile/valeronitrile (85/15, v/v) [43].

2.5. Solar cell fabrication

SOFT and DUAL TiO₂ photoanodes were treated with 0.04 M TiCl₄

Download English Version:

<https://daneshyari.com/en/article/6531534>

Download Persian Version:

<https://daneshyari.com/article/6531534>

[Daneshyari.com](https://daneshyari.com)