



Insights into meso-structured photoanodes based on titanium oxide thin film with high dye adsorption ability



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ARTICLE INFO

Article history:

Received 13 January 2014

Received in revised form 18 April 2014

Accepted 21 April 2014

Available online 30 April 2014

Keywords:

N719 dye adsorption

Morphological properties

Surface roughness

Ordered mesoporous materials

Dye-sensitized solar cells

ABSTRACT

In this work, the absorption of N719 dye on titania films with significantly different morphologies has been investigated. By changing the synthetic approach, we have prepared sol–gel titania films with a flat surface (TiSG), mesoporous films with an ordered porous structure (TiMS) and a reference film from commercial titania P25 using the well-known doctor-blade technique (TiDB). The surface roughness and grain size distribution of titania films has been explored by atomic force microscopy. The effectiveness of the various type of titania films to absorb the N719 dye has been investigated by UV–vis spectroscopy, whereas the dye–titania interaction was examined by Raman spectroscopy. Further information on the structural and morphological properties of titania films were obtained by small angle X-ray diffraction and scanning electron microscopy. Both sol–gel and mesoporous titania films were deposited by spin-coating the solution of titania precursor, which produces films of about 300 nm, much thinner than those afforded by the doctor-blade technique (~6.8 μm). When the thickness of TiMS film was increased up to 1 μm, the absorbance of dye-sensitized titania became also higher, reaching levels similar to those of the reference N719–TiDB film in spite of its lower thickness. Our findings show that the morphological properties of titania substrates affect their ability to adsorb the N719 dye and, in particular, it was observed an enhanced dye adsorption onto meso-structured titania. N719 absorbance normalized to titania film thickness reveals that both the roughness and porosity of titania promote the dye adsorption. The much higher ability of meso-structured photoanodes to adsorb the dye can be attributed to the ordered and highly porous structure of TiMS. The photocurrent–voltage measurements of TiMS and TiDB dye sensitized films with similar thickness (~500 nm) have shown the superiority of N719–TiMS thus suggesting the key role of the mesoporous structure.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are receiving much attention since 1991 as a viable technology for the conversion of sunlight into electricity [1,2]. These devices are very promising for different applications of solar power because they offer many advantages, such as low production cost and their comparatively light overall weight [3].

In DSSCs, ruthenium bipyridyl complexes are typically adsorbed on titania substrates, thus allowing to extend the spectral response of the photoelectrode towards the visible region. The light absorption by the dye is responsible for the excitation of an electron and its subsequent injection into the conduction band of the titania.

This photoinduced electron transfer leads to the production of photocurrent and consequently it is crucial to the device efficiency.

Many factors affect the performance of the DSSCs, such as the composition and structure of the two electrodes, the type of redox electrolytes and the nature of the sensitizers. In particular, the efficiency of the dye–titania photoanode is directly related to the processes that occur at the dye/titania interface. In order to improve the energy conversion process, it is important to achieve an optimal dye loading and dye/titania interaction, which affect both the efficiency of photoinduced electron transfer from the excited state of the dye to the conduction band of the titania and the capacity of light harvesting.

In this context, many efforts have been done in developing strategies for the chemical modification of sensitizers and for the design of new dyes [4–9]. Among them, new panchromatic ruthenium dyes have recently shown a superior potential of light

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harvesting along with good conversion efficiency throughout the entire visible range and the near-infrared region, providing high photocurrent densities [5]. Natural photosensitizers have been also investigated with the aim to lower the cost of the solar cells [6,10]. However, one of the main drawbacks of the sensitizers is a still non-optimal adsorption and dispersion of the dye onto titania surface, which hinders the achievement of high efficiencies.

Besides tailoring new sensitizers with appropriate anchoring groups, it is also necessary to focus the efforts on the optimization of titania films in order to enhance the dye loading and dispersion, thus improving the efficiency of the photovoltaic devices. Some studies were recently addressed to the development of novel titania substrates for DSSCs by using different approaches, such as the introduction of dopant agents and the modification of morphological properties [11–16]. Recent findings have shown that the addition of dopant agents to titania can enhance light absorbance and promote the electron transfer with a consequent increase of energy conversion efficiency [11,12]. It was also reported that the design of bifunctional photoanodes with a double-scale morphology, which comprises a underlayer and a main layer of titania, allows to significantly improve the performance of DSSCs [13,14]. The titania underlayer film ensures a good electronic contact between the main layer and the F-doped tin oxide (FTO) conducting glass and suppresses the back-transport reaction by blocking direct contact between electrolyte and FTO. The main layer, consisting of titania hollow spheres or cluster of nanocrystallites, is responsible for an enhanced light scattering capability. Indeed, hierarchical titania structures usually exhibits excellent light scattering properties and thus enhances light harvesting and power conversion efficiency [15,16]. Some works also discussed the effect of particle size and morphology of titania nanocrystals deposited as paste by the doctor-blade technique [17,18]. In particular, it was observed that the metal-to-ligand charge-transfer (MLCT) absorption bands throughout the visible region of the spectrum, characteristic of ruthenium complexes, was red shifted with the morphology of TiO_2 nanocrystals in the order of quadrilateral < spherical < long crystals and with the increase of the particle size. The main reason is that the morphology and the size of TiO_2 nanocrystals can affect the energy level binding mode between the N719 and the TiO_2 .

In the past few years, high efficiency in DSSC has been reported for photoanode prepared by using titania paste based on Pechini sol-gel method and nanocrystalline titania powder [19]. Moreover, a novel procedure that consists in a modified Pechini method has been recently developed in our group for the synthesis of titania films [20], which have shown excellent performance in the interaction with different species (as enzyme immobilization) [21]. Since the anchorage of the dye onto titania surface has a key role in DSSC, the above-mentioned films could be promising.

In order to achieve superior performance in DSSCs, an attractive strategy is to confine the dyes into a porous structure with a well-defined size, with the aim to attain a high degree of dispersion. The confinement of the dye inside pores could avoid its aggregation and increase the surface of the dye/titania interface. One of the most common routes for the production of mesoporous oxides with high surface area is the sol-gel synthesis in the presence of organic templates, such as block copolymers [22–24]. This process offers many advantages, as low temperature, high scalability and low cost equipments. Recently, ordered mesostructured titania films have been also prepared using block copolymers as the structure-directing agents to obtain lamellar, hexagonal and cubic mesostructures [25–28]. Due to their porous structure, these films have recently shown promising efficiency for applications in DSSC [14,27,29]. Nevertheless, the influence of titania morphology on its capacity to adsorb the dye has not been exhaustively explored so far.

In the present study, the absorption of N719 dye on titania films with significantly different morphologies has been investigated with the aim to evaluate the influence of titania roughness and porosity on the dye loading and on the efficiency of the devices. By modifying the synthetic procedure, we have prepared sol-gel titania films with a flat surface (TiSG), mesoporous films with an ordered porous structure (TiSM) and a reference film prepared from commercial titania using the well-known doctor-blade technique (TiDB). The morphological properties of titania films were investigated by atomic force microscopy (AFM), whereas the extent of N719 dye absorption was evaluated by UV-vis spectroscopy. The interaction between the dye and titania was examined by Raman spectroscopy and further information on the structural and morphological properties of titania films were obtained by small angle X-ray diffraction and field emission scanning electron microscopy (FE-SEM). Moreover, the power conversion efficiency of selected films with similar thickness was investigated by photocurrent-voltage measurements.

2. Experimental

2.1. Synthesis of titania films via sol-gel

Sol-gel titania films were prepared according to a procedure described elsewhere [20], using a modified Pechini method. The solution of titania precursor was deposited on a fluorine-doped tin oxide (FTO) substrate by spin-coating at 2400 rpm for 20 s. Before the deposition of the solution, FTO glass plates (Dyesol, $15 \Omega \text{sq}^{-1}$) were cleaned in acetone using an ultrasonic bath for 30 min and then rinsed with acetone and isopropanol.

After spin coating of titania precursor, the films were annealed on a hot plate at 350 °C for 5 min and calcined in air at 350 or 500 °C for 2 h using a ramp rate of 1 °C/min. The thermal treatment allows to remove the residual organic components and induces the crystallization of titania. The TiO_2 film electrodes calcined at 350 and 500 °C were labeled as TiSG-350 and TiSG-500, respectively.

2.2. Synthesis of mesoporous titania films with soft template

Mesoporous titania films were synthesized using the Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, molar weight of 5800, Aldrich) as template in order to obtain an ordered porous structure with a controlled geometry. The titania precursor solutions were prepared according to the procedures described in the literature using Pluronic surfactant [14,28,30].

In a typical synthesis, 1.4 ml of concentrated HCl were slowly added to 2.1 g of titanium(IV) ethoxide at room temperature. In another flask, 0.65 g of P123 were dissolved in 6 g of 1-butanol and subsequently added to the titanium solution. The system was kept under stirring at room temperature for 3 h. The as-prepared solution of titania precursor was deposited on FTO conducting glass substrates (Dyesol, $15 \Omega \text{sq}^{-1}$) by spin-coating at 2400 rpm for 20 s. After aging at 25 °C for 2 days, optically uniform and transparent films were obtained. These films were calcined at 350 or 500 °C for 2 h using a ramp rate of 1 °C/min to remove the template and the residual organic precursors. The TiO_2 film electrodes calcined at 350 and 500 °C were labeled as TiMS-350 and TiMS-500, respectively.

A thicker film of TiMS-350 was prepared by using a layer of adhesive tape (3 M Magic), as mask, during the deposition by spin-coating to control the thickness of the film. The so-obtained film was labelled as TiMS-S.

2.3. Deposition of commercial titania using the doctor-blade technique

Reference titania films were prepared from commercial titania by using the doctor-blade technique, according to a procedure described elsewhere [31]. A colloidal titania dispersion was prepared by blending 2.5 g of commercial titania P25 (Degussa), 4 ml of 0.1 M nitric acid, 0.08 g of polyethylene glycol (MW 8,000) and 0.2 ml of Triton X100 (Aldrich). The resulting suspension was stirred for 2 h and subsequently ultra-sonicated for additional 2 h. The so-obtained titania paste was deposited on the FTO conducting glass (Dyesol, $15 \Omega \text{sq}^{-1}$). Two edges of the FTO glass plate were covered with a layer of adhesive tape (3 M Magic) to control the thickness of the film; successively the titania paste was spread uniformly on the substrate by sliding a glass rod along the tape spacer. The resulting mesoscopic oxide film was around 6–8 μm thick and opaque. After drying the coated plates were sintered in air for 1 h at 450 °C and labelled as TiDB.

A thinner film of TiDB was prepared depositing the titania paste by spin-coating and using a layer of adhesive tape (3 M Magic) as mask. The so-obtained film was labelled as TiDB-S.

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