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The effect of the number of calcination steps on preparing crack free titania thick templated films for use in dye sensitized solar cells

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ABSTRACT

Crack free titania thick templated films were prepared by evaporation-induced self-assembly (EISA) process and spin coating method with different numbers of calcination steps; then, their application in dye sensitized solar cells (DSSC) was investigated. Wormlike meso-layers prepared at different spin speeds were characterized by TEM analysis. The correlation between spin speed and thickness and porosity of the films were investigated using ellipsometry method. The crystallinity and surface area of the films obtained at a repeated thermal treatment method and different temperatures were investigated by XRD and BET techniques. UV–vis spectroscopy and cross-sectional SEM images were also used to characterize the films. Finally, the mesoporous thick films (5.7 μm) were used in DSSC devices and their photovoltaic performances were examined. The optimum mesoporous film exhibited an open-circuit voltage (V_{OC}) of 0.729 V, short-circuit current density (J_{SC}) of 14.93 mA cm^{-2}, fill factor of 0.68 and a power conversion efficiency of 7.35%.

1. Introduction

Dye-sensitized solar cells (DSSCs) are the most promising alternative to conventional silicon-based photovoltaic devices because of their potential for having low costs and easy manufacturing [1–9].

Normally, DSSCs are composed of a dye-adsorbed nanocrystalline TiO_2 (NC-TiO_2) thick layer (10–15 μm) on a transparent conductive oxide (TCO), electrolyte and Pt counter electrode [1].

Among different nanostructures, nanocrystalline random porous films have been most widely studied as a photoanode in DSSCs. Mesoporous TiO_2 materials are the potentially promising structures which may possibly achieve higher efficiency than NC-TiO_2 films due to their larger surface area. These materials allow more dye adsorption and hence, they have more efficient light absorption compared to NC-TiO_2 [10,11].

According to the literature, initially, Zukalova et al. built a DSSC with a mesoporous titania templated film as photoelectrode in 2005. Their 1-μm-thick mesoporous film showed enhanced solar conversion efficiency by about 50% compared to the device made from traditional random porous NC-TiO_2 films with the same thickness [10]. To improve the efficiency of these cells, numerous activities and further investigations have so far been carried out [11–16]. Although there are many different ways to make a mesoporous templated film, evaporation induced self-assembly (EISA) is the most commonly used process and endows its commonness to it high reproducibility. Dip coating and spin coating techniques are usually used to create a thin layer made of mesoporous titania materials, which is placed on the substrate in the EISA [17,18,22,24]. These thin layers provide only a low surface area of the active materials and, therefore, limit their practical applications. Thus, the increase in the film thickness using layer-by-layer deposition is a necessary prerequisite for obtaining better photovoltaic performances.

The crystallinity of the materials is also an effective factor in the DSSCs. In fact, better crystallinity leads to better photovoltaic performance of the cell and this is due to more effective electron transfer into the film and its transport towards the collecting electrode [11,15].

It should be noted that the synthetic methods employed for the preparation of meso-films by EISA suffer from a time consuming process. This process can take up to one single layer per day for dip coating [10,13,14,19] and three days for spin coating method [20,23]. In these procedures, the coated film is encountered to a relative humidity in a long time for ordering the mesostructure. Calcinations steps are also carried out in a very slow ramp rate to maintain the mesostructure which, in turn, lead to prolongation of the process. Thus, one of the major disadvantages of EISA is its excessive time consuming process. Ordered and disordered meso-films have been used as photoanode in DSSCs. In this regard, general finding in the literature have shown that disordered meso-films, known as ‘worm- like’, are appropriate films

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because of their larger surface area, more dye loading and, consequently, more efficient light absorption as compared to other meso-films [11].

Zukalova et al. prepared mesoporous thin layers and calcined them after each coating. This approach resulted in a high crystallinity with a decrease in the roughness factor after 3–5 layers, and thus the photovoltaic performances got to a plateau [13]. Also, phosphor-doping was applied to increase the crystal growth and to preserve the roughness factor. Nevertheless, the efficiency of the cells made from these films reached a plateau after eight layers with 2.3 μm thickness due to the electron-hole recombination [14]. Alternatively, titania mesoporous thick templated films were prepared with 60 spin coating cycles by Zhang et al. [15]. Stabilization stage was applied after each deposition cycle through heating the fresh film at moderate temperature on a hot plate in a few minutes. After the desirable number of layers was deposited, the calcination stage was performed to overcome the surface area limitations caused by repeated calcinations. The drawback of this work was the appearance of macro-cracks after enhancing the films thickness.

Dewalque et al. reported a dip-coating multilayer deposition following a similar heat treatment route [11]. In this protocol, fewer layers were required to get a thick film. In spite of the enhancement of dye loading and roughness factor (RF), a conversion efficiency plateau was reached after 9 layers because of decreasing the open circuit voltage (Voc) values; this was attributed to low crystallinity of films which were prepared through this method. Their results showed that wormlike meso-films were more appropriate than ordered structures in uptake of dye. In a previous work, we have also shown that wormlike meso films prepared by dip and spin coating methods had more dye loading than gridlike ordered meso films [9].

The mesoporous structure of the film was influenced by many experimental parameters such as preparation conditions of the sol and the film, among which the most studied ones were the relative humidity in dip and spin coating method [21–24,27], and also withdrawal speed in dip coating method [21,23,25–27].

As far as we know, there is no information about the relationship between the spin speed in spin coating method with thickness and porosity of the titania films. As noted, these parameters are very important in DSSCs.

In this study, however, we prepared a 5.7 μm wormlike mesoporous titania film by EISA technique using spin coating method at the shortest time. For the first time, the correlation of spin speed with thickness and porosity of the films were investigated. The crystallinity and surface area of the film obtained at the optimal spin speed were investigated at a repeated thermal treatment method and in different temperatures. Actually, we prepared three series of samples to compare the microstractural properties of the films such as crystallinity and surface area so that a calcination step was applied after every three, five and seven stabilization steps for each sample. Finally, the optimal crack free mesoporous TiO_2 thick films were used in the DSSC devices and their photovoltaic performances were evaluated. The photovoltaic performances of the cells made by the meso-TiO_2 and NC-TiO_2 photoanodes, commonly used in DSSCs, were also compared. Regarding the results, a maximum solar conversion efficiency of 7.35% for the cells made of these mesoporous films was achieved. This is an excellent photovoltaic performance for wormlike mesoporous templated photoanodes prepared by EISA and spin coating method compared to other researches in the literature, despite the notion that no doping or scattering layers were used.

2. Material and methods

2.1. Synthesis of wormlike mesoporous titania thick films

The mother solution was prepared by mixing 1-butanol (Aldrich, 36.3 g) and Pluronic P123 surfactant (Sigma-Aldrich, 4.0 g). Separately, concentrated HCl (Merck, 36 wt%, 9.7 g,) was added to tetraethyl orthotitanate (Merck, 12.7 g) under vigorous stirring, as reported previously [10]. This solution was aged by stirring at ambient temperature for at least 3 h. The films were prepared by spin coating of the solution at the spin speeds of 2000, 2500, 3000 rpm for 20 s onto substrates such as glass slides or FTO conducting glasses (Dyesol, 15 Ω sq^{-1}). To obtain wormlike mesoporous films, the relative humidity in an electronic spin coating chamber was set at 45–50% at 20 °C. Meanwhile, no humidity aging was utilized in this work which, in turn, led to saving time. The intercalation of a stabilization step between each coating cycle made deposition of several layers possible. This stabilization was done through heating the fresh film for 15 min on a hot plate pre-heated at 300 °C. This results in partial condensation of the inorganic network which prevents the redissolution of the film in the next spin coating stage. Solvent, water evaporation, partial contraction and pore merging could also be seen during the heat treatment [6]. Three series of the samples were prepared to compare the microstructural properties such as crystallinity and surface area of the films. Actually, a calcination step was applied after every three, five and seven stabilization steps denoted as S3, S5 and S7, respectively. the calcination steps were performed under air at 350 °C for 2 h (heating rate: 1 °C/min). By repeating the described procedure, thicker films were prepared. Finally, the wormlike mesoporous films were calcined under air for 1 h in the temperature range between 350 and 550 °C (heating rate: 1 °C/min) to evaluate the effect of annealing temperature on the crystallinity of the films. The final calcination step leads to fully condensing the inorganic network, increasing the nanocrystallinity of the mesoporous TiO_2 films, crystallizing the anatase phase and burning out of all surfactant residues, which causes an anatase mesoporous structure [11,15]. All the prepared thick samples were optically transparent.

For the purpose of comparing, a standard non-organized nanocrystalline TiO_2 (NC-TiO_2) photoanode was synthesized based on the method reported by Mallouk et al. [2].

2.2. Fabrication of DSSCs

The TiO_2 thick films coated on FTO substrates were sensitized by their impregnation in 0.3 mM N719 dye (Solaronix) solution in ethanol for two days. In order to prepare Pt counter electrode, a drop of H_2PtCl_6 solution (0.5 mM in isopropanol) was poured on a FTO glass and then the substrate was heated at 385 °C for 15 min under air.

The sensitized photoanode and Pt counter electrode were assembled into a sandwich-like cell. Stretched parafilm was used as a 20–30 μm spacer between the sensitized photoanode (active area of 0.25 cm^2) and platinized electrode. A drop of the redox electrolyte (0.6 M 1,2-dimethyl-3-propylimidazolium iodide, 0.05 M I_2, 0.1 M lithium iodide and 0.5 M 4-*tert*-butylpyridine and 0.1 M guanidinium thiocyanate in acetonitrile) was placed on the top of the sensitized photoanode. Finally, the platinium counter electrode was placed on the photoanode and secured using binder clips.

2.3. Characterization techniques

X-ray diffraction (XRD, Bruker D8 Advance, Cu $K_{\alpha,}$ λ = 1.54 Å, scan rate of 0.03 (2θ/s)) was used to characterize the crystalline phase and crystallinity of the films. A transmission electron microscope (TEM, Phillips-CM200) was applied to study the morphology of the titania templated films. An optical microscope (Olympus BX60) was used to show large cracks of the surface of the mesoporous film. Texture and thickness of the films were investigated by scanning electron microscopy (SEM, KYKY-EM3200). In addition, Ellipsometry analysis was used to measure the porosity and thickness of the films using a SENTECH-SENpro ellipsometer. For this purpose, porosities were calculated according to Lorentz–Lorentz equation [9].

For films thicker than 2 μm, the thickness was checked using cross-sectional SEM micrographs because ellipsometric measurements can be