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Growth of porous light scattering sub-micrometer particle films by occlusion electrolysis for dye-sensitized solar cells

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ABSTRACT

The development of new low-temperature synthetic routes for the growth of light scattering layers is an important issue notably due to their use for light confinement in active films and devices. We present the preparation of porous ZnO made of sub-micrometer sized particles by occlusion electrolysis using the zinc oxide electrodeposition route in a chloride medium. The films show strong light scattering properties. Following this preparation step, the open framework has been conformaly covered by a nanoporous nanocrystalline ZnO material electrodeposited at room temperature and an original hierarchical architecture has been developed. A consequence was a marked increase in the film surface area and a better contact between the deposited layer and the substrate. These films have been used for the preparation of dye sensitized solar cell (DSSC) photoelectrodes after their sensitization by the D149 metal-free organic indoline dye. The cell performances were dramatically increased in the presence of the secondary phase compared to the initial occluded sub-micrometer particle framework layer.

1. Introduction

The preparation of porous ZnO films has been widely studied in recent years for applications in photonics, biosensors, photocatalysis, opto-electronics and photovoltaics [1–11]. Various approaches have been proposed for the synthesis of such films. The use of synthesized preliminary particles at the nanometric or sub-micron scale is attractive since these building blocks can be optimized independently prior to the film deposition. Several techniques have been reported for their assembly as porous layers such as compression [1], screen printing [7], sol–gel [11], electrophoresis [2,6] or occlusion electrolysis [8,9]. Occlusion electrolysis consists of adding particles in a deposition bath and immobilizing them at the electrode surface by electrodepositing simultaneously a matrix of the same [8,9,12,13] or a different material [14]. The technique is soft and performed at low temperatures. Therefore, the initial properties of the particles are preserved and the deposition process is compatible with "fragile" substrates, such as lightweight flexible plastic foils, that cannot stand high temperature processing [15]. The occlusion strategy is more versatile than the approaches involving the direct deposition of material on the support because the particle preparation and the immobilization/deposition steps are separated and, furthermore, the particles and the electrodeposited matrix can be made of different materials.

Highly light scattering films are important for various applications. For instance, they have been successfully used for photon management and light pathway enlargement in the photoelectrodes of dye sensitized solar cells (DSSCs) [16,17]. Their role is to markedly improve the probability of sunlight photons to be absorbed by the dye molecules. This is especially challenging for orange-red photons that are poorly absorbed by the common dyes used with ZnO such as indoline D149 or D205 [18]. Scattering layers are classically prepared by the sol–gel method and require a high temperature sintering treatment that is not compatible with electrodeposited nanoporous ZnO films used in high efficiency solar cells. Therefore developing new techniques of ZnO light scattering layer deposition at low temperature is of importance, notably for DSSCs.

In the present paper, we describe the preparation of sub-micrometer sized ZnO particle films by occlusion electrolysis using a zinc chloride precursor and molecular oxygen for the deposition of the ZnO matrix. The films were porous with large pores. Moreover, due to the size of the particles used (about 400 nm), the films were highly light scattering. In a second step, we filled the open structure with a nanoporous nanocrystalline ZnO material and then developed original hierarchical structures. As a consequence the already developed surface area was further increased and a

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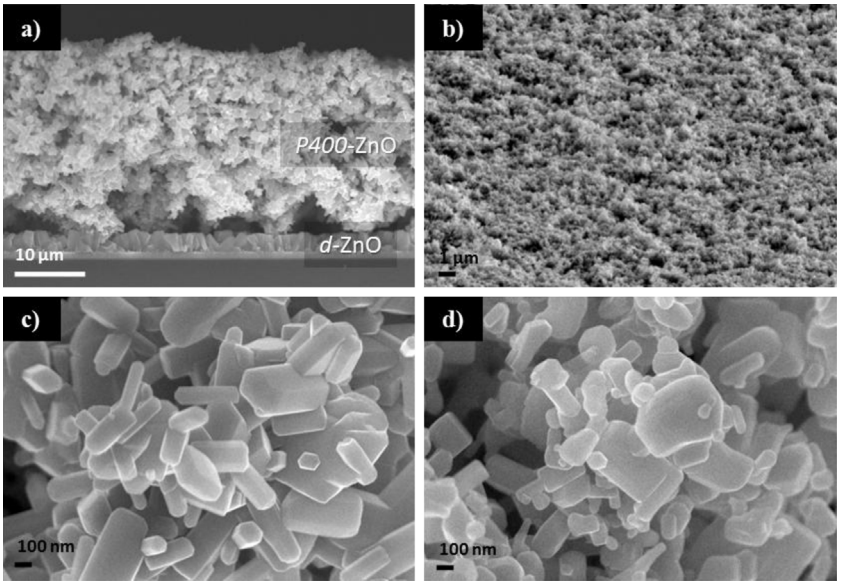

Fig. 1. (a–c) SEM views of the *P400*-ZnO film (a) cross-sectional view; (b) tilted top view; (c) enlarged view. (d) *P400* initial powder.

better contact between the deposited layer and the substrate was achieved. These films were used for the preparation of photoelectrodes after sensitization by an indoline D149 organic dye [19] and the dye-sensitized solar cells showed interesting performances.

2. Experimental

F-doped SnO_2 (FTO) coated glass sheets (TEC-10 from pilkington) were used as the substrates. They were carefully cleaned with detergent, deionized water, acetone and ethanol in an ultrasonic bath for 5 min each. The electrodeposition experiments were carried out in a three-electrode cell [20]. The reference was a saturated calomel electrode (SCE) (with a potential at +0.25 V vs NHE) placed in a separate compartment maintained at room temperature. The FTO/glass substrate was fixed to a rotating electrode and used as the working electrode. The rotation speed was first set to 300 rpm. The bath temperature was controlled at 70 °C. It contained initially 0.1 M KCl (Aldrich) as the supporting electrolyte, 5 mM $ZnCl_2$ (Merck) and was saturated with molecular oxygen by intense bubbling. The counter-electrode was a platinum wire. A thin continuous ZnO layer was then produced on the FTO for 10 min with an applied potential of −1.0 V vs SCE. Then, commercial particles (prolabo), noted *P400*, were added to the bath (8 g L^{-1}). The electrode rotation speed was reduced to 30 rpm and a magnetic barrel was added and rotated at 500 rpm to insure the particle flux toward the electrode. The deposition time was 45 min. After deposition, the film was rinsed thoroughly with milliQ water. To increase the layer surface area, a secondary phase consisting of nanocristalline ZnO was subsequently deposited as described in our previous references [10,21]. The bath contained 5 mM $ZnCl_2$ and 0.1 M KCl and its temperature was maintained at 25 °C. The electrode was rotated at 300 rpm. The applied potential was −1 V vs SCE and the deposition time was 105 min. The reflectance spectra were recorded with a Varian Cary5000 UV-vis-NIR spectrophotometer equipped with an integrating sphere using the S-position and a black mask being placed behind the sample. The films were observed by a JEOL6086 scanning electron microscope (SEM).

For solar cell preparation, after a treatment in an oven at 150 °C for 1 h, the porous ZnO films were immersed upon cooling in a sensitizing solution for 15 min. The solution contained 0.5 mM D149 dye and 1 mM cholic acid in a 1:1 volume mixture of acetonitrile/tert-butanol [18]. The counter-electrode was prepared using a FTO glass substrate and H_2PtCl_6 solution as described elsewhere [18]. The electrolyte composition was 0.05 M I_2 and 0.5 M 1,2, dimethyl, 3-propylimidazolium iodide (DMPII) in acetonitrile. For the *J–V* curves, the solar cells were illuminated with a solar simulator (Abet Technology Sun 2000) filtered to mimic AM 1.5G conditions. The illuminated surface was delimited by a black mask with an aperture diameter of 4 mm (0.126 cm^2). The power density was calibrated at 100 mW cm^{-2} by using a silicon solar cell reference. The *J–V* curves were recorded by a Keithley 2400 digital sourcemeter, using a 0.01 V s^{-1} voltage sweep rate. The R_p and R_s parameters were deduced from the *J–V* curves at 0 V and V_{oc}, respectively.

3. Results and discussion

3.1. Growth of sub-micrometer particle films by occlusion electrolysis

The electrodeposition of ZnO was performed in a chloride medium, using molecular oxygen as a precursor. This precursor was bubbled in the bath prior to and upon the electrodeposition process. The electrochemical reaction at the electrode surface was the reduction of molecular oxygen and hydroxide ion generation [22] according to the reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

Then, zinc oxide deposition occured on the electrode surface according to the reaction [23]:

$$Zn(II) + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O \quad (2)$$

Species distribution diagrams presented in our previous reference [23] show that the Zn(II) species involved at 70 °C is $ZnCl^+$. With the initial conditions used (absence of *P400* in the bath), a dense covering layer (noted *d*-ZnO) was deposited [23]. This layer can be observed on the FTO/glass substrate in Fig. 1a SEM cross-sectional view. In the present study, this dense ZnO layer had two roles: (i) it facilitated the sticking of the particles building blocks upon occlusion electrolysis and (ii), in the solar cell, it played the role of a barrier between the electrolyte and the FTO supposed limit the recombination reactions at this interface.

A layer made of the *P400* particles was then grown by adding the particles in the deposition bath and keeping the deposition

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