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Quasi-solid-state dye-sensitized solar cells employing nanocrystalline TiO_2 films made at low temperature

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ABSTRACT

Quasi-solid-state dye-sensitized solar cells with enhanced performance were made by using nanocrystalline TiO_2 films without any template deposited on plastic or glass substrates at low temperature. A simple and benign procedure was developed to synthesize the low-temperature TiO_2 nanostructured films. According to this method, a small quantity of titanium isopropoxide (TTIP) was added in an ethanolic dispersion of TiO_2 powder consisting of nanoparticles at room temperature, which after alkoxide's hydrolysis helps to the connection between TiO_2 particles and to the formation of mechanically stable thick films on plastic or glass substrates. Pure TiO_2 films without any organic residuals consisting of nanoparticles were formed with surface area of $56\,m^2/g$ and pore volume of $0.383\,cm^3/g$ similar to that obtained for Degussa-P25 powder. The structural properties of the films were characterized by microscopy techniques, X-ray diffractometry, and porosimetry. Overall solar to electric energy conversion efficiencies of 5.3% and 3.2% (under 1sun) were achieved for quasi-solid-state dye-sensitized solar cells employing such TiO_2 films on $F:SnO_2$ glass and ITO plastic substrates, respectively. Thus, the quasi-solid-state device based on low-temperature TiO_2 attains a conversion efficiency which is very close to that obtained for cells consisting of TiO_2 nanoparticles sintered at high temperature.

1. Introduction

Almost two decades ago, dye-sensitized solar cells (DSSCs) were proposed as low-cost alternatives to the conventional amorphous silicon solar cells [1], owing to the simplicity of their fabrication procedures, practically under ambient conditions with mild chemical processes. The overall efficiency of 10.4% placed DSSCs as potential inexpensive alternatives to solid-state devices [2]. For the successful commercialization of DSSCs two important factors have to be taken into account: (a) the low-cost fabrication process, which is approximately 10% (with current technology) of that needed for silicon solar cells [3], and (b) device stability, with lifetime expectancies of at least 10 years for outdoor use [3,4], which is also comparable with that of amorphous silicon. To ensure the durability of the cell, it was considered necessary to replace the liquid electrolyte with quasi-solid state [5], solid [6], polymer electrolytes [7] or p-type inorganic semiconductors [8]. Moreover, the low manufacturing cost by using roll-to-roll coating process creates the need of replacing the glass substrate with light-weighted flexible plastic electrodes, expanding this way the area of DSSCs' applications. Flexible plastic electrodes like polyethylene terephthalate sheet coated with tin-doped indium oxide (PET-ITO) appear to possess many technological advantages (no size/shape limitations, low weight, high transmittance) as they present very low production cost in relation to $F:SnO_2$ (FTO) conductive glasses. The use of such plastic substrates requires that all processes needed for the fabrication of DSSC, including the formation of TiO_2 nanocrystalline films, to be designed at temperatures lower than 150 °C. In the direction of replacing the glass substrates with flexible plastics, mesoporous TiO_2 films have to be prepared at low temperature and also with nanocrystalline dimensions for better efficiency to energy conversion [9–12]. So far, the methods that obtain the most efficient TiO_2 films for DSSCs have been based on high-temperature calcination. High-temperature annealing, usually at 450–500 °C, is necessary to remove organic material needed to suppress agglomeration of TiO_2 particles and reduce stress during calcination for making crack-free films with good adhesion on substrates [13–15]. Besides, high-temperature treatment of films promotes crystallinity of TiO_2 particles and their chemical interconnection for better electrical connection. Low sintering temperature yields titania nanocrystalline films with high-active surface area but

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relatively small nanocrystals with many defects and poor interconnection, thus lower conductivity [16,17]. High sintering temperature for TiO_2 films is then the most efficient method for the preparation of high-performance DSSCs, but it is also a cost-intensive process. In addition, high-temperature treatment of TiO_2 films cannot be applied to flexible plastic electrodes which in recent years emerge as an important technological quest. Different approaches appear in the literature to avoid high-temperature annealing of thick and porous TiO_2 films. Among a variety of methods used for the low-temperature treatment of TiO_2 films like hydrothermal crystallization [18], chemical vapor deposition of titanium alkoxides [19], microwave irradiation [20], ultraviolet light irradiation treatment [21] and sol–gel method [22], the efficiency of DSSCs employing ITO-PET substrates was in the range of 2–3% at standard conditions of $100\,mW/cm^2$ light intensities at AM 1.5 [23].

Herein, we present a very simple and benign method for the formation of pure TiO_2 nanoparticles in films without any further treatment (e.g., hydrothermal). This is an easy method for producing surfactant-free films of nanocrystalline TiO_2 at room temperature with excellent mechanical stability when deposited on glass or plastic substrates for DSSCs. According to this procedure, a small amount of titanium isopropoxide (TTIP) is added to an alcoholic dispersion of commercially available P25-TiO_2 (surface area of $55\,m^2/g$, mean average particle size of 25 nm and 30/70% rutile/anatase crystallinity) powder. The hydrolysis of the alkoxide after its addition helps to the chemical connection between titania particles and their stable adhesion on plastic or glass substrate without sacrificing the desired electrical and mechanical properties of the film. In this study, we demonstrate, for the first time, the development of a completely quasi-solid-state DSSC prepared under ambient conditions. Although many reports have focused on one aspect of the cell, such as room temperature preparation of TiO_2 films on flexible substrates [24] or solid electrolytes [25], there are no studies on the combination of DSSCs with flexible anodes employing quasi-solid-state electrolytes. We believe that the idea of a quasi-solid-state DSSC prepared at low temperature is quite attractive for industrial applications as it could bring merit to the cost reduction by manufacturing the entire cell through a roll-to-roll process.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide (TTIP), was purchased from Fluka. Poly(propylene glycol)bis(2-aminopropyl) ether MW 230, 3-isocyanatopropyltriethoxysilane, 1-methyl-3-propylimidazolium iodide, potassium iodide, iodine, hydrogen hexachloroplatinate(IV) hydrate (H_2PtCl_6) and all solvents were purchased from Aldrich and used as received. Titania powder P25 was provided by Degussa, (Germany, 30% Rutile and 70% Anatase) and Cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium (II) ($RuL_2(NCS)_2$–N3) was provided by Solaronix SA (rue de l'Ouriette 129, 1170 Aubonne VD, Switzerland). SnO_2:F transparent conductive electrodes (FTO, TEC15) $15\,\Omega/sq$ were purchased from Hartford Glass Co., USA and indium-tin Oxide/poly(ethylene terephthalate) (ITO-PET) $60\,\Omega/sq$ from IST. Double distilled water (Mega Pure System, Corning, conductivity: $18.2\,\mu S\,cm^{-1}$) was used in all experiments.

2.2. Preparation of the TiO_2 solution

One gram of P25-TiO_2 powder was added in 10 ml of ethanol followed by magnetic stirring to obtain a homogeneous dispersion. No surfactants were used as templates to the solution. TTIP was mixed in the previous dispersion in various concentrations (varied from 0.017 to 0.18 M). After several minutes, the dispersion was ready to be used either on glass or plastic substrates.

2.3. Film preparation and materials characterization

Films with effective surface area of around $1\,cm^2$ were formed on glass substrate by dip coating ($12.3 \pm 0.5\,cm\,min^{-1}$ withdrawal velocity) within 1 h after solution preparation by using an adhesive tape as a mask cut in the appropriate shape. After the adhesive tape was removed and the round area of the films was cleaned from any spoiled material, the remaining active area of our films was $0.8\,cm^2$. Films could also be formed by casting but we chose the dip-coating method for better reproducibility of film properties. All the films were left to dry in air for 5 min and then were thoroughly rinsed with distilled water several times to wash out any loose material that could be detached from the rest of the film (i.e., as-prepared films). If necessary, to remove any humidity, the TiO_2 films were left to dry in a programmable furnace (Paragon HT-22-D, Thermcraft) at 100 °C for 30 min and cooled down naturally.

A Kristalloflex D500 diffractometer (Siemens) with CuKα ($\lambda = 1.54\,Å$) radiation was employed for X-ray diffraction (XRD) study of TiO_2 crystallinity. A porosimetry apparatus (TriStar 3000, Micromeritics) was used to examine the structural characteristics of TiO_2 material. The proper quantity of TiO_2 particle samples (i.e., 0.1 g) was scraped from the TiO_2 as-prepared film and was characterized. The film morphology was examined with scanning electron microscope (SEM, Hitachi S-4000) which was also used to measure film thickness. High-resolution transmission electron microscope (HR-TEM) with field emission gun at 200 kV was used to examine the film nanostructure. Samples were dispersed in methanol (HPLC grade, Pharmco) using an ultrasonic cleaner (2510R-DH, Bransonic) for 5 min and fixed on a carbon-coated copper grid (LC200-Cu, EMS). In addition, film roughness and nanoparticle morphology were further examined with atomic force microscopy (AFM). The images were obtained with a Digital Instruments Microscope in the tapping mode.

2.4. Fabrication characterization of dye-sensitized photoelectrochemical cell

2.4.1. Dye sensitization of TiO_2 films

The TiO_2 films prepared by the above procedure on FTO glass or ITO-PET plastic substrates were immersed into an 1 mM ethanolic solution of $RuL_2(NCS)_2$ and were left there overnight. The dye-coated electrodes were copiously washed with ethanol and dried in a stream of nitrogen. Before their use in DSSC, the electrodes were left in the oven (100 °C) for 15 min to remove any ethanol or humidity that could be present in the pores of the films.

2.4.2. Preparation of gel electrolyte

For the gel electrolyte applied to the DSSCs, we used a hybrid organic–inorganic material which was prepared according to the following procedure: poly(propylene glycol)bis(2-aminopropyl ether) of molecular weight 230 and 3-isocyanatopropyltriethoxysilane (ICS; molar ratio ICS/diamine = 2) were mixed in tetrahydrofuran (THF) under reflux conditions (64 °C) for 6 h. Under such conditions, the isocyanate group of ICS reacts with the amino groups of poly(propylene glycol)bis(2-aminopropyl ether) (acylation reaction), producing urea connecting groups between the polymer units and the inorganic part. After evaporation of THF under vacuum, a viscous precursor was obtained, which was