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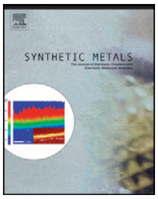

Letter

Using a molten organic conducting material to infiltrate a nanoporous semiconductor film and its use in solid-state dye-sensitized solar cells

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ABSTRACT

We describe a method to fill thin films of nanoporous TiO_2 with solid organic hole-conducting materials and demonstrate the procedure specifically for use in the preparation of dye-sensitized solar cells. Cross-sections of the films were investigated by scanning electron microscopy and it was observed that a hot molten organic material fills pores that are 10 μm below the surface of the film. We characterized the incident photon to current conversion efficiency properties of the solid TiO_2/organic dye/organic hole-conductor heterojunctions and the spectra show that the dye is still active after the melting process.

1. Introduction

Dye-sensitized nanoporous solar cells (DSCs) are an alternative to conventional silicon solar cells because of their high efficiency and potential low cost, see e.g. [1–6] and references therein. The working electrode of a DSC consists of a nanoporous film of semiconductor (usually TiO_2) nanoparticles (with diameters ranging between 10 nm and 100 nm) on a conducting glass substrate. A monolayer of dye molecules is adsorbed onto the surface of the semiconductor nanoparticles which increases the absorption of visible light by the film. The conventional counter electrode contains a conducting glass substrate and a catalytic amount of platinum. Between these electrodes a liquid electrolyte, that fills the nanoporous film completely, is used for electrical contact.

Replacing the liquid electrolyte with a solid-state hole-conductor might lead to more stable devices. Such solid-state dye-sensitized solar cells (SSDSCs), containing the hole conductor 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenyl-amine)9,9′-spirobifluorene was reported by Bach et al. to convert photons to electrons with high yield [7]. Continued research on SSDSCs comprising the same hole-conductor has improved the energy-conversion efficiencies, which today exceeds 5% [8]. Parallel research on other conceivable hole-conductors, such as triarylamine-based molecules [6,9–12] and conducting polymers [13–19] have also been conducted and functional SSDSCs have been fabricated.

A frequently used method to introduce the hole-conductor molecules into the pores of the TiO_2 is based on dissolving the hole-conductor molecules in a solvent where the solution can be introduced into the pores. However, the hole-conductor infiltrates only partially the pores using this method. The infiltration of hole-conductor can be described by the penetration depth [20] and pore-filling [21–23], where the latter resembles the volume fraction between hole-conductor and cavities. These parameters correlate to the light harvesting efficiency and it is therefore of fundamental interest to develop a preparation method in which these can be controlled [6,17]. In the following sections, we present our results on a new method to introduce a solid-state hole-conductor into a nanoporous TiO_2 film. By melting the hole-conductor into the film, we obtain a penetration depth exceeding 10 μm. For the material combinations used in current SSDSCs devices poor charge collection limit constructions with higher thicknesses. However, together with the development of new material combinations, having improved charge collection, the results reported below allow for the fabrication of thicker SSDSCs with enhanced effective light absorption properties.

2. Experimental

Working electrodes with an area of 0.20 cm^2 were prepared by doctor blading a TiO_2 paste (T37, Solaronix) onto conducting glass (back-contact) substrates covered with a TiO_2 blocking layer, created using a spray pyrolysis technique [24]. Various film thicknesses were obtained using different numbers of scotch tape as spacers. The working electrodes were sintered at 500 °C for 30 min and the film thicknesses were thereafter measured using an alpha-step 200 profilometer. Afterwards, the films were sensitized in a 0.2-mM acetonitrile solution of 3-(5-4-(diphenylamino)styryl)thiophen-2-yl)-cyanoacrylic acid, also known as D5 [25,26] (see Fig. 1a), overnight. After rinsing with acetonitrile, the working electrodes were placed on a room-tempered hotplate and a few mg of 4,4′,4′′-tris(*N*,*N*-diphenyl-amino)-triphenylamine (Sensient Imaging Technologies), see Fig. 1b, was spread on top of the dye-sensitized films. The temperature of the hotplate was then increased until the powder melted (255 °C). The melted powder was subsequently doctor-bladed to assure complete coverage of the dye-sensitized film. This simple process removes excess material and leaves a few μm thick hole-conductor layer above the TiO_2 film. The cells were thereafter immediately placed aside for cooling down to room temperature. The X-ray absorption measurements for the hole-conductor before and after the melting procedure showed very similar structures, indicating stability of the

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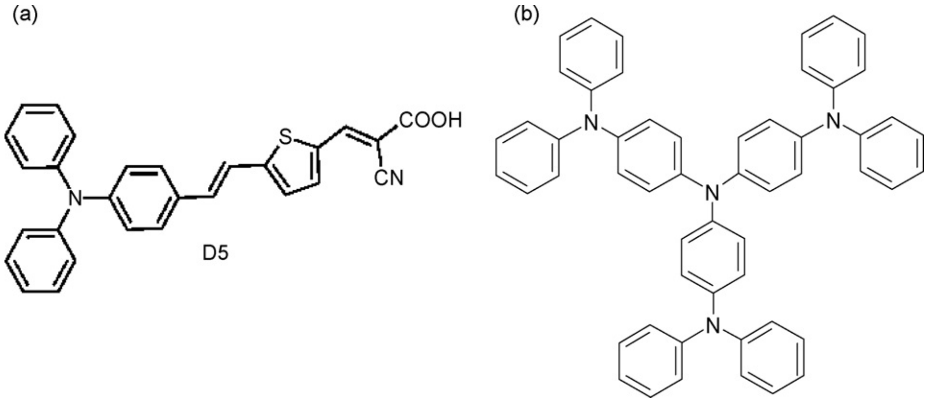

Fig. 1. (a) Molecular structure of the dye and (b) the hole-conductor.

hole-conductor in the melting procedure (see Ref. [26] for experimental details). Silver glue (Hans Wolbring) was applied on top of the hole-conductor as counter electrode. The solar cells were stored at least 24 h prior to characterization. Measurements repeated after 3 weeks (samples stored indoors and exposed to light) showed no decline in efficiency.

Devices with the same hole-conductor were also prepared by spin-coating the hole-conductor from a chlorobenzene solution (11 mM, which was close to saturation) in a procedure similar to that described in Ref. [22]. Before spin-coating (2000 rpm) the hole-conductor was deposited onto the substrate and was allowed to penetrate into the pores for 30 s. This procedure was repeated three times to try to increase the pore-filling. All other preparation steps were similar to the preparation described above.

For the scanning electron microscopy (SEM) measurements of the cross-section, the samples were cut in half by a glass-cutter on the glass side.

Incident photon to current conversion efficiencies (IPCE) were measured using a Keithley 6487 sourcemeter, a Spectral Products CM110 monochromator and a tungsten–halogen light source (Spectral Products). A General Electrics ELH 300 W light source was used for the photovoltage measurements. A Si-photodiode (Hamamatsu S1337-33BR) was used for calibration and IPCE computer software was supplied by Solarena AB. The micrographs of the cross-sections were taken by using a LEO 1550 scanning electron microscope operated at 2 kV acceleration voltage. Several SEM images of the samples were recorded, evenly distributed over the samples (the sample width was 5 mm). All images showed a very similar cross-section, which confirms that the SEM pictures shown below are representative for the entire samples.

3. Results and discussion

First, we examined the overview structure of the different layers in the SSDSC using SEM. In Fig. 2, the cross-section is shown and from the top, the different layers were identified as: non-uniform silver layer (thickness of about 1 μm); hole-conductor layer (thickness of about 3 μm); nanoporous TiO_2 layer (thickness of about 10 μm); spray-pyrolyzed TiO_2 layer (thickness of a few hundred nm); SnO_2:F layer (thickness of a few hundred nm) and glass (substrate at the bottom of the figure). All the layers are in the expected thickness range and the thickness of the hole-conductor overlayer is about 3 μm, that is, the preparation method can be used to fabricate a hole-conductor overlayer thickness to within a few μm. Fig. 3 contains a magnification taken of a nanoporous TiO_2 sample without any hole-conductor (A) together with a magnification from the top (B), middle (C) and bottom (D) part of the nanoporous TiO_2 film of the SSDSC sample containing an infiltrated hole-conductor (see cross-section in Fig. 2). The SEM images in Fig. 3A–D were acquired under identical conditions and can therefore be directly compared to each other. Thus Fig. 3A can be used to compare in more detail the clean TiO_2 nanoporous structure with the structure containing the infiltrated hole-conductor, see Fig. 3B–D, and specifically estimate the penetration depth and qualitatively the pore-filling. In Fig. 3A, the TiO_2 nanoparticles are clearly observed. In the top of Fig. 3B, the interface between the solid hole-conductor and the nanoporous structure can be observed. In the top region of the nanoporous TiO_2 structure, the hole-conductor material is well distributed throughout the network, covering the TiO_2 nanoparticles. The TiO_2 nanoparticles surfaces clearly come out less well defined in Fig. 3B–D compared with Fig. 3A. This is a direct consequence of the coverage of the particles with the hole-conductor material what makes it more difficult to determine the size of individual nanoparticles in contrast to Fig. 3A. The TiO_2 nanoparticles are observed using secondary electrons that will highlight

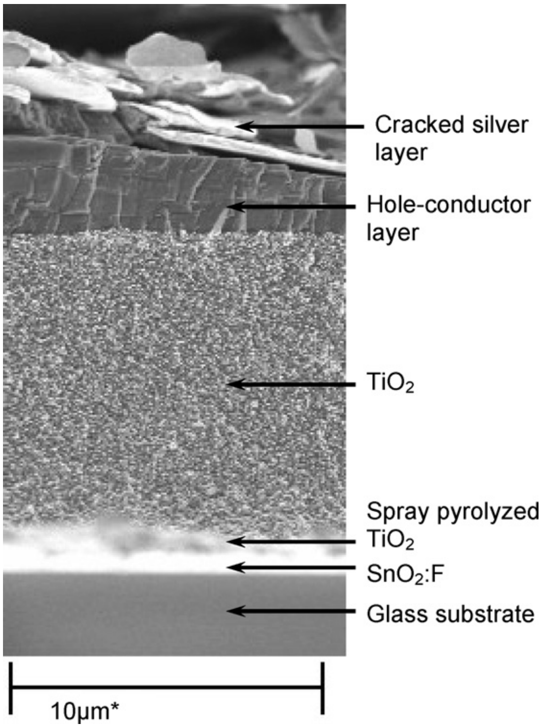

Fig. 2. SEM overview of the cross-section of a SSDSC.