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Flexible dye-sensitized solar cells based on Ti/TiO_2 nanotubes photoanode and Pt-free and TCO-free counter electrode system

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ABSTRACT

Flexible dye-sensitized solar cells (DSSCs) are getting more attention compared to standard glass covered DSSCs due to their unique commercial applications (e.g. tents or sail surfaces) and the possibility of rolling up into a small, portable device. In this work, titania nanotubes (TiO_2 NT) modified with titania nanoparticles (TiO_2 NP) were photoelectrochemically characterized as an anode for flexible dye-sensitized solar cells. The morphology of the prepared electrode materials was inspected using scanning electron microscopy. Electrochemical activity of titania in contact with anaqueous electrolyte containing iodine species was investigated using cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA). The anode with deposited TiO_2 NP exhibits enhanced efficiency of photocurrent generation in comparison to pure titania NT. The new type of comb-shaped Ti electrode with poly(3,4-ethylenedioxythiophene):poly(2-styrenesulphonate) (pEDOT:PSS) layer deposited onto the PET foil substrate was proposed as a counter electrode and compared with a conventional Pt catalytic layer as well as with a typical Pt/FTO counter electrode. Overall photoconversion efficiency of pEDOT-based counter-electrode DSSC reached 0.61% and was almost 40% higher than for counter electrode with Pt.

1. Introduction

Since the breakthrough paper by O'Regan and Grätzel in 1991 [1] dye-sensitized solar cells (DSSCs) are considered as a promising photovoltaic technology mainly due to utilization of low-cost materials and relatively high energy conversion efficiency. A typical DSSC consist of two electrodes deposited onto transparent conductive oxide (TCO) glass substrates and a liquid electrolyte containing I^-/I_3^- active redox centers between them. A dye-sensitized porous nanocrystalline TiO_2 film forms the anode while a thin catalytic platinum (Pt) layer acts as a counter electrode [2]. To date the photoconversion efficiency of over 14% for a standard [3] and almost 9% for a flexible [4] DSSCs has been reported. To reach the demands of industry for novel applications in building-integrated systems, a roll-to-roll mass production of flexible dye-sensitized solar cells have become an interesting opportunity [5]. Another important issue is the total production cost of a DSSC module. It has been reported that the cost of TCO glass substrates is more than 20% of the cost of the entire device [6]. Moreover, the platinum layer (besides excellent catalytic properties) stays also as a cost determining element, and the price for platinum, a noble metal, fluctuates strongly with the political and economic situation [7,8]. Therefore, lightweight, inexpensive, flexible and TCO-free substrates such as plastic (mainly polyethylene terephthalate, PET) or metal (titanium, Ti) or stainless (steel, StSt) foil provide a good alternative [5,9,10]. As the anode a Ti foil is usually used, mainly due to its superior corrosion resistance of passive TiO_2 film [11,12], while StSt or Ti mesh with carbon-based [13] or conductive polymer (usually a poly(3,4-ethylenedioxythiophene)) are utilized as the counter electrode [14,15].

In this paper we report on a flexible, dye-sensitized solar cell consisting of a photoanode formed by titanium dioxide nanotubes grown directly onto Ti plate and then modified with TiO_2 nanoparticles. The comb-shaped Ti pattern deposited onto PET foil forms a counter electrode (Fig. 1). Instead of the commonly used platinum layer, a thin pEDOT:PSS film was applied and tested. Performed electrochemical studies allowed to compare the activity of titania nanotubes with and without deposited TiO_2 nanoparticles which should improve photocurrent and photovoltaic performance [16–18]. The catalytic properties of pEDOT thin film deposited on counter electrode was tested and compared with a conventional Pt catalytic layer. Finally, the overall photoconversion efficiency of complete DSSC device was measured under the standard illumination conditions.

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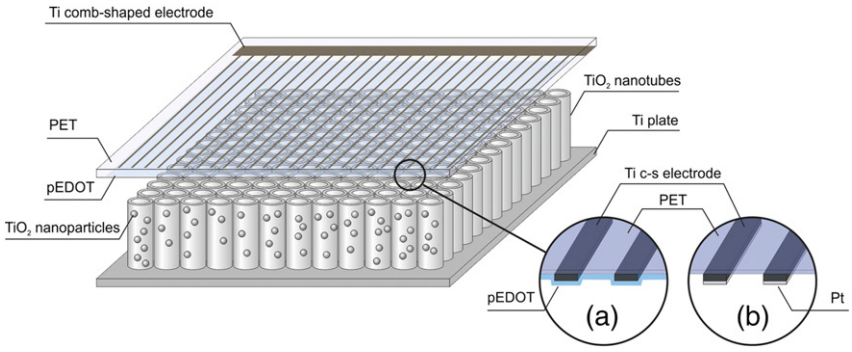

Fig. 1. Schematic diagram of a flexible dye-sensitized solar cell. Close-up of a counter electrode with indicated (a) pEDOT:PSS and (b) Pt cathodic layer.

2. Experimental

2.1. Ti/TiO_2 NT/TiO_2 NP anode preparation

Highly ordered titania nanotubes were prepared via a two-step electrochemical anodization of a Ti plate (Strem, 99.7%) in a fluoride-containing solution. The procedure that leads to the formation of TiO_2 nanotubes was described in our previous report [19]. Anodization was performed in a two-electrode configuration with a platinum grid as a cathode and the Ti plate acting as an anode. Both steps of anodization were performed under the same conditions: temperature (23 °C), electrolyte composition (0.27 M NH_4F in 1%/99% v/v water/ethylene glycol solution) and process parameters (40 V, 2 h). After the first step of anodization, the as-formed nanotubes were removed by overnight etching in an oxalic acid solution (0.5 wt.%). Afterwards, the second anodization process was performed. To remove surface debris, the titanium plates covered with nanotubes were immersed in 0.05 wt.% HF for 180 s. The as prepared amorphous TiO_2 nanotubes were transformed into the anatase crystalline phase by thermal annealing in a tube furnace at 450 °C for 2 h (heating rate 2 °C min^{-1}). In order to decorate nanotubes by titania nanoparticles the annealed electrodes were treated with 40 mM $TiCl_4$ aqueous solution at 75 °C for 30 min, washed with deionized water, and heated again up to 450 °C for 2 h (heating rate 2 °C min^{-1}). After cooling down to 80 °C the electrodes were immersed in a $1 \cdot 10^{-4}$ M solution of N719 dye (Solaronix) in absolute ethanol at room temperature overnight in order to perform sensibilization process of titania surface by dye molecules.

2.2. Ti/PET counter electrode preparation

Counter electrodes (CE) were fabricated by magnetron sputtering (Quorum Q150T) of 100 nm thick Ti layer, through a comb-shaped shadow mask, onto PET foil substrate. The titanium strips having a width of 100 μm arranged in a 1 mm-parallel in intervals were connected to the collecting electrode (Fig. 1). During investigation two different catalytic layers deposited onto CE were compared: a) pEDOT conductive polymer deposited by electrochemical polymerization and b) platinum (Pt) layer (10 nm thick) magnetron sputtered similarly as Ti (compare Fig. 1a and b). Moreover, those two counter electrodes were compared with a typically used Pt/FTO electrode prepared by a thermal decomposition of H_2PtCl_6 (450 °C for 30 min).

The electrochemical deposition of pEDOT:PSS was performed from an aqueous solution containing 0.1 M NaPSS and 0.001 M EDOT, by potentiostatic polymerization at the potential of 1.2 V vs. Ag/AgCl (0.1 M KCl) consuming the charge of 50 mC cm^{-2}. The Ti/PET constituted as a working electrode while a platinum mesh was used as a counter electrode. Finally, the working comb-shaped electrode was washed with deionized water and dried in air.

2.3. Cell assembly

A DSSC flexible device was assembled from the photoanode and the counter electrode connected using 60 μm thick, hot-melted, ionomeric foil (Solaronix), and an electrolyte was injected within a hole in the photoanode which was afterwards sealed with an adhesive tape. The redox electrolyte consisted of 0.6 M 1-propyl-3-methyl-imidazolium iodide (Aldrich), 0.03 M iodine (POCh), 0.1 M guanidine thiocyanate (Aldrich) and 0.5 M 4-tert-butylpiridine (Aldrich) in acetonitrile (POCh) [8].

2.4. Electrodes characterization

Electrochemical measurements (CA, CV, LSV) of TiO_2 NT anodes with and without TiO_2 NP were carried out using an AutoLab PGStat 302N potentiostat-galvanostat system (Methrom, Autolab) in a standard three-electrode setup with prepared electrode materials serving as the working electrodes (geometric surface area in contact with electrolyte equals 0.3 cm^2). The deaerated 0.5 M aqueous solution of K_2SO_4 was used as an electrolyte. An electrochemical cell was equipped with a quartz window enabling illumination of the electrode surface during photoelectrochemical measurements. The photoactive layers were irradiated with a 150 W Xenon lamp (Osram XBO 150) equipped with AM 1.5 filter. An automated light chopper with a period of 20 s was used for modulation of illumination. The irradiance of incident light was measured using a Si reference cell (ReRa) to be 100 mW cm^{-2}. The photocurrent measurements were carried out at +0.5 V vs. Ag/AgCl (0.1 M KCl). The photovoltaic characteristic of the cells was registered under the same illumination conditions (without the chopper) and photocurrent density-photovoltage (J-V) curves were recorded on a SourceMeter (2400, Keithley). Solar cells were tested under back side illumination, i.e. through the counter electrode. The transmittance spectrum of a PET foil and FTO was measured on a Lambda 35 UV–vis spectrometer (Perkin Elmer), while comb-shaped Ti electrode light transmittance (LT) was calculated from the following formula [20]:

$$LT(\%) = \frac{\frac{1}{2}TB \times TL}{\frac{1}{2}TB \times TL + 4 \times \left(\frac{1}{2}W\right) \times \sqrt{\left(\frac{1}{2}TB\right)^2 + \left(\frac{1}{2}TL\right)^2}} \times 100\%, \quad (1)$$

where: TB = 1 mm, TL = 4 mm and W = 100 μm. The cyclic voltammograms of counter electrodes: pEDOT/Ti and Pt/Ti were measured in a three-electrode electrochemical configuration using the same setup as for photoanode characterization. The pEDOT/Ti (or Pt/Ti) was applied as a working electrode, while a Pt mesh as a counter electrode and an Ag/AgCl cell as a pseudo-reference electrode immersed in an acetonitrile solution of 10 mM LiI, 1.0 M I_2 and 0.1 M $LiClO_4$, as used in Ref. [14]. The surface morphology and the cross-section of Ti/TiO_2