Nano Energy (2015) 12, 501–509

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy

ELSEVIER

RAPID COMMUNICATION

High efficiency flexible fiber-type dye-sensitized solar cells with multi-working electrodes

Jia Liang[a,b], Gengmin Zhang[a,c,*], Wentao Sun[a], Pei Dong[b]

[a]*Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing 100871, China*
[b]*Department of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston, TX 77005, United States*
[c]*SIP-UCLA Institute for Technology Advancement, Suzhou 215123, Jiangsu Province, China*

Received 3 September 2014; received in revised form 9 January 2015; accepted 10 January 2015
Available online 21 January 2015

KEYWORDS
Multi-working electrodes;
Flexible;
TiO_2 nanotube arrays;
Dye-sensitized solar cells

Abstract
Novel flexible fiber-type dye-sensitized solar cells (FF-DSSCs) with multi-working electrodes (MWFF-DSSCs) have been developed. In each MWFF-DSSC, all the components are assembled into a flexible plastic capillary tube. A Pt microwire along the axis of the tube is used as the sole counter electrode and a number of Ti microwires surrounding it, which are all covered with highly ordered titanium dioxide (TiO_2) nanotube arrays, are jointly used as the working electrodes. This new configuration brings about good flexibility, capability of harvesting light from all directions and a conversion efficiency competitive with those of the conventional DSSCs. The photovoltaic performances of the MWFF-DSSC with six working electrodes (MWFF-DSSC(6)) are better than those of the MWFF-DSSCs with two to five working electrodes (MWFF-DSSC(x), x=2, 3, 4, or 5) and the FF-DSSC with a single working electrode (SWFF-DSSC). When the as-prepared TiO_2 nanotube arrays are used as the working electrodes, a 6.6% conversion efficiency is obtained from an MWFF-DSSC(6). When the TiO_2 nanotube arrays are treated in the niobium isopropoxide solution, the conversion efficiency is further raised to 9.1% and only suffers a 6.6% relative decrease even under a 180° bending.

Since its invention in 1991, the dye-sensitized solar cell (DSSC) has attracted significant attention as a promising photovoltaic device due to its low cost and convenience in fabrication [1]. So far, tremendous efforts have been devoted to the fundamental and experimental researches on the DSSCs for improving their power conversion efficiencies and compatibilities to practical applications [2]. A conventional

*Corresponding author at: Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing 100871, China
Tel.: +86 10 62751773; fax: +86 10 62762999.
E-mail address: zgmin@pku.edu.cn (G. Zhang).

http://dx.doi.org/10.1016/j.nanoen.2015.01.023
2211-2855/

DSSC is made up of a photoanode (also termed as a working electrode), a counter electrode and an electrolyte filled in the space between them. Generally, the photoanode is a fluorine-doped tin oxide (FTO) glass substrate covered with a dye-sensitized titanium dioxide (TiO_2) film and the counter electrode is a platinized conductive glass [3]. The eventual performance of a DSSC is a synergistic effect of all these components [4–11].

Recently, researchers have been increasingly interested in the flexible DSSCs, which feature lightweight, low cost roll-to-roll process and extensive application perspectives. Such substrates as conducting plastics, metal sheets, and metal wires are used in the flexible DSSCs [6,12–19]. Among them, the metal wires are considered to be more promising than the relatively poorly conducting flexible plastics and opaque metal sheets. Thus the flexible fiber-type dye-sensitized solar cells (FF-DSSCs) based on metal wires are very attractive [20–28]. Although the FF-DSSCs have already exhibited good performances, there is still room for further improvement. First, the use of a platinum (Pt) microwire as the counter electrode sacrifices the advantage of low cost of an FF-DSSC. Second, in the calculation of the conversion efficiency of an FF-DSSC, the product of the diameter and effective length of the working electrode is usually used to represent the cross section of the incident light [6,17–28]. That is, only the light incident to the flank side of the working electrode is taken into consideration and the light incident to other part of an FF-DSSC is ignored. Because the light incident to the part other than the working electrode, which is not utilized effectively, is not included in the computation, the denominator in computing the conversion efficiency is unreasonably underestimated. In contrast, in a conventional DSSC, the photoanode receives all the light incident to the cell. Therefore, for a more reasonable comparison with the conventional DSSCs, the product of the diameter and effective length of the capillary tube, rather than the working electrode, should be used to represent the cross section of the incident light [29]. Accordingly, if the Pt counter electrode can be utilized more efficiently, i.e., larger photocurrent can be extracted from a single Pt microwire, and all the light incident to an FF-DSSC can be utilized, the performances of the FF-DSSCs will probably be further improved.

In this context, FF-DSSCs with multi-working electrodes (MWFF-DSSC(x), x=2, 3, 4, 5, and 6) were designed. As shown in Fig. 1, an MWFF-DSSC(6) contained a Pt microwire counter electrode and six Ti microwire working electrodes. The Ti microwires had been submitted to two-step anodization beforehand and were thus covered with highly ordered titanium dioxide (TiO_2) nanotube arrays. Then they were sensitized with dye molecules. All the electrodes were inserted into a flexible plastic capillary tube with the sole Pt microwire counter electrode surrounded by the six Ti microwire working electrodes. Subsequently electrolyte was injected into the plastic tube. When the Ti microwires covered with as-prepared TiO_2 nanotube arrays were used as the working electrodes, an MWFF-DSSC(6) exhibited obviously higher conversion efficiency than other MWFF-DSSC(x)s (x=2, 3, 4, or 5) and the FF-DSSC with single-working electrode (SWFF-DSSC) in this work. When the TiO_2 nanotube arrays were treated in niobium isopropoxide solution, the conversion efficiency was further improved. Moreover, the high conversion efficiency did not suffer considerable loss under bending.

Similar to the previous works in this lab, TiO_2 nanotube arrays with good orderliness and alignment were obtained by the two-step anodization process [22,30]. Fig. 2a and b shows the top and side view scanning electron microscopy (SEM) images of a typical TiO_2 nanotube array. The nanotube array has a neat and tidy surface and nanotubes in it are uniform in size and alignment. As described in the previous work in this lab, this good orderliness played a favorable role in guaranteeing the good performance of the DSSCs [22]. In the X-ray photoelectron spectroscopy (XPS) results shown in Fig. 2c, the C 1s photoelectron line, which is found in the spectra of all the samples and generally believed to have arisen from adventitious carbon caused by exposure to the atmosphere, is used as the standard for calibration during data processing. In accordance with the previous results in this lab, with the energy of the C 1s line set at 284.6 eV, the energies of the Ti $2p_{1/2}$ and $2p_{3/2}$ lines are identified [22,31]. The oxygen-related lines can also be easily identified. The spectra of both the as-prepared samples and the samples treated in niobium isopropoxide are dominated by the Ti and O lines, confirming that elemental titanium and oxygen were the major elements on all the surfaces of the working electrodes. An analysis on the chemical shifts of the Ti lines suggests that the Ti element existed in the form of TiO_2. In the spectrum acquired from the TiO_2 nanotube array treated with niobium isopropoxide, two lines at 209.7 and 206.8 eV are assignable to Nb $3d_{3/2}$ and Nb $3d_{5/2}$, respectively, indicating that the surface of the TiO_2 nanotube arrays were covered with niobium pentoxide (Nb_2O_5) after the niobium isopropoxide treatment [22,31]. In the X-ray diffraction (XRD) patterns shown in Fig. 2d, all the diffraction peaks are consistent with the anatase phase of TiO_2 (JCPDS no. 21-1272). The absence of Nb_2O_5 peak in the sample treated with niobium isopropoxide is attributed to the thinness of the Nb_2O_5 barrier layer [22,31].

Three types of FF-DSSCs were assembled: (i) an SWFF-DSSC based on an as-prepared TiO_2 nanotube array, (ii) MWFF-DSSC(x)s (x=2, 3, 4, 5, and 6) based on as-prepared TiO_2 nanotube arrays and (iii) an MWFF-DSSC(6) based on Nb_2O_5-covered TiO_2 nanotube arrays. They were all 1.7 cm in length. The SWFF-DSSC and MWFF-DSSC(6), in either the straight or the bending form, are shown in Fig. 3.

As shown in Fig. 3a and b, the working and counter electrodes were extracted at the two ends of the cell in both the SWFF-DSSC and MWFF-DSSC(6). The difference between them was that the SWFF-DSSC contained only one Ti microwire working electrode and the MWFF-DSSC(6) contained six. In the measurement of their photovoltaic performances, the six working electrodes in the MWFF-DSSC(6) were connected together outside the cell using soldering tin, so that the photoelectrons generated on all the working electrodes were utilized. Moreover, as the sole Pt counter electrode was shared by the six Ti working electrodes in the MWFF-DSSC(6), larger photocurrent could be extracted from the Pt counter electrode in the MWFF-DSSC(6) than from that in the SWFF-DSSC. In this sense, the cost on Pt material consumed by per unit current was reduced. As shown in Fig. 3c and d, the MWFF-DSSC(6) was as flexible as the SWFF-DSSC and they were both competitive with the previously reported FF-DSSCs in terms of flexibility [19–22].

The relations between the photocurrent densities (J) and the voltages (V) of the SWFF-DSSC and Nb_2O_5-free MWFF-DSSC(x)s (x=2, 3, 4, 5, and 6) were measured and are given in Fig. 4a.