Materials Letters 119 (2014) 28–31

Contents lists available at ScienceDirect

Materials Letters

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

Efficient dye-sensitized solar cell from spiny polyaniline nanofiber counter electrode

Xiaoxu Chen, Qunwei Tang*, Benlin He

Institute of Materials Science and Engineering, Ocean University of China, Qingdao 266100, Shandong Province, China

ARTICLE INFO

Article history:
Received 18 November 2013
Accepted 24 December 2013
Available online 31 December 2013

Keywords:
Composite materials
Energy storage and conversion
Nanocomposites
Solar energy materials

ABSTRACT

We demonstrate here the growth of spiny polyaniline (PANi) nanofibers on Pt layer through a stepwise control of current density and employment as CE in DSSC. The superiority of this new nanostructure is evaluated by electrochemical characterizations. The resulting PANi nanostructures give an enhanced electrocatalytic activity toward iodides. Careful examination of data and characterizations indicates that the promising properties are impressive to fulfill the task of CEs. A promising power conversion efficiency of 7.66% is obtained in Pt/spiny PANi nanofiber CE in comparison with 5.89% from Pt-only CE and 6.30% from traditional PANi nanofiber CE. This strategy provides new opportunities for fabricating highly efficient DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs), electrochemical devices converting solar energy to electricity characterized by high conversion efficiency, relatively low fabrication cost, zero pollutant emission, and good durability, are honored as promising solution to energy depletion, environmental pollution, and ecological destruction [1]. A typical DSSC comprises a dye-sensitized TiO_2 photoanode, a redox electrolyte containing I^-/I_3^- couples, and a counter electrode (CE). CE is a key component in a DSSC to transfer electrons arriving from external circuit and recover iodides into their base state [2]. The combination of Pt and conducting polymers such as polyaniline (PANi) is believed as an efficient route in enhancing the electrical and electrochemical performances of DSSCs [3]. Electroactive and chemically active PANi nanostructures are highly desirable for applications in DSSCs [4]. The high surface area and high porosity associated with the open nanostructures usually translate into high efficiency for the nanodevices. Electrochemical methods, such as cyclic voltammetric technique, have been widely used for preparing PANi nanofibers with open nanostructure [5]. However, the random pore structures and misalignment of the PANi are not ideal for high power conversion efficiency and fast kinetics. Efficiency of only ~6.5% has been obtained from electrochemical deposited PANi nanofiber CEs [4–6].

In search for more robust PANi CEs, here we report the attainment of spiny PANi nanofibers on a layer of Pt through a stepwise electrochemical deposition as CEs in DSSCs. Results suggest that the spiny PANi nanofiber CE has a much higher charge-transfer kinetics and promotion effect on efficiency enhancement of DSSCs.

2. Results and discussion

Growth of spiny PANi nanofibers: A thin layer of Pt coating was electrodeposited on an FTO glass substrate ($12\ \Omega\ cm^{-2}$) by a potentionstatic method with a potential of -0.3 V for 400 s at room temperature. The supporting electrolyte was a mixing solution consisting of 1 mM H_2PtCl_6 and 20 mM HCl. The growth of spiny PANi nanofibers was carried out by a stepwise control of current density on a conventional CHI660E setup comprising an Ag/AgCl reference electrode, a CE of platinum sheet, and a working electrode of FTO glass supported Pt. This process involved: $0.08\ mA\ cm^{-2}$ for 0.5 h, followed by $0.04\ mA\ cm^{-2}$ for 3 h and another 3 h at $0.02\ mA\ cm^{-2}$.

Assembly of DSSCs and photovoltaic test: Dye-sensitized TiO_2 anode was designed according to reference [7]. The DSSC was fabricated by sandwiching the dye-sensitized TiO_2 anode and FTO supported Pt/spiny PANi nanofiber CE filled by liquid electrolyte. The photovoltaic test of the DSSCs was carried out by measuring the current–voltage (*J–V*) characteristic curves using an Electrochemical Workstation under irradiation of a simulated solar light from a 100 W Xenon arc lamp (XQ-500 W) in ambient atmosphere. The incident light intensity was controlled at $100\ mW \cdot cm^{-2}$ (AM1.5).

3. Results and discussion

The growth of spiny PANi nanofibers on Pt layer involves three steps and the deposition process is shown in Fig. 1a. It is expected

* Corresponding author. Tel./fax: +86 532 66781690.
E-mail address: tangqunwei@ouc.edu.cn (Q. Tang).

0167-577X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.matlet.2013.12.094

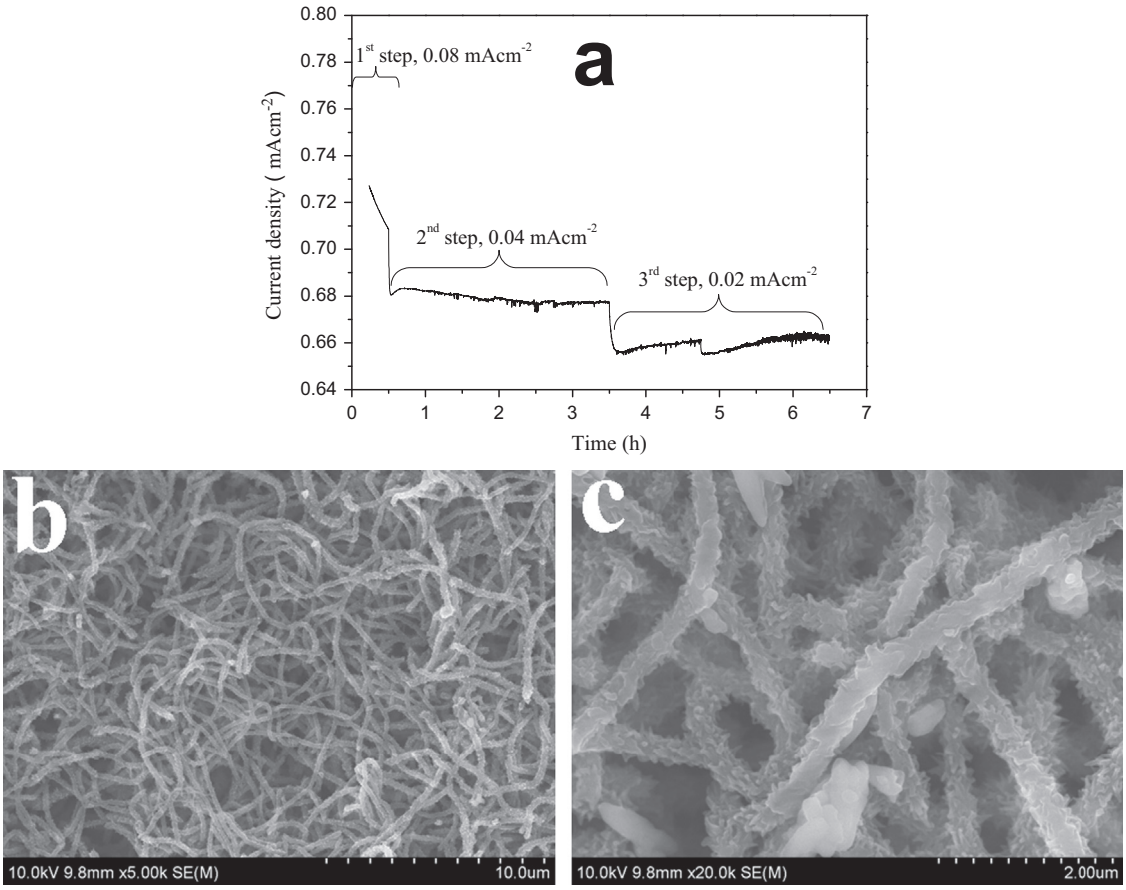

Fig. 1. (a) *i–t* curves for growth of spiny PANi nanofibers on Pt layer, and SEM photographs of spiny PANi nanofibers at (b) low- and (c) high-magnifications.

that the PANi nanoparticles deposited in the first step are nucleation sites for growing of spiny nanofiber structures in the second and third deposition steps with a reduced current density [8]. The PANi films prepared by the proposed method appear to be fairly uniform by visual inspection. The SEM photographs of the spiny PANi nanofibers are shown in Fig. 1b and c, suggesting that the resultant PANi are composed of nanofibers decorated with spiny structures. Different from cyclic voltammetric method deposited PANi nanofibers, the plenty of spiny structures provides high specific surface area and anchoring sites for iodide reduction. Moreover, the porous structure is expected to enhance the loading and to facilitate the migration of I^-/I_3^- redox couples within CE.

The CV curves reflecting electrocatalytic activities of Pt/spiny PANi nanofiber CE, Pt-only CE, and traditional PANi nanofiber CE on I^-/I_3^- redox species are shown in Fig. 2a. The peak positions and shapes of the CV curve from Pt/spiny PANi nanofiber CE is very similar to that of Pt, revealing that Pt/spiny PANi nanofiber CE has a similar electrocatalytic activity to Pt CE. The electroreduction reaction of $I_3^- + 2e \rightarrow 3I^-$ can be employed to elevate the electrocatalytic activity of Pt/spiny PANi nanofiber CE because of its task of reducing redox species. Notably, the combination of spiny PANi with Pt significantly increases the peak current density and therefore electroreductive behavior to I^-/I_3^- redox. To elucidate the relationship between increased bonding sites and diffusion of iodide in a complex CE, Randles–Sevcik theory is employed and presented [9]:

$$J_{red} = Kn^{1.5}ACD_n^{0.5}v^{0.5}$$

where J_{red} is the peak current density of Red_1 ($mA\,cm^{-2}$), K is 2.69×10^5, n is the number of electrons of reduction reaction, A is the electrode area (cm^2), C represents the bulk concentration of I_3^-($mol\,L^{-1}$), D_n is the diffusion coefficient ($cm^{-2}\,s^{-1}$). The diffusivity of Pt/spiny PANi nanofiber CE is $3.77 \times 10^{-5}\,cm^{-2}\,s^{-1}$ which is comparable to $2.75 \times 10^{-5}\,cm^{-2}\,s^{-1}$ of Pt-only CE and $9.41 \times 10^{-6}\,cm^{-2}\,s^{-1}$ of traditional PANi nanofiber CE [10]. Results indicate that the enhanced bonding sites between spiny PANi nanofibers and Pt can accelerate both charge transfer and iodide species within Pt/spiny PANi nanofiber CE. From the stacking CV curves of Pt/spiny PANi nanofiber CE at different scan rates, one can find an outward extension of all the peaks (Fig. 2b). By plotting peak current density corresponding to $I_3^- \leftrightarrow I^-$ versus square root of scan rate, as shown in insert, linear relationships are observed. This result indicates the redox reaction is a diffusion-controlled mechanism on Pt/spiny PANi nanofiber CE [11]. This may be the result from transport of iodide species on CE surfaces.

Nyquist plots in Fig. 2c illustrate impedance characteristics of Pt/spiny PANi nanofiber CE, Pt-only CE, and traditional PANi nanofiber CE. A much lower series resistance (R_s, intercept on the real axis) and charge-transfer resistance (R_{ct}, the first arc) at CE/electrolyte interface are recorded in Pt/spiny PANi nanofiber CE in comparison with traditional PANi nanofiber CE, indicating an enhanced charge-transfer ability. Fig. 2d shows the EIS spectra for the fresh and aged dummy cells with Pt/spiny PANi nanofiber CE. By contrast, the R_{ct} increases gradually which may be due to the failure of CE materials by corrosion of redox electrolyte.

Fig. 3 shows the photovoltaic characteristics of DSSCs from Pt/spiny PANi nanofiber CE, Pt-only CE, and traditional PANi nanofiber CE. The DSSCs employing Pt/spiny PANi nanofiber CE achieve higher J_{sc} than that fabricated using a traditional PANi nanofiber CE. This might be attributed to the Pt/spiny PANi CE having porous structure and higher specific surface area, which provides larger active surface areas for I_3^- reduction. The Pt/spiny PANi nanofiber