Journal of Electroanalytical Chemistry 775 (2016) 280–285

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Ruthenium nanofibers as efficient counter electrodes for dye-sensitized solar cells

Geon-Hyoung An [a], HyeLan An [b], Hyo-Jin Ahn [a,b,*]

[a] Program of Materials Science & Engineering, Convergence Institute of Biomedical Engineering and Biomaterials, Seoul National University of Science and Technology, Seoul 139-743, Korea
[b] Department of Materials Science and Engineering, Seoul National University of Science and Technology, Seoul 139-743, Korea

ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 14 June 2016
Accepted 17 June 2016
Available online 18 June 2016

Keywords:
Dye-sensitized solar cells
Counter electrode
Electrocatalytic activity
Ruthenium

ABSTRACT

The counter electrode has a strong influence on the photovoltaic performance of dye-sensitized solar cells (DSSCs). Thus, we introduce a novel approach where Ru nanofibers consisting of nano-sized grains are used instead of the typical Pt counter electrodes for DSSCs. The Ru nanofibers can be successfully prepared via electrospinning followed by post-calcination and hydrogen reduction. This sequential approach provides a novel nanoarchitecture. This architecture consists of nano-sized grains and a unique network structure, which affords high electrical conductivity. The resultant Ru nanofibers exhibit properties of improved photovoltaic performance: (I) lower charge transfer resistance (12.5 Ω cm^{-2}), (II) higher short-circuit current density (14.77 mA cm^{-2}), and (III) higher photovoltaic conversion efficiency (6.23%), which is comparable to a commercial Pt counter electrode. The improved photovoltaic performance of the counter electrode in the DSSC is attributed to the combined effects of small grain size which results in a high number of electrochemical sites, high electrical conductivity that leads to improved electrocatalytic activity, and a unique network structure that allows for rapid electron transfer and rapid diffusion of the electrolyte.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Since the first report in 1991, dye-sensitized solar cells (DSSCs) have been one of the more anticipated alternatives to the conventional silicon solar cells due to their low cost, relatively high solar conversion efficiency, easy fabrication, and eco-friendly nature [1–5]. In general, DSSCs are composed of a large-band-gap n-type semiconductor that serves as the working electrode, dye molecules that serve as the sensitizer, an iodide/triiodide (I_3^-/I^-) redox-coupled electrolyte and catalysts that serve as the counter electrode [6–8]. The recent research and development of DSSCs has mainly focused on the improvement of their solar conversion efficiency. Among these improvements, the counter electrode performs as the catalyst by reducing the redox species after electron injection and thereby regenerates the dye molecules [9,10]. Therefore, the ideal counter electrode in DSSCs should have a large number of electrochemical active sites, a low charge transfer resistance, and electrochemical stability [9–12]. Currently, Pt is typically used as the counter electrode because of its excellent electrocatalytic activity and high electrical conductivity [9]. However, Pt is very expensive and has limited availability [10]. Therefore, there is a desperate need to find an efficient alternative for Pt as the counter electrode material in DSSCs.

In recent years, the carbonaceous materials (activated carbon, carbon black, carbon nanotube, carbon nanofiber, and graphene), conducting polymers (PEDOT, PEDOT:PSS, PANI, and Ppy), transition metals (Co and Ni), metal and metalloid oxides (Al_2O_3, SnO_2, SiO_2, and Ga_2O_3), metal sulfides (Co_9S_8, FeS_2, SnS_2, and NiS_2), metal carbides (TiC, Cr_3C_2, and VC) and metal nitrides (TiN, VN, and ZrN) have been used as counter electrodes in DSSCs [9–14]. Among them, the transition metals are the most promising choice for the use as the counter electrode due to their rapid redox reactions which owe to their high electrical conductivity [15–17]. However, it is noted that only a few transition metals have been explored as the counter electrode of DSSCs. Among the transition metals, Ru is an attractive material for the counter electrode of DSSCs due to its high electrical conductivity, high electrocatalytic activity, and excellent electrochemical stability over a wide potential range [15–17]. In addition, the cost of Ru is much less than Pt. In addition to cost and electrochemical properties, another important characteristic of an ideal catalyst is its network structure. It is well known that a network structure consisting of one-dimensional nanofibers can provide efficient electron transfer and a rapid diffusion rate of the electrolyte, both of which are responsible for high-efficiency in DSSCs [18–21]. However, the use of Ru nanofibers, which can be

* Corresponding author at: Program of Materials Science & Engineering, Convergence Institute of Biomedical Engineering and Biomaterials, Seoul National University of Science and Technology, Seoul 139-743, Korea.
E-mail address: hjahn@seoultech.ac.kr (H.-J. Ahn).

http://dx.doi.org/10.1016/j.jelechem.2016.06.014
1572-6657/© 2016 Elsevier B.V. All rights reserved.

fabricated by electrospinning, post-calcination, and hydrogen reduction in series, has not yet been studied.

Therefore, we synthesized Ru nanofibers as an alternative to commercial Pt in DSSCs using a sequential process of electrospinning, post-calcination, and hydrogen reduction. This unique strategy allowed for the fabrication of a counter electrode with high electrical conductivity which exhibits higher solar conversion efficiency with excellent electrocatalytic activity compared to commercial Pt. These results indicate that the Ru nanofibers have great potential for being the counter electrode material for high-efficiency DSSCs.

2. Material and methods

2.1. Chemicals

Polyacrylonitrile (PAN, $M_w = 150.000$ amu), Ru(III) chloride hydrate ($RuCl_3 \cdot xH_2O$), *N*,*N*-dimethylformamide (DMF, 99.8%), and *N*-methyl-2-pyrrolidinone (NMP, 99.5%) were purchased from Sigma-Aldrich. All chemicals were used without further purification.

2.2. Synthesis of Ru nanofibers consisting of nano-sized grains

Ru nanofibers consisting of nano-sized grains were synthesized using electrospinning, post-calcination, and hydrogen reduction in sequence. Additionally, carbon nanofibers embedded with Ru nanoparticles and RuO_2-and-Ru nanofiber composites were also synthesized by omitting the post-calcination and reduction step and just the reduction step, respectively. First, 10 wt% PAN and 3 wt% $RuCl_3 \cdot xH_2O$ were dissolved in DMF with vigorous stirring for 5 h to obtain the carbon nanofibers embedded with Ru nanoparticles. For electrospinning, the feeding rate and the voltage were maintained at 0.03 mL h^{-1} and ~13 kV, respectively. The distance between the collector and a 23-gauge needle was set at 15 cm under 10% humidity in the chamber. The as-spun nanofibers were stabilized at 280 °C for 2 h in air and then carbonized at 800 °C for 2 h under a nitrogen atmosphere. In order to remove the CNF matrix, the Ru nanoparticles-embedded carbon nanofibers were calcined in air using a box furnace at 400 °C for 30 min. As a result, RuO_2-and-Ru nanofiber composites were obtained. Then, the hydrogen reduction was carried out to synthesize the Ru nanofibers consisting of nano-sized grains. We thus synthesized three types of the samples: Ru nanoparticles-embedded carbon nanofibers, RuO_2-and-Ru nanofiber composites, and the Ru nanofibers.

2.3. Characterization

The morphologies and structures of the nanofibers were investigated by field-emission scanning electron microscopy (FESEM; S-4800, Hitachi) and transmission electron microscopy (MULTI/TEM; Tecnai G^2, KBSI Gwangju Center). The crystal structures and chemical bonding states of the samples were observed using X-ray diffractometry (XRD; D/Max 2500 V, Rigaku) with CuK_α radiation in the 2θ range of 10°–90° at a step size of 0.02° and X-ray photoelectron spectroscopy (XPS; ESCALAB 250, Thermo scientific) with an AlK_α X-ray source. The XPS spectra were standardized to the C1s core level (284.5 eV).

2.4. Electrochemical characterization

The prepared samples were applied as a counter electrode for DSSCs. Pastes for the counter electrodes, which were made up of each of the resultant samples, ketjen black (KJB, Alfa Aesar), and polyvinylidene difluoride (PVDF, Alfa Aesar) at a ratio of 7:2:1 in *N*-methyl-2-pyrrolidone (NMP, Samchun), were prepared. The PVDF in the counter electrode could innovatively increase the adhesion between the Ru nanofibers and the FTO glass, leading to the improved physical stability of the counter electrode in DSSCs. [6,9,10]. The pastes were then squeeze-printed onto fluorine-doped SnO_2 glass (FTO, 8 Ω/square, Pilkington) and then dried at 100 °C for 12 h. For comparison, the commercial Pt counter electrode was prepared from a solution containing chloroplatinic acid hydrate ($H_2PtCl \cdot xH_2O$, Aldrich) and 2-propanol via spin coating and then annealed at 450 °C for 0.5 h. For fabrication of a working electrode, the TiO_2 paste was formed by mixing TiO_2 (P25, Degussa AG), hydroxypropyl cellulose (HPC, Mw ~80,000 g mol^{-1}, Aldrich), and acetyl acetone (Aldrich) in DI water. The well-dispersed pastes were coated by the squeeze-printing process and subsequently annealed at 500 °C for 1 h. After cooling, the electrode was soaked in 0.5 M solution of N719 dye (Ru-535-bisTBA, Solaronix) in ethanol for 24 h and washed with ethanol to remove the excess dye which had not been physically adsorbed. Finally, sandwich-type cells were assembled with the prepared working and counter electrode and then injected with a liquid electrolyte composed of 1-butyl-3-methylimidazolium iodide (BMII, Aldrich), iodine (I_2, Merck KGaA), guanidine thiocyanate (GuSCN, Aldrich), and 4-*tert*-butylpyridine (4TBP, Aldrich) in acetonitrile/valeronitrile (85:15 (v/v)). The catalytic activity was performed using cyclic voltammetry (CV) with a conventional three-electrode system at a scan rate of 50 mV s^{-1} from −0.3 to 1.1 V. An electrolyte containing 10 mM LiI (Lithium iodide, Aldrich), 1 mM I_2 (Iodine, Merck), and 0.1 M $LiClO_4$ (Lithium perchlorate, Aldrich) in acetonitrile was used. Electrochemical impedance spectra (EIS) was investigated using potentiostat/galvanostat (Ecochemie Autolab, PGST302N) under amplitude of 10 mV s^{-1} in the frequency range from 0.05 to 100 kHz. A solar simulator (PEC L01 with 150 W Xenon Arc Lamp, Peccell) was used to evaluate the current density-voltage (J-V) characteristics under AM 1.5G irradiation (ca. 100 mA cm^{-2}).

3. Results and discussion

Fig. 1a–c show FESEM images of Ru nanoparticles-embedded carbon nanofibers, RuO_2-and-Ru nanofiber composites, and the Ru nanofibers. All samples exhibited an interconnected network structure composed of the one-dimensional nanofibers. This structure can thus provide a rapid electron transfer and a rapid diffusion rate of electrolyte during the photovoltaic process, which results in a high photovoltaic conversion efficiency [18–21]. As shown in Fig. 1a, the FESEM images of the Ru nanoparticles-embedded carbon nanofibers showed smooth

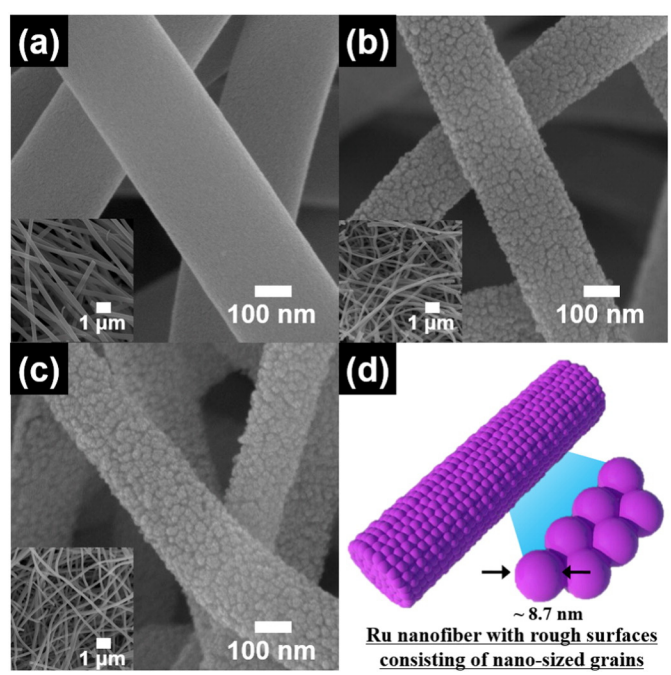

Fig. 1. FESEM images and inserted FESEM images of (a) carbon nanofibers embedded with Ru nanoparticles, (b) RuO_2-and-Ru nanofiber composites, and (c) Ru nanofibers. (d) A schematic illustration of the Ru nanofibers.

Download English Version:

https://daneshyari.com/en/article/217855

Download Persian Version:

https://daneshyari.com/article/217855

Daneshyari.com