Solar Energy 146 (2017) 125–130

Contents lists available at ScienceDirect

Solar Energy

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

Morphology-controlled growth of $NiCo_2O_4$ ternary oxides and their application in dye-sensitized solar cells as counter electrodes

Feng Du [a], Qun Yang [a], Tianze Qin [a], Guang Li [a,b,c,*]

[a] School of Physics and Materials Science, Anhui University, Hefei 230601, China
[b] Anhui Key Laboratory of Information Materials and Devices, Hefei 230601, China
[c] State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai 200050, China

A R T I C L E I N F O

Article history:
Received 18 November 2016
Received in revised form 10 February 2017
Accepted 17 February 2017
Available online 1 March 2017

Keywords:
$NiCo_2O_4$
Controlled synthesis
Counter electrode
DSSCs

A B S T R A C T

In this article, ternary oxides $NiCo_2O_4$ with morphologies of nanosheets, nanorods and nanoflowers have been synthesized by the thermal treatment of the precursors which were fabricated via a hydrothermal process. The materials were then used as counter electrodes (CEs) in dye-sensitized solar cells (DSSCs). The DSSCs equipped with $NiCo_2O_4$ nanoflowers CE achieved excellent power conversion efficiency (PCE) of 8.48%, which is higher than that of counter parts of $NiCo_2O_4$ nanosheets (3.57%), $NiCo_2O_4$ nanorods (6.84%) and Pt (8.11%) CEs. Transmission electron microscopy image shows that the $NiCo_2O_4$ nanoflowers have the best porous 3-dimensional spatial structure. This study offers a self-assembled synthetic route to prepare $NiCo_2O_4$ nanoflowers. The unique structure exhibits high efficient performance and excellent catalytic activity, which may open a new window to use ternary oxides for greatly extending potential applications in dye-sensitized solar cells and other related fields.

1. Introduction

Dye-sensitized solar cells (DSSCs), as a representative of new energy sources, have received much more attention due to their environment-friendly and electrochemistry characteristics (O'regan and Gratzel, 1991; Li et al., 2014; Hao et al., 2013; Yu et al., 2016; Chiu et al., 2016). Generally, photoanode, counter electrode (CE) and electrolyte form a typical DSSCs architecture (Thomas et al., 2014; Hagfeldt et al., 2010; Liang et al., 2016). Meanwhile, the CE plays a crucial role in the operation of DSSCs. It not only conducts the electron between external circuit and cell, but also serves as a catalyst for the reduction of I_3^-. Pt is the benchmark among all CE materials. But its deficiency and exceedingly costly severely restrict its utilization to the wholesale manufacture of DSSCs (Joseph et al., 2010; Imoto et al., 2003; Zhang et al., 2011; Jeong et al., 2014; Yue et al., 2015; Gao et al., 2016). In view of this situation, some binary oxide materials were carried out to replace Pt, such as TaO, WO_2, ZnO and Nb_2O_5, little attention has been paid to the use of ternary oxides (Yun et al., 2012; Wu et al., 2011; Chang et al., 2015; Lin et al., 2011). So many electrochemistry relevant areas reality are involved in the utilization of $NiCo_2O_4$, such as Li-ion battery, supercapacitors and electrocatalytic (Li et al., 2013; Wang et al., 2014; Cui et al., 2008). Recently, we used $NiCo_2O_4$ nanobelts anchored on reduced graphene oxide as a CE in DSSCs, demonstrating decent catalytic activity (Du et al., 2016). However, the poor intrinsic electrical conductivity and bad stability of $NiCo_2O_4$ still restrict its performance although it is higher than many other metal oxides (Sassin et al., 2013). In order to ameliorate these situations, we have optimized special structure and constructed more open channels to facilitate electron and ion by regulating the morphology.

Herein, $NiCo_2O_4$ nanosheets, nanorods and nanoflowers have been synthesized by the thermal treatment of the three individual precursors which were prepared via three different hydrothermal processes. The materials were then coated on a conducting fluorine-doped tin oxide (FTO) conductive glass to construct CEs used in DSSCs. Due to the unique structure characteristics; the DSSCs equipped with $NiCo_2O_4$ nanoflowers CE achieved excellent PCE of 8.48%, which is higher than that of $NiCo_2O_4$ nanosheets (3.57%), $NiCo_2O_4$ nanotods (6.84%) and Pt (8.11%) CEs. Furthermore, cyclic voltammetry (CV) test showed that porous $NiCo_2O_4$ nanoflowers have a great electrochemical rate of the oxidation reduction reaction. Meanwhile, for better understanding of the formation of the porous $NiCo_2O_4$ nanoflowers, time-dependent experiments were carried out by fabricating samples at different hydrothermal reaction time (3 h, 6 h, 9 h and 12 h). The PCE was increased with reaction time. It was found that the sample after 12 h hydrothermal reaction has the highest value of 8.48%. While

* Corresponding author at: School of Physics and Materials Science, Anhui University, Hefei 230601, China.
E-mail address: liguang1971@ahu.edu.cn (G. Li).

http://dx.doi.org/10.1016/j.solener.2017.02.025
0038-092X/

the PCE was 6.29%, 6.84% and 7.46% for the samples with 3 h, 6 h and 9 h hydrothermal reaction, respectively. A possible growth mechanism of $NiCo_2O_4$ nanoflowers were proposed together with observations via the transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

2. Experimental

2.1. Synthesized of $NiCo_2O_4$ nanosheets, nanorods and nanoflowers

$NiCo_2O_4$ nanosheets, nanorods and nanoflowers were synthesized by the anneal method after a simple hydrothermal treatment. In each experiment, the $NiCo_2O_4$ nanosheets reaction precursor solution embraced 1 mmol of $Ni(NO_3)_2{\cdot}6H_2O$, 2 mmol of $Co(NO_3)_2{\cdot}6H_2O$ and 8 mL 2-Aminoethanol, which were dissolved in distilled water (27 mL). The $NiCo_2O_4$ nanorods reaction precursor solution consisted of 1 mmol of $Ni(NO_3)_2{\cdot}6H_2O$, 2 mmol of $Co(NO_3)_2{\cdot}6H_2O$ and 3 mmol of hexamethylenetetramine, which were dissolved in distilled water (35 mL). The $NiCo_2O_4$ nanoflowers reaction precursor solution contained 1 mmol of $Ni(NO_3)_2{\cdot}6H_2O$, 2 mmol of $Co(NO_3)_2{\cdot}6H_2O$ and 3 mmol of hexamethylenetetramine, which were dissolved in a mixture of distilled water (5 mL) and ethanol (25 mL). The three mixtures were stirred by a magnetic stirrer for 1 h to form the transparent solutions. The solutions were transferred to three Teflon-lined stainless steel autoclaves (50 mL capacity), respectively. The autoclaves were put in an electric oven and maintained at 200 °C for 12 h. After restoring to room temperature, the products (precursor) were washed with water and ethanol several times to remove any possible ions and separated by centrifugation followed by drying in a vacuum oven at 60 °C for a couple of hours. The above as-prepared precursors were annealed at 350 °C in air for 2 h with a slow heating rate of 2 °C min^{-1} to gain the $NiCo_2O_4$ nanosheets, nanorods and nanoflowers. For the convenience of description, the as-prepared samples with different structure of nanosheets, nanorods and nanoflowers were labeled as "NCO NS", "NCO NR" and "NCO NF", respectively.

2.2. Fabrication of CE and the DSSCs

The CEs were comprised of 0.02 g ethyl cellulose powder, 0.06 g $NiCo_2O_4$ (NS, NR and NF) and 2 mL ethyl alcohol. The mixtures were ground to form colloids with an agate mortar. Then the colloids were coated on FTO glass by using a doctor-blading method with the assistance of 3 M scotch tapes to form an exposed surface of 0.5×0.5 cm^2 (Yang et al., 2014). After drying naturally, the CEs were obtained by annealing at 400 °C for 60 min with a heating rate of 5 °C min^{-1} under the protection of argon gas.

The DSSCs device was assembled with three key parts: a dye-sensitized photo anode (TiO_2), redox electrolyte and the as-prepared CEs. Thereinto, the TiO_2 films (Dalian HeptaChroma Solar Tech Co., Ltd) were dipped in N719 dye (Dalian HeptaChroma Solar Tech Co., Ltd) solution for 20 h in the darkroom, then rinsed with ethanol and naturally dried in the dark. Moreover 0.5 M LiI, 0.05 M I_2, 0.6 M 1-propy1-2,3-dimethylimidazolium iodide and 0.5 M 4-*tert*-buylpyridine in acetonitrile solution applied as redox electrolyte. The CEs include NCO NS, NCO NR, NCO NF and commercially available Pt.

2.3. Photovoltaic performance of the DSSCs

The crystalline structures of $NiCo_2O_4$ were characterized by Rigaku D/Max-2500 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 0.15406 nm). The microstructures of them were characterized by scanning electron microscopy (SEM; Hitachi S-4800) and transmission electron microscopy (TEM; JEOL, JEM-2100SX). SEM images were performed in a process of blend modes (back scattered electron and secondary electron) and at an acceleration voltage of 1 kV. TEM images were carried out in a process of MAG1 mode and at an acceleration voltage of 200 kV. In the process of TEM test, the samples were achieved by using powder method. Typically, a small amount of product was dispersed in ethanol by continuous ultrasonic treatment. Then a drop or two of the above ethanol dispersion was dropped into a copper grid. The photovoltaic performances of DSSCs were measured by using a solar light simulator (SAN-EI ELECTRIC CO., LTD, XES-402S-CE) under an illumination of 100 mW$\cdot$$cm^{-2}$ and AM 1.5 and using a Keithley 2410 digital source meter. CV tests were performed to investigate the catalytic activity of the CEs in a three-electrode system. Electrochemical impedance spectra (EIS) measurements and Tafel polarization curves were carried out by using an impedance test unit of an electrochemical workstation (ZAHNER ZENNIUM CIMPS-1) at the frequencies ranging from 0.1 to 10^6 Hz with amplitude of 10 mV.

3. Results and discussion

Crystalline structures of those there as-obtained $NiCo_2O_4$ were studied by XRD and the corresponding patterns are shown in Fig. 1. The dominant peaks at about 18.9°, 31.1°, 36.7°, 44.6°, 55.4°, 59.1° and 64.9° are unambiguously indexed as the (111), (220), (311), (400), (422), (511) and (440) crystal planes of $NiCo_2O_4$ (JCPDS Card No. 20-0781). No characteristic peaks can be detected for impurities. This indicates that the as-prepared three samples are high quality of $NiCo_2O_4$ (Wu et al., 2015; Zhu et al., 2014).

Fig. 2 shows representative SEM images of the three obtained $NiCo_2O_4$ with different magnification. It can be found that Fig. 2a and b, c and d, e and f clearly exhibit the nanosheets, nanorods and nanoflowers structure, respectively. Different sizes of nanosheets overlap and agglomerate together. As shown in the middle two images, a mass of nanorods embed and overlap each other. Observation revealed that the as-synthesized nanoflowers have a better 3-dimensional spatial structure compared with nanosheets and nanorods.

CV tests are aimed at evaluating the electrocatalytic activity of the as-synthesized there $NiCo_2O_4$ CEs and Pt CE. In Fig. 3a, the CV cures of the four electrodes reveal obvious redox peaks (Ox 1/Red 1), which can be described by the reaction of Eq. (1).

$$I_3^- + 2e^- \leftrightarrow 3I^- \quad (1)$$

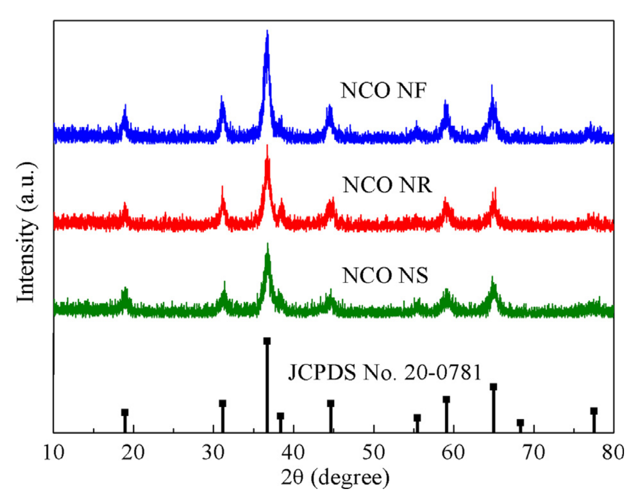

Fig. 1. XRD patterns of as-synthesized NCO NS, NCO NR and NCO NF.