Journal of Power Sources 334 (2016) 44–51

Contents lists available at ScienceDirect

Journal of Power Sources

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

Transparent conducting oxide-free nitrogen-doped graphene/reduced hydroxylated carbon nanotube composite paper as flexible counter electrodes for dye-sensitized solar cells

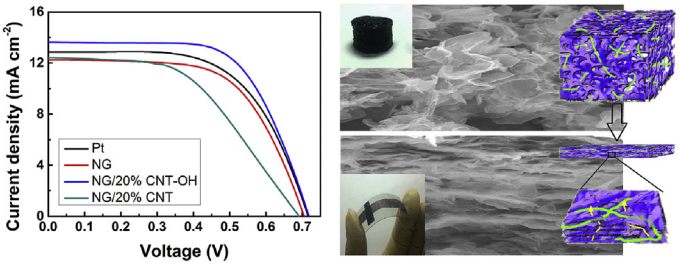
Jindan Zhang, Mei Yu*, Songmei Li, Yanbing Meng, Xueke Wu, Jianhua Liu**

School of Materials Science and Engineering, Beihang University, Beijing, 100191, China

HIGHLIGHTS

- Graphene/CNT composite aerogel (NG/CNT-OH) with hierarchical pores is synthesized.
- NG/CNT-OH has excellent carrier transport ability and high electrocatalytic activity.
- Compressed NG/CNT-OH paper is used as flexible TCO-free counter electrode for DSSC.
- The DSSC performance with NG/CNT-OH paper CE is 6.36% and is higher than using Pt CE.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 July 2016
Received in revised form
23 September 2016
Accepted 4 October 2016

Keywords:
Nitrogen-doped graphene
Carbon nanotube
Hierarchical porosity structure
Counter electrode
Dye-sensitized solar cells

ABSTRACT

Three-dimensional nitrogen-doped graphene/reduced hydroxylated carbon nanotube composite aerogel (NG/CNT-OH) with unique hierarchical porosity and mechanical stability is developed through a two-step hydrothermal reaction. With plenty of exposed active sites and efficient multidimensional transport pathways of electrons and ions, NG/CNT-OH exhibits great electrocatalytic performances for I^-/I_3^- redox couple. The subsequent compressed NG/CNT-OH papers possess high electrical conductivity and good flexibility, thus generating high-performance flexible counter electrodes (CEs) with transparent conducting oxide free (TCO-free) for dye-sensitized solar cells (DSSCs). The flexible NG/CNT-OH electrodes show good stability and the DSSCs with the optimized NG/CNT-OH CE had higher short-circuit current density (13.62 mA cm^{-2}) and cell efficiency (6.36%) than DSSCs using Pt CE, whereas those of the DSSCs using Pt CE were only 12.81 mA cm^{-2} and 5.74%, respectively. Increasing the ratio of hydroxylated carbon nanotubes (CNT-OH) to the graphene oxide (GO) in the reactant would lead to less content of doped N, but better diffusion of electrolyte in the CEs because of more complete GO etching reaction. The design strategy presents a facile and cost effective way to synthesis three-dimensional graphene/CNT composite aerogel with excellent performance, and it can be potentially used as flexible TCO-free CE in other power conversion or energy storage devices.

© 2016 Published by Elsevier B.V.

1. Introduction

There is currently a strong demand for flexible photovoltaic devices to meet the various requirements of modern gadgets [1–3]. Due to their light weight, flexibility and high conductivity, the free-

* Corresponding author.
** Corresponding author.
E-mail addresses: yumei@buaa.edu.cn (M. Yu), liujh@buaa.edu.cn (J. Liu).

http://dx.doi.org/10.1016/j.jpowsour.2016.10.012
0378-7753/© 2016 Published by Elsevier B.V.

standing carbon-based materials are promising for producing wearable or rolling-up electrodes in photovoltaic devices [4,5].

Among the available carbon materials, graphene has attracted many attentions for their outstanding electrical and catalytic properties [6,7]. It has been proved that the lattice defects and oxygen functional groups in the graphene sheets result in well catalytic activity of graphene [8,9]. However, the existence of oxidized defects would simultaneity decrease the electrical conductivity of graphene [10].

It is known that the well-dispersed carbon nanotubes (CNT) show excellent electrical conductivity and extremely large and tunable surface areas [11,12]. Therefore, introduce CNT with excellent conductivity into the graphene with excellent catalytic properties provide a promising way to obtain materials with high electrocatalytic activity and outstanding ability of carrier transport. Whereas, the hydrophobic and easy agglomerate characteristics of CNT [6,13] as well as the strong restack trend of graphene sheets [14] seriously decrease their electronic properties. Therefore, building a three dimension (3D) composite structure in which graphene and CNT are highly interconnected and interlocked is an effective way to obtain high property materials. And simultaneity, the free-standing 3D composite can be used as flexible electrode.

Graphene and CNT composites have been reported before [15,16], and in many of those researches, CNT grew on the graphene sheets to get a 3D structure through chemical vapor deposition (CVD). However, synthesis process based on CVD has high requirements for equipment and is not appropriate for large-scale manufacture.

In our previously work, 3D nitrogen-doped (N-doped) graphene aerogel was synthesized through a simple two-step hydrothermal reaction to solve the restack problem in graphene application [17]. And herein, to increase the conductivity of the synthesized aerogel further, 3D N-doped graphene/reduced CNT-OH composite aerogel (NG/CNT-OH) was synthesized with the two-step hydrothermal reaction using graphene oxide (GO) and hydroxylated carbon nanotubes (CNT-OH) as reactant. The synthesized 3D NG/CNT-OH composite aerogel was subsequently compressed into carbon paper and used as flexible counter electrode (CE) with transparent conducting oxide free (TCO-free, i.e., fluorine-doped tin oxide (FTO) or tin-doped indium oxide (ITO)) for dye-sensitized solar cells (DSSCs) to replace the usually used high-cost Pt-based [18,19] and TCO-based [20] CE. The CNT-OH is chosen as reactant for its better surface hydrophilicity than CNT, and it has the potential to disperse well with less agglomeration. The test results show that the NG/CNT-OH composite aerogel has a hierarchical porosity structure with large numbers of exposed active edge sites and excellent ion transport activity. The graphene building block has an ideal two-dimensional flat surface and the reduced CNT-OH inserts into exfoliated graphene to strengthen the electronic conductivity. Performance tests result show that the composite aerogel displays excellent electrocatalytic activity and multidimensional carrier (electron/ion) transport ability as flexible TCO-free CE for DSSCs, and the power conversion efficiency (PCE) of the DSSCs with NG/CNT-OH is even better than that of DSSCs using Pt or graphene aerogel with non-CNT as CE.

2. Experimental

2.1. Synthesis of NG/CNT-OH aerogel

GO was prepared by oxidation of natural graphite powder according to the modified Hummers' method [21,22]. The CNT and CNT-OH (contains ~3.96% −OH) were bought from BOYUGAOKE, and used without any further purification. 150 mg GO/CNT-OH mixture was dispersed in 30 mL deionized water, and the weight ratio of CNT-OH to the total mixture were 0%, 20%, 40%, 60%, 80%, 100%. Then the GO/CNT-OH aqueous dispersions were completely mixed with 90 μL hydrofluoric acid (HF, 40%) through sonication. The degree of the mixture in this process has important influence on the morphology of the products. The mixed solution was transferred to a 50 mL Teflon-lined autoclave, sealed and heated at 180 °C for 6 h. During the first hydrothermal reaction, the GO and the CNT-OH were reduced and assembled to form a reduced graphene oxide/reduced CNT-OH composite framework (G/CNT-OH). A hydrothermal process using urea as nitrogen source was processed for N-doping and further reduction afterwards. The G/CNT-OH was immersed into 0.1 g mL^{-1} urea aqueous solution in a 100 mL Teflon-lined autoclave and maintained at 180 °C for 12 h. The resulting NG/CNT-OH was then immersed in deionized water to remove any impurities for the following experiments. Then the products were freeze-dried for 8 h to obtain NG/CNT-OH composite aerogel. The yield of NG/CNT-OH compared with non-holey N-doped reduced GO is ~80%. For concentrations of CNT-OH ranging from 0 wt% to 100 wt%, the samples are named as NG, NG/20%CNT-OH, NG/40% CNT-OH, NG/60%CNT-OH, NG/80%CNT-OH and 100%CNT-OH, respectively. In control experiments, CNT was used to synthesis nitrogen-doped graphene/carbon nanotube (NG/CNT) composite aerogel.

2.2. Fabrication of CEs

Slices of NG/CNT-OH with thickness of ~2 mm were cut from the synthesized cylindrical NG/CNT-OH composite aerogel, and the NG/CNT-OH slices were pressed at 20 MPa for 1 min to form NG/CNT-OH papers (~16 μm). Subsequently, the NG/CNT-OH CE was assembled by placing one piece of NG/CNT-OH paper on a polyethylene terephthalate (PET) substrate and fixing with conductive tapes on one hand. (The structure of the NG/CNT-OH CE is shown in supplementary information Fig. S1). The NG/CNT CE was fabricated using the same method. The Pt CE was synthesized through deposit Pt on the FTO and was bought from OPV TECH CO., LTD.

2.3. Assembly of DSSCs

The TiO_2 anodes were fabricated through screen-printing a colloidal paste containing 20 nm sized TiO_2 particles onto a FTO glass followed by annealing at 500 °C. The Organic dye (N719) was used as sensitizer and electrolyte consisted of I^-/I_3^- was used (bought from OPV TECH CO., LTD). Detailed procedures of DSSCs assembly have been described previously [18,23].

2.4. Characterization and measurements

The morphologies of NG/CNT-OH or NG/CNT were characterized by field-emission scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL JSM 2100F). X-ray diffraction (XRD) was collected by a D/MAX2200 X-ray diffractometer with Cu-Ka radiation. X-ray photoelectron spectroscopy (XPS) analysis was carried out with a Thermo escalab 250Xi spectrometer, using monochromated Al-Ka X-rays.

The photovoltaic measurements were performed using an AM1.5 solar simulator (500 W xenon lamp, NBeT, Solar-500) with an intensity of 100 mW cm^{-2}. The photocurrent-voltage (J-V) curves were recorded using a Keithley model 2400 source measurement unit. The Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) measurements were measured by an electrochemical workstation (CHI660e). EIS tests were measured on symmetrical dummy cells (Fig. S2). A symmetrical dummy cell was fabricated from two identical CEs, which were separated by 60-μm thick Surlyn film as a sealant. The cell is filled with the

Download English Version:

https://daneshyari.com/en/article/5150044

Download Persian Version:

https://daneshyari.com/article/5150044

Daneshyari.com