Journal of Power Sources 222 (2013) 518–525

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

A graphene-multi-walled carbon nanotube hybrid supported on fluorinated tin oxide as a counter electrode of dye-sensitized solar cells

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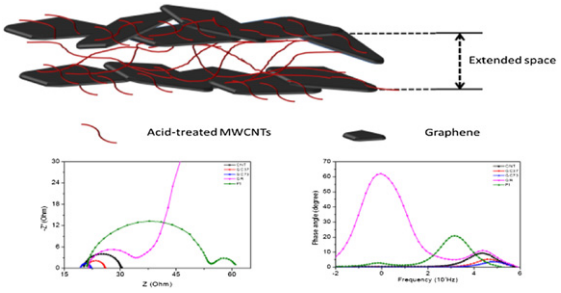
HIGHLIGHTS

- A hybrid material consisting of multi-walled carbon nanotubes and grapheme was used.
- The hybrid material provides a higher charge transfer rate and a lower internal resistance.
- Hybrid electrodes possesses higher rate of charge transfer and lower electron lifetime.
- Hybrid counter electrode cell performance reached 91.6% of platinized electrode.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 May 2012
Received in revised form
16 August 2012
Accepted 21 August 2012
Available online 10 September 2012

Keywords:
Graphene
Carbon nanotubes
Hybrid
Counter electrode
Dye-sensitized solar cells

ABSTRACT

We report a solution-based method to prepare a hybrid material consisting of multi-walled carbon nanotubes and graphene. Raman spectroscopy shows that a decrease in the concentration of defects of hybrid, compared to graphene, which is confirmed by the D/G ratio, implying the repair of the conjugation system. Due to the increased surface areas of graphene and the increased spaces between graphene sheets, results of cyclic voltammetry and electrochemical impedance spectroscopy show that the electrocatalytic ability of the hybrid material affords a higher charge transfer rate, an improved exchange current density, and a lower internal resistance. Transmission and scanning electron microscopy images show that the hybrid counter electrode has a rough and porous structure, resulting in a lower resistance to diffusion, thereby increasing the total redox reaction rate at the counter electrode. Hybrid electrodes have a number of advantages over other electrodes made of graphene or platinum films, including a higher rate of charge transfer, a lower internal resistance, a lower resistance to diffusion, and a lower electron lifetime. The cell performance using a hybrid counter electrode (4.66%) reached 91.6% of that of cells prepared using a platinized fluorinated tin oxide electrode (5.09%).

1. Introduction

Dye-sensitized solar cells (DSSCs) have considerable potential for the development of applications in “green” energy due to their low cost and high performance [1,2]. DSSC devices consist of transparent conductive glass (TCO), sensitized TiO_2 with dye,

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http://dx.doi.org/10.1016/j.jpowsour.2012.08.058

electrolyte, and platinized TCO. The principle of operation of DSSCs is the photo-induced oxidation of a dye molecule on a working TiO_2 electrode; in the process, the oxidized dye molecule is reduced by I^-. The oxidized species diffuses from the surface of the dye to the counter electrode and regenerates I^- with the assistance of a catalyst. Platinum is the catalyst conventionally used in a DSSC because it exhibits a strong electrocatalytic activity for the iodide/triiodide redox species. However, the poor stability and high cost of platinum means an alternative to it is required for the further development of the counter electrode of DSSCs.

The potential of various carbonaceous materials has been demonstrated in the search for alternative catalysts to platinum; these include carbon black [3–5], carbon nanotubes [6–11], and graphite [12,13]. The recent use of the two-dimensional carbon-based material graphene (GR) has shown it to be the most attractive alternative to platinum, due to its high electrical conductivity and high specific surface area [14–18]. Several authors have demonstrated the variable charge transfer resistance and the electrochemical properties of GR [14–18]. Defect-rich GR has been shown to be a favored as an alternative material for use as a counter electrode, as a result of its high concentration of active sites and high specific surface area. However, due to its high aspect ratio, GR is inclined to aggregation, which inhibits its active defect area, thereby leading to an increased internal resistance and the increased diffusion resistance of the redox species [19]. Hence, several authors have demonstrated a novel method of enhancing the electrochemical behavior of GR by incorporating carbon nanotubes (CNTs) into its structure. Choi et al. demonstrated the use of a graphene-based MWCNT (GMWCNT) structure as a counter electrode catalyst through the use of chemical vapor deposition [18,20]. According to electrochemical impendent spectra and performance data, they suggested that GMWCNTs may be a promising material for the counter electrodes of DSSCs. Zhu et al. presented GR-CNTs films by using electrophoretic deposition (EPD) [21] and in so doing achieved a high efficiency of 6.17%. To develop the technology of DSSCs, however, more convenient method of preparing a counter electrode catalyst is required. In our previous study, we demonstrated the use of a carbonaceous hybrid material comprised of multi-walled carbon nanotubes (MWCNTs) and GR, and showed the unique properties of this material for enhancing the rate of charge transfer through the formation of a three dimensional conductive network [22]. In addition, it is possible to control the dispersion and microstructure of the GR through the ratio of GR to MWCNTs, thereby preventing the restacking of GR. Due to the increased spacing of the GR layers, the morphology of the GR may be manipulated through the incorporation of MWCNTs in order to increase the active surface area, thereby improving the electrochemical properties. Furthermore, the high internal resistance is a result of the conducting path of the GR and due to the hopping of the delocalized π-electrons. In the present study, we demonstrate a simple approach for preparing a hybrid carbonaceous material using a one-step solution-based method at room temperature, as shown in Fig. 1. To date, there have been no reports of a GR/MWCNT (GC) hybrid electrode on the fluorinated tin oxide (FTO) fabricated using a solution-based method.

2. Experimental

2.1. Preparation of graphene oxide (GO), GR, and GC hybrid materials

We prepared GO using the method described in our previous study [19]. 10 g of graphite flakes and 50 g potassium permanganate ($KMnO_4$) were stirred in a solution containing concentrated H_2SO_4 and HNO_3 for several days, and this solution was then reacted with H_2O_2 and washed with 5 wt% aqueous hydrochloric acid solution (HCl) to allow the oxidation to be completed and to remove the sulfate ions. The suspension was washed with deionized water and centrifuged repeatedly until the pH of the solution was neutral. Finally, the resulting brown powder was dried in a vacuum at room temperature to obtain GO. The GC hybrid was obtained by means of a chemical reduction using sodium borohydride ($NaBH_4$). GO powder and acid-treated MWCNTs were mixed thoroughly with deionized water in a 250 ml beaker in an ultrasonic bath for 30 min. The mixture was then stirred using with a magnetic bar, and a 0.3 M aqueous solution of $NaBH_4$ was slowly added to the GO solution, thereby causing the reduction of GO to GR. The mixture was washed and centrifuged with deionized water a total of six times, and the resulting black powder was then dried in a vacuum at room

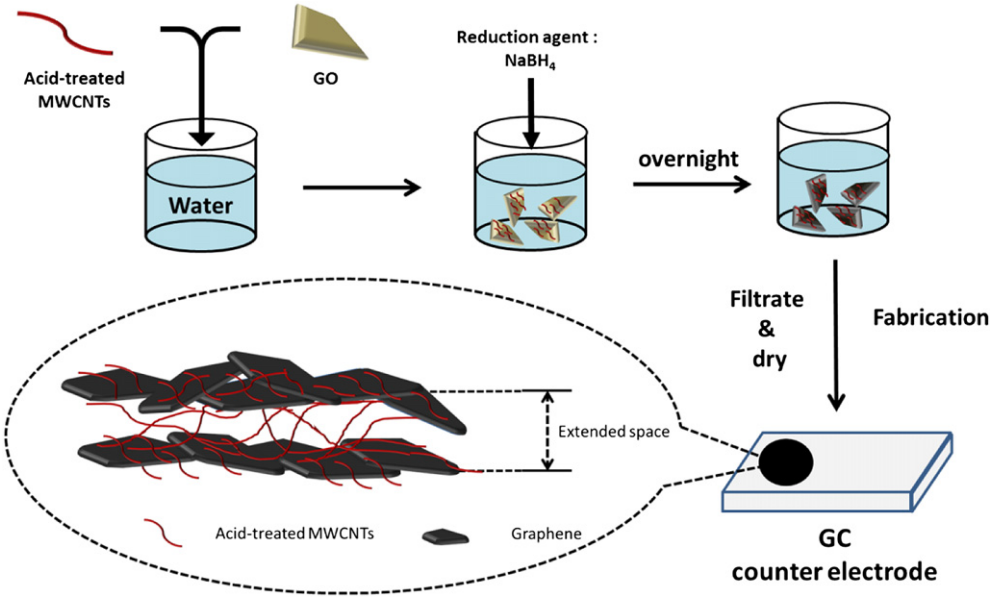

Fig. 1. Illustration of the process used to fabricate the GC counter electrode on FTO.