Organic Electronics 35 (2016) 128–135

Contents lists available at ScienceDirect

Organic Electronics

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

Carbon/carbon nanocomposites as counter electrodes for platinum free dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 19 February 2016
Received in revised form
10 May 2016
Accepted 10 May 2016
Available online 20 May 2016

Keywords:
Carbonaceous materials
Counter electrode
Solar cell
Photovoltaics
Efficiency

ABSTRACT

In this work, carbonaceous materials and their combinations with each other were used as counter electrodes for efficient dye-sensitized solar cells (DSSCs). A small amount of TiO_2 paste was also incorporated in each electrocatalyst to increase the adhesion between the carbon material and the conductive glass substrate. The dispersion of carbonaceous materials in composite films was characterized by transmission electron microscopy (TEM). Electrocatalytic characteristics of carbon/carbon catalysts are systematically investigated by electrochemical techniques, such as cyclic voltammetry and chronoamperometry. Solar cells assembled with carbon/carbon composite counter electrodes were characterized by photocurrent–voltage characteristic and electrochemical impedance spectroscopy measurements. The results indicate that under optimal conditions, the solar cell assembled with carbon/carbon composite counter electrode containing activated carbon, multi-walled carbon nanotube and graphene, shows power conversion efficiency of 10.73%. This photovoltaic performance is comparable with 11.20% for the platinum-based dye-sensitized solar cell. The results exhibit that carbonaceous material is an encouraging alternative for low-cost DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) have got global attention in the past fifteen years because of their easy processing and low-cost when compared to inorganic solar cells [1–3]. DSSC consists of a photo-electrode and a catalytic-electrode with an electrolyte between them. Photosensitizer absorbs light and injects electrons to the conduction band of the semiconductor. The electrolyte, which is in contact with the dye, then donates electrons to the dye, reinstating it to the initial state. The electrolyte then diffuses towards the counter electrode where the reduction reaction takes place. A catalyst is needed for DSSCs to kinetically accelerate the reduction of the redox couple [4,5]. Up to now, platinum (Pt) is a preferred catalyst for the reduction of iodide/triiodide because of its high electrochemical catalytic activity [6,7]. Only a small amount of platinum is sufficient for tri-iodide reduction (50 mg/m^2) [8]. However, the large amount of platinum will be needed for the commercial scale production of DSSCs, which is not abundantly available [9]. Moreover, the other disadvantages of Pt are as follows: high cost, scarcity, corrosion by the.

I_3^-/I^- redox couple electrolyte, and mismatch or non-effectivity in the I-free redox couple electrolyte [7,10]. Therefore, an alternative material is needed, which should be readily available, economical, and capable of showing comparable catalytic properties for tri-iodide reduction [11,12].

Nanocarbon materials have attained much consideration as alternative catalysts for DSSCs due to their low cost [13–16]. The commonly used carbonaceous materials as counter electrodes are graphene [17], carbon nanotubes [18] and activated carbon [19]. These materials generally possess a graphitic structure consisted of two types of graphitic planes, the basal and edge planes [20].Generally, the reduction of the triode is assisted by the edge plane instead of the basal plane because the edge plane comprises comparatively high defective sites [21]. The main advantages of using conventional carbon materials as CEs in DSSCs are their low

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http://dx.doi.org/10.1016/j.orgel.2016.05.014
1566-1199/

cost, high surface area, high electric conductivity, high catalytic activity, high thermal stability, and good corrosion resistance [10,22–24]. However, low chemical stability and poor bonding strength between the carbon film and the substrate are major concerns in the development of Pt-free CEs [25,26].

So far many researchers have used carbonaceous materials as a counter electrode (CE) for low-cost DSSCs. However, to the best of our knowledge, there exists no previous report of DSSCs utilizing carbon/carbon nanocomposites as counter electrodes. Qiquan Qiao et al. [27] used simple mixing technique to prepare nanoscale carbon/TiO_2 composite CE for low-cost DSSCs and found 5.5% efficiency. They used TiO_2 as a binder to bind the carbon particles together. Mingxing Wu et al. [28] utilized nine kinds of carbon materials as counter electrodes for dye-sensitized solar cells. They also used TiO_2 paste as a binder material. Their results showed good electrochemical catalytic activity for triiodide reduction in the DSCs system. Won Jae Lee and his co-workers [29] deposited CNTs on FTO glass substrate by doctor blading and sintered at 250 °C for 1 h. They employed these CEs in DSSCs and found PCE of 6.73%, comparable to that of 7.26% for Pt-based DSSC. An effective counter electrode (CE) was prepared with single-walled carbon nanotubes (SCNTs) by Jung-Geun Park et al. [30] using simple casting technique applying polyvinylpyrrolidone (PVP) as a wrapping agent. DSSCs fabricated with SCNTs-PVP CE presented reasonably high conversion efficiency of 4.5%. D.W. Zhang and his co-workers [31] dispersed graphene (GR) in a mixture of terpineol and ethyl cellulose and then screen printed on glass substrates. They fabricated DSSC with graphene-based counter-electrode and achieved an overall energy conversion efficiency of 6.81% in full sunlight. Likun Pan et al. [32] fabricated reduced GR-carbon nanotubes composite and used as CEs of DSSCs. They achieved maximum power conversion efficiency (PCE) of 6.17%, whereas for Pt-based DSSC was 7.88%.

In this work carbon/carbon nanocomposites electrodes were synthesized that can demonstrate a very good performance. The composition was chosen which utilizes the high surface area of activated carbon (AC), the high conductivity of multi-walled carbon nanotubes (MWCNTs) and good catalytic properties of graphene (GR), enables to fabricate high performance dye-sensitized solar cells. These composites have been prepared by a simple mixing technique. The results indicate that the photovoltaic performance of carbon/carbon CEs is comparable with the conventional sputter-deposited Pt counter electrodes.

2. Experimentation

2.1. Cleaning of glass substrate

FTO glass substrates (2 mm, 7 Ω/seq, Solaronix) were washed with acetone, methanol, and distilled water. First, glass substrates were sonicated (BRANSON 3510) in acetone for five minutes. Subsequently, these substrates were sonicated in methanol for five minutes. Finally, substrates were rinsed with distilled water and dry in an oven (Thermo Scientific V801F) at 200 °C.

2.2. Fabrication of carbon/carbon CEs

MWCNTs (outside/inside diameter of 10–20 nm, length 10–30 μm with purity ˃95% specific surface area (SSA) ˃138 m^2/g) were purchased from “cheap tubes corporation, USA”. Graphene (Specific surface area = 100 m^2/g and average flake thickness = 8 nm) was purchased from “grafen chemical industries Co, Turkey”. While an activated carbon was synthesized from raw fly ash [33]. TiO_2 paste was purchased from Solaronix (T/SP **14451**). TiO_2 paste was used as a binder to hold the material together and also provides the adhesion between electrocatalyst and conductive glass substrates.

a. AC, MWCNTs and GR CEs

These CEs were fabricated by mixing of an exact amount of carbonaceous material (CM) with precise amount of anatase TiO_2 paste. The composition of each electrocatalyst was 90% CM and 10% TiO_2.

b. AC + MWCNTs, MWCNTs + GR, GR + AC CEs

These CEs were fabricated by mixing of an equal amount of AC and MWCNTs with TiO_2. The composition of this electrocatalyst was 45% AC, 45% MWCNTs and 10% TiO_2. Other electrocatalyst i.e. MWCNTs + GR and GR + AC were prepared in the similar manner.

c. AC + MWCNTs + GR CE

This CE was fabricated by mixing of an equal amount of AC, MWCNTs and GR with TiO_2 paste. The composition of electrocatalyst was 30% AC, 30% MWCNTs, and 30% GR and 10% TiO_2.

Each carbon paste was then tape casted on FTO glass substrate. The coated glass substrates were annealed at 450 °C for 30 min. The thickness of each counter electrode was found by using cross sectional images obtained from SEM (JEOL, 6610LV) as shown in. The average thickness of each film was 8 μm. The cross sectional image of AC + MWCNTs + GR is shown in Fig. 1d.

2.3. Fabrication of DSSCs

TiO_2 paste was deposited on FTO substrates and then sintered at 450 °C for 30 min. A 0.5 mM solution of N719 was prepared in methanol for the sensitization of photoanodes. TiO_2 coated glass substrates were soaked in the dye solution for 24 h and then rinsed with ethanol to remove unanchored dye molecules. The photoanodes and CEs were joined together by employing super glue (CA 91730C pacer technology 2011, Taiwan). Finally, an electrolyte (Iodolyte Z-50 (Solaronix), Redox couple: iodide/tri-iodide, Redox concentration: 50 Mm, Additives: ionic liquid, alkylbenzimidazole, thiocyanate, Solvent: 3-methoxypropionitrile) was inserted between two electrodes through dropper to complete the cell. The active area of a cell was 0.20 cm^2. The symmetrical dummy cell Tafel test was fabricated by two identical CEs, and then the electrolyte, similar to that used in assembled DSCs, was filled in the symmetrical dummy cell and sealed with super glue. The active area of dummy cell was 0.20 cm^2.

3. Results and discussion

3.1. Morphological properties of CEs

The SEM micrograph of AC (Fig. 1a) reveals that it possesses meso and micro pores. Few broken particles can also be seen in the SEM micrograph which probably produced during thermochemical activation of raw ash. The porous nature of activated carbon allows a few angstrom wide I_3^- ions to diffuse and get reduced at the surface. The hollow cylindrical nanostructure of MWCNTs is shown in Fig. 1b. The open ends of MWCNTs provide active sites for catalytic reduction reactions owing to the presence of several oxygen containing functional groups [34]. SEM image of graphene with layered-structure is shown in Fig. 1c. The number defective sites in graphene sheets play a crucial role in the catalytic activity of graphene and can be controlled by changing the surface chemical states.