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Carbon nanomaterial based counter electrodes for dye sensitized solar cells

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Abstract

In this paper, we report a new cost effective platinum-free counter electrodes (CEs) for dye sensitized solar cells (DSSCs). The CEs were produced using Graphene Nanoplatelets (GNPs) or multi-wall carbon nanotubes (MWCNTs) or various weight % of hybrid GNPs and MWCNTs mixtures. These materials have been dispersed using PEDOT: PSS polymer and then deposited on fluorine doped tin oxide (FTO) glass as well as on a non-conducting glass substrate by a drop casting method. The testing of these electrodes in DSSCs have demonstrated a power conversion efficiency of up to 4.10% to compare with the power conversion efficiency of 3.90% for the DSSC with a standard Pt based CE. New CEs were also made where both Pt and FTO were completely replaced by the hybrid PEDOT: PSS–GNPs–MWCNT nanomaterials. The DSSC with these new platinum- and FTO-free CEs have demonstrated an efficiency of up to 2.48%.

Keywords: Dye sensitized solar cells; Counter electrodes; Carbon nanomaterials

1. Introduction

Dye-sensitized solar cells (DSSCs) were developed by Gratzel and O'Regan in 1991 (O'Regan and Gratzel, 1991). Since then DSSCs have been intensively investigated because of their potentially lower costs and simple manufacturing process compared to silicon based solar cells (Grätzel, 2001). It is well established that commercialisation of DSSCs requires improvement in three areas: conversion efficiency, long-term stability, and low fabrication costs. DSSCs consist of three adjacent layers: the working electrode (WE) is a transparent conductive oxide (TCO/substrate) coated with a wide-band gap semiconductor mesoporous oxide such as TiO_2 covered with a monolayer of the ruthenium based complex as a photosensitizer. Traditionally the counter electrode (CE) is a TCO substrate coated with Pt. The gap between the two electrodes is filled with an electrolyte which contains an organic solvent with the iodide/tri-iodide (I^-/I_3^-) redox couple. The Pt deposited TCO substrate has been widely used as the standard counter electrode (CE) for DSSCs but both these materials (Pt and TCOs) are very expensive. Therefore it is extremely important to find new cost effective materials and approaches to replace the Pt and TCOs in CEs. Carbon based nanomaterials (e.g. carbon nanotubes, graphene or graphene nanoplates) are particularly attractive as these materials have good electric conductivity and high surface area (Brennan et al., 2011) (Oelhafen and

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Schuler, 2005). The main requirements for a material to be used as a catalyst in a DSSC are a low charge-transfer resistance and high exchange current densities for the reduction of the oxidized form of the charge mediator (Longo and De Paoli, 2003). Furthermore, such materials must possess chemical and electrochemical stability in the electrolyte system used in the cell (Ahmad et al., 2011; Kalyanasundaram and Grätzel, 1998; Papageorgiou et al., 1997). Various other materials rather than Pt, have also been used as electrocatalysts in DSSCs so far such as CNTs (Kim et al., 2012b) graphite (Veerappan et al., 2011), graphene, (Kaniyoor and Ramaprabhu, 2011; Kim et al., 2012b), GNPs + graphene oxide (Kavan et al., 2012), carbon black (Murakami et al., 2006), conducting polymer PEDOT: PSS (Burschka et al., 2012) and PEDOT: PSS + graphene (Hong et al., 2008b). Though, Pt was the best counter electrode material used in DSSCs so far because of its excellent catalytic activity for the reduction of I_3^- ions and good conductivity (Papageorgiou et al., 1997). Various methods have been used for deposition of Pt on TCO glass such as CVD, sputtering, screen printing and spin coating etc. The deposition of Pt by sputtering is the most common technique (Lan et al., 2010). However, sputtering requires an ultra-high vacuum environment and use a large amount of platinum to form one flat surface (Fang et al., 2004). Alongside with these issues Pt has some other disadvantages such as it is a rare and expensive metal. Therefore Pt based CE accounts for approximately 25–35% of the overall price of DSSCs (Lana et al., 2010). Another disadvantage of Pt is that it slowly degrades in I^-/I_3^- medium (Koo et al., 2006). Therefore, it is highly desirable to reduce the amount of Pt in CEs or replace Pt with cheap, stable and readily available materials.

There were reports on high-performance and low platinum loading Pt/Carbon black CE (Li et al., 2009) and Graphene–Pt/ITO CE with significantly reduced Pt loading and enhanced charge transfer (Guai et al., 2012), which have been used in DSSCs. However, ultimately Pt free CE are necessary to achieve a significant cost reduction. Previously, Cruz et al. have prepared stand-alone graphene-based CEs for DSSCs by spray deposition and chemically reduction of GO, followed by thermal annealing under an inert atmosphere. This work resulted in transparent electrodes with transmittance higher than 80%, which have been used to produce DSSCs with energy conversion efficiency of 2.64% (Cruz et al., 2012). Another Pt-free CE was produced from vertically-aligned carbon nanotube forests. The use of this CE enabled to fabricate DSSCs with relatively high efficiency of $5.2 \pm 0.5\%$ which was close to the efficiency ($6.6 \pm 0.7\%$) of the similar Pt containing cells (Anwar et al., 2013). There has been also a report on a graphene and MWCNTs composite CE/DSSC (Velten et al., 2012), in which the authors reported that they have achieved a higher power conversion efficiency with the composite CE (7.55%) compared to graphene (4.62%) and MWCNTs (6.62%) alone as a CE/DSSC but still lower than the Pt/CE (8.8%) standard DSSC.

Furthermore several interesting approaches have been used to increase the electrocatalytic activity of carbon based nanomaterials. For example, a hybrid composite of MoS_2–graphene nanosheet (GNS) was used as a CE in DSSC (Lin et al., 2013). These materials enabled to get power conversion efficiencies of up to 5.81% and 6.24% with hybrid MoS_2 and GNS composite CE and Pt/CE/DSSC respectively. An enhanced catalytic activity for the triiodide reduction was observed for a glassy carbon based CE which was prepared from phenol resins by pyrolysis. In this case the enhanced catalytic activity of CE was attributed to the increase of graphene stacks and active sites in the glassy carbon (Xu et al., 2011).

The main aim of this work is to replace Pt with cheap, readily available and stable carbon based materials. One of the main challenges is that carbon based nanomaterials (CNTs or GNPs) have a very low adhesion to TCO and glass substrate surfaces (Kavan et al., 2012). As a result weakly adhered CNTs/GNPs may easily detach from the TCO or glass substrate as they contact with electrolyte in DSSCs. To address this issue and to improve the efficiency of DSSCs in this work we dispersed MWCNTs, GNPs and hybrids of these two nanomaterials into a PEDOT: PSS aqueous solution and deposited it by a drop casting method on FTO glass. Here we report our studies of these new hybrid carbon based nanomaterials as CEs in DSSCs.

2. Materials and methods

2.1. General procedures

Graphene Nanoplatelets (GNPs) grade 3 was purchased from Cheap Tubes Inc, USA. According to supplier's specification, the GNPs nanoplatelets consisted of 4–5 sheets of graphene, particle diameters less than 2 μm and surface area of 600–750 m^2/g. MWCNTs were purchased from MER Corporation (Catalog # MRGC). According to the manufacturer's specification, the MWCNTS consisted of 8–30 graphene layers, 6–20 nm in diameter and 1–5 μm in length. The working electrodes (TiO_2 layer with 14 μm thickness), counter electrode (Pt coated) were supplied by Solarprint Limited. PEDOT: PSS (Clevios PH 1000) was purchased from Heraeus Clevios GmbH. Organic solvent based High Performance Electrolyte (HPE) was purchased from Dyesol Ltd. Dye (N-719) was purchased from Dyesol Ltd. According to the manufacturer's specification, these electrolytes consist of acetonitrile & valeronitrile with redox couple I^-/I_3^- and some additives. FTO glass (12 Ω/sq) was purchased from Sigma Aldrich. Ultrasonic Bath Grant XB6 (200 W) was used in all sonication experiments. Raman spectra (633 nm) were recorded using a Horiba Jobin Yvon LabRAM-HR (100× objective lens). Scanning electron microscope (SEM) images of the dry film/CEs have been taken using a Zeiss Ultra plus SEM. The electron beam generator was a thermal field emission tungsten tip, with a sintered reservoir of zirconium oxide in the shank. For these samples, the electrons were accelerated between 2 and