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Rapid fabrication and photovoltaic performance of Pt-free carbon nanotube counter electrodes of dye-sensitized solar cells

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ABSTRACT

We fabricated uniform multiwalled carbon nanotube (MWCNT) thin films on fluorine-doped tin oxide (FTO) glass substrates with controlled thickness by an easy and versatile spin-coating process (SCP). Aqueous dispersions of MWCNTs were dropped on the FTO glass substrates and spin-coated to form uniform MWCNT thin films, which were then used as the catalytic medium on the counter electrodes (CEs) of dye-sensitized solar cells (DSCs). For the DSC with an optimized MWCNT-thin-film thickness coated on the CE, the short circuit current density (J_{sc}) was more than that of the conventional Pt-based DSC (10.97 ± 0.13 mA cm^{-2} vs 9.58 ± 0.17 mA cm^{-2}), while its power conversion efficiency (*PCE*) was comparable to that of conventional DSC ($\sim$4.41 ± 0.14% and $\sim$4.69 ± 0.22%, respectively). This suggests that the accumulation of MWCNTs on the CE increases the interfacial contact area between the MWCNTs and liquid electrolyte in the DSC, allowing the rapid reduction of I_3^-. Simultaneously, it decreases the charge transfer resistance owing to rapid electron transport through the MWCNT medium with its relatively high electrical conductivity. Thus, the precisely controlled rapid accumulation of MWCNT thin films by the SCP on the CEs of DSCs is a very promising approach for replacing the expensive Pt metal that is currently used in DSC applications.

1. Introduction

Dye-sensitized solar cells (DSCs) have attracted considerable attention as next-generation solar cells due to their simple manufacturing processes and relatively low production costs (O'Regan and Gratzel, 1991). Typical DSCs consist of a TiO_2 nanoparticle accumulation layer with a sensitizing dye as the photoelectrode, a redox couple containing iodide/triiodide (I^-/I_3^-) in the electrolyte, and a Pt-coated fluorine-doped tin oxide (FTO) glass substrate as the counter electrode (CE). The polychromatic photoabsorption by the dye, fast electron transfer at the TiO_2 photoanode layer, good ion diffusivity in the electrolyte, and efficient reduction of the redox couple at the CE are the key factors that collectively determine the power conversion efficiency (*PCE*) of a DSC. When the dye is excited by sunlight, the CE transfers electrons from the external circuit to the redox couple.

Generally, Pt is used in the CEs of DSCs since it has excellent catalytic activity for the effective reduction of I^-/I_3^- and good electrical conductivity (Hauch and Georg, 2001; Gratzel, 2004; Nazeeruddin et al., 2005; Ahn et al., 2013; Halme et al., 2006; Murakami and Grätzel, 2008; Papageorgiou, 2004; Lee et al., 2010). However, it has the disadvantages of being relatively expensive and easily corroded by the liquid iodide electrolyte (Chiba et al., 2006; Olsen et al., 2000; Luo et al., 2009). These drawbacks have led to the search for proper alternatives to replace Pt catalytic films.

Various carbon nanomaterials, including singlewalled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs) and carbon nanoparticles (CNPs) were synthesized using aerosol/thermal CVD and spraying/compression processes, and then they were used as Pt-free CEs of DSCs. The results showed that SWCNTs, MWCNTs, and CNPs have reasonable catalytic performance (Hashmi et al., 2014; Aitola et al., 2011; Han et al., 2010; Zhang et al., 2011).

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MWCNTs have recently attracted strong interest as practical materials for CEs in DSCs because of their relatively low cost, large specific surface area, and good electrocatalytic activity. Furthermore, they are quite stable in general electrolytes, including the redox couple in the DSCs. Recently, polyelectrolyte-grafted MWCNTs (Han et al., 2010) and graphitic carbon nitride/MWCNT composites (Wang et al., 2016) are introduced into CEs of DSCs, which result in showing excellent electrocatalytic activity for triode reduction and low charge-transfer resistance. However, they require very complex fabrication procedures, and it is also hard to obtain uniform composites.

To use MWCNTs in the CEs of DSCs, the MWCNTs can be coated on an FTO glass substrate through various coating techniques such as electrospraying, doctor blading, electrophoretic deposition, screen printing, hydrothermal deposition, and aerosol deposition (Zhu et al., 2011; Xia et al., 2009; Benard and Chahine, 2001; Suzuki et al., 2003; Ebbesen et al., 1996; Chew et al., 2009; Chen et al., 2009; Han et al., 2010; Ko Kyaw et al., 2012; Roy-Mayhew et al., 2010; Kim et al., 2012; Cha et al., 2010; Siriroj et al., 2012; Hsieh et al., 2011; Li et al., 2010; Ahn et al., 2014; Lee et al., 2009). However, employing these techniques to coat MWCNTs on the FTO glass causes intrinsic problems in fabricating uniform MWCNT thin films; furthermore, precise control of the film thickness is challenging due to highly agglomerated and entangled characteristics of the MWCNTs in solution. Moreover, forming a nonuniform MWCNT thin film on the FTO glass substrate can eventually deteriorate electron transfer in the DSCs. Therefore, a reliable and adjustable method is required to fabricate a uniform distribution of MWCNTs on the substrate.

In this study, we employed a simple and rapid spin-coating process (SCP) to deposit a uniform MWCNT thin film on an FTO glass for use as the CE of a DSC. Furthermore, we systematically examined the photovoltaic performance of the resulting DSCs by varying the thickness of the MWCNT thin films, and then compared the results with a conventional Pt-based DSC.

2. Experimental

2.1. Preparation of MWCNT-dispersed aqueous solution

The MWCNTs (>95% purity) were purchased from CNT Co., Ltd. (Korea) and employed without further treatment. The MWCNTs, synthesized by a thermal CVD process, had an average diameter of ~20 nm and a length distribution of 1–25 μm. The specific surface area was approximately 150–250 $m^2 g^{-1}$.

To fabricate a homogeneous MWCNT-dispersed aqueous solution, we adopted the surfactant addition method. By adding an appropriate surfactant, which serves to interconnect the hydrophobic and hydrophilic surfaces, MWCNTs can be dispersed homogeneously in aqueous solution. In this experiment, carboxymethyl cellulose (CMC, Sigma Aldrich, M_w: 700,000) was used as the surfactant (Cha et al., 2010; Lee et al., 2009; Imoto et al., 2003; Takahashi et al., 2004). In CMC, the hydroxyl functional groups stabilize the MWCNT clusters and allow their homogeneous dispersion in water, probably by surrounding the MWCNT surfaces and overcoming the van der Waals attractions among the MWCNT bundles. We prepared a CMC-added MWCNT aqueous solution containing 1 wt% MWCNTs and 0.15 wt% CMC in deionized water by sonicating with a probe sonicator (Daihan Scientific Co., Ltd.) at 665 W for 30 min.

2.2. Fabrication of MWCNT-deposited CEs by SCP

MWCNT-deposited CEs were fabricated by depositing the MWCNT solution onto FTO glass substrates (SnO_2:F, 7 Ω/sq, Pilkington) by the SCP shown in Fig. 1. SCP can be divided into the following three steps the introduction of the MWCNT droplets, spinning the substrate at constant rotating speed (ω), and drying the MWCNT thin films. The first step involves dispensing sufficient MWCNT solution onto a stationary and then slowly spinning the substrate to prevent the formation of coating discontinuities caused by the drying of solution prior to reaching the substrate edge. During the spinning stage, as the FTO glass substrates are rotated at a constant speed of 3000 rpm for 20 s, the droplet is thinned by centrifugal forces until the solvent is removed, thereby increasing the viscosity to a certain degree. After forming the uniform MWCNT thin film on the FTO glass, the CE is dried on a hot plate at approximately 100 °C for 3 min to increase film adhesion to the substrate by removing the residual solvent. The thickness of the MWCNT thin film could be controlled by the number of spin-coating repetitions ($N_{coating}$). The MWCNT thin films deposited by SCP were additionally heated in an electric furnace at 350 °C for 20 min to remove the surfactant.

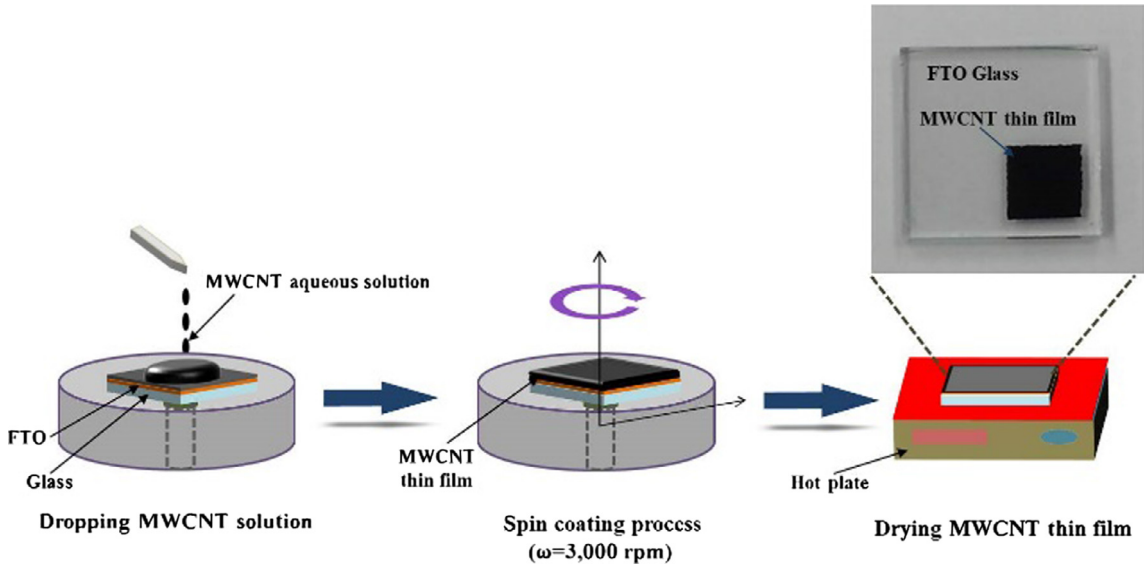

Fig. 1. Schematic of the spin-coating system for fabricating a MWCNT thin film on an FTO glass substrate.