



Enhanced electrocatalytic activity of plasma functionalized multi-walled carbon nanotube-entrapped poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) photocathode



Yong Hoon Rhee^a, Dong June Ahn^a, Min Jae Ko^b, Hwa-Young Jin^b, Joon-Hyung Jin^{c,**}, Nam Ki Min^{a,*}

^a Department of Biomicrosystem Technology, Korea University, Seoul 136-713, South Korea

^b Photo-electronic hybrids research center, Korea Institute of Science and Technology, Seoul 136-791, South Korea

^c Department of Mechanical Engineering, Korea University, Seoul 136-713, South Korea

ARTICLE INFO

Article history:

Received 14 July 2014

Received in revised form 8 September 2014

Accepted 10 September 2014

Available online 16 September 2014

Keywords:

dye-sensitized solar cell
electrocatalytic activity
oxygen plasma-functionalized carbon nanotubes
PEDOT:PSS photocathode
photoelectrochemical cell

ABSTRACT

A composite of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and multi-walled carbon nanotubes (MWNTs) was electrochemically polymerized on a fluorine-doped tin oxide (FTO) substrate and used as a photocathode for a dye-sensitized solar cell. The MWNTs were previously O₂ plasma treated and simultaneously entrapped while the PEDOT:PSS film was electropolymerized. The resulting plasma-functionalized MWNT-entrapped PEDOT:PSS composite showed enhanced electrocatalytic activity for the reduction of I₃⁻ to I⁻, this was confirmed by scanning electron microscopy (SEM), electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), and incident photon-to-current conversion efficiency (IPCE) measurements. An improved energy conversion efficiency by about 13.9% was observed in optimized conditions as compared to a platinized FTO-based photocathode.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Dye-sensitized solar cells (DSSCs) have a great potential for future use as cost-effective reusable energy harvesting devices owing to their low material and production costs, and relatively low CO₂ emission process for the fabrication, as compared to traditional silicon solar cell. With the introduction in recent reports of hybrid DSSCs showing energy conversion efficiencies of 15 % [1], DSSCs have become one step closer to commercialization, even though the perovskite-based hybrid DSSCs utilize environmentally hazardous materials [1,2]. On the other hand, the unit price of DSSCs is practically too high, they are over ten times more expensive to generate one watt power of electricity compared with fossil fuels. One of the reasons for the high price of DSSCs is related to the use of platinized counter electrodes to obtain a sufficient electrocatalytic activity for the reduction of triiodide to iodide on the photocathode surface. Moreover, platinum is incompatible with the flexible substrate-based roll-to-roll process in which the

spin-coated platinum layer commonly needs a high-temperature annealing process. Many efforts have been attempted to replacing this platinum with a relatively low-cost material that has both high conductivity and electrocatalytic activity that are comparable to those of platinum. Examples include tungsten carbides [3], tungsten oxides [4], cobalt sulfides [5], nickel sulfides [6,7], ruthenium dioxides [8], conducting polymer composites [9–13], and various carbon materials such as graphite, carbon nanotubes, and graphene [14–18].

In this study, we introduce a hybrid material composed of well-known poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and multi-walled carbon nanotubes (MWNTs), instead of a new material, these are cost-effective and one of the most frequently-used electrode materials. The insufficient fill factor of pure PEDOT:PSS film was compensated by entrapping the MWNTs [19], the catalytic activity and conductivity of the photocathodes were enhanced by the oxygen plasma treatment of the MWNTs. The oxygen plasma-based functionalization is a more effective and simple way to form evenly-distributed chemical functional groups on the surface of MWNTs than other functionalization methods such as acid-based wet oxidation or ozone treatment [20]. The plasma-functionalized MWNT (pf-MWNT)-entrapped PEDOT:PSS (PEDOT:PSS/pf-MWNT)

* Corresponding author. Tel.: +82 2 925 2296.

** Corresponding author. Tel.: +82 2 324 0344.

E-mail addresses: jjh1023@chol.com (J.-H. Jin), nkmin@korea.ac.kr (N.K. Min).