Available online at www.sciencedirect.com

ScienceDirect

Solar Energy 133 (2016) 524–532

SOLAR ENERGY

www.elsevier.com/locate/solener

Carbon nanohorns based counter electrodes developed by spray method for dye sensitized solar cells

K. Susmitha [a], M. Mamata Kumari [b,c], A. Joseph Berkmans [c], M. Naresh Kumar [d], L. Giribabu [e], S.V. Manorama [e], M. Raghavender [a,*]

[a] Department of Physics, Yogi Vemana University, Kadapa 516003, A.P., India
[b] Department of Materials Science and Nanotechnology, Yogi Vemana University, Kadapa 516003, A.P., India
[c] Department of Metallurgical and Materials Engineering, Indian Institute of Technology, Madras 600036, T.N., India
[d] TKR College of Engineering and Technology, Hyderabad 500097, T.S., India
[e] Inorganic and Physical Chemistry, Indian Institute of Chemical Technology, Hyderabad 500007, T.S., India

Received 4 July 2015; received in revised form 5 March 2016; accepted 28 March 2016
Available online 3 May 2016

Communicated by: Associate Editor Hari M. Upadhyaya

Abstract

The manuscript presents an analysis of the single wall carbon nanohorns (SWCNH) and graphene nanoplatelets (GNP) decorated counter electrodes for Dye Sensitized Solar Cells (DSSCs) application. The systematic catalytic activity and electrochemical performance of the SWCNH and GNP are also studied. SWCNH loaded DSSC showed higher photovoltaic conversion efficiency (4.09%) than the GNP (3.13%) which is attributed to higher average surface roughness area, lower series, charge transfer resistance and electrolyte diffusion impedance values. In addition, the conversion efficiencies increase with higher load of SWCNH up to 3.0 mg. Therefore, the SWCNH material has great potential for application as low-cost counter electrode material for reduction of iodide/tri-iodide redox couple in dye sensitized solar cells.

Keywords: Carbon nanohorns; Dye sensitized solar cell; Electrochemical impedance spectroscopic studies; Pt-free counter electrodes

1. Introduction

Dye Sensitized Solar Cell (DSSC) also called a Grätzel cell was introduced in 1991 (O'Regan and Grätzel, 1999), with attributes such as lower production costs (Razykov et al., 2011), convenient fabrication process and better performance under diffused light which drives the DSSCs to supercede the silicon based solar cells. They are expected to be the next generation solar cells. Typically a DSSC consists of photo anode, an electrolyte with a redox species iodide/tri-iodide (I^-/I_3^-) in an organic solvent, and counter electrode (CE). The anode contains transparent conducting oxide (TCO) coated glass substrate with a mesoporous network of wide band gap metal oxide semiconductor, generally nanosized TiO_2 particles which sensitize a sensitizer. The redox couple in the electrolyte works as mediators and transfers electrons from the cathode to the oxidized dye molecules. I^- reduces the sensitizer and is oxidized to I_3^-, which gets reduced back to I^- at the cathode. In this process, the CE plays vital role in DSSC. Generally, platinum coated TCO glass substrate is used as CE because of its high catalytic activity, delivered a certified efficiency of 11.4% (Han et al., 2012; Upadhyaya et al., 2013) and

* Corresponding author.
E-mail address: toraghavender@rediffmail.com (M. Raghavender).

http://dx.doi.org/10.1016/j.solener.2016.03.059
0038-092X/

resistance against iodine corrosion. To replace platinum counter electrode with a less expensive catalyst, the introduction of carbon derivatives such as mesoporous carbon (Wang et al., 2009), carbon black (Murakami et al., 2006), nanocarbon (Ahmad et al., 2014; Ramasamy et al., 2007), activated carbon (Imoto et al., 2003), and carbon nanotubes (Ahn et al., 2014; Lee et al., 2009) has been initiated. Graphene related materials are integrated into DSSCs as CE material (Devadoss et al., 2014; Zhang et al., 2011) due to their excellent properties such as high catalytic activity (Bu et al., 2013), high charge carrier mobility (Kavan et al., 2011), high optical transmittance (Novoselov et al., 2004; Nair et al., 2008) and chemical stability (Kavan et al., 2012). However, graphene based CE in DSSC reveals lower performance and research in this area is still in progress. Recently, the overture of single wall carbon nanohorns into DSSC applications received major attention (Wang et al., 2008; Casillas et al., 2014; Costa et al., 2013). SWCNHs are a novel group of carbon with an analogous graphitic structure as carbon nanotubes. SWCNH consists of tubular structures with 2–5 nm in diameter and 30–50 nm in length – that associate with roundish aggregates of 100 nm diameter, with high surface area (ca. 300–350 $m^2 g^{-1}$). Further tuning of surface area by chemical or physical oxidation reveals an increase of its specific surface area (up to 1000 $m^2 g^{-1}$) by opening the horn tip, results in the inner tubular area for further accessible to reactants (Cruz et al., 2013; Iijima et al., 1999). SWCNH can be used as a platinum electrocatalyst support, an approach that has already been successfully applied in energy applications like fuel cells (Iijima et al., 1999; Brandao et al., 2011a).

In this report, we have developed counter electrodes using SWCNH with spray method, treated in N_2 atmosphere besides graphene nanoplatelets decorated substrates for comparison. We have demonstrated its application as counter electrodes in dye sensitized solar cells. The essential factors which manipulate the performance of CE were monitored through Cyclic-Voltammetry (C-V), Electrochemical Impedance Spectroscopy (EIS) studies and Current density–Voltage (*J–V*) characteristics. Incorporation of SWCNH material on TCO substrate has been successfully demonstrated with an efficiency of 4.09%.

2. Experimental

2.1. Preparation of aqueous dispersion of SWCNH

The single wall carbon nanohorns were prepared by Arc Discharge method, and oxidized by heat at the 500 °C for 15 min in the air without any flow of oxygen gas. Graphene nanoplatelets were synthesized by reported method (Shen et al., 2009), and for this, graphite powder was heated to 1000 °C in the air for 2–3 min. 115 mL of H_2SO_4 was taken and 5 g graphite was added in the ice bath. $KMnO_4$ (15 g) was added slowly with stirring, and the mixture was then maintained at 35 °C for 30 min. Then Deionized water (230 mL) was gradually added. After 15 min, the mixture was further treated with deionized water (700 mL) and 30% H_2O_2 solution (50 mL). The powder was washed with deionized water until pH 7 was reached, and then dried at 60 °C in a vacuum furnace. A four-necked flask was filled with Styrene (13.5 g), benzoyl peroxide (0.371 g), and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, 0.285 g) and was kept in an oil bath at 120 °C in an N_2 atmosphere under stirring. After 4 h, the solution was reprecipitated four times with toluene/methanol, and then dried in a vacuum oven. In the four neck flask 30 mg of graphene oxide (GO) was well dispersed in 50 mL of DMF and D.I. water (9:1) mixture by sonication for 30 min. 3.2 mM of sodium borohydride was added and the solution was heated in an oil bath at 80 °C for 4 h. After that, PS–T (TEMPO terminated polystyrene) (0.05 g), benzoyl peroxide of 0.016 g, and 0.1 g of acrylamide were added. The oil bath was kept at 125 °C in an N_2 atmosphere under stirring. After 6 h the mixture was cooled to room temperature and precipitated in methanol. The black powder was dispersed in toluene for 48 h, then vacuum-filtered through a 0.4 mm PTFE membrane, washed with D.I. water three times, and heated under vacuum.

The aqueous solutions were yielded with 1 mL of Isopropanol (Merck, Germany) as a solvent ultrasonicated with 0.1 mL of Alpha-Terpineol (Alfa Aesar, USA) along with Ethyl Cellulose (Alfa Aesar, USA), and added to SWCNH weights of 0.5 mg, 1.0 mg, 2.0 mg, 3.0 mg, and 4.0 mg. Then the resultant solution was ultrasonicated with a frequency of 40 kHz at 50 W of ultrasonic wattage.

2.2. Preparation of SWCNH-CE

Prepared aqueous SWCNH solutions were spray coated for developing counter electrodes. The fluorine-doped tin oxide (FTO) glass substrates (TCO22-7 Ω/cm, Solaronix) were used as TCO substrates, drilled with DREMEL 300 using a diamond tipped micro drill, washed with diluted detergent, 0.1 M HCl solution in ethanol and then with acetone, Millipore water, absolute ethanol, and finally cleaned with iso-propanol in an ultrasonicator for 30 min. The cleaned FTO glass substrate was placed on the hot plate at 180 °C, whereas SWCNH solution was loaded into a low-cost spray gun attached to the pure N_2 gas cylinder and flow rate controlled through 0.3 mm micro-tip needled was 1 mL min^{-1}. The sprayed SWCNH films were heated at 150 °C for 30 min in a furnace. Graphene nanoplatelets and platinum decorated CEs were prepared by the same procedure for comparison.

2.3. DSSC fabrication

The DSSC test cells are fabricated as the procedure reported earlier (Giribabu et al., 2008; Susmitha et al., 2015). The anatase TiO_2 nanoparticle based photoanodes are prepared onto cleaned FTO glass substrates (treated