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Synthesis of graphitic carbon nano-onions for dye sensitized solar cells

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Abstract

This study examines dye sensitized solar cells (DSSCs) incorporated with carbon nano-onions as counter electrodes. The synthesized carbon nano-onion nanoparticles were deposited through candle flame synthesis on Cu sputter coated glass substrates. The deposited carbon nano-onions were extensively characterized through scanning electron microscopy, energy disperse spectroscopy, transmission electron microscopy, Raman spectroscopy. It was found that highly graphitic, interconnected carbon nano-onion with mean diameter of around 30 nm can be formed through the proposed method. Cyclic voltammetry and subsequent DSSCs performances indicated that the carbon nano-onion based counter electrode exhibit comparable performances to conventionally used Pt and could be scaled up in industrial production.

Keywords: Carbon nano-onion; Dye sensitized solar cells; Candle synthesis

1. Introduction

Ever since the discovery of carbon nanotubes (Iijima and Ichihashi, 1993; Iijima, 1991), there have been intensive interests in carbon-based nanomaterials due to their unique electronic and mechanical properties. The investigated carbon based nanomaterials include amorphous carbon (Robertson and O'reilly, 1987), diamond (Isberg et al., 2002), fullerene (Liu et al., 1998), nanotubes (Saito et al., 1998; Tune et al., 2010), nano-onion (Ding et al., 2005), nanohorns (Yoshitake et al., 2002), nanofibers (Kothari et al., 2008) and graphene (Novoselov et al., 2004) and have been produced by different deposition techniques such as chemical vapor deposition (CVD) (Kong et al., 1998), arc discharge (Hutchison et al., 2001) and flame synthesis (Height et al., 2004). Typically, the CVD growth of carbon nanomaterials can be achieved by growth on heated catalyst (Fe, Ni or Co) with a flow of carbon containing gases (C_2H_2 or CH_4) (Meyyappan et al., 2003). The proposed growth mechanism is vapor–liquid–solid, with the heated catalyst saturated with C species that results in precipitation and growth of CNTs. Similar mechanism can be modified to produce graphene by flowing of CH_4 over Ni or Cu sheets (Reina et al., 2008; Gomez De Arco et al., 2010).

One of the proposed applications for carbon nanomaterials are in dye sensitized solar cells (DSSCs) (Xia and Yanagida, 2011; Nazeeruddin et al., 2011). Typically, DSSCs solar cells are constructed with fluorine doped tin oxide (FTO) conductive glass/TiO_2 nanoparticle/Ru-based dye/iodine based electrolyte/Pt counter electrode/FTO. In order to scale up for industrial module production of DSSCs, the expensive and rare Pt used in counter electrode must be replaced by an inexpensive alternative material (Kay and Grätzel, 1996). The ideal replacement material

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must possess high electrical conductivity (to inject electron into the electrolyte) and sufficient chemical resistance to the highly corrosive iodine. The obvious candidate is carbon-based nano-materials due to its large effective surface area, high electrical conductivity and chemical stability.

Previous research have already shown that several allotropes of carbon, multiwalled carbon nanotubes (Kyaw et al., 2011; Anwar et al., 2013; Sayer et al., 2010), doped carbon nanotubes (Kyaw et al., 2011; Tantang et al., 2011), graphene (Kavan et al., 2011; Cruz and Pacheco, 2012; Guai et al., 2012), carbon black (Li et al., 2009) and glassy carbon (Xu et al., 2011), have been successfully integrated into DSSCs. Through the utilization of carbon nano-material as counter electrode in DSSCs, acceptable solar cell performances of ~6% has been achieved (Nam et al., 2010). The barrier that prevents a full industrial utilization with most of these nanomaterials are the high production costs associate with expensive manufacturing equipments. Candle synthesis of carbon nanomaterials is a promising process technique due to its simplicity and continuous production in atmosphere without complex apparatus (Merchan-Merchan et al., 2010). Already, high quality MWCNTs has been obtained by flame synthesis of Co catalyst coated substrate via commercially available candles (Li and Hsieh, 2007a).

From processing point of view, a catalyst-less based process is preferred due to reduced contamination and lower process cost. In this study, carbon nano-onions were synthesized by flame synthesis technique on Cu coated glass substrate. The carbon nano-onions were characterized through scanning electron microscopy (SEM), transmission electron microscopy (TEM), Energy dispersive spectroscopy (EDS) electrochemical measurements and Raman spectroscopy. Subsequently, the carbon nano-onions were utilized as counter electrode in DSSCs and demonstrated its potential as a replacement for conventionally used pt.

2. Experimental

Fluorine doped tin oxide (FTO) and Corning glass substrates were cleaned by ultrasonic agitation in acetone, isopropanol (IPA) and distilled water, for 10 min within each solvent. Around 10 nm of Cu thin film was deposited on the substrates using a 2-in. Direct Current (DC) magnetron-sputtering coater using a 99.9% pure Cu target. The substrates were introduced into the sputter chamber (with target-to-substrate distance at 9 cm) and turbo-pumped down to base pressure of around 5×10^{-6} mTorr. Subsequently, high purity argon gases were injected into the chamber using mass flow controllers. For the Cu depositions, the working pressure, power, temperature and duration were set to $\sim 5 \times 10^{-4}$ mTorr, 33 °C, 120 W and 30 s, respectively. Common household candles (Shin Hong Dar Metal Design Ltd.) were used as source of carbon for this study. Typically, such candles consist of 90% alkanes with carbon numbers range from C_{18} to C_{40}. It is important to note that the size and thickness of the obtained carbon nanomaterial could depend on the ingredients used during the manufacturing of candles (e.g. paraffin, beeswax and tallow). The samples were held around 5 cm from the surface of the candle, which is around 600 °C (Li and Hsieh, 2007b) for a period of 30–120 s.

The Scanning electron microscope (SEM) image and film composition of the samples was obtained using an FEI Quanta 400 F Environmental Scanning Electron Microscope (ESEM) equipped with Energy dispersive Spectroscopy EDS. FT-IR spectra were recorded using a FT-IR Bruker IFS 66 V/S spectrometer in a frequency range of 4500–500 cm^{-1}. A Dongwoo Macro Raman spectrometer/PL system was used to obtain Raman spectra and evaluate the quality of the carbon film. Electrical resistivity of the carbon nano-onion paste was determined by scraping carbon nano-material by doctor blade method. The resultant carbon solids were dispersed in IPA solution and spin coated onto glass substrate to for uniform thin film. Four probe measurements were performed to determine the sheet resistance of the films. Cyclic voltammetry measurements were conducted in a conventional three-electrode set-up in 3-methoxypropionitrile solution containing 1 M 1.3-dimethylimidazoliumiodine, 0.5 M 4-tert-butylpyridine, 0.15 M iodine, and 0.1 M Guanidine thiocyanate (Sigma Aldrich). DSSCs were fabricated by doctor blade method ~15 μm of TiO_2 (Degussa) onto pre-cleaned fluorine doped tin oxide. The TiO_2 photoanodes were dye-sensitized by immersion into a 5×10^{-4} M ethanoic solution of ruthenium-based N719 dye for at least 1 day. After the dye impregnation process, the photoanodes were washed with ethanol to remove excess dye. Two types of counter electrodes were fabricated: conventional Pt coated FTO and carbon nano-onion/Cu/Corning substrate. Pt counter electrodes were fabricated by spin coating "Eversolar Taiwan" Pt solution onto cleaned FTO substrates and baked at 450 °C for 10 min to remove organic residues, whereas carbon-onion based counter electrodes were fabricated by aforementioned method for 90 s on copper coated Corning glass. DSSCs were constructed by sandwich a Suryn sheet between the TiO_2 photoanode and Pt coated glass. Then the DSSCs cell were sealed by hot compress the Suryn sheet with redox couple electrolyte, 0.1 M LiI, 50 mM I_2, 0.6 M 1,2-dimethyl-1,3-propylimidazolium iodide, 1 M tert-butylpyridine, and 3-methoxypropionitrile, injected between the counter and photoanode. Current density–voltage (J–V) characteristics were measured using a Keithley 2400 source-measure unit, under illumination (100 mW/cm^2), provided by a solar simulator (Science-tech). Cyclic voltammetry was performed in a three-electrode system in an acetonitrile solution of 0.001 M I_2, 0.01 M LiI and 0.1 M $LiClO_4$.

3. Results and discussion

Fig. 1(a–d) shows the SEM images of carbon nanomaterials synthesized on Cu coated glass substrates for 30 s,