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RAPID COMMUNICATION

Electrospun carbon nanofibers with surface-attached platinum nanoparticles as cost-effective and efficient counter electrode for dye-sensitized solar cells

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Abstract
Dye-sensitized solar cells (DSCs) have attracted incredible attention in recent years as relatively inexpensive alternative to silicon solar cells. Conventionally, a transparent fluoride-doped tin oxide (FTO) conductive glass with a thin layer coating of platinum (Pt) is used as counter electrode in DSCs. The widespread use of Pt as counter electrode in DSCs is due to its catalytic capability for I_3^- reduction in electrolyte. However, Pt is costly and can be affected by the corrosive nature of I^-/I_3^- redox couple, which makes it a less desirable candidate for use in industrial scale manufacturing. In this study, carbon nanofibers with surface-attached Pt nanoparticles were prepared by stabilization and carbonization of electrospun polyacrylonitrile (PAN) nanofibers and subsequent controllable Pt nanoparticle growth on the obtained carbon nanofiber surface through redox reaction. The hierarchical carbon nanofibers with surface-attached Pt nanoparticles (ECNFs-PtNPs) were then employed as cost-effective counter electrode in DSCs. The effects of size, morphology, and loading of Pt nanoparticles on performance of DSCs were investigated. Compared to conventional counter electrode, the counter electrode that was made of ECNFs-PtNPs exhibited larger open circuit voltage (V_{oc}).

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The DSCs that were made with ECNFs-PtNPs counter electrode demonstrated excellent solar energy conversion efficiencies in the range of 7% to 8%.

Introduction

Dye-sensitized solar cells (DSCs) have been widely studied as a potential alternative to conventional solar cells due to their ease of fabrication and high energy conversion efficiency [1–5]. A typical DSC consists of three components: a dye-sensitized nanocrystalline titanium dioxide (TiO_2) electrode (photoanode), a counter electrode, and an electrolyte usually containing a I^-/I_3^- redox couple between the two electrodes [6]. When dye molecules are illuminated with sunlight, photoelectrons are produced and then injected from dye molecules to TiO_2 followed by traveling to counter electrode through an external circuit. Finally the electrolyte regains electrons from the counter electrode and then dye molecules recover lost electrons from the electrolyte.

Counter electrode in DSC is usually composed of a fluorine-doped tin oxide (FTO) conducting glass substrate with a coating of platinum (Pt) [1,6]. Pt possesses an excellent catalytic activity for I_3^- reduction [6–8]. Nonetheless Pt can be corroded by electrolyte with time and more importantly, Pt is a precious metal and its high cost and relative scarcity make it a less desirable candidate for use in industrial scale manufacturing [4,6,7]. In order to make cost-effective DSCs, alternative cheap catalysts and substrates are being sought as counter electrode at level of performance comparable to Pt [9]. Extensive research for suitable candidates to replace Pt counter electrode in DSCs has been conducted and electrode materials such as sulfamic acid-doped polyaniline nanofibers [10], tungsten dioxide nanorods [11], low-cost molybdenum carbide and tungsten carbide [12], and so on have been reported.

Carbonaceous materials have been used as counter electrode in DSCs mainly because of their relatively low cost, electrical conductivity, and corrosion resistance [7]. Some of these materials that have been investigated as potential alternatives to Pt counter electrode include graphite [13], carbon black [14], polyaniline/carbon composite [6], functionalized graphene [7], carbon nanotubes [1,15], graphene-based carbon nanotubes [16], and electrospun carbon nanofibers (ECNFs) [17,18]. ECNFs were investigated for the first time in our previous research and their electrocatalytic performance in DSC device was revealed to be comparable to that of pure Pt [17], indicating a less expensive alternative to Pt counter electrode in DSCs. In order to improve electrical conductivity of ECNFs, a composite counter electrode made of ECNFs and Pt particles has been employed in the following research to improve performance of the ECNFs-based DSCs [18]. In that research, Pt particles were introduced by physical adsorption of Pt precursor on ECNFs surface and subsequent heat treatment. The resultant Pt particles on ECNFs exhibited a wide range of size distribution at level of several hundred nanometers.

Herein a novel carbon nanomaterial was developed by growing Pt nanoparticles onto ECNFs surface through redox reaction in a controllable manner and employed as counter electrode of DSCs. Compared to the approach of heat treatment [18], the advantage of this redox approach is its controllability. By judiciously adjusting Pt growth conditions, the amount, size, and distribution of Pt nanoparticles could be tuned/tailored. DSCs that contained these novel electrospun carbon nanofibers with surface-attached Pt nanoparticles (ECNFs-PtNPs) based counter electrodes achieved excellent device efficiencies, which is equivalent to or even higher than that of DSCs with conventional Pt counter electrode.

Experimental

Materials

Polyacrylonitrile (PAN, Mw=150 kDa) and N, N-dimethylformamide (DMF) were purchased from Sigma-Aldrich (St. Louis, MO). TiO_2 nanoparticle paste and N719 dye (Ruthenizer 535-bisTBA) for DSC assembly were purchased from Solaronix (Switzerland).

Preparation of electrospun carbon nanofibers (ECNFs)

ECNFs were prepared by electrospinning PAN solution followed by stabilization and carbonization. PAN was first dissolved in DMF to make a 10 wt.% solution. The PAN solution was loaded into a 30 ml BD Luer-Lok tip plastic syringe with a stainless-steel needle having an 18 gauge 90° blunt end. The electrospinning setup comprised a high voltage power supply (Glassman High Voltage Inc., Series FX) and a flat 15 in. × 15 in. stainless steel collector plate. In electrospinning, a voltage of 15 kV was applied to the PAN solution while a flow rate of 1.0 ml/h was maintained by using a syringe pump (New Era Pump Systems Inc.). Nonwoven electrospun PAN nanofiber mat was collected on aluminum foil that covered the stainless steel plate. The obtained PAN nanofiber mat was next peeled off the collector for thermal treatment in furnace.

In stabilization process, PAN nanofiber mats were sandwiched between graphite plates and heated at a rate of 1 °C/min from 30 to 280 °C and held there for 6 h in a constant flow of air. Carbonization was carried out by heating the stabilized PAN nanofiber mat in a constant flow of nitrogen gas to 1200 °C at a rate of 5 °C/min and maintained at 1200 °C for 1 h.

Preparation of electrospun carbon nanofibers with surface-attached Pt nanoparticles (ECNFs-PtNPs)

ECNFs-PtNPs were prepared by redox reaction. A 2 in. × 2 in. ECNFs mat was first sonicated and then immersed in a solution