Applied Surface Science 314 (2014) 638–641

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Performance enhancement of dye-sensitized solar cells by incorporating graphene sheets of various sizes

Soumitra Satapathi[a], Hardeep Singh Gill[a], Sriya Das[b], Lian Li[c], Lynne Samuelson[c], Micah J. Green[b], Jayant Kumar[a,*]

[a] Center for Advanced Materials, University of Massachusetts Lowell, Lowell, MA 01854, USA
[b] Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, USA
[c] U.S. Army Natick Soldier Research, Development & Engineering Center, Natick, MA 01760, USA

ARTICLE INFO

Article history:
Received 15 January 2014
Received in revised form 16 June 2014
Accepted 1 July 2014
Available online 8 July 2014

Keywords:
Graphene
Dye sensitized solar cells
Dye-Loading
Porosity

ABSTRACT

Dye-sensitized solar cells (DSSCs) were fabricated using photoanodes made from graphene–TiO_2 nanocomposites. The dependence of the size of graphene sheets on the cell performance was investigated. The experimental results indicated that cells loaded with the smaller graphene sheets yielded larger enhancement. The smaller graphene sheets improved the dye adsorption, leading to higher conversion efficiency. The DSSC incorporated with graphene sheets of 184 nm exhibited the largest enhancement in efficiency (~49%) as compared to the cell without graphene.

1. Introduction

Dye-sensitized solar cells (DSSCs), developed by Grätzel and co workers [1], provide a promising alternative clean and renewable energy source. DSSCs employing semiconducting titanium dioxide (TiO_2) and organometallic dyes can efficiently convert sun light into electricity. Power conversion efficiency up to 12% has been reported [2]. Numerous approaches have been taken so far to enhance the conversion efficiency, including design and synthesis of new sensitizers for better light-harvesting, fabrication of two of more DSSCs in tandem form for broader light absorption, development of novel electrolytes with more suitable redox potential for efficient dye regeneration and charge transport etc. [3–5]. Other approaches, such as utilization of periodic nanostructures for effective light-trapping and metal nanoparticles for better light-absorption using surface plasmon resonance, have been adapted to improve the photovoltaic performance [6–8]. However, there still exist many possibilities for further improvements of the efficiency to meet the requirement for practical applications. Employing nanostructured carbon materials, such as graphene, would be an attractive alternative. Single layer graphene is highly transparent (only one atom thick) and absorbs only 2.3% of the incident light. In addition, graphene exhibits extremely high electron mobility (15,000 $cm^2/(V\,s)$) at room temperature [9]. Furthermore, graphene can be easily derived from graphite, which is naturally abundant and inexpensive. It is well-known that graphene possesses very high specific surface area (2630 m^2/g) [10]. Its unique electronic and optical properties along with its high surface area and ease of synthesis render graphene as a suitable candidate for photovoltaic performance enhancement in DSSCs.

Graphene has recently been incorporated into the photoanodes in DSSCs [11–16]. It has been shown that the incorporation of graphene in the photoanodes leads to enhancement in light-harvesting, faster electron transport and reduces charge-recombination. Enhancement on the photovoltaic performance was achieved. It was reported that the DSSCs with a graphene loading of 0.83–1 wt% yielded the highest power conversion efficiency [13,14]. However, to the best of our knowledge, there is no report on the dependence of graphene sheet size on the device performance in the literature so far. Here, we report the size effect of graphene on the performance enhancement of DSSCs. As the graphene size decreases, both the short-circuit current and the efficiency increase. Dye desorption studies indicated improvement of dye loading in the photoanodes incorporated with smaller graphene sheets.

* Corresponding author.
E-mail addresses: hardeep.gill@student.uml.edu (H.S. Gill), Jayant.kumar@uml.edu (J. Kumar).

http://dx.doi.org/10.1016/j.apsusc.2014.07.003
0169-4332/

2. Experimental

The photoanode in a typical DSSC, is composed of porous semiconducting TiO_2 nanoparticles (NPs) loaded with the sensitizers. The nanoporous photoanode also provides a percolation network for the passage of photogenerated electrons to the transparent conducting oxide substrate. In this study, we have modified the photoanode by heterogeneous mixing of TiO_2 NPs with graphene of various sizes. For better control over the graphene size, we have prepared the graphene dispersions using two different approaches, the modified Hummers method [17] and exfoliation of pristine graphene in the presence of stabilizers [18]. In the first approach, graphene was synthesized by the chemical reduction of graphene oxide with hydrazine monohydrate. Graphene oxide was first made by the modified Hummers method through acid oxidation of graphene nanoplatelets. Subsequently, graphene oxide dispersion was reduced to form reduced graphene oxide by hydrazine monohydrate at 80 °C for 2 h, centrifuged to form homogeneous stable graphene dispersion and dried via evaporation of water.

In the second approach, expanded graphite was tip sonicated for 1 h in surfactant solution (sodium dodecyl benzene sulfonate). The sonicated sample was then centrifuged for 4 h at 5000 rpm to remove large aggregates of graphite, and the supernatant was retained. The characterization of graphene dispersion was reported earlier [18]. Dynamic light scattering (DLS) was used to examine the size distribution of the graphene in the dispersions. A compact thin TiO_2 layer (about 80 nm) was spin-cast onto a fluorine-doped tin oxide (FTO) coated glass substrate by a sol–gel process [19]. The synthesized graphene was then used to fabricate TiO_2–graphene composite photoanodes. Degussa P25 TiO_2 NPs suspension in acetic acid water was prepared. The zeta potentials of the graphene dispersion and the TiO_2 NPs suspension were measured. To investigate the size effect of the graphene sheets on the photovoltaic performance, the graphene prepared by the Hummers method were probe sonicated for different time duration to obtain smaller graphene sheets. The graphene produced by the second method with an average size of 184 nm was used without sonication. The TiO_2 suspension was then mixed with 1 wt% of the graphene sheets. Nanoporous working electrodes were prepared by spin coating the mixture on the top of the thin TiO_2 covered FTO substrates. The surface characteristics of bare photoanode and graphene loaded TiO_2 photoanode were investigated by scanning electron microscopy (SEM).

The composite photoanodes (4 μm thick) with different graphene sizes were used to fabricate the DSSCs. The spin-cast nanocomposite photoanodes were sintered at 450 °C for 4 h and then dipped in 0.3 mM Z907 dye ethanol solution overnight. The chemical structure of the dye is shown in Fig. 1. The platinum coated FTO substrates were used as counter electrodes. The DSSCs without any graphene loading were also fabricated as references (standard cells). The photovoltaic performance of the solar cells was evaluated under simulated AM 1.5 solar irradiation (100 mW/cm^2) in conjunction with a source meter.

3. Results and discussion

Fig. 2(a) shows the cross-sectional SEM image of a TiO_2 photoanode where a large amount of nanoparticles are densely packed. The TiO_2 film is highly porous. Fig. 2(b) shows the cross-sectional SEM image of the graphene–TiO_2 composite film with 1 wt% graphene (184 nm) loading. The image revealed that the graphene sheets were well-dispersed within the TiO_2-NPs. Increase in porosity of the graphene-loaded nanocomposites as compared to that of the TiO_2 films is observed. This led to improvement in the dye loading and to enhancement of the photocurrent in the DSSCs.

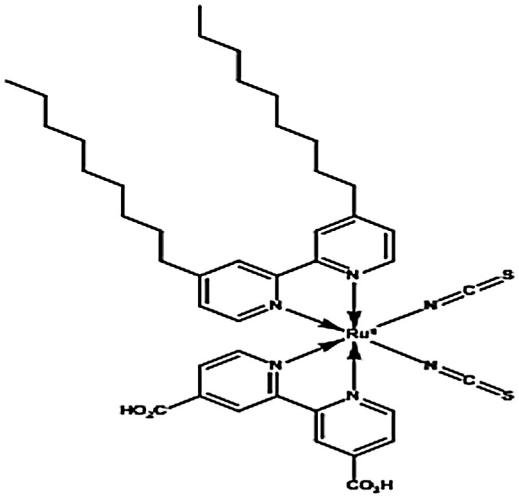

Fig. 1. Chemical structure of Z907 dye.

The zeta potential analysis showed that the graphene surfaces were negatively charged (−42 mV) whereas the TiO_2 nanoparticles were positively charged (around 30 mV). When these two oppositely charged nanomaterials were mixed together, the electrostatic interaction would enable them to adhere on each other. Graphene sheets of different sizes were obtained by probe sonication of the Hummers method synthesized graphene at various time durations. Longer sonication yielded smaller graphene sheets. After 60 min of probe sonication, the size of the graphene decreased to 292 nm. Further sonication for a considerable amount of time did not reduce the size of graphene significantly. The graphene with an average size of 184 nm prepared by the second method was utilized without sonication. Table 1 summarizes the sizes and monodispersities of the graphene sheets used in the DSSCs with or without sonication as determined by DLS.

Fig. 3 shows the current–voltage (I–V) characteristics of the DSSCs. The standard TiO_2 cell without any graphene loading yielded a short-circuit current density (J_{sc}) of 9.76 mA/cm^2, an open circuit voltage (V_{oc}) of 0.68 V, a fill-factor (FF) of 66% with a power conversion efficiency (η) of 4.43%. Upon loading of the 1.2 μm size graphene sheets, 22% increase in J_{sc} and 15% gain in η were attained. 32% and 41% increase in J_{sc} were obtained using 444 nm and 292 nm size graphene, respectively. The highest photovoltaic performance enhancement was achieved by employing the graphene with an average size of 184 nm. A J_{sc} of 14.66 mA/cm^2 and a η of 6.62%

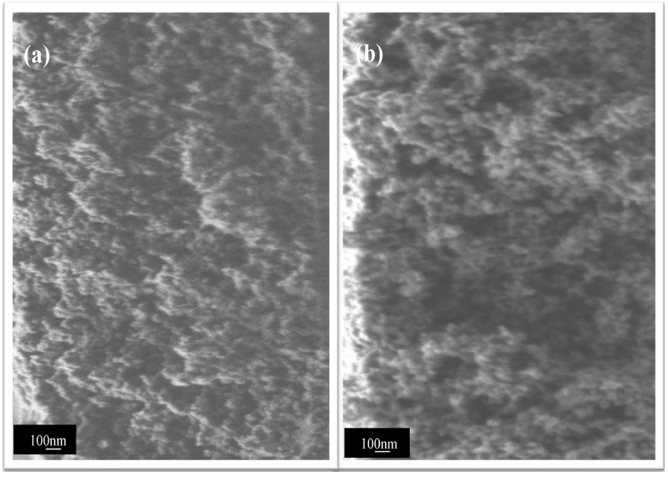

Fig. 2. SEM images of (a) a TiO_2 photoanode and (b) a TiO_2–graphene composite.