Solar Energy Materials and Solar Cells 182 (2018) 314–320

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

NiS/rGO nanohybrid: An excellent counter electrode for dye sensitized solar cell

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ARTICLE INFO

Keywords:
DSSC
Counter electrode
Reduced graphene oxide
Nickel sulfide
Photo conversion efficiency

ABSTRACT

We report the synthesis of a novel nanohybrid based on nickel sulfide (NiS) nanoparticles decorated reduced graphene oxide (rGO) following a facile hydrothermal approach for application as Pt-free counter electrode (CE) in dye sensitized solar cells (DSSC). The DSSC devices fabricated using this NiS/rGO nanohybrid film as CE showed an impressive power conversion efficiency (PCE) of 9.5% and a fill factor of about 0.78 when illuminated by AM 1.5 G simulated solar light. These values are well above those reported previously for DSSCs fabricated with Pt free CE and thus establishes the potential of the NiS/rGO nanohybrid as an excellent low-cost CE material for DSSC fabrication. The improvement in the PCE is due to improved electro-catalytic activity of the NiS/rGO nanohybrid for reduction of the triiodide caused by the synergistic effects of highly catalytic NiS nanoparticles and electrically conductive rGO.

1. Introduction

DSSCs have attracted enormous interest of the researchers as a promising alternative to the silicon solar cell devices for renewable energy harvesting applications because of their low cost and moderately high solar to electric power conversion efficiency (PCE) [1,2]. In general, a conventional DSSC uses a nanocrystalline TiO_2 film as photo anode (PA) on coated with an organic dye, a platinum conductive glass as cathode, often called counter electrode (CE), and an electrolyte generally containing an iodide/triiodide (I^-/I_3^-) redox couple placed between anode and cathode. Consequently, researchers have been working to develop novel materials with tailored properties for PA, CE, electrolyte, and dye, for improved efficiency of the DSSC as each of these components has specific role in the DSSC operation. The CE plays a crucial role in overall DSSC performance as it collects electrons from the external circuit and transfers it to the electrolyte by reducing the I_3^- ions [3]. Although Pt quite well satisfies the prerequisites of a good CE material thanks to its excellent electrical conductivity and electrocatalytic ability, its high cost is a concern for the economic viability of commercial DSSC. Consequently, demand for replacing Pt with low-cost earth abundant materials has been increasing over the past few years [4,5].

Carbon materials, polymers, transition metal sulfides, nitrides, carbides, etc. are among the various alternative materials that are often considered for this purpose [6–12]. Among various transition metal sulfides, nickel sulfide (NiS) is one of the promising candidates due to its high electrocatalytic property, low cost and good chemical and thermal stability [13,14]. Using NiS film as CE, PCE value of as high as 6.82% has been reported recently for DSSC which is comparable with that for Pt-based CE (7.00%) [9]. In another work, Ku et al. prepared a transparent NiS CE and achieved good PCE (6.25%) for a thiolate/disulfide-intervened DSSC [15]. However, the low carrier mobility in nickel sulfide nanoparticles (caused by boundary limits between particles) reduces the DSSC performance. To overcome this, a possible approach could be to combine the highly catalytic nickel sulfide nanoparticles with a phenomenal conductor with large surface area.

Graphene, the two-dimensional nanoscale allotrope of carbon, along with its close derivative, rGO has proved to be a good photoelectric material due to its high electrical conductivity, large surface area and excellent thermal, mechanical and chemical stability [16]. As high quality graphene is very difficult to produce in large scale, rGO offers a very good alternative to most of the applications that exploit the interesting properties of graphene. These interesting properties of graphene and rGO make them suitable for a number of applications including sensors, photocatalysis, batteries, lightweight polymeric composites, supercapacitors, DSSC, etc. [17–25]. For example, Bi et al. reported an efficiency of 5.25% for DSSCs fabricated using a CVD (chemical vapor deposition) grown graphene film decorated with NiS

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https://doi.org/10.1016/j.solmat.2018.03.026
Received 25 August 2017; Received in revised form 15 February 2018; Accepted 13 March 2018

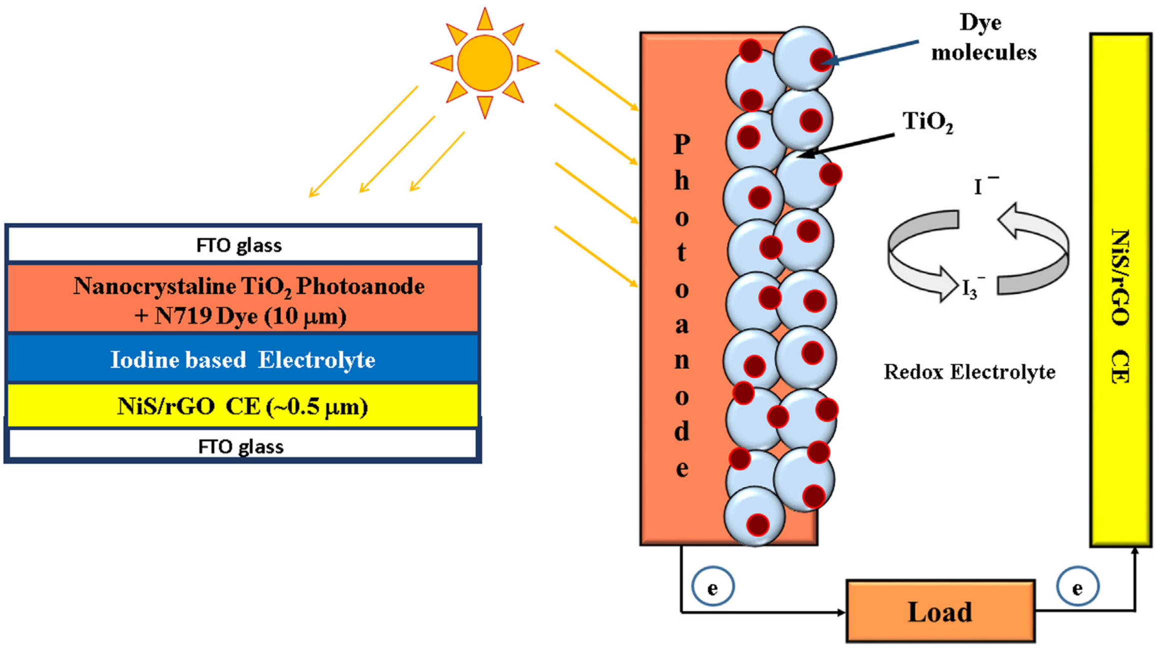

Fig. 1. Schematic diagram of the fabricated DSSC (left) and the working principle (right).

nanoparticles deposited from a Ni precursor by dip coating [24]. However, the CVD method is rather expensive and production of graphene in large quantities using this method is rather difficult. In another work, Lin et al. combined rGO with molybdenum sulfide to develop a novel CE using which they obtained 6% efficiency for the DSSC [25]. All these point to the need for further investigation on NiS and graphene/rGO combination based counter electrodes for development of DSSCs with greater efficiency than those already reported.

Apart from CE material (as discussed above), the sensitizer/dye also plays important role in the DSSC performance. A good dye should possess broad and strong absorption in the visible to near-infrared region and its lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels should be chemically stable for effective charge injection, and restrict recombination [26–28]. Jei et al. used a series of D–π–A based organic sensitizers that contain two 4-*tert*-butylbenzene moieties in the donor part of triphenylamine group and obtained a PCE of 5.35% [29]. Ruthenium based dyes such as N719 have received high demand due to their high absorption in the visible range of solar spectrum, along with excellent electron injection and chemical stability [30–33]. N719 dye has also been used by researchers in fabrication of DSSCs using CE material similar to that of the present work [31–33]. For example, Yue et al. reported DSSCs with MWCNT/WS_2 as CE and N719 as dye and obtained PCE of 6.41% [31].

In the present work, we report the fabrication of a DSSC using a novel CE material comprising NiS/rGO nanohybrid synthesized by a cost-effective and facile hydrothermal method. In order to focus on the influence of the CE material on the DSSC performance we have used N719 dye as standard in our work due to its advantages as discussed above. The morphological analysis confirmed the hybrid nanostructure of rGO sheets well-decorated with NiS nanoparticles. Thin film of this nanohybrid was used as CE instead of Pt to fabricate the DSSC and several devices were tested under standard test conditions for parameters such as fill factor and efficiency. To the best of our knowledge, this is one of the very few studies involving use of metal sulfide and rGO nanohybrid as CE in DSSC made with N719 dye and the efficiency of 9.5% reported in this work is unparalleled to previous reports using similar materials.

2. Experimental section

2.1. Synthesis of NiS/rGO nanohybrid

GO was prepared from expandable graphite flakes following a modified Hummers method [23]. More details on the synthesis as well as information on the chemicals and reagents used in this study can be found in Supplementary information. Next, $Ni(NO_3)_2{,}6H_2O$ (50 mM) was added to 50 ml of GO solution (1 mg/ml) under stirring. After 30 min of stirring 10 ml ethylene glycol was added to the reaction solution. After 20 min stirring 50 ml L-cysteine solution (100 mM) was added to the reaction mixture. L- Cysteine works as sulfur precursor as well as a reducing agent for GO. After 2 h stirring the solution was transferred to a 125 ml teflon lined steel autoclave and sealed. The autoclave was then placed in an oven heated at 160 °C for 18 h allowing the hydrothermal reaction to complete after which it was allowed to naturally cool to room temperature. The product collected from the autoclave was washed several times with deionized water and ethanol before drying at 60 °C for 20 h in vacuum. Bare NiS nanostructures were also synthesized by the same route without the presence of GO in the starting solution.

2.2. Preparation of CE

The CE was made by mixing of NiS/rGO nanohybrid (80 wt%), acetylene black (10 wt%) and PVDF (10 wt%) by grinding them together and then dissolving in N-methyl-2-pyrrolidone. This prepared slurry was then deposited on FTO glass (sheet resistance 7 Ω/□) to make a uniform film over an area of 5 cm × 5 cm by spin coating at 4000 rpm (Apex Instruments, India) followed by drying in air at 100 °C. Typical thickness of the film as measured by electron microscopy is ~400 nm. For comparison, CEs made of bare NiS and bare GO were also prepared by the same procedure.

2.3. Fabrication of the DSSC

The DSSCs were fabricated (Fig. 1) by injecting the I^-/I_3^- redox electrolyte (composed of 0.05 M I_2, 0.1 M LiI, and 0.1 M $LiClO_4$ and dissolved in anhydrous acetonitrile) between the ruthenium based N719 dye-sensitized TiO_2 film (photoanode) and the NiS/rGO