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Highly catalytic nickel sulfide counter electrode for dye-sensitized solar cells

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ABSTRACT

Dye-sensitized solar cells (DSSCs) have been the epicenter of attention for past few decades as a potentially cost-effective substitute for silicon-based solar cells. In DSSCs, the counter electrode (CE) plays a pivotal role in amassing electrons from the external circuit and catalyzing the I_3^- reduction in the electrolyte. In this paper, the development of nickel sulfide (NiS) CEs for DSSCs are studied, emphasizing significant crescendos that assure economical, competent, and stable DSSC systems. Specially, we pinpoint on the design of highly efficient NiS CE, including design ideas, fabrication approaches and characterization techniques that serve as practical replacements to conventional noble metal Pt electrodes. DSSC fabricated with the NiS CE achieved a power conversion efficiency of 5.69% under 1 sunlight illumination (100 mW cm^{-2}, AM 1.5 G).

1. Introduction

Dye-sensitized solar cells (DSSCs) have been the focal point of harnessing solar energy from the past few decades owing to their capability in converting solar energy to electrical energy [1–3]. Enhancements in the efficiency and stability of DSSCs are required for widespread hands-on usage. The DSSCs are fabricated primarily with two electrodes and a redox-active electrolyte. In DSSCs, the photo electrodes are made from TiO_2 which when exposed to light prevents photo corrosion due to their extraordinary chemical stability, subsequently surging the life time [4,5]. The titanium dioxide (TiO_2) centered photo-anodes sensitized with dye (ruthenium based dye), an electrolyte with the I^{3-}/I^- redox couple and Pt (platinum) counter electrode (CE) forms a DSSC. In DSSCs, dye absorbs the molecules for photo generation which plays an integral role in increasing the power conversion efficiency and stability. The redox electrolyte, iodide/triiodide (I^-/I^{3-}) is an essential inorganic constituent in DSSCs that helps in diminishing the power conversion efficiency losses. Prominent optimizations of all cell components are indispensable for promising performance of DSSCs.

The CE is a vital component of DSSCs which is composed of Pt materials. However, Pt being expensive and scarce in nature is replaced with an inferior substitute. Thus, there exists a tradeoff between the cost and quality of the solar cells. The prerequisite of the substitute material is to overcome the challenges associated with Pt-based electrodes and should provide high electrical conductivity and superior catalytic activity simultaneously. The Pt-free materials for DSSCs such as the inorganic materials have fashioned good performances for DSSCs [6]. Among the inorganic materials, nickel sulfide (NiS) has been considered as a favorable alternative to substitute Pt for DSSCs due to its high conductivity, easy fabrication, and excellent catalytic activity. Many other researches have been reported based on NiS CE [7,8]. In this work, we efficaciously synthesized DSSCs assembled with NiS CEs and accomplished comparable photoelectric conversion properties to that based on Pt CE. Chemical bath deposition (CBD) is frequently and economically used methods for the deposition of metal chalcogenide, metal oxide and metal sulfide thin films and is presently drawing and expedient for large area deposition [9]. The low charge transfer resistance (R_{CT}) at the NiS CE/electrolyte interface is detected based from electrochemical impedance spectroscopy, indicating a good electro-catalytic activity of NiS CE ability towards the I^-/I_3^- electrolyte.

The uniqueness in this present work describes the methodical study accomplished for appreciative and applicable composition of materials, which improves the photovoltaic properties of DSSCs which has not been reported previously. In this work, the CBD method has been used for the deposition of NiS thin films. The morphological, optical, and structural properties of the optimized films are deliberated. This report deals with the challenge in fabricating DSSCs with the optimized CE. We have achieved quite

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good photovoltaic conversion efficiency of 5.69%. A representational structure of the TiO_2/dye/NiS DSSC with nano structured NiS CE is depicted in Fig. 1. The photons are absorbed by the dye and the electrons are driven towards the TiO_2 conduction band and hole transfer into the electrolyte upon 1 sun illumination. At the CE, reduction of the oxidized redox system regenerates the reduced redox species.

2. Experimental

2.1. Materials

All chemicals used were purchased from Aldrich and employed without any further purification. FTO substrate with a sheet resistance of 10 Ω/square (Sigma–Aldrich) was used to prepare photo-anodes and CE.

2.2. Preparation of TiO_2 electrode films

The substrates were cleaned ultrasonically using acetone, ethanol, and deionized water for 10 min each and dried with nitrogen gas. The cleaned FTO glasses were dipped in 50 mM of $TiCl_4$ solution for 40 min at 60 °C to form a compact layer of TiO_2 followed by annealing at 450 °C for 30 min. The photo electrodes were prepared using a commercially available nano-porous TiO_2 paste with a particle size of 20 nm (Ti-Nanoixide HT/SP Solaronix) on electrodes having an active area of 0.25 cm^2. Subsequently, the samples were sintered at 450 °C for 30 min for solvent evaporation.

2.3. Fabrication of dye sensitized photoanode

The TiO_2 electrodes were kept in N719 dye for 24 h and then dried with N_2 gas and only then used further.

2.4. Fabrication of NiS counter electrode

NiS thin films were deposited on FTO substrates using CBD. Erstwhile to deposition, FTO substrates were ultrasonically cleaned with acetone, ethanol, and distilled water each for 10 min. The substrate was immersed horizontally into the solution which contains nickel sulfate hexa- hydrate and thioacetamide (TAA) which acts as a source of Ni^{2+} and S^{2-} ions urea and/or TEA (triethanolamine) reagents for depositing NiS thin films. Table 1 shows the in-depth preparation of the NiS CEs thin film. The substrate with growth solution was kept in hot air oven at different conditions of temperature of 70 °C, 80 °C, and 90 °C for 2 h and 1 h deposition time. No visible coating was observed at 70 °C and 80 °C while semi transparent films were observed at 90 °C for 2 h deposition time and thus the optimized condition was achieved. Finally, at different conditions the NiS coated FTOs were cleaned with DI water and are denoted as Sample A–D. The Pt CE is denoted as Sample E. To fabricate the Pt electrode, the cleaned FTO glass substrate was coated with a Pt paste (Pt-Catalyst T/SP, Solaronix) in the active area of ~0.7 cm^2 using the doctor blade method and sintered at 450 °C in air for 10 min.

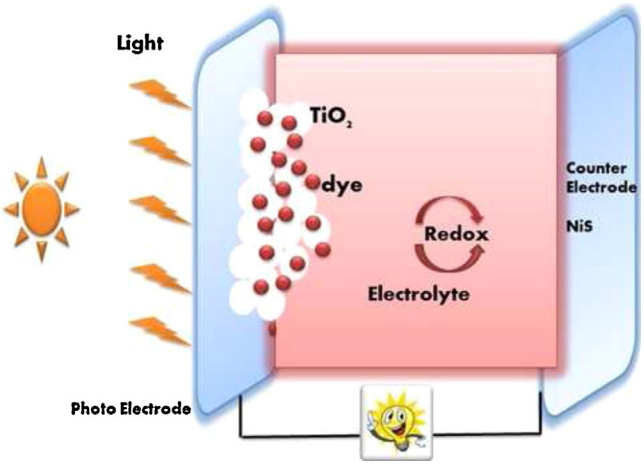

Fig. 1. Schematic structure of TiO_2/dye DSSC based NiS CE.

2.5. Cell fabrication

The dye sensitized TiO_2 electrode and the NiS counter electrode were assembled and sandwiched using a transparent 60 mm thick Surlyn spacer (Dupont). The iodide/triiodide (I^-/I^{3-}) electrolyte was injected through the pin-hole made in the CE.

2.6. Characterization

The surface morphology of NiS thin films was characterized using field emission scanning electron microscope (FE-SEM, S-4200, Hitachi) equipped with an on-system energy dispersive X-ray spectroscopy (EDS) analysis with an operating voltage of 15 kV for elemental compositions. The current–voltage characteristics of the DSSCs was performed under 1 sun illumination (AM 1.5 G, 100 mW cm^{-2}) using ABET Technologies (USA) solar simulator. Electrochemical impedance spectroscopy (EIS) was conducted on DSSC with NiS and Pt CEs using BioLogic potentiostat/galvanostat/EIS analyzer (SP-150, France) under 1 sun illumination and the frequency ranged from 100 mHz to 500 kHz.

3. Results and discussion

3.1. Surface morphology

Fig. 2 shows the surface morphology of deposited NiS thin films on FTO at different preparation conditions such as concentrations of TAA with and without TEA. The NiS film thickness was found to be ~190 nm for Sample B and thickness varied between 150 and 200 nm for other NiS thin films. Adhesion of CE active materials on FTO substrate plays a vital role which determines the power conversion efficiency [10]. If the active material does not adhere properly to the substrate, it may be peeled off from the substrate and released into the electrolyte which could cause the decrease in efficiency of DSSCs. In this study, good adhesion of NiS thin films on

Table 1
NiS thin films deposited on FTO substrate at different preparation conditions.

Nickel sulfide CE	Nickel (M)[a]	Thioacetamide (M)[a]	Urea (M)[a]	Triethanolamine (ml)[b]
Sample A	0.1	0.4	0.8	–
Sample B	0.1	0.4	0.8	2.5
Sample C	0.1	0.8	0.8	2.5
Sample D	0.1	0.8	0.8	–

[a] M: molarity.
[b] ml: milliliter.