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$CoSe_2$/Carbon Thin Films as the Counter Electrode for Dye-Sensitized Solar Cells

Kuo-Chuan Ho[1, 2] and I-Ting Chiu[1]

[1] Department of Chemical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd., Taipei 10617, Taiwan
[2] Institute of Polymer Science and Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Rd., Taipei 10617, Taiwan
Phone: +886–2–2366–0739 E-mail: kcho@ntu.edu.tw

Abstract

Three types of composite films of $CoSe_2$ and carbon ($CoSe_2$/C), which have different morphologies, were obtained on fluorine-doped tin oxide (FTO) substrates via a simple two-step synthesis, *i.e.*, first a pulse-potential electro-deposition and then an annealing process. After the annealing, nanograin (NG)-like, nanorock (NR)-like, and nanoclimbing-wall (NCW)-like films of $CoSe_2$/C were obtained on the FTO substrates. All the annealed $CoSe_2$/C films were used as the counter electrodes (CEs) for dye-sensitized solar cells (DSSCs). The DSSC with the $CoSe_2$/C-NCW exhibits the highest solar-to-electricity conversion efficiency (η) of 8.92±0.03%, which is found to be even higher than that of the cell with a platinum (Pt) CE (8.25±0.03%). The $CoSe_2$/C-NCW was further electro-deposited onto two low-cost, highly porous, and flexible substrates, *i.e.*, nickel foam (NF) and carbon cloth (CC). The DSSC with the $CoSe_2$/C-NCW on NF exhibits a very high η of 10.46±0.23% at 1 sun and an η of 7.90±0.05% at 0.2 sun. The low-weight CC rendered for its DSSC a high η of 9.87±0.06% at 1 sun and an η of 7.83±0.03% at 0.2 sun.

1. Introduction

Recently, dye-sensitized solar cells have attracted more and more attention because the advantages of their high conversion efficiencies, low costs and simple preparation processes. In addition, they can work under low-light intensity and be applied onto flexible substrates. However, the development of DSSCs is limited by the usage of the traditional expensive Pt counter electrode. Thus, the aim nowadays for developing a substitute material is not only to reach high cell efficiency (η) but to maintain a low cost. Among all the potential substitutes, researchers have paid an intensive attention to cobalt selenide due to its earth abundance, high conductivity, and good electro-catalytic ability. Cobalt selenide counter electrode (CE) often possesses a structure of bulk or particles, the lack of directional or low dimensional electron transfer pathways and active surface areas confines the pertinent DSSCs' performance. Since vertically-aligned structures of electro-catalysts were reported to facilitate faster charge transport from the substrate through the electro-catalysts to the electrolyte [1-4], the $CoSe_2$ with such structure is expected to exhibit a high electro-catalytic ability, and thereby give a high η to its DSSC. Besides, carbonaceous materials normally possess oriented charge transfer pathways and excellent conductivities; for this reason, they have been used as the counter electrode materials in DSSCs; they rendered good power conversion efficiencies up to ~8% for their DSSCs [5-9]. Based on the above literatures, a composite film of $CoSe_2$ and a carbonaceous material as the counter electrode material seems to be a promising approach for achieving much higher power conversion efficiency for a Pt-free DSSC.

2. Experiments and Results

In this study, we aim to prepare a low dimensional $CoSe_2$/C with a structure of nano-climbing wall via a simple electro-deposition process. First, the cleaned fluorine-doped tin oxide glasses (1 cm^2) were separately used as the working electrodes for a three-electrode system in three different aqueous bathes containing 5 mM cobalt chloride and 0.75 mM selenourea with pH values of 4.0, 6.0, and 8.0; the obtained $CoSe_2$/C films were denoted as $CoSe_2$/C-4, $CoSe_2$/C-6, and $CoSe_2$/C-8, respectively. A Pt foil and a Ag/Ag^+ electrode were used as the counter and reference electrodes, respectively. A pulse-potential voltage procedure was performed for 100 cycles for each bath; one cycle contained -0.9 V for 6 seconds and 0 V for 4 seconds. Finally, the obtained $CoSe_2$/C films were treated via a post annealing process at 500 ^oC for 30 min in vacuum to obtain a good crystallinity. From the field-emission scanning electron microscopy (FE-SEM) images shown in **Fig. 1**, the $CoSe_2$/C-NG, $CoSe_2$/C-NR, and $CoSe_2$/C-NCW show the nanograin-like, nanorock-like and nanoclimbing wall-like surface morphologies, respectively. Among them, $CoSe_2$/C-NCW simultaneously possesses the two-dimensional (2D) structures and a porous surface, which imply an outstanding electron transfer capability and a great electro-catalytic ability, respectively. In **Fig. 1(e)**, the DSSCs with $CoSe_2$/C-NG, $CoSe_2$/C-NR, and $CoSe_2$/C-NCW CEs give the η's of 8.41%±0.02%, 7.83%±0.02%, and 8.92%±0.03%, respectively. It is notable that the nanoclimbing wall-like $CoSe_2$/C-NCW renders the best η, which is even higher than that of Pt (8.25%±0.03%); therefore, the earth abundant $CoSe_2$/C-NCW is a very promising material to replace Pt. Moreover, a nickel-foam-supported $CoSe_2$/C-NCW on NF reaches higher η of 10.46%±0.23% under 100 mW cm^{-2} and maintained 72% of η under 20 mW cm^{-2} (**Fig. 1(f)**). In **Fig. 1(g)**, the low-weight CC rendered for its DSSC a high η of 9.87±0.06% at 1 sun and an η of 7.83±0.03% at 0.2 sun. It is believed that $CoSe_2$/C-NCW is suitable for both outdoor and indoor electronic devices.

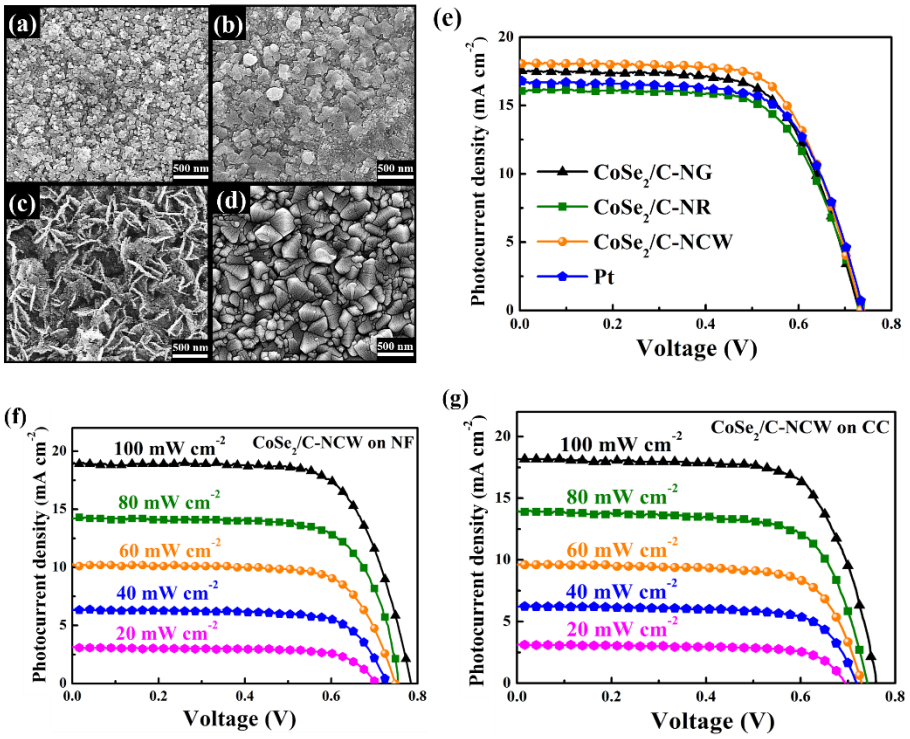

Fig. 1 FE-SEM images of (a) $CoSe_2$/C-NG, (b) $CoSe_2$/C-NR, (c) $CoSe_2$/C-NCW, and (d) Pt film. (e) Photocurrent density-voltage curves of the DSSCs with Pt and $CoSe_2$/C CEs, obtained at 100 mW cm^{-2}. *J–V* curves of the DSSC with the CE of (f) $CoSe_2$/C-NCW on NF and (g) $CoSe_2$/C-NCW on CC, obtained at different light intensities.

3. Conclusions

Three types of $CoSe_2$/C composite films with different morphologies, *i.e.*, nanograins ($CoSe_2$/C-NG), nanorocks ($CoSe_2$/C-NR), and nanoclimbing-walls ($CoSe_2$/C-NCW), were obtained on FTO substrates. The cell with $CoSe_2$/C-NCW reaches the highest efficiency of 8.92±0.03%; this efficiency is even higher than that of the cell with Pt (8.25±0.03%). This highest efficiency is attributed to the best electro-catalytic ability and the fastest charge transfer ability of $CoSe_2$/C-NCW; it can be said that the co-existence of orientated electron transfer pathways and dot-matrix like projections in the film of $CoSe_2$/C-NCW is a desirable hierarchical struture for I_3^- reduction. The cells with the CEs of $CoSe_2$/C-NCW on NF and $CoSe_2$/C-NCW on CC exhibit much higher η's of 10.46±0.23% and 9.87±0.06%, respectively, at 100 mW cm^{-2}. These cells both exhibit good η's at a very dim illumination of 20 mW cm^{-2}, indicating their infinite applications in dim or in indoor electronics. Thus, the $CoSe_2$/C-NCW is a potential replacement for the traditional noble Pt in a DSSC. Moreover, it is environmental-friendly and suitable for various substrates and large-scale roll-to-roll process.

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