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Solution Processed Ni_xS_y Films: Composition, Morphology and Crystallinity Tuning via Ni/S-Ratio-Control and Application in Dye-Sensitized Solar Cells

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ABSTRACT

The design and facile fabrication of highly efficient, cost-effective and earth abundant counter electrode material on an electrode surface is highly desirable for the application of dye-sensitized solar cells (DSSCs). Herein, using a N,N-dimethylformamide based solution process, transition metal chalcogenide Ni_xS_y films have been obtained by spin-coating a $NiCl_2$-thiourea (Ni-Tu) solution combining mild thermal treatment. XRD, SEM and TEM characterizations reveal that the current procedure allows for phase composition (Ni_3S_2, NiS and NiS-NiS_2), crystallinity, morphology (film uniformity and compactness) control of the films through simple adjusting Ni/S ratio in the precursor solution. Electrochemical analysis indicates that the FTO supported Ni_3S_2 and NiS films exhibit excellent electrocatalytic activity toward the reduction of triiodide, resulting in higher photo-electric conversion efficiencies of 6.86% and 6.95% when used as counter electrode in DSSCs, versus 6.66% for Pt. In particular, even without the support of conductive FTO layer, Hall effect measurements and electrocatalytic analysis reveal that pristine Ni_xS_y films exhibit good electrical conductivity and electrocatalytic activity, yielding a highest photo-electric conversion efficiency of 4.41% when used as counter electrode in DSSCs. Our study thus provides a facile procedure which allows for composition, morphology optimization and high performance for low-cost, large-scale DSSC application.

1. Introduction

Dye-sensitized solar cells (DSSCs), which directly convert solar energy into electricity, hold great potential as alternatives to conventional silicon-based solar cells due to its high power conversion efficiency, low manufacturing cost and easy fabrication process (simple, practical, economical) [1–5]. As a critical component of DSSCs, counter electrode (CE) serves to collect electrons from the external circuit and transfer them to the electrolyte, catalyzing the reduction of I_3^- to I^- at CE/electrolyte interface in the case of I^-/I_3^- system [6–9]. Therefore, good electrical conductivity and high electrocatalytic activity are key factors to consider for an efficient CE material [10,11]. Benefiting from the superior electrocatalytic activity, conductivity and stability, noble metals such as platinum (Pt) are at present the most active catalysts for catalyzing the reduction of I_3^-. However, its application in large-scale DSSCs is limited by its high cost and low elemental abundance [12,13]. Motivated by this challenge, the search for cost-effective and earth abundant materials with both good electrical conductivity and excellent electrocatalytic activity has become an important pursuit towards enabling large-scale commercialization of DSSCs. In this regards, various classes of materials such as carbonaceous materials [14–18], conductive polymers [19–21], inorganic compounds including sulfides [22–26], carbides [27–30], nitrides [31,32], oxides [33,34] and selenides [6,10,35–40] have been developed and identified as promising alternatives to Pt.

Among the various electrocatalysts recently developed, nickel sulfides (Ni_xS_y), which exhibits various atomic ratios (Ni_3S_2, NiS and NiS_2) depending on synthetic conditions, has emerged as an efficient candidate with high catalytic activity toward I_3^- reduction [41–47]. For example, Guo et al. synthesized NiS_2 polyhedrons and

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demonstrated high photo-electric conversion efficiency in DSSCs [48]. Fu et al. synthesized NiS/Ni_3S_2 nanorod composite array and α-NiS nanocrystals, respectively, which performed excellent photo-electric performance when comparing with conventionally noble-metal Pt electrode [46,47]. Despite the effort of improving the electrocatalytic activity, it is also necessary to develop method that is suitable for large-scale preparation of Ni_xS_y on an electrode surface, just like the pyrolysis of chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$) to Pt. However, current methods for the preparation of Ni_xS_y films are always energy-intensive and time-consuming [49], followed by complicated deposition procedure which usually results in poor contact between the substrate and catalysts.

In this regard, solution-based process (spin coating or drop-casting of metal precursor solutions or inks) is being developed in an effort to simplify the fabrication procedure for large-scale production [50–52]. However, the main drawback is the use of toxic hydrazine [53] or odorous dithilo-amine solvent [7,24], respectively, which severely restricted the widespread application of this method. Replacing hydrazine or dithilo-amine with an environmentally friendly non-toxic solvent (acetone, N,N-dimethylformamide [42,54], dimethyl sulfoxide [55] and $(NH_4)_2S$ solution [56]) for the deposition of $Cu_{1.8}S$, Ni_3S_2, NiS-NiS_2, CoS_2, $Co_{8.4}S_8$, MoS_2, Cu_2ZnSnS_4 (CZTS), V_2VI_3 chalcogenides (Sb_2S_3, Sb_2Se_3, Sb_2Te_3, As_2S_3, As_2Se_3, As_2Te_3) is highly desirable recently. However, electrocatalytic performance of prepared Ni_xS_y films as CE for DSSCs cannot compete with conventionally noble-metal Pt electrode. Herein, we report on the fabrication of Ni_xS_y films by spin-coating a $NiCl_2$-thiourea (Ni-Tu) complex solution combining mild thermal treatment. In our case, precise phase composition (Ni_3S_2, NiS and NiS-NiS_2), crystallinity, morphology (film uniformity and compactness) control of the films can be achieved through simple adjusting Ni/S ratio in the precursor solution. Interestingly, even deposited on FTO-free glass, our method enables good electrical conductivity of the films according to Hall measurements, which is of great technological importance. Furthermore, we present that our Ni_xS_y films either deposited on FTO or bare glass exhibit excellent electrocatalytic activity toward I_3^- reduction. Finally, using this technique for the preparation of Ni_xS_y films allows us to achieve a highest photo-electric conversion efficiency of 6.95% in DSSC applications, versus 6.66% for Pt under the same conditions.

2. Experimental Section

2.1. Materials

Nickel (II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, 98%), N,N-dimethylformamide (DMF, 99.5%), ethanol (CH_3CH_2OH, 99.7%), acetone (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Concentrated hydrochloric acid (HCl, 36-37%) were received from Beijing Chemical Works. Thiourea (Tu, 99%), chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, Pt ≥37.5%), iodine (I_2, 99.995% metal basis), lithium iodide (LiI, 99.9% metal basis), lithium perchlorate ($LiClO_4$, 99.9% metal basis), guanidinium thiocyanate (GuSCN, 99%), anhydrous acetonitile (C_2H_3N, 99.8%), propylene carbonate ($C_4H_6O_3$, 99.7%) were obtained from Aladdin Reagent Co., Ltd. 1,3-Dimethylimidazolium iodide (DMII) was purchased from Dalian Heptachroma Solar Tech Co., Ltd. The Ruthenium dye (N719) was purchased from Solaronix. 4-tert-Butylpyridine (TBP, 96%) was obtained from Sigma-Aldrich. F-doped SnO_2 transparent conducting glass substrates (FTO) were obtained from Nippon Sheet Glass.

2.2. Preparation of Ni_xS_y and Pt electrodes

Preparation of Ni_xS_y films involved four steps: (1) **Preparation of Ni-Tu solution**: 1 mmol of $NiCl_2{\cdot}6H_2O$ and 0.5–3 mmol Tu were dissolved in 2mL DMF in sequence, which was stirred for at least 30 min to form green homogeneous Ni-Tu solutions (the molar ratios of Ni/S were 1:0.5, 1:0.75, 1:1, 1:2 and 1:3, respectively). We note that for Ni/S ratios at 1:0.5 and 1:0.75, $NiCl_2{\cdot}6H_2O$ cannot be dissolved completely only with the assistance of heating at 60 °C in air. (2) **Ni-Tu solution concentration**: all the Ni-Tu solutions were placed on a hot plate at 85 °C in air to evaporate DMF to 60% of its initial volume under stirring. After cooling down to room temperature, 3 droplets of HCl were added into the concentrated Ni-Tu solutions for long-term stability. (3) **Ni_xS_y film deposition**: spin coat 0.5 mL of the Ni-Tu solution onto the clean FTO and bare glass substrates (500 rpm for 6 s and then 2000 rpm for 60 s, respectively), followed by drying on a preheated hot plate at 80 °C for 5 min. (4) **Annealling**: the as-deposited films were annealed at 400 °C for 30 min under Ar atmosphere to obtain Ni_xS_y films (denoted as Ni_xS_y/FTO and Ni_xS_y/glass, respectively). Pt electrode was prepared as a reference by spin-coating 10 mM of $H_2PtCl_6{\cdot}6H_2O$ in 2-propanol onto the FTO glass, followed by heat treatment in a muffle furnace at 385 °C for 30 min.

2.3. Device fabrication

Nanocrystalline TiO_2 photoanode was purchased from Dalian Heptachroma Solar Tech Co., Ltd. (active area: 0.36 cm^2) and were immersed overnight in a dry ethanol solution (0.3 mM) of N719 dye to obtain dye-sensitized TiO_2 photoanodes. Then the dye-adsorbed TiO_2 photoanode, a drop of electrolyte that consists of 0.6 M DMII, 0.1 M GuSCN, 0.05 M LiI, 0.03 M I_2, and 0.5 M TBP in acetonitrile/propylene carbonate (1:1, v/v), the as-deposited Ni_xS_y and Pt CEs were clamped together to assemble a sandwich-structured DSSC.

2.4. Characterizations

X-ray diffraction (XRD) characterization of the as-deposited Ni_xS_y films was performed at a scanning rate of 5°/min on an Ultima IV X-ray diffractometer with Cu K_α radiation (λ = 1.5406 Å) operating at 40 kV and 200 mA. The morphology of Ni_xS_y films was obtained on an FEI Quanta 250 field emission scanning electron microscopy (FESEM) to analyze the size distribution and film thickness. The transmission electron microscopy (TEM) and high-

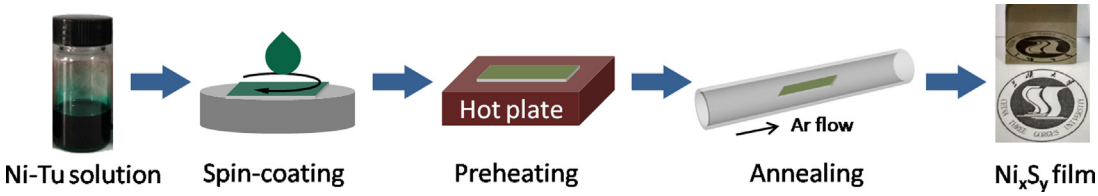

Fig. 1. Schematic illustration of the preparation procedure of Ni_xS_y films.