



Exploring the main function of reduced graphene oxide nano-flakes in a nickel cobalt sulfide counter electrode for dye-sensitized solar cell



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HIGHLIGHTS

- rGO mainly acts as co-catalyst in nickel cobalt sulfide catalyst.
- 2 wt% rGO addition shows optimal catalytic activity of 2.79 Ωcm^2 .
- Under dim light, the requirement of counter electrode is qualitatively discussed.

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ABSTRACT

Addition of carbonaceous materials into transition metal sulfide counter electrode (CE) of a dye-sensitized solar cell (DSSC) is a common method to improve the performance of the CE and consequent photovoltaic performance. This improvement is almost without exception attributed to the improvement of overall conductivity after the carbonaceous material addition; however, the root function of these carbonaceous materials in promoting the solar cell efficiency is seldom discussed. In this study, highly crystallized nickel cobalt sulfide (NCS) micro-particles were mixed with a small portion of home-made reduced graphene oxide (rGO) nano-flakes. This NCS/rGO hybrid is subjected to extensive characterizations including X-ray diffraction, Raman spectroscopy, field emission scanning microscopy and electrochemical impedance spectroscopy. It is found that the rGO acts bi-functionally including a co-catalyst in accelerating the tri-iodide reduction for the main NCS catalysts, conductivity promotor to decrease the series resistance of the CE. Proved by electrochemical impedance spectroscopy, it is confirmed that the decrease in series resistance is less insignificant than that in charge transfer resistance, indicating rGO functions more profoundly as a co-catalyst than as a conductivity promotor. Moreover, an argument to highlight the requirement of a CE in a dim-light optimized DSSC is also proposed.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted academic and industrial interests because of their potential of low cost, colorful, and miniaturized photovoltaics since their discovery in 1991 [1]. More recently, DSSCs are found to be very efficient under dim light environments such as indoor fluorescent light [2]. A typical DSSC includes a photo-anode which is composed of a dye-chemisorbed mesoporous metal oxide (mostly TiO_2) film, an electrolyte system containing a set of redox couple in a proper medium with functional additives, and a catalytic counter electrode (CE) [3]. According to the working mechanism of a DSSC, CE is responsible for

the charge collection during the power generation cycle [4]. Specifically, photo-electrons that travel from photo-anode are collected on the surface of CE by means of electrochemical reduction of the oxidized specie (typically tri-iodide) in the electrolyte. To minimize the activation overpotential of above-mentioned reaction, catalysts are coated on the CE. Ever since the discovery of modern DSSC in 1991 [1], platinum (Pt) has been the dominant catalyst for CE for its excellent catalytic efficiency and durability. However, the rareness of Pt is always a major concern for large scale use. For instance, calculating from the Pt loading on the very-efficient Pt-based CE (thermally reduced Pt cluster with $5 \mu\text{g}/\text{cm}^2$ loading) for DSSC with power conversion efficiency (PCE) over 10% under standard AM 1.5G, 1 sun irradiation [5], the amount of Pt required to generate 1 GW electricity is approximately 500 kg, which is able to produce 17000 fuel cell stacks for Toyota Mirai [6], the first fuel cell vehicle in retail market [7]. Consequently, the development on Pt-free

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catalytic material for CE in DSSC has been deployed a long time ago. To date, these Pt-free candidates can be classified into three categories: carbonaceous materials such as carbon black [8–11], graphite powder [12–14], carbon nanotube [15–17] and graphene [18–20]; transition metal sulfides (TMS) including binary system like cobalt sulfide [21–27] and ternary system like copper indium disulfide [28,29]; and conducting polymers like PEDOT:PSS [30]. Among these Pt-free alternatives, TMS are of particular interest for their versatile crystalline shapes, tunable stoichiometry and superior catalytic capability, rendering them an attractive system for cost-effective, Pt-free CE for massive use. FeS_x [31,32] and Cu_xS [33,34] were the first two TMS materials investigated for CE; then a various binary TMS including CoS_x [21–27], ZnS [35], NiS [36,37], and MoS_2 [38–40] were synthesized by various methods, CEs using these binary TMS also demonstrated promising catalytic performance on tri-iodide reduction. Apart from binary TMS, Pt-free CEs employed with ternary TMS such as CuInS_2 [28,29], CuSbS_2 [41] and NiCo_2S_4 [42–45] or even quaternary TMS such as $\text{Cu}_w\text{Zn}_x\text{Sn}_y\text{S}_z$ were also reported [46,47]. Summarizing above TMS-based CE literature, it is concluded that the catalytic performance toward tri-iodide reduction is closely related to the particle size, the particle shape, the crystalline type and the stoichiometric ratio of these TMS compounds. Notwithstanding the variety of TMS-based CE, it is generally acknowledged all TMS-based CEs have lower intrinsic electrical conductivities because of their nature of metal compound when compared with pure Pt metal. Although the catalytic performance can be tuned by manipulating material properties described above, DSSCs employed with TMS-based CEs generally suffer from more resistive voltage loss when compared with Pt, this deficiency becomes significant on high photocurrent condition (strong irradiation) as the resistive voltage loss is positively proportional to photocurrent. To mitigate this drawback, a small amount of conductive additives such as carbonaceous materials have proposed to hybridize with TMS for the purpose of promoting the electrical conductivity of the electrode [40,48–52]. However, the exact function of these conductive additives in promoting the performance of TMS-based CE is seldom discussed. Most reports listed above merely treated them as pure conducting media and focused on the improvement of overall photovoltaic performance.

For the first time, in this study we found these conductive additives can act as co-catalyst to the main TMS catalyst. Experimentally, we synthesized a ternary TMS, NiCo_2S_4 (NCS), micro-crystals via a facile hydrothermal method; then mixed NCS particles with a small portion of home-made reduced graphene oxide (rGO) nano-flakes. This hybrid material was carefully analyzed by means of X-ray diffraction (XRD), Raman spectra, field emission scanning electron microscopy (FESEM) to characterize its morphology, structure and crystallinity. From electrochemical impedance spectroscopy (EIS), it is confirmed that the addition of rGO in a spray-coated NCS CE accelerates tri-iodide reduction by comparing the charge transfer resistances (R_{CT}) of various CEs. Although the concept of conductive promotor is still valid because the series resistance (R_s) is found to decrease concurrently after rGO addition. However, judging by the experiment results in this study, the decrease in R_{CT} is way profound than the decrease in R_s so that rGO functions as a co-catalyst in NCS CE is major and the effect of conductivity promoting is minor.

2. Experimental

2.1. Synthesis of NCS micro-crystals

Hydrothermal reaction was applied to synthesize NCS micro-crystals. Metal salts including metal chloride hexahydrate (MCH, Acros, 99%) and metal acetate tetrahydrate (MAH, Acros, 98%) were

used as the sources of Ni and Co; thiourea ($\text{CH}_4\text{N}_2\text{S}$) was used as the source of S. Specifically, two experimental sets (shown in Table 1.) were conducted to investigate the property of NCS micro-crystals made from different metal precursors.

After preliminary mixing, the reacting solution was subjected to sonicate for 30 min until a homogenous solution was formed. The homogeneous solution was immediately transferred to a Teflon-coated stainless steel autoclave, followed by heating at 240 °C for 12 h to complete the hydrothermal growth of NCS particles. Finally, the black precipitate in the autoclave was rinsed with deionized water, vacuum-filtrated and centrifuged at 12000 rpm for 2 min sequentially to obtain pristine NCS particles.

2.2. Synthesis of reduced graphene oxide

Modified Hummer's method was applied to synthesize graphene oxide (GO) [53]. Specifically, 0.032 g graphite powder (99%, Acros) was added to a flask containing 50 mL sulfuric acid (98%, Choneye Pure Chemicals) in an icy bath. Subsequently, 3 g KMnO_4 was slowly dropped into the graphite-contained sulfuric acid under agitation in the same icy bath for 2 h. The mixture was then mixed with 100 mL deionized water under agitation. The temperature at this stage was kept at 95 °C for 20 min until the solution became dark brown. The conversion of graphite oxide was completed by adding 10 mL of 30% H_2O_2 solution into the dark brown solution to yield a bright yellow GO solution. The light brown GO powder was obtained by rinsing the yellow GO solution with 5% HCl solution, centrifuging GO solution at 12000 rpm for 5 min and drying the GO precipitate at 65 °C overnight sequentially.

To reduce GO powder, 1 mg of above-prepared GO was dispersed in 120 mL deionized water and sonicated until a homogeneous suspension was formed. Then 10.5 mmol thiourea was immediately added into the suspension. The reacting mixture was transferred into a 150 mL autoclave made with Teflon-lined stainless steel and heated to 240 °C for 12 h then cooled to room temperature naturally. The rGO-contained product was washed with deionized water and ethanol sequentially to remove sulfur-contained residues. Finally, the rGO powders were obtained by centrifuging the product at 12000 rpm for 2 min then drying at 65 °C for 12 h.

2.3. Fabrication of NCS/rGO counter electrode

The mixing of NCS and rGO powders was done by adding 2 wt%, 5 wt%, 10 wt% of rGO into NCS ethanol suspension under vigorous stirring; the resultant mixtures were named as NCS/rGO-2%, NCS/rGO-5% and NCS/rGO-10%, respectively. The mixture solution was subjected to sonicate 60 min to ensure satisfactory suspension. The suspension was then ball-milled continuously for 3 days to obtain a satisfactory homogeneity. The NCS/rGO mixture was coated onto the FTO (7 Ω/sq , NSG, Japan) glass by spraying 0.05 mL above-prepared NCS/rGO mixture with an airbrush (AFC-300A) with a head pressure of approximate 15 psig. The coating area on FTO was controlled as 0.36 cm^2 by a punched sticker. After preliminary drying, the film was annealed at 200 °C in air for 1 h. For

Table 1
Experimental sets for MCH and MAH.

Type of metal salt	MCH	MAH
Co source	6 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	6 mmol $\text{Co}(\text{CH}_3\text{COO})_2$
Ni source	3 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	3 mmol $\text{Ni}(\text{CH}_3\text{COO})_2$
S source	36 mmol thiourea	
Solvent	120 mL deionized water	

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