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Composited $NiSO_4$ and PEDOT:PSS counter electrode for efficient dye-sensitized solar cell based on organic T_2/T^- electrolyte

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ABSTRACT

Ni nanoparticles (~10 nm) were chemically modified in a sulfide containing solution resulting in $NiSO_4$ formation. $NiSO_4$ particle solution was dropped onto conductive glass and used as a dye-sensitized solar cell (DSSC) counter electrode. The efficiency of $NiSO_4$ DSSC when using T_2/T^- electrolyte was ~1.74%. The cell efficiency was significantly increased to ~3.05% after mixing $NiSO_4$ with PEDOT:PSS. This improvement is attributed to an increase in the film electrocatalytic activity as evidenced by CV and EIS measurements.

1. Introduction

Since the breakthrough development of a dye-sensitized solar cell (DSSC) by O'Regan and Grätzel in 1991 [1], DSSCs have continuously received attention from researchers globally. The triiodide/iodide (I_3^-/I^-) electrolyte is normally used in DSSCs. In 2010, Wang et al. obtained a DSSC efficiency of ~6.44% using an organic disulfide/thiolate (T_2/T^-) electrolyte [2]. The advantages of the organic electrolyte over iodine based electrolyte are its high transmittance and low corrosiveness [2,3]. An electrolyte with low corrosiveness, such as T_2/T^-, can function with a wider variety of substrates; including stainless steel, aluminum foil as well as FTO. Although, Wang et al. achieved high efficiency (~6.44%) using Pt as a catalyst [2], Pt is an expensive noble metal and a rare earth material. These issues limit large-scale DSSC production. To minimize DSSC costs and gain customer attention, use of an inexpensive catalyst is imperative, while retaining cell efficiency comparable to Pt based DSSCs.

Several catalysts have been tested in organic electrolyte based DSSCs. These include carbon allotropes [4], conductive polymers [5,6] and metal-sulfide [7–9]. Metal-sulfide catalysts (CoS, WS_2 and PdS) were used in DSSC devices because of their low cost and high stability. Tachan et al. obtained a promising efficiency of ~3.01% from a PdS DSSC using an organic electrolyte [9]. PdS film was fabricated by modifying a Pd sheet in sulfide solution. In a similar manner, by soaking other metals in sulfide solutions, other metal-sulfides could be formed. To our knowledge, there is no report of using nickel sulfide (NiS) as the catalyst in disulfide/thiolate based DSSCs. Thus, in this study, we were interested in modifying Ni nanoparticles to produce sulfide-particles and using them as a catalyst.

2. Experimental method

Preparation of counter electrodes: Ni nanoparticles from QSI-Nano (diameter ~10 nm, shown in Fig. 1a) were modified in 1 M Na_2S, 0.1 M S and 0.1 M NaOH in deionized water for 24 h. The modified particles were separated, rinsed, and then dried at 80 °C for 6 h, $NiSO_4$ particles were obtained. Ni and $NiSO_4$ suspensions were preparing by mixing 0.05 g Ni or 0.05 g $NiSO_4$ in 10 ml deionized-water. Ni-PEDOT:PSS and $NiSO_4$–PEDOT:PSS suspensions was prepared by mixing 0.05 g Ni or 0.05 g $NiSO_4$ in 1 ml PEDOT–PSS and 10 ml deionized-water. CE films were prepared by dropping 70 μl of each suspension on a 1×0.5 cm^2 area of fluoride-doped tin oxide glass (FTO, 8 Ω/sq, Solaronix, SA) and dried at 80 °C for 30 min.

Preparation of working electrodes: Conductive glass (fluoride doped tin oxide glass, FTO, with sheet resistance of 8 Ω/sq, Solaronix), was used as a substrate. The blocking layer was prepared by spinning titanium diisopropoxide bis (2,4-pentanediooate) ($C_{16}H_{28}O_6Ti$) in

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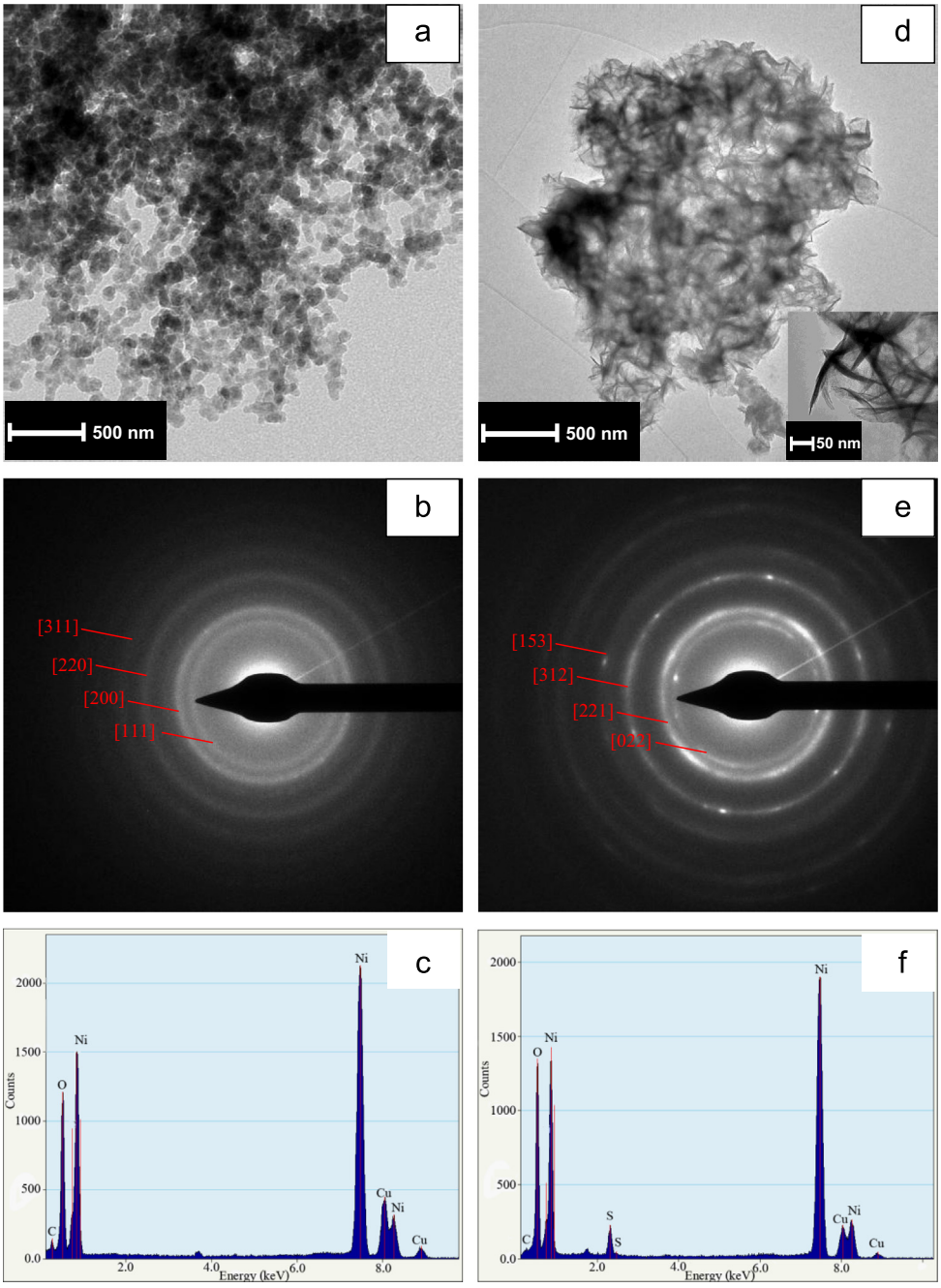

Fig. 1. (a) TEM image, (b) SAED patterns and (c) EDS spectrum of Ni particles scratched from Ni/FTO film. (d) TEM images, (e) SAED patterns and (f) EDS spectrum of $NiSO_4$ particles scratched from $NiSO_4$/FTO film.

isopopanol (1 mL:20 mL) on FTO glass, after that heating at 80 °C for 5 min. The transparent and scattered TiO_2 films, with area of 0.25 cm^2, were coated on the blocking layer by a screen printing technique using the TiO_2 paste PST-18NR and PST-400C, respectively (Catalysts & Chemicals Ind. Co., Ltd.). TiO_2 films were annealed at 500 °C for 1 h, and then were immersed in the dye solution, *cis*-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II)-bis-tetrabutylammonium (N719, Solaronix, 5×10^{-4} M in acetonitrile:tert-butanol at a volume ratio of 1:1) for 24 h at room temperature.

DSSC assembly: Semiclosed DSSCs were assembled using Ni, $NiSO_4$, PEDOT:PSS, Ni-PEDOT:PSS and $NiSO_4$–PEDOT:PSS films as CEs and dye-coated TiO_2 film as WE. Organic electrolyte was filled into the DSSCs. The electrolyte consisted of 0.40 M 5-mercapto-1-methyltetrazole N-tetramethylammonium salt ($NMe_4^+T^-$, prepared as reported in ref. [2]), 0.40 M di-5-(1-methyltetrazole) disulfide (T_2, prepared as reported in ref. [2]), 0.50 M of 4-tert-butylpyridine and 0.05 M of $LiClO_4$ in acetonitrile. The film characterization is discussed in the Supporting information.

3. Results and discussion

Fig. 1a and d reveals the enormous change from nanoparticles to microparticles after chemical treatment. The size of modified particles was ~1 μm. The high magnification TEM image of modified Ni particles, inset in Fig. 1d, reveals the formation of a nanoflower structure on the particle surfaces with the flower diameter of ~5 to 22 nm. Nanoflower formation was also observed by Kung et al. on $CoSO_4$ rod surfaces [7]. The presence of sulfide was determined using EDS in the TEM. The EDS spectrum of Ni nanoparticles in Fig. 1c