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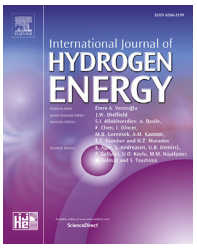

Efficient hydrogen evolution performance of phase-pure NiS electrocatalysts grown on fluorine-doped tin oxide-coated glass by facile chemical bath deposition

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ABSTRACT

The production of hydrogen, the future fuel, on stable, efficient, and robust electrocatalysts represents an attractive approach for the conversion and storage of carbon-free energy resources. In this study, earth-abundant nickel sulfide (NiS) electrocatalyst were grown on fluorine-doped tin oxide (FTO) substrate by a simple and cost-effective chemical bath deposition for hydrogen evolution reaction (HER). Energy dispersive X-ray analysis and X-ray photoelectron spectra indicated the presence of highly pure NiS. The HER performance of the catalyst was examined in alkaline solution (1.0 M NaOH; pH = 13.5). Notably, NiS film prepared at 100 °C demonstrated superior HER activity with an overpotential of 290 mV to afford a current density of 10 mA/cm^2 and a Tafel slope of 143.4 mV/dec which are among the promising results obtained for sulfide-based HER electrocatalysts. The catalyst exhibited 100% faradaic efficiency and electrochemical stability which indicate its potential as noble-metal-free HER electrocatalyst.

Introduction

The increasing global energy demand and environmental concerns over the use of conventional fossil fuels have shifted research direction towards the development of technologies for the production of sustainable, clean, and cost-effective fuels [1,2]. Molecular hydrogen generated from electrochemical water splitting is considered to be a promising alternative for the replacement of fossil fuels. To make hydrogen production sustainable, the water splitting reaction can be proceeded with the help of renewable energy such as solar energy [3]. Water splitting consists of two half reactions: reaction at cathode is the hydrogen evolution reaction (HER) while that at anode is oxygen evolution reaction (OER). Both of these reactions are kinetically hindered due to the multi-step electron/proton transfer process and require suitable, efficient, and stable catalysts to proceed at appropriate rates. For HER, platinum (Pt) and its alloys are the most active catalyst materials but the low reserves and high cost of Pt limit its

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large-scale water splitting application. Therefore, it is necessary to develop low-cost, earth-abundant and efficient HER catalysts for the mass-scale production of hydrogen [2,4].

Many researchers have investigated HER catalysts composed of noble metal-free and earth-abundant elements such as metal carbides (Mo_2C) [5], phosphides (Ni_2P, CoP) [6,7], sulfides (MoS_2, WS_2) [8,9], and selenides ($MoSe_2$) [10]. In addition, metal dichalcogenides (MX_2), in which M = Co, Mo, W, Fe and X = Se and/or S, have been found to show high HER activity owing to the unique pyrite crystal structure of these catalysts [11]. However, most of these catalysts are found efficient in acidic electrolytes in which H_2 evolution occurs as a result of proton discharge. For overall water splitting, the HER and OER catalysts must be used in the same electrolyte. Since the overpotential loss in OER is much larger in acidic media than HER in alkaline solutions and many of OER catalysts are unstable in acidic media, there is need of developing HER catalysts which are stable under alkaline conditions [12]. Recently, Nickel-based catalysts are gaining research focus due to high conductivity, rich redox chemistry, excellent HER activity, and equally high stability in both alkaline and acidic solutions [13–16]. For example, Nan et al. [13] have reported the electrocatalytic performance of NiS nanoparticles of various compositions for HER in strongly alkaline conditions with Ni_3S_2 showing the superior activity compared to NiS_2 and NiS. Wu et al. [17] have reported the synthesis of supported vertical NiS_2 nanosheets and found that the catalysts are equally efficient and stable in both acidic and alkaline solutions. Similarly, Ni_2S_3 has demonstrated robust HER performance in neutral buffer and in natural water [18]. Meanwhile, Nickel sulfides have been found to be promising co-catalysts for photocatalytic hydrogen production [19]. For example, NiS nanoparticle supported CdS (NiS/CdS) and $CdLa_2S_4$ photocatalysts have been shown to demonstrate excellent H_2 evolution [20,21]. These studies thus indicate the potential of nickel sulfides as a HER catalyst for H_2 production.

It is worth noting that NiS exists in various compositions and crystal structures including NiS, NiS_2, Ni_3S_2, and Ni_3S_4, each having different catalytic activity for HER depending on the structure and morphology [13,22]. For instance, NiS nanoframes derived from metal-organic framework have been shown to exhibit good HER activity in 1 M KOH [23]. Wang et al. [14] have synthesized NiS and NiS_2 via hydrothermal method and presented their HER and OER activities in acidic and alkaline solutions for water splitting reaction. In their study, NiS was found to be efficient for OER while NiS_2 showed better electrocatalytic performance for HER. Similarly, Sung et al. [24] have reported that NiS and Ni_3S_2 exhibit different electrocatalytic activity for HER due to the difference in their atomic configuration and crystal structures. The crystal structure and morphology of Ni sulfides depends mainly on synthesis methods. Many techniques such as atomic layer deposition [25], hydrothermal [26], microwave-assisted [13], and metal-organic framework-derived methods have been employed to synthesize Ni sulfide of particular morphology and crystal structures [23,27]. These methods often require high growth temperature and structure directing agents in addition to toxic organic solvents [13,17,26].

In this study, we demonstrate the preparation of phase-pure NiS on fluorine-doped tin oxide (FTO) coated glass at low temperature using one-pot green chemical bath deposition. This method is simple and does not involve the use of any surfactant or toxic organic solvent. Moreover, the experimental parameters can be manipulated to control the structural, morphological, and electrocatalytic characteristics of the deposited material. NiS was coated on pre-cleaned FTO substrates at temperatures ranging from 70 to 100 °C from the aqueous solution of Ni and S precursors with the addition of 10 mL ethanol. The as-prepared samples were annealed at 450 °C under N_2 atmosphere to get crystalline NiS. The prepared samples were examined by various physicochemical characterization to investigate its morphology and crystallinity. Electrochemical characterizations were performed to study the HER activity of the synthesized material. The deposition temperature was found to have influence on the morphology, crystallinity, and HER activity of the synthesized films.

Experimental section

Materials

Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$; Acros organics; 99.5%), nickel chloride hexahydrate ($Ni(II)Cl_2 \cdot 6H_2O$; Junsei Chemicals Co. Ltd; 97%), anhydrous ethanol (Samchun Chemicals; 99%), and sodium hydroxide (NaOH, pellets; Samchun Chemicals; 97%). These chemicals were used as received. For solution preparation electrochemical testing, ultra-pure de-ionized water was used.

Deposition of NiS catalyst on FTO substrates

First, the FTO substrates (FTO, TEC 8, Pilkington glass) of 5 cm × 2.5 cm dimensions were thoroughly washed with common dish-washing detergent and rinsed well with tap water. This step was followed by ultrasonic cleaning in de-ionized water, acetone and isopropanol for 30, 20, and 20 min, respectively. Finally, the substrates were rinsed with de-ionized water and dried with pressurized nitrogen.

NiS electrocatalyst was grown on FTO substrates by procedure illustrated in Scheme 1. To prepare bath solution, 0.5 M $Na_2S_2O_3 \cdot 5H_2O$ and 0.5 M $Ni(II)Cl_2 \cdot 6H_2O$ were dissolved in triply distilled water in separate beakers and stirred for considerable time to make it homogenous. Pre-cleaned FTO coated glass substrate (5 cm × 2.5 cm) was placed in Falcon tube (Corning™ Falcon™ 50 mL) of 50 mL volume with FTO surface towards the wall. The bath solution (50 mL total volume) was prepared by mixing 40 mL of Ni and S precursors (20 mL each) and 10 mL anhydrous ethanol. The tube containing FTO substrate and solution mixture was then kept in oven at different temperatures ranging from 70 to 100 °C. After 4 h of the reaction, the oven was allowed to cool down to room temperature. The samples were taken out from the Falcon tube and rinsed thoroughly with distilled water to remove un-reacted material. Finally, the deposited films were annealed at 450 °C for 1 h in tube furnace under N_2 atmosphere to get the desired crystalline phase of nickel sulfide.

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