SnS and SnS$_2$ Nanocrystals as Effective Electrocatalysts for the Hydrogen Evolution Reaction

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Abstract. We report enhanced electrocatalyst performance for the hydrogen evolution reaction (HER) due to the structural phase change of SnS thin films to SnS$_2$ via a facile low vacuum annealing protocol in the presence of elemental sulfur. This sulfurization process resulting in the increased formation of nanocracks which serve as catalytic sites for hydrogen generation. Compact SnS thin films with large grain sizes demonstrate an improved current density of -6.15 mA/cm$^2$ at relatively low overpotentials as compared to previous reports. After sulfurization, the obtained SnS$_2$ thin films are used as an electrocatalyst for HER for the first time and achieve a significantly higher current density of -27.9 mA/cm$^2$ with a corresponding Tafel slope of 85 mV/dec which can be attributed to a large number of nanoscale active sites. Our results demonstrate the potential of layered tin sulfide compounds as promising electrocatalysts for efficient and large-scale water splitting.

Introduction

Hydrogen has been proposed as a clean, efficient energy resource with zero emission, and a lot of effort have been undertaken recently to develop electrocatalytic/photocatalytic techniques to produce hydrogen efficiently through the HER [1-5]. Efficient electrolytic hydrogen generation relies heavily on active, durable and affordable catalysts to reduce the overpotential and accelerate the kinetics of the HER (HER: $2H^++2e^- \rightarrow H_2$). Although platinum (Pt) group metals have been widely acknowledged as the most active
catalysts for electrolytic water splitting, with very low overpotential requirements even at high reaction rates, they are scarce and expensive and this limits their scalability. Widespread research has been conducted worldwide to design efficient non-precious metal water-splitting catalysts from earth-abundant transition metals for HER[6].

Recently, two dimensional layered transition metal dichalcogenides (TMDs) have emerged as promising electrocatalyst for HER. In TMDs, the active catalytic sites are located at the sulfur edge of the TMDs crystals, whereas the basal planes are catalytically inert [7, 8]. Efforts have been undertaken for the preparation of inorganic metal sulfur compounds such as MoS2 [7-14], Mo2C [15], WS2 [9, 13, 16-18], WSe2 [19], FeS2 [20], NiS2 [20] and CoS2 [20], and are identified as active HER catalysts in both acidic and alkaline solutions. However, most sulphides do not exhibit efficiencies of their theoretical maxima due to the low effective carrier density, Fermi pinning by the surface states of electrode and electrolyte, carrier recombination at boundaries by small grain sizes, and defects leading to carrier recombination at the junction [21-23]. Efficiencies can be enhanced by creating exposed active sites on the surface that can facilitate charge transfer [12, 14]. Furthermore, confirmation of the actual band position of the working electrode with respect to the electrolyte is critical for improving charge transfer efficiency at low overpotentials by correctly identifying the energy barrier at the electrode/electrolyte interface.

As compared to other inorganic materials, tin sulfides and its derivatives such as SnS and SnS2 have attracted significant attention because of their structural multiformity, low cost, unexpected catalytic activity, and high electrical conductivity. The wide absorption range of SnS and SnS2 (SnS band gap ~1.3eV; SnS2 band gap ~2.2) [24, 25] makes them very suitable materials for the application in Li-batteries [26, 27], photovoltaic cells [28, 29], photocatalysts [30-33] and electrocatalysts [34]. Although, SnS has been reported as a photoanode in photoelectrochemical cell [30, 31] or as a cathode material in HER [34], the performance still needs significant improvement. Lee et al., have reported a significant enhancement in the catalytic activity of nanoscale SnS in HER due to the presence of numerous active edge sites, where they have obtained a low current density of about -2.5mA/cm2 at an overpotential of -600 mV. Furthermore, they have improved the HER performance of SnS by combining with n-doped graphene (SnS/N-rGr) and have achieved current densities up to -10 mA/cm² observed at a relatively low over potential of -125 mV [34]. It is possible to enhance SnS electrocatalytic activity by either reducing the intrinsic defects to improve conductivity or by creating more active sites. Although tin sulfide compounds have attractive properties, their application towards HER is significantly limited because of the presence of intrinsic defects, and therefore, synthesis of defect free high quality SnS and SnS2 remains a grand challenge. Here, we describe a facile method for the synthesis of SnS, SnS2 thin film
electrocatalysts and demonstrate their supreme performance toward HER. An intensive literature survey reveals that there is no report about the application of SnS₂ as electrocatalyst in HER.

**Experimental methods**

**Synthesis of mixed phase SnS nanocrystals**

We have used the hot injection method to synthesize SnS nanocrystals consisting of orthorhombic phase SnS hexagonal nanosheets and cubic phase SnS nanoparticles using reaction conditions that have been optimized in previous studies [35-38]. In a typical synthesis protocol, 1.35 g of SnO (Tin (II) Oxide, SHOWA, 99%) was mixed with 13.5 ml OA (Oleic Acid, Sigma Aldrich, 66%-88%) in a three neck flask. The mixture was heated to 120 °C under an argon gas flow under constant magnetic stirring and held there for 15 minutes to remove all the excess water. It was then heated further to 280 °C under low vacuum until it became a clear solution, forming the tin precursor (Sn(OA)X), after which it was cooled down to 190°C. Simultaneously, the sulfur precursor (S-OLA) was prepared by heating a mixture of 0.45 mmol of elemental S powder (sulfur powder, sigma aldrich, 98%) and 9 ml of OLA (Oleylamine, ACROS, 90%) at 155 °C under magnetic stirring in an argon atmosphere. The hot sulfur precursor was quickly injected into the tin precursor by using glass syringes and the final temperature was maintained at 190 °C for 30 minutes before being cooled to room temperature. All chemicals were used without further purification. The resulting SnS nanoparticle solution was then added to ethanol and acetone in the ratio 1:9:9 and centrifuged at 5000 rpm for 15 minutes. This process was repeated several times to wash away all the organic solvents and the final product was dried in vacuum, re-dispersed in hexane for further characterizations.

**SnS and SnS₂ thin films deposition**

To prepare the SnS thin films for electrocatalyst, glass substrates were first coated with Cr/Au (50nm/70nm) using electron beam physical vapor deposition. The synthesized SnS nanocrystals (2mg) were dispersed in toluene (2ml) and spin coated on the glass/Cr/Au substrate followed by vacuum drying for 5 min at 85°C. The obtained SnS thin films can be converted to SnS₂ via a simple annealing step in the presence of S powder. In a typical procedure, the SnS electrode and S powder (0.1g) in separate quartz boat were placed inside a quartz tube. On creation of a low vacuum, both the ends of the quartz tube were sealed and the temperature was raised to 250 °C and held there for 2hr to carry out sulfurization followed by cooling the whole system down to room temperature.

**SnS and SnS₂ electrochemical measurements**

A three electrode cell configuration was utilized with SnS or SnS₂ as the working electrode (WE), platinum as the counter electrode (CE) and Ag/AgCl (3.0 mol/kg KCl) as the reference electrode (RE) in a 0.25M H₂SO₄ electrolyte (pH=0.6) while a radiometer analytical potentiostat (Volta lab PGZ301) was
used to perform electrochemical measurements. Linear sweep voltammetry was employed to obtain polarization plots with a fixed scan rate of 5 mV/s. The obtained polarization data was calibrated with respect to the reversible hydrogen electrode (RHE) by \( E_{RHE} = 0 - (E_{RE} + 0.059 \times pH) \). Mott–Schottky plots were used to estimate the data frequency of 100 kHz in the dark and under the applied potentials from 1.4 to -0.3 V vs RHE.

**Result and discussion**

![XRD data](image)

**Fig. 1.** XRD data for (a) SnS thin film, and (b) SnS\(_2\) thin film.

X-ray diffraction (XRD) analysis of synthesized SnS (JCPDFS 39-0354) and SnS\(_2\) (JCPDS 23-0677) thin films as shown in Fig 1. The SnS thin films deposited by spin coating show a preferred (040) orientation (Fig. 1(a)). In Fig 1(b), the SnS\(_2\) are obtained after sulfurization process which thin films show the preferred orientation with (001). The lattice parameters of orthorhombic SnS are \( a = 4.3283 \), \( b = 11.2015 \), and \( c = 3.9925 \) Å, and SnS\(_2\) are \( a = b = 3.6459 \), \( c = 5.8968 \) Å.[39]

![SEM images](image)

**Fig. 2.** Top and cross sectional SEM image of (a)-(c) SnS thin films, (d)-(f) SnS\(_2\) thin films (after sulfurization).
Fig. 2. shown the SnS and SnS$_2$ thin films top and cross sectional SEM (scanning electron microscopy). Low magnification top view SEM images of SnS and SnS$_2$ thin films demonstrated numbers of nano-cracks, however, the Cr/Au back-contact are not exposing by these nano-cracks. SnS and SnS$_2$ thin films surface elemental distributions are investigate via EDX (Energy-dispersive X-ray spectroscopy) elemental mappings (insets of Fig. 3a, d), the Sn and S elements atomic ratio of SnS thin films approximately 1:1 whereas the SnS$_2$ thin films are 1:2. The EDX elemental mapping results are anastomosis with those obtained from the XRD spectra. Fig. 2b display the high magnification image of the SnS with grain sizes ranging from 200 nm to 400 nm which stacking of larger clusters composed. The SnS thin films are stacking of uniformly dispersed nanocrystals on the substrate throughout the 300 nm thickness of the film. After intensive sulfurization, the SnS$_2$ thin films develop nano-cracks (Fig. 2d) which increases the area of exposed active sites that may contribute to enhanced HER efficiency on the working electrode. As observed in Fig. 2f, the SnS$_2$ thin film thickness increased to ~500 nm, implying the diffusion of the sulfur atoms between the layers of SnS, thus resulting in the expansion of the films. Furthermore, the SnS$_2$ thin films are more compact than SnS thin films.

Fig. 3. (a) TEM image of SnS nanocrystals consisting of orthorhombic phase hexagonal SnS nanosheets and cubic phase SnS nanoparticles. (b) HRTEM image showing crystal planes of cubic phase SnS. (c) TEM image showing top view of SnS nanosheet (Inset: SAED diffraction patterns which can be indexed to orthorhombic-SnS). (d) HRTEM image of top view of SnS nanosheet showing crystal planes of orthorhombic SnS (e) TEM image showing cross sectional view of SnS nanosheet. (f) HRTEM image of SnS nanosheet cross section showing stacked crystal planes of orthorhombic SnS. However, SnS2 thin films
The bright field Transmission Electron Microscopy (TEM) image (Fig. 3a) the particle size of the hexagonal nanoparticles are length 80 nm and width 40 nm. The single crystals projected along the (101) and (\(\overline{1}01\)) direction as shown by the selected area electron diffraction (SAED) pattern (Inset in Fig. 3a). Fig 3b shows the existence of two different microstructures (hexagonal shape nanosheets and spherical nanoparticles) of SnS nanoparticles in the same matrix. According to our previous study [37], a metastable phase consisting of hexagonal nanosheets and spherical nanoparticles is observed in transition from a cubic phase to the more stable orthorhombic phase. The average particle size of the spherical nanoparticles is in the range of 20–40nm. The HRTEM image (Fig. 3c) shows lattice spacing values of 2.78 Å corresponding to the (010) planes of cubic phase SnS. The XRD data of SnS thin films shows a single peak corresponding to the (040) plane of orthorhombic SnS and this is attributed to the stacking of the SnS nanosheets on the substrate and growth along (040) plane after spin coating [40].

The SnS2 thin films corrosion TEM image shows in Fig 3d. The SnS2 thin films TEM text sample are prepare by Focus Ion Beam (FIB), therefore the thin films are inevitably destroyed. However, SnS2 thin films are contact will with Cr/Au substract. The HRTEM image of SnS2 thin films as show lattice spacing values of 5.49 Å corresponding to the (001) planes (Fig. 3e). From Fig 3f, SnS2 thin films has a diffraction ring of (001), (002) and (110) plane.

Fig. 4. (a) HER polarization curves at the scan rate of 5 mV s\(^{-1}\) with 0.25 M H\(_2\)SO\(_4\) for the mixed phase SnS thin films and sulfurized SnS\(_2\) thin films, (b) The corresponding Tafel plots of SnS and SnS\(_2\) thin films.

The electrocatalytic performance of SnS and SnS\(_2\) thin films towards HER was investigated using a conventional three electrode system in a 0.25 M H\(_2\)SO\(_4\) electrolyte with Pt and Ag/AgCl as the counter and reference electrodes, respectively. The applied potential for HER was investigated using a conventional three electrode system in a 0.25 M H\(_2\)SO\(_4\) electrolyte with Pt and Ag/AgCl as the counter and reference electrodes, respectively. The applied potential for HER
polarization is varied from 0.0 V to -0.6 V vs RHE at a scan rate of 5 mV/s for SnS and SnS₂ thin films (Fig. 4a). The SnS thin film electrocatalyst displays an HER current density of -6.15 mA/cm² when the applied potential is -0.6V (Fig. 4a). In comparison, the SnS₂ thin film shows a superior electrocatalytic performance with a current density of -27.90 mA/cm² at the same applied potential.

As shown in Fig. S4, the onset potential for SnS thin films electrocatalyst is -0.134 V for the HER, and SnS₂ thin films electrocatalyst produced a more positive onset potential (-0.327 V). When the applied potential is higher than the open potential the more negative current density would be observed. Tafel slopes (Fig. 4b) are determined by fitting the linear portions of the Tafel plots to the Tafel equation ($\eta = b \log j + a$), where $j$ is the current density, $a$ is the empirical coefficient and $b$ is the Tafel slope. The Tafel plots show slopes of 174 mV/dec for SnS while a lower value of 85 mV/dec is observed for the SnS₂ electrocatalyst. The overall HER mechanism in acidic media is described through three principle steps, namely the Volmer reaction ($H^+ + M + e^- → M - H^*$, Tafel slope ~ 120 mV/dec), the Heyrovsky reaction ($M - H^* + M + e^- → M + H_2$, Tafel slope ~ 40 mV/dec), and the Tafel reaction ($2M - H^* → 2M + H_2$, Tafel slope ~ 30 mV/dec) [41, 42], where M is the electrode surface and $H^*$ is the hydrogen atom. Experimentally, two main pathways through which the HER reaction proceeds are either the Volmer-Heyrovsky reaction or the Volmer-Tafel reaction. The Tafel slope of 85 mV/dec for the SnS₂ electrocatalyst suggests that HER most probably occurs via the Volmer–Heyrovsky mechanism where electron reduction of protons provides a hydrogen atom bound to an active site (Volmer reaction) and also leads to the electrochemical desorption of hydrogen (Heyrovsky reaction). In contrast, for SnS, the HER proceeds through the Volmer reaction as suggested by its large Tafel slope of 174 mV/dec. The relatively lower number of nano-cracks present in SnS thin films which have not been subjected to high temperature annealing results in limiting the rate of HER kinetics due to less active sites as evidenced by the high Tafel slope. Table S1 (Supplementary information) shows a comparative analysis of the current density, applied over potential and Tafel slopes of previously published reports. Our SnS and SnS₂ electrocatalysts show much higher current density and lower Tafel slope as compared to SnS electrocatalysts reported previously [34]. In particular, the SnS₂ electrocatalyst shows much better catalytic performance as that with other binary compounds [11, 12, 15-17, 19] and doped compounds [19].

In general, metal sulfides have not demonstrated efficiencies close to their theoretical maxima because of small grain sizes leading to carrier recombination at grain boundaries and junction defects. In this study, the SnS thin film electrocatalyst is composed of approximately 200 ~ 400 nm hexagonal nanosheets, which can reduce defects due to larger grain size while a thin film (300nm) with the presence of nano-cracks on the surface can enhance the HER. After sulfurization, n-type SnS₂ thin films are obtained by a phase transformation of the SnS thin films with increased number of nano-cracks that provide more
metallic edges for hydrogen adsorption and an easier pathway for electron transport, thus resulting in improved catalytic activity for HER.

Although, SnS$_2$ exhibits excellent catalytic properties for HER, it still requires a high operating overpotential which must be reduced to make it a viable catalyst to replace Pt-group metals which operate at negligible overpotentials. A commonly used protocol to reduce the high operating overpotential is to combine the working electrode with a conductive material (as show in Table S1) as reported previously [10-12, 14, 15, 17, 34]. We will also carry out such experiments to reduce the operating overpotential and enhance catalytic efficiency by incorporating conductive nanomaterials in future studies.

**Conclusions**

In summary, we report the use of layered tin sulfide compounds as high performance electrocatalysts for HER. A simple, non-toxic hot injection method is developed for the synthesis of cubic and orthorhombic SnS nanocrystals that can be spin coated on glass/Cr/Au substrates to form high quality compact thin films which serve as the working electrode. SnS thin films can be converted into SnS$_2$ via a facile sulfurization protocol in low vacuum conditions. The SnS$_2$ electrocatalyst shows superior performance for HER as compared to SnS due to a larger number of exposed active sites while also possessing a higher carrier density, thinner space charge layer and an effective band alignment with respect to the electrolyte at equilibrium conditions. Given our promising findings, we anticipate future advances in tin sulfide materials as a promising alternative to precious metal electrocatalysts for sustainable hydrogen generation.
References