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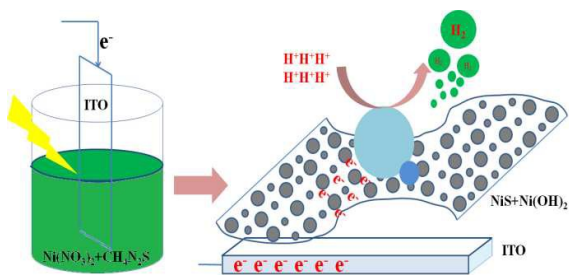


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The Ni-S film prepared by a facile one-step photo-assisted electrodynamic deposition route without any post-treatment exhibits high activity.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

One-step preparation of nickel sulfide/nickel hydroxide films for electrocatalytic hydrogen generation from water

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Received (in XXX, XXX) XthXXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Electrocatalytic reduction of water to molecular hydrogen via the hydrogen evolution reaction (HER) may provide a sustainable energy supply for the future, but its commercial application is hampered by the use of precious metals and high preparation cost. In this work, we report that Ni-S films prepared by one-step photo-assisted potentiodynamic deposition are active HER catalysts in aqueous media. Notably, the Ni-S films showed efficient and robust electrocatalytic activity for the HER in water over a wide pH range. A long-term bulk electrolysis of the Ni-S film exhibited steady current over 22 h without deactivation, demonstrating its superior stability in neutral water. The facile preparation of this Ni-S film, along with its low overpotential, high activity, and long-term aqueous stability, offer promising features for potential use in H₂ evolution applications. A set of characterization techniques, including field emission scanning electron microscopy (FE-SEM), powder X-ray diffraction patterns (XRD) and X-ray photoelectron spectroscopy (XPS), were conducted to detect the composition and structure of the Ni-S film, revealing that its major component is NiS/Ni(OH)₂.

1. Introduction

Increasing awareness of the energy crisis and environmental pollution has stimulated great progress in the development of green renewable energy. Hydrogen is regarded as a potential fuel for renewable energy.¹⁻³ Electrolysis of water is the simplest way to produce hydrogen of high purity at the most economical price and has thus attracted considerable attention. To increase the reaction rate and lower the overpotential, it is necessary to use an efficient hydrogen evolution reaction (HER) electrocatalyst.⁴⁻⁷ Platinum group metals are the best HER catalysts, but they suffer from scarce and high cost limit their application on a large scale. It remains a great challenge to develop inexpensive HER catalysts exhibiting both high efficiency and strong robustness in aqueous media, preferably neutral water.⁸⁻¹²

In recent years, solid-state inorganic compounds offer an alternative strategy to meet this goal and a number of interesting materials have emerged as earth-abundant platinum replacements for HER catalysis, including metal alloys,¹³ nitrides,¹⁴ borides,¹⁵ carbides,^{16, 17} chalcogenides,¹⁸⁻³⁴ and phosphides.³⁵ Among these compounds, metal chalcogenides acquired more and more attention due to their morphology diversity, low price and convenience in fabrication. The typical representatives, such as NiS,¹⁸⁻²¹ CoS,²²⁻²⁵ MoS₂,²⁶⁻³¹ CuMoS₂³² and CuInS₂,^{33, 34} exhibited a high electrocatalytic activity and displayed a comparable or even surpassing performance than that of Pt. Within the group, nickel sulfide (NiS) has been of particular interest because of its superior electrocatalytic activity, earth abundance and low cost.¹⁸⁻²¹ NiS could function as electron collector and electrocatalyst simultaneously.³⁶ In addition, nickel sulfide is

suitable to conduct hydrogen evolution in neutral water, which is the ultimate ideal solvent for water splitting. Moreover, that is favorable to minimize the environmental impact and increase the biocompatibility.¹⁸

However, the procedures to prepare these metal chalcogenides need either a complicated method or a long reaction cycle, which has extremely limited their promotion. Among these methods, the two most common methods also exist some drawbacks. The hydrothermal preparation involved complicated reaction steps, with taking a long time,³⁷⁻³⁹ in the electrodeposition process, though the film of metal chalcogenides was first prepared under common conditions, subsequent heat treatment was necessary for the stability of the catalyst.^{18, 23} Obviously, these methods are complicated or energy-hungry. Therefore, the design of a novel and facile preparation strategy for metal chalcogenides electrocatalysts is still urgent and of great significance.

Herein, aiming to find a way to simplify the production technology of the Ni-S electrode, we report a facile method for preparing Ni-S films. The compound Ni-S was grown on ITO glass substrates by a facile one-step photo-assisted electrodynamic deposition route using inexpensive and nontoxic inorganic salt and thiourea as raw materials without any post-treatment, and the content of electrocatalyst can be controlled by controlling the deposition cycles, expressing a wonderful catalytic activity. Thus, this catalyst maintains its activity for at least 22 h and exhibits a low catalytic onset overpotential (η) of 200 mV and near 100% faradaic efficiency in neutral water.

2. Experimental section

2.1 Materials

Nickel chloride hexahydrate, thiourea, potassium hydroxide, potassium chloride, hexamethylenetetramine, monopotassium phosphate, dipotassium phosphate, hydrochloric acid, sodium sulfate, isopropanol, acetone, ethanol and all other chemical reagents were purchased from commercial vendors and used without further purification.

2.2 Preparation of nickel-sulfide catalyst films on ITO

A three-compartment custom-built electrochemistry cell was used to carry out the photo-assisted electrodynamic deposition of Ni-S film on ITO. The three compartments are separated by a special medium frit. An ITO electrode with an effective area of 1 cm² were used in the working compartment which contains 5 mM nickel chloride and 0.30 M thiourea, while a Ag/AgCl (3M) electrode in reference compartment and a Platinum mesh electrode in counter compartment were exposed to the Na₂SO₄ electrolyte solution used as reference electrode and counter electrode, respectively. The photo-assisted electrodynamic deposition was conducted by cyclic voltammetry at a scan rate of 5 mV s⁻¹ for certain number of cycles within a voltage range of -1.2 to 0.2 V vs Ag/AgCl. To load the Ni-S catalyst onto the electrode, the same solution and procedure was applied for electrochemical deposition with different number of cycles. ITO electrodes were rinsed with ethanol, acetone, and isopropanol solution of potassium hydroxide thoroughly prior to deposition. After deposition, the ITO working electrode was removed from the deposition bath, washed with copious water, followed by drying at room temperature in air.

2.3 Electrochemical Measurements

Electrochemical measurements were performed using a CHI600E three-electrode electrochemical system (Chenhua Instruments Co. Shanghai), with Ag/AgCl electrode used as a reference and Pt wire employed as counter electrode. The Ni-S/ITO electrode served as the working electrode. The raw electrochemical data were collected without any corrections for uncompensated resistance. The amount of H₂ evolved was determined with a gas chromatography (GC-9790) equipped with a thermal conductivity detector (TCD). The electric potential is calculated as follows:

$$E \text{ (V vs RHE)} = E \text{ (vs Ag/AgCl)} + 0.208 + 0.059\text{pH}$$

Electrochemical performance of Ni-S loaded electrode was tested in different specific electrolyte after N₂ purging. Polarization data were obtained at a sweep rate of 0.1 V s⁻¹ by linear scanning voltammetry. The short-term electrochemical stability and hydrogen production activity was measured in buffer solution (pH=6 and pH=7) under different overpotentials. Long-term electrochemical stability measurements were performed at optional overpotential. The electrolyte solution of pH=6 used was 0.2 M KCl with hexamethylenetetramine (HMTA) /HCl buffer in H₂O solution. The potassium phosphate buffer of pH=7 is the most commonly used electrolyte solution. The electrochemical impedance spectra were taken from 0.01 to 10⁵ Hz with an amplitude of 5 mV under various overpotentials.

2.4 Materials Characterization

The size and surface morphologies of the sample were

investigated by field emission scanning electron microscopy (FE-SEM) on a Hitachi S-4800 and transmission electron microscopy (TEM) on a JEM-2100 transmission electron microscope (JEOL, Japan). To identify the composition and phase of sample, powder X-ray diffraction (XRD) patterns were collected using a Bruker-AXS D8 advance diffractometer with Cu K α radiation. To detect the chemical composition and electronic structure of sample, X-ray photoelectron spectroscopy (XPS) analysis was conducted using an ESCALAB 250 Xi (Thermo, USA) X-ray photoelectron spectrometer with Al K α line as the excitation source (h ν = 1484.6 eV) and adventitious carbon (284.6 eV for binding energy) was used as reference to correct the binding energy of sample.

3. Results and discussion

The Ni-S/ITO electrode prepared by photo-assisted electrodynamic deposition showed efficient and robust electrocatalytic activity for the HER in water. Without the light irradiation, the freshly-prepared Ni-S/ITO exhibits poor stability and its catalytic activity decreases quickly. Differences in activity of the two electrodes prepared under different conditions is attributed to the different compositions. Figure 1 displays a scanning electron microscopy (SEM) image of the Ni-S films. The film prepared by photo-assisted electrodynamic deposition appears to be tight and uniform, and disperses evenly over the whole ITO glass substrate. However, the surface of electrode deposited without irradiation is uneven. Also, this result is confirmed by the TEM image of NiS prepared under optimum conditions.

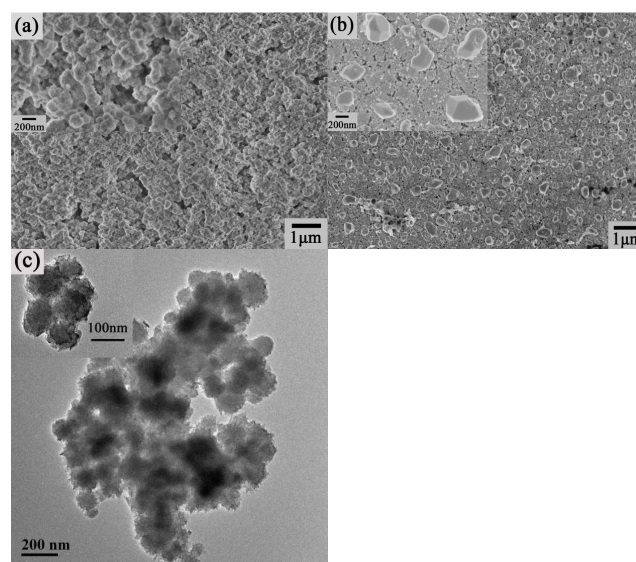


Figure 1. SEM images of as-prepared Ni-S on ITO glass substrates (a) photo-assisted electrodynamic deposition; (b) electrodynamic deposition; (c) TEM images of as-prepared Ni-S by photo-assisted electrodynamic deposition.

X-ray diffraction (XRD) was employed to investigate the composition of the product. As shown in Figure 2, all the diffraction peaks of the sample prepared without irradiation match well with those of NiS (JCPDS 02-0693). However, the

diffraction peaks of the sample prepared by photo-assisted electrodynamic deposition appear to be completely different with the above-mentioned, indicating that its composition is not pure NiS but also likely contains $\text{Ni}(\text{OH})_2$, which is in line with previous observations. The result indicates that the deposit is composed of two phases of NiS and $\text{Ni}(\text{OH})_2$. In addition, the spectrum has peaks at $2\theta = 9.8^\circ$, 28.2° which could be attributed to thiourea derivatives product, which is basically consistent with the reported diffraction peaks of disubstituted thiourea (TU) derivative.⁴⁰

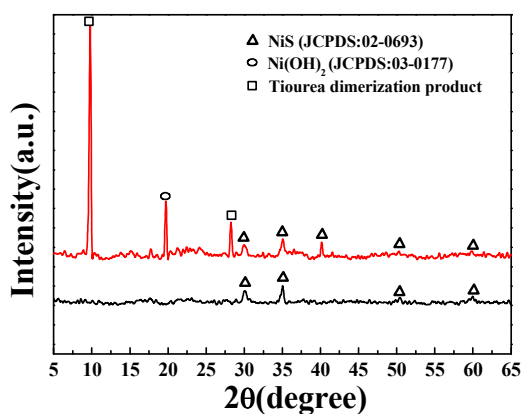


Figure 2. XRD patterns of the Ni-S/ITO as-synthesized, photo-assisted electrodynamic deposition (red line), and electrodynamic deposition (black line).

X-ray photoelectron spectroscopy (XPS) data summarized in Figures 3(a)-(d) provide further support for this hypothesis. Indeed, a Ni 2p peak at 856.3 eV (± 0.5 eV), 873.8 eV (± 0.5 eV) with shoulder at 862.1 eV (± 0.5 eV), 880.9 eV (± 0.5 eV) indicates a Ni^{2+} oxidation state with a mixed composition of NiS/ $\text{Ni}(\text{OH})_2$ (Figure 3(b)). In addition, a single peak at 531.5 eV (± 0.6 eV) in O1s (Figure 3(c)) spectrum can be assigned to OH^- .^{41, 42} Similarly, the S 2p peak at 161-163 eV suggests a S^{2-} oxidation state (Figure 3(d)).^{18,23} By comparing the data with previous XPS studies on Ni, NiO, $\text{Ni}(\text{OH})_2$, and NiS, the presented Ni2p, O1s and S2p spectra can be assigned to Ni^{2+} , OH^- and S^{2-} respectively, in NiS/ $\text{Ni}(\text{OH})_2$.⁴¹⁻⁴³ Hence, it is clear that $\text{Ni}(\text{OH})_2/\text{NiS}$ composite is formed under the present experimental conditions. The peak at ~ 168.5 eV in S2p spectrum is likely due to the thiourea dimerization product.²³ These XPS results are quite consistent with the XRD analysis, as mentioned above.

From the above analysis, a possible photo-assisted electrodynamic deposition mechanism resulting in the formation of a mixed composition of NiS/ $\text{Ni}(\text{OH})_2$ can be explained using two processes as the following reactions:

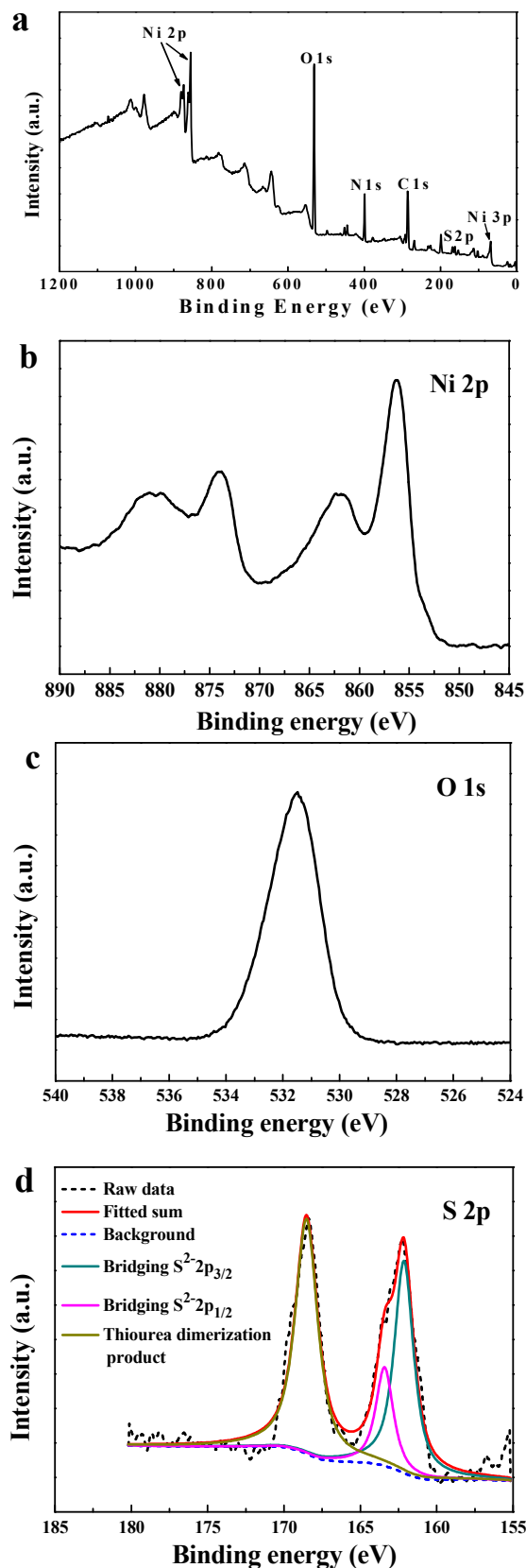
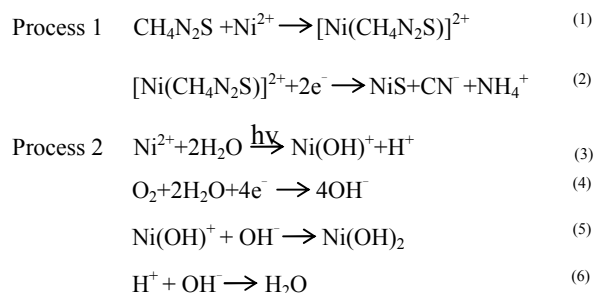


Figure 3. (a) Survey scan XPS spectra in the binding energy range 0-1200 eV and high-resolution spectra, (b) Ni2p, (c) O1s, (d) S2p of Ni-S/ITO.



In the previous studies, several works have proposed the possible electrodeposition mechanism of metal sulfide from TU-containing electrolytes.^{44, 45} The suggested formation mechanism of the NiS deposit is as Process 1. Put simply, Ni^{2+} combine with the corresponding concentration of thiourea to form a Ni^{2+} ions complexes, this complex received external electrons can be electroreduced to NiS. Moreover, dissociative TU molecules will increase rapidly when the TU total concentration exceed that of Ni^{2+} ions and could be polymerized to form thiourea derivatives. According to process 2, Ni^{2+} could react with H_2O under illumination to produce $\text{Ni}(\text{OH})^+$ in a slow reaction process by the reaction (3). Then, $\text{Ni}(\text{OH})^+$ combine with OH^- produced by the reaction (4) to form a $\text{Ni}(\text{OH})_2$. In summary, the composition of the electrode prepared by photo-assisted electrodynamic deposition is a mixture composition of NiS/Ni(OH)₂.

The HER catalysis of the Ni-S film was firstly evaluated in neutral water. Figure 4 shows the polarization curve of Ni-S/ITO in pH 6 buffer solution at a scan rate of 0.1 V s⁻¹. The cathodic scans of four samples prepared by 1, 3, 6, and 9 cycles, respectively, are compared in Fig. 4, where the one of the 6 cycles exhibits the best activity. The polarization curves of a blank ITO electrode and a Pt mesh are also included as a comparison. ITO is not an active HER electrode, while Pt is a highly active, benchmark catalyst, and the polarization data in Fig. 4 are consistent with these known catalytic properties. It is apparent that the blank ITO did not show any HER catalytic activity until -1.0 V vs. RHE,

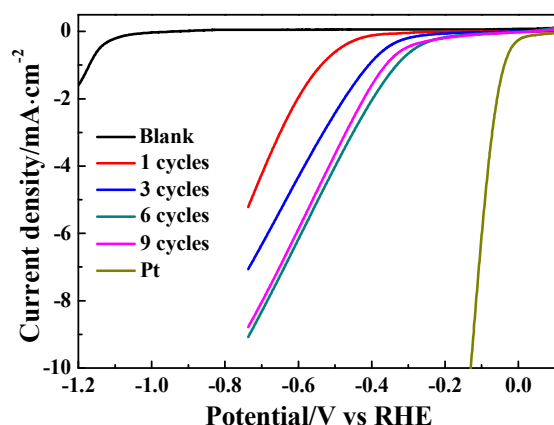


Figure 4. Plots of current density vs potential in buffer solution (pH=6) containing 0.3 mol/L hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), 0.1 mol/L hydrochloric (HCl) and 0.2 mol/L potassium chloride (KCl) for representative samples of Ni-S/ITO with different number of cycles. The bare ITO substrate and Pt are shown as controls.

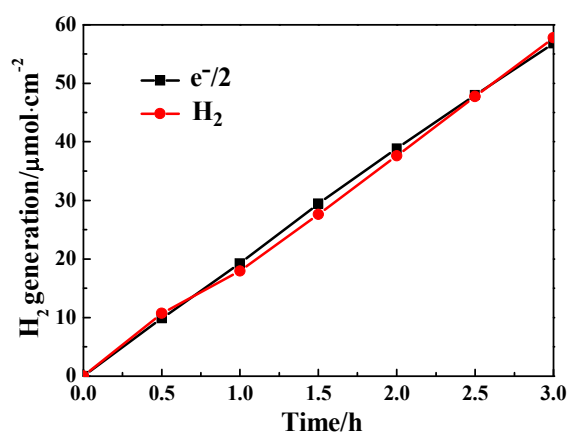


Figure 5. Total hydrogen produced from Ni-S/ITO electrode at -0.4 V vs RHE in buffer solution of pH 6. Also shown is the expected hydrogen evolution calculated from the measured photocurrent assuming 100% faradaic efficiency.

however, a catalytic current was observed for Ni-S/ITO beyond -0.2 V vs RHE. Further scanning towards negative potential produced a dramatic increase in current density.

Next, we investigated the Faradaic efficiency of the Ni-S film in HER catalysis through a chronopotentiometry experiment maintaining a catalytic current of 1 mA for 3 h. As shown in Figure 5, the increasing amount of generated hydrogen was measured by gas chromatography and compared with the theoretical amount assuming that all the passed charges were used to produce hydrogen. The close match of the measured and calculated hydrogen volume demonstrates a 100% faradaic efficiency of Ni-S/ITO in HER electrocatalysis.

In order to assess the long-term stability of the Ni-S film for HER catalysis, an extended electrolysis was carried out. Fig. 6a presents the accumulated charge of Ni-S/ITO in pH 6 buffer solution at -0.7 V vs. Ag/AgCl for 7 h. A nearly linear charge accumulation over time clearly demonstrates the robust durability of the Ni-S film for HER electrocatalysis, which is corroborated by the steady current over the whole process (Fig. 6a, inset). It should be noted that a blank ITO electrode only generated negligible charge build-up under the same conditions. From the very stable catalytic current over the entire electrolysis, it is highly anticipated that the Ni-S film will maintain its catalytic activity for a much longer duration. In addition, we also examined the stability of this electrode at $E = -0.962$ V vs Ag/AgCl, and found that it has the same superior performance with a high current density of 1.5 mA · cm⁻¹ (Figure S1).

We also studied the HER performance of the Ni-S catalyst at extreme pH values. In 0.5 M H_2SO_4 , the catalyst shows a rapid increase in current density when scanning beyond -0.1 V vs RHE (Figure S2), however, subsequent cathodic sweeps led to a quick deactivation of the film, which is most likely due to the dissolution of Ni-S in strong acidic media as the ITO electrode returns to a transparent color after these cathodic scans. Like the problem faced by all metal chalcogenides, the stability of electrode we prepared in strong acid electrolyte is not ideal. On the other hand, in 0.1 M KOH, the Ni-S film exhibits robust HER activity, with nearly linear charge accumulation during 11 h

controlled potential electrolysis (Figure S3).

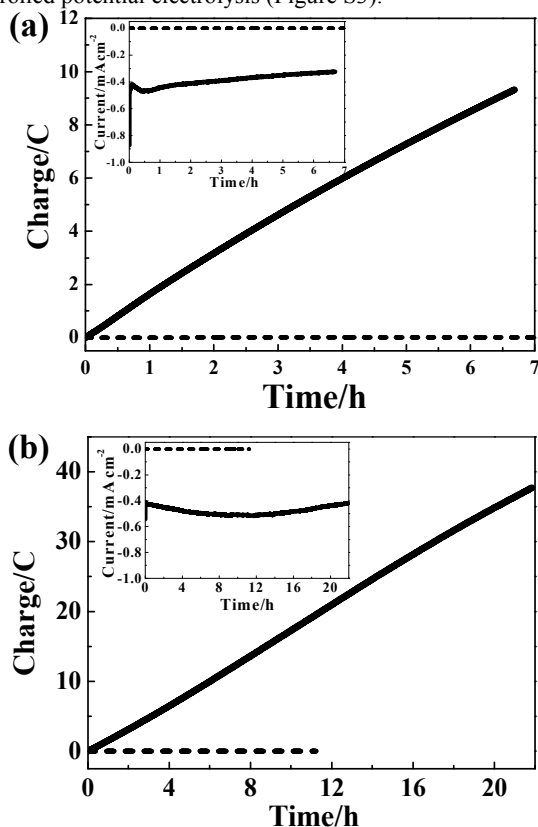


Figure 6. Extended controlled potential electrolysis shows the accumulated charge versus time for Ni-S/ITO (solid) and a blank ITO electrode (dotted) (a) in buffer solution of pH 6 at $E = -0.7\text{V}$ vs Ag/AgCl ($\eta = 138\text{mV}$) and (b) in KPi solution of pH 7 at $E = -0.908\text{V}$ vs Ag/AgCl ($\eta = 287\text{mV}$). Inset: current versus time during the long-term controlled potential electrolysis of Ni-S/ITO (solid) and blank ITO (dotted).

The Ni-S film is also compatible with KPi, the most common electrolyte solution. Figure S4 compares the polarization curves of Ni-S/ITO and blank ITO in 1.0 M KPi electrolyte. Only the former shows a catalytic onset at -0.2V vs RHE followed by a rapid current rise, and the activity persists for at least 22 h as established by a long-term controlled potential electrolysis (Figure 6(b)). To prove this duration is not its maximum duration, we conducted the experiment with a longer duration (36 h) in Figure S5. As been shown in Figure S5, a nearly linear charge accumulation over time clearly demonstrates the robust durability of the Ni-S film for HER electrocatalysis, which is corroborated by the approximate steady current over the whole process. The HER performance was also tested at $E = -0.962\text{V}$ vs Ag/AgCl with $1.3\text{mA} \cdot \text{cm}^{-1}$ current density shown in Figure S6. Hydrogen formation was confirmed by gas chromatography. A 11 h electrolysis of a blank ITO electrode did not generate an appreciable amount of hydrogen under the same conditions, implying that the Ni-S film is a competent and robust HER catalyst in neutral medium. Taken together, these results establish the robust HER activity of the Ni-S catalyst for a wide range of pH values and aqueous reaction media. Then, the XPS data on the sample after the test in KPi solution was characterized to

confirm that materials is stable in the solution in Figure S7. There are no significant change except S 2p peak in Figure S7(d). The peak at $\sim 168.5\text{eV}$ of thiourea dimerization product in S2p spectrum become weak after the test in KPi solution. The reason is that thiourea derivatives was partially decomposed during the reaction, leading to the weak peak. However, the thiourea derivatives is not active ingredient for electrocatalytic hydrogen evolution, and their decomposition hardly effects on the activity of our electrodes. The results indicated that the electrodes was stable in the electrochemical process.

The overall HER activity can be related to the charge transfer resistance (R_{ct}). In order to study this possible mechanism, electrochemical impedance spectroscopy (EIS) was employed to examine the electron transfer process occurring among the Ni-S catalysts and the protons. Figure 7 shows the representative Nyquist plots of Ni-S collected at various overpotentials from 0 mV to 200 mV. The R_{ct} was determined from the semicircle in the low-frequency range. The R_{ct} was much larger than the

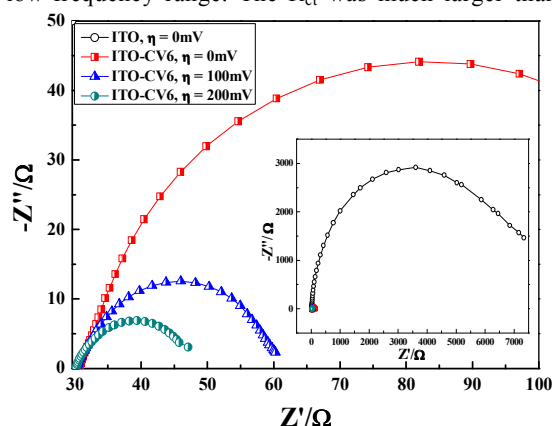


Figure 7. Nyquist plots of Ni-S/ITO at overpotential of 0 mV, 100 mV and 200 mV. All of the spectra were collected by scanning from 0.01 Hz to 10^5Hz with an amplitude of 5 mV in buffer solution of pH 6. The bare ITO substrate are shown as controls.

resistance of the electrode (R_p) and was overpotential-dependent, with the increase of the potential gradually decreases, resulting in the enhanced electrochemical performance, indicating that the R_{ct} dominated the HER reaction.⁴⁶

4. Conclusions

In summary, a NiS/Ni(OH)₂ film prepared by simple photo-assisted potentiodynamic deposition using inexpensive and nontoxic inorganic salt and thiourea as raw materials without any post-treatment is an active, efficient, and robust HER catalyst in neutral pH water, as well as other aqueous media. The prepared electrode possesses a low onset overpotential, high current densities, and 100% faradaic efficiency. Moreover, the Ni-S film exhibited steady current over 22 h with no deactivation, demonstrating its superior stability. These results provide new insights into the facial fabrication of electrodes with high performance and facilitate their practical application in HER field. That plays a certain role in promoting further structure/activity investigations of Ni-S films and related metal chalcogenides for HER.

Acknowledgements

The authors gratefully acknowledge the support from the National Natural Science Foundation of China (No. 20903048, 21275065), the Fundamental Research Funds for the Central Universities (JUSRP51314B), and MOE & SAFEA for the 111 Project (B13025).

Notes and references

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Electronic Supplementary Information (ESI) available: Additional figures and characterization of interest to specialists.

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