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Electrochemical Synthesis of Amorphous Nickel Sulfide Nanostructured Film Photocathode for Solar Hydrogen Production

Mohammed Alghazal[1], Ahsanulhaq Qurashi[1,2,3,*]

[1]Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia
[2]Center of Excellence in Nanotechnology (CENT), King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia
[3]Department of Chemistry, Khalifa University, Abu Dhabi 127788, United Arab Emirates
*Corresponding author: ahsanulhaq06@gmail.com

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Abstract Electrochemical synthesis of amorphous nanostructured films is now well recognized method and here we present experimental protocol for the synthesis of Nickel Sulphide (NiS) amorphous nanostructured film for solar hydrogen production from water feedstock which was used in teaching laboratory in last year of undergraduate and post graduate chemistry students. This proves fascinating laboratory experience that is adopted through modern renewable energy technologies to produce hydrogen from water feedstock. This research area is now well established and expected to be utilized for graduate and undergraduate teaching for advance learning of clean energy processes.

Keywords: *undergraduates, graduates, physical chemistry, materials chemistry, nanotechnology*

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1. Introduction

Materials Electrochemistry is very significant tool which can have multiple applications. In chemistry laboratory other than doing fundamental studies, electrochemical approach can be extended to development of high quality amorphous nanostructured films and clean energy storage and production. Over the years, substantial research is conducted to find an alternative to fossil fuel due to the adverse consequences of the combustion of conventional fuel [1,2]. One of these alternatives is to utilize solar energy which could theoretically cover the world needs of energy [3]. However, there are numerous challenges in harvesting solar energy. Hence, various advanced approaches have been employed to harness solar energy. One of such method is hydrogen generation via photoelectrochemical (PEC) water splitting which was discovered as a viable method by Fujishima et al. [4]. This allows for an efficient energy generation. Fujishima utilized inexpensive Semiconductors materials as photocatalysts in clean energy generation reactions which have high absorbance constant, suitable charger transfer and good alignment of the conducting band with the H_2/H_2O potential [5,6,7,8]. The reaction depends on the formation of the excited electron (e-) and the hole (h^+) in the conducting band and the valance band respectively [9,10]. The reaction has the oxidation and reduction which are shown below. Though the noble metal-based catalysis has excellent performance, but due to their expensive nature they are not considered to be industrially feasible [11]. Thus, catalysis based on low-cost metals is developed [11]. One of them is nickel sulfide based catalyst [11].

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \text{at the anode}$$

$$4H^+ + 4e^- \rightarrow 2H_2 \text{at the cathode.}$$

Nickel Sulfide has been chosen because it is reported to have significant current density [11] which means it has a suitable band gap position for hydrogen generation at cathode. It is also used as co-catalyst by various researchers in similar reactions [12,13,14]. Here in this work we report facile electrochemical approach for the synthesis of NiS on FTO glass substrate.

During this experiment student will understand and learn following practical techniques:

- Cleaning Conducting transparent fluorinated tin oxide substrate surface and finding conductive side by multimeter.
- Electrochemical deposition of Nickel Sulphide in electrochemical cell.
- Surface characterization
- Solar photoelctorchemical hydrogen production
- Accurate data recording and plotting, analysis, and data interpretation.

2. Methods and Materials

2.1. Pre-lab Activities

It would be ideal for students to read the instructions related to electrochemical deposition and solar water electrolysis [5,11]. Also read and understand the preparations of standard solutions. Handle the experiment using full PPE (Gloves, safety googles and lab coat). Execute steps 1-16 while taking break and then write the report.

2.1.1. Apparatus

Potentiostat (Metrohm Autolab Model PGSTAT302N) with NOVA software is used for electrodepositing data collection, with computer connected to potentiostat while collecting data. The counter electrode (CE used as platinum wire obtained from metrohm), reference electrode Ag/AgCl (metroohm) and working electrode WE, Flourinated tin oxide FTO Glass (Solaranix) Susbtrate. Scotch tap used to cover the substrate to open area in three-electrode electrochemical cell (metrohm). Field emission scanning electron microscope (FESEM). FESEM micrographs were acquired through a LYRA 3 Dual Beam instrument (Tescan) operated at an acceleration voltage of 20kV and 10kV furnished with an energy dispersion spectrometer (EDX, Oxford Instruments). Similar potentiostat, Platinum (Pt) and saturated calomel electrode (SCE Ag/AgCl) served as the counter and reference electrodes and NiS/FTO as working electrode(photocathode) for hydrogen generation. A solar simulator (Oriel Sol-3A Newport) delivered artificial solar light irradiation, used for solar light source for collecting hydrogen production data.

2.1.2. Chemicals

Nickel nitrate hexahydrate [$Ni(NO_3)_2{\cdot}6H_2O$, ≥99.0%], thiourea [$SC(NH_2)_2$, ≥99.0%] sodium sulphate (Na_2SO_4), were used as supplied by Sigma-Aldrich .

2.1.3. Note for Instructor

Students should be given instructions on fundamentals of electrochemical deposition, cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry, Also, students should be taught fundamental understanding of surface characterization using scanning electron microscopy and elemental analysis using EDX detector. Finally, how hydrogen produced by photoelectrochemical (PEC) path using water feedstock can be explained theoretically by instructor. Instructor should teach plotting data using excel sheet.

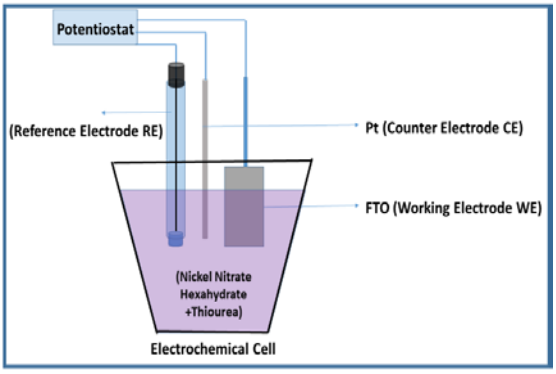
2.1.4. Note for Students

- Measurement unit for distance is often used meter (m) or smaller scale thereof (e.g. mm, µm, nm).
- Measurement for quantities of moles (mol) or divisions/multiples thereof (e.g. mmol).
- Concentrations of particular species/chemicals are mentioned as molarity (M = $mol.L^{-1}$) or divisions/multiples thereof (e.g. µM, mM).
- Measurement unit for volume is liters (L) or divisions/multiples thereof (e.g. µL, mL).

2.2. Experimental Details

2.2.1. Electrochemical Synthesis of Nickel Sulfide Nanostructured Film on FTO Glass Substrate

Step 1. All the electrochemical measurements will be made using a potentiostat using NOVA software connected to computer to control potentiostat. The counter electrode (CE) is Platinum wire, The reference electrode (RE), is 3M KCl in (standard Ag/AgCl). The working electrode is FTO glass substrate fixed in electrochemical cell as shown in schematic 1.



Schematic 1. Three electrode electrochemical deposition of NiS nanostructured amorphous films

Step 2. Clean the FTO glass substrate with ethanol followed by 5 min. sonication in ethanol and dry it and cover the conducting side of substrate with scotch tape to define deposition area.

Step 3. The concentration of nickel (II) nitrate hexahydrate and thiourea, in the electrochemical cell, were 5mM and 0.5M respectively. The electrochemical cell has fluorine doped Tin Oxide (FTO) and platinum as working electrode and counter electrode in the same order with 3M silver/silver chloride reference electrode. After purging the cell for 15 min. with argon, the reaction was done via cyclic voltammetry while maintaining the purging gas. The cyclic voltammetry parameters were limits potentials of 0.200V and -1.200V vs 3M Ag/AgCl electrode, scan rate of 5mV/s, and a total 10 cycles. Figure 1 shows a sample of cyclic voltammogram of the electrochemical synthesis.

Step 4. To start the electrochemical reaction click Nova software, then home button, open library, default procedure, cyclic voltammetry potentiostatic, autolab starting point adjust upper vertex port step potentiostat scan rate, control mode, current range (1mA, 1A, 1µA) run.

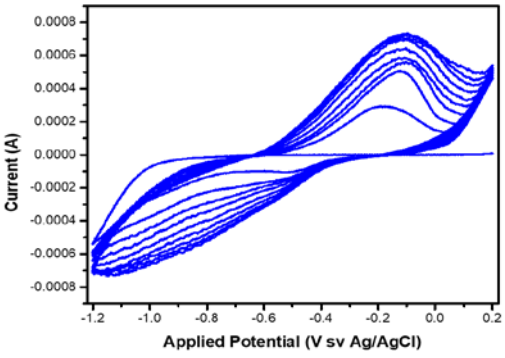


Figure 1. shows Cylic voltammetry for NiS synthesis

Step 5. After the electrochemical deposition, the substrate removed from electrochemical cell dried and found dark grey smooth and uniform as shown in Figure 2.

Figure 2. Photographic image of electrochemically deposited NiS amorphous nanostructured **film**

2.2.2. Surface Characterization of NiS Films

Step 6. Ultrathin 3 nm thick gold film coated by ion beam sputtering on NiS deposited substrate.

Step 7. Above deposited substrate mounted on the Field emission scanning electron microscopy (FESEM) Stub.

Step 8. Field emission scanning electron microscope (FESEM). SEM micrographs were acquired through a LYRA 3 Dual Beam instrument (Tescan) operated at an acceleration voltage of 20 kV and 10kV. Scanned different images to know the films are smooth and nanostructured. The FESEM analysis revealed the irregular surface of the as-synthesis nickel sulfide in Figure 2(a-c) which has many cavities. Conversely, the FESEM images of the treated nickel sulfide in Figure 2 (d-f) displayed nano-cracked surface morphology which exhibits a general smoothness compared to the as-synthesis film.

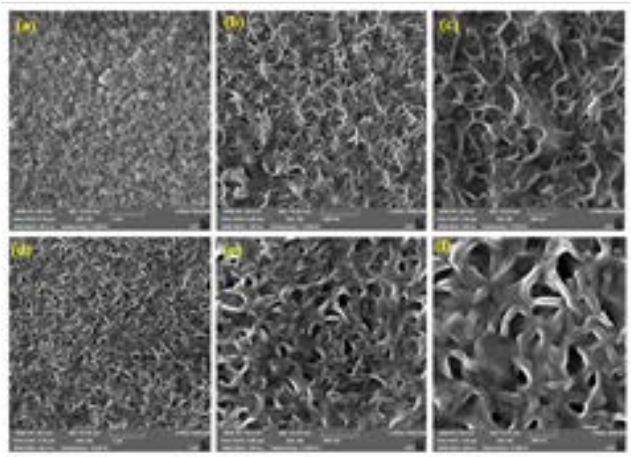


Figure 3. Low and High Magnification FESEM images of NiS nanostructured film grown on FTO substrate

Step 9. SEM furnished with an energy dispersion spectrometer (EDX, Oxford Instruments), which determined the chemical composition and confirmed the essential elements and their surface mapping. These results were confirmed by EDX analysis in Figure 3 where all the elements can be observed. The elemental mapping (not shown in report) shows a homogenous distribution of Ni, C, N, and S on the films which indicates the formation of the catalyst.

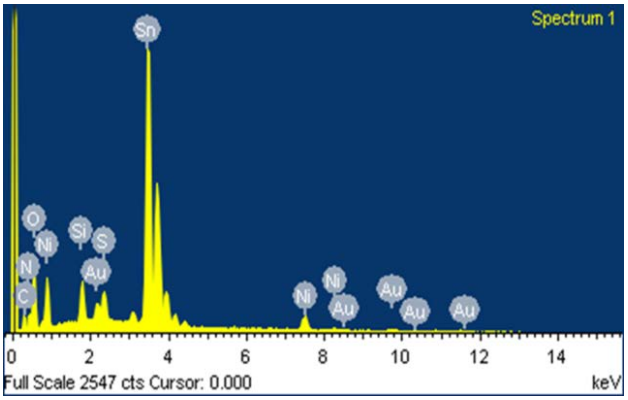


Figure 4. EDX analysis of NiS nanostructured film on FTO glass substrate

2.2.3. Nanostructured NiS Photocathode for Photo-electrochemical Evaluation

Step 10. PEC water splitting was accomplished in a three-electrode PEC cell encompassing a Na_2SO_4 (Sigma Aldrich) electrolyte (pH 7). The fabricated nanocomposite photocathode used as working electrode and controlled by an Autolab potentiostat. Platinum (Pt) and saturated calomel electrode (SCE) served as the counter and reference electrodes. A solar simulator (Oriel Sol-3A Newport) delivered artificial solar light irradiation.

Step 11. To start linear sweep voltammetry (LSV), Click NOVA software, home, open library, default procedure, linear sweep voltammetry, fix voltage between 0 to -1.2V, run in dark and then run while switch on solar simulator to shine sun on working electrode. Save the data.

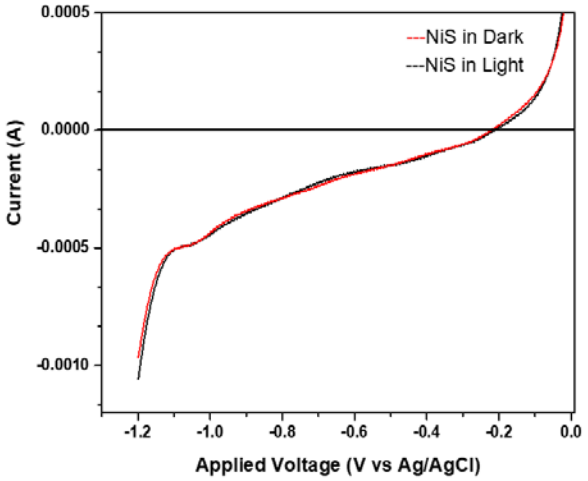


Figure 5. LSV for NiS film in dark and light

Step 12. LSV, I-t chronoamperometry. Figure 5 illustrates the current of nickel sulfide and the reduced nickel sulfide films under light and dark in terms of current density. The figure also shows that the pristine film did not facilitate the evolution of hydrogen as it did not possess a on-set potential at a potential below -1.20V vs Ag/AgCl. The LSV measurements are recorded in the range of 0 to -1.2 V vs Ag/AgCl under regular solar illumination. Figure 5 (a) also depicts the comparative

LSV results of NiS and reduced NiS film under light and dark. It is evident that the dark current is negligible until -1.20 V vs Ag/AgCl. The onset potential for and reduced NiS photocathode is observed at -1.08 V and -1.09 V vs Ag/AgCl under light and dark, respectively. The significant decrease in the onset potential in the case of NiS photocathode can be attributed to the reformation and reduction of nickel which makes the surface more accessible and more conductive as metallic nickel has a high conductivity.

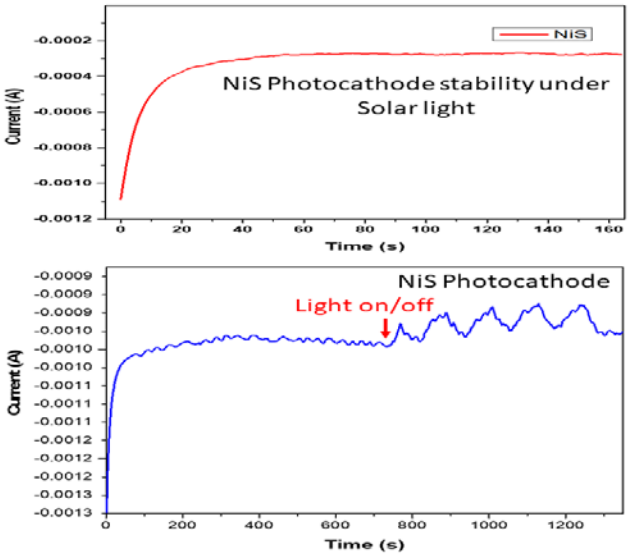


Figure 6. Stability and on of in presence of solar light

Step 13. Click NOVA software, home, open library, default procedure, Chronoamperometry, fix applied voltage. Record signal click duration 1200 seconds interval time 300 second when current stabilized.

Step 14. Again, start chronoamperometry Figure 6 illustrates the periodic chronoamperometric (I-t) results for the hydrogen treated photocathode under dark and light at a cycle of 60 s at -1.20 V vs Ag/AgCl. An increase of 50µA is observed in the photocurrent density of the hydrogen treated photocathode from -950 µA to 1000 µA.

Step 15. NiS electrodes will be dried and stored for other experiments or reproducibility.

Step 16. Solutions will be disposed of safely and glassware rinsed for other experiments.

2.2.4. Report

Step 17. Read the paper from ahsanulhaq et al. and co-workers [22].

Step 18. Plot the clyclic voltammetry (CV) for synthesis of NiS using the excel.

Step 19. Plot the LSV with and without light in excel file and write down your observation report how much current density at which voltage is achieved.

Step 20. Plot the data for stability for time and write the stability of electrode in electrolyte.

Step 21. Plot the data for light chopping on and off and discus

2.2.5. Example Questions

1. What is the rationale for using electrochemical deposition of NiS nanostructured films?
2. What types of information can be gathered by CV?
3. What we observe from FESEM?
4. Why NiS is used as photocathode

2.2.6. Example of Grading

The marks of the report are from 100 % (with partial grading system wherever applicable)

Table 1. Example mark scheme

Weightage	Criteria
15 %	Abstract, introduction and references sections are accurately written and appropriate
15 %	Well-written experimental section, including layout of complete analytical data and plotting
20 %	Clear discussion of electrochemical data
10 %	Correct excel data plotting and figures
10 %	Good write-up and the overall presentation of the report
30 %	Correct answers to questions 1-4

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