A facile route for the synthesis of nickel foam modified WSe₂:CdS nanohybrid as an efficient catalyst for hydrogen evolution reaction (HER)

P Karfa¹, K C Majhi¹, S De¹, R Madhuri¹
¹Department of Applied Chemistry, Indian Institute of Technology (Indian School of Mines) Dhanbad, JH 826004, INDIA
E-mail: paramitakarfa@gmail.com

Abstract. Nickel foam was synthesized via a easy and time consuming method with the help of microwave, the nickel foam was then modified with very impressive rod shaped nanoparticle WSe₂-CdS. The pores of the nickel foam are very clear and uniform in size with the nanoparticle attached in the surface of the foam. The prepared nanohybrid foam (Ni foam@WSe₂-CdS) shows good performance towards hydrogen evolution reaction with small onset potential of -0.30 V and very low tafel slope that is 44 mV/dec. The electrocatalyst was prepared with earth abundant material with low cost of synthesis. Prepared electrocatalyst shows high durability over acidic medium for several time periods with unchanged electrochemical behavior.

Keywords: Nickel foam, Hydrothermal, WSe₂-CdS, Hydrogen evolution reaction

1. Introduction
In recent times two dimensional nanosheet of transition metal dichalcogenides (TMDs) has attracted the researchers, due to their highly efficient electrocatalytic properties. In case of TMDs, X-M-X like layered sandwich structure was observed where M is the metal ions of group IV, V and VI. Here, X is the chalcogen atom (X = S, Se and Te). Diverse properties (chemical, physical, optical, catalytic) of the TMDCs depend mainly on their atomic arrangement. Like that of graphene weak van der Waals interaction works between two adjacent layers and each atom in the same layer are covalently bonded in a hexagonal network. A satisfying stability in strong acids is obtained from these chalcogen atoms decorated on the edges of the transition metal with a beneficial band gap, results in their high catalytic properties [1]. Therefore, emphasize was given on enough edge sites designing and fabrication of the TMDs, which could be possible by the nano scientist via reducing their size to the nanoscale dimensions [2]. Earth abundant material like nickel have been extensively used as an electrocatalyst for HER because of their crystal structure, electrical conductivity, chemical composition, size distribution, low cost etc. However nickel based catalyst also have some limitations like dissolution in acidic medium and many more, but nickel foam have long term stability in acidic or basic medium, very high porosity thus can be used as an good electrocatalyst. Some of the articles reported in nickel foam for HER [3]. Guo et al synthesized CoP nanosheet arrays developed on nickel foam for
outstanding HER activity [4]. Wang et al reported synthesis hierarchical Ni_{3}S_{2}-NiOOH grown on nickel foam for HER [5]. The author reported HER in 1.0 M NaOH with very low overpotential value. Cao et al electrodeposited Ni_{3}P nanospheres on nickel foam as an active catalyst for HER as well as on supercapacitor [6].

Sustainable and renewable energy is the main way out for the great energy crisis and global warming and energy safety issues which can be a substitute of replacing fossil fuels energy [7]. Water splitting proved to be one of the efficient sustainable energy sources at cheap rate [8]. A best electrocatalyst is needed with minimal overpotential (η), high current density to overcome the internal sluggish kinetics of hydrogen evolution reaction (HER). Primary pace towards evolution of hydrogen energy is the use of earth abundant and Pt-free electrocatalysts with high stability in nice potential range [9]. In this work we have made an easy approach for the synthesis of nickel foam and prepared a hybrid with scalable nanometer sized rod shaped WSe_{2}-CdS with high quality and uniformity and explored its activity towards HER. The prepared nanohybrid (Ni_{foam}@ WSe_{2};CdS) showed good HER performances, low TAFEL slope (44 mV/dec) and low overpotential value (230 mV).

2. Experimental

2.1. Chemical reagents consumed

Analytical grade chemicals were used. Sodium tungstate (Na_{2}WO_{4}.2H_{2}O), selenium powder (Se), ethanol, ammonia, sulphuric acid, cadmium sulphate, hydrazine hydrate, sodium hydroxide, dimethyl sulfoxide (DMSO) were purchased from Spectrochem Pvt. Ltd. (India) and Merck (India). Nickel Nitrate, Glycine were purchased from Alfa Aesar (India). All the experiments were conducted in room temperature.

2.2. Instrumentation

Powder X-ray diffraction (XRD) analysis of the samples were taken in Xpert Pro MPD diffractometer with Cu-Kα radiation with 40 KV/mA power. Zeiss SUPRA 55 was used for field emission scanning electron microscopy (FE-SEM) and Energy Dispersive X-ray spectroscopy (EDAX) analysis. All the electrochemical analysis was done on the CH instrument (USA, model number 440D). Every experiments were performed at room temperature.

2.3. Synthesis of rod shaped WSe_{2};CdS

To fabricate rod shaped WSe_{2};CdS nanohybrid, 5.0 mmol of Se powder was dissolved in 10 mL of hydrazine hydrate solution, then 0.41g (2.0mmol) of sodium tungstate and 2.0 mmol of cadmium sulphate were added to the above mixture. Again, 1.0 mmol of l-cysteine (dissolved in 0.3ml of oleylamine) was injected to the above solution maintaining pH of the solution neutral. After that, the solution was kept for constant stirring for 6 hour and poured into a 50.0 mL Teflon lined stainless steel autoclave and placed in the oven keeping the temperature at 200 °C for 36 hours. The product solution was centrifuged at 15,000 rpm, with distilled water and ethanol. Then the product was dried at 60 °C in vacuum for 12 h.

2.4. Synthesis of nickel foam using microwave

Two milimole water-based solution of Ni(NO_{3})_{2}.6H_{2}O was prepared by taking 0.291g Nickel nitrate hexahydrate in 1 mL water. 0.450g of glycine was added to that mixture. Then this mixture was irradiated in microwave oven at 750W for 60s.

2.5. Synthesis of hybrid nickel foam with WSe_{2};CdS (Ni_{foam}@ WSe_{2};CdS)

Nanoparticle of 0.1 g WSe_{2};CdS was dispersed in 10 ml DMF with the prepared nickel foam cut into small pieces with area 1cm² for 24 hours under vigorous stirring. The mixture was then added to 25ml Teflon autoclave for 24 hours. After the reaction the modified foam was washed with water ethanol mixture then dried in vacuum oven for next 48 hours.

3. Result and Discussion

3.1. Compositional and morphological characterization

The XRD of the nanohybrid (Ni_{foam}@WSe_{2};CdS) was successfully done and the XRD spectra of the nanocomposite Ni_{foam}@WSe_{2};CdS shows all the peaks of the nanoparticle and nickel foam which is shown in Figure 1(A). The peaks at 31.5°, 34.4°, 46.7°, 53.9°, 55.6° are due to the WSe_{2}, peaks at
24.48°, 28.3°, 50.9° is due to that of the CdS. Extra peak at 44° and 50° concludes the successful synthesis of nickel foam with JCPDS no 04-0850.

The morphological study of the synthesized nanohybrid has been done by means of FE-SEM analysis. From the Figure 2(A) we can see the clear rod shaped image of the nanoparticle WSe$_2$:CdS of size 100 nm arranged in a homogeneous manner. In figure 2(B) and 2 (C) we can see that the unmodified foam having uniform pores of size less than 10 µm at lower and higher magnification with clear surface having no nanoparticles. After modification the nanoparticle are attached on the surface of the foam beside the pores in haphazard manner can be seen from figure 2(D) and 2 (E). From the EDAX analysis we can tell the homogeneous distribution of W, Se, Cd, S, Ni atoms over the whole nanohybrid shown in figure 2(F). From the EDAX spectra we can say that the nanohybrid is successfully synthesized.
3.2. Electrocatalytic activity and Hydrogen evolution study of the prepared nanocomposite

For the electrochemical measurements as well as HER analysis, nanomaterial modified pencil graphite electrode (PGE) was used. Firstly, the PGE was washed with 6.0 M nitric acid followed by water. The pencil lead which is to be used as an electrode was inserted in a micropipette tip and further modification was carried out. Required amount of nanohybrid material and 5.0 µL of Nafion solution (5 wt %) were dispersed in 1.0 mL of water-ethanol (1:1) solution and was coated dropwise on the pencil graphite electrode. Electrochemical measurements like linear sweep voltammetry (LSV), Cyclic voltammetry (CV) was done in an airtight cell (N2-atmosphere) using a three-electrode system with a nanohybrid modified PGE as the working electrode, Ag/AgCl (in 3.0M KCl electrolyte) as reference electrode, Pt counter electrode. The electrochemical investigation was done in 1N H2SO4 (pH = 0). All potentials were in terms of Ag/AgCl electrode and then converted to reversible hydrogen electrode (RHE), following the equation: 

\[ E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E_{\theta_{\text{Ag/AgCl}}} \]

Here, \( E_{\text{Ag/AgCl}} \) and \( E_{\theta_{\text{Ag/AgCl}}} \) are the experimental potential measured against the Ag/AgCl reference electrode and the standard potential of Ag/AgCl at 25 °C respectively. The electroactive surface area was also analysed using cyclic voltammetry (CV) with 5.0 mM Fe\[(CN)6\]\(^{4-}\) in 1.0 M KCl. The electroactive surface area was estimated according to the Randles-Sevcik equation [5]:

\[ I_p = (2.687 \times 10^5)n^2D^{1/2}v^{1/2}C^0A \]  

where \( I_p \) is peak current, \( A \) is electroactive surface area, \( n \) is number of electrons involved, \( D \) is diffusion coefficient of the analyte, \( v \) is scan rate and \( C^0 \) is concentration of the analyte. The electrocatalytic activity of the electrodes was studied and observed in the Figure 3(A) and Table 1. Modification of bare PGE with nanohybrid (Ni$_{foam}$@WSe$_2$:CdS) increases the charge transfer kinetics by enhancing the electroactive surface area, consequently better current density was obtained at
nanohybrid modified PGE in comparison to the pristine foam modified PGE observed in figure 3(A) thus having high electrocatalytic surface area and high roughness factor for the nanohybrid modified PGE. Optimization through the LSV run was done and it is observed that with 10 mg of the nanohybrid modified PGE electrode and at 5.0 mVs\(^{-1}\) scan rates, 1N H\(_2\)SO\(_4\) as supporting electrolyte noticeable HER activity that is smaller onset potential and high current density is obtained shown in figure 3(B), 3(C), 3(D).

![Figure 3](image_url)

Table 1: Comparision of electroactive surface area, roughness factor of the prepared materials

| Serial no | Electrodes          | Current (Ip) (\(\mu\)A) | Electroactive surface area (A) (cm\(^2\)) | Roughness (R\(_f\)) |
|-----------|---------------------|--------------------------|------------------------------------------|---------------------|
| 1.        | Ni\(_{foam}\)@WSe\(_2\):CdS | 132                      | 0.13                                     | 1.64                |
| 2.        | Unmodified Ni\(_{foam}\)  | 62                       | 0.07                                     | 0.86                |

Tafel slope is an important parameter of electrocatalysts determined by the mechanism, it also give a critical insights into the HER reaction kinetics. The tafel slope can be obtained from linear fitting between linear portion of the polarization curve (LSV)
where \( \eta \) is the overpotential, \( j \) is the current density and the other symbols have their usual meanings.

From the value of tafel slope, there are three possible reaction steps, Volmer reaction step having TAFEL slope (120 mVdec\(^{-1}\)), Heyrovsky reaction step (40 mVdec\(^{-1}\)), Tafel reaction step (30 mVdec\(^{-1}\)). A Tafel plot with small slope value leads to good reaction kinetics for HER and means a slower increase in overpotential with increasing current density.

From the figure 4(A) the LSV plot of the unmodified nickel foam and the nanoparticle modified nickel foam is seen that Ni\(_{\text{foam}}@\text{WSe}_2\)-CdS results the best electrocatalytic activity with lower onset potential of -0.30 V than that of the pristine nickel foam with onset potential -0.44 V. The overpotential value for Ni\(_{\text{foam}}@\text{WSe}_2\)-CdS is 230 mV and that of the pristine nickel foam is 250mV. Smaller the overpotential value means higher is its electrocatalytic activity. The current density of Ni\(_{\text{foam}}@\text{WSe}_2\)-CdS is ~ 80 mA and that of the pristine foam is with 60 mA current density.

\[
\eta = a + \frac{2.3 \ RT}{anF} \ \log (j)
\]  

Figure 4: (A) LSV run and; (B) Cyclic voltammetry runs for both the electrodes.

Cyclic voltammetry (CV) for the nanohybrid was performed at a scan rate of 5 mV \( \text{s}^{-1} \) in the potential range of 0 to -1.3 V for the nanocomposites under the same analytical condition shown in figure 4(B). All the nanocomposites shows a cathodic sweep toward lower potential with a high current density was observed in the nanohybrid modified nickel foam. The Tafel slope of nanohybrid (Ni\(_{\text{foam}}@\text{WSe}_2\)-CdS) was found to be 44 mV/dec and that unmodified nickel is 65 mV/dec. From the TAFEL slope we can conclude that both the electrodes follow Heyrovsky pathway.TAFEL slope of nanohybrid is much smaller than that of the unmodified nickel foam shown in figure 5 (A).

3.3. Stability study of the prepared nanocomposite

Stability is one of the important parameter to justify good HER performances. Cyclic voltammetry was performed to monitor the stability of the electrocatalyst. No such significant change was observed in the cyclic voltammetry data during repetition after 1st, 50th, 100th and 500th cycles respectively recorded in the potential window of 0 to -1.2 V with HER current densities recorded and found as 74, 72 , 70 and 72 mA cm\(^{-2}\) shown in figure 5 (D). From the LSV study we can see that for all the cycles the onset potential is same and also the current density shown in figure 5(B). The higher stability can also be attributed with the unchanged behavior of nanocomposite, after the whole electrochemical study shown in figure 5 (C). The current density and onset potential value was remained almost unaltered for both the cases of fresh and used nanohybrid electrocatalyst (i.e. before and after all the electrochemical studies).
Figure 5: (A) Tafel plot of the materials; (B) LSV plot of the nanohybrid Ni\textsubscript{foam}@WSe\textsubscript{2}:CdS at different cycle; (B) LSV plot before and after electrochemical study; (C) Cyclic Voltammetry plot at different cycle for stability.

4. Conclusion

The prepared nanoparticle WSe\textsubscript{2}:CdS and the nanohybrid with nickel foam were successfully synthesized and were characterized by different characterization method which shows successful synthesis of the materials. Among all the prepared material Ni\textsubscript{foam}@WSe\textsubscript{2}:CdS results the best electrocatalytic activity with much lower onset potential of -0.30 V for hydrogen evolution reaction (HER). So also, electroactive surface area of Ni\textsubscript{foam}@WSe\textsubscript{2}:CdS is found larger than that of the pristine nickel foam making it best electro-catalyst for HER. The prepared nanohybrid with nickel foam also shows a great stability for several months which is very much important parameter as an efficient catalyst.

5. References

[1] Zhou X, Jiang J, Ding T, J. Zhang, Pan B. and Yang J.Q 2014 Nanoscale 19 11046
[2] Yu X, Feng Y, Guan B, Lou X. W. D. and Paik U 2016 Energy Environ. Sci. 9 1246
[3] Gong, M., Wang, D.Y., Chen, C.C., Hwang, B.J. and Dai, H., 2016.. Nano Res. 9 28
[4] Guo, P., Wu, Y.X., Lau, W.M., Liu, H. and Liu, L.M., 2017. Int. J. Hydros. Energy. 42 26995
[5] Wang, X., Liu, R., Zhang, Y., Zeng, L. and Liu, A., 2018. Appl Surf Sci. 456 164
[6] Cao, X., Jia, D., Li, D., Cui, L. and Liu, J., 2018. Chem Eng J. 348 310
[7] Sun C. Zhang J, Ma J, Liu P, Gao D, Tao K and Xu D 2016 J. Mater. Chem. A 4 11234
[8] Wei H, Wang Y, Hu X, Zhou Y and Chen, S. 2012 J Mater Chem. 22 6010
[9] Seo B, Baek D.S., Sa Y.J., Joo S.H. 2016 Cryst Eng Comm. 18 6083
Acknowledgements

Authors are thankful to DST for sponsoring the research projects to Dr. Rashmi Madhuri (Ref. No.: SERB/F/2798/2016-17). The experimental work has been carried out by Ms Karfa with the help of Mr Majhi and Ms De. She and the fellow names are responsible for the data presented.