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# MOF-derived $NiSe_2$ nanoparticles grown on carbon fiber as a binder-free and efficient catalyst for hydrogen evolution reaction

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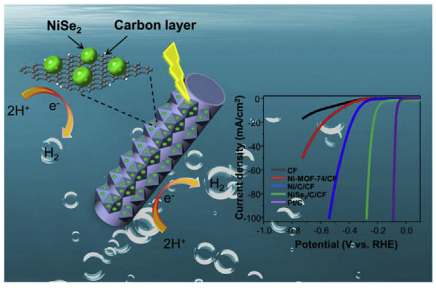
## HIGHLIGHTS

- Approach for the preparation of low-cost and stable catalysts for HER was introduced.
- Binder-free catalyst for HER based on MOF-derived $NiSe_2$/C/CF was constructed.
- $NiSe_2$/C/CF gives a low overpotential of 209 mV, a Tafel slope of 74.1 mV/dec.
- $NiSe_2$/C/CF catalyst exhibits excellent stability under working condition.

## GRAPHICAL ABSTRACT

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## ABSTRACT

It is challenging to grow inexpensive cathode material with superior catalytic properties for hydrogen evolution reaction (HER). Metal-organic frameworks (MOFs) have emerged as powerful platforms to synthesize efficient and ultrastable catalysts for hydrogen production. In this research, $NiSe_2$ nanoparticles were derived from Ni-based MOF, which grown in situ on carbon fiber ($NiSe_2$/C/CF) through pyrolysis and selenization processes. $NiSe_2$/C/CF displays a higher HER performance than that of Ni/C/CF and Ni-MOF-74/CF. Notably, the $NiSe_2$/C/CF electrode gives a low overpotential of 209 mV, a Tafel slope of 74.1 mV/dec, and

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outstanding stability with slight decay after operating for 12 h. The high HER catalytic activity of $NiSe_2$/C/CF is mainly ascribed to the emerging effects of $NiSe_2$ nanoparticles and three-dimensional conductive substrate CF, facilitating active moieties exposure and electron transfer during the electrocatalytic process. Therefore, this work illustrates a novel approach for the preparation of transition metal chalcogenides as low-cost and stable catalysts for HER.



## Introduction

Electrochemical water splitting is a straightforward method to produce hydrogen, which plays an essential role in addressing the issue of clean energy. However, the main disadvantage of water dissociation is that applied overvoltage is required high to surpass the energy barrier for hydrogen evolution reactions (HER). To date, noble metals (e.g., Pt, Pd, Rh) were proved to be the best materials to prepare cathode for electrochemical HER [1]. However, the high-priced of these catalysts inhibited a wide range of industrial processes. A large number of works were carried out to find non-noble metal-related electrocatalysts, such as transition metal oxides [2–5], sulfides [6–9], carbides [10–14], and selenides [15–17] for hydrogen-evolving. In this regard, nickel diselenide has gained growing attention as a potential rival to alter noble metal catalysts by its intrinsically good catalytic activity, outstanding durability, and low production cost [18–20]. However, bulk $NiSe_2$ has low active species, poor conductivity, which is not favorable for electrocatalytic utilizations [21–23]. Its HER activity thus needs to be boosted to become commercial catalysts. Numerous studies have attempted to enhance the HER performance of $NiSe_2$ via various approaches such as designing nanoarchitecture or employing conductive templates. For example, Li et al. prepared $NiSe_2$ nanoparticles with supporting nitrogen-doped graphene toward enhanced HER performance [18]. Nickel foam with a three-dimensional (3D) architecture was evaluated as an ideal skeleton for growth materials to create efficient electrodes for electrochemical applications [24–26]. As a case in point, Zhou et al. create $NiSe_2$ on a nickel foam (NF) platform as an efficient electrode for hydrogen evolving, which is assigned to the emerging effect of catalytic species exposure and fast electron transfer from the high conductivity of NF. This electrode gave an excellent HER catalytic property, which is comparable to Pt/C catalysts. In a similar case in Teng's work, the authors synthesized $NiSe_2$ nanotube arrays on NF as a functional cathode for water dissociation [27]. The effectiveness of NF substrate has been exemplified in a study by Yu and coworkers [28]. However, the drawback of NF is not durable at high temperatures, which is usually used for fabrication catalyst materials [29]. Also, carbon fiber (CF) is employed as a conductive substrate to prepare electrodes in catalytic utilization because of its superior properties, including good chemical stability, high thermal stability, large surface area, and outstanding mechanical strength [30–33]. For instance, Qu et al. deposited $MoSe_2$ nanosheets CF as a 3D cathode for hydrogen evolution [34]. This cathode gave an excellent catalyst with a low overvoltage, which was ascribed to the synergistic engineering of nanosheets and a highly conductive template. Hou and coworkers fabricated Pt/$MoS_2$/CF as a working electrode for HER in an acidic solution, which exhibited remarkable stability with 10 h of operation [35]. Zang et al. used carbon fiber felt (CFF) to grow $MoS_2$ nanolayers as a flexible electrode with outstanding HER activity [36]. Zhang et al. found that the in situ synthesis of $MoS_2$ on carbon cloth (CC) created an electrocatalyst with better performance than the physical preparation of $MoS_2$ with CC [37]. Wang et al. also used CC as a 3D conductive platform to deposit $CoSe_2$ nanocatalysts anchored Co–N-doped carbon matrix for HER [38]. This catalyst displayed a very low Tafel slope comparable with Pt catalyst for hydrogen production. Another work that utilized CC for growth cobalt disulfide nanotube arrays were reported by Guan et al. [39]. The authors found that this material exhibited higher stability than Pt/C catalyst for HER application. Yan and co-workers have confirmed the effectiveness of the CC template [40]. The authors synthesized $WS_2$ and $MoS_2$ on CC through a facial solvothermal process. The electrodes display remarkable durability after 24 h of testing, which is attributed to the good interaction between materials and CC. As mentioned pieces of evidence, the carbon-based substrates' role is significant for preparing efficient, binder-free, and durable electrodes in electrochemical HER. The metal-organic framework was considered ideal for creating unique architecture with high performance in catalysis because of its outstanding properties, such as large surface area and adjustable structural morphology. However, MOFs-derived materials are usually created with powder catalysts, which must use binders (Nafion, polytetrafluoroethylene) to fabricate the working electrodes [41]. This may affect the catalytic activity in the electrochemical reaction, impeding their commercial utilization. Therefore, researchers synthesized the MOFs on conductive substrates, then converted them to nanocatalysts anchored on this template for water dissociation. For example, Wang and coworkers prepared $CoSe_2$ nanoparticles from Co-based MOF nanosheets on CF, which gave an excellent catalytic activity with a Tafel slope of 38 mV/dec [38]. The effectiveness of CF has been proved in a report by Zhan et al. [42]. The authors grow Co-MOF on CF through an active binder carbon nanotube, followed by the oxidation and phosphorization to form CoP nanograins as a highly stable

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electrocatalyst for hydrogen generation. Xie et al. fabricated Ni-doped $CoS_2$ on carbon fiber papers (CFP) as efficient catalysts for oxygen evolution reaction with an overvoltage of 270 mV [43]. Beside Co-MOF, Ni-based MOFs were also used to create Ni compounds for HER. However, the in situ synthesis of Ni-MOF-74 on CF as precursor for preparation $NiSe_2$ has not investigated yet for HER application.

In this study, we introduce a straightforward approach to fabricating $NiSe_2$ nanoparticles from Ni-based MOF, grown in situ on commercial carbon fiber ($NiSe_2$/C/CF) as a binder-free and efficient cathode for hydrogen production in acidic media. $NiSe_2$/C/F exhibits an outstanding catalytic activity with a slight overvoltage of 209 mV at a current density of 10 mA/cm$^2$ and a low Tafel slope of 74.1 mV/dec. Also, this electrode displays remarkable durability, remaining catalytic properties after 10 h. The high performance of $NiSe_2$/C/CF is ascribed to the emerging effects of a conductive substrate and highly active sites of $NiSe_2$ nanoparticles.

## Experimental section

### Materials

Phychemi company provided carbon fiber. Nickel nitrate hexahydrate, Nafion media (5 wt %), 2,5-Dihydroxybenzenedicarboxylic acid ($H_4$DHBDC), Selene powder were supplied from Sigma-Alrich. *N,N*-Dimethylformamide (DMF), Ethanol ($C_2H_5OH$), Sulfuric acid (98%) were bought from Daejung Chemicals & Metals Company Limited. The water utilized in experimental studies was obtained from an instrument of Millipore Mili-Q.

### Synthesis of Ni-MOF-74/CF

The pristine CF (2 cm × 3 cm) was oxidized in air at 450 °C for 30 min to increase the hydrophilic properties for its surface, which is favorable for the growth of MOF crystals. Then, it was rinsed with DI water and ethanol for 15 min. Next, the reaction solution was fabricated by dissolving 0.238 g of $Ni(NO_3)_2 \cdot 6H_2O$ and 0.048 g of $H_4$DHBDC in a mixture solvent (5 ml DMF, 5 ml DI water, 5 ml ethanol). The modified CF was immersed into this reaction solution and heated at 100 °C for 24 h. Finally, the as-prepared Ni-MOF-74/CF was washed with ethanol, accompanied by drying under vacuum at 80 °C for 5 h.

### Synthesis of $NiSe_2$/C/CF

The sample of $NiSe_2$/C/CF was obtained over two steps of calcination and selenization. Firstly, the as-prepared Ni-MOF-74/CF was pyrolyzed at 500 °C for 2 h in nitrogen gas to produce Ni/C/CF. Second, a sample of Ni/C/CF was conducted selenization to create $NiSe_2$/C/CF. In particular, a piece of Ni/C/CF is put in a combustion boat with 50 mg of Se powder at the upstream side, followed by reacting at 350 °C for 2 h under a nitrogen atmosphere. The mass loading of $NiSe_2$/C on CF is approximately 1.0 mg/cm$^2$ determined by the mass change between CF and $NiSe_2$/C/CF.

### Characterization

A SIGMA/Carl Zeiss microscope was chosen to obtain scanning electron microscopy (SEM) images. JEOL-2100F (Japan) electron microscope are adopted for collecting Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images. X-ray diffraction (XRD) data are collected on a D8-Advance/Bruker-AXS with Cu K$\alpha$ radiation. The chemical states of elements in materials were investigated by X-ray photoelectron spectroscopy (XPS). The Raman spectra data were gathered on a Raman microscope (LabRAM-HR) in a frequency zone of 100–3500 cm$^{-1}$.

### Measurements of electrochemical properties

The HER catalytic activities of the catalysts were judged in the electrolyte of 0.5 M $H_2SO_4$ with a potentiostat workstation (Ivium 5612). Carbon rod, $Hg/Hg_2Cl_2$ in KCl (saturated), and as-prepared electrodes (working area of 1.0 cm × 1.0 cm) operated as an auxiliary, reference, and working electrodes. Herein, voltages vs. reversible hydrogen electrode (RHE) are determined from the Nernst equation of E (RHE) = E ($Hg/Hg_2Cl_2$) + 0.059 × pH + 0.241. Polarization curves are recorded in a voltage range of –08–0.1 (vs. RHE) at a scan rate of 10 mV/s, followed by iR correction. Electrochemical impedance spectroscopy (EIS) plots were gathered in frequencies zone of 0.1 Hz–100 kHz. The durable properties of the working electrode were evaluated by utilizing cyclic voltammetry (CV) in a potential window from 0.1 to −0.3 V (RHE) at a scan rate of 100 mV/s and chronoamperometry for up to 12 h at a constant voltage.

## Result and discussion

The synthetic route of nickel diselenides from Ni-based MOF grown on CF is exhibited in Fig. 1. First, Ni-MOF-74 was in situ synthesized on CF (abbreviated Ni-MOF-74/CF) by solvent-thermal method; then it is converted into Ni nanoparticles embedded on carbon layers (Ni/C/CF) at 500 °C, followed by selenization to form $NiSe_2$ nanograins anchored carbon layer array on CF ($NiSe_2$/C/CF). The crystal architectures of CF, Ni-MOF-74/CF, Ni/C/CF, $NiSe_2$/C/CF samples were investigated by XRD spectroscopy (Fig. 2a). A typical peak of CF was identified at about 24.5° indexed to (002) planes, which was appeared in all samples [30]. Two diffraction peaks at 6.8° and 11.7° were observed in the Ni-MOF-74/CF sample that proved the successful growth of Ni-MOF-74 on CF [44–46]. The three peaks of 44.2°, 51.5°, and 75.8° were assigned to the (111), (200), and (220) planes of metallic Ni [19,47], which implied the complete conversion of Ni-MOF-74/CF into Ni/C/CF. The XRD pattern of $NiSe_2$/C/CF exhibits the peaks at 2θ values of 29.9°, 33.4°, 36.7°, 42.6°, 50.5°, 55.2° and 57.5° which were attributed to the (200), (210), (211), 220), (311), (230) and (321) planes (PDF# 88–1711) [20]. Fig. 2b exhibits the Raman spectra peaks of $NiSe_2$/C/CF. Signal frequencies of 149.6, 169.9, 217.5, and 243.7 cm$^{-1}$ are indexed to the $T_g$, $E_g$, $A_g$, and $T_g$ modes of $NiSe_2$ [27]. The high-intensity peaks at 1357, 1590, and 2709 cm$^{-1}$ correspond to the D-, G-, and 2D-band of carbon materials [48].

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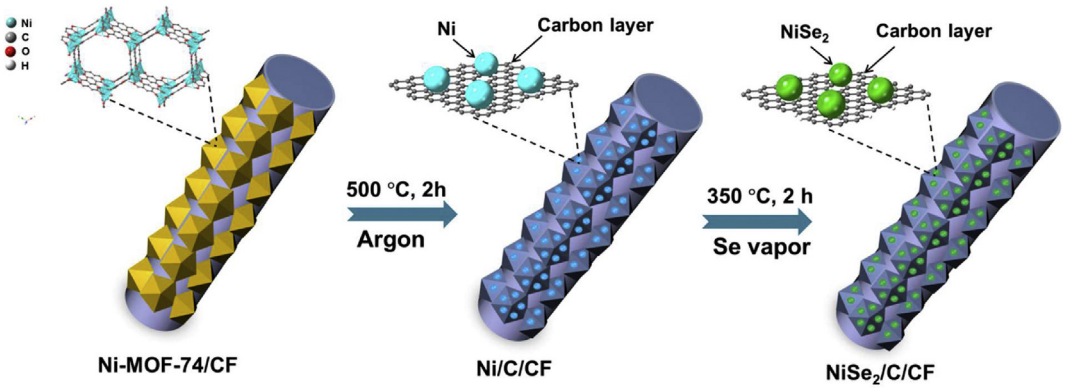


**Fig. 1 – Schematic illustration of the fabrication route of $NiSe_2$/C/CF.**

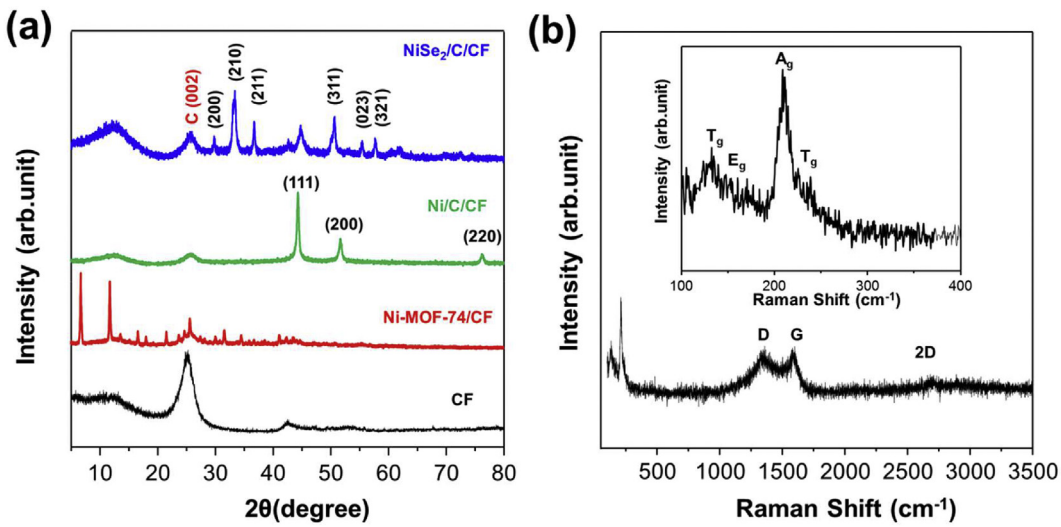


**Fig. 2 – (a) XRD patterns of CF, Ni-MOF-74/CF, Ni/C/CF, and $NiSe_2$/C/CF. (b) Raman spectra of $NiSe_2$/C/CF.**

Fig. 3 exhibits the SEM images of the as-prepared of CF, Ni-MOF-74/CF, Ni/C/CF, and $NiSe_2$/C/CF. CF treated by heat displays a flat surface with a diameter of 8–10 μm, as shown in Fig. 3a and b. As depicted in Fig. 3c, the Ni-MOF-74 crystals uniform cover on CF. Under high magnification, we can see that crystals were connected to create flower-shaped Ni-MOF-74 with a smooth surface (Fig. 3d). After annealed, Ni-MOF-74 converted into Ni nanoparticles embedded on carbon layers, as displayed in Fig. 3e. The surface of $NiSe_2$/C/CF was also changed after selenization was conducted at 350 °C for 2 h (Fig. 3f). The TEM image (Fig. 4a and b) indicates that many $NiSe_2$ nanograins are distributed on carbon frameworks. For the purpose of d-space measurement, HRTEM were analyzed, as shown in Fig. 4c. The d-space is calculated to be 0.296 nm, which was assigned to the (200) facet. The structure of $NiSe_2$/C/CF is further proved by EDS elemental mappings. As shown in Fig. 4d, the elements of Ni, Se and C are uniformly distributed on carbon matrix.

For chemical state analysis, XPS was adopted. Fig. 5a shows the survey spectrum of $NiSe_2$/C/CF and implies the presence of Ni, Se, and C in the compound. As depicted in Ni 2p XPS spectra (Fig. 5b), two prominent peaks located at 853.3 (S1) and 870.6 eV (S1′) are indexed to $Ni^{2+}$ $2p_{3/2}$ and $2p_{1/2}$, respectively, while the oxidation phase of $Ni^{3+}$ is identified at 855.9 eV (S2) and 873.9 eV (S2′). Also, two shakeup excitation of $Ni^{2+}$ was recorded at 861.1 eV (S3) and 880.0 eV (S3') [18,21]. For Se 3d XPS spectra (Fig. 5c), the binding energies of 55.4 eV and 54.5 eV are ascribed to the Se $3d_{5/2}$ and Se $3d_{3/2}$. Also, the existence of a peak at 59.1 eV is suspected of the selenium oxides [23,49]. As depicted in Fig. 5d, C 1s can be devaluated to three peaks, which were assigned to 284.6 eV (C–C), 285.7 eV (C–O), and (287.3 eV (C=O).

The HER properties of the as-prepared working electrodes, including CF, Ni-MOF-74/CF, Ni/C/CF, and $NiSe_2$/C/CF, were investigated in a three-electrode system with acidic sulfuric solution. Fig. 6a displays the polarization curves of CF, Ni-MOF-74/CF, Ni/C/CF, and $NiSe_2$/C/CF and Pt/C. CF did not depict any catalytic activity for hydrogen evolving, whereas the Pt/C electrode depicts the best HER yield. Ni-MOF-74/CF gives a poor HER catalytic performance due to its containing organic component, which causes a high charge transfer resistance. However, when Ni-MOF-74/CF samples were annealed in Argon gas, Ni-MOF-74/CF was transformed into Ni nanoparticles anchored on the carbon layer (Ni/C/CF), which presents a good HER activity. Furthermore, after selenization, $NiSe_2$/C/CF gives a better HER yield than the other working

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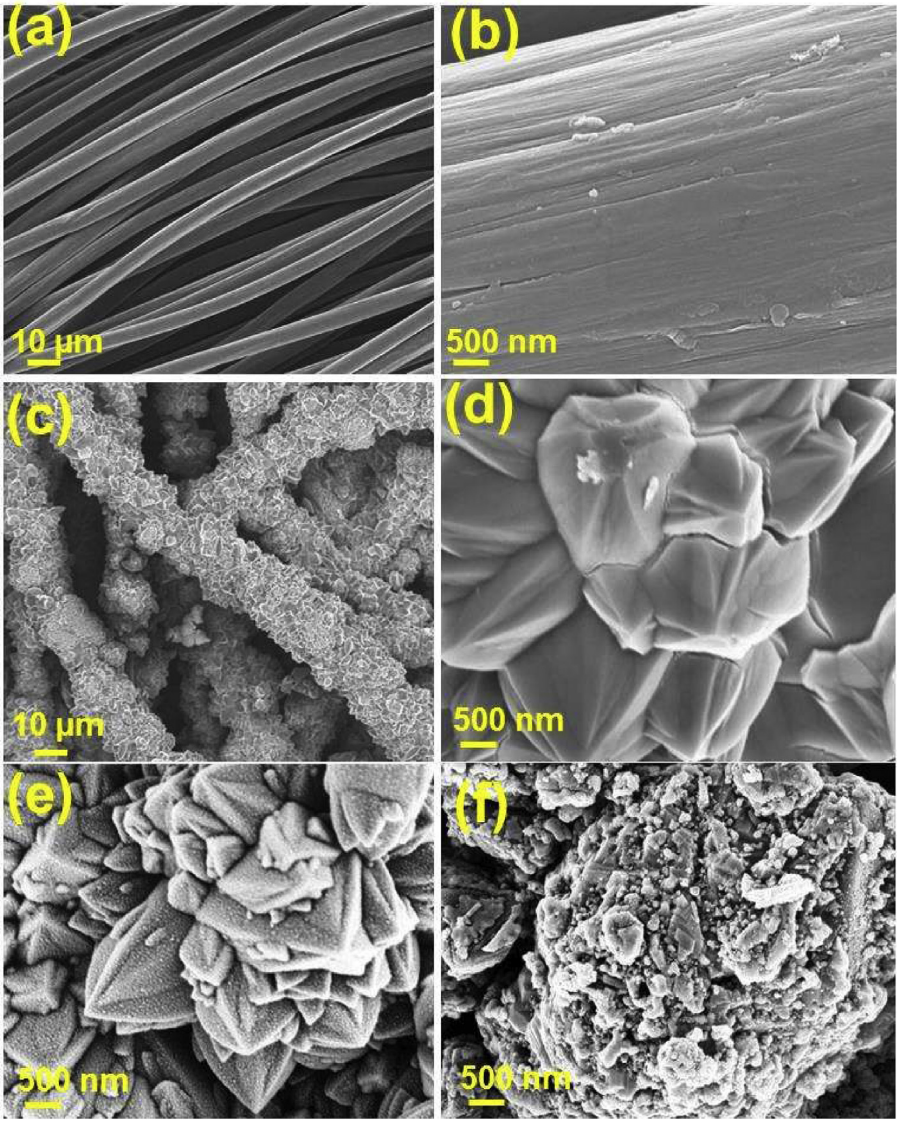


**Fig. 3 – SEM images of (a, b) CF, (c,d) Ni-MOF-74/CF, (e) Ni/C/CF and (f) $NiSe_2$/C/CF.**

electrode. In particular, Tafel slope and overpotential at 10 mA/cm$^2$ were gathered from linear sweep voltammetry (LSV) measurements, as depicted in Fig. 6 b,c. $NiSe_2$/C/CF electrode exhibits an overvoltage of 209 mV, which is smaller than that of Ni/C/CF (341 mV) and Ni-MOF-74/CF (475 mV). Also, the Tafel slope value of $NiSe_2$/C/CF samples is 74.1 mV/dec, which is smaller than that of Ni/C/CF (95.6 mV per/dec) and Ni-MOF-74/CF (117.9 mV per/dec). Theoretically, The mechanism of hydrogen evolving under acidic condition involves two steps. Step 1 (Volmer reaction): proton was adsorbed on the catalyst surface ($H_3O{+}{+}\ e^- \rightarrow H_{ads} + H_2O$), which will generate a slope of ~120 mV/dec. Step 2 may take place two processes. The first process, called the Heyrovsky reaction, occurs the electrochemical desorption ($H_3O{+}{+}\ H_{ads} + e^- \rightarrow H_2\uparrow + H_2O$), which creates a slope of ~40 mV/dec. The second process is called the Tafel reaction, exhibiting chemical desorption ($H_{ads} + H_{ads} \rightarrow H_2$), producing a 30 mV/dec slope. Therefore, we propose that the HER mechanism of $NiSe_2$/C/CF is the combination of the Volmer and Hyrovsky reactions. The changes in HER catalytic performance of the working electrode can be assigned to electrochemically active surface area (ECSA) [50–52]. We thus conduct to determine ECSA, which is related to double-layer capacitances. CV measurements were carried out in a specific potential zone of 0.1–0.2 (V vs. RHE) at seven different scan rates (20–140 mV/s), which only contains non-faradaic current (Fig. S1). Fig. 6d shows the change of current density with scan rates, the slope of these plots is $C_{dl}$. $NiSe_2$/C/CF gives a high $C_{dl}$ value (12.5 mF/cm$^2$) which is about two times and four times higher than Ni/C/CF (6.7 mF/cm$^2$) and Ni-MOF-74 (2.9 mF/cm$^2$). This finding proves that $NiSe_2$/C/CF has the largest effective surface area, which indicates a strong relationship between ECSA and catalytic properties [53]. Impedance measurement was chosen to evaluate the reaction kinetic for hydrogen evolving. Fig. 6e depicts the Nyquist plots of Ni-MOF-74/CF, Ni/C/CF and $NiSe_2$/C/CF. An equivalent circuit (the inset of Fig. 6e) shows two quasi-semicircles, revealing the porosity of MOF-derived materials [54]. Notably, $R_s$, $R_P$, and $R_{ct}$ is indexed to the series

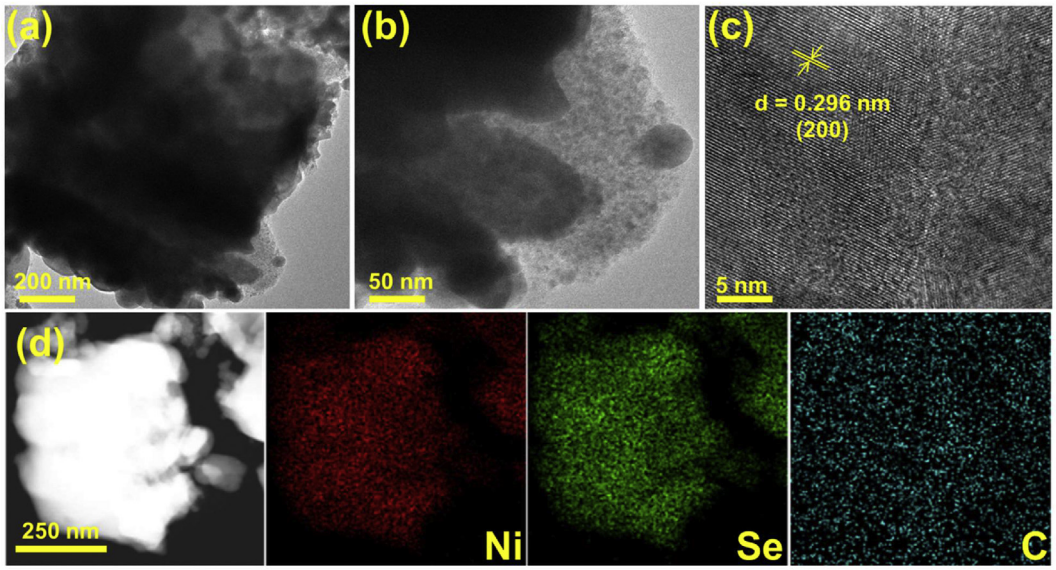


**Fig. 4 – (a, b) TEM images of $NiSe_2$/C/CF. (c) HRTEM image of $NiSe_2$/C/CF. (d) EDS elemental mapping images of $NiSe_2$/C/CF.**

resistance, polarization resistance, and electron transfer resistance, respectively. $R_{ct}$ value of $NiSe_2$/C/CF is 9 Ω, which is lower than that of Ni-MOF-74/CF (62.5 Ω) and Ni/C/CF (14.4 Ω). This indicates that the charge transfer process on $NiSe_2$/C/CF sample is faster than the other electrode in hydrogen evolving.

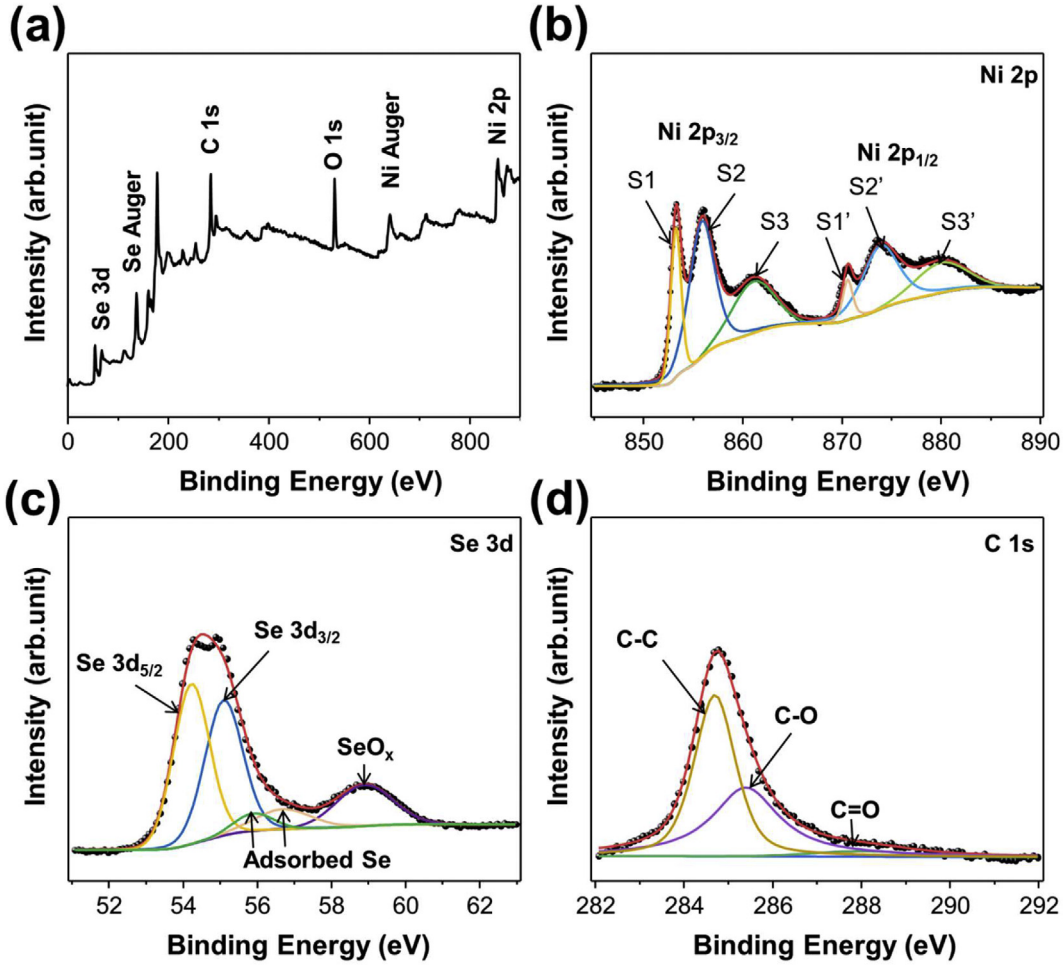


**Fig. 5 – XPS spectra of $NiSe_2$/C/CF: (a) element survey, (b) Ni 2p, (c) Se 3, (d) C 1s.**

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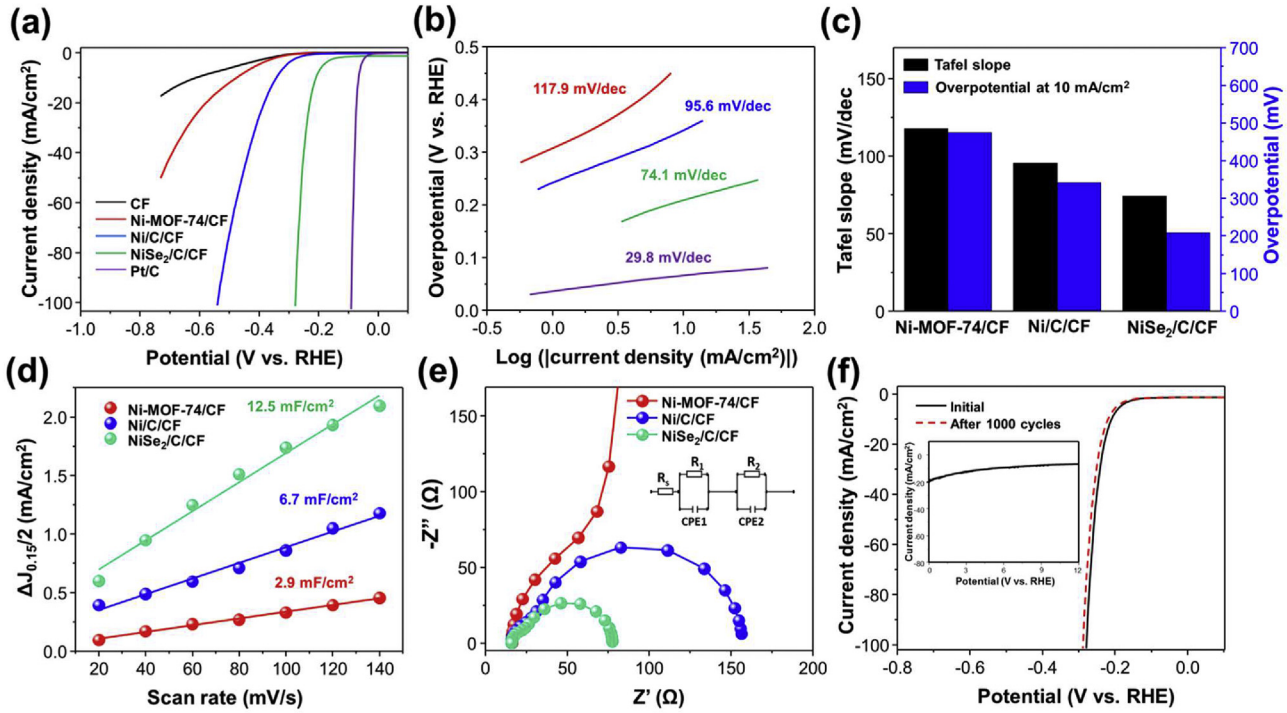


**Fig. 6 – (a) Polarization curves in 0.5 M $H_2SO_4$ (b) the corresponding Tafel slope. (c) Overpotential of as-prepared catalyst at 10 mA/cm$^2$. (d) Estimated $C_{dl}$ of Ni-MOF-74/CF, (e) Ni/C/CF and (f) $NiSe_2$/C/CF. (f) Polarization curves of $NiSe_2$/C/CF before and after 1000 CV cycles. Chronoamperometry test for $NiSe_2$/C/CF at a constant voltage of 209 mV for 12 h.**

For future commercial utilization, the stabilizing of electrocatalysts needs to be scrutinized in a long-term period. LSV of $NiSe_2$/C/CF electrode after 1000 cycles is a slight change compare to the first cycles, as depicted in Fig. 6f. Furthermore, the durability of $NiSe_2$/C/CF was examined at a specific voltage of 230 mV (vs. RHE) through a chronoamperometric analysis. The cathodic current density (20 mA/cm$^2$) of $NiSe_2$/C/CF depicts an approximately 50% decrease in the HER activity after 12 h of hydrogen production (the inset of Fig. 6f). This outcome could be attributed to the consumption of protons and the impeding of the hydrogen bubble on the catalyst's surface [55–57]. After testing for the durability of $NiSe_2$/C/CF, XRD and FE-SEM were analyzed to evaluate the crystal phase and morphological structure of the electrode. XRD pattern (Fig. S2a) reveals that the structure of $NiSe_2$/C/CF built by $NiSe_2$ nanograins anchored carbon layer is unaltered. Besides, the FE-SEM image (Fig. S2b) of $NiSe_2$/C/CF after 12 h of testing is identical before. This implies that $NiSe_2$/C/CF is a durable electrode under acidic conditions for hydrogen production.

## Conclusion

The aim of this work is to design an economical electrocatalyst of $NiSe_2$ nanograins anchored Ni-MOF-derived porous carbon grown on carbon fiber ($NiSe_2$/C/CF) and evaluate its catalytic activities for hydrogen production. This strategy gives emerging effects from $NiSe_2$ nanograins and 3D conductive substrate of CF, facilitating active species exposure and electron transport in the electrochemical HER application. As a result, $NiSe_2$/C/CF electrode displayed a good catalytic performance for hydrogen generation. In particular, $NiSe_2$/C/CF only needs a small overvoltage of 209 mV to achieve a cathodic current density of 10 mA/cm$^2$. Furthermore, this catalyst also maintains catalytic activity after 1000 cycles of testing in the acidic electrolyte. Although this study focuses on nickel diselenide, the findings may well have a bearing on the fabrication of transition metal compounds on CF from MOF precursors for the field of catalysis.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2022.04.127.

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