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SPECIALTY SECTION

This article was submitted to Energy Materials, a section of the journal Frontiers in Materials

RECEIVED 28 July 2022

ACCEPTED 08 September 2022

PUBLISHED 10 October 2022

CITATION

Pi Z-G, Ye H, Han Z, Yu P, Yin Z and Ma X (2022), Promising CoSe₂-CNT composite catalyst for efficient photoelectrochemical hydrogen evolution reaction. *Front. Mater.* 9:1005221. doi: 10.3389/fmats.2022.1005221

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Promising CoSe₂-CNT composite catalyst for efficient photoelectrochemical hydrogen evolution reaction

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CoSe₂ is a typical transition metal chalcogenide and an hydrogen evolution reaction hydrogen evolution catalyst due to its efficient and inexpensive characteristics. In this work, CoSe₂/CNT composite was synthesized through a one-step solvothermal method. Specifically, a current density of 10 mA cm⁻² can be achieved under an overpotential of 163 mV, and the Tafel slope is 69.4 mV dec⁻¹. The reasons for these excellent performances are: 1) the abundant catalytic active sites of CoSe₂; 2) the high conductivity of CNTs; and 3) the synergistic effect between CoSe₂ and CNTs; iv the solar irradiation excites electrons to join the reaction. This work proposes a new way to reasonably design the high-efficiency and low-cost transition metal chalcogenide hydrogen evolution catalysts.

KEYWORDS

HER, solar-irradiation, CoSe₂, CNT, composite

Introduction

In recent years, people have paid more and more attention to renewable energy, such as bioenergy, hydrogen energy, solar energy, *etc.*, because of the decreasing fossil energy and the increasingly severe environmental pollution. Hydrogen has become the focus of attention because of its high energy density, cleanliness, and renewability (Fan et al., 2019; Gao et al., 2018; Li et al., 2020; Yu, Qu, et al., 2016; Yu, Zhang, et al., 2016). Electrocatalysis decomposes water into hydrogen and oxygen, which might be used to tackle energy and environmental problems. The hydrogen evolution reaction (HER) plays a vital role in electrochemical water splitting and has been widely studied (Cao et al., 2022; Yuanmiao Sun et al., 2020; Ji et al., 2020; Zhao et al., 2022). To date, platinum-based materials have been considered to be the best hydrogen evolution reaction catalysts because they have the smallest overpotential, and the Gibbs free energy (ΔG_H) of Pt to adsorb hydrogen is close to zero (Greeley et al., 2006). However, industrial production has been restricted due to few reserves and high prices. Therefore, people are committed to looking for abundant,

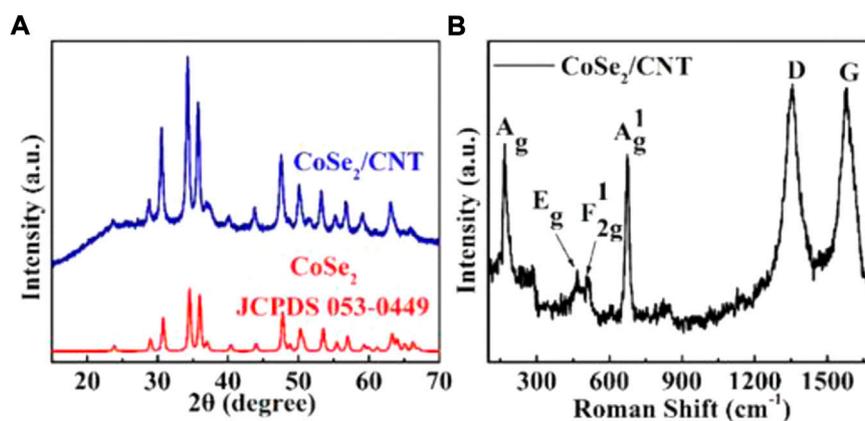


FIGURE 1
(A) XRD patterns and (B) Raman image of CoSe₂/CNTs composites.

low-cost, efficient, and stable catalysts to replace the precious metal platinum-based catalysts (Liu et al., 2016; Ye et al., 2016).

In recent years, people have made great efforts to study the catalytic effects of transition metal sulfides, metal oxides, phosphides, and selenides on HER, proving that these materials are promising electrocatalysts that can replace platinum-based materials. Among these materials, the transition metal selenides MoSe₂ (Deng et al., 2018), WSe₂ (Henckel et al., 2017), NiSe₂ (Sun et al., 2018), and CoSe₂ (Chen et al., 2016) have good catalytic performance, and low cost, so they get extensive studies. Since CoSe₂ has good catalytic activity and durability characteristics, it has been proven to have excellent HER electrocatalytic performance in acidic media (McCarthy et al., 2016; Yang et al., 2021). However, CoSe₂ always agglomerate and leads to a lack of active sites in practical applications. Also, its conductivity is not particularly excellent enough. To address these advantages, pure CoSe₂ is usually prepared into different morphologies and coupled with some conductive substrates, such as carbon cloth, carbon paper, and carbon nanotubes (Lee et al., 2016; Wang et al., 2015). These strategies favor the catalyst exposing many active sites and improving the overall conductivity, which is vital for HER (Yan et al., 2013). For instance, the co-precipitation and annealing methods have been adopted by Chen et al (Wang et al., 2019) to grow CoSe₂ nanosheet arrays on Co-N doped carbon cloth with excellent HER performance. Kang et al. used spray pyrolysis and selenization to make macroporous CoSe₂/CNT composite microspheres, which have good electrocatalytic properties in acid electrolyte (Kim et al., 2017). However, the preparation mentioned above process is quite complicated. On the other hand, the solar assistant electrochemical strategy has recently attracted much attention, which can induce photocarrier generation and further boosts the kinetic process (Ma et al., 2022).

In this work, we employ a simple one-step solvothermal method to successfully synthesize the CoSe₂/CNT composite, which exposes more active sites, increases the composite's electrical conductivity, and improves the overall HER catalytic performance of the material, but also prevents CoSe₂ crystals from clumping together. Importantly, we found that solar-irradiation can excite electrons during catalysis, which boosted the HER effectively. For these reasons, the CoSe₂/CNT composite can drive the current density of 10 mA cm⁻² with only 105 mV, superior to the performance of pure CoSe₂.

Experimental section

Chemicals and materials

The used chemicals and materials include analytical grade Carbon nanotube dispersion, Cobalt Chloride Hexahydrate (CoCl₂·6H₂O, 98%), sodium borohydride (NaBH₄, 98%), selenium (Se, 99.9%). It is worth noting that they were used without being purified further.

Synthesis of CoSe₂/CNT composite

The CoSe₂/CNT method was synthesized based on a classical synthesized method (Yue et al., 2017), wherein the solvent was changed from deionized water to DMF, along with a decreased reaction temperature. First, 671 μL of carbon nanotube solution (41.2 mg ml⁻¹) was dispersed in 20 ml of N, N-dimethylformamide (DMF), and then they were treated with ultrasonic for an hour. Second, 215 mg of selenium powder (Lee et al.) and 128.6 mg of sodium borohydride (NaBH₄) were dissolved in 10 ml of DMF and magnetically agitated to form solution A, which

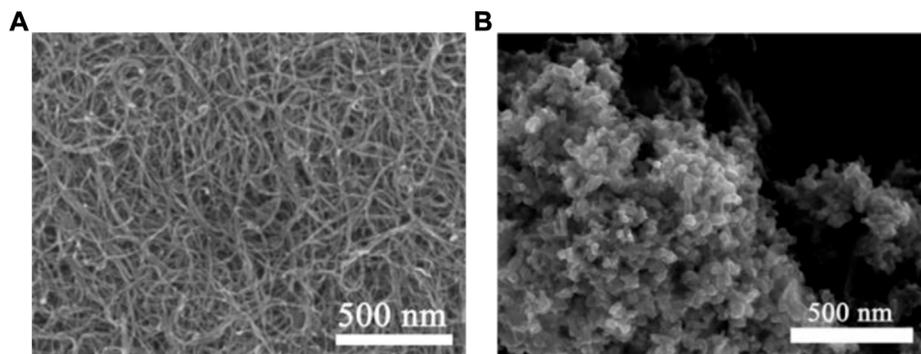


FIGURE 2
(A) SEM image of CNTs, (B) SEM image of pure CoSe_2 .

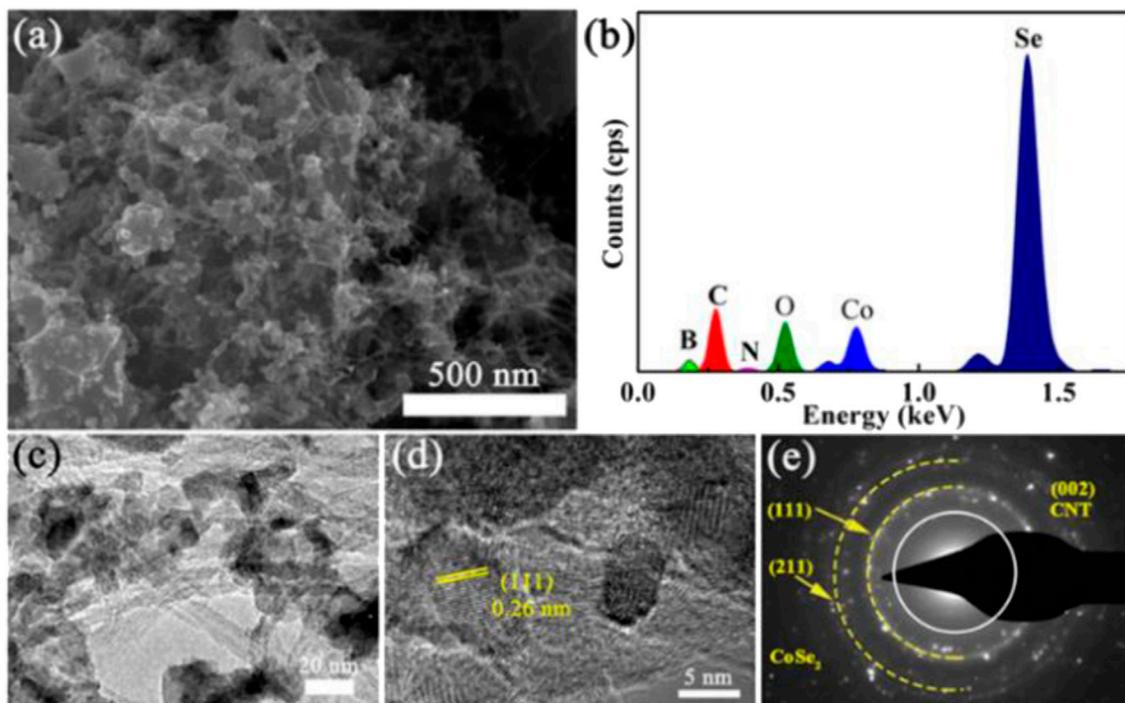


FIGURE 3
(A) SEM image, (B) EDS spectrum, (C) TEM image, (D) HRTEM image, and (E) SAED pattern of CoSe_2/CNT composite.

was mixed for 30 min after adding the dispersed carbon nanotube solution and 323.18 mg of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). Finally, the prepared solution was heated in a 50 ml Teflon-lined autoclave at 200°C for 20 h, and then it was washed with deionized water and ethanol and dried in a vacuum at 60°C for 12 h. CoSe_2/CNT composite was obtained. The synthesis of pure CoSe_2 is the same as the CoSe_2/CNT method.

Preparation of CoSe_2/CNT electrode

20 mg CoSe_2/CNT was ground in mortar for 1–2 h. Then, to obtain uniformly dispersed ink, the NMP contains the CoSe_2/CNT , and 5 wt% of polyvinylidene fluoride (PVDF) (mass ratio: $\text{CoSe}_2/\text{CNT}:\text{PVDF}$ is 9:1) was sonicated for 3 h. The 1 mg/uL ink was evenly coated on hydrophilic carbon paper ($1\text{ cm} \times 1\text{ cm}$,

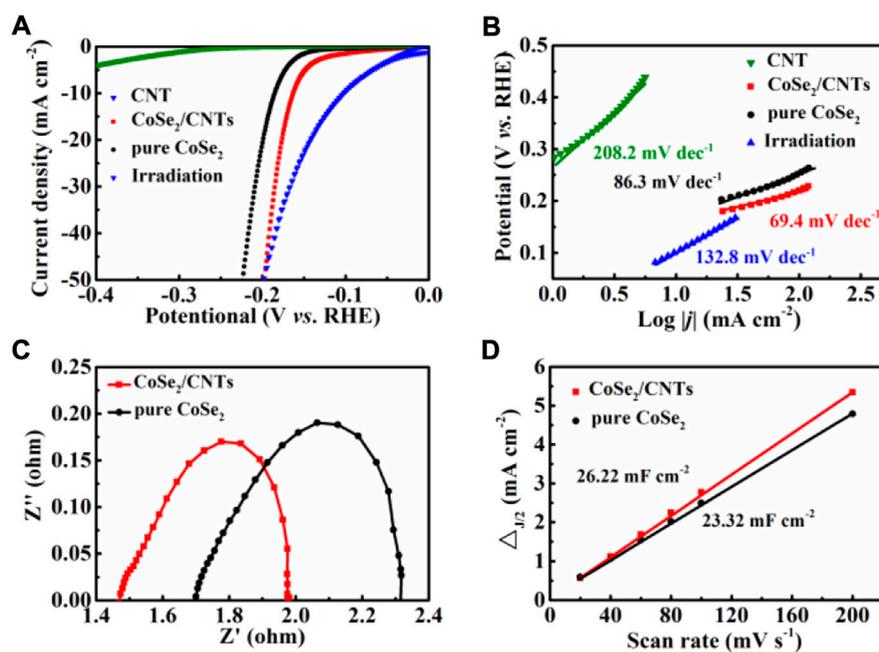


FIGURE 4

(A) Polarization curve, (B) Tafel slopes, (C) electrochemical impedance spectra, and (D) C_{dl} value of different electrodes.

load $\approx 2 \text{ mg cm}^{-2}$) and dried in a vacuum drying oven at 60°C for 12 h.

Characterization

To characterize the morphology and elemental composition of the composite material, we use the scanning electron microscope (SEM) and transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectrometer (EDX). In addition, the crystal structure of the material was characterized by X-ray diffraction (XRD), and the Raman spectrum was measured by a miniature Raman spectrometer (JY; HR800, France) at an excitation wavelength of 488 nm.

Electrochemical experiment

The electrochemical performances such as intrinsic HER activity and durability of the composite were tested by the VMP3 electrochemical workstation (France Bio-logic) in a three-electrode configuration under $0.5 \text{ M H}_2\text{SO}_4$ electrolyte. The electrode we prepared in advance, the saturated calomel electrode (SCE), and the carbon rod was respectively used as the working electrode, the reference electrode, and the counter electrode. The electric potential, which is applied by the reversible hydrogen electrode (RHE), is expressed by formula

$E_{(\text{RHE})} = E_{(\text{SCE})} + 0.059 \text{ V} \times \text{pH} + 0.241 \text{ V}$. The polarization curve is obtained by linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} in the voltage range of $-0.1 \sim -0.7 \text{ V}$. The test condition of electrochemical impedance spectroscopy (EIS) is limited to the frequency parameter of $100 \text{ mHz} \sim 100 \text{ kHz}$ under an overpotential of -0.2 V (vs. RHE). Cyclic voltammetry (CV) is used to measure the electric double-layer capacitance (C_{dl}) at $0.45 \sim 0.55 \text{ V}$ (vs. RHE) is measured by the CV, in which the scan rate ranges from 20 to 200 mV . When the rated voltage is 0.5 V (vs. RHE), the difference between the anode and cathode current densities ($\Delta j = j_a - j_c$) for different scan rates is calculated to obtain the slope and the half is defined as C_{dl} . All overpotentials are corrected by 85% ohm potential drop (iR) compensation.

Results and discussion

Morpho-structural characterization

First, Se powder and NaBH_4 were added to DMF. Then, after the DMF solutions were stirred evenly, the pre-dispersed mixtures of carbon nanotube solution and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with series mass ratios were dispersed into the above solutions. Finally, the one-step solvothermal method is applied to obtain the CoSe_2/CNT composite. In order to analyze the structure and composition, Next, we first performed the XRD test to analyze the structure and composition. As shown in Figure 1A. It can be

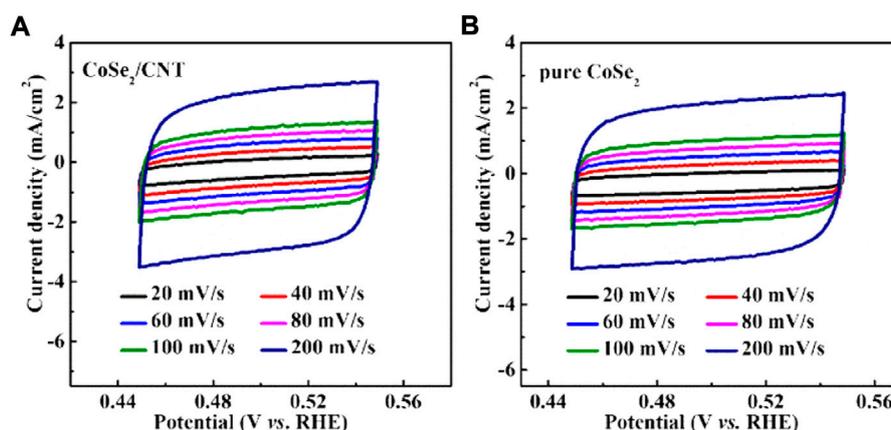


FIGURE 5
CVs were scanned at various rates from 20 to 200 mV s⁻¹: (A) CoSe₂/CNT and (B) pure CoSe₂.

seen that the diffraction peak at 26° is derived from CNTs. CoSe₂/CNTs sample has three prominent diffraction peaks at 30.77°, 34.52°, 35.96°, and there are some small diffraction peaks at 2θ = 28.97°, 47.72°, 50.66°, 53.48°, 55.42°, 56.95°, and 59.27°, corresponding to the orthogonal structure of CoSe₂ (PDF card No. 53-449) (101), (111), (120), (011), (211), (130), (031), (221), (131), and (310) crystal planes, respectively (Fan et al., 2019). No impurities were observed, indicating that a higher purity CoSe₂/CNTs was synthesized. Furthermore, as shown in Figure 1B, the sharp peak at 173.5 cm⁻¹ corresponds to the Se-Se stretching mode of orthorhombic CoSe₂ (o-CoSe₂), which proved the successful synthesis, the high purity as well as high crystalline of CoSe₂/CNTs. The Raman spectra of CoSe₂ show other three typical peaks (E_g, F_{2g}¹ and A_{1g}) at 469, 512 and 674 cm⁻¹, and the peaks at 1,354 and 1,584 cm⁻¹ correspond to the D and G peaks of carbon nanotubes, respectively (Yu et al., 2018).

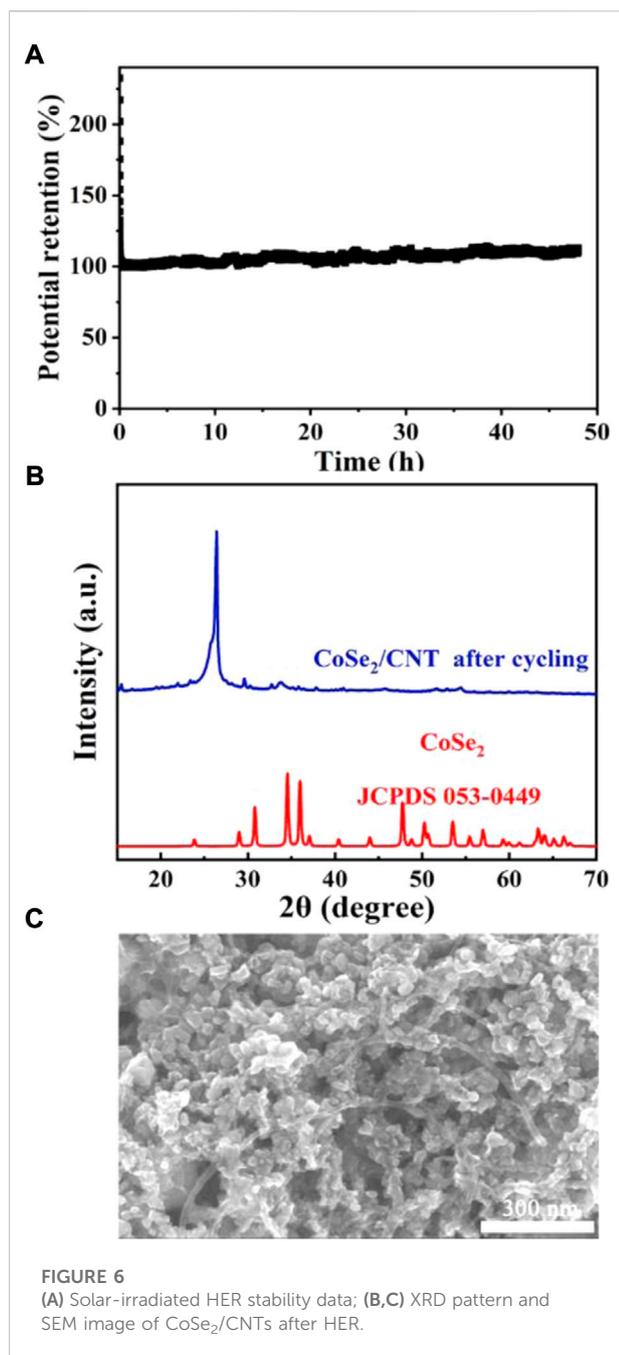
The SEM image shows the morphological information of CNT, pure CoSe₂ and CoSe₂/CNT. The smooth diameter of the CNT surface is shown in Figure 2A and is about 10–15 nm. In Figure 2B, pure CoSe₂ exists in the form of nanoparticles with a size of about 35–50 nm, and the nanoparticles are stacked on each other. It can be seen from Figure 3A that after CoSe₂ and CNT are compounded, CoSe₂ is more uniformly dispersed, and the size is reduced to about 20–35 nm. This should be attributed to the presence of CNT that allowed CoSe₂ to grow on top of them, thereby preventing CoSe₂ stacking. Good contact between CoSe₂ nanoparticles and CNT and further composite nanostructures can enhance the charge transfer ability of CoSe₂. Energy-dispersive X-ray spectroscopy (EDS) analysis is shown in Figure 3B, which indicates that Se is nearly twice that of Co., which conforms to the stoichiometric ratio.

TEM was employed further to study the morphology and structure of CoSe₂/CNT. As shown in Figure 3C, CoSe₂ nanoparticles were grown dispersed on CNT and have smaller

sizes. In addition, the high-resolution TEM (HRTEM) image is shown in Figure 3D, where the lattice spacing is 0.26 nm, which is well to the (111) crystal plane of CoSe₂. Please note that the lattice parameter is consistent with the results calculated by the Bragg equation from XRD data. Figure 3E shows the selected area electron diffraction (SAED) image of the CoSe₂/CNT composite, in which the yellow dotted line and the white circled area correspond to the (111) and (211) crystal planes of CoSe₂ and the (002) crystal plane of CNT, respectively (Shao et al., 2021). The discrete concentric rings prove that the substances in CoSe₂/CNT composites are crystalline. These results confirm that CoSe₂/CNT composite has been successfully prepared (Zhang et al., 2015).

Electrochemical performances

The electrochemical performance of CoSe₂/CNT composites and pure CoSe₂ were measured based on the three-electrode system in 0.5 M H₂SO₄ to study HER performance. As shown in Figure 4, the electrocatalytic performance of pure CoSe₂ and CoSe₂/CNT composite were compared. The current density of the overpotential of CoSe₂/CNT electrode at 163 mV is 10 mA cm⁻² and is super than pure CoSe₂ powder (189 mV) and the CNT (over 450 mV). The main functions of CNT are to improve the conductivity of the composite material and inhibit the growth of CoSe₂. Excited, the HER activity was dramatically enhanced after solar irradiation and only needed 105 mV to drive the current density of 10 mA cm⁻². According to the LSV results, we can obtain the Tafel curve and fit the Tafel equation ($\eta = \log |j| + a$) by the linear region, where η , j , and b are respectively the overpotential, the current density, and the Tafel slope. The value of the Tafel slope is used to compare the catalytic activity of the catalyst. From Figure 4B, the Tafel slope of the CoSe₂/CNT



composite is 69.4 mV dec^{-1} , significantly lower than pure CoSe₂ (86.3 mV dec^{-1}) and CNT (208 mV dec^{-1}), thus proving that the CoSe₂/CNT composite has a faster reaction kinetics.

Commonly, Tafel slopes of 30, 40 and 120 mV dec^{-1} correspond to the mechanisms of Tafel, Heyrovsky or Volmer reactions, respectively. Therefore the CoSe₂/CNT follows the Volmer-Heyrovsky mechanism, and CoSe₂/CNT composites have much better HER performance than pure CoSe₂. It shows that the Tafel for CoSe₂/CNT composites increases to 132 mV dec^{-1} , thus indicating that

the solar irradiation induces a mechanism conversation. This may be derived from the that CoSe₂ is an electronic type semiconductor, wherein abundant electrons were excited to join the reaction by solar irradiation.

In addition, the EIS shown in Figure 4C further verified the reaction kinetics. It can be observed that the ohmic resistance (R_s), i.e., the distance between the intersection of the EIS and the x -axis in the high-frequency region, is the resistance between the interface contact and the electrolyte. The charge transfer resistance (R_{ct}), i.e., the diameter of the semicircle in the high-frequency region, represents the electrocatalytic kinetics of the interface between the electrocatalyst and the electrolyte. The figure indicates that the R_{ct} of the CoSe₂/CNT catalyst is 0.194Ω and lower than that of pure CoSe₂ (0.290Ω), indicating that the CoSe₂/CNT catalyst has faster reaction kinetics in the HER process. The mass transfer resistance (R_{mt}) of the electrode is obtained from the semicircle in the low-frequency region, in which the R_{mt} of the CoSe₂/CNT electrode is lower than that of the pure CoSe₂ electrodes. Based on that the Tafel value changed from 86.3 to $132.8 \text{ mV dec}^{-1}$, it can be considered that solar irradiation has changed govern process from Tafel to the Volmer-Tafel. This is similar to previous literature that photo-induced carriers generated once the catalysts were irradiated and reasonable to explain that the second react step becomes the rate-determining step (Ma et al., 2022).

Electrochemical double-layer capacitance is usually employed to estimate the electrochemically active specific surface area (ECSA). Figure 5 shows the cyclic voltammery curves of CoSe₂/CNT and pure CoSe₂. The linear slope in Figure 4D indicates that the C_{dl} value is 26.22 mF cm^{-2} , significantly greater than pure CoSe₂ (17.39 mF cm^{-2}). It shows that CoSe₂/CNT has higher ECSA, electrode material, and electrolysis. The liquid contact interface has more active sites. CoSe₂/CNT can adsorb more hydrated protons to form the intermediate H_{ads} . The decreased R_{ct} and increased ECSA of CoSe₂/CNT may be derived from the unique structure, which possesses a transfer network for electro and electrolyte and also a space for active center exposure.

Stability is an efficient factor for an ideal HER catalyst. We subsequently measured the stability ability and the morphology and structure conversion information. As shown in Figure 6A, the potential retention was kept around 100%. The corresponding XRD pattern (Figure 6B) is consistent with that before HER, indicating that the structure is maintained well. Figure 6C shows that the sample after HER still expresses particle-like morphology with a size distribution from 20 to 35 nm, similar to pristine CoSe₂/CNT catalyst. The SEM image also shows that the spatial structure is kept. These data certify that the CoSe₂/CNT has good electrochemical stability under solar irradiation. In addition, combining the corresponding excellent and poor HER performances for CoSe₂/CNT

catalyst and CNT and structural maintenance of CoSe₂, it is evidenced that CoSe₂ is the actual catalytic center which follows a behavior of semiconductor-based HER catalyst (Han et al., 2017).

Conclusion

In short, we use a simple one-step solvothermal method to synthesize the CoSe₂/CNTs composite material, which has been proved to have excellent photo electrochemical HER performance, with an overpotential of 105 mV at a current density of 10 mA cm⁻². These excellent properties are attributed to the smaller CoSe₂ nanoparticles, more active sites, the excellent conductivity of CNTs, as well as the ideal photo-electrochemical response. It opens up a new opportunity to develop low-cost, high-efficiency metal compound catalysts.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

Author contributions

ZP: Methodology, Data curation, original draft preparation, writing reviewing. HY: Language help. ZH: Data curation. ZY: Writing-review and editing. PY: Project administration, supervision, funding acquisition, and project guide. XM: Investigation, writing-original draft, data validation.

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Funding

We gratefully acknowledge the support of this research by the National Natural Science Foundation of China (22005078), Research Team Project of Heilongjiang Province (JJ2021TD0011), and the University Nursing Program for Young Scholars with Creative Talents in Heilongjiang Province (UNPYSCT-2020127).

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

The reviewer XY declared a shared affiliation with the authors XM to the handling editor at the time of review.

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Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmats.2022.1005221/full#supplementary-material>

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