

Well-Separated Photoinduced Charge Carriers on Hydrogen Production Using NiS₂/TiO₂ Nanocomposites

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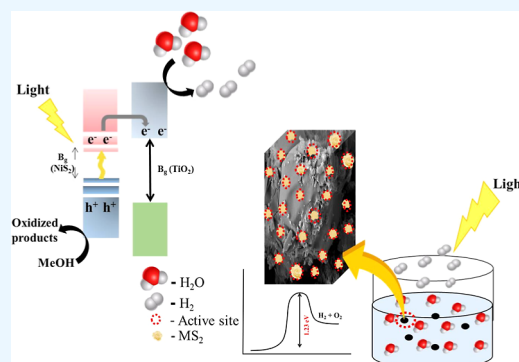
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ABSTRACT: Photocatalytic hydrogen production is a sustainable and greenhouse-gas-free method that requires an efficient and abundant photocatalyst, which minimizes energy consumption. Currently, interests in transition metal chalcogenide materials have been utilized in different applications due to their quantum confinement effect and low band gaps. In this study, different wt % of NiS₂-embedded TiO₂ nanocomposites were synthesized by a facile hydrothermal method and utilized for photocatalytic hydrogen production under extended solar irradiation. Among the materials studied, the highest amount (4.185 mmol g⁻¹) of hydrogen production was observed with 15 wt % of the NiS₂/TiO₂ nanocomposite. The highest photocatalytic activity may be due to the well separation of photoinduced charge carriers on the catalyst, which was confirmed by the electrochemical studies. Thus, we believe that these photocatalysts are promising candidates for future applications.



INTRODUCTION

The photon energy is harvested and converted into chemical fuels within the molecules of H₂ via a solar-driven water splitting process called photocatalytic water splitting.^{1,2} Hydrogen produced by the photoreduction of water is an attractive reaction that will contribute to an ultimate green, sustainable chemistry and does not cause any unwanted emissions like carbon dioxide (CO₂) or carbon monoxide (CO), resulting in an energy revolution.^{3,4} It is a multiple electron and multiple proton process. The sun shines on a catalyst which is dispersed in a pool of water, and then hydrogen gas is readily evolved; but the separation of the evolved H₂ from O₂ is disadvantageous for the photocatalytic process. The problem can be solved by using a Z-scheme photocatalyst system.

A direct Z-scheme photo catalyst possesses band structure configuration and distinctly different charge carrier transfer modes, as shown in Figure 1. In a Z-scheme charge carrier transfer pathway, the photogenerated electrons have strong reduction abilities in the conduction band (CB) of P1, while holes with strong oxidation abilities in the valence band (VB) of P2 are preserved. Simultaneously, the photo generated electrons in the CB of P2 and holes in the VB of P1, which have inferior redox power, tend to recombine.

Therefore, the Z-scheme photocatalyst possesses strong redox abilities for driving photocatalytic reactions and the spatially separated reductive and oxidative active sites. Furthermore, semiconductor photocatalysts with narrow band gaps can be chosen to construct direct Z-scheme

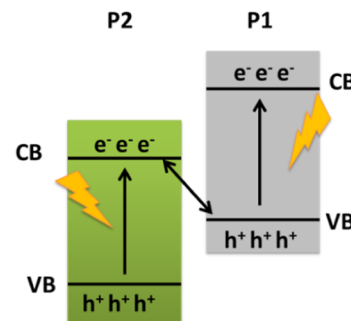


Figure 1. Z-Scheme electron transport.

photocatalysts, thereby broadening the light-harvesting range.⁵ Moreover, this system has a catalyst in powder form and will be an added advantage for large-scale application of photocatalytic water splitting because of its simplicity.⁶

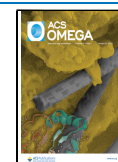
Since the first report on using a catalyst, TiO₂, for photoinduced water splitting in 1972 by Fujima Honda due to their significant characteristics that include strong optical absorption, favorable band edge position, abundant availability,

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and nontoxicity,^{1,6–8} a large number of semiconductor materials have been developed for different photocatalytic applications, such as metal oxides,^{9,10} carbides,^{11,12} metal chalcogenides,^{13–18} graphene,^{19–22} graphitic carbon nitrides,^{23–28} and carbon nanotubes.^{29–34} Among them, NiS₂ has attracted great attention because of its small band gap and high absorption coefficients, which make it suitable for photocatalytic activities by harvesting the visible light of the solar spectrum.³⁵ Therefore, it can overcome the limitations associated with photocatalysts that utilize UV irradiation.

Recently, Ma et al. utilized a facile method to synthesize two-dimensional NiS₂ on nickel foam (NF) for electrochemical hydrogen evolution. It was evidenced that the active sites of NiS₂ help to enhance the overall water splitting reactions.³⁶ In a separate study, NiS₂ catalysts were used to decorate the CdLa₂S₄ nanocrystals using the hydrothermal method for hydrogen generation under visible light irradiation. The NiS₂ loading enhances hydrogen production via the effective separation of electron hole pair. It was also noted in their study, the 2 wt % of NiS₂ loading exhibited remarkable enhancement in the production of hydrogen due to the activation effect of NiS₂ cocatalyst.³⁷ In addition to increasing the photocatalytic activity or efficiency, NiS₂ incorporated with titanium dioxide nanocrystalline develops Z-scheme nanocomposites.

Therefore, this study mainly focuses on synthesizing nanocomposites consisting of different weight percentages of NiS₂ embedded with titanium dioxide (TiO₂) using a facile hydrothermal method. These nanocomposites are intended to be used as photocatalysts for the production of hydrogen from water.

MATERIALS AND METHOD

Materials. Titanium isopropoxide, 98+% for the preparation TiO₂ was purchased from Sigma-Aldrich Norway AS, Oslo, Norway, NiCl₂ anhydrous (Sigma-Aldrich Norway AS) was employed as the precursor of NiS₂; and Na₂S (Sigma-Aldrich Norway AS), ACS reagent, as sulfur source and methanol (Analar NORMAPUR Reag. Ph.Eur., ACS).

Synthesis of NiS₂/TiO₂. NiCl₂ was taken in a beaker containing 40 mL of water. It was stirred with appropriate amount of TiO₂ (hydrothermal synthesis procedure used in previous studies³⁸ was followed here to synthesize this material) by sonication for 10 min at 50 °C. After that, the required amount of Na₂S was added in to it, and the mixture was stirred well. Then, the mixture was transferred into autoclave and kept at 140 °C for 10 h. The product was allowed to cool and centrifuged at 3000 rpm for 2 min and washed with ethanol followed by air drying. Pure NiS₂ nanomaterial was prepared by using a similar method without adding titanium dioxide.

Characterization. The above synthesized materials were characterized by using different techniques, such as powder X-ray diffraction (XRD) spectroscopy. The peak patterns were observed using D8 ADVANCE ECO in a 1 kW copper X-ray tube diffractometer with the scan range from 20 to 70° (2θ). The intensity of light reflected from the nanomaterials was measured using a diffuse reflectance spectroscopy (DRS Cary 100 Bio UV–visible spectrophotometer, Santa Clara, CA, USA) in the wavelength range of 800–200 nm. Scanning electron microscopy (SEM) was employed using Zeiss Supra 55 VP SEM, and the electro chemical measurements were performed with a Bio Logic SP-150 potentiostat.

Hydrogen Production. Hydrogen production experiment was carried out for the synthesized NiS₂/TiO₂ nanocomposite materials and the bare NiS₂ and TiO₂ materials. First, 20 mg of the catalyst was suspended in a 20 mL solution containing a 4:1(v/v) mixture of water–methanol mixture in which, methanol act as a hole-scavenger. The suspension was degassed for 60 min with nitrogen gas prior to irradiation. Then, suspensions were continuously stirred throughout the experiment. A 150 W xenon lamp (Oriental light source: Xenon arc lamp, Scientific Instruments) was used as the source of radiation. Finally, the amount of hydrogen gas produced during the reaction was measured using gas chromatography (Trace 1300, Thermo scientific) with a TCD (thermal conductivity detector). The same study was repeated with the pure water (without methanol) and pure methanol with and without catalysts for comparison purpose.

RESULTS AND DISCUSSION

The pure NiS₂, pure TiO₂, and different weight percentages of NiS₂ embedded titanium dioxide nanocomposite materials (5-,

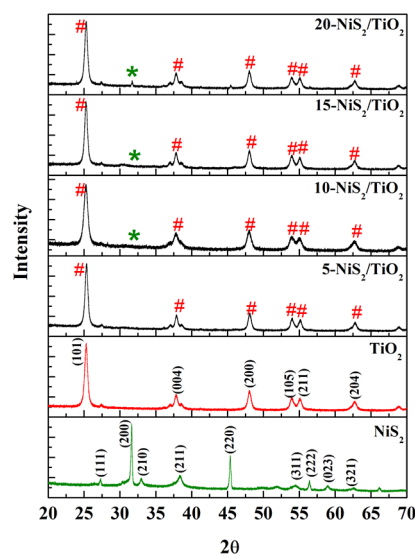


Figure 2. XRD patterns for pristine NiS₂, TiO₂, 5-, 10-, 15-, and 20-NiS₂/TiO₂ nanocomposites.

10-, 15-, and 20-NiS₂/TiO₂) were successfully synthesized by the hydrothermal method, and the XRD results confirmed their formation (Figure 2). The figure further confirms the structural quality, purity, and phase orientations of the prepared nanocomposite materials.

The Figure 2 confirms the formation of the anatase phase TiO₂ along with the crystal plane orientations evaluated by the diffraction angles 25.50, 37.76, 48.10, 53.88, 55.84, and 62.90° related to the planes of (101), (004), (200), (105), (211), and (204), respectively, authenticated from JCPDS 21-1272.³⁹ The peaks obtained at the 2θ values of 27.29, 31.63, 33.00, 38.30, 45.37, 54.49, 56.41, 59.02, and 62.52° due to (111), (200), (210), (211), (220), (311), (222), (023), and (321) diffraction planes of pure NiS₂ matched with JCPDS 11-0099.

The combined peak patterns observed with the mixed NiS₂/TiO₂ nanocomposite materials confirm the impregnation of NiS₂ on TiO₂ nanocrystalline. No other relevant peaks for oxides or any other compounds in XRD peaks further

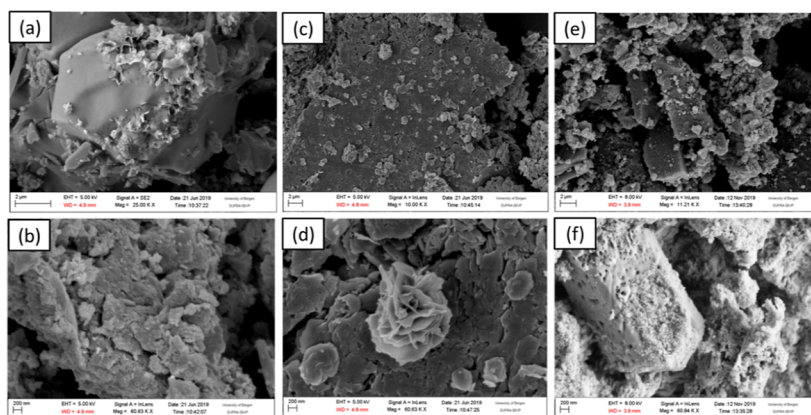


Figure 3. SEM images of NiS₂ (a,b), NiS₂/TiO₂ (c,d), and TiO₂ (e,f) nanomaterials.

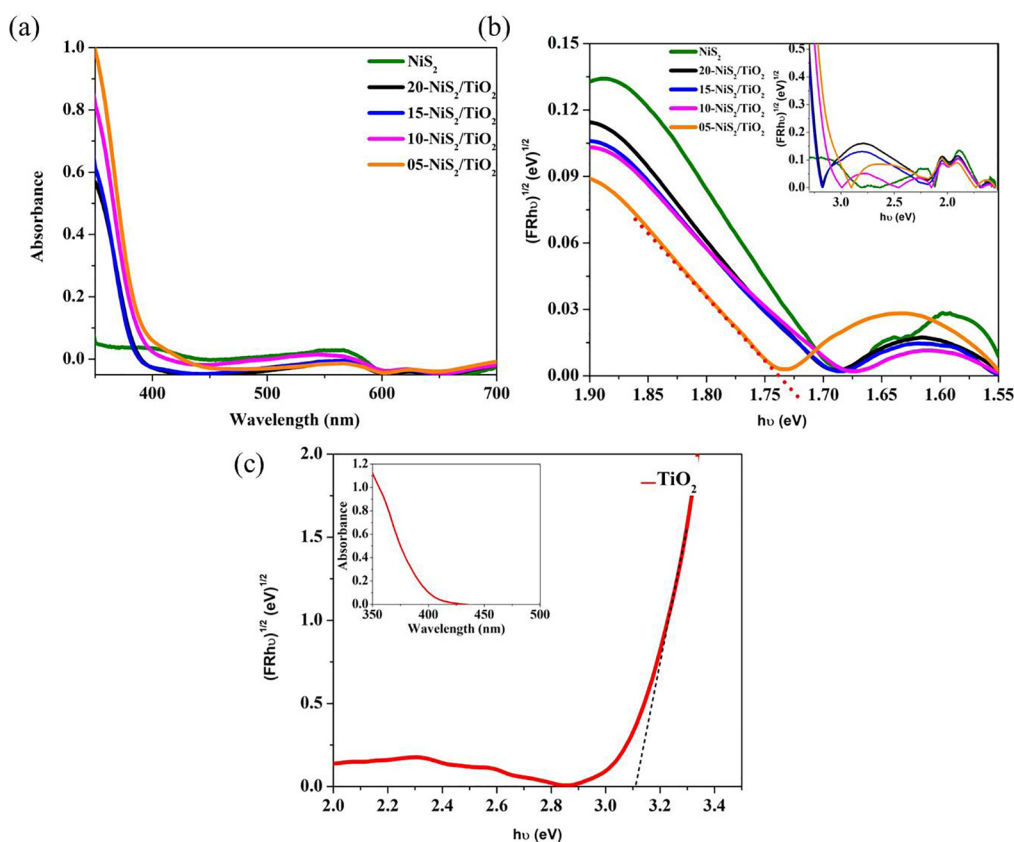


Figure 4. (a) Absorbance vs wavelength plot for NiS₂, 20-, 15-, 10-, and 5-NiS₂/TiO₂ materials, (b) Tauc plot for NiS₂, 5-, 10-, 15-, and 20-NiS₂/TiO₂ materials, and (c) Tauc plot for TiO₂ and onset shows absorbance vs wavelength plot.

confirmed that the NiS₂, TiO₂, and NiS₂/TiO₂ present in its pure forms.

Figure 3 shows the SEM images of pure NiS₂ (Figure 3a,b), 15 wt % of NiS₂ embedded TiO₂ nanocomposite (Figure 3c,d), and pure TiO₂ (Figure 3e,f). The SEM image of NiS₂ shows the flake-like structure material depicted in Figure 3a. The magnification image of Figure 3b clearly indicates the flake-like orientations of this material. Figure 3c,d shows the flake-like flower covered with spongy-like materials for NiS₂ embedded TiO₂ nanocomposites, which also further confirms the presence of NiS₂ on TiO₂ material. Pure TiO₂ materials exhibit a hexagonal rod-like material covered with spongy-like material illustrated in Figure 3e,f.

The weight ratio between Ni and Ti atoms were calculated by using energy-dispersive spectroscopy (EDS) and the values obtained were 4.03, 9.48, 13.82, and 20.11 for 5, 10, 15, and 20 wt % of NiS₂/TiO₂, respectively. The calculated values closely match the expected values; which are tabulated in Table S1.

The optical band gap of these photocatalytic materials, corresponding to the absorbance measurements obtained from DRS (Figure 4a), was determined by plotting the Tauc graph (Figure 4b), which was transformed via the Kubelka–Munk function. $\{[(R\infty)] \text{ vs } E\}$ when $n = 0.5$, for a direct allowed transition, $[K = (R\infty)]$ is an energy-independent constant. Estimates derived from the Tauc plots by extrapolating the steep portion of the plot in Figure 4b to the x -axis suggest the band gaps of these materials. The calculated band gap values of

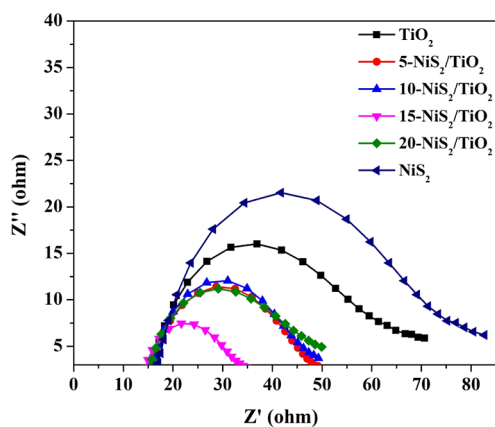
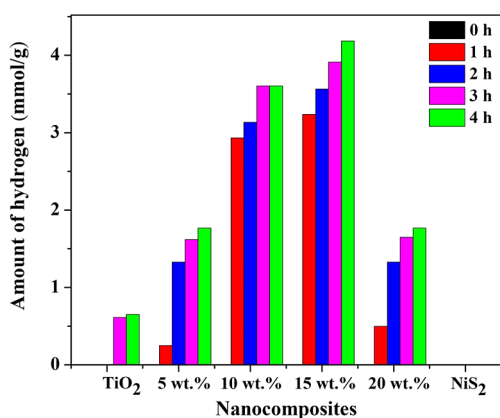


Figure 5. EIS Nyquist plots.

Table 1. R_s Values for TiO_2 , $\text{NiS}_2/\text{TiO}_2$ (5, 10, 15, and 20) and NiS_2 Nanocomposites

materials	R_s value (Ω)
TiO_2	15.96
5- $\text{NiS}_2/\text{TiO}_2$	15.94
10- $\text{NiS}_2/\text{TiO}_2$	15.68
15- $\text{NiS}_2/\text{TiO}_2$	14.42
20- $\text{NiS}_2/\text{TiO}_2$	15.33
NiS_2	17.05

Figure 6. Amount of hydrogen evolution by using NiS_2 , TiO_2 , 5-, 10-, 15-, and 20- $\text{NiS}_2/\text{TiO}_2$ nanocomposites under extended solar irradiation.

nanocomposite materials are 1.738, 1.701, 1.699, and 1.695 eV for 5-, 10-, 15-, and 20- $\text{NiS}_2/\text{TiO}_2$, respectively. These values marginally decrease with increasing the amount of NiS_2 and are the intermediate values between pure NiS_2 (1.690 eV) and pure TiO_2 (3.100 eV).

Electrochemical impedance spectra (EIS), Nyquist plots of pristine TiO_2 , NiS_2 , and different wt % of $\text{NiS}_2/\text{TiO}_2$ (5-, 10-, 15-, and 20- $\text{NiS}_2/\text{TiO}_2$) nanocomposites are illustrated in Figure 5. The solution resistance values [$R_s = 14.42 \Omega$] obtained from the EIS Nyquist plot of 15- $\text{NiS}_2/\text{TiO}_2$ is smaller than that of pristine TiO_2 ($R_s = 15.96 \Omega$) and NiS_2 ($R_s = 17.05 \Omega$) (Table 1). The arc radius of EIS spectra denotes the interface layer resistance occurring at the surface of the electrode. The smaller R_s value and arc radius indicate that there is a very low internal resistance and a higher interfacial charge transfer that improve separation of photoinduced charge carriers over the $\text{NiS}_2/\text{TiO}_2$ photocatalyst.^{40,41}

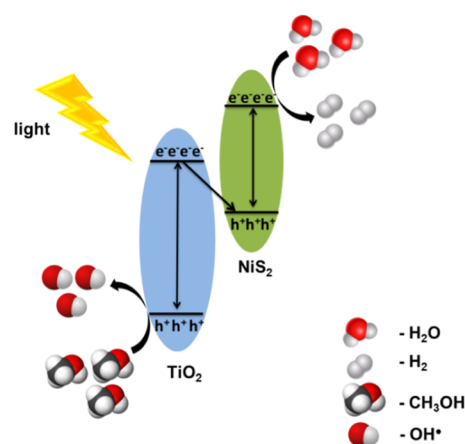
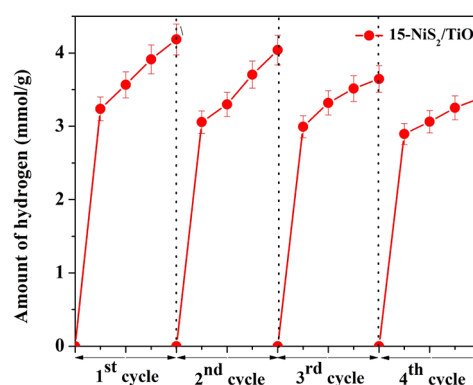
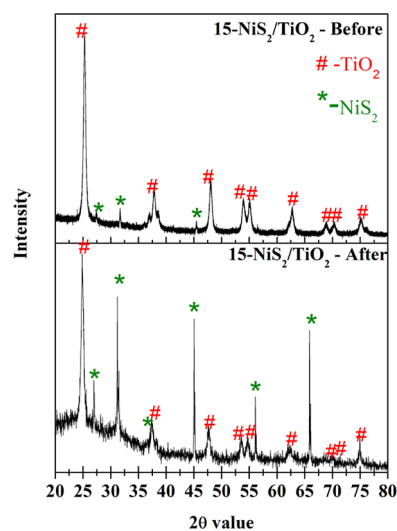


Figure 7. Schematic diagram for the Z-scheme photocatalyst.

Figure 8. Amount of hydrogen production in four cycles by using 15- $\text{NiS}_2/\text{TiO}_2$ under extended solar irradiation.Figure 9. XRD pattern for 15 wt % of $\text{NiS}_2/\text{TiO}_2$ after four cycles of the hydrogen evolution reaction.

The amount of hydrogen evolution was measured with all catalysts prepared in this study under extended solar irradiation. The highest amount (4.185 mmol g^{-1}) of hydrogen evolution was attained with the 15- $\text{NiS}_2/\text{TiO}_2$ nanocomposite after 4 h of light illumination, whereas pure TiO_2 nanomaterial evolved only 0.651 mmol g^{-1} . Notably, no hydrogen was produced with pure NiS_2 material. An increasing trend in the

Table 2. Amount of Hydrogen Production with Different Chalcogenide Materials

material	synthesis method	light source	sacrificial agent	amount of hydrogen evolution ^a	reference
CuS	hydrothermal	450 W xenon lamp	NaS/Na ₂ SO ₃	149 μmol g ⁻¹ h ⁻¹	35
NiS ₂				207 μmol g ⁻¹ h ⁻¹	
FeS				636 μmol g ⁻¹ h ⁻¹	
NiS ₂ quantum dots on g-C ₃ N ₄	hydrothermal	300 W xenon lamp equipped with a UV cut off filter (420 nm)	triethanolamine	4.8 μmol g ⁻¹ h ⁻¹	43
RGO-NiS ₂ synergistic modified g-C ₃ N ₄ aerogel	thermal oxidation, etching-hydrothermal method	300 W xenon arc lamp	triethanolamine	1556 μmol g ⁻¹ h ⁻¹	44
CdS/WS ₂	impregnation-sulfidation	xenon lamp (300 W) (λ > 420 nm) to eliminate ultraviolet light	lactic acid	420 μmol h ⁻¹	45
NiO Layer Over Zn _{1-x} Cd _x S	photodeposition	xenon lamp (HSX-UV 300) equipped with a 420 nm cutoff filter		99.9 μmol g ⁻¹ h ⁻¹	46
dye-sensitized NiS _x on graphene	in situ chemical deposition	Hg lamp (400 W)	H ₂ PtCl ₆	340 μmol h ⁻¹	47
SnS ₂ /TiO ₂	hydrothermal	150 W Xe arc lamp	methanol	196 μmol g ⁻¹	16
CoS ₂ /TiO ₂	hydrothermal	150 W Xe arc lamp	methanol	2550 μmol g ⁻¹	38
NiS/TiO ₂	solvothelmal	300 W xenon lamp	lactic acid	698 μmol g ⁻¹ h ⁻¹	48
NiS ₂ /TiO ₂	hydrothermal	150 W Xe arc lamp	methanol	4185 μmol g ⁻¹	this study

^aIndicate unit variation and the lag in the literature to convert them into a particular unit.

hydrogen evolution was observed with the increase in the NiS₂ content on TiO₂ up to its 15 wt % and then it was found to decrease (1.766, 3.603, 4.185, and 1.767 mmol g⁻¹ for 5, 10, 15, and 20 wt % NiS₂/TiO₂; Figure 6). The higher activity may be due to the well-separated electron hole pairs of the materials with smaller R_s value and arc radius indicate that there is a very low internal resistance and a higher interfacial charge transfer that improve separation of photoinduced charge carriers over the NiS₂/TiO₂ photocatalyst. Although similar band gap values were obtained with all the NiS₂/TiO₂ materials, impregnation of NiS₂ on TiO₂ that may lead the effective separation of electron–hole pairs due to the Z-scheme formation must be acknowledged for this higher H₂ production with 15-NiS₂/TiO₂.

In a typical mechanism, the photon hit on to the catalyst surface ejects the photon from the valence band to the conduction band, and the electrons move from the lower conduction band of TiO₂ to the higher valence of NiS₂ which neutralizes the holes and reduce the recombination with electrons.⁴² On the other hand, methanol may oxidize when capturing the holes in TiO₂ as a sacrificial agent, which may inhibit the formation of oxygen gas (Figure 7). In addition, experimentally, no hydrogen was produced when pure water was tested with the catalyst and pure methanol was tested without the catalyst. Comparatively negligible amount of hydrogen (<0.012 mmol g⁻¹) was obtained with pure methanol with the catalyst under same experimental conditions.

The reusability and, thus, the stability of the catalyst were tested with the 15-NiS₂/TiO₂ material and are shown in Figure 8. Even after four cycles, the amount of hydrogen produced was found to be similar and there were no significant differences obtained (within 5% error) with the catalyst studied. These results indicate that the NiS₂/TiO₂ nanocomposite exhibited excellent stability in water. Furthermore, the structural characteristic was also tested with the used material (15-NiS₂/TiO₂) which was collected and dried after the experiment.

Figure 9 shows the XRD pattern of the 15 wt % of NiS₂/TiO₂ after its fourth cycle, and the peak patterns retained after

the experiment indicate that the material is very stable. The XRD pattern shows an intense peak for NiS₂ compared to the initial material, which may be due to the amorphous nature of TiO₂ after the experiment.

Although a comparison of different studies is still questionable, it can be clearly seen that the catalyst prepared in this work exhibits a reasonably good amount of hydrogen and good stability. Comparing the results obtained in this study with the existing literature can indeed provide valuable insights into the performance of transition metal chalcogenide materials for hydrogen evolution. Despite the variations in experimental conditions, such as the light source, sacrificial agent, and synthesis method, which include carbon nitride, the comparison provides a clear picture of catalysts versus the amount of hydrogen produced. Different morphologies influence the amount of hydrogen production in many studies, as indicated in Table 2.

CONCLUSIONS

NiS₂/TiO₂ nanocomposite materials synthesized by the hydrothermal method exhibited a higher amount of (4.185 mmol g⁻¹) hydrogen evolution. The enhanced photocatalytic activity of the material (15-NiS₂/TiO₂) may be due to the effective electron–hole pair separation, which was supported by the electrochemical studies. Furthermore, the stability of the material can also add value to the use of these materials for future photocatalytic applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c08194>.

Elemental dispersive spectra for 5-, 10-, 15-, and 20-NiS₂/TiO₂ nanocomposites and theoretical and experimental value of ratio between Ni and Ti from EDS analysis (PDF)

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Author Contributions

Conceptualization, S.S. and Y.S.; methodology, S.S. and Y.S.; software, S.S.; validation, S.S., Y.S., D.V., and P.R.; formal analysis, S.S.; investigation, S.S. and Y.S.; resources, D.V., Y.S., and P.R.; data curation, S.S. and Y.S.; writing—original draft preparation, S.S.; writing—review and editing, S.S., Y.S., D.V., and P.R.; visualization, S.S. and Y.S.; supervision, D.V., Y.S., and P.R.; project administration, D.V. and P.R.; and funding acquisition, D.V. and P.R. All authors have read and agreed to the published version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Chen, J.; Wu, X. J.; Yin, L.; Li, B.; Hong, X.; Fan, Z.; Chen, B.; Xue, C.; Zhang, H. One-pot synthesis of CdS nanocrystals hybridized with single-layer transition-metal dichalcogenide nanosheets for efficient photocatalytic hydrogen evolution. *Angew. Chem., Int. Ed.* **2015**, *54*, 1210–1214.
- (2) Nguyen, P. D.; Duong, T. M.; Tran, P. D. Current progress and challenges in engineering viable artificial leaf for solar water splitting. *J. Sci.: Adv. Mater. Devices* **2017**, *2*, 399–417.
- (3) Martha, S.; Chandra Sahoo, P.; Parida, K. M. An overview on visible light responsive metal oxide based photocatalysts for hydrogen energy production. *RSC Adv.* **2015**, *5*, 61535–61553.
- (4) Shanmugaratnam, S.; Yogenthiran, E.; Koodali, R.; Ravirajan, P.; Velauthapillai, D.; Shivatharsiny, Y. Recent Progress and Approaches on Transition Metal Chalcogenides for Hydrogen Production. **2021**, 1–37, doi: .
- (5) Xu, Q.; Zhang, L.; Yu, J.; Wageh, S.; Al-Ghamdi, A. A.; Jaroniec, M. Direct Z-scheme photocatalysts: Principles, synthesis, and applications. *Mater. Today* **2018**, *21*, 1042–1063.
- (6) Kudo, A.; Miseki, Y. Heterogeneous photocatalyst materials for water splitting. *Chem. Soc. Rev.* **2009**, *38*, 253–278.
- (7) Jafari, T.; Moharreri, E.; Amin, A. S.; Miao, R.; Song, W.; Suib, S. L. Photocatalytic water splitting - The untamed dream: A review of recent advances. *Molecules* **2016**, *21*, 900–929.
- (8) Rajaramanan, T.; Shanmugaratnam, S.; Gurunathanan, V.; Yohi, S.; Velauthapillai, D.; Ravirajan, P.; Senthilnathanan, M. Cost Effective Solvothermal Method to Synthesize Zn-Doped TiO₂ Nanomaterials for Photovoltaic and Photocatalytic Degradation Applications. *Catal. Artic.* **2021**, *11*, 690.
- (9) Chakrabarti, S.; Dutta, B. K. Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. *J. Hazard. Mater.* **2004**, *112*, 269–278.
- (10) Liu, Y.; Xie, S.; Li, H.; Wang, X. A highly efficient sunlight driven ZnO nanosheet photocatalyst: Synergetic effect of p-doping and MoS₂ atomic layer loading. *ChemCatChem* **2014**, *6*, 2522–2526.
- (11) Vrubel, H.; Hu, X. Molybdenum Boride and Carbide Catalyze Hydrogen Evolution in both Acidic and Basic Solutions. *Angew. Chem., Int. Ed.* **2012**, *51*, 12703–12706.
- (12) Chen, W. F.; Muckerman, J. T.; Fujita, E. Recent developments in transition metal carbides and nitrides as hydrogen evolution electrocatalysts. *Chem. Commun.* **2013**, *49*, 8896–8909.
- (13) Yao, N.; Tan, T.; Yang, F.; Cheng, G.; Luo, W. Well-aligned metal-organic framework array-derived CoS₂ nanosheets toward robust electrochemical water splitting. *Mater. Chem. Front.* **2018**, *2*, 1732–1738.
- (14) Berkdemir, A.; Gutiérrez, H. R.; Botello-Méndez, A. R.; Perea-López, N.; Elias, A. L.; Chia, C. I.; Wang, B.; Crespi, V. H.; López-Urías, F.; Charlier, J. C.; et al. Identification of individual and few layers of WS₂ using Raman Spectroscopy. *Sci. Rep.* **2013**, *3*, 1–8.
- (15) Mihai, C.; Sava, F.; Galca, A. C.; Velea, A. Low power non-volatile memory switching in monolayer-rich 2D WS₂ and MoS₂ devices. *AIP Adv.* **2020**, *10*.
- (16) Shanmugaratnam, S.; Selvaratnam, B.; Baride, A.; Koodali, R.; Ravirajan, P.; Velauthapillai, D.; Shivatharsiny, Y. SnS₂/TiO₂ Nanocomposites for Hydrogen Production and Photodegradation under Extended Solar Irradiation. *Catalysts* **2021**, *11*, 589–612.
- (17) Shanmugaratnam, S.; Rasalingam, S. Transition Metal Chalcogenide (TMC) Nanocomposites for Environmental Remediation Application over Extended Solar Irradiation. In *Nanocatalysts*, Sinha, I.; Shukla, M.; Eds. 2019, Chapter 6, page75
- (18) Ning, X.; Lu, G. Photocorrosion inhibition of CdS-based catalysts for photocatalytic overall water splitting. *Nanoscale* **2020**, *12*, 1213–1223.
- (19) Gautam, A. K.; Faraz, M.; Khare, N. Enhanced thermoelectric properties of MoS₂ with the incorporation of reduced graphene oxide (RGO). *J. Alloys Compd.* **2020**, *838*, 155673.
- (20) Li, Y.; Wang, H.; Peng, S. Tunable photodeposition of MoS₂ onto a composite of reduced graphene oxide and CdS for synergic photocatalytic hydrogen generation. *J. Phys. Chem. C* **2014**, *118*, 19842–19848.
- (21) Hintze, C.; Morita, K.; Riedel, R.; Ionescu, E.; Mera, G. Facile sol-gel synthesis of reduced graphene oxide/silica nanocomposites. *J. Eur. Ceram. Soc.* **2016**, *36*, 2923–2930.
- (22) Chang, R. J.; Tan, H.; Wang, X.; Porter, B.; Chen, T.; Sheng, Y.; Zhou, Y.; Huang, H.; Bhaskaran, H.; Warner, J. H. High-Performance All 2D-Layered Tin Disulfide: Graphene Photodetecting Transistors with Thickness-Controlled Interface Dynamics. *ACS Appl. Mater. Interfaces* **2018**, *10*, 13002–13010.
- (23) Li, Q.; Zhang, N.; Yang, Y.; Wang, G.; Ng, D. H. L. High efficiency photocatalysis for pollutant degradation with MoS₂/C₃N₄ heterostructures. *Langmuir* **2014**, *30*, 8965–8972.
- (24) Liu, E.; Chen, J.; Ma, Y.; Feng, J.; Jia, J.; Fan, J.; Hu, X. Fabrication of 2D SnS₂/g-C₃N₄ heterojunction with enhanced H₂ evolution during photocatalytic water splitting. *J. Colloid Interface Sci.* **2018**, *524*, 313–324.
- (25) He, K.; Xie, J.; Li, M.; Li, X. In situ one-pot fabrication of g-C₃N₄ nanosheets/NiS cocatalyst heterojunction with intimate interfaces for efficient visible light photocatalytic H₂ generation. *Appl. Surf. Sci.* **2018**, *430*, 208–217.

- (26) Zhang, Z.; Huang, J.; Zhang, M.; Yuan, Q.; Dong, B. Ultrathin hexagonal SnS₂ nanosheets coupled with g-C₃N₄ nanosheets as 2D/2D heterojunction photocatalysts toward high photocatalytic activity. *Appl. Catal., B* **2015**, *163*, 298–305.
- (27) Zhang, Z.; Kang, Y.; Yin, L. C.; Niu, P.; Zhen, C.; Chen, R.; Kang, X.; Wu, F.; Liu, G. Constructing CdSe QDs modified porous g-C₃N₄ heterostructures for visible light photocatalytic hydrogen production. *J. Mater. Sci. Technol.* **2021**, *95*, 167–171.
- (28) Hong, J.; Wang, Y.; Wang, Y.; Zhang, W.; Xu, R. Noble-metal-free NiS/C₃N₄ for efficient photocatalytic hydrogen evolution from water. *ChemSusChem* **2013**, *6*, 2263–2268.
- (29) Olowoyo, J. O.; Kumar, M.; Jain, S. L.; Babalola, J. O.; Vorontsov, A. V.; Kumar, U. Insights into Reinforced Photocatalytic Activity of the CNT - TiO₂ Nanocomposite for CO₂ Reduction and Water Splitting. *J. Phys. Chem. C* **2019**, *123*, 367–378.
- (30) Moya, A.; Barawi, M.; Alemán, B.; Zeller, P.; Amati, M.; Monreal-bernal, A.; Gregoratti, L.; De, V. A.; Shea, P. O.; Vilatela, J. J. Interfacial studies in CNT fibre/TiO₂ photoelectrodes for efficient H₂ production. *Appl. Catal., B* **2020**, *268*, 2–9.
- (31) Hsieh, S.; Chen, W. Synthesis and Characterization of TiO₂/CNT Nanocomposites for Azo Dye Degradation. *Mater. Sci. Forum* **2017**, *909*, 243–248.
- (32) Tahir, M. La-modified TiO₂ /carbon nanotubes assembly nanocomposite for efficient photocatalytic hydrogen evolution from glycerol-water mixture. *Int. J. Hydrogen Energy* **2019**, *44*, 3711–3725.
- (33) Batmunkh, M.; Macdonald, T. J.; Shearer, C. J.; Bat-Erdene, M.; Wang, Y.; Biggs, M. J.; Parkin, I. P.; Nann, T.; Shapter, J. G. Carbon Nanotubes in TiO₂ Nanofiber Photoelectrodes for High-Performance Perovskite Solar Cells. *Adv. Sci.* **2017**, *4*, 1–11.
- (34) Wang, J.; Wang, Z.; Zhu, Z. Synergetic effect of Ni(OH)₂ cocatalyst and CNT for high hydrogen generation on CdS quantum dot sensitized TiO₂ photocatalyst. *Applied Catal. B, Environ.* **2017**, *204*, 577–583.
- (35) Huerta-Flores, A. M.; Torres-Martínez, L. M.; Moctezuma, E.; Singh, A. P.; Wickman, B. Green synthesis of earth-abundant metal sulfides (FeS₂, CuS, and NiS₂) and their use as visible-light active photocatalysts for H₂ generation and dye removal. *J. Mater. Sci. Mater. Electron.* **2018**, *29*, 11613–11626.
- (36) Ma, Q.; Hu, C.; Liu, K.; Hung, S. F.; Ou, D.; Chen, H. M.; Fu, G.; Zheng, N. Identifying the electrocatalytic sites of nickel disulfide in alkaline hydrogen evolution reaction. *Nano Energy* **2017**, *41*, 148–153.
- (37) Yuan, Y. P.; Cao, S. W.; Yin, L. S.; Xu, L.; Xue, C. NiS₂ Cocatalyst Decoration on CdLa₂S₄ Nanocrystals for Efficient Photocatalytic Hydrogen Generation under Visible Light Irradiation. *Int. J. Hydrogen Energy* **2013**, *38*, 7218–7223.
- (38) Shanmugaratnam, S.; Velauthapillai, D.; Ravirajan, P.; Christy, A. A.; Shivatharsiny, Y. CoS₂/TiO₂ in nanocomposites for hydrogen production under UV irradiation. *Materials* **2019**, *12*, 3882.
- (39) Xing, J.; Li, Y. H.; Jiang, H. B.; Wang, Y.; Yang, H. G. The size and valence state effect of Pt on photocatalytic H₂ evolution over platinumized TiO₂ photocatalyst. *Int. J. Hydrogen Energy* **2014**, *39*, 1237–1242.
- (40) Chang, C. J.; Wei, Y. H.; Huang, K. P. Photocatalytic hydrogen production by flower-like graphene supported ZnS composite photocatalysts. *Int. J. Hydrogen Energy* **2017**, *42*, 23578–23586.
- (41) Yang, J.; Wang, X.; Zhao, X.; Dai, J.; Mo, S. Synthesis of uniform Bi₂WO₆-reduced graphene oxide nanocomposites with significantly enhanced photocatalytic reduction activity. *J. Phys. Chem. C* **2015**, *119*, 3068–3078.
- (42) Zhao, J.; Shi, R.; Li, Z.; Zhou, C.; Zhang, T. How to make use of methanol in green catalytic hydrogen production? *Nano Sel.* **2020**, *1*, 12–29.
- (43) Xue, F.; Liu, M.; Cheng, C.; Deng, J.; Shi, J. Localized NiS₂ Quantum Dots on g-C₃N₄ Nanosheets for Efficient Photocatalytic Hydrogen Production from Water. *ChemCatChem* **2018**, *10*, 5441–5448.
- (44) Pan, J.; Wang, B.; Dong, Z.; Zhao, C.; Jiang, Z.; Song, C.; Wang, J.; Zheng, Y.; Li, C. The 2D RGO-NiS₂ dual co-catalyst synergistic modified g-C₃N₄ aerogel towards enhanced photocatalytic hydrogen production. *Int. J. Hydrogen Energy* **2019**, *44*, 19942–19952.
- (45) Zong, X.; Han, J.; Ma, G.; Yan, H.; Wu, G.; Li, C. Photocatalytic H₂ evolution on CdS loaded with WS₂ as cocatalyst under visible light irradiation. *J. Phys. Chem. C* **2011**, *115*, 12202–12208.
- (46) Ning, X.; Zhen, W.; Zhang, X.; Lu, G. Assembly of Ultra-Thin NiO Layer Over Zn_{1-x}Cd_xS for Stable Visible-Light Photocatalytic Overall Water Splitting. *ChemSusChem* **2019**, *12*, 1410–1420.
- (47) Kong, C.; Min, S.; Lu, G. Dye-sensitized NiS_x catalyst decorated on graphene for highly efficient reduction of water to hydrogen under visible light irradiation. *ACS Catal.* **2014**, *4*, 2763–2769.
- (48) Zhang, L.; Tian, B.; Chen, F.; Zhang, J. Nickel sulfide as cocatalyst on nanostructured TiO₂ for photocatalytic hydrogen evolution. *Int. J. Hydrogen Energy* **2012**, *37*, 17060–17067.