

SnO₂@WS₂/p-Si Heterostructure Photocathode for Photoelectrochemical Hydrogen Production

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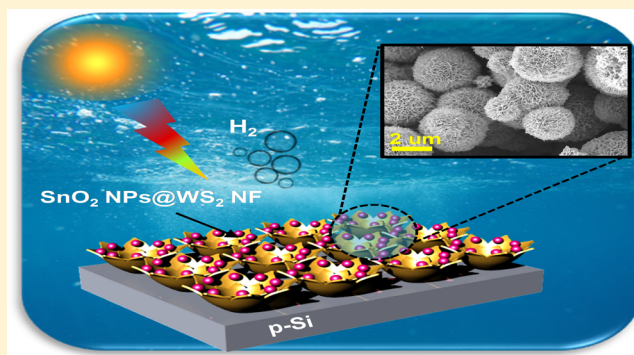
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Supporting Information

ABSTRACT: This study reports an effective method to enhance the performance of photoelectrochemical (PEC) solar water reduction. We design and prepare a SnO₂@WS₂ NF heterostructure on p-Si that has better visible-light absorption as well as low recombination of electron–hole pairs. Consequently, a -3.5 mA cm^{-2} photocurrent density at 0 V versus a reversible hydrogen electrode is obtained using SnO₂@WS₂, and bare SnO₂ and WS₂ photocathodes exhibit values of -0.6 and -0.36 mA cm^{-2} , respectively, showing the combined effects of these two materials for excellent hydrogen evolution reaction performance. Additionally, the photocurrent stability of the sample reveals the improved efficiency for the separation of generated charge carriers. Our study provides experimental and theoretical evidence that SnO₂ doping improves the properties of WS₂ for efficient PEC solar water reduction.



1. INTRODUCTION

Solar water splitting has been considered as an alternative renewable H₂ production method since the introduction of water splitting using a TiO₂ electrode in the 1970s by Fujishima and Honda.¹ However, to date, renewable energy accounts for only 5% of the commercial H₂ production (mainly via electrolysis); the other 95% of H₂ production employs fossil fuels.² As visible light consists of half of the solar radiation, developing active catalysts for direct water splitting remains a major challenge.^{1,3–6} However, considerable progress was made, and new photocatalysts for solar water splitting have recently been discovered.

Due to their interesting and unique properties, transition-metal dichalcogenides (TMDs) and two-dimensional (2D) layered materials such as MoS₂, WS₂, MoSe₂, WSe₂, TaS₂, and TiS₂ are being developed for water splitting.^{7,8} Thus, significant efforts have been directed toward the fabrication of good quality TMD layers. Single-component TMD photocatalysts have poor performance for solar water splitting owing to their low light-absorption range, fast recombination of photo-

generated electrons and holes,^{9–11} and limited edge active sites.¹² Synthesis of nanocomposites by combining different materials is the most promising approach to overcome the limitations of single-component photocatalysts and enhance their performance in photocatalytic water splitting.^{13,14}

Recently, with a narrow band gap of 1.8 eV, WS₂ has attracted attention as a catalyst for photocatalytic water splitting, with strong absorption in the visible region between 400 and 700 nm,^{15–22} and can have a direct band gap when reduced to a monolayer.²³ However, due to the poor generation of electron–hole pairs in the visible region, it has a limited application as a photocatalyst. Thus, combining WS₂ with semiconductors that have a suitable band gap energy is an effective approach to improve the charge separation and thus enhance the photocatalytic activity. For example, Zhong et al.²⁴ combined CdSe quantum dots having different sizes with WS₂

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nanosheets to optimize the band gap energy. The prepared nanocomposite exhibited good stability and high efficiency for H_2 evolution. Additionally, Zou et al.²⁵ decorated WS_2/CN 2D/2D NSs with CdS QDs, obtaining a highly efficient photocatalyst for solar water splitting, which exhibited much higher efficiency than bare CN and WS_2 nanosheets.

In recent years, SnO_2 —a wide band gap (3.5 eV) semiconductor with unique electrical properties, high photoactivity, excellent photocorrosion resistance, and low cost—has attracted considerable attention as a catalyst in the field of humidity sensors and also as an ideal host material for photoelectrodes.^{26–33} However, due to its relatively large band gap, its photoresponse is limited, and in addition, it has fast recombination of electron–hole pairs.

In this study, $\text{SnO}_2@WS_2$ nanoflower (NF) photocatalysts via a simple hydrothermal method were synthesized. As a result, the prepared $\text{SnO}_2@WS_2$ NF photocatalysts exhibited a better photocatalytic activity toward solar H_2 production, and the efficiency is higher than those of SnO_2 and WS_2 NFs alone. The improved performance is attributed to the rich active sites and lower activation barriers for redox reactions of WS_2 , as well as the junction, that is, the intimate contact, between the two photocatalysts SnO_2 and WS_2 , which facilitated the transport of photoexcited carriers at the $\text{SnO}_2@WS_2$ NF interface, resulting in high efficiency. These features make WS_2 NFs promising noble-metal-free cocatalysts in combination with SnO_2 photocatalysts for efficient photocatalytic H_2 evolution. The effect of the loading amount of WS_2 nanoflowers (NF) on the photocatalytic H_2 production activity of the $\text{SnO}_2@WS_2$ NF composites was investigated. Additionally, a possible photocatalytic mechanism of $\text{SnO}_2@WS_2$ was proposed.

2. EXPERIMENTAL SECTION

2.1. Chemical Materials. Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), thioacetamide, oxalic acid, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich, and deionized water (DI) was purchased from Millipore Milli-Q at $18.3 \text{ M}\Omega \text{ cm}^{-1}$ is used.

2.2. Synthesis of WS_2 NFs. The WS_2 NFs were synthesized by the hydrothermal method using a Teflon-lined autoclave. The preparation procedure was as follows. $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (1.2 g) and thioacetamide (1.4 g) were used as W and S sources, respectively.³⁴ The prepared solution was then dissolved in DI. After stirring for a few minutes to get a clear solution, oxalic acid (0.4 g) was added to adjust the pH level to an acidic environment. The prepared sample was put in the sealed autoclave for 24 h at 200°C . Finally, the product was collected and washed with ethanol and distilled water to remove impurities.

2.3. Synthesis of SnO_2 Nanoparticles (NPs). The Sn precursor ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 0.471 g) was weighed and added to 30 mL of DI water followed by stirring for 15 min and the addition of NaOH (0.452 g). After the mixture was stirred for an additional 15 min, 10 mL of DI water with dissolved citric acid (0.176 g) was added. The mixture was stirred again for 15 min and then transferred to a 100 mL autoclave (Figure 1). The hydrothermal reaction was conducted for 6 h at 150°C . Subsequently, the resulting solution mixture was washed three times with DI water.

2.4. Synthesis of $\text{SnO}_2@WS_2$ NFs. $\text{SnO}_2@WS_2$ NFs were synthesized similarly with SnO_2 and WS_2 (Figure 1). The as-fabricated WS_2 (0.1 g) was dispersed in deionized water for a few minutes to get a dispersed solution. In addition, $\text{SnCl}_4 \cdot$

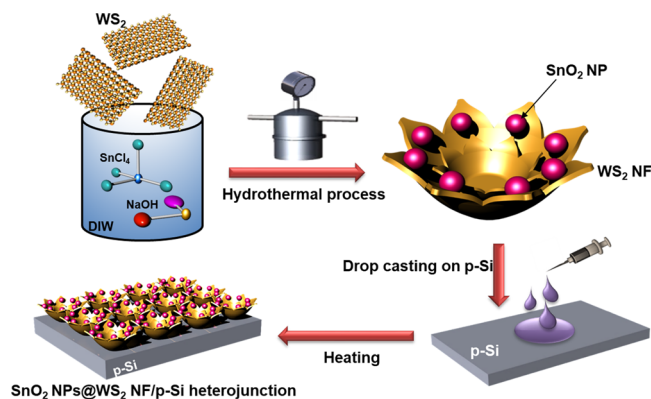


Figure 1. Schematic of WS_2 and $\text{SnO}_2@WS_2$ NF synthesis.

SH_2O (3 mM) and NaOH (21 mM) were used as Sn and O sources, respectively. By varying the concentration of the WS_2 suspension, composites with different SnO_2 -to- WS_2 ratios were prepared and are named $\text{SnO}_2@WS_2$ -1, $\text{SnO}_2@WS_2$ -2, $\text{SnO}_2@WS_2$ -3, and $\text{SnO}_2@WS_2$ -4 (corresponding WS_2 concentration from nanocomposite 0.02 to 0.08 M).

2.5. Device Fabrication. For photoelectrochemical (PEC) measurements, the working electrode was fabricated on p-Si. The p-Si was cleaned with acetone, isopropyl alcohol, and DI water, in sequence, followed by HF washing (10% concentration). Different concentrations of $\text{SnO}_2@WS_2$ NFs were spin-coated at 3500 rpm for 60 s followed by drying at 40°C in air for 15 min. Then the backside p-Si was then scratched for a good contact and coated by an InGa alloy. Finally, Cu wires were attached using Ag paste, and the backside was covered completely by epoxy. The samples were thereafter left to dry in preparation for the measurement of the PEC performance.

2.6. PEC Measurement. A saturated calomel electrode (SCE), a Pt mesh, and $\text{SnO}_2@WS_2$ NFs coated on p-Si were employed as the reference, counter, and working electrodes, respectively. The hydrogen evolution reaction (HER) activity was measured using linear sweep voltammetry with a scan rate of 10 mV s^{-1} . All measurements were performed in 0.5 M H_2SO_4 with iR compensation. Electrochemical impedance spectroscopy (EIS) was performed at a potential of -250 mV versus a reversible hydrogen electrode (RHE) in the frequency range of 100 kHz to 0.1 Hz. Additionally, the photocurrent stabilities of all the samples were tested. All the potentials were referenced to the RHE using the Nernst equation:

$$E(\text{RHE}) = E(\text{SCE}) + 0.24 \text{ V} + 0.059\text{pH} \quad (1)$$

2.7. Material Characterization. The compositions of the samples were analyzed via X-ray diffraction (XRD) analysis (Bruker D8 Advance X-ray diffractometer) using $\text{Cu K}\alpha$ radiation. Field-emission scanning electron microscopy (FESEM, Zeiss 300 VP) images were obtained at an acceleration voltage of 50 kV. X-ray photoelectron spectroscopy (XPS, VG Scientific Ltd., England) was performed under a vacuum pressure of at least $1 \times 10^{-5} \text{ mbar}$ using $\text{Mg K}\alpha$ radiation (1250 eV) and a constant pass energy of 50 eV to confirm the presence of W, S, Sn, and O. Transmission electron microscopy (TEM) was also performed. Raman spectroscopy was conducted to investigate the structures and sizes of the synthesized samples.

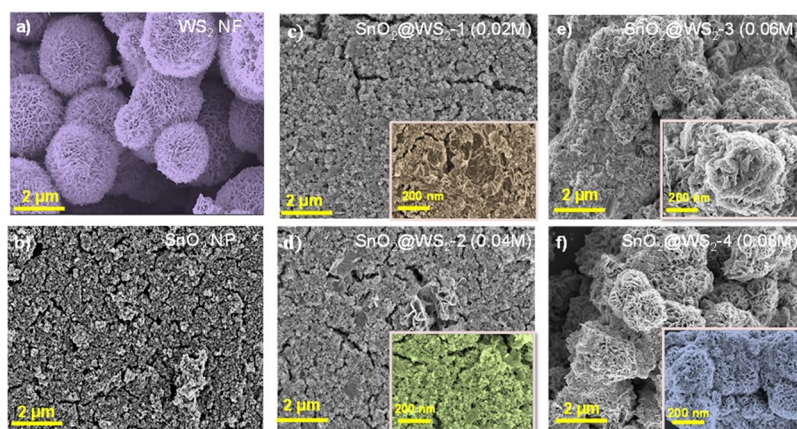


Figure 2. FESEM images: (a) WS₂ NF, (b) SnO₂ NP, (c) SnO₂@WS₂-1 (0.02 M), (d) SnO₂@WS₂-2 (0.04 M), (e) SnO₂@WS₂-3 (0.06 M), and (f) SnO₂@WS₂-4 (0.08 M).

3. RESULTS AND DISCUSSION

The microstructure and morphology of the as-prepared WS₂ NFs, SnO₂, and different SnO₂@WS₂ samples were observed via FESEM and TEM, and the results are shown in Figures 2 and 3. The surface morphology of the flowerlike WS₂ is clearly

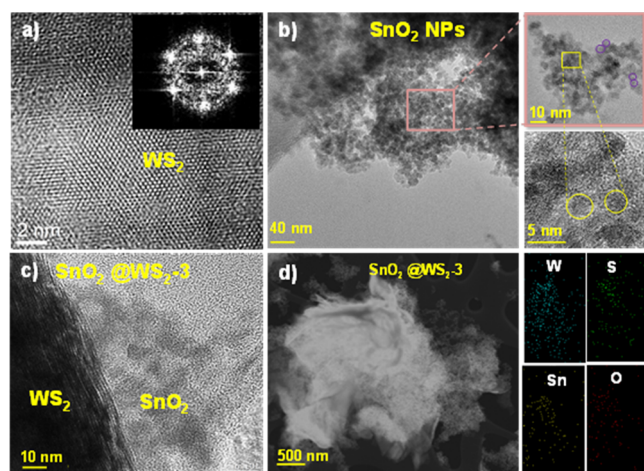


Figure 3. TEM images: (a) WS₂ NF, (b) SnO₂ NP, (c) HRTEM image of SnO₂@WS₂-3, and (d) the corresponding scanning TEM-EDS elemental maps of S, W, Sn, and O for the as-prepared SnO₂@WS₂-3.

observed in Figure 2a. The insets in Figure 2 show high-magnification SEM images. The WS₂ NFs had an average size of 1–2 μm. The crystallographic structures of WS₂ NF, SnO₂, and SnO₂@WS₂ hybrid nanocomposites were examined via XRD analysis and Raman spectroscopy, as shown in Figure S1a,b. The peaks of the WS₂ NFs and SnO₂ NPs show the hexagonal WS₂ NFs and tetragonal SnO₂, respectively. The NF structures provided a larger surface area and more active sites than the NSs,²¹ improving the HER performance. The morphology of pure SnO₂ (Figure 2b) comprised spherical NPs with a size of 10–20 nm. The SnO₂@WS₂ hybrid structures having different concentrations of WS₂ from 0.02 to 0.08 M were used, while the amount of SnO₂ NPs and the reaction conditions were kept fixed. The morphology of the as-prepared SnO₂@WS₂ heterostructure, which consisted of WS₂ NFs and SnO₂ NPs, was also examined with different concentrations, as shown in Figure 2c–f. In general, the

surface morphology varied for the different composites. As the concentration of WS₂ NFs increased from SnO₂@WS₂-1 to 4, WS₂ NF area also increased. As shown in Figure 2c, the SnO₂ NPs occupied the entire observed area in SnO₂@WS₂-1, corresponding to the smallest amount of WS₂ NFs, and the amount of WS₂ NFs gradually increased from SnO₂@WS₂-2 (Figure 2d) to SnO₂@WS₂-4 (Figure 2f) in which the WS₂ fully covered the area. In Figure 2f, a large area of WS₂ NFs is observed. TEM was performed to examine the crystal structure of the as-prepared WS₂ NF and SnO₂@WS₂ hybrid structures. The sample with the highest performance was chosen. High-resolution TEM (HRTEM) revealed the stacking of WS₂ (002). Figure 3a shows a hexagonal crystal structure similar to that reported previously.³⁵ Additionally, the WS₂ exhibited a characteristic layered structure. The size of the SnO₂ NPs was in the range of 10–20 nm (Figure 3b). In agreement with the FESEM image (Figure 2e), the SnO₂ NPs with sizes in the range of 10–20 nm were well deposited on the surfaces of the WS₂ NFs, as shown in Figure 3c. In the SnO₂@WS₂-3 composite, SnO₂ NPs outside the WS₂ NFs were observed, owing to the strong binding and interaction between the SnO₂ NPs and WS₂ NFs. Under a higher magnification, the lattice fringes at the edge of the WS₂ NFs and SnO₂ NPs were clearly observed. HRTEM and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed to show the atomic distribution of SnO₂ and WS₂ in the SnO₂@WS₂ hybrid structure (Figure 3d). The EDS revealed the uniform distributions of Sn, O, W, and S.

All the four composites, that is, SnO₂@WS₂-1 to -4, were analyzed via XPS (Figure 4). The XPS full-survey, W4f, and S2p spectra of the SnO₂@WS₂-3 sample were obtained. Figure 4a shows a typical XPS survey spectrum of SnO₂@WS₂-3 with the corresponding atomic ratio, exhibiting peaks associated with W, S, Sn, and O. The XPS analysis verified the constituent atomic ratios of all the prepared SnO₂@WS₂ composites, indicating a high amount of WS₂ as the concentration increased from 0.02 to 0.08 M (Figure S2). Compared with the W4f spectrum of pure WS₂, the SnO₂@WS₂-3 composite sample exhibited a higher binding energy because of the SnO₂, as shown in Figure 4b. The slight shifts of W4f_{7/2} and W4f_{5/2} peaks to higher binding energies in SnO₂@WS₂-3 compared with WS₂ indicate the combination of WS₂ and SnO₂ NPs. The W4f_{7/2} and W4f_{5/2} peaks were positioned at 32 and 34 eV, respectively, for bare WS₂ and at 32.9 and 34.4 eV, respectively, for SnO₂@WS₂-3, confirming the combination

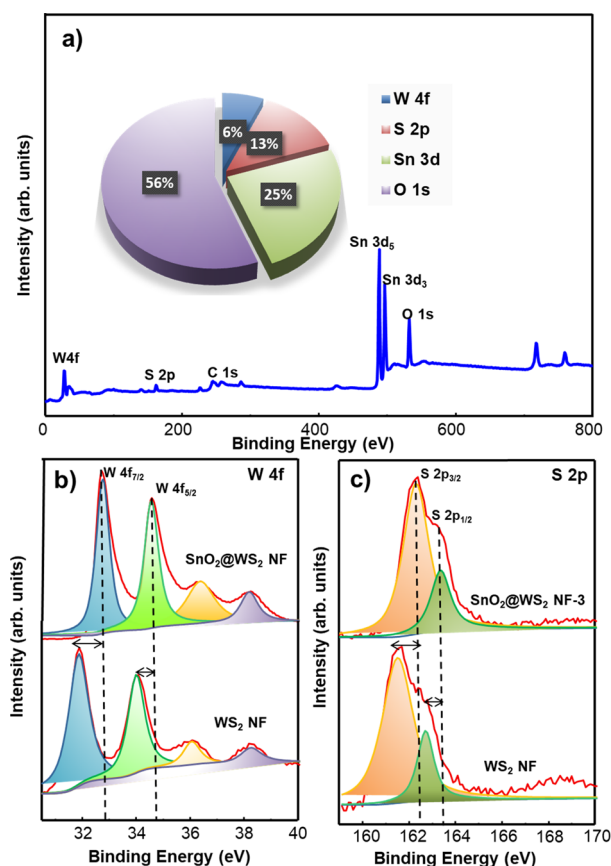


Figure 4. (a) Full-survey XPS spectra. (b) High-resolution XPS W4f peak and (c) high-resolution XPS S2p peak of WS₂ NFs and SnO₂@WS₂-3.

of SnO₂ and WS₂. Similarly, there was a slight shift in the S2p peak of the SnO₂@WS₂-3 sample (from 161.9 to 162.4 eV and 163 to 163.6 eV for S2p_{3/2} and S2p_{1/2}, respectively), as shown in Figure 4c. Additionally, the Sn3d and O1s peaks for all the samples were analyzed. The Sn3d_{3/2} and Sn3d_{5/2} peaks for different composites were similar in shape and in position at 495.7 and 487.3 eV, respectively,³⁶ as shown in Figure S3a.

The photocatalytic H₂ production activities of the prepared SnO₂, WS₂, and SnO₂@WS₂ hybrid were examined in the presence of a H₂SO₄ aqueous solution under solar-visible-light irradiation ($\lambda > 420$ nm), as shown in Figure 5. As shown in Figure 5a, the current density at 0 V when WS₂ alone was used as a photocatalyst was very low, implying that WS₂ has low performance for photocatalytic H₂ evolution, similar to the previously reported papers.^{37,38} Additionally, bare SnO₂ showed low photocatalytic activity, with a current density of -0.6 mA cm⁻² at 0 V. The photocatalytic activity of the SnO₂@WS₂ hybrid catalysts was much higher than those of pure WS₂ and SnO₂. The photocurrent density of SnO₂@WS₂ significantly increased compared with those of planar WS₂ and SnO₂ because the formed SnO₂@WS₂ heterojunction enhanced the carrier transport kinetics and suppressed the charge recombination. When 0.02 M (SnO₂@WS₂-1) WS₂ was loaded on SnO₂, the current density was enhanced to -1.2 mA cm⁻² at 0 V. When the WS₂ loading amount increased to 0.04 M (SnO₂@WS₂-2), the H₂ evolution rate was further enhanced to -1.9 mA cm⁻². The maximum H₂ evolution rate of -3.5 mA cm⁻² at 0 V was achieved at a loading amount of 0.06 M (SnO₂@WS₂-3). When the amount of WS₂ was further

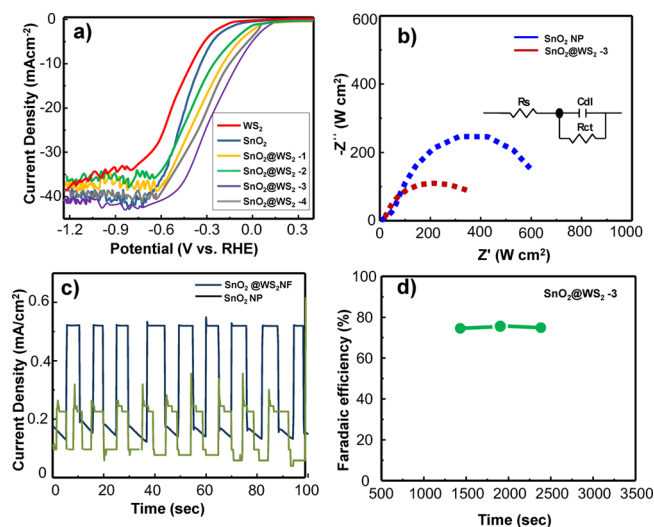


Figure 5. (a) HER polarization in 0.5 M H₂SO₄, (b) EIS analysis, (c) photocurrent stability of the bare WS₂ and SnO₂@WS₂ NF catalysts, and (d) faradaic efficiency of SnO₂@WS₂-3.

increased to 0.08 M (SnO₂@WS₂-4), the photocatalytic H₂ evolution rate decreased to 2.4 mA cm⁻². This reduction could have occurred because the heavy loading of WS₂ hindered the light absorption of SnO₂. The charge transfer and the interfacial charge transfer kinetics performance were obtained via EIS and analyzed by the Nyquist plot (Figure 5b). Additionally, the effect of the coupling of WS₂ and SnO₂ and the separation and migration of generated charges for the prepared SnO₂ and SnO₂@WS₂-3 photocatalysts were studied by using PEC measurements. Figure 5c presents the photocurrent response spectra of SnO₂ and SnO₂@WS₂-3 photoelectrodes under alternating visible-light irradiation. As shown, both the SnO₂ and SnO₂@WS₂-3 photoelectrodes responded rapidly to the on/off visible-light irradiation, confirming the visible-light response characteristic of SnO₂. More importantly, the SnO₂@WS₂-3 photoelectrode exhibited significantly higher photocurrent intensity than the SnO₂ photoelectrode, implying more efficient separation and migration of the photogenerated charges, which enhanced the photocatalytic activity. Gas chromatography measurement was used to examine the faradaic efficiency and the generation H₂. As a result, the as-optimized SnO₂@WS₂-3 exhibited high faradaic efficiency of $80 \pm 2\%$ as shown in Figure 5d.

Figure 6a presents the UV-vis spectra of SnO₂, WS₂, and SnO₂@WS₂-3. Clearly, the SnO₂ showed a lower absorption region, while the SnO₂@WS₂-3 showed optical absorbance in the visible-light region, exhibiting an absorption edge around 565 nm with a band gap energy of 2.1 eV. For the sample with a small amount of WS₂, the surface area was insufficient for the excessive SnO₂ to form a heterojunction with the WS₂. Based on the obtained band gap energy of SnO₂@WS₂, the photocatalytic mechanism of the SnO₂@WS₂ composites was proposed, as shown in Figure 6b. The SnO₂ NPs were first excited, producing electrons and holes. Due to a large band gap energy, the pure SnO₂ sample encountered easy recombination of generated electrons and holes and showed poor catalytic activity. However, after coupling SnO₂ with WS₂, the generated electrons could easily transfer from SnO₂ to WS₂ because of the lower band gap energy. In this case, the separation of photogenerated electron-hole pairs within SnO₂ would be significantly enhanced, which can be attributed to the

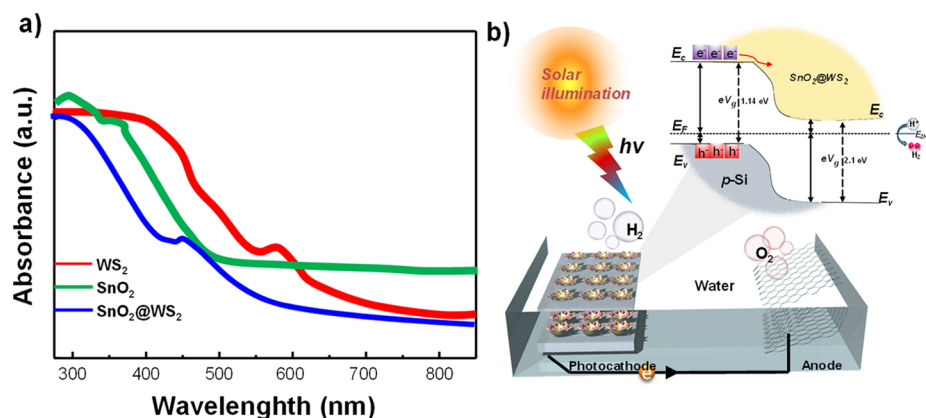


Figure 6. (a) UV-vis spectra of SnO_2 , WS_2 , and $\text{SnO}_2@\text{WS}_2$ and the corresponding band gap energy. (b) Schematic of the photocatalytic H_2 evolution mechanism of the $\text{SnO}_2@\text{WS}_2$ NF catalysts under visible light.

heterostructure formed at the edge between SnO_2 and WS_2 . The collected electrons in WS_2 would then reduce H^+ , generating H_2 , because the ECB potential of $\text{SnO}_2@\text{WS}_2$ was lower than the reduction potential of H^+/H_2 .

4. CONCLUSIONS

A $\text{SnO}_2@\text{WS}_2$ hybrid with different molar ratios of WS_2 was synthesized by a simple hydrothermal method. The $\text{SnO}_2@\text{WS}_2$ hybrid structures showed significantly enhanced photocatalytic activity compared with SnO_2 and WS_2 under visible-light irradiation. According to the results of XPS, the photocurrent stability, and EIS, the improved photocatalytic activity was attributed to the intimate interface contacts of SnO_2 and WS_2 , which had effective transfer and separation of generated electrons. Furthermore, we proposed a mechanism to explain the enhanced photocatalytic performances of the $\text{SnO}_2@\text{WS}_2$ hybrid structures. The synthesized $\text{SnO}_2@\text{WS}_2$ hybrid structure is a promising photocatalyst and can be used as a reference for other SnO_2 -based materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.9b09623>.

Figures showing the XRD patterns, Raman spectra, atomic ratios, O1s peaks, Sn3d peaks, and current density comparison at 0 V of WS_2 NFs, SnO_2 , and $\text{SnO}_2@\text{WS}_2$ of different concentrations (PDF)

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Notes

The authors declare no competing financial interest.

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