Noble-Metal-Free Ni$_x$S$_y$-C$_3$N$_5$ Hybrid Nanosheet with Highly Efficient Photocatalytic Performance

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Abstract: The construction of highly efficient, low-cost and noble-metal-free photocatalysts depends on photocatalytic technology. Recently, N-rich C$_3$N$_5$ has been explored as a novel carbon nitride material with a much narrower band gap (~2.2 eV) than that of traditional C$_3$N$_4$ (~2.7 eV). Planting noble-metal-free active sites on C$_3$N$_5$ to improve its photocatalytic activity is of great significance. Herein, 2D Ni$_x$S$_y$ nanosheet is facially loaded on 2D C$_3$N$_5$ using a hydrothermal procedure under a low temperature. Due to the quick separation of photogenerated carries between C$_3$N$_5$ and Ni$_x$S$_y$, this inexpensive noble-metal-free Ni$_x$S$_y$-C$_3$N$_5$ hybrid nanosheet is highly efficient and stable as a multifunctional catalyst in various applications, including photocatalytic H$_2$ production from water and NO removal. Impressively, the apparent quantum yield (AQY) value for H$_2$ production reaches 37.0% (at 420 nm) on optimal Ni$_x$S$_y$-C$_3$N$_5$ hybrids, which is much higher than that of Pt-C$_3$N$_5$ material. This work opens an avenue to the fabrication of low-cost and noble-metal-free catalysts for multifunctional photocatalytic applications.

Keywords: Ni$_x$S$_y$-C$_3$N$_5$ hybrid; photocatalysis; H$_2$ production; NO removal; noble-metal-free catalyst

1. Introduction

Semiconductor-based photocatalytic technology is one of the most promising strategies for solving the ever-increasing energy crisis and addressing environmental pollution as well as concerns for public health [1–4]. Although numerous efforts have been made since the pioneering work on TiO$_2$ photoelectrodes for water splitting in 1972 [5–7], the industrialization of this technology is still unrealized due to its inefficiency and problems with implementation. In general, the photocatalytic conversion efficiency is influenced by light absorption, photogenerated carrier separation and surface reduction-oxidation reactions. Previous research has shown that the aforementioned three factors cannot be fully satisfied in one semiconductor, and the construction of hybrid materials, such as a design co-catalyst or active sites on semiconductors and semiconductor-based heterojunctions, is an effective strategy to combine the advantages of different materials to enhance photocatalytic efficiency [3,8–13]. Thus, the design of robust hybrid materials is an essential element in the photocatalytic field.

Of the various semiconductors used in photocatalytic investigation, carbon nitride has drawn enormous attention because of its low cost, metal-free status, suitable band positions, stability, environmental-friendliness, etc. [2,14–17]. Recently, a boron-doped and nitrogen-deficient strategy was reported to adjust the band positions of C$_3$N$_4$ nanosheets; Z-scheme carbon nitride-based heterostructures were fabricated with high solar-to-hydrogen efficiency (1.16% under one-sun illumination) for photocatalytic water splitting using Pt and Co(OH)$_2$ as H$_2$ and O$_2$ evolving co-catalysts, respectively [18,19]. Lin et al. reported...
the controlling of the reactive facets based on a carbon nitride PTI/LiCl− single crystals for photocatalytic water splitting with the assistance of Pt/Co as co-catalysts [16]. In addition, C3N4 was decorated with oxygen-vacancy-rich BiOBr sheets to form a hybrid, which exhibited excellent photocatalytic CO2 reduction and NO removal efficiency [20]. However, the performance of C3N4-based materials is seriously limited by its wide band gap (~2.7 eV). Recently, a new type of N-rich carbon nitride (C3N4) was synthesized using various precursors [21–26]. The structure of C3N5 and C3N4 is very similar, except that some terminal amino groups on C3N4 are replaced by terminal 1,2,4-triazole or 1H-1,2,3-triazole on C3N5 [24]. C3N5 could absorb visible light wavelengths longer than 600 nm and exhibited potential application in the fields of water splitting [25,26], pollutant removal [21,26], gas adsorption/sensing [25], N2 fixing [23] and photovoltaics [22]. Recently, the photocatalytic H2 production activity of C3N5 prepared from 3-amino-1,2,4-triazole was comprehensively investigated with Pt as a co-catalyst by our group [27]. However, the precious Pt is not practical for wide application. The design of low-cost noble-metal-free co-catalysts on C3N5 has not yet been reported in the literature. The unique visible light absorption and band position of C3N5 that can afford NO removal by the photocatalytic oxidation procedure, which has yet to be investigated, will be of great significance for atmosphere purification.

Herein, following the above hypothesis, 2D nickel sulfide (NiSx) is hybridized with 2D C3N5 to construct a noble-metal free hybrid (NiSx-C3N5) using a facial hydrothermal method at 120 °C. The photocatalytic H2 production and NO oxidation properties of this hybrid are evaluated to illustrate the potential application of this material. Experimental results show that NiSx-C3N5 is a highly efficient, low-cost photocatalyst for H2 production, even exceeding Pt-C3N5, and can produce sufficient active species participating in converting NO into harmless N-containing species such as NO3−. The present work will promote the development of low-cost photocatalytic materials to address energy and environmental issues.

2. Results and Discussion

2.1. Characterization

Figure 1 depicts the X-ray diffraction (XRD) patterns of NiSx and the NiSx-C3N5 hybrid obtained by the facial hydrothermal method at 120 °C; NiSx-160 °C is listed for comparison. As revealed in Figure 1a, strong diffraction peaks are observed for bare NiSx material, indicating its high crystallinity, and the NiSx material prepared under hydrothermal conditions at 120 °C primarily contains NiS (PDF card of 65–3419), while some weak peaks corresponding to Ni3S4 (PDF card of 47–1739) can be seen. This result demonstrates that the prepared NiSx is composed of NiS and NiS4, with NiS as the main component. To obtain nickel sulfide with a single phase of NiS or NiS4, the hydrothermal temperature for nickel sulfide preparation is adjusted and is shown in Figure 1a and Figure S1. As can be seen, the nickel sulfides obtained under temperatures from 100 to 170 °C are mixed phases of NiS and NiS4, with the main phase changing from NiS to Ni3S4. Taking NiSx at 160 °C (NiSx-160 °C) as an example (Figure 1a), it is mainly composed of Ni3S4 but some small peaks corresponding to NiS can also be found. It should be noted that a new phase of NiSx in Ni3S4 is observed when the hydrothermal temperature is increased to 200 °C. The above result reveals that it is difficult to prepare nickel sulfide with a single phase using this facial method. Notably, it has been reported that nickel sulfides have multiple crystalline phases (i.e., NiS, Ni3S4, Ni3S2, NiS2, Ni2S6, and Ni3S8) depending on the relative concentration of nickel and sulfur precursors in the synthetic system, and the mixed phase of these nickel sulfides have exhibited better performance [28–30]. Thus, the materials containing NiSx mentioned in the following sections are all synthesized under 120 °C unless otherwise specified.

As displayed in Figure 1b, two distinct peaks corresponding to (100) and (002) planes of C3N5 are observed, which is in agreement with our previous work and the related literature [23,25,27]. For the hybrid of NiSx-C3N5, the two peaks for C3N5 exhibit no obvious shift, indicating that the present hydrothermal procedure does not destroy the
basic structure of C$_3$N$_5$. Briefly, no obvious peaks corresponding to Ni$_3$S$_y$ are found for 1.0 wt% Ni$_3$S$_y$-C$_3$N$_5$, which is likely due to the low loading amount of Ni$_3$S$_y$. However, some weak peaks attributed to Ni$_3$S$_y$ are observed when the loading amount of Ni$_3$S$_y$ is increased to 3.0 wt%, indicating the successful fabrication of the Ni$_3$S$_y$-C$_3$N$_5$ hybrid.

![Figure 1. XRD patterns of (a) Ni$_3$S$_y$ prepared using a hydrothermal procedure at 120 and 160 °C, and (b) C$_3$N$_5$ and Ni$_3$S$_y$-C$_3$N$_5$ with different Ni$_3$S$_y$ loading amounts prepared using a hydrothermal procedure at 120 °C.](image)

Generally, C$_3$N$_5$ exhibits the micro morphology of 2D nanosheet according to our previous work. Figure 2 displays the TEM images of Ni$_3$S$_y$ and Ni$_3$S$_y$-C$_3$N$_5$ hybrids. In brief, Ni$_3$S$_y$ exhibits irregular 2D nanosheets (Figure 2a), which is similar to that of C$_3$N$_5$. HRTEM images of Ni$_3$S$_y$ (Figure 2b) confirm the fact that it is composed of NiS and Ni$_3$S$_y$, and clear lattice fringes of 0.25 and 0.28 nm corresponding to NiS (101) and Ni$_3$S$_y$ (311), respectively, are observed. This result is in good agreement with the above-mentioned XRD analysis. As depicted in Figure 2c for 1.0 wt% Ni$_3$S$_y$-C$_3$N$_5$, the sheets of Ni$_3$S$_y$ and C$_3$N$_5$ contact tightly with each other, indicating that the Ni$_3$S$_y$-C$_3$N$_5$ is a 2D/2D nanosheet hybrid and the hydrothermal procedure for Ni$_3$S$_y$ preparation has no obvious influence on the structure of C$_3$N$_5$. C$_3$N$_5$ possesses an amorphous structure as shown in our previous work. The HRTEM image of 1.0 wt% Ni$_3$S$_y$-C$_3$N$_5$ (Figure 2d) conveys that amorphous C$_3$N$_5$ is combined with Ni$_3$S$_y$, for which clear lattice fringes of 0.25 and 0.28 nm corresponding to NiS (101) and Ni$_3$S$_y$ (311), respectively, are also be observed. The TEM results confirm the successful fabrication of the Ni$_3$S$_y$-C$_3$N$_5$ hybrid.

To further investigate the components of the hybrid, we performed scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) element mapping of 1.0 wt% Ni$_3$S$_y$-C$_3$N$_5$, as shown in Figure 3. As seen in the figure, Ni$_3$S$_y$-C$_3$N$_5$ exhibits the basic morphology of nanosheets, which is in good agreement with the results of TEM. In addition, the hybrid is composed mainly of C, N, Ni and S elements, and each element disperses uniformly in the observed region from the mapping images. The high dispersion of Ni$_3$S$_y$ on C$_3$N$_5$ will be favorable for subsequent photocatalytic performance.

Figure 4 and Figure S2 show the XPS spectra of Ni$_3$S$_y$-C$_3$N$_5$ to determine the state of each element in the hybrid. As exhibited in the survey spectrum of Figure S2a, C, N, Ni and S are all observed in 1.0 wt% Ni$_3$S$_y$-C$_3$N$_5$, indicating the successful fabrication of the hybrid, which is in good agreement with the above results of XRD, TEM and SEM analyses. The regional spectra of C 1s and N 1s (Figure S2b,c) are similar to that of C$_3$N$_5$ in our previous work [27], and no obvious shift is observed for the corresponding peak position, revealing that the hydrothermal procedure for the Ni$_3$S$_y$-C$_3$N$_5$ preparation has no obvious influence on the structure of C$_3$N$_5$. The high-resolution XPS spectrum of S 2p is shown in Figure 4a, in which the peak at ~168 eV represents the residual sulfate group originating from the hydrothermal procedure. Two peaks at ~162.3 and ~163.1 eV corresponding to S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively, are observed, demonstrating the existence of a metal-sulfur (Ni-S) bond and sulfur ion [30–32]. Two distinct spin-orbit peaks at ~855 (Ni 2p$_{3/2}$) and 873 eV (Ni 2p$_{1/2}$), along with two satellite peaks (identified as “Sat.”), are observed in the
high-resolution XPS spectrum of Ni 2p (Figure 4b), suggesting the existence of nickel ions in the Ni$_x$S$_y$-C$_3$N$_5$ hybrid [30,31,35]. These results further confirm that the Ni$_x$S$_y$-C$_3$N$_5$ hybrid was successfully constructed.

**Figure 2.** TEM and HRTEM images of Ni$_x$S$_y$ (a,b) and 1.0 wt% Ni$_x$S$_y$-C$_3$N$_5$ (c,d).

**Figure 3.** SEM and element mapping images of 1.0 wt% Ni$_x$S$_y$-C$_3$N$_5$.

The DRS spectra of Ni$_x$S$_y$, C$_3$N$_5$ and Ni$_x$S$_y$-C$_3$N$_5$ were recorded to provide a direct comparison of their light absorption properties, which play an important role in photocatalytic performance. As revealed in Figure 5, C$_3$N$_5$ exhibits strong absorption in the visible light wavelength longer than 600 nm due to its narrow band gap (~2.25 eV), as shown in our previous work [27]. Ni$_x$S$_y$ can absorb the whole visible light region due to its black color. In addition, the visible light absorption property of Ni$_x$S$_y$-C$_3$N$_5$ displays the combination of the two components, demonstrating the successful construction of the Ni$_x$S$_y$-C$_3$N$_5$ hybrid. The excellent visible-light-responsive ability of Ni$_x$S$_y$-C$_3$N$_5$ is favorable for photocatalytic applications.
Our previous work demonstrated that no obvious H$_2$ production was observed on pristine C$_3$N$_5$ due to the lack of co-catalyst [27]. In addition, the control experiment displayed that H$_2$ production is extremely limited on pristine Ni$_3$S$_y$. As depicted in Figure 6a, the H$_2$ production rate can be greatly elevated when 0.5 wt% Ni$_3$S$_y$ is loaded on C$_3$N$_5$, demonstrating that Ni$_3$S$_y$ can facilitate the separation of photogenerated carriers of C$_3$N$_5$ and serve as an active site for H$_2$ production. This result is in good agreement with the literature, where nickel sulfide is widely taken as a catalyst for photo- or electro-catalytic water reduction [31–35]. The influence of Ni$_3$S$_y$ loading amounts on the H$_2$ production rate of Ni$_3$S$_y$-C$_3$N$_5$ was also investigated and is shown in Figure 6a. The H$_2$ production rate increases when increasing the loading amount of Ni$_3$S$_y$, and a platform is obtained when the fraction of Ni$_3$S$_y$ changes from 1.0 wt% to 3.0 wt%. However, a decrease in photoactivity is observed for 4.0 wt% Ni$_3$S$_y$-C$_3$N$_5$, which may be related to the influence of excessive Ni$_3$S$_y$ on the visible light absorption of C$_3$N$_5$. Generally, the initial amount of the S source should be higher than that of the Ni source in the nickel sulfide preparation process. Thus, taking 3.0 wt% Ni$_3$S$_y$-C$_3$N$_5$ as an example, the influence of the initial mol ratio of Ni/S (Ni(NO$_3$)$_2$/TAA) on the H$_2$ production rate was investigated and is shown in Figure S3; the optimal Ni/S reaction condition is confirmed as 1/3, and the highest H$_2$ production rate is ~1595 µmol/h.

2.2. Photocatalytic H$_2$ Production Performance

The photocatalytic activity of Ni$_3$S$_y$-C$_3$N$_5$ was first evaluated for H$_2$ production under visible light irradiation (λ > 420 nm), with TEOA as the sacrificial reagent. The DRS spectra of Ni$_3$S$_y$ were recorded to provide a direct measurement of the photoabsorption properties. As shown in Figure 5, Ni$_3$S$_y$ displays strong absorption in the visible light wavelength longer than 600 nm due to its narrow band gap (~2.25 eV), which can be greatly elevated when 0.5 wt% Ni$_3$S$_y$ is loaded on Ni$_3$S$_y$-C$_3$N$_5$. Therefore, the photocatalytic activity of Ni$_3$S$_y$-C$_3$N$_5$ was explored as an example, the influence of the initial mol ratio of Ni/S (Ni(NO$_3$)$_2$/TAA) on the H$_2$ production rate was investigated and is shown in Figure S3; the optimal Ni/S reaction condition is confirmed as 1/3, and the highest H$_2$ production rate is ~1595 µmol/h.
As mentioned above, the main phase of Ni$_3$S$_4$ is NiS, while a slight amount of Ni$_3$S$_4$ also exists in the catalyst. To explore the main phase of nickel sulfide, which plays a dominant role in photocatalytic H$_2$ production activity, taking 3.0 wt% Ni$_3$S$_y$-C$_2$N$_5$ as a reference, the sample of 3.0 wt% Ni$_3$S$_y$-C$_2$N$_5$-160 (prepared at 160 °C hydrothermal treatment, with the main component of Ni$_3$S$_y$ being Ni$_3$S$_4$; see Figure 1a) was also tested for H$_2$ production under the same photocatalytic condition. As shown in Figure 6b, the difference in H$_2$ production rates between 3.0 wt% Ni$_3$S$_y$-C$_2$N$_5$ and 3.0 wt% Ni$_3$S$_y$-C$_2$N$_5$-160 is slight, demonstrating that both NiS and Ni$_3$S$_4$ in Ni$_3$S$_y$ can act as electron traps and active sites to greatly enhance the photocatalytic activity for H$_2$ production. To evaluate the efficiency of the Ni$_3$S$_y$ co-catalyst, Pt nanoparticle, a widely used co-catalyst in photocatalysis, was taken as reference. As shown in Figure 6b, the H$_2$ production rate of 3.0 wt% Ni$_3$S$_y$-C$_2$N$_5$ is higher than that of 1.0 wt% Pt-C$_3$N$_5$ (the optimal Pt loaded amount is 1.0 wt% according to our previous work [27]), NiS [33,34] and NiS/C$_3$N$_4$ [36,37] materials (see Table 1). This result conveys that the present Ni$_3$S$_y$ may be a competitive alternative to noble metals such as Pt as a co-catalyst utilized in photocatalytic H$_2$ production.

Table 1. The comparison of the photocatalytic H$_2$ production performance of the Ni$_3$S$_y$-C$_3$N$_5$ with some reported catalysts.

| Photocatalysts | Reaction Conditions | H$_2$ Production Rate ($\mu$mol g$^{-1}$ h$^{-1}$) | Ref. |
|---------------|-------------------|-----------------|-----|
| Pt/C$_3$N$_5$ | 300 W Xe lamp ($\lambda > 420$ nm), TEOA | 28,956 | [27] |
| NiS/ZnIn$_2$S$_4$ | 320 W Xe lamp ($\lambda > 420$ nm), Lactic Acid | 3333 | [33] |
| NiS/CQDs/ZnIn$_2$S$_4$ | 300 W Xe lamp ($\lambda > 420$ nm), TEOA | 568 | [34] |
| g-C$_3$N$_4$/1.5% NiS | 300 W Xe lamp ($\lambda > 420$ nm), TEOA | 395 | [36] |
| NiS/g-C$_3$N$_4$ | 300 W Xe lamp ($\lambda > 420$ nm), TEOA | 16,400 | [37] |
| Ni$_3$S$_y$-C$_3$N$_5$ | 300 W Xe lamp ($\lambda > 420$ nm), TEOA | 35,444 | this work |
Taking 3.0 wt% Ni$_x$S$_y$-C$_3$N$_5$ as a model, the change tendency of AQY values along with the irradiated wavelength is shown in Figure 6c; the AQY values decrease gradually when the monochromatic light changes from 420 to 700 nm. This result demonstrates that the photocatalytic H$_2$ production of Ni$_x$S$_y$-C$_3$N$_5$ is dominated by its visible light absorption property. The highest AQY value is 37.0% at 420 nm light irradiation, which is higher than that of Pt-C$_3$N$_5$ exhibited in our previous work [27]. In addition, the Ni$_x$S$_y$-C$_3$N$_5$ hybrid can also work under 700 nm monochromatic light irradiation with an AQY value of 0.2%.

To evaluate the cyclicity and durability of the present hybrid material for H$_2$ production, a long-term test under visible light irradiation was conducted on 3.0 wt% Ni$_x$S$_y$-C$_3$N$_5$. As revealed in Figure 6d, the hybrid exhibits excellent stability for H$_2$ production in the four test runs during a total of 16 h of visible light irradiation. The stability of Ni$_x$S$_y$-C$_3$N$_5$ is also confirmed by the XRD and DRS curves of the photocatalytic H$_2$ production test, as depicted in Figure 7. No obvious change in the peak number and position is observed for Ni$_x$S$_y$-C$_3$N$_5$ before and after the photocatalytic test. In addition, there is only a slight change in the visible light responsive property of Ni$_x$S$_y$-C$_3$N$_5$ after the photocatalytic test when compared with the pristine material. The nickel concentration in the solution after the photocatalytic reaction was determined to be 20.3 ppb by ICP-MS. Thus, the leaching rate of Ni was 0.14%, which is negligible. These results further confirm the structural stability of Ni$_x$S$_y$-C$_3$N$_5$ during the photocatalysis procedure.

**Figure 7.** Comparison of (a) XRD and (b) DRS curves of pristine and light irradiated Ni$_x$S$_y$-C$_3$N$_5$.

### 2.3. Photocatalytic NO Oxidation Performance

Figure 8a depicts the photocatalytic NO oxidation performance of Ni$_x$S$_y$-C$_3$N$_5$ and C$_3$N$_5$; quick removal of NO is observed, and the removal ratio reaches equilibrium during a short (~20 min) test in the continuous flow reaction system. The control experiment shows that no obvious activity for NO removal is observed on the pristine Ni$_x$S$_y$. The NO removal efficiency on pristine C$_3$N$_5$ is ~35%, which can be attributed to its wide light absorption property and suitable band position for O$_2$ molecular activation and the generation of reactive oxygen species (ROS, such as •OH, •O$_2^-$ and $^1$O$_2$), which participate in the subsequent photocatalytic NO oxidation. Generally, the production of •O$_2^-$ and $^1$O$_2$ follows the equations of $\text{O}_2 + e^- \rightarrow •\text{O}_2^-$ and $\text{O}_2^- + h^+ \rightarrow 1\text{O}_2$ [11,38]. In addition, the production •OH follows the procedure of $\text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \rightarrow •\text{OH}$, since the VB position of C$_3$N$_5$ is more negative than the potential of •OH/H$_2$O (2.38 V vs. NHE, pH = 0) according to our previous work [11,27]. The corresponding NO removal value can be improved to ~40% when 0.5 and 1.0 wt% Ni$_x$S$_y$ are loaded on C$_3$N$_5$, which is much higher than that of the C$_3$N$_4$ materials [see Table 2] [39–41]. However, a decrease in NO removal efficiency is observed with a higher loading amount of Ni$_x$S$_y$ (such as 3.0 wt%). It should be noted that excessive Ni$_x$S$_y$ may cover the surface of C$_3$N$_5$ and then influence the light absorption by C$_3$N$_5$. The improved photocatalytic performance is related to the electron transfer between C$_3$N$_5$ and Ni$_x$S$_y$, as well as the enhanced efficiency for ROS generation, as will be discussed in the following section. The durability of 1.0 wt% Ni$_x$S$_y$-C$_3$N$_5$ on photocatalytic NO removal was tested under 2 h of light irradiation, as shown in Figure 8b;
the removal ratio is maintained in the long-term test, revealing the excellent photocatalytic stability of Ni$_x$S$_{1-x}$C$_3$N$_5$. The cycling performance of 1.0 wt% Ni$_x$S$_{1-x}$C$_3$N$_5$ on photocatalytic NO removal is depicted in Figure 8c; there is only a slight decrease after six test runs, demonstrating the excellent photocatalytic repeatability of the present hybrid. Generally, the products of photocatalytic NO oxidation are considered to be NO$_2$ and NO$_3^-$. The production of NO$_2$ is directly recorded on the NO$_x$ analyzer shown in Figure 8d. For NO$_3^-$ detection, the irradiated Ni$_x$S$_{1-x}$C$_3$N$_5$ samples are re-dispersed in water and then filtered. Finally, the transparent filtrate is analyzed by ion chromatography with NaNO$_3$ as a reference. As displayed in Figure 8e, the production of NO$_3^-$ during NO removal is confirmed qualitatively. Notably, the selectivity for NO$_3^-$ production is estimated to be ~70%, based on NO removal efficiency and residual NO$_2$ amount (Figure 8a,d).

![Figure 8.](image)

**Figure 8.** (a) Comparison of photocatalytic NO removal behaviors on Ni$_x$S$_{1-x}$C$_3$N$_5$ and Ni$_x$S$_{1-x}$C$_3$N$_5$. Durability (b) and cyclability (c) of photocatalytic NO removal on 1.0 wt% Ni$_x$S$_{1-x}$C$_3$N$_5$. Detection of NO$_2$ (d) and NO$_3^-$ (e) during photocatalytic NO removal on Ni$_x$S$_{1-x}$C$_3$N$_5$.

**Table 2.** The comparison of the photocatalytic NO removal performance of the Ni$_x$S$_{1-x}$C$_3$N$_5$ with some reported catalysts.

| Photocatalysts | Reaction Conditions | NO Removal Efficiency (%) | Ref. |
|---------------|---------------------|---------------------------|------|
| Mo-g-C$_3$N$_4$/g-C$_3$N$_4$ | flow reactor, metal halide lamp, >420 nm | 36.0 | [39] |
| g-C$_3$N$_4$/BO$_x$:NO$_x$ | flow reactor, metal halide lamp, >420 nm | 30.2 | [40] |
| N-Vacancies g-C$_3$N$_4$ | flow reactor, Xe lamp, >420 nm | 32.8 | [41] |
| Ni$_x$S$_{1-x}$C$_3$N$_5$ | flow reactor, visible LED | 40.0 | this work |

Generally, photogenerated h$^+$ and the series of ROS play significant roles in the photocatalytic NO oxidation procedure. To explore active species that participate in the reaction of NO removal, a series of trapping agent experiments were conducted, in which Na$_2$C$_2$O$_4$, tert-butanol (TBA), p-benzoquinone (PBQ) and β-carotene were used as scavengers for h$^+$, •OH, •O$_2^-$ and •O$_2$, respectively [42]. As can be seen in Figure 9a, the photocatalytic NO removal efficiency is inhibited to different extents when different trapping agents are added, demonstrating that all of the above-mentioned species can participate in the procedure for NO removal. In addition, the dominant species are •O$_2^-$ and •O$_2$, since the NO removal efficiency is greatly inhibited when the two species are captured. Electron spin resonance (ESR) spectra were recorded to monitor the formation of
the main active species of ⋅O₂⁻ and ¹O₂. As revealed in Figure 9b,c, characteristic signals for DMPO-⋅O₂⁻ and TEMPO (product of TEMP oxidized by ¹O₂) were detected [42–44], and the signal intensity for NiₓSₓ-CₓN₅ was higher than that of pristine CₓN₅ under light irradiation, demonstrating that greater amounts of ROS can be generated on the NiₓSₓ-CₓN₅ hybrid. The result of the EPR analysis is in good agreement with the results of the photocatalytic performance.

![Figure 9](image-url)

**Figure 9.** (a) Trapping agent experiments for photocatalytic NO removal. ESR spectra of DMPO-⋅O₂⁻ (b) and TEMPO (c) for ROS detection.

BET analysis was first conducted to explore the factors affecting the high photocatalytic performance of NiₓSₓ-CₓN₅ compared with CₓN₅. As shown in Figure S4, the specific surface area of NiₓSₓ-CₓN₅ (10.32 m²/g) is almost equal to that of CₓN₅ (10.60 m²/g), showing that this factor cannot afford the enhanced photoactivity for NiₓSₓ-CₓN₅. Considering that nickel sulfide is often taken as an active site for H₂ production in the field of photo-and electro-catalysis, the influence of NiₓSₓ on the separation of e⁻/h⁺ pairs generated from CₓN₅ under light excitation was investigated using steady-state and time-resolved PL as well as photocurrent-time and EIS behaviors. As depicted in Figure 10a, the PL intensity of CₓN₅ is dramatically quenched by NiₓSₓ, demonstrating that the loading of NiₓSₓ can significantly restrain the e⁻/h⁺ recombination of CₓN₅ under light excitation and NiₓSₓ can serve as electron traps to facilitate the photogenerated electron transfer from CₓN₅ to NiₓSₓ [15,45]. This viewpoint is further supported by the time-resolved fluorescence spectra (TRFS) shown in Figure 10b; the PL decay rate on NiₓSₓ-CₓN₅ is slower than that of pristine CₓN₅, and the fluorescence lifetime of NiₓSₓ-CₓN₅ (11.56 ns) is longer than that of pristine CₓN₅ (8.50 ns), demonstrating that the recombination of photogenerated e⁻/h⁺ pairs on CₓN₅ is restrained by NiₓSₓ through efficient internal electron transfer [15,46]. The generation and separation of e⁻/h⁺ pairs on NiₓSₓ-CₓN₅ and CₓN₅ is also reflected in their photocurrent-time behaviors. Figure 10c shows the change tendency of photocurrent curves of the two materials along with commutative light-on and light-off operation. The high current value was recorded when the work electrode was irradiated by the Xe-lamp, and the value vanished suddenly when the light was turned down, indicating that the current is generated after the material is excited. In addition, the generation of photocurrent...
is repeatable. Moreover, the photocurrent value recorded on Ni$_{x}$S$_{y}$-C$_{3}$N$_{5}$ is much higher than that of C$_{3}$N$_{5}$, demonstrating that the separation of $e^-/h^+$ pairs in Ni$_{x}$S$_{y}$-C$_{3}$N$_{5}$ under light irradiation is greatly improved. This result is in accordance with the conclusions of the PL analysis. A smaller radius was obtained on Ni$_{x}$S$_{y}$-C$_{3}$N$_{5}$ from the EIS Nyquist plots, as shown in Figure 10d, revealing the lower charge transfer resistance of Ni$_{x}$S$_{y}$-C$_{3}$N$_{5}$ [15,47]. The above results convey that Ni$_{x}$S$_{y}$-C$_{3}$N$_{5}$ possesses quicker internal charge migration than bare C$_{3}$N$_{5}$.

![Figure 10. Comparison of steady-state (a) and time-resolved (b) fluorescence spectra as well as photocurrent-time (c) and EIS (d) behaviors of C$_{3}$N$_{5}$ and Ni$_{x}$S$_{y}$-C$_{3}$N$_{5}$.](image)

Based on the above results, the mechanism for photocatalytic H$_2$ production or NO oxidation is proposed. Under visible light irradiation, C$_{3}$N$_{5}$ is excited and generates $e^-/h^+$ pairs. Ni$_{x}$S$_{y}$ can harvest the $e^-$ on the CB of C$_{3}$N$_{5}$, and then the trapped electrons participate in subsequent surface reactions. For H$_2$ production, the collected electrons on Ni$_{x}$S$_{y}$ react with adsorbed H$_2$O molecules and H$_2$ is produced. The residual h$^+$ on the VB of C$_{3}$N$_{5}$ is consumed by TEOA, and subsequently the whole photocatalytic H$_2$ production procedure is accomplished. In the process of photocatalytic NO oxidation, the activation of O$_2$ is considered the first step according to most reported studies. The generation of ROS such as •O$_2$-, $^1$O$_2$ and •OH are enhanced by Ni$_{x}$S$_{y}$, as discussed in the above section. These ROS and the residual h$^+$ on the VB of C$_{3}$N$_{5}$ can then participate in the NO oxidation procedure along with the formation of NO$_3^-$ and NO$_2$.

3. Materials and Methods

3.1. Material Preparation

All chemicals used were purchased commercially and used without purification. C$_{3}$N$_{5}$ was prepared by heating 3-amino-1,2,4-triazole under 500 °C in air according to our previous work [27]. Generally, Ni$_{x}$S$_{y}$-C$_{3}$N$_{5}$ was synthesized by the hydrothermal method at 120 °C. In brief, C$_{3}$N$_{5}$ was dispersed in 40 mL deionized water, followed by the addition of Ni(NO$_3$)$_2$ and thioacetamide (TAA) with a mol ratio of 1:3, and then transferred into a 100 mL Teflon-lined autoclave. Finally, the autoclave was sealed and kept at 120 °C for 12 h. The precipitate was washed with distilled water and absolute ethanol several times after the autoclave cooled to room temperature. The obtained samples were dried in vacuum at 80 °C for 12 h. The loading amount of Ni$_{x}$S$_{y}$ on C$_{3}$N$_{5}$ was calculated based on
the initial input Ni ion mass fraction, and a series of Ni$_x$S$_y$-C$_3$N$_5$ hybrids with an Ni$_x$S$_y$ loading amount varying between 0.5 and 4.0 wt% were prepared by changing the amount of Ni(NO$_3$)$_2$ and TAA accordingly. Pristine Ni$_x$S$_y$ was also prepared by the same method in the absence of C$_3$N$_5$. Notably, all the materials containing Ni$_x$S$_y$ in the following section were prepared under 120 °C hydrothermal conditions unless otherwise specified.

3.2. Catalyst Characterization

XRD patterns were recorded on a powder X-ray diffractometer with Cu Ka radiation (D8 Advance Bruker Inc., Munich, Germany). TEM and HRTEM images were acquired using FEI TALOS F200. SEM and EDS mapping images were acquired using Gemini Sigma 300. The Brunauer–Emmett–Teller (BET) specific surface area was evaluated using a nitrogen adsorption–desorption apparatus (ASAP 2040, Micrometrics Inc., Norcross, GA, USA), with all samples degassed at 120 °C for 12 h prior to measurements. The valence state of each element in the catalyst was analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectroscopy. A Shimadzu UV-3100 recording spectrophotometer and fluorescence spectrometer (F-4600, Hitachi Inc., Tokyo, Japan) were used to record UV-vis diffuse reflectance (DRS) and PL spectra measurements, respectively. Time-resolved fluorescence spectra (TRFS) were obtained on an Edinburgh FLS 1000. Electron paramagnetic resonance (EPR) spectra were recorded on a JES-FA200 EPR Spectrometer. DMPO (5,5-dimethyl-1-pyrroline-N-oxide) was used as radical spin-trapped reagent for •OH and •O$_2^-$. TEMP (2,2,6,6-tetramethylpiperidine) was used as the trapping agent for $^1$O$_2$ [11].

The photocurrent and electrochemical impedance measurements were recorded on a CHI 660D electrochemical workstation (Chenhua Instrument, Shanghai, China) with a conventional three-electrode configuration. Pt foil and Ag/AgCl (saturated KCl) were used as the counter electrode and reference electrode, respectively. The working electrode was made by spreading catalyst/nafion slurry on FTO glass and 0.1 M Na$_2$SO$_4$ aqueous solution was used as the electrolyte.

3.3. Photocatalytic Activity Tests

The photocatalytic H$_2$ production rate and AQY measurements were carried out on a top-irradiated reaction vessel containing catalyst and sacrificial reagent (TEOA) connected to a closed gas system with a 300 W Xe-lamp (PLS SXE300, Beijing Perfectlight Inc., China) equipped with a cutoff filter ($\lambda > 420$ nm) or band-pass filters ($\lambda = 420, 500$ nm etc.); the operation system is shown in Figure S5. The H$_2$ production rate was detected by a GC (SP7820, TCD detector, 5 Å molecular sieve columns, and Ar carrier), and AQY values were calculated according to our previous report [27]:

\[
AQY = 2 \times \frac{\text{Number of evolved H}_2\text{ molecules}}{\text{Number of incident photons}}
\]

For photocatalytic NO removal, a continuous flow reactor under ambient conditions was adopted, as per our previous work [11]. The volume of the rectangular reactor was 4.5 L (30 cm $\times$ 15 cm $\times$ 10 cm). A 25 mg catalyst was dispersed into the mixture of ethanol and water and then transferred into a culture dish with a diameter of 12 cm, and the dish was then placed in the reactor after the solvent was evaporated. A 30 W visible LED (General Electric) was used as a light source. The gas (containing NO and air) flow rate through the reactor was controlled at 1000 mL/min by a mass flow controller with an initial NO concentration of ~600 ppb. The NO and NO$_2$ concentrations were recorded on a NO$_x$ analyzer model T200 (Teledyne API). The generation of NO$_3$$^-$ was detected by ion chromatography on Thermo DIONEX ICS-900.

4. Conclusions

In summary, a low-cost and noble-metal-free 2D Ni$_x$S$_y$-C$_3$N$_5$ hybrid photocatalyst was facially fabricated by a hydrothermal procedure under a low temperature and analyzed using a series of methods. The tight contact between 2D Ni$_x$S$_y$ and 2D C$_3$N$_5$ sheets facilitates
internal photogenerated electron transfer from C$_3$N$_5$ to Ni$_x$S$_y$, which is demonstrated by steady-state and time-resolved PL spectra as well as light-switched photocurrent behavior. The Ni$_x$S$_y$-C$_3$N$_5$ hybrid possesses multiple photocatalytic applications (H$_2$ production from water and NO removal) with high activity and stability. In particular, the optimal Ni$_x$S$_y$-C$_3$N$_5$ photocatalyst exhibits a high AQY value of 37.0% at 420 nm, exceeding Pt-C$_3$N$_5$ material and revealing the potential of the Ni$_x$S$_y$ in photocatalytic water splitting. This work not only demonstrates a simple method with which to construct a high-efficiency noble-metal-free hybrid photocatalyst, but it also exhibits the potential applications of such a photocatalyst in various fields.

**Supplementary Materials:** The following are available online at [https://www.mdpi.com/article/10.3390/catal11091089/s1](https://www.mdpi.com/article/10.3390/catal11091089/s1), Figure S1, XRD patterns of Ni$_x$S$_y$ prepared under different hydrothermal temperatures; Figure S2, XPS survey spectrum of Ni$_x$S$_y$-C$_3$N$_5$ (a) and high-resolution spectra of C 1s (b) and N 1s (c); Figure S3, Influence of mole ratio of Ni/S on the H$_2$ production activity of 3.0 wt% Ni$_x$S$_y$-C$_3$N$_5$; Figure S4, Comparison of nitrogen adsorption–desorption isotherms between C$_3$N$_5$ and Ni$_x$S$_y$-C$_3$N$_5$; Figure S5, Photograph of photocatalytic H$_2$ production system.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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