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Article

Ni nanoparticles as electron-transfer mediators and NiS_x as interfacial active sites for coordinative enhancement of H₂-evolution performance of TiO₂

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ABSTRACT

The development of efficient photocatalytic H₂-evolution materials requires both rapid electron transfer and an effective interfacial catalysis reaction for H₂ production. In addition to the well-known noble metals, low-cost and earth-abundant non-noble metals can also act as electron-transfer mediators to modify photocatalysts. However, as almost all non-noble metals lack the interfacial catalytic active sites required for the H₂-evolution reaction, the enhancement of the photocatalytic performance is limited. Therefore, the development of new interfacial active sites on metal-modified photocatalysts is of considerable importance. In this study, to enhance the photocatalytic evolution of H₂ by Ni-modified TiO₂, the formation of NiS_x as interfacial active sites was promoted on the surface of Ni nanoparticles. Specifically, the co-modified TiO₂/Ni-NiS_x photocatalysts were prepared via a two-step process involving the photoinduced deposition of Ni on the TiO₂ surface and the subsequent formation of NiS_x on the Ni surface by a hydrothermal reaction method. It was found that the TiO₂/Ni-NiS_x photocatalysts exhibited enhanced photocatalytic H₂-evolution activity. In particular, TiO₂/Ni-NiS_x(30%) showed the highest photocatalytic rate (223.74 μmol h⁻¹), which was greater than those of TiO₂, TiO₂/Ni, and TiO₂/NiS_x by factors of 22.2, 8.0, and 2.2, respectively. The improved H₂-evolution performance of TiO₂/Ni-NiS_x could be attributed to the excellent synergistic effect of Ni and NiS_x, where Ni nanoparticles function as effective mediators to transfer electrons from the TiO₂ surface and NiS_x serves as interfacial active sites to capture H⁺ ions from solution and promote the interfacial H₂-evolution reaction. The synergistic effect of the non-noble metal cocatalyst and the interfacial active sites may provide new insights for the design of highly efficient photocatalytic materials.

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1. Introduction

In recent years, photocatalytic H₂ evolution from water splitting by semiconductors has been considered a promising solution for serious energy crisis and environmental issues

[1–13]. Among various semiconductors, TiO₂ as a traditional photocatalyst has attracted enormous interest for photocatalytic H₂ evolution owing to its good chemical stability, low cost, and nontoxicity [14–25]. Unfortunately, bare TiO₂ exhibits low H₂-evolution activity from pure water owing to the rapid re-

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combination of photogenerated electron–hole pairs, which severely limits its practical applications [26–32]. Recently, surface cocatalyst modification has been regarded as one of the most ideal strategies for realizing efficient photocatalytic H₂ evolution [33–39]. Noble metals (such as Pt [20,40], Au [41,42], Ag [43,44], and Pd [45,46]) as well-known cocatalysts have been extensively demonstrated to improve the photocatalytic H₂-evolution performance of TiO₂ and other photocatalysts. The enhanced activity can mainly be attributed to the fact that the noble metals can rapidly capture and transfer electrons from the semiconductor surface. In addition to rapid electron transfer, an effective interfacial catalysis reaction for H₂ production is important for achieving highly efficient cocatalyst-modified photocatalysts [36,47,48]. Consequently, various approaches for loading catalytic active sites on the surface of noble metals have been developed [42,49,50]. For example, Chio et al. [49] reported that the adsorption of SCN[−] ions on the surface of Ag nanoparticles accelerated interfacial electron transfer to increase the activity of Ag in Ag/TiO₂ for photocatalytic H₂ production. Furthermore, our recent works confirmed that SCN[−] and Ag₂S, which were selectively loaded on metallic Au and Ag surfaces, respectively, as efficient H₂-evolution active sites greatly promoted the interfacial H₂-evolution reaction rate [42,50]. These reports clearly reveal that the synergistic effect of noble metals (such as Au and Ag) and interfacial catalytic active sites (such as SCN[−] and Ag₂S) can greatly improve the photocatalytic H₂-evolution performance of photocatalysts (such as CdS and TiO₂).

In addition to noble metals, many studies on non-noble metals as electron-transfer mediators in photocatalytic processes have been reported. For example, low-cost and earth-abundant metals (such as Cu, Bi, Co, and Ni) have been used to modify photocatalysts [51–55]. Because almost all these metals lack interfacial catalytic active sites, methods for loading effective catalytic active sites on non-noble metals have been extensively explored [54,56,57]. For instance, Lv et al. [56] prepared a graphene-Cu-TiO₂ photocatalyst with Cu and graphene as cocatalysts, and the photocatalytic H₂-evolution performance of TiO₂ with the Cu-graphene synergetic cocatalyst was approximately 5 times higher than that of graphene-TiO₂. Furthermore, Jiang et al. [54] reported the successful coupling of monodisperse Bi nanoparticles with g-C₃N₄ to increase the photocatalytic performance for NO removal. In fact, a shell of amorphous bismuth oxide (BiO_x) was formed on the surface of Bi owing to the rapid oxidation of Bi when exposed to air at room temperature. As a result, the improved performance of g-C₃N₄ was attributed to the synergistic effect of Bi and BiO_x. Moreover, Wen et al. [57] demonstrated that the simultaneous loading of metallic Ni interface layers and amorphous NiS dual-layer electron cocatalysts enhanced the photocatalytic H₂-evolution performance of g-C₃N₄. The above reports strongly demonstrated a general and very effective strategy for improving the photocatalytic performance of various photocatalysts, namely, the simultaneous loading of non-noble metals (such as Cu, Bi, and Ni) and other cocatalysts (such as graphene, BiO_x, and NiS) that exhibit excellent synergistic effects. In this case, the non-noble metals acting as electron co-

catalysts (or electron-transfer mediators) can rapidly transfer electrons, while the other cocatalysts function as interfacial catalytic active sites for promoting the interfacial catalytic reaction. However, very few reports on the interfacial active sites of non-noble-metal-modified photocatalysts are available, and the mechanism of the improved performance remains unclear. Therefore, it is quite important to develop new interfacial active sites and determine a reasonable mechanism for the enhanced H₂-evolution activity of metal-modified photocatalysts.

In this study, highly efficient TiO₂ photocatalysts co-modified with Ni nanoparticles as electron-transfer mediators and NiS_x as interfacial catalytic active sites (denoted as TiO₂/Ni-NiS_x) were synthesized via a two-step process including the photoinduced deposition of Ni nanoparticles on the TiO₂ surface and the subsequent formation of NiS_x by a hydrothermal reaction method. It was found that the TiO₂/Ni-NiS_x photocatalyst exhibited enhanced photocatalytic H₂-evolution activity compared with TiO₂, TiO₂/Ni, and TiO₂/NiS_x. Based on the experimental results, a synergistic effect mechanism of Ni and NiS_x was proposed to account for the improved photocatalytic performance. This work may provide new insights for the smart design and development of highly efficient photocatalytic materials for various potential applications.

2. Experimental

All chemicals were of analytical grade. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), titanium dioxide (TiO₂-P25), sodium sulfide (Na₂S), and ethanol (CH₃CH₂OH) were purchased from Shanghai Chemical Reagent Ltd. (China).

2.1. Preparation of photocatalysts

Untreated commercial TiO₂ (P25) was used as the TiO₂ photocatalyst.

The Ni-modified TiO₂ photocatalyst (TiO₂/Ni) was prepared using a photodeposition method. In a typical experiment, 50 mg of TiO₂ powder was dispersed in 80 mL of ethanol as a sacrificial reagent. To this solution, 0.5 mL of Ni(NO₃)₂/ethanol solution (3 mg mL^{−1}) was added, such that the amount of Ni with respect to TiO₂ was controlled at 3 wt%. After it was bubbled with nitrogen for 15 min to remove dissolved oxygen, the suspension was illuminated using four low-power LEDs (3 W, 365 nm, Shenzhen Lamplic Science Co. Ltd., China) for 120 min under stirring. Finally, the products were collected by filtration, washed three times with ethanol, and dried at 40 °C for 24 h to obtain the TiO₂/Ni photocatalyst.

The TiO₂/Ni-NiS_x photocatalysts were prepared via the formation of NiS_x from Ni under hydrothermal conditions. First, 50 mg of the TiO₂/Ni powder was dispersed in 15 mL of distilled water under stirring, and to this a certain amount of Na₂S solution (0.1 mol L^{−1}) was added. After vigorously stirring for 60 min, the resulting mixture was transferred into a Teflon-lined stainless-steel autoclave and heated at 170 °C for 10 h. After naturally cooling to room temperature, the sample was washed with distilled water three times and dried at 40 °C overnight to obtain the TiO₂/Ni-NiS photocatalysts. To investigate the effect

of the NiS_x concentration on the photocatalytic performance of TiO_2/Ni photocatalysts, the amount of Ni converted to NiS_x with respect to TiO_2 was controlled at 10 wt%, 30 wt%, and 50 wt%. The resulting samples were denoted as $\text{TiO}_2/\text{Ni-NiS}_x(10\%)$, $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$, and $\text{TiO}_2/\text{Ni-NiS}_x(50\%)$, respectively. For comparison, an NiS_x -modified TiO_2 ($\text{TiO}_2/\text{NiS}_x$) photocatalyst was prepared using a method similar to that used for the preparation of $\text{TiO}_2/\text{Ni-NiS}_x$, and excess Na_2S solution was added to induce the complete conversion of Ni to NiS_x .

2.2. Characterization

X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima III X-ray diffractometer (Japan) with a $\text{Cu K}\alpha$ radiation source and at a scan rate (2θ) of $10^\circ \text{ min}^{-1}$. The morphologies of various samples were observed by field emission scanning electron microscopy (FESEM, JSM-7500, JEOL, Japan), and energy-dispersive X-ray spectroscopy (EDS) results were recorded using an X-Max 50 EDS detector (Oxford Instruments, UK). The morphological features were further examined by high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan). Moreover, high-angle annular dark-field (HAADF) TEM images and EDS mapping were acquired using an electron microscope (TitanTM Themis 200, FEI, USA) with an energy-dispersive X-ray spectrometer fitted on the microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi system (Thermo Scientific, UK) with a $\text{Mg K}\alpha$ source. All the binding energies were referenced to the C 1s peak of surface adventitious carbon at 284.8 eV. UV-vis absorption spectra were collected with a UV-vis spectrophotometer (UV-2450, Shimadzu, Japan) using BaSO_4 as a reflectance standard.

2.3. Photocatalytic H_2 -evolution activity

The photocatalytic H_2 -evolution activity of the samples was evaluated using a method similar to that used in our previous reports [16,50]. The experimental details were as follows. The photocatalyst (50 mg) was dispersed in 80 mL of ethanol solution (25 vol%) in a 150 mL three-necked Pyrex flask under constant stirring at room temperature. Four low-power LEDs (3 W, 365 nm, Shenzhen Lamplic Science Co. Ltd., China) placed 3 cm away from the reactor were used as the irradiation source to trigger the photocatalytic reaction. Before each experiment, the system was bubbled with nitrogen for 15 min to remove dissolved oxygen. Finally, gas (0.4 mL) was intermittently sampled through a septum, and the amount of hydrogen was analyzed using a gas chromatograph (Shimadzu GC-2014C, Japan, with nitrogen as a carrier gas) equipped with a 5 Å molecular sieve column and a thermal conductivity detector. The quantum efficiency (QE) was calculated according to the following equation: $\text{QE} (\%) = \text{number of reacted electrons} / \text{number of incident photons} \times 100 = \text{number of evolved } \text{H}_2 \text{ molecules} \times 2 / \text{number of incident photons} \times 100$.

2.4. Photoelectrochemical measurements

Photoelectrochemical (PEC) measurements were conducted on an electrochemical workstation (CHI660E, Shanghai Chenhua, China). All the PEC measurements were performed in a 0.5 mol L^{-1} Na_2SO_4 electrolyte solution using a standard three-electrode configuration (a platinum plate as the counter electrode, a standard Ag/AgCl (saturated KCl solution) electrode as the reference electrode, and the working electrode). The working electrode was prepared on fluorine-doped tin oxide (FTO) conductor glass as in our previous works [42,50]. Linear sweep voltammetry (LSV) curves were obtained in the potential range of -0.4 to -1.4 V (vs Ag/AgCl) at a 5 mV s^{-1} scan rate without light irradiation. The i - t curves were collected at the bias potential of the open circuit (approximately -0.2 V) during repeated ON/OFF illumination cycles. The electrochemical impedance spectra were collected in the frequency range of 0.001 – 10^6 Hz with an ac amplitude of 10 mV at the open circuit voltage.

3. Results and discussion

3.1. Synthesis strategy for $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalysts

In this work, the steps for the preparation of $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalysts can be described as the initial photodeposition of metallic Ni nanoparticles on the TiO_2 surface and the subsequent formation of NiS_x on the Ni surface, as shown in Fig. 1. First, the TiO_2 powder (Fig. 1(A-a)) is dispersed in anhydrous ethanol to form a white suspension (Fig. 1(B-a)). After the addition of the $\text{Ni}(\text{NO}_3)_2$ /ethanol solution, $\text{Ni}(\text{II})$ ions are reduced to form metallic Ni nanoparticles and then photodeposited on the TiO_2 surface under illumination to obtain TiO_2/Ni [58] (Fig. 1(A-b)). In this case, the color of TiO_2/Ni suspension changes to gray (Fig. 1(B-b)), indicating the successful deposition of Ni nanoparticles on the TiO_2 surface. Furthermore, when the resultant TiO_2/Ni sample is redispersed in an Na_2S solution and treated in a hydrothermal autoclave at 170°C under autogenous pressure, NiS_x is gradually generated on the surface of the Ni nanoparticles by the effective reaction of metallic Ni and S^{2-} [59] to form the $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalyst (Fig. 1(A-c)). Owing to the formation of the black-colored NiS_x phase, the final $\text{TiO}_2/\text{Ni-NiS}_x$ sample shows an obvious gray-black color (Fig.

Fig. 1. Graphical illustration for the synthesis of various samples. (a) TiO_2 ; (b) TiO_2/Ni ; (c) $\text{TiO}_2/\text{Ni-NiS}_x$.

1(B-c)). Therefore, it is believed that $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalysts were successfully prepared using the above photodeposition and hydrothermal method.

3.2. Morphologies and microstructures of $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalysts

To confirm the successful synthesis of $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalysts, the as-prepared samples were characterized by XRD, FESEM, and TEM. Fig. 2 exhibits the XRD patterns of all samples. The diffraction peaks of pure TiO_2 (Fig. 2(a)) can be indexed to anatase TiO_2 (JCPDS 21-1272) and rutile TiO_2 (JCPDS 21-1276). The TiO_2/Ni (Fig. 2(b)), $\text{TiO}_2/\text{Ni-NiS}_x$ (Fig. 2(c–e)), and $\text{TiO}_2/\text{NiS}_x$ (Fig. 2(f)) samples display slightly weaker peak intensities than pure TiO_2 , which might be ascribed to the successful loading of Ni and NiS_x cocatalysts on the TiO_2 surface. However, the lattice and phase structures of TiO_2 are well maintained, suggesting that the loading of Ni and NiS_x cocatalysts on the TiO_2 surface has no obvious effect on the crystal structure of TiO_2 . Moreover, no diffraction peak of Ni is observed for TiO_2/Ni , which may be because of the main characteristic peak of Ni at $\sim 44.5^\circ$ being shielded by the (210) peak of rutile TiO_2 at $\sim 44.1^\circ$. Furthermore, the NiS_x -containing samples do not exhibit diffraction peaks corresponding to nickel sulfide owing to its limited amount and amorphous state.

Fig. 3 shows FESEM images of the TiO_2 , TiO_2/Ni , $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$, and $\text{TiO}_2/\text{NiS}_x$ samples. The TiO_2 sample (Fig. 3(A)) exhibits an irregular morphology with a wide size range of 20–60 nm. The TiO_2/Ni sample (Fig. 3(B)) has a similar morphology to that of pure TiO_2 . However, the corresponding EDS result reveals a new Ni signal in addition to Ti and O signals, indicating the successful loading of Ni. For the $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$ (Fig. 3(C)) and $\text{TiO}_2/\text{NiS}_x$ (Fig. 3(D)) samples, new S signals are observed and the amount of S increases from 0.19 at% to 0.87 at%, although these samples also show similar morphologies to those of TiO_2 and TiO_2/Ni samples. To further observe the morphology and structure of $\text{TiO}_2/\text{Ni-NiS}_x$, TEM images of $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$ were recorded, as illustrat-

Fig. 2. XRD patterns and the typical diffraction peaks of various samples (a) TiO_2 ; (b) TiO_2/Ni ; (c) $\text{TiO}_2/\text{Ni-NiS}_x(10\%)$; (d) $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$; (e) $\text{TiO}_2/\text{Ni-NiS}_x(50\%)$; (f) $\text{TiO}_2/\text{NiS}_x$.

Fig. 3. FESEM/EDS results of various samples. (A) TiO_2 ; (B) TiO_2/Ni ; (C) $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$; (D) $\text{TiO}_2/\text{NiS}_x$.

ed in Fig. 4. Fig. 4(A) and (B) reveal obvious lattice planes with spacings of ~ 0.352 and ~ 0.203 nm, which correspond to the (101) plane of anatase TiO_2 and the (111) plane of metallic Ni [15,58], respectively. In addition, NiS_x in an amorphous state is homogeneously dispersed on the surface of metallic Ni, and Ni-NiS_x is closely connected to the TiO_2 nanoparticles. Furthermore, the elemental mapping results (Fig. 4(C–C5)) also demonstrate the presence of Ni-NiS_x on the TiO_2 surface. It is clear that S is mainly distributed on the Ni surface and the density of Ni is obviously higher than that of S, suggesting that NiS_x has been successfully loaded on the surface of the metallic Ni nanoparticles. According to the above results, metallic Ni and NiS_x were successfully loaded on the TiO_2 surface to form $\text{TiO}_2/\text{Ni-NiS}_x$ by the present facile strategy.

The successful loading of Ni and NiS_x on the TiO_2 surface

Fig. 4. (A, B) TEM images and (C–C5) HAADF-STEM and EDS mapping images of $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$.

Fig. 5. (A) XPS survey spectra and the high-resolution XPS spectra of (B) Ni 2p and (C) S 2p for various samples. (a) TiO_2 ; (b) TiO_2/Ni ; (c) $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$; (d) $\text{TiO}_2/\text{NiS}_x$.

was demonstrated by XPS, which revealed the component elements and their chemical states in the $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalyst. The XPS survey spectra in Fig. 5(A) show that the $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalyst is composed of Ti, O, C, S, and Ni. The TiO_2/Ni sample (Fig. 5(B-b)) reveals a peak at around 852.9 eV, indicating the presence of metallic Ni [58], in addition to peaks at the binding energies of 855.7 and 873.2 eV, which are attributed to Ni 2p_{3/2} and Ni 2p_{1/2} of Ni(II) [15,60], respectively. For $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$ (Fig. 5(B-c)), the peak intensity of metallic Ni gradually decreases while that of Ni(II) increases, suggesting that NiS_x is formed from Ni nanoparticles by the effective reaction of metallic Ni and S^{2-} under a high temperature and autogenous pressure [59]. Further investigation indicates that $\text{TiO}_2/\text{NiS}_x$ (Fig. 5(B-d)) exhibits a lower peak intensity of metallic Ni than $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$ owing to the greater extent of conversion from Ni to Ni(II). As shown in Fig. 5(C), the peak at around 167.9 eV can be attributed to S^{2-} in NiS_x . With increasing amounts of NiS_x , the peak intensity of S is obviously enhanced. Therefore, the XPS results strongly demonstrate that the $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalyst was successfully prepared.

UV-vis spectra can be used to determine the optical absorption of the samples. As shown in Fig. 6, the absorption boundary of the white TiO_2 sample (Fig. 6(a)) is around 390 nm, in accordance with the band energy of TiO_2 [15,48,61]. Compared

with pure TiO_2 , the deep-gray-colored TiO_2/Ni sample (Fig. 6(b)) shows significantly enhanced visible-light absorption, which can be attributed to the absorption of metallic Ni. When Ni is partly converted into NiS_x , the color of the $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$ sample (Fig. 6(c)) becomes slightly lighter than that of the TiO_2/Ni sample, leading to a decreased absorption intensity in the visible region. Once Ni is completely converted into NiS_x , the $\text{TiO}_2/\text{NiS}_x$ sample (Fig. 6(d)) turns black and exhibits enhanced optical absorption. Based on the above results, it can be concluded that the loading of metallic Ni and NiS_x has a considerable influence on the optical absorption properties of TiO_2 .

3.3. Photocatalytic performance and mechanism

The photocatalytic performance was evaluated by detecting the H_2 -evolution rate of various samples under UV-light irradiation (Fig. 7(A)). Pure TiO_2 (Fig. 7(A-a)) exhibits a low photocatalytic H_2 -evolution activity with a rate of only $10.10 \mu\text{mol h}^{-1}$ and a QE of 0.58%. After the surface photodeposition of metallic Ni nanoparticles, the resultant TiO_2/Ni sample (Fig. 7(A-b)) shows an improved H_2 -evolution rate ($27.91 \mu\text{mol h}^{-1}$ with a QE of 1.59%) owing to the rapid transfer of photogenerated electrons from the TiO_2 surface to the metallic Ni nanoparticles. With the formation of NiS_x on the metallic Ni surface, the H_2 -evolution performance of all the $\text{TiO}_2/\text{Ni-NiS}_x$ samples is further improved. In particular, $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$ (Fig. 7(A-d)) achieves the highest photocatalytic rate ($223.74 \mu\text{mol h}^{-1}$ with a QE of 12.78%), which is greater than those of TiO_2 , TiO_2/Ni , and $\text{TiO}_2/\text{Ni-NiS}_x$ (Fig. 7(A-f)) by factors of 22.0, 8.0, and 2.2, respectively. To verify the stability of H_2 evolution, a

Fig. 6. UV-vis absorption spectra of various samples. (a) TiO_2 ; (b) TiO_2/Ni ; (c) $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$; (d) $\text{TiO}_2/\text{NiS}_x$.

Table 1

The H_2 -evolution rate and quantum efficiency (QE) of the various samples.

Sample	H_2 -evolution rate ($\mu\text{mol h}^{-1}$)	QE (%)
TiO_2	10.10	0.58
TiO_2/Ni	27.91	1.59
$\text{TiO}_2/\text{Ni-NiS}_x(10\%)$	66.42	3.80
$\text{TiO}_2/\text{Ni-NiS}_x(30\%)$	223.74	12.78
$\text{TiO}_2/\text{Ni-NiS}_x(50\%)$	120.80	6.90
$\text{TiO}_2/\text{NiS}_x$	99.75	5.70

Fig. 7. (A) The photocatalytic H₂-evolution activity of various samples of (a) TiO₂, (b) TiO₂/Ni, (c) TiO₂/Ni-NiS_x(10%), (d) TiO₂/Ni-NiS_x(30%), (e) TiO₂/Ni-NiS_x(50%), and (f) TiO₂/NiS_x; (B) The cycling runs of the photocatalytic H₂-evolution activity of the TiO₂/Ni-NiS_x(30%).

recycling test was performed with the TiO₂/Ni-NiS_x(30%) sample and the results are displayed in Fig. 7(B). After recycling four times, the TiO₂/Ni-NiS_x(30%) sample still shows steady and highly efficient H₂ evolution, indicating that this sample has good recyclability.

The above results demonstrated that the loading of Ni-NiS_x on the TiO₂ surface effectively improved the photocatalytic H₂-evolution activity of the TiO₂ photocatalyst. Hence, it is very valuable and meaningful to explore the photocatalytic H₂-evolution mechanism of TiO₂/Ni-NiS_x (Fig. 8). Pure TiO₂ usually exhibits a low photocatalytic H₂-evolution activity owing to the rapid recombination of electron-hole pairs and the slow interfacial reaction. After the deposition of highly conductive Ni on the TiO₂ surface, the TiO₂/Ni sample shows a slightly improved photocatalytic H₂-evolution activity owing to the rapid transfer of photogenerated electrons by metallic Ni. However, the TiO₂/Ni sample still shows a limited performance because of the lack of interfacial catalytic active sites for the photocatalytic H₂-evolution reaction. Interestingly, it has been reported that nickel sulfide can act as interfacial catalytic active sites for photocatalytic H₂ evolution owing to the fact that interfacial or unsaturated S atoms can efficiently capture H⁺ ions from solution [62–65]. Accordingly, loading NiS_x on the Ni surface significantly enhanced the photocatalytic activity of the resultant TiO₂/Ni-NiS_x photocatalysts. The improved performance can be attributed to the excellent synergistic effect of Ni as an electron-transfer cocatalyst and NiS_x as interfacial active sites. In this case, after the implantation of the highly conductive Ni nanoparticles between the TiO₂ photocatalyst and the NiS_x cocatalysts, the photogenerated electrons in the conduction band of TiO₂ can be rapidly transferred to metallic Ni ow-

ing to the formation of intimate Schottky junctions between metallic Ni and TiO₂. Subsequently, the collected electrons in metallic Ni with sufficiently high potentials can be driven to NiS_x for the H₂-evolution reaction because the overpotential of metallic Ni is much higher than that of NiS_x [57]. Furthermore, NiS_x functions as interfacial catalytic active sites to adsorb H⁺ ions from solution effectively and further promote the subsequent interfacial H₂-evolution reaction. Therefore, the excellent synergetic effect between metallic Ni and NiS_x on the TiO₂ surface can simultaneously achieve the effective transfer of photogenerated electrons and the interfacial H₂-evolution reaction.

To confirm that Ni and NiS_x promote the H₂-evolution reaction, the photoelectrocatalytic performance of various samples was investigated. Using LSV measurements (Fig. 9(A)), the TiO₂/Ni sample was found to show a lower overpotential than the TiO₂ sample owing to the fast transfer of electrons by metallic Ni. For the TiO₂/Ni-NiS_x(30%) sample, the overpotential dramatically decreases, suggesting that NiS_x forms better interfacial active sites than metallic Ni, thus providing excellent kinetics for efficiently reducing H⁺ to H₂. However, the TiO₂/NiS_x sample displays a slightly increased overpotential compared with the TiO₂/Ni-NiS_x(30%) sample. This difference can be attributed to the lack of an electron-transfer mediator in the TiO₂/NiS_x sample, resulting in a slow rate of electron transfer that affects the subsequent interfacial H₂-evolution reaction. In fact, efficient photocatalytic H₂-evolution materials require not only rapid electron transfer but also an effective interfacial catalysis reaction for H₂ production. Therefore, both the metallic Ni electron-transfer cocatalyst and the NiS_x interfacial active sites are important for the H₂-evolution reaction of TiO₂. Furthermore, the transient photocurrent responses (Fig. 9(B)) and electrochemical impedance spectra (Fig. 9(C)) of the TiO₂/Ni-NiS_x(30%) sample exhibit the highest photocurrent density and the smallest arc radius, respectively, among the various samples, indicating that this sample has the highest separation efficiency of photogenerated carriers. According to the above results, it can be concluded that the excellent synergistic effect of metallic Ni nanoparticles as electron-transfer cocatalysts and NiS_x as interfacial active sites in the TiO₂/Ni-NiS_x system contributes to its enhanced photocatalytic H₂-evolution activity.

Fig. 8. The photocatalytic H₂-evolution mechanism of TiO₂/Ni-NiS_x.

Fig. 9. (A) Linear sweep voltammetry (LSV) curves, (B) transient photocurrent responses, and (C) electrochemical impedance spectra (EIS) of various samples. (a) TiO_2 ; (b) TiO_2/Ni ; (c) $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$; (d) $\text{TiO}_2/\text{NiS}_x$.

4. Conclusions

$\text{TiO}_2/\text{Ni-NiS}_x$ photocatalysts were prepared via a two-step process involving the photodeposition of Ni on the TiO_2 surface and the subsequent formation of NiS_x on the Ni surface by a hydrothermal reaction method. The resultant $\text{TiO}_2/\text{Ni-NiS}_x(30\%)$ sample achieved the highest photocatalytic activity, which was greater than those of TiO_2 , TiO_2/Ni , and $\text{TiO}_2/\text{NiS}_x$ by factors of 22.2, 8.0, and 2.2, respectively. The improved H_2 -evolution performance of $\text{TiO}_2/\text{Ni-NiS}_x$ was attributed to the excellent synergistic effect of Ni and NiS_x , where the Ni nanoparticles functioned as an effective mediator to transfer electrons from the TiO_2 surface and NiS_x served as interfacial active sites to capture H^+ ions from solution and promote the H_2 -evolution reaction. This study not only provided the promising idea of using the synergistic effect of non-noble metal cocatalysts and interfacial active sites but also highlighted the potential applications of highly efficient TiO_2 photocatalysts for energy transformation.

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Graphical Abstract

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Ni nanoparticles as electron-transfer mediators and NiS_x as interfacial active sites for coordinative enhancement of H_2 -evolution performance of TiO_2

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The $\text{TiO}_2/\text{Ni-NiS}_x$ photocatalyst exhibited enhanced H_2 -evolution performance due to the excellent synergistic effect of Ni nanoparticles as electron-transfer mediators and NiS_x as interfacial active sites to promote H_2 evolution.

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Ni纳米粒子作为电子转移剂和NiS_x作为产氢界面活性位协同增强TiO₂光催化制氢性能

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摘要: 作为一种传统的半导体光催化材料, TiO₂因具有低价易得、无毒性及稳定性好等优势而一直受到研究者的关注. 理论上, TiO₂的能带结构可满足分解水制氢的条件. 然而, 研究发现TiO₂本身的光催化制氢性能较低, 主要是由于TiO₂被光激发后生成的电子和空穴尚未到达材料表面参与反应, 就在其体相内发生复合, 导致电子参与有效光催化制氢反应的几率较低. 近年来, 为提高TiO₂的制氢性能, 研究者主要通过半导体耦合、元素掺杂、形貌调控和助剂修饰等方式对TiO₂进行改性. 其中, 助剂表面修饰由于用量少、条件温和并且对主体材料结构影响很小而成为一种常见和有效的改性手段. 最常用的电

子助剂是贵金属如Au, Ag, Pt和Pd. 当TiO₂表面沉积微量的贵金属纳米粒子时, 导带上的光生电子被贵金属捕获并迅速转移, 将H⁺在贵金属表面发生界面还原反应生成H₂, 从而有效提高了制氢效率. 除了贵金属电子助剂外, 还有一些价格较低、产量丰富的非贵金属如Co, Cu, Ni和Bi等也可以作为电子助剂应用于光催化制氢, 在提高制氢性能的同时也降低了光催化剂的成本. 但在大多数情况下, 这些金属材料(除贵金属Pt以外)本身都不能作为有效的界面催化活性位点, 表现出较低的界面析氢速率, 导致金属-半导体光催化材料的产氢活性低. 因此, 进一步对金属表面进行改性、增加界面催化活性位点、促进其界面产氢催化反应, 对于提高金属-半导体光催化材料的制氢性能非常重要.

在金属作为电子传输介质修饰半导体材料的制氢过程中, 电子传输介质快速转移光生电子和有效捕获溶液中的H⁺直接进行界面催化还原反应生成H₂这两个步骤都十分关键. 在制备金属-半导体光催化材料时, 对于通常的金属材料本身都不能作为界面催化活性位点、缺乏有效的界面产氢活性位点的问题, 可通过在金属表面进一步修饰作为界面催化活性位点的基团或离子来解决. 本文采用先将Ni纳米粒子光沉积在TiO₂表面、再在水热条件下在Ni纳米粒子表面生成NiS_x的两步法合成了以Ni作为电子转移介质、以NiS_x作为界面催化活性位点共修饰的高效TiO₂光催化剂(称为TiO₂/Ni-NiS_x). 研究表明, 优化后的TiO₂/Ni-NiS_x光催化的最高制氢速率(223.74 μmol h⁻¹)分别是纯TiO₂, TiO₂/Ni和TiO₂/NiS_x样品的22.2, 8.0和2.2倍. 性能增强的原因是Ni纳米粒子作为电子传输体、NiS_x作为界面催化活性位点同时提高了光生电子的转移速率和界面催化反应速率, 即Ni和NiS_x两者协同作用增强了TiO₂光催化制氢性能. 这种非贵金属助剂和界面活性位点协同作用的方法为设计高制氢性能催化剂提供了新的思路, 并有望在光催化领域得到应用.

关键词: 二氧化钛; 电子转移剂; 界面活性位; 协同作用; 光催化制氢

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