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Integrating noble-metal-free NiS cocatalyst with a semiconductor heterojunction composite for efficient photocatalytic H₂ production in water under visible light

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ABSTRACT

Photocatalytic water splitting is an economical and sustainable pathway to use solar energy for large-scale H₂ production. We report a highly efficient noble-metal-free photocatalyst formed by integrating amorphous NiS with a CdS nanorods (NRs)/ZnS heterojunction material for photocatalytic H₂ production in water under visible light irradiation ($\lambda > 420$ nm). The results show that the photocatalytic H₂ production rate reaches an optimal value of up to 574 $\mu\text{mol}\cdot\text{h}^{-1}$ after the loading of NiS, which is more than 38 times higher than the catalytic activity of pure CdS NRs. The average apparent quantum yield is $\sim 43.2\%$ during 5 h of irradiation by monochromatic 420 nm light. The present study demonstrates the advantage of integration strategies to form not only semiconductor heterojunctions but also photocatalyst-cocatalyst interfaces to enhance the catalytic activity for photocatalytic H₂ production.

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1. Introduction

Photocatalytic H₂ production from water splitting is an attractive approach for solar energy conversion [1,2]. Since the first report of water splitting by TiO₂ electrode 1972 [3], great efforts have been devoted to the development of TiO₂-based photocatalysts [4–12]. Unfortunately, TiO₂ can only absorb ultraviolet light owing to its wide band gap. Therefore, photocatalysts that are active for H₂ evolution under visible light irradiation are highly desirable. Among these visible light-responsive photocatalysts, CdS has proven to be a promising candidate for photocatalytic H₂ production, benefiting from its good absorption of visible light and sufficiently nega-

tive conductive band potential for proton reduction [13–17]. However, CdS alone usually suffers from rapid recombination of photogenerated charge carriers and photocorrosion, which hampers its activity and practical application [15,18]. Many approaches have been developed to address this issue, including doping metal elements [19], loading a cocatalyst [20–22], and fabricating heterojunctions with other suitable semiconductors [23–27]. In recent years, the formation of a CdS/ZnS heterojunction has been investigated for visible light-driven photocatalytic H₂ production [28–31] and was found to enhance the photocatalytic H₂ production. However, the photocatalytic efficiency of these CdS-based systems remains quite low.

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Alternatively, noble-metal-based cocatalysts, such as Pt and PdS, have been loaded on a CdS/ZnS nanocrystal photocatalyst to further enhance the performance for photocatalytic H₂ production [28]. However, the high cost and scarcity of these cocatalysts limits their practical application on a large scale. Therefore, it is highly desirable to develop active, robust, and low-cost noble-metal-free cocatalysts for H₂ production. Among these noble-metal-free cocatalysts, NiS has been demonstrated to be an efficient cocatalyst over CdS [22,32,33], C₃N₄ [34–36], and Cd_{1-x}Zn_xS [37,38] for H₂ production. However, there have been no reports on the H₂ production over a noble metal-free NiS cocatalyst modified by CdS NRs/ZnS heterojunctions.

In this study, we report a highly efficient ternary hybrid photocatalyst obtained by integrating amorphous NiS nanoparticles with a CdS NRs/ZnS heterojunction through a facile chemical deposition loading method for photocatalytic H₂ production in an aqueous Na₂S/Na₂SO₃ solution under visible light irradiation. Under optimal conditions, the rate for H₂ production is improved more than 38 times when compared with pure CdS and the average apparent quantum yield is 43.2% at 420 nm. A possible mechanism for the enhanced performance is proposed.

2. Experimental

2.1. Materials

CdCl₂·2.5H₂O (99.0%), thiourea (NH₂CSNH₂, 99.0%), ethylenediamine (C₂H₄(NH₂)₂, 99.0%), NiCl₂·6H₂O (98.0%), Zn(NO₃)₂·6H₂O (99.0%), Na₂S·9H₂O (98.0%), and Na₂SO₃ (97.0%) were purchased from Innochem or Aldrich and used without further purification.

2.2. Synthesis of the photocatalysts

CdS NRs and CdS NRs/ZnS composites were synthesized according to our previous reports with slight modification [21,29]. To prepare the CdS NRs, 10.125 mmol of CdCl₂·2.5H₂O and 30.375 mmol of thiourea (CH₄N₂S) were added into a 100-mL Teflon-lined autoclave filled with 60 mL of ethylenediamine. The autoclave was maintained at 160 °C for 48 h and allowed to cool to room temperature. Yellow solid products were collected by centrifugation, and washed with distilled water and ethanol for several times. The final product was then dried at 60 °C overnight. In a typical preparation procedure for CdS NRs/ZnS, 101 mg (0.7 mmol) CdS NRs and 20 mg (0.095 mmol) citric acid were added to 50 mL distilled water. The mixture was ultrasonicated for 10 min and then maintained at 40 °C for 2 h with stirring. After cooling to room temperature, 20 mL aqueous solution of 20.8 mg (0.07 mmol) of Zn(NO₃)₂·6H₂O was slowly added into the above reaction solution, followed by stirring for another hour. Next, 20 mL aqueous solution containing 0.14 mmol Na₂S was slowly added to the solution and the solution was then stirred for 0.5 h. Finally, the product was collected by centrifugation and washed with water and ethanol three times each and dried under vacuum overnight to obtain the product.

Various amounts of NiS were loaded onto the CdS NRs/ZnS samples by in-situ chemical deposition. In a typical procedure, *x* (*x* = 0, 10, 100, 400, 1000) μL NiCl₂ aqueous solution (20 mmol/L) was added dropwise to a suspension of the CdS NRs/ZnS photocatalyst (2.0 mg) dispersed in 0.25 mol/L Na₂S/0.35 mol/L Na₂SO₃ solution just before the photocatalytic H₂ production experiment, and the corresponding samples were labelled as N0, N1, N2, N3, N4, respectively. For comparison, NiS modified CdS NRs was also prepared in a similar procedure except for the addition of CdS NRs instead of CdS NRs/ZnS, and the resulting sample was referred to as CN. The 1 wt% Pt-modified CdS/ZnS (Pt/N0) sample was prepared according to a previous report [42].

2.3. Characterization

The crystal diffraction patterns of the photocatalyst samples were investigated by powder X-ray diffraction (XRD, D/max-TTR III) using graphite monochromatized Cu K_α radiation of 1.54178 Å, operating at 40 kV and 200 mA. The scanning rate was 10° min⁻¹ from 10° to 70° (2θ). Scanning electron microscopy (SEM) was performed on a JSM-6700F microscope. Transmission electron microscopy (TEM) images were collected on a JEM-2010 electron microscope operated at an acceleration voltage of 200 kV. The UV-vis diffuse reflectance spectra were obtained using a UV-visible spectrophotometer (SOLID 3700 UV-vis spectrometer). X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 250 X-ray photoelectron spectrometer.

2.4. Photocatalytic H₂ production

Photocatalytic H₂ production experiments were carried out in a 50 mL round-bottom flask at room temperature. A 300 W Xe-lamp equipped with a 420 nm cut-off filter was used to provide the visible light irradiation. In a typical photocatalytic reaction, 2.0 mg of the photocatalyst powder sample was dispersed in a 20 mL aqueous solution containing 0.25 mol/L Na₂S and 0.35 mol/L Na₂SO₃. Before irradiation, the solution was bubbled with high purity nitrogen for 15 min to remove the air. Methane was used in the reactor as the internal standard. The amount of evolved H₂ was determined by gas chromatography (GC) equipped with a TCD detector. The apparent quantum yield (AQY) was measured using a 300-W Xe-lamp equipped with a 420 nm (±5 nm) bandpass cut-off filter. The light intensity was approximately 8.9 mW cm⁻² and the illuminated area for the reactor was approximately 1.44 cm². The AQY was calculated based on the following equation:

$$\begin{aligned} \text{AQY}(\%) &= \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\% \\ &= \frac{\text{number of evolved H}_2 \text{ molecules} \times 2}{\text{number of incident photons}} \times 100\% \end{aligned}$$

2.5. Photocurrent measurement

Photocurrent experiments were conducted on a CHI 602E instrument in a standard three-electrode system with the pho-

Fig. 1. Powder XRD patterns of CdS, N0, N2, and NiS samples.

to catalyst-coated FTO as the working electrode (an active area of 1.0 cm²). A Pt wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. A 300-W Xe lamp with a cut-off filter ($\lambda > 420$ nm) was used as the light source, and the electrolyte was sodium sulfate (Na₂SO₄, 0.5 mol L⁻¹) solution. The applied potential for the measurement was 0 V versus Ag/AgCl (saturated KCl).

3. Results and discussion

The crystal structures of the as-prepared photocatalyst samples were revealed by powder XRD measurements. Fig. 1 shows the XRD patterns of CdS, N0 (CdS/ZnS), N2

(NiS-CdS/ZnS sample with an optimal amount of NiS) and NiS samples. It was clearly seen that all the diffraction peaks could be well indexed to a hexagonal structure (JCPDS #77-2306) for the CdS sample, which indicated the formation of crystalline hexagonal CdS. The N0 sample showed patterns similar to CdS but had no diffraction peaks from ZnS, owing to the low content and weak crystallization of ZnS in N0, which was consistent with our previous results [29]. NiS was introduced to prepare the N2 sample but the diffraction peaks still showed no significant changes and no obvious crystalline NiS peaks were observed. For comparison, the XRD patterns of pure NiS prepared by the same method were also collected and no appreciable diffraction peaks were observed, which indicated the amorphous nature of NiS under the present conditions.

SEM measurements were employed to investigate the morphologies of different samples. Fig. 2(a) shows the SEM image of CdS and it could be observed that the CdS sample was composed of NRs with a diameter of 30–60 nm and a length of 0.5–2 μ m. When the surface of CdS was modified with ZnS, the resulting N0 sample showed a morphology similar to that of CdS. The element composition for both CdS and N0 samples were measured by EDX (Fig. 1(d) and (e)). The results showed the presence of Cd, S, Cu, Au, and C elements in the CdS sample. For the N0 sample, in addition to the main Cd and S signals from the CdS, an elemental Zn signal was also present, which suggested that ZnS had been loaded on the CdS surface. The pure NiS sample was composed of small nanoparticles of ~100 nm size (Fig. S1). When NiS was loaded onto a CdS NRs/ZnS sample, the corresponding N2 sample also showed a similar morphology (Fig. 2(c)) and new signals for elemental Ni were observed in the EDX analysis (Fig. 2(f)). All the above results

Fig. 2. SEM images and the corresponding EDX patterns of various photocatalyst samples. (a, d) CdS; (b, e) N0: CdS NRs/ZnS; (c, f) N2: NiS-CdS NRs/ZnS.

Fig. 3. EDX mapping of the elemental distribution (a–d) and HR-TEM image (e) of the N2 sample.

indicated that the ternary NiS–CdS NRs/ZnS composite was successfully synthesized.

To identify the elemental distributions of Cd, S, Zn, and Ni, and to obtain the structural information, TEM-mapping and HRTEM measurements were performed. Fig. 3(a)–(d) clearly shows the signals of Cd, S, Zn, and Ni elements in a single nanorod. The width difference between Cd and Zn elements suggested the ZnS was only on the surface of the CdS. In addition, the Ni element, which was loaded by the chemical deposition method, was also distributed on the surface of the CdS NRs. The HRTEM image of the N2 sample exhibited fringes with a lattice spacing of 0.34 nm, which corresponded to the (002) lattice plane of CdS. Another obvious lattice fringe on the surface of CdS with a width of 0.27 nm could be attributed to the (200) plane of ZnS. In addition, the NiS particles on the surface of NRs showed no obvious lattice fringes, which suggested the amorphous nature of NiS on the photocatalyst, and this was consistent with the XRD results.

XPS was conducted to investigate the element valence states and the surface composition of the N2 sample. As shown in Fig. 4(a), the photocatalyst composite was mainly composed of Cd,

S, Zn, O, C, and Ni elements in the survey scan. The O element was proposed to arise from the absorbed gaseous molecules and a C element was used as the reference to correct the binding energies. Fig. 4(b) shows the high resolution spectrum of Cd. The main peaks located at 405.0 and 411.7 eV were attributed to Cd 3d_{5/2} and Cd 3d_{3/2}, respectively [39]. The high resolution spectrum of S is shown in Fig. 4(c) and the binding energies of S 2p_{3/2} and S 2p_{1/2} were 161.4 and 162.5 eV, respectively [40]. The high resolution spectrum of Zn 2p exhibited two peaks at 1045.3 and 1022.2 eV (Fig. 4(d)) [41]. Fig. 4(e) shows the high resolution spectrum of Ni 2p and the observed binding energy of Ni 2p_{3/2} at 856.4 eV suggested the existence of NiS [37].

The UV-vis diffuse reflectance spectra of the CdS, N0, N2, and NiS samples are displayed in Fig. 5. It can be seen that the absorption intensity of CdS started to increase at ~520 nm indicating a band gap of ~2.4 eV, which was consistent with the value reported in the literature [20,21]. For the N0 sample, no obvious change could be observed in the visible light owing to the fact that ZnS is transparent at these wavelengths. Based on the absorption spectrum, NiS showed a typical metallic character in our investigations, which could not be directly used for visible light-driven H₂ production. By modifying the N0 sample with NiS to obtain the N2 sample, the absorption intensities (500–1200 nm) increased and a darker color was formed. In addition, no significant edge shift was observed for N2, which suggested that NiS was not doped into the semiconductor to change the band gap.

The activities for H₂ production of the as-prepared photocatalyst samples were evaluated under visible light irradiation ($\lambda > 420$ nm) using Na₂S/Na₂SO₃ as sacrificial electron donors. As shown in Fig. 6(a), the H₂ performance was remarkably

Fig. 4. (a) XPS survey spectrum of the N2 sample. High-resolution XPS spectra of Cd 3d (b); S 2p (c); Zn 2p (d); Ni 2p (e).

Fig. 5. The UV-vis diffuse reflectance spectra of CdS, N0, N2, and NiS samples.

promoted by the introduction of NiS. The best of our samples was determined to be N2, which produced the maximum amount of H₂ in our experiments at an average rate that reached 574 $\mu\text{mol}\cdot\text{h}^{-1}$, while the average rates were 206, 312, and 12 $\mu\text{mol}\cdot\text{h}^{-1}$ for N1, N3, and N4, respectively. The results indicate that a proper amount of NiS can highly promote the H₂ production performance in a CdS NRs/ZnS heterojunction. However, if the content of NiS is too high, a negative effect is seen, probably arising from the fact that a large amount of NiS may shield the light absorption and block the active sites on the surface of the CdS NRs/ZnS heterojunction. The Pt-modified CdS/ZnS (Pt/N0) was also prepared and used for comparison (Fig. S2). Only a ~ 2 times higher H₂ evolution rate was observed when 1 wt% Pt was loaded onto CdS/ZnS. However, the performance of Pt/N0 was still much lower than that of the N2 sample, which indicated the beneficial role of NiS in the present system. In the control experiments, pure CdS showed a low photocatalytic activity of $\sim 15 \mu\text{mol}\cdot\text{h}^{-1}$ (Fig. 6(b)), which could be attributed to the fast recombination of photogenerated electron-hole pairs. The photocatalytic performance of CdS NRs modified by either NiS (CN sample) or ZnS (N0 sample) was indeed improved when compared with that of pure CdS. How-

ever, the catalytic activity was far inferior to that of the N2 sample, which strongly suggested the essential synergistic effect of both NiS and ZnS to achieve a highly efficient photocatalytic H₂ performance.

We also investigated several other first-row transition metal-based sulfides, such as cobalt sulfide, iron sulfide, copper sulfide, and manganese sulfide, as cocatalysts for integration with the CdS NRs/ZnS heterojunction photocatalyst. All the cocatalysts were loaded by the same in situ chemical deposition method, using amounts equal to the amount of NiS used for sample N2. The results are illustrated in Fig. S3. The H₂ production rates were 92, 43, and 98 $\mu\text{mol}\cdot\text{h}^{-1}$ for cobalt sulfide, iron sulfide, and copper sulfide, respectively. It was evident that NiS showed the best activity among all of these transition-metal sulfides.

The apparent quantum yield (AQY) of the NiS-modified CdS NRs/ZnS sample (N2) was measured under a 300 W Xe lamp with a 420 nm (± 5 nm) band-pass filter. As shown in Fig. 7(a), the H₂ production rate was stable during the evaluated time and the amount of H₂ reached $\sim 177 \mu\text{mol}$ in total after 5 h with an average AQY value of $\sim 43.2\%$. This result indicated that NiS-modified CdS NRs/ZnS was an exceptional photocatalyst to improve the electron-hole pair separation and subsequently enhance the photocatalytic H₂ production. Good activity is vital but catalytic stability is also a key factor for a photocatalyst. In this present study, three cycles of H₂ production were carried out for the photostability testing of the N2 sample. As shown in Fig. 7(b), the sample did not show any significant decrease in H₂ production, which indicated the good stability under the present conditions for photocatalytic H₂ production. In addition, the SEM image and XRD data of NiS-CdS NRs/ZnS after irradiation for H₂ production were also collected, as shown in Fig. S4. The morphology and XRD patterns were similar to the sample before irradiation, further proving the stability of the photocatalyst during the H₂ production reaction.

To investigate the possible mechanism for the enhanced photocatalytic H₂ production performance, the transient photocurrent response curves of CdS, N0, and N2 on FTO electrodes were recorded using an electrochemical potentiostat under visible light irradiation ($\lambda > 420$ nm). As shown in Fig. 8,

Fig. 6. (a) Photocatalytic H₂ production rates of NiS-CdS NRs/ZnS samples. (b) Photocatalytic H₂ production rates of CdS, NiS-CdS (CN), CdS/ZnS (N0), NiS-CdS/ZnS (N2), and NiS.

Fig. 7. (a) Time courses of H₂ production and apparent quantum yield using N₂ photocatalyst in 0.25 mol L⁻¹ Na₂S/0.35 M Na₂SO₃ aqueous solution under 420 nm monochromatic light irradiation. (b) Cyclic runs for the photocatalytic H₂ production using N₂ photocatalyst in 0.75 mol L⁻¹ Na₂S/1.05 M Na₂SO₃ aqueous solution under visible-light irradiation ($\lambda > 420$ nm).

Fig. 8. Transient photocurrent responses of CdS (black), CdS NRs/ZnS (N0, red), and NiS-CdS NRs/ZnS (N2, blue) samples in 0.5 mol L⁻¹ Na₂SO₄ aqueous solution under visible light irradiation at 0 V vs. Ag/AgCl (saturated KCl).

the results showed that all the photocatalysts exhibited fast photocurrent responses to visible light. When the working electrode was exposed to the dark, the photocurrent densities rapidly decreased to zero, which suggested that the photogenerated electrons were transported to the FTO electrodes to produce photocurrent under irradiation. Notably, the N2 electrode exhibited the best photocurrent performance, better than those of the CdS and N0 electrodes, which indicated that the N2 sample could achieve the most efficient charge transport and separation, and this was consistent with the photocatalytic H₂ production activity.

Building on the above discussion, a proposed mechanism is shown in Scheme 1. Under visible light irradiation, CdS serves as a photosensitizer to absorb photons and generate electron-hole pairs. With the introduction of ZnS, more electrons can be used [28–30] because when NiS is integrated with the CdS NRs/ZnS heterojunction photocatalyst, the NiS can accept electrons from CdS NRs/ZnS and provide active reduction sites where protons are efficiently reduced to H₂. Therefore, the recombination process of the electron-hole pairs in NiS-CdS NRs/ZnS is effectively suppressed, leading to a highly improved

Scheme 1. The proposed reaction mechanism during photocatalytic H₂ production.

photocatalytic H₂ production activity.

4. Conclusions

We report a novel ternary hybrid photocatalyst that is composed of an amorphous NiS cocatalyst and CdS/ZnS NRs fabricated by a facile in-situ chemical deposition method. Owing to the synergistic effect between the NiS cocatalyst and CdS/ZnS heterojunction, the photocatalyst composite exhibits an H₂ production rate of 574 μmol·h⁻¹ under visible light irradiation ($\lambda > 420$ nm) and an average AQY of 43.2% for the N2 sample in 0.25 mol/L Na₂S and 0.35 mol/L Na₂SO₃ aqueous solution at 420 nm. The hydrogen production performance using N2 shows that our new catalyst has among the best catalytic activity for noble-metal-free CdS-based photocatalysts for H₂ production in water under visible light. Since the ternary amorphous NiS-CdS NRs/ZnS hybrid photocatalyst is made of earth-abundant elements and can be facily prepared, it has great potential for large-scale photocatalytic H₂ production.

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Graphical Abstract

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An excellent photocatalytic H₂ production rate for an amorphous NiS cocatalyst facily deposited onto a CdS nanorods (NRs)/ZnS heterojunction material is observed in water under visible light irradiation ($\lambda > 420$ nm).

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硫化镍修饰的硫化镉/硫化锌异质结复合光催化剂用于高效光催化产氢性质的研究

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摘要: 光催化水分解是一种经济而且可持续的利用太阳能来制备洁净能源氢气的方式, 因此寻找和开发高效稳定的光催化剂已成为光催化产氢领域的研究热点. CdS因其具有高效、廉价、较负的导带位置等优点而引起人们的关注. 然而, 由于CdS本身光生电子/空穴对易复合, 以及存在光腐蚀等不足, 限制了其实际利用. 为了提高CdS的光催化水分解产氢性质, 人们开发了构建异质结和负载助催化剂等策略. 近年来, ZnO, g-C₃N₄, TiO₂等半导体已被证实可以与CdS一起形成II型异质结来促进光生电子和空穴的分离, 进而提升光催化产氢性质. 此外, 传统的type I型CdS/ZnS异质结也被证实能提高光催化产氢速率. 研究表明, ZnS一方面能够钝化CdS表面态, 另一方面ZnS半导体中存在缺陷能(V_{Zn} , I_{S}), 有利于转移CdS价带的空穴, 最终大幅度提高了整个体系的光催化活性. 在适用于CdS的各种助催化剂中, 由于常用的Pt, Pd和Ru等贵金属的高成本严重限制了它们的实际应用, 所以近年来基于过渡金属的各种非贵金属助催化剂(包括MoS₂, Ni₂P, FeP, Ni₃N, NiS, Ni(OH)₂等)得到了广泛的研究. 我们采用原位化学沉积法将无定型的NiS助催化剂修饰在CdS/ZnS异质结表面, 开发出廉价高效的NiS-CdS/ZnS三元产氢光催化体系. 在该三元体系中, NiS和ZnS分别用于促进CdS导带上光生电子和价带的光生空穴的分离及利用, 从而使得高能的CdS的光生电子转移到NiS表面并应用于光催化产氢, 而高能的CdS的光生空穴被应用于氧化牺牲剂Na₂S和Na₂SO₃, 最终实现了整个体系的高效光催化产氢活性及稳定性.

我们首先利用水热合成法得到大量的CdS纳米棒, 然后使用化学浴沉积法在CdS表面沉积一定量的ZnS壳层, 制备出CdS/ZnS异质结. 光照前, 采用原位化学沉积法将NiS颗粒负载在CdS/ZnS表面. 光催化产氢的性能测试表明, 当初始加入镍盐(20 mmol/L)量为100 μL 时, 所得样品N2(NiS-CdS/ZnS)产氢效率最高(574 $\mu\text{mol}\cdot\text{h}^{-1}$), 分别是CdS/NiS, CdS/ZnS和CdS的16.2, 5.6和38倍. 复合材料的表观量子效率高达43.2%. 由此可见, NiS助催化剂和CdS/ZnS异质结存在协同效应, 实现了三元体系的高效的光催化产氢性能. 瞬态光电流测试结果表明, ZnS和NiS的加入能有效地促进光生电子/空穴的分离和利用. X射线衍射结果表明, CdS以六方相的形式存在, 负载ZnS和NiS之后没有明显变化. 高分辨透射电子显微镜照片和元素分布证实了NiS-CdS/ZnS复合材料中ZnS和NiS富集在纳米棒表层, 其中NiS没有明显晶格条纹. 紫外-可见漫反射结果表明, NiS和ZnS的负载后, 复合材料的吸收边和纯相的CdS相近, 而加入NiS助催化剂使得复合催化剂的颜色变黑, 进而增加了可见光的吸收.

关键词: 光催化产氢; 硫化镉/硫化锌半导体; 异质结; 硫化镍

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