Construction of CdS/Ni$_3$S$_2$ Heterojunctions for the Enhancement of Hydrogen Production

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Abstract: The CdS/Ni$_3$S$_2$ heterojunction is prepared by a two-step hydrothermal method. The structure and crystalline phase are proved by SEM, TEM and XRD. The photocatalytic hydrogen production performance of the CdS/Ni$_3$S$_2$ heterojunction exhibits about ~24 times enhancement that of pure CdS. It may be ascribed to the CdS with narrow band gap could increase the solar utilization. What’s more, the Ni$_3$S$_2$ with quick photon-generated electrons transferring could improve the separation of photon-generated carriers.

1. Introduction

Energy is the most important issue for the social development. With the quick growth of the global energy requirement, the traditional non-renewable energy sources, such as fossil fuels etc., are gradually exhausted, and the new recyclable energy has become the focus of researches [1]. Especially the solar energy, as an environmental friendly, rich and clean energy, is considered to be an effective energy source for resolving the resource shortages and environmental pollution [2]. Nowadays, particularly the photocatalytic hydrogen production via water splitting, with the green process and clean combustion products, has become the current hot point. Up to now, lots of methods have been reported to enhance the photocatalytic hydrogen production, such as surface heterojunction modification, elements doping, etc. There, the co-catalyst modification, with the easy preparation and high efficiency, is reported as the hot topics. Unfortunately, the noble metal Pt, reported with the best hydrogen evolution co-catalytic properties, is so rare and expensive that restricting its application in the fields of photocatalysis gravely [3,4]. There, the transition metal sulfides, with the catalytic high activity, are relatively inexpensive and can be regarded as the replacements of precious metals, such as NiS$_2$, MoS$_2$, WS$_2$ and so on.

On the other hand, the semiconductor CdS, with a narrow band gap of 2.4 eV, exhibits an remarkable visible-light responsive characteristics and is considered as an ideal foundational photocatalytic materials. Recently, many graphene-like co-catalysts have been applied to incorporate with CdS to construct multi-component nanosystem for high-efficient photocatalytic performance [5-7]. However, the photocatalytic performance of the CdS is often plagued by the low photo-generated electron-hole separation efficiency and poor photostability [7-11]. Therefore, how to solve above problems would be the most important issues for enhancing the photocatalytic HER performance of the CdS system. As reported, theNi$_3$S$_2$, with the remarkable electron acception and high charge transferring, is regarded as the effective co-catalyst in promoting water splitting hydrogen production of the CdS system [12-16].

In this work, we prepared the CdS/Ni$_3$S$_2$ heterojunction by hydrothermal method and evaluated the photocatalyst performance via the water splitting hydrogen production. It is obvious that the hydrogen
production performance of CdS/ Ni$_3$S$_2$ heterojunction exhibits significantly improvement about ~24 times than that of the pure CdS and the mechanism of the HER enhancement is discussed.

2. Material and Methods

2.1 Preparation of CdS
Hydrothermal preparation of CdS, dissolve Cd(COOH)$_2$•2H$_2$O and a certain amount of thiourea into 30 ml of ultrapure water, stirring for 30 min, and sonicating for 30 min. Then the above solution was placed in a 50 ml reactor at 180 °C for 24 h. The resulting green powder was washed with deionized water and dried in a vacuum oven at 60 °C.

2.2 Combination of CdS and Ni$_3$S$_2$
0.3g of CdS, 0.06g NiCl$_2$•6H$_2$O and 0.04g of thiourea were added to 50 ml of DI water. After 10 minutes ultrasonication, the solution was stirred for another 30 minutes. Then transfer the mixture to 50ml Teflonlined autoclave at 180 °C for 24h. The green product was washed 3 times with absolute ethanol and deionized water, and then centrifuged at 60 °C for 8 h.

2.3. Characterization
The phase composition of the prepared sample was determined by XRD, using Cu Kα (λ = 1.5406) radiation by X-ray diffraction (XRD, Bruker D8 Discover). The micromorphology of the samples were characterized by scanning electron microscopy (FESEM Hitachi S-4800). The PL spectra were recorded by a Hitachi F-7000 spectrofluorimeter at the excitation wavelength of 400 nm. The UV-vidiffuse reflectance spectra were obtained by the UV-vis spectrophotometer (Hitachi-U3900).

2.4. Photocatalytic activity
Evaluation of photocatalytic performance by a typical method, 50 mg of the as-prepared sample was pour into100ml solution that mixed 90 ml of DI water, and 10 ml triethanolamine (TEOA) . It becomes a homogeneous solution that is ultrasonically dispersed after 20 minutes. The performance tested by a closed gas circulation system and a gas chromatograph(GC-7900) with 300W light source. We kept the temperature of the catalyst at around 10 °C by circulating water throughout the experiment.

3. Results and discussion

![Figure 1. The XRD patterns of the CdS, CdS/ Ni$_3$S$_2$ and Ni$_3$S$_2$.](image)

Fig. 1 is the XRD patterns of the CdS, CdS/ Ni$_3$S$_2$ and Ni$_3$S$_2$. As revealed, the XRD pattern of the as-prepared CdS obtains the peaks at 26.5°, 43.6°, 51.8°, which are ascribed to the (002), (110), (112)
plan of the CdS (JSPDS-41-1049). Further, with the deposition of the Ni$_3$S$_2$ the new peaks at 37.7°, 44.3° could be attributed to the (003), (202) planes of the Ni$_3$S$_2$, and correspond to the pure Ni$_3$S$_2$.

![SEM images of CdS and CdS/Ni$_3$S$_2$ composites](image)

Figure 2. SEM of (a) CdS particles (b) CdS/Ni$_3$S$_2$ composites (c) Ni$_3$S$_2$

Fig. 2 is the SEM, as revealed, the pure CdS is block particle (Fig. 2a). Further, with the deposition of the Ni$_3$S$_2$, the obvious uniform nanoparticles could be observed in the surface of the CdS (Fig. 2b). Fig. 1c is the typical molybdenum disulfide (Ni$_3$S$_2$), which is uniform nanoparticles and correspond to the Fig. 2b.

![PL and UV-Vis spectra](image)

Figure 3. (a) PL spectrum of CdS and CdS/Ni$_3$S$_2$, (b) UV–Vis diffuse reflectance spectra of CdS, CdS/Ni$_3$S$_2$, and Ni$_3$S$_2$

Figure 3a is the PL of the CdS and CdS/Ni$_3$S$_2$, as revealed, the CdS/Ni$_3$S$_2$ observed a lower PL than the pure CdS, which indicates that the recombination of the CdS/Ni$_3$S$_2$ is much lower than the pure CdS, and is benefit for the photocatalytic HER performance. Figure 3b displays the UV-visible absorption spectra of CdS/Ni$_3$S$_2$ heterojunction with different modification. It’s obvious that, the CdS obtains an absorption edge located at about 500nm, which corresponds to the band gap of the CdS. Further, with the deposition of the Ni$_3$S$_2$, the nano-heterojunction exhibits a red shift relative to the band gap of CdS, and obtains an increasing about the utilization of light, which is benefit for the photocatalytic enhancement.
Figure 4. H$_2$ production of CdS, CdS/Ni$_3$S$_2$ and Ni$_3$S$_2$

There, the photocatalytic hydrogen production performances of the as-prepared samples at different stages are shown in Figure 4. As revealed, the CdS/Ni$_3$S$_2$ exhibits a remarkably superior photocatalytic activity than that of the single CdS and Ni$_3$S$_2$, though the best absorption is obtained as the pure Ni$_3$S$_2$, which manifests that the band gap of the heterojunction and the quickly photon-generated transferring of the Ni$_3$S$_2$ would be more important than the visible light absorption. There, by calculation, the CdS/Ni$_3$S$_2$ obtains an excellent photocatalytic HER performance of about ~813.9umol/g·h and exhibits an obvious enhancement of about ~24 times than that of the pure CdS. Therefore, the introducing of the suitable Ni$_3$S$_2$ could improve the photocatalytic hydrogen production performance of the CdS efficiently.

4. Conclusions

In this work, we have successfully prepared the CdS/Ni$_3$S$_2$ heterojunctions by the hydrothermal method. As shown, the photocatalytic hydrogen production of the CdS/Ni$_3$S$_2$ exhibits an obvious enhancement of about ~24 times than that of the pure CdS, which could be ascribed that the CdS with narrow band gap could increase the solar utilization and the Ni$_3$S$_2$ with quickly photon-generated electrons transferring could improve the separation of photon-generated carriers, such properties is benefit for the photocatalytic HER performance. Consequently, we provide a new sight for exploring the renewable solar energy.

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