
Kai He\textsuperscript{a}, Liejin Guo\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}International Research Centre for Renewable Energy & State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Shaanxi 710049, China (Kai He will present the paper at the conference)

Abstract

In the present study, CdS nanorod particles with the stacking fault structures were hydrothermally synthesized through a dissolution-recrystallization approach in concentrated ammonia solvent, for the first time. It was clear that concentrated ammonia solution contained a large number of hydroxyl ions and large numbers of ammonia. Comprehensive characteristics were performed to investigate the influence of stacking fault structures on the photocatalytic activity and stability of CdS nanorod particles. Transmission electron microscopy (TEM) images revealed that the CdS catalyst included many nanorods with stacking fault structures. Stacking fault structures were obviously observed within CdS nanorods with the length ranging from 70 to 200 nm and diameter ranging from 20 to 65 nm, respectively. It revealed that the formation of CdS nanorod particles with stacking faults was contributed to the dissolution-recrystallization process. There were many structural units for cubic phase changing to hexagonal phase in the CdS crystals in the process of hydrothermal resulting in forming a large number of stacking fault structures. Photo-generated electrons and holes migrating directionally along the nanorods direction and the stacking fault structures in some nanorods could promote the separation of photo-generated electrons and holes, which enhanced the activity of visible-light-driven photocatalytic hydrogen production. Through the photocatalytic hydrogen production experiments, CdS nanorod particles with the stacking fault structures showed much higher photocatalytic activity than CdS particles prepared by the conventional hydrothermal method using the water as the hydrothermal solvent.

Keywords: CdS Nanorods; Stacking fault structures; Photocatalytic hydrogen production

* Corresponding author. Tel.: + 86-29-82663895; fax: + 86-29-82669033.
E-mail address: lj-guo@mail.xjtu.edu.cn.
1. Introduction

Some researchers had studied that the ZnS with the stacking fault structures contained many structural units of changing for cubic phase to hexagonal phase. [1] The Cd and Zn for the same subgroup elements should have the similar chemical properties, so we concluded that some CdS catalysts should contain the stacking fault structures. It was known that the stacking fault structure was closely related to the formation of twins which efficiently prevent the recombination of photoinduced free electrons and holes. [2, 3] This study, for the first time, using a new synthetic method with concentrated ammonia as the hydrothermal solvent, successfully synthesized the CdS nanorods with the stacking fault structures. The activity of photocatalytic hydrogen production for the CdS synthesized by the new synthetic method was much higher than that of CdS with conventional hydrothermal method using water as the hydrothermal solvent.

2. Experimental

2.1 Synthesis

Cadmium acetate and thioacetamide with equimolar amount were added into a Teflonlined autoclave (100ml) containing 80 ml of 25% (w/w) ammonia, which was maintained at 230°C for 72 h, and then cooled naturally in air. The resulting precipitates collected by centrifugal separation were washed with deionized water and absolute ethanol several times and then dried under vacuum for 24 h at 80°C. CdS prepared by this method was denoted as CdS-N.

The other CdS catalysts for comparison were synthesized using deionized water as the hydrothermal solvent instead ammonia, under the remaining conditions unchanged. CdS prepared by this method was denoted as CdS-H.

2.2 Photocatalytic hydrogen production

Photocatalytic reactions for hydrogen production from water under visible light were performed in a side-irradiation Pyrex cell with uniformly stirring, of which efficient irradiation area was 15.90 cm², and nitrogen was purged to remove oxygen through the cell before reaction. The catalyst (0.1 g) was added into the solution (180 ml) containing Na₂S (0.35 M) and Na₂SO₃ (0.25 M) as the electron donors, and the temperature of solution was kept at 35°C using circulating water. The solution was irradiated by visible light (λ>420 nm) through a cutoff filter from the Xe lamp (300 W), and the irradiation power after the filter was measured by the fiber optic spectrometer to be 55 mV cm⁻². The amount of hydrogen was tested by the gas chromatography (NaX zeolite column, TCD detector, N₂ as carrier gas). The apparent quantum yield (AQY) measured by a 420 nm band-pass filter and a fiber optic spectrometer was defined using the following eqn (1). The energy conversion efficiency was defined by the following eqn (2) (ΔG/ mol¹: the standard Gibbs energy for the chemical reaction forming the product(s) P; R_p/mol s⁻¹: the rate at which the products are formed; E_s/J s⁻¹ m⁻²: the total incoming light irradiance; A/m²: the irradiated area). [3]

\[
AQY (%) = \frac{\text{The number of reacted electrons}}{\text{The number of incident photons}} \times 100
\]

\[
= \frac{\text{The number of evolved H₂ molecules} \times 2}{\text{The number of incident photons}} \times 100
\]

\[
\eta_e = \frac{\nabla G_p^0}{E_s A} R_p
\]
3. Results and discussion

CdS-H did not form the nanorod structure shown in Fig. 1 a and c. Figure 1 b and d show the images of CdS-N, which formed the nanorod structure and the stacking fault structure. Fig. 1 e shows the XRD patterns of CdS-H and CdS-N. It indicated that both of cubic phase and the hexagonal phase existed in CdS-N, which was the key factor in improving the activity of photocatalytic hydrogen production. Fig. 1 f shows the UV-vis absorption spectra of CdS-N and CdS-H. The absorption edge of CdS-N became narrower than that of the CdS semiconductors had been reported in the literatures. It was mainly attributed to many structural units of changing for cubic phase to hexagonal phase in the CdS-N with a large number of stacking fault structures.

Fig. 1 TEM images (a, b, c, d); XRD patterns (e); UV-vis absorption spectra (f)

4. Effects of hydrothermal temperature

Fig. 2 (a, b, c, d, e) shows the TEM images of CdS-N synthesized at different hydrothermal temperatures (120°C, 150°C, 180°C, 230°C and 260°C, respectively). With the hydrothermal temperature increasing, the stacking fault structures became much more and clearer; the lengths and diameters of nanorods became much longer. However, when the temperature reached to 260 °C, the nanorods disappeared and the stacking fault structures were also not observed. Fig. 2 (f) shows the XRD patterns of CdS nanorod particles synthesized at different hydrothermal temperatures of 120°C, 150°C, 180°C, 230°C and 260°C, respectively. It revealed that, as the temperature increasing, the proportion of hexagonal phase gradually increased, so there would be many structural units for cubic phase changing to hexagonal phase in the CdS crystals resulting in forming a large number of stacking fault structures. When the hydrothermal temperature was risen to 260 °C, obtained from the TEM images of CdS, the stacking fault structures and nanorods disappeared. The UV-vis absorption spectra of CdS-H and CdS-N synthesized with different hydrothermal temperatures at 120°C, 150°C, 180°C and 230°C noted as CdS-N (1, 2, 3, 4) are shown in Fig. 2 (g). It revealed that the absorption edges of CdS-N (1, 2, 3, 4) were larger than that of the CdS-H, which attributed to many structural units of changing for cubic phase to hexagonal phase in the CdS-N with a large number of stacking fault structures. The activity of photocatalytic hydrogen production for
CdS nanorod particles synthesized at different hydrothermal temperatures (120°C, 150°C, 180°C and 230°C, respectively), is shown in Fig. 2 (h). With the increasing of temperatures, the amount of hydrogen gradually increased, which reached a maximum of 188.3 μmol when the temperature was increased to 230 °C. When the temperature reached to 260 °C or continued to rise, the stacking fault structures and nanorods disappeared.

5. The comparison for the activity of hydrogen production

Fig. 3 (a) shows the visible-light-driven activity of photocatalytic hydrogen production of CdS-H and CdS-N. The average rate of photocatalytic hydrogen production for CdS-N was 37.66 μmol / h without Pt loading, while the average rate of photocatalytic hydrogen production for CdS-H was only 10.68 μmol / h. The average photocatalytic hydrogen production rate of CdS-N with 2.0 wt% Pt-loading was 5357 μmol g⁻¹ h⁻¹, with the quantum yield as high as 23.0% at 420 nm by eqn (1) and the energy conversion efficiency as high as 4.0% by eqn (2). Compared with the CdS prepared by the solvothermal, thermolysis and template method, [6-9] the photocatalytic activity of CdS-N was much higher. Because of the different band gaps between cubic phase and hexagonal phase, the electrons of valence band in the hexagonal phase were transition to the conduction band in the cubic phase leading to promoting the effective separation of photo-generated electrons and holes shown in Fig. 3 (d), [5] which could enhance the activity of photocatalytic hydrogen production for CdS-N. The Roman spectra was also measured for CdS-H and CdS-N synthesized with different hydrothermal temperatures at 120°C, 150°C, 180°C and 230°C noted as CdS-N-1, CdS-N-2, CdS-N-3 and CdS-N-4, shown in Fig. 3 (b). Compared with the CdS-H, a blue shift can be observed about CdS-N (1, 2, 3, 4) implied its better microstructure, which can ensure the integrity of the CdS crystal to enhance the stability of CdS-N. Fig. 3 (c) shows the activity of photocatalytic hydrogen production of CdS-N for 120 h, with 0.25 M Na₂SO₃/0.35 M Na₂S as the sacrificial agent, which was replaced once every 12 h. It can be seen from the figure that the photocatalytic activity of CdS-N had almost no decrease during 120 h, indicating that the CdS-N showed perfect stability for photocatalytic hydrogen production.
6. Conclusions

In summary, our work, for the first time, using a new synthetic theory with concentrated ammonia as the hydrothermal solvent, successfully synthesized the CdS nanorods with the stacking fault structures, and the research for its activity of photocatalytic hydrogen production shown that it was higher than that of CdS synthesized by the conventional hydrothermal method using the water as the hydrothermal solvent. Compared with previous work, [6],[10] the CdS synthesized using the new theory also showed a perfect stability. Hydrothermal temperature on the morphology, structure and activity of photocatalytic hydrogen production for the CdS nanorods had been also studied to obtain the optimum synthesis conditions for such catalysts. This new synthetic theory, for synthesizing CdS with nanorods and a clear stacking fault structure which could effectively promote the separation of photoinduced electrons and holes resulting in increasing the activity of photocatalytic hydrogen for CdS, could be considered for synthesizing many new photocatalysts with the higher activity of photocatalytic hydrogen production.

Acknowledgements

The work was financially supported by the National Natural Science Foundation of China (Grant No. 51236007 and No.51121092).

References


