Construction of MoS2/CaTiO3 Heterojunctions for the Enhancement of Photocatalytic Hydrogen Production

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Abstract: The MoS2/CaTiO3 heterojunctions is prepared by the hydrothermal co-deposition method. The results of XRD, SEM and TEM imply that the MoS2/CaTiO3 heterojunctions is synthesized successfully. The absorption band pf the MoS2/CaTiO3 heterojunctions exhibit a red shift and increase the utilization of sunlight. The photocatalytic hydrogen production activity of the MoS2/CaTiO3 heterojunctions expresses a higher improvement about 10 times, compared to the pure CaTiO3. It was ascribed to MoS2 as co-catalyst can drive the transfer of photon-generated carriers to promote the photon-generated carrier separation.

1. Introduction

Nowadays, with the increasing of the demand for energy, and limited by the non-renewable energy, the exploring of the new energy would be an important issue [1,2]. Solar energy, as an inexhaustible and clean energy source, is regarded as an efficient way to solve the energy shortage and environment pollution problems, especially the solar photocatalytic split water to produce hydrogen, which has been considered as the hot issue in currently [3,4]. In the past few decades, most of the researches have payed attention to pyrochlores (A2B2O7), spinels (AB2O4) or perovskites (ABO3) [5-7]. Particular the perovskite CaTiO3, with a wide band gap, low cost and nontoxicity, has been reported as an ideal material and lots of inspiring results have been achieved, such as the doping, composition and surface modification [8-10]. Due to the position of its valence band and conduction band, it is considered as an efficient way to enhance photocatalytic hydrogen production.

On the other hand, the MoS2, as a co-catalyst, is used to increase the hydrogen production efficiency of photocatalytic materials, which could be attributed to the fact that the MoS2 can improve the separation efficiency of photogenerated electrons and holes in photocatalytic materials [11]. Further researches demonstrated that, the MoS2 with different physical dimensions, including 0D, 1D or 2D have been widely applied and enhance the photocatalytic hydrogen production obviously [12-14].

In this work, the MoS2/CaTiO3 heterojunctions was prepared by the hydrothermal co-deposition method. The nanostructure and photocatalytic hydrogen production were examined. The results indicate that the photocatalytic activity improved obviously. What’s more, the mechanism of the nanostructure was studied [15].

2. Experiment

2.1. Materials
All the chemicals are analytical grade and purchased from Aladdin Industrial Corporation (shanghai, China).

2.2. Synthesis of the MoS2/CaTiO3 heterojunction
The MoS2/CaTiO3 heterojunctions were prepared by the two-step hydrothermal method. Typically, Ca(NO3)2•4H2O (1.66g) was put into the deionized water (20 mL). Then, tetrabutyl titanate (1.7 mL) was added into the solution with stirring for 1h. Next, NaOH (0.37g) were put into the solution with stirring for 1h at ambient temperature. The mixture was poured into the teflon-lined stainless steel vessel and the hydrothermal treatment was carried out for 24 h at 200°C. The precipitate was washed twice with deionized water, diluted acetic acid and ethanol after cooling to room temperature. The precipitate was dried for 8h at 80°C. Then, samples were annealed at 500 °C for 4h with a rate of 5 °C min⁻¹. Secondly, 10 mg Na2MoO4•2H2O and 18 mg C2H5NS were dispersed into deionized water (10 mL). 75 mg CaTiO3 was added in the solution with ultrasonic for 1h. Then the hydrothermal treatment was carried out for 24 h at 200°C. The precipitate was washed twice with deionized water and ethanol. The precipitate was dried for 8h at 80°C. Samples with Na2MoO4•2H2O of 0 mg, 10 mg, 20 mg and 30 mg were labelled as Ca-Mo-0, Ca-Mo-1, Ca-Mo-2 and Ca-Mo-3.

2.3. Characterization
The micromorphology of the samples was characterized by scanning electron microscopy (FESEM Hitachi S-4800) and transmission electron microscopy (TEM JEM-2100). The phase composition of the as-prepared samples were determined by X-ray diffraction (XRD, Bruker D8 Discover) using Cu Kα (λ = 1.5406 Å) radiation at 40 kV and 40 mA. The UV–vis diffuse reflectance spectra were obtained by the UV–vis spectrophotometer (Hitachi-U3900). The PL spectra were recorded by a Hitachi F-7000 spectrofluorimeter at the excitation wavelength of 360 nm.

2.4. Photocatalytic activity
Photocatalytic activity of the MoS2/CaTiO3 heterojunctions was tested by photocatalytic hydrogen production using gas chromatograph (Techcomp GC-7900). A 300W Xe arc lamp was used as light source. For the photocatalytic experiment, 50 mg samples were suspended in 100 mL solution (90 mL water and 10 mL methanol, methanol as the sacrifice agent). Before the experiment, high purity Ar gas was evacuated for 20 min to remove the dissolved oxygen from the reactor, and the suspension was put in the ultrasonic bath for 20 min. In the whole reaction, keep it at room temperature.

3. Results and discussions

Fig. 1. The XRD spectra of the CaTiO3 modified with different ratio of MoS2.
Fig.1 is the XRD figure of the different ratio of MoS2 modified CaTiO3. In the pattern, the diffraction peaks of Ca-Mo-0 could be in agreement with (101), (121), (202), (221), (223), (242) and (323) crystal planes of the CaTiO3 (PDF-42-0423) [10]. As the amount of MoS2 increases, the new diffraction peaks appear and increase. However, the crystallinity of MoS2 is weak, but MoS2 modified CaTiO3 appeared
a stronger peaks at 29.1°. It corresponded to the (004) plane of MoS₂. At about 25°, this low peaks was attributed to the substrate. There are no other obvious peaks present in all curves, which manifests that the samples are composed of MoS₂ and CaTiO₃.

The morphology of different ratio MoS₂/CaTiO₃ nanoheterojunction is showed in Fig.2. Fig.2a is SEM of the pure CaTiO₃. And it showed stepped and its long and width were approximately 1.5 μm and 350 nm. Fig.2b-d are SEM of Ca-Mo-1, Ca-Mo-2 and Ca-Mo-3. With the amount of MoS₂ increasing, it showed that the morphology of MoS₂ was from small particles to rhombus particles. The size of MoS₂ increased from 40nm to 150nm. It corresponded to the result of photocatalytic hydrogen production.

Fig.2. The SEM of as-prepared CaTiO₃ with different ratio of MoS₂, (a) Ca-Mo-0, (b) Ca-Mo-1, (c) Ca-Mo-2, (d) Ca-Mo-3.

Fig.3. The TEM of the sample, (a) the TEM of Ca-Mo-2, (b) the interface of the MoS₂ particles and CaTiO₃ ladder, (c) HRTEM of Ca-Mo-2.

Fig.4. The UV-vis absorption spectra of CaTiO₃ modified with different ratio of MoS₂.
Fig.3 is the TEM picture of the Ca-Mo-2 heterojunction. As shown in Fig.3a, the ladder samples covered with some small particles and rhombus particles obtain diameter of about 40 nm and 150 nm, which corresponds to the SEM. Fig.3b is the interface of the MoS$_2$ and CaTiO$_3$. Fig.3c is the HRTEM of the MoS$_2$ and CaTiO$_3$, the lattice spaces of 0.308 nm and 0.381 nm are ascribed to the (004) plane of MoS$_2$ and (101) plane of CaTiO$_3$. It illustrated the plane of MoS$_2$ is corresponded to the result of XRD.

Fig.4 displays the UV-visible absorption spectra of MoS$_2$/CaTiO$_3$ heterojunction with different modification. In the figure, MoS$_2$/CaTiO$_3$ nanostructure exhibit a red shift relative to the band gap of CaTiO$_3$ and increase the utilization of light. It obvious that the absorption edge of CaTiO$_3$ located 350 nm. MoS$_2$ has a narrower band gap and the enhanced photocatalytic hydrogen production is ascribed to the absorption enhancement.

![Fig.5](image1.png)

**Fig.5.** The PL of the MoS$_2$/CaTiO$_3$ with different ratio.

![Fig.6](image2.png)

**Fig.6.** MoS$_2$/CaTiO$_3$ heterojunction photocatalytic hydrogen production activity.
Fig. 5 displays the PL of the MoS$_2$/CaTiO$_3$ heterojunction with different ratio under the excitation of 360 nm. What’s more, the PL would be regarded as an efficient way to investigate the separation of the photo-generated carriers [16]. With the ratio of MoS$_2$ increasing, the intensity of peak is lower and lower. It illustrated the separation of the photo-generated carriers become more effective and the higher efficiency of charge immigration with the concentration of MoS$_2$ increasing. The Ca-Mo-3 exhibits the lowest PL, but the H$_2$ production of Ca-Mo-3 is not the highest. It is ascribed to MoS$_2$ is surrounding the base material.

Fig. 6 shows the photocatalytic hydrogen production of MoS$_2$/CaTiO$_3$ heterojunction with different ratio. The pure CaTiO$_3$ (Ca-Mo-0) reveals weaker H$_2$ production of 9.32 μmol/g-h. And the Ca-Mo-2 exhibits the highest H$_2$ production of 88.89 μmol/g-h, which is nearly 10 times than the Ca-Mo-0. The Ca-Mo-1 and Ca-Mo-3 show H$_2$ production of 44.63μmol/g-h and 18.60μmol/g-h. It obvious that MoS$_2$ modified CaTiO$_3$ with different ratio is enhancing. It is interesting that the H$_2$ production of Ca-Mo-2 is higher than Ca-Mo-3. Although the PL intensity of Ca-Mo-3 is lower than Ca-Mo-2, CaTiO$_3$ is surrounded by MoS$_2$ and cannot contact water to react fully.

4. Conclusions
In our work, we have successfully prepared the MoS$_2$/CaTiO$_3$ heterojunctions by the two-step hydrothermal method. The photocatalytic hydrogen production of the MoS$_2$/CaTiO$_3$ is enhancing larger. It was ascribed to MoS$_2$ as co-catalyst can drive the transfer of photon-generated carriers to promote the photon-generated carrier separation [17]. Consequently, we open a new sight for exploring renewable energy and make a great design for materials.

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