Facile synthesis of Co-doped MoS$_2$/TiO$_2$ composite as an enhanced photocatalyst for hydrogen evolution

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Abstract. MoS$_2$/TiO$_2$ composite was prepared through a simple solvothermal route by combining the layered MoS$_2$ and TiO$_2$ nanosheets. Then, when preparing MoS$_2$/TiO$_2$ composite, cobalt acetate was added to prepared Co-doped MoS$_2$/TiO$_2$ photocatalyst. The experimental results show that the photocatalytic activity of the Co-doped MoS$_2$/TiO$_2$ composite is significantly improved compared with that of the undoped MoS$_2$/TiO$_2$ composite in the aspect of photocatalytic hydrogen production from water. The enhanced activity should be mainly ascribed to the more exposed active sites and broadened absorption region due to the doping of Co ions.

1. Introduction

The direct conversion of water into hydrogen fuel through artificial photosynthesis is considered to be an effective method to alleviate energy crisis and solve environmental degradation [1, 2]. Recently, functional two-dimensional (2D) layered materials have attracted extensive attention in the field of photocatalytic hydrogen production due to their novel structural characteristics and unique properties [3, 4]. On the one hand, 2D semiconductor is an excellent cocatalyst support with a large specific surface area, which is conducive to the dispersion of cocatalysts. On the other hand, nano-level 2D layered cocatalyst has a large number of hydrogen evolution reaction sites, which leads to the improvement of photocatalytic activity.

Due to the advantages of high efficiency, low cost, rich crustal content, stability and non-toxicity, 2D anatase TiO$_2$ nanosheet (NS) with exposed (001) facet is considered as one of the most promising photocatalysts [5-7]. At present, the strategy to design efficient hydrogen-producing catalyst based on the NS is mainly to load precious metals, so as to form a 0D - 2D composite structure [8-10]. Although the loading of precious metals can effectively promote the separation of photogenerated electron-hole on TiO$_2$ NS, due to the limited contact interface between precious metals and TiO$_2$ NS, the photocatalytic activity of these materials is usually relatively low. The high price of precious metals also limits their widespread use. Therefore, there is an urgent need to develop a non-noble metal cocatalyst modified TiO$_2$ NS composite photocatalyst with a larger and closer contact interface. Recent studies have found that MoS$_2$ is an excellent catalyst for photocatalysis and electrocatalysis for hydrogen production due to the presence of a large number of exposed edges and sulfur edge active sites [11-15]. Coupling anatase TiO$_2$ NS with lamellar MoS$_2$ will increase the contact interface and charge transfer...
rate, thus greatly improving the photocatalytic activity of the 2D-2D composite. In addition, element doping (substituting or gap filling) can effectively regulate the Fermi level or band gap of the semiconductor and obtain better photoelectric performance. In layered materials, doped atoms can also be inserted into layers or generate new crystalline phases.

We first designed and synthesized the MoS$_2$/TiO$_2$ composite photocatalyst, in which the anatase TiO$_2$ NS with exposed (001) facet was used as the light-trapping semiconductor, and the 2D layered MoS$_2$ was used as the photocatalytic cocatalyst for hydrogen production. Secondly, in the process of synthesis, we also doped Co into the MoS$_2$/TiO$_2$ NS to regulate its structure. The photocatalytic performance was greatly improved through changing the doping concentration.

2. Experimental Section

2.1 Synthesis of TiO$_2$ NS

25 mL tetrabutyl titanate was measured and poured into a beaker. 3 mL hydrofluoric acid (40%) was added under stirring. After stirring for about 5 min, the solution was transferred to a 100 mL polytetrafluoroethylene (PTFE) autoclave. The autoclave was sealed and put into the oven. After heated to 180 °C and kept for 24 h, the autoclave was cooled to room temperature. The obtained white precipitate was centrifuged and washed for three times with 0.1 mol/L NaOH solution, and then the supernatant was centrifuged and washed with deionized water to be neutral. The final product was dried under vacuum at 60 °C for 12 h.

2.2 Hydrothermal synthesis of MoS$_2$/TiO$_2$ NS

40 mL deionized water was first measured and poured into the beaker, and then 55.3 mg of TiO$_2$ NSs powder prepared above was weighed and added into the water for ultrasonic dispersion. Then thiourea (52.6 mg) and sodium molybdate dihydrate (25.13 mg) were added successively and ultrasonic dispersion was conducted. Dispersion was then stirred for 5 min, and transferred into a 50 mL PTFE autoclave. After heated to 200 °C for 24 h, the autoclave was cooled to room temperature. The precipitate was centrifuged and washed three times with deionized water and then centrifuged and washed once with anhydrous ethanol. The final product was dried under vacuum at 60 °C for 12 h.

2.3 Hydrothermal synthesis of Co-doped MoS$_2$/TiO$_2$ NS

The synthesis of Co-doped MoS$_2$/TiO$_2$ NS is the same as that of MoS$_2$/TiO$_2$ NS, except that a certain amount of cobalt tetrahydrate was added.

2.4 Material characterization

X-ray diffraction (XRD) was performed on Rigaaku corporation UltimaLV X-ray diffractometer using Cu Kα radiation (I = 1.5406 Å). The measurements were done in reflection geometry and diffraction angles, 2θ, were scanned at a rate of 0.016 s$^{-1}$. The morphologies of samples were investigated using scanning electronic microscopy (SEM, Verios 460L) and high-resolution transmission electronic microscopy (TEM with FEG, Talos F200X).

2.5 Photocatalytic performance measurements

The experiment of photocatalytic hydrogen production was carried out under the condition of Labsolar-IIIAG hydrogen production system. The light source used for simulating sunlight was xenon lamp (300 W). The experimental steps were as follows: firstly, 20 mg as-obtained photocatalysts was dispersed in 60 mL deionized water, and then appropriate Na$_2$SO$_3$ and Na$_2$S were added successively as hole sacrificial agents, and their concentrations were 0.35 mol/L and 0.25 mol/L, respectively. During the reaction, the light source was about 10 cm away from the reaction liquid level, and the yield of H$_2$ was measured by gas chromatography (GC7900, Techcomp) online detection system. Gas chromatography was equipped with a TCD detector, and chromatographic column was 5Å molecular sieve packed column.
3. Results and Discussion

Figure 1. (a) SEM image of TiO$_2$ NS; (b) SEM image of MoS$_2$/TiO$_2$ NS; (c) TEM image of TiO$_2$ NS; (d) TEM image of MoS$_2$/TiO$_2$ NS; (e) TEM image of Co-doped MoS$_2$/TiO$_2$ NS; (f) HRTEM image of Co-doped MoS$_2$/TiO$_2$ NS.

Figure 1a and c are the SEM and TEM images of TiO$_2$ NS, respectively. As shown in the figure, the morphology of these TiO$_2$ NS is relatively uniform, all of which are flaky structures with a size of about 50 nm*40 nm*4 nm. Figure 1b and d are respectively the SEM and TEM images of MoS$_2$/TiO$_2$ NS. As can be seen from the figure, the original square NS become irregular in shape after the loading of layered MoS$_2$, and at the same time, there is also the formation of curly NS structure, which is ascribed to the growth of layered MoS$_2$ on the surface of TiO$_2$ NS. In order to further improve the photocatalytic performance of MoS$_2$/TiO$_2$ NS, we doped Co element into it. As can be seen from Figure 1e, after Co doping, the number of layer MoS$_2$ coating on TiO$_2$ NS is very few, even single layer coating. This may be because the doped Co ions enlarge the layer spacing between MoS$_2$, resulting in fewer layers of MoS$_2$. In addition, normally, as shown in Figure 1f, the lattice spacing of (002) facet of MoS$_2$ should be 0.62 nm, but this value increases to 0.82 nm after Co doping.

Figure 2. XRD patterns of the as-obtained samples.
Figure 2 shows the X-ray diffraction (XRD) patterns of the synthesized samples. All the diffraction peaks of the solvothermal synthesis TiO$_2$ NS are consistent with those of anatase TiO$_2$ standard card (JCPDS No.21-1272) without any impurity. When the MoS$_2$ was coated by solvothermal method, the obtained samples only show the diffraction peak of TiO$_2$, but no obvious diffraction peak of MoS$_2$ was detected, which may be caused by the low loading or poor crystallinity of the loaded MoS$_2$. Similarly, the samples doped with Co only show the diffraction peak of TiO$_2$.

![Figure 2. X-ray diffraction (XRD) patterns of the synthesized samples.](image)

**Figure 2.** X-ray diffraction (XRD) patterns of the synthesized samples.

In order to analyze the elemental composition of the sample, the sample was tested by X-ray energy spectrum (EDX). As shown in Figure 3, Ti, O, Mo, S, and Co were detected in the Co-doped MoS$_2$/TiO$_2$ NS, and the content of Mo element is only 3.91 wt%. This further indicates that the MoS$_2$ is indeed loaded on the TiO$_2$ NS, but the diffraction peak of MoS$_2$ does not appear on the XRD spectrum due to the low loading or poor crystallinity.

![Figure 3. EDX spectra of Co-doped MoS$_2$/TiO$_2$ NS.](image)

**Figure 3.** EDX spectra of Co-doped MoS$_2$/TiO$_2$ NS.

The UV-vis absorption spectrum can reflect the absorption of photocatalyst in the UV-visible region. It can be seen from Figure 4a that, compared with that before the MoS$_2$ was loaded, the photocatalysts loaded with MoS$_2$ show significant absorption in the visible region. Moreover, with the increase of Co doping amount, the absorption intensity of visible region also increases. This shows that loading MoS$_2$ on the surface of TiO$_2$ broadens its absorption range to a certain extent, and wide absorption of photocatalysts is a necessary condition for photocatalytic reaction.

![Figure 4.](image)

**Figure 4.** (a) UV-vis absorption spectra of the as-obtained samples. (b) Photocatalytic hydrogen evolution of the as-obtained samples.

The photocatalytic efficiency of the sample prepared in this experiment was evaluated by its photocatalytic hydrogen production performance. As shown in Figure 4b, pure TiO$_2$ NS shows poor photocatalytic activity, and the hydrogen production efficiency was only about 0.15 mmol/g/h. When MoS$_2$ was loaded, the efficiency of hydrogen production was better than that of TiO$_2$ NS, improved to about 0.25 mmol/g/h. It is well known that doping appropriate transition metal ions in semiconductor photocatalyst can significantly improve its photocatalytic efficiency. In this experiment, we investigated...
the influence of Co doping with different proportions on the photocatalytic performance of MoS$_2$/TiO$_2$ NS. As can be seen from Figure 5, with the increase of Co doping amount, the efficiency of photocatalytic hydrogen production first increases and then decreases. When doped with 5 wt% Co, the photocatalytic hydrogen production efficiency was the highest, reaching 0.72 mmol/g/h, and the photocatalytic hydrogen production efficiency of MoS$_2$/TiO$_2$ NS was increased by about two times.

In order to better understand the reasons for the performance improvement of Co-doped MoS$_2$/TiO$_2$ NS photocatalyst, we analyzed its possible mechanism on the basis of experiment and theory. In general, the possible reasons for the performance improvement are as follows: on the one hand, it may be that the interlayer doped metal ions increase the interlayer spacing of MoS$_2$, and the interlayer interaction force is weakened, making it easier to be stripped into 2D ultrathin NS with few layers, thus exposing more active sites; on the other hand, doped metal ions can also adjust the band structure of semiconductor and change the light absorption region, so as to enhance its photocatalytic activity.

4. Conclusion

MoS$_2$/TiO$_2$ NS was first prepared by combining the layered MoS$_2$ and TiO$_2$ NS through a simple solvothermal route. The experimental results show that the photocatalytic activity of this photocatalyst is significantly improved compared with that of TiO$_2$ NS in the aspect of photocatalytic hydrogen production. Cobalt acetate was then added when preparing MoS$_2$/TiO$_2$ composite photocatalyst, and Co-doped MoS$_2$/TiO$_2$ NS photocatalyst was obtained. The experimental results show that the photocatalytic activity of the photocatalyst doped with MoS$_2$/TiO$_2$ NS is significantly improved compared with that of the undoped MoS$_2$/TiO$_2$ NS in the aspect of photocatalytic hydrogen production from water. It should be mainly ascribed to the more exposed active sites and broadened absorption region due to the doping of Co ions.

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