Synthesis and Characterization of MoS₂/Graphene-TiO₂ Ternary Photocatalysts for High-Efficiency Hydrogen Production under Visible Light

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ABSTRACT

Ternary MoS₂/graphene (G)-TiO₂ photocatalysts were prepared by a simple hydrothermal method. The morphology, phase structure, band gap, and catalytic properties of the prepared samples were investigated by X-ray diffraction, Raman spectroscopy, scanning electron microscopy, UV-vis spectrophotometry, and Brunauer-Emmett-Teller surface area measurement. The H₂ production efficiency of the prepared catalysts was tested in methanol-water mixture under visible light. MoS₂/G-TiO₂ exhibited the highest activity for photocatalytic H₂ production. For 5 wt.% and 1 wt.% MoS₂ and graphene (5MT-1G), the production rate of H₂ was as high as 1989 μmol⁻¹h⁻¹. The catalyst 5MT-1G showed H₂ production activity that was ~ 11.3, 5.6, and 4.1 times higher than those of pure TiO₂, 1GT, and 5MT, respectively. The unique structure and morphology of the MoS₂/G-TiO₂ photocatalyst contributed to its improved hydrogen production efficiency under visible light.

Key words : Heterojunction, Hydrogen production, Visible light

1. Introduction

Increasing environmental pollution and energy consumption are the two most serious problems facing humanity today, due to which, the development of techniques for the efficient utilization of solar energy has attracted much attention.^{1,2)} As a renewable clean energy source, solar energy can be used to decompose water into hydrogen and oxygen over a photocatalyst, which can be further stored in the form of chemical energy or converted into a fuel.³⁻⁶⁾ In view of their low cost, unique structure and excellent physicochemical properties, both TiO₂ and MoS₂ are of great interest as photocatalyst materials.⁷⁻⁹⁾ However, there are inherent disadvantages when using TiO₂ or MoS₂ alone that severely limit their practical application, but it has been observed that TiO₂ and MoS₂ are highly complementary.^{10,11)} This finding has led to much research effort in recent years to form MoS₂/TiO₂ composites to improve photocatalytic activity.¹²⁻¹⁶⁾ However, although both TiO₂ and MoS₂ can be

easily prepared using low-cost methods, the reported synthesis procedures for MoS₂/TiO₂-based composites are complex, expensive, and are not satisfactory in terms of performance.¹⁷⁾ The most advantageous among these processes is that involving ex-situ synthesis in being low cost and is scalable. However, TiO₂ and MoS₂ in the obtained MoS₂/TiO₂-based composite material have weak interfacial interaction and their dispersion in the composite is highly inhomogeneous. Hence, a considerable fraction of MoS₂ does not make sufficient contact with the TiO₂ skeleton, which affects the stability and electrical conductivity of the composite.¹⁸⁾ In in-situ synthesis, the most common methods used to make a strong interfacial contact between MoS₂ and TiO₂ in the prepared MoS₂/TiO₂ composite are through hydrothermal and solvothermal reactions. However, it has been observed that the MoS₂/TiO₂-based composite prepared by this method exhibits structural instability due to a lattice mismatch between TiO₂ and MoS₂. This results in a considerable amount of MoS₂ that is not adequately contacted to TiO₂, leading to an unstable interface during photocatalysis.¹⁹⁻²⁰⁾ The interface between the constituent components is an important criterion that affects the performance of composite materials; hence, adhesion at the interface must be strictly controlled in MoS₂/TiO₂-based composites. At present, the photocatalytic activity of MoS₂/TiO₂ composites is still low under visible light because of the lack of active catalytic reaction sites to enable the effective separation of electron-hole pairs. Therefore, several strate-

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gies have been employed to increase the photocatalytic hydrogen production efficiency of these composites, for example, by extending the light utilization range to the visible region, improving bonding at the interface or through additives such as graphene that can be supported on MoS₂/TiO₂ to form a ternary composite. Graphene (RGO) has a high specific surface area and excellent electrical conductivity and has therefore been widely used as a co-catalyst to prevent agglomeration and enhance the electron transfer ability of the catalyst. Therefore, the introduction of RGO into the MoS₂/TiO₂ composite is expected to effectively improve the photocatalytic activity.²¹⁻²⁴ Xiang synthesized a TiO₂/MoS₂/RGO (T/MG) composite photocatalyst by a two-step hydrothermal method, in which, TiO₂ nanoparticles were grown on the surface of layered MoS₂/RGO (MG). Under the UV light irradiation, the photogenerated electrons on TiO₂ could be transferred to both MoS₂ and G promoters, which effectively improved the separation and migration efficiency of the charge carriers. As a result, the ternary T95M5G sample showed a high photocatalytic activity of 2066 $\mu\text{mol}^{-1}\text{h}^{-1}$, which was 4 times that of the binary T/100 M0G sample.¹⁵ Li and his team used glucose to improve contact between TiO₂ and MoS₂ to promote the adhesion of MoS₂ to the TiO₂ surface in MoS₂@TiO₂ composites.¹⁶ The strong interfacial interaction between MoS₂ and TiO₂ and the large-area contact significantly improved stability and resulted in effective charge transfer. In this study, we have developed a method to increase the transmission efficiency of photogenerated electron holes by adsorbing MoS₂ on the surface of graphene. Moreover, the morphology and interfacial properties of TiO₂ were modified by hydrofluoric acid using glucose and a surfactant as chelating agents. These two modifications enhanced interaction at the MoS₂/G-TiO₂ interfaces and greatly improved both H₂ production efficiency and stability of the MoS₂-G/TiO₂ composite under visible light.

2. Experimental Procedure

2.1. Materials

Sodium molybdate dihydrate (Na₂MoO₄·2H₂O), thiourea (H₂NCSNH₂), hydrochloric acid (HCl), polyvinylpyrrolidone ((C₆H₉NO)_n), sodium dodecylbenzenesulfonate (C₁₈H₂₉NaO₃S), tetrabutyl titanate (C₁₆H₃₆O₄Ti), diethanolamine (C₄H₁₁NO₂), ethanol (C₂H₆O) and glacial acetic acid (C₂H₄O₂) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphene oxide slurry was obtained from Shan dong Yuhuang New Energy Technology Co., Ltd. All reagents were of analytical grade and no further purification was required. Distilled water was further purified before use.

2.2. Synthesis of MoS₂/G Photocatalyst

Sodium molybdate (0.363 g) and thiourea (0.324 g) used as molybdenum and sulfur sources, respectively, were mixed with a known quantity of graphene oxide and dissolved in

20 mL of 1.48 mmol/L sodium dodecylbenzene sulfonate solution in water. Hydrochloric acid (3 mmol) of was added dropwise to this solution After stirring for 30 min, the resulting solution was transferred to a Teflon-lined autoclave (30 mL) and heated at 220°C for 20 h. The obtained precipitate was collected by centrifugation, washed three times with distilled water and ethanol and dried in an oven at 60°C for 12 h.

2.3. Synthesis of MoS₂/G-TiO₂ Photocatalyst

MoS₂/G-TiO₂ photocatalyst was synthesized by a hydrothermal method. In the first step, MoS₂/G (24 mg), glucose (50 mg) and 0.9 g of polyvinylpyrrolidone (PVP) were added to a mixture of acetic acid (4 mL) and ethanol (16 mL). Next, 1 mL of hydrofluoric acid was added dropwise and stirred for 20 min using a magnetic stirrer. The solution was then sonicated for 45 min using an ultrasonic cell grinder (1000 W). Tetrabutyl titanate (1.7 mL) and diethanolamine (0.4 mL) were added to ethanol (7.5 mL) and stirred for 30 min, and this solution was added dropwise to the MoS₂/G mixed solution under magnetic stirring and left stirring for 45 min. Finally, the mixed solution was transferred to a polytetrafluoroethylene-lined autoclave (30 mL) and heated to 180°C for 10 h. The obtained precipitate was collected by centrifugation, washed three times with distilled water and ethanol and dried in an oven at 60°C for 12 h. The samples were labeled as 1GT-2M, 1GT-4M, 1GT-5M, 1GT-6M, 1GT-8M, and 1GT-10M, depending on the MoS₂ content. Samples with different G contents were labeled 5MT-0.25G, 5MT-0.5G, 5MT-0.75G, 5MT-1G, 5MT-1.25G, and 5MT-1.5G.

2.4. Characterization

Crystal structures were determined by X-ray powder diffraction (XRD) using a Bruker D8 Advance diffraction with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$, 40 keV, 40 mA). Raman measurements were performed using a Via Reflex micro-Raman spectrometer with excitation at a wavelength of 532 nm. The size and morphology of the samples were investigated by scanning electron microscopy (SEM) (JOEL, JSM-7500F). Ultraviolet (UV)-visible absorption spectra were taken with the help of a UV-vis spectrophotometer (SolidSpec-3700, Japan). The laser beam was focused by a 50 $\times$ objective lens to a $\sim 1 \mu\text{m}$ spot on the surface of the sample. Specific surface areas were determined from N₂ adsorption isotherms measured at 77 K (JW-BK132F) using the Brunauer-Emmett-Teller (BET) equation

2.5. Photocatalytic hydrogen production performance

An On-line photocatalytic hydrogen production system (AuLight, Beijing, and CELSPH₂N) was used to measure the photocatalytic hydrogen production at the ambient temperature of 20°C. Photocatalytic H₂ production experiments were carried out in a closed gas circulation and evacuation system fitted with a top Pyrex window. The photocatalyst (25 mg) was dispersed in 50 mL of methanol-water mixture

(containing 10 mL of methanol and 40 mL of deionized water). Photocatalytic experiments were conducted in a single compartment Pyrex reactor of volume $\sim 196 \text{ cm}^3$ having a flat window $\sim 19.6 \text{ cm}^2$ area for illumination. A 300-W Xe lamp (545 mW/cm^2) equipped with an optical cutoff filter of 420 nm was employed for visible-light excitation; the intensity of the light source was estimated to be 180 mW/cm^2 . Gas evolution was observed only under photo-irradiation, and the evolved gases were analyzed using an online gas chromatograph (SP7800, TCD, $5 \text{ \AA}$ molecular sieve, N_2 carrier gas). To evaluate the stability of the photocatalyst, the photocatalyst was separated from the suspension after the first 8 h of hydrogen production run, washed with water, and dried at 60°C . The recovered photocatalyst was then used in the next hydrogen production run under the same conditions.

3. Results and Discussion

3.1. Characterization of catalysts supports

3.1.1. XRD analysis

The results of XRD analysis of MoS_2 , TiO_2 , 5MT and 5MT-1G are shown in Fig. 1. In the XRD pattern of 5MT and 5MT-1G, there are several strong and narrow peaks corresponding to (002), (101), (103) and (105) crystal planes of MoS_2 (standard PDF card, No. JCPDS37-14920) indicating the high crystallinity of the nanosheets.²⁵⁻²⁸ The diffraction peaks at 26.5° , 37.5° and 47.8° can be attributed to reflections from the (101), (004) and (200) crystal planes of TiO_2 (standard PDF cards JCPDS75-1621). Diffraction peaks due to carbon species in the photocatalyst could not be observed due to its low mass ratio and the low diffraction intensity of G.²⁹⁻³¹ Therefore, Raman spectroscopy was used to analyze the composition of the material.³²

3.1.2. Raman spectral analysis

The Raman spectrum of pure MoS_2 , which is taken to be

Fig. 1. XRD patterns of pure TiO_2 , MoS_2 , 5MT (5% $\text{MoS}_2/\text{TiO}_2$) and 5MT-1G (5% $\text{MoS}_2/1\%\text{G-TiO}_2$) photocatalysts.

Fig. 2. Raman spectra of bulk MoS_2 , 5MT (5% $\text{MoS}_2/\text{TiO}_2$) and 5MT-1G (5% $\text{MoS}_2/1\%\text{G-TiO}_2$).

the reference sample, is shown in Fig. 2. Raman spectra of both 5MT and 5MT-1G show the two characteristic peaks at 387 and 406 cm^{-1} corresponding to MoS_2 ³³ originating from E_{2g}^1 and A_{1g} vibration modes, which represent, respectively, the inter-layer displacement of S atoms and the outward symmetric displacement of S atoms along the c-axis. In addition, the frequency difference between the two characteristic Raman peaks is $\sim 19 \text{ cm}^{-1}$, which confirms that the MoS_2 sheet is very thin.³⁴⁻³⁶ Peaks at 151, 514 and 635 cm^{-1} are characteristic of TiO_2 .¹⁵ As compared to 5MT, two more peaks of 1350 cm^{-1} and 1600 cm^{-1} can be seen in the 5MT-1G sample, which are characteristic peaks of G. Raman spectra thus demonstrate that the composite $\text{MoS}_2/\text{G-TiO}_2$ photocatalyst was successfully prepared.³³

Fig. 3. SEM images of (a) graphene oxide; (b) MoS_2/G ; (c) magnified image showing clusters of MoS_2/G and (d) 5MT-1G (5% $\text{MoS}_2/1\%\text{G-TiO}_2$).

3.1.3. SEM characterization

SEM images (Fig. 3(a)) show that graphene oxide is a large area nanosheet where self-assembled MoS₂ spheres are seen adsorbed on the graphene surface, the edges of the graphene sheet are slightly folded (Fig. 3(b)). The MoS₂ spheres are self-assembled from MoS₂ monolayers and have uniform diameters in the range 50–100 nm. An ultra-thin nano-MoS₂ layer was clearly observed in Fig. 3(c), indicating that the MoS₂ crystal form in the MoS₂/G material also grows along the sheet. In Fig. 3(d), the morphology of the 5MT-1G catalyst can be seen, which consists of a sphere composed of MoS₂ sheets and graphene that are uniformly dispersed in the TiO₂ matrix during ultrasonic dispersion to form a perfectly mixed MoS₂/G-TiO₂ photocatalyst.

3.1.4. UV-vis spectroscopic analysis

Figure 4 shows the UV-vis absorption spectra of the catalysts. All samples absorbed both UV and visible light as expected, confirming the photocatalytic activity of the composite catalyst in visible light. The pure TiO₂ sample shows an absorption edge at ~ 387 nm corresponding to a band gap of 3.2 eV¹⁵⁾ and the absorption onset of MoS₂ is at 461 nm. The exciton peak at 688 nm corresponding to the band gap of 1.8 eV emitted by brillouin region K in MoS₂ can be clearly observed in the composite materials and in pure MoS₂, proving the successful surface modification of TiO₂ by MoS₂.²⁵⁾ As compared to pure TiO₂, the absorption of 5MT, 1GT, and 5MT-1G is stronger in the visible range. Upon the

Fig. 4. UV-vis spectra of TiO₂, 1GT (1%G/TiO₂), 5MT (5%MoS₂/TiO₂), and 5MT-1G (5%MoS₂/1%G-TiO₂).

Table 1. BET Surface Area of the Photocatalysts

Sample	S _{BET} (m ² /g) ^{a)}
TiO ₂	12.2
1%G/TiO ₂	69
5%MoS ₂ /TiO ₂	101.7
5%MoS ₂ /1%G-TiO ₂	205.8

^{a)}Obtained from BET method.

addition of MoS₂ and graphene, a red shift in the absorption edge occurs accompanied by increase in absorption strength.

3.1.5. Surface area of the catalysts

Table 1 lists the specific surface area values of the catalysts. As-prepared 1GT has a surface area of 69 m²/g, while the surface area of 5MT is found to be 101.7 m²/g, thus

Fig. 5. Photocatalytic H₂ production activity of (a) samples with different mass ratio of MoS₂; (b) Samples with different mass ratios of G; (c) photocatalytic H₂ evolution cycle test for 5MT-1G photocatalyst consisting of 5% MoS₂ and 1% G under 300 W xenon lamp (λ > 420 nm), 0.025 g of cat. Dispersed in 50 mL of (20%) methanol in wat.

showing that the SSA values are increased, respectively, by 5.7 and 8.4 times, as compared to that of pure TiO_2 ($12.2 \text{ m}^2/\text{g}$). A dramatic increase in surface area is observed for layered MoS_2 and RGO-embedded TiO_2 systems. Thus, the specific surface area of the 5MT-1G photocatalyst is as high as $205.8 \text{ m}^2/\text{g}$. Combining MoS_2 and RGO improves the structure of TiO_2 , leads to a favorable synergistic effect, creates more reactive sites, increases visible light absorption, and results in better charge separation and electron transfer efficiency.

3.2. Analysis of the photocatalytic hydrogen evolution activity and its mechanism

As shown in Fig. 5(a) and 5 (b), we have studied the effect addition of MoS_2 and G of different mass loading on the photocatalytic hydrogen production activity of TiO_2 . The photocatalytic efficiency of pure TiO_2 under visible light is only $176 \mu\text{molg}^{-1}\text{h}^{-1}$ and the photocatalysts 1GT and 5MT showed slightly higher photocatalytic activity, with H_2 generation rates of $401 \mu\text{molg}^{-1}\text{h}^{-1}$ and $557 \mu\text{molg}^{-1}\text{h}^{-1}$, respectively. Photocatalytic hydrogen production is increased with increase in both MoS_2 and G content. It can be speculated that the quantum confinement effect of MoS_2 promotes charge separation and the excellent charge transfer capacity of G enhances the photocatalytic activity. When the MoS_2 content is 5 wt.% with 1 wt.% G, the H_2 generation rate reaches a maximum of $1989 \mu\text{molg}^{-1}\text{h}^{-1}$, which is 12.9 times higher than that of TiO_2 . Further increasing the content of MoS_2 in the catalyst results in a decrease in photocatalytic activity, this could be due to the higher MoS_2 and G concentration in TiO_2 , which is not conducive to charge separation and photo-generated electron migration.

A tentative mechanism is proposed to explain the high H_2

production rate of the $\text{MoS}_2/\text{G-TiO}_2$ photocatalyst, as illustrated in Fig. 6. Under visible light, photo-generated electrons in TiO_2 are excited and transferred onto the surface. Being a good two-dimensional layered conductor, the redox potential of graphene is slightly lower than the CB of anatase TiO_2 . Graphene can combine with the cluster formed from nano-layered MoS_2 to enhance its electrical conductivity. The cluster formed by self-assembly of nano MoS_2 layer has a large number of exposed edges and unsaturated active S atoms and therefore acts as a good co-catalyst. The photo-generated electrons in the CB of TiO_2 can be transferred to the clusters in nano MoS_2 layers through the graphene sheets (which act as a conductive electron transport “highway”) enabling fast charge transfer (Fig. 6). Some of the electrons approaching the edge of MoS_2 react directly with adsorbed H^+ in H_2O to produce H_2 due to the presence of unsaturated active S atoms in the co-catalyst, which can accept electrons and act as active sites for H_2 generation. Furthermore, the stability of 5MT-1G was tested by repeating the photocatalytic H_2 production four times (Fig. 5(c)) and the change in hydrogen production was less than 10%. This result demonstrates the high stability and excellent catalytic activity of our composite catalyst in photocatalytic hydrogen production.

4. Conclusions

The $\text{MoS}_2/\text{G-TiO}_2$ photocatalyst prepared in this work has a high visible light catalytic hydrogen production activity and excellent stability. Results show that the special heterojunction structure in the composite enhances the separation efficiency of photogenerated carriers and improves charge transfer efficiency. Moreover, the high specific surface area

Fig. 6. Schematic showing the mechanism of photocatalysis of $\text{MoS}_2/\text{G-TiO}_2$.

effectively increases the number of active sites at the reaction sites and also tailors the forbidden band width to increase visible light utilization.

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