Synthesis and Characterization of MoS$_2$/Graphene-TiO$_2$ Ternary Photocatalysts for High-Efficiency Hydrogen Production under Visible Light

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(Received April 17, 2019; Accepted May 7, 2019)

ABSTRACT

Ternary MoS$_2$/graphene (G)-TiO$_2$ 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 H$_2$ production efficiency of the prepared catalysts was tested in methanol-water mixture under visible light. MoS$_2$/G-TiO$_2$ exhibited the highest activity for photocatalytic H$_2$ production. For 5 wt.% and 1 wt.% MoS$_2$ and graphene (5MT-1G), the production rate of H$_2$ was as high as 1989 µmol h$^{-1}$. The catalyst 5MT-1G showed H$_2$ production activity that was ~11.3, 5.6, and 4.1 times higher than those of pure TiO$_2$, 1G, and 5MT, respectively. The unique structure and morphology of the MoS$_2$/G-TiO$_2$ 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. 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 energy can be used to decompose water into hydrogen and oxygen. However, although both TiO$_2$ and MoS$_2$ are of great interest as photocatalyst materials, there are inherent disadvantages when using TiO$_2$ or MoS$_2$ alone that severely limit their practical application, but it has been observed that TiO$_2$ and MoS$_2$ are highly complementary. This finding has led to much research effort in recent years to form MoS$_2$/TiO$_2$ composites to improve photocatalytic activity. However, although both TiO$_2$ and MoS$_2$ can be easily prepared using low-cost methods, the reported synthesis procedures for MoS$_2$/TiO$_2$-based composites are complex, expensive, and are not satisfactory in terms of performance. The most advantageous among these processes is that involving ex-situ synthesis in being low cost and is scalable. However, TiO$_2$ and MoS$_2$ in the obtained MoS$_2$/TiO$_2$-based composite material have weak interfacial interaction and their dispersion in the composite is highly inhomogeneous. Hence, a considerable fraction of MoS$_2$ does not make sufficient contact with the TiO$_2$ skeleton, which affects the stability and electrical conductivity of the composite. In in-situ synthesis, the most common methods used to make a strong interfacial contact between MoS$_2$ and TiO$_2$ in the prepared MoS$_2$/TiO$_2$ composite are through hydrothermal and solvothermal reactions. However, it has been observed that the MoS$_2$/TiO$_2$-based composite prepared by this method exhibits structural instability due to a lattice mismatch between TiO$_2$ and MoS$_2$. This results in a considerable amount of MoS$_2$ that is not adequately contacted to TiO$_2$, leading to an unstable interface during photocatalysis. 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 MoS$_2$/TiO$_2$-based composites. At present, the photocatalytic activity of MoS$_2$/TiO$_2$ 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-
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 MoS$_2$/TiO$_2$ 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 MoS$_2$/TiO$_2$ composite is expected to effectively improve the photocatalytic activity.\textsuperscript{21-24} Xiang synthesized a TiO$_2$/MoS$_2$/RGO (T/MG) composite photocatalyst by a two-step hydrothermal method, in which, TiO$_2$ nanoparticles were grown on the surface of layered MoS$_2$/RGO (MG). Under the UV light irradiation, the photogenerated electrons on TiO$_2$ could be transferred to both MoS$_2$ 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 μmol\(^{-}\)• g\(^{-}\)\(\text{H}_2\)\(\text{L}^{-}\)h\(^{-}\)\(^1\), which was 4 times that of the binary T/100 M0G sample.\textsuperscript{15} Li and his team used glucose to improve contact between TiO$_2$ and MoS$_2$ to promote the adhesion of MoS$_2$ to the TiO$_2$ surface in MoS$_2$/@TiO$_2$ composites.\textsuperscript{16} The strong interfacial interaction between MoS$_2$ and TiO$_2$ 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 MoS$_2$ on the surface of graphene. Moreover, the morphology and interfacial properties of TiO$_2$ were modified by hydrofluoric acid using glucose and a surfactant as chelating agents. These two modifications enhanced interaction at the MoS$_2$/G-TiO$_2$ interfaces and greatly improved both \(\text{H}_2\) production efficiency and stability of the MoS$_2$/G/TiO$_2$ composite under visible light.

2. Experimental Procedure

2.1. Materials
Sodium molybdate dihydrate (Na$_3$MoO$_4$·2H$_2$O), thiourea (H$_2$NCSNH$_2$), hydrochloric acid (HCl), polyvinylpyrrolidone (C$_9$H$_9$NOSO$_2$), sodium dodecylbenzenesulfonate (C$_{17}$H$_{33}$NaO$_2$S), tetrabutyl titanate (C$_{18}$H$_{36}$O$_4$Ti), diethanolamine (C$_{4}$H$_{12}$N$_{2}$O$_{4}$), ethanol (C$_{2}$H$_{6}$OH) and glacial acetic acid (C$_2$H$_4$O$_2$) 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 MoS$_2$/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 MoS$_2$/G-TiO$_2$ Photocatalyst
MoS$_2$/G-TiO$_2$ photocatalyst was synthesized by a hydrothermal method. In the first step, MoS$_2$/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 MoS$_2$/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 MoS$_2$ 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 Kα radiation (λ = 1.5406 Å, 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× objective lens to a ~ 1 μm spot on the surface of the sample. Specific surface areas were determined from N$_2$ 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 CELSPH, N) was used to measure the photocatalytic hydrogen production at the ambient temperature of 20°C. Photocatalytic \(\text{H}_2\) 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...
Photocatalytic experiments were conducted in a single compartment Pyrex reactor of volume ~ 196 cm$^3$ having a flat window ~ 19.6 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 Å 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 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 $E_{12g}$ 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 ~ 19 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 MoS$_2$/G-TiO$_2$ photocatalyst was successfully prepared.\(^{37}\)
3.1.3. SEM characterization

SEM images (Fig. 3(a)) show that graphene oxide is a large area nanosheet where self-assembled MoS$_2$ spheres are seen adsorbed on the graphene surface, the edges of the graphene sheet are slightly folded (Fig. 3(b)). The MoS$_2$ spheres are self-assembled from MoS$_2$ monolayers and have uniform diameters in the range 50–100 nm. An ultra-thin nano-MoS$_2$ layer was clearly observed in Fig. 3(c), indicating that the MoS$_2$ crystal form in the MoS$_2$/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 MoS$_2$ sheets and graphene that are uniformly dispersed in the TiO$_2$ matrix during ultrasonic dispersion to form a perfectly mixed MoS$_2$/G-TiO$_2$ 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 TiO$_2$ sample shows an absorption edge at ~ 387 nm corresponding to a band gap of 3.2 eV$^{25}$ and the absorption onset of MoS$_2$ 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 MoS$_2$ can be clearly observed in the composite materials and in pure MoS$_2$, proving the successful surface modification of TiO$_2$ by MoS$_2$.$^{25}$ As compared to pure TiO$_2$, the absorption of 5MT, 1GT, and 5MT-1G is stronger in the visible range. Upon the

addition of MoS$_2$ 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 m$^2$/g, while the surface area of 5MT is found to be 101.7 m$^2$/g, thus

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
</tr>
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<tbody>
<tr>
<td>TiO$_2$</td>
<td>12.2</td>
</tr>
<tr>
<td>1%G/TiO$_2$</td>
<td>69</td>
</tr>
<tr>
<td>5%MoS$_2$/TiO$_2$</td>
<td>101.7</td>
</tr>
<tr>
<td>5%MoS$_2$/1%G-TiO$_2$</td>
<td>205.8</td>
</tr>
</tbody>
</table>

$^a$ Obtained from BET method.

Fig. 4. UV-vis spectra of TiO$_2$, 1GT (1%G/TiO$_2$), 5MT (5%MoS$_2$/TiO$_2$), and 5MT-1G (5%MoS$_2$/1%G-TiO$_2$).

Fig. 5. Photocatalytic H$_2$ production activity of (a) samples with different mass ratio of MoS$_2$; (b) Samples with different mass ratios of G; (c) photocatalytic H$_2$ evolution cycle test for 5MT-1G photocatalyst consisting of 5% MoS$_2$ 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 m$^2$/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 m$^2$/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 of 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 μmol·h$^{-1}$·g$^{-1}$ and the photocatalysts 1GT and 5MT showed slightly higher photocatalytic activity, with H$_2$ generation rates of 401 μmol·h$^{-1}$·g$^{-1}$ and 557 μmol·h$^{-1}$·g$^{-1}$, 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 μmol·h$^{-1}$·g$^{-1}$, 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 MoS$_2$-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$_2$O 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 MoS$_2$-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
effectively increases the number of active sites at the reaction sites and also tailors the forbidden band width to increase visible light utilization.

Acknowledgments

This work was financially supported by the Major Projects of Natural Science Foundation of Anhui province (1808085ME129), Natural Science Research in Anhui Colleges and Universities (KJ2018ZD050), Outstanding Young Talents Support Program in Colleges and Universities (gyqZD2018056), and College Students' Science and Technology Innovation Foundations (2018-242).

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