ZnO@MoS$_2$ Core–Shell Heterostructures Enabling Improved Photocatalytic Performance

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Abstract: This work reports the fabrication of ZnO@MoS$_2$ core–shell micro/nanomaterials and their photocatalytic performances. First, the ZnO@MoS$_2$ core–shell micro/nanorods heterostructures were grown by a two-step, hydrothermal method. Second, X-ray diffraction, scanning-electron microscopy, Raman spectra, and UV-visible spectra were applied to confirm and characterize the ZnO@MoS$_2$ core–shell micro/nanorods. Third, methylene blue was employed to investigate the photocatalytic performance of the ZnO@MoS$_2$ core–shell micro/nanorods heterostructures. It was found that the shape of the MoS$_2$ shell layer depended on the growth time. The shell layer was composed of MoS$_2$ nanoparticles before the growth time of 6 h and then turned into MoS$_2$ nanosheets. It was also found that the photocatalytic performance was significantly affected by the growth time of the MoS$_2$ nanosheets. When the growth time of the MoS$_2$ nanosheets was between 6 and 10 h, ZnO@MoS$_2$ core–shell heterostructures grown for 6 h exhibited a best photocatalytic efficiency value of 69.24% after 3 h catalysis.

Keywords: growth time; photocatalytic performances; ZnO@MoS$_2$ core–shell heterostructures

1. Introduction

Nowadays, widely applied, organic reagents cause a large amount of organic pollutants [1], which are considered a major threat to human health and survival. Therefore, the harmless treatment of organic pollutants has become a hot topic in past decades [2,3]. One of the green approaches is employing semiconductor materials to degrade the organic pollutants into non-toxic compounds under sunlight [4,5]. A great work has been carried out to pursue highly efficient, semiconductor photocatalysts, such as a single crystal TiO$_2$, zinc oxide (ZnO) CdS, etc. [6–8]. Among the highlighted, semiconductor photocatalysts, ZnO has attracted particular attention and has been studied numerous times due to its outstanding properties [3]. First, ZnO has versatility, availability, and low toxicity [9], which means low cost and environmental protection. Significantly, ZnO has a 3.37 eV band gap and high photo-responsivity (60 meV), which make it suitable for oxidation and reduction reactions by absorbing visible light for significant solar energy harvesting [10]. However, ZnO still suffers from some deficiency in photocatalysis. On the one hand, the photocatalytic reaction of ZnO is limited by the low, solar-energy conversion efficiency caused by the intrinsic, wide-band gap; high recombination rate of photo-generated, charge carriers; and possible photo-corrosion. On the other hand, the chemical stability of ZnO should not be ignored. In our previous study, we demonstrated that ZnO thin film can be easily etched by a 0.001 mol/L hydrochloric acid solution. In practice, organic-dye sewage is most likely to be acidic, which might allow it to cut down on ZnO materials.

One way to solve the first issue is by fabricating ZnO micro/nanomaterials. ZnO micro/nanomaterials possess large specific surface areas, quantum effects, and piezoelectric photoelectron effects. These perfect effects can greatly improve the solar-energy conversion
efficiency. Another effective method is to bring in co-catalysts, such as metal nanoparticles (Pt, Ag, Co, etc.) with graphene, graphene oxide, and transition metal dichalcogenides (i.e., MoS$_2$, WS$_2$, etc.) [6,9,11]. Among the above co-catalysts, MoS$_2$ exhibits nice chemical stability [10], indicating that the ZnO@MoS$_2$ core–shell nano-structure should be an outstanding photocatalyst. In this regard, MoS$_2$ nanosheets have been widely studied [9,10]. In numerous previous successful studies, the growth time of the MoS$_2$ nanomaterials with a hydrothermal method was over 10 h [12–15]. On the premise of ensuring efficient catalysis, shortening the growth time of the MoS$_2$ nanosheets can bring in two benefits. One is that saving time means saving source materials and cost. The other is that saving time results in improving production efficiency. As the famous quote says, “time is money; time is efficiency”. Therefore, cutting down on growth time is meaningful for the ZnO@MoS$_2$ core–shell nano-structure photocatalyst on the premise of ensuring efficient catalysis.

In this work, we explored ZnO@MoS$_2$ core–shell heterostructures that benefited from the excellent chemical stability and synergetic photocatalytic performance of the MoS$_2$ nanosheets. The MoS$_2$ nanosheets’ growth time was also investigated for effectively saving growth time on the premise of ensuring efficient catalysis.

2. Experimental Section

2.1. Growth of ZnO Micro/Nanorods

A total of 1.616 g of zinc acetate (Zn(CH$_3$COO)$_2$, purity of 99.5%) and 0.8 g of hexamethylenetetramine (C$_6$H$_{12}$N$_4$, purity of 99.5%) were added into the mixed solution of 15 mL of ethylene glycol (CH$_2$OH), purity of 99.5%) and 20 mL of deionized water and then stirred at 60 $^\circ$C for 1 h to obtain a uniform, precursor solution. Afterward, the precursor solution and clean indium tin oxide (ITO) substrates were transferred into an autoclave. The closed autoclave was put into a precision oven, and a growth process was carried out at 85 $^\circ$C for 5 min. After the growth process, ZnO micro/nanorods were achieved on the ITO substrates. The as-received ZnO micro/nanorods on ITO substrates were washed by deionized water to remove the residual precursor solution and dried at 80 $^\circ$C for 30 min.

2.2. Fabrication of ZnO@MoS$_2$ Core–Shell Heterostructures

High purity sulfur (S, 99.9%) powder and molybdenum oxide (MoO$_3$, 99.5%) were added to 20 mL of octane (C$_8$H$_{18}$, 99.5%) and then stirred at 60 $^\circ$C for 1 h to achieve the precursor solution for growing the MoS$_2$ shell layer on the as-received ZnO micro/nanorods (the core). Similarly, the precursor solution for growing MoS$_2$ and the as-received ZnO micro/nanorods on ITO substrates were put into another autoclave. The growth process was performed in the precision oven at 180 $^\circ$C for 1, 6, 8, and 10 h to synthesize the ZnO@MoS$_2$ core–shell heterostructures with different thicknesses of the MoS$_2$ nanosheets shell layer.

2.3. Characterization of the ZnO Micro/Nanorods and ZnO@MoS$_2$ Core–Shell Heterostructures

X-ray diffraction (XRD, X’Pert Pro MFD, PANalytical, Almelo, Netherlands) determined the structure of the as-received ZnO micro/nanorods and ZnO@MoS$_2$ core–shell heterostructures samples. Scanning electron microscopy (SEM, ZEISS Sigma 500, Jena, Germany, working voltage of 15 kV) was used to characterize the morphology of the as-received samples. An energy dispersive spectrometer (EDS) was employed to confirm the elements of the samples. An energy dispersive spectrometer (EDS) was employed to confirm the elements of the samples. Raman spectra (LabRAM HR UV-NIR, Paris, France) laser wavelength of 488 nm) and ultraviolet-visible spectra (Shimadzu, UV3600Plus, Kyoto, Japan) were conducted to detect the optical properties of the samples. A photochemical reactor (OCRS-K, mercury lamp as the light source, working power of 500 W) was utilized to investigate the photocatalytic properties of the as-received nano-structures.

3. Results and Discussion

XRD was applied to determine the crystalline structure of the three samples, and the results are shown in Figure 1. The XRD pattern of a blank ITO substrate was also taken
for comparison. From Figure 1, one can see clearly that, apart from the ITO peaks, the patterns for the ZnO@MoS$_2$ core–shell heterostructures samples have some peaks that can be well-indexed to ZnO (JCPDS:36-1451). Strangely, no independent peaks are assigned to MoS$_2$. However, when Mo$_3$S$_3$ (JCPDS:40-0972) or Mo$_{15}$S$_{19}$ (JCPDS:40-0936) are taken as a reference, three or four peaks appear in the same positions as those of ZnO or ITO. This result indicates that MoS$_2$ with rich sulfur vacancies is possibly fabricated on ZnO. Further analysis should be carried out to confirm the fabrication of MoS$_2$.

![Figure 1](image_url)

**Figure 1.** XRD patterns of the ITO substrate and the as-received ZnO@MoS$_2$ core–shell heterostructures under the MoS$_2$ growth time of 6, 8, and 10 h.

Furthermore, the element mapping images from SEM were deployed to confirm the fabrication of MoS$_2$ directly. Figure 2a is an SEM image of the ZnO@MoS$_2$ core–shell heterostructure with the MoS$_2$ shell grown for 1 h, and Figure 2b–e are the element mapping images corresponding to O, S, Zn, and Mo elements, respectively. The O signal is from the ZnO microrod and ITO substrates, while the Zn signal comes from the ZnO microrod due to the high working voltage of 15 kV. Accordingly, as can be seen, the shapes of S, Zn, and Mo are in the same position as the ZnO microrod of Figure 2a, indicating that MoS$_2$ has been achieved after hydrothermal growth, and ZnO micro/nanorods have been almost decorated with the MoS$_2$ shell layer. At the same time, in Figure 2f, the corresponding energy dispersive X-ray spectrometry (EDX) pattern of Figure 2a also verifies the existences of S and Mo. Therefore, the ZnO@MoS$_2$ core–shell heterostructures have been fabricated by the two-step hydrothermal method.

Except the element mapping images, the Raman spectrum is another technology used to confirm the fabrication of MoS$_2$ directly. As shown in Figure 3, when the MoS$_2$ growth time is 6 h, the intense peak of ZnO micro/nanorods at ~437 cm$^{-1}$ is sharply decreased, and a very weak peak at about 406.4 cm$^{-1}$ turns up. As the MoS$_2$ growth time is increased to 8 h, the peak at 406 cm$^{-1}$ becomes more prominent, and a new and weak peak at 377.3 cm$^{-1}$ appears. When the MoS$_2$ growth time is up to 10 h, the peaks at 406.4 cm$^{-1}$ and 377.3 cm$^{-1}$ can be seen distinctly. Meanwhile, the peak at 325 cm$^{-1}$ gradually becomes weaker and disappears as the growth time of MoS$_2$ is from 6 h to 10 h. According to previous publications [16–19], the peaks located at 377.3 cm$^{-1}$ and 406.4 cm$^{-1}$ can be assigned to the $A_{1g}$ mode of MoS$_2$ and to $E_{2g}$ mode of the Mo–S bond, respectively. These results are well-matched with those of the MoS$_2$ fabricated by the hydrothermal method [7]. Thus, the ZnO@MoS$_2$ core–shell heterostructures have been successfully achieved by two-step hydrothermal growth.
Figure 2. (a) SEM image of the as–received ZnO@MoS₂ core–shell heterostructure with the MoS₂ growth time of 1 h and its element mapping of (b) O, (c) S, (d) Zn, and (e) Mo. (f) Its corresponding EDX pattern.

Figure 3. Raman spectra of the as–received ZnO micro/nanorods and the as–received ZnO@MoS₂ core–shell heterostructures under the MoS₂ growth time of 6, 8, and 10 h.
It should be noted that the intensities of the peaks at 406.4 cm\(^{-1}\) and 377.3 cm\(^{-1}\) are about one-twentieth of that of the ZnO peak at ~437 cm\(^{-1}\). The intensity of the Raman peak is dependent on the quality and thickness of the materials based on our previous experiments. In this work, the ZnO materials are single microrods or nanorods, while the MoS\(_2\) materials are nanosheets. The quality and thickness of the ZnO micro/nanorods are much better than those of the MoS\(_2\) nanosheets. As a result, the Raman peak’s intensity of the ZnO micro/nanorods is much higher than that of the MoS\(_2\) nanosheets. Moreover, the peak at ~437 cm\(^{-1}\) for the ZnO@MoS\(_2\) heterostructures should be from the ZnO micro/nanorods, thanks to its super-strong intensity.

Much recent research has suggested that ZnO micro/nanorods produced by hydrothermal method exhibit smooth surfaces. In contrast, the MoS\(_2\) fabricated by the hydrothermal method usually endows rough surfaces or nanosheet-like structures. This means the surface diversification can be taken as an indirect method to just the hydrothermal growth of the MoS\(_2\) on the ZnO micro/nanorods. Figure 4a represents the SEM image of ZnO micro/nanorods. The SEM image shows that the as-grown ZnO samples consist of micro-rods with a typical diameter of ~2 \(\mu\)m and many small white particles. The SEM images recorded at high magnification clearly show the smooth surfaces of the ZnO micro/nanorods and the presence of the ZnO nanorods (Figure 4b).

Figure 4. SEM images of (a) the as-received ZnO micro/nanorods and (b) the as-received ZnO@MoS\(_2\) core–shell heterostructures grown for 1 h, (b,d) are the corresponding high-resolution SEM images of (a,c), respectively, and (e,f) are ZnO microrods and (b) ZnO@MoS\(_2\) core–shell heterostructures of (a,c) respectively. The insert picture of Figure 2b is the ZnO nanorods in Figure 2a marked by a red circle.
Furthermore, the insert SEM image in Figure 4b steads for the area in Figure 4a marked by a red circle at high magnification, which exhibits the ZnO nanorods, too. The ZnO samples grown hydrothermally in this work are the ZnO micro/nanorods. As illustrated in Figure 4c, after hydrothermal growth of MoS$_2$, the micro/nanorods become grayish and rough. Figure 4d, a high magnification SEM image, displays the rough surface of micro/nanorods modified with small particles. A single microrod of the ZnO and the ZnO@MoS$_2$ grown for 1 h are applied for comparison, as shown in Figure 4e,f, respectively. By comparing these two figures, the surface of the ZnO@MoS$_2$ microrod is much rougher than that of the ZnO microrod, suggesting the growth of MoS$_2$ again. Based on the discussion above, after the hydrothermal growth of the MoS$_2$, the ZnO@MoS$_2$ heterostructures have been obtained successfully.

According to our experiment, when the growth time is less than 6 h, the MoS$_2$ shell layer is composed of nanoparticles. When the MoS$_2$ growth time is 6 h, the surface morphology of the ZnO@MoS$_2$ core–shell heterostructures is very distinct from that grown for 1 h, as shown in Figure 5a,b as well as Figure 4d. As shown in Figure 5a, the bottom turns rough with the feature of MoS$_2$ nanosheets. Additionally, clearly, MoS$_2$ shell layers are well-decorated on the ZnO micro/nanorods (in Figure 5b). The MoS$_2$ nanosheets at the bottom grow significantly and more densely as the growth time is increased to 8 h, as shown in Figure 5c. However, it can be observed in Figure 5d that the growth rate of the MoS$_2$ nanosheets is slower than those of the bottom. Unfortunately, the MoS$_2$ nanosheets grown for 10 h have turned poor at the bottom, as illustrated in Figure 5e. Maybe due to the slow growth rate, the MoS$_2$ nanosheets on the ZnO micro/nanorods still keep the shape of the nanosheets well (Figure 5f).

Methylene blue solution is introduced to evaluate the photocatalytic performance of the ZnO@MoS$_2$ core–shell heterostructures. Furthermore, the ZnO micro/nanorods were chosen as a reference for comparison. Figure 6a illustrates that the ZnO@MoS$_2$ core–shell heterostructures grown for 6 h show the best photocatalytic performance. It is also found that the photocatalytic performance of the ZnO@MoS$_2$ core–shell heterostructures decreases as the MoS$_2$ growth time ranges from 6 to 10 h. Furthermore, the photocatalytic performance of the ZnO@MoS$_2$ core–shell heterostructures grown for 10 h is almost the same as that of the ZnO micro/nanorods. Based on previous work, the photocatalytic efficiency ($\eta$) is calculated from the following formula [19]:

$$\eta = \frac{(C_0 - C)}{C_0} \tag{1}$$

where $C_0$ and $C$ are the methylene blue initial solution concentration and the methylene blue concentration after photocatalytic degradation. According to this formula, the photocatalytic efficiency of the ZnO@MoS$_2$ core–shell heterostructures grown for 6, 8, and 10 h are 69.24%, 64.52%, and 58.34%, respectively. Moreover, the photocatalytic efficiency of the ZnO micro/nanorods is 58.13%. These results suggest that the growth time of the MoS$_2$ nanosheets shell layer has been significantly reduced for the ZnO@MoS$_2$ core–shell nano-structure photocatalyst on the premise of ensuring efficient catalysis. Furthermore, these results are comparable to those reported by Fu et al. [2] when grown for 24 h. In recent years, ZnO@ZnS@MoS$_2$ [20], ZnO@CdS@MoS$_2$ [21], ZnO@MoS$_2$@rGO [22], and ZnO@MoS$_2$@ polyaniline [23] dual heterojunctions have been developed to highly enhance photocatalytic performance. Moreover, MoS$_2$@ZnO heterojunctions have also been demonstrated to be highly efficient photocatalysts [4,24]. The photocatalytic efficiency of this work is close to that of the reports mentioned above. It can be found that, in most of these reports, the growth time of the MoS$_2$ nanosheets is over 10 h. Ref. [4] reported rapid growth of the MoS$_2$@ZnO heterojunctions by electric spark erosion, which is our future goal. It is well-known that the longer the growth time, the thicker the thickness of the MoS$_2$ shell layer. Normally, it is believed that the thicker thickness of the MoS$_2$ nanosheets shell layer leads to better photocatalytic efficiency. However, the photocatalytic efficiency is reduced when the growth time is increased in this work. The photocatalytic efficiency changing trend of the MoS$_2$ growth time in this work matches with the report by...
Putritama et al. [9]. However, the MoS$_2$ nanosheets shell layer increases the contact angle and shows inactive catalytic sites in Ref. [9], which reduces the photocatalytic efficiency of the ZnO@MoS$_2$ heterostructures.

Figure 5. SEM images of the as-received ZnO micro/nanorods and the as-received ZnO@MoS$_2$ core–shell micro/nanorods under the MoS$_2$ growth time of 6, 8, and 10 h: (a,c,e) correspond to MoS$_2$ (the bottom); (b,d,f) correspond to the as-received ZnO@MoS$_2$ core–shell heterostructures.

It is well-known that photocatalytic efficiency is significantly affected by light absorption. UV-visible spectra are employed to characterize the light absorption of ITO substrate, ZnO micro/nanorods, and ZnO@MoS$_2$ core–shell heterostructures with the MoS$_2$ growth time of 6 h, as illustrated in Figure 7. Compared with the blank ITO substrate, the ZnO micro/nanorods reveal a slightly higher light absorption in the range from 290 to 350 nm. The ZnO@MoS$_2$ core–shell heterostructures show a much higher light absorption in the range from 290 to 600 nm in the three samples. Accordingly, a higher light absorption usually results in a higher photocatalytic efficiency. It also can be confirmed by the color change of the methylene blue after photocatalytic degradation, as shown in the insert picture of Figure 7. The reason for the higher photocatalytic efficiency of the ZnO@MoS$_2$
core–shell heterostructures may be due to three aspects. The first is the rich sulfur vacancies in the MoS2 nanosheets shell layer [11,12]. The sulfur vacancies on the surface of the MoS2 shell layer have been demonstrated to be the active sites of the catalytic reactions. The more sulfur vacancies there are, the higher the photocatalytic efficiency is. The second is attributed to the heterojunction of MoS2/ZnO [2,15,25]. It has been demonstrated that the MoS2 chemically bonded to ZnO under high-pressure growth conditions to form the MoS2/ZnO heterojunction [2]. It should be noted that a strong internal field is set up by the MoS2/ZnO heterojunction, which leads to a significant promotion in the spatial separation of the photogenerated carriers [2]. The photogenerated carriers are believed to be the power source of the photocatalytic action. This indicates that the enhanced internal field created by the MoS2/ZnO heterojunction favors the photocatalytic efficiency. The third is the specific surface area enhanced by the MoS2 nanosheets. It is widely accepted that the MoS2 nanosheet’s shell layer owns a more extensive specific surface area than that of the ZnO micro/nanorods [11]. A bigger and rougher surface can absorb more organic dyes, suggesting a better photocatalytic efficiency [11].

Figure 6. Photocatalytic ability of the as-received ZnO micro/nanorods and the as-received ZnO@MoS2 core–shell heterostructures grown for 6, 8, and 10 h on methylene blue with a photocatalytic time of 3 h: (a) absorption spectra and (b) photocatalytic efficiency.

Figure 7. Absorption spectra of ITO substrate (black line), the as-received ZnO micro/nanorods (red line), and the as-received ZnO@MoS2 core–shell heterostructures (blue line) grown for 6 h and the insert picture is of the methylene blue solution after a 3 h photocatalytic reaction: (a) without any photocatalyst, (b) ZnO micro/nanorods, and (c) ZnO@MoS2 core–shell heterostructures grown for 6 h.

However, as the growth time exceeds 6 h, the photocatalytic efficiency of the ZnO@MoS2 core–shell heterostructures is reduced and kept down as the growth time is increased. As mentioned above, the thickness of the MoS2 nanosheet’s shell layer is thicker as the growth
time is increased. On the one hand, increasing the MoS2 nanosheet’s shell layer thickness will weaken the light absorption of the MoS2/ZnO heterojunction or ZnO micro/nanorods and further cut down on the spatial separation of the internal field [10]. Accordingly, this leads to a reduction in the photocatalytic efficiency. On the other hand, an increase in the MoS2 nanosheet’s shell layer thickness indicates an increase in the migrated path of the photogenerated carriers [9], which means that the recombination probability between the photogenerated carriers and the internal defects is increased. Meanwhile, the life of the photogenerated carriers is usually short, revealing that the photogenerated carriers would be possibly recombined before they migrate to the surface of the MoS2 nanosheet’s shell layer.

4. Conclusions

The ZnO@MoS2 core–shell heterostructures have been successfully fabricated by a two-step hydrothermal method. The surface morphology of the MoS2 shell layer is significantly affected by the growth time. Before 6 h, the MoS2 shell layer consists of nanoparticles. When the growth time is up to 6 h, the MoS2 nanoparticles have been turned into the MoS2 nanosheets. It is also found that the photocatalytic performance of the ZnO@MoS2 core–shell heterostructures is reduced as the growth time is increased from 6 to 10 h. Therefore, the growth time of the MoS2 nanosheet’s shell layer has been effectively reduced on the premise of ensuring the ZnO@MoS2 core–shell nano-structure’s photocatalytic efficiency.

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