Effect of annealing temperature on the photocatalytic performance of ZnO@MoS_2 composite materials

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Abstract. In this work, we report the ZnO@MoS2 composite materials prepared by a hydrothermal method, and the effect of annealing temperature on the photocatalytic performance of ZnO@MoS2 composite materials. It is found that annealing temperature plays an important role in the formation of MoS2 surface morphology, resulting in the dense films and a reduction of nanostructure nummber and active sites by enhancing temperature. Furthermore, ZnO@MoS2 composite materials annealed at 50 oC possess a higher photocatalytic degradation efficiency of 62.88% on methylene blue solution compared with ZnO materials or other samples.

Keywords: Hydrothermal method; ZnO@MoS2 composite materials; annealing temperature; photocatalytic performance.

1. Introduction

ZnO is a typical third-generation semiconductor material. ZnO has many advantages such as good photoelectric performance [1], abundant source materials, good biological and environmental compatibility, and good photocatalytic performance [2]. ZnO has been widely used in light-emitting diodes [1], photodetectors [3, 4], biosensors [5], sewage treatment [2, 6], etc. However, ZnO materials are prone to hydrolysis, which severely limits the application of ZnO. Especially in sewage treatment, ZnO needs to be soaked in sewage for a long time, and hydrolysis will drastically reduce its photocatalytic performance. Therefore, the surface of ZnO needs to be modified with a protective layer. While avoiding the hydrolysis of ZnO, it is necessary to further improve its photocatalytic performance [6]. MoS2 has stable chemical properties, does not hydrolyze, and can form a heterojunction with ZnO, which significantly improves the photocatalytic performance [6]. This work will hydrothermally grow the MoS2 nanosheet film layer on a film composed of ZnO micron/nanopillars to obtain a ZnO@MoS2 composite material. At the same time, this work also studies the effect of annealing process on the photocatalytic performance of ZnO@MoS2 composite materials.

2. Experimental details

Firstly, ZnO micro/nano pillars on ITO substrates were prepared by a hydrothermal method. The precursor solution was prepared with zinc acetate as the zinc source, hexamethyltetramine as the catalyst, polyethylene glycol as the buffer, and deionization as the solvent. The required reagents are added to deionized water, and magnetically stirred at 60 °C for 1 hour to obtain a clear and uniform precursor solution of 0.02 mol/L. The prepared precursor solution and the cleaned indium tin oxide (ITO) substrate were put into the autoclave, and the reaction solution was kept at 85 °C for 5 minutes to obtain the ZnO micron/nano column sample. And 2 minutes clean of deionized soak was used to remove residual reagents.

Then, the MoS2 shell layer was prepared on the ZnO micron/nano column sample using the hydrothermal method again. In order to avoiding the corrosion of the ZnO micron/nano column samples caused by the second hydrothermal, Mo2O3, high-purity S powder, octylamine and absolute ethanol were taken as the reaction system for the synthesis of MoS2, and the reaction time is 6 h. After cleaning and drying, the samples were annealed at 50 oC, 100 oC and 150 oC to improve the crystalline quality of MoS2 and the combination with ZnO, in order to obtain better photocatalytic performance.

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After the preparation, X-ray diffractometer (XRD, X'Pert Pro MFD), micro-focus Raman spectrometer (LabRAM HR UV-NIR), and high-resolution field emission scanning electron microscope (SEM, ZEISS Sigma 500) were used to detect the prepared samples. A photochemical reaction instrument (OCRS-K) was applied to test the photocatalytic performance of the photocatalytic performance on methylene blue solution. And an ultraviolet (UV) spectrophotometer (Shimadzu UV-2550) was employed to detect the photocatalytic effect of the prepared samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of ZnO@MoS2 composite materials without and with different annealing temperature. The star marks are corresponding to the peaks of ITO. The other peaks are assigned to ZnO peaks. There is no single peak belonged to MoS2. It seems that MoS2 does not have grown on ZnO. In fact, based on the PDF car of MoS2 in the XRD database, the peaks' locations of MoS2 are the same with those of ITO or ZnO. Besides, according to the reference of [6], MoS2 should be prepared on ZnO. Therefore, it is necessary to employ other techniques to identify the presence of MoS2.

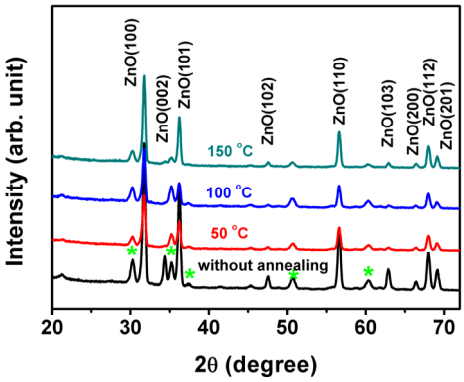


Fig.1 XRD patterns of ZnO@MoS_2 composite materials without and with different annealing temperature

SEM is taken to study the surface morphology of the prepared samples, as shown in Fig. 2(a) to 2(c). Before the growth of MoS_2, the ZnO surfaces are very smooth [7]. Significantly, dense nanosheets have been coated on the surfaces of ZnO materials after the preparation of MoS2. Normally, such nanosheets should be MoS_2. That is to say, ZnO@MoS2 composite materials have been successfully prepared on ITO substrates. Furthermore, as the annealing temperature is increased, the MoS_2 film consisted of nanosheets become dense, and the number of nanosheets or nanostructure is decreased. This indicates that annealing temperature plays an important role in the formation of MoS2 film surface.

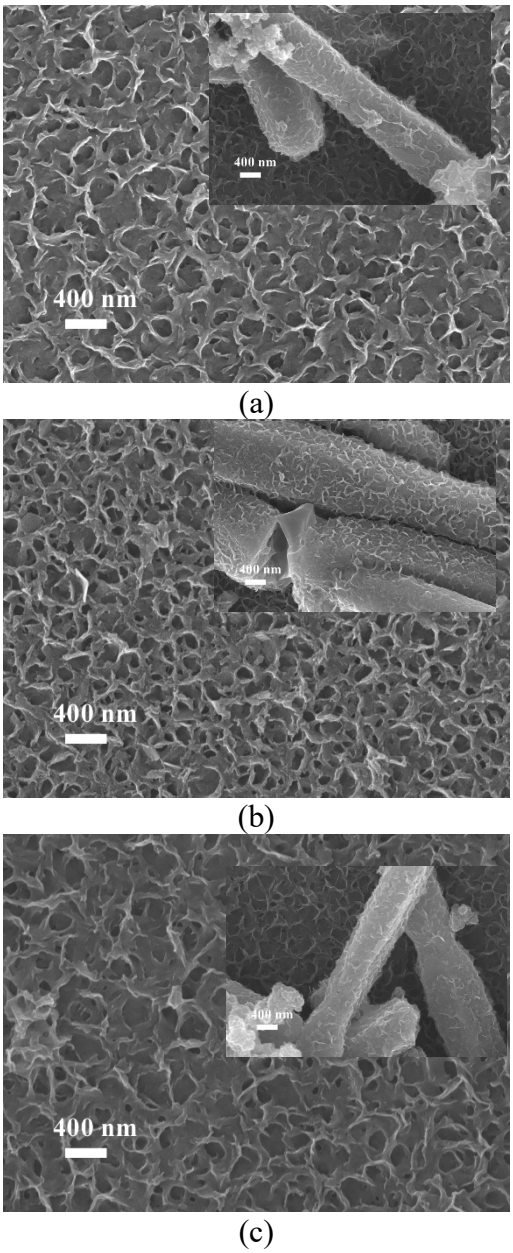


Fig.2 ZnO@MoS_2 composite materials with different annealing temperature: (a) 50 oC, (b) 100 oC, and (c) 150 oC

Raman spectra are carried out to confirm the MoS2, too. As shown in Fig. 3, seven sharp peaks can be found in the typical ZnO material. When it turns to the ZnO@MoS2 composite materials, most peaks of ZnO have been gone, and a wide peak is located in 328.5 cm-1, which should be composed of few peaks. It has been reported that MoS2 have two strong peaks located in about 405 cm-1 and 355 cm-1 in the Raman spectra [8]. Besides, after annealing, due to oxidation, new peaks are located in around 280 cm-1 and 335 cm-1, which is assigned to molybdenum oxide [9]. Indication, ZnO materials also have a peak in 332.5 cm-1 as shown in Fig.3. Based on what has been mentioned above, the wide peak located in 328.5 cm-1 may be mainly composed of the response of ZnO@MoS2 and a small part of molybdenum oxide. This result clearly means that MoS2 has been prepared on ZnO material. Moreover, during the annealing process, MoS2 has been slightly oxidized into molybdenum oxide.

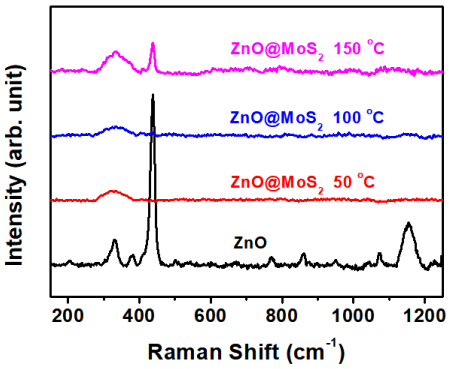
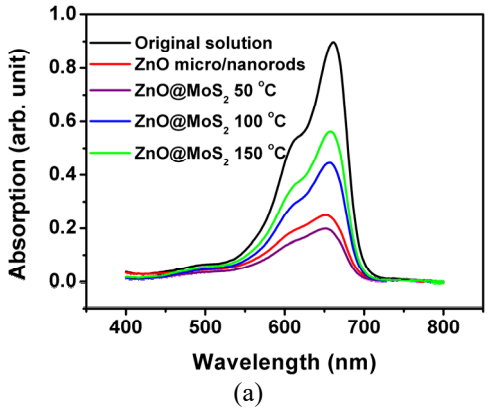


Fig.3 Raman spectra of ZnO and ZnO@MoS_2 composite materials

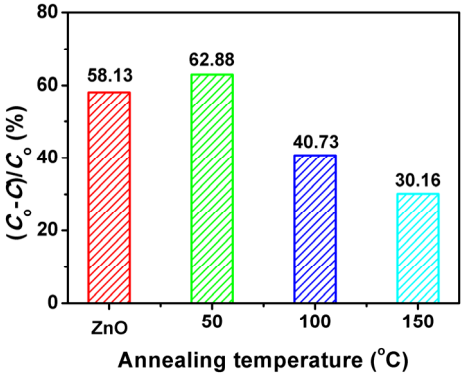
Fig. 4(a) is the absorption spectra of methylene blue solution treated with ZnO and ZnO@MoS2 composite materials. It can be seen clearly that ZnO@MoS2 composite materials has the best photocatalytic degradation efficiency. And unfortunately, further enhancing the annealing temperature leads to a decrease of photocatalytic degradation efficiency for the ZnO@MoS2 composite materials. Normally, photocatalytic degradation efficiency (E) can be calculated with the below formula [10]:

$$E = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

Herein, C0 is the original concentration of methylene blue solution, C is the concentration of methylene blue solution after the photocatalytic degradation reaction. According to this formula and the data from Fig.4(a), photocatalytic degradation efficiency for the ZnO materials and ZnO@MoS2 composite materials annealing at 50 oC, 100 oC and 150 oC are 58.13%, 62.88%, 40.73% and 30.16% respectively (in Fig. 4(b)). Compared to the ZnO materials, ZnO@MoS2 composite materials annealing at 50 oC own more nanostures and active sites, as illustrated in Fig. 2(a). Accordingly, more active sites result in higher photocatalytic degradation efficiency. Unfortunately, in a higher annealing temperature, active sites (Uusually point defects) on the MoS2 surfaces will be repaired through oxidation. 62.88% photocatalytic degradation efficiency in this word is compared to that of MoS2/MoO3 composite materials [10].



(a)



(b)

Fig.4 (a) Absorption spectra of methylene blue solution treated with ZnO and ZnO@MoS_2 composite materials; (b) Photocatalytic degradation efficiency of ZnO and ZnO@MoS_2 composite materials on methylene blue solution

4. Conclusion

ZnO@MoS2 composite materials have been prepared by a hydrothermal method. XRD, SEM, Raman spectra and UV spectrophotometer are deployed to analyze the structural, surficial, and optical properties of ZnO@MoS_2 composite materials with annealing. It is found that annealing temperature significantly affects the surface morphology of ZnO@MoS_2 composite materials, and leads to a reduction of active sites as the annealing temperature is over 50 oC. It is also found that ZnO@MoS_2 composite materials annealing at 50 oC reveal the best photocatalytic degradation efficiency of 62.88% on methylene blue solution. Higher annealing temperature reduces the photocatalytic degradation efficiency of ZnO@MoS_2 composite materials due to the reduction of active sites caused by oxidation. This work indicates that the annealing process should be improved to ensure the active sites.

Acknowledgements

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