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SHORT COMMUNICATION

Interface Influence on Photocatalytic Properties of Ag_2MoO_4/ZnO Heterojunctions

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Abstract:

Ag_2MoO_4/ZnO heterostructures were synthesized by a co-precipitation method in room temperature. XRD studies have showed the formation of the heterostructures containing wurtzite-type structure with hexagonal phase (ZnO) and spinel-type cubic structures (Ag_2MoO_4). The crystal morphologies and sizes were observed by field emission scanning electron microscopy (FE-SEM). The photocatalytic activities were evaluated by the degradation of rhodamine B (RhB) under ultraviolet light irradiation.

Keywords: heterojunction; photocatalysis; silver molybdate; zinc oxid

1. Introduction

Photocatalysis has attracted intensive attention as a cost-effective, green chemical technology [1]. Synthetic dyes are massively produced and widely used in many areas nowadays, while most of them are the hazardous materials in the wastewater. Because they are environmentally harmful and not quite prone to degradation, the daily life and health of human beings are imperceptibly influenced by these synthetic dyes [2]. Therefore, the development of efficient methodology or technology to decompose these synthetic dyes becomes emergency issues for environment remediation. Various reports demonstrated that adsorption and photocatalytic degradation are the conventional, effective, and economical methodologies in wastewater purification and environmental protection over the past decades [3-5]. However, the advancement of heterostructured oxides based semiconductor photocatalysts have received an enormous consideration in the field of environmental remediation due to their excellent growth with unique surface morphology and tunable properties [6]. Then, coupling Ag_2MoO_4 with other semiconductors can be an effective way to reduce the recombination rate during the photocatytic process [7]. In this work, Ag_2MoO_4/ZnO heterostructures were performed for using in photocatalytic degradation of rhodamine B (RhB).

2. Results and Discussion

Fig. 1 (a-c) shows the XRD pattern obtained for the Ag_2MoO_4 crystals, ZnO crystals and Ag_2MoO_4/ZnO heterostructures, respectively. Ag_2MoO_4 crystals present a spinel-type cubic structure with space group ($Fd\bar{3}m$) and point-group symmetry (O_h^7) (Fig 1(a)). ZnO crystals with wurtzite-type structure and hexagonal phase are shown in Fig. 1 (b). However, the XRD pattern shown in Fig. 1 (c) have demonstrated peaks matched either with Ag_2MoO_4 or ZnO crystals, confirming with successful the formation of the Ag_2MoO_4/ZnO heterostructure [8]. For all the

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compositions were obtained fine and intense diffraction peaks, corresponding to samples with high degree of crystallinity [9]. No deleterious phase has been observed.

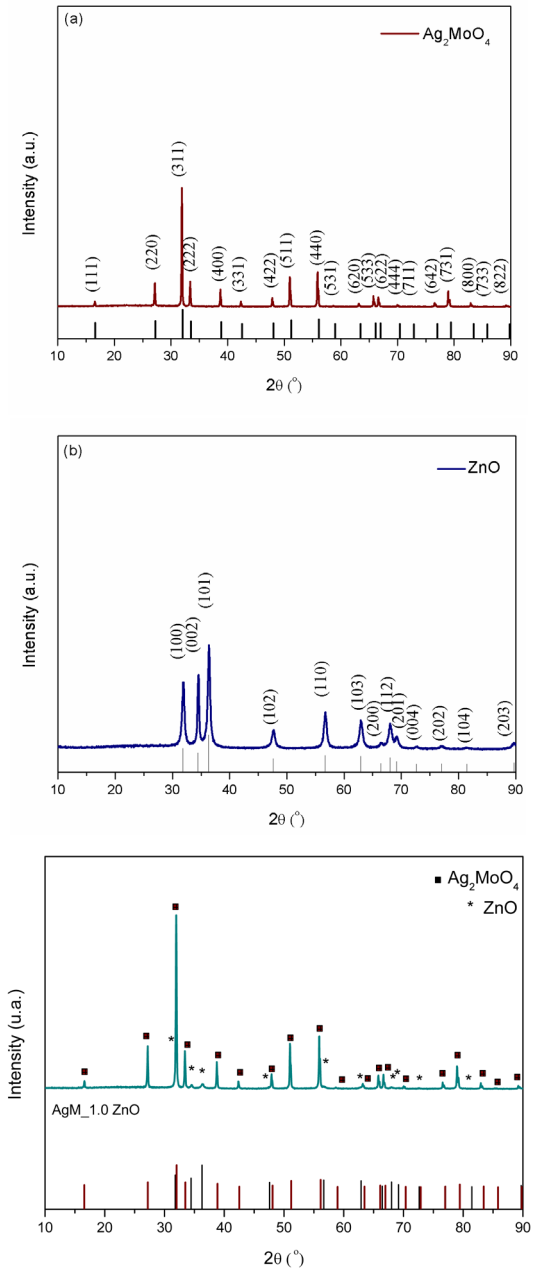

Figure 1. XRD patterns of: a) Ag_2MoO_4 crystals, b) ZnO crystals, c) Ag_2MoO_4/ZnO heterostructure.

Fig. 2(a) illustrates FE- SEM images of the pure Ag_2MoO_4 microcrystals prepared by coprecipitation method. We can observe the formation of a system composed of several irregular microcrystals ranging in size from approximately 4 to 5 μm. (Fig. 2(b)) shows ZnO agglomerated and irregular particles ranging in size from approximately 0.3 to 1 μm. For the heterostructures (Fig 2 (c-d)) the presence of heterojunctions between Ag_2MoO_4 and ZnO can be observed, with ZnO adhered to the surface of the Ag_2MoO_4 particles, preserving the morphologies of the materials.

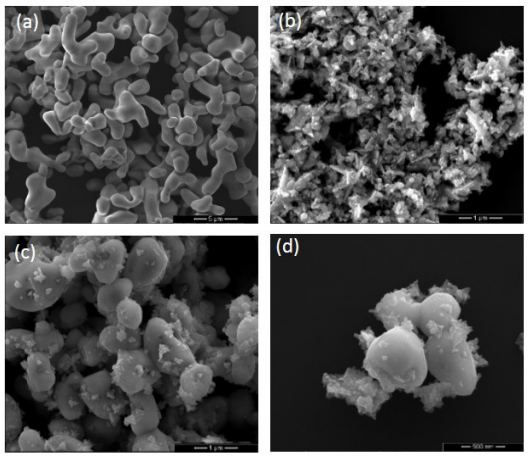

Figure 2. FE-SEM images of a) Ag_2MoO_4 crystals, b) ZnO crystals, c-d) Ag_2MoO_4/ZnO heterostructure.

Fig. 3 (a) shows the fotocatalytic process of RhB with different catalysts, where C_0 and C_n are the equilibrium absorbance of RhB solution in the equilibrium adsorption state in the dark, and the absorbance of the solution after light irradiation in a period of time, respectively. Pure photocatalysts, Ag_2MoO_4 and ZnO, displays an intermediate photocatalytic activity, with 43% and 42% in 90 min, respectively. However, the results revealed that the as-prepared heterostructure Ag_2MoO_4/ZnO exhibited the most photocatalytic activity, where almost 75% degradation of RhB observed in same time for others samples. From this, it can be observed that the heterojunction formed between Ag_2MoO_4/ ZnO can make strong interfacial effect, with intermediate E_{gap}, which contributes to the efficient charge transfer at the interface of the heterostructure with the consequent elevation photocatalytic performance [10].

According to previous studies, the kinetics of RhB photodegradation using Ag_2MoO_4/ZnO as photocatalysts can be ascribed to a pseudo-second-order reaction (Figure 3(b)). We applied this order model as expressed by equation (X) to obtain the rate constant (*k*) of catalyst [11].

$$\frac{1}{[C_n]} = \frac{1}{[C_0]} + kt \qquad (1)$$

where, k is the rate constant and t is the time. Compared to pure materials, the heterostructure sample show satisfactory photocatalytic degradation under UV irradiation. The rate constants of pure Ag_2MoO_4, ZnO and Ag_2MoO_4/ZnO samples are 0.00824, 0.00851, 0.0293 $Lmol^{-1}min^{-1}$, respectively. Therefore, it is verified that the heterostructure is a more effective photocatalyst than pure materials.

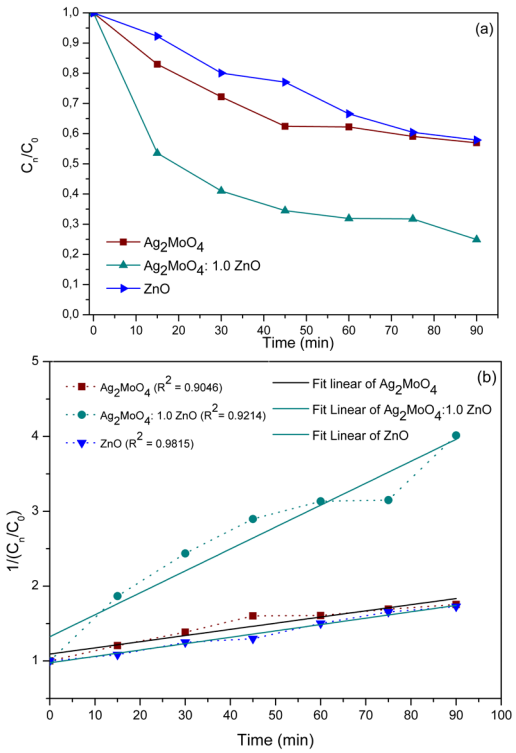

Figure 3. a) Photocatalytic degradation for the pure compounds and heterostructures; b) Pseudo-second order plots for the photocatalytic decomposition of RhB dye.

3. Material and Methods

Synthesis

First, Ag_2MoO_4 crystals were prepared by the co-precipitation method at room temperature from an aqueous solution of molybdate (VI) sodium dihydrate ($Na_2MoO_4.2H_2O$) (99% purity, Sigma-Aldrich) and silver nitrate (99% purity, Aldrich). Thus, the product has been washed and dried at 60 ºC for 6 h.

Separately, zinc nitrate hexahydrate ($Zn(NO)_3.6H_2O$) (99% purity, Aldrich) was dissolved in 300 mL of deionized water with constant stirring. Then, NaOH (5 mol/L) was added into zinc nitrate solution to generate a certain white precipitate and left for 6 h under constant stirring at room temperature for stabilization of the ZnO crystals formed. The resulting precipitate was washed with deionized water and dried at 60 ºC for 6h.

Ag_2MoO_4/ZnO heterostructures were prepared by ultrasonic- assisted co-precipitation method. Separately, $AgNO_3$ was dissolved in 25 mL of deionized water and Na_2MoO_4 in 40 mL of deionized water, forming two distinct solutions. A certain amount of ZnO was dissolved in 40 mL deionized water, and dispersed by ultrasound for 3 min, then $AgNO_3$ solution was added in this ultrasonic media. Subsequently, Na_2MoO_4 solution was added drop by drop under stirring for 10 min. Then, Ag_2MoO_4/ZnO heterostructures were formed by the growth of silver molybdate particles surrounded by ZnO particles (1.0 mol % of ZnO) attached on the silver molybdate surface. Posteriorly, these heterostructures were washed by deionized water and dried for 24 h at 60 °C.

4. Conclusions

Compared to the precursor, the as-obtained Ag_2MoO_4/ZnO heterostructures have showed an enhanced photocatalytic activity in the photodegradation of rhodamine B (RhB). These results are very promising for environmental remediation because of the unique physical and chemical properties, stable and inexpensive of these materials. It originates to the enhanced catalytic performance and makes it easy to use in an extensive range of applications in various energy and environmental field. Future works will be developed to determine the causes of photocatalysis and photodegradation mechanisms.

Acknowledgments

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References and Notes

[1] Wang, Z.; Lv, J.; Zhang, J.; Dai, K.; Liang, C. *Appl.*

Surf. Sci. **2018**, *430*, 595. [Crossref]

[2] Tian, Q.; Wu, W.; Yang, S.; Liu, J.; Yao, W.; Ren, F.; Jiang, C. *Nanoscale Res. Lett.* **2017**, *12*, 221. [Crossref]

[3] Travlou, N. A.; Kyzas, G. Z.; Lazaridis, N. K.; Deliyanni, E. A. *Langmuir*. **2013**, *29*, 1657. [Crossref]

[4] Chen, C.; Ma, W.; Zhao, J. *Chem. Soc. Rev*. **2010**, *39*, 4206. [Crossref]

[5] Kyzas, G. Z.; Siafaka, P. I.; Lambropoulou, D. A.; Lazaridis, N. K.; Bikiaris, D. N.; *Langmuir* **2014**, *30*, 120. [Crossref]

[6] Kundu, S.; Ma, L.; Chen, Y.; Liang, H. *J. Photochem. Photob. A: Chem*. **2017**, *346*, 249-264. [Crossref]

[7] Jiao, Y.; Chen, F.; Zhao, B.; Yang, H.; Zhang, J. *Colloids Surface A*. **2012**, *402*, 66. [Crossref].

[8] Abraham, N.; Rufus, A. U. C.; Philip, D. *Spectrochimica Acta Part A: Mol. Biomol. Spect*. **2018**, *200*, 116. [Crossref]

[9] Ehsan, M. F.; Bashir, S.; Hamid, S.; Zia, A.; Abbas, Y.; Umbreen, K.; Ashiq, M. N.; Shah, A. *Appl. Surf. Sci.* **2018**, *459*, 194. [Crossref]

[10] Cao, W.; An, Y.; Chen, L.; Qi, Z. *J. Alloys Comp.* **2017**, *701*, 350. [Crossref]

[11] Malagutti, A. R.; Mourão, H. A. J. L.; Garbin, J. R.; Ribeiro, C. *Appl. Catal. B* **2009**, 90, 205. [Crossref]