

Photocatalytic degradation and inactivation of *Escherichia coli* by ZnO/ZnAl₂O₄ with heteronanostructures

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Received 22 October 2012; accepted 13 May 2013

Abstract: ZnO/ZnAl₂O₄ nanocomposites with heteronanostructures were successfully prepared by co-precipitation method. The as-prepared samples were characterized by HRTEM, TEM, XRD, BET, TG-DTA, and UV-Vis spectra techniques. The photocatalytic activities of the as-prepared samples were evaluated by the photocatalytic degradation of methyl orange and inactivation of *Escherichia coli* in suspension under the irradiation of the simulated sunlight. The effects of compositions, calcination temperatures, concentration of photocatalysts and light source on the photocatalytic activities were systematically studied. The results show that when the concentration of ZnO/ZnAl₂O₄ photocatalyst with the starting Zn to Al molar ratio of 1:1.5 calcined at 600 °C is 1.0 g/L, the maximum photocatalytic degradation rate of 98.5% can be obtained in 50 min under the irradiation of the simulated sunlight. Under the same conditions, an inactivation rate of 99.8% for *E. coli* is achieved in 60 min.

Key words: ZnO/ZnAl₂O₄; photocatalysis; degradation; inactivation; heterojunction

1 Introduction

Since the first application of TiO₂ photocatalyst under UV irradiation for microbial inactivation by MATSUNAGA et al in 1985 [1], much effort has been devoted to developing semiconductor photocatalysts with high photocatalytic activities in air purification, disinfection, and water treatment process [2–4]. Among various semiconductor photocatalysts, the heterostructures fabricated by the coupling of different semiconductor materials possess significant advantages for promoting the separation of electron–hole pairs and achieving a higher photocatalytic activity compared with single-phase photocatalyst [5,6]. ZnO is well known as a preferable material for a variety of environmental applications due to its high photosensitivity, non-toxic nature, low cost and chemical stability [7,8]. It is even more efficient than TiO₂ in the photodegradation [9]. However, the quick recombination of e[−] and h⁺ pairs is the major limitation in achieving high photocatalytic

efficiency. Studies indicated that the composite between ZnO and another nonsensitive semiconductor (usually having very wide band gap), e.g., In₂O₃ ($E_g=3.6$ eV) [10], SnO₂ ($E_g=3.8$ eV) [11], and NiO ($E_g=3.5$ eV) [12], also has been proved to be an effective method to improve their photocatalytic activity. Spinel ZnAl₂O₄ with a broad bandgap of 3.8 eV has attracted considerable attention since it can be used as catalyst [13], and catalyst support [14] due to its high thermal stability, low surface acidity, and high specific surface area [15].

In the present work, ZnO/ZnAl₂O₄ heterostructure photo-catalyst with high photocatalytic activity was synthesized. Subsequently, the composition, morphology and UV-absorbing properties of the resulting nanocomposites were systematically investigated by HRTEM, TEM, XRD and UV-Vis spectra techniques. Finally, the photocatalytic activities of the ZnO/ZnAl₂O₄ nanocomposites were evaluated by the degradation of methyl orange (MO) and inactivation of *Escherichia coli* (*E. coli*).

2 Experimental

2.1 Sample synthesis

Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were employed as starting materials. Firstly, a mixture of Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O with a certain Al to Zn molar ratio (varying from 1.1 to 2) in the starting materials was dissolved into deionized water to form a clear solution with a total cationic concentration of 30 mmol/L. Subsequently, aqueous ammonia was added under constant stirring to the above solution until pH reaching 7–8 to ensure complete precipitation. The gel solution was aged for 24 h before filtration. After filtration and washing with distilled water and ethanol several times, the obtained sample was dried in an oven at 80 °C overnight. Finally, the samples were obtained after calcination at different temperatures (500, 600, 700, 800 and 900 °C).

2.2 Sample characterization

The crystalline phase and the crystal size of the samples were identified by X-ray diffraction (XRD, Bruker D8) using Cu K_α radiation (wavelength 1.5418 Å) at a scan speed of 0.05 (°)/s, a voltage of 40 kV and a current of 300 mA. High resolution transmission electron microscopy (HRTEM) images were recorded on JEOL JEM–2010 high-resolution transmission electron microscope. The accelerating voltage was 200 kV. UV-Vis diffuse reflectance spectra of the samples were obtained using UV-Vis spectrophotometer (UV–2550, Shimadzu, Japan). BaSO₄ was used as a reflectance standard in the UV-Vis diffuse reflectance experiment. Brunauer–Emmett–Teller (BET) surface area (SBET) was determined with the nitrogen absorption isotherms apparatus (ST–08 analyzer).

2.3 Photocatalytic activity measurement

The photocatalytic reaction was carried out in a self-made tube-shaped quartz reactor including three layers connected with gas collecting devices. The reaction temperature was kept at (25±0.2) °C by controlling the external circulation water in the water jacket of the reactor during the entire experiment. The photocatalyst powder (0.6 g) was dispersed by a magnetic stirrer in 600 mL MO solution with the concentration of 25 mg/L. A 150-W xenon lamp with λ=200–900 nm was used as the simulated sunlight source. The luminous intensity was measured at 100 mW/m² by the auto-range ST–85 optical radiometer (Photoelectric Instrument Factory of Beijing Normal University). Prior to light illumination, the suspension was strongly magnetically stirred for 30 min in dark for adsorption/desorption equilibrium. During irradiation,

the catalyst was kept in suspension state by a magnetic stirrer. Samples for analysis were extracted through pipette every 10 min and centrifuged immediately. Decoloration rate is presented as $(\rho_0 - \rho_t)/\rho_0 \times 100\%$, where ρ_0 is the initial concentration of MO solution and ρ_t is the concentration of MO solution after the irradiation time t .

Under the same conditions, photocatalytic activity was measured by inactivation of *E. coli* (DH 5a) provided by the Biology Laboratory of Hunan Institute of Science and Technology, China. *E. coli* was in Luria–Bertani (LB) nutrient solution at 37 °C for 18 h with shaking, and then washed by centrifugation at 4000 r/min. The treated cells were then re-suspended and diluted to 10⁹ colony-forming units (CFU/mL) with 0.9% saline. All materials used in the experiments were autoclaved at 121 °C for 25 min to ensure sterility. The diluted cell suspension and photocatalyst were added to a 600-mL beaker with a cover. The final photocatalyst concentration was adjusted to 0.2–1.0 g/L, and the final bacterial cell concentration was 1×10⁶ CFU/mL. The reaction mixture was stirred with a magnetic stirrer throughout the experiment. The light source for photocatalysis was the 150-W Xe arc lamp. For comparison, the disinfection under natural sunlight was made with identical solar irradiance, and the solar irradiance was monitored with a Daystar solar meter (USA). A bacterial suspension without photocatalyst was irradiated as a control and the reaction mixture with no light irradiation was a dark control. Before and during the light irradiation, aliquots of the reaction solution were immediately diluted with saline and the samples with the appropriate dilution were incubated at 37 °C for 24 h in nutrient agar medium. Then the colonies were counted to determine the number of viable cells. Survival ratio of *E. coli* was calculated as the ratio of the number of viable colonies remaining after exposure to the number of viable colonies the present initially experimental conditions to.

3 Results and discussion

3.1 Characterization

3.1.1 TG–DTA analysis

Figure 1 shows the TG–DTA curves of ZnO/ZnAl₂O₄ sample with the starting Zn to Al molar ratio of 1:1.5. The total mass loss occurs in the temperature range of 20–500 °C. The first mass loss before 200 °C may be attributed to the evaporation of absorbed water, meanwhile the corresponding endothermic peak is observed from the thermogravimetric curve. The second mass loss occurs at 200–320 °C, and the corresponding exothermic peak at about 280 °C can be ascribed to the decomposition of the residual organic compounds. The third mass loss at

320–500 °C is due to the decomposition of the nitrate and synthesis of the ZnAl_2O_4 compounds, and then the mass loss becomes almost constant when the temperature is more than 600 °C. The corresponding endothermic peak at about 700 °C is perhaps owing to the forming of ZnO.

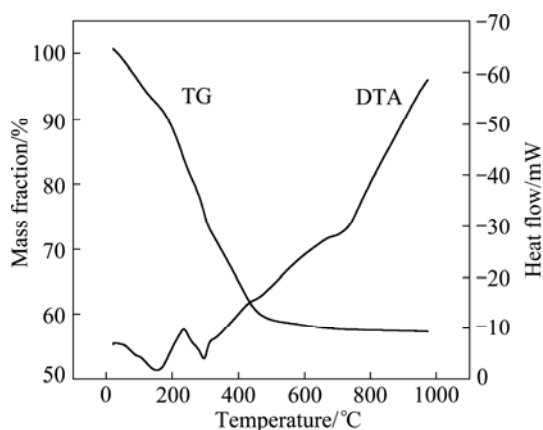


Fig. 1 TG-DTA curves for precursor ZnO/ZnAl₂O₄ sample

3.1.2 XRD analysis

Figure 2 shows the XRD patterns of the ZnO/ZnAl₂O₄ nanocomposites with the starting Zn to Al molar ratio of 1:1.5 calcined at different temperatures. We can clearly see that the sample calcined at 500 °C shows a pure phase of spine ZnAl_2O_4 without any other compositions. The diffraction peaks at $2\theta=31.22^\circ$, 36.81° , 44.73° , 55.63° , 59.33° and 65.25° are ascribed to the typical spine structure of ZnAl_2O_4 (JCPDS card No. 05-0669). This is mainly because of the poor crystallization of the as-grown sample at the low calcination temperature. When the temperature is increased to 600 °C, a phase transition appears. The sample shows a mixed phase of ZnAl_2O_4 and ZnO. When the calcination temperature is higher than 600 °C, the peaks become sharp (the peak width at half-height decreased) as the calcination temperature increases. This

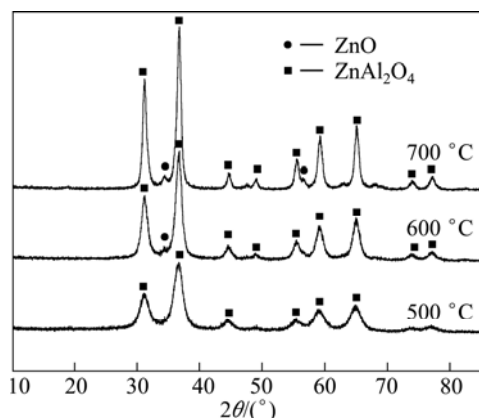


Fig. 2 XRD patterns of ZnO/ZnAl₂O₄ samples calcined at different temperatures

means that the crystallinity of samples is improved, and the crystal grains grow bigger when the calcination temperature increases.

3.1.3 BET surface area

The ZnO/ZnAl₂O₄ nanocomposites with the starting Zn to Al molar ratio of 1:1.5 calcined at different temperatures varied a lot in the BET surface areas, and their values are listed in Table 1. The BET surface areas of samples decrease when the calcination temperature increases. The sample calcined at 500 °C shows the highest BET surface area of 68.38 m²/g. The BET surface area of sample calcined at 600 °C decreases a little (55.92 m²/g). And the values for the samples calcined at 700 and 800 °C become smaller (25.38 and 22.72 m²/g, respectively). When the sample was calcined at 900 °C, the BET surface area is even smaller (e.g., 11.35 m²/g), only about 1/5 of the value of the sample calcined at 600 °C. The sample calcined at 500 °C has a large BET surface area, but poor crystallinity, which may result in relatively low photocatalytic activity. On the basis of the above analysis, 600 °C is regarded as the optimum calcination temperature in our experiments.

Table 1 BET surface Areas of ZnO/ZnAl₂O₄ samples

Sample No.	Calcination temperature/°C	Starting Zn to Al mole ratio	BET area/(m ² ·g ⁻¹)
a	500	1:1.5	68.38
b	600	1:1.5	55.92
c	700	1:1.5	25.38
d	800	1:1.5	22.72
e	900	1:1.5	11.35

3.1.4 TEM and HRTEM images

Figure 3 shows the TEM and HRTEM images of ZnO/ZnAl₂O₄ nanocomposites with the starting Zn to Al molar ratio of 1:1.5 calcined at 600 °C. Figure 3(a) shows that the sample is irregularly spherical and its particle size is relatively identical. The particle size of sample is 15–20 nm. More detailed morphology about the ZnO/ZnAl₂O₄ nanocomposites is indicated by HRTEM (Fig. 3(b)). HRTEM image reveals that both ZnO and ZnAl₂O₄ form a heterojunction nanostructure proven by well-defined lattice fringes: the spacing of 0.26 nm represents the lattice-resolved (001) crystalline plane of ZnO phase, and the spacing values of 0.28 nm and 0.46 nm correspond to the (220) and (111) facets of ZnAl₂O₄ phase, respectively, which are in good agreement with the report in Ref. [16].

3.1.5 UV-Vis DRS analysis

The diffuse reflectance spectrum for the synthesized ZnO/ZnAl₂O₄ nanocomposites with the starting Zn to Al molar ratio of 1:1.5 calcined at 600 °C is presented in

Fig. 4. For comparison, the spectra of pure ZnO and ZnAl_2O_4 synthesized are also plotted. The $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ sample shows a certain absorption in the visible light region (the wavelength ranging from 400 to 800 nm), while no absorption can be observed for pure ZnO and ZnAl_2O_4 . For ZnO, the CB bottom and the VB top lie at

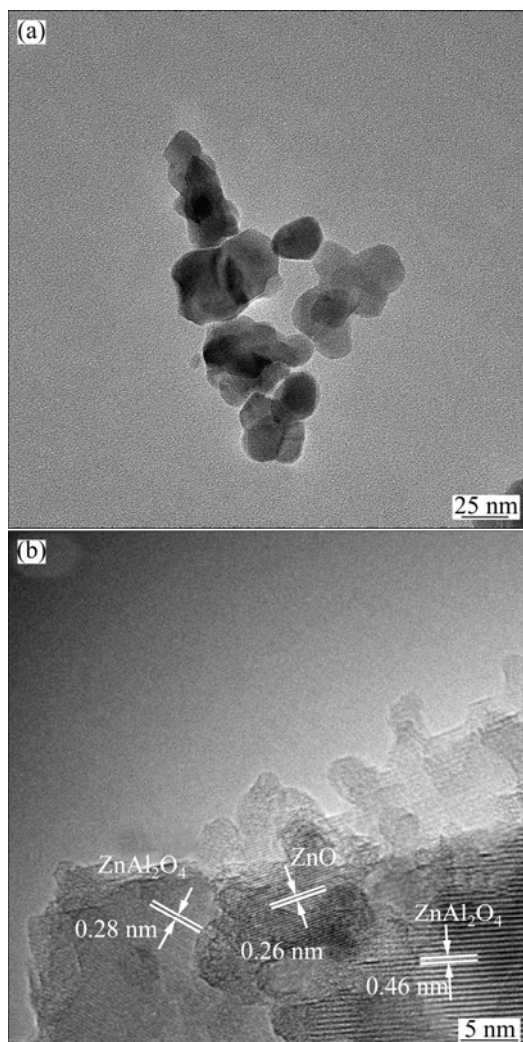


Fig. 3 TEM (a) and HRTEM (b) images of $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ nanocomposites

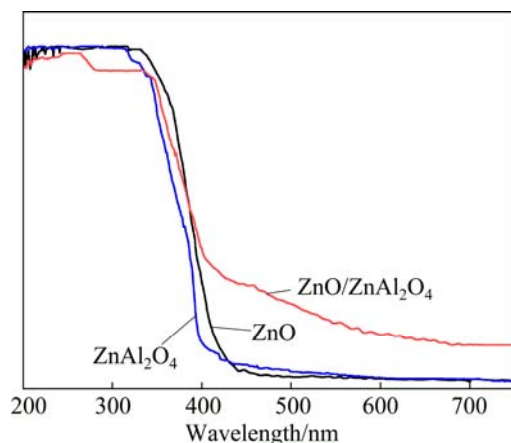


Fig. 4 UV-Vis DRS of samples

–4.19 and –7.39 eV, respectively, with respect to absolute vacuum scale (AVS). While for ZnAl_2O_4 , the CB bottom and VB top lie at –3.36 and –7.16 eV vs AVS, respectively. Both the CB bottom and the VB top of ZnO lie below the CB bottom and VB top of ZnAl_2O_4 , respectively. When they are coupled together, the middle band gap (2.97 eV) between the CB bottom of ZnO and the VB top of ZnAl_2O_4 forms, which may be the main reason for the absorption in the visible light region.

3.2 Photocatalytic activity

3.2.1 Effect of $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ composition on photocatalytic degradation activity

Figure 5 shows the degradation of MO in the presence of $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ nanocomposites with different starting Zn to Al molar ratios calcined at 600 °C under the irradiation of the simulated sunlight. It can be seen that the photocatalytic activities of $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ samples first increase with the molar ratio of Zn to Al decreasing to 1:1.5, and then slightly decrease when the molar ratio exceeds 1:1.5. $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ sample with Zn to Al molar ratio of 1:1.5 is found to be the most active, with a photocatalytic activity about 3.5 times higher than that of pure ZnO sample. The reason is attributed to the existing of heterojunction and the content of ZnO in the $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ nanocomposite. When they are coupled together to form a heterostructure, photons may be absorbed in both ZnO and ZnAl_2O_4 and form the e^- and h^+ pairs. The electrons at the CB bottom of ZnAl_2O_4 would migrate to the ZnO; whereas holes at the VB top of ZnAl_2O_4 would remain there. On the other hand, the holes at the VB top of the ZnO would migrate to ZnAl_2O_4 , and electrons at the CB bottom of ZnO remain there. Such process is energetically favorable and the photogenerated e^- and h^+ pairs can be efficiently separated, which is regarded as the key factor for the

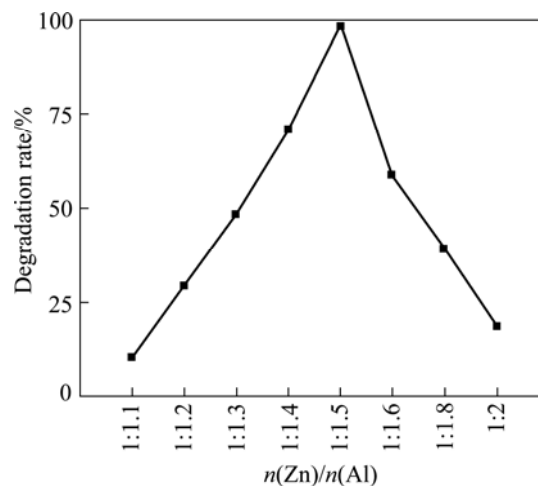


Fig. 5 Photocatalytic activities of $\text{ZnO}/\text{ZnAl}_2\text{O}_4$ with different starting Zn to Al molar ratios

enhancement of photocatalytic activities of the ZnO/ZnAl₂O₄ sample [16]. Furthermore, the heterojunction photocatalysts where one component is grown or deposited on the other, and one must control over the coverage because of complete and sparse coverage of one component on the other will reduce the catalytic efficiency [17]. Thus, the optimum content of ZnO is proposed to contribute the enhancement of utilization of light, which can favorably improve the photocatalytic activities [18,19]. Therefore, Zn to Al molar ratio of 1:1.5 in the starting materials is found to be the optimum composition for ZnO/ZnAl₂O₄ samples.

3.2.2 Effect of calcination temperature on photocatalytic degradation activity

Figure 6 reveals the photocatalytic activities of the ZnO/ZnAl₂O₄ nanocomposites with the starting Zn to Al molar ratio of 1:1.5 calcined at different temperatures. From Fig. 6, the photocatalytic activities vary greatly for the samples. The sample calcined at 600 °C shows the highest photocatalytic activity. The maximum photocatalytic degradation rate of MO within 50 min is obtained. For the other samples calcined at 500, 700, 800, and 900 °C, the degradation rates of MO within 50 min are estimated to be 89.3%, 94.2%, 93.9%, and 91.4%, respectively. The difference in photocatalytic activity may be ascribed to the BET surface area and the crystalline quality of the nanocomposition. Although the sample calcined at 500 °C possesses a larger specific surface area, the photocatalytic activity is lower, which may be ascribed to the relatively poor crystallinity. The sample calcined at 600 °C shows a better crystalline quality. The photocatalyst with good crystallization can provide a shorter migration distance for electrons and holes and reduce the chances of their recombination. Therefore, the photocatalytic reaction efficiency is accelerated and the catalytic activity is improved [20,21]. The high photocatalytic activity of sample calcined at

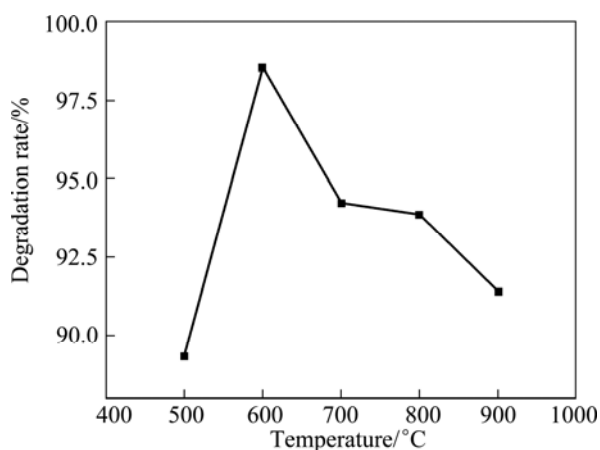


Fig. 6 Photocatalytic activity of ZnO/ZnAl₂O₄ sample calcined at different temperatures

600 °C is also attributed to the higher specific surface area than that of the sample calcined at 700, 800, or 900 °C (shown in Table 1). A larger surface area provides more surface active sites for the adsorption of reactants molecules, making the photocatalytic process more efficient [22].

3.2.3 Effect of ZnO/ZnAl₂O₄ concentration on photocatalytic inactivation activity

The photocatalytic activities of four different concentrations of ZnO/ZnAl₂O₄ (0.2–1.0 g/L) under simulated sunlight are shown in Fig. 7. It is clear that with the increase of concentration of ZnO/ZnAl₂O₄, the photocatalytic inactivation activity is correspondingly increased, reaching a plateau at 1.0 g/L. The photocatalytic inactivation rate of *E. coli* achieves 99.8% in 60 min. While the inactivation rate of 95.9% (inactivation rate = $1 - \rho/\rho_0$) is obtained using 0.5 g/L photocatalyst, which has been obviously attributed to the increase in the number of photons that can be absorbed by ZnO/ZnAl₂O₄ before reaching a maximum corresponding to the total absorption of the incident radiation [23,24].

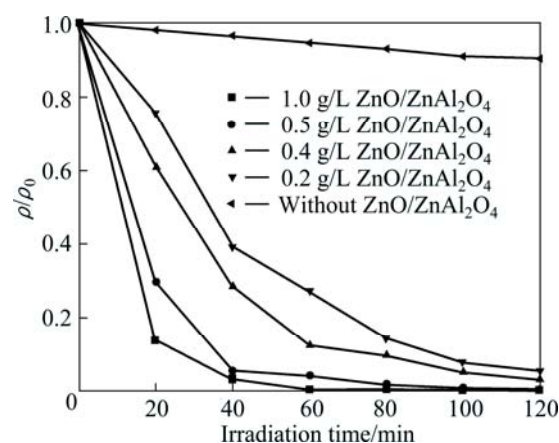


Fig. 7 Photocatalytic inactivation of *E. coli* with different concentrations of ZnO/ZnAl₂O₄ under simulated sunlight (Zn to Al molar ratio 1:1.5; calcination temperature 600 °C; irradiation power 100 mW/m²; initial concentration of *E. coli* 10⁶ CFU/mL)

3.2.4 Effect of light source on photocatalytic inactivation activity

Figure 8 displays the photocatalytic inactivation of *E. coli* by ZnO/ZnAl₂O₄ under different light sources. The survival ratio of *E. coli* falls initially, followed by a slow diminishing in the presence of ZnO/ZnAl₂O₄ under simulated sunlight and natural sunlight illumination. It clearly demonstrates the effective photocatalytic inactivation of *E. coli* by ZnO/ZnAl₂O₄ under sunlight irradiation. The inactivation response is probably due to the DNA damage to the bacteria caused by the reactive oxygen species (ROS) produced by irradiation [25]. The corresponding photocatalytic inactivation of *E. coli* by

photolysis (without catalyst) is also shown for comparison. No significant inactivation is observed for *E. coli* both under simulated sunlight irradiation and natural sunlight. However, when the system in the presence of ZnO/ZnAl₂O₄ is in the dark, a significant decrease in the number of viable *E. coli* bacteria is observed, although the inactivation of the *E. coli* by ZnO/ZnAl₂O₄ in the dark is small compared with the photocatalytic inactivation, which is consistent with the previous reports [26]. The results show that the osmotic stress may change the permeability of the cell wall, allowing the transfer of the smaller ZnO/ZnAl₂O₄ particles through the cell wall, as suggested by the results of HUANG et al [27], although the outer membrane of Gram-negative bacteria have been reported to limit the permeability to many chemical compounds [28,29].

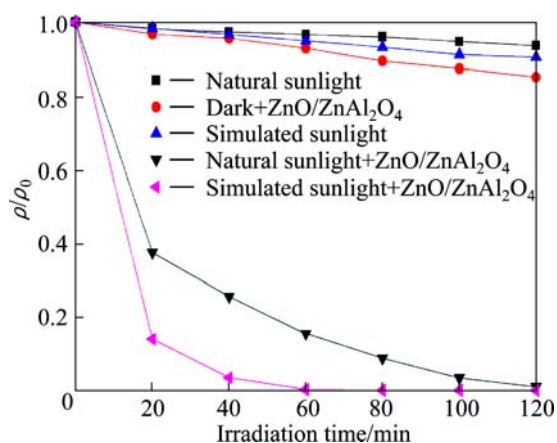


Fig. 8 Photocatalytic inactivation of *E. coli* under different light source (Zn to Al molar ratio 1:1.5; calcination temperature 600 °C; ZnO/ZnAl₂O₄ concentration 1.0 g/L; irradiation power 100 mW/m²; initial concentration of *E. coli* 10⁶ CFU/mL)

4 Conclusions

1) The ZnO/ZnAl₂O₄ nanocomposites exhibit excellent photocatalytic activity for degradation of MO and inactivation of *E. coli* under the irradiation of the simulated sunlight, which may be attributed to the fact that ZnO and ZnAl₂O₄ can form heterojunction structure.

2) The photocatalytic degradation activity of the ZnO/ZnAl₂O₄ nanocomposites can be improved by varying the concentration of ZnO/ZnAl₂O₄, the molar ratio of Zn to Al and calcination temperature. When the concentration of ZnO/ZnAl₂O₄ is 1.0 g/L, the maximum activity is obtained at the molar ratio of Zn to Al of 1:1.5 and calcination temperature of 600 °C.

3) For comparison, the photocatalytic inactivation of *E. coli* was performed under the same conditions. A 99.8% inactivation rate of *E. coli* was obtained in 60 min.

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ZnO/ZnAl₂O₄ 异质结光催化剂的光催化降解和杀灭大肠杆菌性能

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摘 要: 通过共沉淀法制备 ZnO/ZnAl₂O₄ 纳米异质结光催化剂, 利用 HRTEM、TEM、XRD、BET、TG-DTA 和 UV-Vis DRS 测试方法对样品进行表征。在模拟太阳光照射下, 通过测定甲基橙溶液的光催化降解率和对大肠杆菌的杀灭率来评价样品的光催化活性。研究催化剂的组成、焙烧温度、催化剂的用量和不同光源对样品光催化活性的影响。结果表明, 当原料中 Zn 与 Al 摩尔比为 1:1.5 时, 在 600 °C 焙烧所得的催化剂具有最佳光催化活性。在模拟太阳光照射下, 在 50 min 内 1.0 g/L 光催化剂对甲基橙的降解率达 98.5%; 在 60 min 内, 在相同条件下对大肠杆菌(10⁶ CFU/mL)的杀菌率达到 99.8%。

关键词: ZnO/ZnAl₂O₄; 光催化; 降解; 杀菌; 异质结

(Edited by Hua YANG)