Preparation and Photocatalytic Performance of Porous ZnO Micron Powders

Rui Niu, Qing Yang,[†] Xucheng Zhang

Faculty of Materials Science and Engineering, Xi'an University of Technology, No.5 South Jinhua Road, Xi'an 710048, China

[†] Corresponding author: yangqing@xaut.edu.cn

Received: 25 December, 2019; Accepted: 12 February, 2020; Published: 14 March, 2020

Porous ZnO micron powders are obtained by thermal oxidation in air. The as-obtained powders are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), nitrogen adsorption, and ultraviolet-visible spectrophotometer, and the photocatalytic degradation of methyl orange (MO) is evaluated. The results indicate that, with the increase in thermal oxidation temperature, the nanoparticles on the surface of porous ZnO gradually grow and connect to each other, and the porous structure is destroyed, which results in the decrease in the specific surface area. Porous ZnO obtained at 800°C exhibits the best photocatalytic performance for MO degradation. The highest degradation rate is 0.043 min^{-1} using 10 mg of the ZnO powders and 10 mg L^{-1} of the MO solution.

Keywords ZnO micron powder; Porous structure; Thermal oxidation; Photocatalytic degradation

I. INTRODUCTION

Water resources have been polluted by industrial wastewater, and organic-dye wastewater is one of the main pollution sources. Photocatalytic technology is one of the catalytic technologies, and certain semiconducting materials are employed as catalysts to degrade environmental pollutants. The method has advantages such as simple processes and low costs, and it can completely oxidize and decompose most of the toxic organic compounds that cannot be or are difficult to be biodegraded at normal temperature [1].

ZnO is an n-type semiconducting metal oxide with a wide band gap (3.37 eV) and a high exciton binding energy (60 meV), and have advantages of being chemically stable, non-toxic, inexpensive, etc. [2, 3]. The specific surface area of ZnO can be increased sharply by reducing the particle size. Thus, the nano-sized ZnO with a high surface activity can be applied as a high-efficient photocatalyst [4]. However, the recycling of the photocatalyst in practical applications becomes difficult with the decrease in the particle size. The morphology of ZnO plays an important role in photocatalytic performance, and there is a certain relationship between the photocatalytic activity and the specific surface area [5].

Therefore, the preparation of ZnO powders with large size and high specific surface area is expected.

The hierarchical porous ZnO microspheres synthesized by the microwave hydrothermal method exhibited excellent photocatalytic activity for methylene blue (MB) degradation [6]. In addition to the high specific surface area, there are certain oxygen defects on the surface of the porous structure, which can resist the recombination rate of photogenerated electrons and holes so that the photocatalytic activity is improved [7]. Furthermore, a porous ZnO film was grown simply by thermal oxidation of a ZnS film [8]. In this research, we prepared the porous ZnO micron powders by thermally oxidizing ZnS micron powders and investigated the effect of the oxidation temperature on the morphology and the photocatalytic performance.

II. EXPERIMENTAL

ZnS powders (particle size; 2–4 μm , purity; >99.9%) were tiled in a crucible and placed in a tube furnace which was open to the air. The preparation of porous ZnO by thermal oxidation in air was performed at 700–1000°C for 20 min. The phase composition, morphology, the specific sur-

Figure 1: XRD spectra of the ZnS and ZnO powders obtained at different thermal oxidation temperatures.

face area, and the optical band gap of the as-prepared ZnO powders were characterized by X-ray diffraction (XRD), Zeiss-Merlin scanning electron microscopy (SEM), nitrogen adsorption (ASAP2000), and ultraviolet (UV)-visible spectrophotometer (U-4100), respectively.

The photocatalytic performance of the as-prepared ZnO powders was evaluated by the photodegradation of methyl orange (MO) under UV light irradiation. A reaction system was set up by adding an appropriate amount of the ZnO powders into the 50-mL MO solution at room temperature. The obtained suspension was dispersed for 30 min by an ultrasonic cleaner, and then stirred for 30 min in darkness by a magnetic stirrer to ensure an adsorption-desorption equilibrium between the ZnO powders and the MO molecules. Then, the mixed solution was placed in an optical reactor, and the mercury lamp (300 W, the main wavelength of 365 nm) was turned on to start the photocatalytic reaction. A small amount of suspension was taken and centrifuged every 10 min. The absorbance of the supernatant was measured by a UV-visible spectrophotometer (UV-8000S) at 463 nm, and the photocatalytic performance of porous ZnO was analyzed.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD spectra of the ZnS and ZnO powders obtained at different thermal oxidation temperatures. Compared with the PDF card JCPDS No. 36-1451, ZnS was completely transformed into ZnO with a hexagonal structure after thermal oxidation. The XRD peak intensity of ZnO increased with the increase in the oxidation temperature from 700°C to 1000°C. The reason is that, with the increase in temperature, the grain size is increased, the defects in the crystals are decreased, and the crystallinity is increased. The high crystallinity can promote the transfer of photogenerated electrons and holes from the bulk to the surface of photo-

Figure 2: SEM images of the ZnO powders obtained at different thermal oxidation temperatures. (a) 700°C, (b) 800°C, (c) 900°C, and (d) 1000°C.

catalyst, thus enhancing the photocatalytic performance [9].

Figure 2 shows SEM images of the ZnO powders obtained at the different thermal oxidation temperatures. The ZnO powders exhibited a porous structure formed by the interconnection of the nanoparticles. During the thermal oxidation process, oxygen diffused inward and reacted with zinc and sulfur. The formation of the porous structure can be attributed to the evaporation of volatile sulfur oxides at elevated temperatures [8]. When the oxidation temperature was raised from 700°C to 1000°C, the nanoparticles on the surface of porous ZnO obviously grew from 154 nm to 590 nm, and the porous structure was destroyed.

Figure 3 shows nitrogen adsorption-desorption isotherms of the ZnO powders obtained at different temperatures. The adsorption-desorption isotherms are type-IV curves with H3 hysteresis [10], which confirms the presence of the nanoporous structure after thermal oxidation. The maximum spe-

Figure 3: Nitrogen adsorption-desorption isotherms of the ZnO powders obtained at different thermal oxidation temperatures: (a) 700°C, (b) 800°C, (c) 900°C, and (d) 1000°C.

cific surface area was $6.16 \text{ m}^2 \text{ g}^{-1}$ for porous ZnO obtained at 800°C , which was slightly larger than that obtained at 700°C . When the temperature was higher than 800°C , the specific surface area decreased sharply. The reason is that the nanoparticles on the surface of porous ZnO gradually grew and connected to each other so that the porous structure was destroyed and the pores decreased, which led to the decrease in the specific surface area of porous ZnO.

Figure 4(a) shows the UV-visible absorption spectra of the ZnO powders obtained at different temperatures. The absorption peaks are mainly in the ultraviolet regions of 300–380 nm. Figure 4(b) shows the plots of $(ahv)^2$ vs. $h\nu$ of porous ZnO. The optical band gap can be calculated by $ahv = C(h\nu - E_g)^{1/2}$, where α is an optical absorption coefficient, and C is a constant for a direct transition [11]. The optical band gap of porous ZnO increased with the increase in the thermal oxidation temperature. This may be related to the number of defects in the crystals. The defects in the crystals decreased with the increase in temperature. This led to the narrower width of the band-tailed localized state and widening of the luminous energy gap when the free exciton recombined, resulting in a blue shift in the UV absorption spectra [12].

Figure 5 shows the absorption spectra of MO degraded by

Figure 4: (a) UV-visible absorption spectra of ZnO powders obtained at different thermal oxidation temperatures, and (b) plots of $(ahv)^2$ vs. $h\nu$.

Figure 5: Absorption spectra of MO degraded by the ZnO powders obtained at different thermal oxidation temperatures: (a) 700°C , (b) 800°C , (c) 900°C , and (d) 1000°C .

the ZnO powders. Porous ZnO exhibited an excellent photocatalytic effect on the MO solution. When porous ZnO absorbed the UV light, it generated the electrons and holes, which reacted with H_2O or O_2 adsorbed on the surface of ZnO and generated more strongly oxidative free radicals, which freely oxidize and degrade MO. The possible reaction mechanism can be represented as follows [13]:

Therefore, with the increase in the light irradiation time, the number of the free radicals in the solution increased, MO was degraded into small inorganic molecules, and the concentration of the MO solution continued to decrease.

Figure 6(a) shows the degradation curves of MO by the ZnO powders. A decolorization rate percentage of MO was calculated by $D = (1 - C/C_0) \times 100\%$, where C_0 is the initial concentration of MO, and C is the concentration of MO at an instant time. MO was not degraded at the dark reaction stage. After the 80-min light irradiation, MO in the blank group was only degraded by 13.7%, while MO mixed with porous ZnO was almost degraded.

Figure 6(b) shows the plots of the pseudo-first-order kinetic model. The degradation kinetics of MO can be expressed by $\ln(C_0/C) = kt$, where k is the pseudo-first-order rate constant and t is the irradiation time. Generally, the plot of the pseudo-first-order kinetic model represents the photocatalytic degradation activity at the interface of the catalyst and organic pollutants.

The results indicated that porous ZnO obtained at 800°C exhibited the highest degradation efficiency with a degradation rate of 0.043 min^{-1} . The highest degradation efficiency was due to the largest surface area of porous ZnO obtained at 800°C . The large specific surface area increased the contact probability of the MO molecules with free radicals, improved the ability to adsorb organics, and, thus, enhanced the photocatalytic performance. Particularly, the specific surface area of porous ZnO obtained at 900°C was much less than that obtained at 800°C , but their degradation efficiency values were similar. The reason can be attributed to

Figure 6: (a) Degradation curves of MO by the ZnO powders obtained at different thermal oxidation temperatures, and (b) plots of pseudo-first-order kinetic model.

the large band gap of porous ZnO obtained at 900°C. The band gap of porous ZnO became wider so that the photo-generated electrons and holes had a stronger redox capacity, and, thus, the photocatalytic activity was enhanced [14]. Therefore, the photocatalytic performance of porous ZnO was determined by both of the specific surface area and the band gap.

The amount of the catalyst added to the solution has an important effect on the degradation rate. The 10 mg L⁻¹ MO solution was mixed with 5–20 mg of the ZnO powders obtained at 800°C to perform the photodegradation reactions. The degradation curves were fitted by the pseudo-first-order kinetics, and the results are shown in Figure 7. With the increase in the amount of porous ZnO, the active sites of hydroxyl radicals on the surface of catalyst increased, which improved the photocatalytic performance. However, when the amount of porous ZnO was too high, the suspended particles in the solution increased, the light transmittance of the system decreased, the light scattering intensified, and the light absorption capacity of porous ZnO decreased. Thus, the increase in the degradation rate decreased continuously. The degradation rate at 60 min with different amounts of porous ZnO is shown in Figure 7(c). The optimal addition amount of porous ZnO was 10 mg.

The initial concentration of the MO solution also affects the degradation rate of MO. The MO solutions with the concentrations between 5 mg L⁻¹ and 20 mg L⁻¹ were mixed with 10 mg of the ZnO powders obtained at 800°C to perform the photodegradation reactions. The degradation curves were fitted by pseudo-first-order kinetics, and the results are shown in Figure 8. With the increase in the reaction time, the degradation rate increased, but the increase in

the degradation rate decreased continuously. The main reason is that, in the photocatalytic reaction, the occurrence of degradation depended on the diffusion and adsorption of the MO molecules on the surface of porous ZnO. As the reaction proceeded, the driving force for diffusion in the solution decreased, and the contact probability between the MO molecules and the surface of porous ZnO decreased.

In addition, the degradation rate decreased with the increase in the initial concentration of the MO solution, and finally tended to be moderate. This is mainly due to two points: first, with the increase in the initial concentration of the MO solution, most of the active sites on the surface of porous ZnO were occupied. The higher the concentration of the MO solution, the lower the light transmittance, and the less the number of photons participating in the photocatalytic reaction. Thus, the photodegradation rate of porous ZnO decreased [15]. Second, the absolute removal amount was limited. The degradation rate tended to be lowered with the increase in the concentration of the MO solution and finally was kept at the fixed value, which was related to the nature of the catalyst. The degradation rate at 60 min with different initial concentrations of the MO solution is shown in Figure 8(c). The optimal initial concentration of the MO solution was 10 mg L⁻¹.

IV. CONCLUSIONS

Porous ZnO micron powders were prepared by thermal oxidation of ZnS micron powders. With the increase in the oxidation temperature from 700°C to 1000°C, the nanoparticles on the surface of porous ZnO gradually grew up from 154 nm to 590 nm and were connected to each other so that

Figure 7: (a) Degradation curves of MO by different amount of the ZnO powders obtained at 800°C, (b) plots of pseudo-first-order kinetic model, and (c) the degradation rate at 60 min.

Figure 8: (a) Degradation curves of MO with different initial concentration by the ZnO powders obtained at 800°C, (b) plots of pseudo-first-order kinetic model, and (c) the degradation rate at 60 min.

the porous structure was destroyed. At the same time, the specific surface area of porous ZnO showed a decreasing trend. Porous ZnO obtained at 800°C exhibited the best photocatalytic performance for MO degradation, and the degradation rate was 0.043 min⁻¹. The optimal amount of porous ZnO and the initial concentration of the MO solution were 10 mg and 10 mg L⁻¹, respectively.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Grant Nos. 51471132, 51202191) and Shaanxi Province Science Fund for Distinguished Young Scholars (2018JC-027).

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