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Investigation of Photocatalytic Degradation of Methyl Orange by Using Nano-Sized ZnO Catalysts

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Abstract

Nano-sized ZnO catalysts were prepared by a direct precipitation method under the optimal conditions (calcination of precursors at 550˚C for 120 min). The as-synthesized ZnO catalysts were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and UV-Vis spectroscopy. The photocatalytic properties of ZnO nanoparticles were investigated via methyl orange (MO) as a model organic compound under UV light irradiation. The influence of operating parameters on MO degradation including the amount of ZnO catalysts, pH value of solutions, and the photodegradation temperature was thoroughly examined. In addition, the kinetic process of photocatalytic degradation of MO using nano-sized ZnO catalyst was also examined, and the degradation of MO follow the first order kinetics.

Keywords: ZnO Nanoparticles, Photocatalytic Degradtion, Methyl Orange

1. Introduction

Semiconductor photocatalysts such as TiO_2 and ZnO nano-particles have attracted much attention in recent years due to their various applications to the photocatalytic degradation of organic pollutants in water and air and dye sensitized photovoltaic solar cell [1-3]. Among these semiconductor photocatalysts, TiO_2 is the most commonly used owing to its stable, harmless and inexpensive properties. However, two typical defects including only exciting by high energy UV irradiation and a low quantum yield rate resulted from a low rate of electron transfer to oxygen and a high rate of recombination between excited electron/hole pairs, limit the photo-oxidation rate of TiO_2 nanoparticles. In order to improve the photocatalytic efficiency of TiO_2 nanoparticles, most studies have been focused on the modification of TiO_2 doped by metal ions, especially transition metal ions, which make it possible for TiO_2 to absorb visible light by increasing the charge separation [4,5]. In addition, combination of different kinds of semiconductor photocatalysts also is a promising way to improve the photocatalytic efficiency [6]. Recently, ZnO nanoparticles appear to be a suitable alternative to TiO_2 nanoparticles used for the photodegradation of pesticide carbetamide [7], herbicide triclopyr [8], pulp milling bleaching wasterwater [9], 2-phenylphenol [10], phenol [11], reactive blue 19 [12], and acid red 14 [13]. The substitution of TiO_2 by ZnO used for photo-degradation is ascribed to the photo-degradation mechanism of ZnO being similar to that of TiO2 [3,14]. K. Gouvea *et al.* has confirmed that ZnO exhibits a better efficiency than TiO_2 in photocatalytic degradation of some reactive dyes in aqueous solution [15]. As we known, ZnO nanoparticles can be synthesized by various approaches including sol-gel processing, homogeneous precipitation, mechanical milling, organometallic synthesis, microwave method, spray pyrolysis, thermal evaporation and mechanochemical synthesis. However, ZnO nanoparticles fabricated by the abovementioned methods are prone to aggregate due to the large surface area and high surface energy. In order to improve the dispersion, it is necessary to modify the surface of ZnO nanoparticles. Some researches have revealed several physical and chemical methods for modifying the surface of ZnO nanoparticles. The chemical surface modification, which can be classified as surface grafting and esterification, is the most promising method because of the strong covalent bond between the surface modified particles and polymer chains. In previous researches, the ZnO nanoparticles were ever modified by SiO_2 [16], PMMA [17] and PSt [18], and the influence of particles on the mechanical properties of polymer matrix was studied.

In the present article, the nano-sized ZnO catalysts were prepared by a direct precipitation method under the optimal conditions (calcination of precursors at 550˚C for 120 min). The surfaces of ZnO nanoparticles fabricated by a direct precipitation method are not modified by SiO_2, PMMA and PSt. The effect of various experiment parameters such as the amount of ZnO catalyst, pH of solutions, the photodegradation temperature, and the initial concentration of MO on the degradation of the MO has been thoroughly examined with an aim to quantitatively probing the regulation of photocatalytic activity of ZnO nano-sized particles fabricated by a direct precipitation method.

2. Experimental

2.1. Preparation and Characterization

Nano-sized ZnO particles in this study were prepared by a direct precipitation method. $Zn(NO_3)_2$, $(NH_4)_2CO_3$, ethanol and de-ionized water were used in the experiments. All the reagents used in this study were the analytical grade. The synthetic procedures of nano-sized ZnO particles were also thoroughly introduced elsewhere [19]. As is reported in our recent study [20], the nano-sized ZnO particles fabricated by a direct precipitation method via the calcination of precursors at 550˚C for 120 min have the optimal photocatalytic activity. As a result, the nano-sized ZnO particles synthesized by the calcination of precursor at 550˚C for 120 min were used as catalysts in this study. The specific surface area of nano-sized ZnO particles synthesized by the calcination of precursor at 550˚C for 120 min was determined by nitrogen absorption Brunauer-Emett-Teller (BET) method. The BET measurements were performed on a Micromeritics ASAP 200 instrument. The 26.58 m^2/g of BET specific surface area was obtained. The structural properties of these nano-sized ZnO particles were investigated by the θ-2θ method of X-ray diffraction (XRD) with a Cu $K_{\alpha 1}$ (λ = 0.154 nm) radiation at 40 kV and 30mA using a multipurpose XRD system (PANalytical). The morphology and particle size of these nano-sized ZnO particles were also analyzed by a scanning electron microscope (SEM, JXA840). SEM photographs for the nano-sized ZnO particles were recorded (LEO 435) at 30 kV from samples covered with a thin gold film.

2.2. Photocatalytic Degradation

The MO solutions in concentrations varied from 5 to 50 mg/L (5, 10, 20, 30, 40 and 50) were prepared through dissolving MO powders in ultra pure water, respectively. The concentration of MO solution was determined by measuring the value at approximately 464 nm using a UV-Vis spectrophotometer 756PC (China). The reaction suspensions were prepared by adding nano-sized ZnO particles into the abovementioned MO solutions. The suspensions were ultrasonically sonicated for 20 min and magnetically stirred in dark for 45 min to ensure an adsorption/desorption equilibrium. The reaction suspensions containing MO and nano-sized ZnO photocatalyst were irradiated by a 300 W high-pressure mercury lamp with continuous stirring. In addition, the pH of MO solution adjusted by adding NaOH or HCl solutions was measured using Elico LI120. Absorbance measurements were also recorded in the range of 200-600 nm, using a UV-vis spectrophotometer. The photocatalytic degradation efficiency of the MO solutions was calculated with the following formula: $\eta = \frac{A_0 - A}{A_0} \times 100\%$, where A_0 is the absorbance of MO dye solution before the illumination, A is the absorbance of MO solutions in suspension after time t.

3. Results and Discussion

The XRD pattern of ZnO nanoparticles synthesized via the calcination of precursor at 550˚C for 120 min is showed in **Figure 1**. It could be seen that the diffraction peaks were more intensive and narrower implying a good crystalline nature of the as-synthesized ZnO product, and all of the peaks can be well indexed to hexagonal phase ZnO reported in JCPDS card (NO.36-1451, a = 0.3249 nm, c = 0.5206 nm). Diffraction peaks related to the impurities were not observed in the XRD pattern, confirming the high purity of the synthesized product. The average crystalline size (L) of the nano-sized ZnO particles can be calculated from the Debye-Scherrer formula [21]:

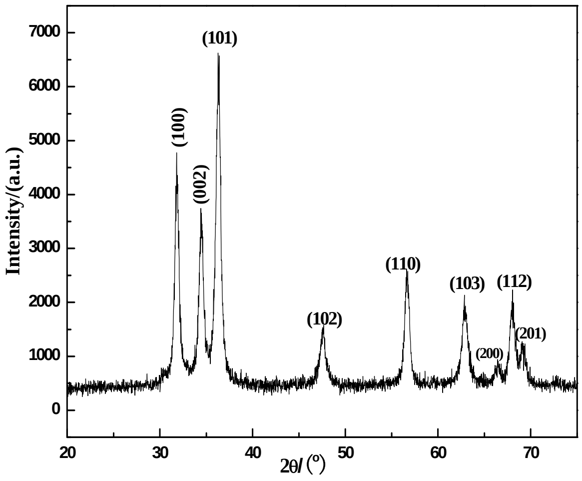

Figure 1. XRD patterns of nano-sized ZnO particles synthesized by a direct precipitation method with the calcination of precursor at 550˚C for 120 minutes.

$L = \frac{0.89\lambda}{\beta \cos\theta}$, where L is the crystalline size (in nm), λ is the wavelength (in nm), β is the full width at half maximum intensity (FWHM--in radian), and θ is the Bragg diffraction angle (°). The average crystalline size of ZnO product synthesized was figured out from the Debye-Scherrer formula to be about 17.3 nm. Typical SEM image of the ZnO nano-particles calcinated at 550˚C for 120 min is shown in **Figure 2**. The ZnO nanoparticles are reasonably uniform in size, and the morphology of the ZnO nano-particles takes on pseudo-spherical shape. The average size of the ZnO nanoparticles is approximately 20 nm, which is consistent with the crystallite size estimated from the XRD analysis shown in **Figure 1.**

The photocatalytic activity of ZnO nanoparticles was assessed according to the photo-degradation kinetics of MO solutions. The dependence of the amount of ZnO nanoparticles on the photodegradation efficiency of 1*l* MO solutions with an initial concentration of 10 mg/*l* at the neutral pH value was shown in **Figure 3**. Experiments show that the photo-degradation efficiency of MO solution increases with the increase of amount of ZnO photocatalysts, after which it reaches the highest value of catalyst amount (2.5 g/*l*), and then decrease. This observation can be explained in terms of availability of active sites on the surface of catalyst and the penetration of UV light into the suspension [22]. The total active surface area of ZnO nano-particles increases with the increase of catalyst dosage. On the other hand, with an increase in the turbidity of the MO suspension, the penetration of UV light will decrease as a result of the increased scattering effect.

The effect of pH in the range of pH 3.0 – 11.0 on the photo-catalytic degradation rate of MO was investigated. The photodegradation efficiency of 1*l* MO solution with an initial concentration of 10 mg/*l* (ZnO concentration = 2.5 g/*l*) as a function of pH of MO solutions were shown in **Figure 4**. The strong effect of pH on the photodegradation efficiency of MO solution was observed. The highest removal rate of MO was obtained at a pH of 7.0.

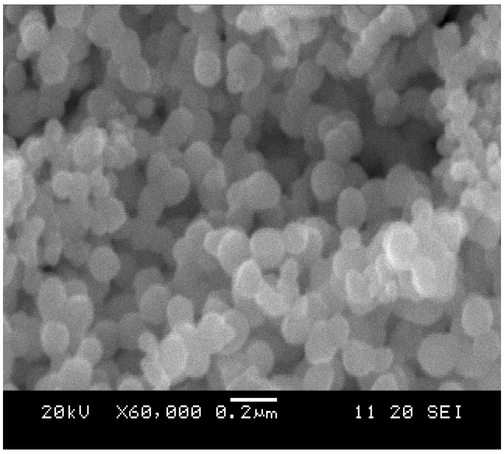

Figure 2. The SEM image of nano-sized ZnO particles synthesized by a direct precipitation method with the calcination of precursor at 550˚C for 120 minutes.

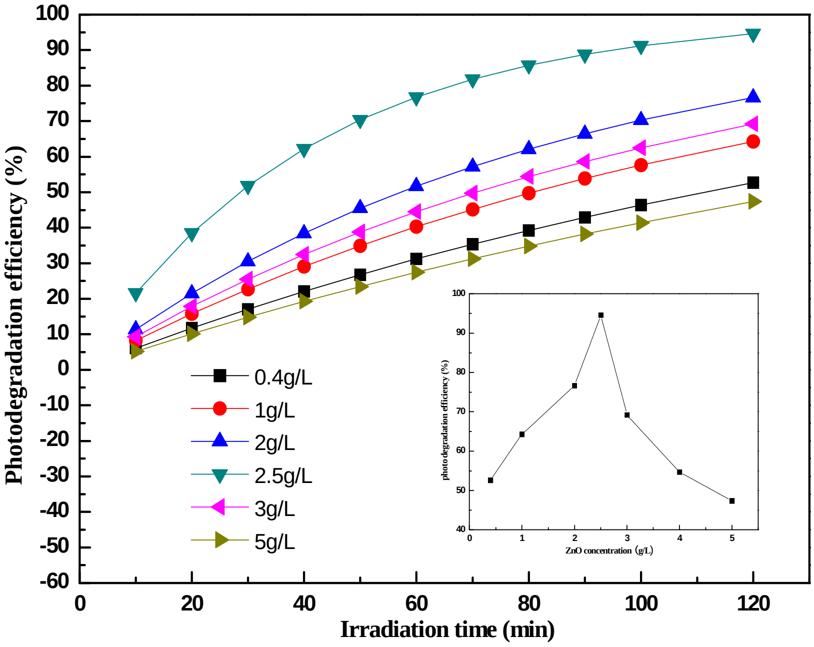

Figure 3. The effect of ZnO amount on the photodegradation efficiency of MO solutions.

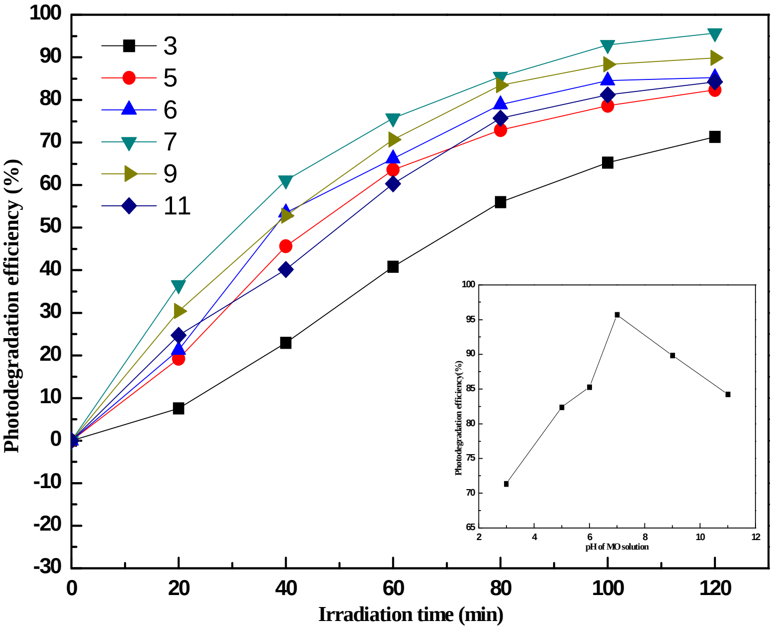

Figure 4. Effect of pH on the photodegradation efficiency of methyl orange at different irradiation times.

However, when TiO_2 nanoparticles were utilized to catalyze the photo-degradation of MO, the higher removal rate of MO was obtained at lower pH values, which is reported in literature [23]. The effect of pH on the photodegradation of MO using ZnO catalysts can be explained as follows. As is pointed out by E. Topoglidis *et al.* [24], the point of zero charge (PZC) of nano-sized ZnO particle is about a pH of 9.30. Above the pH value, the surfaces of nano-sized ZnO particles are negatively charge. Below the pH value, the surfaces of nano-sized ZnO particles are positively charged. Methyl orange molecules have negative charges in a wide pH value range. Therefore, when the MO solution pH value is below the PZC, the MO anions should be readily adsorbed on the surfaces of nano-sized ZnO particles.

As is described by H. Tian *et al.* [1], the photocatalytic degradation efficiency of MO solutions with nano-sized TiO_2 catalysts changes with the temperature variation of the MO solutions. Hence, the effect of MO solution temperature on the degradation efficiency of MO catalyzed by ZnO nano-particles was also discussed in the range from 20˚C to 70˚C at 10˚C intervals in this study. It can be seen in **Figure 5** that at the first stage, the photo-degradation ratios of MO ascend with the increase of solution temperature from 20˚C to 50˚C, and begin to decrease at a temperature beyond 50˚C. However, in many cases, the higher the temperature is, the quicker the chemical reaction rate does. The experimental results shown in **Figure 5** can be explained as follows. At an elevated temperature, the adsorbability of nano-sized ZnO particles to MO becomes low. The lower adsorbability of MO will weaken the direct hole oxidation on the surface of nano-sized ZnO catalysts.

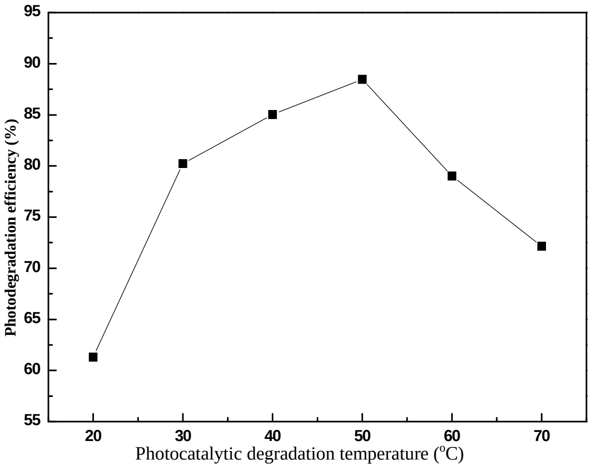

Figure 5. Influence of solution temperature on photodegradation efficiency of methyl orange(MO initial concentration of 10 mg/*l*, ZnO amount of 2.5 g/*l*, solution acidity of pH 7.0 and total volume of 1*l*.

The photocatalytic decomposition of MO organic pollutants on the surface of ZnO nano-particles also follow a pseudo first-order kinetic law, and can be expressed as $-ln\left(\frac{C}{C_0}\right)=kt$, where C and C_0 are the reactant concentration at time $t = t$ and $t = 0$, respectively, k and t are the pseudo-first-order rate constant (reaction rate constant) and time, respectively [25]. The relationships between $-\ln(C/C_0)$ and irradiation time (Reaction time) are shown in **Figure 6**. It is obvious that there exists a linear relationship between –ln(C/C_0) and irradiation time. The pseudo-first-order rate constant k and linear regression coefficient (R) for MO solutions with different initial MO concentrations are summarized in **Table 1**, respectively.

According to the Langmuir-Hinshelwood model, the fact that the decrease of reaction rate constant with the increase of the initial concentration of MO solutions obtained from **Table 1** could be explained as follows. The organic MO is firstly adsorbed on the surface of nano-sized ZnO particles, and then the photocatalytic decomposition takes place under UV irradiation. With the increase of the initial MO concentrations, the MO molecules congregate on the surface of nano-sized ZnO catalysts. However, quenching between these excited MO molecules irradiated by UV will take place [26]. The quenching probability could also increase with the increase of the initial MO concentrations. Consequently, the photocatalytic efficiecncy of MO solutions is decreased with the increase of the initial MO concentrations.

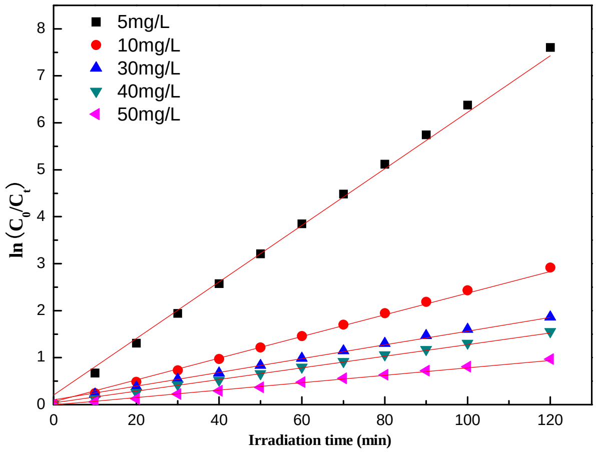

Figure 6. Kinetics of the methyl orange degradation catalyzed by ZnO nanoparticles.

Table 1. Reaction rate constant of MO photocatalytic decomposition with different initial concentration.

Experiments	ZnO concentration (g/*L*)	Initial concentration of MO solutions (mg/*L*)	*k* (*constant*)	R^2
1	2.5	5	0.063812	0.9999
2	2.5	10	0.024304	0.9999
3	2.5	30	0.016148	0.9975
4	2.5	40	0.013099	0.9997
5	2.5	50	0.007942	0.9982

4. Conclusions

The nano-sized ZnO catalysts were prepared via the calcination of precursors at 550˚C for 120 min. A series of experiments were carried out to study the effects of the amount of photocatalyst, a pH value of MO solutions, and reaction temperature on the photocatalytic degradation efficiency of MO solutions. The photodegradation efficiency increases with the increase in the amount of ZnO photocatalyst. Once the amount of ZnO photocatalyst is beyond the highest value of catalyst amount (2.5 g. l^{-1}), the photo-degradation efficiency of MO solution begin to decrease. The photocatalyst capacity of ZnO towards the methyl orange solutions strongly depends on the pH of MO solutions, and the MO solutions catalyzed by ZnO nano-particles has good photodegradation efficiency at a central pH value. The photodegradation ratios of MO solutions ascend with the increase of the MO solution temperature from 20 to 50˚C, and they begin to decrease at temperature beyond 50˚C.

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