Degradation kinetics for photocatalytic reaction of methyl orange over Al-doped ZnO nanoparticles

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A B S T R A C T

Al-doped ZnO nanoparticles with different Al concentrations were prepared and employed as photocatalysts for the degradation of methyl orange. The samples were characterized by XRD, FE-SEM, XPS, BET, UV–vis DRS and photoluminescence techniques. The kinetic behavior could be described in terms of the Langmuir–Hinshelwood model. The adsorption equilibrium constant increased with increasing Al concentration and the reaction rate constant showed a maximum at 3% Al. It can be deduced that the enhancement of photocatalytic activity of ZnO by addition of Al could be attributed not to increase of surface area but to effective suppression of photoinduced electrons and holes.

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Introduction

Heterogeneous photocatalytic decomposition of organic pollutants is quoted to be one of the most promising processes for air and water decontamination. A wide range of organics can be oxidized into CO_2 and H_2O on an illuminated semiconductor photocatalyst at ambient temperature and pressure. Band gap excitation of semiconductors generates electron–hole pairs that can initiate redox reactions that oxidize the adsorbed organic molecules. An efficient semiconductor photocatalyst must have suitable band-gap energy and chemical stability over long irradiation times. TiO_2 is known to be the most active photocatalyst for organic oxidation. However, certain studies have reported that zinc oxide (ZnO) exhibits a better activity in photocatalytic decolorization of some dyes as compared with TiO_2 [1,2].

Zinc oxide, which is a highly degenerate semiconductor with a wide band gap of 3.22 eV, has emerged as one of the most promising oxide materials because of its numerous industrial applications in the fields of piezoelectric transducers, UV devices, chemical and gas sensors, light-emitting diodes and lasers.

However, it was claimed that ZnO as a photocatalyst has several drawbacks including the fast recombination rate of photogenerated electron–hole pair and a low quantum yield in the photocatalytic reactions in aqueous solutions, which obstruct commercialization of the photocatalytic degradation process [3,4]. Consequently, there has been a lot of interest in improving the photocatalytic activity of ZnO. Various methods, including morphological change in nano-scale [5,6], coupling with other materials such as carbon nanotube and graphene [7], introducing surface defects [8], and doping with transition metals, were proposed as suitable modifications of ZnO photocatalyst for the degradation of organic compounds. Among them, one simple and effective approach, which has recently received much attention, is to dope transition metals into the photocatalyst [9,10].

A number of transition metals such as Co [11], Ag [12], Mn [13], Pd [14], Bi [15], Sm [16], Al [17], Ce [18], were used as dopants for ZnO to improve its photocatalytic activity. Among these doped ZnO materials, Al-doped ZnO (AZO) has received considerable attention because of its unique physico-chemical properties as well as the merit of cheap raw materials.

Consequently, the effect of Al doping on the photocatalytic efficiency of AZO has been studied extensively. Hsiao et al. [19] indicated that the doping of Al in ZnO increases the specific surface area which results in a better activity in the photocatalytic decomposition of methylene blue under UV irradiation. Recently Ahmad et al. [17] also reported that, in the photocatalytic

degradation of methyl orange under visible light irradiation, the AZO photocatalyst doped with 4% Al exhibits higher activity compared to undoped ZnO and they attributed the enhanced activity to extended light absorption, inhibition of electron–hole pair's recombination and increasing adsorptivity of reactant molecules on the surface of catalyst powders. On the contrary, Saber et al. [20] proposed that the improvement of photocatalytic activity of AZO in the photocatalytic decomposition of naphthol green B in the presence of sunlight irradiation is mainly attributed to the reduction of band gap by the addition of Al. AZO films were also used as photocatalysts for the decomposition of methyl orange under UV and sunlight and found to have a excellent photocatalytic activity [21]. This observation was attributed to the extra electrons provided by the aluminum atoms. Although, in many photocatalytic reactions, the doping of ZnO with Al shows the improvement of photocatalytic activity, the role of Al in the enhancement of photocatalytic activity of AZO is still uncertain and needs to be further studied. Furthermore, it was reported recently that the ZnO doped with low concentration of transition metals, such as Mn, Co, Ni and Cu, has a lower photocatalytic activity than undoped ZnO for the degradation of methyl orange [22].

In the present study, the Al-doped ZnO (AZO) materials having different Al contents were prepared and used as photocatalysts for degradation of methyl orange (MO). Methyl orange azo dye is commonly used as a coloring agent in several applications, such as textile, paint, ink, plastic, and cosmetic industries [23]. The degradation kinetics of MO on AZO photocatalysts was studied and obtained kinetic parameters were used to examine the role of Al dopant in the enhancement of photocatalytic activity of AZO for the degradation of methyl orange. We also investigated the effects of Al doping on the physico-chemical properties and photocatalytic activity of AZO.

Experimental

Catalyst preparation

Al-doped ZnO (AZO) samples were prepared by a simple precipitation method. $Zn(NO_3)_2 \cdot 6H_2O$ and NH_3 solution were used as starting materials and the aluminum dopant source was $Al(NO_3)_3 \cdot 9H_2O$. Typically, $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in distilled water to prepare 0.3 M solution of zinc nitrate and then 0.3 M NH_3 solution was added dropwise into the zinc nitrate solution with continuous stirring. The white precipitates were obtained and they were still stirred vigorously at 75 °C for 2 h. After being cooled to room temperature, these precipitates were filtered and rinsed with distilled water several times until it became neutral. The collected precipitates were dried at 100 °C for 24 h and followed by calcination at 500 °C for 2 h. Depending on the required concentration of Al-doping, the corresponding amount of $Al(NO_3)_3 \cdot 9H_2O$ was added to the solution of zinc nitrate. Al-doping concentration was varied from 1 to 8 mol%.

Catalyst characterization

Crystal structures of the prepared AZO samples were examined by X-ray diffractometer (XRD, Philips X'pert diffractometer) using Cu-Kα radiation in the diffraction angle range $2\theta = 10$–$90°$. The effect of doping concentration on crystallite size was also investigated and the crystallite size was calculated using the Scherrer's formula [10]:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where D is the average crystallite size, β is the full width at the half maximum of the diffraction peak, θ is the Bragg angle, λ is the wavelength of X-ray used and k is a constant.

The morphology of the synthesized AZO particles was visualized by field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F).

X-ray photoelectron spectroscopy (XPS, THERMO VG SCIENTIFIC, MultiLab2000) was also utilized to analyze the chemical bonding state of various species in AZO particles. The binding energies were corrected for the charge shift using the C 1s peak of graphitic carbon (BE = 284.6 eV) as a reference.

The specific surface areas of AZO samples were determined by nitrogen adsorption and desorption at 77 K using the surface area and pore size analyzer (Quantachrome NOVA 100e).

The light absorption properties of the AZO catalysts were investigated by UV–vis diffuse reflectance spectroscopy (DRS, Varian Cary 100).

The adsorption properties of AZO catalysts in the dark were also evaluated by monitoring the concentration of a MO solution which contacted the AZO catalysts at 30 °C under continuous stirring [24]. In this experiment, the initial concentration of MO solution was 20 mg/L and 1 g of AZO photocatalyst was added to 100 mL of MO solution. The progress of adsorption was monitored by measuring the concentration of MO in the solution at desired contact time.

Room temperature photoluminescence (PL) spectra of AZO catalysts were obtained on a spectrofluorophotometer (Fluorescence Spectrophotometer F-4500, Hitachi). The excitation wavelength was 325 nm and spectra were obtained in the range of 300–600 nm.

Photocatalytic activity measurement

The photocatalytic activities of AZO catalysts were evaluated using MO as a probe molecule for photodegradation. The photocatalytic reactions were carried out using a 100 mL Pyrex reactor with a quartz window. The AZO suspension concentration was 4 g/L and the concentrations of MO in the suspension were adjusted to 10–50 mg/L. The light source was a 300 W Xe-arc lamp (Newport). Prior to photoreaction, the suspension was magnetically stirred in the dark for 60 min to establish an adsorption/desorption equilibrium condition. The reaction suspension was then irradiated with constant stirring. During the photocatalytic reaction, samples were taken out at given time intervals and immediately centrifuged at 10,000 rpm to remove particles. The analysis of concentration of MO was carried out by measuring of the absorbance of MO at 470 nm by using a UV spectrometer (Shimadzu UV-240 spectrophotometer).

In order to facilitate discussions, similar photocatalytic reactions were also conducted using methylene blue (MB) as a probe compound since MO and MB are known to be typical anionic and cationic dyes, respectively. In this experiment, the concentration of MB was 20 mg/L and AZO samples with 1 and 5% Al were used as photocatalysts since those AZO catalysts showed the lowest and highest adsorption capabilities in the case of MO photodegradation.

Results and discussion

Characterization of samples

Fig. 1 shows the XRD patterns of prepared AZO catalysts. The XRD patterns of AZO samples display characteristic peaks that matched well with wurtzite structure of ZnO (JCPDS 05-0664). No diffraction peaks of element or oxide of Al are detected. Similar phenomena were reported by Navale et al. [25] who prepared the