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Photocatalytic degradation of an azo textile dye with manganese-doped ZnO nanoparticles coated on glass

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ABSTRACT

Mn doped ZnO nanocomposite thin film coated on glass by a simple spin-coating method was used to degrade an azo textile dye from aqueous environment. Mn doped ZnO nanocomposite thin film was characterized by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The photo-reduction activity of photocatalyst was evaluated using an azo textile dye as organic contaminant irradiated only with UV light from mercury bulb. The processing parameter such as the pH value also played an important role in tuning the photocatalytic activity. The maximum photodecomposition rate was achieved at pH=6, and a novel model about the absorption of azo dye on the surface of the catalysts was proposed.

Keywords: Photocatalytic degradation; Mn doped ZnO thin film; Composite thin film; Nanoparticle; Azo dye.

1. Introduction

Photocatalytic degradation of organic pollutants in water using semiconductive particles, such as TiO_2 and ZnO, has attracted extensive attention. ZnO is a suitable alternative to TiO_2 as it has a similar band gap energy (3.2 eV), larger quantum efficiency than TiO_2 and higher photocatalytic efficiencies have been reported [1–5]. ZnO is a low cost alternative photocatalyst toTiO_2 for decolorization of organics in aqueous solutions [6-7]. Pure metal oxides have disadvantages of low quantum yield and the fast recombination rate of photogenerated electron–hole pair. The presence of metals on semiconducting metal oxides which act as electron–hole separation centers can enhance the degradation efficiency of photocatalytic reactions [8]. The finely divided powder photocatalyst can be dispersed in the irradiated aqueous solution as slurry [9-10]. However, from a practical point of view it may not be possible to use catalyst suspension in slurry because of the filtration problems linked to the small size of the photocatalyst particles for catalyst recycling and obtaining clean, powder-free water. Because of this reason, attempts have been made to immobilize the catalyst on rigid supports. It has been shown that it is possible to deposit photocatalyst on various rigid supports of different nature such as glass and stainless steel [11-12]. In the past decade we have reported that metal oxide photocatalysts could degrade environmental pollutants [13-18].

Here we are interested in the photocatalytic decolorization of textile dye contaminants by the manganese-doped zinc oxide photocatalyst. The Mn-doped ZnO photocatalyst was synthesized and the photocatalytic decolorization of azo dye was carried out over the photocatalyst coated on glass under irradiation. In this work, manganese-doped zinc oxide nanostructure thin films have been prepared via sol-gel spin-coating method, in which manganese were homogeneously incorporated into the lattice of ZnO nanostructure. Degradation of an azo dye was used as a probe reaction to evaluate the role of Mn in photocatalytic activities of ZnO thin film in response to UV light irradiation

2. Experimental

Manganese-doped zinc oxide sol was synthesized via spin-coating sol–gel method. A sample of $Zn(CH_3COO)_2.2H_2O$, $(Mn(OAc)_2.2H_2O)$, monoethanolamine (MEA) and 0.5 ml de-ionized water were dissolved in 15 ml isopropyl alcohol at 60 ^{o}C for 60 min under vigorous stirring. The stoichiometry of manganese was controlled by dissolving the precursor $(Mn(OAc)_2.2H_2O)$ in anhydrous ethanol. Manganese-doped zinc oxide was prepared by spin-coating method and dried at 275 $^{\circ}$C for 10 min. Films were annealed at 550 $^{\circ}$C for 60 minutes. The deposition was repeated to obtain a film with different thicknesses. The structure and crystalline size were determined by XRD diffraction (Bruker D8 advanced X-ray diffractometer: Cu Kα radiation, Scan rate 0.03 2Θ s^{-1}). Film morphology was characterized by Philips XL-30 scanning electron microscopy (SEM) with accelerating 10 kV. The initial and final pH values were measured by pH/conductivity-meter, Schott Instruments GmbH, Mainz, Germany. Degradation of dye solutions was monitored by a Double beam UV-visible spectrophotometer (Varian Cary 500 Scan). The photocatalytic degradation experiments were carried out in a simple oxidation reactor (Fig. 1). Concentration was measured by spectrophotometer at λmax of 535 nm (Varian Cary 500 Scan).

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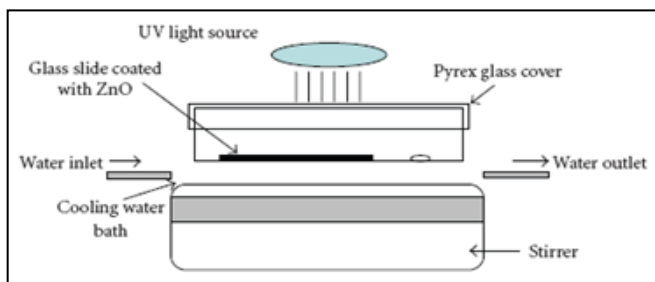 E-mail:habibi@chem.ui.ac.ir, habibi284@gmail.com

Fig.1. The diagrammatic representation of the experimental setup used for photocatalytic experiments: glass slide coated with manganese-doped zinc oxide thin film

In all experiments, doubly distilled water was used throughout this study and the initial pH of solutions was adjusted as appropriate by addition of either HCl or NaOH. The results of blank experiments under similar conditions but without the addition of catalysts indicated that there was a negligible loss of solution volume due to the UV irradiation and reactor open to the air and also the loss of substrate was negligible.

3. Results and Discussion

3.1. Structure and morphology of manganese-doped zinc oxide thin film

XRD patterns of the manganese-doped zinc oxide nanostructure thin film samples were shown in Fig. 2. The diffraction peaks of each sample were quite similar to those of ZnO, which could be indexed as the hexagonal wurtzite structure ZnO. These results confirmed the formation of single phase hexagonal ZnO. It is shown that the diffraction peaks are relatively strong, and the peak positions matched well the standard data for bulk ZnO. Therefore, all samples crystallized in a wurtzite structure with a high crystallinity [19-23]. The mean crystallite size L was determined from the broadening β of the most intense line, for each polymorph, in the X-ray diffraction pattern, based on the Scherer equation using the full-width at half maximum of the peaks where λ is the radiation wavelength, k = 0.90 and θ the Bragg angle [24]. The average particle size of manganese-doped zinc oxide nanoparticles are 48 nm.

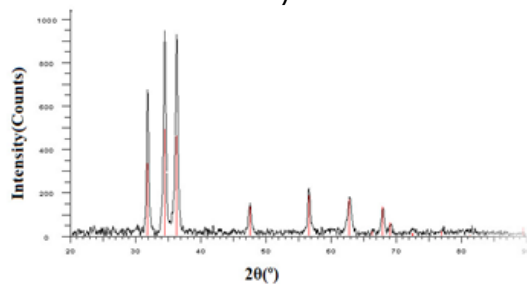$$L = \frac{k\lambda}{\beta\cos\theta}$$

Fig. 2 The XRD pattern of the manganese doped zinc oxide thin film coated on glass by spin-coating and annealed at 550 ºC.

The scanning electron microscopy image of manganese-doped zinc oxide thin film is shown in Fig. 3. As shown in Fig. 3, the film is assembled by the spherical nanoparticles that are distributed uniformly and monodispersely in the film. The average crystalline size of manganese-doped zinc oxide nanoparticles in the film annealed at 500 ºC is about 48 nm and a granular surface.
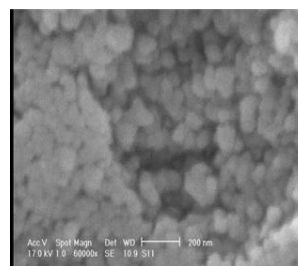

Fig. 3. SEM image of manganese-doped zinc oxide nanostructure thin film coated on glass by spin-coating and annealed at 550 ºC

3.2 Photodegradation of azo dye by manganese-doped zinc oxide thin film

Fig. 4 shows the $\ln(C_0/C)$ versus time curves of the azo dye photocatalytic decolorization using manganese -doped zinc oxide thin film photocatalyst, where C_0 and C were the concentrations of the primal and remaining azo dye, respectively. Curve shown in Fig. 4 was linear, revealing that the kinetic data of the azo dye photocatalytic decolorization fit well to the first-order reaction kinetic model. Assuming first-order reaction kinetics for the photocatalytic oxidation process, the decolorization rate constant was determined from the equation $\ln(C_0/C_t)=-kt$, where C_0 and C_t are the dye concentrations at times 0 and t , respectively, and k is the first-order rate constant.

Photodegradation experiments were carried out at dye concentration 5 to 20 mg/L, reaction temperature 25 ºC, catalyst loading 5 glass slides coated with manganese-doped zinc oxide thin film. The rate of photocatalytic degradation of manganese-doped zinc oxide thin film catalysts is higher compared to pure ZnO thin film. The self-degradation of azo dye without involving photocatalysts was negligible under UV light irradiation [25, 26].
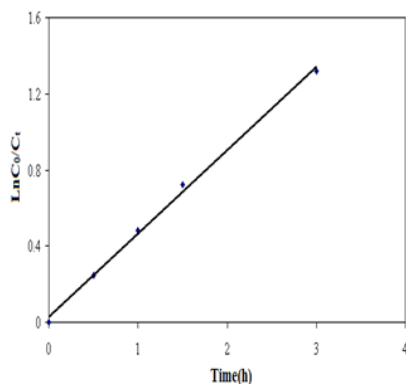
Fig. 4. Effect of UV-irradiation time on the degradation of azo textile dyes at initial concentration 10 mg/L in de-ionized water using manganese-doped zinc oxide nanostructure thin film coated on glass by spin-coating and annealed at 550 °C

Under the irradiation of manganese -doped zinc oxide thin film catalysts manganese acts as an electron scavenger, which may react with the superoxide species and prevent the holes–electrons recombination, and thus increases photooxidation efficiency [27-31].

The effect of initial dye concentration is attributed to the so-called shielding effect; after exceeding the optimal amount, the dye reduces the penetration of the light in the solution. Mineralization of the dyes was confirmed by monitoring the evolution of CO_2 by gas chromatography. The stoichiometry amounts of CO_2 evolved in neutral media were consistent with TOC assays. Final products were, in all cases, CO_2, NH_4^+ and NO_3^- and SO_4^{2-} ions. Results confirm the complete mineralization of the dyes.

4. Conclusion

The manganese -doped zinc oxide thin film sols have been prepared by sol–gel spin-coating method with a flat glass as substrate. The film was characterized by means of XRD and SEM. The manganese-doped zinc oxide thin film has been employed in photocatalytic oxidation of azo dye. The manganese-doped zinc oxide thin film-supported commercial glass is a promising and efficient catalyst to degrade organic pollutants. Glass coated manganese-doped zinc oxide thin film can be used repeatedly over a long time with small loss of efficiency.

Acknowledgments

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