Photocatalytic Activity of Manganese-Doped ZnO Nanocrystalline Powders

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Abstract
ZnO nanocrystalline powders doped with up to 5 at% manganese were synthesized and their photocatalytic activity was studied. Doped ZnO powders were prepared using a sol-gel process. The crystal structure and grain size of the particles were characterized by X-ray diffractometry and optical properties were studied using UV-Vis spectroscopy. The photoactivity of undoped and doped ZnO nanocrystalline powders was evaluated by monitoring the photo-bleaching of the aqueous solutions of Rhodamine B dye in the presence of ZnO under simulated sunlight. The results showed that up to 3 at% manganese were successfully doped into the nanocrystalline ZnO and that manganese-doping reduced the photocatalytic activity of ZnO.

Keywords: ZnO, nanocrystalline powder, photocatalysis, synthesis, doping, manganese.

INTRODUCTION
The detrimental effects of UV-radiation are having an increased impact on Australian society. With the highest rate of skin cancer in the world, more than 1,200 Australians lose their lives every year as a result of UV exposure [1]. Significant environmental problems are also resulting from UV-induced degradation of organic materials such as timbers, textiles, plastics, paints and dyes. The development of suitable UV-shielding agents is therefore of great importance [2,3].

ZnO is a semiconductor having a wide bandgap energy of ~ 3.3 eV. It is considered as one of the most effective UV shielding materials owing to their broader UV absorption spectrum, lower toxicity and higher physical/chemical stability than organic UV absorbers [4]. However, the inherent photocatalytic properties of ZnO have been a major obstacle for the utilisation of ZnO powders in UV protection applications. ZnO generates reactive free radicals upon illumination by UV light, acting as a photocatalyst. In ZnO, UV light excites electrons from the valence band to the conduction band to form electron – hole pairs. These can migrate to react with oxygen or hydroxide species on the particle surface, resulting in the production of free radicals such as hydroxyl radicals (OH) and superoxide (O2-). These free radicals, in turn, can degrade organic polymer substrates and/or change the colour of the substrates which the ZnO is supposed to protect [5,6].

While modification of photocatalysis has been widely investigated, the research has been directed mainly towards enhancing the photoactivity of TiO2 [5]. Despite the industrial importance of ZnO as a UV blocking agent [4], experiments involving the reduction of the photocatalysis of ZnO have scarcely been reported. One approach to eliminate the photocatalytic activity is to dope ZnO with impurity ions. It is generally considered that dopant ions create defects in the crystal lattice that act as trapping sites of the excitons, promoting recombination of electron-hole pairs, resulting in reduced photocatalytic activity [7]. For example, the doping of manganese ions in ZnO creates deep traps within the bandgap, which may act as electron-hole recombination sites [8].

This study investigates the photocatalytic properties of un-doped and manganese doped zinc oxide. Several samples with different doping levels were synthesised using the thermal decomposition of zinc carbonate and then examined for their photoactivity. The photocatalytic activity was studied by using UV-Vis spectroscopy, to observe how each sample degraded a common dye when exposed to UV light.
METHODS AND PROCEDURES

The starting materials, Zn(CH₃COO)₂•2H₂O (Aldrich, >99.0%), Na₂CO₃ (Aldrich, >99.5%) and Mn(CH₃COO)₂•4H₂O (Aldrich, >99%) were used without further purification. Initially, the synthesis of zinc carbonate was attempted via the reaction

\[
\text{Zn(CH₃COO)₂•2H₂O + Na₂CO₃ → ZnCO₃ + 2Na(CH₃COO) + H₂O}
\]

In a typical synthesis of undoped ZnO, a solid mixture of 1, 3, and 5 mol% Mn(CH₃COO)₂•4H₂O was separately dissolved in 50 ml of deionised water. Next, the Na₂CO₃ solution was added into the Zn(CH₃COO)₂•2H₂O solution to form white precipitates. The precipitates were separated from the supernatant using a centrifuge and further washed with deionised water to remove reaction by-products until the salinity of the supernatant becomes less than 100 ppm. The separated precipitates were dried in air at 60°C and then heat treated at 300°C for 1 hour. For the synthesis of manganese-doped ZnO, a solid mixture of 1, 3, and 5 mol% Mn(CH₃COO)₂•4H₂O in Zn(CH₃COO)₂•2H₂O was dissolved in 50 ml of deionised water and then mixed with an aqueous solution of Na₂CO₃, followed by the same procedure as for undoped ZnO.

The crystal structure of the nano-powders was characterized by X-ray powder diffraction (XRD) measurement using a Philips PW-1729 X-ray diffractometer with Cu-Kα radiation. For the determination of the shift in diffraction peak positions, corundum powders were used as an internal standard and the scanning step of 0.01° was employed. The mean crystallite size was estimated from the width of the six diffraction peaks in the diffraction angle range between 30 and 65°, using the Debye-Scherrer equation [9].

Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis of the white precipitate was conducted using a Netzsch STA 409 PC system under a constant N₂-gas flow. The specific surface area of the powder was analysed by the Brunauer-Emmett-Teller (BET) gas absorption method using a Micromeritics Tristar 3000 system. All powders were dried at 150°C for 1 hour under a high purity nitrogen gas prior to BET analysis. UV-Vis diffuse reflectance measurements were carried out on dried powder samples using a Varian Cary 300Bio spectrophotometer equipped with an integrating sphere, Labsphere DRA-CA-30I.

Rhodamine B (RhB) was used as a probe molecule to evaluate the photocatalytic activity of doped and undoped ZnO nanoparticles in response to UV and visible light irradiation. The characteristic optical absorption peak of RhB at 554 nm was chosen to monitor the photocatalytic degradation process. The experiment was carried out according to the following procedure: 8 mg of the dried powder was dispersed in 50 ml of RhB aqueous solution in a 100 ml beaker. The suspension was stirred in the dark for 1 hour to ensure the establishment of adsorption and desorption equilibrium of RhB on the particle surface. Subsequently the suspension was irradiated with simulated sunlight using an Atlas Suntest CPS+ instrument equipped with 150 W xenon lamp and a filter (coated quartz dish). At given intervals, 3 ml of the suspension was extracted and then centrifuged at 6000 rpm for 10 min to separate the nanoparticles from the supernatant. UV-Vis specular absorbance spectra of the supernatant were measured with a Varian Cary 3E spectrophotometer using a quartz cuvette having an optical path length of 10 mm.

RESULTS AND DISCUSSION

The dried precipitate obtained by mixing Zn(CH₃COO)₂•2H₂O and Na₂CO₃ solutions was examined by XRD and DTA-TG analyses. Fig. 1(a) shows an XRD spectrum of the undoped white precipitates before heat treatment. The indexed peaks in the spectrum are closely matched with the available powder diffraction of hydrozincite Zn₅(CO₃)₂(OH)₆ (JCPDS Card No. 19-1458, 89-1397, and 89-0511), suggesting that the white precipitates were formed via the reaction

\[
5\text{Zn(CH₃COO)₂•2H₂O} + 5\text{Na₂CO₃} → \text{Zn₅(CO₃)₂(OH)₆ + 10Na(CH₃COO) + 7H₂O + 3CO₂.}
\]

In fact, extensive effervescence was observed during the mixing of Na₂CO₃ and Zn(CH₃COO)₂•2H₂O solutions, suggesting the generation of CO₂ gas via the above reaction path. In the XRD patterns of some of the replicates of the precipitates, a small amount of smithsonite ZnCO₃ (JCPDS Card No. 08-0449) along with hydrozincite was evident (spectra not shown). The precipitates doped with manganese showed the same characteristics in the powder colour and XRD patterns as the undoped precipitates.

Fig. 2 shows the DSC-TG curves of the precipitates. It is evident that the thermal decomposition of hydrozincite started from ~230°C. The weight loss during the thermal decomposition was ~24wt%, nearly the same as the theoretical value of 26.0 wt% expected for the complete decomposition reaction of hydrozincite, Zn₅(CO₃)₂(OH)₆ → 5ZnO + 3H₂O + 2CO₂. In order to ensure the completion of thermal decomposition from hydrozincite to ZnO, the doped and undoped hydrozincite precipitates were heat treated at 300°C. As shown in Fig. 1(b-e), the XRD spectra of undoped and doped ZnO after heat treatment consist solely of the diffraction patterns as the undoped precipitates.

The doping effects on the mean crystallite sizes and specific surface area are shown in Fig. 3. As the doping level increases, the crystallite size decreases slightly, while specific surface area shows marked increase.
Fig. 1: X-ray diffraction patterns of the undoped powders (a) undoped ZnO before heat treatment and (b) undoped, (c) 1 at%, (d) 3 at%, (e) 5 at% manganese-doped ZnO after heat treatment.

Fig. 2: TGDTA curves of the undoped precipitate. This is due to the fact that dopant ions inhibit crystal growth and sintering between grains during heat treatment. Similar observation was previously reported [10].

It was observed that the position of the diffraction peak at ~34° shifted to lower angles as the doping level increased. Since the particular peak is associated with (002) lattice plane, the c-axis lattice constant was calculated from the diffraction angle of the peak as shown in Fig. 4. It is evident that the lattice parameter gradually expands as the doping level increases and that the lattice parameter reaches its maximum above the doping level of ~3 at%.

Previous studies of manganese-doped ZnO thin films have taken the observed lattice parameter expansion as evidence that the dopant cation is incorporated into ZnO solid solution in the divalent state [11]. The Mn$^{2+}$ ion is characterised by a slightly larger size (0.066 nm) compared to Zn$^{2+}$ (0.060 nm). As a consequence, substitution of Zn$^{2+}$ ions with Mn$^{2+}$ would be expected to cause an expansion of the unit cell. Similar behaviour has been observed in other experimental studies regarding transition metal-doped ZnO powders [7,12] and thin films [13].

The saturation of the lattice parameter at ~3 at% of doping level indicates that, using the current doping method, the solubility limit of manganese in ZnO crystal lattice is close to 3 at% and the excess manganese ions may be precipitated out on the particle surfaces.

Fig. 3: X-ray crystallite size (closed circle) and BET specific surface area (open square) as a function of Mn doping level.

Fig. 4: C-axis lattice constant as a function of Mn doping level.
Fig. 5 shows the diffuse reflectance spectra of dry powders. It is evident that the increased doping level resulted in a progressive decrease in diffuse reflectance in the visible light range. In the spectra of the samples doped with 1 and 3 at% manganese, additional broad absorption below ~ 560 nm (~ 2.2 eV) is evident. This is consistent with a previous experimental study by Rao et al. [14], which found that manganese-doped ZnO powders exhibit a broad absorption band in the range of 450-500 nm as a result of the $^6A_I(S) \rightarrow ^4T_I(G)$ transition at Mn$^{2+}$ sites.

The diffuse reflectance in the UV range below ~ 365 nm was nearly zero for all the samples, due to the bandgap absorption of light. The reflectance spectra showed no evidence for the blue-shift of the bandgap energy by manganese-doping, contrary to the previous finding by Samanta et al. [15].

Fig. 6 shows the absorption spectra of RhB under irradiation of simulated sunlight in the presence of undoped ZnO. The irradiation time is indicated in the figure. The peak height gradually decreases as the irradiation time increases, indicative of the degradation of RhB by the photocatalytic activity of ZnO. The absorption spectra showed no change without irradiation or without ZnO. It is also evident in Fig. 6 that the peak position shifted toward lower wavelengths with increased irradiation time. The peak shift is due to the formation of photo-degradation intermediates species that have absorption peaks in the range between 502 and 541 nm [16].

The intensity of the RhB absorption peak in the absorbance spectra is plotted in Fig. 7 for undoped and doped ZnO powders as a function of irradiation time. The intensity was normalised with the initial value at the beginning of irradiation. Since photoactivity is also dependent on powder’s surface area, the intensity was further normalised using the specific surface area of each powder. As evident in Fig. 7, the photo-induced degradation of RhB was significantly slower in the presence of doped ZnO than undoped ZnO. The powders doped with 1 and 3 at% manganese showed nearly the same amount of photoactivity, while the powder doped with 5 at% manganese showed the greatest reduction in photoactivity. This is rather surprising, as the XRD data indicates that 5 at% exceeded the doping limit and hence the powder contains no more than 3 at% of crystal-doped manganese. Thus the results suggest that undoped manganese ions that are possibly on the particle surface have some effect to reduce photoactivity.
If manganese ions are located on the particle surface, manganese itself may oxidise RhB molecules without help of photo-generated free radicals. However, as in the case for undoped ZnO, without irradiation of simulated sunlight, the absorption spectra showed no change even in the presence of doped ZnO. Hence the degradation of RhB was caused only by UV light via photocatalysis of doped ZnO.

CONCLUSION
ZnO nanocrystalline powders doped with up to 5 at% manganese were prepared using a sol-gel process. The powder consisted of primary particles of ~10 nm in diameter and had a high specific surface area. XRD study revealed that up to ~3 at% manganese ions were doped in the ZnO crystal lattice. The photoactivity of undoped and doped ZnO nanocrystalline powders was evaluated by monitoring the photo-bleaching of the aqueous solutions of Rhodamine B dye in the presence of ZnO under the simulated sunlight. Manganese doped zinc oxide exhibited significantly reduced photoactivity compared to undoped zinc oxide. This reduction is important for ZnO nanoparticles to be used as UV shielding agents to protect organic substrates. Further investigation is planned for (i) the determination of the location of manganese ions, (ii) the study of the photocatalytic activity of manganese doped ZnO in the doping level lower than 1 at% and (iii) the mechanism of the reduction of photocatalysis by manganese ions on particle surfaces.

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