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Synthesis and Photocatalytic Activity of Doped Zinc Oxide Nanoparticles

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Abstract— In this study, we have investigated the effect of doping with cobalt and manganese oxide on the photocatalytic activity of nanoparticulate zinc oxide. Zinc oxide powders with controlled particle size, minimal agglomeration, and controlled chemical composition were manufactured by mechanochemical processing. The photocatalytic activity of the powders was measured using the spin trapping technique with electron paramagnetic resonance spectroscopy. It was found that the addition of cobalt oxide decreased the yield of photogenerated hydroxyl radicals. In contrast, doping with manganese oxide was found to substantially increase the rate of radical production.

Keywords- zinc oxide; nanoparticles; photocatalysis; mechanochemical synthesis

I. INTRODUCTION

Irradiation of zinc oxide (ZnO) with sufficiently energetic ultraviolet (UV) light results in the promotion of electrons to the conduction band and the consequent formation of holes in the valence band. Once created, these photogenerated charge carriers can migrate to the surface of the ZnO where they can undergo redox reactions with adsorbed molecules in a process known as heterogeneous photocatalysis [1].

The phenomenon of heterogeneous photocatalysis has attracted considerable interest as a technique for the destruction of intractable chemical waste. Experimental studies have shown that photocatalysis on ZnO nanoparticles can effectively mineralize hazardous organic compounds into CO₂, H₂O, and simple mineral acids. However, practical application of photocatalysis for this purpose has been limited by the low photonic efficiency of the process. The majority of photogenerated charge carriers undergo recombination rather than reacting with adsorbed molecules [2].

In applications as an optically transparent UV-shielding agent, such as topical sunscreens, the photocatalytic activity of nanoparticulate ZnO must be minimised so as to prevent the degradation of any organic compounds that are present. It has previously been demonstrated that photoinduced mineralization can lead to a reduction in the efficacy of UV-shielding agents [4].

The successful exploitation of nanoparticulate ZnO for use in various technological applications requires the development of techniques for controlling its photocatalytic activity. A key

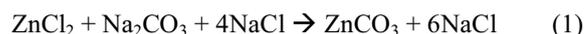
factor determining the activity of a photocatalyst is the rate of charge carrier recombination relative to that of interfacial charge transfer. A high rate of charge carrier recombination inevitably decreases the number of free electrons and holes that are available to react with adsorbed molecules and thereby generate free radicals.

Previous experimental studies have shown that doping can markedly affect the performance of photocatalysts by altering the dynamics of charge carrier recombination and interfacial charge transfer. In this study, we have investigated the effect of doping with cobalt and manganese oxide on the photocatalytic activity of nanoparticulate zinc oxide.

II. EXPERIMENTAL

A. Powder Synthesis

Aqueous suspensions of ZnO were manufactured by a three-stage process consisting of high-energy milling, heat-treatment, and washing. In the first stage of processing, mechanical milling was used to induce reaction between anhydrous chloride precursors and Na₂CO₃ in the presence of NaCl diluent, as given by (1):



Heat-treatment was then used to form the final oxide phases through thermal decomposition of the ZnCO₃. In the final stage of processing, washing with deionised water was used to remove the NaCl by-product. Doped ZnO powders were synthesised by the same overall method using reactant mixtures for which a given amount of the ZnCl₂ was substituted with either MnCl₂ or CoCl₂.

B. Characterisation Techniques

The chemical evolution of reactant mixtures during processing was followed by x-ray diffraction (XRD) using a Siemens D500 diffractometer with Cu-K_α radiation.

Specific surface area of the washed powders was measured by five-point BET gas adsorption using a Micromeritics Tristar instrument. All powders were vacuum degassed at 150°C for 1

hour prior to analysis. The specific surface area was used to derive estimates of the average particle diameter by $D = 6 / S\rho$, where D is the average particle diameter, S is the specific surface area, and ρ is the density.

Washed powders were examined by transmission electron microscopy (TEM) using a JEOL 2000FX microscope with a beam energy of 80 keV. Samples for TEM were prepared by ultrasonically dispersing a small quantity of the aqueous slurry in a 0.10wt.% solution of stearic acid in hexane and then evaporating a drop of this dispersion on a carbon coated specimen grid.

C. Photocatalytic Testing

Samples for photocatalytic testing were prepared by diluting the washed ZnO slurries down to a solids content of 0.04wt.% with Milli-Q water. Following dilution, the slurries were subjected to intense ultrasonication for 15 minutes in order to disperse the particles within the suspension. Immediately prior to measurement of the photocatalytic activity, 1 mL of a 25 mM solution of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) spin-trap was added to 10 mL of the powder suspension.

The photocatalytic activity of the washed ZnO powders was characterised by measuring the hydroxyl radical concentration as a function of irradiation time using the spin-trapping technique with electron paramagnetic resonance (EPR) spectroscopy [4]. Aqueous suspensions were irradiated with 300 nm light whilst within a quartz flat cell that was located in the cavity of the EPR spectrometer. Irradiation used a 1 kW Hg-Xe lamp with a monochromator to select the wavelength. The concentration of photogenerated hydroxyl radicals was measured as a function of time by recording the intensity of the first central line of the first derivative EPR spectrum of the DMPO-OH spin adduct.

III. RESULTS AND DISCUSSION

A. Powder Synthesis

Figure 1 shows the XRD pattern of $\text{ZnCl}_2 + \text{Na}_2\text{CO}_3 + 4\text{NaCl}$ following (a) milling for 6 hours, (b) heat-treatment at 400°C for 1 hour, and (c) washing. The pattern of the as-milled powder consists solely of diffraction peaks corresponding to nanocrystalline NaCl. The disappearance of all other diffraction peaks indicates that chemical reaction of the precursors occurred during milling and resulted in the formation of an amorphous or at least poorly crystalline ZnCO_3 product phase. Subsequent heat treatment resulted in a sharpening of the NaCl peaks and the appearance of new peaks corresponding to ZnO. Following washing only those peaks corresponding to ZnO remained, which indicates the successful removal of the NaCl by-product.

Figure 2 shows a representative bright field TEM image of a washed ZnO powder that was synthesized by mechanochemical processing. As shown, the powder consists of well dispersed single crystal particles with a reasonably narrow size distribution. The high degree of particle dispersion is a consequence of the synthesis technique. The nanoparticles of ZnO are formed simultaneously with an intervening salt

matrix. This salt matrix maintains the physical separation of the particles during processing, thus preventing the formation of agglomerates [5].

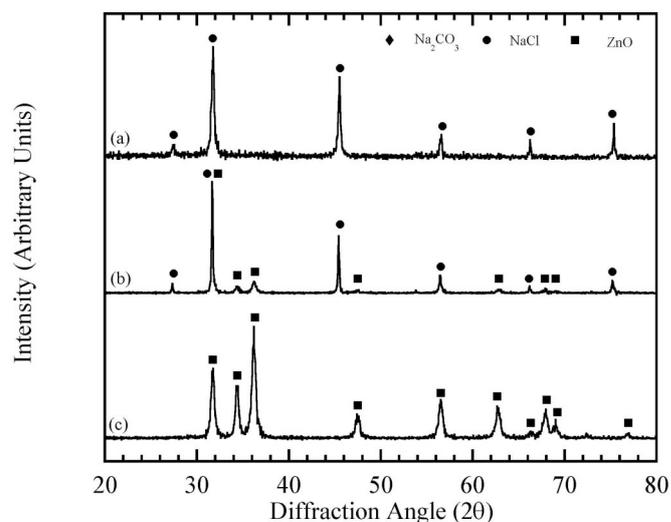


Figure 1. XRD pattern of $\text{ZnCl}_2 + \text{Na}_2\text{CO}_3 + 4\text{NaCl}$ following (a) milling for 6 hours, (b) heat treatment at 400°C for 1 hour, and (c) washing with deionised water.

The synthesis of Mn_2O_3 by mechanochemical reaction of $\text{MnCl}_2 + \text{Na}_2\text{CO}_3 + 4\text{NaCl}$ was found to exhibit a phase evolution during processing similar to that displayed by the ZnO synthesis system. Reaction of the precursors occurred during milling and resulted in the formation of a powder consisting of nanocrystalline MnCO_3 grains embedded within a matrix of NaCl. Subsequent heat-treatment and washing yielded an aqueous suspension of Mn_2O_3 .

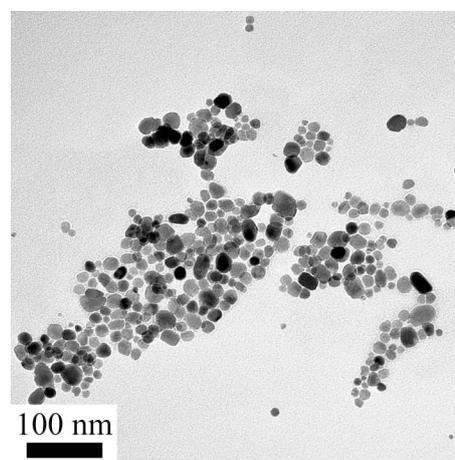


Figure 2. Bright field TEM image of a washed ZnO powder that was synthesized by mechanochemical processing.

The $\text{CoCl}_2 + \text{Na}_2\text{CO}_3 + 4\text{NaCl}$ system for the synthesis of Co_3O_4 was found to exhibit significantly different behaviour during processing. Rather than inducing chemical reaction, milling merely resulted in mixing and microstructural refinement of the starting reactant mixture. Chemical reaction

with the consequent formation of Co_3O_4 only occurred during post-milling heat treatment.

Nanoparticles of doped ZnO were successfully synthesised by combining the basic reactant mixture for the synthesis of ZnO with those of the corresponding dopant. For all dopant levels (1-5 mol.%), the combined reactant mixtures gave single phase ZnO solid solutions. The Co doped powders ranged in colour from pale to dark green depending on the dopant level, which is consistent with previous experimental observations of CoO-ZnO solid solutions [6]. The Mn-doped powders exhibited a characteristic brown colour [7].

As shown in Figure 3, the addition of dopants to ZnO was found to have a significant effect on the specific surface area of the powder. In the case of Mn-doping, the surface area increased monotonically with the dopant level up to approximately $64 \text{ m}^2/\text{g}$ for a doping level of 5 mol.%. For the Co-doped ZnO, the specific surface area was roughly constant at approximately $50 \text{ m}^2/\text{g}$.

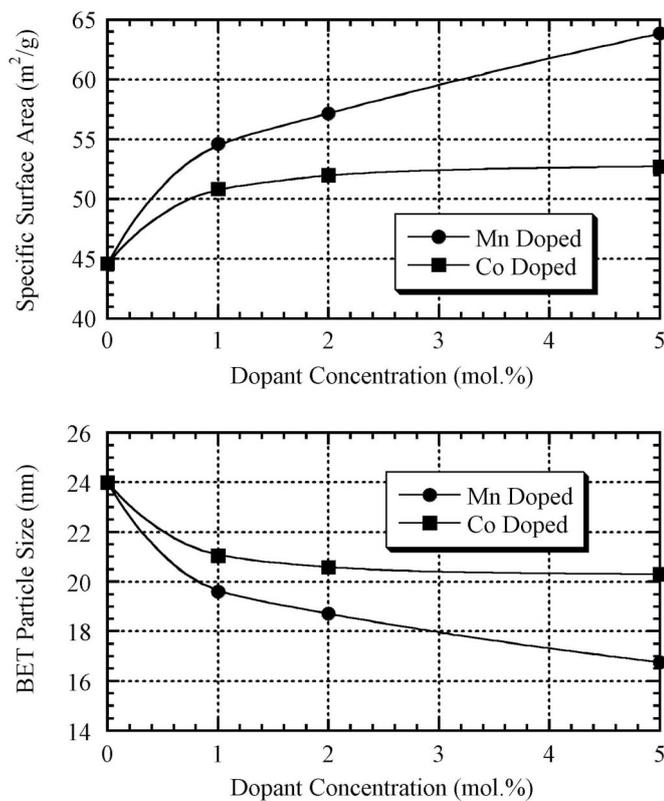


Figure 3. Specific surface area and equivalent particle diameter of the Mn and Co doped ZnO powders as a function of the dopant concentration.

B. Photocatalytic Activity

The absorption of sufficiently energetic UV light by particulate ZnO results in the formation of electron-hole pairs through a process of electronic excitation between the valence and conduction bands. Photogenerated charge carriers either undergo recombination, become trapped in metastable states, or migrate to the surface of the ZnO where they react with adsorbed molecules. In an air saturated aqueous environment, the photogenerated electrons and holes undergo reaction with

dissolved molecular oxygen, surface hydroxyl groups, and adsorbed water molecules to form hydroxyl ($\cdot\text{OH}$) and superoxide (O_2^-) radicals, as shown by (2) and (3):



The hydroxyl radical is generally accepted to be the active species that is responsible for the mineralization of organic pollutants [1]. The activity of a particulate photocatalyst in an aqueous environment can therefore be evaluated by measuring the hydroxyl radical production as a function of exposure time.

Figure 4 shows the concentration of the DMPO-OH spin-adduct as a function of irradiation for aqueous suspensions of Mn-doped ZnO powder. For given duration of irradiation, the doped powders gave a higher yield of hydroxyl radicals compared to the undoped ZnO, indicating an improvement in the photocatalytic activity. The activity was maximized for a dopant level of 2 mol.%. A further increase in the dopant concentration to 5 mol.% resulted in a drop in activity.

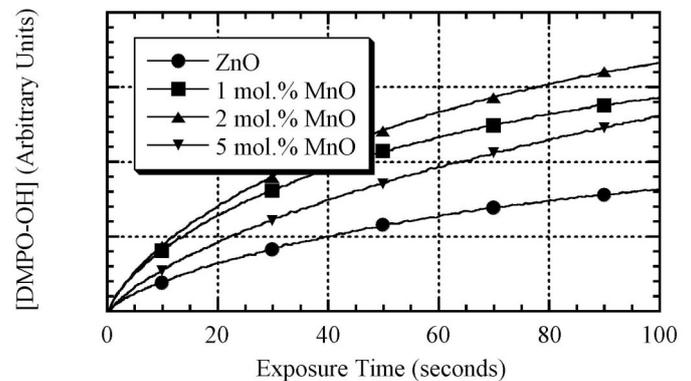


Figure 4. DMPO-OH concentration as a function of time for aqueous suspensions of Mn-doped ZnO.

The higher specific surface area of the doped powders compared to the undoped ZnO is contributing factor to the enhanced photocatalytic activity. A higher specific surface area would increase the number of active surface sites where the photogenerated charge carriers could undergo interfacial charge transfer.

The enhancement in photocatalytic activity arising from the addition of suitable dopants has been attributed to the formation of shallow trapping sites in the crystal lattice [9]. These sites are able to temporarily trap the photogenerated charge carriers thereby separating the arrival time of the electrons and holes at the surface of the photocatalyst. By separating the arrival time of electrons and holes, the probability of recombination is reduced and the charge carriers are more likely to undergo interfacial transfer and react with adsorbed molecules to generate free radicals.

The results obtained in this study show that there is an optimal Mn-doping level for which the photocatalytic activity

of ZnO is maximised. This is consistent with previous studies regarding the effect of doping. The existence of an optimal doping level has been attributed to the occurrence of multiple trapping at high doping levels, which reduces the apparent mobility of the photogenerated charge carriers and thereby renders recombination more likely [8].

Figure 5 shows the concentration of the DMPO-OH spin-adduct as a function of irradiation for aqueous suspensions of Co-doped ZnO powder. The addition of Co to ZnO resulted in a progressive decrease in the production of hydroxyl radicals, which indicates a decrease in photocatalytic activity.

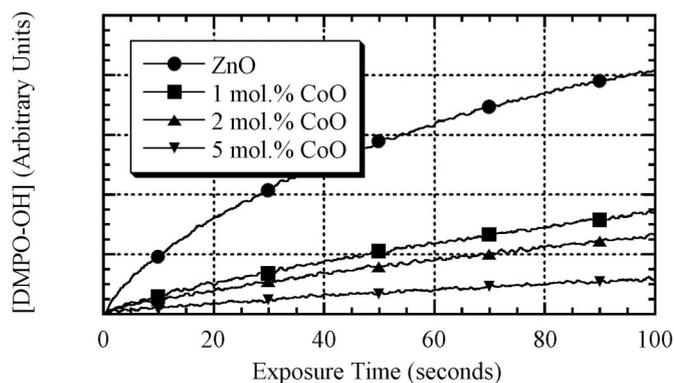


Figure 5. DMPO-OH concentration as a function of time for aqueous suspensions of Co-doped ZnO.

The reduction in photocatalytic activity arising from the incorporation of CoO can be attributed to the creation of deep trapping sites. A deeply trapped charge carrier will recombine with its counterpart generated by a subsequent photon so that the overall effect is to promote charge carrier recombination, thus reducing photocatalytic efficiency.

IV. SUMMARY AND CONCLUSIONS

Mechanochemical processing of anhydrous chloride precursors with Na_2CO_3 in the presence of NaCl has been used to manufacture powders of pure and doped ZnO nanoparticles. The photocatalytic activity of these powders was evaluated by measuring the hydroxyl radical production as a function of irradiation time using the spin-trapping technique with electron paramagnetic resonance spectroscopy. It was found that the photocatalytic activity of nanoparticulate ZnO can be substantially increased through doping with Mn. In contrast, doping with Co was found to suppress the photocatalytic activity of nanoparticulate ZnO.

The results obtained in this study demonstrate that the photocatalytic activity of nanoparticulate ZnO can be optimized for different applications through the addition of transition metal oxide dopants.

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