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Local structure and photocatalytic property of sol–gel synthesized ZnO doped with transition metal oxides

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Abstract ZnO nanoparticles doped with up to 5 at% of Co and Mn were prepared using a co-precipitation method. The location of dopant ions and the effect of doping on the photocatalytic activity were investigated. The crystal structure of nanoparticles and local atomic arrangements around dopant ions were analyzed by X-ray absorption spectroscopy. The results showed that the Co ions substituted the Zn ions in the ZnO wurtzite phase structure and induced lattice shrinkage, while Mn ions were not completely incorporated in the crystal lattice. The photocatalytic activity under simulated sunlight was characterized by the decomposition of Rhodamine B dye molecules. It was revealed that Co-doping strongly reduced the photocatalytic activity but Mn-doping showed a weaker effect on the reduction of the photoactivity.

Introduction

Zinc oxide is an important semiconducting material having a broad range of applications including transparent conductive oxides [1], ultraviolet (UV) light absorbers [2], and photocatalysts [3]. Since the band gap energy of bulk ZnO crystals is around 3.3 eV [4], UV rays with wavelength under 375 nm can be absorbed by ZnO and hence ZnO has

been regarded as an excellent UV shielding material with a broad UV absorption characteristics and photo-fastness compared with other organic and inorganic UV shielding materials.

The absorbed UV rays excite valence electrons onto the conduction band. When these photo-excited electrons and holes move to the particle surfaces where water and oxygen molecules reside, highly active free radicals such as superoxide (O_2^-) and hydroxyl ($\bullet OH$) are generated and undergo secondary reactions such as the decomposition of organic compounds [5]. This phenomenon called photocatalysis is useful for many applications, such as water-splitting, organic pollutant scavenging, and anti-fouling [6] and much effort was made to enhance the photocatalytic property of semiconductor nanoparticles [7–10]. However, the degradation of organic molecules by the photocatalysis, including color fading [11], textiles aging [12], and even DNA and RNA damage [13], has been raising industrial and academic concerns for the safe use of ZnO as effective UV shielding agents.

In order to decrease the photocatalytic activity, the generation of free radicals needs to be suppressed. In general, two approaches can be considered for the reduction of photocatalysis in semiconductor nanoparticles. The first approach is the surface coating on nanoparticles, which block the contact between excited electrons/holes and oxygen/water molecules [14]. This approach has drawbacks as more materials are required to form barrier layers around particles which often results in higher production costs of the UV screening agents. The second approach is impurity doping to create chemical and, in some cases, physical defects in the crystal lattice that would act as the trapping and recombination sites of the excitons [15].

In this study, transition metal atoms (Mn and Co) were introduced as impurities in ZnO crystallites to tailor the photocatalytic property. The ionic radii of Mn (0.066 nm)

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and Co (0.058 nm) are similar to that of Zn (0.060 nm) and hence crystal doping of Mn and Co into the Zn sites is expected [16]. They are also known to form deep energy levels within the bandgap, which may act as an efficient charge recombination sites [17, 18]. Different amounts of dopants, namely, 1, 2, 3, and 5 at% were introduced to sol-gel synthesized ZnO crystalline nanoparticles. The doping process was extensively studied from raw materials to final products. X-ray absorption near edge structure (XANES) analysis was used to identify the oxidation states of dopant atoms. The local atomic arrangements and coordination states of doping elements were characterized by extended X-ray absorption fine structure (EXAFS) analysis. The change in photocatalytic activity was analyzed via the decomposition of Rhodamine B (RhB) dye molecules under simulated sunlight in the presence of nanopowders.

Experimental

Sample preparation

Co-doped and Mn-doped ZnO was synthesized separately by using a sol-gel co-precipitation method to form doped zinc carbonate hydroxide and subsequent heat treatment to decompose zinc carbonate hydroxide into ZnO:

The raw materials were $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Aldrich >99.0%), NaOH pellets (Chem-Supply 97%), Na_2CO_3 (Aldrich >99.0%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Aldrich >98.0%), and $\text{Mn}(\text{CH}_3\text{COO})_2$ (Fluka, 98%), all of which were used without further purification. First, a mixed transparent solution-A of Zn^{2+} and dopant ions with a fixed atomic ratio (Dopant: Zn^{2+} = 1:99, 1:49, 1:32.3 and 1:19) was prepared in distilled water. At the same time, NaOH and Na_2CO_3 were also dissolved in distilled water to prepare another solution-B which would be used as a precipitant. Then, the solution-A was added into the solution-B drop-wise with continued magnetic stirring at the speed of 500 rpm. The precipitate was immediately formed during the mixing of the two solutions. After 1.5 h of aging, the slurries were washed with distilled water several times using a centrifuge at the speed of 7,000 rpm (Eppendorf centrifuge 5417R) until the salinity of the supernatant becomes less than 100 ppm. The washed powders were oven dried under 80 °C. Finally, the dried samples were heat-treated at 400 °C for 1 h to decompose doped Zn carbonate hydroxide into doped ZnO.

Powder characterization

The morphology of the synthesized particles was characterized by transmission electron microscopy (TEM) using a Philips CM-120 microscope with the beam energy of 120 kV. TEM specimen was prepared by evaporating a drop of the nanoparticle dispersion on a carbon-coated specimen grid.

The crystal phase of the as-prepared particles was characterized by X-ray powder diffraction (XRD) measurement using an X-ray diffractometer (Panalytical X'Pert PRO MRD) with Cu K α radiation at a step width of 0.02°. The operation voltage and current were set at 40 kV and 30 mA, respectively.

X-ray absorption spectroscopy (XAS) experiments were performed at the BL20B beamline (Australian National Beamline Facility) which was located in Photon Factory, Tsukuba, Japan. The samples were diluted with boron nitride to minimize the effects of self absorption and then filled in the $5 \times 10 \text{ mm}^2$ cells on the sample holder. The K-edge spectra of Zn, Mn, and Co elements were measured separately in a fluorescence mode. The Average program [19] was used to average raw data. The EXAFS data analysis was carried out using the Ifeffit software package [20].

Simultaneous thermogravimetric/differential scanning calorimetry (TG/DSC) measurements of undoped and doped zinc carbonate hydroxide were performed on a Netzsch STA 409 thermal analyzer to characterize the phase transformation during the heat treatment, using heating rates of 10 °C/min and nitrogen flowing rates of 100 mL/min. The pyrolysed samples were also diluted with distilled water to 0.01 g/L at pH = 7, which were used to measure the zeta potential using a Malvern Zetasizer Nano instrument. A Varian Cary 3E spectrophotometer was used to measure the absorption spectra of the washed ZnO and doped ZnO powders at the wavelength range of 200–800 nm. The actual doping levels in the powders were characterized using a Varian SPECTRAA-240 Atomic Absorption Spectroscopy instrument in the flame mode.

Photocatalysis test

The photocatalytic activity of the washed powders was measured by monitoring the degradation of RhB dye solution in the presence of the powder samples under simulated sunlight irradiated using an ATLAS Suntest equipment. For each measurement, 0.012 g of the powder sample was added into 100 mL of RhB aqueous solution having the concentration of 0.0096 g/L. The temperature of the solution was regulated to 37 °C and the simulated sunlight was irradiated up to 3 h. Three milliliters of the suspension was extracted every 30 min and then

centrifuged to separate the nanoparticles from the supernatant. UV–Vis absorbance spectra of the supernatant were measured with a Varian Cary 3E spectrophotometer. The intensity of the optical adsorption peak around 554 nm, which is a characteristic absorption band of RhB, was used to monitor the rate of dye degradation.

In order to assess the influence of powders' surface area on photocatalytic property, the specific surface area of the particles was analyzed by the Brunauer–Emmett–Teller (BET) gas absorption method using a Micromeritics Tristar 3000 system. The result was also used to normalize the degradation rate of RhB.

Results and discussion

Structural and optical properties of doped ZnO

The synthesized ZnO nanopowders showed different colors at different doping levels. For Co-doped samples, the color changed from pure white, light green to dark green as the Co composition increased from 0 to 5 at%, while the color changed from pure white, yellowish to dark brown as the Mn composition increased from 0 to 5 at%. Figure 1a shows a typical bright field TEM image of undoped ZnO. It is evident that the powder consisted of agglomerated nanoparticles with the sizes between 10 to 50 nm. The TEM images of 5 at% Co-doped ZnO and 5 at% Mn-doped ZnO (Fig. 1b, and c) showed similar particle sizes. It was observed that the undoped ZnO and other Co-doped and Mn-doped samples with different doping levels appeared nearly identical under TEM.

The XRD patterns of synthesized undoped ZnO, Mn oxides, Co oxides, Co-doped ZnO and Mn-doped ZnO were shown in Fig. 2. The XRD patterns of Mn oxides and Co oxides correspond to the JCPDS-ICDD index card No. 24-0734 (Mn_3O_4) and 42-1467 (Co_3O_4), respectively. For undoped and doped ZnO, only the wurtzite phase

Fig. 2 XRD patterns of undoped, Co-doped, and Mn-doped ZnO

corresponding to the standard crystallographic data in the JCPDS-ICDD index card No. 36-1451 was observed. No separated phase of dopants appeared was evident in the XRD pattern.

Figure 3 shows the correlation between the nominal and measured doping levels for Co- and Mn-dopings. The real doping levels were closer to the nominal values for Co than Mn. Moreover, the Co-doping levels had a better linear correlation between real and nominal values. Hereafter, we use nominal dopant levels to identify the samples in the text.

The UV–Vis transmittance spectra of undoped and doped ZnO are shown in Fig. 4. As shown in Fig. 4a and c, the increased doping level for both Co and Mn resulted in a

Fig. 1 Bright-field TEM images of undoped and doped ZnO nanoparticles: **a** pure ZnO, **b** 5 at% Co-doped, **c** 5 at% Mn-doped

Fig. 3 The correlation between nominal and real doping levels

decrease in optical transmittance in the visible light range, while retaining good absorption property in the UV-light range. The bandgap energy of the samples were calculated by extrapolating the linear portion of the plot $(\alpha h\nu)^2$ versus $h\nu$ to the $(\alpha h\nu)^2 = 0$ axis (Fig. 4b, d) [21, 22]. The estimated bandgap energy of Co-doped and Mn-doped ZnO at low doping levels (1–3 at%) were close or slightly larger than the value of pure ZnO (3.24 eV), while the bandgap energy of 5 at% Co-doped ZnO was lower than 3.24 eV. This red-shift in bandgap energy, which was also observed

by other groups [23, 24], is mainly caused by the *sp-d* exchange interactions between the band-electrons and the localized d-electrons of the Co^{2+} ions at Zn sites [25].

Location of dopants

XANES was carried out to investigate the location of the dopant ions within the Zn lattice. The possible locations of the dopant ions are: (1) the surface of the ZnO nanoparticles, (2) the Zn sites within the ZnO crystal lattice or (3) interstitial sites in the ZnO crystal lattice. Figure 5a shows the normalized Co K-edge XANES spectra of Co-doped ZnO, CoO, Co_3O_4 , and a tetrahedral (T_d) coordinated Co reference sample $[\text{Co}(\text{MeIm})_2]_n$ after the background was subtracted. The peak at “A” in Fig. 5a is usually referred to as a pre-edge peak and is assigned to a $1s \rightarrow 3d$ transition [26, 27]. The intensity of the peak A is reflective of the coordination environment; a tetrahedral cobalt compound will have higher intensity than an octahedral compound [28]. This effect can be seen in Fig. 5a, where the tetrahedral (T_d) reference had a substantially higher pre-edge peak than CoO in which Co is present in octahedral (O_h) sites. This correlation indicates that the majority of doped Co-ions in ZnO were present at the tetrahedral sites, indicative of Co substituting Zn in the ZnO crystal lattice.

XANES rising edge energy is indicative of oxidation states, which is also shown in Fig. 5a as the peak “B”. The rising edge energy positions of Co-doped ZnO samples

Fig. 4 UV–Vis transmittance spectra and estimation of band gap energies of undoped, Co-doped, and Mn-doped ZnO: **a** UV–Vis transmittance spectra of undoped and Co-doped ZnO, **b** estimation of band gap energies of undoped and Co-doped ZnO, **c** UV–Vis transmittance spectra of undoped and Mn-doped ZnO, **d** estimation of band gap energies of undoped and Mn-doped ZnO

Fig. 5 K-edge XANES spectra for Co-doped, Mn-doped ZnO, and reference samples: **a** Co-doped ZnO and reference samples at Co K-edge, **b** Mn-doped ZnO and reference manganese oxides samples at Mn K-edge

were similar to each other and to that of the T_d reference and CoO reference, indicating that the oxidation state of most of the Co ions in Co-doped ZnO systems were +2.

Figure 5b shows the Mn K-edge XANES spectra of Mn-doped ZnO, MnO, and Mn_3O_4 . A pre-edge peak A is observed in all spectra, which is characteristic of transition metal ions [26, 27]. In the series of Mn-doped ZnO samples, the positions of peaks/shoulders B and C did not shift when Mn-doping level increased. The peaks B and C of Mn-doped ZnO samples resemble in both energy and intensity to those of Mn_3O_4 that contains both Mn^{2+} and Mn^{3+} as well as Mn T_d and O_h sites [29, 30]. This result indicates that not all the Mn ions substituted Zn sites in ZnO crystal lattice.

In addition to the XANES data, the interpretation of EXAFS can also be used to elucidate the location of the Co ions. Figure 6 shows k^3 -weighted Co K-edge EXAFS and

Fig. 6 k^3 -weighted EXAFS oscillation functions; **a** Co K-edge for Co-doped ZnO, CoO, Co_3O_4 , and Zn K-edge for undoped ZnO, **b** Mn K-edge for Mn-doped ZnO, MnO, Mn_3O_4 , and Zn K-edge for undoped ZnO

Mn K-edge EXAFS compared with the Zn K-edge EXAFS for undoped ZnO.

In Fig. 6a, the shapes of EXAFS oscillation for Co-doped ZnO are nearly the same as that of undoped wurtzite phase ZnO but are quite different from those of CoO and Co_3O_4 . This result suggests that the local atomic arrangement around Co ions in doped ZnO was similar to that of Zn in undoped ZnO. The increased noise in the $Co_{0.01}Zn_{0.99}O$ spectrum at high k range is likely caused by self absorption phenomena [31].

On the other hand, in Fig. 6b, it is shown that the shape of Mn K-edge EXAFS $k^3\chi(k)$ oscillation for all the Mn-doped ZnO samples were significantly different from those of Zn K-edge ZnO, Mn K-edge MnO, and Mn_3O_4 . If only the low k area ($2\text{--}8\text{ \AA}^{-1}$) is considered, the EXAFS oscillations of Mn-doped ZnO showed similar trend with that of Mn_3O_4 , which suggests that the local atomic

Fig. 7 Fourier transforms of the EXAFS $k^3\chi(k)$ spectra: **a** Co K-edge radial distribution functions for Co-doped ZnO, CoO, Co₃O₄, and the Zn K-edge radial distribution function for undoped ZnO, **b** Mn K-edge radial distribution functions for Mn-doped ZnO samples, MnO, Mn₃O₄, and the Zn K-edge radial distribution function for undoped ZnO

arrangement around Mn ions in doped ZnO was similar to that of Mn in Mn₃O₄, which also correlates with the interpretation of XANES data, where the only difference between Mn₃O₄ and Mn-doped Zn could be attributed to self absorption phenomena.

The phase-corrected EXAFS $k^3\chi(k)$ spectra were then Fourier transformed into radial distribution functions in R space to show the coordination states. For example, in the Fourier transforms of Zn K-edge EXAFS of undoped ZnO, the first peak at 1.9 Å corresponds to the first coordination shell with four oxygen atoms. The second peak at 3.3 Å represents the second coordination sphere, consisting of 12 Zn atoms at the distance of 3.3 Å. In Fig. 7a, the radial distribution functions of Co-doped ZnO samples, CoO and Co₃O₄ around Co ions are compared with that of undoped

ZnO around Zn ions. The radial distribution functions of Co-doped ZnO samples around Co ions showed nearly identical peak positions with those of undoped ZnO around Zn ions, indicating that the majority of Co²⁺ ions substituted the Zn²⁺ position in the ZnO crystal lattice [28, 32], which supports the results of the XANES analysis described above.

In Fig. 7b, the radial distribution functions around Mn ions in Mn-doped ZnO, MnO, and Mn₃O₄ samples are compared with that of undoped ZnO around Zn ions. For Mn-doped ZnO, the radial distribution functions around Mn ions were quite different from those around Zn ions in undoped ZnO and Mn ions in MnO. When dopant levels increased to 5 at%, the second and third peaks gradually appeared at ~2.63 and ~3.41 Å, respectively, which were similar to the peak positions of Mn₃O₄. Therefore, the majority of Mn ions did not replace Zn ions in the wurtzite crystal structure [24]. This conclusion is consistent with a previous study by Erwin et al. [33] who found that the Mn²⁺ ion was difficult to substitute Zn²⁺ ions in wurtzite structure. The likely reason for the difficulty in Mn-doping is also attribute to the radii of the ions. The ionic radius of Mn is 0.066 nm, larger than Zn (0.060 nm) and Co (0.058 nm). Hence, the substitution of Zn sites with Co ions is expected to occur more commonly than with Mn ions.

Effects of doping processes on the location of dopants

The process to form Co and Mn-doped ZnO consisted of two steps, namely (i) sol–gel co-precipitation of doped zinc carbonate hydroxide and (ii) thermal decomposition of doped zinc carbonate hydroxide into doped ZnO. In order to elucidate the effect of the synthesis routes on the location of dopant ions, the local structure of dopants ions in the zinc carbonate hydroxide was also studied by EXAFS.

In Fig. 8, the radial distribution functions of Mn-doped, Co-doped, and undoped zinc carbonate hydroxide at Mn, Co, and Zn K-edges, respectively, are shown. The radial distribution function of Co-doped zinc carbonate hydroxide has the shape and peak positions similar to that of undoped zinc carbonate hydroxide, indicating that the majority of Co²⁺ ions substituted the Zn²⁺ position in the crystal lattice of zinc carbonate hydroxide at the co-precipitation stage. On the other hand, the radial distribution function of Mn-doped zinc carbonate hydroxide has the shape and peak positions different from that of undoped zinc carbonate hydroxide, suggesting that Mn²⁺ ions did not replace Zn²⁺ at the co-precipitation stage. Hence, the state of crystal doping before thermal decomposition appears to influence the successful replacement of Zn²⁺ ions with dopants in ZnO.

Further pyrolysis analysis of as-prepared manganese carbonate hydroxide, cobalt carbonate hydroxide, zinc

Fig. 8 Fourier transforms of the EXAFS spectra of zinc carbonate hydroxide, Co-doped zinc carbonate hydroxide, and Mn-doped zinc carbonate hydroxide

Fig. 9 TG curves of as-prepared manganese carbonate hydroxide, cobalt carbonate hydroxide, zinc carbonate hydroxide, Co-doped zinc carbonate hydroxide, and Mn-doped zinc carbonate hydroxide

carbonate hydroxide, Co-doped zinc carbonate hydroxide, and Mn-doped zinc carbonate hydroxide was shown in Fig. 9 which reveals the decomposition temperature of those compounds. For the as-prepared manganese carbonate hydroxide, cobalt carbonate hydroxide, and zinc carbonate hydroxide, the decomposition temperature decreased gradually from 320, 260 to 225 °C. For the as-prepared Co-doped zinc carbonate hydroxide, the thermal decomposition occurred between 225 and 300 °C and no separated decomposition stage was observed, indicating a uniform decomposition process. For the as-prepared Mn-doped zinc carbonate hydroxide, two decomposition stages were observed. The first stage at around 260 °C

Fig. 10 Zeta potential of undoped ZnO, Co-doped ZnO, Mn-doped ZnO, Co_3O_4 , and Mn_3O_4

represents the decomposition of zinc carbonate hydroxide with major mass loss. A slight mass loss appeared at around 350 °C. The data suggest that inhomogeneous doping occurred during the precipitation process which has led to the formation of inhomogeneous phases after thermal decomposition, possibly consisting of undoped ZnO and Mn_3O_4 .

Furthermore, the results of zeta potential measurements in Fig. 10 provide another clue for the location of dopants. The zeta potential of as-synthesized Mn_3O_4 and Co_3O_4 by pyrolysis were -34.8 and $+29.8$ eV, respectively. However, the zeta potential of 5 at% Co-doped ZnO was $+16.4$ eV which is very close to the value of undoped ZnO ($+15.9$ eV) while the zeta potential of 5 at% Mn-doped ZnO was only $+7.98$ eV. The lower zeta potential of Mn-doped ZnO may be caused by the negative zeta potential of Mn_3O_4 that were precipitated on the particle surface, suggesting the possibility of Mn dopants concentrated on the particle surfaces (i.e., surface doping).

Photocatalytic activity

Figure 11 shows the doping effects on the BET specific surface area. The value of specific surface area does not differ much among the samples. For Co-doped ZnO, the surface area showed a general descending trend as the dopant level increased. For Mn-doped ZnO, it increased with dopant level.

Figure 12a and b show the relative change in the intensity of the optical absorption peak of RhB as a function of irradiation time. In the y axis, C is the absorbance value of RhB at each irradiation time interval at the wavelength of 554 nm and C_0 is the absorbance value before the irradiation when the adsorption and desorption equilibrium was achieved. The data was normalized using the BET specific surface area of each sample. It is evident that the photo-induced degradation of RhB was

significantly slower in the presence of doped ZnO than undoped ZnO. Higher doping levels resulted in stronger reduction of RhB decomposition for both Co-doped ZnO and Mn-doped ZnO. Figure 12c also shows the calculated RhB degradation rate assuming the first-order kinetics [14, 34]. The doping level of 1 at% induced a significant decrease in the photo-degradation rate, down to 24.3% of the original value for Co-doped ZnO and down to 66.6% for Mn-doped ZnO. When doping level was increased to 5

at%, the photo-degradation rate decreased to 8.6% for Co-doped ZnO and to 33.3% for Mn-doped ZnO.

The mechanism of decreased photocatalytic activity by successful lattice doping of Co in ZnO is considered to be not by creating physical defects but mainly by introducing deep band gap energy levels between the valence and conduction bands that would act as efficient recombination centers for photo-generated excitons [18, 35]. The recombination of electrons and holes inside the particles will give the charge carriers less chance to generate $\cdot\text{OH}$ and O_2^- free radicals on particle surfaces [36]. As for the case of Mn-doped ZnO, the cause of the reduction in photocatalytic property may be attributed to the physical defects and increased oxidation state of Mn ions, which may act as trapping sites for photo-generated charges and promote the recombination of electron and holes and decrease the chance to generate $\cdot\text{OH}$ and O_2^- free radicals on particle surfaces [37, 38].

Conclusion

In this study, a sol-gel co-precipitation method and subsequent heat treatment were used to synthesize ZnO nanopowders that are Co-doped and Mn-doped up to 5 at%. Synchrotron X-ray absorption spectra and zeta potential measurements were used to investigate the locations of dopant ions in the nanopowders. It was shown that Co ions

Fig. 11 BET specific surface areas of undoped, Co-doped and Mn-doped ZnO

Fig. 12 Relative change in the intensity of the optical absorption peak at 554 nm of RhB as a function of irradiation time: **a** with Co-doped ZnO, **b** with Mn-doped ZnO, **c** RhB degradation rate calculated assuming first-order kinetics

successfully replaced the Zn ions in the ZnO crystal lattice which may have created deep bandgap energy levels for the recombination of photo-generated electrons and holes. It was demonstrated that 5 at% Co-doping can effectively decrease the photocatalytic activity of ZnO down to <10% of the original reaction rate. Mn ions failed to substitute Zn ions in the ZnO crystal lattice and the majority of Mn may have precipitated on the particle surfaces. Nevertheless, the photocatalytic activity was also reduced by Mn-surface-doping with less efficacy than Co-lattice-doping.

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