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Photocatalytic activity of cobalt-doped zinc oxide thin film prepared using the spray coating technique

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Abstract

We report on the synthesis, characterization and photocatalytic activity of ZnO: Co thin films coated onto amorphous glass substrates by sol–gel spray coating technique. Structural and optical properties of the films were evaluated using x-ray diffractometer (XRD) and uv–vis spectrophotometer (UV–Vis), respectively. XRD patterns showed that the samples exhibited hexagonal wurtzite structure. The addition of cobalt reduced the (0 0 2) peak. This doping also reduces transparency and optical band gap. The band gap (E_g) markedly decreased from 3.20 eV to 3.00 eV for undoped ZnO and ZnO: Co with 10 mol% of doping concentration, respectively. Our thin films exhibited good structural, optical and photo cataytic properties. In this study, ZnO with 4 mol% of Co was observed to have the highest photocatalytic activity with methylene blue (MB) degradation of about 76.31% for 2 h under UV irradiation.

1. Introduction

ZnO is a direct wide band gap (3.2 eV at room temperature) II–IV compound semiconductor which has been used in many applications. ZnO is preferred due to its abundance, low cost, and environmentally friendly nature. ZnO can be used for diodes [1], optoelectronics [2], biosensors [3] gas sensors [4], transparent conductive oxide [5], anti-bacterial agents [6] and photo catalysts [7]. Metal ions doping such as Ag^+, Al^{3+}, and Co^+ have been applied to improve structural, optical and photocatalytic properties of ZnO. Co metal ion is preferred because its ionic radius (0.58 Å) matches that of Zn (0.60 Å) and hence, a significant red-shift can be obtained [8, 9]. There are many methods to synthesis ZnO: Co thin films such as sol–gel [10], RF magnetron sputtering [11], ultrasonic spray method [12, 13], sol–gel spin coating [14] spray pyrolysis [15, 16], and pulsed laser deposition [17]. Petkova *et al* studied the effect of Cobalt ion on ZnO thin films prepared by spray deposition. The suggested optical properties and band gap were influenced by Co^{2+} and Cr^{2+} in the ZnO thin films. This study is interesting in the field of photo catalysis since optical properties and band gap both play important roles [18].

In our reseach, we focused ourselves on the preparation of undoped ZnO and ZnO:Co thin films using the spray coating technique. Effects of Co doping concentration on structural and optical properties were evaluated using XRD and UV–vis spectrophotometer. We also evaluated the photocatalytic activity of all prepared samples using MB under solar radiation.

2. Materials and method

Undoped ZnO and ZnO:Co thin films were synthesized using the spray coating technique. Procedures for precursor preparation and schematic diagram of spray coating technique can be seen in figures 1 and 2, respectively. Zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was dissolved into isopropanol ($(CH_3)_2CHOH$) with a concentration of 0.5 M and stirred at room temperature for 30 min. Some drops of monoethanolamine (MEA) were added into the solution to make ZnO precursor clear. Cobalt nitrate hexahidrate ($(Co(NO_3)_2 \cdot 6H_2O$ was added into the solution as a cobalt source for ZnO:Co precursor with molar percentages of 0%, 2%, 4%, 6%, 8% and 10% which are denoted

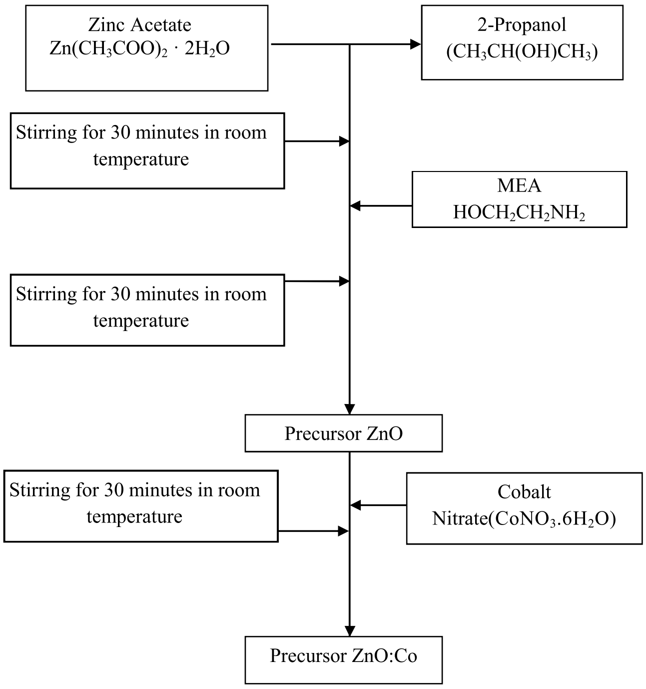

Figure 1. Flowchart of precursors ZnO and ZnO:Co preparation.

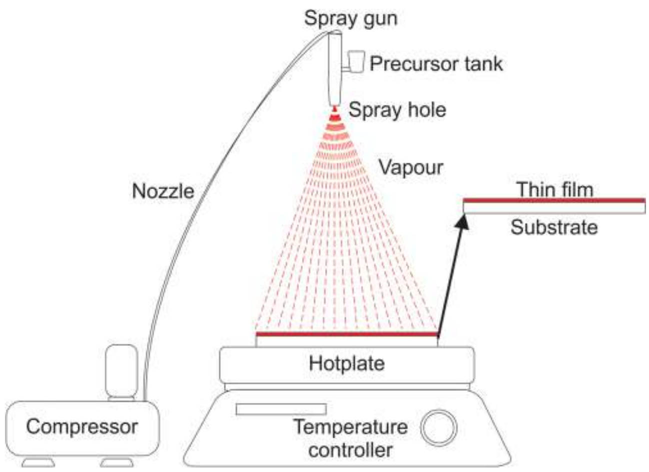

Figure 2. Schematics of the spray coating technique.

as ZnO, ZC2, ZC4, ZC6, ZC8, and ZC10, respectively. Deposition process on amorphous glass substrates was conducted at 450 °C hotplate temperature. Prior to deposition, the glass substrates were cleaned using acetone, methanol and distilled water.

Obtained thin films were then characterized using XRD and UV–vis spectrophotometer to evaluate their structural and optical properties, respectively. Shimadzu 6100/7000 XRD was used with angles that range from 0.02° to 2θ, and from 20° to 60°. Transmittance and absorbance spectra were obtained from Shimadzu UV–vis which records waves in the range of 300–800 nm. The photocatalytic test was conducted under solar radiation using methylene blue (MB) as pollutant for the samples. MB solution was made by adding MB powder into water with a concentration of 10 mg l^{-1}. Each prepared sample was placed into a 50 ml of MB solution. After 2 h of solar irradiation, MB solution of each sample was taken to measure its optical absorbance using UV–vis. The initial absorbance of MB (C_0) and final absorbance of MB (C_t) were measured to calculate the photocatalytic efficiency using equation (1).

$$\%\text{Degradation} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\% \quad (1)$$

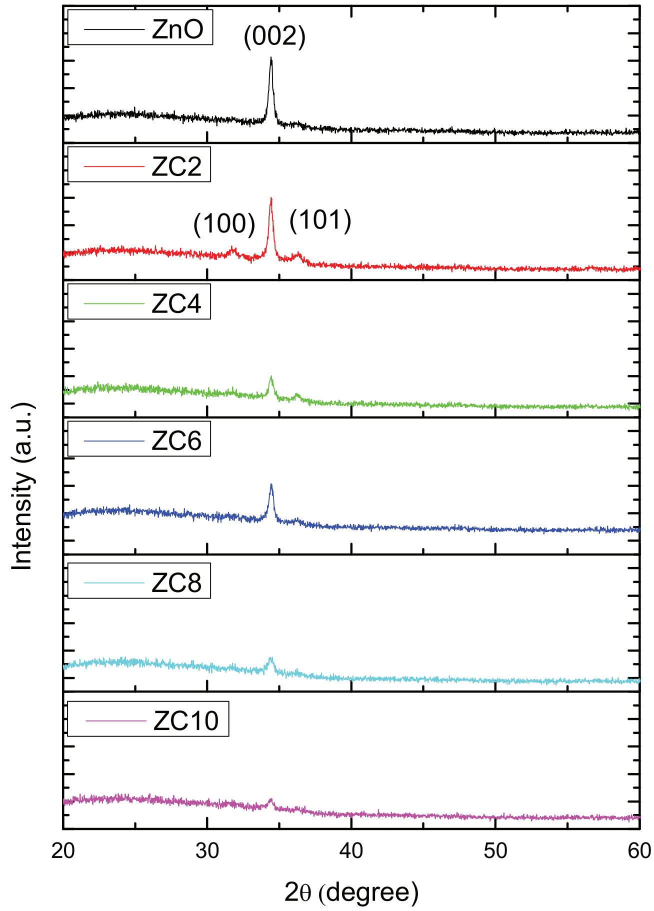

Figure 3. XRD pattern of as-synthesized ZnO:Co thin films.

Table 1. Angle shift, FWHM and band gap energy of as-synthesized thin films.

Samples	2θ at (0 0 2)	FWHM (deg.)	E_g (eV)
ZnO	34.419 31	0.341 79	3.20
ZC2	34.413 66	0.362 13	3.16
ZC4	34.425 22	0.382 12	3.12
ZC6	34.434 41	0.389 70	3.14
ZC8	34.391 48	0.467 04	3.07
ZC10	34.378 08	0.384 25	3.00

3. Results and discussion

3.1. Crystal structure

The crystal structure and preferred orientation of obtained undoped ZnO and ZnO:Co thin films were analyzed the XRD method and are shown in figure 3. All peaks are confirmed as hexagonal quartzite structure (JCPDS No. 36-1451, Zincite phase) and there is no peak related cobalt or other phases that can be detected. These results indicated that Co ions have successfully occupied the lattice site of ZnO rather than the interstitial ones [10]. We can see that (0 0 2) plane is the highest peak for all samples and becomes shorter with increasing Co content. Decrease in peak intensity and increase in full width at half maximum (FWHM) confirm reduced crystallinity of ZnO:Co thin films compared to undoped ZnO thin film.

The FWHM and angle shift from (0 0 2) plane can be deduced and is presented table 1. Cobalt metal contributes to degradation of crystallite size due to incorporation of Co into ZnO lattice [14]. We also noted that the angle of (0 0 2) plane slightly shifted to higher angle for ZC2, ZC4, and ZC6 and back to lower angle for ZC8 and ZC10. These changes are thanks to the small difference of ionic radii between Co^{2+} (0.58 Å) and Zn^{2+} (0.60 Å) [19]. Zinc ions might be replaced by cobalt ions and cause crystal defects that slightly change the angle of (0 0 2) plane to higher and lower angles. Results in this research are very much similar to those obtained by Caglar, in which deposition of ZnO:Co (~5%) thin film was carried out using the spin coating method at 3000 rpm for 30 s with 10× repetitions, after which, the resulting film was sintered at 650 °C for 1 h [10]. Results of XRD test show that

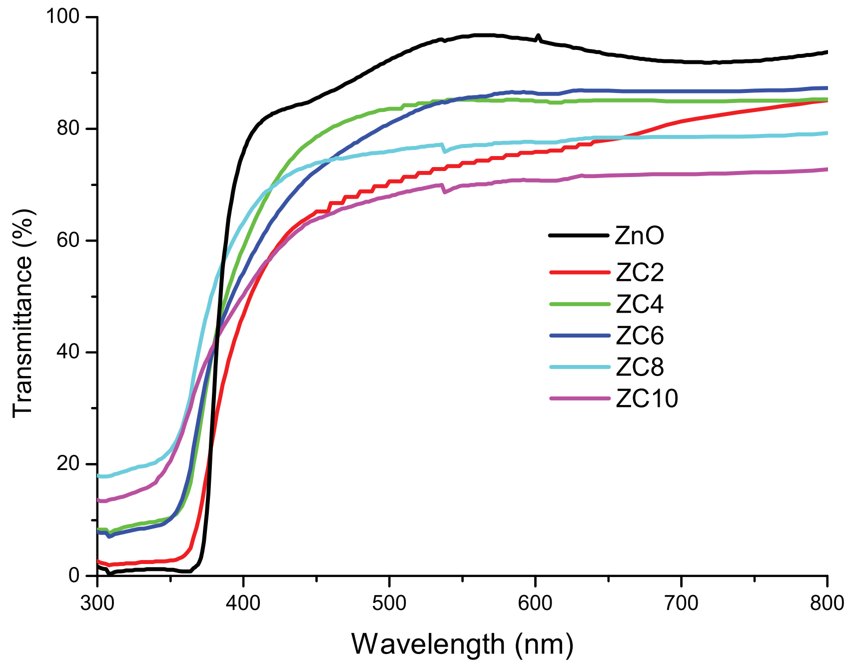

Figure 4. Transmittance spectra of undoped ZnO and ZnO:Co thin films.

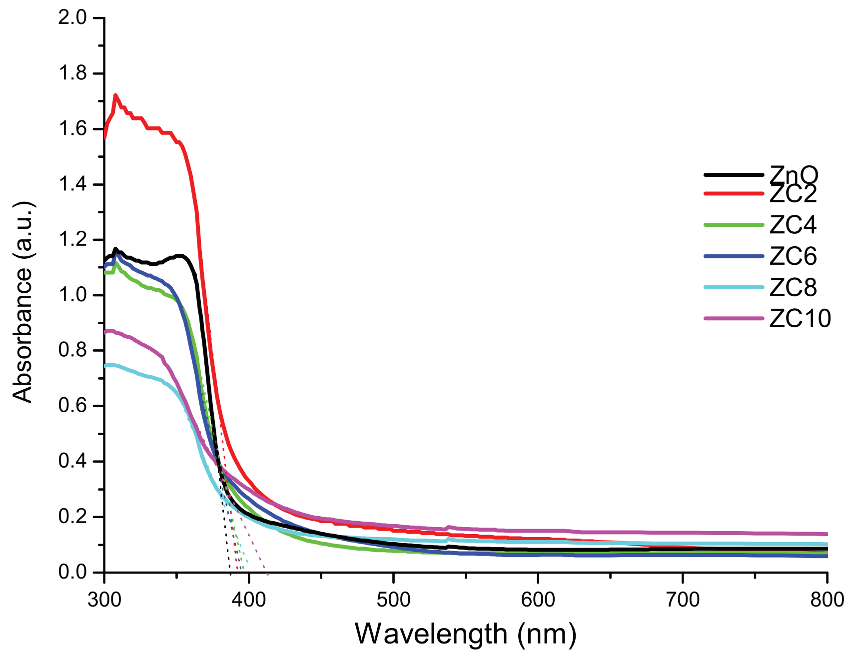

Figure 5. Absorbance spectra of undoped ZnO and ZnO:Co thin films.

the thin film has main diffraction peak of (0 0 2), with the other diffractions at (1 0 0) at (1 0v1). The addition of Co also lowers crystal quality as Co occupies the top spot of Zn lattice. It is not due to insertion of Co ion into the lattice between Zn and O. Poongodi *et al*, 2015 also reported that Co atom addition for ZnO:Co deposition using the spin coating method resulted in lower crystal quality as it yields new diffractions planes of (1 0 2), (1 1 0), (1 0 3) and (1 1 2). Other than that, he also found that Co addition increases lattice strain [10].

3.2. Optical properties

Figure 4 shows optical transmittance spectra of all prepared thin films deposited on glass substrates. Undoped ZnO has higher transparency than the other films at about 80%–90% in the visible light region. The higher Co doping concentration, the lower the transparency of ZnO:Co thin films within the visible light region. We can conclude that the addition of Co reduces the transparency of thin films. It might be caused by defects in ZnO lattice as confirmed with our XRD results.

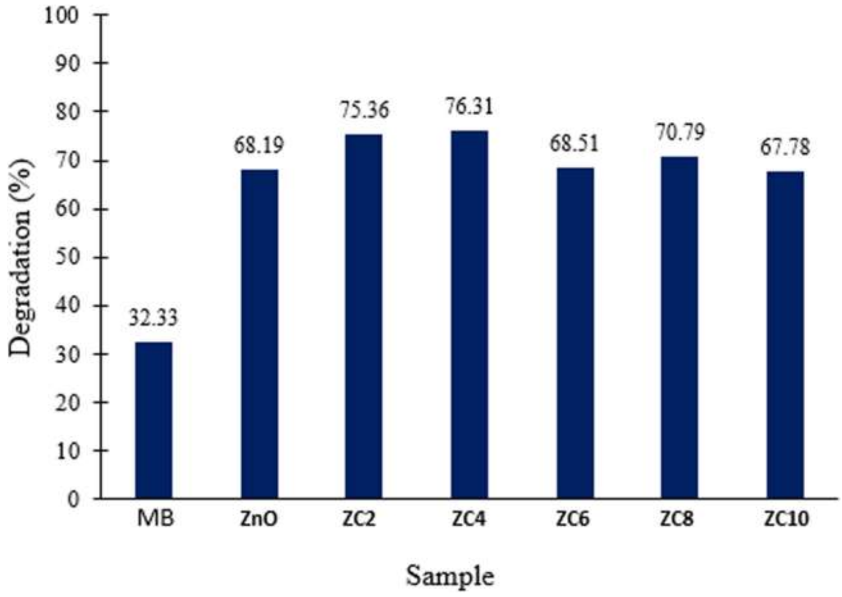

Figure 6. Photocatalytic degradation of MB under UV irradiation for 2 h.

Figure 5 shows the absorbance spectra of all prepared samples. The band edge of ZnO:Co thin films slightly shifted to lower wavelength (red shift). Optical band gap (E_g) in eV of thin films can be estimated directly from absorbance spectra using the following equation,

$$E_g = \frac{hc}{\lambda} = \frac{1240}{\lambda} \tag{3}$$

Where h is Planck constant $= 6.626 \times 10^{-34}$ J s, c is speed of light $= 2.998 \times 10^{8}$ ms^{-1}, and λ is cut-off wavelength in nm [14, 20]. Values of optical band gaps can be seen in table 1 and they decrease with increase of Co doping concentration to 3.20 eV and 3.00 eV, for undoped ZnO and Co doped ZnO 10%, respectively. Results in this research are very much similar to those of Poongadi *et al* and Kao *et al* which showed that adding Co concentration on ZnO lowers the value of energy band gap [19, 20]. This change in energy band gap is due to the red shift mechanism, which means that when Co ions replaces Zn in a ZnO lattice, the result is narrower energy band gap because of interaction exchanges among sp-d electrons in the conduction band at Zn orbital, and d electrons in the Co orbital [21]. These results differ from that of Caglar, which showed that addition Co concentration caused changes in energy band gap, due to the blue shift phenomenon [10]. This result indicated that the Co doped ZnO can be more useful for photocatalytic application, since low band gap semiconductor is expected to absorb solar energy efficiently [14].

3.3. Photocatalytic activity

The photocatalytic activity of all prepared samples is displayed in figure 6. MB photo degradation without any catalyst has the lowest percentage of about 32.33%. Cobalt doping obviously enhanced the photo degradation after 2 h of UV irradiation. The highest percentage is obtained by ZC4 at about 76.31%. Higher doping concentration reduces photocatalytic performance. It proved that 4 mol% of Co is the best amount to improve the photocatalytic activity of ZnO. In the previous study, Co ions contributed to increase oxygen vacancy and crystal defects [22]. These two important parameters are important to enhance the photocatalytic activity of ZnO. Our results are similar to the other study that showed higher MB degradation about 88% for ZnO:Co (3%) sample prepared by spin coating method [23]. Another factor that plays significant role in photocatalytic degradation is the value of band gap energy of ZnO:Co film. Smaller band gap energy will increase the absorption of light.

4. Conclusion

Undoped ZnO and ZnO:Co thin films have been successfully deposited onto glass substrates using the spray coating technique. XRD results indicated that all films were hexagonal wurtzite with a strong peak of (0 0 2) plane. The peak angle shifted to higher angles for ZC2, ZC4, ZC6 and shifted back to lower angles for ZC8 and ZC10 due to small differences in ionic radii between Co^{2+} and Zn^{2+}. Crystallinity decreased with the increase of Co dopant content. The increase affects transmittance and absorbance spectra. Transparency of films decreased and band edge of films slightly shifted to higher wavelength (red shift). The optical band gap of thin films decreased with the increase of Co concentration to 3.02 eV and 3.00 eV for undoped ZnO and ZC10, respectively. ZC4 is the best sample for photocatalytic degradation of MB under UV light irradiation.

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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