Structural and optical properties of Fe-doped ZnO thin films prepared by Sol–Gel spin coating process and their photocatalytic activities

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Abstract

Pure and Fe-doped zinc oxide nanocrystalline films were prepared via a sol–gel method using spin coating process. Pure and Fe-doped zinc oxide, containing 2 to 8% Fe, were annealed at 500°C for 2 h. The thin films were prepared and characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), field emission scanning electron microscopy (FE-SEM) and UV-visible spectroscopy. The XRD results showed that ZnO has hexagonal wurtzite structure and the Fe ions were well incorporated into the ZnO structure. As the Fe level increased from 2 wt% to 8 wt%, the crystallite size reduced in comparison with the pure ZnO. The transmittance spectra were then recorded at wavelengths ranging from 300 nm to 1000 nm. The optical band gap energy of spin-coated films also decreased as Fe doping concentration increased. In particular, their optical band gap energies were 3.75, 3.6, 3.5, 3.45 and 3.3 eV doping concentration of 0%, 2%, 4%, 6% and 8% Fe, respectively. The performance of the pure and doped ZnO thin films was examined for the photocatalytic activity using organic dyes (methyl orange, methyl blue, methyl violet). The samples ZnO with concentration of Fe showed increased photocatalytic activity with an optimal maximum performance at 0.8 wt%.

Key words

Zinc oxide thin films spin coating, photocatalytic activities.

Article info

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Introduction

Zinc oxide (ZnO) is a semiconductor compound of the II-VI family, with wide and direct band gap of (3.37 eV) [1] and large exciton binding energy (60 meV) at room temperature in the ultraviolet (UV) range abundant in nature, nontoxic and environmental friendly photocatalyst [2]. It has high catalytic efficiency with low cost, so that is one of the most widely used photocatalysts. [Because the intrinsic defects prevailing in materials, has effective in modulating the activity of the photocatalyst [3]. For example, some authors examined that introduction of surface oxygen vacancies in ZnO was an effective way to produce visible response and enhance photocatalytic activity [4-6]. Many process such as dopant, higher temperature annealed [4, 7] were used to make defects and then improve the photocatalytic activity. It is usually agreeable that surface defects are useful to the photocatalytic activity [8]. In addition, zinc oxide has high defect and many forms of defects occur in ZnO thin films such as oxygen vacancy and zinc vacancy [9]. At first the crystallite size of ZnO nanocrystalline is decide the properties of ZnO. Where, the presence of the defects can it altered structure properties of ZnO [10]. The ZnO photocatalyst thin films must be absorb not only ultraviolet radiation but also visible light, to achieve better photocatalytic efficiency in many applications [11]. To absorb visible light of solar spectrum, the energy band gap should be decreased by doping [12]. Many methods, such as hydrothermal method [13], sol-gel method [14], plasma-enhanced chemical vapor deposition (PECVD) [15], rf-magnetron sputtering [16], electro spinning [17] and so on are used to produce ZnO or doped ZnO thin films [18]. Among these techniques, the sol–gel method is attractive because of its simplicity, capability to produce good-quality films at a large scale, lower crystallization temperature, safe operation, low cost of equipment, and easy adjusting composition and dopants.

In this study, Fe:ZnO thin films were deposited and characterized through sol–gel spin coating. The photocatalytic activities of these films were also evaluated as a function of doping concentration and enhanced.

Experimental

1. ZnO preparation

Twenty five ml of methanol was mixed with 25 ml isopropanol (IPA), a 1.0975 g of zinc acetate was added to prepare 0.1M of ZnO seed solutions. The mixtures were vigorously stirred at 60 °C for 1 h. Subsequently, monooethanolamine (MEA) was added drop wise to the solution under constant stirring at 60 °C for 12 h, which was used as a stabilizer. Different molar concentration (2 %, 4 %, 6 %, and 8 %) of ferric nitrate as dopant was dissolved in the ZnO sol after the reagent was thoroughly
mixed. The solution was aged at room temperature for 24 h prior to the deposition process, where a transparent and homogenous solution was obtained. ZnO gel was deposited on the glass substrate by using spin coating method. Then, the films were dried at 150 °C for twenty min and annealed at 500 °C for 2 h.

2. Characterization of nanocrystalline ZnO Fe-doped films

The crystal structure of ZnO films was analyzed using X-ray diffraction (XRD) system (Shimadzu X-ray diffraction) with CuKα1 radiation at λ=1.54 Å. From Scherrer–Debye formula, was calculated the average crystallite size [19]

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \text{ (nm)} \]  

(1)

where k = 0.94, λ =1.54060 Å, \( \beta \) = Full Width Half Maximum (FWHM) and \( \theta \) = Diffracting angle.

Also was calculated the micro-strain from the relation [20]:

\[ \varepsilon = \frac{|a_{	ext{CPD}} - a_{	ext{XRD}}|}{a_{	ext{CPD}}} \times 100\% \]  

(2)

Film thickness was measured by interferometry Fizeau using a He–Ne laser (0.632 μm). The morphologies of the resulting films were characterized by atomic force microscopy (AFM) (CSPM-5000) and scanning electron microscopy (SEM) (VEGA TE Scan). The optical transmittance and absorbance measurement were performed with UV/Vis spectrophotometer (UV-1800 Shimadzu) with double beam at a wavelength range from 300–1000 nm.

3. Photocatalytic degradation of organic dyes

The photocatalytic activity of pure and Fe-doped ZnO samples was determined from the degradation of methyl orange (MO), methyl blue (MB) and methyl violet (MV) were chosen as the target compounds during its catalytic decomposition. The MO, MB and MV are organic water soluble dyes found in waste waters and are potentially toxic.

Photocatalytic experiments were carried out in reactor of a static cylindric flask of 500 mL, coated by aluminum foil. The photodegradation reactor was equipped with two lamps TUV 6W G6 T8 quartz lamps, placed lamps on reactor. Each of the two lamps emitted a broad range of UV light, of \( \lambda_{\text{max}} = 254 \text{ nm} \).

Was measured value initial concentration of (MO), (MB) and (MV) before irradiation and then measure concentration of (MO), (MB) and (MV) at each interval of time after irradiation. The pure and Fe-doped ZnO coated slides were immersed in the dyes solution, and stirring under a magnetic stirrer. The samples were exposed to illumination up to 60 minutes for each sample in the dyes solution, the reaction was maintained at room temperature. Period the pure and Fe-doped ZnO thin films were irradiated with two lamps 6W (UV) light source with central wavelength emission at 254 nm. Furthermore, in each typical catalytic run, the dyes solution of catalyst free was illuminated under the same reaction conditions and was used as a control. No significant decrease in dyes concentration observed after UV light exposure in the absence of catalyst. This indicates that the photochemical degradation was negligible under UV-A irradiation with low energy. The absorbance of (MO), (MB) and (MV) solutions was supervised at periods of 15 min and monitored photocatalytic degradation of methyl orange (MO), methyl blue (MB) and methyl violet (MV) using UV–Vis spectrophotometer (UV-1800 Shimadzu) with double beam at a wavelength range from 300–1000 nm. After 60 min of irradiation, the
absorbance is registered at $\lambda_{\text{max}}$ that is 460 nm for methyl orange (MO), 660 nm for methyl blue (MB) and 560 nm for methyl violet (MV) respectively. The concentration of the dyes solutions were 100 mg/L.

**Results and discussion**

1. **XRD analysis**

The X-ray diffraction analysis for thin films of zinc oxide in various Fe-doping levels, namely 0, 2, 4, 6 and 8 wt. %, are shown in Fig. 1. All thin films are polycrystalline, with hexagonal wurtzite ZnO structure, and the peak positions of the films were found to be in good agreement with the established standards (JCPDS No. 36-1451). An XRD patterns was achieved to study the orientation and crystal quality of the deposited pure and ZnO with different doping concentrations thin films (Fig. 1). Based on Fig. 1, the crystal growth orientation of pure and Fe doped with 2 % thin film has preferential growth along (101) and (100) planes, followed by (002), (110), (103), (102) and (112). It was observed that, by increasing the Fe doping concentration, the intensity of all diffraction peaks occurs in general. An addition to, the intensity of all the diffraction peaks was found decreasing with increasing Fe doping concentration. This caused by the formation of the stresses resulting from the effects of disorders or defects created by the Fe ions in the ZnO lattice structure [21], or because the kinetics of crystal growth has effected by chemical reactivity of the dopant [22], due to the low chemical reactivity of the iron in the zinc oxide lattice compared to the zinc, adding iron into ZnO lattice decreased the crystal growth speed and hence the crystallite sizes. This result is matches with the results of other authors, Mahmoudi et al. [21], ZnO nanoparticles doped with Fe were prepared by sol-gel method using Fe(NO$_3$)$_3$.9H$_2$O as the dopant and X-ray diffraction results exhibited that the higher concentration of Fe doping give rise weakening of crystalline which is identical to our experimental result. Wang et al. [23] were deposited ZnO doped with Fe on glass and Silicon substrates by using magnetron sputtering method, XRD results exhibited that the FWHM increased and the intensity of diffraction peak decreased with increasing iron doping content, showing that the crystalline quality of ZnO thin film decrease gradually. However, the results are very various for other authors with other growth techniques and dopant sources Salaken et al. [24].

![Fig. 1: XRD pattern of ZnO thin films for different doping concentrations of Fe.](image-url)
2. Effect of iron doping on crystallite size
The crystallite size of ZnO thin films was calculated by using Eq. (1) as shown in Fig. 2. The sizes of the zinc oxide crystallite, which was calculated to be 31.23, 11.08, 9.98, 9.90, and 9.53 nm, correspond to the peak of (101) plane, with a Fe doping in solution of 0, 2, 4, 6 and 8 wt% respectively. As shown, increased Fe concentration decreases the average crystallite size, and this behavior is caused by the increase in strain as a result of the increase in Fe concentration as shown in Fig. 3 was calculated using equation. This result is in good agreement with [25].

3. Effect of iron doping on lattice parameters
The increasing doping concentration lead to decrease of all the lattice constants (a=b, c) of the thin film as shown in Fig. 4. Shows all the lattice constants, had decreased value compared with pure ZnO film. These reducing was attributed to the ionic radius of Zn$^{2+}$ is larger than that of Fe$^{3+}$, suggesting that when Fe$^{3+}$ replaces Zn$^{2+}$ in the lattice substitutionally, it results in a smaller lattice constants of doped films than that of pure ZnO film [26].

4. Effect of iron doping on diffraction peak angle of XRD
Fig. 5 shows the relation between difference angle of (101) peak with Fe doping concentration. From figure we observed that the (101) peak position was shifted to the lower angle with increasing doping concentration. A similar result is also reported by Mahmoudi et al. [21]. While, the researchers Salaken et al.[24]
exhibited that the (101) peak the considerable shifts towards higher angle direction with the increase of doping level. The solubility of the dopant depends on the ionic radius and the valence states. In Fe doped ZnO thin films, for maintaining charge neutrality, Fe ions need to have a valence of +2 in order to substitute Zn\(^{2+}\) ionic sites. When adding Fe in the ZnO lattice, for holding charge neutrality, the lattice structure are expected to deform by the Fe\(^{3+}\) ions [26]. And taking into consideration the ionic radii, the ionic radius of Zn\(^{2+}\), Fe\(^{2+}\) and Fe\(^{3+}\) are 0.074, 0.078 and 0.068 nm, respectively. Thus, the ionic radius of Zn\(^{2+}\) is larger than Fe\(^{3+}\) by 8.1%, whereas that of Zn\(^{2+}\) is smaller than that of Fe\(^{2+}\) by 5.4%. Due to the difference of ionic radii between Fe\(^{2+}\) and Fe\(^{3+}\) so that both will result in different types and magnitudes of strain, when Fe\(^{2+}\) and Fe\(^{3+}\) substitute lattice sites in site of Zn\(^{2+}\) substitutionally. If Fe substitute lattice sites in site of Zn\(^{2+}\) substitutionally in the form Fe\(^{2+}\), due to Zn\(^{2+}\) has smaller ionic radius than that of Fe\(^{2+}\), it will lead to compression strain in the film [27], so that the peaks of XRD is shifting towards smaller angle direction (as shown in our experimental and by researchers Mahmoudi et al.[21]). And if Fe substitute lattice sites in site of Zn\(^{2+}\) substitutionally in the form Fe\(^{3+}\), due to Zn\(^{2+}\) has larger ionic radius than that of Fe\(^{3+}\), it will lead to tensile strain in the film, so that the peaks of XRD is shifting towards larger angle direction (as shown by the researchers Salaken et al.).

When Fe ions occur in ZnO mainly in the form of Fe\(^{2+}\), due to its larger ionic radius of Fe\(^{2+}\) than that of Zn\(^{2+}\), it will produce to compression strain in the film [27]. A visualization of this situation in XRD patterns is shifting of the peak towards smaller angle direction. On the contrary, if Fe ions occur in ZnO mainly in the form of Fe\(^{3+}\), due to its smaller ionic radius than that of Zn\(^{2+}\), it will lead to tensile strain in the film, producing a shifting of the peak towards bigger angle direction in XRD patterns.

**Fig. 5**: The variation of 2\(\theta\) (101) for ZnO thin film with Fe doping concentrations.

5. Morphological analysis

Fig.6 reveals the 3D and cumulating distribution AFM images of pure ZnO thin films doped with 2, 4, 6 and 8 % Fe concentrations. The average grain size, which is measured from AFM analysis using software, of doped and nondoped synthesized ZnO films ranged from 100 nm to 72 nm. AFM results show that adding Fe to ZnO thin films causes the films to become rough and porous and have a small grain size. This result is in good agreement with [22]. Table 1 shows the grain size, roughness values, and root mean square of ZnO thin films.

Fig.7 shows the field emission scanning electron microscopy (FE-SEM) images displaying the top view of the ZnO thin films for pure and doping with 4% on glass substrate. The FE-SEM images clearly illustrate the formation of flake-like nano-sized crystallite with more or less uniform structure of ZnO. The morphology of the films appears to be due to the growth and clustering of initial nuclei.
Doped films have randomly oriented and distinct flake shape structure. These results are in agreement with that of previous studies [24]. The SEM image with low magnification of ZnO film shows smooth ganglia-like hills (Fig. 5).

![Image of SEM images with low magnification of ZnO film](image)

**Fig. 6**: AFM Images for pure and Fe-doped ZnO films (A) Pure ZnO (B) Fe-ZnO 2% (C) Fe-ZnO 4% (D) Fe-ZnO 6% (E) Fe-ZnO 8%.

**Table 1**: Grain size and root mean square of surface obtained from AFM data.

| No. | Thin films    | Grain size (nm) | Root Mean Square $S_q$ (nm) | Roughness Average $S_a$ (nm) |
|-----|---------------|-----------------|-----------------------------|-----------------------------|
| 1   | Pure ZnO     | 100             | 0.982                       | 0.85                        |
| 2   | 2% Fe-ZnO    | 96              | 2.98                        | 2.63                        |
| 3   | 4% Fe-ZnO    | 84              | 2.92                        | 2.52                        |
| 4   | 6% Fe-ZnO    | 82              | 2.72                        | 2.36                        |
| 5   | 8% Fe-ZnO    | 72              | 3.24                        | 2.71                        |
6. Optical analysis

The band gaps of thin films are calculated using the following equation [28]:

\[ \alpha h\nu = A (h\nu - E_g)^r \]  \hspace{1cm} (3)

where \( \alpha \) is the coefficient of absorption, \( h \) is the Planck’s constant, \( E_g \) is the optical energy band gap of the material, \( \nu \) is the frequency of light, \( r \) is the factor controlling the direct and indirect translation of the electrons from the valence band to the conduction band, \( A \) is constant, and \( h\nu \) is the energy of photon. Fig. 8 shows the relationship between \((\alpha h\nu)^2\) and energy of photon \(h\nu\). The results indicate that an increase in the Fe content from 0 % to 8 wt. % leads to a decrease in the energy band gap from 3.75 eV to 3.3 eV, as shown in Fig.8. This reduction in energy gap is caused by the presence of prohibited impurities that led to the formation of donor levels within the energy gap near the conduction band. These results are in agreement with those of [29]. Interestingly, to achieve better photocatalytic efficiency, band gap energy of pure and Fe-doped zinc oxide thin films photocatalysts must have to be decreased [11].

![Image](image_url)

*Fig.7: The FE-SEM image (top view) of ZnO thin films: (A) Pure ZnO (B) Fe- ZnO 4%.*

![Image](image_url)

*Fig.8: \((\alpha h\nu)^2\) versus photon energy plot of (A) pure ZnO thin films (B) with different doping concentration of Fe.*
Photocatalytic activity

The photoreactivity of semiconductor is very sensitive to the morphology, crystal structure, phase composition and shape [30]. Also, the photocatalytic efficiency depends on the band structure, the electronic interaction between semiconductor and adsorbates, and the adsorption dynamics of substrate and intermediates [30]. The reaction is initiated by absorption of light with energy equal or higher than the energy band gap and the generation of electron hole pair on ZnO surface. The methyl orange (MO), methyl blue (MB) and methyl violet (MV) reacts with electrons produced on the zinc oxide thin films under UV irradiation. The technicality of the photocatalytic activity has been illustrated elsewhere [31]. Fig. 9 shows the absorbance spectra of the (a) methyl orange (MO) at 460 nm, (b) methyl blue (MB) at 660 nm and (c) methyl violet (MV) at 560 nm as a function of irradiation time on the zinc oxide for pure and doped thin films immersed in the dyes solution. It was concentration of the solutions were 100 mg/L. In order to confirm the photocatalytic activity, the spectrum was recorded at various time periods. The test was reduplicated with three sets of thin films at similar conditions and the results were reproducible.

Fig. 9 shows the absorbance decreases with irradiation time, which suggests the photocatalytic activity of methyl orange (MO), methyl blue (MB) and methyl violet (MV). Further it can be observed the rate of decrease in absorbance is great in the case of films doped with 8%. The decreasing of the absorbance band (MO) at 460 nm, (MB) at 660 nm and (MV) at 560 nm is very remarkable suggesting high photoreactivity. However, in our experiment, all the thin films doped with Fe showed noticeable increased photodegradation compared with pure ZnO. Fig. 9 showed that the 8% Fe-doped catalyst has higher values of photocatalytic activity than of the 2%, 4% and 6% Fe-doped thin films catalysts, and required only 60 min to decompose in aqueous solution. This can be related to the many reasons: (1) due to higher specific surface area, surface morphology, crystal structure and the enhanced photoresponse of the films. The film doped with 8% had higher surface roughness (surface roughness = 3.24 nm compared with 0.98, 2.98, 2.92, and 2.72 nm of the film doped with 0%, 2%, 4%, and 6% respectively). The effective surface area increases with increase the surface roughness which in turn improved the photodegradation [32]. (2) Introducing Fe in the ZnO lattice leads to increased absorption in the UV light range [4, 7] (as shown by reducing energy band gap). Therefore, the electronic interaction between Fe species and ZnO leads to the visible light photocatalytic activity of zinc oxide thin films. Where, the formation dopant energy levels of iron in the energy band gap of zinc oxide leads to the change in energy band gap [33]. The oxidation activity of ZnO photocatalyst thin films is enhanced, when the oxidation-reduction potential of the electrons and holes is increased [34].
Fig. 9: Absorbance of an aqueous solution with irradiation time of the ZnO films immersed in it. (A) for methyl orange (MO). (B) methyl blue (MB). (C) methyl violet (MV). Inset: absorption spectra of aqueous solution (100 mg/l) degraded by a ZnO film.

The photocatalytic degradation can be calculating by using the relation [35].

\[ \ln \frac{C}{C_0} = -k \times t \]  

where C is the concentration of MB, MO and MV (mg/l) at each interval of time in mg/l, \( C_0 \) is the initial concentration, t is the irradiation time in minutes and k is the rate constant.

The degradation (%) can be calculated using the relation [35]:

\[ \text{Degradation} (\%) = (\frac{C_0 - C}{C}) \times 100 \]

The photocatalytic activity of the different zinc oxide samples was estimated by calculating the rate constant (k values) from the slope of the diagram in Fig. 10. The k values and the degradation (%) of MO, MB and MV (Fig.11) exhibiting the photocatalytic activity of zinc oxide thin films are given in Table 2.

One can conclude that the surface morphology of sol-gel films, energy gap and the crystallites sizes have effect on the photocatalytic activity of the thin films. The results exhibited the higher photocatalytic activity can obtained by significantly advanced surface. Thin films with Fe doping are hopeful and efficient catalysts for the decomposition of organic pollutants by photocatalytic oxidation.
Fig.10: The relation between $\ln \frac{C}{C_0}$ with irradiation time for zinc oxide thin films. (a) MO, (b) MB and (c) MV solution.

Fig.11: Degradation of aqueous MO, MB and MV solution as a function of irradiation light time of the ZnO thin films immersed in it.
**Table 2: Illustrate the rate constant (k) and degradation (%) of the (a) MO, (b) MB and (c) MV (100 mg/l) solution.**

| samples     | K min\(^{-1}\) for MO | Degradation in 60 min | K min\(^{-1}\) for MB | Degradation in 60 min | K min\(^{-1}\) for MV | Degradation in 60 min |
|-------------|------------------------|-----------------------|------------------------|-----------------------|------------------------|-----------------------|
| Pure ZnO    | 0.0072                 | 54                    | 0.00358                | 24                    | 0.0057                 | 41                    |
| 2% Fe       | 0.0081                 | 62                    | 0.00405                | 28                    | 0.00669                | 48                    |
| 4% Fe       | 0.009                  | 72                    | 0.0051                 | 43                    | 0.00865                | 68                    |
| 6% Fe       | 0.0102                 | 84                    | 0.00607                | 56                    | 0.0111                 | 95                    |
| 8% Fe       | 0.0116                 | 101                   | 0.0071                 | 64                    | 0.0143                 | 135                   |

**Conclusions**

ZnO:Fe thin films were prepared through simple and low cost spin-coating sol-gel method. The deposited film was 300 nm thick, and XRD studies of as-deposited samples show polycrystalline structure with hexagonal wurtzite structure of ZnO and Fe:ZnO thin films. With Fe doping from 0–8 wt. %, the prepared film has energy band gap of approximately 3.75 eV to 3.3 eV. It was found that Fe concentration affect surface roughness, grain size, absorption of UV light and photocatalytic activity of the samples. The photocatalytic activity of the samples was enhanced by all these factors. The optimum concentration of iron under UV light is 8%, degradation process with irradiation time UV light for 60 min. Moreover, the photocatalytic activity of thin films against which indicates the photodegradation of MO, MB and MV under UV light irradiation (354 nm, 6 W) has been developed in this research.

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