Investigation of photocatalytic activity of ZnO prepared by spray pyrolysis with various precursors

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Abstract. Semiconductor photocatalysts such as ZnO has attracted much attention in recent years due to their various applications for the degradation of organic pollutants in water, air and in dye sensitized photovoltaic solar cell. In the present work, ZnO thin films were prepared by ultrasonic spray pyrolysis by using different precursors namely: acetate, chloride and zinc nitrate in order to investigate their influence on ZnO photocatalytic activity. The films crystalline structure was studied by mean of X-ray diffraction measurements (XRD) and the films surface morphology by Scanning Electron Microscopy (SEM). The films optical properties were studied by mean of UV–visible spectroscopy. The prepared films were tested for the degradation of the red reactive dye largely used in textile industry. As a result, we found that the zinc nitrate is the best precursor to prepare ZnO thin films suitable for a good photocatalytic activity.

1. Introduction

Semiconductor-assisted photocatalysis has recently emerged as an efficient method for conversion of photon energy into chemical energy and environmental purification [1, 2]. Among the semiconducting catalysts, zinc oxide (ZnO) has been extensively studied due to its low cost, non-toxicity, outstanding stability, and high efficiency [3-5]. ZnO is an n-type semiconductor with wide band gap (3.3 eV), large exciton binding energy (60 meV). Illuminated ZnO material with ultraviolet (UV) light can generates electron/hole pairs. These electrons and holes can migrate and initiate redox reactions with water and oxygen, by which they degrade organic molecules adsorbed on the surface of a photocatalyst [6, 7]. It is well known that ZnO thin films morphology controls its properties and subsequently their relevant potential applications. ZnO thin films were mainly used in : biomedical [8], piezoelectricity, biosensors, photocatalysis [9-11], biotechnology [12], light emitting diodes (LED’s), laser systems [13] transparent electrodes [14], gas sensors [15,16], solar cells [17] and cosmetic products [18]. Various techniques have been used for ZnO thin films deposition namely: magnetron sputtering [19], reactive evaporation [20], chemical vapor deposition (CVD) [21], pulsed laser deposition (PLD) [22] and spray pyrolysis [23]. Among these methods, spray pyrolysis technique has several advantages, such as, simplicity, safety and vacuum less equipments. It is widely used and succeeded in oxide metallic thin films production [24-26].
In the present paper we studied the influence of the solution nature and properties on the characteristics of ZnO thin films on the photocatalytic activity.

2. Experimental

The ZnO films were grown onto glass substrates; using a Spray Pyrolysis Equipments (HOLMARC). Three different solutions, with 0.1 M molarity were prepared by mixing zinc salts with methanol. The used salts are zinc acetate, zinc nitrate and zinc chloride with 99.9995% of purity. ZnO thin films were deposited with the prepared solutions on well cleaned glass substrates with methanol and distilled water. The prepared solutions are then sprayed on the heated glass substrates by a pneumatic pump with flow rate of 100µl/min. During deposition, the substrate temperature is kept at 350°C. Deposition time for each precursor was 5 min. The crystalline structure was studied by X-ray diffraction measurements (XRD) and the films surface morphology was characterized by means of Scanning Electron Microscope (SEM). The UV–Visible transparency of the films is performed by Shimadzu UV–3101 PC spectrophotometer within the wavelength range of 200–800 nm. The films thickness and refractive index were derived from optical transmission measurement. The films electrical conductivity was carried out using D.C electrical measurements in dark and at room temperature. In the present work, we have studied the photocatalysis application of ZnO thin films prepared by various precursors for study the degradation of the red reactive dye largely used in textile industry. The used solution was prepared from red reactive 184 powder dissolved in distilled water to obtain a solution with concentration of 4*10^-6 mole/l. ZnO samples were placed inside a beaker containing 250 ml of polluted solution in contact with ZnO layer placed in horizontal position. The ZnO sample is exposed to an UV irradiation with a wavelength of 365nm and 2W power.

3. Results and discussion

3.1 Films structure

Figure 1 shows XRD spectra of different films deposited with the three studied salts. As can be seen, the ZnO films prepared from zinc nitrate and zinc chloride were polycrystalline with hexagonal wurtzite structure. While, films prepared with zinc acetate exhibits an amorphous phase due to the absence of any relevant peak. The XRD diffraction pattern of both films deposited using nitrate and zinc chloride are composed with several peaks assigned to (101), (002), (101), (110) planes as shown in figure1. We noticed that when we using a chloride as a precursor, diffraction peak, assigned to the plane (002) became the preferential orientation indicating that the film have the Wutrzite hexagonal and the growth is achieved along the axis c normal to the substrate surface. However in the case of zinc nitrate precursor, the deposited film shows that the plane (101) is the most intense peak. The XRD results are in good agreement with Lehraki et al [27] results, they reported that the ZnO thin films obtained by zinc chloride are polycrystalline and the zinc acetate has an amorphous phase.

![Figure 1. XRD diffraction pattern of ZnO thin films obtained by various precursors: (a) zinc acetate, (b) zinc nitrate and (c) zinc chloride.](image-url)
Figure 2 shows typical SEM images of ZnO films prepared using the three different precursors. As shown, the films morphology depends strongly on the nature of the used precursor. Film prepared with zinc nitrate as starting solution is porous and exhibits a non continuous network (figure 2.a). While film prepared with zinc chloride exhibits a rough surface morphology and non continuous structure (figure 2.b). However as can be seen in figure 2.c, zinc acetate precursor yields to a dense and continuous structure film structure with a smooth surface. Due to its structure, zinc nitrate films have a larger specific surface than the others films, consequently this precursor will offers larger reactive surface with the environment which is required for gas sensing or for water treatment.

3.2. Optical properties

In figure 3 we have reported the transmittance spectra of UV-visible range of ZnO films prepared with different precursors. The film deposited with zinc acetate (figure 3(a)) has the higher transparency of 87% than films deposited with zinc nitride and zinc chloride (curves 3.b and c). This is due to the smooth surface of the former. It is well known that rough surface causes the light scattering resulting in transmittance reduction. This explains the low transmittance measured in films deposited with zinc chloride and nitride despite that they have better crystallinity then the films deposited with zinc acetate. Since these films have rough surfaces as can be seen in SEM images (figure 2).

Figure 3. UV-visible transmittance spectrum of ZnO thin films deposited at 350 °C using different salts: (a) Zinc acetate-(b) Zinc nitride-(c) Zinc chloride.
The optical band gaps of films have been estimated from the plot of their absorption coefficient as a function of photon energy and using Tauc formula for direct band gap semiconductors [28]:

\[(\alpha h\nu)^2 = B (E_g - h\nu)\].

Where \(\alpha\) is a absorption coefficient, \(B\) is a constant, \(h\) is Planck constant, \(E_g\) is the energy band gap and \(\nu\) is incident photon frequency.

Films optical band gap are found equal to 3.12 and 3.20 eV for films prepared with zinc nitrate and zinc acetate respectively. While the optical gap of film deposited with zinc chloride is close to its value for ZnO bulk material which is 3.27 eV because of the good crystallinity of this film. The films thickness, refractive index and optical band Eg deduced from optical transmittance spectra were reported in Table 1.

**Table 1:** thickness, band gap, refractive index, degradation rate \(k\) and conversion rate of ZnO thin films deposited with different precursors.

| ZnO precursors | d (nm)   | Eg (eV) | n     | Rate \(k\) \((10^{-4})\) | Conversion rate (%) |
|----------------|----------|---------|-------|--------------------------|----------------------|
| Nitrate        | 209.936  | 3.12    | 1.88  | 18                       | 36                   |
| Chloride       | 202.463  | 3.25    | 1.93  | 6.58                     | 17                   |
| Acetate        | 134.864  | 3.20    | 1.69  | 8.56                     | 20                   |

3.3. Electrical properties:

Figure 4 shows the variation of the electrical conductivity, of ZnO thin films deposited by various precursors, measured in the dark and at room temperature. As can be seen the conductivity of films obtained with zinc nitrate have the slightly larger conductivity value \(7.23 \times 10^{-5} (\Omega \cdot \text{cm})^{-1}\). This is due to the fact that film prepared with this precursor is dense and continuous in contrary to others ones.

![Conductivity graph](image)

**Figure 4.** Variation of the conductivity for the three precursors.

3.4. Photocatalytic activity:

We have studied the variation of absorbance spectra of polluted solution after different UV light exposure times. The wavelength region is ranged from 450 to 600 nm; this broad absorption band is a characteristic of the used red dye. The absorption peak intensity is used as signature of the dye degradation. From the variation of this absorption peak with exposure time, we concluded that the
photo degradation is more significant when solution is in contact with film prepared using zinc nitrate than the ones prepared with zinc acetate and zinc chloride films.

To have more insight on the photo degradation kinetics and the influence of ZnO precursors, we have monitored the variation of the intensity of the absorption located at 542 nm. We have reported in figure 5 the variation of the ratio \( C/C_0 \), where \( C \) is the peak intensity at time \( t \) and \( C_0 \) is the peak intensity before light exposure. As can be seen, the photo degradation is more important when using film obtained with zinc nitrate salt, the ratio is reduced with increasing exposure time; it reaches 0.64 after 240 minutes of irradiation. However in the case of zinc acetate and zinc chloride films salt source, the ratio is slightly reduced up to 0.78 and 0.83 after 240 minutes, respectively. As can be seen in figure 6, the photocatalytic decomposition of red pollutant, in contact with the surface of ZnO thin films of the three precursors, follow a pseudo first-order kinetic law, it can be expressed as [31]:

\[
-Ln \left( \frac{C}{C_0} \right) = kt
\]

Where \( C \) and \( C_0 \) are the reactant concentration at time \( t \) and \( t = 0 \), respectively and \( k \) rate constant (reaction rate constant) [29].

In table I we have reported the calculated value of the rate \( k \) for the all ZnO thin films. Zinc nitrate film is characterized by a larger rate \( k \) then the other films. The conversion rate defined as \( \tau = \left( C_0 - C(t)/C_0 \right) \times 100 \), is an interesting quantity that can yield information about the pollutant degradation, it represents the relative quantity of removed pollutant from the solution. In figure 6 we have reported the variation of the conversion rate obtained with all ZnO thin films. In the case of zinc nitrate film, 36 % of pollutant is removed after 240 minutes of exposure time, while only less than 22% and 17% are removed when using zinc acetate and zinc chloride films, respectively. The discrepancy in the photocatalysis activity of all thin films of ZnO may found explication in the difference between their microstructure. As deduced from SEM images, zinc nitrate and zinc chloride films are rough and have a porous structure while zinc acetate film is smoother and has a continuous structure. Therefore, the reactive specific surface of the first film is larger than in the others films, thereafter, more reactive surfaces are available for the water than in the other ones (acetate and chloride). The same conclusion has been outlined by Li et al [32] in ZnO/CuO structure, they reported that a material with an open and porous surface exhibit higher degradation efficiency. So, the reactive specific surface is one of the important parameters to controller the photocatalytic activity of ZnO thin films.

Figure 6. Evolution temporal of the conversion rate of dye red pollutant during its degradation in contact with ZnO thin films deposited by various salts.

4. Conclusion:
In order to investigate the influence of the precursor’s salt nature, we have studied the ZnO thin films deposited with spray pyrolysis by different precursors. The obtained ZnO thin films are polycrystalline
when using zinc nitrate and zinc chloride, however using zinc acetate salt leads to an amorphous film microstructure. From this investigation we inferred that the starting salt source nature and morphology of the Zn salt play an important role on the photocatalytic activity. Thin and porous films offer more reactive sites due to the large surface to volume ratio and larger charge transfer, thereafter their better photocatalytic activity. According to the obtained films SEM images and to morphologies, we concluded that zinc nitrate source is the best precursor for the preparation of ZnO thin film suitable to the red dye photo degradation.

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