# Synthesis and structural characterizations of ZnO /$TiO_2$ Nanocomposites by Wet-Chemical Routes

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***ABSTRACT*****:** *ZnO/ TiO2 nanocomposites were synthesized via sol-gel technique. The synthesized ZnO/ TiO2 nanocomposites have been characterized structurally and optically by using X-ray diffraction (XRD), UV-Visible spectroscopy and Photoluminescence Study. Using the Full proof program X-ray diffraction of ZnO/TiO2 nanocomposites was analyzed. The program fitted and refined with the experimental XRD data by two methods; Le Bail fitting and Rietveld refinement. Experimental profiles of the XRD data were fitted by Pseudo-Voigt functions. The analyses revealed that ZnO/TiO2 nanocomposites have a hexagonal phase structure. A good agreement between experimental and simulated patterns was obtained. The obtained data from the Full Prof Refinement were used to calculate the average crystallite size and related parameters for ZnO/TiO2 nanocomposites.*

***Keywords: ZnO/ TiO2 nanocomposites, X-ray diffraction (XRD), UV-Visible spectroscopy and Photoluminescence***

## 1. INTRODUCTION

Metal oxide nanoparticles attract great attention in recent years on account of their special electronic and chemical properties. Among the metal oxide semiconductors, TiO2 and ZnO have been investigated extensively due to their chemical stability and efficient photocatalytic properties. Zinc oxide has achieved applications in various areas such as optical, piezoelectric, magnetic, and gas sensing properties, and apart from this, zinc compounds have been generally regarded as safe [1]. Titanium oxide (TiO2) is the most widely used metal oxide for environmental applications, paints, electronic devices [2], gas sensors [3] and solar cells [4, 5]. It is a well-known semiconductor with an excellent photocatalytic property that has been widely used in environmental pollutant elimination [6, 7], antibacterial dopes, self-clean buildings, etc. [8]. Its unique antibacterial properties make the material a candidate for applications in medical devices and sanitary ware surfaces. However, their are still problems

needed to be dissolved concerning its application in photocatalysis. For most of the photocatalytic decomposition processes, photonic efficiency is relatively low, and furthermore, photocatalytic reactions on TiO2 nanoparticles can usually be induced only by ultraviolet light, which limits the application of TiO2 as a photocatalyst with visible light [9]. It is expected that the composites of ZnO and TiO2would exhibit useful applications in photocatalysis. As to this, recently, several papers concerning the enhancing of TiO2 photocatalytic activity have been reported. Most of them concern modifying the photocatalysts by doping with ions [10, 11], or coupling TiO2 to other oxides[12] for instance to ZnO [13]. Coupled semiconductor photocatalyst of TiO2/ZnO has been investigated to enhance the photodegradation efficiency of TiO2 catalyst by a number of researchers and its effect on improving photocatalytic efficiency was reported [9, 13-15].On the contrary, some studies found that the coupling of ZnO and TiO2 semiconducting powders was not so beneficial to enhance the photoreactivity for the studied reaction [16, 17]. Research in this area is of both scientific and applied significance.

In this work, ZnO/TiO2 nanocomposites were synthesized by the sol-gel method. Compared with the above-mentioned methods, this method has four advantages: (1) it is very cheap and facile because of not requiring any complex equipment and complicated operations; (2) the reaction is environmentally friendly since the byproducts are sodium chloride, (3) the reaction is safe and quick and (4) the high yield. Prepared ZnO/ TiO2 nanocomposites were characterized by X-ray diffraction (XRD), Morphology and Elemental analysis, UV-Visiblespectroscopyand Photoluminescence Study. Using the Fullprof program X-ray diffraction of ZnO/TiO2 nanocomposites was analyzed.

## 2. MATERIALS AND METHODS

The ZnO/ TiO2 nanocomposites were prepared by means of the sol-gel method. For the preparation of, 5 g zinc chloride was dissolved in 10 ml ethanol and the obtained solution was added to 70 ml benzyl alcohol under continuous stirring at room temperature. To this mixture, 4 ml TiCl4 was slowly added. The obtained orange liquid was stirred continuously at 60°C for 8 hours. Thus obtained materials were left for aging at room temperature. The resulting white thick suspensions were centrifuged at 4500 rpm for 15 min and the supernatant was discarded by decantation. The white precipitates were then washed two times with absolute ethanol and three times with diethyl ether (1×20 ml). After every washing step, the solvent was separated by centrifugation. The collected material was dried in air overnight and then ground into a fine

powder. The obtained powders were calcinated at 200°C which yields to ZnO/ TiO2 nanocomposites.

**Characterization method**

The structure of the prepared ZnO/ TiO2 nanocomposites was investigated from the X-ray diffraction patterns obtained using a Riagu Mini Flexell Desktop Diffractometer(using CuKα radiation at a wavelength of 1.5406 Å). Optical properties were studied using a UV-VIS spectrophotometer (JASCO -V-670) in the wavelength range of 300 - 1000 nm. The luminescence studies were carried out using Fluoromax 4 spectrophotometer.

## 3. RESULTS AND DISCUSSION

### 3.1. Structural analysis

The XRD patterns of the ZnO/ TiO2 nanocomposites prepared by the sol-gel method are shown in Figure 2. The XRD patterns ZnO/ TiO2 nanocomposites reveal the formation of well-crystalline single-phase materials. No extra peaks corresponding to any other secondary phases are observed. The obtained XRD patterns of the ZnO/ TiO2were compared with the standard data for ZnO (JCPDS card No. 80-0075) and for TiO2(JCPDS card No.21-1272).The XRD patterns for the composite system revealed the presence of reflections from both ZnO and TiO2 in equal strength representing the equal crystalline distribution of phases within the sample. The lattice parameters were calculated from 2θ values in the X-ray diffraction patterns by using Fullprof program computer programming. The XRD structural parameters obtained are given in Table 1.

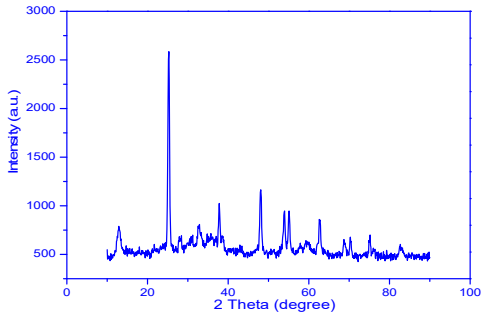


**Figure 2. The XRD patterns of the ZnO/ TiO2 nanocomposites prepared by sol-gel method**

From the diffracting profiles, the diffraction angle (2θ) and intensity lines are measured with high accuracy. Possible directions in which the films diffracted the beam of monochromatic X-rays are determined by Bragg's law

$$2d \sin\theta = n\lambda$$

Where, d is Lattice spacing, θ is Glancing angle of X-rays, n is Order of diffraction and λ - Wavelength of X-rays.

The crystallite size has been calculated using Scherer's formula from the XRD data.

$$D = (K\lambda/\beta \cos\theta) \text{ (nm )}$$

Micro strain (ε) were calculated using,

$$\varepsilon = \beta / (4 \tan\theta)$$

The existence of stacking faults gives rise to a shift in a peak position of different reflection planes with respect to an ideal position of fault free sample. The relation between stacking faults probability (α) with a peak shift in terms of (β) is given by

$$\alpha = [2\pi^2 / 45(3\tan\theta)^{1/2}] \beta \text{ (Å)}$$

where,$\alpha$ - is the stacking fault

β - is the full width at half maximum

A dislocation is an imperfection or crystallographic irregularity or a defect formed within the material. As the dislocation density increases the material becomes harder. It has been shown that the dislocation density increases while crystallite size decreases with increasing strain and ultimately these parameters reach saturation values. Above a certain crystallite size limit (~20 nm) the strength of materials increases with decreasing crystallite size. The dislocation density (δ) has been determined using values of lattice constant, FWHM, θ, and crystallite size.

**Table 1.** ***Structural parameters of ZnO/ TiO2 nanocomposites***

| S.No | 2θ (°) | FWHM (°) | Crystallite Size D (nm) | Dislocation Density (δ) | Elastic strains | Stacking faults probability (Å) |
|---|---|---|---|---|---|---|
| 1. | 25.26 | 0.4741 | 17.95 | 47.8542 | 0.0092 | 0.0044 |
| 2. | 37.81 | 0.4297 | 20.43 | 27.3760 | 0.0054 | 0.0032 |
| 3. | 48.05 | 0.4731 | 19.21 | 54.9846 | 0.0046 | 0.0031 |
| 4. | 53.90 | 0.5804 | 16.05 | 55.4897 | 0.0049 | 0.0035 |
| 5 | 53.91 | 0.4843 | 19.24 | 61.0773 | 0.0041 | 0.0029 |
| 6 | 55.09 | 0.5020 | 18.65 | 29.6293 | 0.0041 | 0.0030 |
| 7 | 62.70 | 0.5504 | 17.66 | 58.7851 | 0.0039 | 0.0031 |
| 8 | 68.83 | 0.5795 | 17.37 | 53.9183 | 0.0036 | 0.0030 |
| 9 | 70.33 | 0.3785 | 26.83 | 25.2228 | 0.0023 | 0.0019 |

### 3.2. Optical Properties

The absorption spectra of ZnO/ TiO2 nanocomposites are shown in Figure 2. The sample exhibit a sharp falling at the absorption edge which is an indication of good crystallinity. The band gap values of the sample are determined using the Tauc plot analysis. From the investigations, the absorbance is high in the ultraviolet region and found to be less absorbance above 350 nm in the entire visible region. The cut off wavelengths has been observed to be lesser than 350 nm and have a sharp absorption edge.

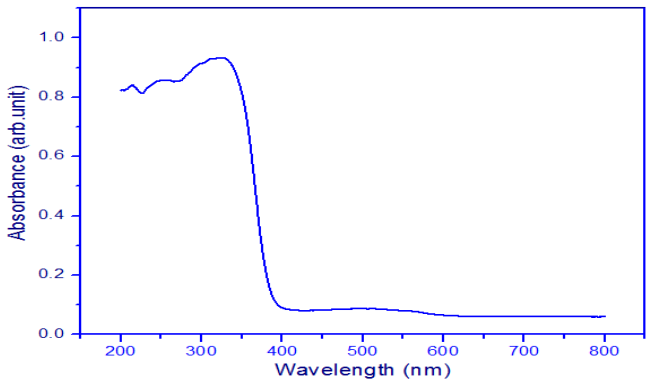


**Figure 2 Optical absorbance spectra of ZnO/ $TiO_2$ nanocomposites**

From the transmittance spectra, it was found to be increasing with the increase of the wavelength of the incident light and the transmission is around 80% in 375nm and further increases up to 85% at a higher wavelength. The transmittance (T) vs wavelength (λ) spectra have been taken and shown in Figure 3. It is observed that the optical transmittance is a maximum of 85% in the IR region.

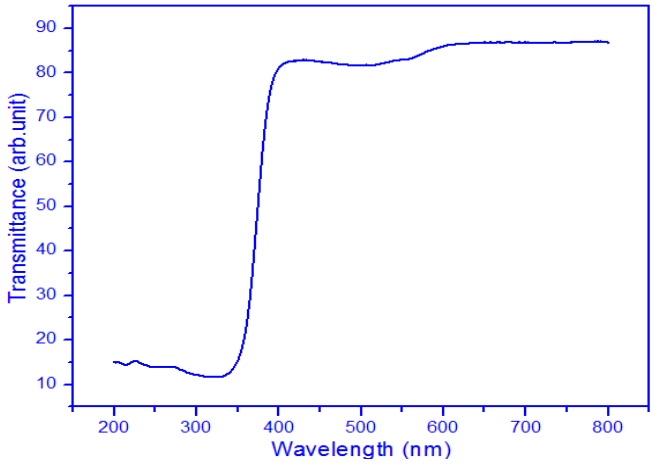


**Figure 3 Optical transmittance spectra of ZnO/ $TiO_2$ nanocomposites**

The optical band gap values have been calculated using the fundamental absorption, which corresponds to electron excitation from the valence band to the conduction band. The relation between absorption coefficient α and incident photon energy (hν) are given by the equation

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

where A is a constant, $E_g$ is the bandgap of the material and the exponent n depends on the type of transition.

Tauc plots between $(\alpha h\nu)^2$ and energy have been plotted and the linear portions of the graphs were extrapolated to meet the energy axis as shown from Figure 4from which the energy bandgap has been determined as 3.3 eV. The presence of a single slope in the curves suggests that ZnO/ $TiO_2$ nanocomposites are in a single phase in nature and the type of transition is direct and allowed.

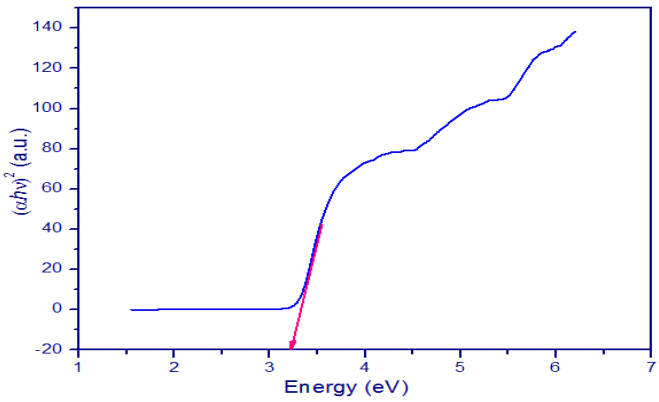


**Figure 4. The optical band gap of ZnO/ $TiO_2$ nanocomposites**

### 3.3. Photoluminescence Spectra

Photoluminescence (PL) spectroscopy has also been used to determine the bandgap since the most common radiative transition in the semiconductor occurs between the states at the bottom of the conduction band and the top of the valence band.PL spectra observed for ZnO/ TiO2 nanocomposites were indicated in Figure 5. In the present, study the blue emission peak occurring around ~ 435 nm (2.85eV) is attributed to the presence of oxygen vacancies Vo°. The yellow band seen at 571nm is linked to the presence of singly as well as doubly ionized Vo.

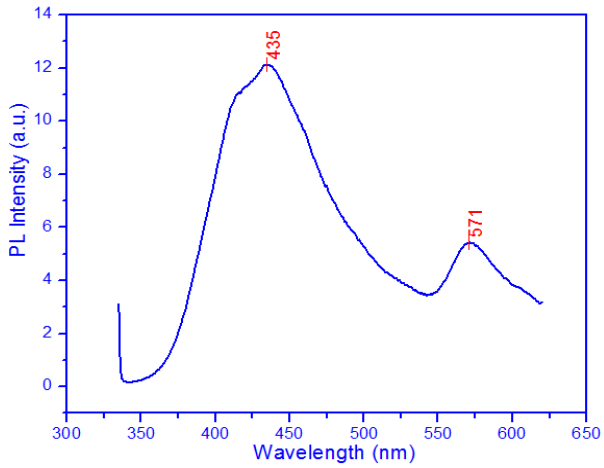


**Figure 5. Photoluminescence spectra of ZnO/ $TiO_2$ nanocomposites**

### 3.4. SEM Analysis

SEM is a scanning electron microscope that illustrates the sample surface by scanning with a beam of high-energy electrons. X-rays in the SEM can be used to identify the elemental composition of a sample by a technique known as energy dispersive x-ray (EDX). The surface morphology of ZnO/ TiO2 nanocomposites synthesized by the sol-gel method can be seen in Figure 6. The ZnO/ TiO2 nanocomposites have a uniform particle shape and size with a low level of agglomeration because they did not form a large cluster. The agglomeration can usually be demonstrated by the formation of a large cluster.

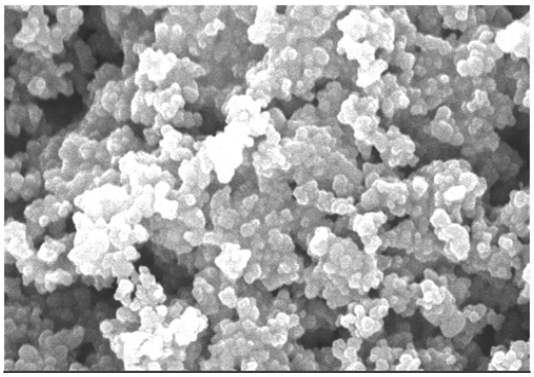

**Figure 6. SEM images of ZnO/ $TiO_2$ nanocomposites**

## 4. CONCLUSION

ZnO/ TiO2 nanocomposites were synthesized by the sol-gel method. The XRD patterns ZnO/ TiO2 nanocomposites reveal the formation of well-crystalline single-phase materials. The structural parameters were calculated from 2θ values in the X-ray diffraction patterns by using Fullprof program computer programming. The crystallite size has been calculated using Scherer's formula and found to be19.27nm. From the investigations of UV-Vis spectra, the absorbance is high in the ultraviolet region and found to be less absorbance above 400 nm in the entire visible region. The cut off wavelengths has been observed to be lesser than 350 nm and have a sharp absorption edge. The energy bandgap has been determined as 3.3 eV. In PL spectra, the blue emission peak occurring around ~ 435 nm (2.85eV) is attributed to the presence of oxygen vacancies Vo°. The yellow band seen at 571 nm is linked to the presence of singly as well as doubly ionized Vo. ZnO/ TiO2 nanocomposites have a uniform particle shape and size with a low level of agglomeration because they did not form a large cluster. The agglomeration can usually be demonstrated by the formation of a large cluster.

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