# Thermal and Antibacterial Properties of ZnO / TiO2 Nanocomposite

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Abstract:  $ZnO/TiO_2$  nanocomposite was prepared by wet chemical reaction method and the structural, optical and thermal properties of the synthesized sample were studied by XRD, UV-Visible absorption microscopy, DSC and TG/DT analysis. The XRD pattern showed a set of well defined diffraction peaks, which could be indexed to the wurtzite hexagonal phase of ZnO. Moreover, characteristic diffraction peaks corresponding to TiO<sub>2</sub> were observed. DSC analysis of the sample indicated two exothermic reactions at temperatures 94°C and 256.7°C. The TGA curve shows a multistage decomposition of the sample. The antibacterial activity of the ZnO/TiO<sub>2</sub> was evaluated for *three different bacteria* by agar disc diffusion assay and the results clearly showed that ZnO/TiO<sub>2</sub> nanocomposite has remarkable antibacterial effect and this effect is concentration-dependent. While increasing the concentration of TiO<sub>2</sub>, more microbial toxicity was observed.

# Keywords- ZnO, TiO<sub>2</sub>, nanocomposite, XRD, antibacterial.

# I. INTRODUCTION

In recent years, the unique and fascinating properties of nanostructured materials have triggered tremendous motivation among scientists to explore the possibilities of using them in industrial and biotechnological applications. Inorganic materials such as metal and metaloxides have attracted lots of attention over the past decade due to their ability to withstand harsh process conditions [1-3]. Zinc Oxide (ZnO), a wide band gap (3.36 eV) II-VI compound semiconductor, has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics [4-6]. ZnO has received increasing attention as antibacterial agent in recent years among the various metal oxides studied for their antibacterial activity, as ZnO nanoparticles are highly toxic to prokaryotic cells. Titanium oxide (TiO<sub>2</sub>) is a well known semiconductor with excellent photocatalytic property that has been widely used in environmental pollutant elimination [7,8], antibacterial dopes, self-clean buildings [9], etc. Its unique antibacterial properties make the material a candidate for applications in medical devices and sanitary ware surfaces. Recently, the use of inorganic antimicrobial agents, such as Titanium and Zinc compounds, has received increased attention. The key advantages of inorganic anti-microbial agents are improved safety and stability, which are lacking in organic antimicrobial agents. The aim of this work was to synthesize ZnO/TiO<sub>2</sub> nanocomposite powder by wet-chemical route and to study their structural, thermal and antibacterial properties.

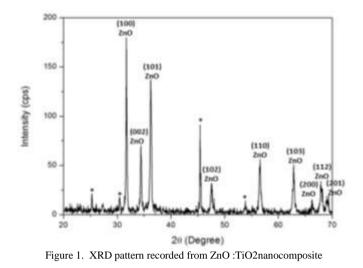
### II. EXPERIMENTAL

ZnO/TiO<sub>2</sub> nanocomposite was prepared by wet-chemical reaction method. The aqueous solution of 6.1326 g of Zinc acetate dihydrate, 0.3995g of TiO<sub>2</sub> and 4.4 g of Sodium hydroxide were mixed by magnetic stirrer at 100°C for an hour. The slurry was ultrasonicated for 30 minutes and centrifuged at the 1600 rpm for 30 minutes. The precipitate obtained was filtered, washed thoroughly with ethanol and distilled water. The washing procedure was repeated for several times and then the collected residue was dried in an oven at 200°C for 2 hours then the dried powder was ground to fine powder.

#### III. RESULTS AND DISCUSSION

#### A.X-Ray Diffraction Analysis

A typical XRD pattern of the ZnO/TiO<sub>2</sub> nanocomposite is shown in Fig. 1. The XRD pattern shows a set of well defined diffraction peaks, majority of the peaks could be indexed to the wurtzite hexagonal phase of ZnO. In addition, diffraction peaks corresponding to TiO<sub>2</sub> (JCPDS 78-2486) and ZnTiO<sub>3</sub> (JCPDS 26-1500) are observed. The average crystal size of the nanoparticles was calculated by using the Scherer formula is predicted to be ~33 nm. Thus, the XRD pattern clearly reveals the formation of ZnO/TiO<sub>2</sub> nanocomposite.



**B.** UV-absorption Analysis

The room temperature optical absorption spectrum of  $ZnO:TiO_2$  nanocomposite is shown in Fig.2. A strong UV absorption band at around 372 nm is assigned to the ZnO band – to – band transition. The energy band gap measured from the UV absorption spectrum is found to decrease (3.34 eV) in comparison with bulk ZnO (3.37 eV). This study shows that the ZnO/TiO<sub>2</sub> nanocomposite absorbs more visible light and therefore this Zn)/TiO<sub>2</sub> can be used as an efficient photocatalyst under visible light irradiation.

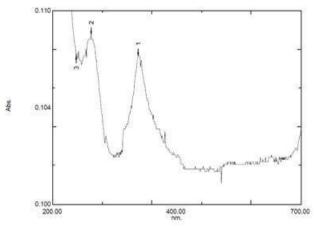


Figure 2. UV-Vis. Absorption spectrum of ZnO/ TiO2 Nanocomposite

#### C. Thermal Analysis of ZnO/TiO<sub>2</sub> Nanocomposite

The DSC study of ZnO/TiO<sub>2</sub> nanocomposite was carried out using a calorimeter (Netzsch DSC204F1) under nitrogen atmosphere. The testing temperatures were from  $0 - 350^{\circ}$ C. The reaction enthalpy (J/g) and residual heat of reaction were carried from the area under the DSC peaks. The result of the thermal analytical study of ZnO: TiO<sub>2</sub> nanocomposite is presented in Fig. 3.The DSC curve of ZnO:TiO<sub>2</sub> nanocomposite shows two prominent peaks at 94°C and 256.7°C. The exothermic peak at 94°C is associated with the decomposition of residual OH groups and the condensation of non bounded oxygen which causes the weight loss and exothermic peak at 256.7°C is possibly related to the crystallization of ZnO.

The TG/DTA analysis of ZnO/TiO<sub>2</sub> nanocomposite is shown in Fig. 4. The TGA curve exhibits three apparent mass losses, the first one between  $(0-100)^{\circ}$ C is due to the loss of residual solvent and water. The second and third mass loss observed in the region  $(100 - 220)^{\circ}$ C and  $(220-599)^{\circ}$ C is due to thermal decomposition of organics. The DTA curve shows two exothermic peaks around 149.2°C and 255.7°C indicating that there might exist weak interactions between TiO<sub>2</sub> and ZnO nanoparicles.

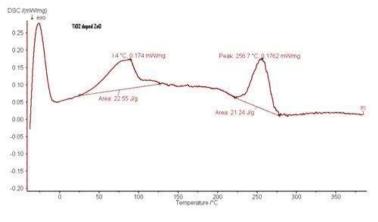


Figure 3. DSC curve of ZnO:TiO2 Nanocomposite

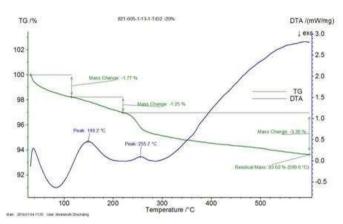


Figure 4. TG/DTA curves of ZnO: TiO2Nanocomposite

### D. Antibacterial Study

Earlier studies have demonstrated that ZnO nanoparticles have antibacterial activity on both gram positive and negative bacteria including *E.coli* and also reported that the antibacterial activity of ZnO is dependent on the size and concentration of the particles [7-9]. In the present study, our interest was to determine whether  $ZnO/TiO_2$  nanocomposite can inhibit the growth or kill different bacterial strains.

The bacteriological tests were conducted with *Staphylococcus aureus*, *E. coli* and *Bacillus subtilis* by agar diffusion method [13]. It was observed from the study that the zone of inhibition increases as the concentration of  $TiO_2$  in ZnO increases (Fig 5).



Figure 5. Antibacterial activity of  $ZnO / TiO_2$  nanoparticles of different concentrations (20, 30, and 40 mol %) were tested against bacteria by a disc diffusion method

#### IV. CONCLUSION

Synthesis of  $ZnO/TiO_2$  nanoparticles was achieved by using wet-chemical reaction method. The structural characterizations using XRD of the sample demonstrated that product was crystallite. The energy band gap calculated from UV absorption spectrum was found to decrease due to decrease in covalency and an increase in

the iconicity observed in the iono-covalent ZnO due to TiO<sub>2</sub> doping. DSC analysis of ZnO/TiO<sub>2</sub> ensures that two exothermic reactions were taken place at around 94°C and 256.7°C. TGA analysis of the sample supports the results of DSC analysis that weight loss were observed around at 100°C and 250°C, respectively. This study also shows that ZnO/TiO<sub>2</sub> nanocoposite has antimicrobial activity against *Staphylococcus aureus*, *E. coli* and *Bacillus subtilis*.

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#### REFERENCES

- L. Fu, Z. Liu, Y. Liu, B. Han, P. Hu, L. Cao, D. Zhu, "Beaded cobalt oxide nanoparticles along carbon nanotubes: Towards more highly integrated electronic devices" Adv.Mat., vol.17, pp. 217-221, January 2005.
- [2] S. Makhluf, R. Dror, Y. Nitzan, Y. Abramovich, R. Jelnek, A.Gedanken, "Microwave-assisted synthesis of nanocrystalline MgO and its use as a bacteriocide" Adv. Funct. Mat., vol2005, 15, pp. 1708–1715, October 2005.
- [3] P. K. Stoimenov, R. L. Klinger, G. L. Marchin, K. J. Klabunde, "Metal oxide nanoparticles as bactericidal agents" Langmuir, vol. 18, pp. 6679–6686, July 2004..
- [4] K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, H.Hosono, Thin-film transistor fabricated in single-crystalline transparent oxide semiconductor" Science, vol.300, pp. 1269–1272, May 2003.
- [5] S. Y. Lee, E. S. Shim, H. S. Kang, S. S. Pang, J. S. Kang, "Fabrication of ZnO thin film diode using laser annealing" Thin Solid Films, vol. 473, pp. 31-34, February 2005.
- [6] R. Konenkamp, R. C. Word, C. Schlegel, "Vertical nanowire light-emitting diode" Appl. Phys. Lett., vol. 85, pp. 6004–6006 December 2004.
- [7] J. Polleux, A. Gurlo, N. Barsan, U. Weimar, M. Antonietti, M. Niederberger, "Template-free synthesis and assembly of singlecrystalline Tungsten oxide nanowires and their gas-sensing properties" Angewandte Chemie. Int. Edn., vol.45, pp. 261-265, December 2005.
- [8] C. McCullagh, J. M. C. Robertson, D. W. Bahnemann, P. K. J. Robertson, "The application of TiO2 photocatalysis for disinfection of water contaminated with pathogenic micro-organisms: a review" Res Chem Intermed, Vol. 33, pp. 359–375, March 2007.
- [9] A. Sobczynski and A. Dobosz, "Water purification by photocatalysis on semiconductors" Pol. J. Environ. Stud., vol.10, pp.195-205, February 2001.
- [10] Y.W. Baek and Y. J. An. "Microbial toxicity of metal oxide nanoparticles (CuO, NiO, ZnO, and Sb2O3) to Escherichia coli, Bacillus subtilis, and Streptococcus aureus" Sci Total Environ., vol. 409, pp. 1603–1608, March 2011.
- [11] Z. Huang, X. Zheng, D. Yan, G. Yin, X. Liao, Y. Kang, Y. Yao, D. Huanq. "Toxicological effect of ZnO nanoparticles based on bacteria" Langmuir, vol.24 pp.4140-4144, March 2008.
- [12] P. C Maness, S. Smolinski, D.M. Blake, Z. Huang, E. J. Wolfrum, W. A. Jacoby. "Bactericidal activity of photocatalytic TiO<sub>2</sub> reaction: toward an understanding of its killing mechanism" Appl.Environ. Microbiol., vol65, pp.4094-4098. September 1999.
- [13] P. Nagarajan, V. Rajagopalan. "Enhanced bioactivity of ZnO nanoparticles—an antimicrobial study" Sci. Technol. Adv. Mat. Vol.9 pp. 1-7, March 2008.