SOL-GEL/HYDROTHERMAL SYNTHESIS OF MIXED METAL OXIDE OF TITANIUM AND ZINC (TiO_2/ZnO) NANOCOMPOSITES THROUGH DIRECT CHEMICAL METHOD

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ABSTRACT

Mixed metal oxides of titanium and zinc nanocomposites were prepared through sol-gel method under hydrothermal condition using titanium oxy-(1, 2 - pentadione) and zinc acetate without hazardous additives. The resulting composites were characterized by X-Ray Diffractometer (XRD), Scanning Electron Microscope (SEM) and the optical property was determined from the ultraviolet/visible spectrum. The reactions were performed at 90^{O}C and 180^{O}C at different time intervals, in order to determine optimal condition for the formation of the nanoparticles.

Keywords: Nanocomposites, Titanium dioxide, Zinc oxide, Particle sizes, Optical property, X-Ray Diffraction.

INTRODUCTION

Nanostructured metal oxides like titanium dioxide and zinc oxide are regarded as an important class of nanomaterials for their wide range of interesting properties. These properties make them useful for a wide range of applicability for instance, in dye-sensitized solar cells (DSSC) [Seok-Sung *et. al*, 2003], photocatalytic degradation for wastewater purification [Houšcová *et. al*, 2008], magnetic storage, optical and miniaturized electrical devices [Lipeng *et. al,* 2006]. However, these interesting applications depend on the particle sizes and structural morphologies of these metal oxides which are strongly influenced by the synthetic processes [Marci *et. al*, 2001]. In principle, it is possible to process any solid material into nanostructures with proper control on synthetic parameters [Elderstein and Cammarata, 1996]

Titanium dioxide (TiO_2) nanoparticles, a functional semiconductor with an electronic band-gap of 3.3 eV is one of the most extensively studied materials due to its catalytic, electrical, optoelectronic and cosmetology applications. In addition, Fujishima and Honda (1972) discovered that glass coated with titanium dioxide has self-cleaning and anti-fogging properties. However, TiO_2 faces the challenges of higher recombination rate of electron-hole pairs leading to rapid loss of efficiency over a short period of time. Efforts were made to increase its efficiency by successfully doping with other semiconductors like zinc oxide, aluminium oxide and other metal oxide. Zinc oxide (ZnO), another extensively studied semiconducting and piezoelectric material with a direct wide band gap of 3.4 eV which possess an energy-band structure and physical properties similar to those of TiO_2, but has higher electronic mobility that would be favourable for electron transport, with reduction in recombination loss, when used in photovoltaic cell.

Majority of the synthetic processes employed for the production of TiO_2-ZnO nanoparticles use either titanium alkoxides or salts as precursors. For instance, Maolin *et. al* (2010) prepared ZnO/TiO_2 via homogenous hydrolysis of metal alkoxides at low temperature, while Houšcová et al (2008) extensive work on the binary oxide, involved using titanium sulphate and thioacetamide for the synthesis. On the other hand, Seok-Sung *et. al*, (2003) prepared TiO_2/ZnO nanocomposites by cathodic electrodeposition of dye and ZnO on TiO_2-coated ITO glass. One of the versatile method of generating metallic oxide network is through sol-gel process. Sol-gel process leads to the formation of inorganic network by hydrolysis and condensation reaction. It involves the generation of colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase [Nierderberger and Pinna, 2009]. It is important to note that the nature of the products in liquid

phase is highly dependent on the following parameters; the type of the precursor used, concentration, temperature, additives, pressure and in some cases light [Chemseddine, 2000]. In this paper, we report a simple temperature-dependent sol-gel chemical method, without the use of any hazardous solvents, for the synthesis of TiO_2-ZnO nanoparticles using titanium oxy-(1, 2-pentadione) also known as titanium (IV)oxide acetylacetonate and zinc acetate as the precursors.

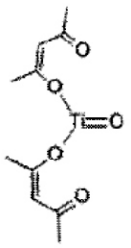
EXPERIMENTAL

Materials

Titanium oxy -(1,2-pentadione) (99%), zinc acetate (99%), methanol, distilled water. All reagents were analytical grade and used without further purification.

Synthesis of TiO_2-ZnO nanoparticles at 90°C and 180°C

The synthesis was carried out according to the following procedure: 0.67g of titanium oxy (1, 2-pentadione) was added to 5ml of distilled water with vigorous stirring. Then 5ml of methanol was added to the above mixture. Then in another beaker, 0.33g of zinc acetate was added to 5ml of distilled water, and then 5ml of methanol was added to the solution. The two solutions were then mixed together under room temperature, this was transferred into a Teflon-lined stainless steel autoclave (Fig.1.), and clean glass slides were placed in the autoclave and kept level during the hydrothermal process. The reaction temperature and time was set at 90°C for six and twelve hours in an electric oven. The whole process was repeated at 180°C for six and twelve hours for comparative studies. The equation for the reaction is given as:



$$+ \quad \text{H-OH} \quad (OR)_3\text{-Ti-OH} + \text{ROH} \quad \text{(hydrolysis)}$$

$$(OR)_3\text{-Ti-OH} + (OR)_3\text{-Ti-OH} \quad (OR)_3\text{-Ti-O-Ti-}(OR)_3 + \text{H-OH} \quad \text{(condensation)}$$

The formation of zinc oxide network from zinc acetate follows the same synthetic routes.

As the number of -Ti-O-Ti- bond increases, aggregation tends to occur in which they begin to interknit into a network forming gel.

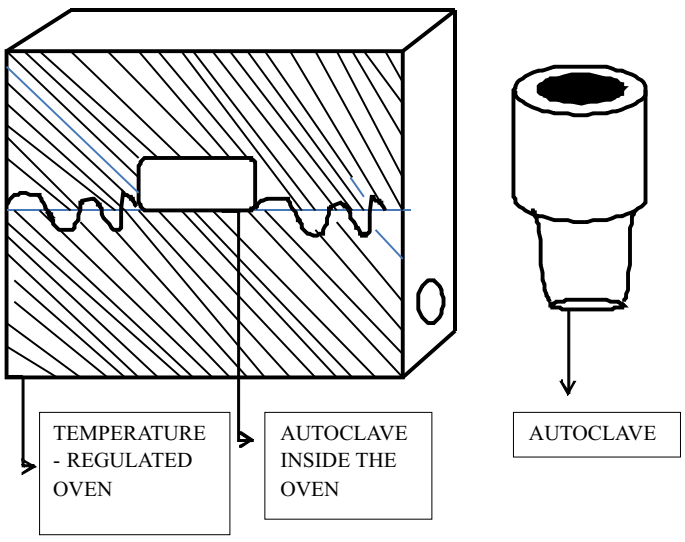


Figure 1: Schematic Representation of the Hydrothermal Set-up (Inset: Autoclave Diagram)

Characterization

The elemental compositional analyses were carried out using Energy-Dispersive X-ray spectrometer. The morphologies and sizes of the synthesized products were characterized with Scanning Electron Microscope (Nova NanoSEM 50 series). The images were processed and particle sizes determination were done using imageJ software; a Java-based imaging Software [Abramoff *et. al*, 2004]. Copper grids coated with holey carbon support film were used to prepare the samples for SEM observations. The X-ray diffraction patterns of the products were obtained using a Rigaku D-max 2200 diffratometer with Cu*Ka* radiation and crystallite sizes were calculated using Sherrer equation. The optical property of the formed TiO_2-ZnO nanoparticles was obtained on ultraviolet/visible spectrophotometer.

RESULTS AND DISCUSSION

Elemental Compositional Analyses

Elemental composition was carried out by energy dispersive X-ray spectrometer (Fig. 2A&B.) in order to have detailed qualitative and quantitative information about all the elements present in the sample. This was done by scanning different portion of representative grains (Fig.2.), to give spectra denoting the existence and the amount in percentage of each element present in the sample. The spectra of the prepared sample confirmed the presence of titanium, zinc and oxygen; the constituent elements of titanium dioxide and zinc oxide. The carbon and silicon detected were from the coating and the machine [Flewitt and Wild, 2003]. The major constituents being titanium (average weight and atomic percentage: 32.40, 14.92), zinc (average weight and atomic percentage: 14.76, 4.94) and oxygen (average weight and atomic percentage: 35.29, 48.56). The EDX gave the stoichiometry ratio of titanium to zinc as two to one, which was in accordance with the ratio of the precursors.

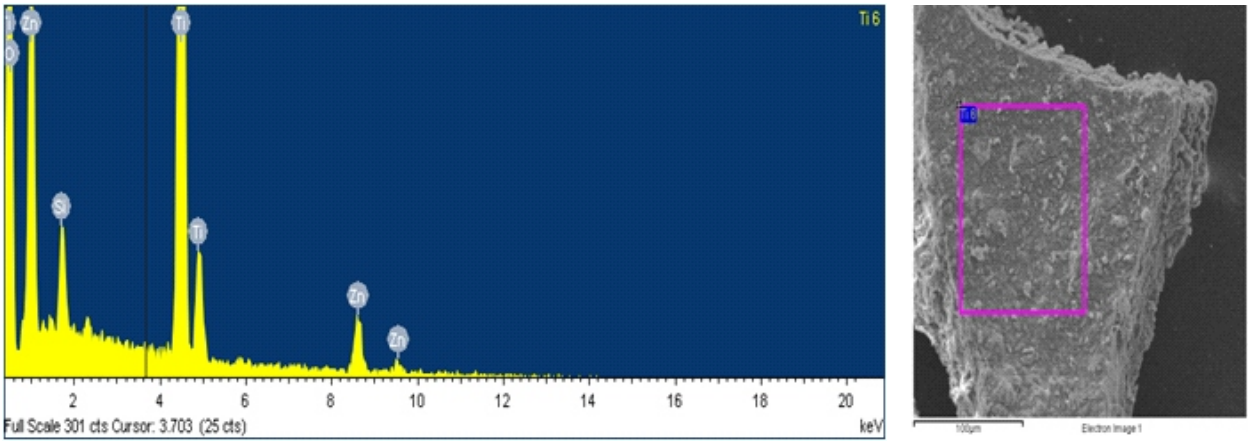


Figure 2A: Energy Dispersive Spectrum of a Representative Grain

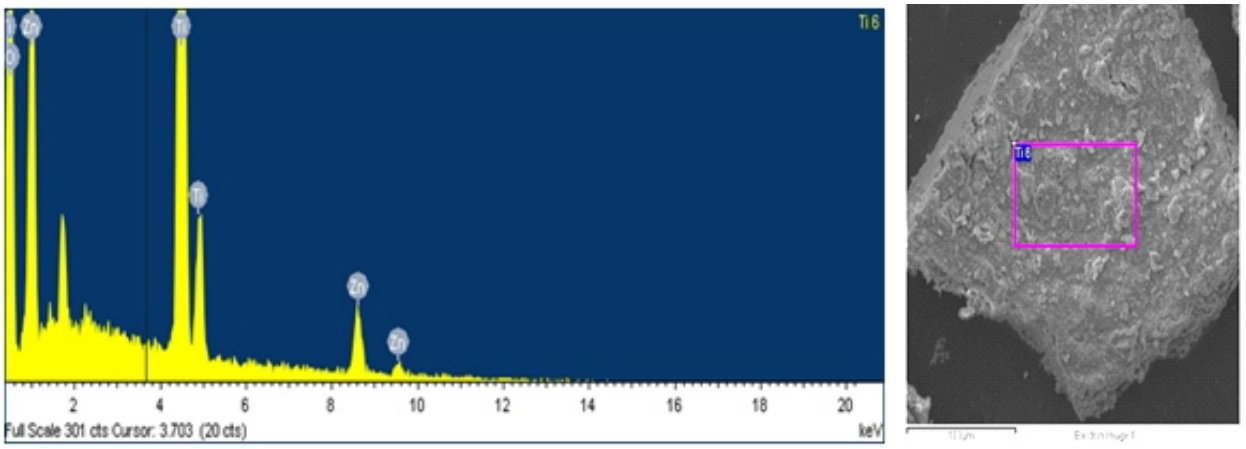


Figure 2B: Energy Dispersive X-ray Spectra of Representative Grains

THE X-RAY DIFFRACTION RESULTS

The fundamental studies of possible thermodynamically equilibrium alloys of TiO_2-ZnO binary system had been shown to produce three major compounds of the type Zn_2TiO_4 (spinel ortho-titanate), $ZnTiO_3$ (perovskite meta-titanate) and $Zn_2Ti_3O_8$ (cubic) at higher temperatures of >500^{O}C for sol-gel methods [Dulin and Rase, 1960; Bartram and Slepetys, 1961; Chang *et. al*; 2004 and Obradović *et. al*, 2005], however studies done at lower temperatures <200^{O}C using the same methods led to the formation TiO_2 and ZnO composites [Maolin et al, 2010; Ali and Hassan, 2008; Houšková *et. al* 2008; Houšková *et. al*, 2007; Mane *et. al*, 2005)

The X-ray diffraction pattern obtained for synthesis at 90^{O}C for 6 and 12 hours (Fig.3A.) showed the product obtained was made up of mixtures of the titanium oxide (Ti_3O_5), rutile phase of titanium dioxide (TiO_2) and zinc acetate hydrate. This showed that at this temperature, zinc acetate was not hydrolysed and according to phase diagram equlibria, there is no possibility of the incorporation of the zinc acetate molecules into the crystal lattice of the titanium dioxide. The XRD pattern showed both sharp and broad peaks indicating the mixtures to be of micro- and nanoparticle sizes [Thamaphat *et. al*, 2008]

The diffraction spectra at 180^{O}C remain the same for 6 and 12 hours [Fig.3B.] with the formation of Titanium dioxide (anatase) and zinc oxide nanocomposites. The characteristics diffration peaks 2 = 26.5^{o}, 36.5^{o}, 38.5^{o}, 48.5^{o} and 55.5^{o} which corresponds to TiO_2 (anatase) and those peaks at 31.8^{o}, 34.4^{o}, 47.7^{o} and 56.9^{o} corresponding to ZnO were observed [Markoç and Özgür, 2009]. The XRD spectrum showed no other apparent phases of the titanuim dioxide and zinc oxide respectively which was in contrast to Houscova *et. al*, (2008) attempt at preparing TiO_2-ZnO nanoparticles through sol-gel method from metal sulphates precursors, with the addition of thioacetamide and sintering at 600^{O}C. It yielded mixture of different products in various phases, whereas, Maolin *et. al* (2010) obtained neat TiO_2-ZnO through sol-gel method at temperature ~200, using tetrabutyl titanate and zinc acetate as precursors. This shows that the choice of precursors and conditions of synthesis played important role to the type of products obtained through this method.

The observed anomalies in the peaks and the slight shift of the peaks to higher 2 values than those reported in the literatures for TiO_2 and ZnO, were probably due to small dimension of crystallites sizes [Zanchet et al, 2000; Bryan and Gamelin, 2005]. The average crystal sizes obtained at 180^{O}C were calculated to be approximately 44-70nm using the Sherrer equation [Patterson, 1989]

$$T \quad \frac{K}{B\cos}$$

Where K is the particle factor (particle factor is 0.9 if the shape is spherical), *B* is the peak half-width, and are the incident angle and X-ray wavelength of 0.152nm respectively.

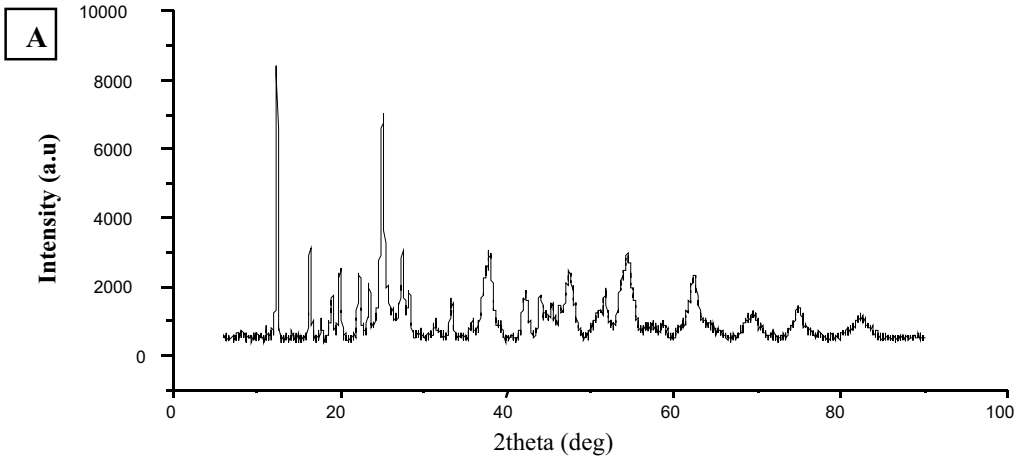


Figure 3A: XRD Spectrum of TiO2-Zn(OOCCH$_3$)$_2$ at 90^{O}C.

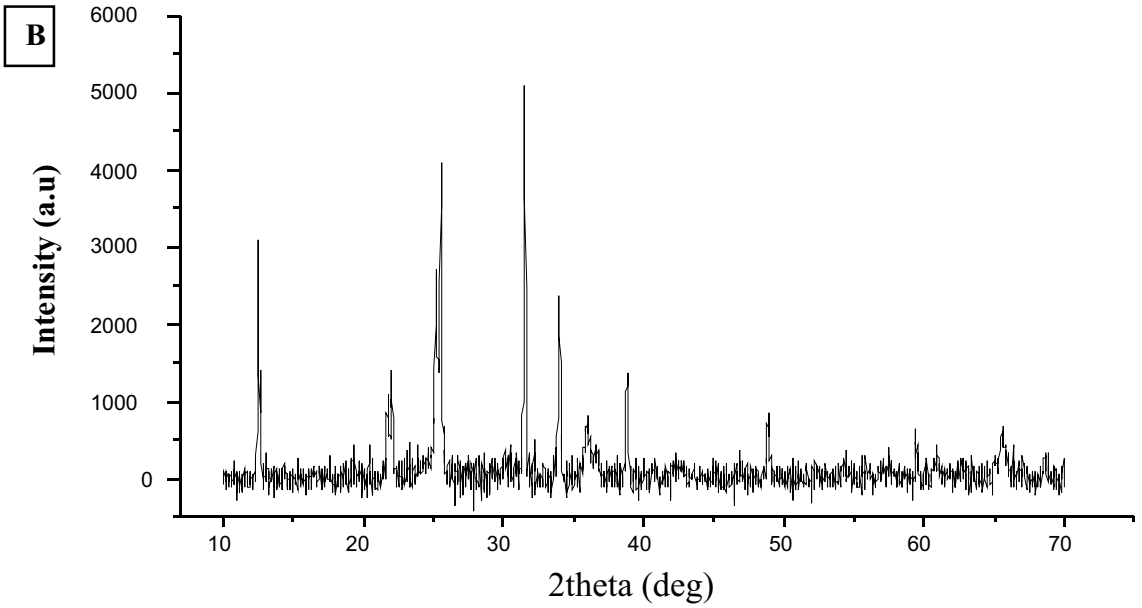


Figure 3B: XRD Spectrum of TiO_2-ZnO at 180^{O}C

SCANNING ELECTRON MICROGRAPH IMAGES

The SEM image obtained for the preparation temperature of 90^{O}C (Fig. 4), in which the XRD result indicated formation $TiO_2/Zn(OOCH_3)_2$, showed a zeolite-like topography with well-defined cages of 2-3 μm and chanel thickness of 174-387nm. This interesting cage and channel topology could be as a result of the evaporation of the water molecules trapped in the zinc acetate lattice.(Capilla and Aranda, 1979).

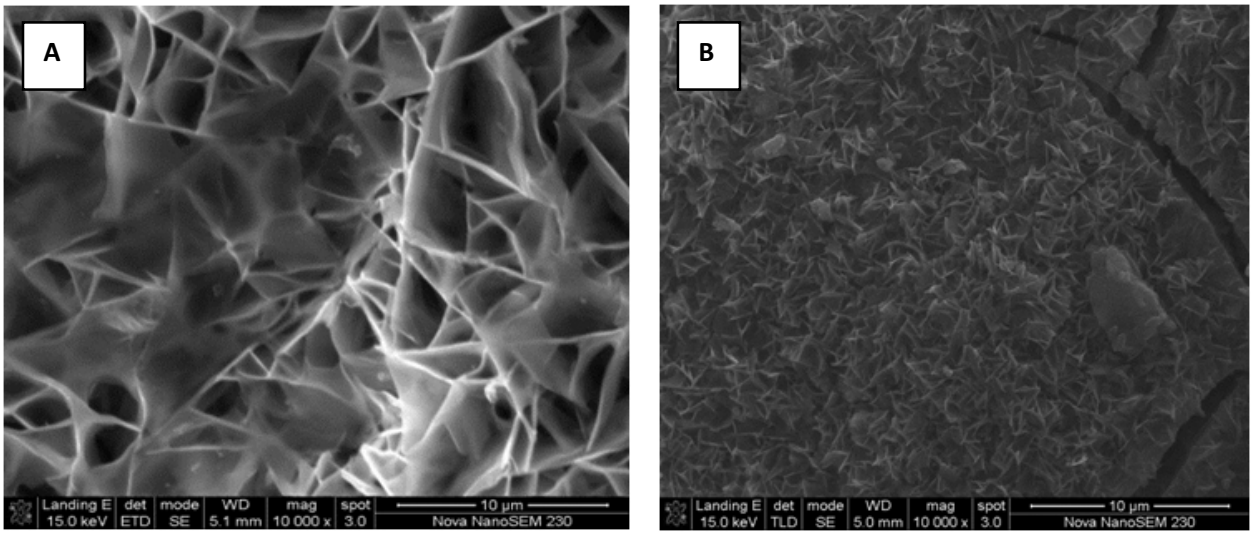


Figure 4: SEM Images of $TiO_2/Zn(OOCCH_3)_2$ Mixtures Prepared at 90^{O}C at Low Magnification (A) 6hrs (B) 12hrs

The SEM images obtained for the composites at 180^{O}C were different from that of 90^{O}C (Fig. 5), the micrographs shows that the original nanoparticles coagulated to form flake-like bigger grains which are like crumbled cookies. These original nanoparticles are planar spheres with diameter ranging from 49- 90nm corresponding to those calculated from x-ray diffraction pattern. This planar spherical structure were also reported by Houšcová *et. al* (2007) and Perkgoz *et. al* (2011) and experimentally provides large surface activation area for enhanced photocatalytic reactions to occur (Perkgoz *et. al,* 2011).

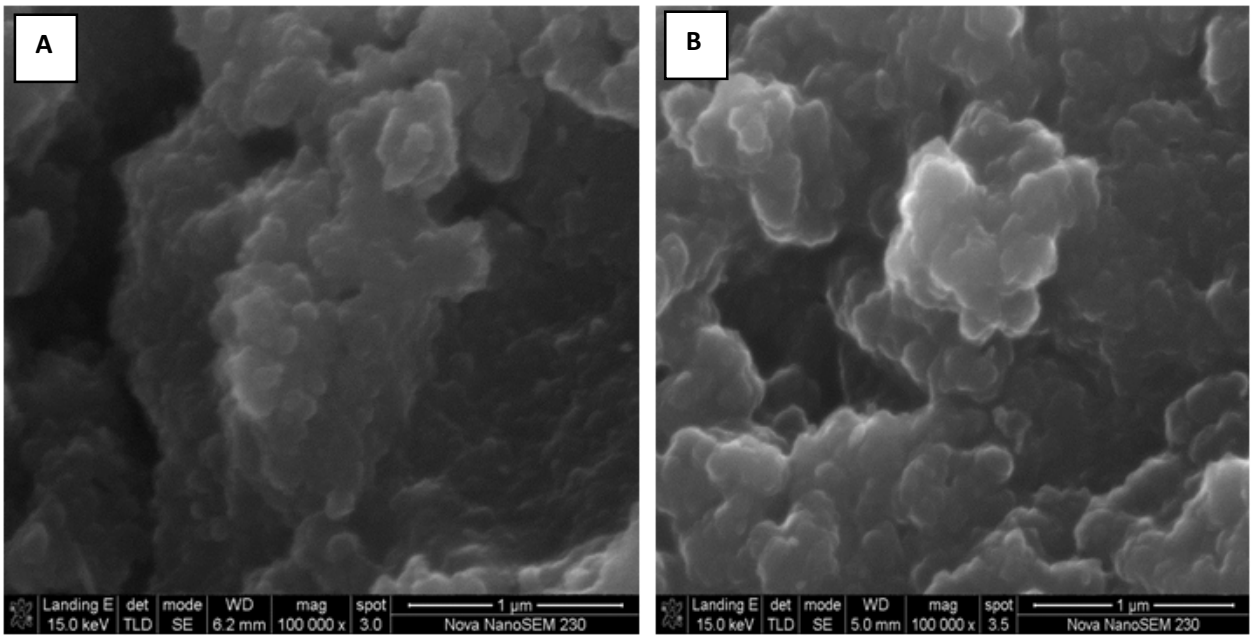


Figure 5: SEM Images of Representative Product Obtained at 180^{O}C for (A) 6 and (B) 12 hrs

ULTRAVIOLETVISIBLE SPECTRUM

Titanium dioxide and zinc oxide do not normally absorb photons in the visible range of the electromagnetic spectrum because they are made up of wide bandgap energies [Markoç and Özgür, 2009]. The relationship between absorption wavelength and band gaps of a semiconductor are inversely related, in that, the increase in absorption wavelength means shorter band gap and vice versa [Lee and Kang, 2010]. The advantage of shorter band gap is the ease at which excited electrons move from the valence to the conduction band in a semiconductor.

According to the literature, TiO_2 and ZnO individually absorbs photons at wavelegth of 376 and 365nm respectively, corresponding to bandgap energies of 3.3 and 3.4 eV (Burdar et al. 2000; Markoç et al, 2009; Chemseddine, 2000). However, the uv-vis spectrum (Fig. 6.) of the prepared TiO_2-ZnO nanocomposites showed a red-shifting in the absorption band towards the near ultraviolet and visible region; around 480-600nm corresponding to 2.53-2.01 eV band gap energies. Similar reported researches also correlate this observed shift of TiO_2-ZnO nanocomposites towards the visible region, for instance, the work done by Maolin *et. al* (2010), Mane *et. al* (2005), Ali and Hassan (2008), Perkgoz *et. al* (2011) supported this observation. It should be noted that, TiO_2 and ZnO individually, are photoinactve at these wavelengths and for the composite to be active, it means there has been a narrowing in the band gap. This phenomenon happened due to the fact that, as a composite with smaller dimensions, its electrons and holes possess different redox energy level for conduction and valence bands. This TiO_2 (anatase) and ZnO could make use of their indirect bandgaps which have narrower bandgap energies than the direct one. The net overall bandgap is reduced facilitating inter-particle tranfer of electron from conduction band of TiO_2 to conduction band of ZnO and vice versa when irradiated with near UV and visible light [Perkgoz *et. al*, 2011; Ou et al, 2006; Ali *et. al*, 2010]. It has been one of the contributing factors to efficient photocatalytic and photovoltaic properties of semiconductor composites (Reddy *et. al*, 2002; Valencia *et. al*, 2010). This feature also make it an attractive materials for usage in dye-sensitized solar cells [Lee and Kang, 2010].

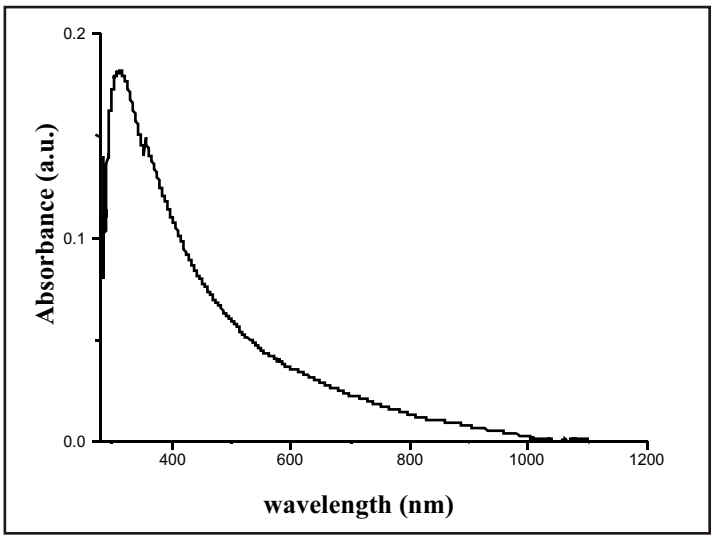


Figure 6: Ultraviolet-visible Spectrum of TiO_2/ZnO Nanocomposite Prepared at 180^{O}C for 12hrs

CONCLUSION

In this paper, the syntheses of TiO_2/ZnO nanocomposites were successfully done at 180^{O}C using titanium oxy- (1, 2-pentadione) as the precursor, at 95^{O}C, the zinc acetate was unable to hydrolyse to the corresponding zinc oxide yielding composites with cage-like topography. The X-ray diffraction pattern showed that there were no chemical bonding between titanium dioxide and zinc oxide, only the formation of composites with particles sizes ranging from 70-180nm correlating with the scanning electron micrograph measurements. Images showed the formation of spherical coagulates with planar surface topography. Its ultraviolet/visible spectrum showed it possesses an electronic transition towards the visible region making it very useful in dye-sensitized solar cells and as photocatalyst.

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