Temperature Dependence of ZnO-TiO_2 Nanocomposites Thin Films Prepared by Sol-gel Spin Coating Method

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Abstract

This research aims to prepare the temperature dependence of ZnO-TiO_2 nanocomposites thin films by sol-gel precipitation and spin coating methods. Zinc acetate dihydrate was used to prepare the ZnO precursor and distilled water was used as solvent. On the other hand, titanium tetrachloride was utlised for the synthesis of TiO_2 anatase nanopowder. The structural properties of synthesized ZnO-TiO_2 nanocomposites were characterized by X-ray Diffraction (XRD). Scanning Electron Microscope (SEM) was used to determine the surface morphology of prepared ZnO-TiO_2 nanocomposites. The optical properties and energy band gap were analysed by UV-Vis spectroscopy. In this study, the temperature dependence of ZnO-TiO_2 nanocomposites thin films were synthesized excellent photocatalytic properties with cost effective and versatile modified sol-gel spin coating technique.

Keywords: *XRD, SEM, UV-Vis spectroscopy, ZnO-TiO_2 Nanocomposite Thin Films*

1. INTRODUCTION

The coupling of two semiconductors can be enhanced both electro-optical properties than a single semiconductor[1]. The coupling of various semiconducting oxides is very useful to absorb a wide range of solar radiation (both UV and visible regions) and to obtain a more efficient electron-hole pair separation and higher photocatalytic activity will be attained[2]. Many researchers have been used many semiconducting oxides such as ZnO, TiO_2, CuO, SnO_2 and the as-prepared composite oxides films to fabricate (explore) the possibilities of promoting the efficiency of perovskite solar cells[3]. Mostly, the composites can found by TiO_2 nanoparticles and other inorganic oxides. Both TiO_2 and ZnO are n-type semiconductor oxides that have excellent properties and extensive application and have attracted a lot of research interest because they possess physical and chemical properties such as non-toxicity, high reactivity the nanoscales, highly abundant and cheap. ZnO and TiO_2 have similar energy bandgaps.Energy bandgap of TiO_2 semiconductors is 3.2 eV (anatase) while ZnO has a wide bandgap energy 3.37 eV and also it has higher electron mobility about 60 meV at room temperature. But ZnO and TiO_2 intrinsic semiconductors characteristics are different while ZnO is direct bandgap energy; TiO_2 is an indirect semiconductor[4, 5]. Higher electron mobility in ZnO thin film will reduce the electron recombination rate by making the injection of a photoexcited electron into the conduction band become easier to promote the performance of solar cell[6]. ZnO is a popular n-type semiconductor oxide which occurs naturally in the form of zincite. Since ZnO is thermally stable at room temperature which is a significant advantage in UV light-emitting devices, UV lasers, field-effect transistors, photoelectrons, gas sensors, solar cells, piezoelectric generators, and photocatalysis[7].TiO_2 is a well-known semiconductor due to its high photocatalytic activity, non-toxic nature and stable in aqueous solution and low cost[8,9]. But TiO_2 thin film has two drawbacks during the photocatalytic process which are the low use of solar spectrum and the relatively high electron-hole recombination rate[10-12]. Since TiO_2 and ZnO have excellent properties and similar bandgap energy, these drawbacks can be possibly overcome by composite these two nano-semiconductor to enhance the photocatalytic efficiency[13].

2 EXPERIMENTAL PROCEDURES

2.1 *Sample preparation of ZnO/ TiO_2 nanocomposites thin films by Sol- gel Spin coating method*

The ZnO/ TiO_2 nanocomposites were synthesized by incorporating with TiO_2 nanopowder and ZnO by using sol-gel method. TiO_2 nanopowder was synthesized by co-precipitating methods by preparatinon of titanium oxide from titanium tetrachloride. The resulting TiO_2 nanopowders were dried at 500 ºC for 2hrs. Zinc acetate dehydrate was dissolved in distilled water to form 1.215 M solution and the as-prepared TiO_2 nanopowder was dissolved in distilled water which was magnetic stirred as 70 ºC for 30 min and cool to room temperature. And then, TiO_2 and ZnO solutions were mixed. The resulting mixture was stirred about 30 min and then cooled to room temperature. An aqueous solution of sodium hydroxides was prepared and stirred at 60 ºC for 15 min and then this solution was cooled to room temperature. The cooled NaOH solution was added drop by drop to the ZnO-TiO_2 solution at room temperature and the resulting solution was stirred vigorously for 6hrs. The ZnO/ TiO_2 precipitation was obtained. After that the mixture solution was put to settle down for 24hrs. And then the upper parts of the solutions were decanted to the beaker and filtered and washed for several times and then adjusted the pH level to get ZnO/TiO_2. To evaporate water, those samples was dried at 100 ºC for 28hrs and then calcined at 500 ºC for 2hrs and ground into powder. The as-prepared ZnO/ TiO_2 nanocomposites powder and 2methoxyl ethanol were mixed and then stirred for 30 min and spin coating for 30 s with 2500 rpm to obtain ZnO/ TiO_2 nanocomposites thin film. The as-prepared these films were calcined at 300 ºC, 400 ºC, 500 ºC, 600 ºC for 1 hr. Fig 1 showed the block diagram of sample preparation of ZnO/TiO_2 nanocomposites thin films.

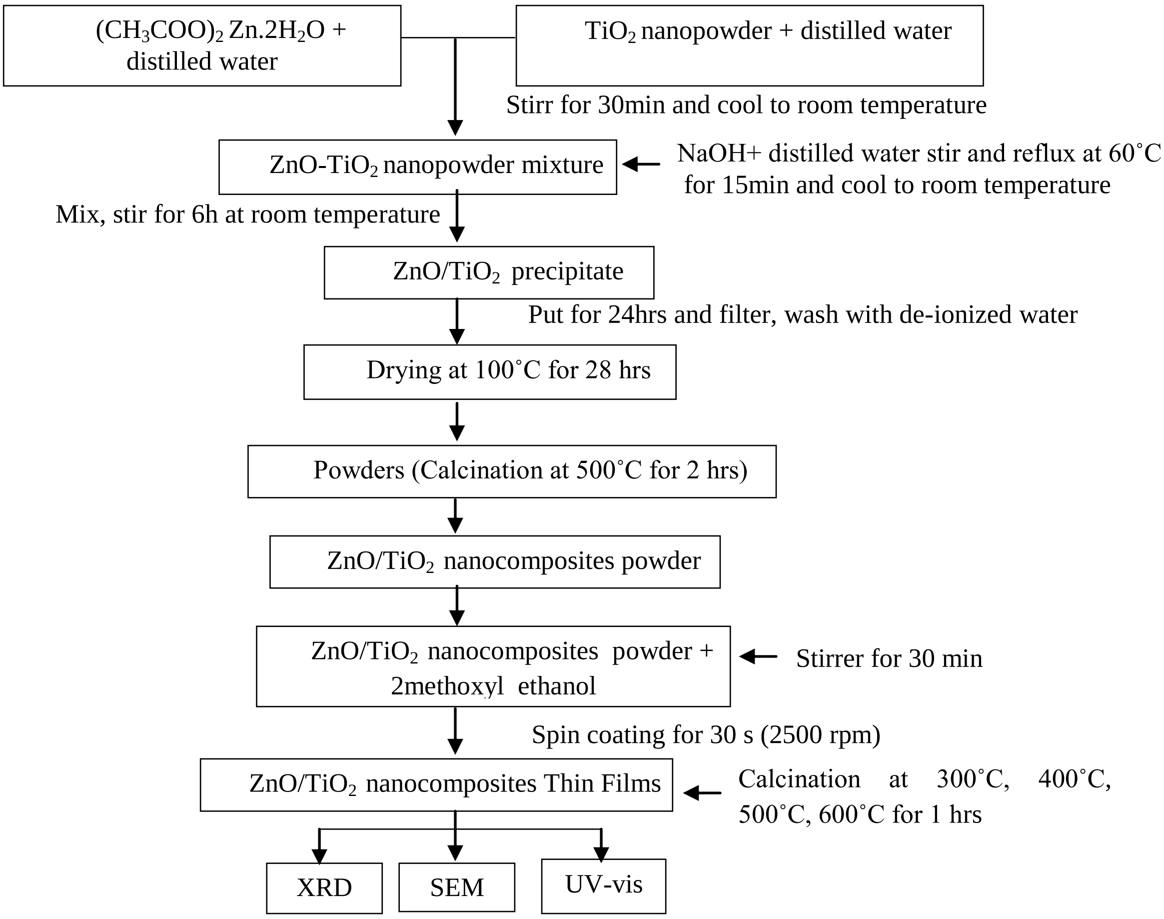

Fig. 1. The block diagram of sample preparation of ZnO/TiO_2 nanocomposites thin films

3. RESULTS and DISCUSSION

3.1 *X-ray Diffraction Analysis of ZnO/TiO_2 nanocomposites thin films*

XRD-analysis was carried out to study the crystal structure and properties of ZnO/TiO_2 nanocomposites thin films at different substrate temperatures. It was performed using monochromatic Cu-K_α radiation (λ =1.54056 Å) operated at 40 kV (tube voltage) and 50 mA (tube current). Specimen was scanned from 10º to 70º in diffraction angle, 2θ with step-size of 10º /min. The reference profile was used as 89-4203>Anatase,syn TiO_2 and 99-0111>ZnO-Zincite, JCPDS library files to identify the observed XRD spectral lines. Fig 2 represented peak comparison of XRD patterns for ZnO/TiO_2 nanocomposites thin films at different substrate temperatures by using Sol-gel Spin coating method. This indicates that hexagonal phase was present in the ZnO/TiO_2 nanocomposites thin films. No impurity peaks were not observed, indicating that the samples were pure. The lattice parameters of TiO_2 are a = b = 3.29 Å, c = 5.23 Å with the hexagonal symmetry. The lattice distortion (c/a) of ZnO/TiO_2 nanocomposites thin films is 1.6. Crystalline size of TiO_2 thin films for all identified peaks which were calculated by using the Debye- Scherrer's equation;

$$D = \frac{k\lambda}{B\cos\theta}$$

where, D is the crystallite size, k is the Scherrer's constant (0.899), λ is the wavelength of X-ray (1.54056 Å), B is the full width at half maximum of the diffraction peak, and θ is the Bragg diffraction angle. The experimental results of the observed lattice parameters, c/a and average crystallite sizes are tabulated in Table 1.

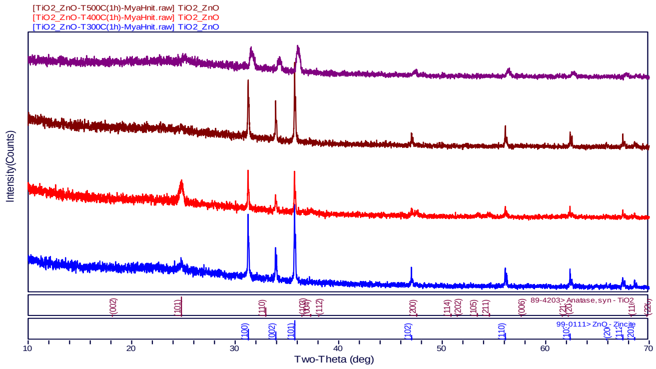

Fig. 2. Represented peak comparison of XRD patterns for ZnO/TiO_2 nanocomposites thin films at different substrate temperatures

Table 1. Average lattice parameters, c/a and average crystallite sizes at different temperatures

Temperature (°C)	Avg: a=b (Å)	Avg: c (Å)	Calculated c/a	Avg: Crystallite size(nm)
300	3.3	5.24	1.6	50.09
400	3.29	5.23	1.6	41.26
500	3.29	5.25	1.6	54.89
600	3.26	5.21	1.6	23.36

3.2 *SEM Analysis of Zno/TiO_2 nanocomposites thin films at Different Temperatures*

Microstructural properties of ZnO/TiO_2 thin films at different temperatures were characterized by using JEOL JSM- 5610 LV Scanning Electron Microscope. Fig 3 (a-d) shows the SEM analysis of ZnO/ TiO_2 nanocomposites thin films at different temperatures exhibit grained microstructure with small crystallite size. The grain sizes were calculated by using well known bar code system. Bar code size was 2 μm with magnification of 15 k . The average grain size of ZnO/TiO_2 thin films were found to be 8.09 μm,8.96 μm ,10.71μm, and 11.35 μm respectively at 300 °C, 400 °C, 500 °C and 600 °C . These figures indicated that most of the grain size was regular structure and a few number of large grain size were found. It looks fairly dense and rough. These consisted of well-defined grain but marked difference. This fact indicated that structural properties were influenced by different temperatures. From the images, it was clearly found that the little amount of pores and grain growth were examined with the increase in process temperatures. The orientation of grain was towards left for all images.

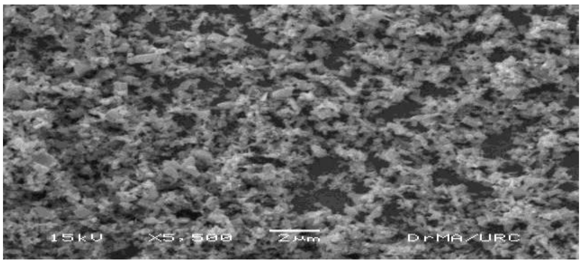

Fig. 3.(a) SEM image of ZnO/TiO_2 thin film at 300 ºC

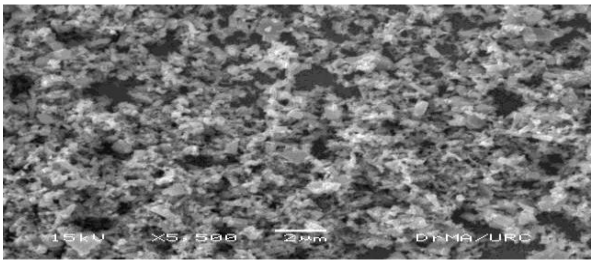

Fig. 3.(b) SEM image of ZnO/TiO_2 thin film at 400 ºC

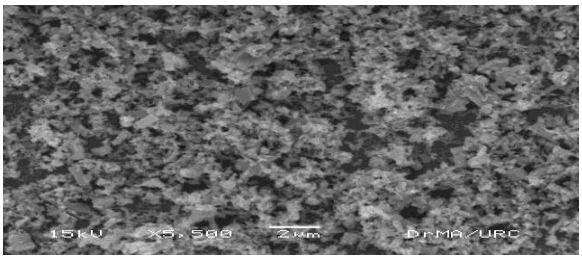

Fig. 3.(c) SEM image of ZnO/TiO_2 thin film at 500 ºC

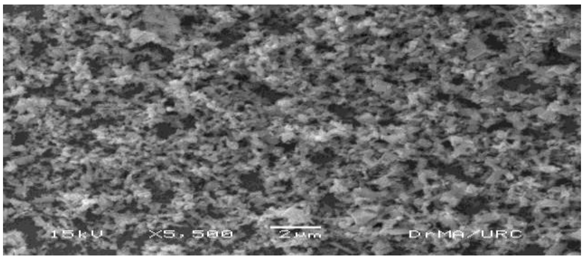

Fig. 3.(d) SEM image of ZnO/TiO_2 thin film at 600 ºC

3.3 *UV-vis Analysis of ZnO/TiO$_2$ nanocomposites thin films at Different Temperatures*

The absorption spectrum and the energy band gap of ZnO/TiO$_2$ nanocomposite films were performed using UV-vis spectrometer (SMIMADZU). Fig 4 (a-d) showed the absorption spectra of 2-methoxyl ethanol to absorb photons from visible light spectrum. It was found that the maximum absorption of wavelength obtained by ethanol is in the visible region. The wavelength range of spectrum laid between 400 nm to 700 nm. The ZnO/TiO$_2$ nanocomposite films showed good absorption level of Ultraviolet and visible regions. The intensity of absorption peak increases with increasing temperature and the ZnO/TiO$_2$ Nanocomposite thin films were dispersed in the aqueous solution with no evidence for aggregation in UV- Vis absorption spectrum. Table 2 showed the average energy band-gap of ZnO/TiO$_2$ nanocomposite films at different temperatures.

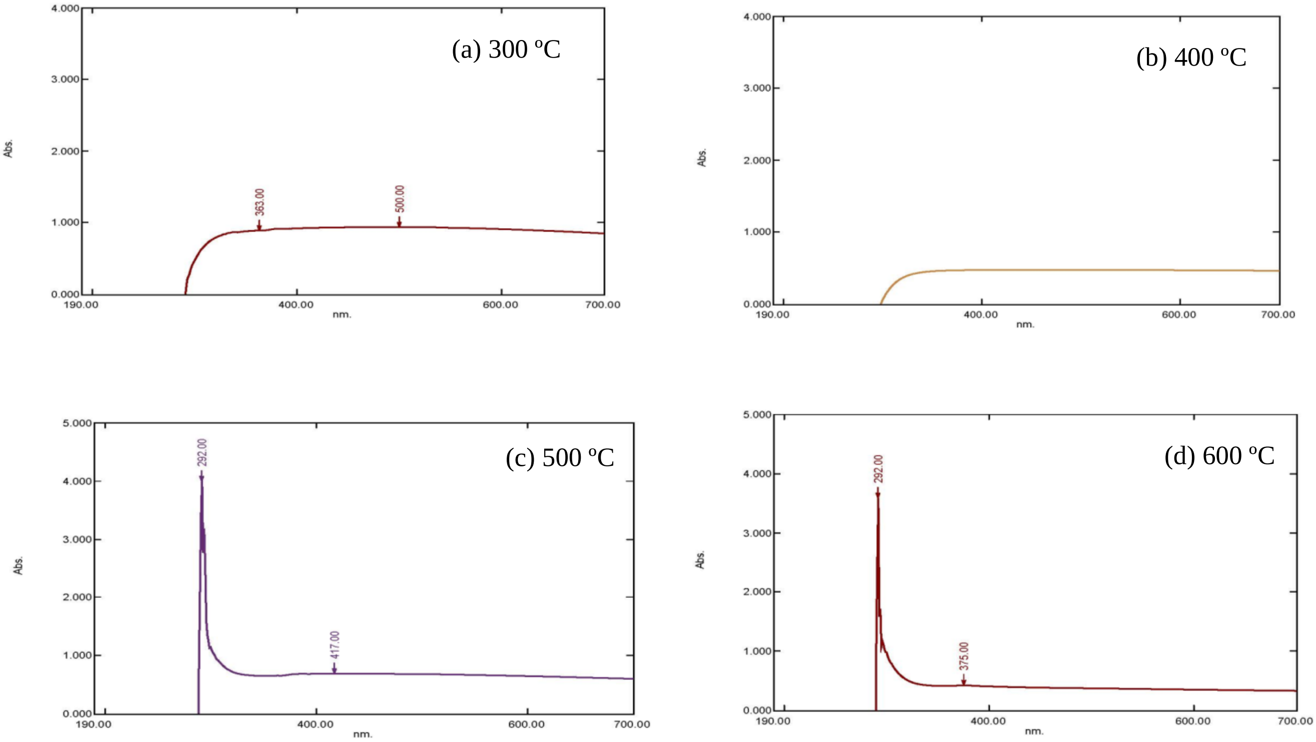

Fig .4. The absorption spectra of ethanol to absorb photons from visible light spectrum at (a) 300 ºC, (b) 400 ºC, (c) 500 ºC and (d) 600 ºC

Table 2. The average energy band-gap of ZnO/TiO$_2$ nanocomposite films at different temperatures

Temperature (ºC)	Avg Energy Bandgap (eV)	Standard Energy Bandgap(eV)
300	3.44	3.2 – 3.8
400	3.52	3.2 – 3.8
500	3.67	3.2 – 3.8
600	3.78	3.2 – 3.8

4. CONCLUSIONS

In this research work, the synthesis and characterization of ZnO/TiO$_2$ nanocomposites thin film were successfully implemented by Sol gel, spin coating methods.The average crystallite size of ZnO/TiO$_2$ nanocomposites thin film was found to be 50.09 nm at 300ºC ,41.26nm at 400 ºC, 54.89nm at 500 ºC and 23.36 nm at 600 ºC respectively. The fabrication and characterization of ZnO/TiO$_2$ thin films have been deposited on glass substrate by spin coating method at different substrate temperatures. According to XRD analysis, all the peak heights and peak positions of different temperatures were in good agreement with library files of XRD machine. The XRD pattern revealed that these films were hexagonal structure. According to

XRD analysis, the smallest crystalline sizes of ZnO/TiO_2 thin films was found to be about 23.36 nm at 600 ºC .From SEM images, SEM analysis was examined to be smooth, uniform, crack free and agglomerated spread layers of ZnO/TiO_2 thin films. This suggested that agglomerated grain size increases with increasing process temperatures**.** The experimental finding resulted from this research work indicated that the crystal structure, phase formation and surface morphology of ZnO/TiO_2 thin films were influenced by annealing different temperatures. UV-Vis showed that the dominant sharp band of ZnO/TiO_2 thin films was observed around UV –visible range. The intensity of absorption peak increases with increasing temperatures. Therefore this ZnO/TiO_2 nanocomposite films can be used as the electron transporting layers for perovskite solar cell.

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