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Structural Characterization and Synthesis of ZnO / TiO2 Nano Composites

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Abstract: Titanium dioxide (TiO2) has many characteristics such as strong oxidation state, biocompatibility and acceptable mechanical properties; TiO2 is among the materials that are frequently used in biological and medical applications. Nowadays, increasing efficiency of titanium dioxide involves doping it with elements such as silver, zinc and iron and is being favored. In this study, nanoparticles of TiO2 with ZnO were synthesized by the impregnation method. ZnO nanoparticles were impregnated with different concentrations of TiO2 and the result was compared and evaluated. In order to identify the present phases in the structure, X-ray diffraction analysis was used. Also for the characterization of the nanocomposites Field Emission Scanning Electron Microscope (FESEM), Ultraviolet-visible spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FTIR), and were used The results showed that impregnation method could successfully produce Nanocomposites of ZnO-TiO2 with the expected combination.
Keywords: Titanium dioxide, Zinc, Emission Scanning Electron Microscope (FESEM), Ultraviolet-visible spectroscopy (UV-Vis), Fourier-transform infrared spectroscopy (FTIR), solar cells, Structural characterization, nanometer ZnO/TiO_2 composite powder, composite structure of nano-TiO_2.

1 Introduction

Titanium dioxide is an important photo-catalysis material. Its characters include the high activity in photo-catalyzing organic materials, stability in chemical property, bearing the chemical and photochemical erosion and non-toxicity. It has great potential in disposing of sewage, purifying the air, etc. [1-3]. However, titanium dioxide is wide-gap material, it only absorbs the ultraviolet light part of the solar spectrum and the efficiency of using solar energy is low so that its applications are limited.
Using the coupling between Nano-particles can increase the efficiency of using solar energy to a great extent and increase the speed and efficiency of photo-catalyzing organic matters. The Nano-composition and developing new techniques for it becomes a hot spot in this field. Nano-ZnO and TiO_2 are important in the research of nanometer materials field. They have good performance and wide applications in optics and photo-electrochemistry [5, 6]. Documents show that nanometer ZnO/TiO_2 composite powder has great scattering power for visible light of 400-700 nm and has great abilities to absorb the ultraviolet radiation of 200-350 in the spectrum. So that it has great ability to prevent ultraviolet radiation and it improves a lot compared with sole-functioned nanometer ZnO and TiO_2 powder [7, 8].
The purpose of this article is to look for simple ways and techniques to prepare Nano-ZnO and the composite structure of nano-TiO_2 to provider a wider basis for the research of its performances in the future. We used X-ray diffraction, transmission electron microscope etc. to characterize the phase and appearance and analyses the performance of the products.

2 Experimental Section

2.1 Synthesis of ZnO/TiO_2 nanocomposites

In this experiment, different material concentrations of non-composite material of ZnO/TiO2 is synthesized and then after preparing their dough, they used in solar cells. Zn $(NO_3)2 6H_2O$ with 99.8% purity was received from Fisher Scientific in powder form. Commercial anatase TiO_2 (98%) was purchased from Acros Organics and utilized as a support for the synthesis of ZnO/TiO_2 composite. All chemicals were used without further modifications. Deionized water that was used in the composite synthesis was obtained from the laboratory. Wet incipient wetness impregnation method was used for the synthesis of ZnO/TiO_2 composite to achieve the higher loading of ZnO

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on the surface of commercial anatase TiO_2 support 1.36 g of Zn $(NO_3)26H_2O$ was dissolved in 2 mL of deionized water for preparation of 3%ZnO/TiO_2 composite. A homogenous mixture of this solution was obtained by stirring it for 30 min with an electromagnetic stirrer at room temperature. Meanwhile, 10 g of TiO_2 with an average diameter of 200 nm was dried at 200 C for 1 h. The dried TiO_2 was further immersed into the Zn solution and mixed vigorously with a stirrer for 15 min to achieve a homogenous absorption of Zn solution over the surface of TiO_2. The ZnO/TiO_2 composite was aged at 110 C for 24 h inside an oven. The synthesized composite was then calcined at 400 C for 5 h with a ramp of 4 C/min by using a muffle furnace for removal of metal counter ions and adsorbed water in the prepared composite. Finally, the calcined sample was stored in a sample bottle for further use in DSSCs. Similarly, 2.27 g and 4.56 g of Zn $(NO_3)26H_2O$ was used for the synthesis of 5%ZnO/TiO_2, and 10%ZnO/TiO_2 composites, respectively.

2.2 Characterization of ZnO/TiO_2 composites

After preparing intended Nanocomposites, analysis has been done for comparing of synthesized Nanocomposite with industrial TiO2 power that is, X-ray diffraction (XRD), field-emission-scanning-electron-microscopy(FE-SEM), Ultraviolet-visible spectroscopy (UV-Vis) and Fourier-transform infrared spectroscopy (FTIR) analyses.
Instruments used for morphology character finding of the level has been done using an electronic scanning microscope of field development (FE-SEM), made by TE-SCAN Company and pyro symmetry of absorption by BETBELSORPMINI Instrument.
Characterization of the structure was done with the use of x-ray diffraction STOE-IPDS 2T diffractometer. Optic characterization composed of ultraviolet and seen absorb spectrum in room temperature by Spectrophotometer with ocean optics HR 4000 spectrometer and infrared spectroscopy has been done by FTIR WQF-51OFT- IR spectrometer.

3 Results and Discussion

3.1 X-ray diffraction (XRD)

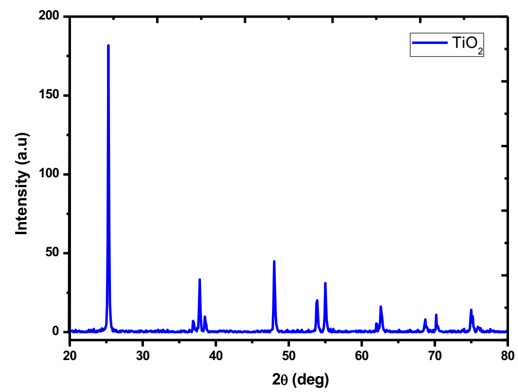
XRD analysis of bare TiO_2 and ZnO/TiO_2 composites were given in Figure 1. These XRD charts are drawn by X' Pert High Score software. XRD pattern and corresponding characteristic 2θ values confirmed that TiO2 particles in the composites are distinguished as anatase phase due to diffraction peaks obtained at 25.3, 37.8, 48.1, 53.9 and 55.1, 62.8, 68.9 and 75.3. The peaks appeared at 31.7, 34.3, 36.9, and 70 were corresponding to zincate ZnO [9]. The presence of minor peaks at 31.7, 34.3 and 36.9 for 3%ZnO/ TiO_2 were due to the allow amount of ZnO. Therefore, increasing the loading of ZnO elevated the peaks of ZnO. Based on the XRD analysis, it can be concluded that composite samples consisted of anatase TiO_2 and zincate ZnO. Based on XRD analysis we can conclude that charts of synthesized Nanocomposites have TiO_2 anatase phase and ZnO Wurtzite structure. Optic properties have a direct relationship with Nano sizes. Optic spectrum, and density of optic spectrum that is semiconductor changes when its size changes. Nanoparticles gained with data of the main part in each material with Scherer formula that is as follows:

$$D = (K \times \lambda)/(\beta \cos\theta) \quad (1)$$

Where K is Scherer fix number= 0/9 and λ is x-ray wave length=1/54a and β is peak width in the middle of maximum height and θ is brag diffraction angle and D is particles size based on Nanometer. Distance between Nano grid pages can be calculated from brag rule that is shown in relation2.

$$d = n\lambda / \sin\theta \quad (2)$$

By using Scherer formula and data of x-ray diffraction spectrum, size of Nanoparticles in the middle for different loading of ZnO is 50 nm.



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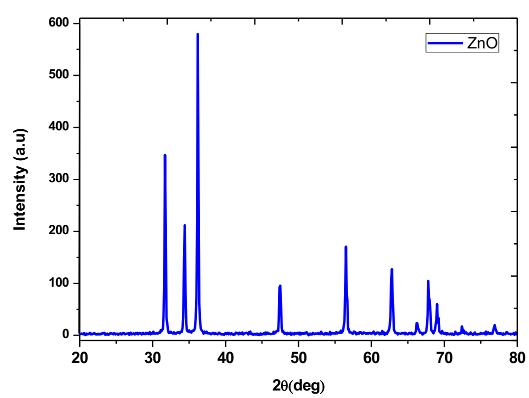

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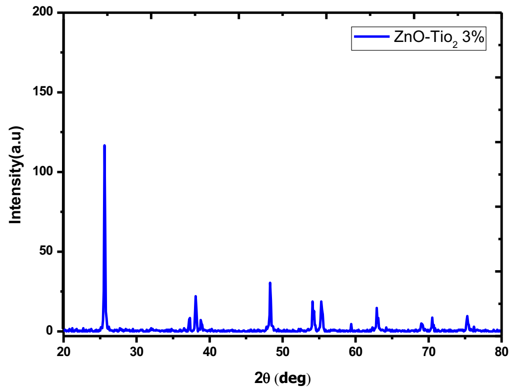

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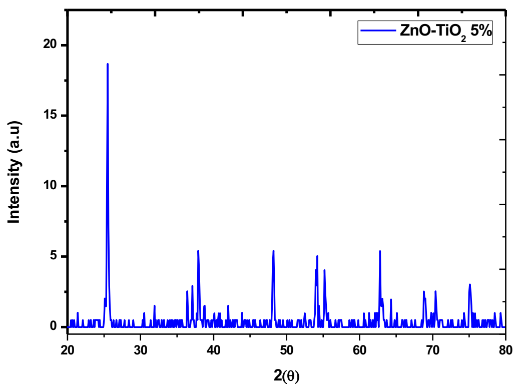

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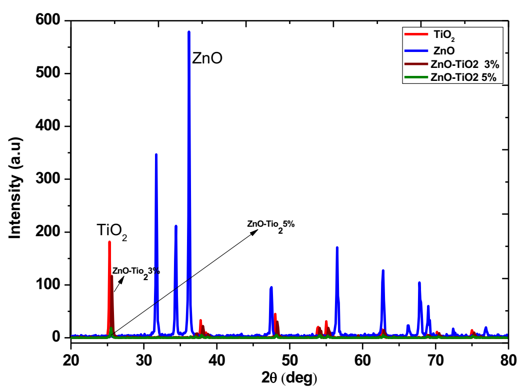


(e)

Figure 1. XRD pattern of (a) bare TiO2 (b) ZnO (c) 3% ZnO/TiO_2(d) 5% ZnO/TiO_2 and (e) XRD for all samples

3.2 Measuring field-emission-scanning-electron-microscopy (FE-SEM)

The FE-SEM images of calcined ZnO/TiO2 composites at different ZnO loading are given in Figure 2. The impregnation of ZnO over TiO_2 is evident from the comparison of FE- SEM images of bare TiO_2 (Figure 2(a–b)) and synthesized composites at different loading of ZnO (Figure 2(c– e)). At a lower amount of ZnO, TiO_2 was the main component of the synthesized composites and ZnO was widely dispersed on the surface of TiO2. It also showed that the dispersion of ZnO was homogeneous over the surface of support for 10%ZnO/TiO_2. Image analysis clearly showed an increase in surface coverage of TiO2 by ZnO on increasing the loading of ZnO. Figure 2. at 1 μm magnification demonstrates the slight agglomeration and irregular spherical morphology of the calcined ZnO/TiO_2 composites [10]. The particle size of the synthesized composites was laid in the range of 15 nm– 100 nm with an average particle diameter of 50 nm. But because of the high density of Nanoparticles and tendency of the gathering of very big particles by using Scherer equation, the size of these Nanoparticles is the reason for particles scattering.

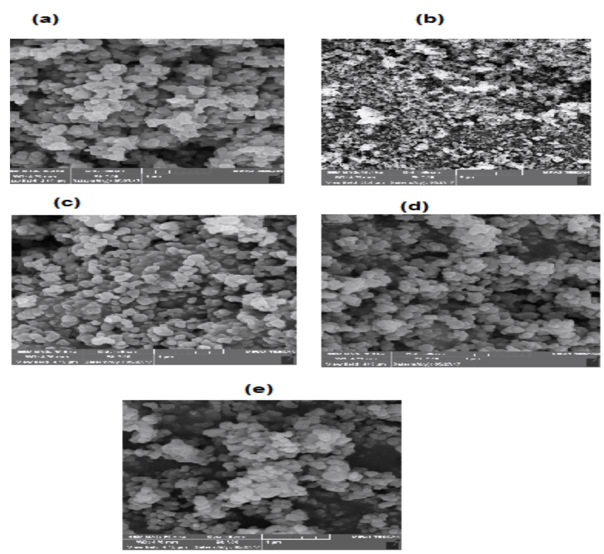
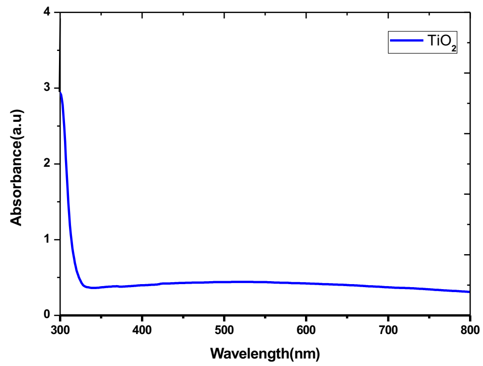


Figure 2. FE- SEM images of ZnO/TiO_2 composites (a) bare TiO_2 at 1 μm (b) bare TiO2 at 5 μm (c) 3% ZnO/TiO2 at 1 μm (d) 5% ZnO/TiO_2 at 1 μm (e) 10% ZnO/TiO_2 at 1 μm.

3.3 Ultraviolet-visible spectroscopy

One of the amazing methods for Nanoparticle analysis is using binders of the visible area and ultraviolet electromagnetic waves that are properties of adsorption and ultra-emit. Figure 3. is ultraviolet and visible adsorption binder of industrial powder TiO_2, ZnO and Nanocomposites of ZnO/TiO_2. As you can see in industrial powder, titanium dioxide has the highest adsorption invisible part, and in zinc oxide powder we have the highest adsorption in the ultraviolet region. Spectroscopy curve of visible-ultraviolet of Nanocomposites as we can see in curves when ZnO loading increased, adsorption is more in the ultraviolet region. Adsorption in visible region decreases with much loading of ZnO. This decrease in adsorption is related with a decrease of photoanode level because of ZnO saturation in TiO_2 level and this is a reason of efficiency decrease or load increase of ZnO.



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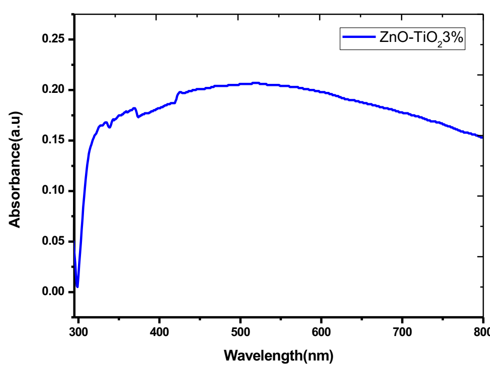

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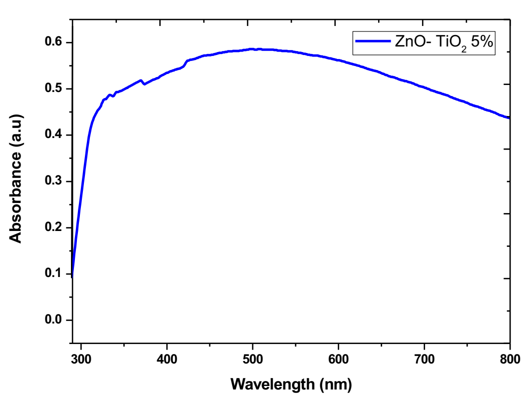

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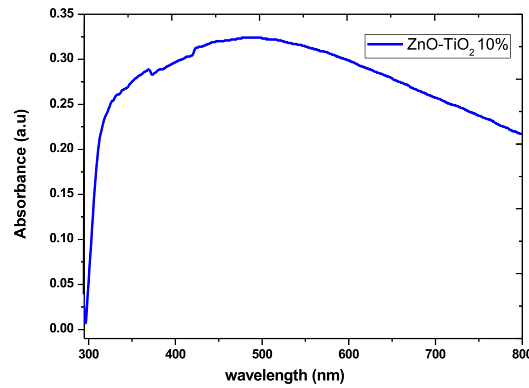


(d)

Figure 3. Ultraviolet visible spectroscopy of (a) bare TiO_2 (b) 3% ZnO/TiO_2(c) 5% ZnO/TiO_2 (d) 10% ZnO/TiO_2

The problem in Nanocomposite is the energy gained from Taok equation. Adsorption coefficient α is good with adsorption area that adsorption amount (A) and samples thickness (t) gained from equation (3).

$$\alpha = 2.3026A/t \quad (3)$$

So the attenuation coefficient (k) gained from equation (4).

$$k = \alpha\lambda / 4\pi \quad (4)$$

Nanoparticle energy loss can be gained from equation (5).

$$\alpha h\nu = k[(h\nu - Eg)] \wedge (n) \quad (5)$$

In this equation, α is optic adsorption coefficient, $h\nu$ is adsorption photon energy, Eg is energy loss and k is attenuation coefficient. Another important parameter that has been calculated from ultra violet-adsorption spectrum curve is the depth of penetration that is equal to the absorption coefficient. The invisible wavelength and depth of penetration is high but in ultraviolet wavelength because of powerful electron bit, conducting electron and descent photons reaches to least amount. Figure 4 is Taok curve of Nano composites. As you see Nanocomposite energy loss in comparison with titanium dioxide energy loss (3.22 eV) increased and by much loading of ZnO Nanocomposite energy loss increased.

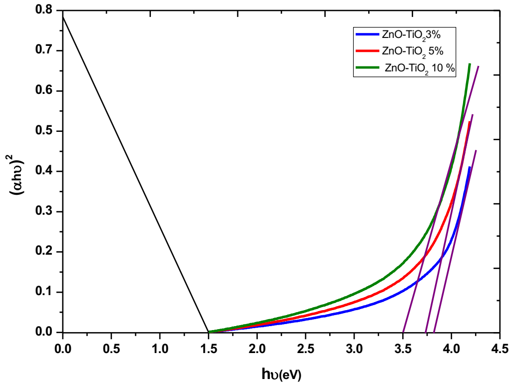
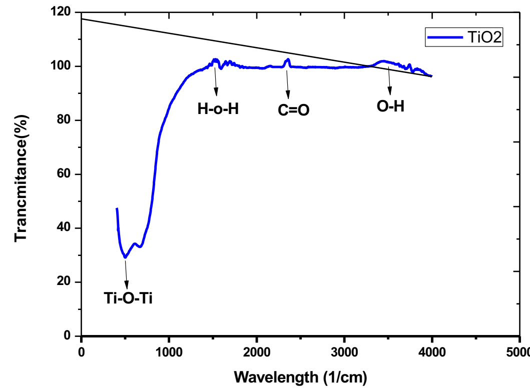
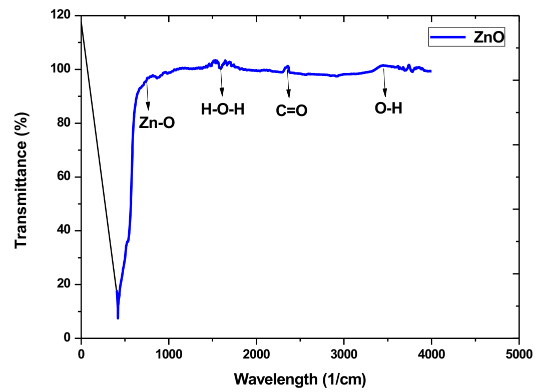


Figure 4. Bnd gap of (a) 3% ZnO/TiO_2 (b) 5% ZnO/TiO_2(c) 10% ZnO/TiO_2



(a)



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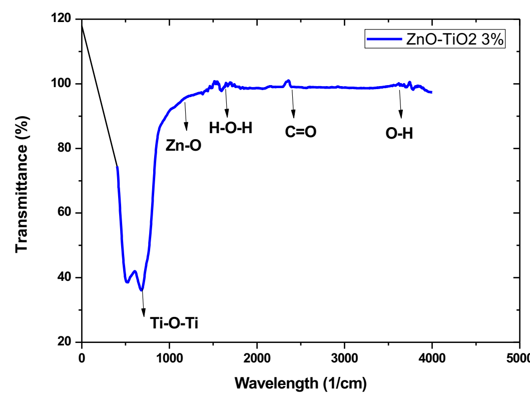

(C)

Figure 5. Fourier-transform infrared spectroscopy of (a) bare TiO_2 (b)ZnO (c) 3% ZnO/TiO_2

3.4 Fourier-transform infrared spectroscopy (FTIR)

This technique works based on measuring the vibrating frequency of chemical bonds between atoms. Gained spectrum in infrared spectroscopy of Fourier Transform for the industrial powder of TiO_2 and ZnO for synthesized Nanocomposites is shown in figure 5. In the spectrum of industrial powder of TiO_2 there are peaks in 400-900 cm-1 that is for tensile vibrations of TiO of anatase of TiO_2. Peaks in region 1630, 3450 cm-1 are for bending and the tensile band of O-H bond that confirmed the existence of hydroxyl group in TiO_2 and existence of these peaks is the probability of their adsorption in ion level of Ti+4. Also, the peak in 2345 cm-1 is for linked vibrations of C=O. This situation shows that in industrial powder level of TiO_2 there are a little water and CO2 that is absorbed from the air's atmosphere. In the infrared spectrum of ZnO industrial powder, is a strong band in 469 cm-1 that is for tensile frequencies of Zn-O. Peaks in 1630 and 3450 cm-1 are for bending and a tensile band of O-H. As you can see three peaks in ZnO industrial powder is exists in a spectrum of industrial powder of TiO_2. In figure 5, the infrared spectrum for synthesized Nanocomposite is shown. As you can see a band in 469 cm-1 exists that is for the tensile frequency of Zn-O and there are peaks in 400-900 cm-1 that is for tensile vibrations of Ti-O of anatase phase of TiO_2 that is a confirmation of the existence of two materials of titanium dioxide and zinc oxide in synthesized Nanocomposites. Also three other peaks we can see that are those who existed in industrial powder and as we said because of Little adsorption of water and CO_2 from the air, it can have a negative effect in solar cell efficiency and synthesis should be done with high accuracy and in an isolated environment that peaks become very little.

4 Conclusions

We used impregnation method to prepare ZnO/TiO_2 nano-composite structure with TiO_2 nano powder as the base. ZnO covers TiO_2 nano powder evenly. Scanning electron pictures are done from Nanocomposite powder and then we saw that these materials have a useful structure. X-ray diffraction is also done for structural properties finding and by using results they knew synthesized material and crystal structure parameters of that gained. Visible optic adsorption spectrum is done for properties finding of material and they saw that %3 ZnO/TiO_2 Nanocomposite had high adsorption towards other composites and it can be compared with pure TiO_2. Compared with pure TiO_2, ZnO/TiO_2 nano-composite structure has a better ability to absorb ultraviolet light.

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