

Investigation on the structural, morphological and photochemical properties of spin-coated TiO₂ and ZnO thin films prepared by sol-gel method

ABSTRACT

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Received: 15 November 2012

Received in revised form 11 Feb 2013

Accepted: 17 March 2013

In this study, TiO₂ and ZnO nanofilms were prepared by sol-gel spin-coating method. Nanofilms were characterized by X-ray Diffraction (XRD), Energy Dispersive Analysis of X-ray (EDX), Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FE-ESM). Structural and morphological properties of nanofilms were investigated. The average crystalline size of TiO₂ and ZnO nanoparticles which were obtained from the ignition of sols were obtained 80 and 50 nm, respectively. The morphological properties of nanofilms showed that the TiO₂/ZnO nanocomposite film was strongly related to the steps of coating. Also, photocatalytic degradation of methylene blue on the surface of these nanofilms under UV light irradiation was studied and results were compared to each other.

Keywords: Zinc Oxide; Titanium dioxide; Nanoparticles; Thin film; Photocatalyst; Coatings.

INTRODUCTION

Nowadays, the production of thin layers of materials like zinc oxide and titanium dioxide is very important because of their attractive applications such as transparent conducting oxide (TCO) arise from the combination of optical transparency, the electrical conductivity in doped zinc oxide [1], high photocatalytic activation [2], information technology devices including displays, solar cells and sensors [3], photoconducting properties [4], high dielectric constant and is transparent to visible light [5]. In recent years, ZnO and TiO₂ nanostructures have attracted great attention in both fundamental studies and application. Zinc oxide, ZnO, is an inexpensive n-type semiconductor with a wide band gap of 3.3 eV, which crystallizes in the hexagonal wurtzite structure. This property makes it good candidate as host materials for the visible and infrared emission of various rare-earth ions [6].

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Also, among the photocatalysts, nanocrystalline TiO_2 is widely used in water and air purification, in self-cleaning process and as bactericide under light irradiation. Photocatalysis with TiO_2 anatase is more efficient than rutile or brookite. Nanocrystalline anatase is commonly prepared with high surface area having a high degree of crystallinity [7].

During the last years, ZnO thin films have been studied extensively due to their potential applications, as piezoelectric transducers, optical waveguides, acousto-optic media, surface acoustic wave devices, conductive gas sensors, transparent conductive electrodes, solar cell windows, and varistors [8-10]. On the other hand, TiO_2 self-cleaning property can be bestowed on many different types of surface, and some TiO_2 -based self-cleaning products such as tiles, glass, and plastics have been commercially available. TiO_2 self-cleaning coatings are finding increasing applications in buildings, public furniture and auto industry. The self-cleaning mechanism is mainly based on TiO_2 photocatalysis, where photo-induced electron-holes catalyze reaction on the surface [11-15].

A rich variety of techniques about the preparation of thin films including sputtering [16], chemical vapor deposition (CVD) [17], spray pyrolysis [18], and sol-gel process [19-22] are known. Among these methods, the sol-gel method not only enables easy fabrication of a large area thin film at a low cost, but also easily controls over the film composition and uniformity of thickness [23]. Sol-gel spin-coating processing technique presents an inexpensive alternative for fabrication of thin film. The chemical composition can be controlled with relative ease and large area fabrication of the thin film can be achieved by sol-gel technique in a cost effective way [24].

In this paper, the TiO_2 and ZnO nanofilms were prepared by the sol-gel spin-coating method and different coating conditions were investigated on the structural, morphological properties and thickness of nanofilms. TiO_2 and ZnO sol firstly synthesized by a simple sol-gel route from an available reagents and then spin-coating was performed to obtain thin layer films. Nanofilms were used to study on the photodegradation of methylene blue and the photocatalytic properties of them were compared to each others.

EXPERIMENTAL**Material**

Titanium isopropoxide, $\text{Ti}(\text{OC}_3\text{H}_7)_4$, acetyl acetone, $\text{C}_5\text{H}_8\text{O}_2$, ethanol, $\text{C}_2\text{H}_5\text{OH}$, zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, isopropanol, $\text{C}_3\text{H}_8\text{O}$, and diethanolamine, $\text{C}_4\text{H}_{11}\text{NO}_2$, were purchased from Merck Company and used without further purification as starting materials.

Fabrication of TiO_2 Sol

Titanium isopropoxide was used as a precursor and TiO_2 sol was prepared at room temperature as follows. At first, 9.6 ml of TTIP (0.0325 mol) was added into 5.16 ml of acetyl acetone (0.05 mol) and vigorously stirred at room temperature. The molar ratio of $\text{Ti}(\text{OC}_3\text{H}_7)_4$: $\text{C}_5\text{H}_8\text{O}_2$ was 2:3. Then 30.5 ml of ethanol (0.525 mol) was added drop wise into the solution with a burette at a speed of one drop per second under continues stirring. It is observed that the color of mixture was yellow while ethanol was added completely. Subsequently, to obtain final sol, the solution was agitated for 2 hours at room temperature.

Preparation of TiO_2 Nanofilm

Transparent TiO_2 nanofilm was prepared on the soda-lime glass precursor (25*25 mm) as substrate by using spin-coating method with (VMC409, 500-6000 rpm) spin-coater after 2 days of sol preparation. Prior to the coating process, the glass was washed with de-ionized water, ethanol and acetone, respectively in ultrasonic bath for 15 minutes. The initial voltage was 12 V and the power of spin-coater system was 24 W. The speed of rotation was 1500 rpm for 160 seconds. Finally, the coated substrate was placed into the furnace for 2 hours with the heating rate of 2°C min^{-1} to obtain TiO_2 nanofilm.

Synthesis of ZnO Sol and Preparation of ZnO Nanofilm

Firstly, 6 g (0.03mol) zinc acetate dihydrate was added in to the isopropanol. The mixture was stirred at 40°C for 30 minutes and diethanolamine was then added. The molar ratio of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ to $\text{C}_4\text{H}_{11}\text{NO}_2$ was 3:2. The final solution was agitated at this temperature for 2 hours and ZnO sol was obtained. At the end, ZnO nanofilm was coated on the glass substrate after 2

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days of sol preparation by spin-coating method with the same properties which was used in previous section.

Preparation of Nanocomposite films

The preparation of the TiO_2/ZnO and ZnO/TiO_2 nanofilms was conducted by spin-coating process using glass as substrate. In this section, three methods suggested for preparing the combined nanofilms and subsequently the results were compared to each others.

- **Spin-Coating of ZnO Sol over TiO_2 Nanofilm**

After that TiO_2 nanofilm was calcined in the step 2.3, a thin layer of ZnO sol was coated on its surface and calcined at 600°C for 2 hours to obtain TiO_2/ZnO nanofilm.

- **Spin-Coating of TiO_2 Sol over ZnO Nanofilm**

Unlike the previous step, this time a thin layer of TiO_2 was coated on the surface of ZnO nanofilm which was calcined in the step 2.4 and was heat treated at 600°C for 2 hours to obtain ZnO/TiO_2 nanofilm.

- **The TiO_2/ZnO Nanocomposite Film from Direct Mixing of the Sols**

The TiO_2/ZnO nanocomposite film was also prepared via sol-gel process from directly mixing TiO_2 and ZnO sols. The obtained ZnO sol was added directly into the TiO_2 sol. The molar ratio of ZnO to TiO_2 was 3:1. The mixture of sols was stirred for 15 minutes. The prepared sol was coated on to the substrate surface via spin-coating method at the speed of 2000 rpm for 130 seconds. The coated substrate was then calcined at 600°C for 2 hours.

RESULTS AND DISCUSSION

Characteristics of Nanofilms

- **XRD Analysis**

The XRD patterns of nanofilms showed an amorphous structure. So, determination of phases was carried out when the sol was ignited and the crystallinity of TiO_2 and ZnO nanoparticles was recorded by X-ray diffraction (XRD) using a diffractometer with $\text{Cu } K_\alpha$ radiation (STOE, STADI-P, 40 kV).

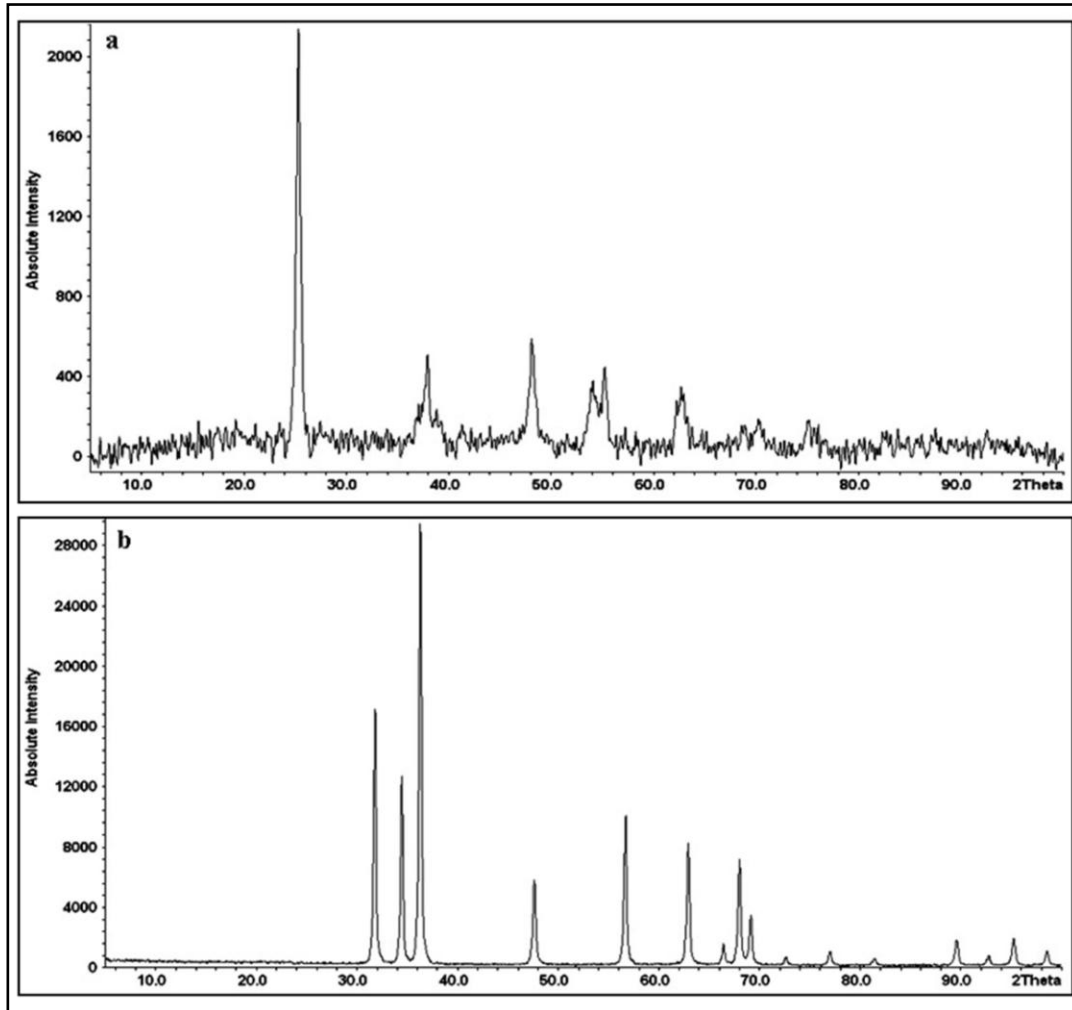
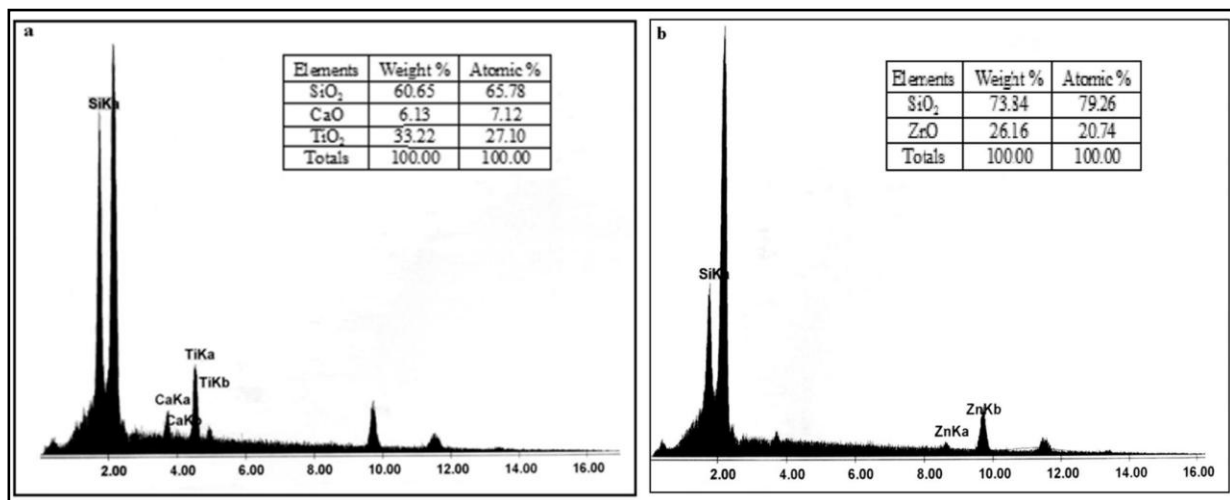
Figure 1 (a and b) show XRD patterns of TiO_2 and ZnO nanoparticles. Figure 1a showed that TiO_2 nanoparticles were obtained and the sample was included single crystalline phase of anatase. It is demonstrated that the sol process was completely performed on to the reagents and the ignited gel had same properties of initial sol but in crystalline form. According to this result, the amorphous TiO_2 could be well crystallized under ignition process. The average crystalline size of TiO_2 nanoparticles was 80 nm. XRD pattern of ZnO nanoparticles which was shown in Figure 1b indicated that single phase of zinc oxide was obtained after ignition and the average size of nanocrystals was 50 nm.

- **EDAX Analysis**

In order to clarify the element composition of the prepared nanofilms and evaluating of approximate atomic ratio, the EDAX analysis was conducted. Figure 2 (a and b) showed the EDAX analysis of nanofilms. The EDAX analysis revealed the presence of Ti and Zn elements in the nanofilms. The presence of titanium (Ti) indicated that TiO_2 film has been successfully formed on the substrate (Figure 2a). The zinc (Zn) was also found present in ZnO nanofilm (Figure 2b). Also, some components such as CaO and SiO_2 were observed which were from the substrate glass.

- **SEM Images**

The morphology of nanofilms was characterized by using scanning electron microscopy (Philips-XL30) with an accelerating voltage of 15-30 KV. SEM images of nanofilms were shown in Figure 3 (a and b). According to Figure 3 (a), it can be seen that cracks formed on the surface of TiO_2 nanofilm. Also the spherical crystalline particles with size of approximately 38 nm were found on its surface. In the case of ZnO nanofilm, Figure 3(b), it is observed that the surface structure of nanofilm contains crystalline particles which are uniformly dispersed and the surface has not any cracks unlike TiO_2 nanofilm.

Fig. 1. XRD patterns of a) TiO_2 and b) ZnO nanoparticles.Fig. 2. EDAX analysis of a) TiO_2 and b) ZnO nanofilms

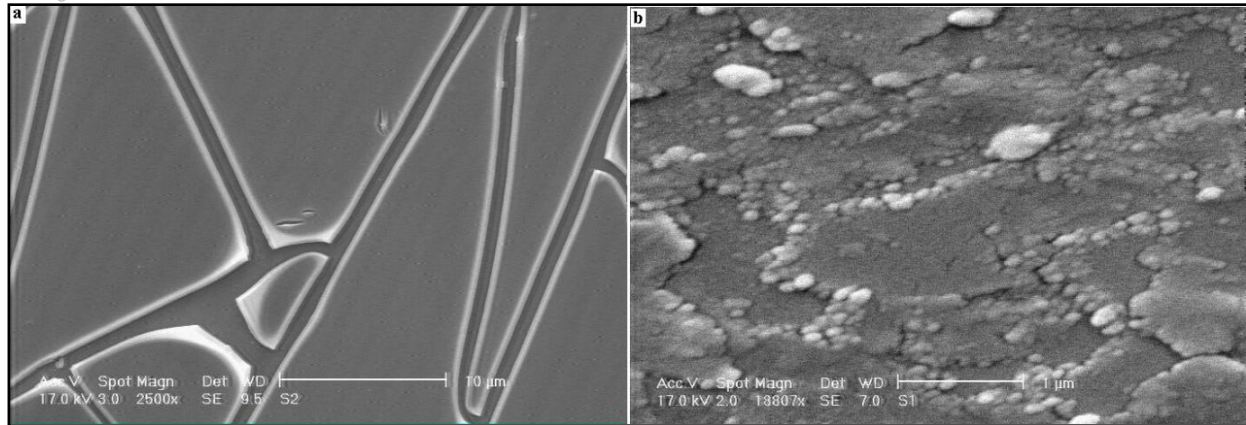


Fig .3. SEM images of a) TiO₂ and b) ZnO nanofilm

Field Emission Scanning Electron Microscope, (S-4160 Model, 15 kV, Hitachi) was employed to determine the crystallinity and thickness of TiO₂/ZnO nanofilm which prepared from direct mixing of two sols. The surface

structure of nanofilm has no cracks. The spherical crystalline particles are clearly observed in Figure 4(a, b). The thickness of obtained nanofilm was about 84-88 nm that was presented in Figure 4 (c, d).

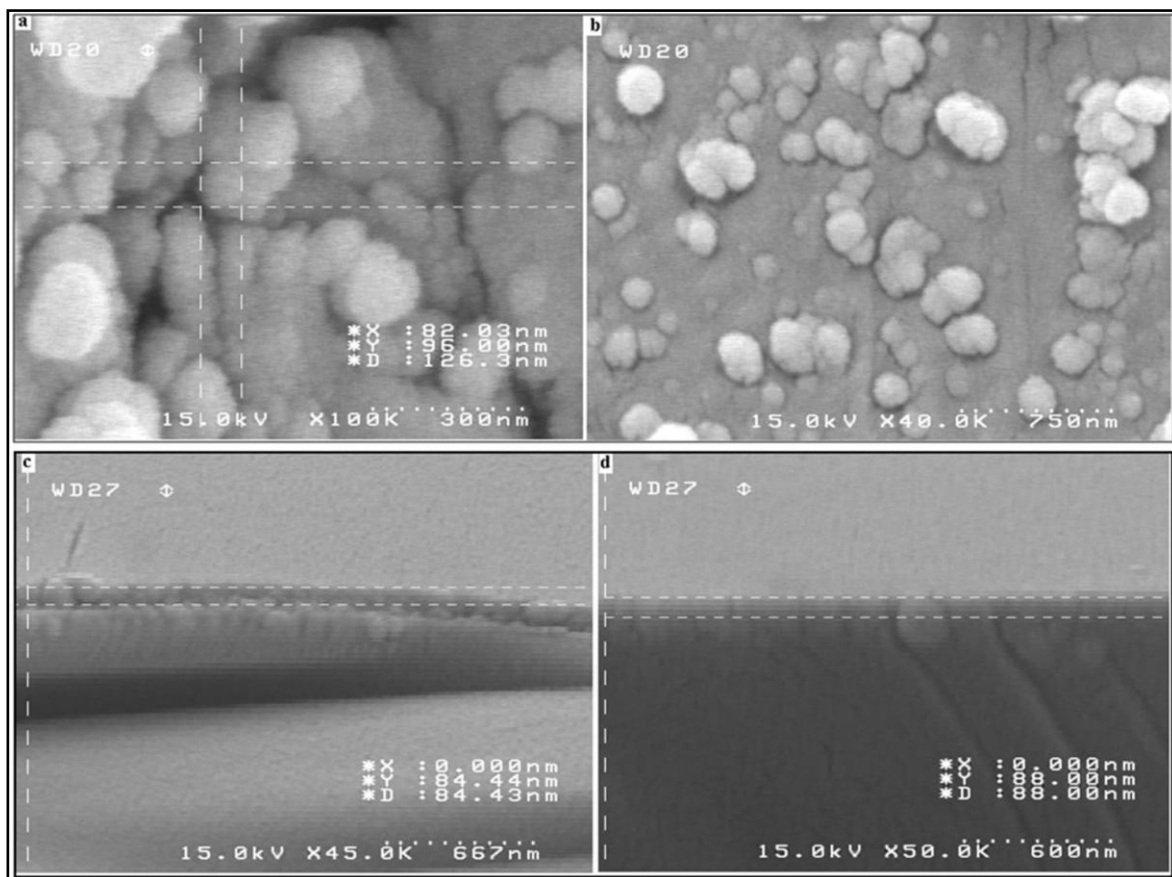


Fig. 4. FESEM images of TiO₂/ZnO nanofilm prepared from direct mixing of two sols.

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Photodegradation Properties of Nanofilms

The photodegradation of methylene blue was investigated on the surface of TiO₂, ZnO and TiO₂/ZnO nanofilms which treated from direct mixing of two sols, respectively. Degradation calculated from equation:

$$X = \frac{A_0 - A}{A_0}$$

Where X is degradation percentage, A₀ is initial absorption of and A is absorption after several minutes. Degradation of methylene blue on the surface of TiO₂ and ZnO are shown in Figure 5 (a and b). Photocatalytic removal efficiency was about 50 and 80% for TiO₂ and ZnO nanofilms, respectively after 180 minutes. It is demonstrated that the ZnO has a better structure and operation than TiO₂. Also, it can be concluded that the uniform shape and good band gap of ZnO nanofilm have an efficient role in the reaction.

Degradation of methylene blue on the surface of TiO₂/ZnO, ZnO/TiO₂ and TiO₂/ZnO (from direct mixing) is shown in Figure 6 (a-c). The degradation percentage of the film which was

treated in accordance with step 2.5(a) and 2.5(b) were 35 and 12% after 100 minutes. Whereas, the degradation percentage of the film prepared in step 2.5(c) was about 20% after the same time.

It is expected that UV light is able to break the bonds of dyes. In this case, the dye has several chromophore points and the compound has broken at these sites which is the main cause to observe the adsorption in visible region. Based on the results, it cannot assumed that the hetero-junction compound was formed by combining the two sols, because these compounds can be formed if one compound (one metal oxide) can be entered in the lattice of one other. Totally, it is concluded that the degradation was carried out by one of the metal oxide in the case of TiO₂/ZnO and ZnO/TiO₂ nanofilms as the data showed. It means that the coating of one sol on the surface of the glass which was coated by another sol, due to decreasing the effect of first layer to best destruction. In the case of nanofilm which was prepared from direct mixing of two sols, it is very low probable that one compound was introduced into the lattice of the other. However, results have not shown more difference between the degradation percentages.

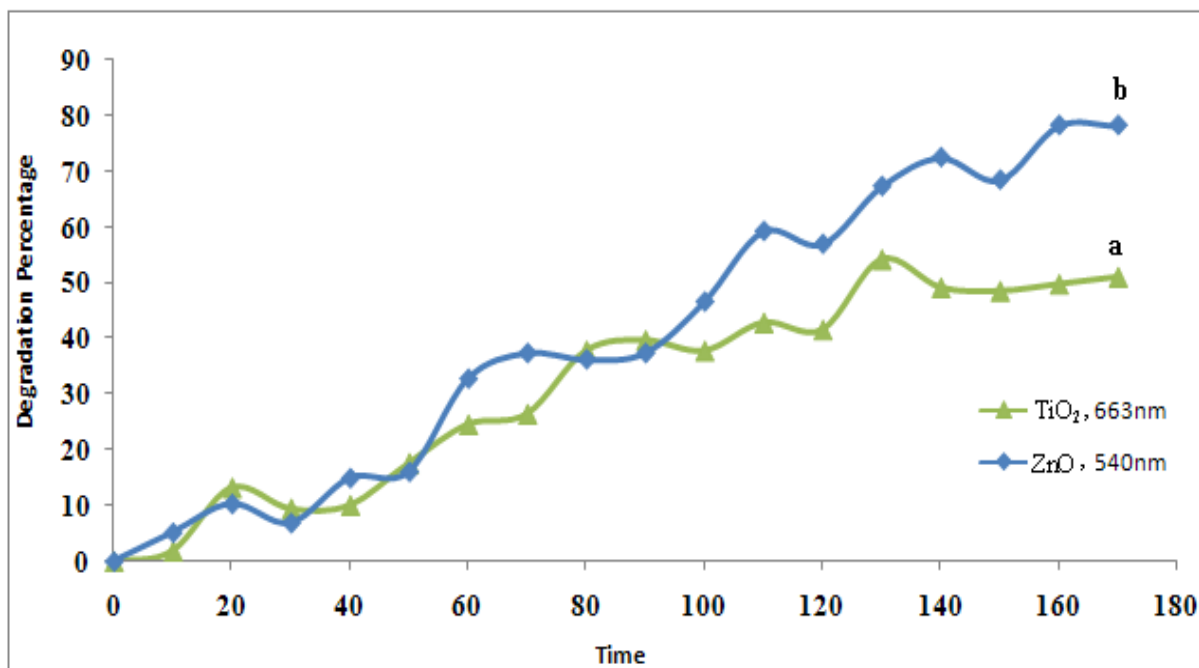


Fig. 5. Degradation percentage of MB on the surface a)TiO₂ and b) ZnO nanofilms.

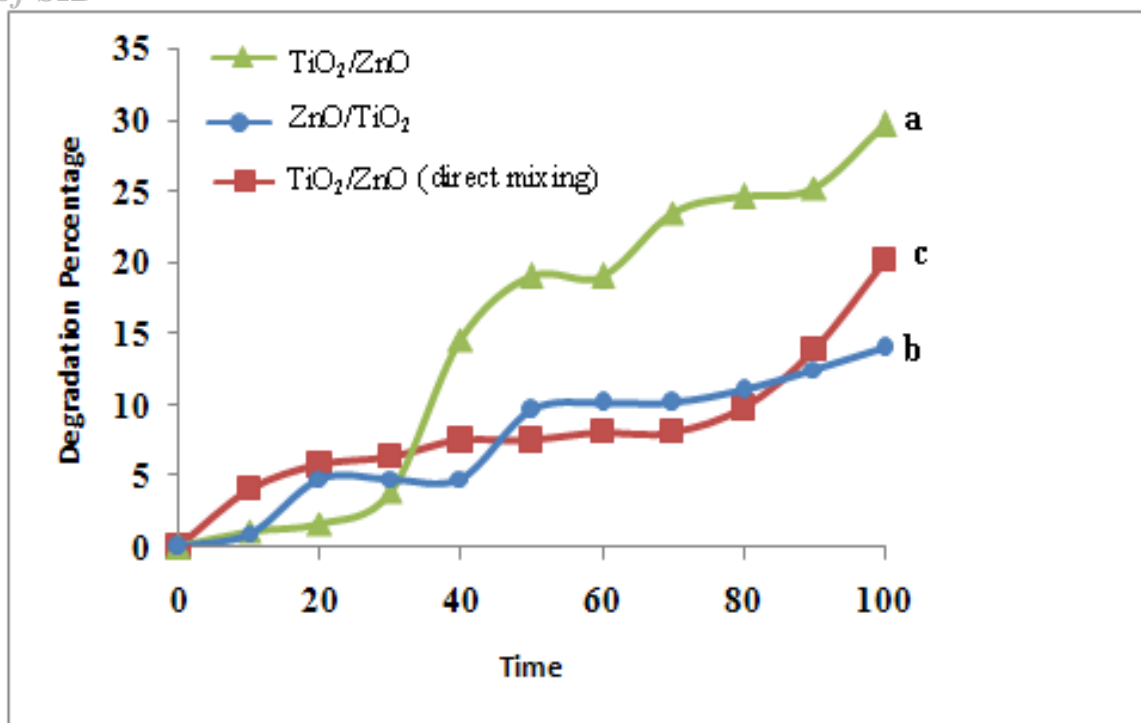


Fig. 6. Degradation percentage of MB on the surface a) TiO₂/ZnO, b) ZnO/TiO₂ and c) TiO₂/ZnO (direct mixing) nanofilms.

CONCLUSIONS

In summary, TiO₂ and ZnO nanofilms were prepared by sol-gel spin-coating method. Characterization of nanofilms showed that several cracks were present on the surface of the TiO₂ film. In the case of ZnO film no crack was observed. Some extent agglomerates dispersed uniformly on the surface of ZnO film. The EDAX analysis revealed homogeneous distribution of Ti and Zn elements in the films. The TiO₂/ZnO nanocomposite film could be successfully prepared via sol-gel process from both single coating of TiO₂/ZnO and directly mixing of TiO₂/ZnO sols. Microstructural morphology and the crystallization of the TiO₂/ZnO nanocomposite films were strongly related to the steps of coating. According to results, it is demonstrated that TiO₂/ZnO nanofilm which prepared from direct mixing of two sols has better thickness and crystallinity compared with TiO₂/ZnO and ZnO/TiO₂ nanofilms.

These nanofilms were employed to photocatalytic destruction of methylene blue in the presence of UV light irradiation. Results showed that the photodegradation percentage of TiO₂/ZnO nanofilm which prepared from direct mixing of two

sols was 20% which is contributed to physical adsorption of ZnO. It seemed that ZnO has an important role in enhancement of separation of electron-hole pairs and can increase the photocatalytic degradation.

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Cite this article as: N. Mastali *et al.*: Investigation on the structural, morphological and photochemical properties of spin-coated TiO₂ and ZnO thin films prepared by sol-gel method.

Int. J. Nano Dimens. 5(2): 113-121, Spring 2014