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Synthesis of Gd doped TiO_2 Thin Film for Photocatalytic Degradation of Malachite Green

Hasan ESKALEN[*1], Süleyman KERLİ[2]

Abstract

In this research work, a simple spray pyrolysis method was employed to synthesized gadolinium (Gd) doped titanium oxide (TiO_2) thin film. The crystal structure and morphology of the sample was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). According to XRD measurements, no apparent crystal peak was observed. The thickness of the prepared film was found to be 228 nm from SEM observation. The optical transmittance and bandgap energy of the synthesized thin film was investigated by using UV-Vis spectroscopy. The high transmission of the thin film was found in the visible region. The optical bandgap energy of the prepared film was found to be 2.85 eV. The photocatalytic degradation of malachite green solution was studied. As a result of the photocatalytic experiment, the thin film could be used as an effective photocatalyst for malachite green dye.

Keywords: Spray pyrolysis, XRD, SEM, TiO_2, malachite green

1. INTRODUCTION

The increasing interests of researchers from science and industry have been focused on thin films because of the full range of application areas from energy to radiation shielding [1–3]. One of the significant application areas of the thin film is obviously photocatalyst since, among different reasons, especially massive industrialization pollute water that causes unsafe drinking water [4]. The photocatalysis is a valuable and kindly green (since renewable solar energy is utilized) methods to remove toxic organic complexes from wastewater [5]. Semiconductor-based photocatalytic materials have been used for water treatment because of their high potentials [6].

The titanium oxide (TiO_2) has an environmentally friendly nature, low cost, and excellent photocatalytic activity [6]. Moreover, TiO_2 has chemical stability, high redox reactivity, high thermal resistance, and low toxicity [7,8]. Despite all the superior features about TiO_2, the use of visible light is limited. This material only uses about 45 % solar energy of visible light and ~4 % of ultraviolet light [7]. Concerning this drawback, doping TiO_2 with metal and non-metal elements can enhance visible light absorption that can

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increase photocatalytic activity [9,10]. Boron can place two different positions as an interstitial and substitutional position in TiO_2 lattice and the interstitial boron-doping remarkably increase the photocatalytic activity of TiO_2 film was founded [11]. The enhanced optical absorption was found at boron and nitrogen co-doped TiO_2 synthesized by the sol-gel method [12]. The ZnO/TiO_2 solution of the thin film prepared and photocatalytic activities were investigated recently [13]. The decrease in optical bandgap energy of Cu doped TiO_2 was reported [14]. Gadolinium (Gd) 0-6 % doped TiO_2 was synthesized by sol-gel spin coating methods, and their photocatalytic degradation activity of Rhodamine-B (RhB) dye was studied [15]. TiO_2 was doped Gd, and La same time decrease optical bandgaps and so increase photocatalytic activity was reported [16].

Herein, we explored 10 % Gd doped TiO_2 thin film synthesized by a spray pyrolyzed method. This method is preferred because it has many advantages such as low cost and not requiring vacuum environment. Moreover adjusting the molarity of the solutions, controlling the substrate temperature, and compatible for industry since large area can be coatable with this method [17,18]. The structural, morphological and optical properties of the prepared gadolinium doped TiO_2 thin film were characterized by the X-ray diffraction, SEM, UV-Vis spectroscopy method. The photocatalytic degradation performance of the film was investigated.

2. MATERIALS AND METHOD

The 10 at% Gd doped TiO_2 thin film was obtained by the spray pyrolysis method. Titanium chloride ($TiCl_4$) and gadolinium nitrate ($GdN_3O_9{\cdot}6H_2O$) chemicals were used for thin-film synthesizes. These chemicals were prepared atomic rate of 10/90 (Gd/Ti) in 40 ml pure water and 5 ml ethanol. The temperature of substrates adjusted set as 450 °C and the solution was sprayed the glasses substrates. The diffraction pattern of the obtained thin film was measured using the XRD device (Philips X'Pert PRO brand XRD device (CuKα, λ=0.154056 nm)). The measurement range of the equipment is adjusted from 10˚ to 90˚, the step interval will increase by 0.055 and the waiting time will be 0.5 seconds in each step. The morphological features of the produced film were examined by using the ZEISS EVO LS10 scanning electron microscope (Scanning Electron Microscope). UV-Vis (Ultraviolet) spectrophotometer measurements were conducted using the Shimadzu UV-1800, UV-Vis spectrophotometer device.

3. RESULTS AND DISCUSSION

The crystal structure of gadolinium-doped titanium oxide thin film was not apparent at the obtained XRD results which is shown Figure 1. As seen in the figure, no clear crystalline peak was found in the X-ray pattern. It is believed that the amorphous structure is dominant in this film. In literature, a similar study conducted by Chobba et al., Gd element from 0 to 5 percent was doped to titanium oxide nanoparticle and the XRD results demonstrated that the intensity of peaks decreased with the increasing amount of Gd concentration [19]. There are also some other studies in which the intensity of TiO_2 peaks was reduced by introducing the Gd element to the system [20,21]. In our study, differs from the mentioned works, the concentration of Gd elements was highest with 10 % and this is the main reason for the TiO_2 crystal structure was not apparent at the obtained XRD results.

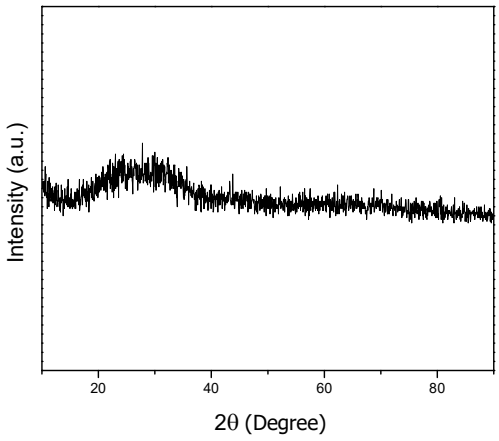

Figure 1 XRD diffraction pattern of 10 % Gd doped TiO_2 thin film

Electron microscopy (SEM) images of 10 % Gd doped TiO_2 thin film obtained by the spray

pyrolysis method are shown in Figure 2. The thickness of the film obtained from SEM photographs was measured as approximately 228 nm. Besides, SEM photographs show that thin films have agglomerations at some points and are generally more uniform and more homogeneous.

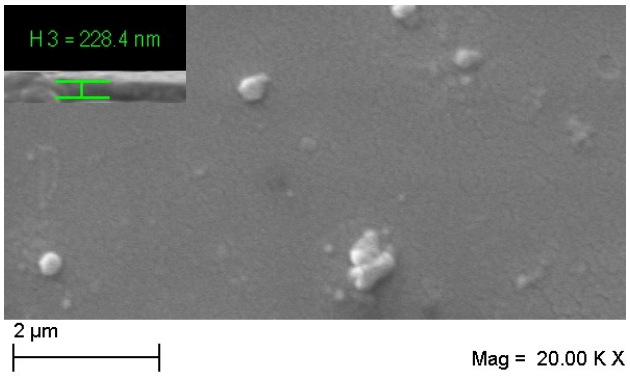

Figure 2 SEM image of 10 % Gd doped TiO_2 thin film. Inset cross-section image of the film

Figure 3 (a) shows the transmission spectra of gadolinium-doped titanium oxide thin film. As can be clearly seen from this figure, the film has a high transmission value of about 94% at 900 nm. Also, it was observed that the optical transmittance of the film decreases inclined with the wavelength. The bandgap energy of the 10 % Gd doped TiO_2 thin film was obtained from the line of the linear section intersects the hv axis $(\alpha h\nu)^2 = 0$. The $(\alpha h\nu)^2 \sim h\nu$ graph relation of Gd doped TiO_2 film was demonstrated in Figure 3b. The optical bandgap energy (Eg) of the thin film was found 2.85 eV and the result is suitable with the previously studied related to doping rare-earth metal in the TiO_2 matrix [22,23]. The oxygen atoms are loosed and free electrons are generated with doping Gd element to TiO_2 matrix and the redshift in the absorbance band is due to the transition of an electron from the valance band to 4f energy level of Gd [22].

Photocatalytic degradation of the 10 % Gd doped TiO_2 thin film was performed with 2 ppm malachite green dye solution under solar light simulator cabin (300W Luzchem Photoreactor). The photocatalytic performance of the used thin film was measured by using UV-Vis spectroscopy as a function of reaction time. The maximum absorption of malachite green solution was recorded at 618 nm and a minor absorption peak at 424 nm. The 2 ppm (10 mL) malachite green solution put into the petri dish and the thin film was kept in the dark for 40 min to achieved absorption desorption equilibrium. After then the petri dish was placed into a solar simulator and regular circulation of the solution was made with the help of magnetic stirrer. The samples were taken from the solution at proper time intervals from 0 min to 110 min, and the samples were analyzed at UV-Vis spectrometry in ranging from 400-700 nm.

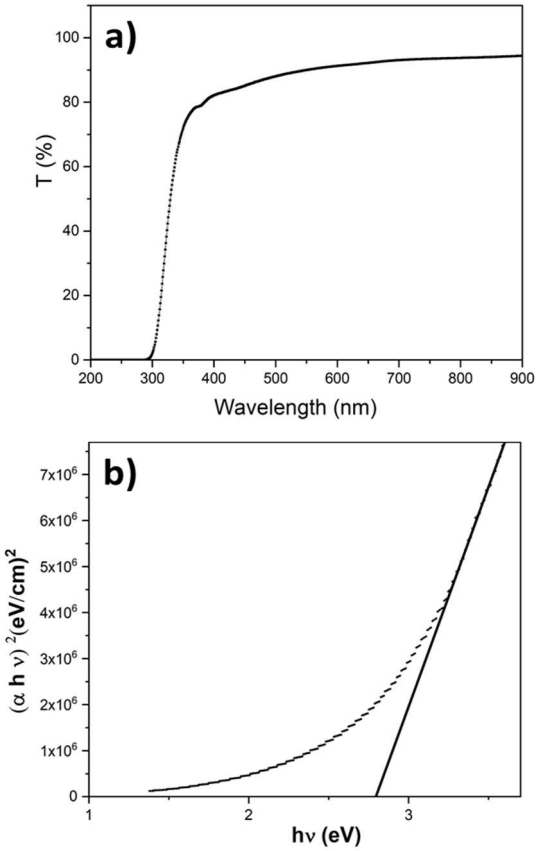

Figure 3 (a) The transmission spectrum of 10 % Gd doped TiO_2 thin film, (b) estimated optical bandgap of the prepared film

The degradation efficiency of the example was found by using the equation:

$$DE = \left(1 - \frac{C_t}{C_0}\right) \text{ x } 100 \qquad (1)$$

where DE implies degradation efficiency, C_0 is the initial concentration, C_t is the represent concentration at the sampling time. The change in

UV-Vis spectra of 10 % Gd doped TiO_2 thin film as a function of time is illustrated in Figure 4. As seen from this figure, the maximum absorption peak linearly decreases as the reaction time increase. The initial green color of solution change to almost white after 110 min of reaction.

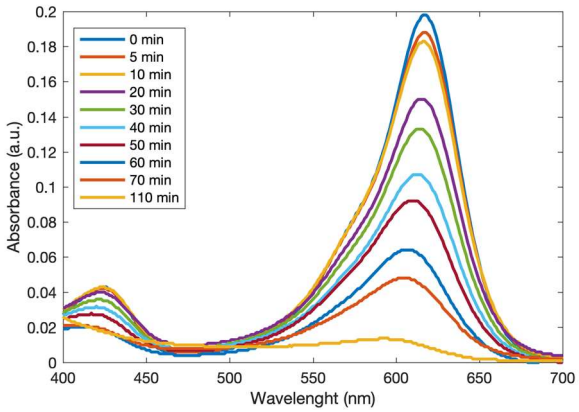

Figure 4 Uv-vis spectra of photocatalytic degradation of 10 % Gd doped TiO_2 as a function of time

The photocatalytic degradation efficiency of the prepared film is given in Figure 5. The self-degradation and 10 % Gd doped TiO_2 film degradation are clearly seen from the figure. The efficiency of the film was reached 87 % in 110 min. The Gd element as a doping agent of TiO_2 has an exciting specification, and the photocatalytic performance of TiO_2 may enhance or reduce with introducing Gd elements. The enhancement of the concert with Gd doping might be attributed to the 4f level of the lanthanide [19]. However, the irradiation environment, annealing of film and doping concentration changes to the photocatalytic performance of the mentioned system [19,23,24]. So further studies are needed.

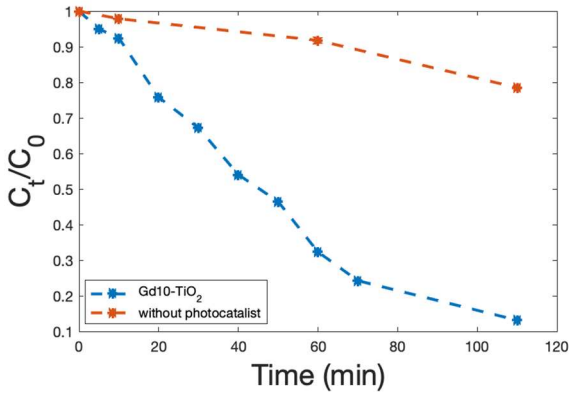

Figure 5 The photocatalytic degradation efficiency of malachite green by 10 % Gd doped TiO_2

4. CONCLUSION

In this study, 10 % Gd doped TiO_2 thin film was successfully synthesized by a simple spray pyrolysis method. The crystal structure of the sample was examined, and no apparent crystalline peak was observed. The thickness of the prepared film was found as 228 nm from SEM observation. The transmission feature of the 10 % Gd doped TiO_2 film was examined by a UV-Vis spectrometer and a highly transparent thin film was found. The optical bandgap energy of the synthesized film was seen as 2.85 eV. The photocatalytic degradation of malachite green solution was examined, and the synthesized thin film can be used as an active photocatalyst for malachite green dye, but further studies are needed to Gd doped TiO_2 thin films. These findings may contribute to the development of new insight on Gd doped TiO_2 thin films.

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The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

Authors' Contribution

All authors have contributed in experimental study and writing of the manuscript equally.

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The authors declare that this document does not require an ethics committee approval or any special permission.

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