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Synthesis of Titanium Oxide thin Films by Spray Pyrolysis Method and its Photocatalytic Activity for Degradation of Dyes and Ciprofloxacin

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Titanium oxide (TiO_2) thin film was obtained using the spray pyrolysis method. The structural properties of the obtained thin film were examined by X-ray diffraction (XRD) and it was found that it had a tetragonal structure. The morphological features were examined with scanning electron microscopy (SEM). In addition, the optical properties of the film were examined and the bandgap energy was calculated. Photocatalytic properties of TiO_2 thin film on different dyestuff and antibiotic were investigated. Methyl blue and malachite green were used in the dye degradation test of the thin film. In particular, it was found to have a high degradation of 86 % after 100 minutes on malachite green. Moreover, the degradation on ciprofloxacin after 90 minutes was found as 93 %. The reusability ciprofloxacin antibiotic was investigated and it was found that synthesized TiO_2 thin film has excellent stability and reusability.

Keywords: TiO_2, methyl blue, malachite green, ciprofloxacin.

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Introduction

Environmental pollution has now become a critical problem that treat the quality of human life. As a result of the radical change of laws and regulations on the prevention and control of environmental pollutants, the issue of handling organic pollutants has become the focus of interest by the relevant enterprises and industry [1-2]. Some of the contaminants in the water are organic compounds containing dyes and antibiotic residues. It is known that some wastewaters that originated from dyes contaminate freshwater sources and land. Indeed, these also have a carcinogenic effect [3]. The chemical compounds with antibacterial properties, also known as antibiotics, are one of the most used pharmaceuticals for curing humans and animal diseases [4-5]. Ciprofloxacin (CIP) is a broad spectrum second generation fluoroquinolone antibiotics and play a critical role for treatment of diseases like pharyngitis, sinusitis and bronchitis [6], but pharmaceutical manufacturing, hospitals and excretion from human are the three common contamination ways of the CIP [4,7-8]. So, it essential to eliminate CIP from aqueous solutions.

In recent years, the photocatalytic performance of some alloys [9-10] and semiconductors [11-14] have attracted the intense attention of scientists. Titanium dioxide (TiO_2) is semiconductor powders and has a remarkable band gap and it has three different kinds of crystalline structure anatase, rutile and brookite [15-16]. It has been used as an excellent photocatalyst material due to nontoxicity, low cost, chemical stability, light resistance, high refractive index and photoinduced performance [2,17-19]. Many different methods are utilized to synthesized TiO_2 thin films such as chemical vapor deposition, pulsed laser deposition, chemical bath deposition, sol-gel method, spray pyrolysis [20-21].

Among these methods, spray pyrolysis methods is the easiest, low-cost techniques and it is remarkably suitable for relatively large surface area coating.

In the present study, the TiO_2 thin film on glass substrate was synthesized by spray pyrolysis method. In the synthesizing process, titanium chloride was used. The structural morphologic and optical properties of the synthesized thin film were examined. The main goal of this study investigates photocatalytic degradation performance of the prepared thin film by degradation ciprofloxacin antibiotic and two different dyes including malachite green and methyl blue dye in aqueous solution under solar light simulator. Moreover, the recycling performance of the thin film is also studied.

I. Experimental

Titanium oxide film was synthesized by using the spray pyrolysis technique on a glass substrate (26×76 mm). Titanium chloride ($TiCl_4$, Merck) chemical was used to prepare a thin film. Titanium chloride (0.6 ml) was dissolved in 40 ml of purified water. After then, 5 ml of ethanol added to the prepared solution under magnetic stirrer. The temperature of heater was set at 450 °C and the prepared solution was sprayed to the glass substrate. The prepared film was annealed at 570 °C in air for 1 hour.

The diffraction pattern of the TiO_2 thin film was investigated by using Philips X'Pert PRO. The morphological properties of the produced film were examined using ZEISS EVO LS10 scanning electron microscope, and the optical properties of the prepared films were studied using Shimadzu UV-1800 UV-VIS spectrophotometer. In photocatalytic measurements, a 300 W solar simulator (LuzchemPhotoreactor) was used.

The photocatalytic performance of the synthesized film was investigated. Methyl blue (5 ppm) and malachite green (2 ppm) were used for dye degradation in 20 ml solution into a petri dish under continuous stirring by the help of magnetic stirrer. Ciprofloxacin (5 ppm) was used for antibiotic degradation. Two TiO_2 thin films were used in all experiments. The first film was used for photocatalytic degradation of dyes and the other one was used in the antibiotic degradation experiment and reusability test. In all test prepared solutions keep in dark for 40 min to achieve absorption-desorption equilibrium. The antibiotic degradation experiment was repeated 4 times and for each test the solution only changed with freshly prepared ones and the same film was used.

II. Results and discussion

The XRD results of the TiO_2 thin film obtained with the spray pyrolysis technique at 450 °C substrate temperature are shown in Figure 1. In the XRD graph, especially 2θ peaks (101) and (004) were prominently observed. From these results, it can be explained that the thin film has a tetragonal structure and its anatase form. It also complies with Reference code: 96-101-0943. From similar studies, Hosseinzadeh et al. used titanium (IV) butoxide as a titanium oxide source and found similar XRD results with films obtained with Ultrasonic-assisted spray pyrolysis technique [22]. Moreover, there are titanium oxide thin films that Dundar et al. obtained with similar structures [23].

The SEM image of the titanium oxide thin film is shown in Figure 2. As can be seen in the figure, although there are roughnesses at some points, it is generally smooth and well sticks to the glass. The transmittance spectrum of the TiO_2 film is shown in Figure 3a. It has been observed that the optical transmittance of the film decreases with a decrease in wavelength. The optical absorption method was used to determine the bandgap of produced thin film. The bandgap of the material by the absorption method was obtained by using the Tauc plot. In Figure 3b, the bandgap values of the TiO_2 film was found to be approximately 3.33 eV. The calculated bandgap value of TiO_2 thin film is suitable with literatures [24-25].

The photocatalytic performance of the synthesized TiO_2 thin film was investigated through degradation of methyl blue, malachite green dyes and ciprofloxacin antibiotic under solar light simulator. The absorbance of MB for different reaction times is given in Figure 4.

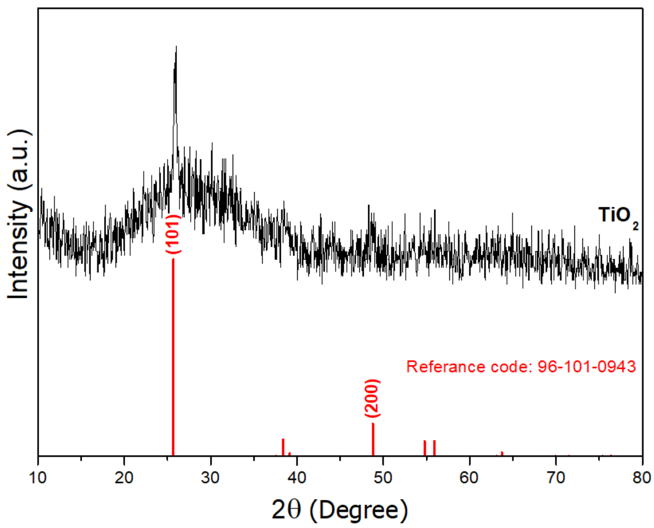

Fig. 1. XRD patterns of TiO_2 thin film.

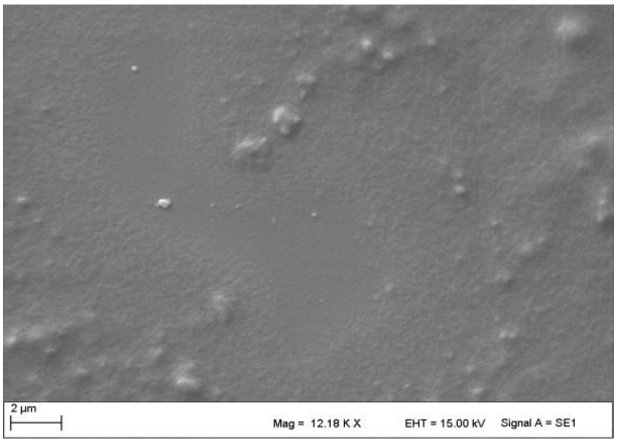

Fig. 2. SEM surface image of TiO_2 thin film.

The reference peak for methyl blue (MB) closed to 600 nm was selected and as is demonstrated in the figure, this peak gradually decreased with increasing reaction time. The experiment was performed 60 min and after this time, degradation efficiency was reached to 65.52 %. The degradation efficiency of MB as a function of reaction time is given in Figure 4 inset. The degradation efficiency η of the thin film was measured using the following equation:

$$\eta = \frac{(C_0 - C)}{C_0}\ x\,100, \qquad (1)$$

where C_0 and C are the initial concentration and concentration at the sampling time respectively. The photocatalytic performance of 2 ppm malachite green aqueous solution dye was investigated and before the experiment, synthesized thin film, which was used in MB dye degradation cleaning with double distilled water and dried in an oven at 40 °C for 24 hours. The absorbance spectra of malachite green dye as a function of the reaction time is given in Figure 5. The reference peak was around 619 nm and the decrease in this peak was used for evaluation photocatalytic degradation efficiency. The degradation efficiency of malachite green dye is given in Figure 5 inset. After 100 min reaction under solar simulator, about 86 % malachite green dye was degraded.

The self-degradation of malachite green was also studied. The absorbance spectra of only malachite green dye without thin film under solar simulator are given in Figure 6. As seen from this figure, after 100 min irradiation of solar simulator, the absorption peak of malachite green was decreased. 23.5 % malachite green dye was self-degraded under solar simulator. This result also verified that synthesized TiO_2 thin film was an effective catalyst for the degradation of malachite green dye

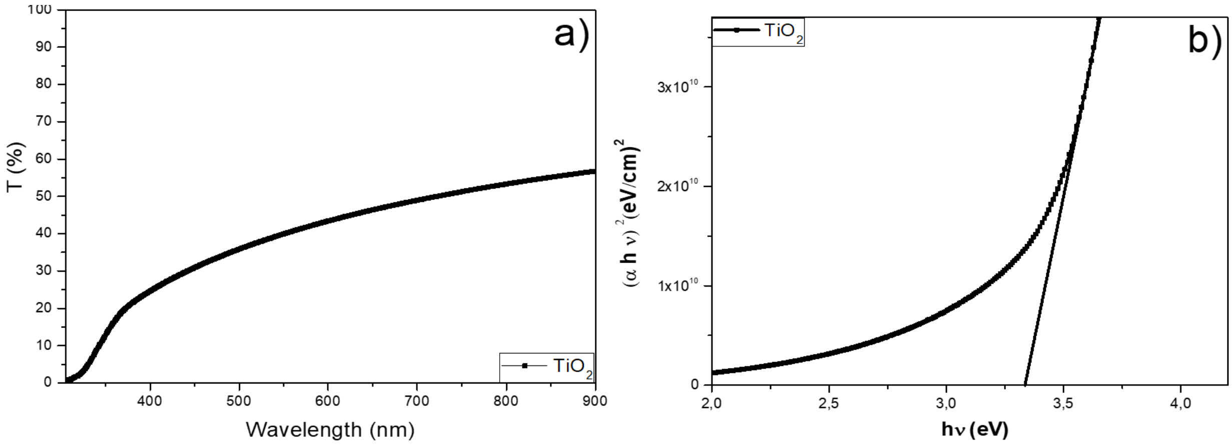

Fig. 3. (a) Transmittance, (b) the optical bandgap (Eg) of TiO_2 thin film.

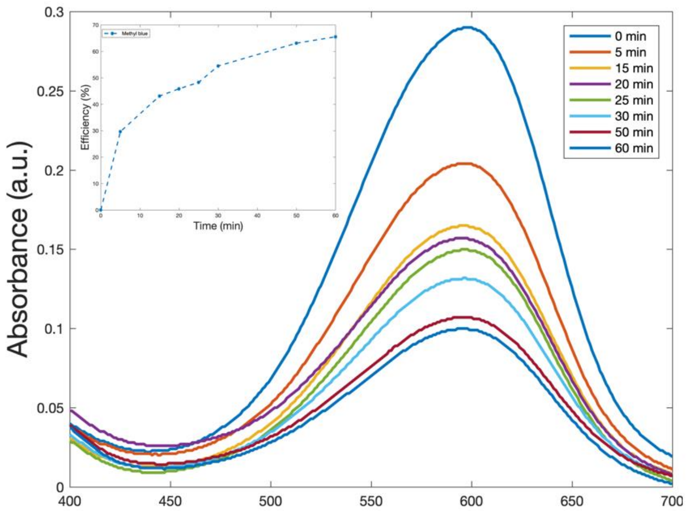

Fig. 4. The photocatalytic performance of MB dye under solar simulator with TiO_2 thin film, inset degradation efficiency TiO_2 thin film.

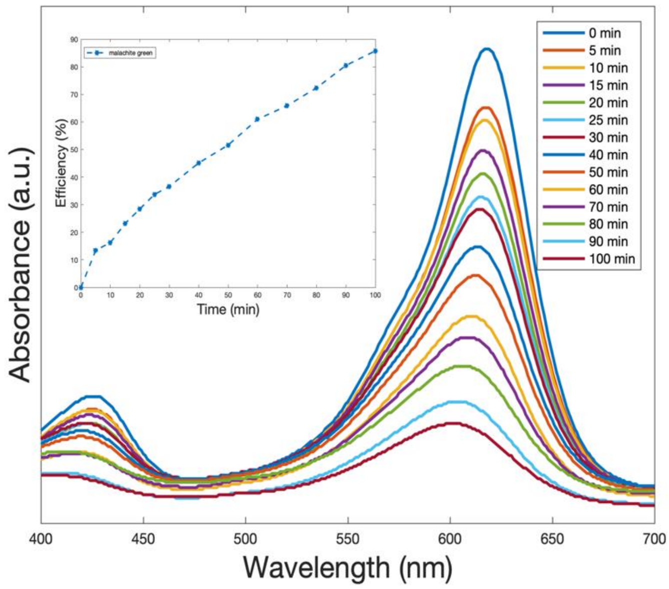

Fig. 5. The photocatalytic performance of malachite green dye under solar simulator with TiO_2 thin film, inset degradation efficiency TiO_2 thin film.

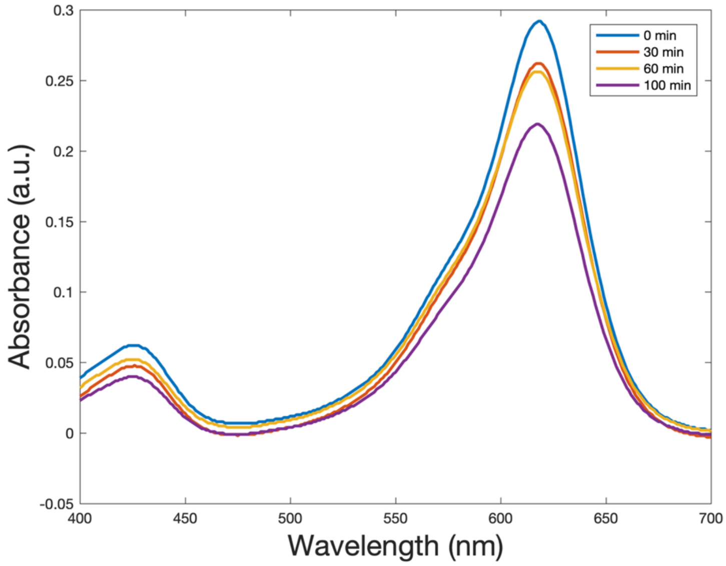

Fig. 6. The self-degradation of malachite green dye under solar simulator as a function of reaction time.

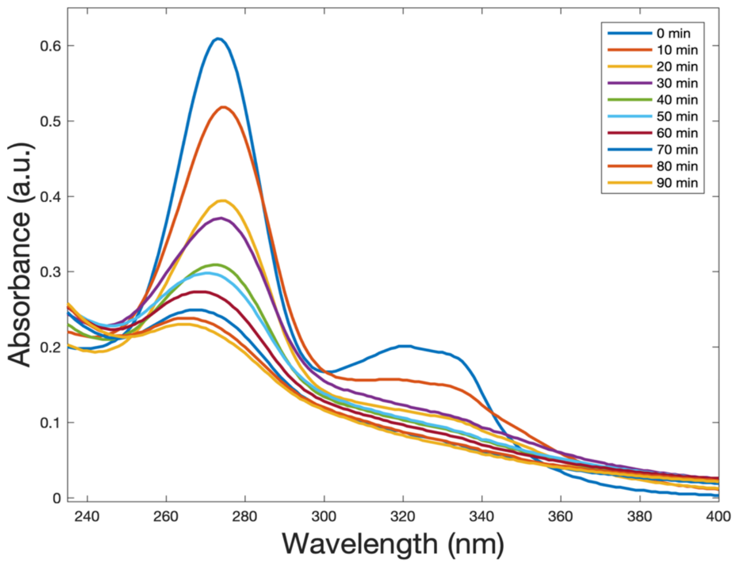

Fig. 7. The absorption spectra of CIP in the presence of TiO_2 thin film.

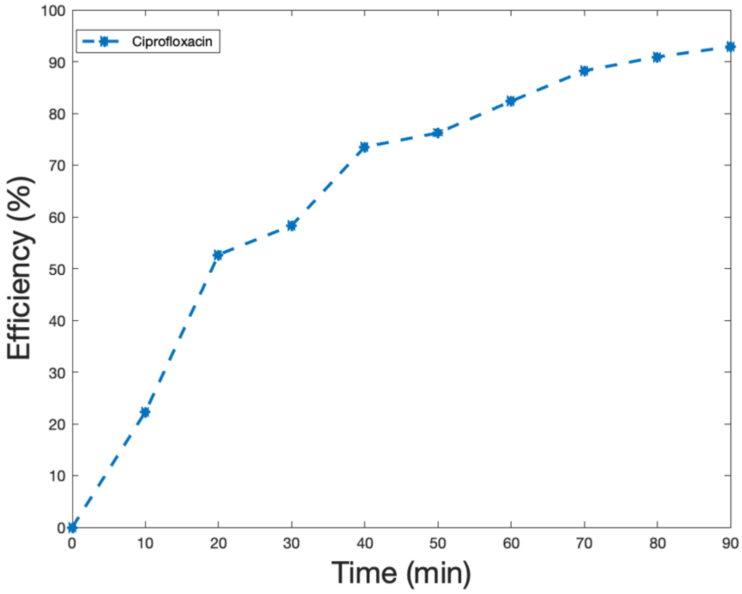

Fig. 8. The photocatalytic degradation of CIP with TiO_2 thin film as a function of reaction time.

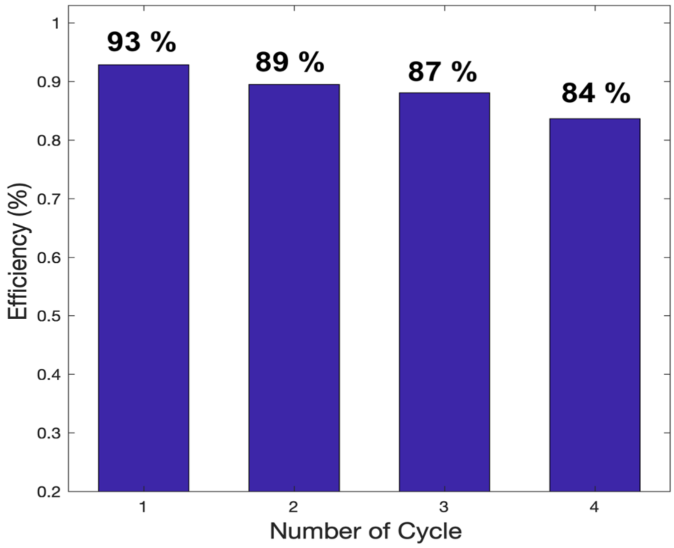

Fig. 9. The reusability of the TiO_2 thin film.

The other synthesized TiO_2 thin film was used for the CIP experiment. The concentration of CIP is chosen as 5 ppm, (commonly used standards as the photocatalytic experiment that is conducting with thin films) and 20 ml aqueous solution was used. The absorption spectra of CIP with TiO_2 thin film under solar light simulator are demonstrated in Figure 7. The reference peak of CIP was selected around 273 nm and the decrease of this peak as a function of reaction time is apparently seen from the figure. The peak position of CIP moves to lower wavelength, i.e. blueshift is observed with increasing reaction time and after 90 min irradiation, the wavelength of peak move to 265 nm. This blueshift was associated with the aromatic ring opening process [26-27]. At the first stage of the experiment, TiO_2 thin film and CIP left in dark for 40 min for providing absorption-desorption equilibrium. The photocatalytic degradation efficiency of TiO_2 thin film with CIP antibiotic is demonstrated in Figure 8. The photocatalytic efficiency of TiO_2 thin film has significantly enhanced when compared to malachite green dye. Although the photocatalytic reaction time of malachite green dye is longer than CIP, the removal rate of CIP is higher than the malachite green dye. The removal rate of malachite green dye was reached to 86 % with 100 min irradiation, but the removal rate of CIP was reached to 93 % with 90 min irradiation.

The photocatalytic stability and reusability is an essential parameter for industrial applications, and photocatalytic stability of the synthesized TiO_2 thin film was studied. The recycling experiments are conducted under a solar light simulator for four cycles with the same condition of the experiment. After each cycle, TiO_2 thin film was washed with distilled water and dried at oven at 40 °C for 24 hours. As seen in Figure 9 the stability of TiO_2 thin film did not decrease significantly after four-cycle. These results implied that the synthesized TiO_2 thin film posses excellent cycle stability. A recent study related to the reusability of boron and cerium doped TiO_2 catalysts demonstrates that photocatalytic degradation of CIP is decreased from 93

% to 69 % at the end of the fifth cycle [28]. The photoactivity of TiO_2 thin film ascribed by the illustrated solar light irradiation might generate electron-hole pairs that can react with water to produce hydroxyl and superoxide radicals, and they can oxidize and mineralize the CIP molecules [29].

Conclusion

In this study, TiO_2 thin film was successfully synthesized by spray pyrolysis methods on glass substrate. The synthesized film was characterized by using several analytical instruments. It was determined by XRD measurements that TiO_2 thin film was in anatase form. Bandgap of the obtained film was found to be 3.33 eV. The photocatalytic effect of this film on dyestuffs and antibiotics was investigated. As a result of the experiments, it was found that methyl blue degradation was approximately 65 % after 90 minutes, malachite green degradation was 86 % after 100 minutes, and antibiotic degradation was 93 % after 90 minutes. Degradation experiments on ciprofloxacin were carried out using the same film for 4 times and it was found that the effect of photocatalytic degradation decreased by 9 % at the end of 4 experiments. From here it is understood that the photocatalytic degradation reusability of titanium thin films is quite high.

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Синтез тонких плівок оксиду титану методом розпилювального піролізу та його фотокаталітична активність для розкладання барвників та ципрофлоксацину

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Тонкі плівки оксиду титану (TiO_2) отримано методом розпилювального піролізу. Структурні властивості отриманих плівок досліджували за допомогою дифракції X-променів (XRD) та встановлено наявність тетрагональної структури. Морфологічні особливості досліджували за допомогою скануючої електронної мікроскопії (SEM). Крім того, досліджено оптичні властивості плівки та розраховано ширину забороненої зони. Досліджено фотокаталітичні властивості тонкої плівки TiO_2 на барвник та антибіотик. У тесті розкладання барвника тонкої плівки використано метиловий синій та малахітовий зелений. Зокрема, було виявлено високу деградацію 86 % через 100 хвилин на малахітовому зеленому. Більше того, деградація ципрофлоксацину через 90 хвилин виявилася 93 %. Досліджено антибіотик ципрофлоксацину та встановлено, що синтезована тонка плівка TiO_2 має чудову стабільність.

Ключові слова: TiO_2, метиловий синій, малахітовий зелений, ципрофлоксацин.