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Degradation of Contaminated Industrial Waste Water using Sol-Gel Derived Ru-doped TiO_2 Photocatalytic Films

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Abstract

In this study, Ru-TiO_2 films were deposited on glass substrates with a sol-gel route for degradation of contaminated industrial water. A solution with the Ru/Ti molar ratio of 0.05 was prepared using ruthenium and titanium based precursors. Solution characterizations were made using a turbidimeter and pH meter. The gel films, prepared by the sol-gel drop casting method, were dried at 300°C for 10 minutes and subsequently heat-treated at 500°C for 5 minutes in air. After that, the oxide thin films were annealed at 600°C for 60 minutes in air. In order to evaluate the phase structure, microstructure, optical, and photocatalytic properties of the coatings, they were investigated using XRD, SEM, and UV/Vis spectrophotometer, respectively. The obtained phase was mostly anatase TiO_2. Photo-oxidation experiments were performed to obtain the photocatalytic activity of the films on impure water using an UV light source. The absorption spectrum of the water samples taken from Cigli Industrial Plant and Gediz River in Izmir/Turkey showed that they have absorbance bands in the range of 300 nm and 500 nm. The Ru doped TiO_2 films exhibited highly photocatalytic activity to decompose organic species in contaminated waters. The degradation percentage ratios were calculated as 75% and 62% for two different industrial water samples.

Keywords: İmpure or (contaminated), water degradation, photocatalytic activity, sol-gel method, and TiO_2 thin film.

Sol-Jel ile Elde Edilen Ru katkılı TiO_2 Fotokatalitik Filmler Kullanılarak Endüstriyel-Kirli Suların Ayrıştırılması

Özet

Bu çalışmada, sol-jel yöntemiyle cam altlıklar üzerine hazırlanmış Ru katkılı TiO_2 filmler endüstriyel kirli suların temizlenmesi için kullanılmıştır. 0,05 Ru/Ti molar oranı içeren çözelti rutenyum ve titanyum esaslı prekürsörler kullanılarak hazırlanmıştır. Hazırlanan bu çözeltinin karakterizasyonu, türbidimetre ve pH metre kullanılarak gerçekleştirilmiştir. Sol-jel damlatma metodu ile hazırlanan jel filmler hava ortamında 300°C'de, 10 dakika süre ile kurutulmuş ve hemen ardından 500°C'de 5 dakika süreyle ısıl işleme tabi tutulmuştur. Son olarak bu oksit filmler yine hava ortamında 600°C'de ve 60 dakikada tavlamaya maruz bırakılarak film oluşturma işlemi tamamlanmıştır. Bu kaplamaların faz yapısını, mikroyapısını, optik ve fotokatalitik özelliklerini incelemek için sırasıyla XRD, SEM ve UV/Vis spektrofotometre teknikleri kullanılmıştır. Elde edilen faz, büyük oranda anataz TiO_2 yapısındadır. Foto-oksidasyon deneyleri, üretilen oksit filmlerin UV ışık kaynağı kullanılarak kirli su içinde fotokatalitik aktivitelerinin belirlenmesi için gerçekleştirilmiştir. Çiğli Sanayi Bölgesi'nden ve Gediz Nehri'nden alınan kirli su örneklerinin absorbans spektrumları özellikle 300 nm ile 500 nm dalgaboyları arasında yüksek absorbans bandı sergilemişlerdir. Sentezlenen Ru katkılı TiO_2 filmlerin endüstriden alınan su örneklerindeki organik kirliliklerin parçalanmasında çok yüksek fotokatalitik aktiviteye sahip oldukları gösterilmiştir. İki farklı su örneği için parçalanma yüzde oranları %75 ve %62 olarak hesaplanmıştır.

Anahtar Kelimeler: Fotokatalitik aktivite, kirli suların temizlenmesi, sol-gel yöntemi, TiO_2 ince film.

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INTRODUCTION

Anatase titanium dioxide (TiO_2) is a well-known semiconductor material for photocatalytic applications on account of its high catalysis efficiency, relatively low cost, high photo-activity, and large suitability for removing various kinds of organic pollutants (Zhang et al. 200, Shen et al. 2010). Anatase Titania has been used for the degradation of organic pollutants, cancer cells, and viruses in the form of nano-crystalline powders, thin-films, and particles (Macwan-Pragnesh et al. 2011). The photocatalytic activity occurs at the semiconductors' surface when the applied light energy is greater than or equal to the band-gap energy interacting with the oxygen to produce an oxidizing effect on the pollutants. Thanks to the band gap energy of anatase Titania (3.2 eV) the energy of the photons fall into the UV portion of the electromagnetic spectrum of higher energy (typically $\lambda \leq 380$ nm). Once the TiO_2 is irradiated with UV light, the electrons are excited from the valance band to the conduction band and create an electron-hole pair. These photo electron-hole pairs have produced an oxidizing potential that is sufficient to oxidize most of the organic pollutants (Ugurlu, 2010, Macwan-Pragnesh et al. 2011).

Many studies have been performed to modify TiO2 with non-metals, such as B, C, N, F, and S to effectively extend the photo response from the UV to the visible light region (Dong et al., 2009). Among these non-metal dopants, doping TiO_2 with nitrogen has been regarded as one of the most effective approaches to improve photocatalytic activity of TiO_2 in the visible region and provides effective routes for degradation of various environmental pollutants (Dong et al. 2009). Asahi et al. (2001) found that N-doped TiO_2 powder (anatase) improves the absorbance by 5–20% in the wavelength range of 400–500 nm. Moreover, noble-metal-loaded catalysts of the type M/TiO_2 have been employed in photocatalytic reactions mainly because (1) they have high electron affinity and hence increase the lifetime of the exactions, thus slowing the recombination of the charge carriers (i.e. electrons and holes) and (2) they are good hydrogenation catalysts since they promote the dissociative adsorption of hydrogen as Hads. Therefore high rates of hydrogen evolution can be expected for metals with a low H_2 over potential (i.e. Pt) and a similar phenomenon can be expected that metals with high over potential (i.e. Ru) will stabilize (Ransit et al. 1995). Matsunagaa et al., (2009) reported the photocatalytic activity of Ru-doped TiO_2 powder as a rutile phase. They obtained a decrease on the reflectivity of 20–80% in the range of 420-750 nm for Ru-doped TiO_2 powder (rutile).

The photo activity of the semiconductor thin films can be enhanced by several methods such as depositing noble metals, surface modification, and doping. Doping as a substitutional exchange of ions can be explained by Goldschmidt Rules (Choi et al. 2010) which consist of four conditions: (1) the ions of an element can extensively replace those of another in ionic crystals if their radii differ by less than approximately 15%, (2) ions whose charges differ by one unit substitute readily for one another provided electrical neutrality of the crystal is maintained. If the charges differ by more than one unit, substitution is generally slight, (3) when two different ions can occupy a particular position in a crystal lattice, the ion with the higher ionic potential forms a stronger bond with the anions surrounding the site, and (4) substitutions may be limited, even when the size and charge criteria are satisfied, when the competing ions have different electro negativities and form bonds of different ionic character (Choi et al. 2010). These doped cations shift the threshold for photonic excitation of the TiO_2 towards the visible range. Based on these conditions, Ru might be a more suitable material for doping of TiO_2 film because the atomic radii of Ru (0.056 nm) (Doi et al. 1999) is close to the atomic radii of Ti (0.060 nm) (Shah et al. 2002).

The film structure of TiO_2 is an ideal form for photocatalytic activity when compared to the powder form. Compatibility of powder catalysts is not suitable for application in terms of the disadvantages of the powder form on stirring during the reaction and also separation of catalyst after the operation. On the other hand, the film form can be directly deposited or fixed on the reactor medium and etc. There are several thin film deposition methods like plasma enhanced chemical vapor deposition, ion beam induced chemical vapor deposition, wet process, sol–gel electrophoresis deposition, reaction with hydrogen-bearing gas, anodic oxidation, and sol–gel process (Matsunagaa et al. 2009). Among these techniques, the sol-gel method has some advantages such as simple and easy fabrication, suitable for any substrates and large

areas, good homogeneity, ease of composition control, low processing temperature, and good optical properties. Furthermore, the sol-gel process is also an efficient way to produce thin, transparent, and multi layered films on various substrates including glass (Brinker et al. 1990, Lucic-Lavcevic et al. 1998, Lin et al. 1998, Wang et al. 1999, Kim et al. 2002, Sonawane et al. 2002, Gartner et al. 2004, Celik et al. 2006).

The contamination of our environment has been pointed out as one of the major problems of our society. The industrial and agricultural activities contribute to the increase in the pollution of soil, surface, and groundwater (Merabet et al. 2009, Parilti 2010). In this study, contaminated water samples were taken from the Cigli industrial plant (WS-A) and Gediz River (WS-B), respectively (Izmir, Turkey). If this region is taken into account in details, there are too many industrial organizations and agricultural fields which leads to an increase of water contamination (Isık 2000, Minareci et al. 2004).

To the best of our knowledge, only a few researches have been performed on the effect of Ru doping of TiO_2 films for photocatalytic activity (Ranjit et al. 1995, Wetchakun et al. 2008, Kim et al. 2011). In this study, Ru-doped TiO_2 films prepared by the sol-gel method were employed to develop a suitable and efficient water treatment method to remove the organic compounds present in wastewater samples. The phase structure, surface morphology, and photocatalytic activity of the films were investigated.

MATERIALS AND METHODS

Ruthenium-doped TiO_2 Film Preparation

The Sol-gel technique is used to produce Ru-doped TiO_2 (Ru-TiO_2) films. The Sol-gel film synthesis can be summarized as; (1) dissolving precursors to obtain suitable stoichiometry, (2) preparing homogenous solutions, and applying a coating process, (3) applying several heat treatments for removing volatile and organic contents, and (4) obtaining an intended phase structure. Based on the synthesis mechanism summarized above; the precursor (Ruthenium (III) chloride - Alfa Aesar) was dissolved in isopropanol and glacial acetic acid as a solvent and chelating agent, respectively. After the prepared solution was mixed using a magnetic stirrer at room temperature for 15 min, titanium isopropoxide (Ti[$OCH(CH_3)_2$]4, Alfa Aesar) was added to the solution. The precursors were added to the solutions to obtain an Ru/Ti molar ratio of 0.05. The final solution was stirred for 1 h with a magnetic stirrer to obtain a homogenous solution. The schematic rep-resentation of the sol-gel process is shown in Fig. 1.

Ru-TiO_2 films were deposited on glass substrates with a dimension of 15mm× 15mm×3mm. Deposition steps include; ultrasonic cleaning of the substrates in a methanol medium, deposition of the solutions on the cleaned substrates at room temperature, and applying heat treatments according to the determined regimes from the obtained data from the process optimization steps of the mechanism. The optimization of the process was applied using the differential thermal analysis – thermogravimetry (DTA-TG) results of a previous research performed in our laboratories and summarized here. As mentioned in this research, the same heat treatment regimes were followed. The coatings were dried at 300°C for 10 min and subsequently heat treated at 500°C for 5 min in air. The process was repeated six times to increase the thickness of the coating. In order to obtain a polycrystalline phase structure, the multilayered thick films were annealed at 600°C for 60 min in air.

Solution and Film Characterization

In order to produce thin films, it is very important to optimize the solution properties for the sol-gel method. The solution characteristics (pH and turbidity) of this method were measured using a standard pH meter (Mettler Tolede electrode) and TB-1 Velp Scientifica Model turbidimeter, respectively.

X-ray diffraction (XRD, Rigaku, D/MAX-2200/PC) with a Cu-Kα irradiation wavelength of λ=0.15418 nm was used to identify the phase structures of the film. The surface morphologies were examined using a scanning electron microscope (SEM, JEOL, JSM 6060) to decide whether the coatings have suitable surface morphologies for photocatalytic degradation or not. As an important part of the film characterization, the refractive index and thickness-band gap measurements were evaluated at room temperature by refractometer (Abbe) and spectrophotometer (V-530 JASCO UV/VIS), respectively.

The photocatalytic activities of the Ru-TiO_2 films were measured based on the degradation of the organic content of wastewater samples WS-A

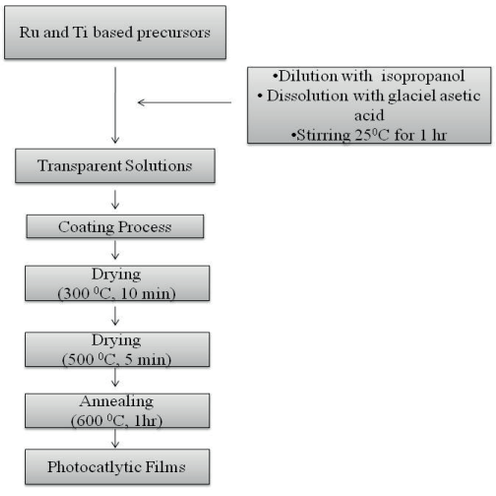

Fig. 1. A Flow chart of sol–gel processing for Ru-TiO_2 films.

and WS-B taken from the Cigli Industrial Plant and Gediz River in Izmir, TURKEY, respectively. Samples taken from these sources were reported to include photocatalytically degradable food and petroleum products (Çelik et al. 2003, Çelik et al. 2011). Before using these water samples, they were filtered by 9.5 μm filter paper (Munktell) in order to eliminate large pieces. Then 10 mL samples of WS-A and WS-B were placed in separate beakers. The Ru-TiO_2 films on the glass substrates were then immersed in the beakers for 24 h under UV irradiation (Philips TUW series UV Lamp UV-C, 254 nm wavelength) with air ventilation in a box with dimension of 45x45x60 cm. The UV-VIS absorption spectra of the irradiated wastewater samples were measured by UV-VIS spectrophotometer (V-530 JASCO UV/VIS). The degradation percentages of the WS-A and WS-B samples were calculated from the absorption spectrum curves by using pure deionized water as a reference medium.

RESULTS AND DISCUSSION

Solution Characterization

The data obtained from the turbidity measurements are used to determine whether the solutions are dissolved properly or not. The unit of the turbidity data is nephelometric turbidity units (ntu). This value defines the homogenation quality of the solutions with a value between 0 ntu and 1000 ntu. The more the value of the turbidity is closer to 0 ntu the more the precursors are completely dissolved in a solvent medium. In the experiments, the turbidity value of the solution was 130 ntu, which is acceptable to deposit the solutions.

The mechanism of the sol-gel reactions is so complex due the fact that there are so many mechanisms which affect the influence rate of hydrolysis and condensation. Many factors in the sol–gel process including temperature, pH, catalyst, nature of the solvent, and the type of salt and alkoxide-based precursors (Brinker et al. 1990). The pH value of the solutions is an important factor among these parameters. Owing to this reason, the pH value of the solution was found to be 0.41. In construction of three dimensional polymeric gel networks in the sol-gel process, the pH value plays an important role. While the ramified structure is randomly formed in acidic conditions, separated clusters are formed from the solutions showing basic characters (Pierre 1998, Zeman et al. 2002, Guillard et al. 2002, Onar et al. 2007, Celik et al. 2007). Furthermore, it can be noted that these factors influence the film formation characteristic after gelation. For instance, homogeneous, continuous, and textured films can be produced using optimum pH values. Therefore, there is a strong correlation between the film structure and gelation for further processing.

Crystalline Structure Analysis

The XRD pattern of the annealed thin film is depicted in Fig. 2. According to the pattern, anatase type TiO_2 (JCPDS: 21-1272) with a crystalline structure which corresponds to the tetragonal system was strongly observed with a low amount of rutile type TiO_2 (JCPDS: 21-1276) which also has a tetragonal crystal structure. It is well known that anatase phase of TiO_2, which is thermodynamically less stable than the rutile phase and transforms into the rutile phase at elevated temperatures, has an important role in photocatalytics (Macwan-Pragnesh et al. 2011). Depending on these results, a nearly pure TiO_2 anatase phase was determined to afford phocatalytic activity. It can also be seen that the peaks at 2θ of 25.32, 36.98, 37.84, 38.60, 48.07, 53.95, 55.10, 62.16, 68.84, and 70.34 are assigned to (1 0 1), (1 0 3), (0 0 4), (1 1 2), (2 0 0), (1 0 5), (2 1 1), (2 1 3), (1 1 6), and (2 2 0) lattice planes of the anatase TiO_2. Since the amount of Ru addition to the structure is too low, any peaks related to Ru based structures were not observed in the diffraction pattern.

Surface Morphology

Fig. 3a., 3b., and 3c denote SEM micrographs of Ru-TiO_2 films on a glass glide substrate at the

magnifications of 500x, 1000x, and 5000x, respectively. As seen in the microstructure images at different scales of focusing, island like structures, caves, and channels were obtained. It was noticed that the sizes of the square-like islands were found to be approximately 5μm x 5μm and the widths of the channels are approximately 400 nm. All these microstructural features show that there is a very large catalyst surface. In so far as the applied production route containing thermal shock with instant temperature changes, small cracks and pinholes can easily form in the coatings. The process was repeated six times to make the coatings thicker. In this case small cracks, pinholes, and island-like structures form when the film thickness is increased.

Photocatalytic Activity

The photocatalytic activity of Ru-TiO_2 thin films was characterized by the absorbance spectrum of the degraded WS-A and WS-B samples under UV light. Fig. 4a and 4b show the photo-degradation effect of the immersion of WS-A and WS-B samples with Ru-TiO_2 films' after being irradiated for 24 hours under UV light, respectively. Notably, both samples show absorbance bands in the range of 300 nm and 500 nm. Note that the absorbance values of these spectra increase with the increasing organic content in the water samples since organic solvents may have significant UV absorption (Power et al. 1998, Guillard et al. 2004, Onar et al. 2007, Celik et al. 2007). As seen in Figures 4a and 4b, both samples show characteristic absorption bands at 400 nm. Ru-TiO2 films exhibit active behaviors for photocatalytic degradation of organic species in water samples and the degradation percentages of WS-A and WS-B water specimens were calculated as ≈ 75 % and ≈ 62 %, respectively.

The basic mechanism for TiO_2 based photocatalytic degradation is proposed to involve the generation of an electron-hole (e^-/h^+) pair, leading to the formation of hydroxyl radicals ($_\bullet OH$), superoxide radical anions (O_2-), and hydroperoxyl radicals ($_\bullet OH$) as shown below (Dionysiou et al. 2000, Daneshvar et al. 2003, Da Silva et al. 2003):

$$TiO_2 + h\nu \rightarrow TiO_2\,(h^+ + e^-) \quad (1)$$

$$H_2O_{(ads)} + h+ \rightarrow {}_\bullet OH + H^+ \quad (2)$$

$$OH^- + h^+ \rightarrow {}_\bullet OH \quad (3)$$

$$O_2 + e^- \rightarrow O_2{}_\bullet - \quad (4)$$

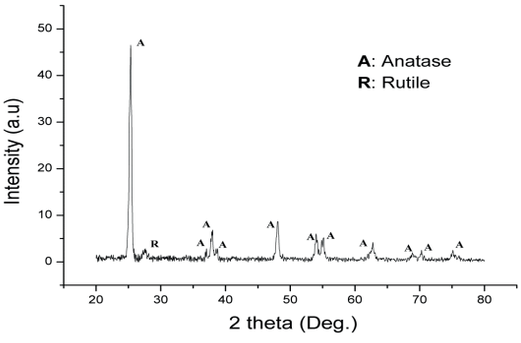

Fig. 2. The XRD patterns of Ru-TiO_2 thin films produced on glass substrate.

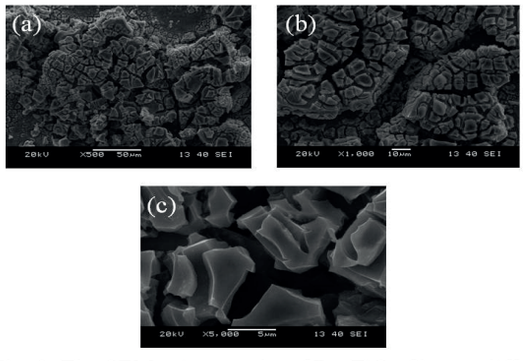

Fig. 3. The SEM micrographs of Ru-TiO_2 films at different magnifications.

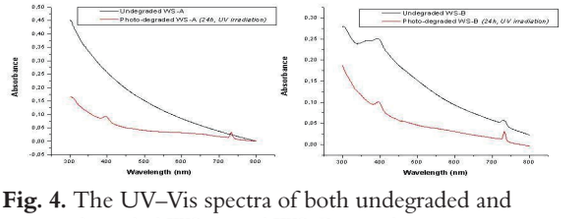

Fig. 4. The UV–Vis spectra of both undegraded and degraded WS-A and WS-B samples.

$$O_{2(ads)} + e^- + H+ \rightarrow HO_2 \quad (5)$$

The organic pollutants are attacked and oxidized by the radicals formed through the mechanisms detailed above. In addition to hydroxyl radicals, superoxide radical anions and in some cases the positive holes help the degradation mechanism of organic impurities (Zang et al. 2005).

The photocatalytic activity of TiO_2 depends on several parameters such as crystalline structure, recombination rate of electron-hole pairs, and the surface hydroxyl group (Eshaghi et al. 2011). The crystalline structure has a very important role on the efficiency of the photocatalytic activity. Several studies proved that the anatase phase of TiO_2 has a higher photodegradation effect than the rutile phase

(Zhang et al. 2005, Kim et al. 2009, Shen et al. 2010, Macwan-Pragnesh et al. 2011). This noticeable distinction might be a result from the oxidation and reduction potentials of the photo generated e^- and h^+ in the conduction and valance bands for the anatase and rutile phases.

In addition, the photo generation of an electron-hole pair which can either recombine or dissociate in their bands has a significant effect on the photocatalytic process. The band gap energy value of the TiO_2 semiconductor material is 3.2 eV and is related to the number of photo-generated electron-hole pairs under UV light irradiation. If the band gap energy can be decreased, a larger number of electron-hole pairs can be generated for the same irradiation energy resulting from the change in the photocatalytic rate. In this study, the band gap energy values of pure and ruthenium-doped TiO_2 films was measured as 3.2 eV and 2.99 eV showing the effect of Ru.

Photo-active Ru-TiO_2 films were successfully fabricated by a very simple, efficient, and cost-effective deposition method. The following results can be summarized as follows:

(1) The turbidity and pH values are important in controlling the quality of films and gelation reactions, respectively. The ionic structures of the precursors assist with the increase in acidic behavior. Thus, the pH value was found as 0.41 and the turbidity value as 130 ntu which is a reasonable value when compared with 1000 ntu.

(2) The phase structure and microstructure are suitable for the activity of the films. High intensity pure anatase phase with a small amount of rutile phase was determined from the XRD results. The obtained microstructure assists to increase the catalyst surface because of cracks, pinholes, and cavity islands.

(3) The optical band gap of the film is 2.9 eV which is lower than that of the pure anatase TiO_2. This result demonstrates that doping helps the activity of film.

(4) The photocatalytic efficiency percentages of WS-A and WS-B water specimens, in which the Ru-TiO_2 films were immersed was found to be 75 % and 62 %, respectively. The efficiency of the films can be studied with different stoichiometries to increase the values closer to 100%.

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