Comparison of Surface Properties of B$_2$O$_3$-Doped TiO$_2$ and Non-Doped Thin Films with Sol-Gel Method

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Abstract
Titanium dioxide (TiO$_2$) is a widely used material in nanotechnological applications. Especially in photocatalytic and optical applications, TiO$_2$ thin films are an indispensable material. Metal-doped thin films are of interest to researchers for the development of these properties.

In this study, the effect of boron oxide (B$_2$O$_3$) additive on surface properties in coating TiO$_2$ thin films on soda-lime glasses was investigated. In the experimental study, alkoxide solutions with a source of boron and titanium were used. TiO$_2$ sol was prepared with Sol-Gel method. In addition, the sol was prepared by adding Trisopropyl borate. Condensation and polymerization steps were completed in acid catalysis and the solution was obtained. In the home-made dip coater device, the solution is coated on the surface. The substrate was immersed in solution at constant speed for a specified time (approximately 30 seconds). It was then withdrawn at the same speed. The surface properties of dried thin films have been characterized by applying morphological analysis (Scanning Electron Microscope) and contact angle measurement tests. The surface shows hydrophilic properties, as an angle of less than 90 degrees occurs on the uncoated glass surface. As is seen contact angle image of TiO$_2$, an angle of 11.83 degrees has occurred on the surface of TiO$_2$ coated glass. As is seen contact angle image of boron oxide coated glass, an angle of 24.12 degrees has occurred on the surface of B$_2$O$_3$ coated glass. As is seen contact angle image of TiO$_2$ and boron oxide coated glass, an angle of 6.12 degrees has occurred on the surface of TiO$_2$ and B$_2$O$_3$ coated glass. So, although the surface is very close to the superhydrophilic degree, it is hydrophilic as the contact angle of the surface is greater than 5 degrees.

As a result, the B$_2$O$_3$-doped TiO$_2$ coated surface was found to have better hydrophilic properties than the non-doped TiO$_2$ surface. It has been observed that the boron oxide-doped TiO$_2$ coated glass material has a superhydrophilic value.

Keywords: B$_2$O$_3$-Doped TiO$_2$, Sol-Gel, Superhydrophilic.

B$_2$O$_3$-Katkılı TiO$_2$ ve Katkısız İnce Filmlerin Yüzey Özelliklerinin Sol-jel Yöntemi ile Karşılaştırılması

Öz
Titanyum dioksit (TiO$_2$) nanoteknolojik uygulamaları yaygın olarak kullanılan bir malzemedir. Özellikle fotokatalitik ve optik uygulamalarda, TiO$_2$ ince filmler vazgeçilmez bir malzemedir. Metal katkılı ince filmler, bu özelliklerinin geliştirilmesi için araştırmacılarnın ilgisini çekmektedir.

Bu çalışmada, bor oksit (B$_2$O$_3$) katkıının, TiO$_2$ ince filmlerinin soda-kireç camları üzerine kaplanmasında yüzey özellikleri üzerindeki etkisi araştırılmıştır. DeneySEL çalışmada, bor ve titanyum kaynağı olan alkoksit çözeltileri kullanılmıştır. TiO$_2$ sol, Sol-jel yöntem ile kaplanmıştır.

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yöntemle iki hazırlandı. Ek olarak, Sol, Trizisopropil Borat eklenerek hazırlanmıştır. Asit katalizinde yoğunlaşma ve polimerizasyon aşamaları tamamlanmış olup özeltil elde edilmiştir. Ev yapımı sol-jel dal DMA kaplama cihazında, özeltil yüzeye kaplanmıştır. Kullanıldığı mekanik düzene, taşıştırıcı belli bir düsey hızla çözeliti daldırıp aynı hızla (yaklaşık 30 saniye) çıkarma işlevi görzüktedir.

Kurutulmuş ince filmlerin yüzey özellikleri, morfolojik analiz (taramalı elektron mikroskobu) ve temas açısından ölçüm testlerinin uygulanmasıyla karakterize edilmiştir. Cam kaplanmış durumda 90 dereceden küçük olduğu için hidrofil bir özellik göstermektedir. TiO$_2$ kaplanmış cam örnekine ise 11.83 derecelik bir açı yaparak 0 dereceye yakın olduğundan bu hidrofil bir özellik göstermektedir. B$_2$O$_3$ kaplı cam yüzeyinde 24.12 derecelik bir açı meydana geldiği için yüzey hidrofil özellikler göstermiştir. TiO$_2$-Boroksit kaplı cam örnekımız ise 0 dereceye yakın bir özellik göstermektedir. TiO$_2$ ve B$_2$O$_3$ kaplı cam yüzeyinde 6.12 derecelik bir açı meydana gelmiştir. Bu nedenle, yüzey süperhidrofilik dereceye çok yakın olması rağmen, yüzeyin temas açısından 5 dereceden büyük olduğu için yüzey hidrofiliktir.

Sonuç olarak, B$_2$O$_3$ katıklı TiO$_2$ kaplı yüzeyin, katıksız TiO$_2$ yüzeyinden daha iyi hidrofilik özelliklere sahip olduğu bulunmuştur. Bor oksit katıklı TiO$_2$ kaplamalı cam malzemenin süperhidrofilik bir değere sahip olduğu gözlenmiş.

Anahtar Kelimeler: B$_2$O$_3$-Katıklı TiO$_2$, Sol-Jel, Süperhidrofilik.

1. Introduction

Nowadays, research and development work in the field of nanotechnology is growing rapidly, focusing on nanomaterials that include high performance and new functions [1]. Recently, TiO$_2$ thin films with hydrophilic properties have been attracting intense attention. TiO$_2$ thin films have many advanced functions and features, such as anti-decay, deodorization, sterilization and anti-fogging. Therefore, in order to increase the surface area of TiO$_2$ and the hydrophilicity of the surface, metals, rare elements, nitrogen or iron are doped to TiO$_2$ films [2-5]. In order to compare the morphology and microstructure of different films by coating, the sol-gel dip-coating method may be preferred [6-7].

Sol-gel method is one of the most widely used techniques in which glass, glass-ceramic or composite materials can be produced by preparing the solution, gelling and removing the solvent from the system [8-9]. Sol-gel dip coating method is simple, economical and functional. Furthermore, dip-coating method, the substrate to be coated is prepared it is based on the fact that it is dipped in the solution at a certain speed and withdrawn from the solution again at the same speed. This method is one of the most preferred methods among sol-gel coating methods [10].

In this study, different solutions for TiO$_2$ and B$_2$O$_3$ were prepared by sol-gel method. On the other hand, the prepared solutions were coated to the surface with a homemade dip-coater devices. The microstructure of the prepared surfaces was examined with scanning electron microscopy (SEM). The contact angles of the surfaces were also examined with the contact angle measurement device. As a result of the investigations, it was observed that the glass material coated with TiO$_2$ has a better hydrophilic property than the glass material coated with B$_2$O$_3$. In addition, it has been observed that the TiO$_2$ coated glass material doped with B$_2$O$_3$ has a superhydrophilic property.

2. Material and Method

2.1. Preparation of TiO$_2$ solution

In this study, 1,854 ml of titanium (IV) Isopropoxide and 10 ml propanol was added to the glass beaker after cleaning the material to be used. Then, the mixture was placed in the magnetic stirring apparatus and stirred for 30 minutes. 2 ml of nitric acid and pure water were added to the mixture of titanium (IV) isopropoxide-propanol. In order not to evaporate the solution, the lid of the solution was kept closed at each stage.

2.2. Preparation of B$_2$O$_3$ solution

2,298 ml of Trisopropyl borate and 10 ml propanol was added to the glass beaker after cleaning the material to be used. Then, the mixture was placed in the magnetic stirring apparatus and stirred for 30 minutes. 2 ml of nitric acid and pure water were added to the mixture of B$_2$O$_3$-propanol. In order not to evaporate the solution, the lid of the solution was kept closed at each stage.

2.3. Coating of Thin Films

In our study, dip coating method was used to cover films. The thin films are carefully placed in the dip-coater devices. The substrate was immersed in solution at constant speed for a specified time (approximately 30 seconds). It was then withdrawn at the same speed. In addition, the surface plane of the solution with the carrier surface was kept perpendicular. The carrier was given an angle of 5-7 degrees without disturbing the steepness of the plane. If this slope is not given, completely drainage cannot be achieved when the lower limit of the carrier is withdrew of the solution at the same time. Therefore, in intermediate heat treatments, the solution can't be dried completely.

3. Results and Discussion

3.1. Contact Angle Measurements

The magnitude of the contact angle depends on the relative magnitude of the gravitational forces (cohesion forces) between the liquid's own molecules and the gravitational forces (adhesion forces) between the liquid and solid [11]. The greater the size of the cohesion forces than the size of the adhesion forces, the greater the contact angle between the liquid and solid.

As shown in Figure 2.1., the surface shows hydrophilic properties, as an angle of less than 90 degrees occurs on the uncoated glass surface.
As shown in Figure 2.2., an angle of 11.83 degrees has occurred on the surface of TiO$_2$ coated glass. Therefore, since the contact angle is close to 0 degrees, the surface shows a hydrophilic property.

As shown in Figure 2.3., an angle of 24.12 degrees has occurred on the surface of B$_2$O$_3$ coated glass. Therefore, the surface showed hydrophilic properties.

As shown in Figure 2.4., the SEM image taken from the surface of the TiO$_2$ coated glass shows that the surface has a homogeneous structure.

As shown in Figure 2.5., the SEM image taken from the surface of the TiO$_2$ coated glass doped with B$_2$O$_3$ shows that the surface has a heterogeneous structure.

**3.2. SEM Analysis**

Scanning electron microscope images of prepared surfaces are as follows;

As shown in Figure 3.5., the SEM image taken from the surface of the TiO$_2$ coated glass shows that the surface has a homogeneous structure.

As shown in Figure 3.6., the SEM image taken from the surface of the TiO$_2$ coated glass doped with B$_2$O$_3$ shows that the surface has a heterogeneous structure.

**4. Conclusions and Recommendations**

In this study, it was observed that the glass material coated with TiO$_2$ has better hydrophilic properties than the glass material coated with B$_2$O$_3$. It has been observed that the surface of boron oxide and TiO$_2$ coated glass to the fact that material is superhydrophilic. However, differences in surface thickness were observed due the TiO$_2$ coated glass surface doped with B$_2$O$_3$ was not homogeneous. So, it has been a heterogeneous coating.
In future studies, the characteristics of surfaces can be studied by adding different materials to TiO$_2$-coated surfaces.

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**References**

[1] Shibuya, M., & Miyauchi, M. (2009). Site-Selective Deposition of Metal Nanoparticles on Aligned WO$_3$ Nanotrees for Super-Hydrophilic Thin Films. Advanced Materials, 21(13), 1373-1376.

[2] Banerjee, S., Gopal, J., Muraleedharan, P., Tyagi, A. K., & Raj, B. (2006). Physics and chemistry of photocatalytic titanium dioxide: visualization of bactericidal activity using atomic force microscopy. Current science, 90(10), 1378-1383.

[3] Chen, D., Huang, F., Cheng, Y. B., & Caruso, R. A. (2009). Mesoporous anatase TiO$_2$ beads with high surface areas and controllable pore sizes: a superior candidate for high-performance dye-sensitized solar cells. Advanced Materials, 21(21), 2206-2210.

[4] Nahar, M. S., Hasegawa, K., & Kagaya, S. (2006). Photocatalytic degradation of phenol by visible light-responsive iron-doped TiO$_2$ and spontaneous sedimentation of the TiO$_2$ particles. Chemosphere, 65(11), 1976-1982.

[5] Luca, D., Mardare, D., Iacomi, F., & Teodorescu, C. M. (2006). Increasing surface hydrophilicity of titania thin films by doping. Applied surface science, 252(18), 6122-6126.

[6] Ilkhechi, N. N., Ghorbani, M., Mozammel, M., & Khajeh, M. (2017). The optical, photo catalytic behavior and hydrophilic properties of silver and tin co doped TiO 2 thin films using sol–gel method. Journal of Materials Science: Materials in Electronics, 28(4), 3571-3580.

[7] Li, H., Zhao, G., Han, G., & Song, B. (2007). Hydrophilicity and photocatalysis of Ti1–xVxO2 films prepared by sol–gel method. Surface and Coatings Technology, 201(18), 7615-7618.

[8] Zhang, W., Tu, J., Long, W., Lai, W., Sheng, Y., & Guo, T. (2017). Preparation of SiO2 anti-reflection coatings by sol-gel method. Energy Procedia, 130, 72-76.

[9] Zhang, Z., Zhang, P., Guo, L., Guo, T., & Yang, J. (2011). Effect of TiO2–SiO2 sol–gel coating on the cpTi–porcelain bond strength. Materials Letters, 65(7), 1082-1085.

[10] Faustini, M., Louis, B., Albouy, P. A., Klemmel, M., & Grosso, D. (2010). Preparation of sol–gel films by dip-coating in extreme conditions. The Journal of Physical Chemistry C, 114(17), 7637-7645.

[11] Loeb, G. I., & Schrader, M. E. (Eds.). (2013). Modern approaches to wettability: theory and applications. Springer Science & Business Media.