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# Synthesis of V, Er and Ce Substitued $TiO_2$ Films via Sol-gel Method to Degrade Cyanide Content in Waste Water Under UV/Sunlight Source

**Erkan ÇAKIROĞLU[1], Mustafa EROL[1, 2, *], Sibel KOCAKUŞ[3] and Erdal ÇELİK[1, 4, 5]**

[1] *Dokuz Eylul University, Engineering Faculty, Department of Metallurgical and Materials Engineering, Buca, Izmir*

[2] *Dokuz Eylul University, The Graduate School of Natural and Applied Sciences, Buca, Izmir*

[3] *Marmara University, Department of Physics, Istanbul*

[4] *Dokuz Eylul University, Center for Production and Applications of Electronic Materials (EMUM), Buca, Izmir*

[5] *Dokuz Eylul University, Graduate School Natural and Applied Sciences, Department of Nanoscience and Nanoengineering, Buca, Izmir*

*e-posta: m.erol@deu.edu.tr*

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***Key words***
Sol-gel; $TiO_2$; Cynide; Waste water

**Abstract**

In this study, Vanadium (V), Erbium (Er) and Cerium (Ce) substituted $TiO_2$ films were deposited on glass substrates via sol-gel technique in industrial scale in order to provide photocatalytic degradation of cyanide in waste water. Structural, microstructural and electrical properties of the thin films were examined and thin films coated on glass substrates were used as the photocatalyzer in the photocatalytic degradation of cyanide in waste waters under UV/sunlight source. It was found that 85-90 % efficiency was obtained in degradation of cyanide in waste water using modified $TiO_2$ films.

# UV/Güneş Işığı Kaynağı Altında Atık Sudaki Siyanür İçeriğini Gidermek İçin Sol-jel Metodu ile V, Er ve Ce Katkılandırılmış $TiO_2$ Filmlerin Sentezlenmesi

***Anahtar kelimeler***
Sol-jel; $TiO_2$; Siyanür; Atık su

**Özet**

Bu çalışmada, atık sudaki siyanürün fotokatalitik bozunmasını sağlamak için kaplanmış altlıklar üzerine endüstriyel ölçekte sol-jel tekniğiyle Vanadyum (V), Erbiyum (Er) ve Seryum (Ce) kakılandırılmış $TiO_2$ filmlerin cam altlıklar üzerine kaplanmıştır. İnce filmlerin yapısal, mikroyapısal ve elektriksel özellikleri incelenmiş ve cam üzerine kaplanmış filmler UV/güneş ışık kaynağı altında atık sularda siyanürün fotokatalitik bozunmasında fotokatalizör olarak kullanılmıştır. Modifiye edilmiş $TiO_2$ filmler kullanılarak atık sulardaki bozunmada % 85-90 verim elde edildiği bulunmuştur.



## 1. Introduction

Presence of free and complex cyanides in industrial effluents is a problem of major concern thanks to the well-known toxicity of these species for living organisms, even at low concentrations. Of particular concern is the discharge of large volumes of cyanide-contaminated waste water from gold cyanidation plants. At present most of the world's gold production is achieved using cyanide leaching on account of its simplicity and high efficiency. Ore containing only a few ppm of gold can be solubilized with aqueous solutions of sodium or calcium cyanide at pH 10–12 either by agitation leaching of finely ground material or heap leaching of crushed product. In some cases gold recovery can reach 98–99 % after leaching at ambient temperature for 24–48 hours (Hafizah and Sopyan, 2009). Thus, several methods have been proposed for treating the industrial wastewater polluted by cyanides, including chemical, biological and photocatalytic treatments; among them the photocatalytic oxidation process using a semiconductor catalyst under UV-light radiation has been proposed as an attractive, clean and

efficient method for cyanide elimination (Yao and Wang, 2010). The process has several advantages over competing processes. These are: (1) complete mineralization, (2) no waste disposal problem, (3) low cost, and (4) only mild temperature and pressure conditions are necessary [3]. There are numerous study and information available on the photocatalytic mineralization process in terms of reactions and mechanism, degradation of individual compounds, comparison of different photocatalysts (Xiao, *et.al.,* 2006). Degradation of cyanides in waste water by $TiO_2$ photocatalyst was studied by many research groups in literature (Valde´s, *et.al.*, 2008; Chen and Oh, 2010). Most of the studies were indicated on degradation of cyanides using pure $TiO_2$ photocatalysts. Differently from their studies this work was carried out substitution of V, Er, Ce for Ti ion in the crystalline $TiO_2$ structure. Due to substitution defects formed in the crystal lattice of $TiO_2$ through doping with metallic ions, they changed its crystallinity and restrained the composition of photoproduced electrons and cavities to influence its photocatalytic activity (Sayılkan, et.al., 2007). According to mentioned above, this work aimed to investigate effects of substitution in to structural, morphological, electronic and photocatalytic properties of the films produced on glass substrates using sol-gel method. Nevertheless, V, Er and Ce substituted $TiO_2$ films deposited on glass substrates via sol-gel technique were used to provide photocatalytic degradation of cyanide in waste in industrial scale.

## 2. Material and Method

Precursor solution was prepared by dissolving appropriate amounts of tetraisopropyl orthotitanate ($C_{12}H_{28}O_4Ti$, Merck) in isopropanol, ($(CH_3)_2CHOH$, Merck). Also calculated amounts of vanadium (III) chloride ($VCl_3$, Merck), erbium (III) chloride ($ErCl_3$, Merck) and cerium (III) nitrate hexahydrate ($CeN_3O_9.6.0H_2O$, Merck) were dissolved in previous titanate solution to yield substitutions of V, Er and Ce respectively. In order to form chealation reactions, small amounts of glacial acetic acid and hydrochloric acid were added to solutions. Subsequent to solution preparation, the solutions were stirred via magnetic strirrer 30 minutes at room temperature. In order to determine solution qualities generally determination of turbidity and pH values are important issues on homogeneity and sol electrochemistry respectively. Due to this reason, turbidity and pH values of the prepared solutions were determined using turbidimeter (VELP TB1 Model) and pH meter (MP 230, Mettler-Toledo). Prepared solutions were drop casted on glass substrates to obtain first deposition layer. After the deposition, the obtained films were dried in an incubator at 300 $^oC$ for 10 minutes. The mentioned heat treatment was afforded to improve adhesion forces between glass and solution interface besides removing volatile and some organic content. In order to obtain solid like gel, structure films were dried at 500 $^oC$ for 5 minutes in air. As mentioned above, process approved for the first deposition layer was repeated for five times two obtain thicker and denser films. Finally produced films were annealed at 600 $^oC$ for 1 hour to acquire anatase structured $TiO_2$.

X-ray diffraction (XRD, Rigaku D/MAX-2200/PC) patterns of the films were determined to identify phase structure by means of a diffractometer with a CuKα irradiation. The surface properties and topographies of the films were examined using scanning electron microscopy (SEM, JEOL JSM 6060). An industrial scale specific photocatalytical setup was prepared which contains; $CN^-$ circulated in an alkaline character bath, UV-C lamp and photocatalyst at the bottom surface of the bath. The $CN^-$ decomposition percentage was determined according to titrimetric CN- measurement technique (EPA 9014).

## 3. Results and Discussion

Production of highly efficient $TiO_2$ photocatlyst is directly affected from solution characterization as mentioned in experimental section. Turbidity and pH measurements results were listed in Table 1. According to first column of Table 1, the measured turbidity values are in the range of 3.33 and 10.30 which were found to be too low if compared to the

maximum turbidity value 1000 ntu. This low turbidity values addresses that almost homogenous solutions were synthesized. Therefore the obtained turbidity values of the solutions are acceptable for this application. Other column of Table 1 indicates acidic character of the solutions between 1.32 and 4.70 as pH values. As known, acidic character of the solutions points out branchy and slow gelation which is preferred for thin film applications.

**Table 1.** Turbidity and pH values of the prepared solutions

| Solutions | Turbidity (ntu) | pH |
|---|---|---|
| $TiO_2$ | 10.3 | 4.70 |
| $V-TiO_2$ | 5.42 | 1.78 |
| $Er-TiO_2$ | 8.12 | 1.32 |
| $Ce-TiO_2$ | 3.33 | 2.20 |

XRD patterns of pure $TiO_2$, $V\text{-}TiO_2$, $Er\text{-}TiO_2$ and $Ce\text{-}TiO_2$ photocatalyst films were represented in Figure 1. It has been well known that anatase phase of $TiO_2$, which is less stable than rutile phase thermally and transfers into rutile phase at elevated temperatures, has an important role in photocatalysis (Taoda, 2008). Based on these results, any rutile peak was not identified for pure $TiO_2$ film. Anatase peaks (JPDS:021-1272) were identified with low intensity rutile peaks (JPDS:021-1276) for $V\text{-}TiO_2$, $Er\text{-}TiO_2$ and $Ce\text{-}TiO_2$ films. Phase formation temperature which is applied in this research was also reported as 600°C in much study in the literature to obtain sol-gel derived pure crystalline anatase structure (Saito, 1998; Sayılkan, *et.al*., 2006). By this way, the obtained rutile peaks can be explained as a decrease in the phase formation temperature of rutile structure down to 600°C. Any dopant element peaks such as $VO_x$, $ErO_y$ and $CeO_z$ were not observed in the patterns because of their low concentration in the catalyst materials.

Microstructures of the films determined via SEM were represented in Figure 2. Note that in this case a granular island-like structure was obtained from these coatings. This island-like and crackly structure was considered as a result of different thermal expansion characteristics of susbtrate and film at elevated temperatures. In thought of photocatalytic manner, the obtained structure is found to be better than a crack free and low roughness surface. It is interesting to note here that increasing surface roughness and crack number causes an increase in the surface area which means more photoproduced electrons for degradation.

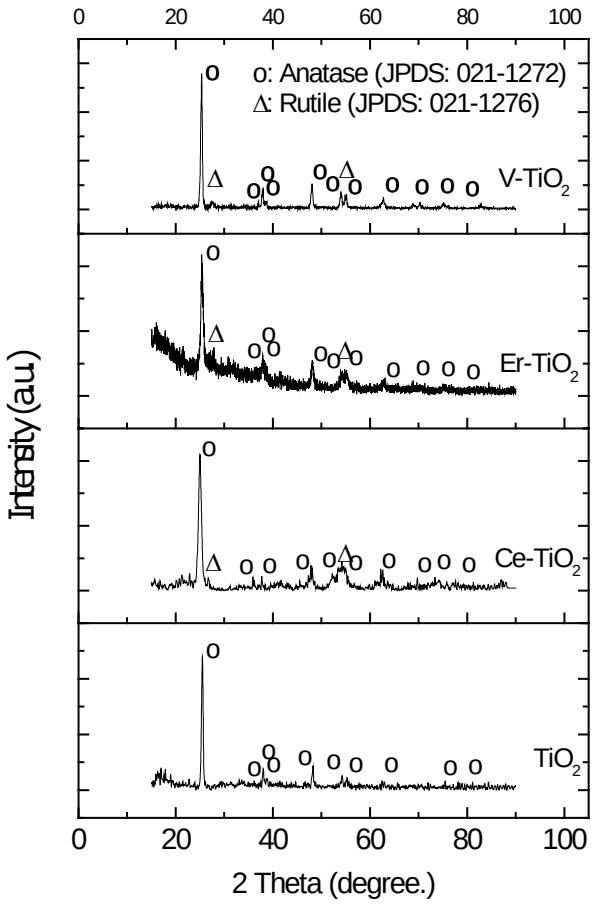
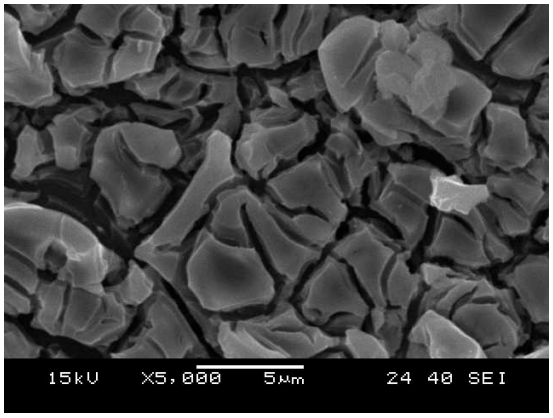



**Figure 1.** XRD patterns of pure $TiO_2$, $V\text{-}TiO_2$, $Er\text{-}TiO_2$ and $Ce\text{-}TiO_2$ photocatalyst films




(a)

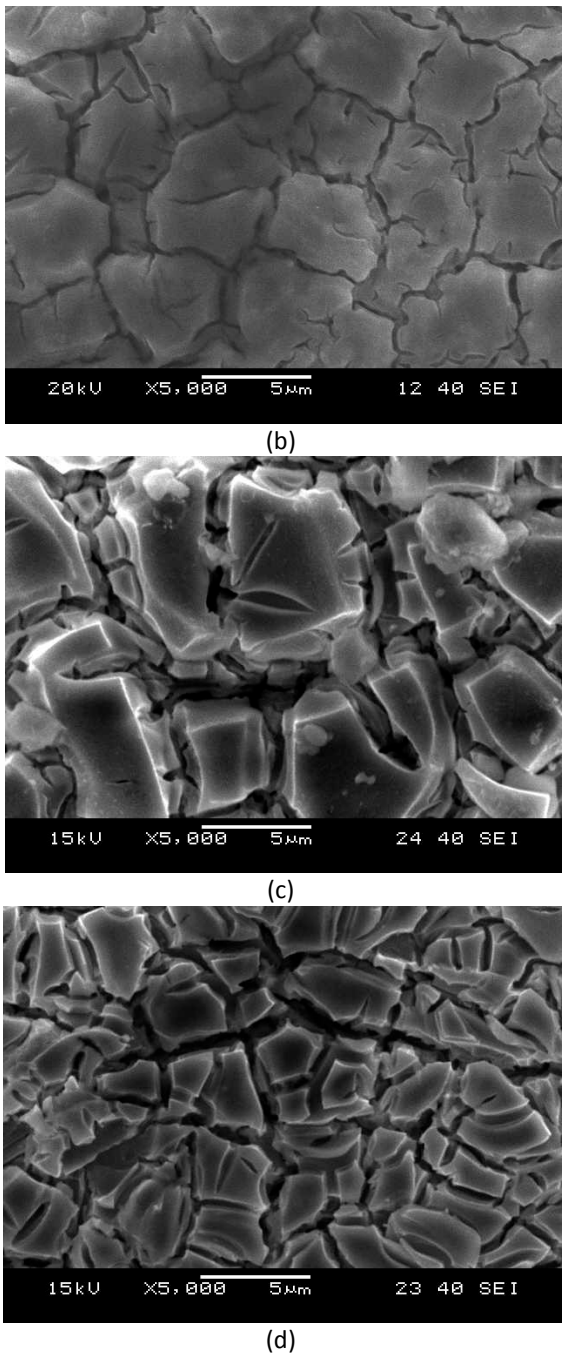



**Figure 2.** SEM micrographs of (a) $TiO_2$, (b) V-$TiO_2$, (c) Er-$TiO_2$ and (d) Ce-$TiO_2$ films.

As mentioned elsewhere (Sparrow. and Woodcock, 1988; Staunton, 1991), experimental setup containing CN solution with concentration 0.8 g/L and $TiO_2$ based photocatalytical films radiated with a UV-C lamp was installed. Time versus CN concentration was recorded using titrimetric method. The obtained results were illustrated in Figure 3, showing CN degradation of the wastewater with concentration 0.8 g/L of CN as a function of processing time using $TiO_2$, V-$TiO_2$, Er-$TiO_2$ and Ce-$TiO_2$ photocatalys films. It was found that the best photocatalyst film is V-$TiO_2$ in this research. Worth nothing here is that once dopant elements such as V, Er and Ce are substituted into $TiO_2$ structure, photocatalytic degradation percentage increased.

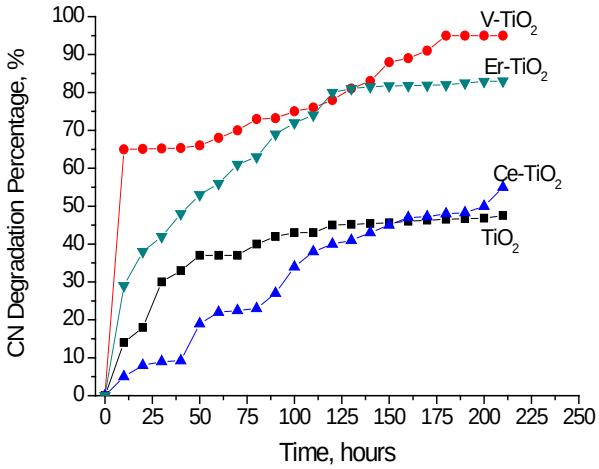



**Figure 3.** CN degradation of the wastewater with concentration 0.8 g/L of CN as a function of processing time using $TiO_2$, V-$TiO_2$, Er-$TiO_2$ and Ce-$TiO_2$ photocatalyst films.

## 4. Conclusion

V, Er and Ce substituted $TiO_2$ films deposited on glass substrates via sol-gel technique were successfully utilized to provide photocatalytic degradation of cyanide in waste. The measured turbidity values which are acceptable for this application are in the range of 3.33 and 10.30. Acidic character of the solutions were determined in the range of 1.32 and 4.70 as pH values. Anatase phase were found for V-$TiO_2$, Er-$TiO_2$ and Ce-$TiO_2$ films. Any dopant element peaks such as $VO_x$, $ErO_y$ and $CeO_z$ were not observed in the patterns because of their low concentration in the catalyst materials. The granular island-like structure was obtained from these coatings. In thought of photocatalytic manner, the obtained structure is found to be better than a crack free and low roughness surface. It was found that the best photocatalyst film is V-$TiO_2$ in this research. When dopant elements such as V, Er and Ce are substituted into $TiO_2$ structure, photocatalytic degradation percentage increased.

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