Surface & Coatings Technology 271 (2015) 207–216

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Photocatalytic degradation of cyanide in wastewater using new generated nano-thin film photocatalyst

Ayşegül Pala [a,b,*], Ruti Ruth Politi [c], Güneş Kurşun [b,c], Mustafa Erol [d], Fatma Bakal [c,e], Gülek Öner [c], Erdal Çelik [b,e,f]

[a] *Dokuz Eylul University, Center for Environmental Research and Development, Tinaztepe Campus, 35397 Izmir, Turkey*
[b] *Dokuz Eylul University, Center for Production and Application of Electronic Materials, Tinaztepe Campus, 35397 Izmir, Turkey*
[c] *Dokuz Eylul University, The Graduate School of Natural and Applied Sciences, Tinaztepe Campus, 353987 Izmir, Turkey*
[d] *Izmir Katip Çelebi University, Department of Material Science and Engineering, Çiğli Main Campus, 35160 İzmir, Turkey*
[e] *Dokuz Eylul University, Department of Metallurgical and Materials Engineering, Tinaztepe Campus, 35397 Izmir, Turkey*
[f] *Dokuz Eylul University, Department of Nanoscience and Nanoengineering, Tinaztepe Campus, 35397 Izmir, Turkey*

## ARTICLE INFO

*Keywords:*
Sol–gel method
Spin coating
Photocatalytic degradation
Nanotechnology
$K_2La_2Ti_3O_{10}$ photocatalyst
Cyanide degradation

## ABSTRACT

This study investigates the possibility of using new generated potassium lanthanum titanates ($K_2La_2Ti_3O_{10}$, KLTO) photocatalyst thin films and $CeO_2$ buffer layer produced using sol–gel method to remove cyanide from wastewater. DTA–TG, FTIR, XRD, XPS, SEM, AFM and profilometer analyses were performed to determine the thermal, structural and morphological characterization of the thin film photocatalysts, respectively. In order to provide the highest photocatalytic activity, new generated photocatalytic films with KLTO/$CeO_2$ architecture were coated on Si (100) substrates and the cyanide degradation experiments were carried out. In this respect, initial concentration, pH of cyanide and light intensity were chosen as variables and their single and joint effects on removal of cyanide from wastewater were investigated. ATLAS Suntest CPS + which simulates solar radiation was used as illumination source for the photocatalytic degradation of cyanide. ANOVA statistical test was carried out to understand the effectiveness of the variables. The degradation experiments were fitted to first order reaction law. The maximum degradation efficiency of cyanide was found to be 99.87% at pH of 10 and light intensity of 750 W/m$^2$ by using 100 mg/l cyanide initial concentration after 5 hour irradiation.

## 1. Introduction

The upward trend of water contamination causes many environmental problems [1]. The presence of cyanide in wastewater is an important issue because of the toxic effect. There are many different treatment processes which are usually used for industrial wastewater treatment facilities [2]. Advanced treatment methods are improved to remove persistence and toxic matters. Photocatalytic oxidation processes are one of the types of advanced treatment method and are suggested to treat polluted water [2,3]. In recent years, photocatalytic specialized on materials and devices are increased not only in academic case but also in industrial applications [4,5]. Photocatalytic semiconductors drew attention because of the ability to remove the pollutants. Photocatalysis is a substance which creates chemical oxidation reaction with the presence of light like chlorophyll in photosynthesis process. When photocatalysis is exposed to the light like photosynthesis process, the activation of the photocatalysis will occur. The most powerful and cheap photocatalyst known is titanium dioxide ($TiO_2$) and the semiconductor structure provides this photocatalytic function. It has high chemical stability, non-toxicity and high oxidation power [6]. Photocatalytic process is started with the absorption of light by the presence of the semiconductor structure. Semiconductors are constituted with an energy gap which are separated two energy band called valance and conductivity band. If photocatalysis which is exposed to photon energy is on the own energy gap, it gives its energy to an electron which is in valance band and electron is reached to the conductivity band. At the end of this reaction, electron–hole pairs occur. Electron–hole pairs which are located in valance and conductivity band become power supply. The size of energy gap and position affects photocatalytic reactions [7]. After the improvements of $TiO_2$, new approaches are enhanced like perovskite type layered materials. It has been realized that these types are more active than $TiO_2$. Ion exchange occurs immediately with perovskite type layered structures in terms of the geometry. One of them is lanthanum-titanates ($K_2La_2Ti_3O_{10}$—KLTO). $La_2Ti_3O10^{2-}$ octahedral perovskite layers and substitutional K ions constitute the structure. This structure provides hydration of toxic and persistent organic matters in aqua solutions with the presence of UV light; in this way it presents high photocatalytic activity [8]. Recently, the layered perovskite photocatalyst KLTO has drawn attention due to its unique properties, for instance, optical properties, electrical transport properties, and especially its

---

[*] Corresponding author at: Dokuz Eylul University, Center for Environmental Research and Development, Tinaztepe Campus, 35397 Izmir, Turkey. Tel.: +90 232 301 70 96; fax: +90 232 453 11 43..
*E-mail address:* aysegul.pala@deu.edu.tr (A. Pala).

http://dx.doi.org/10.1016/j.surfcoat.2014.12.032
0257-8972/

photocatalytic activity. In addition, a lot of derivatives of KLTO can be generated due to replace with other elements [9].

The objective of this study is to synthesize and characterize the new generated KLTO thin film photocatalyst on $CeO_2$ buffer layer/Si (100) plate substrate with the aid of nanotechnological methods called sol–gel and spin coating and to examine their effect on wastewater treatment. Buffer layer method was used to enhance the coating efficiency and adhesion quality. The effect of various parameters on cyanide degradation such as the initial concentration of cyanide in wastewater, pH and the light intensity was examined. ANOVA statistical test was realized to understand the statistical significance of the variables.

## 2. Material and method

New photocatalytic films with KLTO/$CeO_2$ architecture (Fig. 1) were grown on Si (100) plate substrates using as innovative approaches according to flow chart about preparation of substrate, buffer layer and photocatalyst film (see Fig. 2 for details). Highly pure Si with (100) orientation (99.99%) was utilized to coat multilayer films as a substrate. Prior to coating process, Si (100) plate substrates with 2 cm × 2 cm × 0.5 mm of dimension were cleaned at room temperature for 15 min in air by rinsing in acetone in an ultrasonic bath to remove organic contaminants, particles and metallic contaminants on the substrate and subsequently dried at room temperature.

### *2.1. Preparation of the multilayers*

$CeO_2$ film was used to improve adhesion characteristics of KLTO as a buffer layer. The buffer layer was produced on Si (100) by means of sol–gel techniques. For preparation of $CeO_2$ films, Ce based alkoxide material, methanol and glacial acetic acid were used as precursors, solvent and chelating agent respectively. Chemical properties of all materials are given in Table 1 for $CeO_2$ film production. Cerium (III) acetyle–acetone hydrate was dissolved in methanol and glacial acetic acid and the obtained solution was consequently stirred at room temperature for 60 to 120 min in air until it became transparent. After the solution preparation, $CeO_2$ buffer layer was deposited on Si (100) substrate by sol–gel including spin coating system. Thanks to the optimum outcomes with typical spin coating technique, this process was used to make buffer layer application. Here $CeO_2$ film was selected for a buffer layer not only for increasing the crystallographic harmony [11], but also for improving adhesion characteristics between KLTO top layer and Si (100) substrate as mentioned just before. The gel coated Si (100) samples were dried at a temperature of 300 °C for 10 min and then heat treated at temperature of 500 °C for 5 min in air. As a final process, the obtained $CeO_2$ films were annealed at 700 °C for 60 min in air as seen in Fig. 2.

Layered perovskite structured potassium lanthanum titanate $K_2La_2Ti_3O_{10}$ (KLTO) was used as a photocatalytic material. The KLTO films were coated on $CeO_2$/Si (100) samples through sol–gel techniques. As for preparation of KLTO films, K, La and Ti based alkoxide materials, propionic acid, glacial acetic acid and triethanolamin were utilized as precursors, solvent, chelating agent and surface activator respectively. Chemical properties of all materials are summarized in Table 1 for KLTO film production. In order to prepare the solution, lanthanum (III) 2,4 pentanedionate hydrate was mixed with solvent and chelating agent till it is dissolved. To reduce the surface tension and provide good wettability properties, triethanolamine was added into the obtained solution. After this process, potassium 2,4 pentanedionate hydrate compound was put into the beaker and the mixing process was continued as far as potassium based precursor was dissolved. Inasmuch as the temperature of sublimation of the potassium is low, the nimiety of potassium based precursor compound was added according to the literature [10]. Ti based solution was separately prepared using titanium (IV) isopropoxide and solvent, and then added into the previous solution with lanthanum and potassium. The final solution having potassium, lanthanum and titanium was mixed in ultrasonic mixer at 45–50 °C for 30 min in air until they became transparent. After the production of this solution, gel films were deposited on $CeO_2$/Si (100) substrate by spin coating technique. In this technique, an excess amount of the prepared solution was placed on the substrate, which was rotated at high speed in order to spread the fluid by centrifugal force. The film thickness was adjusted by changing the rotation speed, the rotation time, and the concentration of the used solution. KLTO was coated to increase film thickness 5 times in this system. To obtain the multilayer coating, the gel films were dried at 300 °C for 10 min and heat treated at 500 °C for 5 min in air. As a last stage of this procedure, the samples were annealed at the range of temperature of 1150 and 1300 °C for 8 h in air.

**Fig. 1.** KLTO/$CeO_2$/Si (100) architecture for photocatalytic applications.

### *2.2. Characterization of solutions and films*

The turbidity, pH and contact angle values of the prepared solutions were measured to better understand the properties of the Ce-based and K, La, and Ti based solutions. Turbidity tests were performed by

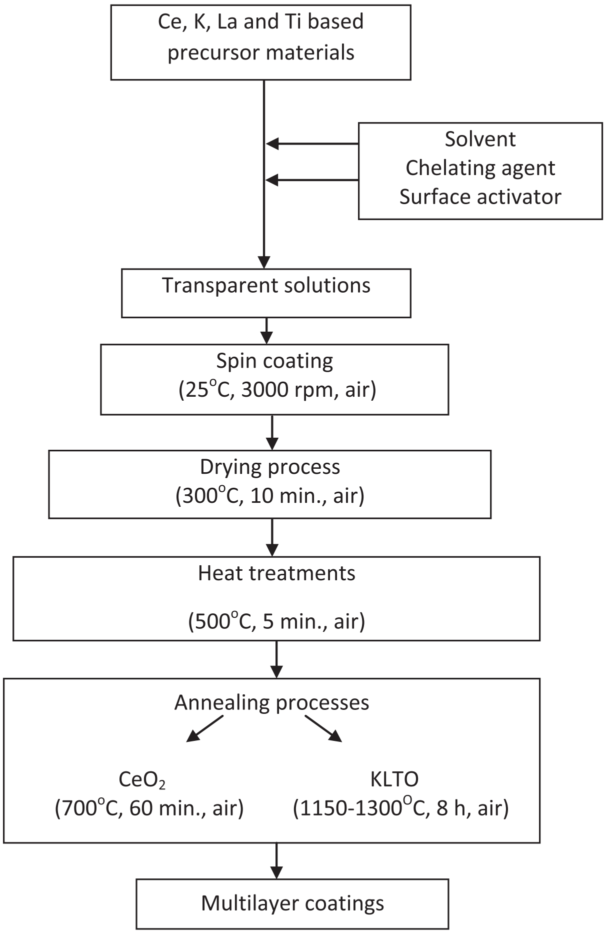

**Fig. 2.** Flow chart for general production of $CeO_2$ and KLTO layers. In this chart, $CeO_2$ and KLTO were separately produced using sol–gel method. The preparation of the films was the same until annealing process.