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# Sol–gel fabrication and enhanced optical properties, photocatalysis, and surface wettability of nanostructured titanium dioxide films

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ABSTRACT

$TiO_2$ photocatalytic film, annealed at temperatures of 500 °C and 700 °C, was prepared on $SiO_2$ pre-coated glass via sol–gel technique for photocatalytic purposes and effects of catalyst-type on its properties were investigated by an X-ray diffractometer (XRD), Scanning Electron Microscope, UV–vis spectrophotometer, and contact angle measurements. The XRD results showed that present phases depend upon catalyst used in the solution and phase transformation behaves in a temperature-dependent manner. For the layers derived from sols containing acidic catalysts, the anatase structure dominated and exhibited much better photocatalytic activity. The results indicated that the sample derived from sol comprises $H_2SO_4$ as catalyst, and exhibits anatase grains with the lowest size. This could be the reason for its better photocatalytic activity. Finally, samples derived from sol containing acidic catalysts showed superhydrophilicity and superior cleaning ability.



## 1. Introduction

During the past decade, interest in thin films such as nanostructure titania ($TiO_2$) has been widespread due to its excellent chemical and physical properties [1] like stability [2], high transmittance in the visible spectral region [1,3], high refractive index, high dielectric constant and wide band gap [4,5]. The latter and low absorption coefficient of $TiO_2$ make it suitable for solar cells, optical devices, self-cleaning, semiconductor for various photonic devices, and photocatalytic applications [6–9]. It is well-known that titanium dioxide crystallizes in three polymorphic states of rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Anatase may transform into rutile at any temperature between 600 and 1000 °C [10]. Practically, the anatase phase has been developed for its photocatalytic properties [3,8,11,12] and is widely used in solar cell applications, primarily owing to its wide band gap [4,9]. From this point of view, factors affecting $TiO_2$ crystallinity, such as deposition method, substrate chemical, and heat treatment temperature, e.g., seem important to prevent polymorphic transformations [13].

Anatase and rutile phases could commonly be obtained either as powders or as thin films by sol–gel techniques. Sol–gel technique, among the chemical methods, has been properly developed to make $TiO_2$ films because of appropriate homogeneity, facile composition control, moderate equipment cost, and good optical properties [7,8,10,14]. This method best allows tailoring of macro- or nanostructures [15,16]. The main advantage of the process features here is the low temperature used to prepare materials, which inhibits anatase-to-rutile phase transformation [17].

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Although anatase is known as a metastable form, interesting properties of $TiO_2$ thin films are referred to it [13,18]. Thus, conditions must be controlled in a way that offers anatase as the final structure. Since the $TiO_2$ thin film properties depend on its thickness, composition, crystallinity and morphology [19], it is important to control the sol–gel constituents to optimize these characteristics. Nevertheless, the effect of acidic or alkaline catalysts on the final product has not been studied yet.

In this paper, the effect of catalyst type on the $TiO_2$ film properties, applied on glass samples provided from the windshield, is investigated by means of adding diethanolamine (DEA) as alkaline catalyst and hydrochloric acid (HCl), nitric acid ($HNO_3$) and sulfuric acid ($H_2SO_4$) as acidic catalysts to the sol. Finally structure, morphology, photocatalytic activity, and surface wettability of prepared thin films have been studied.

## 2. Experimental procedures

### 2.1. Sample preparation

Windshield (in the dimension of 100 mm × 20 mm × 2 mm) pre-coated with a $SiO_2$ layer was used as the supporting substrate. The procedures for the silica layer preparation and its characteristics have been presented in detail elsewhere [20]. The $TiO_2$ films were prepared via sol–gel dip-coating technique and synthesized as follows. Titanium tetraisopropoxide (TTIP, Panreac) was used as a precursor to prepare $TiO_2$ sol. A mixture of 0.3 M X (X is the catalyst and can be DEA, HCl, $HNO_3$, and $H_2SO_4$), 10 M isopropanol (i-PrOH) and deionized water was added to a mixture of TTIP and i-PrOH under continuous magnetic agitation in laboratory atmosphere at room temperature. Water addition is in such content that $n_\alpha$ in $n_\alpha = n_{acid}/n_{H2O}$ is established to be 0.3. Detailed information of the sols is represented in Table 1.

The substrates were dipped in the sol and withdrawn at a rate of 1 mm $s^{-1}$ to make a gel film. The coated films were dried for 48 h at room temperature to allow slow solvent evaporation and condensation reactions due to rapid sol–gel reaction of titania precursor, following by drying at 100 °C with the heat rate of 10 °C $min^{-1}$; held at this temperature for 30 min. This heat treatment would improve the adhesion of film on substrate and release residual stresses. The temperature of the furnace was subsequently increased to the final temperature (500 °C and 700 °C with the same heat rate, to investigate the annealing temperature effect on microstructural properties) and held at this temperature for 30 min to accomplish the crystallization of gel films. Finally, the films were cooled in the furnace to room temperature.

**Table 1**
Constituent molar ratios for different sols.

| Sol | TTIP | i-PrOH | DEA | HCl | $HNO_3$ | $H_2SO_4$ | $H_2O$ |
|---|---|---|---|---|---|---|---|
| S.DEA | 1 | 25 | 0.3 | – | – | – | 1 |
| S.CL | 1 | 25 | – | 0.3 | – | – | 1 |
| S.N | 1 | 25 | – | – | 0.3 | – | 1 |
| S.S | 1 | 25 | – | – | – | 0.3 | 1 |

### 2.2. Characterization of $TiO_2$ films

The main phase present was identified and the crystalline size of the $TiO_2$ thin films was determined by an X-ray diffractometer (XRD) (D8 Advance, Bruker Co., Germany) using monochromatic Cu-Kα radiation operated at 40 kV and 30 mA at a scan speed of 0.02 s per step with an increment of 0.02° per step. The crystalline size was calculated from X-ray line broadening analysis by the Scherrer formula. The nanoparticle size and morphology of films were characterized by field-emission-scanning electron microscopy (FE-SEM, Hitachi S-4160). Windshield chemical composition was determined by the XRF test (ARL model 8410) with ASTM C 982-97 reference standard.

Optical properties of the thin films deposited on $SiO_2$ pre-coated glass substrates were examined with the normal incident transmittance measured by UV–vis Spectroscopy (Perkin-Elmer model Lambda 25). Finally, the effect of catalyst-type on the hydrophilicity of the $TiO_2$ films was investigated by measuring the contact angle of water droplet on the film under an ambient condition at room temperature, in the dark and 1 and 2 h after UV radiation using an OCA 15-plus (Dataphysics).

### 2.3. Evaluation of photocatalytic activity

Photocatalytic activity of the $SiO_2$–$TiO_2$ films was evaluated by investigating degradation of Methylene Blue (MB) dye, used as a model pollutant. For the photodegradation investigation, the $SiO_2$–$TiO_2$ films on glass substrates were immersed in an aqueous solution of MB ($6.25 \times 10^{-5}$ M), then irradiated with UV light for different intervals of 15, 30, 45, 60, 90, 120 and 150 min. Next, degradation of the MB was determined by measuring absorbance of the MB of each decanted solution using a UV–vis spectrophotometer (CECIL SERIES CE-2040) at a maximum wavelength of $\lambda_{max} = 664$ nm. The kinetics of the degradation of the MB dye was described with the Langmuir–Hinshelwood (L–H) kinetic model.

## 3. Result and discussion

### 3.1. Structural properties

In order to compare the crystalline composition and crystal size of the films derived from different sols (at two diverse annealing temperatures of 500 °C and 700 °C), the XRD test was employed. It should be noted that the crystallinity of the films depends on their chemical composition and the annealing temperature is known to affect the relative proportions of anatase to rutile phase and $TiO_2$ phase transformation anatase-to-rutile. Factors such as preferential grain orientation, morphology, nucleation sites, and growth of rutile phase may influence XRD results [11,16]. Crystalline phases and their crystalline size identified by XRD measurements for the films derived from sols containing various kinds of catalysts are listed in Table 2.

Here, Spurr and Myers' method [21] has been applied to determine anatase to rutile ratio which utilizes the ratio of (110) peak intensity of rutile phase in the angle ($2\theta$) of 27.355° to those of anatase phase in the (101) plane with