

# CHALLENGES AND OPPORTUNITIES IN FABRICATION OF PHOTOCATALYTIC, SUPERHYDROPHILIC AND SELF-CLEANING COATINGS: AN OVERVIEW

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## ABSTRACT

*In the last 10 years, self-cleaning applications using thin films have become a subject of increasing interest. The self-cleaning property has been known to be a mutual effect between photocatalysis and hydrophilicity. It is the synergetic effect of photocatalysis and hydrophilicity that improves and maintains the self-cleaning effect. Photocatalytic TiO<sub>2</sub> provides a promising route to produce self-cleaning coating surfaces. To date, titanium dioxide (TiO<sub>2</sub>) based coatings are the most successful photocatalytic self-cleaning coatings utilized in practical applications. Antifogging mirror or self cleaning glass can be realised utilising photoinduced hydrophilicity of titanium dioxide. Application fields of functional titanium dioxide coating is now expanding rapidly not only in application of glasses but also in application for polymer, metal and ceramic materials. The coating layers of TiO<sub>2</sub> films prepared from a sol-gel precursor were deposited on glass substrate using the coating techniques. Dip-coating the TiO<sub>2</sub> optical film two and three times resulted in superhydrophilic surfaces. Increasing number of dipping times was found to increase the photocatalytic activity.*

**Keywords:** Dip-Coating, Hydrophilicity, Photocatalysis, Self-Cleaning, Titanium Dioxide.

## 1. INTRODUCTION

The utilization of solar irradiation to supply energy or to initiate chemical reactions is already an established idea. When a wide-band gap semiconductor like titanium dioxide (TiO<sub>2</sub>) is irradiated with light, excited electron-hole pairs result and these can be applied in solar cells to generate electricity or in chemical processes to create or degrade specific compounds during the chemical process[1]. The photocatalysis property helps to decompose the organic substances that come in contact with the surface and thus prevent them from building up. The hydrophilicity helps in cleaning more effectively as the water spread over the surface instead of remaining as droplets which helps to collect the dirt better, make the surface dry faster, and moreover, prevent

the undesirable water streaking or spotting on the surface[2-3]. Because of its thermostability and photocatalytic properties,  $\text{TiO}_2$  is one of the most widely used materials for self-cleaning application[4-5]. The ability to engineer the  $\text{TiO}_2$  to have superhydrophilic property on surfaces is also an advantage[3]. Superhydrophilic property of the surface allows water to spread completely across the surface rather than remaining as droplets, the result is  $\text{TiO}_2$ -coated glass which is antifogging and self-cleaning[6]. For practical applications such as mirrors, window glasses, windshields of automobiles, etc, transparent self-cleaning  $\text{TiO}_2$  films on glass substrates have a high potential[7-8]. One of the most interesting aspects of  $\text{TiO}_2$  is that the photocatalysis and hydrophilicity can take place simultaneously on the same surface even though the mechanisms are completely different[9]. This is the reason that the film has a self-cleaning effect. However, very little attention has been focused on the relationship between the photocatalysis, hydrophilicity and self-cleaning effect. The synergetic effect of photocatalysis and hydrophilicity is very important in sustaining the self-cleaning effect[3]. The synergetic effect of photocatalysis and photo-induced hydrophilicity is the main factor that makes Titanium oxide ( $\text{TiO}_2$ ) the first choice for large-scale applications in the field of antifogging and self-cleaning coatings. The  $\text{TiO}_2$  hydrophilic surfaces can be easily obtained by UV activation, resulting in the generation of surface oxygen vacancies at bridging sites and conversion of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  sites, which support the dissociative water adsorption and formation of water layers on the film surface[10-11].  $\text{TiO}_2$ -based coatings are widely used in outdoor environments where UV light from sunlight is generally sufficient to preserve wettability properties of the material during the day. Moreover, the ability of light to control the wettability of the surface by generating an amphiphilic (hydrophilic and oleophilic) character has also been proved, which results in a  $\text{TiO}_2$ -coating with antifogging and self-cleaning properties[10]. The advanced wettability properties of these materials are not only suitable for self-cleaning purposes but also crucial for a plethora of many other applications like for example in biomedical related fields, where surface wettability can play an important role in protein adsorption, cell adhesion and proliferation[12]. Liquids separation, especially oil/water separation, and liquid transportation driven by a gradient in the interfacial tensions acting at the phases interface, are other promising applications in which the superwettability of  $\text{TiO}_2$  can be effectively exploited, provides new opportunities for the development of cutting-edge technologies and strategies in these areas[13]. However, the need for UV light to assume the highly hydrophilic behavior precludes their choice when designing indoor applications and when the hydrophilic character must be preserved at night[14-15]. The main concern of hydrophilic or superhydrophilic separation materials in oil/water separation application is that they are readily susceptible to contamination by low surface-energy substance such as oil owing to their intrinsically high surface energy[16]. As the wettability of a solid surface is governed by chemical compositions and geometrical structures, superhydrophilic and underwater superoleophobic materials are generally fabricated by creating hierarchical micro/nano-structures on hydrophilic substrates, or by surface modification of an appropriate rough surface with hydrophilic materials[17-18].

## **II. EXPERIMENTAL PROCEDURE**

### **2.1 Preparation of $\text{TiO}_2$ precursor solution**

In order to obtain  $\text{TiO}_2$  sol, a precursor solution was prepared that follows Legrand-Buscema et al.[19]. Firstly, 0.3 M titanium-isopropoxide (TTIP, Fluka) dissolved in isopropanol (IPA, Fluka) and was stirred at room

temperature for 30 minutes. Then, acetylacetone (Acac, Merck) added to make 10:3 molar ratio of titanium isopropoxide to acetylacetone. The mixture was used as chelating agent for the stabilization of the solution. The mixture obtained then stirred for the duration of 30 minutes more. Acetic acid was added afterward to help initialize hydrolysis by creating esterification reaction with isopropanol. As a result transparent yellow solution was obtained.

## **2.2 Preparation of P25 Degussa TiO<sub>2</sub> solution for coating**

A mixture of P25 Degussa TiO<sub>2</sub>/Terpineol anhydrous (Fluka)/Ethyl cellulose (Fluka) having weight ratio of 1:7:1 was prepared. The mixture stirred vigorously and continuously until homogeneous white solution was obtained. The TiO<sub>2</sub> precursor and P25 Degussa TiO<sub>2</sub> mixture were used for film fabrication by dip coating, spin coating and screenprinting. Soda lime glass slides were used as substrates. The glass slides were ultrasonicated with DI water, acetone, ethanol and isopropanol for 15 minutes each, respectively. The coated films were dried at 60°C for 30 minutes and calcined at 450°C for 4 h in air[20]. Smooth and uniform TiO<sub>2</sub> films were selected for characterization.

## **III.RESULTS AND DISCUSSION**

### **3.1 Microstructure and thickness of the films**

Among all film coating techniques, dip coating was the only technique that yielded homogenous TiO<sub>2</sub> films. Figure.1(a)-(c) are the AFM micrographs showing the surface morphologies of TiO<sub>2</sub> films dip-coated for one, two and three times, respectively. Figure.1(d) shows an AFM micrograph of P25 Degussa TiO<sub>2</sub> film prepared by screen printing. The technique which involves dip coating of the TiO<sub>2</sub> from the prepared precursor resulted in a denser film than screen printed P25 Degussa TiO<sub>2</sub> film. However, by screen printing it was not possible to prepare smooth films from the in-house prepared TiO<sub>2</sub>, due to the difference in sizes of primary particles and viscosity of the precursor. Increasing dip coating time of the TiO<sub>2</sub> film from the prepared precursor from one to three times resulted in thicker and less rough films (Table 1). The TiO<sub>2</sub> film screen printed from P25 Degussa was found to be much thicker than the films prepared by dip coating. The roughness of P25 Degussa film is three orders of magnitude higher than that of the dip-coated films.

	<b>Thickness(nm)</b>	<b>Roughness(nm)</b>
<b>Number of Dipping Times</b>		
<b>One</b>	116.5	0.451
<b>Two</b>	252.5	0.2337
<b>Three</b>	360	0.1952
<b>P25 screen printing</b>	980	2.402

Table 1: Thickness and Roughness of the TiO<sub>2</sub> films prepared by one to three dipping times and screen printing [21].

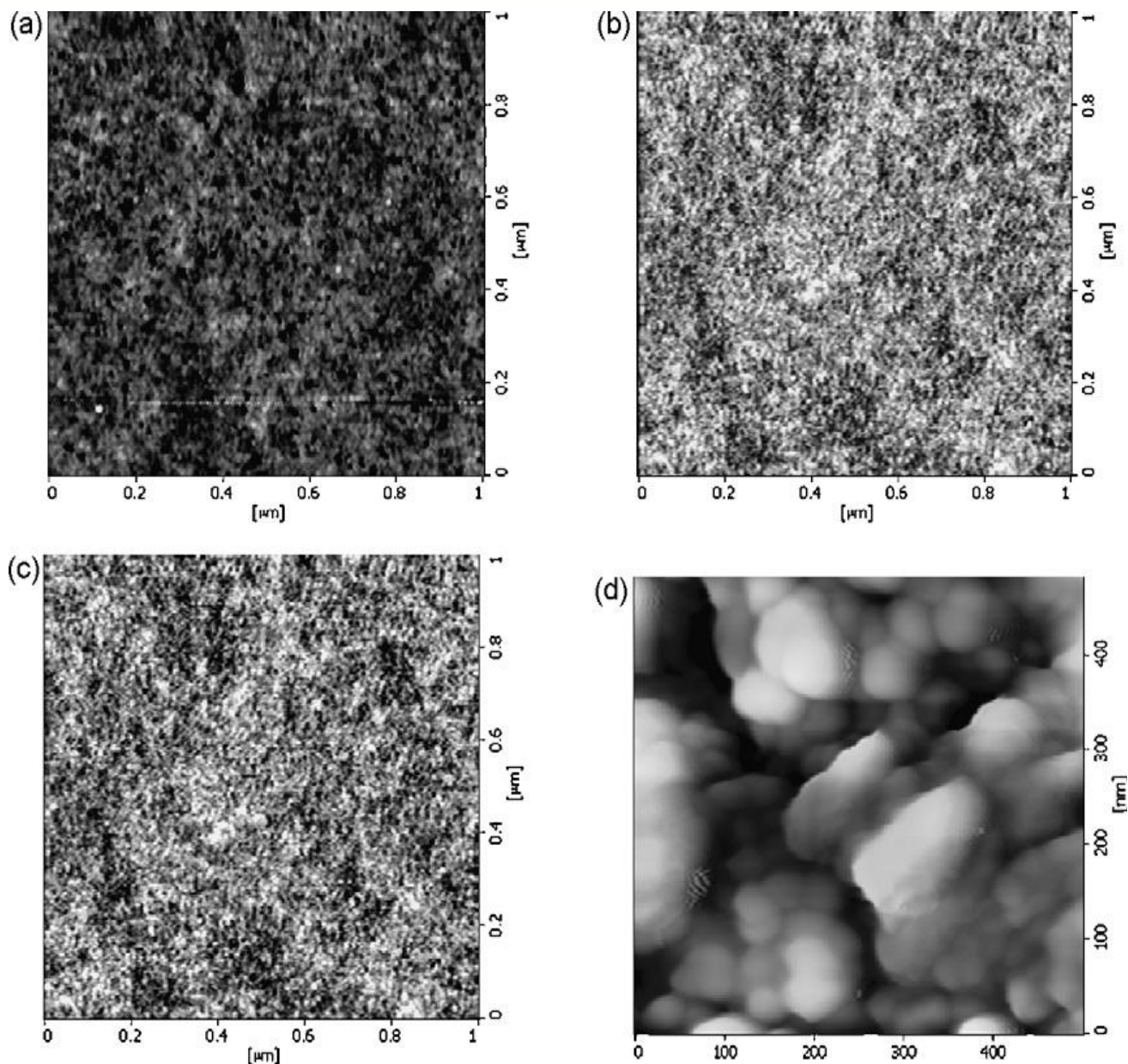


Figure 1: AFM micrographs of the  $\text{TiO}_2$  thin films dipped for (a) one time, (b) two times, (c) three times and (d) P25 Degussa in screen printed films[21].

### 3.2 Photocatalytic activity of the film

In order of the photocatalytic activity, the  $\text{TiO}_2$  films prepared from the precursor have inferior photocatalytic activities to the  $\text{TiO}_2$  films from P25 Degussa. The differences in photocatalytic activity could be contributed from the differences in the phases present, surface morphology, and surface areas. From the AFM results, the films produced from the  $\text{TiO}_2$  sol was found to be much smoother which means less surface area for absorption leading to lower catalytic activity when compared to the P25 film. Further, for sample fabricated from P25, it was observed that there exist a combination of the two phases, anatase(A) and rutile(R). It has been reported that



a combination of the anatase and rutile phase could provide higher photocatalytic activity[22]. On comparing the effect of number of times of dip coating, it was observed that the film dip-coated three times exhibits a higher photocatalytic activity. On Investigating the XRD results, the number of dip coating time increases and the XRD peak got sharper. Sharper XRD peak indicates that a larger particle size or a more well-ordered crystallites (Fig. 2). The more ordered structure which is directly associate with the lower concentration of defects would make the recombination of electrons and holes less favoured and thus could be the reason for higher photocatalytic activity observed for the sample dip-coated for three times[1].

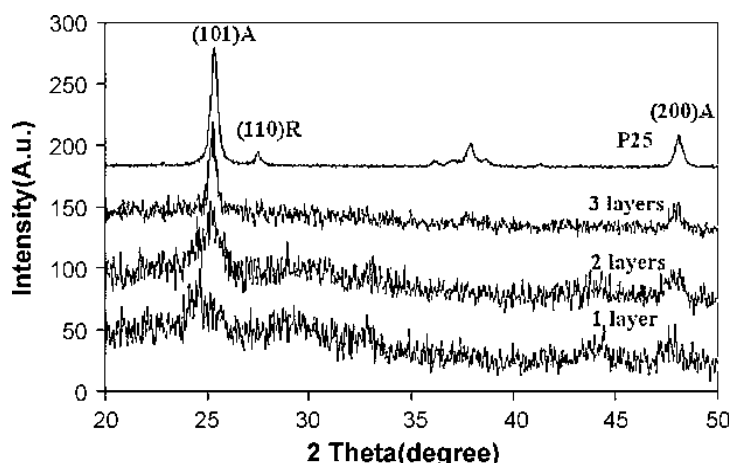


Figure 2: XRD patterns, P25 Degussa TiO<sub>2</sub> film and TiO<sub>2</sub> films dip-coated three, two and one time from a prepared TiO<sub>2</sub> precursor[21].

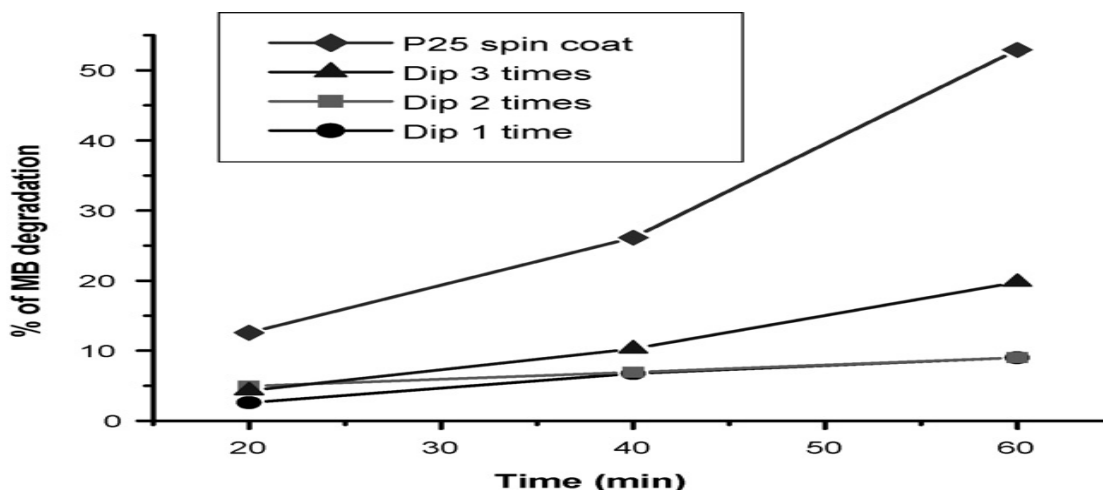


Figure 3: A comparison of the photocatalytic activities of TiO<sub>2</sub> prepared by dipping coating (a) one time, (b) two times, (c) three times and (d) screen printed P25 Degussa[21].

### 3.2 Hydrophilicity of the film

In order of the hydrophilicity, the TiO<sub>2</sub> films dip-coated two and three times showed superhydrophilic nature, as compared to screen printed one layer of P25 Degussa (Table 2). For the P25 Degussa screen printed TiO<sub>2</sub> film, superhydrophilic property caused by its porous structure that enables fast water absorption[23]. Moreover, in the case of the dip-coated TiO<sub>2</sub> films, calcinations temperature at 450 °C was reported to be the best for pure anatase phase in the TiO<sub>2</sub> films as it is observed to be responsible for the superhydrophilicity of the TiO<sub>2</sub> films[2]. The hydrophilicity is also believed to relate to the density of surface hydroxyl of the TiO<sub>2</sub> films. The surface hydroxyl can combine with water molecules to form hydrogen bond, results in wettability. The mass density of the film is also known to affect the superhydrophilicity. Moreover, the dip-coated TiO<sub>2</sub> films have preferred orientation which has been observed to be in favor of hydrophilicity. The dip-coated anatase TiO<sub>2</sub> films in this study is observed to have all the properties required for superhydrophilicity. The self-cleaning is a mutual effect of hydrophilicity and photocatalysis, the three times dip-coated TiO<sub>2</sub> films provides the most promising results[24].

Contact Angle (Degree)	
Number of Dipping Times	
One	8
Two	Almost 0
Three	Almost 0
P25 screen printing	Almost 0

Table 2: Contact angle of water on the TiO<sub>2</sub> films[21].

### 3.4 OPTICAL QUALITY OF THE FILM

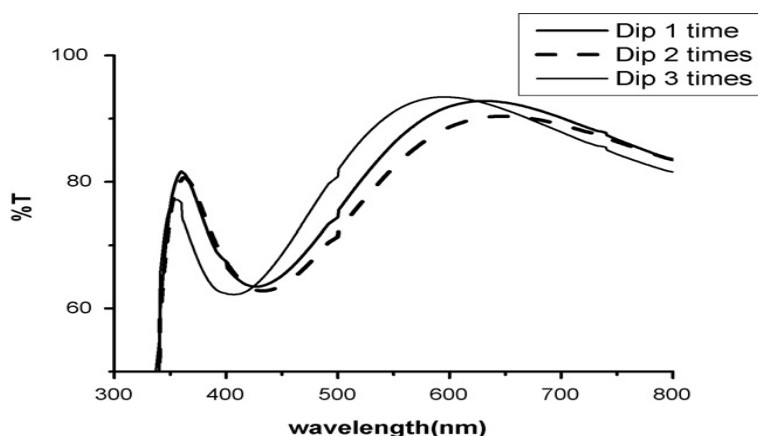


Figure 4: UV Spectra of TiO<sub>2</sub> dip-coated films one to three layers[21].

In (figure.4) UV transmission spectra of dip-coated films are shown. Results indicated that all films prepared by dip coating allow a good transmission of light in the visible region.

#### IV.CONCLUSION

The TiO<sub>2</sub> optical film coated from titanium isopropoxide which is dissolved in isopropanol, in presence of acetylacetone as a chelating agent and acetic acid. Dip coating technique was the only technique that resulted in most favourable smooth films. Dip coating the TiO<sub>2</sub> optical layers two and three times resulted in superhydrophilic surfaces. The superhydrophilicity of the prepared dip-coated TiO<sub>2</sub> films were observed, due to pure anatase(A) TiO<sub>2</sub> with preferable orientation. The increase in number of dipping times was observed to increase the photocatalytic activity. The best self-cleaning TiO<sub>2</sub> film was obtained by dip coating the prepared TiO<sub>2</sub>precursor three times using glass slide substrates.

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