



## INCORPORATION OF CHITOSAN AND GLASS SUBSTRATE FOR IMPROVEMENT ON ADSORPTION, SEPARATION AND STABILITY OF TiO<sub>2</sub> PHOTOCATALYSIS

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### ABSTRACT

*It has been demonstrated that the single TiO<sub>2</sub> has high capabilities for photodegradation process for all types pollutants. However, TiO<sub>2</sub> are still far from becoming a potential candidate for photocatalytic system due to weakness for the adsorption process, separation as well as dissolution during the treatment. Therefore, this study highlights on the highly adsorption, easy separation and promising stability of TiO<sub>2</sub>(S<sub>T</sub>) photocatalyst by fabrication of Chitosan-TiO<sub>2</sub>(S<sub>T</sub>) supported glass substrate (Cs-TiO<sub>2</sub>(S<sub>T</sub>)/Glass substrate) photocatalysts. Cs with abundant R-NH and NH<sub>2</sub> groups promotes adsorption sites of synthetic dyes. Meanwhile, present of glass substrate support increase the stability and easy separation of the photocatalysts. The fabrication process Cs-TiO<sub>2</sub>(S<sub>T</sub>)/Glass substrate has been done through dip-coating methods. Further analyzed by the adsorption photodegradation with Methyl Orange (MO) as a model of synthetic dyes compound. Approximately, 70% of total removal of MO by optimize 8 layers of photocatalyst analysis has been achieved within 1 hour of UV irradiation. Besides that, the adsorption photocatalyst has been achieved about 50% when no exposure of light for 15 minutes irradiation. It concluded that, a suitable photocatalytic conditions and sample parameters, possessing the Cs-TiO<sub>2</sub>(S<sub>T</sub>) gave the benefits of adsorption-photodegradation practice in the abatement of wastewater contaminants.*

**Keywords:** Photodegradation, Waste water, Treatment, Aromatic compounds, Photocatalyst, Nanomaterials, Semiconductor, Chitosan, Synthetic dyes

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### 1. INTRODUCTION

It has been verified that many aromatic compounds derived from synthetic dyes could be successfully degraded and effectively mineralization to end products, which are CO<sub>2</sub>, H<sub>2</sub>O, and nutrient acids [1, 2]. Various environmental applications to remove synthetic dyes in water and air have been utilized using the photocatalytic properties of Titanium Dioxide (TiO<sub>2</sub>)

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nanoparticles, which is a very well-known semiconductor, used as a photocatalyst, due to the stability of its chemical structure, biocompatibility, and physical, optical, and electrical properties [3, 4]. Furthermore, it was reported that dyes, metal ions, organic acids, and pesticide effectively possess the ability to adsorb Chitosan (Cs), due to its high adsorption potentials. A variety of useful features of Cs make it a versatile adsorbent, which is evident in the electrostatic attraction between the  $-NH_2$  functional groups and the solutes, both of which are capable of generating the adsorption of organic substrates by Cs [5, 6]. The chelating groups ( $-NH_2$  and  $-OH$  groups assist as coordination and reaction sites, respectively) on the Cs is attributed to the binding ability of Cs for synthetic dyes [7] while the adsorption process that is simply mediated by Cs is amongst the most successful technique that were effectively used against inorganic, organic, and heavy metal pollutants from polluted water bodies [8]. The combined effects of Cs and  $TiO_2$  were known as adsorption–photodegradation that are coated on a glass substrate (Cs– $TiO_2$ /Glass), demonstrate an improvement when used to treat or pre-treat dye-containing wastewater under visible light. The immobilization of Cs– $TiO_2$  photocatalyst onto a glass substrate also assist in the separation upon the photocatalysis process [9].

In this study, reactive  $TiO_2$  (SY) was coated or incorporated into Cs onto the smooth surface of the glass substrate (separately using that different  $TiO_2$ (SY)). It is expected that this would be incredibly useful in the investigation of the mixed effect of adsorption–photodegradation, mediated by Cs– $TiO_2$ (SY) photocatalyst. The actual photocatalytic degradation process, which makes use of  $TiO_2$ (SY), has been shown to be extremely successful in degrading MO, which is representative of synthetic dye compounds. Furthermore, the presence of Cs was acknowledged to have a very encouraging effect on the adsorption capability of the  $TiO_2$ (SY) nanoparticles. Therefore, it was expected that both  $TiO_2$ (SY) and Cs respective advantages are compatible upon the glass substrate, resulting in a diverse approach in dealing with several wastewater pollutants, especially for the synthetic dyes. Glass substrates demonstrated distinctive advantage as a photocatalyst support, such as retaining transparency even after the immobilization of the photocatalyst, which allows for the penetration of light, improving its photocatalytic activities. A byproduct of this approach is that the photocatalyst will gain large surface areas. Other benefits of a glass substrate include superior adsorption properties, higher surface area, and increased surface or reduced charge recombination.

## 2. MATERIALS AND METHODOLOGY

### 2.1. Chemicals

The chemicals required in this work were Titanium isopropoxide (purity, 97%),  $Ti[OCH(CH_3)_2]_4$  and acetic acid (purity, 99%),  $CH_3CO_2H$ , all of which were procured from Sigma-Aldrich, and sodium chloride, NaCl, which was purchased from Merck. The commercial Cs (medium molecular weight) MO was obtained from Sigma-Aldrich. De-ionized water was used to prepare all the standard solutions.

## 2.2. Synthesis of TiO<sub>2</sub> Nanoparticles

Titanium isopropoxide (TTIP), acetic acid glacial, and deionized water were used to synthesize TiO<sub>2</sub> via the sol-gel method. Initially, a TTIP (2.8 ml; 97%) solution was mixed in concentrated/pure acid acetic acid glacial (6ml; >90%). After that, TTIP was titrated slowly into the acetic acid glacial solution. Next, DI water (36 ml) was slowly added under vigorous stirring at an ambient temperature and mixing/rate of 350 - 500 rpm for 5 hours.

Once a clear solution was obtained (sol), the mixture was stirred for another hour at 80°C. To keep the reaction temperature constant, the beaker was covered with an aluminum foil and a thermometer was placed near the surface of the mixture. The solution was subsequently converted to a gel mixture at a reaction temperature of 60°C. The continuation of the reaction will eventually result in a white suspension, which was subsequently dried overnight (12 hours 80°C) until it is amorphous, resulting in dried TiO<sub>2</sub> nanoparticles (yellowish color). Next, the TiO<sub>2</sub> nanoparticles was manually grounded using an agate mortar. TiO<sub>2</sub> powder (0.70 g) was calcined for 5 hours at 500°C, and directly stored in a controlled humidity and temperature conditions.

## 2.3. Fabrication of Cs-TiO<sub>2</sub> Supported Glass Substrate

Glass substrate (25×75 mm) was used to retain and fix the prepared Cs-TiO<sub>2</sub> photocatalyst. Initially, the glass substrate was thoroughly cleaned and dried prior to being deposited into the prepared solution. The whole glass substrate was manually dipped in the Cs-TiO<sub>2</sub> viscous solution at a uniform immersion rate, resulting in a coated diameter of (25×55 mm). The readily dipped glass substrate was dried at 100°C for 4 hours alternately after each dipping process. The glass substrate itself helps vary the amount (weight ratio) or layers of Cs-TiO<sub>2(SY)</sub> that was coated onto the glass substrate. The dipping process was repeated for 2, 4, 6, and 8 layers of Cs-TiO<sub>2</sub> photocatalyst on the glass substrate. Herein, the TiO<sub>2(SY)</sub> with Cs samples were called Cs-TiO<sub>2</sub>/Glass photocatalyst. The photocatalyst of Cs-TiO<sub>2</sub> formed on the glass substrate will be responsible for adsorption and photodegradation reactions. Otherwise, it was stored in the dark to avoid pre-activation by visible light or sunlight (UV-light).

## 2.4. Adsorption and Photodegradation of Cs-TiO<sub>2</sub> Supported Glass Substrate

The working solution, with MO concentration of 10 ppm, was placed into a Pyrex reactor. Then, the sample of MO solution was stirred with a magnetic bar for 10 minutes to obtain a uniform concentration of the samples. After that, the Cs-TiO<sub>2</sub>/Glass was added into the sample. Irradiation was conducted using a UV-light lamp (6 W, λ = 365 nm) as its energy source. For the first 15 minutes, the sample was allowed to adsorb on the surface of the photocatalyst to attain adsorption-desorption equilibrium in dark conditions. The MO sample was taken after finish the process. After that, the sample was irradiated with a UV-light lamp for the next hour. A sample of MO solution was taken at 10, 20, 30, 40, 50, and 60 minutes.

The photocatalytic activity of Cs-TiO<sub>2</sub>/Glass systems was evaluated by measuring the time dependence of the concentration loss of a degraded compound. Usually, this involve dyes, such as

Methyl Orange, Methylene Blue, or environmental pollutants, such as phenol. For this study, MO was used as a model pollutant. Furthermore, the absorbance data of the MO samples were obtained from the optical spectra recorded on a UV-VIS Shimadzu - UV-3101PC, with wavelengths ranging from 200–800 nm.

### 3. RESULTS AND DISCUSSION

#### 3.1. Adsorption and Photodegradation of Cs-TiO<sub>2(SY)</sub> Supported Glass Substrate

##### 3.1.1. Effect on Initial Concentration

Figure 1 show the adsorption and photodegradation performance of Cs-TiO<sub>2(SY)</sub> supported glass substrate photocatalysts samples at multiple MO initial concentrations (5, 10, 15, and 20 ppm). The summary of both adsorption and photodegradation are illustrated in Figure 2.

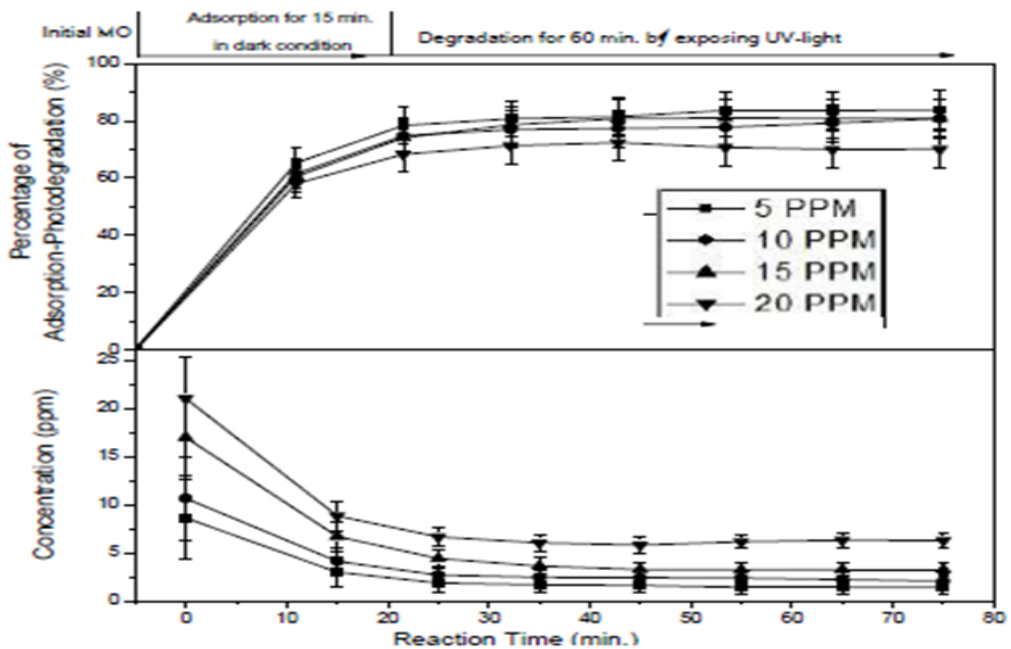


Figure-1. The adsorption and photodegradation of photocatalysts with different initial concentration

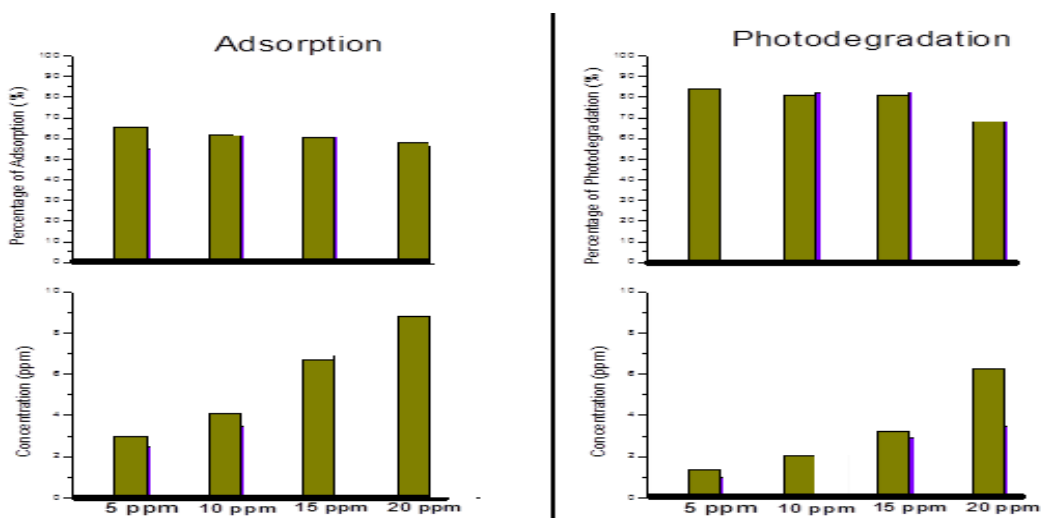


Figure-2. Summary on adsorption and photodegradation of photocatalyst at different number of initial concentration

Generally, different initial concentrations of MO insignificantly effected the adsorptions of the photocatalysts. This applies for MO with concentrations of 5 ppm and 10 ppm. Moreover, the adsorption values increased significantly, to 65%, when an MO with a concentration of 15 ppm was used for the pollutant medium. However, the adsorption value was reduced to 60% when the MO concentration reached 20 ppm. However, at an MO concentration of 10 ppm, the adsorption process was slightly reduced for photocatalyst to 62%. At an initial concentration of 15 ppm, the photocatalyst samples demonstrated some reduction of 60% for adsorption properties. Finally, using an MO with a concentration of 20 ppm as the pollutant medium resulted in adsorption values of 75%.

It is expected that at higher concentrations, the ratio of the initial number of the available adsorption sites to the dye molecules was low, thus the number of available adsorption sites becomes lower, which subsequently reduced the rate of removal of dyes. Moreover, as higher concentrations of MO was used, the relationship between MO concentrations of particular obtainable adsorption by the Cs-TiO<sub>2</sub>(SY)/Glass photocatalyst to the MO pollutant medium is rather minimal. Moreover, the number of obtainable adsorption by the Cs-TiO<sub>2</sub>(SY)/Glass photocatalyst decreased to the subsequent adsorbed MO [10].

Under UV light irradiation, the photocatalyst recorded a significant photodegradation of almost 85% when 5 ppm was used as the starting initial concentration. Next, the photodegradation process decreased to 70% as the initial concentration used was increased to 20 ppm. Furthermore, the photocatalyst was effectively photodegraded until 15 ppm of the initial concentration, with 80% of photodegradation percentage. The process decreased the photodegradation percentage when the initial concentration was 20 ppm. The photocatalytic system become more saturated at higher concentrations of MO, consequently resulting in lesser breakthrough and exhaustion time compared to lower initial concentrations.

The improvement on adsorption, as well as the photodegradation, was brought about by the saturation of active sites on the catalyst's surface with the MO molecules. Moreover, the MO

solution was rendered darker at higher concentrations, which might block or reduce the penetration of light that helps initiate further reaction with the catalyst for photodegradation (loss of light-energy). Moreover, the following formation of hydroxyl radical was reduced as well [11-13]. Indeed, the adsorption ability of the photocatalysts can be related to the characteristics of Cs molecules (the functional groups). The functional groups NH, NH<sub>2</sub>, and OH can function as chelation sites, where the MO pollutant medium could be adsorbed. This can be further explained by the fact that the adsorption process of Cs towards MO utilizes electrostatic attraction formed between the Cs and MO solute [7]. Furthermore, TiO<sub>2</sub>(SY) used in the process initiated the photodegradation process when exposed to UV-light as its source of energy, which will help further degrade the MO pollutant medium [14, 15]. The contact between Cs and TiO<sub>2</sub>(SY) in the context of this work initiated the highest adsorption process and further improved the degradation capabilities of TiO<sub>2</sub>(SY) under UV-irradiation.

### 3.1.2. Effect on pH of Pollutant Medium

The adsorption, as well as the photodegradation of photocatalysis was further analyzed at different pHs (2, 4, 6, 8 and 10) of the MO pollutant medium (Figure 3 and 4)

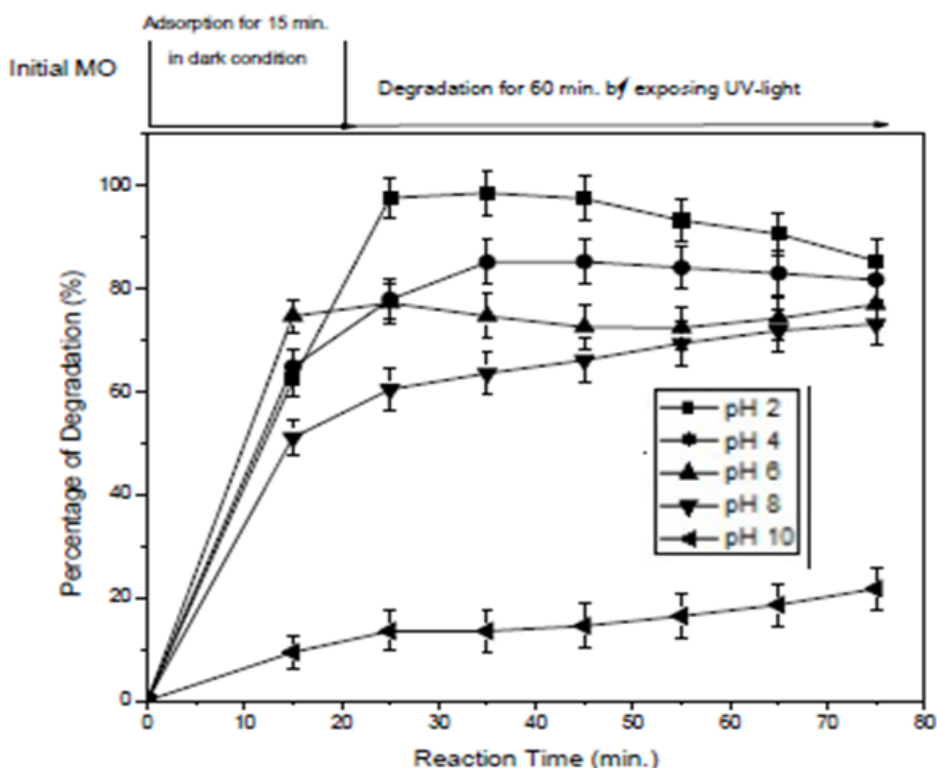


Figure-3. The adsorption and photodegradation of photocatalysts with different initial concentration

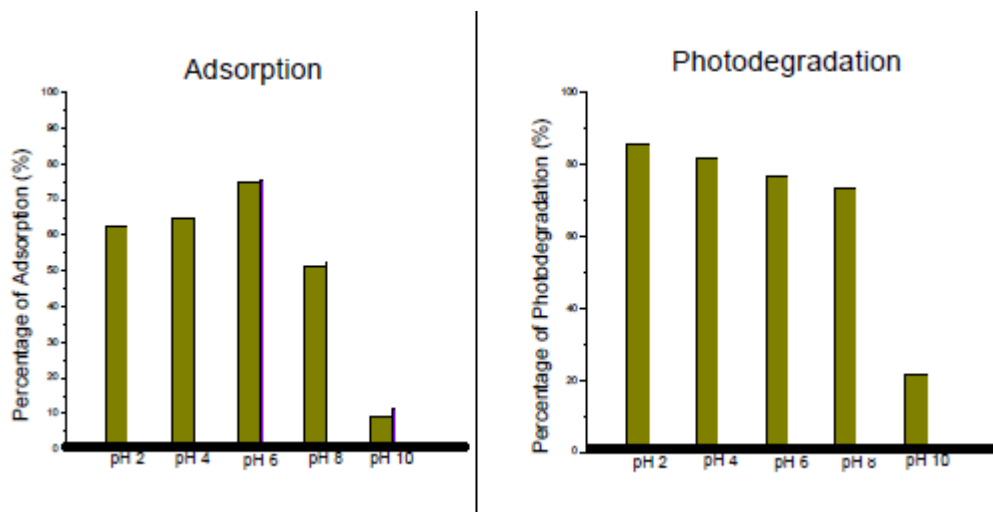


Figure-4. Summary on adsorption and photodegradation of photocatalyst at different pH medium

At pHs of 2 to 6, the percentage of adsorption increased from 60% to 75%. However, the percentage of adsorption at pHs 6 to 10 slightly decreased from 75% to 10%. Furthermore, the percentage of photodegradation demonstrated improvements once the adsorption process was completed. For the photodegradation process, the percentage of photodegradation demonstrated a reduction tendency when pHs 2 to 10 was used as the pollutant medium. At that rate, the photodegradation was recorded to be 91% to 25% for photocatalysts. Generally, the percentage of adsorption activity was determined to be 62% and 72% photocatalysts, which contributed to the highest adsorption process by the MO solution at a pH of 2. Furthermore, the photodegradation of photocatalysts could reach 85%.

The mechanism between the activity of adsorption-photodegradation by photocatalyst and initial pH of MO can be explain based on the concentration of  $H^+$  and  $OH^-$  ions present in the MO medium. It depends on the nature of the MO being used to adsorb and degrade. Furthermore, most industrial effluents contributing to dye waste will not usually be generated at neutral pH. According to Akpan and Hameed [16] most study confirmed that the use of catalysts such as  $TiO_2(SY)$  is effective for degradation at lower pHs, similar to the ones reported elsewhere, which is attributed to the strong electrostatic field of the Cs- $TiO_2(SY)$ /Glass photocatalyst enhancing photocatalytic performance between the surface of  $TiO_2(SY)$  catalyst with positive charges, and the charges from solution, which is mostly negative [13, 17]. However, lower pHs could adversely affect the catalyst during the photocatalytic process [16] making it necessary that the adsorption characteristics of MO on the surface of Cs- $TiO_2(SY)$ /Glass photocatalyst is investigated prior to the extended photodegradation process. According to Liu, et al. [10] Cs could be used as an adsorbent at an optimal pH of between 3-6. For the Cs- $TiO_2(SY)$ /Glass photocatalyst, high adsorption was obtained at a pH of 2 due to the protonation of the  $-NH_3$  groups in Cs prior to adsorption. The process can be explained by the fact that the MO can be contained within an aqueous solution, after which the sulfonate groups ( $R-SO_3Na$ ) of the absorbed MO are dissociated, rendering them anionic for absorption to the MO ions. At this

point, the adsorption process is completed, due to the electrostatic attractions between the adsorbent surface, as well as the MO anions. However, the decrease of MO adsorption can be explained by the competition of the abundant presence of  $\text{OH}^-$  ions in the basic solution for the adsorption sites with MO anions [10]. The recombination of holes and photoelectrons can be avoided when the MO pollutant medium was adsorbed by the photocatalyst media. This can be explained by the fact that the MO molecules can only be degraded near the surface of the Cs-TiO<sub>2(SY)</sub>/Glass photocatalyst by the  $\cdot\text{OH}$  free radical. Furthermore, superoxide free radicals are generated by irradiating the Cs-TiO<sub>2(SY)</sub>/Glass photocatalyst. This basically means that higher percentages of MO molecules was adsorbed on the surface of Cs-TiO<sub>2(SY)</sub>/Glass photocatalyst, which translate into extended degradation time for the MO molecules [18].

#### 4. CONCLUSION

In a nutshell, combined Cs and TiO<sub>2(SY)</sub> results in an advanced and highly efficient adsorption and photodegradation for MO synthetic dye purification. The Cs functions as the host material for the adsorption site of TiO<sub>2(SY)</sub>, which consequently results in better dispersion and separation of photocatalyst in a pollutant medium. Cs provides the unique components related to the presence of polar groups (OH and NH<sub>2</sub>), while TiO<sub>2(SY)</sub> could help by further degrading the MO by being supported by the UV-light as its energy source to influence photodegradation. Moreover, Cs, along with TiO<sub>2(SY)</sub>, would transform their respective chains by being stretched onto glass surfaces. Furthermore, it will also straighten itself on the smooth glass surfaces, or form hydrophobic minuscule domains via the dip-coating method. It can also be used on compact glass substrates, which also helps curtail movements.

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