Processing of Nanostructured TiO$_2$ and Modification of Its Photocatalytic Behavior for Methylene Blue Degradation

Mohammad Sajjadnejad$^a$,* Hooman Karimi Abadeh$^b$

$^a$ Department of Materials Engineering, School of Engineering, Yasouj University, Yasouj, Iran
$^b$ Department of Materials Science and Engineering, School of Engineering, Shiraz University, Shiraz, Iran

**ABSTRACT**

In this work, sol-gel process was chosen to produce a photocatalytic film to degrade methylene blue. To study the structural and morphological properties, a base sol of TTIP, I-PrOH, and DEA were created. Then, with addition of 45 g/L PEG 2000, 30 g/L TiO$_2$ and 15 g/L PEG 2000+30 g/L TiO$_2$, three other additional sols were produced. The results of the thermogravimetry and differential thermal analysis indicated that a calcination temperature of 550 °C is sufficient to calcinate all four layers formed in four sols. Structural X-ray studies showed that, calcination temperature is dependent of the composition. The results of this study revealed that, substrate will have an effect on the photocatalytic behavior. It was concluded that the rough sand blasted surface because of creating more film islands that enhances photocatalytic behavior is a better substrate surface condition. Degradation of Mb showed that as a result of more TiO$_2$ corporation in the film produced by the fourth sol, the fourth sol is superior in terms of photocatalytic behavior. Also it was found that, degradation of Mb is dependent on the initial concentration; and the higher initial concentration, the lower is the efficiency.
Introduction

TiO$_2$ has been used and studied extensively for its outstanding photocatalytic behavior [1-3]. Non-toxicity, chemical stability in aqueous environments, and inexpensiveness made this material a desirable semiconductor for industrial purposes. Due to inherent practical problems of using powder catalysts for water treatment and purification processes, i.e. homogenizing the powder throughout the whole medium and separation after treatment, immobilized TiO$_2$ films have been extensively researched and utilized.

Diverse techniques such as sputtering [4], electrospinning [2], chemical vapor deposition [5-7] and sol-gel [8-14] can be used to produce a desirable TiO$_2$ film. Among all these methods, sol-gel has been widely used due to its low cost, desirable homogeneity, and low processing temperature. There are two feasible methods for producing the TiO$_2$ films, the alkoxide route and non-alkoxide route. Inorganic salts (TiCl$_4$) are used in alkoxide route as the starting material for reactions, then after removing the inorganic anion of these salts results the desired TiO$_2$ from the film is achieved. However, halides are notoriously challenging to be removed and often remain in the material. The TiO$_2$ films produced by the non-alkoxide route possess high density and are crystalline [15].

Microstructure, density and phase identity of the film are the key factors in shaping the photocatalytic behavior of a film. The TiO$_2$ film produced from the mentioned process fabricated a network of material; so a calcination step should be carefully designed and undertaken to achieve the optimum photocatalytic properties, otherwise extensive deterioration of quality will occur.

Modified alkoxide sol-gel method has been extensively evaluated. The phenomena was first studied by Balasubramanian et al. [15] in 2004 and has established that a more sensitive TiO$_2$ photocatalyst can be produced by incorporating P-25 powder into an isopropoxide sol. Chen et al. [16,17] found out that this improvement is due to the grain reduction size, higher number of pores, micro-cracks and crystalline material on the surface of the coating. Polyethylene gelycol (PEG) addition to alkoxide solution and its beneficial application to increase the thickness of TiO$_2$ film and morphology was first reported by Kato et al. [18]. Many researches expanded this new finding and produced a rather well understanding of the PEG effect on TiO$_2$ film produced by sol gel method [19-22]. There are also many studies assessed the crystal size and phase transformation during the calcination steps [23,24].

One of the main organic pollutants of many industries such as pharmaceuticals, dyeing, printing, paper and ink industries is an organic solution called methylene blue (Mb). Fortunately, this aqueous contamination can easily be removed by using a photocatalysis method. There are several advantages in utilizing this route such as cost-effectiveness, solar light energy source, and operation near the ambient temperature.

The aim of this study is to synthesize nanostructured TiO$_2$ film using sol-gel containing both P-25 and PEG. Then the structure and morphology of the synthesized TiO$_2$ films to used as an effective photocatalyst to degrade Mb in environment were evaluated. It was found that, the TiO$_2$ powder (Degussa, P-25), is a standard material for photocatalytic applications, containing anatase and rutile phases in a ratio of about 3:1.

Experimental

Materials and chemicals

TiO$_2$ films were produced using sol-gel method to study structural and morphological properties by XRD and SEM, respectively. To get clearer understanding of different affecting parameters, four different sols were prepared.
Table 1. Different materials used to create sols

| Material                        | Original company and purity (%) | Chemical formula and molar mass |
|--------------------------------|---------------------------------|--------------------------------|
| Titanium isopropoxide (TTIP)   | Aldrich (97%)                   | C_{12}H_{28}O_{4}Ti (284.215 g/mol) |
| Isopropyl alcohol (i-PrOH)     | Merck (99.99%)                  | C_{3}H_{8}O (60.10 g/mol)        |
| Diethylamine (DEA)             | Aldrich (99%)                   | C_{4}H_{11}N (73.14 g/mol)       |
| Polyethylene glycol (PEG)      | Merck (99.9%)                   | C_{2n}H_{4n+2}O_{n+1} (2000 g/mol) |

Figure 1. Sols that were used in this study

Table 1 presents the materials that were used to synthesize the sols. Methylene blue with the chemical formulae was used to assess which TiO$_2$ film possesses superior photocatalytic behavior.

Preparation of TiO$_2$ films by Sol-Gel method

A base sol and three derivative sols were prepared. To prepare the base sol, TTIP, i-PrOH and DEA were evaluated in terms of DEA:TTIP=4:1. Stirring was done for 2 h and then deionized water in terms of H$_2$O:TTIP=2:1 in molar ratio was added. To prepare the three other sols, 15 g/L PEG 2000, 30 g/L TiO$_2$ and 15 g/L PEG 2000+30 g/L TiO$_2$ were added to the base sol respectively. The ratios were chosen based on the reviewed literature [15-17]. Figure 1 schematically shows the constituents of different sols.

Dip coating method was utilized to produce the TiO$_2$ films required. Initially two substrates were used. 304 stainless steel and glass, 304 stainless steel showed preferential properties (for the reasons that will be explained) so the rest of the experiments were done on this substrate. The withdrawal rate was chosen to be 13.5 cm/min$^{-1}$ and in order to increase film thickness 1 to 6 dipping cycles were performed. After each dip-coating cycle, specimens were dried for 2 h at 120 °C to obtain the crystallized anatase phase. Subsequently each sample was calcined in an oven at 400 °C to 700 °C. To minimize the nucleation of cracks in the coating surface, a slow heating rate of 3 °C/min$^{-1}$ was chosen.

Characterization technique

To evaluate the thermal decomposition properties of the assynthesized dried zero gel samples, a thermogravimetry and differential thermal analyzer (PL-STA-1640, Polymer Laboratories Santtom Redcraft, UK) was used. By the means of a heating rate of 5 °C/min$^{-1}$ temperature rose from 25 °C to 900 °C. X-ray diffraction (XRD) analysis was performed using an EQUINOX 3000 INEL with Cu (kα) radiation
to determine the present phases and crystalline size calculated from Debye-Scherrer equation [19].

\[ L = \frac{k\lambda}{\beta \cos \theta} \]

Where \( L \) is crystalline size that is equal to multiplication of Debye-Scherrer constant \((k=0.89)\) in the X-ray radiation wavelength \((0.15481 \text{ nm for Cu (Kα)})\) divided by full-width half-maximum of diffraction \((\beta)\) peak at \(2\theta\). Morphology, thickness and chemical composition of the coatings were studied using scanning electron microscopy (SEX) (Seron Tech, AIS 2100) equipped with the energy dispersive X-ray spectroscopy (EDAX).

**Results and discussion**

**TGA/DTA and UV-visible analysis**

Figures 2 and 3 depict the overall weight loss curve if TGA/DTA for as-synthesized zero gel TiO₂. As can be seen in the TG curve (Figure 2), the total weight loss happens in several steps, the first of being at 12% between 25 to 235 °C as a result of removal of physisorbed water and solvent molecules from porous gel networks. The second step occurs at the temperature ranging from 235 to 450 °C and 30% weight loss was observed as a result of removal of DEA with boiling point of 268 °C [25]. In the third step, 15% weight loss was evident as a result of removal of strongly chemisorbed water molecules and residual organic species [1]. All these weight losses are proven by the small peaks that are showed in DTA curve (Figure 3). Amorphous to anatase TiO₂ transformation happens at 500 °C as a broad exothermic peak can be seen at this temperature. The curvature of the graph flattens beyond 550 °C which is an indication that a calcination temperature of 550 °C is enough to achieve the crystallization and removal of organic species.

**Figure 2.** TG curve of the base sol derived TiO₂

![Figure 2](image)

**Figure 3.** DTA curve of the base sol derived TiO₂

![Figure 3](image)
**Structural Studies by X-ray**

XRD patterns from the calcined base sol at different temperatures (400-700 °C) are shown in Figure 4. Two main peaks at 25.4° and 27.5° corresponded to the anatase (101) and rutile (110) peaks, respectively [13]. As the film was mostly amorphous before the calcination step, no distinctive peak can be seen before 400 °C; however, as calcination happens at 400 to 500 °C, sharper peaks can be seen as temperature rises. This is in agreement with the results of DTA analysis. The existence of other observable peaks such as anatase (200) and anatase (004) was an indication that the film was polycrystalline. According to these figures, anatase to rutile formation occurs at 500 to 600 °C, and at 700 °C the film is completely made of rutile.

To compare the phase transformation of base sol with other sols, forth sol (PEG+P25) was chosen for XRD analysis at the same temperatures of base sol. It was found that, the crystalline phases were observed even at 400 °C. This is the influence of P-25 addition that possesses anatase and rutile phases. The other interesting change that can be inferred is a distinctive shift in calcination temperature to 600-700 °C.

**Figure 4.** X-ray diffraction spectra of coatings from (a) the base and (b) fourth (containing PEG+P25) sols that were calcined at 400 °C to 700 °C.

For the best photocatalytic behavior, the favorable anatase to rutile phase ratio is 70 to 30, thus there was a need in calculating the optimum calcination temperature. Crystallite sizes are presented in Table. It was found that, the crystallite size increased with temperature elevation. Crystallite sizes were calculated using the Scherrer’s equation and anatase to rutile phase ratio was determined using the spur equation by utilizing peak intensities of anatase (101) and rutile (110).

\[
F_A = 100 - \left( \frac{1}{1 + 0.8 \left( \frac{I_A}{I_R} \right)} \right) \times 100
\]

Where \(F_A\) is the weight percentage of anatase phase and \(I_A\) and \(I_R\) are peak intensities of the anatase (101) and rutile (110), respectively. To achieve the optimum ratio desired, calcination temperature for the base sol determined to be between 500 to 600 °C and for the forth sol 500 °C. Agglomerated nanoparticles in the SEM micrographs of TiO\(_2\) film immobilized in the base sol are presented in Figure 5.

| Calcination temperature (°C) | Base sol crystallite size | Fourth sol crystallite size | Vol.% of anatase from base sol | Vol.% of anatase from forth sol |
|-----------------------------|--------------------------|-----------------------------|-------------------------------|-------------------------------|
| 400                         | 30 (A)                   | 19 (A)                      | 100                           | 74                            |
| 500                         | 35 (A)                   | 21 (A)                      | 92                            | 71                            |
| 600                         | 42 (R)                   | 21 (A)                      | 18                            | 67                            |
| 700                         | 52 (R)                   | 24 (R)                      | -                             | 28                            |

**Table 2.** Results from XRD measurements for TiO\(_2\) films
Effects of substrate nature and condition on crack formation

To achieve a better understanding of the effect of surface roughness on the coated films, a smooth and rough sand blasted surface was utilized. Average diameter of the islands between cracks and the covered surface area were calculated using the Clemex software. Figure 6 a and b show that the rough sand blasted substrate possess smaller islands and smaller crack covered surface area as a result of more favorable condition for nucleation. This will lead to a more favorable condition for photocatalytic activity as it will increase the surface area available for the related reactions to happen, thus for the remainder of the study a rough sand blasted surface was chosen. The data extracted from Clemex software is presented in Table 3.

Effect of substrate on Mb degredation

Figure 7 depicts the morphology of the coatings that were produced by 4 cycles of dip-coatings from 4 different sols mentioned and then subsequently calcined at 500 °C. EDS studies (Figure 8) indicated that, the amount of TiO$_2$ in the film increased with addition of PEG and P-25. It theorized that this addition may increase the photocatalytic behavior of the films. To test this, degradation of Mb by photolysis was utilized. First, a small amount of Mb was degraded with no substrate and then the same test was performed with mentioned film substrate. As it can be inferred from Figure 9, photolysis of Mb was enhanced by addition of P-25. However, the best result was achieved in the PED+P-25 film. In Figure 9, the vertical axis is the amount of maintained Mb in the solution, so as it decreased the degradation efficiency was improved.

Apart from the increased presence of TiO$_2$ in the film several other mechanisms are responsible for this behavior. P-25 loading produced more cracks on the film. This is the direct result of p-25's low permeability and high density that in turn decreases the permeability of TiO$_2$ film, thus formation of more cracks on the film [26]. On the other hand, PEG increases the roughness of the layer because of its removal during calcination step which lead to formation of more porosities [21]. Also, PEG limits water absorption in favor of direct dye absorption [27] not only at the surface of the photocatalytic film, but also at the increased porosities that are present in the film [28].
**Figure 6.** SEM images of the TiO$_2$ immobilized on (a) smooth and (b) rough stainless steel

![SEM images of TiO$_2$ immobilized on stainless steel](image)

**Table 3.** Average diameter of the islands and crack surface percentage that were calculated using Clemex software

|                  | Sand blasted (rough) | Smooth |
|------------------|----------------------|--------|
| Crack area percentage | 24%                 | 35%    |
| Average diameter of islands (µm) | 60                  | 37     |

**Figure 7.** SEM images of the surface morphology of TiO$_2$ films immobilized from different sols

![SEM images of TiO$_2$ films immobilized from different sols](image)

**Effect of initial concentration of Mb**

As seen in Figure 10, the photo degradation of Mb decreased as the initial concentration increased. Several other studies reported the same behavior for photo degradation of organic compounds and dyes [31, 32]. It was theorized that when the initial concentration of dye increased in the solution, the amount of absorbed Mb molecules on the surface of TiO$_2$ increased, limiting the direct interaction of other molecules with generated holes and
hydroxyl radicals. Also, a higher amount of Mb molecules in solution bulk absorbs an amount of UV light itself and lessen the amount of photons that reach the surface of TiO$_2$ film. This in turn decreased the hydroxyl radical flux [33] that ultimately resulted in a weaker degradation of Mb at higher initial concentrations.

**Figure 8.** EDS analysis of the films produced from the (a) base sol (b) second sol (c) third sol and (d) fourth sol.

**Figure 9.** Photodegradation of Methylene blue on TiO$_2$ samples prepared from different sols

**Figure 10.** Effect of initial Mb concentration on photodegradation of Methylene blue
Conclusion

Sol-gel process was chosen to produce a photocatalytic film to degrade methylene blue. To study the structural and morphological properties for sols were produced. Results of TGA/DTA tests indicated that a calcination temperature needed for four sols to calcinate. The XRD results revealed that, calcination temperature was dependent on composition. It was also found that, the substrate may affect the photocatalytic behavior and steel substrates with a sand blasted surface deemed superior. Additional tests indicated that, the increased dip coating cycles increased the nucleation and formation of cracks on the film. Degradation of Mb showed that as a result of more TiO_2 corporation in the film produced by the fourth sol, the photocatalytic behavior of the fourth sol is superior. The last tests of this research study indicated that, degradation of the Mb is dependent on the initial concentration and a higher initial concentration reduced the efficiency.

Disclosure statement

No potential conflict of interest was reported by the authors.

ORCID

M. Sajjadnejad †: 0000-0001-5112-1791

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