# Visible light induce photocatalytic activity of Ag<sup>+</sup> doped TiO<sub>2</sub> thin film prepared by sol-gel technique

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#### Abstract:

The photocatalytic activities of a  $TiO_2$  thin film with various dopant concentrations of Ag were investigated. Pure and doped  $TiO_2$  thin films were synthesized using sol-gel dipcoating method using surfactant and was then characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet-visible (UV-Vis) spectroscopy. The results showed that  $TiO_2$  has anatase phase only. As the  $Ag^+$  concentration increased from 0 atomic % to 1 atomic %, the photocatalytic activity induced up to 0.75 atomic %, in comparison with the pure  $TiO_2$ . The optical absorption shifts of the visible light region (red shift) and the band gap decreases for  $Ag^+$  doped  $TiO_2$  film were investigated. The photocatalytic activities of the  $TiO_2$  films were evaluated based on the degradation of congo red dye. The tailoring in the band gap and small crystallite size were attributed to high activities of  $Ag^+$  doped  $TiO_2$  thin films compared to pure  $TiO_2$ .

*Keywords:* Sol-gel technique,  $Ag^+$ -doped TiO<sub>2</sub>, thin film, Visible light, Photocatalytic activity

# 1. Introduction:

Titanium dioxide (TiO<sub>2</sub>) is well established as the most efficient and effective photocatalyst for the photochemical applications because of its functionality, durable stability and non-toxicity. Titanium dioxide has widely been employed in the process of degrading unwanted pollutants and coloring agents water [1, 2]. The most widely used photo-catalysis process is slurry phase reaction; however, this process suffers from the requirement of additional separation process which automatically increases the cost of the process. This inherent property which has negatively affected the application of photocatalyst in powder form for photocatalysis has prompted various researches leading to the development of reusable photocatalysts. Over past two decades now, much research leading to the development of TiO<sub>2</sub> film on a suitable inert supports have been conducted. However, the first problem arises at the point is related to the thin coating of the catalyst. Since the photo-catalytic action occurs at the liquid-solid interface, only a part of the photocatalyst is in contact with the reactant. Hence, the overall rate may be limited to mass transport of the pollutant to the catalyst

surface. The second problem is that a good contact between reactants and photocatalyst required along with, efficient exposure of the photocatalyst to irradiation through the whole interior of the reactor.

TiO<sub>2</sub> is active only under ultraviolet (UV) light because of its large band gap energy (3.2 eV) and the solar energy contains only about 6-7% of UV light. Thus, expansion of new approaches to modify the electronic band gap structure of TiO<sub>2</sub> for visible light response with strong interfacial charge carrier transfer process would be of great interest from the stand point of its practical and widespread use. In order to utilize extensive spectrum of incident photon energies, many strategies are developed to tailor the band gap absorption to visible region like metal/non metal ion doping [3, 4], co-doping with external ions [5, 6], noble metal deposition [7, 8] and sensitization by organic dyes or inorganic complexes [9, 10] and self doping [11, 12].

The aim of this study is to synthesize an Ag doped  $TiO_2$  for visible light response for photocatalytic activity and to compare it with a pure  $TiO_2$  film. In the present study, the mutual dip coating sol-gel process with surfactant-assisted method is reported as a potential and simple technique for pure and Ag<sup>+</sup> doped  $TiO_2$  anatase films synthesis.

## 2. Materials and methods:

The following chemicals in this study were purchased: Titanium (IV) isopropoxide (Ti(OiPr)<sub>4</sub>, 98% Aldrich), absolute ethanol (EtOH, Merck), ethyl acetoacetate (EAA, 98% Merck), 2-methoxyethanol (MeO (CH2)<sub>2</sub>OH, >99% Sigma-Aldrich), tetraethoxysilane (TEOS, 99% Merck), concentrated HNO<sub>3</sub> (65% Merck), Congo Red (dye content ca. 50% Sigma-Aldrich), Pluronic F127 (Surfactant, Sigma), and deionized water. The AgNO<sub>3</sub> was used as the precursor for Ag metal ion doping and the concentrations of Ag<sup>+</sup> ions was varied from 0, 0.25, 0.5, 0.75 to 1 at.%. The coating was done as follows: The glass slides were cleaned with a solution containing 5 mL concentrated HNO<sub>3</sub> and 200 mL distilled water in ultrasonic bath for 20 min, and then with ethanol to remove possible stains from the glass slides. First a dense SiO<sub>2</sub> barrier layer was deposited on the glass slides ( $25 \times 70 \times 1$ mm) to avoid diffusion of Na<sup>+</sup> ions from the glass substrate to the TiO<sub>2</sub> film during calcination and possible inhibition of photocatalytic activity [13]. The details of the SiO<sub>2</sub> and TiO<sub>2</sub> sol and it's films preparation technique were reported in our previous work [13].

The UV-visible transmittance spectra of the pure and Ag doped various TiO<sub>2</sub> films were recorded on a Shimadzu UV-1601 UV-vis spectrophotometer. XRD patterns of the film's powder were measured by D8 Advanced X-ray solution with an alpha 1 configuration using CuK<sub>1</sub> radiation (1.5406A°) in a wide-angle range (2 $\theta$ ) from  $20^{\circ}$  to  $60^{\circ}$  with a step-angle of  $0.0342^{\circ}$  was measured. The average particles sizes were determined from the Scherrer's equation [14] using the broadening of the (101) anatase peak reflection. The photocatalytic films were also characterized by Field Emission Scanning Electron Microscopy (FE-SEM) by the means of a Field Emission Zeiss SUPRA 35VP instrument. Top surface images were acquired by adopting accelerating voltage at 5 kV. The photocatalytic activity of synthesized pure and Ag doped  $TiO_2$  thin films were evaluated by the degradation of an azo dye Congo red (5 mg  $L^{-1}$ , CR dye concentration) under visible light irradiation with batch system. The 1000 W tungsten halogen lamp equipped with a UV cut off filters (Wavelength  $\lambda > 380$  nm) was used as a visible light source (the average light intensity was 60 mW cm<sup>-2</sup>). After every 10 min interval, clear solution was analyzed using UV-Visible spectrophotometer (UV-1601 Shimadzu, Japan) at CR maximum absorbance,  $\lambda_{\text{max}} = 498 \text{ nm}$ .

#### 3. **Results and discussion:**

#### **3.1.** X-ray diffraction (XRD):

Fig. 1 depicts XRD patterns of all TiO<sub>2</sub> film's powder samples (0, 0.25, 0.5, 0.75 to 1 at.%.) calcined at 500°C for 2 h. Evidently, all the reflections belong to anatase phase (peaks appeared at  $2\theta = 25.3^{\circ}$ ,  $38.2^{\circ}$ ,  $48.1^{\circ}$ ,  $54.2^{\circ}$  and  $55.3^{\circ}$  corresponding to (101), (004), (200), (105) and (211) reflections, respectively) and no additional reflections belonging to others phase were observed. It is well known that among crystalline phases of TiO<sub>2</sub>, anatase is photocatalytically most active [15, 16]. The average crystallite size was determined from the Scherrer's formula using the broadening of the (101) anatase peak. The crystallite size were reduced from 20.8 nm to 14.5 nm for Ag<sup>+</sup> doping 0 to 0.75, at.%. Further increase in Ag<sup>+</sup> doping crystallite size was not reduced.



Fig. 1: X-ray diffraction of pure and Ag<sup>+</sup> doped TiO<sub>2</sub> films.

### **3.2.** UV-Vis transmittance:

Fig. 2 depicts the UV-Vis transmittance spectra of pure and doped TiO<sub>2</sub> films (0, 0.25, 0.5, 0.75 to 1 at.%). The transparency of all TiO<sub>2</sub> films above 410 nm over the whole visible light region is as high as about 65%. As Ag<sup>+</sup> doping increases from 0 to 0.25, 0.5, 0.75 to 1 at.%, there was a remarkable induced red shift in transmittance in the range of 380-410 nm due to the introduction of Ag<sup>+</sup> ion in TiO<sub>2</sub> film. Fig.2 clearly show that absorption of UV light noticeably increased up to 0.75 at.% doping. These results indicate that absorption of longer wavelength of light can be controlled and increased up to 0.75 at.% doping in a film. The contributing effects of TiO<sub>2</sub> doping film on degradation of CR dye pollutant were further confirmed from photocatalytic degradation. It can be seen from Fig.2 that there is an enhancement in the absorption of 0.75 at.% doped TiO<sub>2</sub> film well agreement with photocatalytic degradation results. The observed performance highlights a direct correspondence between the pure and doped TiO<sub>2</sub> films with its crystallite size and the photocatalytic degradation of dye Congo red.



Fig. 2: UV-visible transmission spectra of pure and Ag<sup>+</sup> doped TiO<sub>2</sub> films.

## 3.3. FE-SEM analysis:

Fig. 3 depicts FE-SEM employed to characterize the surface morphology of the highly photocatalytic active 0.75 at.% doped  $TiO_2$  film. The FE-SEM image of  $TiO_2$  film is clearly exhibiting a homogeneously well-defined spherical nano crystallite structure with clear interstices between the crystallites without any cracks and slightly porous surface. The porous surface can play an important role in the photocatalytic activity since the photocatalytic reaction occurs at the surface, and a larger surface area provides for more photocatalytic reactions to take place [13].



Fig. 3: SEM images of 0.75 at.% doped TiO<sub>2</sub> film.

## 3.4. Photocatalytic activity of films

The photocatalytic activities of synthesized pure and doped TiO<sub>2</sub> thin films were evaluated by the degradation of an azo dye Congo red under visible light irradiation. For this purpose the 1000 W tungsten halogen lamp (the average light intensity was 60 mW cm<sup>-2</sup>) equipped with a UV cut off filters (Wavelength  $\lambda > 380$ nm) was used as a visible light source. Fig. 4 shows that the photocatalytic degradation efficiency of azo dye Congo red is a function of irradiation time. All Ag<sup>+</sup> doped TiO<sub>2</sub> films showed well photocatalytic degradation of Congo red under visible light irradiation expect pure TiO<sub>2</sub> film. However pure TiO<sub>2</sub> film also shows slight<del>ly</del> activity under the visible light irradiation [15, 16]. It is interesting to note that after 0.75, at.%. doping, neither significant induces in red shift in transmittance nor significant changes in the degradation rate of CR dye. These results suggest that the optimum concentration of dopant in TiO<sub>2</sub> film for the highest degradation of CR dye.



Fig. 4: Photocatalytic degradation of Congo red dye under visible light.

#### **Conclusions:**

The doping of  $TiO_2$  thin film with  $Ag^+$  ions is found to be effective in shifting the activation energy from UV range to the visible range. This makes the photocatalysis process effective, efficient and economical. The principal advantages of synthesized films are crack free transparent, uniformly, excellent photocatalytic activity and most importantly good adhesion with substrate,  $TiO_2$  films make it a good applicant to be considered in emerging wastewater engineering applications.

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