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Synthesis of nanocrystalline TiO₂ thin films by liquid phase deposition technique and its application for photocatalytic degradation studies

NOOR SHAHINA BEGUM* and H M FARVEEZ AHMED

Department of Post-Graduate Studies and Research in Chemistry, Central College Campus, Bangalore University, Bangalore 560 001, India

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Abstract. A transparent, high purity titanium dioxide thin film composed of densely packed nanometer sized grains has been successfully deposited on a glass substrate at 30°C from an aqueous solution of TiO₂-HF with the addition of boric acid as a scavenger by liquid phase deposition technique. From X-ray diffraction measurement, the deposited film was found to be amorphous and turns crystalline at 500°C. The deposited film showed excellent adherence to the substrate and was characterized by homogeneous flat surface. TiO₂ thin films can be used as a photocatalyst to clean up organohalides, a class of compound in pesticides that pollute the ground water. Photocatalytic degradation experiments show that indanthrene golden orange dye undergoes degradation efficiently in presence of TiO₂ thin films by exposing its aqueous solution to ultraviolet light. The suitable surface structure and porosity increases the photocatalytic activity. It was also observed that hemin doped TiO₂ thin films break up organohalides at a surprisingly high rate under visible light.

Keywords. TiO₂ thin film; LPD technique; photodegradation.

1. Introduction

Considerable interest has been generated in recent years to develop materials, which can provide sufficient photosensitivity in UV/visible region. TiO₂ is well known as an efficient photo catalyst, active only under UV light and has attracted a great deal of attention with the increase in number of recent environmental problems. However, the use of powder catalyst results in disadvantages of stirring during the reaction and separation after the reaction (Negishi *et al* 1995). Preparation of TiO₂ catalyst as a thin film will make it possible to overcome these disadvantages and to extend it to industrial applications. Generally, the preparation methods of metal oxide thin film are broadly classified as dry and wet processes. Dry processes are vacuum evaporation, sputtering, chemical vapour deposition, etc (Meng and Dos Santos 1993; Battiston *et al* 1994; Lobl *et al* 1994) and the wet processes are sol-gel, spray pyrolysis, liquid phase deposition, etc (Nagayama *et al* 1988; Richardson and Rubin 2000; Yu *et al* 2000; Deki *et al* 2001). However, there are several engineering problems associated with sol-gel and spray pyrolysis such as the requirement of special and costly apparatus for the deposition of films and these methods are not suitable for coating the substrate with a large surface area or complex morphology. Hence, in our present studies, a latest and simple novel wet process known as liquid phase deposi-

tion (Nagayama *et al* 1988; Richardson and Rubin 2000; Deki *et al* 2001) has been adopted to develop thin films of bare TiO₂ and hemin doped TiO₂ to overcome some of these problems. The resultant films have been characterized structurally and optically. The morphology and composition of the films were ascertained by SEM and EDAX. The TiO₂ thin film is applied as a photocatalyst for the photodegradation of indanthrene golden orange dye (IGOR). TiO₂ thin film is doped with hemin, a naturally occurring substance. The hemin doped TiO₂ thin film was found to increase the rate of degradation under visible light.

2. Experimental

2.1 Preparation of TiO₂ thin films

TiO₂ powder was supersaturated in 5% aqueous HF. The concentration of titanium ion was adjusted to 0.384 mol/dm³. This solution was then diluted to 0.15 mol/dm³ of titanium ion with distilled water and used as a precursor solution. The sodium silicate glass after degreasing and washing with double distilled water was immersed into the treatment solution and suspended vertically. The boric acid solution, ~0.05 mol/dm³, was added, which acts as a free F⁻ scavenger and shifts the equilibrium to one side. The solution was maintained at 30° for 40 h. After 40 h, the sample was taken out from the treatment solution, washed with distilled water and dried at room temperature. Calcinations of deposited film were carried out at

*Author for correspondence (noorsb@rediffmail.com)

various temperatures. The hemin doped TiO_2 was also prepared by mixing the powder hemin in different proportions to the above precursor solution.

2.2 Photocatalytic degradation

TiO_2 films were settled in aqueous IGOR solution of concentration, 100 mg/dm^3 , in a beaker. A pressure mercury lamp of about 200 W was used as light source. The solution was bubbled with air during irradiation. The concentration of aqueous IGOR was determined with a UV-visible spectrophotometer by measuring the absorbance between 200 and 700 nm. IGOR showed intense band at about 470 nm.

2.3 Characterization of deposited films

X-ray diffraction spectra were obtained from an X-ray diffractometer (type PW 3710 based tube anode: $\text{CuK}\alpha_1$: 1.54056 and $\text{CuK}\alpha_2$: 1.54439). Optical properties were studied by using UV-vis-NIR, scanning spectrophotome-

ter (type, Shimadzu-2003, Japan) in the wavelength range 300–1400 nm. The structural properties and chemical composition of coating were studied using scanning electron microscope and EDAX (type: Leica Cambridge Ltd./Leica S440i for SEM and Oxford link software for EDAX).

3. Results and discussion

The surface morphology of the TiO_2 film and hemin doped TiO_2 films were recorded by scanning electron microscopy (figure 1a) which indicates that the films are homogeneous with amorphous background. The film annealed above 400°C exhibited a uniform distribution of grains with an average grain size of about 50–100 nm (figure 1b). The SEM of hemin-doped TiO_2 thin film shows the compact structure with the segregation of hemin atoms (figures 1c and d).

The chemical composition of the TiO_2 and hemin doped TiO_2 films were also analysed by using EDAX spectra (figures 2a and b). The EDAX data confirmed that

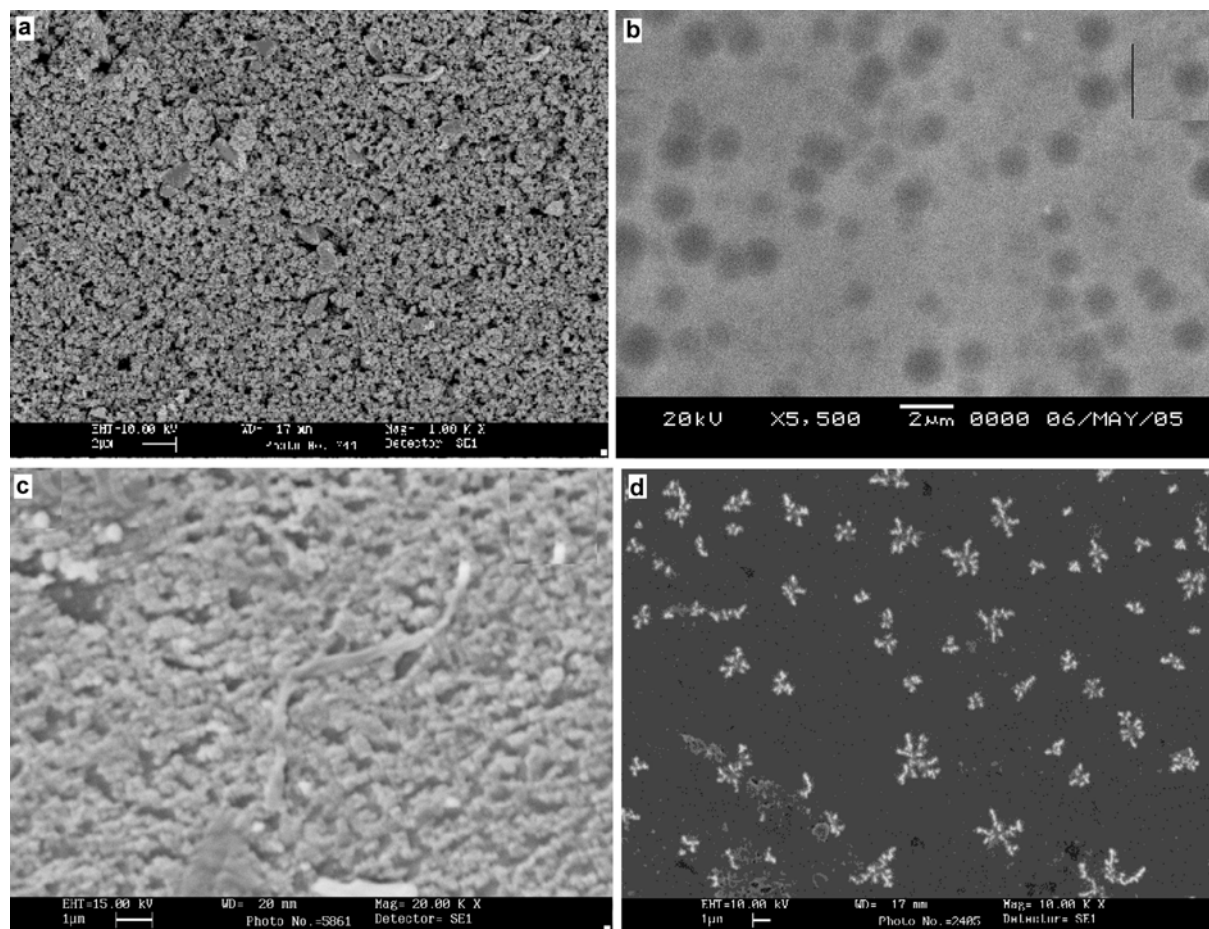


Figure 1. Scanning electron micrographs of **a.** TiO_2 thin films annealed at 300°C . **b.** TiO_2 thin films annealed at 400°C , **c.** hemin-doped TiO_2 thin films annealed at 300°C and **d.** hemin-doped TiO_2 thin films annealed at 400°C showing the segregation of hemin atoms in TiO_2 matrix.

the as deposited film and the film annealed at 500°C are nearly stoichiometric and indicates the peaks for TiO₂ and Fe atoms. This confirmed the formation of hemin-doped TiO₂ thin film.

The XRD pattern of TiO₂ thin films annealed at different temperatures is shown in figure 3. The broad and diffused X-ray diffraction patterns of as deposited film and film annealed up to 200°C indicate that the films are amorphous in nature. However, the films calcined at 400°C and above are polycrystalline and exhibited diffraction peaks with predominantly [101] orientation at 2θ equal to 25°. At 500°C, a very sharp peak is observed which can be attributed to the formation of anatase phase.

In the present investigation, the UV-visible spectra of TiO₂ thin films were recorded in the wavelength range 300–1400 nm. The optical absorption and transmittance spectra of TiO₂ thin films annealed at different temperatures are shown in figures 4 and 5. The as deposited film shows minimum absorption, but the absorption decreases

with increasing annealing temperature of the films (figure 4). Similarly the as deposited film exhibited high trans-

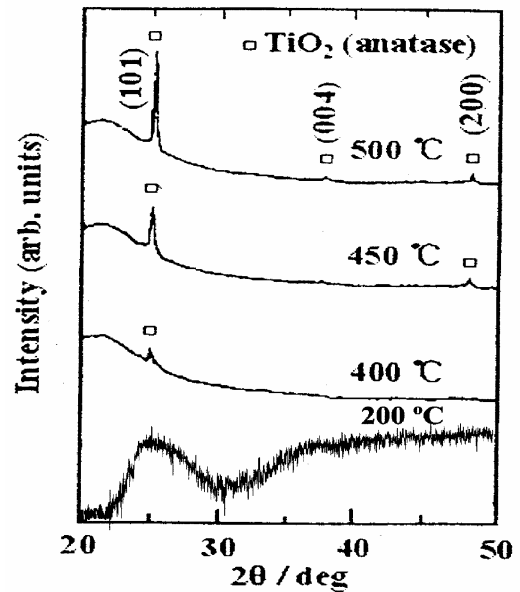


Figure 3. XRD pattern of TiO₂ thin films at different temperatures.

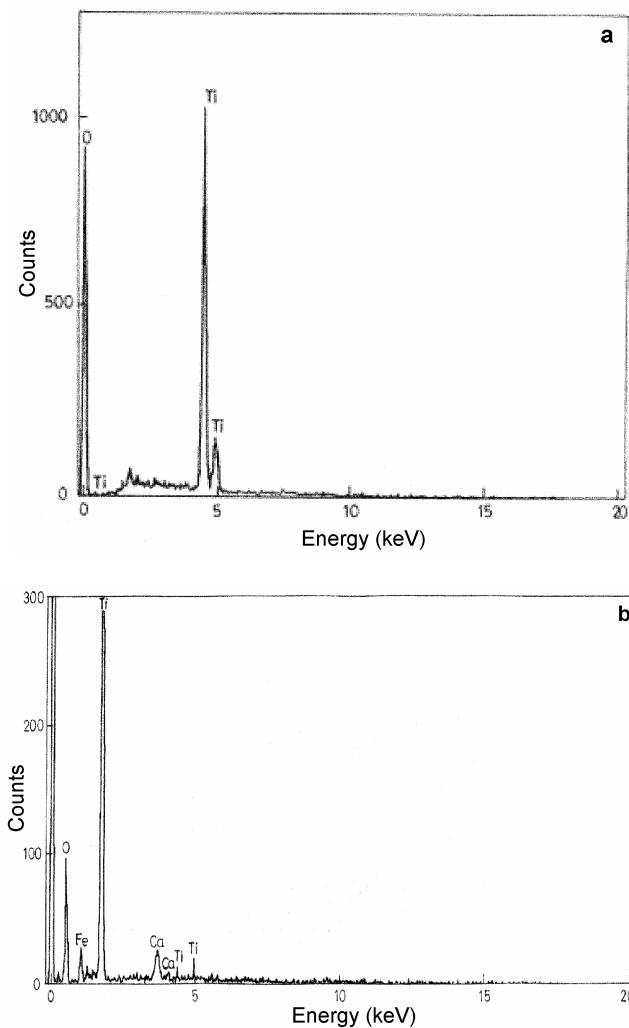


Figure 2. a. EDAX spectra of pure TiO₂ thin film and b. TiO₂ thin film doped with hemin.

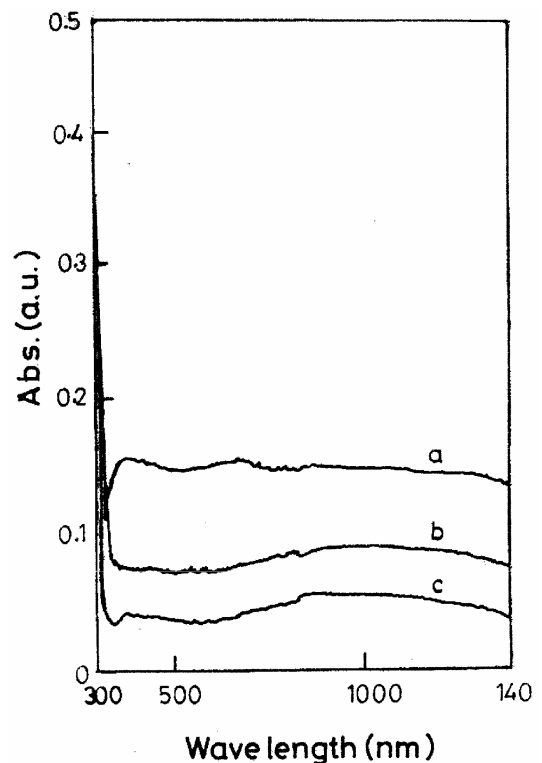


Figure 4. UV absorption spectra of TiO₂ thin films annealed at different temperatures (curves (a) absorption spectra of TiO₂ thin film annealed at 500°C, (b) absorption spectra of the film annealed at 300°C and (c) absorption spectra of the film annealed at 200°C).

mittance in the visible region with a sharp absorption edge between 350 and 400 nm (figure 5). However, transmittance decreases with increase in temperature. The high transmittances indicate smooth surfaces and relatively good film homogeneity. Absorption coefficient of the films can be calculated from transmittance and reflectance data. By determining the absorption coefficient, α , the optical band gap, E_g , can be calculated using the relation (Ramana *et al* 1997)

$$ah\nu = (h\nu - E_g)^n,$$

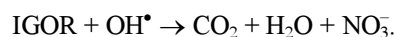
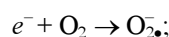
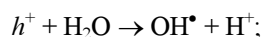
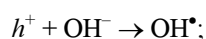
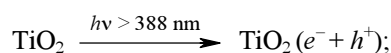
where $h\nu$ is the photon energy, n the exponent that determines the type of electronic transition causing the absorption and can take the values 1/2, 2/3, 2 and 3/2. The optical band gap for direct allowed transition was found to be around 3.2 eV and this is in good agreement with the theoretically reported values.

3.1 Photocatalytic degradation of indanthrene orange dye (IGOR)

Titanium dioxide is a well known photocatalyst in presence of UV light. However, thin films of TiO_2 also exhibit photocatalytic activity under UV light and degrade organic pollutants very effectively and overcome the di-

fficulties of powder catalyst (Negishi *et al* 1995; Kishimoto *et al* 1998). In addition, the same catalyst can be used repeatedly, which is not possible in case of powder catalyst. The rate of degradation increases with increasing number of OH^- , the amount and life time of holes, the surface area which the reactant can contact, transmittance and crystallinity of TiO_2 thin films etc. Hence, thin films of TiO_2 annealed at 500°C degraded organic dye effectively. The photodegradation of indanthrene orange dye will occur when TiO_2 thin film is illuminated by light of wavelength, 388 nm, in presence of water containing dissolved oxygen and organic dye. Many organic compounds are known to degrade to CO_2 and water under these conditions (Yuan and Zhang 1991; Andrew Burns *et al* 2002). The primary step in photodegradation is certainly the generation of electrons and holes within TiO_2 particles.

3.2 Mechanism



The photogenerated conduction band electron (e^-) gets trapped by the dissolved oxygen to form superoxide ion, $\text{O}_2^{\bullet-}$. IGOR is attacked by hydroxyl radicals formed in the above equations and generates organic radicals or some other intermediates. Eventually all the parent compounds and intermediates are oxidized into CO_2 and NO_3^- (Yu *et al* 2000; Mayer and Obare 2004).

Figure 6a shows a decrease in the concentration of IGOR with time. After 70 min, the concentration almost reduces to 0.02 g. Unfortunately, the large bandgap of TiO_2 lies in UV range, so that only 5–8% of sunlight photons have the requisite energy to activate the catalyst. A visible light ($\lambda = 400\text{--}800 \text{ nm}$) catalyst would be much more effective and efficient in degradation process.

It is evident from figure 6b that hemin, when anchored with TiO_2 thin film, shows excellent photocatalytic activities for the visible light photodegradation of IGOR compared with non-doped TiO_2 thin films. In fact, TiO_2 doped with 0.1 mg hemin degraded about 80% of the dye within a short reaction time. Whereas 0.15 mg of hemin doped TiO_2 thin film reduces the concentration of the dye to almost zero. This is attributed to the fact that the Fe^{3+} ion present in hemin is activated to its reduced form, Fe^{2+} , which traps the electron and increases the lifetime of holes. Electron trappings reduce surface recombination and facilitate the holes to diffuse to the particle surface and participate in the oxidation reaction and hence photodegradation is predominant.

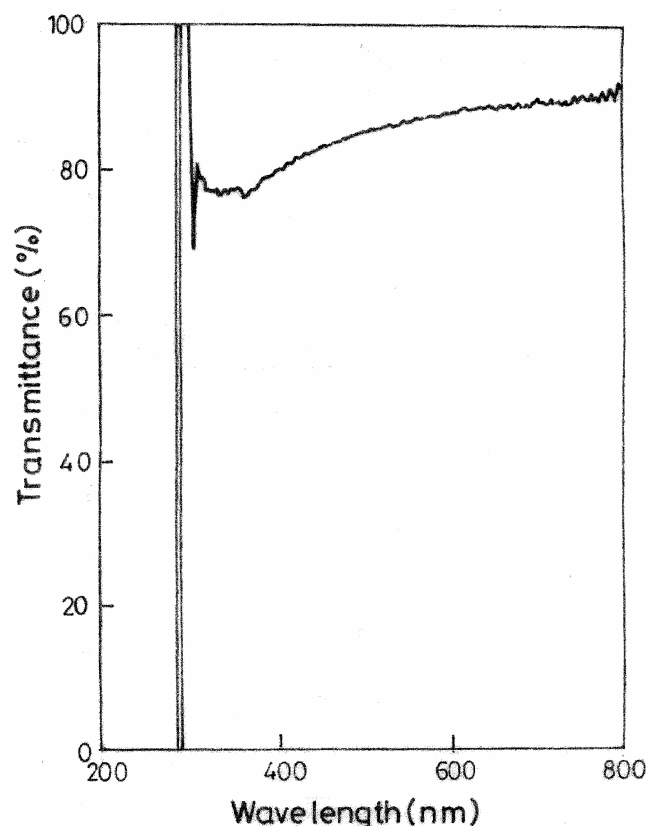


Figure 5. UV transmittance spectra of TiO_2 thin film annealed at 400°C .

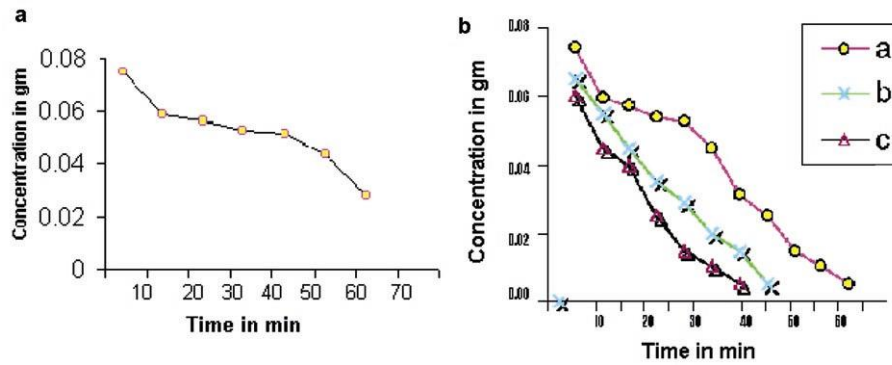


Figure 6. Photodegradation of IGOR organic dye by a. bare TiO₂ thin film and b. hemin-doped TiO₂ thin films (curves (a) TiO₂ thin film without hemin, (b) with 0.1 mg hemin and (c) with 0.15 mg hemin).

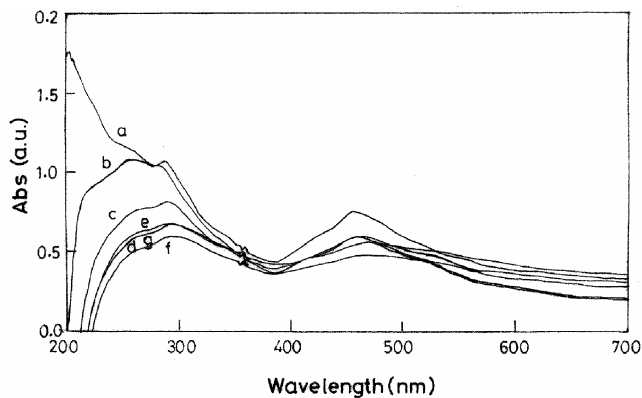


Figure 7. UV absorption spectra recorded for IGOR aqueous solution during photodegradation recorded at every 10 min interval using bare TiO₂ thin film.

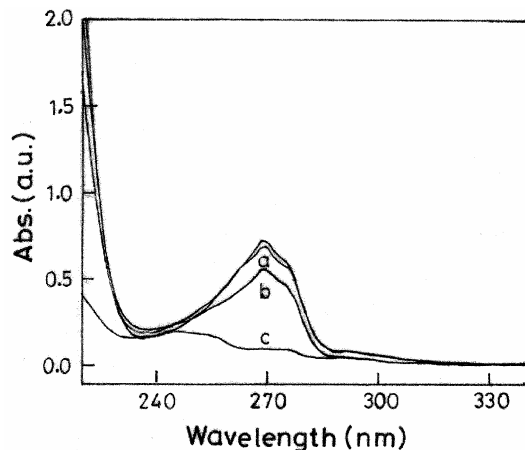


Figure 8. UV absorption spectra of IGOR aqueous solution during photodegradation recorded by using hemin-doped TiO₂ thin film with different concentrations of hemin (curves (a) without hemin, (b) with 0.1 mg hemin and (c) with 0.15 mg hemin).

Similarly, figures 7 and 8 show the UV-vis spectra of IGOR aqueous solution before and after degradation with

bare TiO₂ thin film and with hemin-doped TiO₂ thin film, respectively. The absorption of light gradually decreases with time.

4. Conclusions

Transparent and homogeneous TiO₂ thin films have been prepared by a highly economical technique known as liquid phase deposition technique (LPD) on soda lime glass. The UV-vis spectrum shows the optical band gap of TiO₂ thin films to be 3.2 eV which is in good agreement with theoretical values. The XRD pattern of thin films shows a single anatase phase at 500°C with some orientation effect in [101] peak. The photocatalytic activity of TiO₂ thin film has been investigated. The film annealed at 500°C degraded the organic dye effectively in presence of UV light. However, the hemin-doped TiO₂ thin films degraded the dye at a surprisingly high rate under visible light. The rate of degradation increases with increasing concentration of hemin.

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