PHOTOCATALYTIC ACTIVITY OF NANO-TiO_2 ON GLASS IN BUILDING ENVELOPE

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Abstract: Titanium dioxide is manufactured by processing naturally occurring titanium containing rutile (TiO_2) or ilmenite ($FeTiO_3$) minerals. Sri Lanka has vast deposits of ilmenite which is the major raw material in TiO_2 production. However, Sri Lanka currently does not produce any type of value added TiO_2 pigments. With the growth of nanotechnology, nano-TiO_2 is now produced worldwide using different methods varying the particle size from 1 nm to 100 nm. Nano-TiO_2 has the tightly controlled particle size that increases both the refractive index and light scattering properties as a result of the uniform particle size distribution and additional surface area. Nano-TiO_2 is particularly interesting in UV resistant surface coatings where it can act as a UV reflector. Because of the higher photocatalytic activity nano-TiO_2 can be used for anti-fogging coatings where nano-TiO_2 incorporated into outdoor building materials can substantially reduce concentrations of airborne pollutants such as volatile organic compounds and nitrogen oxides and as photocatalyst coating which assist in deactivation of bio-contaminants. In this investigation nano-TiO_2 and pigmentary TiO_2 were synthesized using titanyl sulfate precursor, which can easily be produced by Sri Lankan ilmenite with sulfuric acid according to the sulfate process. Synthesized nano-TiO_2 was characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) methods. The photocatalytic activity of nano-TiO_2 was assessed by the degradation of bromothymol blue in aqueous solution. Nano-TiO_2 coated on glass showed a higher photocatalytic activity and self cleaning effect that can effectively be used in building envelops.

Keywords: Ilmenite, Nano-TiO_2, Photocatalytic effect, Self cleaning glass

1 Introduction

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO_2. Titanium dioxide has been extensively studied because of its unique properties and wide verity of applications, for example semiconductor electrodes, gas sensors, self cleaning materials and as pigments with enhanced photodegradation activity on visible light [1]. Titanium dioxide has been widely used as a photocatalyst for solar energy conversion and environmental applications because of its low cost, non toxicity and excellent photoactivity. When TiO_2 is irradiated by sunlight with a wavelength less than 387 nm (ultraviolet range), electrons is passed across the band gap into the conduction band, leaving holes in the valence band. These holes have high oxidation power, thus can easily react with adsorbed hydroxide ions to produce hydroxyl radicals, the main oxidizing species which are responsible for the photooxidation of organic compounds [2]. As a new material, nano-sized TiO_2 is of great interest of many scientists in the recent years. Its small size and large specific surface area allow for certain unique unusual physio-chemical properties [1, 2]. Nano- TiO_2 has the tightly controlled particle size that increases both the refractive index and light scattering properties as a result of the uniform particle size distribution and additional surface area. Because of the higher photocatalytic activity, nano-TiO_2 can be used for anti-fogging coatings where nano-TiO_2 incorporated into outdoor building materials can substantially reduce concentrations of airborne pollutants such as volatile organic compounds and nitrogen oxides and as photocatalyst coating which assist in deactivation of bio-contaminants. Recently large number of studies appeared based on the photocatalytic activity of TiO_2 for oxidation of organic chemicals, obviously the most potential environmental friendly process. In general, two methods of application of TiO_2 in photocatalysis have emerged, one as highly dispersed fine particle on porous support materials and suspended fluids in liquid medium and another as their films [3]. However the application of TiO_2 as a film is one of the easiest ways out of those two methods. TiO_2 thin films are prepared by coating the substrate with TiO_2 sol by different techniques such as chemical vapor deposition, chemical spray pyrolysis, electrodeposition and sol-gel methods [3]. Each method has its

own advantages and disadvantages. In this present work, we have developed a very simple, efficient and cost-effective method for deposition of thin films of TiO_2 on glass to be used in building envelops. Main objectives of this work is to find the ways of producing nano-TiO_2 and pigmentary TiO_2 by titanyl sulfate precursor which can easily be produced from Sri Lankan ilmenite with sulfuric acid according to the sulfate process [4]. Photocatalytic activity and self cleaning effect of synthesized nano-TiO_2 coated on glasses are also investigated.

2 Material and methods

2.1 Preparation of TiO_2 precursor sol

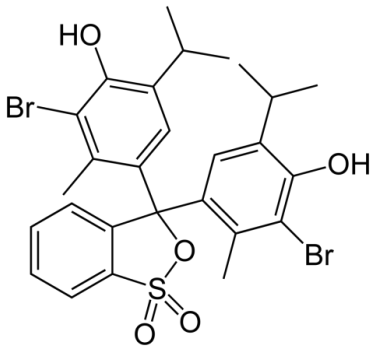
In the preparation of titanium precursor sol, 25 mL of titaniyl sulfate (99.9%, Sigma-Aldrich) was added drop wise to 50 mL of distilled water while stirring at room temperature. Then the pH of the titanium solution was adjusted to pH=3 by adding 3 mol L^{-1} ammonia solution drop wise while stirring to form a white precipitate. The precipitate formed was separated and washed several times to remove NH^{4+} and $SO4^{2-}$. The precipitate was then dispersed in distilled water. This dispersed solution was added drop wise in to 100 mL of 30% H_2O_2 solution while stirring at room temperature. A yellow colored solution with a yellow precipitate was formed indicating the formation of peroxo titanium complex. This solution was stirred for 12 hours at 600 rpm. The precipitated gel was separated by centrifugation at 9000 rpm and washed several times with distilled water. Then precipitated gel was dispersed in 100 mL distilled water and refluxed for 5 hours at 100 °C to obtain TiO_2 sol to be coated as thin film of TiO_2 on glass substrate.

2.2 Preparation of thin film of TiO_2

Glass slides were used as substrates for the deposition of the TiO_2 film. Before the deposition, glass substrates were ultrasonically cleaned using acetone and ethanol respectively. Finally they were thoroughly washed with water and dried. TiO_2 thin film was deposited on substrate by a dip-coating process at room temperature. Substrates were immersed in the TiO_2 sol prepared for 30 minutes and dried at room temperature followed by the drying at 100 °C for 1 hour in an oven. In order to obtain nano-TiO_2 powder, the TiO_2 sol prepared was oven dried at 105 °C and calcined at 800 °C for 1 hour. For comparative study, pigmentary TiO_2 was synthesized using titanyl sulfate solution according to the sulfate process used for the manufacturing of TiO_2 pigment from ilmenite ($FeTiO_3$) [4].

2.3 Photocatalytic decomposition of bromothymol blue on nano-TiO_2 films

The photocatalytic activity of the prepared nano-TiO_2 particles and TiO_2 thin films were evaluated by studying the degradation of bromothymol blue in an aqueous solution under diffused light. One piece of 50 mm × 20 mm glass side having TiO_2 thin films on both sides were dipped in a Petri dish containing the indicator (1.7×10^{-5} mol L^{-1}, 20.00 ml) and exposed to diffused light for 48 hours. Same experiment was carried out by adding 0.5 g of nano-TO_2 powder in to a Petri dish instead of a glass slide. The change in the concentration of bromothymol blue was estimated from the changes in the absorbance in the range of 300 nm to 700 nm using UV-Visible spectrophotometer (SHIMADZU UV-3600, UV-VIS-NIR Spectrophotometer). The maximum absorbance peaks of bromothymol blue are at 428 nm and at 614 nm. The structure of bromothymol blue is shown below.



Bromothymol blue

2.4 Characterization

The crystallinity of the synthesized TiO_2 powder samples were determined by X-ray diffraction (XRD) technique using Brucker D8 Focus X-ray Diffractometer with Cu Kα radiation. The average particle size was estimated by applying the Scherrer equation to the apparent full-width-at-half maximum intensity (FWHM) of the (101) peak of anatase TiO_2 [2], as follows:

$$d= (k\lambda) / (\beta \cos \Theta),$$

where d denotes the average crystallite size, k = 0.9, λ = 0.15405 nm is the X-ray wavelength of Cu-Kα, β is the full-width of the peak measured at the half-maximum intensity (FWHM) and Θ is the Bragg angle of the peak.

Synthesized TiO_2 powder samples were also studied by using UV-Vis absorption spectrum in a wavelength range from 300 nm to 700 nm employing SHIMADZU UV-3600; UV-VIS-NIR Spectrophotometer. FT-Raman spectra of the TiO_2 powder samples were studied using Bruker Vertex80 coupled with Ram-FT module (RAM II) FT-IR Spectrophotometer. For the FT-Raman experiment a CaF_2 beam splitter and InGaAs detector were used with sample illumination by a laser operating at 1064 nm. Scanning Transmission electron microscopy (STEM) at an operating voltage of 30 kV and scanning electron microscopy (SEM) at an operating voltage of 20 kV using Hitachi SU 6600 FE-SEM were carried out to ascertain the particle size and the morphology of TiO_2 powder samples synthesized.

3 Results and discussions

3.1 X-ray diffraction

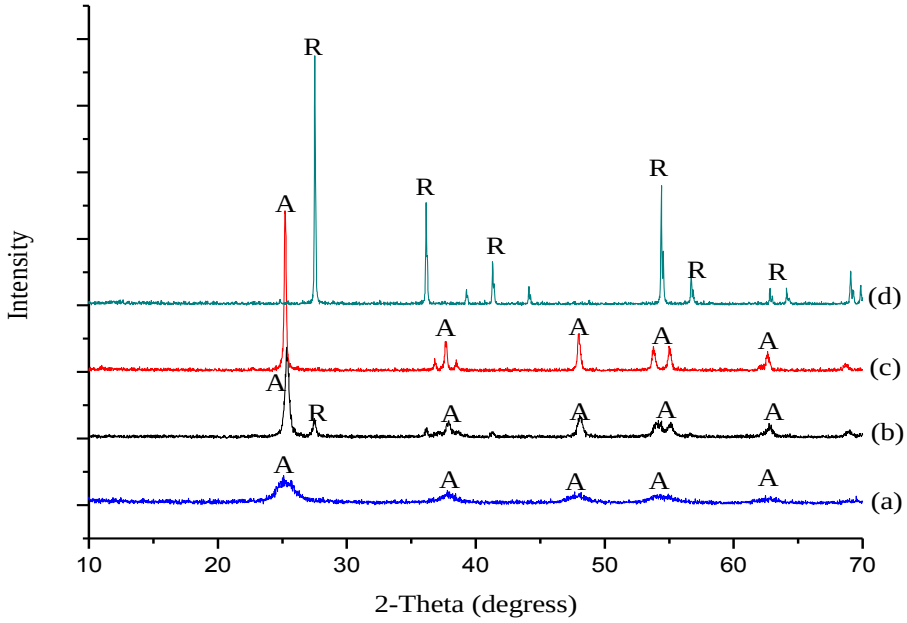


Figure 1: *XRD patterns of the TiO_2 powders: (a) TiO_2 coated on glass, (b) commercial nano-TiO_2, (c) nano-TiO_2 synthesized at 800 °C, (d) pigmentary TiO_2*

The powder XRD patterns of TiO_2 powder samples are shown in Figure 1. The XRD pattern of commercial nano-TiO_2 sample (< 30 nm, Degussa) is given in Figure 1 (b) and it mainly contains the anatase form of TiO_2 with modest amount of rutile. Figure 1 (d) presents the XRD pattern of pigmentary TiO_2 synthesized according to the sulfate process given. The only crystal type found in this pigmentary TiO_2 sample was rutile crystal type. Figure 1 (a) and (c) are X-ray diffraction

diagrams of TiO_2 coated on glass surface and nano-TiO_2 synthesized at 800 °C respectively. Higher peak intensity of anatase in Figure 1 (c) shows the increase in the crystallinity due to use of higher temperature in the synthesis process.
The X-ray diffraction pattern of anatase crystal type TiO_2 samples give three major distinctive peaks at 25.3°, 37.9°, 48.0° corresponding to (101), (004) and, (200) crystal planes respectively, where as rutile crystal type TiO_2 samples give three major distinctive peaks at 27.5°, 36.9°, 54.4° corresponding to (110), (004) and, (200) crystal planes respectively.
In general, FWHM of XRD peak corresponds to the crystal size of the materials. When the width is broader, the crystallites exhibit smaller size. The Scherrer equation was used to determine the average particle size of the nano-TiO_2. The average particle size of the nano-TiO_2 coated on the glass and nano-TiO_2 powder synthesized at 800 °C was found to be 10 nm and 60 nm diameters.

3.2 Raman spectroscopy

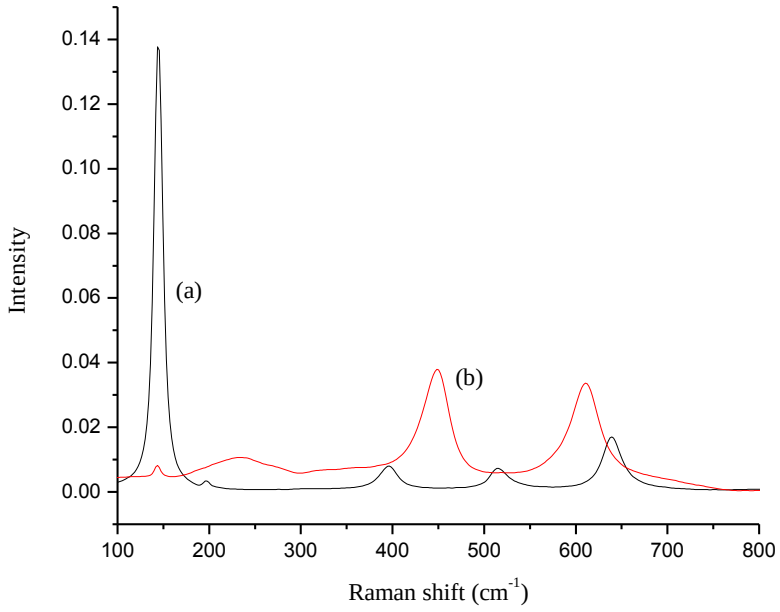


Figure 2: *Raman spectra of the TiO_2 powders: (a) nano-TiO_2 synthesized at 800 °C, (b) pigmentary TiO_2*

Raman spectroscopy can be used to examine the crystal structure of TiO_2 samples as a more sensitive technique compared to X-ray diffraction method for the identification of anatase and rutile crystals in a variety of natural and synthetic materials over a wide range of concentrations [5, 6]. Raman spectra of nano-TiO_2 synthesized at 800 °C and pigmentary TiO_2 synthesized are shown in Figure 2 (a) and (b) respectively. Figure 2 (a) shows Raman shifts at 145, 396, 515, and 639 cm^{-1} for nano-TiO_2 synthesized at 800 °C indicating only anatase crystal phase is present without any impurities. Figure 2 (b) gives Raman shift at 449 and 611cm^{-1} for pigmentary TiO_2 synthesized according to the sulfate process. Pigmentary TiO_2 contained only rutile type crystal according to its Raman spectrum.
Figure 3 (a) and (b) show the Raman spectra of commercial nao-TiO_2 and the TiO_2 coated on glass. Raman spectroscopy results revealed that the TiO_2 coated on the glass slide was only in the anatase crystal form.

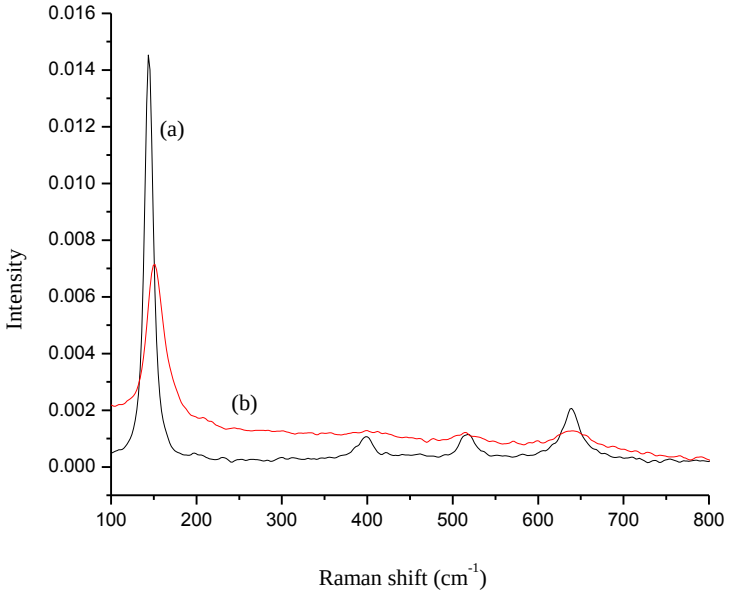


Figure 3: *Raman spectra of the TiO_2 powders: (a) commercial nano-TiO_2, (b) TiO_2 coated on glass*

3.3 UV-visible diffuse reflectance spectroscopy

The UV–visible diffuse reflectance spectra of the TiO_2 samples are shown in Figure 4 (a) and (b). Both commercial nano-TiO_2 and nano-TiO_2 synthesized at 800 °C gave the maximum absorption band at 205 nm wavelength. The spectra show shoulders near 350 nm and bases which approach zero at about 400 nm. The absorption quickly increased above 350 nm due to the absorption of light caused by the excitation of electrons from the valence band to the conduction band of TiO_2.

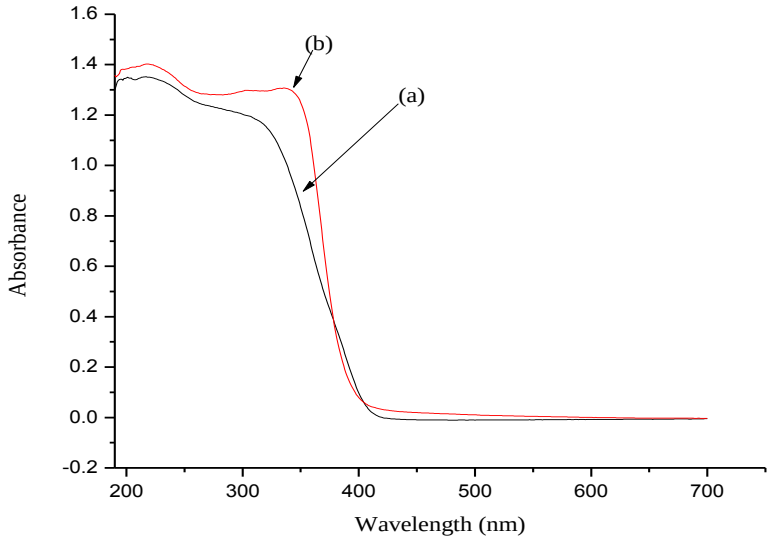


Figure 4: *UV–visible diffuse reflectance* spectra *of the TiO_2 powders: (a) commercial nano-TiO_2 (b) nano-TiO_2 synthesized at 800 °C*

3.4 Surface Morphology

STEM and SEM images of nano-TiO_2 synthesized at 800 °C are shown in Figure 5. Experimental results show the morphological homogeneity with grain size falling mostly in the rage of 20 nm to 60 nm, with soft agglomerates. These spheres consist of many small short rod shaped crystals of TiO_2 crystals due to agglomerations. STEM and SEM images also reveal that particle sizes of nano-TiO_2 synthesized at 800 °C were in agreement to the values determined by using XRD data. In order to investigate nao-TiO2 powder, EDX analysis was also carried out. The EDX analysis shows that nao-TiO_2 synthesized at 800 °C contains only titanium and oxygen elements and there is no impurity in the sample.

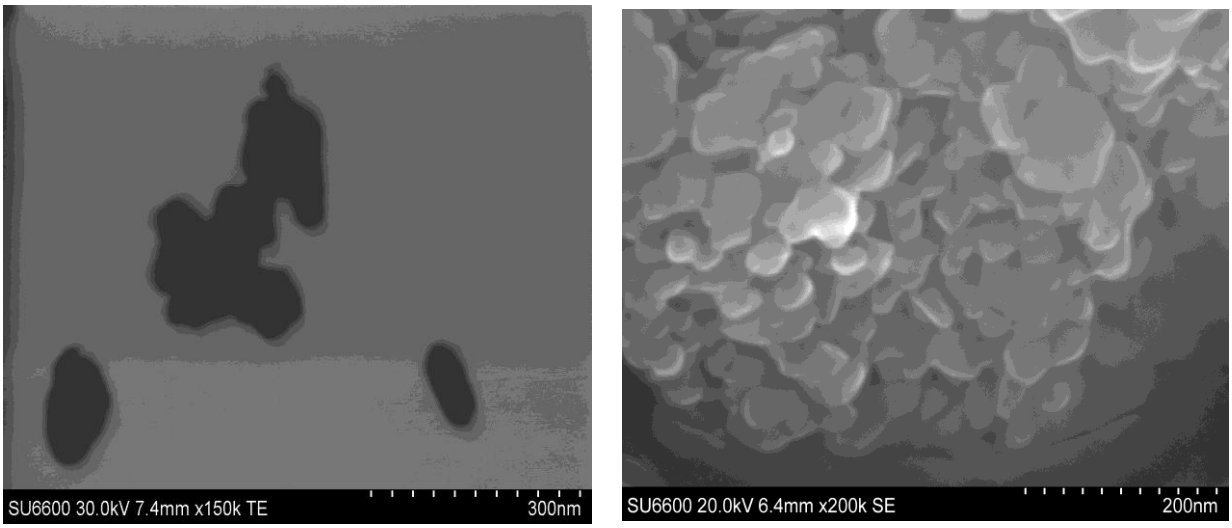


Figure 5: STEM and *SEM images of the nano-TiO_2 synthesized at 800 °C*

3.5 Photocatalytic activity

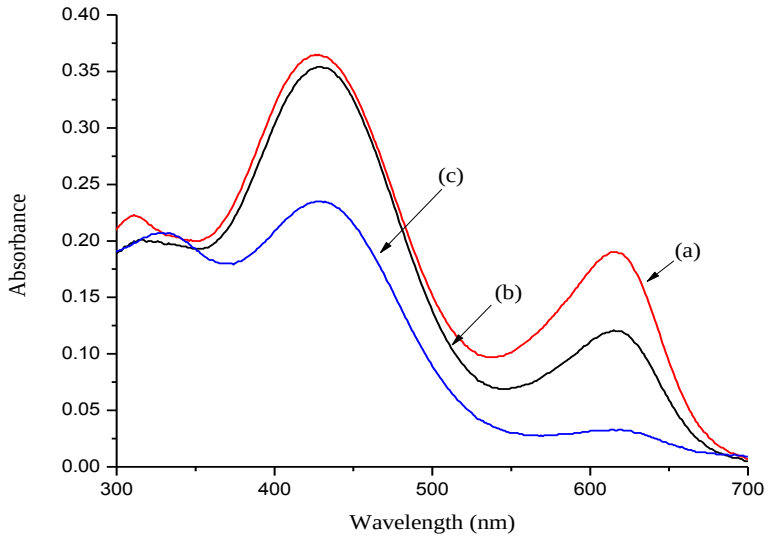


Figure 6: *UV-Vis spectra of reaction product of bromothymol blue solution: (a) with uncoated glass (control), (b) with the TiO_2 coated on glass, (c) with nano-TiO_2 powder after exposing to diffused light for 48 hrs.*

The photocatalytic activity of the thin film TiO_2 was determined by photo-oxidation of bromothymol blue. Figure 6 (a) represents the UV- visible absorption spectrum of bromothymol blue in water (1.7×10^{-5}) after exposing to diffused light for 48 hours with an uncoated glass slide dipped. Figure 6 (b) and (c) are spectra of bromothymol blue in water (1.7×10^{-5}) after exposing to diffused light for 48 hours with a TiO_2-coated glass slide dipped and with 0.5 g of nano-TiO_2 powder respectively.
Figure 6 (b) showed that the reduction of absorbance at 614 nm in bromothymol blue solution was mainly due to the photocatalytic capabilities of TiO_2 thin film coated on glass. Figure 6 (c) shows the significant decrease in absorbance both at 428 nm and 614 nm indicating that most of the bromothymol blue has been photo-oxidized by nano-TiO_2 with diffused light. The maximum percentage of photo-oxidation of bromothymol blue was 82.6% at 614 nm by nano-TiO_2 under diffused light.

5 Conclusions

A simple and inexpensive technique has been established to prepare nanocrytalline TiO_2 powder and thin films from aqueous solution at room temperature. According to XRD analysis the particle size of the nano-TiO_2 particles increased up to 60 nm with an increase in the temperature. Nano-TiO_2 synthesized is in pure anatase form where it shows a higher level of photocatalytic activity. The thin TiO_2 film preparation process involved in research is quite simple and a low temperature route. The photocatalytic activity of nano-TiO_2 was assessed by the degradation of bromothymol blue in aqueous solution. Nano-TiO_2 coated on glass showed a higher photocatalytic activity and self cleaning effect that can effectively be used in building envelops. This method can be implemented on a wide range of applications, involving the deposition of photocatalytic TiO_2 films on low thermally resistant materials, such as plastics. Therefore, value added nano-TiO_2 can easily be produced from Sri Lankan ilmenite ($FeTiO_3$). Nano-TiO_2 coated glass has potential for the effective and efficient photocatalytic and self cleaning effect and in a commercial context may provide savings with respect to both time and energy.

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