

Self-Cleaning Finish on Cotton Textile Using Sol-Gel Derived TiO₂ Nano Finish

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Abstract: *TiO₂ Nano Particles have been synthesized using titanium tetrachloride as precursor through Sol-gel technique. The characterization of synthesized particles was done in XRD and FTIR analysis. It is revealed from XRD and FTIR spectroscopy that the TiO₂ nano particle formation. Subsequently the synthesized particles were applied on the Cotton textile woven fabrics using pad patch method using 1 wt% of acrylic binder. While coating three different concentration of TiO₂ Nano particles were maintained. The self cleaning action of nano coated fabric has been quantified by measuring photo catalytic degradation of stain due to visible light irradiation. %of Decrease in K/S value is increased with respect to increase in TiO₂ concentration as well as duration of visible light irradiation.*

Keywords: *TiO₂ Nano particles, Self-cleaning property, Nano-Sol, Photocatalysis*

I. Introduction

Functional textiles are generally classified in functions related to basic properties, comfort properties, safety and new functions. The functional application oriented textile products can be further classified in to two types such as general apparels and special apparels (Chi-Chung,2002). Sensitivity /appearance functions and health /cleanliness functions are further divided as branch of comfort functions. Textile finishing has always led to introduction of new technical properties, which are useful in diversified end uses. Technological diversification in finishing decides the performance domain of fabrics and renders it special functional properties. There has been a continuous improvement and innovation in the area of chemistry related to textile finishing. Recently high demand has created among the customer about the high technology textile products.

Ever since the introduction of Nano particles in textiles, efforts were on to produce finished fabrics with multiple functional performances. It was demonstrated in recent years that Nano technology can be used to enhance textile attributes, such as fabric softness, durability, and breathability, water repellency, fire retardancy, anti-microbial properties, and the like in fibers, yarns, and fabrics (Sawhney A P S et al, 2008). Lee et al (2003) reported the use of nano silver particles for imparting antimicrobial properties. Yadav et al (2006) reported that use of ZnO nano particles the antimicrobial as well as UV protection can be achieved. Photocatalysis have gained higher attention in recent years because these materials enable low energy and low cost (Herrmann, J, M, 2005 & Karuanakaran, C et al, 2008). The Catalytic activity of TiO₂ is based on the electron/hole pair information due to photo excitation (Kamal K Gupta et al, 2008). More over Nano level TiO₂ exhibits higher photo-catalytic properties behave of having large surface area. In addition to that photo catalytic activity of TiO₂ Nano particle coating depends strongly on the phase, the crystallite size, porosity of the coatings and the particles size are formed during synthesis (Kamal K Gupta et al, 2008). Among the photocatalysts, TiO₂ Nano particles are widely used in air and water purification and self-cleaning process (Laoufi, N. A et al, 2008). TiO₂ coating attempts on surfaces such as glass, textile, cement and plastics was done in various places (Coronado, J, M. et al, 2008). Coleman et al (2005) reported that TiO₂ has three types of crystal structures in nano level called anatase, rutile and brookite. Anatase types of TiO₂ nano particles are generally having high photo catalysis. Several techniques

As reported by Chen, X et al (2007) major efforts have been devoted to the development of methods for their synthesis, and numerous, fundamentally different ways of preparation have been postulated some of them being sol-gel, sol, hydrothermal and solvothermal methods, micelle and inverse micelle methods, direct oxidation methods, chemical and physical vapour deposition methods and also electrodeposition, sonochemical and microwave deposition methods. However, when we take into consideration the application of TiO₂ nanoparticles on textile substrates it should be kept in mind that the low-temperature methods for the synthesis is highly preferable. Therefore, the wet chemistry methods such as sol-gel or hydrothermal methods are used to obtain textiles with self-decontaminating properties. As these methods are most promising ones. The sol-gel method (Andersson et al, 1995) is performed by the hydrolysis of a titanium precursor, usually titanium(IV) chloride or titanium tetraisopropoxide (TIP) in a mixture of water and alcohol in acidic conditions. It involves the reaction of hydrolysis of a corresponding Ti precursor and a subsequent polymerization reaction leading to the formation of the liquid sol phase.

This paper titanium tetrachloride has been utilized as precursor for TiO₂ nano particles using sol-gel techniques. The synthesized nanoparticle are then characterized using XRD, FTIR and SEM. Then Nano particle then applied on the fabric by pad –dry cure method in different concentration. The self cleaning action of TiO₂ studied.

II. Experimental

2.1 Photocatalytic Mechanism of TiO₂

The development of nano technology, used to get self-cleaning fabrics is to apply photocatalytic materials on the textile substrate. By utilizing the photoreaction induced by photocatalytic material, when the textile substrate expose to certain irradiations, irradiations with higher energy than the band gap of the photocatalytic material, the organic contaminants will be degraded into air and water on the photocatalytic material surface. (Malik T. et al., 2013) Titanium dioxide gets a lot attention during past decades and is taken as one of the most promising photocatalytic materials that could be used in textile industry for many advantages such as low band gap, UV protection. (Hashimoto, k et al., 2005)

The mechanism of photoreaction induced by TiO₂ was extensively studied and explained by many researchers, some of them are Dastjerdi R. and Montazer M.(2010), Yuranova T. et al (2007) and Chen X. and Mao S.(2007), when TiO₂ nanoparticles are irradiated by light, usually ultraviolet light (UV), with energy equal to or higher than its band gap (>3.0 eV), electrons on the TiO₂ surface are excited and will escape from valence band to the conduction band, leading to formation of electron- hole pairs on the surface – excited negative charged electrons in the conduction band and positive charged holes in the valence band. The created pairs can recombine, radiatively or get trapped and react with other materials absorbed on the photocatalyst. The pairs will cause redox reactions at the surface, the negative electrons (e⁻) will combine oxygen to produce super oxide radical anions (O₂⁻), the positive electric holes (h⁺) will act with water to generate hydroxyl radicals. Ultimately, all the formed highly active oxygen species will oxidize organic compounds to carbon dioxide (CO₂) and water (H₂O). Hence, titanium dioxide can decompose common organic matters in the air such as odour molecules, bacteria and viruses. However, it has been demonstrated that the intensity of photocatalytic activity of titanium dioxide is affected by its physical and chemical properties such as crystallinity, shape, size of the particles and surface area. The mechanism of generation of oxidative radicals and photodecomposition of organic compounds could be seen in below figure.

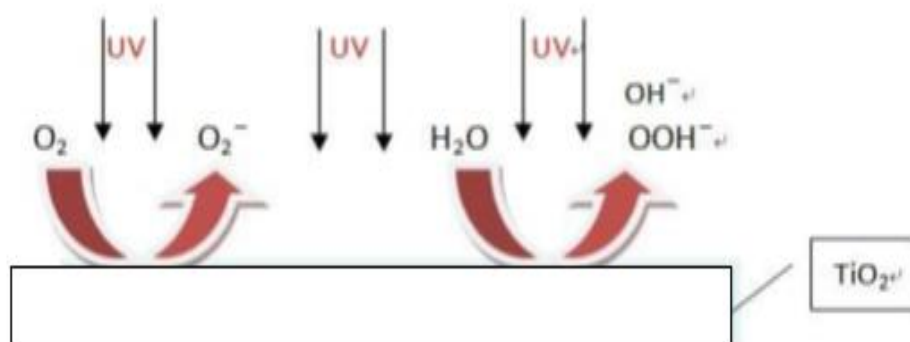


Fig.1- shows the highly oxidative radicals produced under UV light by TiO₂

III. Materials

The cotton plain woven fabric with well bleached. The construction parameters are as follows, ends per inch 96 and pick /inch is 75 .Warp and weft counts are 40s Ne .The cloth GSM is 135.The titanium tetrachloride precursor were procured from Raj enterprises ,Mumbai. Lissapol-N surfactant was used as capping agent during the sonication process.

IV. Methods

4.1 Synthesis of TiO₂ Nano particle using titanium tetrachloride

As per the procedure reported by Parthasarathi(2009) titanium tetrachloride (TiCl₄) was taken as a precursor .The said chemical was hydrolyzed by adding 1.0 M ammonia drop-wise to prepare a stock solution, in which the concentration of titanium was 5.45M. During the reaction ,the yellow cakes of TiO(OH)₂ were formed first, which was then dissolved with added ammonia solution to form an aqueous TiCl₄ solutions. This stock solutions remained in a stable state without precipitation even after 5 months at room temperature. Finally ,ammonia solution with a concentration of 4.5M HNO₃ was added to the stock solutions with various concentrations of Ti 4+ for precipitation. This solution was poured into reactor and placed in oven at 90^oc for precipitation. TiO₂ precipitates were repeatedly cleaned by distilled water and dried at 80^oc for 6 h.

4.2 TiO₂ Nano coating on fabric

Nano-particle were applied on the fabric using pad-dry-cure method. Before initiating the coating process, the fabric samples were dried at 100 °C for 5 min. in oven to remove the moisture content .. The coating were prepared 1.0Wt% of TiO₂ nano particles and 1.0% acrylic binder on weight of the solutions. Subsequently sonication process was initiated for 30 min in the solution bath to ensure the even application on the fabric. The surfactant of 0.5% Lissapol-N is added in the bath as a capping agent. The cotton fabric was immersed for 1-2 min in aqueous nano solution then passed over the padding mangle to remove the excess amount solution. A 100% wet pick up maintained for all the samples. After the padding the fabric was dried for 4 min at 80°C and then cured for 30 min at 100 °C. Similarly 2% nano particle coating is also done

V. Characterization of Nanoparticles

The nano-particles size, shape, chemical and physical structures were characterized through the following procedures

5.1 X-Ray Diffraction (XRD)

The Crystallinity of the nanostructures was done by XRD spectrum using SHIMADZU-XRD 6000 advanced X-rays Diffractometer equipped with a Cu K α radiation, $\lambda=1.5406\text{\AA}$, applied voltage 30kV and current 30 mA. The dried nanoparticles deposited as randomly oriented power onto a plexiglass sample container, and the XRD patterns were recorded at angle 10⁰-80⁰c, with a scan speed of 5⁰/min, sampling pitch of 0.02⁰ ND PRESET TIME OF 0.24 S. The crystallite domain diameters(D) were obtained from XRD using the Debye-Scherrer's equation, as shown below

$$D = \frac{0.89\lambda}{\Delta W X \cos\theta}$$

Where λ is wave length of the incident X beam (1.5406 Å for Cu α); θ is bragg's diffraction angle; and ΔW is the full width of the X-ray pattern line at half peak-height in radians

The XRD Spectra of TiO₂ Nano-particle is shown in figure no.2. It shows the well defined peak of TiO₂ Nano particles presence. The XRD spectra of TiO₂ Nano-particles synthesized using TiCl₄ shows distinctive peaks at 29.9, 38, 47.8, 57, 64.5 and 74.6 respectively

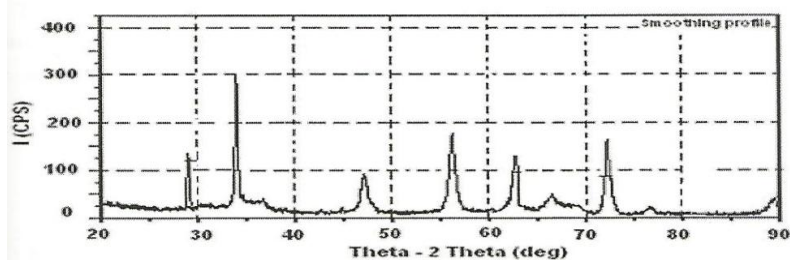


Fig.2-XRD Pattern of TiO₂ nano particle synthesized by TiCl₄

5.2 FTIR Spectroscopy

SHIMADZU-FTIR 8400S with a spectral range of 4000-400 cm^{-1} was utilized to study the nano particle presence. Spectra with resolution of 0.9 -1.0 cm^{-1} and given as ratio of 200 single beam scans to the same of background scans in pure KBr. KBr was grounded to fine power and mixed with samples [2% w/w].

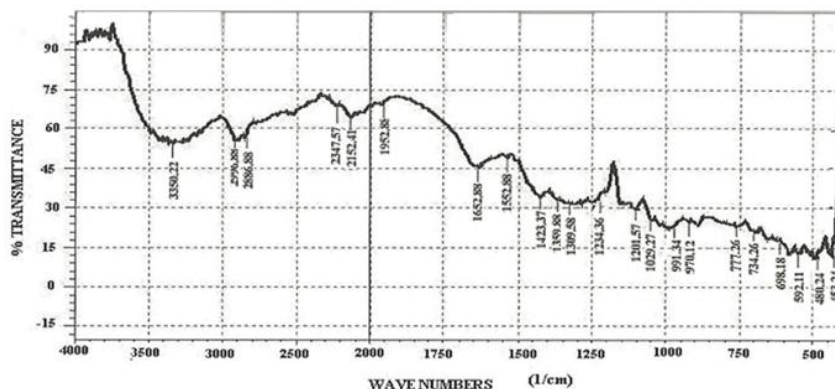


Fig.3-FTIR Spectrogram of TiO₂ nano-particle synthesized using TiCl₄

The above FTIR spectra for TiO₂ coated cotton fabrics. The diffraction spectrogram of TiO₂ nano particles synthesized shows absorption band of TiO₂ near 482 cm⁻¹. The peak at 3000 and 1200 cm⁻¹ indicate the presence of -OH and C=O residues due to atmospheric moisture and CO₂ respectively.

5.3 SEM Analysis

JEOL-JSM-6360 –SEM analyzer was used to predict the samples. The treated fabric samples were mounted on a specimen stub with double sided adhesive tape, coated with gold in a sputter coater and examined.

Figure 2 shows the SEM image of TiO₂ nano particle coated cotton plain woven textile fabrics. The diagram proved that nano particles are well dispersed and embedded on the surface of the fibre. Some places in the diagram (a) shows the uneven and agglomerated patch coating, which is due to larger nano particle size. More over the particle size place an important role in determining their adhesion on the fabric.

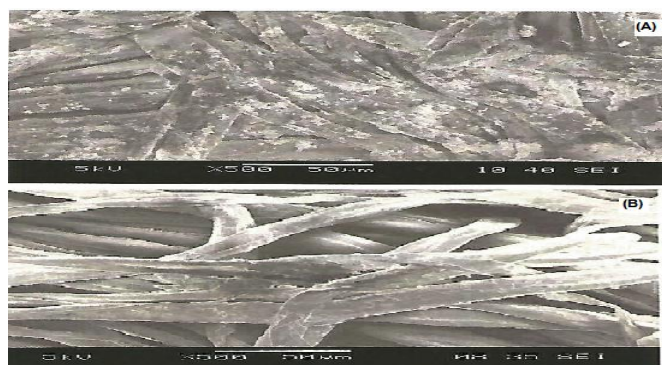


Fig.4-SEM image of TiO₂ Nano particle coated fabric produced from Sol-gel technique.

5.4 Evaluation of Self-cleaning action

As reported by (Kamal, K. et al 2008) The self-cleaning activity was assessed for the Nano coated textile fabric is by exposing the samples containing adsorbed coffee stain to visible irradiation. The measured quality of 6% coffee solution was introduced on the fabric and was allowed to spread. One half of each stain on the fabric was exposed to sunlight for 12-48 h, while the other half was covered with a black paper to prevent its irradiation from sun light. The exposed part of the stain was compared with that of covered part for self-cleaning action. Premier Color scan SS5100A Spectrophotometer was used to measure the change in K/S value.

$$\text{The K/S value of exposed part} = \frac{\left(\frac{K}{S}\right)_{\text{un expected}} - \left(\frac{K}{S}\right)_{\text{expected}}}{\left(\frac{K}{S}\right)_{\text{un expected}}} \times 100$$

Where K is the absorption; and S is scattering.

The self-cleaning property of TiO₂ Nano coated textile fabric is analysed and reported in graphical form shown as fig.5. The K/S value of coffee stained cotton fabrics were measured in various Nano-TiO₂ coated structures in different duration of 12, 24 and 48 h. The percentage of decrease in K/S value for the exposed samples in higher concentration of TiO₂ Nano coating. The rate of change in deterioration is also depends upon the duration as well. Higher the duration the percentage of decrease in K/S value is increased.

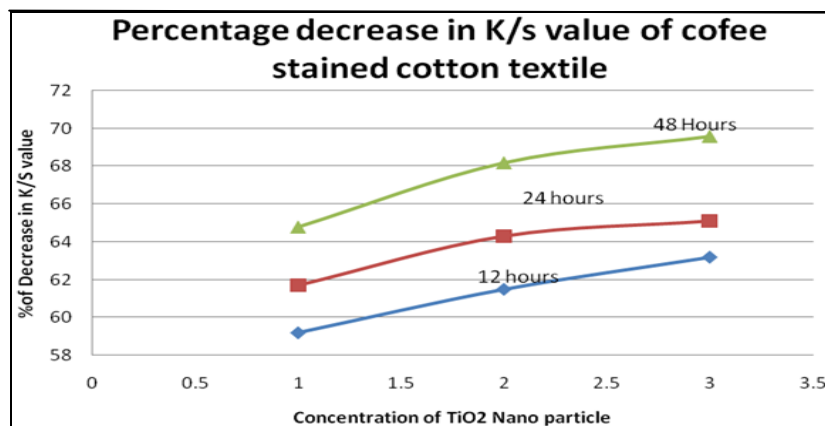


Fig.5-percentage of decrease in K/S Value of Coffee stained cotton fabric in various Nano TiO₂ concentrated coating

VI. Conclusion

- TiO₂ Nano particle were synthesized through Sol-gel technique. The XRD spectra analysis indicated the presence of Nano particle and then FTIR analysis again conformed the TiO₂ Nano particle formation.
- Coating of TiO₂ Nano particles were done well through Pad-Batch technique .
- SEM Image demonstrated that the even coating of TiO₂ Nano particle over the surface of the cotton textile.
- The coated Textile structure demonstrates the significant self –cleaning activity when exposing under UV light spectrum.
- It is also confirmed that the percentage of TiO₂ Nano particle increases with increase in Self-cleaning activity and the High duration of exposing under UV light will also accelerate the Self-cleaning action.

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