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Durable Self Cleaning Property on Cotton Fabric by Synthesised TiO_2 Nanoparticles at Room Temperature

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Abstract

In this study, synthesis and optimization of titanium dioxide nanoparticles were carried out at room temperature by sol-gel technique using Box-Behnken design of experiment. Titanium dioxide nanoparticles were characterised using UV-visible spectrophotometer in which the band gap energy was determined as 3.31 eV, particle size analyser (PSA) analysed size of nanoparticles as 250 nm and scanning electron microscope (SEM) showed uniform distribution of nanoparticles on surface of fabric. The titanium dioxide nanoparticles were applied on cotton fabric through pad-dry-cure method to develop self-cleaning property on cotton fabric. The stain degradation property was evaluated initial and after 20 washes and determined significant decrease in K/S value with increase in concentration of nanoparticles. There is no significant effect on inherent properties of fabric to be found.

Keyword: Box-Behnken; Cotton; Nano-TiO_2; PSA; Photo-catalysis; Self-cleaning; Sol-gel

Introduction

Nanotechnology being the engineering of functional system at molecular scale has the ability to dramatically alter the properties of material at nanoscale. It has opened up the possibility of creating new products to function in a much better way than was possible earlier [1]. The concept of self-cleaning on account of its unique features and wide range of applications in various fields has acquired an astounding interest [2]. In early days, Wax, silicones, Polyfluorinated carbons and polyvinyl chloride were used as self-cleaning agents. In recent years, Nano TiO_2 has gained significant attention due to its high photo-catalytic activity and is associated with high crystallinity which prevent the electron-hole recombination and high surface area which increases of number of active sites on the photo-catalytic surface. Nanomaterials have been prepared through physical methods such as Sputter Deposition, Chemical Vapour Deposition, Electric Arc Deposition, Ion Beam Techniques and chemical methods such as hydrothermal synthesis, Sono-chemical synthesis, Sol-gel method, Nucleation and Growth technique. Sol-gel method is preferred due to ease of synthesizing and extracting high performance nanoparticles [3]. Anatase-based Nano-TiO2 is capable to impart self-cleaning property to textile [4]. Generally red wine and coffee stains were photo-degraded on textiles treated with Nano TiO_2 for its self-cleaning properties [5]. The self-cleaning property is activated by light and is evaluated by color strength value (K/S) of stain after exposure [6].

This study involves the synthesis of titanium dioxide (TiO_2) nanoparticles by sol-gel technique and is characterized using Particle Size Analyser and Scanning Electron Microscope. The TiO_2 nanoparticles are applied on cotton fabric using acrylic binder with finishing technique of dip-pad-dry-cure to test for stain degradation property.

Material and Methods

Mechanism of photo-catalysis

TiO_2 being semi-conductive in nature, under illumination acts as a strong oxidizing agent by lowering the activation energy for the decomposition of compounds. The illumination of surface of TiO_2 induces a pair of electrons and holes. The electron of valence band of TiO_2 becomes excited and the excess energy of the excited electron promotes electron to conduction band of titanium dioxide thereby creating negative-electron (e-) and positive-hole (h+) pair. This stage is referred to as semiconductor's photo-excitation state. The energy difference between valence band and conduction band is known as "Band gap". The band gap energy, Eg of TiO_2 (Anatase) is 3.2 eV, which corresponds to photons with a wave length of 388 nm [7]. The positive-hole of TiO_2 breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion [8].

Oxidative reactions due to photo catalytic effect:-

$UV + MO \rightarrow MO\ (h + e^-)$ Where MO stands for metal oxide

$H^+ + H_2O \rightarrow H^+ + \bullet OH$

$2h^+ + 2H_2O \rightarrow 2H^+ + H_2O_2$

$H_2O_2 \rightarrow HO\bullet + \bullet OH$

The reductive reaction due to photo-catalytic effect:-

$e- + O_2 \rightarrow \bullet O^{2-}$

$\bullet O^{2-} + HO_2 + H_+ \rightarrow H_2O_2 + O_2$

$HOOH \rightarrow HO\bullet + \bullet OH$

The hydroxyl radicals are generated in both the reactions (Figure 1).

Materials

Pre-treated plain woven cotton fabric having specification 40s Ne (14.8 tex) count in both warp and weft, 140 ends/inch, 72 picks/inch fabric set and 126 GSM fabric mass was procured from Vardhman Textiles, Baddi, India. The precursor Titanium (IV) iso-propoxide (AR

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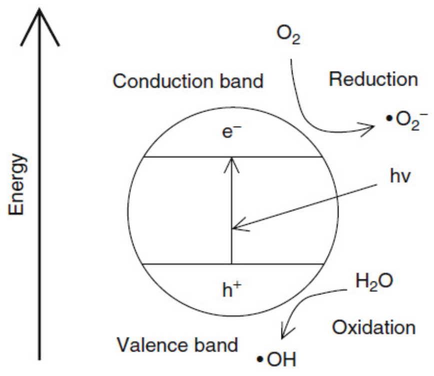

Figure 1: Mechanism of photo-catalysis.

grade) was procured from Sigma Aldrich, US and Deionized water as catalyst was used for hydrolysis of titanium dioxide. Hydrochloric acid (35.4%) was procured from SDFCL, Mumbai. Isopropyl alcohol, used as solvent, was procured from SDFCL, Mumbai; Acrylic acid was procured from SDFCL, Mumbai, used as acrylic binder.

Instruments used in the study include Glassware, electronic weighing balance (Mettler Toledo, Switzerland),magnetic stirrer with hot plate (ABC India), hot air oven (ABC India), Sonicator (LABMAN & Elmasonic), UV vis Spectrophotometer (Lambda 365), particle analyser (Beckman Coulter), padding mangle (EEC, Bombay), drying and curing chamber (EEC, bombay), Weather-o-meter, Launder-o-meter (RBEE Mumbai), Universal Testing Machine (Aimil), Air permeability tester.

Methods

Synthesis of TiO_2 nanoparticle: 0.01 moles of Titanium (IV) iso-propoxide were dissolved in 60ml of propanol and stirred well until a clear solution is obtained and this solution was marked as solution A. 0.02 moles of water were taken in beaker and 60 ml of propanol was added to it and the solution obtained was marked as solution B. The solution B was taken in conical flask and placed on magnetic stirrer with magnetic bead inside the flask and solution A was taken in burette. The solution A was then poured into solution B at 25 °C for 20 minutes. After the pouring was completed, the solution in the flask was kept on stirrer for another 10 minutes for completion of the reaction. The nanosol was transferred to petri dish and heated at 90 °C for 5 hours to evaporate the propanol and the yellowish white powdery substance was obtained and stored in plastic container. This set up was prepared in order to stop alcohol from getting evaporated out of the reactor set up and to achieve better stoichiometric control over the reaction.

Optimization of synthesis of TiO_2 nanoparticle: The optimization of synthesis of TiO_2 nanoparticles with best possible conditions and parameters were carried out using Box and Behnken of Design Expert® Software. At preliminary stage, the time of addition of precursor to catalyst and the time of stirring have significant effect on absorption value of TiO_2 Nano particles [9]. According to Box-Behnken design, 29 numbers of experiments were carried out with four variables A: Precursor to catalyst ratio (1:4), B: Solvent (25 ml), C: Time of addition (20 minutes), D: Time of stirring (10 minutes) and three levels as low (-1), medium (0) and high (+1).

The data were analysed by statistical tools by using two techniques. The first technique involves the study of response surface plot to observe the absorption value of the synthesized titanium dioxide nanoparticles. The second technique involves development of regression equation for the output parameters and using these equations to get the optimized conditions giving maximum absorbance for the titanium dioxide nanoparticle.

Characterisation of nanoparticles

The Nano particles were characterised for their size shape and structure and distribution of Nano particles on fabric using following techniques.

Ultraviolet-Visible (UV-Vis) spectrophotometer

Since the optical absorption of TiO_2 ranges between wavelength of 200 to 400 nm and reveals strong absorbance peak [8], the band gap energy was determined based on optical absorption coefficient using energy relation and UV spectrum peak value (absorption):

$E=h\nu$,

Where h is planks constant,

$\nu=c/\lambda$

Where, c is the speed of light in vacuum, λ is the wave length of the spectrum.

This was done using UV Vis spectrophotometer (Model Lambda 365)

Particle size analysis

The size distribution of Nano particles were determined using particle size analyser, using particle analyser (Beckman Coulter). The conditions under which particle size measurement was done are temperature 25°C, viscosity 0.88 cP and measuring range 1-1000 nm.

Scanning electron microscopy

The Nano finished fabric sample was made conductive with gold by vacuum sputter coating. The fabric surface is imaged by scanning with high energy beam of electrons using SEM.

Application of nanoparticle on cotton fabric

The cotton fabric was dried at 100°C for 5 minutes to remove excess moisture content. The finishing bath was prepared with TiO_2 nanoparticles of concentrations such as 0.5%, 1.0%, 1.5% on the weight of fabric along with acrylic binder in concentration of 0.5% on the weight of fabric. The pre-treated cotton fabric was treated separately with TiO_2 Nano particles of different concentrations for 10 minutes followed by padding under a pressure of 10 Kgf/cm^2 at a speed of 20 m/minute with 75% expression at 40°C and drying at 800°C and was cured at 150 °C for 5 minutes.

Self-cleaning effect of TiO_2 nanoparticles

TiO_2 Nano finished cotton fabric sample was dipped with 2% coffee solution for uniform staining and a part of it was covered with back opaque cardboard while the other part was exposed to simulated source of UV light in weather-o-meter for 10, 20 and 40 hours. The exposed area of stained sample was compared with that of covered area in terms of their K/S values to measure photo degradation of coffee stain on exposed and covered part using spectrophotometer (Data color).

$$\%\,Decrease\,in\,\frac{K}{S}\,of\,exposed\,part=\frac{K/S_{unexposed}-K/S_{exposed}}{K/S_{unexposed}}$$

Where K is absorption, S is scattering [10].

Physical testing of TiO_2 nano finished fabric

The untreated and Nano TiO_2 treated cotton fabric was conditioned at temperature 20 ± 2°C and Relative humidity of 65% and tested for physical properties such as Fabric mass (ASTM D 3776), tensile strength (ASTM D 5035), Tearing strength (ASTM D 1424), Air permeability (ASTM D 737) and whiteness index (AATCC 110).

Results and Discussion

Optimization of synthesis of TiO_2 nanoparticles

Surface plots of the data for absorption value are shown in Figure 2 for titanium dioxide nanoparticles. With increase in amount of water used as catalyst, the absorption value is increased initially and then decrease. The absorption value is decreased with increase in amount of propanol used as solvent. The absorption value increased with increase in time of addition of precursor to catalyst and at optimum time of stirring. These results were compared with the results of the regression equations to obtain the optimized conditions for the treatment.

Analysis of data using regression equation technique

The data was analysed using statistical tools to obtain regression equation for the response variable: Absorption of titanium dioxide nanoparticles.

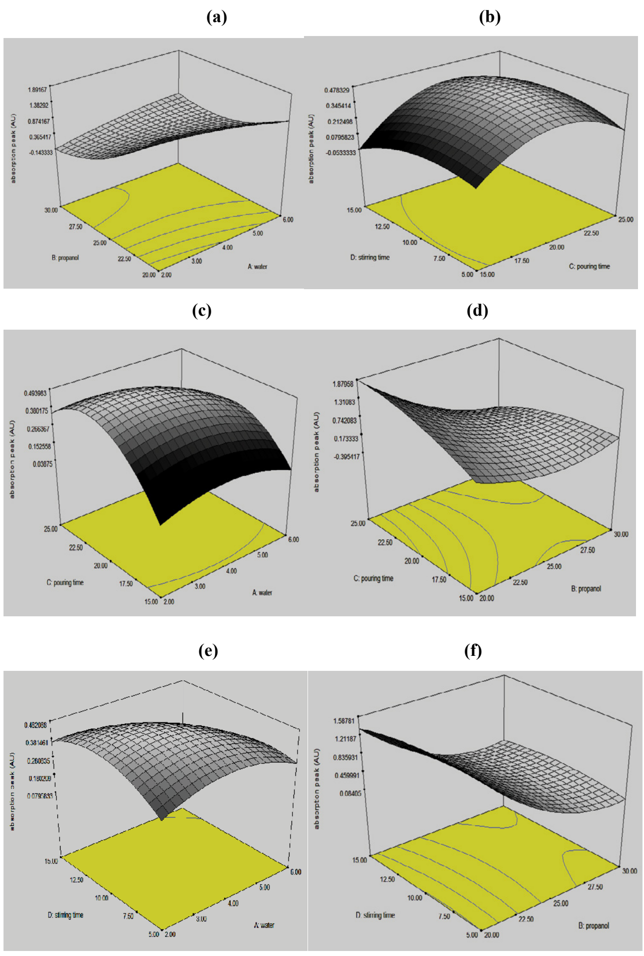

Figure 2: Surface response plots showing relative effects of different process parameters on absorption peak of synthesized TiO_2 nanoparticles.

Regression equation for absorption in terms of coded values at $R^2 = 0.8253$

$$Y = 4.03 - 0.52A - 0.78B + 0.88C + 8.50D - 0.02A^2 + 0.01B^2 - 9.75C^2 - 4.55D^2 + 0.03AB - 6.25AC - 7.50AD - 0.01BC + 2.70BD + 1.90CD$$

These equations were then used to predict the optimized combination of the parameters that will give maximum absorption as 1.34 AU at 375 nm wavelength for the titanium dioxide nanoparticle. The optimized condition is shown in table which also shows the predicted value of absorption for titanium dioxide nanoparticles. These are consistent with the observations obtained in the study of the surface plots (Tables 1-3).

Variables	Level of Variables		
Independent Variables	**Low (-1)**	**Medium (0)**	**High (+1)**
A: Precursor to catalyst Ratio	1:2	1:4	1:6
B: Solvent (ml)	20	25	30
C: Time of Addition (minutes)	15	20	25
D: Time of Stirring (minutes)	5	10	15
Dependent Variables			**Goal**
Y: Absorption (AU)			**Maximize**

Table 1: Box-Behnken design with variables and levels.

Run	Water (ml)	Propanol (ml)	Pouring time (min)	Stirring time (min)
1	4	20	20	5
2	4	20	25	10
3	6	25	20	5
4	4	25	20	10
5	6	30	20	10
6	4	25	20	10
7	2	25	20	15
8	4	20	15	10
9	4	25	20	10
10	2	25	20	5
11	6	25	25	10
12	4	30	15	10
13	2	25	25	10
14	4	25	25	15
15	4	25	25	5
16	4	25	20	10
17	4	30	20	5
18	6	25	20	15
19	6	20	20	10
20	6	25	15	10
21	2	25	15	10
22	4	30	25	10
23	4	20	20	15
24	4	30	20	15
25	4	25	15	5
26	2	20	20	10
27	4	25	20	10
28	4	25	15	15
29	2	30	20	10

Table 2: Treatment conditions for optimization of titanium nanoparticles using Box-Behnken.

It can be concluded that with increase in molar ratio of titanium (IV) iso-propoxide to water, the absorption of the nanoparticles will be greater. It required optimum amount of propanol and more time of addition of precursor to catalyst with decreased stirring time (Table 4).

Characterization of TiO_2 nanoparticles

The TiO_2 Nano particles were characterized by UV-Vis spectrophotometer and particle size analyser (PSA) for analysing particle size distribution and scanning electron microscope (SEM) for analysing uniform distribution of Nano particles on surface of cotton fabric.

UV-visible spectroscopy: The TiO_2 nano particles showed the peak at wavelength of 375 nm with 1.34 AU absorption value. The band gap energy was calculated as 3.31 eV.

Particle Size Analysis: The particle size distribution of TiO_2 nanoparticles were determined using particle size analyser. TiO_2 Nano particle of size 250 nm was obtained by synthesis from titanium tetra iso-propoxide as precursor at room temperature. The intensity distribution for the maximum peak is at 5.1.

Scanning electron microscope: The TiO_2 nanoparticles are uniformly distributed and well-embedded on the surface of fabric. The adherence of Nano particles on the surface depends on particle size. The larger particle agglomeration tends to detach from fibre surface, while smaller particles cohere into fibre matrix.

Analysis of stain degradation: The self-cleaning property of TiO_2 Nano finished cotton fabric was quantified by stain degradation analysis. This is done by comparison of K/S value of unexposed and exposed part of coffee stained cotton sample to determine the percentage decrease in K/S value for initial and after 20 wash (as per ISO 6330). The self-cleaning property increases with the increase in concentration of TiO_2 nanoparticles and increase in duration of exposure to light.

Effect of Nano TiO_2 on physical properties of cotton fabric: The physical properties such as fabric mass, tensile strength, Air permeability of untreated and Nano TiO_2 treated cotton fabric were tested as per ASTM test methods as shown in Table 4. There is no significant variation in case of fabric mass and permeability while there is a slight increase in tensile strength (Figures 3-6).

Parameter	Optimized Value
Titanium (IV) Iso-propoxide (g)	1.42
A: Precursor to catalyst ratio	01:05
B: Solvent (ml)	20
C: Time of Addition (minutes)	25
D: Time of Stirring (minutes)	7
Absorption (AU)	**1.34***

Table 3: Optimized treatment conditions for synthesis of titanium dioxide.

Physical Property	Untreated Fabrics	0.5% TiO_2	1.0% TiO_2	1.5% TiO_2
Fabric Mass (g/m²)	126	126.1	126.3	127
Tensile Strength (Newton)				
Warp	397	406	438	459
Weft	204	207	210	222
Air Permeability (cm³/cm²/s)	34.59	34.59	34.45	34.61
Whiteness Index	72	71.8	71.5	71.5

Table 4: Physical properties of untreated and TiO_2 Nano-treated cotton fabric.

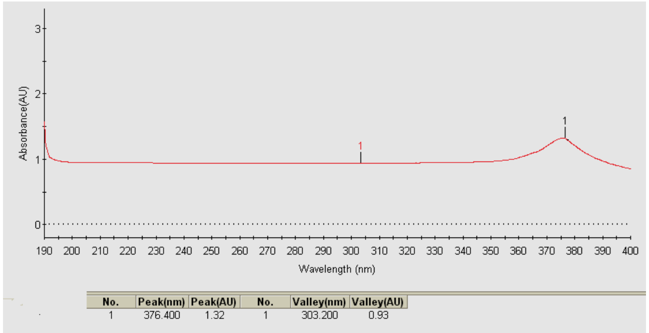

Figure 3: UV- spectrum peak value (absorption) Lambda 365.

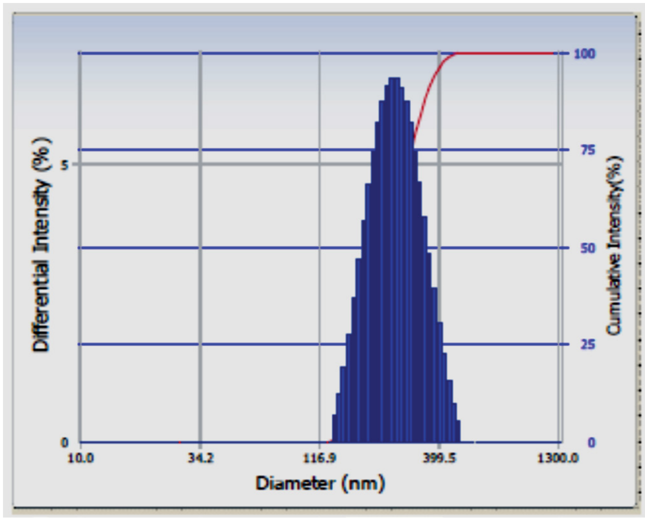

Figure 4: Particle size analysis of TiO_2 Nano particles.

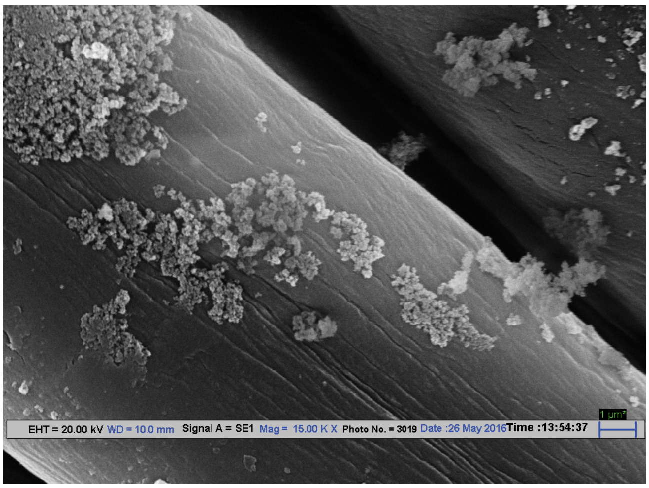

Figure 5: SEM photograph of nanoTiO_2 treated cotton fabric sample.

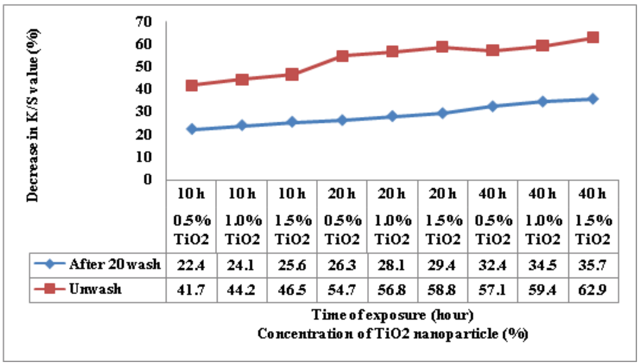

Figure 6: Percentage decrease in K/S value of coffee stained cotton sample after exposure for unwash and after 20 wash.

Conclusion

In this study, the titanium dioxide nanoparticles were synthesized and optimized at room temperature using sol-gel method using. From particle size analysis, the size of the Nano particle was found to be 250 nm. The TiO_2 nanoparticles were distributed evenly on surface of fabric as captured in SEM image and showed good self-cleaning effect on cotton fabric up to 40 hours and sustained up to 20 wash. The novelty in the work is there is no effect on whiteness of treated fabrics due to selection of metal alkoxide precursor during synthesis.

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