Salar Zohoori,
*Loghman Karimi,
**Ali Nazari

Photocatalytic Self-cleaning Synergism Optimization of Cotton Fabric using Nano $SrTiO_3$ and Nano TiO_2

Department of Textile Engineering,
Yazd Branch,
Islamic Azad University,
Yazd, Iran
Email: s_textile@yahoo.com

*Young Researchers and Elites Club,
Science and Research Branch,
Islamic Azad University,
Tehran, Iran

**Art & Architectural Department,
Yazd Branch,
Islamic Azad University,
Yazd, Iran

Abstract

Titanium dioxide (TiO_2) and Strontium titanate ($SrTiO_3$) are well-known photocatalysts. Today, the photocatalytic activity of dyes on fabrics has attracted much attention. Therefore in this study the photocatalytic activity of nano strontium titanate mixed with nano titania was examined while being coated on cotton fabric under UV irradiation at different nano material concentrations and various pHs. The Central Composite Design (CCD) was used for different variables based on Design Expert software. The crystal size and phase of nano titania and strontium titanate were characterised by XRD. The cotton fabrics stained with two common synthesised dyes were treated under 400 W UV irradiation for 30 hours and their self-cleaning properties were investigated by reflectance spectrophotometer. SEM photos show the pervasion of nano materials. The results show that samples treated with $SrTiO_3$ and TiO_2 have higher values of ΔE as compared with those treated with TiO_2 or $SrTiO_3$ alone.*

Key words: *nano TiO_2, nano $SrTiO_3$, photocatalytic, optimization, self-cleaning.*

Introduction

One of the important photocatalysts which is active in the UV area (because of its wide band gap) is strontium titanate ($SrTiO_3$) [1 - 3]. It has many applications because of its large polarisation and high dielectric constant [4], and due to its excellent physical and chemical properties, such as the structure and thermal stability, it is considered as one of the favorable photocatalysts [5]. Today a wide range of nanoparticles and nano structures can be immobilised on fabrics, which brings new properties to the final clothing product. In recent years, the photocatalytic activity of nano TiO_2 has gained much attention because of its abilities to purify pollutions [6, 7]. TiO_2 can exist in both crystalline and amorphous forms. In the case of photocatalytic, the amorphous form is inactive. There are three crystalline phases of TiO_2: anatase, rutile and brookite. Anatase and rutile are both tetragonal in structure while the brookite structure is orthorhombic [8].

Strontium titanate has cubic, tetragonal, orthorhombic and other phases, near 105 K of which it becomes distorted from a cubic structure and takes on a tetragonal one, and is kept in that phase till 0 K [9, 10]. Also the tetragonal phase of strontium titanate can transform into a orthorhombic structure by small perturbation [10]. The photocatalytic activity of titania is affected by many parameters, such as the particle size, crystal structure and phase, the intensity and wavelength of irradiation, solution pH, the preparation method, and surface absorption of contaminants. While it is used on a nano scale, its photocatalytic activity is enhanced because of the increase in the effective surface area and the expansion of the band gap [11 - 14].

Strontium titanate is also active under UV irradiation because its band gap is similar to that of titania (Eg = 3.2 eV) [1, 15 - 17], which makes $SrTiO_3$ a good candidate for coupling TiO_2 as it has been reported in previous works that the photocatalytic activity of materials (such as Zn) can be improved by the supporting and doping of $SrTiO_3$ [18 - 22]. Also retarding a charge recombination between excited electrons in the conduction band and holes in the valence band, which are formed by UV irradiation, is one of the performance improvements of TiO_2 photocatalysts. Supporting the nano particle of $SrTiO_3$, into which excited electrons in the conduction band of TiO_2 can be injected, is one of the methods to increase the charge separation efficiency of TiO_2 [23, 24]. In order to graft nano materials onto cotton fabric, cross-link agents must be used to attach them. In previous works, succinic acid has been used as a cross-link agent and the results reported were good for coating nano titania on cotton fabric [25 - 28].

In this paper, we investigated and reported on the influence of $SrTiO_3$ along with TiO_2 on cotton fabric to improve the self-cleaning property. For this purpose the photo degradation of Dark Green BN and Reactive Orange were quantified. The focus of this study was on implementing a central composite design to optimise the self-cleaning properties of these fabrics. The best treatment condition to obtain Δ*E** on the treated cotton will subsequently be discussed.

***Table 1.** Formulations for fabric treatments.*

Sample code	$SrTiO_3$%	TiO_2%	pH
1	0.50	0.10	4.00
2	0.10	0.30	
3	0.50	0.50	
4	0.10	0.50	
5	0.50	0.10	
6	0.30	0.50	
7	0.10	0.10	
8	0.10	0.10	
9	0.40	0.30	4.75
10	0.30	0.10	5.50
11	0.10	0.30	
12	0.50	0.50	
13	0.50	0.10	7.00
14	0.10	0.50	
15	0.10	0.10	
16	0.50	0.50	
17	0.50	0.10	
18	0.10	0.50	
19	0.10	0.10	
20	0.30	0.30	
21 (Blank)	0.00	0.00	-

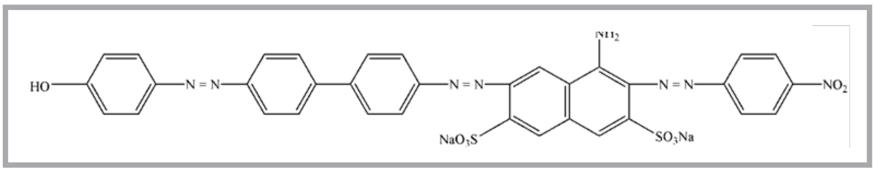


Figure 1. Structure of dark green.

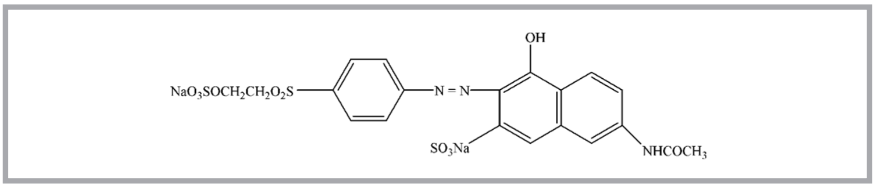


Figure 2. Structure of reactive orange.

Table 2. Variance analysis of samples.

Source	Sum of Squares	df	Mean Square	F Value	P-Value Prob > F	
Model	223.91	9	24.88	7.13	0.0025	Significant
A-Nano TiO_2	73.44		73.44	21.04	0.0010	
B-Nano $SrTiO_3$	80.34		80.34	23.02	0.0007	
C-pH	12.89		12.89	3.69	0.0836	
AB	7.23		7.23	2.07	0.1807	
AC	0.92	1	0.92	0.26	0.6193	
BC	8.02		8.02	2.30	16.04	
A^2	3.41		3.41	0.98	0.3459	
B^2	4.13		4.13	1.18	0.3022	
C^2	8.75		8.75	2.51	0.1445	
Residual	34.90	10	3.49			
Lack of Fit	34.82	5	6.96	445.03	< 0.0001	Significant
Pure Error	0.078	5	0.016			
Cor Total	258.8	19				

Experimental

Materials

Nano titania from the Degussa company (P25), nano powder of strontium titanate from Aldrich (517011) with a particle size of less than 100 nm, succinic acid from Merck, sodium hypophosphate from Fluka, and two common textile dyes: Dark Green BN (CI 30295) and Reactive Orange (CI 17907), were prepared.

Methods

To coat cotton fabric by nano materials, the fabric samples were washed with distilled water at 75 °C for an hour in order to remove wax and impure materials. Three baths of succinic acid (6% wt/wt) and sodium hypophosphate (4% wt/wt) were prepared (bath 1 - pH = 4, bath 2 - pH = 4.75, bath 3 - pH = 5.5). Also another bath was set up without succinic acid (bath 4: pH = 7). Washed cotton fabric was immersed in the baths for an hour and dried in an oven for 3 minutes at 75 °C. During this process, for the preparation of a precursor solution of nano materials, nano strontium titanate and titania suspension were sonicated for 30 min at 50 °C at various supporting concentrations (***Table 1*** see page 91). The cured fabric was immersed in nano material suspension for an hour at 75 °C. To fix the nano materials, the fabric was kept in an oven at 100 °C for 2 minutes. Finally it was washed with distilled water in an ultrasonic bath for 10 minutes.

The crystal size and phase of the coated nano materials were characterised by x-ray diffraction (XRD); Bruker, D8ADVANCE, Germany and an x-Ray tube anode: Cu; wavelength: 1.5406 Å (Cu Ka); Filter: Ni. Scanning Electron Microscopy (Philips, SEM, XL3, 15 Kv, Netherland) was used to determine the structure of nano materials on the fabric. The samples were stained by two common dyes: dark green BN (***Figure 1***) and reactive orange (***Figure 2***) and were irradiated using a UV-A 400 W lamp (Philips, HPA 400s, Belgium) for 30 h.

In the CIELAB system, colour is expressed in terms of CIE L*, a* and b* values, where L* defines lightness, a* denotes the red-green value, and b* indicates the yellow-blue value. Determination of Δa*, Δb*, ΔL* and the total colour difference (Δ*E**) between the cured stained samples before and after irradiation was made using a reflectance spectrophotometer (BYK Gardner, India, with CIELAB 1976 colour space and D65-light source). The total colour difference (Δ*E**) was calculated according to ***Equation 1***.

$$\Delta E* = \sqrt{(\Delta a*)^2 + (\Delta b*)^2 + (\Delta L*)^2} \quad (1)$$

Hence Δ*E** of the coated samples under UV radiation , and the degree of discoloration and self-cleaning of the different samples were compared.

Experimental design

The central composite design was used for an experimental plan with three variables including the amounts of TiO_2, $SrTiO_3$ and different pH conditions. Details of the design for cotton samples with nano TiO_2 (0.00% - 0.50%) and nano $SrTiO_3$ (0.00% - 0.50%) and different pHs are presented in ***Table 1***. Also the impact of the variables on the results Y (Δ*E**) was adjusted using the following second order polynominal function (***Equation 2***):

$$Y = b_0 + \sum b_i X_i + \sum b_{ij} X_i X_j + + \sum c_i X_i^2 i \geq j \quad i,j = 1,2,3 \quad (2)$$

where b_0 is an independent term according to the mean value of the experimental plan; b_i denotes the regression coefficients that explain the influence of the variables in their linear form; b_{ij} indicates the regression coefficients of the interaction terms between variables, and c_i shows coefficients of the quadratic form of variables.

Results and discussions

Self-cleaning and properties

Variance analyses of the samples (ANOVA Table) are presented in ***Table 2*** and diagrams of Δ*E** are shown in ***Figure 3***. According to the results of the ANOVA table and diagrams, the self-cleaning of the samples increases by enhancing nano TiO_2 (***Figure 3.a***). When the photocatalyst is illuminated by a light of energy higher than its bandgap energy, electron–hole pairs diffuse out to the surface of the photocatalyst. At the surface, the electrons and holes can either take part

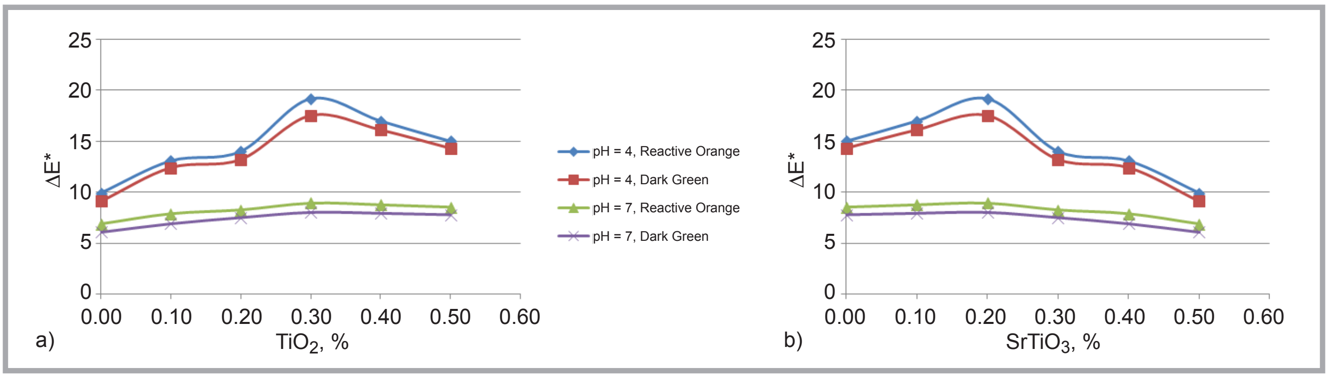


***Figure 3.** ΔE* of samples (by percentage of nano a) TiO_2) and b) $SrTiO_3$).*

in the chemical reaction with electron donors and acceptors or recombine. In the absence of a suitable electron and hole scavengers, the recombination of electron–hole pairs will occur within a very short time. Therefore the observed enhancement of the self-cleaning activity of TiO_2 supported by $SrTiO_3$ is thought to be explained on the basis of the increase in charge separation efficiency, and the fact that electrons in the conduction band of TiO_2 excited by UV irradiation are injected into the conduction band of $SrTiO_3$ to suppress recombination between the electrons and holes in TiO_2.

Investigating the effect of nano $SrTiO_3$ shows that the sample's self-cleaning property is increased by increasing nano $SrTiO_3$ till 0.2%, and then it suddenly drops down (***Figure 3.b***).

Also in this regard, the self-cleaning of samples in an acidic condition is higher than at a neutral pH. As is shown, the ΔE^* of reactive orange dye is higher both in an acidic and non-acidic condition.

The effect of pH is the same as in ***Figure 3.a***, and also reactive dye has a better self-cleaning property. In both figures (3 .a and 3.b), it is clear that the ΔE^* of the acidic condition is higher. In an acidic condition, nano particles can graft onto the fabric and thus the self-cleaning property increases. Also the higher homogeneity of nano particles on the surface of cotton fabric in these samples is another reason for better self-cleaning.

To achieve more reliable results, two different type of dyes were investigated: monoazo dye (Reactive Orange) and trisazoic dye (Dark Green). By comparing the self-cleaning of the two dyes, it was observed that the self-cleaning of reactive dye is higher. Therefore it can be concluded from the chromophore structure of dyes that trisazo dye is more stable than monoazo dye (***Figures 1*** and ***2***).

Statistical analysis

For the samples treated, the analysis of variance (ANOVA) is presented in ***Table 2***. According to the ANOVA results, the models of self-cleaning (ΔE^*) fit-

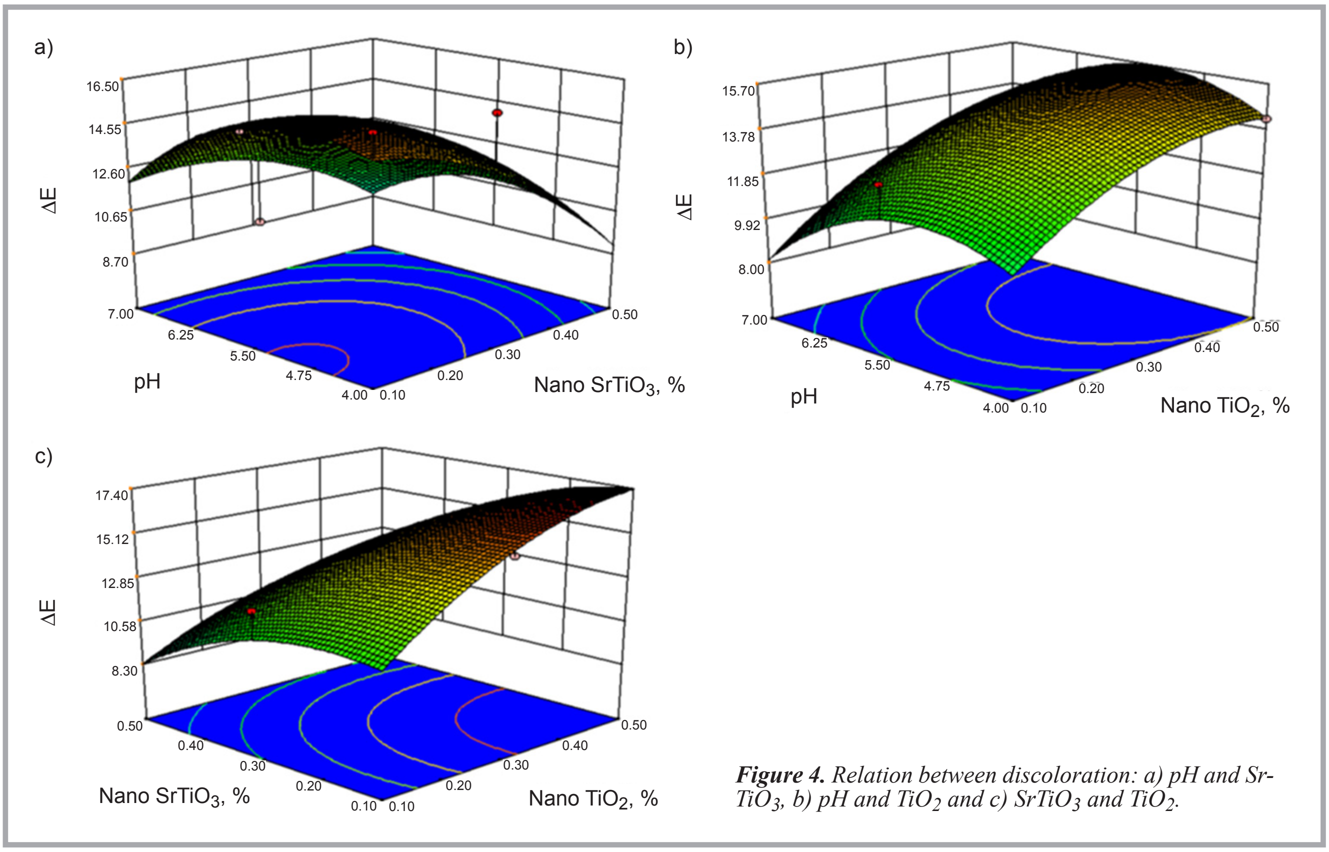


***Figure 4.** Relation between discoloration: a) pH and $SrTiO_3$, b) pH and TiO_2 and c) $SrTiO_3$ and TiO_2.*

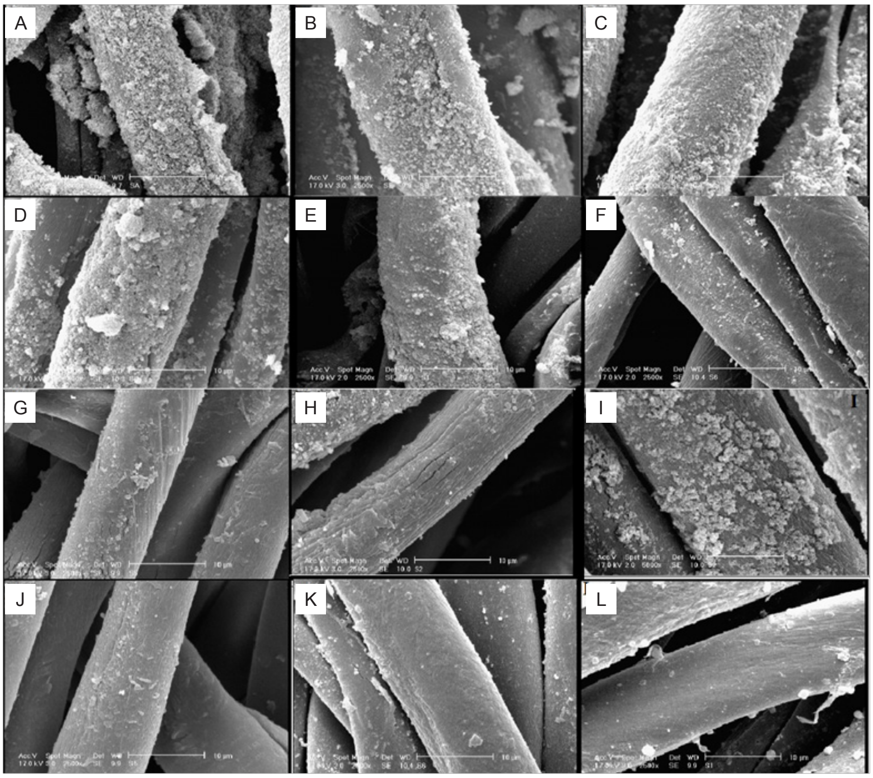


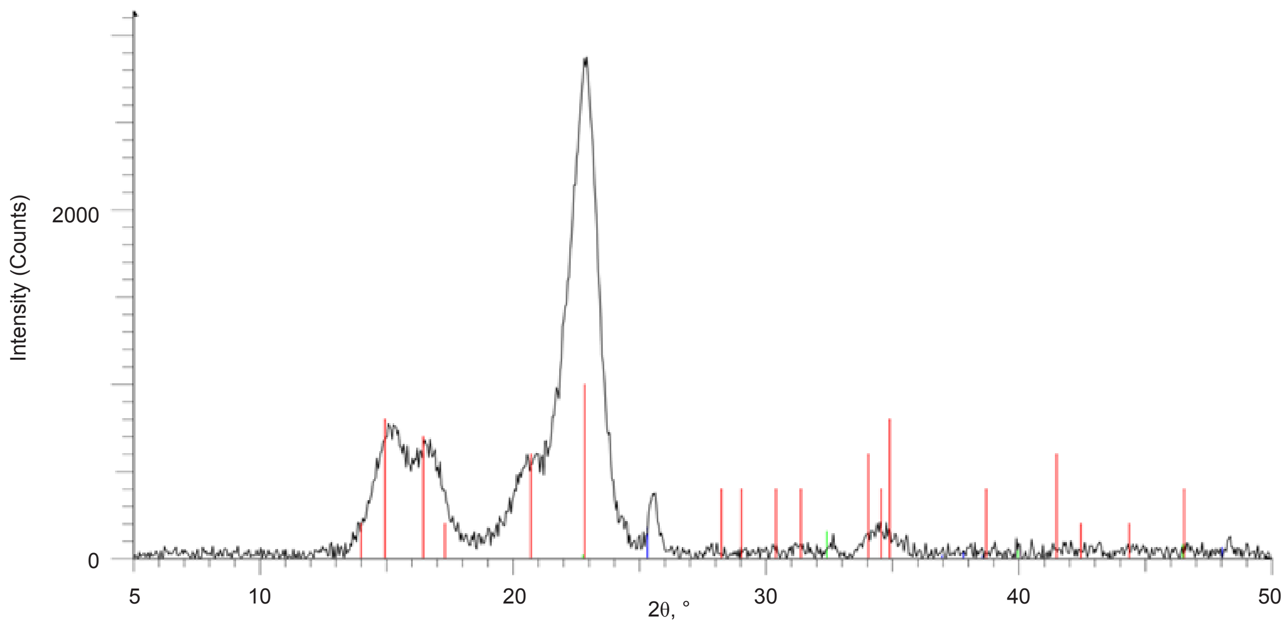
Figure 5. *SEM of samples A) 0.5%TiO_2, B) 0.4% TiO_2 + 0.1% $SrTiO_3$, C) 0.3% TiO_2 + 0.2% $SrTiO_3$, D) 0.2% TiO_2 + 0.3% $SrTiO_3$, E) 0.1% TiO_2 + 0.4% $SrTiO_3$, F) 0.5% $SrTiO_3$, G) 0.5% TiO_2, H) 0.4% TiO_2 + 0.1% $SrTiO_3$, I) 0.3% TiO_2 + 0.2% $SrTiO_3$, J) 0.2% TiO_2 + 0.3% $SrTiO_3$, K)0.1% TiO_2 + 0.4% $SrTiO_3$, L) 0.5% $SrTiO_3$; (A - F acidic condition, G - L non-acidic condition).*

ted using Design-Expert software are given in ***Equation 3*** and ***Figure 4*** (see page 93).

$$\begin{aligned}\Delta E^* = &-9.73128 + \\ &+ 29.37157 \times \text{nano } TiO_2 + \\ &- 0.33169 \times \text{nano } SrTiO_3 + \\ &+ 7.93211 \times pH + \\ &- 18.66465 \times \text{nano } TiO_2 \times \text{nano } SrTiO_3 + \\ &+ 0.88380 \times \text{nano } TiO_2 \times pH + \\ &+ 2.59174 \times \text{nano } SrTiO_3 \times pH + \\ &- 29.65512 \times \text{nano } TiO_2^2 + \\ &- 33.48608 \times \text{nano } SrTiO_3^2 + \\ &- 0.87118 \times pH^2\end{aligned} \quad (3)$$

SEM

Figure 5.A - 8.L) illustrates the SEM of cotton fabric treated with nano materials. In ***Figure 5.A***, we can see the fabric that is treated only with nano titania (0.5%) in an acidic condition, showing the good contribution of nano particles. ***Figure 5.B*** has 0.4% nano titania in addition to 0.1% nano strontium titanate. ***Figure 5.C***, which has the best ΔE^*, contains 0.3% nano titania in addition to 0.2% nano strontium titanate. As is shown, the particles have good pervasion and are more homogenous on the surface of the fabric. ***Figure 5.D***



Sample identification and quantification

Line colour	Compound name	Formula	Particle size, nm
(red)	Native cellulose	(C6H12O6)x	-
(blue)	Anatase, syn	TiO2	21.91
(green)	Tausonite, syn	SrTiO3	43.13

Figure 6. *XRD pattern.*

contains 0.2% titania with 0.3% nano strontium titanate. In ***Figure 5.E***, 0.1% nano titania with 0.4% nano strontium titanate is used. These were all in acidic conditions. ***Figure 5.F - 5.L***) has the same percentage of nano materials, but in a non-acidic condition.

X-ray diffraction analysis

The crystalline phase and size of nano particles on the fabric were studied by XRD (***Figure 6***). The beam signal volume is derived from cotton, which is considered as the main substrate. The average crystal size was 219.1 and 431.3 Å for nano titania and nano strontium titanate, respectively. For nano titania, three main peaks of anatase were observed at 25.5, 38 and 48°, and for strontium titanate the peak of Tausonite was observed at 32.5, 40 and 46.5°. Quantification analysis of titanium dioxide shows that the average percentage of anatase and rutile are 84 and 16% respectively. Hence it is excellent for photocatalytic activity.

Conclusion

The purpose of this study was to investigate the self-cleaning properties of cotton fabric treated with nano TiO_2 and $SrTiO_3$ at different pHs, which were optimised using a statistical model. The results demonstrated that cross-linking in acidic pH improves the grafting of nano materials. Also supporting nano titanate with nano strontium titanate at ratio of 0.2% ($SrTiO_3$)/0.3% (TiO_2) has the highest effect of discoloration in comparison with other ratios and also in comparison with nano titania. By increasing the amount of nano strontium titanate, the self-cleaning increases, but then it suddenly drops down, which is due to the bigger particle size of nano strontium titanate compared with nano titania.

References

1. Yan J-H, Zhu Y-R, Tang Y-G, Zheng S-Q. Nitrogen-doped $SrTiO_3/TiO_2$ composite photocatalysts for hydrogen production under visible light irradiation. *Journal of Alloys and Compounds* 2009; 472: 429-433.
2. Avudaithai M, Kutty TRN. Ultrafine powders of $SrTiO_3$ from the hydrothermal preparation and their catalytic activity in the photolysis of water. *Materials Research Bulletin* 1987; 22, 5: 641-650.
3. Karimi L, Zohoori S, Yazdanshenas ME. Photocatalytic degradation of azo dyes in aqueous solutions under UV irradiation using nano-strontium titanate as the nanophotocatalyst. *Journal of Saudi Chemical Society* 2011, doi:10.1016/j.jscs.2011.11.010.
4. Lee S-J, Thiyagarajan P, Lee M-J. Synthesis and characterization of strontium titanate powder via a simple polymer solution route. *Journal of ceramic processing research* 2008; 9, 4: 385-388.
5. Puangpetch T, Sreethawong T, Chavadej S, Yoshikawa S. Synthesis and Photocatalytic Activity in Methyl Orange Degradation of Mesoporous $SrTiO_3$ Photocatalyst Prepared by Surfactant-assisted Templating Sol-Gel Method. In: *The 2nd Joint International Conference on "Sustainable Energy and Environment (SEE 2006)"*. E-056 (O) 1-23 November 2006, Bangkok, Thailand.
6. Dubas ST, Kumlangdudsana P, Potiyaraj P. Layer-by-layer deposition of antimicrobial silver nanoparticles on textile fibers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2006; 289: 105-109.
7. Starkova O, Yang J, Zhang Z. Application of time–stress superposition to nonlinear creep of polyamide 66 filled with nanoparticles of various sizes. *Composites Science and Technology* 2007; 67: 2691-2698.
8. Watson S, Beydoun D, Scott J, Amal R. Preparation of nanosized crystalline TiO_2 particles at low temperature for photocatalysis. *Journal of Nanoparticle Research* 2004; 6: 193-207.
9. Boudali A, Driss Khodja M, Amrani B , Bourbie D, Amara K , Abada A. First-principles study of structural, elastic, electronic, and thermal properties of $SrTiO_3$ perovskite cubic. *Physics Letters A* 2009; 373, 8-9: 879-884.
10. Ríos S, Ruediger A, Jiang AQ, Scott JF, Lu H, Chen Z. Orthorhombic strontium titanate in $BaTiO_3$-$SrTiO_3$ Superlattices. *Journal of Physics: Condensed Matter* 2003; 15, 21: L305-L309.
11. Simonsen ME, Jensen H, Li Z, Søgaard EG. Surface properties and photocatalytic activity of nanocrystalline titania films. *Journal of Photochemistry and Photobiology A: Chemistry* 2008; 200: 192-200.
12. Yu J, Zhou M, Cheng B, Yu H, Zhao X. Ultrasonic preparation of mesoporous titanium dioxide nanocrystalline photocatalysts and evaluation of photocatalytic activity. *Journal of Molecular Catalysis A: Chemical* 2005; 227, 1-2: 75-80.
13. Zhang Q, Chakraborty AK, Lee WI. Preparation of titania nanotape array and its photocatalytic property. *Journal of Physics and Chemistry of Solids* 2008; 69, 5-6: 1450-1453.
14. Wahi RK, Yu WW, Liu Y, Mejia ML, Falkner JC, Nolte W, Colvin VL. Photodegradation of Congo Red catalyzed by nanosized TiO_2. *Journal of Molecular Catalysis A: Chemical* 2005; 242: 48-56.
15. Subramanian V, Roeder RK, Wolf EE. Synthesis and UV-Visible-Light Photoactivity of Noble-Metal-$SrTiO_3$ Composites. *Industrial & Engineering Chemistry Research* 2006; 45: 2187-2193.
16. He HY. Comparison Study of Photocatalytic Properties of $SrTiO_3$ and TiO_2 Powders in Decomposition of Methyl Orange. *International Journal of Environmental Research* 2009; 3, 1: 57-60.
17. Chang CA, Ray B, Paul DK, Demydov D, Klabunde KJ. Photocatalytic reaction of acetaldehyde over $SrTiO_3$ nanoparticles. *Journal of Molecular Catalysis A: Chemical* 2008; 281, 1-2: 99-106.
18. Wang G-Y, Qin Y, Cheng J, Wang Y-J. Influence of Zn doping on the photocatalytic property of $SrTiO_3$. *Journal of Fuel Chemistry and Technology* 2010; 38, 4: 502-507.
19. Jiao Z, Chen T, Xiong J, Wang T, Lu G, Ye J, Bi Y. Visible-light-driven photoelectrochemical and photocatalytic performances of Cr-doped $SrTiO_3/TiO_2$ heterostructured nanotube arrays. *Scientific reports* 2013; 3, doi:10.1038/srep02720.
20. Zhang H, Guashuai M, Xingping M, Bei W. Fabrication and Photocatalytic Property of One-Dimensional $SrTiO_3$/Nanostructures. *International Journal of Photoenergy* 2013.
21. Zhang X, Huo K, Hu L, Wu Z, Chu PK. Synthesis and photocatalytic activity of highly ordered TiO_2 and $SrTiO_3/TiO_2$ nanotube arrays on Ti substrates. *Journal of the American Ceramic Society* 2010; *93*, 9: 2771-2778.
22. Ng J, Xu S, Zhang X, Yang HY, Sun DD. Hybridized nanowires and cubes: a novel architecture of a heterojunctioned $TiO_2/SrTiO_3$ thin film for efficient water splitting. *Advanced Functional Materials* 2010; *20*, 24: 4287-4294.
23. Karimi L, Zohoori S. Superior photocatalytic degradation of azo dyes in aqueous solutions using $TiO_2/SrTiO_3$ nanocomposite. *Journal of Nanostructure in Chemistry* 2013; *3*, 32.
24. Cao T, Li Y, Wang C, Shao C, Liu Y. A facile in situ hydrothermal method to SrTiO3/TiO2 nanofiber heterostructures with high photocatalytic activity. *Langmuir* 2011; *27*, 6: 2946-2952.
25. Chen C-C, Wang C-C. Crosslinking of cotton cellulose with succinic acid in the presence of titanium dioxide nanocatalyst under UV irradiation. *Journal of Sol-Gel Science and Technology* 2006; 40: 31-38.
26. Meilert KT, Laub D, Kiwi J. Photocatalytic self-cleaning of modified cotton textiles by TiO_2 clusters attached by chemical spacers. *Journal of Molecular Catalysis A: Chemical* 2005; 237: 101-108.
27. Karimi L, Mirjalili M, Yazdanshenas ME, Nazari A. Effect of Nano TiO_2 on Self-cleaning Property of Cross-linking Cotton Fabric with Succinic Acid Under UV Irradiation. *Photochemistry and photobiology* 2010; 86, 5: 1030-1037.
28. Zohoori S, Karimi L. Effect of nano $SrTiO_3$ supporting nano TiO_2 on self-cleaning of cotton fabric. *Fibers and Polymers* 2013; 14, 6: 996-1000.

Received 19.07.2012 Reviewed 21.10.2013