

Nano TiO₂ Based Self-Cleaning Fabric Technology

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1. INTRODUCTION

Nanocrystalline titanium dioxide films have received much attention as photocatalyst in practical applications such as environmental purification [1–3], deodorization [4], sterilization [5], anti-fouling [6] and self-cleaning glass [7,8] due to their high oxidizing ability, nontoxicity, long term stability and low cost. It is well known that anatase titania is more efficient as a photocatalyst than rutile and brookite titania [9]. Sol–gel processes offer an attractive means of producing anatase TiO₂-based thin films at a low temperature which can extend the application of anatase TiO₂ to substrates with low thermal resistance.

Much work has been focused on the nucleation of anatase by various low temperature methods such as hot water treatment of silica–titania coatings [10–12], sol–gel derived silica–titania coatings exposed to water vapor [13]. It has been reported that anatase TiO₂ sols can be synthesized by hydrolysis of titanium n-butoxide in nitric acid aqueous solution and subsequent reflux at a low temperature of 75 °C [14]. However, this product is composed of a mixture of anatase and brookite, rather than pure anatase.

Recently, several studies have reported nanocrystalline TiO₂ films on textiles prepared at relatively low temperatures. *Nature* has reported [15] that Daoud and Xin [16] successfully grown anatase nanocrystallites on cotton fabrics and these fabrics could be made into self-cleaning clothes that tackle dirt, environmental pollutants and harmful microorganisms. The anatase phase could be obtained on the cotton textile surface by a boiling water treatment for 3 h after a fabric treatment using an ethanol-based sol–gel titania [16]. Later on, Kiwi *et al* [17–20] reported the preparation of self-cleaning wool-polyamide, polyester and cotton textiles coated with TiO₂. In their work, the TiO₂ colloidal solution was prepared using titanium tetraisopropoxide as the precursor in 2-propanol acidified by nitric acid, then the TiO₂ solution was hydrothermally treated for 16 h

at 100 °C. However, it was amorphous TiO₂ [18] or pure rutile TiO₂ [17] that was attained on the textiles, which is less photoactive than anatase TiO₂ [9, 21]. Furthermore, the use of organic solvents is not desired because it makes the whole chemical approach not environmentally friendly. TiO₂ colloid prepared using an aqueous based sol-gel process at 80°C was also amorphous TiO₂ [20], which was used to fabricate SiO₂/TiO₂ coating on cotton. The TiO₂/SiO₂ films on the cotton were obtained by immersing the cotton in a mixture of TiO₂ colloid and commercial SiO₂ solution, subsequently followed by thermal treatment at 100 °C for 1 h. However, the long treatment time is not feasible in the industrial textile application. More environmentally friendly aqueous based single phase anatase TiO₂ was developed by Qi and Xin [22–24] and the self-cleaning effects were investigated on cotton and polyester substrates. Daoud *et al.* [25, 26] investigated self-cleaning wool by the chemical modification and anatase coating processes.

Constrained by TiO₂'s low quantum efficiency, high band gap (located at the UV wavelength range), hydrophobic nature, utilizing TiO₂ as highly active photo – catalyst for visible light self – cleaning fabrics, however, remains challenging. Recently, various possible strategies toward this intrinsic limitation including doping TiO₂ with inorganic or metallic species, such as SiO₂ [20, 23, 27], Au [28], Ag [29 – 30], S [31], N [31], or bonding spacer [19], or photo – sensitizing TiO₂ with organic dyes those were often efficient but unstable [32]. The object of this work is to strengthen the visible light self – cleaning properties of TiO₂, and to improve the hydrophilicity of the surface of the treated fabrics as well.

In the present study, an aqueous based sol–gel process was used instead of the ethanol. The work also reported that a highly active rutile Au/TiO₂/SiO₂ photo – catalyst with hydrophilic nature, by embedding Au and Si species using sol – gel nanotechnology. Undoped and doped TiO₂ sols were prepared at a temperature as low as 60 °C by hydrolysis and condensation of titanium tetraisopropoxide in an acidic aqueous solution. TiO₂ thin

films were produced on cotton fabrics from colloidal sols by a simple dip-pad-dry-cure process. Self-cleaning properties of the fabrics treated with both undoped and doped TiO_2 were studied including colorant decomposition activity, ability to decompose organic materials and stains such as red wine and coffee stains.

2. EXPERIMENTAL

Preparation of TiO_2 sol

Titanium tetraisopropoxide (Aldrich, 97%) was added dropwise into acidic water containing 0.4% nitric acid (Aldrich, 37%), and acetic acid (Aldrich, 99.9%) under vigorous stirring. The mixtures were heated at 60 °C, and kept vigorously stirring overnight. The concentration of TiO_2 is 1.0 wt%.

Preparation of Au/ TiO_2 /Silica Nanosol

Au/ TiO_2 /silica nanosols with different concentrations were synthesized as follows. In a typical procedure, predetermined amount of $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ aqueous solution ($9.55 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, International Laboratory, USA), and 2 ml tetra-ethyl-ortho-silicate (TEOS, International Laboratory, USA) were added drop-wise into 200 ml as-prepared 1 wt% TiO_2 aqueous solution under vigorous stirring at about 60 °C for 10 min. The amount of $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ aqueous solution of 0.5 ml were used. And then the flask was moved to a self-made ultraviolet light source chamber under UV irradiation (UV intensity is around 1.2 mW/cm^2) at ambient temperature for minutes.

Preparation of TiO_2 and doped TiO_2 films

The as-prepared sols were used to prepare TiO_2 and doped TiO_2 films on woven white cotton fabrics by a dip-pad-dry-cure process. The substrates were dipped in TiO_2 sol for 1 min, and pressed with an automatic padder. The wet pick-up is about 70%. The substrates were dried at 80°C for 5 min in a preheated oven and finally cured at 120°C for 3 min in a preheated curing oven.

Characterization

The structure and morphology of the TiO_2 and doped TiO_2 films on cotton fabrics were investigated using field-emission scanning electron microscopy (FESEM, JSM-6335F at 3.0 kV, JEOL, Tokyo, Japan). The crystal phase of titania and doped titania solid powder extracted from the sols was studied by X-ray diffraction spectroscopy (XRD, Bruker D8 Discover

X-ray diffractometer) operating at 40 kV and 30 mA.

Assessment of degradation activities of coffee and red wine stains

The degradation activities of a red wine stain (Carlo Rossi California Red, 11.5% alc/vol) and a coffee stain (Nestle, 1.8g 100% pure soluble coffee power/150ml hot water) were evaluated. Untreated, TiO_2 and doped TiO_2 treated white fabrics were cut into 4.5cm x 6.5cm respectively.

One drop of red wine and coffee were applied onto the treated fabrics and untreated fabrics using 10 ml medical syringe with pinhead close to the fabric surface when dropping.

Then the irradiation of all samples were carried out in Xenotest Alpha LM light exposure and weathering test instrument (air cooled xenon arc lamp, irradiance 4.5 mW/cm^2 at 300-400 nm Wavelength, Xenotest Alpha LM, Heraeus Industrietechnik, Hanau, Germany). The red wine and coffee stained fabrics were irradiated with predefined durations.

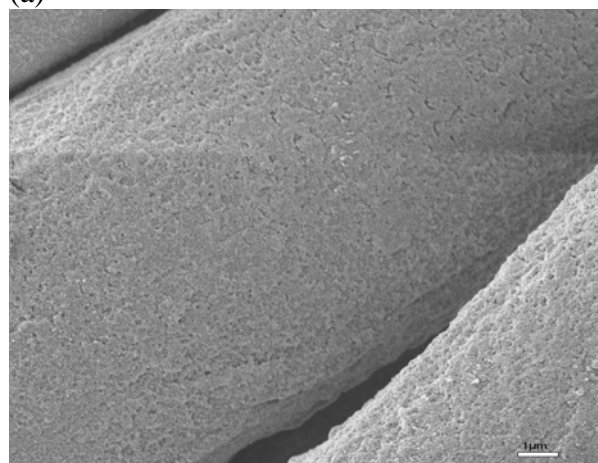
3. RESULTS AND DISCUSSION

SEM images

Figure 1 shows SEM micrographs of TiO_2 and doped TiO_2 treated cotton fibres.

The surface structure of TiO_2 treated cotton fibres in Figure 1a shows that TiO_2 layer has been formed on cotton fibres and the layer looks uniform, while the surface of the doped TiO_2 treated cotton fibres is very porous.

(a)



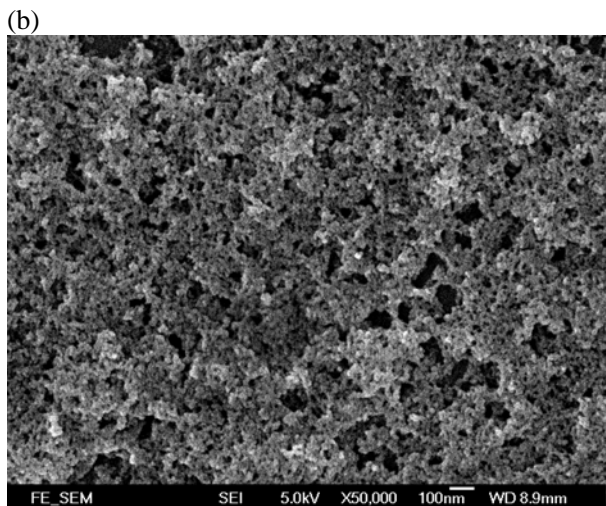


Figure 1 SEM images of (a) titania treated cotton fibres and (b) doped titania treated cotton fibres.

XRD patterns

According to JCPDS Card No: 21-1272 (JCPDS Catalogue), it can be seen that the TiO₂ investigated here is a mixture of anatase and rutile phase. The pH and the calcinations temperature should be responsible for the mixed crystallites. The Au peaks can not be observed due to the low concentration.

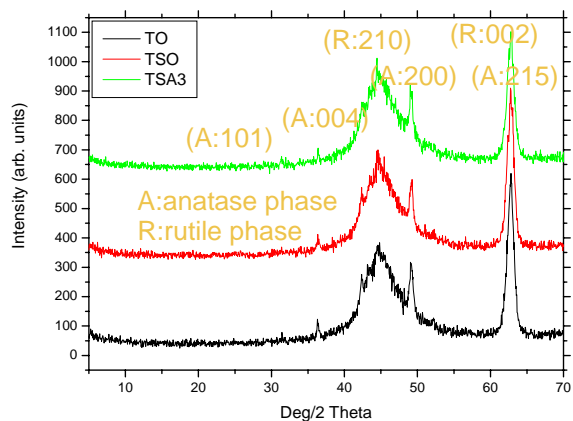


Figure 2 XRD patterns of pure TiO₂ and doped TiO₂. TO: TiO₂ only, TSO: SiO₂/TiO₂, TSA3: Au/SiO₂/TiO₂.

Degradation of coffee and red wine stains

Figure 3 presents the degradation of coffee stains and red wine stains on untreated white cotton and TiO₂ treated white cotton fabrics before and after 20 h of light irradiation.

It can be seen that coffee stains and red wine stains on TiO₂ treated cotton fabrics were discolored significantly after 20h of light irradiation, respectively.

However, the discoloration of coffee stains and red wine stains on untreated white cotton was not obvious after 20 h of light irradiation.

This indicates that TiO₂ films on cotton fabrics can effectively degrade coffee stains and red wine stains while untreated cotton fabrics have no degradation activities for coffee stains and red wine stains.

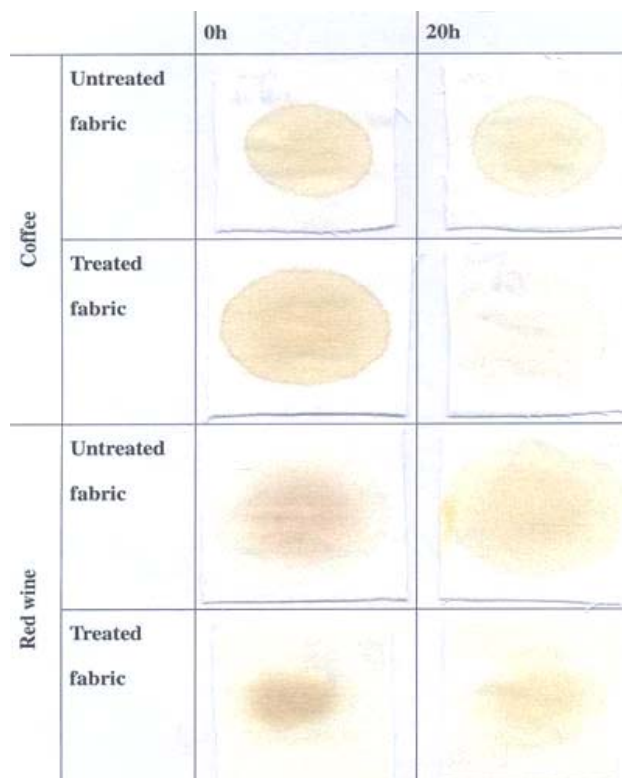


Figure 3 Stain removal test using coffee stains and red wine stains. The images shown are the exposed sides of untreated and TiO₂ treated white cotton fabrics before and after 20 h of light irradiation in Xenotest Alpha LM light exposure and weathering test instrument.

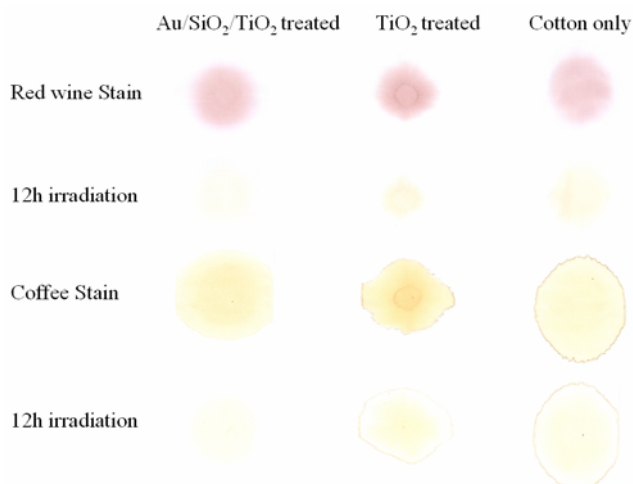


Figure 4 presented the degradation results of a red wine stain and a concentrated coffee stain, respectively, on pristine woven cotton fabrics, TiO₂ treated white woven cotton fabrics, and Au/TiO₂/Silica coated white woven cotton fabrics after 12 h visible light irradiation using a Suntest solar simulator with a light intensity of 6460 lux.

It can be seen that the Au/TiO₂/Silica treated fabrics are hydrophilic enough to disperse the stains as much as possible. On the contrary, TiO₂ treated fabrics are slightly hydrophobic that keep the stains from spreading. The hydrophilic improvement of TiO₂ was observed from the red wine and coffee stained samples. The condensation step for sol-gel process was not conducted in this study, thus make sure that the surface of Au/TiO₂/Silica nanoparticles have more hydrophilic groups than those of TiO₂ only.

4. CONCLUSIONS

Nanocrystalline TiO₂ and doped TiO₂ films were prepared on cotton fabrics by a near room temperature sol-gel process. The TiO₂ nanocrystallite treated fabrics showed significant self-cleaning performance as demonstrated by degradation of coffee stains and red wine stains under light irradiation. The

nanocrystalline TiO₂ treated cotton fabrics have high potential in commercial applications for self-cleaning cotton textiles.

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REFERENCES

- [1] Y. Nosaka, K. Koeuma, K. Ushida, and A. Kira, *Langmuir*, 12(3), 736-738 (1996).
- [2] X. Fu, W. A. Zeltner, and M. A. Anderson, *Appl. Catal. B Environ.*, 6(3), 209-224 (1995).
- [3] A. Heller, *Acc. Chem. Res.*, 28 (12), 503-508 (1995).
- [4] I. Sopyan, M. Watanabe, S. Murasawa, K. Hashimoto, and A. Fujishima, *J. Electroanal. Chem.*, 415(1-2), 183-186 (1996).
- [5] Y. Kikuchi, K. Sunada, T. Iyoda, K. Hashimoto, and A. Fujishima, *J. Photochem. Photobiol. A: Chem.*, 106(1-3), 51-56 (1997).
- [6] Y. Paz, Z. Luo, L. Rabenberg, and A. Heller, *J. Mater. Res.*, 10 (11), 2842-2848 (1995).
- [7] S. Fukayama, K. Kawamura, T. Saito, T. Iyoda, K. Hashimoto, and A. Fujishima, Proceedings of the Extended Abstracts of the 187th Meeting of the Electrochemical Society, The Electrochemical Society, Pennington, NJ, USA, 1995.
- [8] N. Negishi, T. Iyoda, K. Hashimoto, and A. Fujishima, *Chem. Lett.*, (9), 841-842 (1995).
- [9] K. Kato, A. Tsuzuki, H. Taoda, Y. Torii, T. Kato and Y. Butsugan, *J. Mater. Sci.*, 29(22), 5911-5915 (1994).

- [10] A. Matsuda, Y. Kotani, T. Kogure, M. Tatsumisago, and T. Minami, *J. Am. Ceram. Soc.*, 83(1), 229-231 (2000).
- [11] A. Matsuda, T. Matoda, T. Kogure, K. Tadanaga, T. Minami, and M. Tatsumisago, *J. Sol-Gel Sci. Technol.*, 27 (1), 61-69 (2003).
- [12] A. Matsuda, T. Matoda, K. Tadanaga, T. Minami, and M. Tatsumisago, *J. Am. Ceram. Soc.*, 88(6), 1421-1426 (2005).
- [13] H. Imai, and H. Hirashima, *J. Am. Ceram. Soc.*, 82(9), 2301-2304 (1999).
- [14] Y. Hu, and C. W. Yuan, *J. Cryst. Growth*, 274(3-4), 563-568 (2005).
- [15] M. Peblow, *Nature*, 429, 620 (2004).
- [16] W. A. Daoud, and J. H. Xin, *J. Am. Ceram. Soc.*, 87(5), 953-955 (2004).
- [17] A. Bozzi, T. Yuranova, and J. Kiwi, *J. Photochem. Photobiol., A: Chem.*, 172(1), 27-34 (2005).
- [18] A. Bozzi, T. Yuranova, I. Guasaquillo, D. Laub, and J. Kiwi, *J. Photochem. Photobiol., A: Chem.*, 174(2), 156-164 (2005).
- [19] K. T. Meilert, D. Laub, and J. Kiwi, *J. Mol. Catal. A: Chem.*, 237(1-2), 101-108 (2005).
- [20] T. Yuranova, R. Mosteo, J. Bandata, D. Laub, and J. Kiwi, *J. Mol. Catal. A: Chem.*, 244(1-2), 160-167 (2006).
- [21] A. Fujishima, K. Hirashima, and T. Watanabe, "TiO₂ Photocatalysis: Fundamental and Applications", BKC, Tokyo, 1999.
- [22] K. H. Qi, W. A. Daoud, J. H. Xin, C. L. Mak, W. Tang, and W. P. Cheung, *J. Mater. Chem.*, 16(47), 4567-4574 (2006).
- [23] K. H. Qi, X. Q. Chen, Y. Y. Liu, J. H. Xin, C. L. Mak, and W. A. Daoud, *J. Mater. Chem.*, 17(33), 3504-3508 (2007).
- [24] K. H. Qi, J. H. Xin, W. A. Daoud, and C. L. Mak, *Int. J. Appl. Ceram. Tec.*, 4 (6), 554-563 (2007).
- [25] W. A. Daoud, , Leung, S. K., Tung, W. S., Xin, J. H., Cheuk, K., and Qi, K., Self-cleaning Keratins, *Chem. Mater.*, 20(4), 1242-1244 (2008).
- [26] W. S. Tung, and W. A. Daoud, *J. Colloid Interf. Sci.*, 326(1), 283-288 (2008).
- [27] T. Yuranova, V. Sarria, W. Jardim, J. Rengifo, C. Pulgarin, G. Trabesinger, J. Kiwi. *J. Photochem. Photobiol. A: Chem.*, 188(2-3), 334-341 (2007).
- [28] M. J. Uddin, F. Cesano, D. Scarano, F. Bonino, G. Agostini, G. Spoto, S. Bordiga and A. Zecchina. *J. Photochem. Photobiol. A: Chem.*, 199(1), 64-72 (2008).
- [29] T. Yuranova, A. G. Rincon, C. Pulgarin, D. Laub, N. Xantopoulos, H.-J. Mathieu, and J. Kiwi. *J. Photochem. Photobiol. A: Chem.*, 181(2-3), 363-369 (2006).
- [30] M.J. Uddin, F. Cesano, S. Bertarione, F. Bonino, S. Bordiga, D. Scarano, and A. Zecchina. *J. Photochem. Photobiol. A: Chem.*, 196(2-3), 165-173 (2008).
- [31] R. Bacsá , J. Kiwi, T. Ohno, P. Albers, and V. Nadtochenko, *J. Phys. Chem. B.*, 109(12), 5994-6003 (2005).
- [32] H. Li, Z. Bian, J. Zhu, Y. Huo, H. Li, and Y. Lu. *J. Am. Chem. Soc.*, 129, 4538 - 4539 (2007).