

APPLICATION OF SELF-CLEANING TREATMENT ON COTTON AND PES/CO FABRIC USING TiO₂ AND SiO₂ COATING SYNTHESIZED BY SOL-GEL METHOD

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ABSTRACT

The photocatalytic activity of TiO₂–SiO₂ coated and TiO₂ coated on 100% cotton and PES/Co fabrics was investigated through the self-cleaning of red wine stains and coffee stains. It was shown that a TiO₂ species could be produced at temperatures of 25 °C, 40 °C and 60 °C with acceptable photo-activity and TiO₂–SiO₂ nanocomposites were prepared by a sol-gel process at a low temperature. The discoloration of red wine and coffee led to CO₂ evolution that was more efficient for TiO₂–SiO₂ coated cotton for samples than of TiO₂ coated ones. The textile surface did not show any change after several consecutive light-induced discoloration cycles of a red wine stain and coffee stain. The structural properties of these nanocomposites were characterized with scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The scanning electron microscope (SEM) photo showed that the TiO₂–SiO₂ layer is thicker than TiO₂ layer on the cotton fabric and PES/Co fabric and the Ti-particles were always surrounded by amorphous SiO₂ and never alone by themselves. The TiO₂–SiO₂ nanocomposites were coated onto cotton and PES/Co fabrics by a simple dip-pad-dry-cure process.

Keywords: self-cleaning, fabric, TiO₂–SiO₂, coating, sol-gel method.

1. INTRODUCTION

The term of “making clothes wash themselves” has become more popular in recent years, when fabric only need a spot of sunshine to get rid of those spills and stains during usage. The method developed is a saving efficient way to grow special nanostructures, which can degrade organic matter when exposed to light, directly onto textiles. In the research field of self-cleaning in recent years, crystalline TiO₂ has received much attention due to their interesting properties as photocatalyst. Nano-sized particles show high photoactivity due to their large surface area per unit mass and diffusion of the electron/holes before recombination [1]. The commercial use of TiO₂ as photocatalyst is becoming widespread in the areas of: (a) for water purification; (b) air purification; (c) sterilization/disinfection; and (d) systems involving applications of the recently

reported superhydrophilic effect [1]. A several studies also report the nucleation of anatase at relatively low temperatures: (a) from sol-gel coated substrates exposed to boiling water; (b) at 100 °C from sol-gel exposed to water vapor; (c) at temperatures 60–180 °C from TiO₂-SiO₂ films exposed to water vapor [1–3]. In the last case, the treatment with water vapor reduced the temperature necessary to produce anatase crystallites in the sol-gel films to temperatures below 100 °C by phase separation of the TiO₂ from the SiO₂; (d) anatase nano-crystals were produced more recently on cotton fabrics from the TTIP alkoxide solution at low temperature by sol-gel process with grain sizes of ~20 nm. The anatase phase was attained on the cotton textile surface by boiling the textiles in water for 3 h [1, 4, 5].

It was concluded that self-cleaning fabrics have been successfully prepared by depositing and grafting TiO₂ nanoparticles via an aqueous sol process at low temperature. Anatase TiO₂ nanoparticles were well developed in size of 3–5 nm. These TiO₂-coated cotton fabrics possessed distinct self-cleaning properties, such as bactericidal activity and photocatalytic decomposition of dyes. The photocatalytic activity of the treated fabrics was fully maintained upon several numbers of photodegradation cycles [2]. In addition, the photocatalytic activity of TiO₂-SiO₂-coated cotton textiles were investigated through the self-cleaning of red wine stains. The discoloration of red wine led to CO₂ evolution that was more efficient for TiO₂-SiO₂-coated cotton for samples than of TiO₂-coated ones. The textile surface did not show any change after several consecutive light-induced discoloration cycles of a red wine stain. By high-resolution transmission electron microscopy (HRTEM), the TiO₂-SiO₂ layer thickness on the cotton fibers was detected to 20–30 nm. The TiO₂ and SiO₂ were both observed to have particle sizes between 4 and 8 nm. Further electron microscopy work coupled with energy dispersive spectroscopy (EDS) showed that the Ti-particles were always surrounded by amorphous SiO₂ and never alone by themselves [4]. Infrared spectroscopy revealed that no modification of the cotton could be detected after photo-discoloration processes with TiO₂-SiO₂, taking a wine stain as model compound. The mixed TiO₂ and SiO₂ colloids lead during the dip-coating and subsequent thermal treatment on cotton to an organized structure of highly dispersed TiO₂ particles always surrounded by amorphous silica [4, 6, 7, 8]. Therefore, this study demonstrates that the photocatalytic activity of TiO₂-SiO₂ coated and TiO₂ coated on 100% cotton and PES/Co fabrics can be successful by the self-cleaning of red wine stains and coffee stains. It was shown that a TiO₂ species could be produced at low temperatures with acceptable photo-activity on non-heat resistant materials and TiO₂-SiO₂ nanocomposites could be prepared by a sol-gel process at a low temperature.

2. MATERIALS AND METHODS

2.1. Materials

Titanium tetra isopropoxide (TTIP, 97 % purity), methyltrimethoxysilane (MTMS, 98 % purity), SiO₂ nanoparticles (5–15 nm) were purchased from Sigma – Aldrich. The other chemicals used to include ammonia (28 % – 30 %), acetic acid (99.9 %), nitric acid (70 %) were purchased from Xilong Chem Co. Ltd. (China). The commercial 100 % cotton fabrics, woven weave, weight 135 g/cm², warp density 90 threads cm⁻¹, weft density 85 threads cm⁻¹, scoured and bleached (supplied by X28 Co, Viet Nam) were used. PeCo 65/35 fabrics, warp density 51 threads cm⁻¹, weft density 27 threads cm⁻¹. Samples were prepared with the size of 4 cm × 12 cm.

2.2. Preparation of TiO₂ nanosols

Titanium tetra-isopropoxide (TTIP, 5 ml) was added dropwise into 100 mL acidic water containing 1 mL nitric acid 70 % and 10 mL acetic acid 99.9 % under stirring. The mixtures were heated at different temperatures, namely 25, 40 and 60 °C, and kept vigorously stirred for 16 h, pH = 1–2. The prepared TiO₂ nanosols were named as A25, A40 and A60.

2.3. Preparation of TiO₂–SiO₂ composite colloids

The SiO₂ powder (5–15 nm) was added to TiO₂ nanosol (A60) and dispersed in an ultrasonic bath for 15 min. The TiO₂/SiO₂ mixture was kept for 12 h to form TiO₂–SiO₂ composite particles (pH = 3–5). The TiO₂–SiO₂ layers in a 1:1, 1:2, 2:1 volume mixture made up of the TiO₂ colloid A60 and SiO₂. The prepared TiO₂/SiO₂ nanocomposites were named as B1, B2 and B3, respectively.

2.4. Coating process

The as-prepared TiO₂ nanosols and TiO₂–SiO₂ composite colloids and were used to prepare thin coatings on substrates (cotton fabrics and PeCo fabrics) by a dip-pad-dry-cure process. The cleaned substrates were dipped in TiO₂ sols and TiO₂–SiO₂ composite colloids for one minute, pressed with a padder at a nip pressure of 2.75 kg/cm² to keep the same amount of TiO₂ and TiO₂–SiO₂ composite on each of the fabric substrates. After 5 min, the padded fabrics were put in ammonia gas for neutralization to get pH = 7 of the fabric surface. The substrates were dried at 80 °C for 5 min in a preheated oven and finally cured at 120 °C for 3 min.

2.5. Characterization

The structure and morphology of these coatings were investigated using scanning electron microscopy (SEM, Hitachi S4800). The chemical composition of the samples was identified by infrared spectrometer (IR, Tensor 27, Bruker). The characterization experiments were implemented at Ho Chi Minh city Academy of Science and Technology, Vietnam.

2.6. Evaluation of the textile cleaning action

The textile cleaning action was evaluated by the discoloration of a wine stain and coffee stain, which was added on to the bleached fabrics surface, after 0, 4, 8 and 24 h in a solar light irradiation. The test was implemented at Textile-Dyeing Laboratory of Thanh Cong Textile Garment Investment Trading Joint Stock Company (TCG), Vietnam.

3. EXPERIMENTAL RESULTS

3.1. Assessment of water absorbance of TiO₂–SiO₂ coated fabric

Figure 1 describes the water absorption ability of the cotton fabric treated with sol TiO₂ with at different of temperature of 25°, 40°, and 60° without the exposedness to UV. The three samples show the round shape water drops with the contact angle between the water drop and the fabric surface is greater than 90°. This demonstrated that fabric surface coated with sol TiO₂ became hydrophobic.

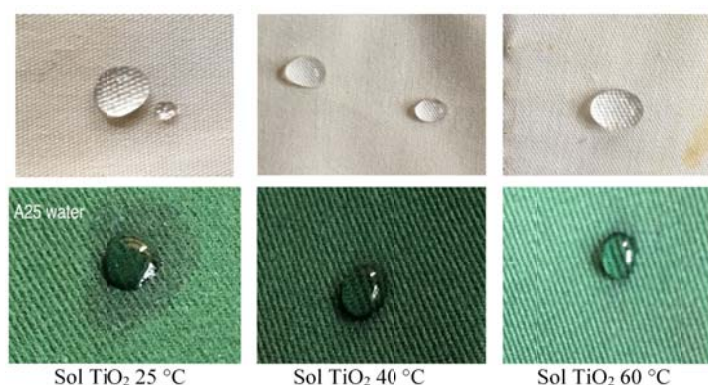


Figure 1. Water absorbance capacity of cotton (upper line) and PeCo (under line) fabrics treated with sol TiO_2 at different temperature.

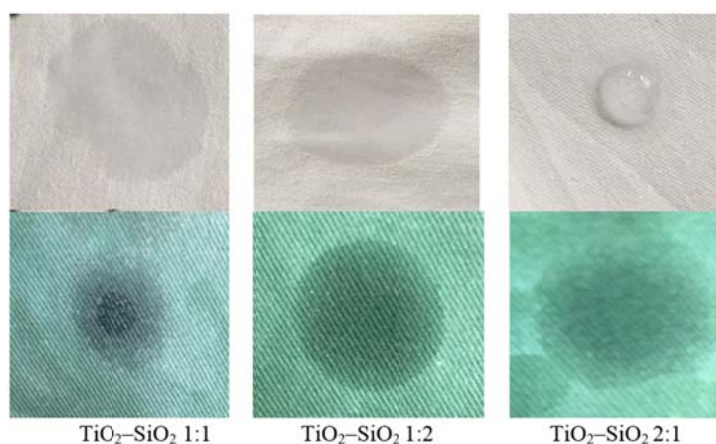


Figure 2. Water absorbance capacity of cotton (above) and PeCo (under) fabrics treated with TiO_2-SiO_2 colloids at different mixing ratio.

However, when dripping the water drop on the fabric surface coated with the TiO_2-SiO_2 colloids (Figure 2), the water drops will spread out the fabric surface. This can be said that the fabric coated with TiO_2-SiO_2 colloid have higher capability of water absorbance than the one coated with only sol TiO_2 and untreated fabric. The differences when coating on cotton and PeCo fabrics are also introduced in Figure 1. The angle of three water drop possessed a contact angle smaller than 30° . The FI-IR spectra of coated PeCo fabrics in Figure 3 can be used to explain this phenomena, where we found only double covalent bond $C=O$. When this bonding reacts to the bonding of $Ti-O-Ti$ and $Ti-O-Si$, the inverse chemical reaction occurs that make the PeCo fabric surface have the higher water absorbance than untreated fabric.

As shown in Figure 2, the water drops on fabric coated with TiO_2-SiO_2 colloids tended to spread out immediately to fabric surface. The drops were almost completely contacted with fabric surface. The percentage of transmittance illustrated in Figure 3 and Figure 4 also proved that the absorption ability of the PeCo fabric coated with sol TiO_2 and TiO_2-SiO_2 colloids is higher than that of cotton fabric. The percentage of transmittance of the ion bonds of PeCo samples is lower than that of the cotton samples. Figure 3 showed that, at the peak 1713 cm^{-1} , there is the appearance of the stretching vibration $C=O$. These peaks 1272 cm^{-1} , 1407 cm^{-1} and

2890 cm^{-1} are respected to the stretching vibration C–H. The peak 1532 cm^{-1} showed the appearance of the bonding of carboxylic group and Ti atoms. This bonding improves the oxidation of the sol TiO_2 coating and TiO_2 – SiO_2 colloid coating leading to the easier and faster photocatalytic activity. Figure 4 presents the specific FT–IR spectra of untreated cotton fabric and cotton fabric treated with sol TiO_2 (60 °C) and the TiO_2 – SiO_2 2:1 colloid. Three spectra have the similar profile. The values in the range of 3100–3600 cm^{-1} correspond to O–H stretching vibration. The peaks 1000 cm^{-1} , 1500 cm^{-1} and 2997 cm^{-1} present the C–H vibration. By observation the lowest line corresponds to cotton fabric treated with sol TiO_2 at 60 °C, there is the appearance of the Ti–O–Ti bonds respect to the wavelength ranges 450–700 cm^{-1} . The appearance of Ti–O–Si bond in the coating $\text{TiO}_2/\text{SiO}_2$ at the peak 897 cm^{-1} notices the stable bonding of Si–Ti. This bonding surface acidity of the nano mixture $\text{TiO}_2/\text{SiO}_2$ and also increases the photocatalytic activity of the $\text{TiO}_2/\text{SiO}_2$ coating on the cotton fabric.

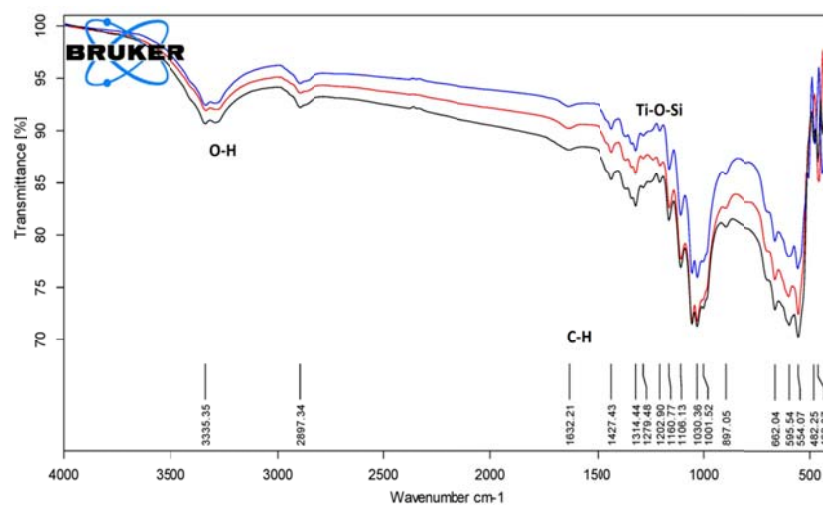


Figure 3. FT–IR spectra of untreated cotton fabric (upper line), treated with TiO_2 – SiO_2 colloids 2:1 (middle line) and treated with sol TiO_2 A60 (lower line).

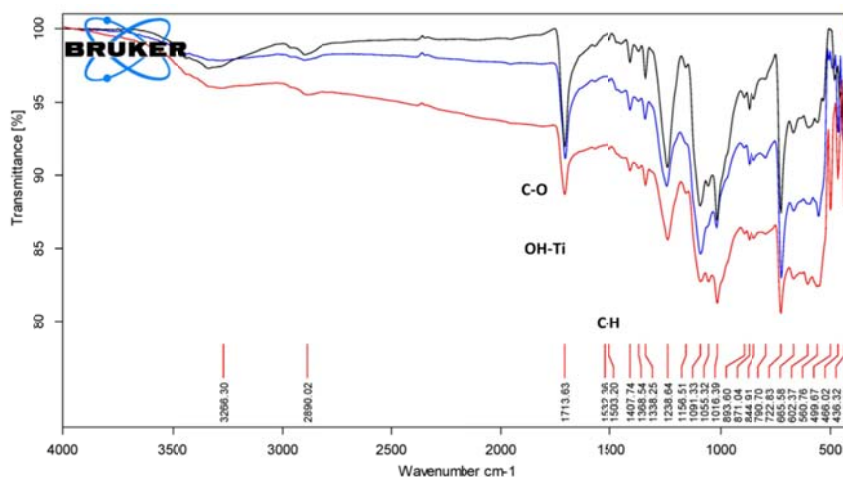


Figure 4. FT–IR spectra of untreated cotton fabric (upper line), treated with TiO_2 – SiO_2 colloids 2:1 (middle line) and treated with sol TiO_2 A60 (lower line).

Those remarks are illustrated by SEM image of coated fabric as shown in Figure 5. We found a thin but most homogenous coating film on fabric treated with TiO₂ A60 and a very dense film coated on fabric treated with TiO₂-SiO₂ 2:1.

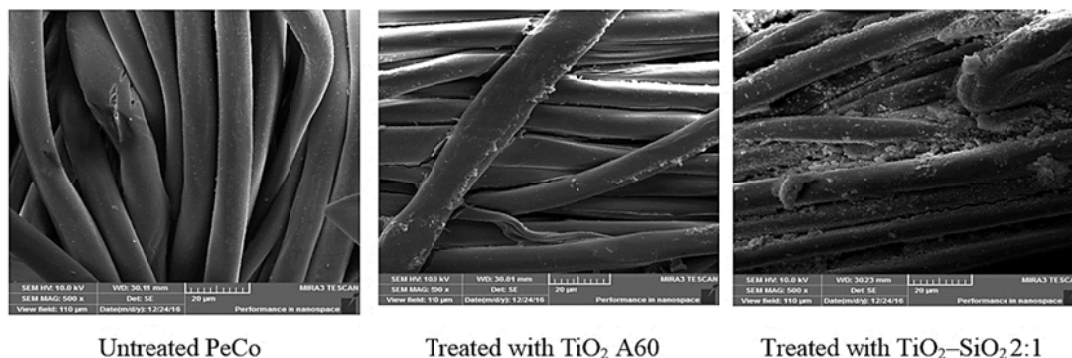


Figure 4. SEM image of untreated and treated PeCo fabric.

3.2. Assessment of self-cleaning ability of TiO₂-SiO₂ coated fabric

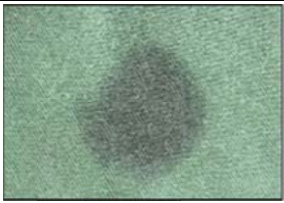
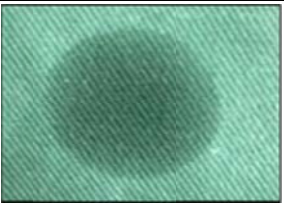
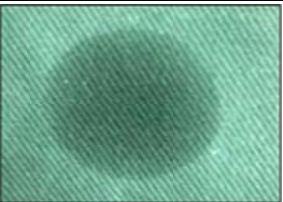



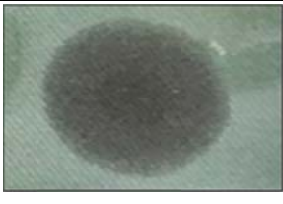
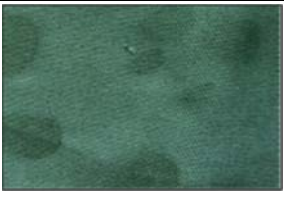

On the surface of untreated fabric, the coffee and wine stains have remained even after 4 h, 8 h then 20 h exposure time as displayed in Table 1 and Table 2. When coating with sol TiO₂ at all three heating mixture of 25 °C, 40 °C and 60 °C, the self-cleaning effect occurred. The discoloration can be clearly seen only after 4h sunlight exposure. The discolorations continued intensively until 8 h and almost disappeared until 20 h. Among them, the samples treated with sol TiO₂ A60 exhibited the best self-cleaning effect.

Table 1. Red wine stain on treated cotton fabric after different exposure time.

Discoloration Time	0 h	4 h	8 h	20 h
Untreated fabric				
Treated with sol TiO ₂ A60				
Treated with TiO ₂ -SiO ₂ 2:1				

Treated with different mixture ratio of the $\text{TiO}_2\text{-SiO}_2$, the self-cleaning capability of fabric is greater than that treated with only sol TiO_2 . We could see the intensive discoloration of stain at 8h exposure time and the vanishing of stain at 20 h exposure time.

Table 2. Coffee stain on treated PeCo fabric after different exposure time.

Discoloration Time	0h	4h	8h
Untreated fabric			
Treated with sol TiO_2 A60			
Treated with $\text{TiO}_2\text{-SiO}_2$ 2:1			

This proved the impact of nano SiO_2 in the mixture of $\text{SiO}_2\text{-TiO}_2$ on the self-cleaning ability of coated fabric. The nano SiO_2 created the thin film on the fabric surface and prevented the stain from penetrating into the fiber structure. When the TiO_2 coating film in fabric surface is exposure to sunlight, the photocatalytic activity occurred and generated the pair of electron (e^-) and hole (h^+) which receive the energy from the unstable cation from “pigment” color inside the red wine and coffee stains. The electrons received energy to overcome the restricted area and move up to the path of TiO_2 .

The self-cleaning ability of PeCo samples coated with the sol TiO_2 and $\text{SiO}_2\text{-TiO}_2$ colloids is higher than that of the cotton samples. According to table 1 and 2, the stains are completely disappearing after 8 hours. The PeCo fabric mainly consists of C=O , C-O , $-\text{O-C=O}$, $-\text{COH}$, $-\text{COOH}$ bonding, therefore during padding processes of TiO_2 and $\text{TiO}_2\text{-SiO}_2$ on the fabrics, these ion bonding make a huge of nano molecules connect together to form a thick and homogenous film attached on the fiber structure of the fabric. This will form the bigger anatase crystals size than usual. The photocatalytic activity happened faster leading to the faster stain discoloration.

4. CONCLUSIONS

This study demonstrated that that self-cleaning capacity of cotton and PeCo fabrics can obtain when treated with TiO_2 nano solution prepared at 60°C and with nano $\text{TiO}_2\text{-SiO}_2$ 2:1 colloids synthesized by sol-gel method. The coating film on surfaces protected the cotton and PeCo fabric from stains, even with hard stains such as wine or coffee stains. The nano TiO_2

acted as semiconductor photocatalyst with the support of nano SiO₂ forming a film on fabric that prevent stain from penetrating deeply in to the fiber structure and accelerate the faster discoloration. The preparation can be simply and effectively done at laboratory atmosphere. The fibers maintain their original shape and the coating made a homogenous film on fabric surface as illustrated by SEM images. The influence of treatment on tensile strength and other physical properties of fabric as well as the antibacterial properties of sol-gel TiO₂-SiO₂ can be investigated in future work of this study to confirm the effectiveness of this treatment on commercial fabric.

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