

## Preparation and the light transmittance of TiO<sub>2</sub> deposited fabrics

Yang Xu, Ning Wu, Qufu Wei, Xiubiao Pi

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**Abstract** Nanoscale titanium dioxide (TiO<sub>2</sub>) films were deposited on the surface of polyester nonwovens by using direct current reactive magnetron sputtering. The effect of oxygen flow on the surface structures and properties of the fabrics was investigated in this article. The surface morphology, microstructure, and the chemical composition of TiO<sub>2</sub>-coated fibers were characterized by atomic force microscope, X-ray diffraction, and X-ray photoelectron spectroscopy. The effect of oxygen flow on deposition rate, white degree, and light transmission properties of the fabrics with nanoscale TiO<sub>2</sub> films were examined. The test results proved that the oxygen flow was a key factor in sputter processing. The deposition speed decreased and the white degree of the fabric increased with increasing oxygen flow. The ultra-violet absorption by the polyester nonwoven fabric with TiO<sub>2</sub> coatings was also enhanced as the oxygen flow increased in a proper range.

**Keywords** Magnetron sputtering, Titanium dioxide, Nonwoven fabric, Transmittance, AFM, XPS

### Introduction

Functional textiles have attracted a lot of attention in recent years due to their great potential application in many industries. Nanoscale titanium dioxide (TiO<sub>2</sub>), with the excellent properties of photocatalysis and ultra-violet (UV) shielding,<sup>1</sup> has been applied to the textile industry for bringing some special properties to

these common fabrics, such as antibacterial, self-cleaning, and UV protection.

Considering the advantages of TiO<sub>2</sub> films, a great deal of effort has been used to search for effective methods of making TiO<sub>2</sub> functional materials for a wide range of applications. Various techniques have been developed and employed to produce TiO<sub>2</sub>-coated fabrics,<sup>2–6</sup> such as the sol-gel method, vacuum evaporation, sputtering, and so on.

The sol-gel method is one of the most widely used techniques because of its simple process. This kind of method, however, does not adapt to preparing uniform and compact functional films in a large area. The bad adhesive force between the fabric and the function films also cannot satisfy the need for lengthy and repeated usage.<sup>7</sup> In addition, the chemical pollution caused by a wet process is another serious disadvantage. Magnetron sputtering—an environmentally friendly process—is a better technique for preparing nanoscale TiO<sub>2</sub> functional films. This is because sputtering alone can offer better adhesion between the fabric and the function films. The TiO<sub>2</sub> films deposited by magnetron sputtering under ideal vacuum conditions can arouse a special interest in functional textiles. Sputtering can also be used in large-area deposition and achieve high quality TiO<sub>2</sub> films even at low substrate temperatures,<sup>8</sup> which can increase the practical use of fabrics effectively in many areas.

The structure and properties of TiO<sub>2</sub> films prepared by magnetron sputtering can be modified and controlled by process parameters such as sputtering pressure, sputtering power, and oxygen partial pressure. Thus, the influence of those parameters on the structure and properties is an interesting and necessary subject to study.<sup>9</sup> In this paper, nanoscale TiO<sub>2</sub> functional films deposited under different oxygen flows by a direct current (DC)-reactive magnetron sputtering process were investigated.

Y. Xu, N. Wu, Q. Wei (✉), X. Pi  
Key Laboratory of Eco-textiles, Ministry of Education,  
Jiangnan University, Wuxi, Jiangsu 214122, China  
e-mail: qfwei@jiangnan.edu.cn

## Experimental

### Materials preparation

The substrate used in this study was commercial spunbonded polyester nonwovens with a mass of  $100 \text{ g/m}^2$ . Before sputter coatings, the material was first washed with ethanol and distilled water. The material was then dried in an oven at  $40^\circ\text{C}$  for 24 h.

### Sputter coating

A DC-reactive magnetron sputter coating system (JZCK-420B) was used to prepare coated fabrics. A high purity Ti target (diameter 50 mm; purity 99.99%) was mounted on the cathode. The sputtering direction of Ti atoms was set from the bottom up to the surface of the substrate to avoid the deposition of impurities onto the substrate. The distance between target and substrate was 60 mm. To avoid the deformation of fabrics caused by high temperature, water cooling equipment was used to bring down the temperature of the substrate during the sputtering. The working chamber was first evacuated to a base pressure of  $1.5 \times 10^{-3} \text{ Pa}$  prior to introducing the high purity argon gas (99.99%) as the bombardment gas and the high purity oxygen gas (99.99%) as the reacting gas. During sputtering, the substrate holder was rotating at a speed of 100 rpm to ensure that  $\text{TiO}_2$  particles uniformly deposited on the substrate. Prior to the sputter coating, the target was discharged in argon gas for about 5 min to remove the oxides on its surface. The sputtering pressure was set at 0.3 Pa. The power used for sputtering was set at 70 W. The argon gas flow was set at 80 sccm.  $\text{TiO}_2$ -deposited fabrics were prepared at different oxygen gas flow rates. The thickness of the deposited layer was examined by a quartz crystal detector FTM-V during the sputtering process. The thickness of the  $\text{TiO}_2$  coating was about 100 nm in this work.

### Surface characterization

#### AFM characterization

Benyuan CSPM4000 atomic force microscope (AFM) (Guangzhou, China) was employed to scan the morphology and distribution of nanoscale  $\text{TiO}_2$  on the fabric surfaces. All images were obtained at ambient conditions and images were analyzed by the Imager 4.40 Software equipped with CSPM4000 AFM.

#### X-ray photoelectron spectroscopy and X-ray diffraction analysis

The X-ray photoelectron spectroscopy (XPS), a type of Thermo ESCALAB 250 (USA), was used to analyze

the elemental composition of the functional fabrics. The measurements were performed at a base pressure of  $10^{-6} \text{ Pa}$ , using a  $\text{Al K}\alpha$  ( $h\nu = 1486.6 \text{ eV}$ ) source. The source was operated at a power of 225 W. All XPS spectra were calibrated with the  $\text{C1s}$  peak at 284.6 eV. The spectra were recorded in the constant analyzer energy mode with analyzer pass energies of 20 eV.

The structure of  $\text{TiO}_2$  thin films deposited on the fibers was characterized by X-ray diffraction (XRD, X'Pert MPD PRO, Holland) with  $2\theta$  angle in the range of  $30\text{--}55^\circ$  using  $\text{Cu K}\alpha$  radiation.

### Whiteness and transmittance analysis

To analyze the influence of oxygen flow on the surface color of nanoscale  $\text{TiO}_2$ -coated fabric, the WSD-III whiteness meter (Kangguang, Beijing, China) was employed to compare the whiteness of samples by measuring Hunter Whiteness (Wh). During the experiment, black canister was used to set the whiteness meter to zero, and then adjusted it to 100% by using GSB-A67002-86 standard chinaware white. The result of each sample was the average of 30 measurements.

The SP-1700 UV-visible (UV/Vis) spectroscopy (Spectrum Instrument, Shanghai, China) with a deuterium lamp was introduced to examine the samples' transmittance in the wavelength range between 250 and 850 nm.

## Results and discussion

### Effect of oxygen flow on deposition rate

The particle deposition rate of the  $\text{TiO}_2$  film at different oxygen flow rates is shown in Fig. 1. It indicates that the deposition rate evidently decreases as oxygen flow rate increases. When the oxygen flow increases from 0 to 24 sccm, the deposition rate declines by almost 85%. This is because as oxygen flow increases, the colliding chemosynthesis—probability of titanium atom and

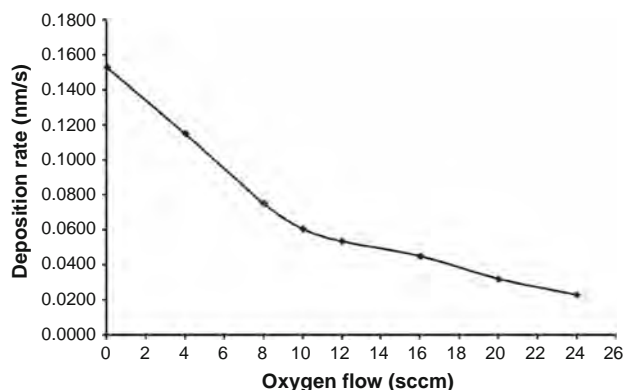
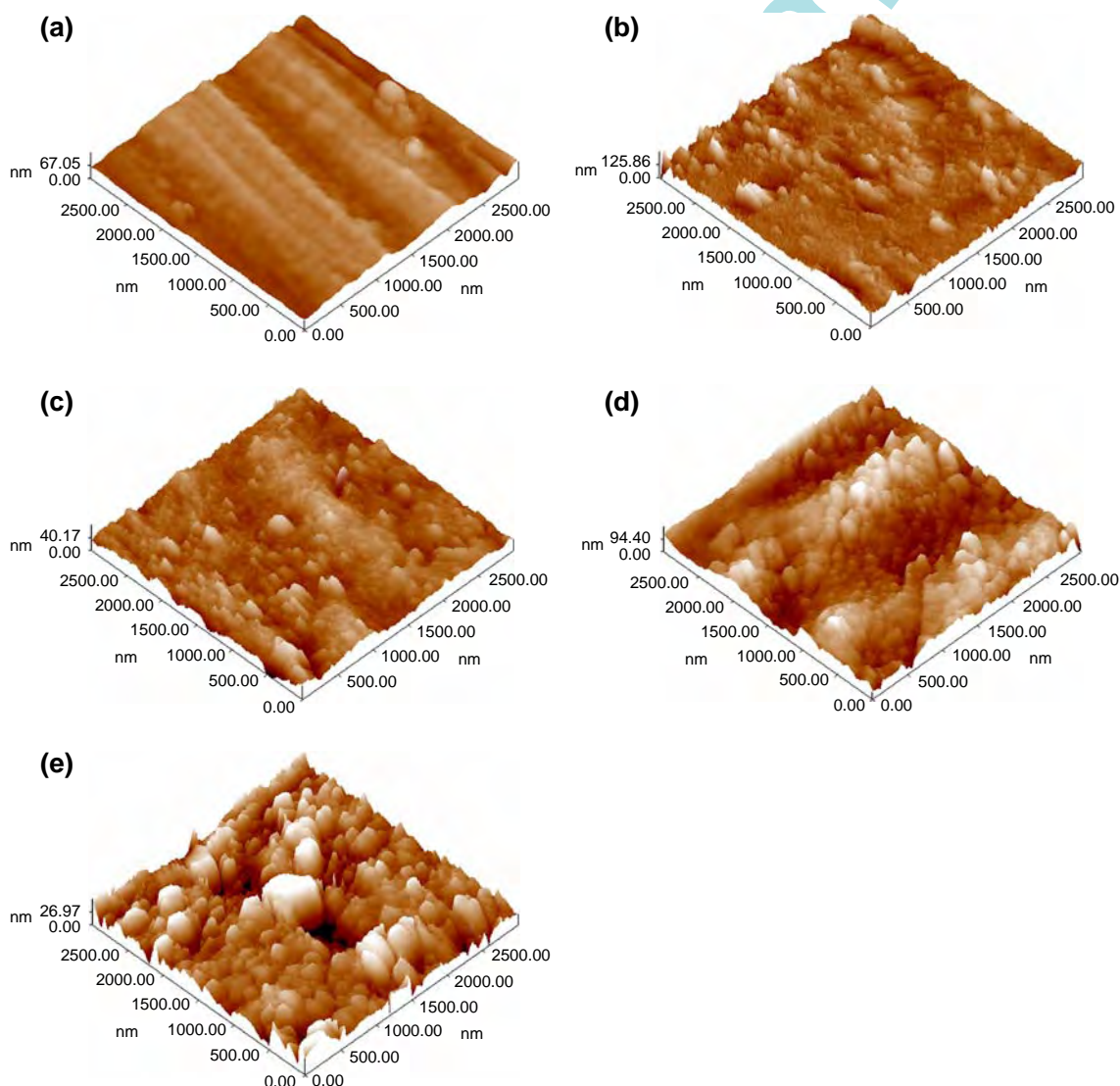


Fig. 1: Deposition rate with different oxygen flow rates

oxygen molecules—also increases before it reaches the substrate, which will directly affect the deposition rate of the functional structures. On the other hand, an increasing oxygen flow rate will cause oxidation of the surface of the titanium target. The sputtering rate of colliding oxidation material formed on the surface of the target is also usually significantly less than the rate of sputtering of the elemental target material.<sup>10</sup> Thus, the deposition rate decreases with the increasing degree of target surface oxidation. It is also observed in the experiments that more serious oxidation occurs on the target surface if oxygen flow rate continues to increase. In this case, the arc light of the target changes from blue white to orange gradually, and the sputter process becomes unstable. The sputter rate eventually goes down to almost zero, which is referred to as “target poisoned” phenomenon.<sup>11</sup>

### Surface morphology

AFM images reveal the change in the surface micro-structure of the polyester fibers before and after the TiO<sub>2</sub> coating, as shown in Fig. 2. It appears that the morphology of the polyester fiber without treatment is relatively smooth, with a groove-like structure on its surface as presented in Fig. 2a, which may be formed during the manufacturing process. Compared to the original sample, the TiO<sub>2</sub> coating significantly alters the surface characteristics of the fibers. The details of the sputtered TiO<sub>2</sub> nanoclusters on the polymer fibers prepared at 4, 8, 12, and 16 sccm oxygen flow rates can be seen from the high magnification AFM images obtained by the 3–3 μm scan, as illustrated in Figs. 2b, 2c, 2d, and 2e, respectively. The AFM images clearly show the sputtered particles covering the fiber surface



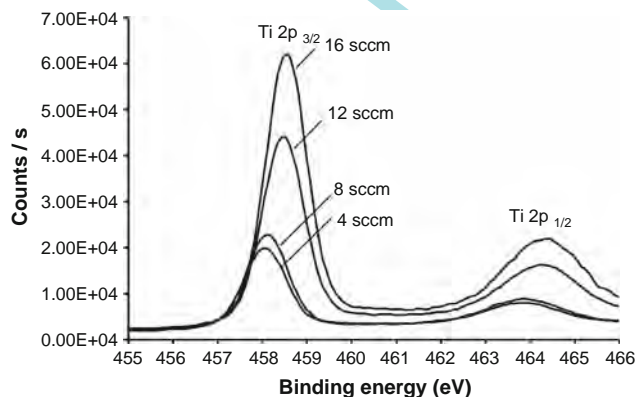
**Fig. 2: Surface morphology at different oxygen flow rates: (a) original sample; (b) 4 sccm; (c) 8 sccm; (d) 12 sccm; (e) 16 sccm**

when the thickness of the deposited films reaches 100 nm. The sputtered particles have smaller diameters and better smoothness because the oxygen flow is lower. It is clearly indicated that the diameters of the sputtered particles are enlarged and the surface roughness is increased as the oxygen flow increases, as revealed in Fig. 2. The diameters of the sputtered particles deposited at an oxygen flow of 4, 8, 12, and 16 sccm are 23.2, 28.3, 34.4, and 37.2 nm, respectively, as analyzed by Imager Software. It appears that there are some large clusters on the fiber surface, but they are the assemblies of the small grains sputtered together. The AFM software picks up the grains based on their profile boundary. The theory of mobility can be used to explain the phenomena.<sup>12</sup> The mobility is mainly influenced by the energy of the particles. The lower oxygen flow will cause the high energy of particles deposited on the substrates, and the small particles can be acquired with the high particle spread rate and low aggregation. The big particles will be obtained with high oxygen flow, low spread rate, low energy, and high aggregation.

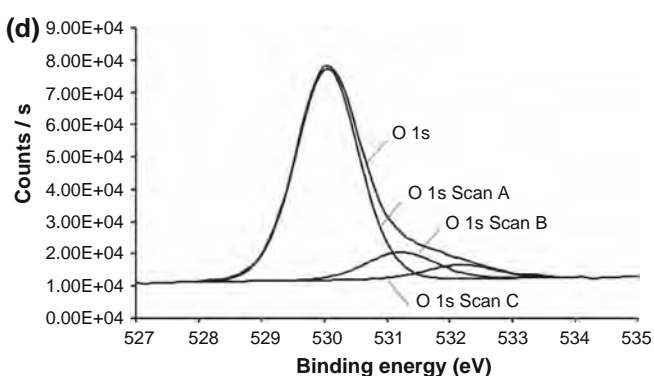
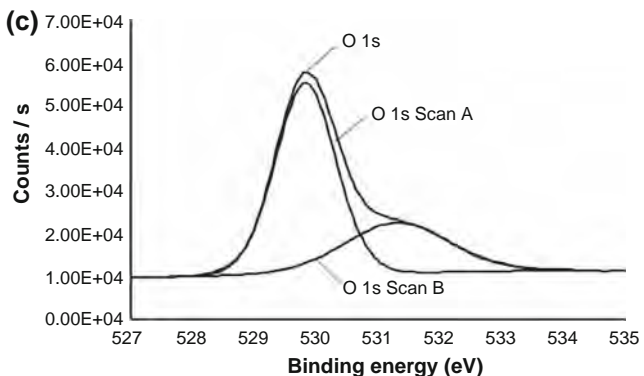
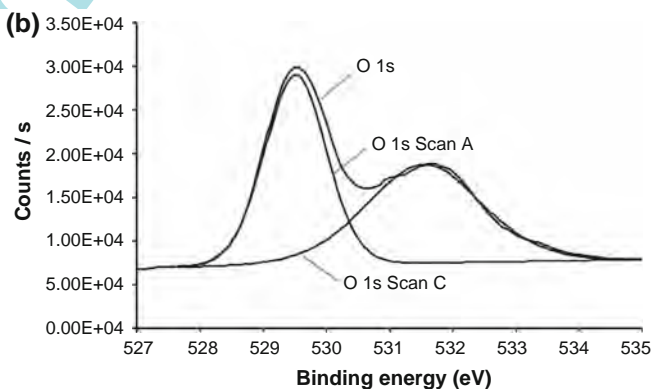
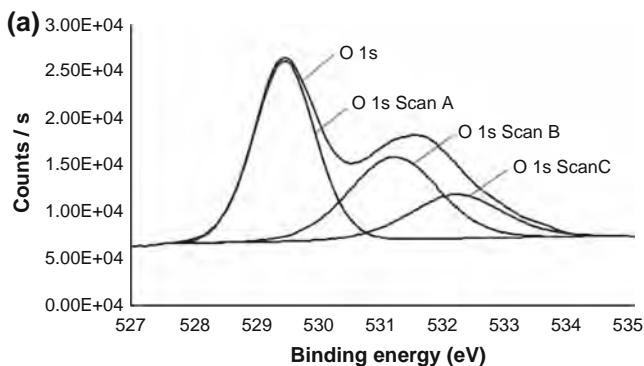
**XPS and XRD analysis**

XPS spectra of O 1s and Ti 2p of the samples deposited at an oxygen flow of 4, 8, 12, and 16 sccm are shown in Figs. 3 and 4, respectively. The O 1s spectra can be

resolved into two or three peaks corresponding to O 1s Scan A, O 1s Scan B, and O 1s Scan C, as indicated in Fig. 3. The O 1s Scan A peak located at about 529.5 eV is assigned to O<sup>2-</sup> in TiO<sub>2</sub>; O 1s Scan B peak situated at about 531.5 eV is assigned to O<sup>2-</sup> in H<sub>2</sub>O chemically and physically adsorbed on the films<sup>8</sup>; and O 1s Scan C peak located at 532.3 eV may be related to organic surface contamination. The Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> peaks are very symmetrical and the binding energies are about 458.05, 458.1, 458.45, 458.55 eV and 463.80, 463.90, 464.25, 464.35 eV, assigned to Ti<sup>4+</sup> in TiO<sub>2</sub> with



**Fig. 4: XPS spectra of Ti 2p region of samples with deposition at the oxygen flow rates of 4, 8, 12, and 16 sccm**



**Fig. 3: XPS spectra of the O 1s region of samples with deposition at the different oxygen flow rates: (a) 4 sccm; (b) 8 sccm; (c) 12 sccm; (d) 16 sccm**

a peak separation of 5.8 eV,<sup>13,14</sup> as illustrated in Fig. 4. No evident shoulder is observed at lower binding energies, which would attest to the presence of point defects due to oxygen vacancies. The magnetron-sputtered Ti atoms and titanium suboxides are easily oxidized in air to form TiO<sub>2</sub> because Ti is a hard metal with high sublimation enthalpy.<sup>14</sup> It should be noted from the Ti 2p and O 1s Scan A spectra, however, that the Ti–O binding energies shift slightly to the high region and the intensities of the Ti 2p and O 1s peaks increase with the increasing flow of oxygen. It may be inferred that the oxygen content increases and oxygen vacancies decrease with the increase of oxygen flow in the coated films.

It is also observed that the full width at half-maximum (FWHM) of Ti 2p peaks of the samples are 1.14, 1.12, 1.10, and 1.11 eV, tending to the FWHM at Ti 2p for the TiO<sub>2</sub> single crystal standard (1.1 eV).<sup>15</sup> It is indicated that the crystalline degree of TiO<sub>2</sub> grains increases with the increase of oxygen flow. The XRD patterns in Fig. 5 also confirm the effect of oxygen flow on the crystal structure of the deposited TiO<sub>2</sub> grains. The sample with a 4 sccm oxygen flow rate shows no obvious observed diffraction peaks and exhibits amorphous structure, but the sample with a 12 sccm oxygen flow rate is partially crystalline and shows the trend of anatase crystalline structure, as indicated in Fig. 5.

### Effect of oxygen flow on fabric whiteness

Hunter Whiteness (Wh) of fabric samples is shown in Fig. 6. When there is no oxygen added in the sputtering process, the substance deposited on the substrate is not the transparent and colorless nanostructured titanium dioxide particles,<sup>16</sup> but basically metal titanium atoms. The whiteness is the lowest, as shown in Fig. 5, and the surface color looks blue-purple. When a low oxygen flow is used, the sputtered titanium atoms cannot react sufficiently since the number of available oxygen molecules that can collide with the sputtered titanium atoms is very small. So the substance partially deposited

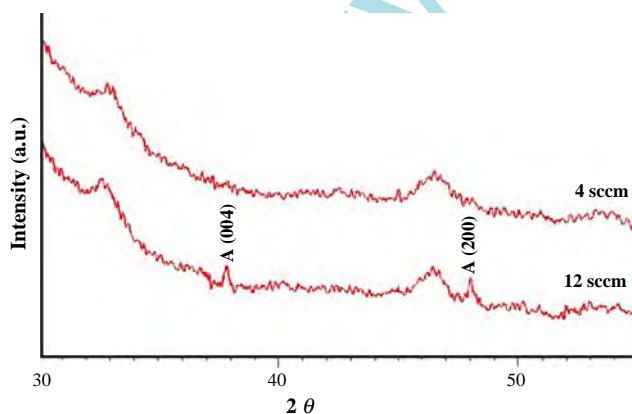


Fig. 5: XRD spectra of TiO<sub>2</sub> thin films deposited at different oxygen flow rates of 4 and 12 sccm

on the substrate surface is weak stoichiometric titanium oxide. The oxygen deficiency induces a modification of the absorption bands and, as a consequence, blue-colored samples.<sup>17</sup> It is also shown in Fig. 6 that the sample's whiteness gradually increases from about 36 up to 86% as the oxygen flow rate increases from 4 to 12 sccm. The observed sample's whiteness gradually becomes stable and close to the whiteness of the original sample when the oxygen flow rate is higher than 12 sccm. This is because the sputtered titanium atoms collide sufficiently with the oxygen molecules, synthesizing a large amount of stoichiometric compound, and the functional structural layer is almost composed of pure TiO<sub>2</sub> as oxygen flow increases. Whiteness is very close to the original sample, indicating a transparent and colorless property of TiO<sub>2</sub> film within the visible spectrum.<sup>16</sup> This also means that after the oxygen flow rate reaches 12 sccm, further increases in the oxygen flow have little effect on the film composition because the films have already been fully oxidized. The small difference in whiteness compared to the original sample is probably due to the lack of vacuum in the process, and impurity affects the whiteness.

### Optical transmittance

The optical transmittance of the polyester nonwoven deposited with TiO<sub>2</sub> films under different oxygen flows is shown in Fig. 7. It shows that the original sample has the transmittance of about 30% in the range from 400 to 850 nm, indicating a good transmittance of visible light. The Ti sputter coating without oxygen significantly alters the optical properties of polyester nonwoven, as displayed in Fig. 7. The transmittance of UV light and visible light in the range of 300–850 nm is considerably reduced to a level below 5%, revealing the light-shielding effect of the Ti coating. The UV/Vis spectra in Fig. 7 also clearly reveals the effect of oxygen flow on the transmittance of the samples deposited by the reaction of Ti with oxygen. It indicates that the optical transmittance in the range of 400–850 nm increases from about 5 to over 20% as the oxygen flow increases from 4 to 16 sccm. This is

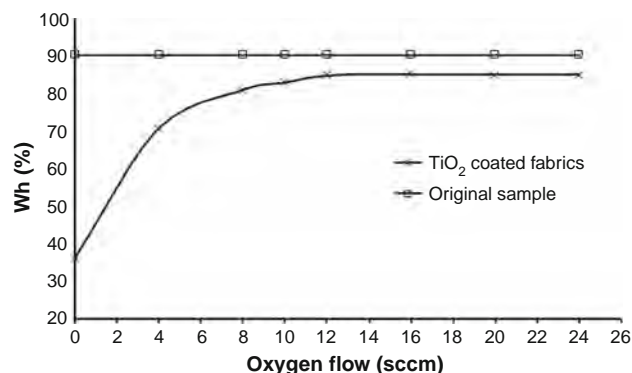


Fig. 6: Hunter Whiteness

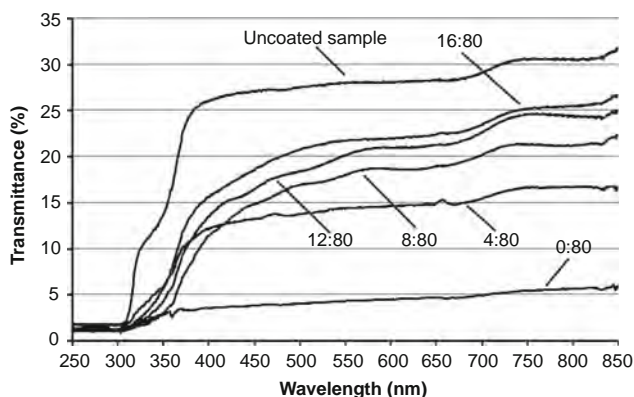


Fig. 7: Transmittance spectra

because the transmittance of polyester nonwoven with TiO<sub>2</sub> films is related to the absorption of films. And as the absorption increases, the transmittance decreases. One of the main reasons affecting the absorption of the TiO<sub>2</sub> films is the substoichiometry of oxidation. The high absorbing suboxide components can be easily formed under low oxygen flow rates, and adequate oxygen can repair oxygen vacancies. The relationship between absorption coefficient and concentration of free carriers can be written as<sup>18</sup>

$$a_f = \frac{N_e^2 \lambda_0^2}{8m * \pi^2 n c^3 \tau} \quad (1)$$

where  $a_f$  is the absorption coefficient,  $N_e$  is the concentration of free carriers,  $n$  is the refractive index,  $m^*$  is the effective mass of free carriers,  $\lambda_0$  is the absorption wavelength, and  $\tau$  is the relaxation time. Equation (1) indicates that the absorption coefficient of TiO<sub>2</sub> thin films is directly proportional to the concentration of free carriers—namely, a twofold concentration of oxygen vacancies. Hence, the substoichiometry of the TiO<sub>2</sub> films induced by insufficient oxygen content is the main cause of transmittance differences. This also coincides with the change in the samples' color as affected by oxygen flow. The transmittance of coated samples deposited under 4 sccm of oxygen is lower, which indicates that the films have more oxygen vacancies. The number of oxygen vacancies decreases and the whiteness and the transmittance of coated fabrics gradually correspondingly increases as the oxygen partial pressure increases.

Surface morphology is another main factor affecting the transmittance of TiO<sub>2</sub>-coated fabrics. The TiO<sub>2</sub> films are almost fully oxidized when the oxygen flow is over 8 sccm. The higher oxygen flow rates cause the increase in surface roughness of the deposited films, which is proved by AFM scans, and the transmittance of coated fabrics decreases.

The transmittance drops gradually from 30 to less than 3% in the range of 400–300 nm, and all samples show very low transmittance in the wavelength between 250 and 300 nm as presented in Fig. 7. It is

also observed that in the wavelength between 300 and 400 nm, the transmittance of the UV light through the samples deposited with the nanoscale TiO<sub>2</sub> is much smaller than that of the uncoated sample. This is because the nanoscale TiO<sub>2</sub> is agitated under the UV light, and the energy is used to excite the valence electrons to the conduction band. Therefore, the samples acquire antiultraviolet property after deposited with the nanoscale TiO<sub>2</sub> films.

## Conclusion

In this article, TiO<sub>2</sub> thin films have been deposited on spun-bonded polyester nonwovens under different oxygen flow. Oxygen flow was an important factor in the sputtering process. The results showed that oxygen flow could not only influence the whiteness and transmissivity of these coated fabrics, but also the morphology of fiber surface. The whiteness increased and the deposition rate decreased as the oxygen flow increased. Meanwhile, the transmission of UV radiation decreased, as the oxygen flow increased from 8 to 16 sccm. The investigation revealed that the polyester fabric deposited with nanoscale TiO<sub>2</sub> under a 12 sccm oxygen flow rate was more practical in the current process.

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