

Research Article

Preparation and Photocatalytic Activity of TiO₂-Deposited Fabrics

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Nanoscale titanium dioxide (TiO₂) photocatalytic films were deposited on the surface of polyester nonwovens by using direct current reactive magnetron sputtering. The effects of coating thickness on the surface structures and properties of TiO₂-coated fabrics were investigated by X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), and scanning electron microscope (SEM). The photocatalytic activity of the functional nonwoven fabrics was evaluated by the degradation of methylene blue. The test results proved that the grain sizes of the sputtered clusters increased and the coating layer became more compact with the increase of film thickness, but the composition of the sputtered films did not have any significant change. At the same time, the photocatalytic activity of TiO₂-coated fabrics mostly depended on the film thickness which could lead to the optimum thickness for a particular application.

1. Introduction

Polyester (PET) nonwoven materials are increasingly used in many industries ranging from wipes to filters due to their unique fibrous structures and relatively low cost [1]. Because of these increasing applications, it is desirable to produce such nonwoven materials with specially designed surface properties, such as surface abrasion, surface adsorption, and surface biocompatibility [2]. However, the surfaces of PET fibers are often not ideal for a particular application. The inert nature of PET fibers has hindered the expanding applications of PET nonwovens.

Nanoscale titanium dioxide (TiO₂), with excellent properties of photocatalysis [3], has been developed and employed to modify the surface of common nonwovens by various deposition techniques such as chemical vapor deposition, sol-gel deposition, and magnetron sputtering [4–6]. 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 weak adhesive force between the fabric and the function films also cannot satisfy the need for lengthy and repeated usage [7]. In addition, the chemical pollution caused by a wet

process is another serious disadvantage. The magnetron sputtering technique, an environmentally friendly process, has emerged as one of the most promising techniques. It permits large-scale deposition of high-quality films at high deposition rates, and metal target can be used for fabrication of large-scale uniform coatings with a high or low density at a relatively low deposition temperature [8]. It is especially important for thermal sensitive substrates such as PET materials, which cannot endure high temperatures.

It was reported that the structure and properties of TiO₂ films prepared by magnetron sputtering can be modified and controlled by process parameters such as coating thickness, sputtering gas Ar:O₂ ratio, sputtering power, and sputtering pressure [9]. Therefore, the analysis of the coating microstructure with different thickness and its influence on the photocatalytic activity of the TiO₂-coated fabrics is an interesting subject to study.

In this study, nanoscale TiO₂ films were deposited on the surface of PET nonwovens by using direct current (DC) reactive magnetron sputtering at room temperature. In order to correlate the effect of the thickness on the coating structure and photocatalytic properties, three samples with different thicknesses (20, 60, and 100 nm) were produced. X-ray photoelectron spectroscopy (XPS), atomic

force microscopy (AFM), scanning electron microscope (SEM), and photocatalytic tests were employed to study surface chemical composition, morphology, microstructure, and photocatalytic activity of the materials, respectively.

2. Experimental

2.1. Materials Preparation. Commercial spunbonded polyester nonwovens (100 g/m^2) were used as the substrate in this study. It was first washed with ethanol and distilled water before sputter coatings and then dried in an oven at 40°C for 24 h. The dried samples were further cut into a size of $6 \times 6 \text{ cm}$ for sputtering.

2.2. Sputter Coating. Sputtering coatings of TiO_2 were performed onto the flexible nonwovens in a magnetron sputter coating system (Shenyang Juzhi Co., Ltd.). A high-purity titanium (Ti) target (diameter: 50 mm; purity: 99.99%) was mounted on the cathode. The target was placed below the substrate holder at a distance of 60 mm. During sputtering, the substrate holder was kept rotating at a speed of 100 rpm to ensure the uniform deposition on the surface of the nonwoven substrate. The sputter chamber was first pumped to a base pressure of $1.5 \times 10^{-3} \text{ Pa}$ before introducing bombardment gas (argon gas 99.999%) and reacting gas (oxygen gas 99.999%). Based on the previous investigation [10], argon and oxygen gas-flow rates were set at 80 and 12 mL/min, respectively. Coating was performed at pressure of 0.5 Pa with a power of 50 W. The thickness of the deposited layer was examined by a quartal crystal detector FTM-V (Shanghai, China) during the sputtering process.

2.3. XPS Analysis. X-ray photoelectron spectroscopy (XPS), a type of Thermo ESCALAB 250 equipment (USA), was used to analyze the elemental composition of the functional fabrics. Measurements were run at a base pressure of 10^{-6} Pa using an Al $K\alpha$ ($h\nu = 1486.6 \text{ eV}$) source and the source was operated at a power of 225 W. All XPS spectra were calibrated with the C 1s peak at 284.6 eV. The spectra were recorded in CAE mode (constant analyzer energy) with analyzer pass energies of 20 eV.

2.4. Surface Morphology by AFM. Morphology and distribution of nanoscale TiO_2 on the fibre surfaces were examined using Benyuan CSPM3300 Atomic Force Microscope (Guangzhou, China). Scanning was carried out in contact mode AFM with a silicon cantilever. All images were obtained at ambient conditions and analyzed by the Imager 4.40 Software equipped with CSPM3300 AFM.

2.5. SEM Analysis. A SEM instrument (S-4800, HITACHI, Japan) operated at 5 kV was used to observe the cross-section structure and analyze the growth model of TiO_2 films. Samples were coated with platinum in order to prevent charge buildup during SEM observations.

2.6. Photocatalytic Activity. The photocatalytic activity of the prepared TiO_2 -coated nonwovens was tested by using

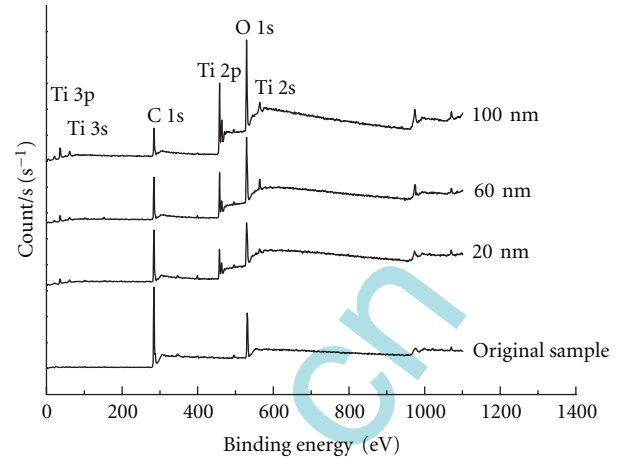


FIGURE 1: XPS survey spectra of samples.

decomposition of methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}-\text{Cl}-3\text{H}_2\text{O}$) under UV irradiation of ZXC II ultraviolet lamp (245 nm, 30 W, Shanghai, China) [11, 12]. This was done in a lightproof container in order to avoid possible complicating effects of illumination. Test samples with a certain area were dipped into an aqueous MB solution with a concentration of 5 mg/L and pH 6.5. The absorbance of the solution was measured every 30 min by 721 spectrophotometer (Shanghai, China) at a wavelength of 665 nm [13].

The decolorizing ratio A_t was calculated using the following equation [14]:

$$A_t = \frac{(C_{0t} - C_t)}{C_{0t}} \times 100\%, \quad (1)$$

where C_{0t} and C_t represent the absorbency of the MB solution for the uncoated and TiO_2 -coated samples in t minutes, respectively. The experiments were repeated for three times; herein, the average values were reported.

3. Results and Discussion

3.1. XPS Analyses. XPS analysis provides information about film composition and chemical state.

Figure 1 shows the XPS survey spectra of uncoated and coated TiO_2 PET nonwovens. Photoelectron peaks for C and O are shown in uncoated samples. Presence of peaks, binding energy of C 1s (285.0 eV) and O 1s (531.0 eV), have been related to organic surface of polyester [15]. Ti photoelectron peaks were observed in XPS survey spectra of coated samples, whereas there was no Ti photoelectron peak in uncoated samples. Peak intensity of Ti and O is obviously increased and C is significantly reduced with the increase in coating thickness. Moreover, peak-binding energies for Ti 2p_{3/2} and Ti 2p_{1/2} peaks of 20 nm, 60 nm, and 100 nm coated films are all about 458.2 eV and 464.0 eV, assigned to Ti^{4+} in TiO_2 with a peak separation of 5.8 eV [16]. It indicates that the increase in coating thickness seems not to have any significant influence on the composition of the sputtered TiO_2 on the PET nonwoven fabric surface.

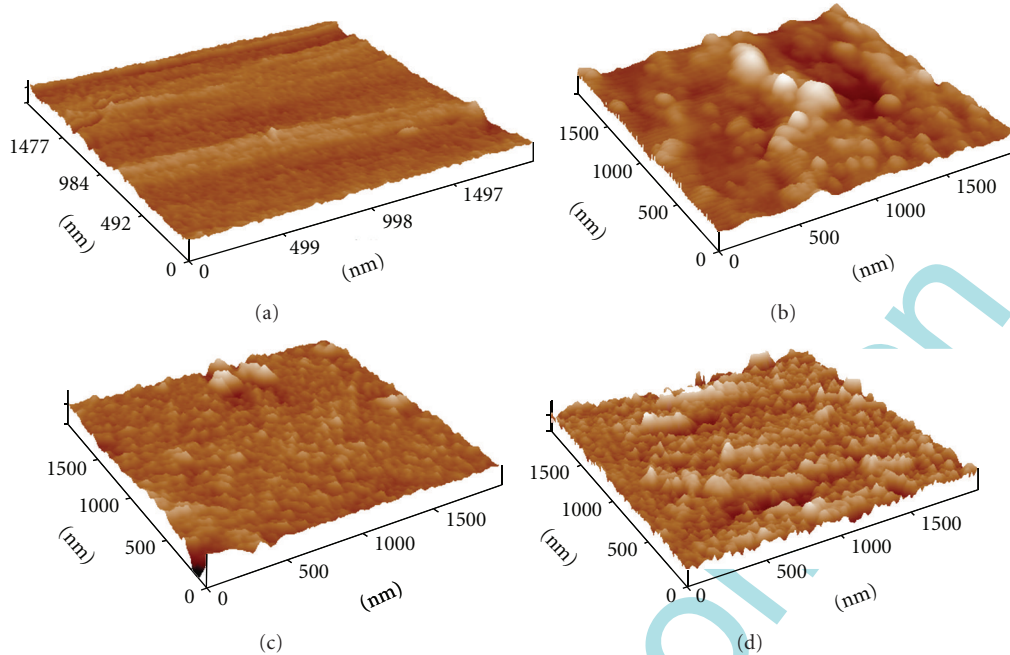


FIGURE 2: AFM images of uncoated and coated PET fiber surface at the scan size of 2000×2000 nm (a) uncoated, (b) 20 nm, (c) 60 nm, and (d) 100 nm.

3.2. Comparison in Surface Morphology. AFM images reveal the change in the surface microstructure of the polyester fibers after the TiO_2 coating, as shown in Figure 2.

It is clearly shown that uncoated PET fiber has a relatively smooth surface with some microdefects such as microcracks and point defects on its surface (Figure 2(a)). They might have been formed during the manufacturing process. The sputter coatings of TiO_2 significantly altered the surface characteristics of the PET fibers (Figures 2(b)–2(d)). TiO_2 clusters scattered on the PET fiber surface after 20 nm coating, but the clusters have variable sizes from less than 20 nm to over 50 nm (Figure 2(b)). Intrinsic defects on PET surface may be responsible for the rough and loose structure of coating surface, because sputtering particles are preferential nucleation and growth at the defect location of substrate surface in the initial film growth stage [17]. As the coating thickness is increased to 60 nm, TiO_2 clusters coated on the PET fiber surface have coalesced and looked more even. Average size of the sputtered TiO_2 cluster is about 31.5 nm and compact coating is formed (Figure 2(c)). AFM image in Figure 2(d) indicates that the increased coating thickness from 60 nm to 100 nm leads to more compact distribution of the TiO_2 clusters on the fiber surface. The growth of the TiO_2 clusters is also observed and the size of the sputtered TiO_2 cluster is increased to 35.1 nm. This is attributed to the collision of the sputtered TiO_2 grains. The increase in sputter coating thickness leads to the growth of the TiO_2 clusters and more compact deposition.

3.3. Microstructure of Film Cross-Section. TiO_2 -coated PET nonwoven with 100 nm thickness was broken for the SEM imaging. Broken section image of TiO_2 films provided

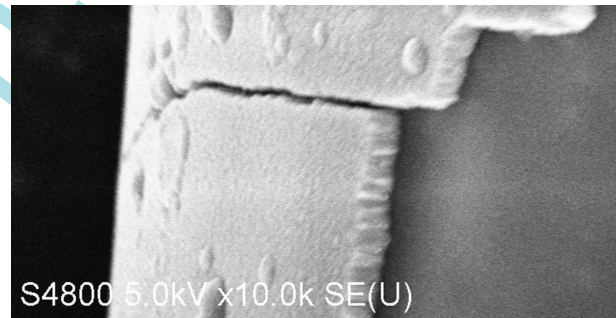


FIGURE 3: Section image of 100 nm thick film.

a more detailed picture of the microstructure and their evolution from the interface to the outer surface, as shown in Figure 3. It clearly reveals that TiO_2 layers exhibit a columnar microstructure with the columns extending throughout the film thickness. This also implies that the growth of TiO_2 on PET fiber surface belongs to the island growth mode (Volmer-Weber mode) including nucleation, island growth, impingement and coalescence of islands, and development of a continuous structure as well as film growth [18]. This microstructure might originate from the low adatom mobility of the sputtered particles on the low-temperature substrate surface [19].

3.4. Photocatalytic Activity. The photocatalytic activity of TiO_2 -coated fabrics was evaluated by photocatalytic decomposition of MB in its aqueous solution. Figure 4 shows the absorbency of MB aqueous solutions tested with original and TiO_2 -coated fabrics under different film thickness. The

TABLE 1: Decolorizing ratios of MB aqueous solutions tested with uncoated and TiO₂-coated fabrics.

Film thickness	Original sample	20 nm	60 nm	100 nm
Absorbance C_{240}	0.340	0.220	0.135	0.130
Decolorizing ratio A_{240} (%)	—	35.29	60.29	61.76

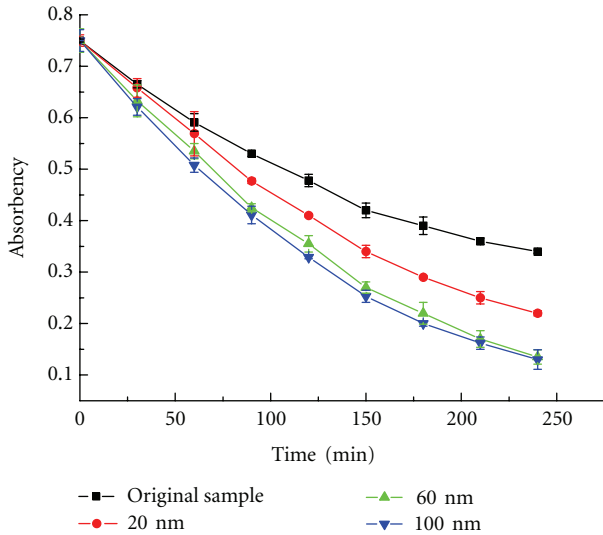


FIGURE 4: Effects of film thickness on the absorbency curve of methylene blue solution.

average results of three absorbency measurements were reproducible with standard deviation typically less than $\pm 3.0\%$. The decolorizing ratios calculated from (1) are shown in Table 1.

In photocatalytic tests, it was found that when fabric samples with a certain area were, respectively, immersed into the same quantitative MB aqueous solution, samples would turn into blue due to its adsorption of MB molecules. And with concentration decreasing, the color of MB solution faded and absorbency decreased. The absorbency of MB aqueous solution with the original fabric would tend to stabilize after a period of time because of the surface adsorption/desorption equilibrium [20], but there is a slightly downward trend shown in Figure 4. It may be due to the chemical decomposition of MB induced by UV radiant energy [21]. Under the same test conditions, significant decrease in the absorbency is observed for the 20 nm coated fabric compared to the uncoated fabric. This indicated that the TiO₂ film deposited on the nonwoven surface exhibits decomposition ability of methylene blue. The decolorization ratio $A_{240\text{min}}$ was 35.29% shown in Table 1. When the coating thickness increased to 60 nm, $A_{240\text{min}}$ increased to 60.29%, indicating excellent photocatalytic properties. It then increased slowly to 61.76% when the coating thickness is increased to 100 nm. The change of decolorization ratio with different film thicknesses can contribute to the evolution of the film morphology. Photocatalytic processes

are chemical reactions on the surface. Thus, the photocatalytic activity of final TiO₂ film depends strongly on their structures, surface morphology, and total surface area. The increase of surface area should improve the efficiency of the process because it implicates larger contact surfaces exposed to the pollutants [22]. TiO₂ films of 60 nm thickness are more uninterrupted, even than 20 nm films, more even surface structure and smaller particle size contribute to the increase in surface area of the deposited films. This was proved by AFM scans and photocatalytic activity of coated fabrics. When film thickness is increased to 100 nm, the surface roughness and compactness are enhanced, but the surface morphology and particle size only change little, resulting in slight increase in surface area and photocatalytic activity.

Another factor that should have been noted is the thickness of the film. It has effect on both the transmission of UV light in the film and the transportation distance that the electrons and holes produced under UV irradiation need to travel to reach the surface of the film [23]. When the film thickness is relatively thin, the number of photoexcited electron-hole pair grows with the increase of film thickness and photocatalytic activity improved. However, when the film keeps growing thicker, the number of photoexcited electron-hole pair that could move to the photocatalyst surface and participate in the desired photocatalysis reaction remains stable. So, when the film thickness grows to a certain range, the degradation rate would not change evidently with the increase of the film thickness.

4. Conclusions

This study has compared the effect of film thickness on grain growth and microstructure and chemical composition as well as photocatalytic activity of TiO₂ coatings deposited by DC magnetron sputtering at room temperature. The sputter coatings formed nanoscale clusters scattered or covered on the fiber surface subject to the film thickness. Film thickness affected the grain size of the TiO₂ clusters. With increase in film thickness, grain size of the sputtered clusters increased and coating layer became more compact, but the composition of the sputtered films did not have any significant change. The photocatalytic test results proved that film thickness plays an important role in the photocatalytic activity of the TiO₂-coated fabric. It is believed that there existed a critical thickness related to the photocatalytic activity of TiO₂ thin films. When the film thickness is below the critical thickness, the photocatalytic activity of TiO₂ thin films increases with the thickness increasing. But once the film thickness exceeds the critical thickness, the film thickness has little influence on the photocatalytic activity of the TiO₂ thin films.

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