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Electrical and optical properties of polyester fabric coated with Ag/TiO_2 composite films by magnetron sputtering

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Abstract

Silver/titanium dioxide (Ag/TiO_2) composite films were successfully deposited on polyester fabric by using direct current (DC) magnetron sputtering and radiofrequency (RF) magnetron reaction sputtering techniques with pure Ag and Ti targets. Atomic force microscope and X-ray photoelectron spectroscopy were used to examine the structure and composition of Ag/TiO_2 composite films. Anti-ultraviolet properties and antistatic properties of the Ag/TiO_2 coated fabric were investigated, and structural color of the Ag/TiO_2 coated fabric was also analyzed. The experimental results showed that the composite films deposited on textile substrates were even and dense. It was also found that Ag in Ag/TiO_2 composite films was elemental silver, but Ti in Ag/TiO_2 composite films was completely oxidized, and existed in TiO_2 form. Compared with the original fabric samples, anti-ultraviolet properties and antistatic properties of the fabrics deposited with Ag/TiO_2 composite films were improved significantly; meanwhile, different structural colors of the coated fabrics were generated.

Keywords

silver/titanium dioxide composite film, magnetron sputtering, electrical properties, optical properties, polyester fabric

With the development of science and technology and the improvements in living standards, people are paying increasing attention to the demand for better properties of functional textiles, such as safety, comfort, etc. Multifunctional finishing is the technology that blends two or more functional properties in a textile material to improve product quality and add value.[1] In order to achieve the goal of multifunctional properties, various advanced and innovative technologies have been applied to functional textiles.[2–4] In recent years, methods of functional finishing have mainly included the use of functional finishing agents, new functional fibers, and the magnetron sputtering technique, as well as some other methods.

Magnetron sputtering technology possesses many advantages, such as a uniform film thickness, many sputtering materials, strong binding strength between deposited film and substrate, environmental protection, and so on. Magnetron sputtering technology can prepare super-hard films, corrosion and friction resistant films, superconducting films, magnetic films, optical films, and other special films. It has been considered as a very effective deposition method of thin film.[5–13]

In this work, metallic silver (Ag) and titanium dioxide (TiO_2) films were deposited on a textile substrate by magnetron sputtering technology. Silver has excellent electrical, optical, and chemical properties, whereas titanium dioxide has high photocatalytic activity, good chemical stability, and environmental friendliness.[14,15]

The silver film was prepared on the textile substrate by magnetron sputtering and then the titanium dioxide

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film was further deposited on the Ag-coated textile substrate by magnetron sputtering. Meanwhile, due to the interference effect of thin films, structural color was generated on the surface of the textile substrate. The structure and composition of the composite films were analyzed by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Anti-ultraviolet properties and antistatic properties of samples were tested, and structural colors of samples were also analyzed by Color-Eye 7000A GretagMacbeth.

Experimental details

Materials

The substrate material consisted of white plain woven fabric, 100% polyester.

The fabrics were cut into 5 cm diameter circular samples, and washed in the acetone solution, then vibrated 30 min by KQ-50B type ultrasonic cleaners to remove impurities on the surface of the fabrics. Then they were repeatedly washed with deionized water and put into an oven at 60°C to dry.

Target materials used were 99.99% silver (Ag) and 99.99% titanium (Ti), respectively.

Deposition of Ag/TiO2 composite films

The sputtering unit (JPG-450 type) was used in the experiment. The preparation process of Ag/TiO_2 composite films was as follows: silver thin film was first deposited on the base fabric using silver target by direct current (DC) magnetron sputtering, then, titanium dioxide thin film was further deposited on the silver coated fabric using titanium target by radiofrequency (RF) magnetron sputtering. Silver thin film is easily oxidized and tarnished in the atmospheric environment.[16,17] In our experimental trials, it was found that the silver film oxidized in high vacuum oxygen environment when titanium target was reactively sputtered on the silver film. The color of fabric samples looked black, and it would not generate any structural colors. Accordingly, we tried to use a layer of titanium film to protect the coated silver film, and then deposit the TiO_2 film using reaction sputtering. Due to the protection by titanium film, silver film would not be oxidized, and structural color could be generated. Therefore, the preparation process of Ag/TiO_2 composite films was set. The silver film was first prepared on the base fabric using silver target by DC magnetron sputtering, then, the titanium film was prepared on the silver coated fabric using titanium target also by DC magnetron sputtering. Finally, the titanium dioxide films with different thicknesses were prepared on the titanium films using titanium target by RF magnetron reaction sputtering.

The silver sputtering was performed using argon (Ar) as sputtering gas with a gas flow rate of 20 mL/min, a base pressure of 1.5×10^{-3} Pa, a rotating speed of 10 r/min, a working gas pressure of 0.8 Pa, a sputtering power of 70 W, and for a sputtering time of 10 min.

The titanium film was deposited also using argon (Ar) as sputtering gas with a gas flow rate of 50 mL/min, a base pressure of 1.5×10^{-3} Pa, a rotating speed of 10 r/min, a working gas pressure of 0.8 Pa, a sputtering power of 100 W, and for a sputtering time of 10 min.

In the preparation of titanium dioxide films, argon (Ar) was also used as the sputtering gas and oxygen (O_2) was used as reaction gas. Gas flow rates of Ar and O_2 were set as 20 mL/min and 10 mL/min, respectively. Other processing parameters included a base pressure of 1.5×10^{-3} Pa, a rotating speed of 10 r/min, and a working gas pressure of 0.8 Pa. The sputtering power was set as 476 W, 582 W, and 627 W, respectively. The sputtering time was set as 30 min, 40 min, and 60 min.

For all of the samples, the deposition of silver films and titanium films was conducted under fixed conditions, but the preparation of titanium dioxide films was performed under different conditions, as detailed in Table 1.

Characterizations

The chemical composition and valence state of the deposited composite films on the textile substrate were analyzed by XPS (Escalab 250Xi, England). Monochromatic Al K_α radiation was used as the X-ray source.

The surface morphologies of composite films on the textile substrate were examined by AFM (CSPM4000,

Table 1. Sample details

Experimental sample No.	Sputtering power (W)	Sputtering time (min)
1#	476	30
2#	476	40
3#	476	60
4#	582	40
5#	582	60
6#	627	30
7#	627	60

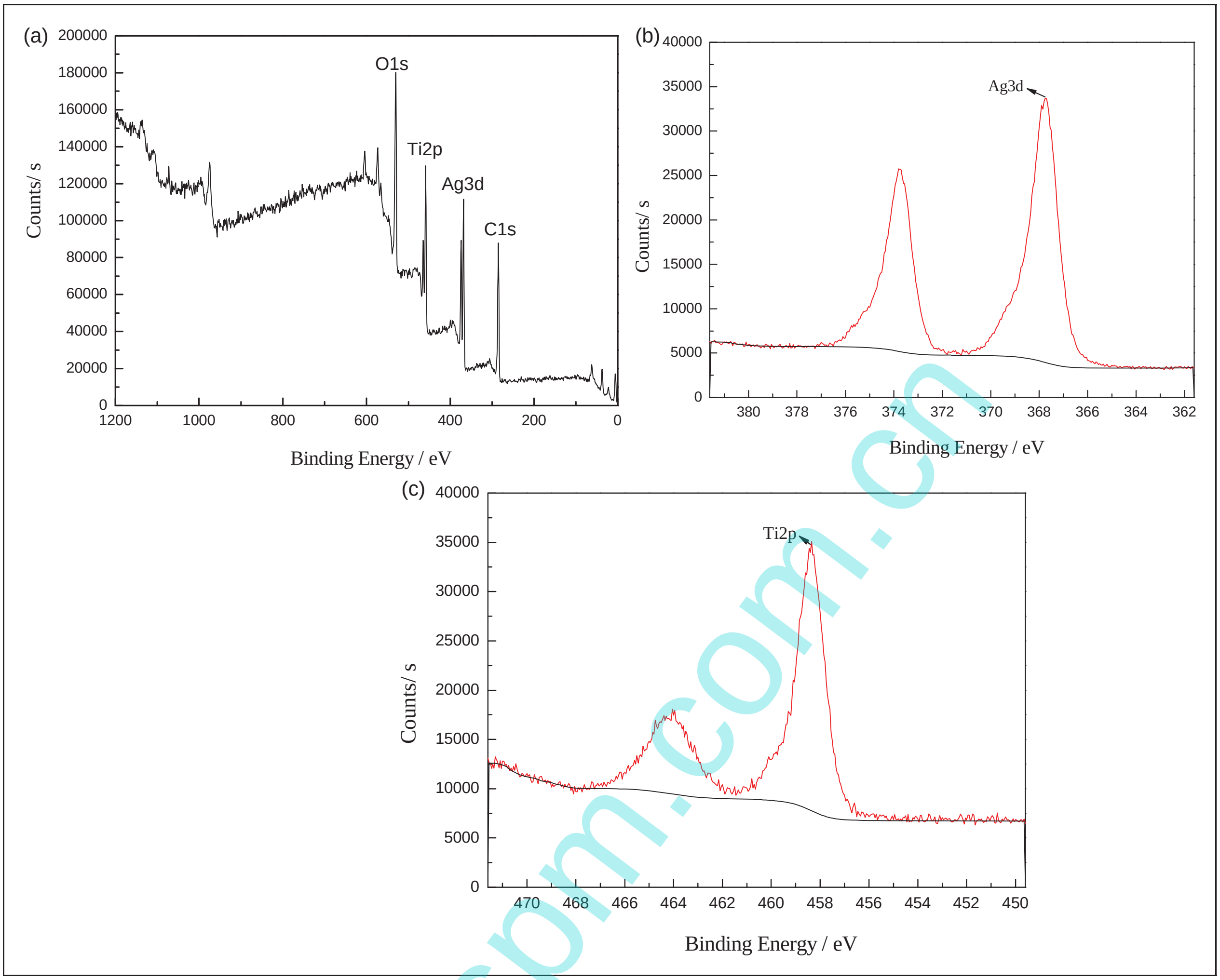

Figure 1. X-ray photoelectron spectroscopy of Ag/TiO_2 composite films: (a) full spectrum; (b) Ag 3d peak; (c) Ti 2p peak.

Guangzhou). The tapping mode was used with a horizontal resolution of 0.1 nm and a vertical resolution of 0.01 nm. The scanning frequency was 1.0 Hz and the scanning size was 5000 nm × 5000 nm.

According to GB/T18830-2009, anti-ultraviolet properties of the coated fabrics were tested by ultraviolet transmittance analyzer (UV-1000F, Lapsphere, America). The evaluation indexes of anti-ultraviolet properties included solar UV-A spectral transmittance (*T*(UVA)), solar UV-B spectral transmittance (*T*(UVB)), and ultraviolet protection factor (UPF). Each sample was tested five times, and the average values were reported.

According to GB/T12703.1-2008, antistatic properties of the coated fabrics were tested by static honestmeter (H0110/V1, Shishido Electrostatic Ltd, Japan). The samples were stored in controlled atmosphere conditions (temperature = 20 ± 2°C and humidity = 35 ± 5%) of experimental environment for 24 h to humidify before testing. Applied voltage was 10 kV. The evaluation indexes of anti-ultraviolet properties were static half period and instantaneous electrostatic voltage. Each sample was tested six times, and the average values were used.

The color and lightness of the coated fabrics were tested using a spectrophotometer (Color-Eye 7000A, GretagMacbeth, America) with a light source of D65 according to the 1931 norm of the Commission International de l'Eclairage (CIE). The angle of incidence was 10°. Color properties of the samples can be described using the L*, a*, b* scale. Each sample was tested four times, and the average values were used. The color strength values (K/S values) were calculated with the same apparatus.

Results and discussion

Composition analysis and valence state of composite films

Because of magnetron reaction sputtering, the valence states of Ti and Ag were the most critical. By comparison, the experimental results of samples 1#–7# were

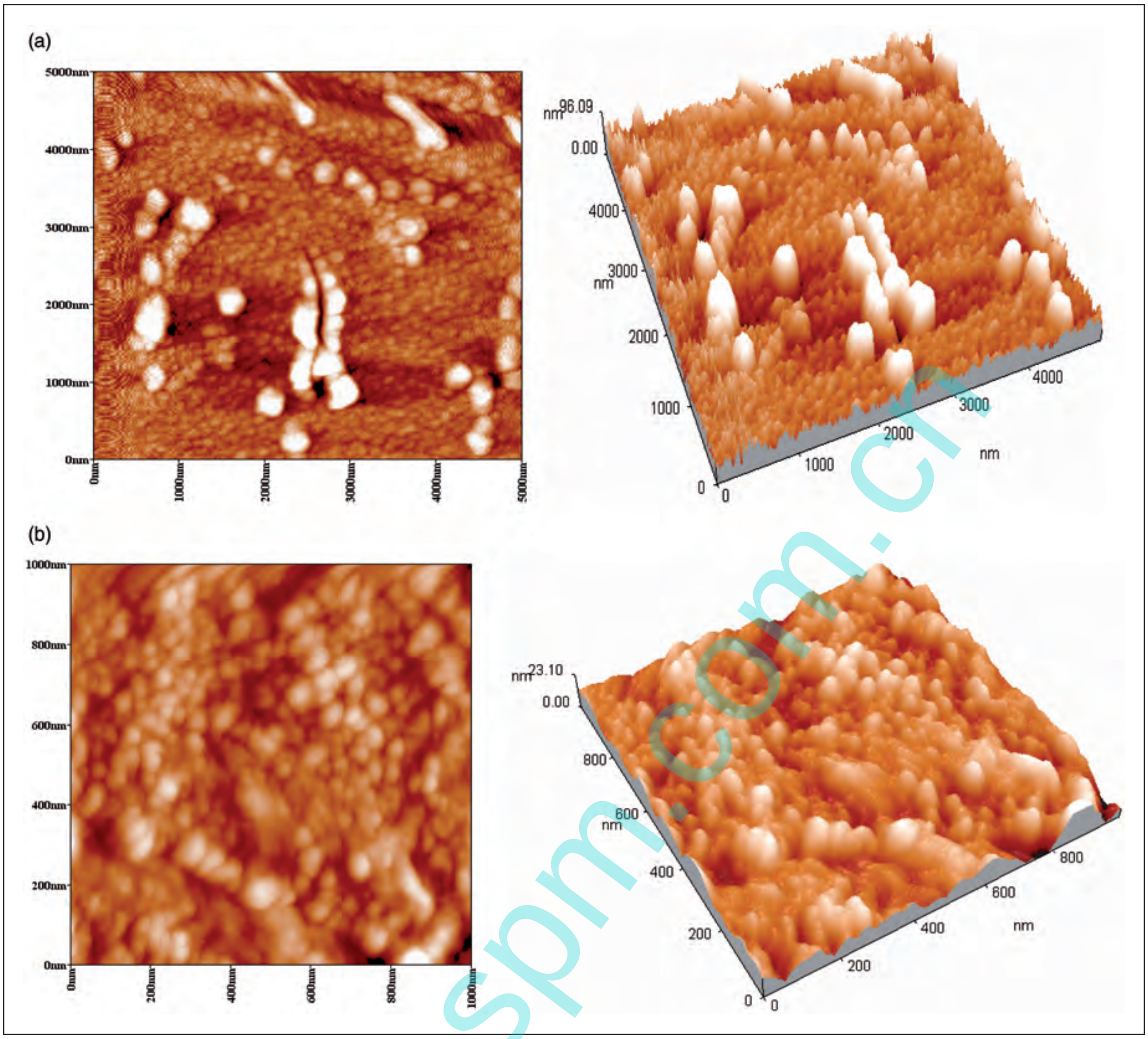

Figure 2. AFM images of (a) the Ag film and (b) of the Ag/TiO_2 composite films for sample 1#.

Table 2. Experimental results of anti-ultraviolet properties

	T(UVA) (%)		T(UVB) (%)		UPF	
Samples	Average value	Standard deviation	Average value	Standard deviation	Average value	Standard deviation
Original fabric	38.35	0.46	5.30	0.14	9.62	0.86
Fabric coated with silver film	5.22	0.23	4.20	0.13	23.01	2.34
Fabric coated with titanium dioxide film	27.12	0.16	4.46	0.22	14.68	1.06
1#	3.88	0.03	3.62	0.10	27.36	1.18
2#	3.82	0.14	3.57	0.05	27.74	0.76
3#	3.76	0.22	3.59	0.09	27.74	0.54
4#	4.23	0.04	3.99	0.12	24.86	1.58
5#	3.72	0.11	3.45	0.11	28.70	2.29
6#	4.06	0.20	3.77	0.07	26.23	0.76
7#	3.52	0.13	3.33	0.08	29.88	1.75

Table 3. Experimental results of antistatic properties.

	Static half period (s)		Instantaneous electrostatic voltage (V)	
Samples	Average value	Standard deviation	Average value	Standard deviation
Original fabric	>180		650	10.95
Fabric coated with silver films	2.69	0.32	420	11.85
Fabric coated with titanium dioxide films	97.70	1.54	590	10.23
1#	34.29	0.75	560	5.77
2#	28.71	0.54	500	9.76
3#	35.87	0.68	570	7.99
4#	3.83	0.42	490	0
5#	4.54	0.38	490	7.11
6#	5.18	0.63	460	9.87
7#	12.99	1.02	500	9.21

Table 4. Technical requirements of static half period

Grade	Requirements
A	$\leq$2.0 s
B	$\leq$5.0 s
C	$\leq$15.0 s

similar. For all of the samples, except for the sputtering time and the sputtering power, the other sputtering parameters were the same; therefore, sample 7# was used as a representative in XPS analysis.

The photoelectron spectra of the 7# sample were obtained by XPS, and the full spectrum, Ag 3d peaks, and Ti 2p peaks are displayed in Figure 1.

In Figure 1 it can be seen that the full spectrum characteristic peaks for all elements of interest, and they are Ti, Ag, O, and C. Because the binding energy of Ag along with the valence state change was very small, the valence state analysis of Ag was relatively difficult. In Figure 1(b), the position of the Ag 3d peak was 367.75 eV and the result was consistent with the binding energy of simple atomic Ag. At the same time, using a metal target under the condition of vacuum sputtering, it can be sure that Ag in Ag/TiO$_2$ composite films is elemental silver. From the binding energy of Ti analysis, it can be seen that the position of the Ti 2p peak was 458.36 eV. With refer to the work of He et al.,[18] this means that Ti was completely oxidized and existed in TiO$_2$ form.

Surface morphology

Figure 2 shows AFM images of the Ag film and Ag/TiO$_2$ composite films for the 1# sample.

In Figure 2, the surface of Ag film deposited on the textiles substrate was relatively dense and uniform. The average particle diameter of the Ag film was about 57.6 nm, and the surface average roughness of the Ag film was 24.6 nm. Compared with the Ag film, the surface of the Ag/TiO$_2$ composite films for the 1# sample was relative rough and dense. The average particle diameter of the Ag/TiO$_2$ composite films for the 1# sample was about 32.8 nm, and the surface average roughness was 51.1 nm.

Anti-ultraviolet properties

Table 2 shows the anti-ultraviolet properties of different samples, where T(UVA) and T(UVB) represent solar UV-A spectral transmittance and solar UV-B spectral transmittance. The smaller the transmittance value, the higher the anti-ultraviolet properties. Conversely, the greater the UPF, the higher the anti-ultraviolet properties. According to GB/T18830-2009, if the values of T(UVA) are less than 5%, and the values of UPF are greater than 40, this means that the sample is a ultraviolet protection fabric.

From Table 2 it can be seen that the anti-ultraviolet properties of the original sample were the lowest, followed by sample coated with titanium dioxide film. The anti-ultraviolet properties of the samples coated with Ag/TiO$_2$ composite films were close to those of the sample coated with silver films. The values of T(UVA) and T(UVB) for samples 1#–7# were less than 5%, and the values of UPF were close to 30. Because the original fabric was very thin, the values of UPF could not achieve 40. Nevertheless, compared with the original samples, the anti-ultraviolet properties of the fabric deposited with Ag/TiO$_2$ composite films were improved greatly.

Antistatic properties

Table 3 shows the static half period and the instantaneous electrostatic voltage values of the samples. Higher static half period values mean higher antistatic properties and lower ones mean lower antistatic properties. For the values of the instantaneous electrostatic voltage, the trend is the opposite. As shown in Table 3, it is observed that the antistatic properties of the original fabric were the lowest, and the antistatic properties of the fabric coated with silver film were the highest because of the electrical conductivity of metal film. Titanium dioxide film is a semiconductor materiel; hence, the antistatic properties of the fabric coated

Figure 3. Coloring of fabric coated with Ag/TiO_2 composite films prepared by magnetron sputtering.

Table 5. L*a*b* scale values of Ag/TiO_2 composite films

	ΔL*		Δa*		Δb*	
Samples	Average value	Standard deviation	Average value	Standard deviation	Average value	Standard deviation
1#	−18.440	0.154	16.961	0.143	20.477	0.088
2#	−32.992	0.206	14.134	0.098	−12.959	0.201
3#	−25.414	0.095	5.701	0.067	14.523	0.145
4#	−30.586	0.047	10.894	0.024	3.417	0.206
5#	−33.634	0.083	7.546	0.123	−3.218	0.114
6#	−24.144	0.147	7.495	0.108	14.228	0.123
7#	−35.105	0.125	0.085	0.113	−1.588	0.109

with titanium dioxide film were higher than the original fabric, and lower than the fabric coated with silver film. The antistatic properties of the fabrics coated with Ag/TiO_2 composite films were much higher than the fabric coated with titanium dioxide film, and little lower than the fabric coated with silver film because of the electrical conductivity of silver film.

According to GB/T12703.1-2008, technical requirements of static half period are shown in Table 4.

From Tables 3 and 4 it can be seen that the antistatic properties of the 4# and 5# samples met the technical requirements of grade B, 6# and 7# samples met the technical requirements of grade C, and other samples were below grade C. However, the antistatic properties of the coated samples were much higher than the original sample and the samples coated with titanium dioxide films. This indicates that the antistatic properties of the fabric coated with Ag/TiO_2 composite films are increased greatly compared with the original samples.

Structural color analysis

According to the principle of thin-film interference,[19] using the reflection of silver metal film and the transmission and reflection of transparent metal oxide TiO_2 film, the optical path difference was formed, and the structural colors were created on the polyester fabrics coated with Ag/TiO_2 composite films.

The structural colors of different samples are representative colors after processing, as shown in Figure 3. The colors of samples 1#–7# were, respectively, dark yellow, blue, blackish green, yellow, dark blue, reddish brown, and black blue. The observed colors in Figure 3 could be expressed with the maximum absorption wavelength in the visual wavelength range since the peak position determined the color of composite films.

Figure 4 shows the K/S value curves of different samples. The K/S value is a constant, in which K represents an absorption coefficient and S represents a scattering coefficient. The K/S value exhibits a linear relationship with the dyeing depth.

From Figure 4 it can be seen that the positions of absorption peaks for samples 1#–7# were observed at wavelengths of 470 nm, 460 nm, 530 nm, 490 nm, 520 nm, 470 nm, and 590 nm, respectively, corresponding to the colors of dark yellow, blue, blackish green, yellow, dark blue, reddish brown, and black blue. This is consistent with the results shown in Figure 3. The K/S values of samples 1#–7# at the peaks were 4.691, 5.478, 6.234, 6.447, 5.669, 5.617, and 5.938. The larger the K/S value, the deeper the sample color. The K/S values of samples 1#–7# indicate that the color of all the samples tended to be dark.

The L*a*b* values for the samples are shown in Table 5. L* is an indication of the lightness, the a* axis indicates red (positive) to green (negative), and b* indicates yellow (positive) to blue (negative).

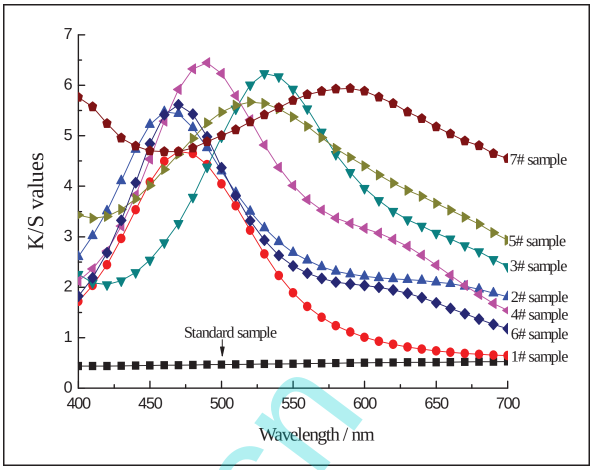

Figure 4. Comparison of K/S values for Ag/TiO_2 composite films.

In Table 5, Δ refers to values of samples minus values of standard samples, and the standard sample is the original sample. From Table 5, it can be seen that the values of ΔL* for samples 1#–7# were negative, indicating that the lightness of the samples had decreased and that they were dark. The values of Δa* for samples 1#–6# samples were positive, and the bigger the values indicated that the colors of samples were closer to red. The values of Δa* for sample 7# was close to zero, indicating that the color of sample was close to green. The values of Δb* for samples 1#, 3#, 4#, and 6# were positive, and the bigger the values indicated that the colors of samples were closer to yellow. The values of Δb* for samples 2#, 5#, and 7# were negative, and the bigger the values indicated that the colors of samples were closer to blue. Analysis of these results indicates that the measured chromaticity values for samples 1#–7# correspond with the results shown in Figures 3 and 4.

Conclusions

Ag/TiO_2 composite films were successfully deposited on polyester fabric using DC magnetron sputtering and RF magnetron reaction sputtering techniques with pure Ag and Ti targets. Ag/TiO_2 composite films deposited on textile substrates were even and dense. According to XPS analysis, in Ag/TiO_2 composite films, Ag was elemental silver, whereas Ti was completely oxidized and existed in TiO_2 form. Compared with the original fabric, anti-ultraviolet properties and antistatic properties of the fabric coated with Ag/TiO_2 composite films were improved greatly. Meanwhile, different structural colors of the fabric coated with Ag/TiO_2 composite films were generated. The colors of samples 1#7# were, respectively, dark yellow, blue, blackish green, yellow, dark blue, reddish brown, and black blue.

Declaration of Conflicting Interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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