Structural coloration and ultraviolet protective fabrication on fabrics coated with SiO₂/TiO₂ multilayer films via a magnetron sputtering method

Mei-Lin Huang¹,², Ying-Zhu Wu¹ and Sheng-Guo Lu²

Abstract
Interference structural colors and excellent ultraviolet (UV) protection performance were prepared by coating SiO₂/TiO₂ composite multilayer film on polypropylene non-woven fabrics (PP-NW) and polyester woven fabrics (PET-W) via a magnetron sputtering method. The colors on the coated structured film of “substrate/[TiO₂/SiO₂]k/air” (TSk) and “substrate/[SiO₂/TiO₂]k/air” (STk) (k=2, 3, 4, 5) was confirmed to be the interference structural colors. The positions and numbers of the strongest reflection peaks of the reflection-reducing type of TSk film and the reflection-enhancing type of STk film were consistent with theoretical calculations. The optical properties obtained from depositing the same STk film on PP-NW and PET-W were different. The reflectivity of the STk film was greater than the TSk film. The STk-coated samples with the PET substrate have a higher reflectivity than samples with the PP substrate because of the higher refractive index of PET. The reflection-enhancing film structure and higher refractive index substrate improved the film reflectivity. This research offered a theoretical basis and practical guidance for structural coloration and functional fabrication on fabric substrates.

¹School of Textile Material and Engineering, Wuyi University, Jiangmen, China
²School of Materials and Energy, Guangdong University of Technology, Guangzhou, China

Corresponding authors:
Ying-Zhu Wu, School of Textile Material and Engineering, Wuyi University, No. 22 dongcheng street, Jiangmen 529000, China.
Email: wuyingzhull11@163.com

Sheng-Guo Lu, School of Materials and Energy, Guangdong University of Technology, No. 100 West Waihuan Road, Guangzhou Higher Education Mega Center, Panyu District, Guangzhou 510006, China.
Email: sglu@gdut.edu.cn
Keywords
structural color, SiO₂/TiO₂ film, magnetron sputtering, textile coloration, UV protection

Introduction
Nano-materials can coat the surface of textiles and prepare structural colors. Magnetron-sputtered coatings are an effective way to achieve colors in anhydrous media while avoiding the need for water and secondary chemicals typical of traditional textile printing and dyeing.¹⁻⁵ Magnetron sputtering is a physical vapor deposition (PVD) process for depositing a thin film on a substrate under high vacuum conditions (Figure 1(c)). Argon (Ar) positive ions and new electrons is generated under the action of a high-intensity electric field by electrons collide with Ar atoms. Ar positive ions with high energy bombard the cathode target surface, the target molecules or atoms are subsequently sputtered on the substrate to form a thin film. These films offer interference and diffraction: The intensity of interference light is related to the optical thickness and refractive index of each layer of the film. Thus, it is necessary to comprehensively consider the refractive index of the film and the refractive index of the textile substrate. One can then consider using a reflection-reducing coating or a reflection-enhancing coating. Figure 1(a) shows that rays two and three are reflected from the upper and lower surfaces by incident light 1.

By considering half-wave loss, the optical path difference (OPD; ΔL=OPD=(AB+BC)-AD) between lights two and three can be expressed via the equations below.⁹

\[
ΔL = 2d \sqrt{n_2^2 + n_1^2 \sin^2 θ_1}, \quad \text{(reflection − reducing film, } 1 = n_1 < n_2 < n_s) \tag{1}
\]

\[
ΔL = 2d \sqrt{n_2^2 + n_1^2 \sin^2 θ_1 + \frac{λ}{2}}, \quad \text{(reflection − enhancing film, } 1 = n_1 < n_2 > n_s) \tag{2}
\]

Here, d is the physical thickness of the film. Terms n₁, n₂, and nₙ are the refractive indices of air, film, and substrate, respectively. Term θ₁ and θ₂ are the incident angle and refraction angle of visible light, respectively. M₁ and M₂ are the film and the substrate, respectively.

However, the interference conditions are different for the two series thin films of the reflection-reducing film (1 = n₁ < n₂ < nₙ) and the reflection-enhancing film (1 = n₁ < n₂ > nₙ). In contrast to reflection-reducing (transmission-enhancing) films, reflection-enhancing films (n₂ > nₙ) generally have a refractive index higher than that of the substrate material in order to increase the reflectivity of the film surface. As long as n₂ > nₙ, no matter what the value of n₂d is, the reflectivity is improved or unchanged compared with the pristine sample without coating. For a single-layer film (Figure 1(a)), assuming the maximum reflection wavelength is λ, the condition for optical constructive
interference (obtained highest brightness) at normal incidence ($\sin \theta_1 = 0$) can be written as

\[ \Delta L = 2n_2d = m\lambda, \quad \text{(reflection – reducing film, } 1 = n_1 < n_2 < n_s, m = 1, 2, \ldots \text{)} \]

\[ \Delta L = 2n_2d + \frac{\lambda}{2} = m\lambda, \quad \text{(reflection – enhancing film, } 1 = n_1 < n_2 > n_s, m = 1, 2, \ldots \text{)} \]

(3) \hspace{1cm} (4)

However, it is sometimes difficult to achieve high reflectivity in a single-layer film and improve the brightness of the structural color via interference. It is sometimes necessary to enhance the reflection through a multi-layer structure to enhance the interference structural color. Multi-layer reflection-enhancing films are thus generally formed by alternately stacking high and low refractive index materials (Figure 1(b)). The optical thickness ($n \times d$) of each layer is a quarter of the wavelength ($\lambda/4$) of a certain light.

Figure 1. Schematic diagram of interference on single-layer film (a); periodic stacking of a multilayer film (b); magnetron sputtering (c) and three kinds of stepped film with single-layer, double layer, and stacking bilayer (d).
The reflected light vector and vibration direction from each reflected surface participate in the superposition and are the same. Thus, the composite amplitude increases with increasing number of film layers. This in turn increases the reflectivity. For multilayer films, the conditions for optical constructive interference (obtained highest brightness) at normal incidence \((\sin \theta_1 = 0)\) are

\[
\begin{align*}
\Delta L = 2(n_A d_A + n_B d_B) &= \frac{m}{2} \lambda, \quad \text{(reflection - reducing film, } n_A < n_B < n_S, m = 1, 2, \ldots), \\
\Delta L = 2(n_A d_A + n_B d_B) + \frac{\lambda}{2} &= \frac{m}{2} \lambda, \quad \text{(reflection - enhancing film, } n_B < n_A > n_S, m = 1, 2, \ldots) 
\end{align*}
\]

The quarter-wavelength rule and the light interference principle as well as equation (5) indicate that constructive interference of structural color (the brightest color) occurs when the optical thickness of the film \((n_A d_A + n_B d_B)\) is equal to half the wavelength \((\lambda/2)\) in reflection-reducing films \((n_A < n_B < n_S)\). Equation (6) shows that constructive interference of structural colors (the brightest color) occurs (Table 1) for a reflection-enhancing film \((n_B < n_A > n_S)\) when the optical thickness of the film \((n_A d_A + n_B d_B)\) is equal to an odd multiple of the quarter-wavelength \((\lambda/4)\). Thus, to use the thin film interference method for structural coloration, the thickness and refractive index of each layer of the multilayer structure in the thin film must be optimized. The reflectivity of the reflected light must be concurrently examined. A higher reflectivity leads to brighter colors perceived by the human eye. Prior work\(^{10}\) has shown that—when the optical thickness of each layer in a multilayer structure film is equal to \(\lambda/4\) and \(3\lambda/4\), respectively—the reflection spectrum of the former is wider, but the reflection spectrum of the latter is narrower which increases the color saturation.

We show here a typical reflection-reducing film of a multilayer structure substrate/\((H_B L_A)_k/\text{air}\) \((n_A < n_B < n_S)\) in which \(L_A\) is the film layer with low refractive index \(n_A\); \(H_B\) is the film layer with a high refractive index \(n_B\); \(k\) is the double-layer film stacking (repetition) times \((k=1,2,3\ldots \ldots)\). For this periodic stacking of double-layer reflection-reducing films, the maximum interference reflected light intensity can be calculated according to equation (7).\(^{13}\) Here, \(n_1, n_A, n_B, n_S\) is the refractive index of the air, the outermost film, the second film, and the substrate, respectively. The reflectivity of multilayer films is related to \(k\) while a bigger \(k\) value leads to higher reflectivity (Figure 2(a)).

| \(nd \text{ or } n_A d_A + n_B d_B\) | \(\frac{1}{4} \lambda\) | \(\frac{1}{2} \lambda\) | \(\frac{3}{4} \lambda\) | \(\lambda\) | \(\frac{5}{4} \lambda\) | \(\frac{3}{2} \lambda\) | \(\frac{7}{4} \lambda\) | \(2\lambda\) |
|---|---|---|---|---|---|---|---|---|
| Reflection-reducing film | dark | bright | dark | bright | dark | Bright | dark | bright |
| Reflection-enhancing film | bright | dark | Bright | dark | bright | dark | bright | dark |
The maximum interference reflected light intensity of the single-layer reflection-reducing film (k = 0, n₂ < n₅) is given below

$$ R = \left\frac{n_1 - \left(\frac{n_B}{n_A}\right)^{2k} \times n_S}{n_1 + \left(\frac{n_B}{n_A}\right)^{2k} \times n_S}\right)^2. \quad (7) $$

The maximum interference reflected light intensity of the single-layer reflection-reducing film (k = 0, n₂ < n₅) is given below

$$ R = \left[1 - \left(\frac{n_B}{n_S}\right)^{2}\right]^2. \quad (8) $$

A single layer of film should be added in a reflection-enhancing multilayer film due to the half-wave loss. Structural films of substrate/Hₐ/(LₐHₐ)ᵏ/air (n_B < n_A > n_S) are usually used with odd total layers of 1, 3, 5, 7, 9, 11, 13 (2k-1, k = 1, 2, ...). In this
reflection-enhancing multilayered film structure, the maximum reflected light intensity (reflectivity) is \(^{14}\)

\[
R = \left[ \frac{n_1 - \left( \frac{n_A}{n_B} \right)^{2k} \times \left( \frac{n_A^2}{n_S} \right)} {n_1 + \left( \frac{n_A}{n_B} \right)^{2k} \times \left( \frac{n_A^2}{n_S} \right)} \right]^2
\]

The maximum interference reflected light intensity of the single-layer reflection-enhancing film (\(k = 0, n_2 > n_S\)) is given by equation (10).\(^{12}\) This is related to optical thickness and refractive index. Figure 2(b) shows that different reflectivity values are obtained for single layer films with different refractive indices (here, \(n_1 = 1.0, n_S = 1.5\)).

\[
R = \left[ \frac{n_1 - n_S}{n_1 + n_S} \right]^2
\]

Yin et al.\(^{14}\) reported that a reflectivity of 70% was obtained for three layers (\(k = 2\)) of multilayer reflection-enhancing films. Zinc sulfide (ZnS, \(n_A = 2.40\)) was used for its high refractive index layer, magnesium fluoride (MgF\(_2\), \(n_B = 1.38\)) for the low refractive index layer, and silicon dioxide (SiO\(_2\), \(n_S = 1.50\)) as the substrate. The reflectivity is increased to 98.7% and 99.8% for a film with nine layers (\(k = 4\)) and 13 layers (\(k = 6\)), respectively. This confirms the situation in Figure 2(a).

When we set \(Y = \left( \frac{n_A}{n_B} \right)^{2k} \times \left( \frac{n_A^2}{n_S} \right)\), equation (9) can be transformed into

\[
R = \left[ \frac{n_1 - Y}{n_1 + Y} \right]^2
\]

Since \(n_1 = 1\), the derivation can be

\[
R = \left[ 1 - \frac{2}{Y + 1} \right]^2 = \left[ 1 - \frac{2}{\frac{1}{Y} + 1} \right]^2
\]

The functional diagram of the relationship between the \(Y\) value and the reflectance \(R\) is made by equation (12) as shown in Figure 2(c). When \(Y < 1\), a smaller \(Y\) implies a larger \(R\); when \(Y > 1\), a larger \(Y\) implies a larger \(R\); but always \(R \leq 1\). In reflection-enhancing films, there is \(n_B < n_A > n_S\), and then \(\left( \frac{n_A}{n_B} \right) > 1\) and \(\left( \frac{n_A^2}{n_S} \right) > 1\). For \(Y = \left( \frac{n_A}{n_B} \right)^{2k} \times \left( \frac{n_A^2}{n_S} \right) > 1\); thus, the \(Y\) value is as large as possible to enhance the reflectivity, i.e. a greater difference in refractive index between two layers leads to a higher reflectance \(R\). A larger reflectivity leads to more vibrant and higher brightness in the structural color. Similarly, a greater difference in refractive index between the high-refractive index film and the substrate leads to greater reflectivity of the film surface. This implies a stronger interference effect and a more vibrant color.\(^{15}\) At the same time, a key indicator for the evaluation of dyeing
performance in the textile industry is the dyeing depth. This is expressed by the K/S value derived from the Kubelka-Munk (K-M) equation\(^\text{16,17}\) as follows

\[
\frac{K}{S} = \frac{(1 - R)^2}{2R}
\]  

(13)

Here, \(K\) is the K-M absorption coefficient of the measured object, \(S\) is the K-M scattering coefficient, and \(R\) is the reflectance (%) of the solid sample. Generally, the \(K\) and \(S\) values are not calculated separately, but the ratio of \(K/S\) is calculated and called the K/S value.\(^\text{18}\) The relationship between \(K/S\) and reflectivity \(R\) can be obtained according to equation (13); here, \(A+R=1\) where \(A\) is the absorption rate (Figure 2(d)). A larger K/S value implies a darker color and vice versa. Therefore, the K/S value has a linear relationship with color brightness and can represent the color depth of the fabric surface. Here, K/S can also partially represent the brightness of the structural colors.

The three mechanistic factors that modulate the structural color are the refractive index, periodic nanostructure, and incident light angle. These can be understood from the interference phenomenon of multilayer structures. To modify the organizational color, one can change the refractive index of the film, i.e. select materials with different refractive indices as the film material. This is one of the key issues in color control. The second modifies the physical thickness of the film to change the optical thickness. Changing the thickness of the film layer or the refractive index of the material will change the optical path difference of the interference; thus, causing the wavelength of the interference light to change and changing the hue of the color. A third step amends the refractive index ratio of the two film materials or the number of layers stacked to increase the reflectivity, i.e. the color intensity. This improves the brightness or vividness of the color.

Artificial structural colors imitate natural biological structural colors.\(^\text{3,19}\) Qin et al.\(^\text{20}\) found that the colors of the Papilio wings are derived from the interference structural color of the multilayered film structure. This multilayered film structure has nine stacking periods, and each period includes a chitin layer with a thickness of about 113 nm and a refractive index of about 1.58. The air-isolation layer has thickness of about 86 nm and a refractive index of about 1.20. A total thickness of 199 nm is seen in one period. Studies have shown that choosing an appropriate refractive index film is a key issue in the preparation of structural colors. For example, coating a ZnS-SiO\(_2\) multilayer film on plastic parts can lead to colorful interference structural colors\(^\text{21}\) in which ZnS is a high refractive index material (\(n = 2.35–2.4\)), and SiO\(_2\) is a low refractive index material (\(n = 1.45–1.5\)). A layer of metal is first sputtered on the fabric substrate as a reflective layer and then a metal oxide medium is sputtered as an optical interference/absorption layer to form a multilayered film such as Ag/Ag\(_2\)O\(^\text{22}\), Ag/TiO\(_2\),\(^\text{9,23–26}\) Ag/ZnO,\(^\text{27}\) and Al/TiO\(_2\).\(^\text{28}\) The combined effect of the two layers of thin films on visible light was used to generate interference structural color. The results later showed that these structural films conform to the principle of thin film interference, and the thickness of the outer dielectric film determines the hue of the coated fabric; thus, the structural color can be controlled or adjusted by the thickness of the outer dielectric film.\(^\text{9}\)
TiO$_2$ ($n = 2.55$) and SiO$_2$ ($n = 1.45$) are often used as optical antireflection or reflection enhancement films due to their high refractive index contrast. In the early stage of our research, periodic films of alternating layers of different dielectric materials are plated on polyester non-woven fabrics and mulberry silk fabrics to prepare textile structural colors. TiO$_2$ is sputtered first followed by SiO$_2$. This is repeated for three to four cycles until an interference structural color is obtained (see Figure 1(b) for the multilayer film structure). This multilayer film is an anti-reflection film structure with an insufficient structural color brightness. Some studies have deposited “substrate/[SiO$_2$/TiO$_2$]$^k$/air” (ST$k$) periodic multilayer films to obtain structural color, but the film can crack due to an increase in thickness when the number of lamination periods is greater than five although a sol-gel deposition is used. Here, PP-NW fabrics and PET-W fabrics with different refractive indices are selected as substrates to prepare reflection-reducing “substrate/[TiO$_2$/SiO$_2$]$^k$/air” (TS$k$) and reflection-enhancing type ST$k$, respectively. The bilayer stacking times ($k$) is selected to be less than or equal to 5. The difference between the two film structures and the structural color prepared on different substrates is then compared. The reflectivity of the film is then studied to improve the structural color brightness. Structural color textiles with excellent UV protective properties are investigated.

**Experimental**

**Experimental materials and film preparation**

A magnetron sputtering instrument was used for coating (W500, China Shenyang Scientific Instrument Co., Ltd). The film was formed by sputtering upward with the substrate fixed on the top and the target installed on the bottom (Figure 1(c)). The substrates were polypropylene (average refractive index 1.49) hot-rolled non-woven fabric (PP-NW) (white, 80 g/m$^2$) and polyester (average refractive index 1.6) woven fabric (PET-W) (white, 79.1 g/m$^2$). The substrates were cut into circular shapes with a diameter of 5 cm, cleaned with absolute ethanol in an ultrasonic cleaner, and then dried in a hot air-drying oven for use. Titanium dioxide (TiO$_2$) (refractive index 2.55) and silicon dioxide (SiO$_2$) with circular specifications of $\phi 75$ mm×4 mm and purity of 99.99% were provided by Shenzhen Zhongchengda Target Co., Ltd as targets. A custom W500 magnetron sputter machine (Shenyang Scientific Instruments Co., Ltd) was used for coating.

TS$k$ films with bilayer stacking times ($k$) of 2, 3, 4, and five were prepared on PP-NW. ST$k$ films with a double-layer stacking time of three were coated on PP-NW and PET-W, respectively. Radio frequency (RF) sputtering was used with targets of TiO$_2$ and SiO$_2$. The distance between the target and the substrate was set to 50 mm, the background pressure was $5 \times 10^{-3}$ Pa, the flow ratio of argon (Ar, 99.999%) and oxygen (O$_2$, 99.999%) was 35:20 (ml/min), the working air pressure was 1.0 Pa, and the sputtering power was 85 W. The physical thicknesses of a single-layer SiO$_2$ film and a single-layer TiO$_2$ film were designed to be 100 nm. We previously showed that the deposition rates of single-layer SiO$_2$ and TiO$_2$ films sputtered on mica sheets under the same sputtering conditions were 1.85 and 1.47 nm/min, respectively. Thus, the deposition times of single-layer
SiO2 films and single-layer TiO2 films were 54 min and 68 min, respectively. A detailed structure of the film and related experimental parameters were shown in Table 2.

**Testing and characterization**

Structural colors were characterized using a multi-angle spectrophotometer (R1, Shanghai Fuxiang Instruments and Equipment, China) in a reflection mode with incident angles varying from 10° to 60° (10° intervals). The samples’ morphology was characterized by a super depth-of-field microscope (VHX-7000, KEYENCE, Japan).

The ultraviolet (UV) (290–400 nm) absorption and transmission properties of the samples were tested via a UV transmission and protection performance tester (NF021, Ningbo Spinning Instrument, China) according to GB/T18830-2009. The output of T (UVA)\textsubscript{AV} (transmittance of ultraviolet rays in the A-band 315–400 nm), T (UVB)\textsubscript{AV} (transmittance of ultraviolet rays in the B-band 280–315 nm), and UPF\textsubscript{AV} (Ultraviolet Protection Factor) were abbreviated as UVA, UVB, and UPF. This can be called a “UV protection product” when the UPF>40 and UVA<5%. The material is marked as 40+ when 40<UPF≤50 and UVA<5%, which means that the protective effect is very good. It is marked as 50+ when UPF>50 and UVA <5%, which means that the protection effect is excellent. A higher UPF value means better UV protection.

**Results and discussion**

**Color charactering and surface morphology of TSk films coated on PP-NW**

The colors of the TSk films on PP-NW changed with increasing stacking k (k = 2, 3, 4, 5) of the bilayer film as shown in Figure 3(a). The number of reflection peaks in the visible light wavelength range increased sequentially as the k value increased (Figure 3(b))—this suggests that the number of strong peaks that produce constructive interference when visible light is incident on the stacking multilayer film is not equal. This observation agrees with the theory of interference structural color in that the reflection curve of visible light incident on a film with a constant refractive index will exhibit a series of sinusoidal reflection peaks. Moreover, the samples’ colors were confirmed to be the interference structural colors that changed with observation angle (Figure 3(c)).

**Table 2.** Sputtering parameters and the film’s structure.

| NO. | Sample | Film structure | Double-layer stacking times (k) | Film thickness/nm |
|-----|--------|----------------|---------------------------------|-------------------|
| #1  | PP-TS2 | PP-NW/[TiO2/SiO2]\textsuperscript{2} | 2                              | 400               |
| #2  | PP-TS3 | PP-NW/[TiO2/SiO2]\textsuperscript{3} | 3                              | 600               |
| #3  | PP-TS4 | PP-NW/[TiO2/SiO2]\textsuperscript{4} | 4                              | 800               |
| #4  | PP-TS5 | PP-NW/[TiO2/SiO2]\textsuperscript{5} | 5                              | 1000              |
| #5  | PP-ST3 | PP-NW/[SiO2/TiO2]\textsuperscript{1} | 3                              | 600               |
| #6  | PET-ST3| PET-W/[SiO2/TiO2]\textsuperscript{3} | 3                              | 600               |
The hue of the coated fabrics was related to the film thickness (or optical thickness) and the incident angle (or viewing angle). The uniformity of the film thickness directly affected the consistency of the hue or color while the transparency of the film determines the color purity and brightness. The refractive index and extinction coefficient (or absorptivity) of nanofilms closely affected the color rendering effect. The optical thickness (refractive index × physical thickness) within a certain range must satisfy the condition of constructive interference for increasing the reflectivity or brightness. The absorption of the film affects the intensity of the reflected light. Smaller absorption implies greater reflection, and thus a more obvious interference phenomenon. The film may also show structural color due to constructive interference of the reflected light. Therefore, the absorption of light by the film should largely be considered to determine whether the color presented is the interference structural color or the intrinsic absorption color of the film or the substrate.

Figure 3(a) shows that a sample’s color is different at different surface position precisely because of the different observation angles (also the incident angles). Thus, the colors have an iridescent effect, thus confirming the law of structural color. The reflectivity of PP-TS2 in Figure 3(b) is lower than that of PP-pristine, and thus the sample brightness is a little lower. Figure 3(c) shows the multi-angle reflectance spectrum of the PP-TS5 with a bilayer stacking of 5 times. There are three strong peaks on the reflectance curve corresponding to 448 nm, 574 nm, and 742 nm—this implies that the three wavelengths of the reflected light incident on the multilayer film produce constructive interference. The strongest reflection peak of PP-TS2 is at 625 nm; those of PP-TS3 are at 467 nm and 774 nm; and those of PP-TS4 are at 464 nm and 647 nm (Table 3).
For the TSk films coated on PP-NW, the visible light interference meets equation (6) by considering the half-wave loss between the bottom-most TiO$_2$ film and the substrate. For $n_A < n_B > n_S$, it meets

$$2k(n_A d_A + n_B d_B)\cos \theta + \frac{\lambda}{2} = m\lambda. \ (n_A < n_B > n_S, \ \theta = 60^\circ, \ m = 1, 2, \cdots) \quad (14)$$

Because $\cos 60^\circ = 0.5$, the above formula becomes

$$k(n_A d_A + n_B d_B) = m\lambda - \frac{\lambda}{2} = \left( m - \frac{1}{2} \right)\lambda \quad (15)$$

Here, $n_A$ is 1.45 for SiO$_2$, $n_B$ is 2.55 for TiO$_2$, $n_S$ is 1.5 for PP-NW, $d_A$ is 100 nm, and $d_B$ is 100 nm leading to

$$400k = m\lambda - \frac{\lambda}{2} = \left( m - \frac{1}{2} \right)\lambda \quad (16)$$

Through these calculations, we see that the theoretical value of the strongest reflection peak position of the TSk films coated on PP-NW is obtained for samples with different bilayer stacking times (Table 4).

Upon comparing Table 3 and Table 4, we see that the theoretical calculation is generally consistent with the actual. When $k$ is small (2, 3, 4), the actual peak wavelength of the strongest reflection is smaller than the theoretical value perhaps because the actual refractive index of each film is less than the theoretical average value. When $k$ is larger (5), the theoretical value is closer to (or even consistent with) the experimental value because the total thickness of the composite film increases. The influence of the refractive index variability is also reduced. The strongest reflection peak is located at 800 nm when $k$ is 1. This exceeds the visible light range and confirms the reflection curve of the pristine sample shown in Figure 3(b), i.e., a sinusoidal characteristic that is vague.

Furthermore, STk ($k=3$) films were coated on PP-NW and PET-W. Because $n_B < n_A > n_S$ (here, $n_A$ is 2.55 for TiO$_2$, $n_B$ is 1.45 for SiO$_2$), equation (6) is also applicable and is theoretically the same as that of the TSk films coated on PP-NW. In Figure 3(b), the PP-ST3 sample has two strongest reflection peaks at 484 nm and 750 nm ($\theta = 60^\circ$). These are basically consistent with the theoretical analysis shown in Table 4. Structural colors are obtained on sample PP-ST3 and PET-ST3 (Figure 4(a)). Thin film with structural colors is

| Sample | The strongest reflection peak/nm |
|--------|---------------------------------|
| PP-TS2 | — | 625 | — |
| PP-TS3 | — | 467 | — |
| PP-TS4 | — | 464 | — |
| PP-TSS | 448 | — | 574 | — |

**Table 3.** The strongest reflection peak position of the samples ($\theta = 60^\circ$).
Table 4. The theoretical reflection peak positions of PP-NW/[TiO₂/SiO₂]³⁰⁰⁰⁰ (θ = 60°).

| Stacking times (k) | m | The strongest reflection peaks/nm |
|--------------------|---|----------------------------------|
| 1                  | 1 | —                                |
| 2                  | 2 | —                                |
| 3                  | 3 | 320 —                            |
| 4                  | 3 | —                                |
| 5                  | 4 | —                                |
| 6                  | 5 | —                                |

Color features and surface morphology of STₖ films coated on PP-NW and PET-W

The strongest reflection peak is at 438 nm for PET-ST3. This is different from the PP-ST3 sample. Comparing Figures 4(d) and (e), we see that the absorption peak of the reflection curve of PET-ST3 corresponds to a wavelength (426 nm) larger than that of PP-ST3 (415 nm), which means that the absorption is red-shifted. The strongest reflection peak of PET-ST3 corresponds to 438 nm and is smaller than that of PP-ST3 (484 nm). This means that the reflection is blue-shifted. Different results were obtained on the same structured film (ST3) coated on different substrates. This may be due to other factors such as the substrate structure, refractive index, and surface shape. However, the exact reasons require further study. The strongest peak positions of the reflection curves of PP-ST3 and PET-ST3 both move to shorter wavelengths with increasing incident angle, i.e. there is a blue shift. This also shows that the sample colors have iridescent effects. This is a key feature of structural colors, thus suggesting that these colors are interference structural colors. The phenomenon with the strongest reflection peak and the peak position in the reflection curve are blue-shifted with increasing incident angle consistent with equation (14). The wavelength (λ) of the light wave where constructive interference occurs becomes shorter, and the wavelength corresponding to the maximum reflectance moves to the short wavelength direction, i.e. the reflection peak is blue-shifted.

Upon comparing the TSK film and the STₖ film, we see that the relative reflectance of the reflection-reducing TSK films is within the range of 110% (θ=60°) when the k value is (k=2–6) (Figure 3). Figure 4 shows that the maximum relative reflectivity of the reflection-enhancing STₖ films is high up to 270% (θ=60°) only when k is 3. This suggests that the visible light reflectivity values of the two structural films are different; the STₖ film can have higher reflectivity. In these two composite structure films (structure of 2k but not 2k+1, substrate/(LBHA)⁴/air (n_B < n_A)), the reflectivity R is expressed as
Figure 4. (a) Structural colors of PP-ST3 recorded with optical pictures in different viewing angles; (b) Surface morphology and color of PP-ST3; (c) Surface morphology and color of PET-ST3; (d) Multi-angle reflection spectrum of PP-ST3; and (e) Multi-angle reflection spectrum of PET-ST3. (In (b) and (c), image-1 is an optical digital photo of the sample; image-2 is a photo under a certain magnification, and it can be seen that the coating/film is colored; image-3 show that the film with structural colors covered the fiber well under a super-depth-of-field microscope, and the illustration inside is a schematic diagram of the fabric structure.).
\[
R = \left[ n_1 - \left( \frac{n_A}{n_B} \right)^{2k} \times n_S \right] \left[ n_1 + \left( \frac{n_A}{n_B} \right)^{2k} \times n_S \right]^{2}
\] (17)

For the TSk films coated on PP-NW, the refractive indices of TiO\textsubscript{2} and SiO\textsubscript{2} are 2.55 (n\textsubscript{B}) and 1.45 (n\textsubscript{A}), and substrate PP and PET are 1.49 and 1.6, respectively. Equation (17) is used to measure the reflectivity of PP-TS3, PP-ST3, and PET-ST3: 81.73, 91.32 and 91.9%, respectively. The reflectivity of the PP-ST3 is higher than that of PP-TS3, and PET-ST3 is higher than PP-ST3. This also implies that the reflectivity of the reflection-enhancing film deposited on the same substrate is higher than that of the anti-reflection film. The PP-ST3 sample and the PET-ST3 sample are both anti-reflection films, and the latter has a larger refractive index of the PET substrate than the former; thus, the reflectivity is also relatively large. The results indicate that reflection-enhancing structural films and a substrate with a relatively large refractive index can improve the reflectivity.

**Ultraviolet protection performance and breathability**

The UV protection performance results of the samples are shown in Figure 5. Results show that UV protection performance of samples PP-ST3 and PET-ST3 are excellent according to criterion GB/T18830-2009. From a mechanism point of view, the UV protection performance of the multilayer film coated samples increases with the stacking time, which should be directly assigned to the result of the increase in the reflectance to UV and even visible light (Figure 5(a)). Samples of PP-pristine and PET-pristine have a UPF of 9.84 and 51.60, respectively (Figure 5(b)). For a series of TSK films, a higher bilayer stacking time resulted in a higher UPF value. The UV protection performance of PP-ST3 and PET-ST3 is greatly improved by coating the reflection-enhancing film of STk.

![Figure 5.](image-url)
The PET-woven fabric had the highest UV protection performance with UPF of 1124, UVA of 1.48%, and UVB of 0. We concluded that the coating increases the reflectance of the samples for UV, visible light, and even near-infrared light. In general, higher visible light reflectivity leads to better UV protective performance. The use of the reflection-enhancing structural film improves the UV protective performance.

**Conclusion**

Reflection-reducing and reflection-enhancing multilayer films were prepared by coating SiO$_2$/TiO$_2$ multilayer films, and their optical properties were compared. The colors prepared on the structured films of PP-NW/[TiO$_2$/SiO$_2$]$^k$ ($k = 2, 3, 4, 5$), PP-NW/[SiO$_2$/TiO$_2$]$^3$, and PET-W/[SiO$_2$/TiO$_2$]$^3$ were confirmed to be interference structural colors. The positions and numbers of the strongest reflection peaks of the reflection-reducing T$^k$s film and the reflection-enhancing S$^k$t film were consistent with theory. The optical properties obtained by depositing the same S$^k$t film on PP-NW and PET-W were different. The reflectivity of the S$^k$t film was greater than that of the T$^k$s film. The reflectivity of the PP-T$^3$s sample, PP-ST$^3$s sample, and PET-ST$^3$s sample were 81.73, 91.32, and 91.9%, respectively. The S$^k$t-coated samples with a PET substrate have a higher reflectivity than samples with a PP substrate because of the higher refractive index of the former’s substrate. The reflection-enhancing film structure and higher refractive index substrate improved the reflectivity of the film and the UV protection performance. The UPFs of the PP-ST$^3$s sample and the PET-ST$^3$s sample were 746.96 and 1124, respectively. These were much higher than the pristine sample. The results indicate that the composite film—especially the reflection-enhancing films with structural color effects—enabled the samples to obtain excellent UV protective properties. This research offered a theoretical basis and practical guidance for structural coloration and functional fabrication on fabric substrates via sputtering coating.

**Declaration of Conflicting Interests**

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

**Funding**

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was supported by the Science and Technology Planning Project of Guangdong Jieyang City (skjcx033) and Guangdong Science and Technology Major Special Fund (2019-252).

**ORCID iD**

Mei-Lin Huang  [https://orcid.org/0000-0003-4762-2061](https://orcid.org/0000-0003-4762-2061)
References

1. Huang M, Lu S-G, Ren Y, et al. Structural coloration and its application to textiles: a review. *J Text* 2019; 111: 1–9, DOI: 10.1080/00405000.2019.1663623

2. Mo-xin LI, Dan-yan W, Cheng Z, et al. Metasurface-based structural color: fundamentals and applications. *Chin Opt* 2021; 14: 900–926, DOI: 10.37188/co.2021-0108

3. Zhang Z, Chen Z, Shang L, et al. Structural Color Materials from Natural Polymers. *Adv Mater Tech* 2021; 6: 2100291–2100299, DOI: 10.1002/admt.202100296

4. Li K, Li C, Li H, et al. Designable structural coloration by colloidal particle assembly: from nature to artificial manufacturing. *iScience* 2021; 24: 102121–20210130, DOI: 10.1016/j.isci.2021.102121

5. Yang B, Cheng H, Chen S, et al. Structural colors in metasurfaces: principle, design and applications. *Mater Chem Front* 2019; 3: 750–761, DOI: 10.1039/c9qm00043g

6. Kinoshita S, Yoshioka S, Miyazaki J, et al. Physics of structural colors. *Rep Prog Phys* 2008; 71: 076401, DOI: 10.1088/0034-4885/71/7/076401

7. Shao J, Liu G and Zhou L. Biomimetic nanocoatings for structural coloration of textiles. In: Hu J (ed). *Active Coatings for Smart Textiles*. Elsevier, 2016, pp. 270–300.

8. Huang M-L, Wu Y-Z, Fan F, et al. Antibacterial and ultraviolet protective neodymium-doped TiO₂ film coated on polypropylene nonwoven fabric via a sputtering method. *J Eng Fibers Fabr* 2021; 16: 252–257, DOI: 10.1177/15589250211025257

9. Yuan X, Xu W, Huang F, et al. Structural colors of fabric from Ag/TiO₂ composite films prepared by magnetron sputtering deposition. *Int J Clothing Sci Tech* 2017; 29: 427–435, DOI: 10.1108/ijcst-04-2016-0038

10. Xi L, Yi L, Jia-wen L, et al. Influence of the Optical Multi-Film Thickness on the Saturation of the Structural Color Displayed. *Adv Natural Sci* 2010; 13: 317–323, DOI: 10.3968/j.ans.1715787020100302.039

11. Penselin SA and Steudel A. Fabry-Perot-Interferometerspiegelungen aus dielektrischen Vielfachschichten. *Z Angew Phys* 1955; 142: 21–41, DOI: 10.1007/BF01330054

12. Ya-lu T and Guang H. Relationship between AR coating Reflectance and Coating Refractive Index and Film Thickness. *J HuaiYin Inst Tech* 2008; 17: 86–88, DOI: 10.3969/j.issn.1009-7961.2008.03.021

13. Land MF. A multilayer interference reflector in the eye of the scallop, pecten maximus. *J Exp Biol* 1966; 45: 433–447, DOI: 10.1242/jeb.45.3.433

14. Zhongwen Y and Aihua X. Calculation of Reflectance of Optical Films. *J Nanyang Normal Univ* 2007; 6: 24–27, DOI: 10.3969/j.issn.1671-6132.2007.03.008

15. Xinyuan S. Structural Chromogenesis and Dyeing and Finishing (3). *Dyeing and Finishing* 2005; 31: 45–48, DOI: 10.3321/j.issn:1000-4017.2005.19.015

16. Haisong X. The application research of Kubelka-Munk theory to automatic color matching in textile dyeing. *Acta Photonica Sinica* 1998; 27: 338–341, DOI: 10.1088/0256-307X/15/12/010

17. Amirshahi MTP S. H. and Pailthorpe M. Applying the Kubelka-Munk equation to Explain the color of blends prepared from precolored fibers. *Text Res J* 1994; 64: 357–364, DOI: 10.1177/004051759406400608
18. Huang M-L, Cai Z, Wu Y-Z, et al. Metallic coloration on polyester fabric with sputtered copper and copper oxides films. *Vacuum* 2020; 178: 109489, DOI: 10.1016/j.vacuum.2020.109489
19. Dumanli AG and Savin T. Recent advances in the biomimicry of structural colours. *Chem Soc Rev* 2016; 45: 6698–6724. DOI: 10.1039/c6cs00129g
20. Youhua Q, Feng L, Haiwei Y, et al. One-dimensional photonic structures on the wings of a phoenix butterfly. *Chin Sci Bull* 2007; 52: 2101–2106, DOI: 10.3321/j.issn:0023-074x.2007.18.001
21. Guoshun C and Zengyou W. A colorful high-brightness thermal film, 7. China: Patent CN201720082817., 2017.
22. Zhang X, Jiang S, Cai M, et al. Magnetron sputtering deposition of Ag/Ag2O bilayer films for highly efficient color generation on fabrics. *Ceram Int* 2020; 46: 13342–13349, DOI: 10.1016/j.ceramint.2020.02.113
23. Diop DK, Simonot L, Martínez-García J, et al. Spectral and Color Changes of Ag/TiO2 Photochromic Films Deposited on Diffusing Paper and Transparent Flexible Plastic Substrates. *Appl Spectrosc* 2016; 71: 1271–1279, DOI: 10.1177/0003702816680000
24. Yuan X, Liang S, Ke H, et al. Photocatalytic property of polyester fabrics coated with Ag/TiO2 composite films by magnetron sputtering. *Vacuum* 2020; 172: 109103, DOI: 10.1016/j.vacuum.2019.109103
25. Yuan X, Wei Q, Chen D, et al. Electrical and optical properties of polyester fabric coated with Ag/TiO2 composite films by magnetron sputtering. *Text Res J* 2015; 86: 887–894, DOI: 10.1177/0040517515595034
26. Yuan X, Xu W, Huang F, et al. Structural colour of polyester fabric coated with Ag/TiO2 multilayer films. *Surf Eng* 2016; 33: 231–236, DOI: 10.1080/02670844.2016.1216264
27. Yuan X, Xu W, Huang F, et al. Polyester fabric coated with Ag/ZnO composite film by magnetron sputtering. *Appl Surf Sci* 2016; 390: 863–869, DOI: 10.1016/j.apsusc.2016.08.164
28. Yuan X, Ye Y, Lian M, et al. Structural Coloration of Polyester Fabrics Coated with Al/TiO2 Composite Films and Their Anti-Ultraviolet Properties. *Materials (Basel)* 2018; 11. DOI: 10.3390/ma11061011
29. Zambrano DF, Villarroel R, Espinoza-González R, et al. Mechanical and microstructural properties of broadband anti-reflective TiO2/SiO2 coatings for photovoltaic applications fabricated by magnetron sputtering. *Sol Energ Mater Sol Cell* 2021; 220: 110841, DOI: 10.1016/j.solmat.2020.110841
30. Xu YJ, Liao JX, Cai QW, et al. Preparation of a highly-reflective TiO2/SiO2/Ag thin film with self-cleaning properties by magnetron sputtering for solar front reflectors. *Sol Energ Mater Sol Cell* 2013; 113: 7–12, DOI: 10.1016/j.solmat.2013.01.034
31. Lihua Y and Wenqin D. Optical properties of fabric with multiple structural colors. *Chin J Textiles* 2016; 037: 83–88, DOI: 10.13475/j.fzxb.20141005106
32. Yasuda T, Nishikawa K, Furukawa S, et al. Structural colors from TiO2/SiO2 multilayer flakes prepared by sol–gel process. *Dyes Pigm* 2012; 92: 1122–1125, DOI: 10.1016/j.dyepig.2011.08.006
33. Lihua Y and Wenqin D. Effect of magnetron sputtering process parameters on the excellent structural color of polyester fabrics. *J Wayi Univ (Natural Sci Edition)* 2015; 29: 16–22, DOI: 10.3969/j.issn.1006-7302.2015.03.005
34. Yongchong R, Meilin H, Xiaoru W, et al. Influence of sputtering pressure of radio frequency magnetron sputtering on the surface coating of polyester fabric. *J Wayi Univ (Natural Sci Edition)* 2017; 31: 66–69, DOI: 10.3969/j.issn.1006-7302.2017.04.010