

# Preparation and Characterization of Lignin-TiO<sub>2</sub> UV-shielding Composite Material by Induced Synthesis with Nanofibrillated Cellulose

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It is desirable to develop biodegradable ultraviolet (UV)-shielding materials from renewable resources, as the demand for sustainability is ever increasing. In this work, a novel lignin-TiO<sub>2</sub> UV-shielding composite was synthesized successfully *via* a hydrothermal method induced by nanofibrillated cellulose (NFC). Comprehensive characterization showed that the lignin-TiO<sub>2</sub>@NFC composite induced by NFC had good nanoparticle size, shape, and thermal stability. The sunscreen performance of lignin-TiO<sub>2</sub>@NFC was investigated *via* mixture with unmodified hand cream. The UV-visible (vis) transmission spectra results revealed that the unmodified cream with 10 wt% lignin-TiO<sub>2</sub>@NFC absorbed approximately 90% of UV light in the full UV band (200 nm to 400 nm), which indicated that lignin-TiO<sub>2</sub>@NFC had a good UV-shielding ability.

*Keywords:* TiO<sub>2</sub>; Lignin; Cellulose nanofibril; UV-shielding

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## INTRODUCTION

In recent years, the amount of ultraviolet (UV) radiation has increased with the destruction of the ozone layer, and the overexposure of UV radiation causes negative effects on human health and material stability (Slaper *et al.* 1996; Dong *et al.* 2018). Therefore, the research and development of UV-shielding materials has aroused extensive interest in academia and industry. In this field, titanium dioxide (TiO<sub>2</sub>) is widely investigated as an inorganic UV-shielding agent due to its ability to reflect, scatter, and absorb a wide range of ultraviolet radiation (Sambandan and Ratner 2011). However, the poor dispersibility and strong photocatalytic degradation hazard of TiO<sub>2</sub> impair its application (Xiao *et al.* 2013).

In the process of preparing TiO<sub>2</sub> by traditional sol-gel method, nucleation and the growth of secondary particles in the precipitation process cannot be well controlled. In addition, nanoparticles agglomerate easily, and this method requires sintering to obtain crystals, so their structure cannot be easily controlled (Dinh *et al.* 2009). The generation of TiO<sub>2</sub> with suitable particle size and good dispersibility *via* a simple and fast method is a research area of great interest (Rockafellow *et al.* 2009; Zhou and Fu 2013). The template method can effectively control the morphology, structure, and size of synthesized nanomaterials, so it has become an important method of preparing nanomaterials (Giese *et*

*al.* 2015). Dong *et al.* (2002) used the polymer template with a groove structure and found that TiO<sub>2</sub> sol infiltrated with appropriate concentration can be used to obtain fibrous TiO<sub>2</sub> after solvent evaporation, but the polymer material is difficult to obtain with this method.

As it is a natural high polymer, nanocellulose is also used as a template for the preparation of nano-TiO<sub>2</sub>. Several studies have reported the successful application of cellulose templates in the preparation of TiO<sub>2</sub> with specific morphology. The two main features of cellulose templates are a uniform network formed in aqueous solution and nucleation sites formed by a large amount of surface hydroxyl groups (Marques *et al.* 2006). Miao *et al.* (2006) dispersed cellulose in titanium tetrabutyl oxide to prepare TiO<sub>2</sub> of 10 nm to 20 nm size. In addition, Zhou *et al.* (2007) used cellulose nanocrystals (CNC) as a morphology inducer to synthesize square nano-TiO<sub>2</sub>. Wei *et al.* (2012) used CNC to prepare mesoporous TiO<sub>2</sub> in different shapes. The authors claimed that reactions between the hydroxyl groups of the long-chain CNC and TiO<sub>2</sub> precursor provided a physical barrier to prevent the growth and aggregation of the TiO<sub>2</sub> precursor and promote the spherical structure by self-assembly. Chen *et al.* (2016a) prepared TiO<sub>2</sub> composite material with high dispersion, small grain size, and high specific surface area induced by CNC.

Studies have demonstrated that inorganic TiO<sub>2</sub> nanoparticles have some side effects in sunscreen materials (Zaccariello *et al.* 2017). In sunlight, inorganic TiO<sub>2</sub> nanoparticles have photocatalytic activity that produces reactive species, such as O<sub>2</sub><sup>-</sup> and OH radicals and other reactive oxygen species (ROS), such as H<sub>2</sub>O<sub>2</sub>, which can damage cellular components, including DNA, proteins, lipids, and membranes (Sander *et al.* 2002). To eliminate the photocatalytic activity of TiO<sub>2</sub>, inorganic or polymeric thin layers have been coated onto the surface of TiO<sub>2</sub> nanoparticles. The inorganic coating layers included zeolite, silica, and alumina (Jaroenworarluck *et al.* 2006; Shen *et al.* 2006; Zhang *et al.* 2009).

Excessive use of inorganic coatings could lead to poor light transmittance in the UV-screening product. Inorganic particles are not easily dispersed in creams, which greatly limits their application in skincare products. Morlando *et al.* (2018) utilized the antioxidant properties of chitosan to capture the free radicals generated by the photocatalytic activity of TiO<sub>2</sub>. However, the prepared chitosan/TiO<sub>2</sub> nanocomposite particles had weak UV absorption capacity.

Lignin is the most abundant aromatic polymer (Kai *et al.* 2016). It has a natural phenylpropane skeleton and contains functional groups such as phenolic hydroxyls, double bonds, and carbonyls. The structural properties of lignin suggest that it has excellent free radical scavenging ability, good UV-absorption, and antioxidant properties (Pan *et al.* 2006; Qian *et al.* 2016; Li *et al.* 2018). Hambarzumyan *et al.* (2012) used lignin as a UV-shielding material, and they reported the use of a UV-blocking nanocomposite coating based on lignin that exhibited high transmittance in the visible spectrum. The use of lignin to capsule chemical sunscreens improves the UV-blocking performance of chemical sunscreens. In addition, lignin has been employed to modify the properties of TiO<sub>2</sub>. Nair *et al.* (2016) combined lignin with TiO<sub>2</sub> *via* a ball-milling method. The composite obtained by this method had low thermal stability and poor UV-shielding. Chen *et al.* (2016b) prepared lignin/TiO<sub>2</sub> UV-shielding composite material *via* a sol gel method, and they found that the precursor of TiO<sub>2</sub> was bound with the oxygen-containing functional groups in lignin and formed stable complexes during the hydrolysis process. Morsella *et al.* (2016) prepared lignin/TiO<sub>2</sub> composites *via* UV irradiation in THF (tetrahydrofuran) solution, and they found that lignin can effectively reduce the photocatalytic activity of TiO<sub>2</sub>. However, large amounts of organic solvents, such as tetrahydrofuran and glutaraldehyde, were used,

but these are toxic and not suitable for skincare products (Li *et al.* 2019). The study of UV-shielding of lignin showed that lignin exhibited antioxidant properties and acted as a free radical scavenger due to the presence of the phenolic hydroxyl groups; the phenolic hydroxyl groups also act as a proton donor and can stabilize the resulting radicals *via* substituents and delocalization (Sun *et al.* 2014). Ibrahim *et al.* (2019) employed lignin to scavenge the hydroxyl radicals generated from the photocatalytic activity of TiO<sub>2</sub> by forming a lignin/TiO<sub>2</sub> composite. The results showed that lignin can reduce phototoxicity and scavenge the hydroxyl radicals. Therefore, the use of lignin replacing the inorganic coating to modify TiO<sub>2</sub> improves the UV-blocking performance of chemical sunscreens and may enhance the antioxidant properties of chemical sunscreens. It is a great idea to use NFC, taking advantage of its characteristic functional groups and orderly spatial structure, together with lignin, to induce TiO<sub>2</sub> crystal growth and control the particle size, while completing the surface lignin coating at the same time.

In this study, multi-hydrogen-bond reticulated NFC was prepared with high dispersion through enzymatic hydrolysis and high-pressure homogenization. Lignin-TiO<sub>2</sub> composite materials were prepared by using NFC as the inducer and an alkali lignin one-step solvothermal method. The influences of UV-shielding properties, antioxidant properties, thermal stability, and the dynamic mechanical properties of the composite material were studied. The composite materials can be added to skin care products and has excellent anti-ultraviolet ability and good application prospect.

## EXPERIMENTAL

### Materials

The NFC suspension (solid content was 1.08%) used bleached softwood pulp as the raw material, and it was made with 68.9 MPa (10,000 psi) and homogenized 10 times by using the microjet high pressure homogeneous machine (LMZO; Microfluidics International Corporation, Newton, MA, USA). The diameter of the resulting NFC was about 87 nm. The alkali lignin (solubility: H<sub>2</sub>O, pH: 10.5) was purchased from Sigma-Aldrich (Shanghai, China). The titanium butoxide, which was 98% pure, was obtained from Mike Chemical Instrument Co. Ltd. (Hangzhou, China). The unmodified hand cream used was Dabao SOD hand cream, which was purchased from Dabao Cosmetics Co. LTD (Beijing, China); its main ingredients contain glycerin and silicone oil.

### Synthesis of TiO<sub>2</sub> and TiO<sub>2</sub>@NFC

The TiO<sub>2</sub> precursor was prepared *via* the solvothermal method. Five mL of titanium butoxide (5.0 g) was introduced into 25 mL of anhydrous ethanol, and the mixed solution was stirred with a magnetic stirrer at room temperature at 400 r/min for 30 min. Then, 10 mL of the NFC suspension (solid content was 1.08%) was slowly added, and stirring continued until white clouding occurred. Next, the suspension liquid was transferred to the high temperature and high-pressure reactor for reaction at 120 ° for 2 h. Colloids were allowed to form for 24 h at room temperature. Finally, the gel was dried under a vacuum for 12 h. The powder obtained from grinding in the mortar was nano-TiO<sub>2</sub> induced by nanocellulose and used without further purification; it was named TiO<sub>2</sub>@NFC. For comparison, TiO<sub>2</sub> samples were prepared according to the above preparation method by replacing the nanocellulose suspension with 10 mL of H<sub>2</sub>O.

### Synthesis of Lignin-TiO<sub>2</sub>@NFC

Five mL of titanium butoxide (5.0 g) was introduced into 25 mL of anhydrous ethanol, and the mixed solution was stirred with a magnetic stirrer at room temperature at 400 r/min for 30 min. Then, 0.1 g of alkali lignin was added to the 10 mL of NFC suspension with stirring. Next, all suspension liquid was transferred to the high temperature and high-pressure reactor for reaction at 120 °C for 2 h. The colloids were allowed to form for 24 h at room temperature. Finally, the gel was dried under a vacuum for 12 h. Finally, the resultant yellow powder was the lignin-TiO<sub>2</sub> composite; it was named lignin-TiO<sub>2</sub>@NFC.

### X-ray Diffraction (XRD) Analysis

The crystal structure of TiO<sub>2</sub> and the composite material hybrids were recorded with an X-ray diffractometer (XRD, Bruker D2 Phaser, Bruker Corp., Karlsruhe, Germany). The scanning angle ( $2\theta$ ) ranged from 10° to 80° with a step increment of 0.02°.

### Fourier Transform Infrared (FT-IR) Spectroscopy Analysis

The FT-IR spectra of the TiO<sub>2</sub> and the prepared composite material hybrids were obtained on a Fourier transform infrared spectrometer (NICOLET5700; Thermo Fisher Scientific, Madison, WI, USA) using a KBr disc containing finely ground samples (1 %). Ten scans were taken for each sample recorded from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup> with a resolution of 0.5 cm<sup>-1</sup>.

### Scanning Electron Microscopy (SEM) Analysis

The morphology analysis of the TiO<sub>2</sub>@NFC and lignin-TiO<sub>2</sub>@NFC were recorded with a scanning electron microscope (JSM-5610LV; JEOL Ltd., Tokyo, Japan).

### X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (K-Alpha; Thermo Fisher Scientific, Madison, WI, USA) equipped with a monochromatic Al K $\alpha$  X-ray source (1486.6 eV) was utilized to characterize the elemental chemical states of lignin-TiO<sub>2</sub>@NFC.

### Thermogravimetric Analysis (TGA)

The thermal analysis (TGA) and differential thermal analysis (DTG) of the TiO<sub>2</sub>@NFC and lignin-TiO<sub>2</sub>@NFC were conducted on a thermal analyzer (PYRIS I; PerkinElmer, Waltham, MA, USA). Four mg of lignin was placed on an aluminum crucible and heated from 25 °C up to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere (40 mL/min).

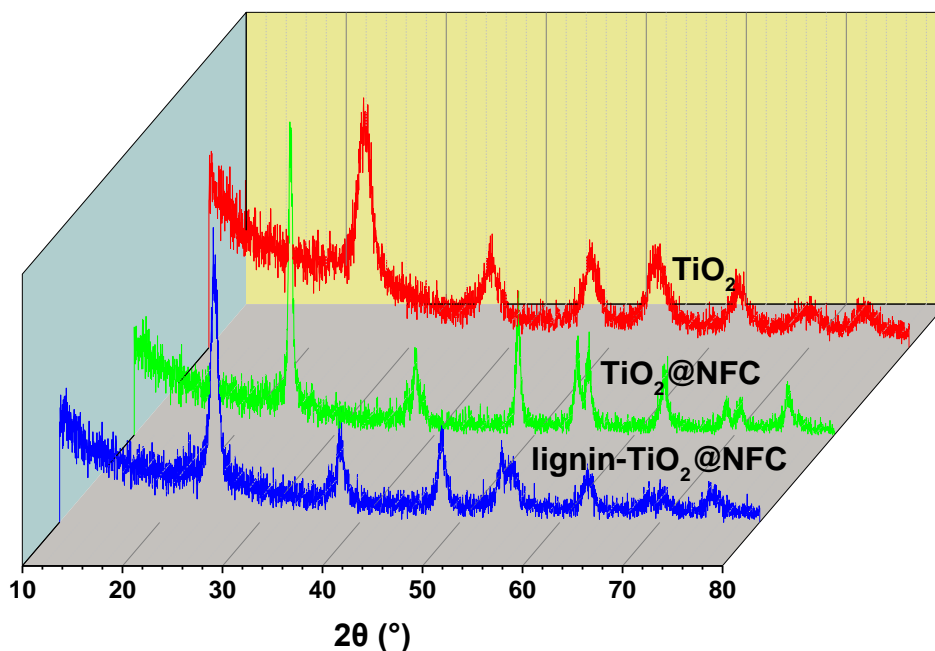
### UV-blocking Performance

The solid particles (TiO<sub>2</sub>@NFC and lignin-TiO<sub>2</sub>@NFC) were added to the hand cream in different mass ratios and stirred for 8 h to make a uniform sunscreen. A 3M (Hangzhou, China) medical porous tape with an area of 12.5 cm<sup>2</sup> was pasted on a clean transparent quartz plate with a thickness of 2 mm, and the sunscreen sample was evenly coated on the tape. The tape sample was placed in a dark place and dried for 30 min. The ultraviolet transmittance of samples at 290 nm to 400 nm was measured with a UV-visible (UV-vis) spectrometer (Cary 60; Agilent Technologies Co., Ltd., Palo Alto, USA).

## RESULTS AND DISCUSSION

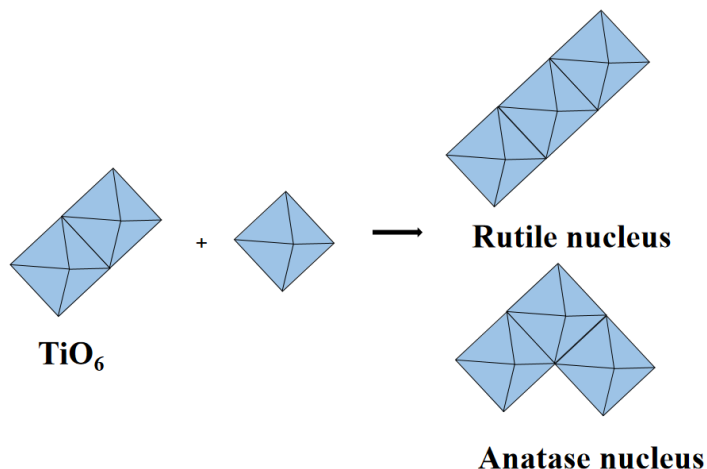
### X-ray Diffraction

The XRD patterns of the composite material hybrids are shown in Fig. 1. The diffraction angles of 25.4°, 37.9°, 47.9°, 53.9°, 55.1°, 62.7°, 68.8°, 69.9°, and 75.5° corresponded to the (101), (004), (200), (105), (211), (204), (116), (220), and (215) interplanes of the anatase TiO<sub>2</sub> phase (JCPDS No. 21- 1272). Figure 1 shows the XRD patterns of the cellulose nanofibers with the TiO<sub>2</sub> coating and the lignin coating. As demonstrated in the XRD patterns, some XRD peaks of the composite materials were still identifiable by referring to JCPDS No. 21- 1272 due to the low crystallinity of the NFC (Zhang *et al.* 2019). Since lignin is amorphous in nature and lacks ordered structure, the XRD diffractograms of both composites did not show any diffraction peak and that can be referred to lignin, and no other crystalline by-products are formed even after the formation of lignin-TiO<sub>2</sub>@NFC composite (Ibrahim *et al.* 2019). The results showed that the TiO<sub>2</sub>@NFC and lignin-TiO<sub>2</sub>@NFC had increased crystalline structures, which may have been due to the fact that NFC is more malleable and spatial than TiO<sub>2</sub> because of its silk-like and broom-like structure; in addition, the hydrogen bonds in NFC are stronger, and chemical bonds are more frequent, which results in a better induction effect (Chu *et al.* 2019).



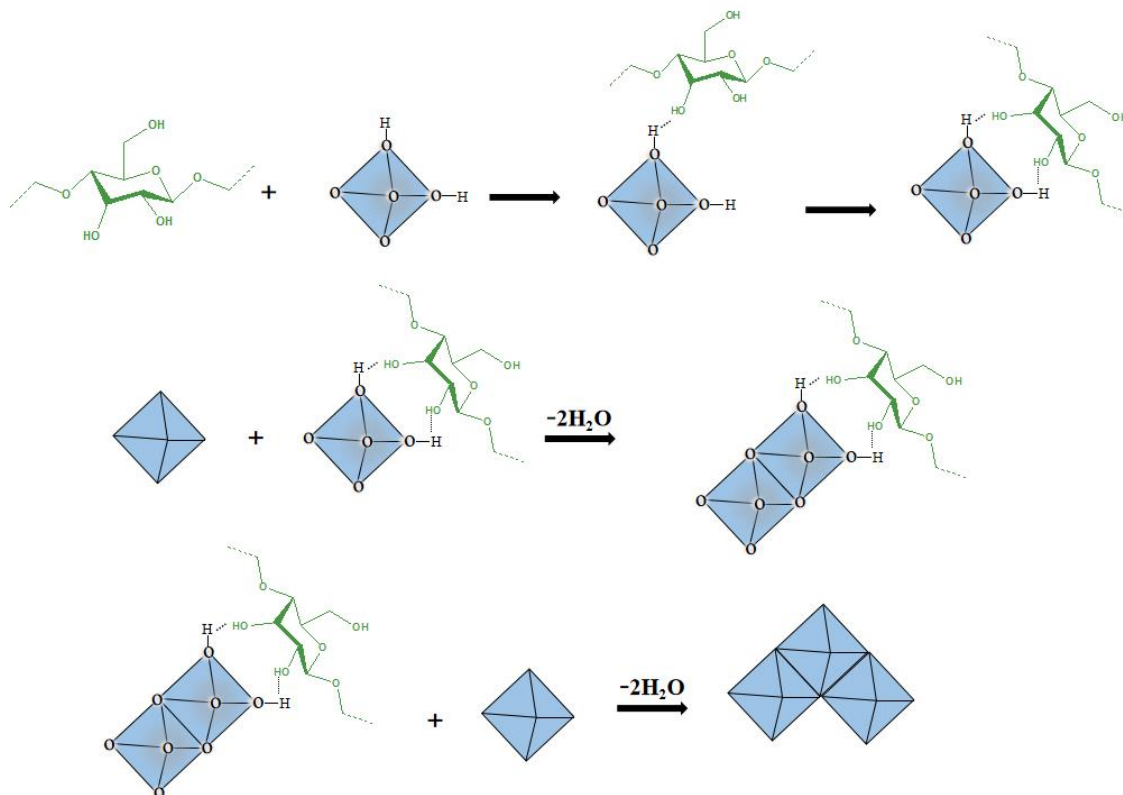
**Fig. 1.** The XRD patterns of the prepared composite materials

Many hydroxyl groups on the surface of NFC can form hydrogen bonds with TiOH<sup>3+</sup> and adsorb on the surface of the TiO<sub>2</sub> crystal unit, which promotes heterogeneous nucleation and growth of crystals. Therefore, structured TiO<sub>2</sub> nanocrystalline can be induced under relatively low temperature and simple conditions. The specific mechanism is shown in Fig. 2.



**Fig. 2.** The schematic illustration of the evolution process of the TiO<sub>2</sub> crystal

The steric resistance effect caused by the adsorption of NFC on the surface of the TiO<sub>2</sub> crystal unit affects the stacking mode of the third TiO<sub>6</sub> octahedron, and the third TiO<sub>6</sub> octahedron is more inclined to connect with the second TiO<sub>6</sub> octahedron from the back. Therefore, this promoted the generation of an anatase phase with a folded linear structure, and NFC and CNC were nano-sized in both the length and width directions. In addition, NFC was uniformly prepared under high pressure, with better solubility, a larger specific surface area, more exposed hydroxyl groups, and a free anion terminal, which created electrostatic interaction with Ti<sup>4+</sup>. Therefore, the crystals prepared under double steric hindrance were better.



**Fig. 3.** The proposed mechanism of the evolution process of TiO<sub>2</sub> crystals in the presence of NFC

## FT-IR Analysis

Figure 4 presents the FT-IR spectra of the pure  $\text{TiO}_2$  and the prepared composite material hybrids. Broad and strong bands at  $3430\text{ cm}^{-1}$  were observed for all samples, and they were attributed to the hydroxyl groups in the phenolic and aliphatic structures of lignin. Compared with that of lignin, the spectrum of lignin- $\text{TiO}_2$ @NFC exhibited a new broad absorption band in the range  $400\text{ cm}^{-1}$  to  $800\text{ cm}^{-1}$ , which was due to the stretching vibration of the Ti-O bands (Li *et al.* 2011). In addition, one single band at approximately  $1631\text{ cm}^{-1}$  was also found for lignin- $\text{TiO}_2$ @NFC hybrid due to the bending vibration of Ti-O bands. This indicated the formation of intermolecular hydrogen bonding between groups of the lignin surface and the  $\text{TiO}_2$  surface (Hu *et al.* 2007). Combined with the above results, the composite materials were prepared successfully *via* cellulose nanofibril induction.

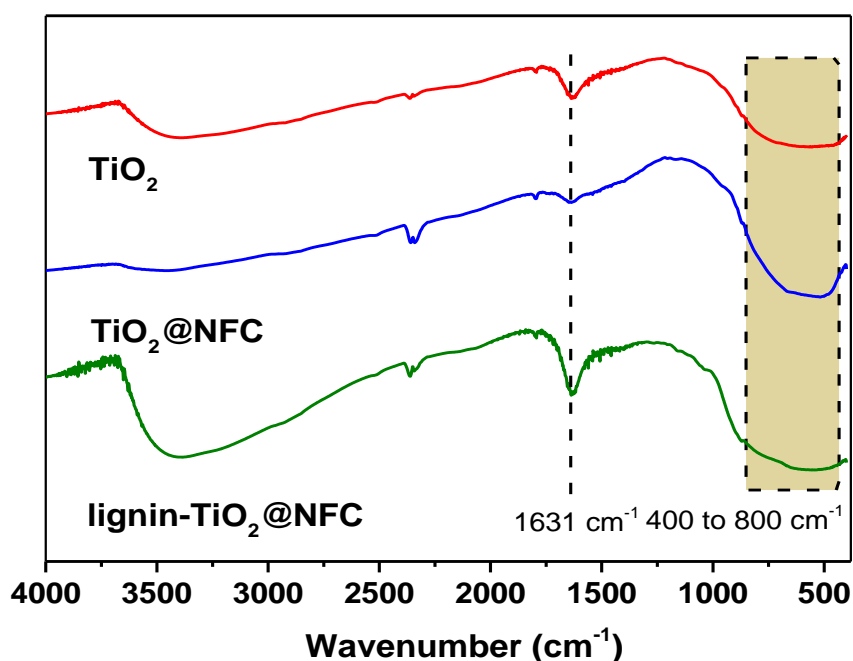
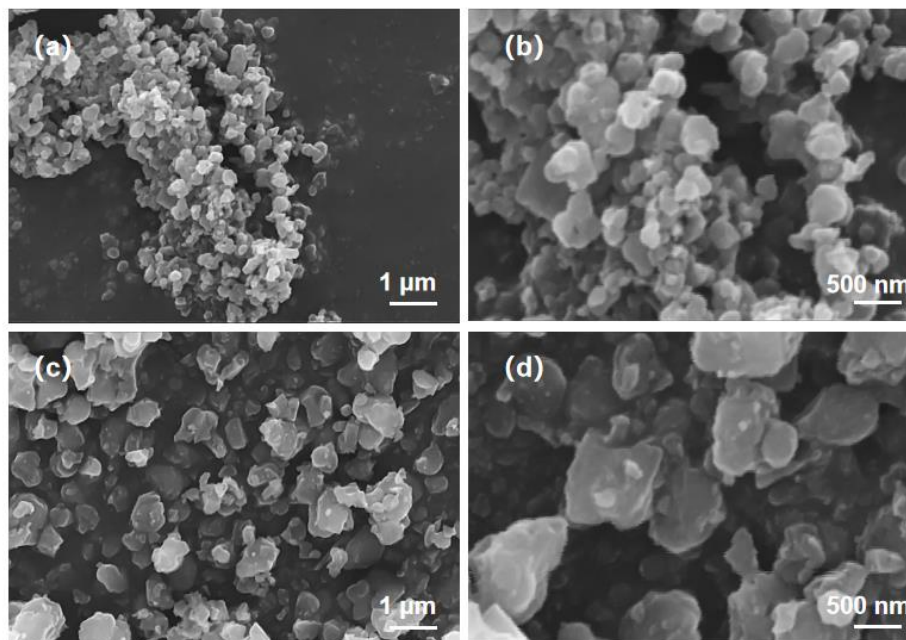


Fig. 4. The FT-IR spectra of  $\text{TiO}_2$  and the prepared composite materials

## SEM Analysis

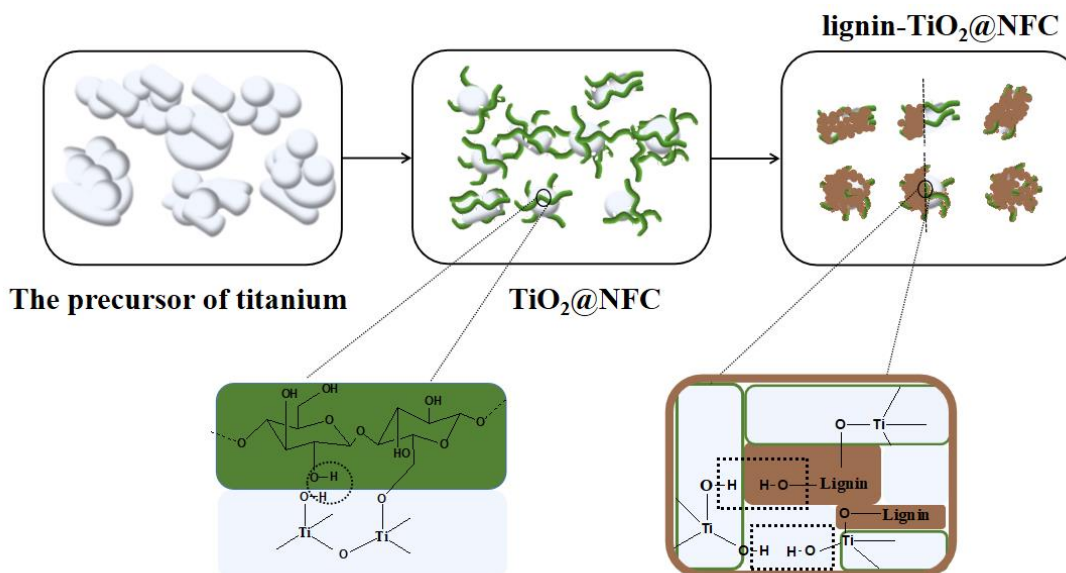
Figure 5 shows that the  $\text{TiO}_2$ @NFC prepared by the NFC-induced synthesis had a uniform nanometer size, and the lignin- $\text{TiO}_2$ @NFC composite material prepared with the same method increased in size. The size and degree of agglomeration of the composite materials were better than those reported by Morsella *et al.* (2016). As demonstrated in Fig. 5, the introduction of NFC solved the aggregation problem of  $\text{TiO}_2$  and induced the formation of lignin- $\text{TiO}_2$ @NFC composite material in a flake shape due to its special structure and chemical properties. Compared to nanoparticles with a spherical structure, the lamellar structure of lignin- $\text{TiO}_2$ @NFC has a UV shielding effect, and a better UV shielding effect can be achieved with lignin- $\text{TiO}_2$ @NFC with a small amount of doping (Chen *et al.* 2019). Because it does not affect the physical stirring of the blank cream, it can alleviate the danger of nanoparticle infiltration, such as penetrating into facial skin and greatly improve safety.





**Fig. 5.** The SEM images of the composites: (a)  $\text{TiO}_2@\text{NFC} \times 20.0\text{k}$ ; (b)  $\text{TiO}_2@\text{NFC} \times 50.0\text{k}$ ; (c) lignin- $\text{TiO}_2@\text{NFC} \times 20.0\text{k}$ ; (d) lignin- $\text{TiO}_2@\text{NFC} \times 50.0\text{k}$

The preparation mechanism of the small grain size and high activity titanium dioxide with cellulose nanofibril as the template is shown in Fig. 6.



**Fig. 6.** Preparation mechanism of the novel Lignin- $\text{TiO}_2$  induced with NFC

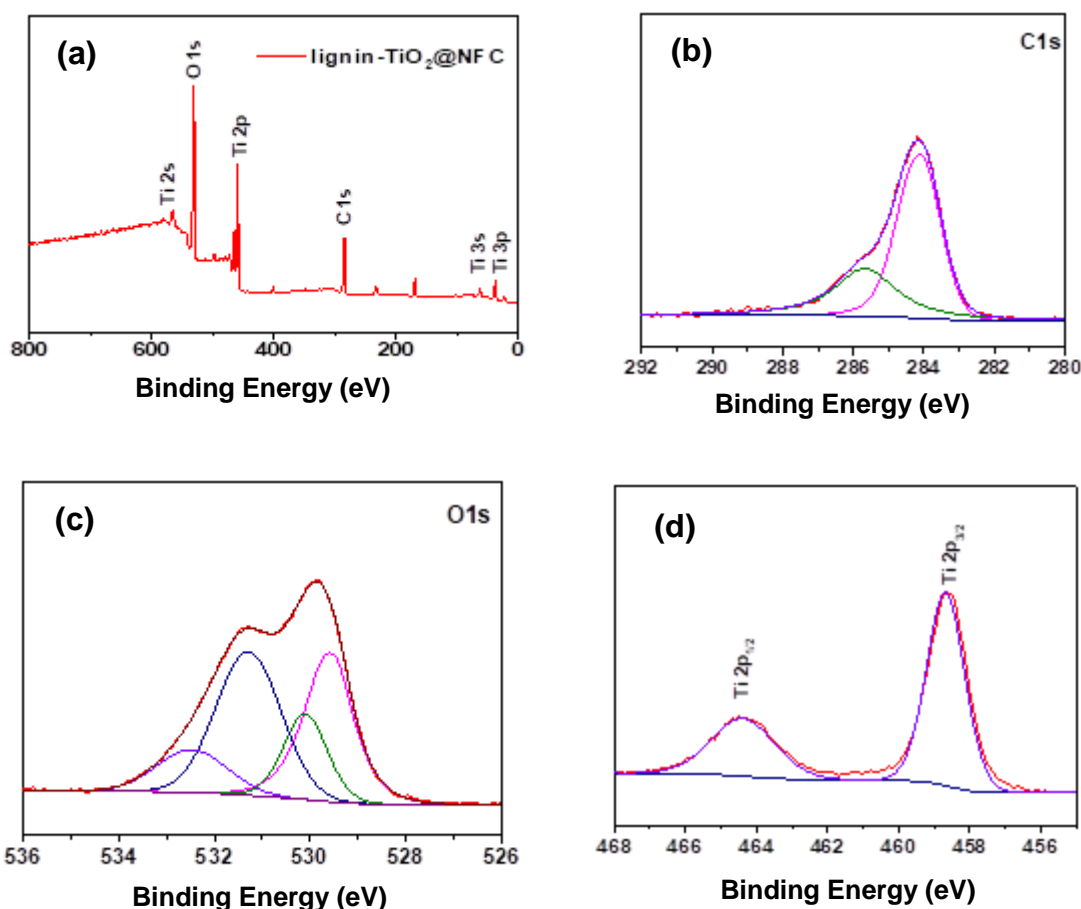
Because they were affected by the hydroxyl groups of NFC macromolecules, the growth and aggregation of  $\text{TiO}_2$  precursor were inhibited. Lignin also plays a role in promoting and inducing the crystallization of titanium dioxide due to its phenolic hydroxyl group and spatial structure. The composite materials achieved uniform immobilization and coating structure of titanium dioxide induced by lignin and cellulose. Nanoscale composite



materials were obtained without subsequent treatment to weaken the photocatalytic effect of lignin in the subsequent composite materials on titanium dioxide and the synergistic anti-ultraviolet effect.

### XPS Analysis

The chemical composition of the lignin-TiO<sub>2</sub>@NFC was elucidated by XPS. The XPS survey spectra of the lignin-TiO<sub>2</sub>@NFC confirm that the lignin-TiO<sub>2</sub>@NFC contains the elements of C, O, and Ti, as shown in Fig. 7a. In Fig. 7b, the main peak locked at 284.3 eV is assigned to C-C bonds, whereas the other peak at 285.6 eV corresponds to C-O bonds. The presence of carbon-oxygen polar bonds can contribute to the absorption of the Ti precursor and the nucleation of the TiO<sub>2</sub> nanoparticles on the surface of NFC (An *et al.* 2007). The O1s spectra of lignin-TiO<sub>2</sub>@NFC is shown in Fig. 7c.



**Fig. 7.** (a) XPS survey spectra of lignin-TiO<sub>2</sub>@NFC. High resolution of XPS spectra for (b) C1s, (c) O1s, and (d) Ti2p

The O1s spectra show a chemical linkage between lignin, NFC, and TiO<sub>2</sub>. Peaks at 529.3 and 531.5 eV correspond to Ti-O-Ti bonds and surface hydroxyl groups, respectively, while those at 529.8 and 532.9 eV are classified as C-O-Ti bonds and C-O bonds, respectively (Yu *et al.* 2018). The Ti2p spectrum of the lignin-TiO<sub>2</sub>@NFC contains peaks for Ti2p<sub>3/2</sub> and Ti2p<sub>1/2</sub> located at 458.6 and 464.4 eV, respectively, but they are shifted to lower binding energies than pure TiO<sub>2</sub>. This indicates that C-O-Ti bonds in the lignin-

TiO<sub>2</sub>@NFC, which lowers the energy of the Ti peak, indicating that some degree of molecular interactions exist between the lignin-TiO<sub>2</sub>@NFC (Yang *et al.* 2018). The presence of C-Ti-O bonds demonstrates that lignin was coated on the surface of TiO<sub>2</sub> by esterification-based dehydration condensation. The XPS results also confirmed the preparation mechanism of the novel lignin-TiO<sub>2</sub> induced with NFC, as shown in Fig. 6.

### Thermal Analysis

The thermal stabilities of the prepared composite materials were tested by TG. Figure 8 shows that the TiO<sub>2</sub>@NFC sample mainly suffered from severe weight loss at approximately 300 °C, which was largely due to the degradation of NFC. Figure 9 shows that the lignin-TiO<sub>2</sub>@NFC sample also suffered from severe weight loss at approximately 300 °C, whereas TiO<sub>2</sub> remained stable above 500 °C.

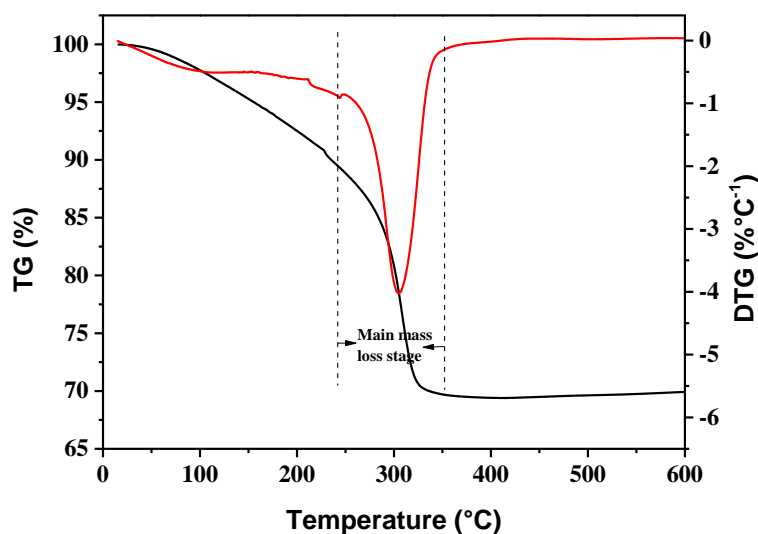


Fig. 8. The TG and DTG curves of the prepared TiO<sub>2</sub>@NFC

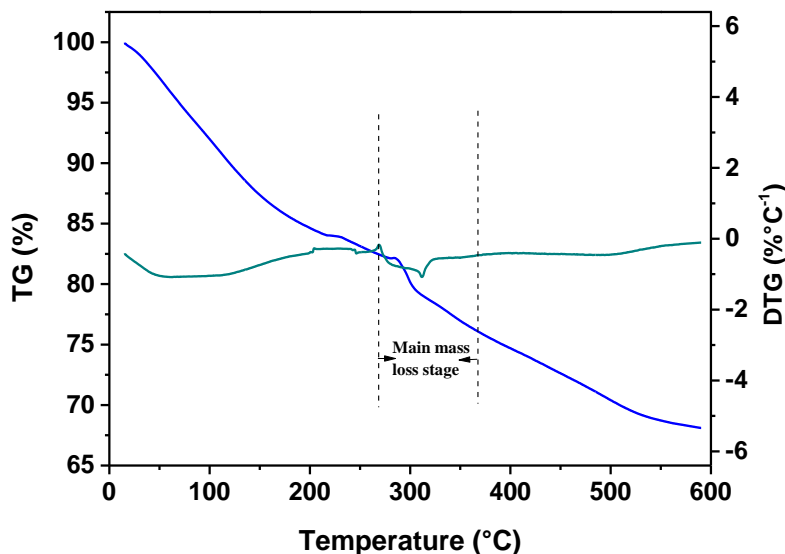
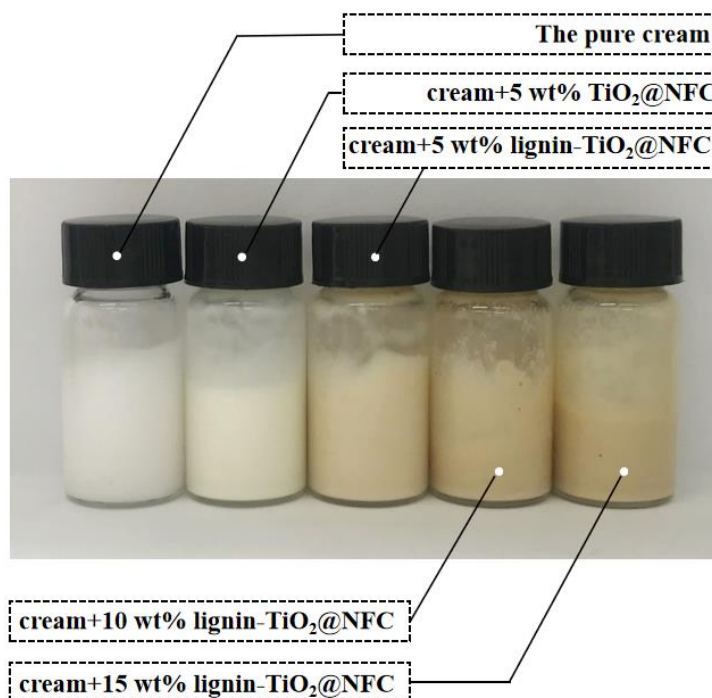


Fig. 9. The TG and DTG curves of the prepared lignin-TiO<sub>2</sub>@NFC

The char residue of lignin-TiO<sub>2</sub>@NFC at 600 °C was 68.1 wt%, which indicated that the lignin-TiO<sub>2</sub>@NFC had better thermal stability, and the load of lignin-TiO<sub>2</sub>@NFC was approximately 31.9%. The results showed that the thermal stability of lignin-TiO<sub>2</sub>@NFC was similar to that reported by Wu *et al.* (2019) but differed from that of TiO<sub>2</sub>@NFC and lignin, which showed a relatively stable decline. This indicated that lignin-TiO<sub>2</sub>@NFC was not simply a physical combination of TiO<sub>2</sub>@NFC and lignin but rather a stable chemical bond.

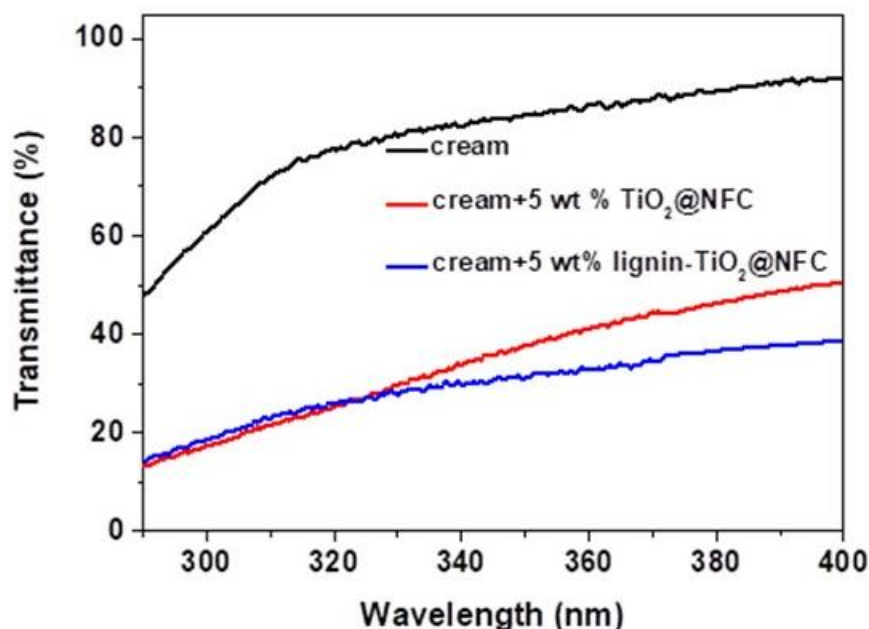
### UV-blocking Performance

TiO<sub>2</sub> is the most commonly used physical sunscreen. Lignin-TiO<sub>2</sub> is both a macromolecular dispersant and a natural sun blocker. Coating lignin on the surface of TiO<sub>2</sub> can improve its dispersity and enhance its UV-blocking property. Therefore, the sunscreen performance of lignin-TiO<sub>2</sub> was investigated and compared with TiO<sub>2</sub> and the unmodified cream physical mixture. The cream matrix was mixed with 5 wt% TiO<sub>2</sub>@NFC, 10 wt% lignin-TiO<sub>2</sub>@NFC, and 15 wt% lignin-TiO<sub>2</sub>@NFC for 8 h until the composite materials were evenly dispersed. The sunscreen performance of lignin-TiO<sub>2</sub> was investigated and compared with TiO<sub>2</sub> and the unmodified cream physical mixture. The cream matrix was mixed with 5 wt% TiO<sub>2</sub>@NFC, 5 wt% lignin-TiO<sub>2</sub>@NFC, 10 wt% lignin-TiO<sub>2</sub>@NFC, and 15 wt% lignin-TiO<sub>2</sub>@NFC. The cream matrix mixtures with 5 wt% TiO<sub>2</sub>@NFC, 5 wt% lignin-TiO<sub>2</sub>@NFC, 10 wt% lignin-TiO<sub>2</sub>@NFC, and 15 wt% lignin-TiO<sub>2</sub>@NFC were all faint yellow, which was lighter than the color of commonly used BB and therefore acceptable (Fig. 10).



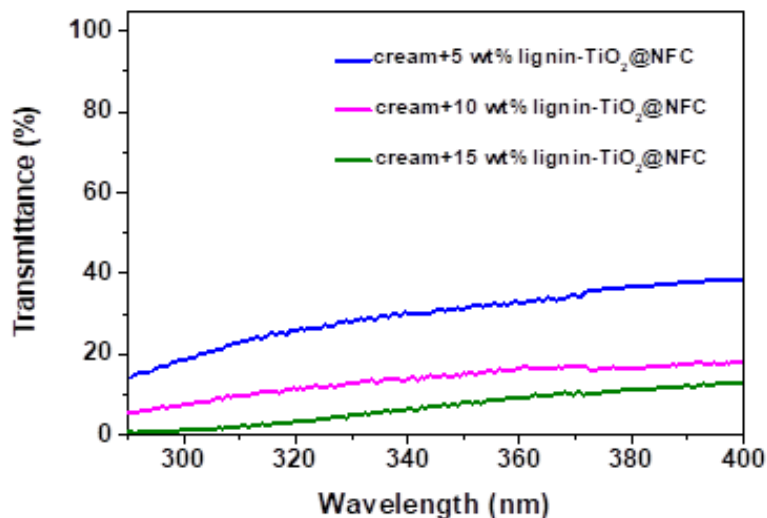
**Fig. 10.** Image of the unmodified hand cream with 5 wt% TiO<sub>2</sub>@NFC and the 5 wt% lignin-TiO<sub>2</sub>@NFC, 10 wt% lignin-TiO<sub>2</sub>@NFC, and 15 wt% lignin-TiO<sub>2</sub>@NFC physical mixtures

Figure 11 shows the typical UV transmittance of the unmodified hand cream and the cream blended with 5 wt% TiO<sub>2</sub>@NFC and 5 wt% lignin-TiO<sub>2</sub>@NFC in the UVA and UVB areas. The unmodified hand cream exhibited poor UV-blocking performance and higher transmittance. With the same 5% concentration, the transmittance of lignin-TiO<sub>2</sub>@NFC was lower than that of TiO<sub>2</sub>@NFC in the UVA areas, whereas the transmittance of lignin-TiO<sub>2</sub>@NFC was close to TiO<sub>2</sub>@NFC in the UVB areas. Due to the presence of chromophore groups in the lignin which reduces the light transmittance of composite materials. The lignin-TiO<sub>2</sub>@NFC significantly reduces the UVA (320 nm to 400 nm) and UVB (280 nm to 320 nm) transmittance because of the uniform distribution and synergistic effect between the TiO<sub>2</sub> and lignin components (Rukmanikrishnan *et al.* 2020). Therefore, the UV shielding effect of lignin-TiO<sub>2</sub>@NFC was superior.



**Fig. 11.** Typical UV transmittance of the unmodified hand cream and the cream blended with 5 wt% TiO<sub>2</sub>@NFC and 5 wt% lignin-TiO<sub>2</sub>@NFC and the physical mixture in the UVA and UVB areas

Then, the typical UV transmittance of the unmodified hand cream and the cream blended with 5 wt% lignin-TiO<sub>2</sub>@NFC, 10 wt% lignin-TiO<sub>2</sub>@NFC, and 15 wt% lignin-TiO<sub>2</sub>@NFC in the UVA and UVB areas were studied. Figure 12 shows that, as input amount increased, the UV shielding effect became more obvious. Compared to 5 wt% lignin-TiO<sub>2</sub>@NFC, the input amount of 10 wt% lignin-TiO<sub>2</sub>@NFC was greatly improved, whereas the effects of 10 wt% lignin-TiO<sub>2</sub>@NFC and 15 wt% lignin-TiO<sub>2</sub>@NFC were similar. However, higher dosages of composite materials would demulsify the sun cream, and the 15 wt% input amounts of the nanocomposites dispersed well in the unmodified hand cream. In addition, 10 wt% lignin-TiO<sub>2</sub>@NFC was the best dosage, and it could absorb approximately 90% of UV light in the full UV band (200 nm to 400 nm), which indicated the lignin-TiO<sub>2</sub>@NFC had a good UV-shielding property.



**Fig. 12.** Typical UV transmittance of hand cream blended with 5 wt% lignin-TiO<sub>2</sub>@NFC, 10 wt% lignin-TiO<sub>2</sub>@NFC, and 15 wt% lignin-TiO<sub>2</sub>@NFC and the physical mixture in the UVA and UVB areas

## CONCLUSIONS

1. In this work, a novel lignin-TiO<sub>2</sub> UV-shielding composite was synthesized successfully *via* a hydrothermal method induced with NFC, and the TiO<sub>2</sub> was synthesized *via* the same method without the addition of lignin.
2. Comparison of the characterization results of TiO<sub>2</sub> and lignin-TiO<sub>2</sub> showed that the lignin-TiO<sub>2</sub>@NFC had anatase nanoparticles with good thermal stability.
3. The UV-vis transmission spectra results revealed that the unmodified hand cream containing 10 wt% lignin-TiO<sub>2</sub>@NFC could absorb approximately 90% of UV light in the full UV band (200 nm to 400 nm), which indicated that the lignin-TiO<sub>2</sub> induced by NFC had a good UV-shielding property.

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