Study of Particle Reduction Method and Particle Size Effect on TiO$_2$ as Near-infrared Reflector Coating in Cotton Fabric

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A near-infrared (NIR) reflector in cotton clothes may prevent several dermatological problems. TiO$_2$ is commonly used for the NIR reflector coating in cotton. The NIR reflectance value is expected to increase if smaller TiO$_2$ particles were used. A simple mechanical process of ultrasonic wet-milling to reduce the TiO$_2$ particle size is proposed in this study. The reduction process utilizes ultrasonic cavitation by an ultrasonic homogenizer has succeeded in reducing the particle size from 170 to 80 nm as indicated by particle size measurement results and as supported by transmission electron microscopy results. The wet-milling particles of 80 nm TiO$_2$, along with 170 and 280 nm TiO$_2$, were used to coat cotton fabrics. Optimization of the coating process was performed using citric acid and chitosan as binder agents. The effect of citric acid and chitosan was studied through NIR spectroscopy, scanning electron microscopy, and X-ray fluorescence. From the NIR spectroscopy characterization results, it is found that the fabrics which are coated with the smallest TiO$_2$ particle size (80 nm) indeed show highest NIR reflectance among others.

Keywords NIR reflector; Fabric coating; Ultrasonic wet-milling; Titanium dioxide

I. INTRODUCTION

Clothing made from cotton is commonly used in summer or warm/hot weather since it can release heat from a human body quickly, which make the wearer feels cooler and cozier. Unfortunately, cotton easily transmits the near-infrared (NIR) ray from the sun to the surface of our body. The NIR spectrum accounts for about 52% of the sunlight energy [1], so it is quite dominant among the other energy spectra. This means that the NIR spectrum carries high energy which potentially causes dermatological problems such as skin aging or apoptosis [2].

These problems motivate some researchers to develop NIR reflector coatings on the cotton fabric surface. This coating utilizes reflective particles inside the coating layer to prevent the NIR wave radiation that propagates through the fabric by altering the physical properties of the particles like the refractive index or color of the fabric [3]. Many previous studies use titanium dioxide (TiO$_2$) as a reflective coating material since it has a white color and a high refractive index as well as it is not soluble in water, non-toxic, and could act as a good antipollution component [4, 5]. TiO$_2$ exhibits strong oxidizing power under irradiation of the ultraviolet light in a water and oxygen containing environment. Thus, it gives ability of decomposition and/or oxidization of most of organic and/or inorganic compounds that are proven to be beneficial for the destruction of microorganisms and bacteria [4]. Various studies have shown TiO$_2$ utilization for antibacterial and self-cleaning in cotton fabric. A research by Zahid et al., who used manganese-doped photocatalytic
TiO$_2$ nanoparticles to functionalize cotton fabric, showed 100% reduction of *Staphylococcus aureus* (Gram-positive) and *Klebsiella pneumoniae* (Gram-negative) populations within 120 min under sunlight irradiation [6]. In 2019, Zhang *et al.* treated cotton fabric with amino-capped TiO$_2$ which exhibited a bacterial reduction rate of both *S. aureus* and *E. coli* for more than 99% [7]. One of the latest related studies in this topic is given by Tudu *et al.*, who succeeded in preparing superhydrophobic cotton fabric by a simple immersing technique with a mixture of perfluorodecytrimethoxyxilane and TiO$_2$ nanoparticles [8]. The result showed properties of great self-cleaning, stain resistance, rust stain resistance, and anti-water absorption ability of the coated cotton fabric.

One of the concepts used to explain the interaction between the wave radiation and the material is the Kubelka-Munk (KM) theory, which is widely accepted for explaining the optical properties of complex systems such as powders and inhomogeneous systems [3]. In previous researches, the KM theory is favorable to be used as a model function to explore electrical properties such as a band gap [9] or optical properties such as scattering and reflection behaviors [10]. Gudla *et al.* have used this theory to determine absorption and scattering coefficients of TiO$_2$ particles embedded in polyurethane to help understanding reflection spectra [11]. According to the KM theory, the increase of the reflectance is directly proportional to the decrease of the reflector particle size [12]. Therefore, for TiO$_2$ coating, the intensity of the reflected NIR wave is expected to increase as the TiO$_2$ particle decreases.

However, previous studies regarding the TiO$_2$ nanoparticle were usually conducted by using two separated materials [12], and only a few used a modification of the larger particles. The use of commercial TiO$_2$ nanoparticle products may simplify the fabrication process of UV reflective coating, but it will increase the fabrication cost as those products are expensive. Thus, it is more economical to use the TiO$_2$ nanoparticles obtained from in-house size reduction method of TiO$_2$ microparticles as proposed in this manuscript. But the reduction process of the TiO$_2$ microparticle is mostly done through the chemical process, which generally requires a long and complicated step. Some previous studies employed precipitation [13] or a sol-gel process to create smaller particles [14]. This process, although successful in producing TiO$_2$ in the nanometer-range particles, needs various stages and takes a long time. In a mechanical approach, ball milling is a quite favorable method. Although considered as a simple and easy method [15], this process also takes a long time, i.e., around 2 to 5 h [15, 16]. There are also studies on annealing [17] and calcination [18] processes to control the size reduction, but they require high working temperatures.

In the present research, a much simpler mechanical process of ultrasonic wet-milling was proposed to reduce the TiO$_2$ particle size prior to be used as an NIR reflector coating on the surface of cotton fabric. The reduction in the TiO$_2$ particle size is expected to occur through the mechanical effect of ultrasonic cavitation using an ultrasonic homogenizer at a certain amplitude range, which usually takes only less than 2 h to be processed [19]. The reflection performance of the TiO$_2$ reflection coating with a small particle size was then compared with two other larger particle coatings. The results of the present research are expected to help the development of nanotechnology, especially in the field of anti-NIR coating as an effort to find a simpler particle-size reduction method and as a part of a development of a better NIR reflection performance.

II. MATERIALS AND METHOD

A. Materials

Two types of TiO$_2$ powder in the rutile phase, both from Brataco Chemical, Indonesia, with particle sizes of around 280 nm (TiO$_2$-a) and 170 nm (TiO$_2$-b) were used. Citric acid (C$_6$H$_{12}$O$_7$) purchased from Brataco Chemical and chitosan synthesized in Advance Processing Material Laboratory, Engineering Physics Department, Institut Teknologi Bandung were used as binders of the TiO$_2$ coating on the cotton fabric surface. Demineralized water, filtered to remove impurities but not distilled, was used as a suspension medium for a particle-size reduction process and a coating synthesis process, and also as a dispersion medium in measuring the particle size. The density of demineralized water was measured experimentally and was about 0.985 g mL$^{-1}$.

B. Size reduction of the TiO$_2$ particle

TiO$_2$-b was processed in ultrasonic wet-milling to produce TiO$_2$ with a smaller particle size of 80 nm (TiO$_2$-c). The process was started by dispersing 2.59 g of TiO$_2$-b in 50 mL demineralized water to produce 5 wt% of TiO$_2$ suspension. Then, the suspension was stirred manually before being sonicated using an ultrasonic homogenizer (3000 MP, Bio-Logics). According to Hielsher [19], the amplitude range for particle reduction using sonication milling is around 40–120 μm. Based on this information and device specifications, the sonication amplitude used in this study was 50 μm. The TiO$_2$ suspension was sonicated for 30 min with a 5-s pause in every 1 min. The suspension was then centrifuged for 15 min at 7000 rpm to obtain only the small TiO$_2$ particles. The supernatant was then separated from the resulting sediment to be evaluated using a particle size analyzer (PSA) (SZ-100, Horiba) and a transmission electron microscope (H-9500, Hitachi).

C. Coating process of TiO$_2$ on the cotton fabric

The coating process was performed for each TiO$_2$ sample (TiO$_2$-a, TiO$_2$-b, TiO$_2$-c) on the cotton fabric surface. The process was based on the method described in the paper by Kustningsih *et al.* [20] with a slight modification. The process started with mixing 10 mg of TiO$_2$ and 70 mg of citric acid in 60 mL of demineralized water using a magnetic stir-
rer with the velocity of 600 rpm for 30 min. Next, 30 mg of chitosan was added to the mixture and the stirring was continued for another 30 min. Finally, a piece of cotton fabric with the same weight as the chitosan was added to the mixture, and the stirring was continued for 1 h. The fabric was then washed using detergent in demineralized water and dried using an oven at 80°C for 30 min. These fabric samples were named as in Table 1.

All samples were characterized using a NIR spectrometer (NIRQuest, Ocean Optics) and a scanning electron microscope (SU3500, Hitachi). NIR spectroscopy characterization was performed to determine the percentage of incoming infrared that was reflected by each piece. Average reflectance values for each sample were obtained by dividing the total reflectance values with the total number of measured wavelengths. Characterization by scanning electron microscopy (SEM) was needed to observe coating’s morphology on the cotton fabric surface. Characterization using X-ray fluorescent (XRF) (Orbis Micro, EDAX) was also conducted to determine the type of elements and the amount of each element contained in the samples.

### III. RESULTS AND DISCUSSION

#### A. Particle characterization and reduction process

The particle size distribution of the TiO$_2$-b powder before and after sonication milling is shown in Figure 1. From this figure, it can be seen that there is a significant shift in the size distribution of the TiO$_2$ powder after ultrasonic wet-milling compared to that before sonication. The particle size decreases significantly after the ultrasonic wet-milling process. It was obtained that the average diameters of TiO$_2$-b and TiO$_2$-c are 170 and 80 nm, respectively.

The milling process using an ultrasonic homogenizer relies on the concept of ultrasonic cavitation. Particles’ grinding through this phenomenon utilizes the collapse of vacuum bubbles caused by absorption of high-intensity ultrasonic wave energy [19]. The vacuum bubbles occur due to the cycle of the pressure drop from the sonication process, which is influenced mostly by the intensity of the wave acceleration or the oscillation amplitude [19]. Cavitation is a phenomenon where the bubbles collapse violently because they can no longer absorb energy during high pressure cycle of the sonication process. A larger oscillation amplitude or pressure difference could generate a more violent cavitation that can give a better result on particle deagglomeration and can produce a more homogeneous dispersion [21].

It should be noted that the homogeneity of the TiO$_2$-c powder is lower than that of TiO$_2$-b. The ultrasonic wet-milling process might not homogeneously reduce the particle size of the TiO$_2$-b powder for several reasons, such as the frequency, the amplitude, the duration, and the density of the suspension. To increase the homogeneity of the sonication result, centrifugation was performed to separate larger and smaller particles. A higher speed and a shorter time of centrifugation are expected to yield a more homogeneous particle-size distribution because the size of the particles left in supernatant decreases in this configuration. Overall, the PSA results prove that the reduction process through ultrasonic wet-milling is successfully performed.

A more detailed characterization of the TiO$_2$-c particles was conducted by transmission electron microscopy (TEM). The observation was performed at a 300-kV operation voltage and a magnification of 100 k ×. TEM imaging result is shown in Figure 2. The size and the shape of the TiO$_2$-c particles could be clearly understood from the imaging results. As can be seen in the image, it is clear that the particle size is not homogeneously distributed. Although most of the particles have a size around 80 nm, other particles have a bigger size around 90 and 100 nm. This

### Table 1: List of the cotton fabric samples, average reflectance values, and XRF characterization results for each sample.

| Sample | Treatment          | Average reflectance | Weight ratio (%) |
|--------|--------------------|---------------------|------------------|
|        |                    |                     | TiO$_2$ | CaO |
| A      | Coated with TiO$_2$-a | 45%                | 97.4   | 2.7 |
| B      | Coated with TiO$_2$-b | 51%                | 98.9   | 1.2 |
| C      | Coated with TiO$_2$-c | 54%                | 96.9   | 3.2 |
| D      | Uncoated Fabric     | 43%                | 95.6   | 4.5 |

Figure 1: Particle size distribution from the PSA characterization of TiO$_2$ before (TiO$_2$-b) and after (TiO$_2$-c) sonication milling.
result is compatible with the results of the PSA characterization. However, it is also clear from this result that the size reduction process is successfully performed since most of the particles have a size under or around 100 nm, which are smaller than the TiO$_2$-b particle size.

The shape of the particles is irregularly spherical. Most of the particles seem to have a combination of a spheric-cubic shape, shown by a clear straight line and angle in some parts while a round in the other parts. This shape actually corresponds to the shape of the TiO$_2$ rutile phase. The particles of the TiO$_2$ rutile type are present in irregularly shaped round particles, while the particles of the TiO$_2$ anatase type are found to be spherical in shape [22]. This result shows that the TiO$_2$ phase does not change from rutile to anatase. This is considered not unusual since the rutile phase is thermodynamically the most stable form of TiO$_2$ [3], while the anatase phase is metastable and has a less constrained structure which enhances its kinetics of the formation [23]. Although it can be stated that the ultrasonic wet-milling process has no effect to the TiO$_2$ phase transformation from rutile to anatase, the effect of this process on the phase transformation from anatase to rutile still needs to be investigated further.

**B. Surface morphology**

The SEM observation was performed for each fabric sample at a 10-kV acceleration voltage and a magnification of 2 k×. Surface morphology of each sample is shown in Figure 3. These pictures depict that there are more TiO$_2$ particles bonded together in sample B rather than in samples A and C. This result suggests that the binder weight ratio might be higher in sample B. TiO$_2$ with different particle sizes seems to have their own binding character in the fabric. The TiO$_2$-c particles that stick to the sample C fibers look more tenuous and smoother, and do not accumulate too much. On the other hand, the TiO$_2$-a and TiO$_2$-b particles agglomerate quite a lot in the cotton fabric. However, the TiO$_2$-a particles still a bit lumpier than other TiO$_2$ particles. This agglomeration might occur due to several reasons such as insufficient washing duration and the distribution inhomogeneity of the binder and the TiO$_2$ particles. This particle agglomeration might decrease the reflection ability of TiO$_2$-a.

**C. NIR reflection properties of cotton fabric**

The reflection measurement results of four pieces of coated cotton fabrics are shown in Figure 4, and the reflectance average values for each sample are listed in Table 1. Sample C has the highest reflectance value with the average of 54%, followed by sample B with 51%. Sample A has the lowest reflectance value of 45%, which is just a little bit higher than that of sample D (43%). These results prove that the reflectance value does relate to the differences in the particle size.

In the term of the relation between the particle size and the reflection value, these measurement results have a significant correlation with the KM theory. This theory is suitable for describing optical properties in the complex structure which both absorption and scattering phenomena occur. Since TiO$_2$ in the rutile phase has a non-spherical particle, as depicted in the TEM imaging result, this theory is applicable for the current study. Basically, the theory describes the relation between the reflectance value with absorption ($k$) and scattering ($S$) properties as follows:

\[
 f(R_\infty) = \left( \frac{1 - R_\infty}{2R_\infty} \right)^2 = \frac{k}{S}.
\]

Here, $R_\infty$ and $f(R_\infty)$ are the absolute diffuse reflectance.
Figure 4: Spectral reflectance curves of cotton fabric with different treatments. The measured NIR region is divided into four regions.

and the KM function of the absolute diffuse reflectance, respectively. The scattering coefficient $S$ is assumed to be constant over the wavelength region measured [9], and thus the reflectance is mostly affected by the absorption coefficient $k$. As the particle size increases, the depth of the light penetration increases and absorption is also enhanced, leading to the decrease in reflectance [12].

There is another factor that affects the reflection property. Coating with small particles creates a large number of grains with different crystal orientations so that the scattering process is enhanced and the penetration depth is decreased along with the increase of the grain boundaries [12]. This is the main factor for the increase of reflectance and inhibition of the propagation of the infrared waves with smaller particle coatings. It is also important to consider the band gap manipulation as the particle size decreases. Previously, Lin et al. [5] investigated the relationship between the particle size and the TiO$_2$ photocatalytic property by using the transformed diffuse reflectance technique which was based on the KM theory. The band gap changes as a function of the particle size, which may contribute to the reflection performance of the material.

It can be seen in Figure 4 that reflectance of each fabric sample is quite stable in a wavelength region between 897 and 1330 nm and, then, starts to decrease and becomes unstable, especially from 1580 nm onwards until 2500 nm with strong absorption at around 1600 and 2250 nm. These results are actually quite similar to other previous studies. Menning et al. reported that their coatings had a reflectance of about 80% in the range of 800–1200 nm [24]. The NIR reflectance measurements of TiO$_2$ nanoparticle and micro-particle powders by Jeevanandam et al. showed that the reflectance value of nanoparticles was significantly high in the region between 750 and 1300 nm but gradually decreased between 1300 and 2500 nm [12]. This phenomenon may happen because of the combination and overtone band caused by an anharmonic oscillation in the NIR and mid-IR region, that is in the wavelength range from 2500 to 25000 nm [25]. Meanwhile, according to Jeevanandam et al. [12], nanocrystalline metal oxides possess a higher surface area compared to microcrystalline metal oxides and, thus, have stronger absorption features. The strong absorption effect already affects the final part of the NIR wavelength range near 2500 nm. The reflectance measurement results in this study indicate that this effect begins to emerge after the wavelength of 1300 nm. Inconsistency of the shape of the reflectance curves will be discussed in detail in Section III.F.

Qualitatively, it appears that the difference in the average reflectance values of the reflectance curves is not the same among four samples. There is a quite huge gap (or difference) between the curves of sample A and sample B, while the gap between those of sample A and sample D is quite small (Figure 4). According to Fang et al. [3], this might have happened because of differences in the ratio of the weight of the binder, which is chitosan in the present case, on each fabric sample. The observation result of surface morphology of the fabric by SEM, as can be seen in Figure 3, has already indicated such a suggestion. This encourages another observation on the weight amount of the TiO$_2$ particle in the fabric surface since it is suspected that there has been a different amount of the TiO$_2$ particle on each fabric sample.

| Table 2: NIR reflectance curve characteristics for each wavelength range. |
|-----------------|----------------|----------------|
| Range          | Wavelength (nm) | Curve characterization |
| Range 1 (R-1)  | 897–1330        | Stable          |
| Range 2 (R-2)  | 1330–1635       | Have some ripples |
| Range 3 (R-3)  | 1635–2230       | Have several peaks and dips |
| Range 4 (R-4)  | 2230–2536       | At the lowest position |

D. XRF analysis

XRF measurements at 40 kV and 355 μA were carried out to determine the amounts of constituent elements on each sample. The result is shown in Table 1. Only two elements were detected in the measurements from the uncoated fabric; they are TiO$_2$ and CaO. Calcium exists in the cotton fabric as one of inorganic cations from raw fiber, found both in the lumen and in the pectin fraction, where it serves as a cross-linking agent and accounts for approximately 14% of the total cationic content [26]. On the other hand, titanium or its oxide compound usually added later in the cotton fabric as antimicrobial and sunlight-resistant agents for cotton fabrics intended for outdoor use [26]. As mentioned before, results from previous studies have suggested the addition of titanium or titanium oxides for these applications [6, 7].
It can be understood from Table 1 that each coated fabric sample has a different amount of the TiO\(_2\) weight percentage compared to the uncoated fabric. Sample A gains 1.8% TiO\(_2\) more than the uncoated fabric, while sample B gains 3.3% and sample C gains 1.3%. The weight ratio of TiO\(_2\) bonded to sample B is indeed more than those of other coated fabrics. This result also matches the surface morphology observation from the SEM characterization (Figure 3) and indicates that chitosan is not equally distributed on each fabric sample so that the amount of the TiO\(_2\) particles coated on each fabric surface is also different. Accuracy in the weight measurement of citric acid and chitosan as a crosslinking agent along with the stirring time and speed can be a significant reason for the occurrence of this condition.

E. Effect of TiO\(_2\) amount on the reflectance

Different amounts of a TiO\(_2\) addition on each fabric sample might affect the reflectance value. To negate the effect of this amount difference, the inverse variation of the average reflectance gain is calculated based on the XRF results listed on Table 1 to predict the reflectance gain of each sample at the same amount of TiO\(_2\) from the uncoated sample. This data processing is done with the assumption that there is a linear relationship between the percent of the mass of the reflector and the reflectance value. In processing the reflectance data, a simple inverse variation equation is used to correlate it with an increase in the mass percentage. The inverse variation equation used is as follows:

\[
\Delta R_d = \frac{\Delta W_d}{\Delta W_a} \times \Delta R_a,
\]

where \(\Delta R_a\) and \(\Delta R_d\) are actual and desired percent reflection gains of the fabric sample, respectively, and \(\Delta W_a\) and \(\Delta W_d\) are actual and desired weight percent gains of the fabric sample, respectively.

Table 2 shows the division of four different wavelength ranges for each coated fabric sample. These divisions are based on the NIR reflectance curve characteristics. The average reflectance gains for each range were then processed using the inverse variation method, by using the data of the TiO\(_2\) weight percent gain of each coated fabric sample and the weight percent of sample C as the reference. The processed data were then plotted to describe such correlation.

![Figure 5: Average of desired reflectance gain (\(\Delta R_d\)) of fabric samples after inverse variation. The relationship between the particle sizes is described using exponential trendline. It should be noticed that \(\Delta R_d\) of sample C in R-1 (blue dots) overlaps that of sample C in R-2 (red dots), since their values are quite similar.](image)

These data are listed in Table 3, and the plot can be seen in Figure 5.

The inverse variation result (Table 3) shows that, although decreasing, the average reflectance gains of sample B and sample A still maintain their positions as the second-best and the least reflector fabric samples. The pattern of plots in Figure 5 shows that the correlation between the particle size and the reflectance gain is still moderately similar in all wavelength ranges. Generally, the average reflectance value gradually decreases as the wavelength increases. The highest reflectance gain is achieved in R-1, followed by R-2, R-3, and R-4. But the difference between the average reflectance gains of sample C (80 nm) in R-1 and R-2 is very small, indicating a higher reflectance stability in the wider wavelength range, which is throughout the whole wavelength range of R-1 and R-2, compared to other samples. These results denote that the particle size is indeed the most important factor in the reflectance of a material compared to other factors such as the binder amount.

| Sample | TiO\(_2\) weight gain (%) | \(\Delta R\) | Information |
|--------|--------------------------|-------------|-------------|
|        |                          | R-1 | R-2 | R-3 | R-4 | \(\Delta R\) |
| A      | 1.8 \((\Delta W_d)\)    | 2.9 | 1.9 | 1.2 | 1.1 | \(\Delta R_a\) |
|        | 1.3 \((\Delta W_d)\)    | 2.1 | 1.4 | 0.9 | 0.8 | \(\Delta R_d\) |
| B      | 3.3 \((\Delta W_d)\)    | 9.8 | 8.9 | 7.6 | 5.9 | \(\Delta R_a\) |
|        | 1.3 \((\Delta W_d)\)    | 3.9 | 3.5 | 3.0 | 2.3 | \(\Delta R_d\) |
| C      | 1.3 \((\Delta W_d)\)    | 12.5| 12.5| 11.4| 8.6 | \(\Delta R_a\) |
|        | 1.3 \((\Delta W_d)\)    | 12.5| 12.5| 11.4| 8.6 | \(\Delta R_d\) |
F. Effect of NIR wavelength to the shape of the reflection curves

Inconsistency of the shape of the reflectance curves along different wavelength ranges, i.e., R-1, R-2, R-3, and R-4, is caused by overtones and combination bands of the NIR region. Overtones occur at approximately multiples of the fundamental vibrational frequency when anharmonic oscillation is dominant [27]. Two or more vibrational modes can interact in such a way as to cause simultaneous energy changes and give rise to absorption bands called combination bands [27]. The NIR spectra consist of many significant overlapping of overtones and numerous combination bands. Therefore, understanding of the NIR spectra becomes more complex and is not directly interpretable as in other spectral regions [28]. However, it might still be able to predict the reasons for the curves’ shape from the NIR absorption bands as they are related to the overtone and combination bands in the NIR region [29], as can be listed in Table 4.

Comparing the NIR absorption bands with the measurement result of the NIR reflectance curves in Figure 3, it can be recognized that the curve shapes in R-1 and R-2 are more stable than those in other ranges, because the wave spectra in higher-order (i.e., second and third) overtones tend to be less complicated due to the concept of the local modes. The main idea of the local mode model is to treat a molecule as if it were made up of a set of equivalent diatomic oscillators [30]. The absorption bands in the spectrum can, thus, be interpreted as if they are originated from the local modes that makes the spectra in R-1 and R-2 appear more stable compared to other regions [30].

Fluctuation in the reflection curves happens at 1635 nm or higher wavelength regions of R-3 and R-4 (Figure 3), because they correspond to the first overtone and combination band regions, respectively. In these regions, the spectra have a more complex structure compared to those in the second and third overtone regions. Therefore, the reflectance curves fluctuate more in the R-3 and R-4 regions than in the R-1 and R-2 regions. The spectra tend to show a strong absorption especially at around 1660 and 2250 nm. It is known that those wavelengths depict C−H and O−H stretching modes, respectively [29]. Since absorption of the NIR radiation by organic molecules is primarily caused by O−H, C−H, C=O, and N−H groups [28], it is understandable that reflectance might be low in the R-3 and R-4 regions. It is also known that the NIR combination bands appear between 1900 and 2500 nm [27], meaning that there are strong absorption bands due to the combination of the C−O and C−H stretching at around 1900 and 2500 nm, respectively [31]. This strong absorption in the combination bands matches the shape of the reflectance curves in R-4 where the curves show their lowest reflectance.

IV. CONCLUSION

The coating process of cotton fabric using three sizes of TiO$_2$, that are TiO$_2$-a (280 nm), TiO$_2$-b (170 nm), and TiO$_2$-c (80 nm), with citric acid and chitosan as the binders has been successfully conducted. TiO$_2$-c was prepared by the ultrasonic wet-milling process of the TiO$_2$-b powder to achieve smaller TiO$_2$ particles using an ultrasonic homogenizer, proved by the characterization using PSA and TEM. NIR spectroscopy, SEM, and XRF characterization of the coated fabrics was performed to assess the effect of particle size on reflectance of the coated samples.

Reflectance of the NIR radiation decreases as the TiO$_2$ particle size increases, since the fabric coated with the smallest particle TiO$_2$-c shows highest reflectance, followed by TiO$_2$-b and TiO$_2$-a. The results are in accordance with the concept of the KM theory and wave diffraction. It can be concluded that the simple particle-size reduction method proposed in this study is relevant for the development of TiO$_2$ coating as an NIR reflector. In the future, it is suggested to investigate the variation of other variables in the ultrasonic wet-milling, such as temperature and dispersion medium, and their effect on the size reduction. Considering the trend of preceding studies, further studies should also be encouraged in the term of the TiO$_2$ size reduction effect on the antibacterial and self-cleaning properties that TiO$_2$ is renowned for.

The SEM images and the XRF results show that chitosan as a binder agent is not homogeneously distributed in all fabric samples. This affects the weight percent and the reflectance gain of each fabric sample. Data processing on samples’ reflection gain by the inverse variation method.
validates that the reflectance of the NIR radiation decreases as the TiO$_2$ particle size increases and, thus, simultaneously proves that the particle size plays a major role in controlling reflectance. Nonetheless, studies regarding correlation of the TiO$_2$ concentration and the particle size with the NIR reflectance are suggested to be performed in a more detailed manner in the future.

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