Research Article

Fabrication and Characterization of TiO_2/GO/ZnO Composites Coated Cotton Fabric for Improved Hydrophobic Property

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ABSTRACT

This research focused on the hydrophobic properties of improving the cotton fabric coated with TiO_2/GO/ZnO composites (TNPsGZ composites) powder using the dip-dry-cure method. The Fourier-transform infrared spectroscopy (FT-IR) revealed that TNPsGZ composites contained peaks associated with titanium dioxide (TiO_2), graphene oxide (GO), zinc oxide (ZnO) and polyvinylpyrrolidone (PVP). The optical microscopic photographs demonstrated the TNPsGZ composite layer on the surface of the cotton fabric. The Scanning Electron Microscope (SEM) images confirmed that the TNPsGZ composites were evenly distributed on the surface of the cotton fabric. FT-IR spectra of the coated-TNPsGZ cotton fabric revealed the presence of C=O bond, C-O bond, O-H bond, C1-O-C4 cellulose bond and C=O bond of PVP. The coated-TNPsGZ cotton fabric significantly outperforms the pristine cotton fabric in terms of hydrophobic properties. As the results of this research, the contact angle of the coated-TNPsGZ cotton fabric ranged from 70° to 85° while the pristine cotton fabric showed 0°.

Keywords: Titanium Dioxide, Graphene Oxide, Zinc Oxide, Hydrophobic

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Introduction

Clothing, an indispensable necessity for individuals across all age groups and genders, becomes particularly vital in tropical climates like Thailand and Southeast Asia, where soaring temperatures often lead to issues such as perspiration and staining [1]. Among the various fabrics available, cotton stands out as a preferred choice, valued for its hygroscopicity, air permeability, biodegradability, and static-free properties. Its ability to provide comfort and excellent ventilation makes it an ideal choice for hot and humid environments. However, despite its many merits, cotton's susceptibility to water absorption remains a persistent challenge, especially in areas prone to heavy rainfall or high humidity levels [2].

In recent years, the burgeoning interest in super-hydrophobic fabrics has sparked attention owing to their potential applications across various industries, ranging from outdoor apparel to medical textiles [3]. In response to this burgeoning demand, researchers have been exploring innovative coating techniques to augment the hydrophobic properties of cotton fabric [4]. One auspicious approach involves the utilization of composite coatings comprising titanium dioxide (TiO_2), graphene oxide (GO), and zinc oxide (ZnO).

The combination of TiO_2, GO, and ZnO offers a synergistic blend of properties that can significantly enhance the performance of fabric coatings. Titanium dioxide (TiO_2), with its excellent photocatalytic properties, provides durability and stability to the coating [4], while graphene oxide (GO) is known for its exceptional mechanical strength and two-dimensional structure, its functional groups create a rough and hydrophobic surface, effectively repelling water molecules and preventing their penetration into underlying materials [5]. Additionally, zinc oxide (ZnO) contributes UV-blocking and antibacterial properties, further enhancing the functionality of the fabric coating [6].

In this work, the TNPsGZ composites were synthesised using the ultrasonic method. Subsequently, the TNPsGZ composite powder was characterised using Fourier Transform Infrared Spectroscopy. The TNPsGZ composites were coated on the cotton fabric using the dip-dry-cure method. The coated cotton fabric was examined for morphology and chemical structural properties. Further, hydrophobic cotton fabric was investigated.

Materials and Method

Materials

The cotton fabric (100%) was purchased from Bulliontex Co., Ltd. Graphene oxide single layer (GO) was purchased from Graphene Laboratories Inc. Ethanol (99.7-100%) was purchased from BDH AnalaR®. Titanium dioxide nanoparticles (Degussa P25), Polyvinylpyrrolidone (PVP), zinc oxide (ZnO), and isopropanol (IPA) were purchased from Chemipan Thailand. All the compounds were of analytical grade, no additional purification was required. Deionised water was used throughout the research.

Preparation of TNPsGZ composites

1. Synthesis of titanium dioxide/graphene oxide (TG) composites

Graphene oxide (GO) (0.06 g) was dispersed into ethanol (200 mL) under ultrasonic-assisted conditions for 45 minutes to obtain the homogeneous solution. After that, TiO_2 (1.94 g) was slowly added to the GO suspension under vigorous stirring conditions at 80°C for 2 hours. GO and TiO_2NPs were sonicated for 3 hours to obtain TG suspension.

2. Synthesis of the TNPsGZ composites

ZnO (3 g) was dispersed into TG (10 mL) suspension and isopropanol (40 mL) under ultrasonic-assisted conditions for 90 minutes to obtain a homogeneous solution. The suspension was dried at room temperature and ground into powder. Subsequently, 16 g of polyvinylpyrrolidone was slowly added to DI (200 mL) water. Following this, 2 g of TiO_2 NPs/GO/ZnO powder was added to the solution under ultrasonic-assisted conditions for 90 minutes and stirred at 75°C to obtain the TNPsGZ composite solution.

Coating of cotton fabric

The pristine cotton fabrics were dipped in the TNPsGZ composite solution at 75°C for 30 minutes. Subsequently, the specimens were dried at 120°C for 30 minutes. The coating and drying steps were repeated until the desired number of layers was achieved (1, 3, 5 and 7 layers) to investigate the effect of the number of coating layers on hydrophobicity. All specimens were cured for 30 minutes at a consistent temperature of 130°C.

Characterization

The study used various techniques to examine the prepared TNPsGZ composite powder and to evaluate the properties of the pristine cotton fabric and the TNPsGZ-coated cotton fabric. The prepared fabrics were placed on a diamond crystal for Fourier transform infrared (FT-IR) analysis, while the TNPsGZ composite powders were prepared in potassium bromide (KBr) pellets. The attenuated total reflection (ATR) spectra were captured in the frequency range of 400-4000 cm^{-1} using a Bruker FT-IR Alpha spectrometer. The contact angle system (OCA) was used to determine the wettability of the pristine cotton fabric and the TNPsGZ-coated cotton fabric. Images were taken every 10 seconds after placing a 5 μL water droplet on the surface. Contact angle measurements repeat three different locations on the sample and take the average value. The morphology were determined using a scanning electron microscope (SEM) (JEOL JSM-6480LV).

The fastness of fabric

The fastness (wash durability) of the coated cotton fabric was carried out according to the AATCC (American Association of Textile Chemists and Colorists) test method 61 (2010), The non-ionic solution was dissolved in the water at 40°C, for 30 minutes. Subsequently, the specimen was placed in the washing machine and prepared solution was added. The washing machine lid was closed and the wash cycle was initiated with the specified temperature and duration. Once the wash was complete, the water was drained from the machine. The specimen was transfered to a 4-litre beaker filled halfway with distilled water at room temperature. The solution was gently stirred for 1 minute and then the beaker was positioned so that water flowed over the test piece for an additional 1 minute. In the case of multiple test pieces, each one was washed separately. Finally, the excess water was removed and the test piece was allowed to dry at a temperature not exceeding 60°C.

Results and discussion

Analysis of Functionalized Samples

Qualitative chemical analyses by FT-IR, the FT-IR spectra of TiO_2, GO, ZnO, and TNPsGZ composites are shown in Figure 1. In the TiO_2 spectrum (Figure 1(a)), peaks attributed to Ti-O-Ti and Ti-O stretching vibrations were observed within the range of 500 to 1000 cm^{-1}, indicating the presence of titanium dioxide. The broad band at 3409 cm^{-1} represented stretching vibrations of O-H bonds. The peaks at 1397 and 1626 cm^{-1} represented stretching vibrations of the C=O bond and the bending of the O-H bond, respectively [7]. The FT-IR analysis of ZnO is shown in Figure 1(b). According to Bashir et al [8], the 550 to 1000 cm^{-1} region was attributed to the Zn-O group (778 and 872 cm^{-1}). The absorption peak at 1447 cm^{-1} represented the stretching vibration of C=C, while the peak at 1626 cm^{-1} represents the stretching vibrations of the C=O bond. The peak indicated the presence of the O-H bond at 3439 cm^{-1}. The peaks observed in the GO spectrum (Figure 1(c)) are in agreement with Kumar et al [9], which a variety of oxygen configurations in the structure include the -OH bending vibration (1049 cm^{-1}), the vibration modes of epoxide (C-O-C) (1200-1320 cm^{-1}), sp^2-hybridized C=C (1500-1600 cm^{-1} in-plane vibration), carboxy group (COOH) (1650-1750 cm^{-1}) and hydroxyl group (C-OH) (3000-3800 cm^{-1}). Furthermore, the FTIR spectra (Figure 1(d)) of the TNPsGZ composites displayed characteristic peaks, with the broad absorption peak at 680 cm^{-1} representing the Zn−O stretching vibration in ZnO. Additionally, the characteristic peaks of GO, including 1626 cm^{-1} attributed to the skeletal vibration of unoxidized graphite domains, asymmetric vibrations of C-H at 2922 cm^{-1} and O-H stretching at 3456 cm^{-1} [10]. According to this weight ratio of TiO_2:ZnO, it is not surprising that the dominance of the peak in the range of 400-1000 cm^{-1} is Zn-O.

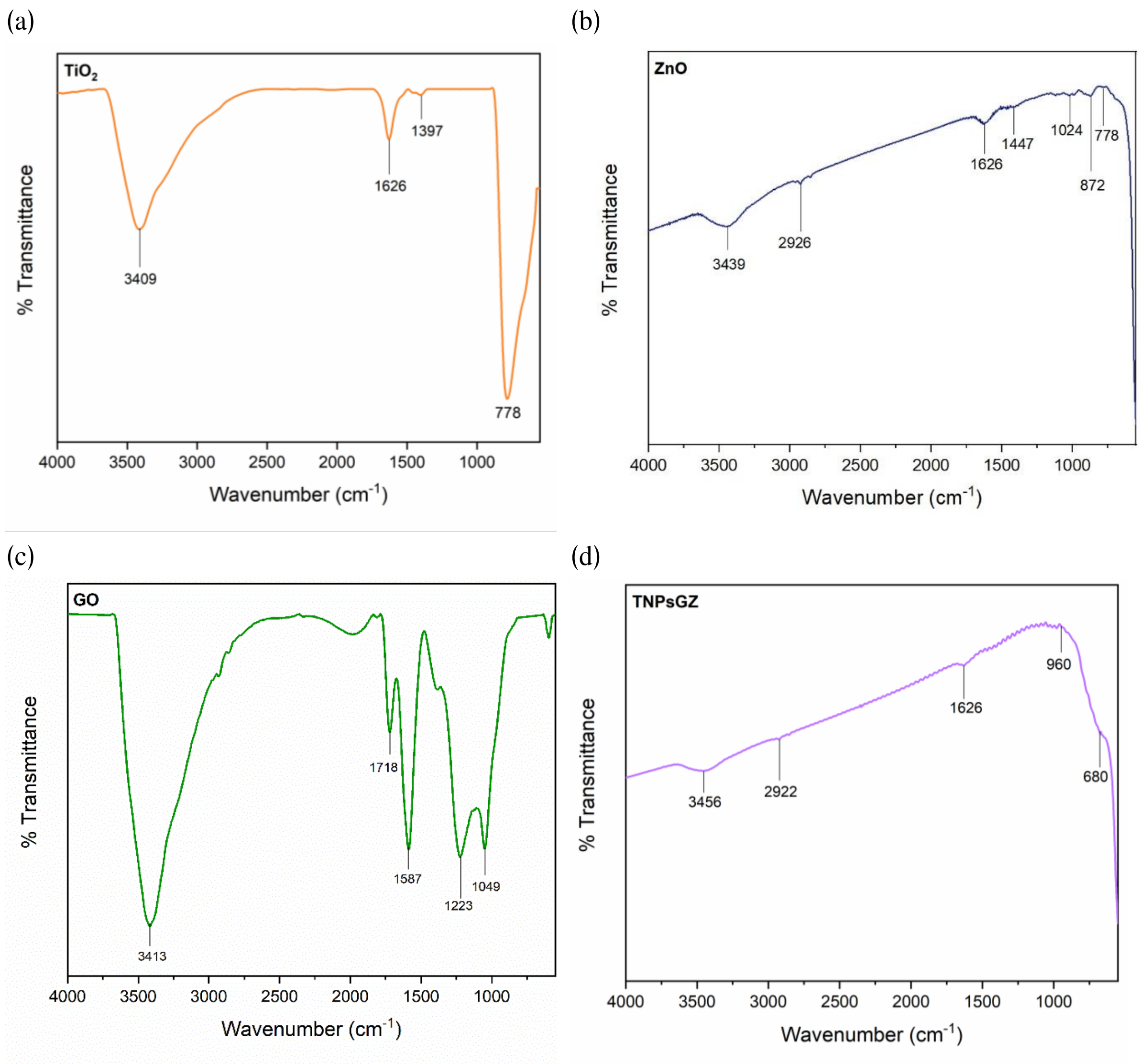


Figure 1 Typical FT-IR spectra for (a) TiO_2 NPs, (b) ZnO, (c) Graphene oxide and (d) TNPsGZ composites.

Characteristics of the pristine cotton fabric and the TNPsGZ-coated cotton fabric

1. Fabric appearance

Figure 2 represents the pictures of the TNPsGZ-coated cotton cloth which is pre- and post-curing. The coating of white cotton fabric using the TNPsGZ composites with different numbers of coating layers has resulted in the original colour. Moreover, the colour of the TNPsGZ-coated cotton cloth remained unchanged after the curing process.

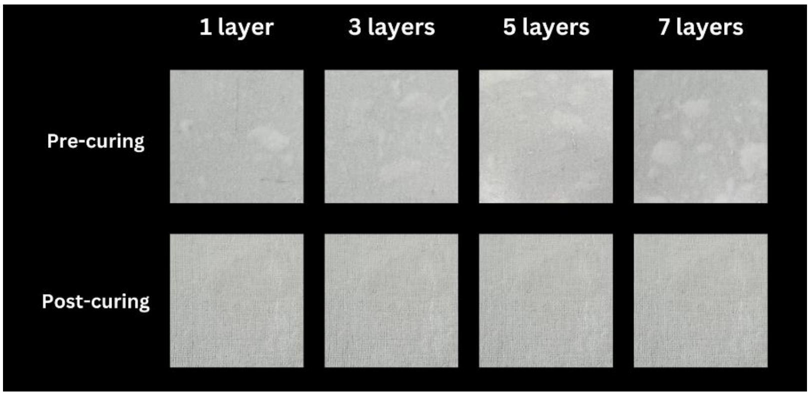


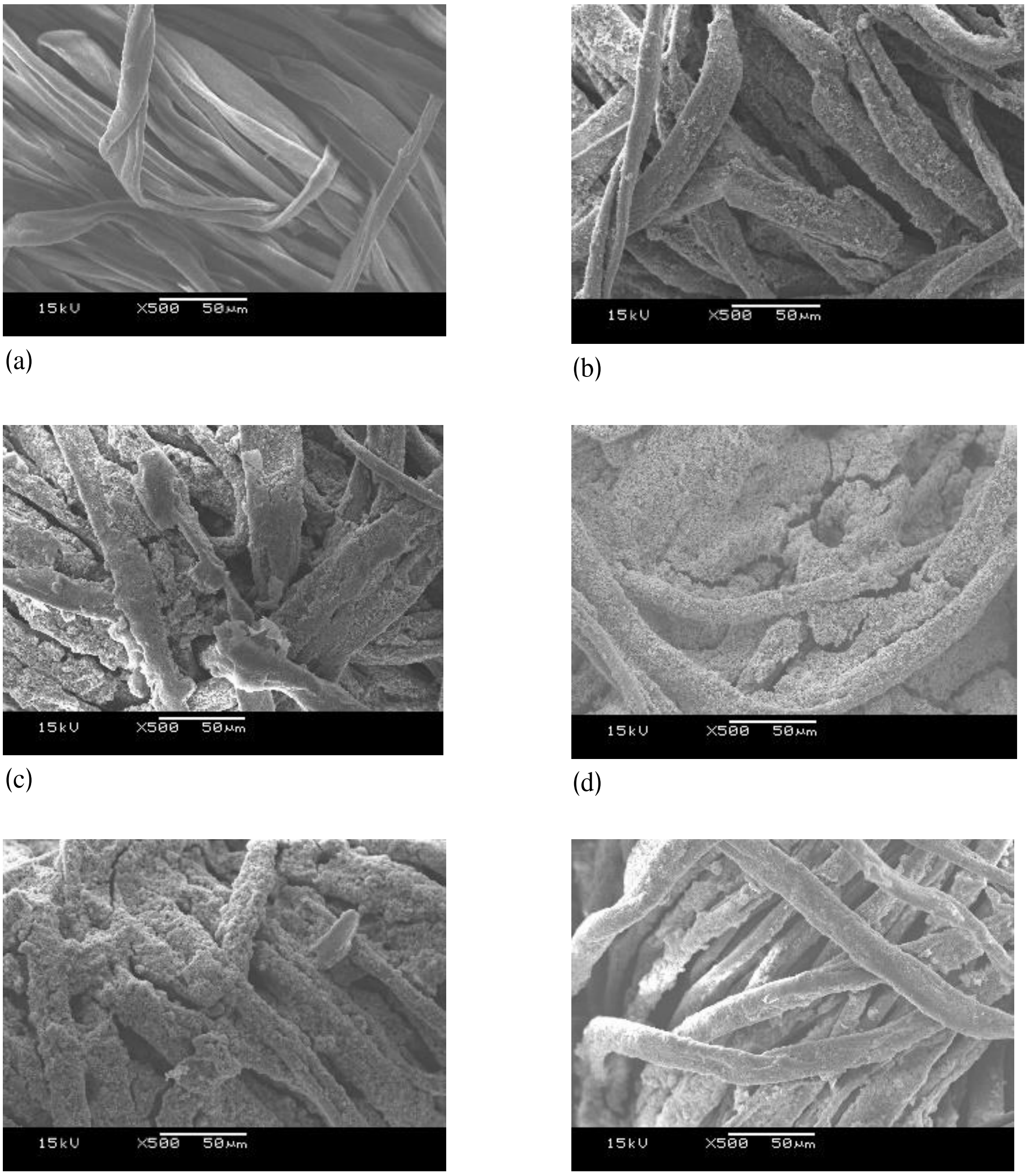
Figure 2 Appearances of the TNPsGZ-coated cotton cloth with different numbers of coating layers: pre- and post-curing process.

2. Surface morphology of fabrics

The SEM images were applied for a clearer revealing of the morphology of the TNPsGZ coated layer on the cotton fabric as shown in Figure 3. The yarns of the pristine cotton fabric have a smooth surface with no evidence of nanocomposites (Figure 3(a)). After the first coating, TNPsGZ particles were observed and uniformly distributed on the fibre surface (Figure 3(b)). When the cotton yarn was dipped into TNPsGZ composite solution at the beginning of the process, the cotton yarn permitted more TNPsGZ particles to be coated onto the cotton yarn surface. The use of PVP as a binder was found to bind the TNPsGZ particles onto the cotton yarn. Moreover, the increasing number of coating layers found that the TNPsGZ particles integrated to form a TNPsGZ thin film on the cotton fibre surface (Figure 3(d-e)). After one wash (Figure 3(f)), the photograph reveals the TNPsGZ particles coated on the cotton fabrics tightly adhering to the cotton fabric surface.

3. Analysis of functionalized fabrics

The chemical surface of the pristine cotton fabric, the TNPsGZ-coated cotton fabric, and the TNPsGZ-coated cotton fabrics after one wash were studied by FT-IR analysis. The spectra were taken in transmittance mode as shown in Figure 4. Figure 4(a) exhibits the FT-IR spectrum of pristine cotton according to Vaideki et al and Ahmad et al [11, 12]. The FT-IR spectrum of the pristine cotton fabric shows the vibrational modes of C=O stretching, C-O stretching and O-H deformation mode in the region 1,200 to 1,700 cm^{-1}. The presence of OH-C=O reveals the peak in the 2,800 cm^{-1} region. The broad peak at 3,100 to 3,500 cm^{-1} in the spectrum indicates the O-H stretching vibration of the H-bonded hydroxyl (OH) group. The peak at 891 cm^{-1} introduces asymmetric stretching of C1-O-C4 of cellulose. As the above result, peaks observed in the TGZ/PVP composite spectrum at 3407 cm^{-1} were attributed to the stretching vibrations of hydroxyl (O–H) groups, indicating the presence of PVP on the coated fabrics. Furthermore, the asymmetric CH_2 stretch (2943 cm^{-1}) and symmetric CH_2 stretch (2892 cm^{-1}) peaks were observed, highlighting the presence of aliphatic hydrocarbons. The presence of the C=O stretch band at 1646 cm^{-1} is characteristic of pure PVP. Moreover, the spectra of the multilayers TNPsGZ coated cotton fabrics have increased in the peak intensity (Figure 4(b)). Additionally, the −C−N stretching vibrations and −C−H bending vibrations of the PVP polymer were observed at 1422 and 1280 cm^{-1}, respectively, further confirming PVP's presence in the TNPsGZ composites [13]. The FT-IR spectra analysis of the washed cotton fabric as shown in Figure 4(c) revealed noteworthy changes. The spectra showed a peak intensity reduction in the band at 1650 cm^{-1}, suggesting potential alterations in the fabric's chemical composition or structure due to the washing process. These findings underscored the importance of considering the effects of washing and other environmental factors on the performance and durability of coated fabrics.



(a) (b)

(c) (d)

(e) (f)

Figure 3 The SEM photographs of the cotton fabric (a) the pristine cotton fabric and the TNPsGZ-coated cotton fabric (b) a single-layer coating, (c) a triple-layer coating, (d) a quintuple-layer coating, (e) a septuple-layer coating and (f) a single-layer coating after one wash.

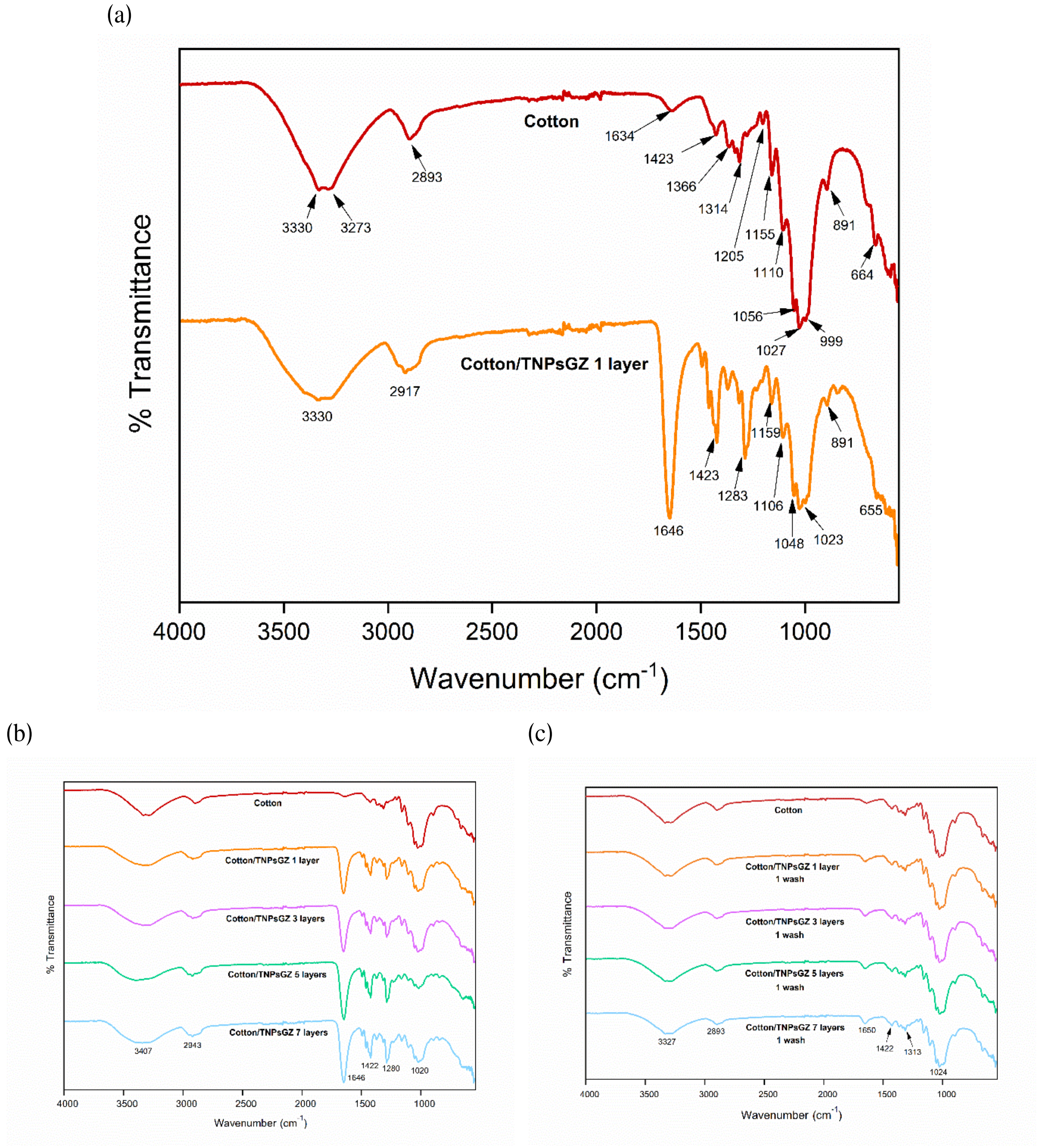


Figure 4 FT-IR spectra of (a) the pristine cotton fabric and one layer of the TNPsGZ-coated cotton fabric, (b) the pristine cotton fabric and the different coated layers of the TNPsGZ-coated cotton fabric and (c) the pristine cotton fabric and the different coated layers of the TNPsGZ-coated cotton fabric after one wash.

4. Hydrophobic property of fabrics

The contact angle was examined to clarify the surface wettability of the pristine and the modified cotton fabric. The water droplet was immediately absorbed by the pristine cotton fabric and there was no contact angle. The water contact angle result of the TiO_2-, ZnO- coated and the different coated layers of the TNPsGZ-coated cotton fabric is shown in Figure 5. It can be seen that the TiO_2-coated cotton fabric has a good hydrophilic property and a water contact angle record of 0°. The ZnO-coated cotton fabric displayed hydrophobic behaviour which an average water contact angle was 78.5°. After TNPsGZ was coated on the cotton fabric, the water absorption of the cotton fabric increased. The average water contact angles of water droplets on the TNPsGZ-coated cotton fabric ranged from 70° to 85°. However, increasing the number of coated layers did not affect the contact angle of the coated fabrics. After one wash, the contact angle decreased to 29° which was due to the wash-off of the coated layer on the cotton fabric surface. Leaching was confirmed by the surface morphology of the TNPsGZ-coated cotton fabric after washing which was characterised by SEM as provided in Figure 2(f).

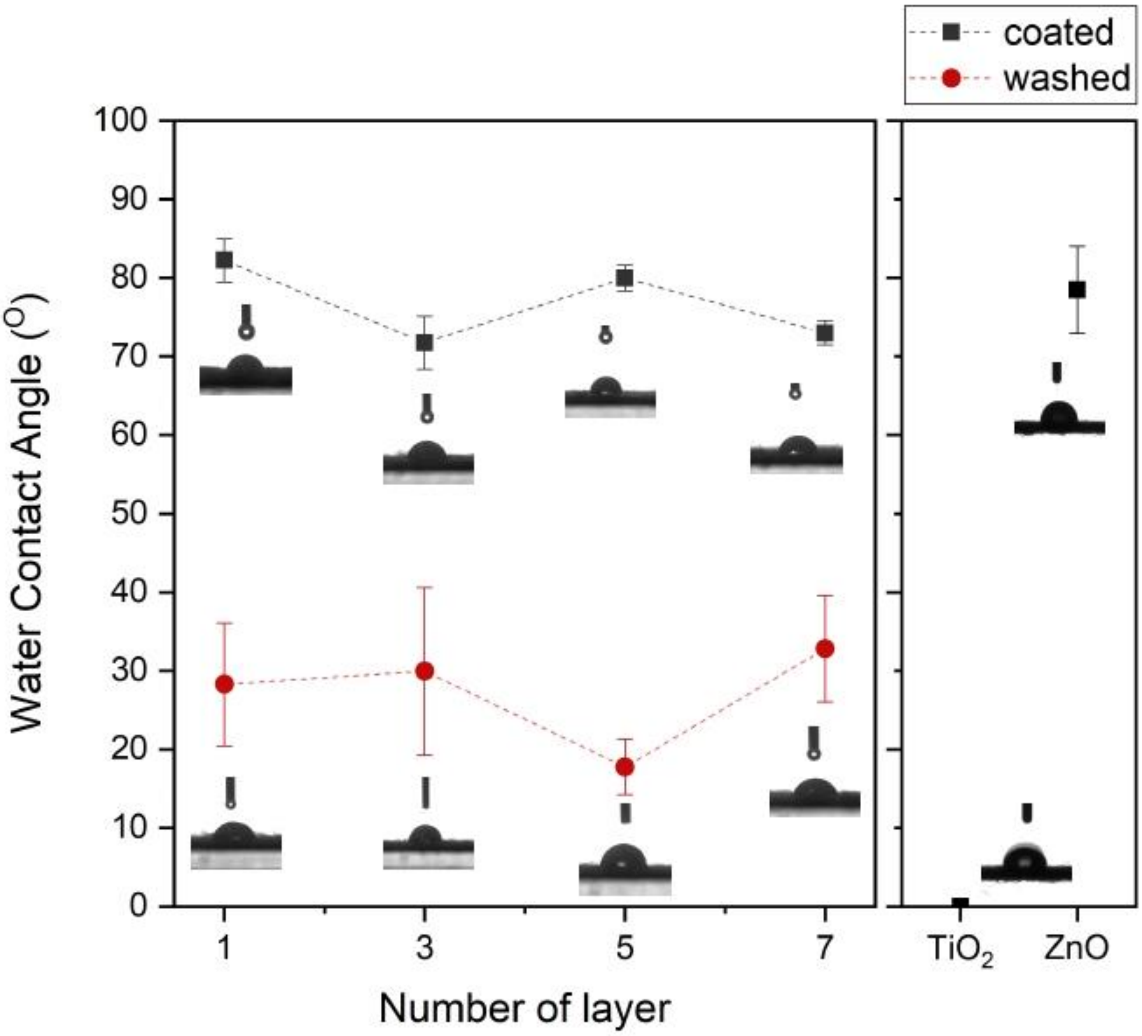


Figure 5 The shape of water droplets and contact angles on the surface of the single layer of TNPsGZ-coated on cotton fabric (black line) and the single layer of TNPsGZ-coated on cotton fabric after one wash (red line).

Conclusion

To provide hydrophobic properties of cotton fabric, the TNPsGZ composites were coated on the cotton fabric using a dip-dry-cure method. This technique has many advantages such as low cost, user-friendly and non-destructive. SEM revealed that coated under this condition, the TNPsGZ composites uniformly covered each cotton fabric sample with no signs of splintering. The TNPsGZ composites and PVP were proven to be effective for producing hydrophobic cotton fabrics with higher water contact angles than the pristine cotton fabric. For the 1-layer coated sample, the water contact angle value was 85°. Unfortunately, while a change to the water contact angle value of the coating layer composed of TNPsGZ composites was observed, this value was less than 90° on the mixed nanoparticles system. This hindered the pursuit of the motivation for this research wherein it was hoped to create tertiary nanocomposites that could become super hydrophilicity. Better hydrophobicity properties would have been gained if a suitable choice of TiO_2, ZnO and PVP was used.

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