Conductive, superhydrophobic, and microwave-absorbing cotton fabric by dip-coating of aqueous silk nanofibers stabilized MWCNTs and octadecanoyl chain bonding

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Abstract Compared to previously reported methods, we developed a facile dip-coating method to endow cotton fabric (CF) with satisfactory conductivity, superhydrophobicity and microwave absorption performance based on the combination of multi-walled carbon nanotubes (MWCNTs) and hydrophobic octadecanoyl chain bonding. Silk nanofibers (SNFs) derived from silk were adopted as dispersant to prepare individually dispersed MWCNTs via ultrasonication and homogenization processes. The non-covalent functionalization of MWCNTs enabled by SNFs wrapping was superior to organic functionalization, which could keep the carbon backbone of MWCNTs intact and thus preserved their complete electron tube structure and electronic properties. The adhesion of MWCNTs coated to CF (MWCNT-CF) was enhanced via dipping coating and thermal treatment induced chemical immobilization cycles. Octadecanoyl chain-tethered MWCNT-CF (C18-MWCNT-CF) was manufactured by further treatment with stearoyl chloride to achieve superhydrophobicity. Compared with pristine CF ($1.04 \times 10^{10} \Omega/$sq), the C18-MWCNT-CF exhibited excellent conductive property with surface resistivity reaching 55 $\Omega$/sq with the MWCNT loading content of 247.5 mg/g and possessed a relatively greater microwave absorption performance of $-36.08$ dB at 9.28 GHz with merely 2.7 mm thickness. Compared with other similar materials, the as-prepared C18-MWCNT-CF showed outstanding comprehensive performance, which was the highest value reported in the literature. Meanwhile, C18-MWCNT-CF exhibited robust superhydrophobicity even after 20 scratching cycles due to the combination of octadecanoyl group tethering and the increased

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surface roughness. The biodegradable and recyclable C18-MWCNT-CF exhibited reasonable electrical conductivity, superhydrophobicity and microwave absorption that promises an ideal application prospect in the field of smart textile and wearable electronic devices.

**Graphical abstract**

![Graphical abstract](image)

**Keywords**  Multi-walled carbon nanotubes · Cotton fabric · Conductive · Superhydrophobic · Microwave absorption

**Introduction**

As we all know, intelligent textiles are materials and structures that can sense and respond to environmental changes. In recent years, conductive textiles have managed to become one of the fastest growing branches of intelligent textiles in that they have taken its region among the most leading products. As the literature reviews have shown, the significance of conductive cotton fabric (CF) is ordinarily associated to their extensive application fields, such as medical, space, defense, industrial fields in which they create added value (Gao et al. 2021; Luo et al. 2019). The electrical conductivity and antistatic property are very essential in the use and production of CF. The static electricity or electrostatic behavior generated on the surface of CF can cause consumers to be subjected to electronic shock during product use or manufacturing process, breaking down of sensitive electronic equipment, ignition in environments where flammable vapor and dust exists as well as rapid contamination of fabrics (Su et al. 2020). Therefore, it is crucial to incorporate conductive materials into fibrous system to prepare flexible wearable devices based on CF materials.

Due to the superior electrical conductivity and highlighted microwave absorption performance, multi-walled carbon nanotubes (MWCNTs) have become a promising candidate for the preparation of multifunctional CF (Sethi et al. 2017). It is widely accepted that construction of multifunctional CF composites can be realized by combined manipulation of functionalization or mechanical dispersion of
MWCNTs (Ma et al. 2010; Ruoff and Weng 2018). A variety of biomolecules, including protein (Liang et al. 2020; Fang et al. 2018), peptide (Mann et al. 2020; Geng et al. 2019), silk nanofibers (Tan et al. 2020) and nucleator/DNA (Sun et al. 2020) have been applied to realize stripping and aqueous dispersion of defect-free MWCNTs. Compared with similar methods using industrialized surfactants and organic solvents, these stripping methods have significant environmental and economic benefits, and also endowed untied MWCNTs with improved biocompatibility and potential functionalization of biomolecules (Anaya-Plaza et al. 2021). Silk materials have been utilized to prepare multifunctional composite biomaterials because of their biocompatibility, mechanical properties, adjustable biodegradability, versatile processability (Cheng et al. 2017; Dong et al. 2016; Xiao et al. 2017) and strong interaction between silk proteins and various hydrophobic nanomaterials such as MWCNTs (Zhao et al. 2020). The bearing of a plenty of hydroxyl groups on the CF surface provides numerous possibilities for subsequent modification through adjusting the surface wettability toward superhydrophobic CF-based composites (Luo et al. 2019; Lam et al. 2019).

Recently, CF combined with functional nanomaterials have attracted enormous attention for their considerable application in the fields of flexible wearable devices, smart textiles, strain sensors or health monitoring and so on. For instance, Xue (Xue et al. 2020) developed a superhydrophobic, flame-retardant and conductive CF via layer-by-layer assembly method based on the combination of poly(ethyleneimine), ammonium polyphosphate and MWCNTs. Interestingly, Sadi (Sadi et al. 2019) provided simple and facile fabrication techniques to load conductive components onto textiles for wearable applications involving dip-coating of single-walled CNTs and polydopamine templating. Zheng (Zheng et al. 2019) designed a conductive superhydrophobic CF by assembling carboxylated and aminated MWCNTs followed by modification with polydimethylsiloxane, which was claimed to exhibit a high capability under the chosen arrangement of investigations. However, the dispersion of CNTs and the adhesion between CNTs and CF in the above literature required further improvements involving the selecting or designing highly efficient dispersant of MWCNTs and promoting the durability of functional CF composites to meet the practical application. Therefore, more effective assembly methods to enhance the adhesion between the loaded conductive CNTs and the fiber substrates are highly demanded.

In this work, an efficient strategy for waterborne MWCNTs dispersion stabilized by silk nanofibers (SNFs) was developed. Functional CF composites were fabricated by dip-coating of individually dispersed MWCNTs and surface bonding of octadecanoyl groups. The biocompatible SNFs obtained from cheap and abundant waste silk was used as dispersant to prepare individually dispersed MWCNTs. The chemical reactions between active groups of SNF and abundant hydroxyl groups on CF facilitated the enhanced adhesion of MWCNTs towards CF and provide active sites for subsequent superhydrophobic treatment. The conductivity, superhydrophobicity and microwave absorption performance of multifunctional CF composites were investigated systematically. Furthermore, abrasion and tensile tests were carried out to verify the robustness of the modified CF against mechanical forces to evaluate their potential applications in wearable electronic devices, medical care and strain sensors.

**Experimental section**

**Materials**

The commercial MWCNTs used in study were purchased from Nanjing XFNANO Materials Tech Co., Ltd (serial number: XFQ041). This kind of MWCNTs has an average diameter of 10−20 nm, length of 20−100 μm and purity of 95%. Cotton fabric (cellulose content = 95−98%, length = 25−35 mm, linear density = 2.12−1.56 dtex, surface hydroxyl content = 12%) and silk were purchased from the local market, Hefei, China. Sodium hydroxide, urea, stearoyl chloride, acetone, anhydrous ethanol, and triethylamine (TEA) were obtained from Aladdin Industrial Co.; Ltd. Methylene blue was bought from Yashilin Ltd. Co. Unless otherwise noted, all reagents were of analytical grade and used without further purification. Ultrapure water was made in-house.
Preparation of silk nanofibers dispersant (SNFs)

Silk nanofibers were prepared via procedures reported previously (Zhuo et al. 2018). First, the waste silk was smashed by a pulverizer and then sieved through 60 and 80 mesh standard screens to collect uniform particulate silk. The collected silk was ultrasonically rinsed with ultrapure water and anhydrous ethanol, respectively, the pretreated silk was dried at 50 °C for subsequent use. 20 g of silk was put into a three-necked flask containing appropriate amount of deionized water under magnetic stirring. Then the stoichiometric sodium hydroxide and 5 g of urea were added to adjust pH to about 11. SNFs (5wt%) were obtained after the silk was hydrolyzed for 1d at 90 °C under alkaline condition.

Aqueous dispersion of SNFs stabilized MWCNTs

The water dispersion of SNFs stabilized MWCNTs comprised the following specific steps. In brief, 2.6 g of MWCNTs, 2.6 g of SNFs, and 94.8 g of deionized water were mixed together. The above suspension was ultra-sonicated at 40 kHz for 30 min and then homogenized at 12,000 rpm for 5 min at room temperature to obtain SNFs stabilized MWCNTs dispersion with a solid content of 2.6 wt%.

Deposition of MWCNT dispersion on CF

Pristine CF samples were cut to 3 × 3 cm in dimension and washed multiple times with ultrapure water and anhydrous ethanol sequentially to remove dust and then dried in an oven at 65 °C for 6 h. Subsequently, CF was immerged into MWCNTs dispersion (5 mg/mL) for 15 min, rinsed with ultrapure water, and then dried at 60 °C as the first dipping-drying process. The prepared sample was labeled as MWCNT-CF-n. Four cycles of dipping-drying process were performed to obtain the MWCNTs treated CF, coded as MWCNT-CF-1, MWCNT-CF-2, MWCNT-CF-3, and MWCNT-CF-4, respectively.

Loading capacity of MWCNTs on pure CF

In the current work, the pristine CF was soaked in the MWCNTs dispersion (5 mg/mL) for adsorption. The weights of pure CF and MWCNT-CF-n were recorded as \( m_1 \) and \( m_2 \), respectively. Loading capacity of MWCNTs (MWCNTs/pure CF (mg/g)) can be calculated according to the following formula:

\[
LC = \frac{m_2 - m_1}{m_1}
\]

Fabrication of conductive, superhydrophobic, and microwave-absorbing cotton fabric (C18-MWCNT-CF)

1 g of MWCNT-CF-n and 2 mL of TEA were dispersed in a flask containing 15 mL of acetone in the ice bath by mechanical stirring. Then, 2 mL of stearoyl chloride were added dropwise under stirring. After the solution was stirred in a sealed flask for 1 d at 20 °C, the octadecanoyl groups tethered MWCNT-CF (C18-MWCNT-CF) was obtained after washing thoroughly with acetone and drying under vacuum overnight for performance tests later.

Microwave absorption measurement

For electromagnetic parameter measurements, the absorbers were made by mixing the as-prepared SNFs-MWCNTs with paraffin at the mass loading ratio of 3:7 and pressed into a coaxial cylinder (3.0 and 7.0 mm, inner and outer diameters). The relative electromagnetic parameters were measured by a vector network analyzer (Agilent N5224A, USA) in the frequency range 2−18 GHz. Typically, the performance of microwave absorber significantly depends on their complex permittivity, permeability, and impedance matching. The microwave absorption performance can be represented by reflection loss (RL) based on the transmit line theory (Li et al. 2017). The RL was calculated using the equations:

\[
RL = 20\log\frac{Z_{in} - Z_0}{Z_{in} + Z_0}
\]

\[
Z_{in} = Z_0 \sqrt{\frac{\mu}{\varepsilon}} \tanh(j2\pi f d \sqrt{\mu_\varepsilon\varepsilon_\varepsilon})
\]

where \( Z_{in}, Z_0, f, d, \) and \( c \) are the input impedance, free space impedance, microwave frequency, layer thickness of the testing absorber, and microwave velocity in free space, respectively (Li et al. 2016).
Characterization

The morphologies of MWCNTs and CF samples were evaluated by scanning electron microscopy (SEM) at 200 kV. MWCNTs samples were prepared by drying a diluted suspension (in water) on silicon wafer and CF samples were adhered directly onto conductive tape. The surface chemical compositions of SNFs were investigated by means of Fourier transform infrared spectroscopy (FT-IR) and CF samples were characterized by attenuated total reflectance (ATR) FT-IR. The X-ray photoelectron spectroscopy (XPS) measurement was conducted on ESCALAB 250Xi to analyze valence of elements. The samples were examined by X-ray diffraction (XRD) using a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation (λ = 1.54 Å) and a scan range of 2θ = 10 ~ 70°. The sheet resistivity of the CF samples was conducted by a four-point probe meter (SZT-2A, China). The water contact angle (WCA) was performed using a contact angle instrument (DSAIONKZ, Germany) with deionized water droplets of 5 μL at ambient temperature, and the obtained WCA of each sample was the average of five measurements at the different positions. The thermal decompositions of pristine CF, MWCNT-CF-n, and C18-MWCNT-CF were studied by thermogravimetric analysis (TGA), which was performed with a STA-449F3 apparatus in air with a heating rate of 20 °C/min.

Results and discussion

Fabrication of superhydrophobic, conductive and microwave-absorbing CF

The synthesis of SNFs and the process of stabilizing MWCNTs in water medium to fabricate a multifunctional CF were briefly introduced in Fig. 1. Aqueous SNFs were obtained after the silk was hydrolyzed with the help of urea under alkaline condition. With the incorporation of SNFs, aqueous dispersion of
SNFs stabilized MWCNTs was prepared via ultrasonication and homogenization assisted liquid-phase method. The unwound MWCNTs are stabilized by electrostatic repulsive interactions with SNFs dispersant (Paredes and Villar-Rodil, 2016). Notably, SNFs include aromatic amino acid residues, such as tyrosine, tryptophan, and phenylalanine, which have strong π-π interactions with the surface of MWCNTs (Liang et al. 2020). The β-sheet structure, as well as the high negative charge density, endowed SNFs with hydrophobicity and good aqueous dispersibility, allowing the SNFs to act as a surfactant to prevent the restacking of MWCNTs in water (Bai et al. 2014) (Fig. 1a). As shown in Fig. 1b, the placed water droplet wetted the cotton fibers and was absorbed fast representing the obvious hydrophilicity of pristine CF. Subsequently, MWCNTs deposited CF was fabricated by dip-coating and thermal treatment induced chemical immobilization cycles, which were labeled as MWCNT-CF-n. The octadecanoyl chains tethered MWCNT-CF (C18-MWCNT-CF) was obtained after further treatment with stearoyl chloride. Compared with the water droplet on the surface of pristine CF, the C18-MWCNT-CF demonstrated an obviously varied wettability and the water droplet maintained a nearly spherical shape exhibiting prominent water repellency.

Structure and morphology of MWCNTs and C18-MWCNT-CF

The successful preparation of SNFs dispersant was verified by FT-IR characterization (Fig. 2). Compared with the spectrum of pristine silk (Liu et al. 2017), the characteristic peaks of SNFs were associated to the amide III stretching vibration at about 1290 cm⁻¹, and amide I (C═O or asymmetric carboxylic group vibration) at around 1689 and 1630 cm⁻¹. Besides, the newly appearing absorption peaks at 3448 and 3351 cm⁻¹ corresponding to N − H, and the peak of 1160 cm⁻¹ originating from the existence of C − N.

To confirm the successful tethering of the octadecanoyl chain, characterization of CF samples was carried out by using ATR FT-IR, which were shown in Fig. 3a. Compared with the spectrum of pristine CF, the newly appearing absorption peaks at 3448 and 3351 cm⁻¹ corresponding to N − H, and the peak of the 1160 cm⁻¹ originating from the existence of C − N.
the C═O stretching vibration at 1816 cm$^{-1}$, and C−H deformation vibration at 1707 cm$^{-1}$ were assigned to the existence of octadecanoyl groups. These results confirmed that the octadecanoyl groups were chemically bonded on the CF surface by esterification reactions between active hydroxyl groups of cotton fiber and stearoyl chloride.

To further verify the above reaction mechanism, the local chemical composition of the surface was detected by XPS (Fig. 3b). Compared with pristine MWCNTs, the XPS spectrum of the modified MWCNTs showed new peaks of N element, indicating that SNFs were successfully introduced on the surface of the modified MWCNTs. After dip-coating of aqueous SNFs stabilized MWCNTs and octadecanoyl chain bonding processes, the appearance of N 1 s and Cl 2p signals testified the successful immobilization of SNFs-MWCNTs and octadecanoyl groups on the surface of CF, respectively. In Fig. 3c and d, C 1s peaks of MWCNTs must be deconvoluted with sp$^2$ and sp$^3$ carbons properly. The peak 284.8 eV may be assigned as sp$^2$ carbon (C═C). Pristine MWCNTs are mainly composed of sp$^2$ carbon which contribute to electrically conductive of MWCNTs. The addition of SNFs on the pristine MWCNTs led to deconvolution of the spectrum into three peaks, namely the original two peaks and a new C−N peak at 286.5 eV (Fig. 3c, d). Moreover, different from the C 1s peak spectra of pristine CF, the new peaks located at 285.8 and 288.1 eV of C18-MWCNT-CF, corresponding to the binding energies of C−N/C−O and O−C═O (Fig. 3e, f). These XPS analyses are consistent with that of ATR-FTIR results, verifying the successful introduction of SNFs-MWCNTs and octadecanoyl groups.

Fig. 4 XRD patterns of a pristine MWCNTs, b pristine CF, and c C18-MWCNT-CF

Fig. 5 SEM images of pristine MWCNTs (a, b) and SNFs-stabilized MWCNTs with different scale (c, d). And optical photograph of pristine MWCNTs (the inset of b) and SNFs-stabilized MWCNTs aqueous dispersion (the inset of d)
The X-ray diffraction data collected on the pristine CF, pristine MWCNTs, and C18-MWCNT-CF samples were shown in Fig. 4. Compared with pristine MWCNTs (Fig. 4a), the characteristic diffraction peak of C18-MWCNT-CF appeared at 2θ = 26.06° corresponding to the (002) crystal plane (Liu et al. 2021). The untreated CF and treated CF had the same peak located at 35.2°, which attributed to the crystalline structure of CF, suggesting that crystalline structure of treated CF was not destroyed. The noncovalent interaction between SNFs and MWCNTs preserved the inherent characteristic of MWCNTs backbone and is superior to chemical modification, which retained the intact structure and electronic properties.

The surface morphology of pristine MWCNTs and SNFs-stabilized MWCNTs were investigated via SEM analyses. Without the addition of SNFs dispersant, pristine MWCNTs agglomerated into microsized bundles even after ultrasonication and homogenization processes due to the fact that the commercialized MWCNTs are supplied in the form of heavily entangled bundles (Fig. 5a, b). With the incorporation of SNFs dispersant, microsized MWCNTs bundles disappeared and were scattered into well-dispersed MWCNTs with the wrapping of SNFs (Fig. 5c). The disentangled MWCNTs are stabilized and prevented from the restacking. With the further enlargement of magnification, the aggregates of MWCNTs were hardly examined (Fig. 5d). As shown in the inset of Fig. 5d, no precipitation was observed in 5 mg/mL MWCNTs dispersion whether the sample bottle was placed upside down, which was in sharp contrast to the observation of Fig. 5b. These results suggested that SNFs was a suitable biomolecule to
effectively disperse MWCNTs and efficiently stabilize them in water.

As can be seen in Fig. 6a, b, the pristine CF presented quite a smooth surface without visible impurities (Cheng et al. 2018). Compared with that of pristine CF, the deposition of MWCNTs on the CF surface was presented in the form of gray tubes with a size of approximately 20–30 nm (Fig. 6c, d). It was observed that the connected MWCNTs formed a conductive network owing to the extended percolative structure. With the enlargement of magnification, MWCNTs appeared to be adhered tightly on CF due to the cross-linking reactions between amino groups of SNFs and hydroxyl groups of CFs during drying process (Fig. 6d). After octadecanoyl chain tethering, a mass of grooves emerged on the surface of C18-MWCNT-CF owing to the detachment of tiny cotton fibers during reaction and stirring processes (Fig. 6e, f). To achieve superhydrophobicity, the key is to construct micro/nano roughed hierarchical surface (Zhang et al. 2017). Compared with the pristine CF, the combination of the enhanced surface roughness induced by MWCNTs disposition and the hydrophobic octadecanoyl group bonding dramatically strengthened the hydrophobicity of C18-MWCNT-CF. The post-treatment did not destroy the conductive network of MWCNTs in the coating and weaken the adhesion of MWCNTs towards CF surface, which is expected to achieve high conductivity and hydrophobicity.

**Properties of multifunctional CF**

**Superhydrophobic durability of CF**

The wetting behaviors of pristine CF and C18-MWCNT-CF were explored using WCA measurements. As displayed in Fig. 7a, the WCA of pristine CF was approximately 26° and upon approaching, the water droplet was adsorbed completely within 2 s due to the abundant hydrophilic hydroxyl groups of pristine CF. The hydrophilicity of CF was enhanced by the disposition of SNFs stabilized MWCNTs, and the water droplets were quickly absorbed so that the contact angle can’t be captured (Movie S1). The octadecanoyl chain-tethered C18-MWCNT-CF was expected to enable the hydrophilic CF with superhydrophobic characteristics after the active sites of CF and SNFs were reacted with stearoyl chloride. Therefore, C18-MWCNT-CF
displayed superhydrophobicity with a WCA of about 154° due to the increased surface roughness induced by hydrophobic octadecanoyl chain (Fig. 7b and Movie S2) (Fan et al. 2019). The pristine CF was wetted as soon as it was immersed in common contaminated liquids (dyed with methylene blue), and the CF was dyed after being taken out (Fig. 7c1, c2). However, C18-MWCNT-CF possessed obviously antiwetting performance remarkable towards the examined water (dyed with methylene blue), milk, and coffee due to the superhydrophobicity of C18-MWCNT-CF (Fig. 7d).

Fine sand as pollutant was placed on the surfaces of the C18-MWCNT-CF and pristine CF. As presented in Fig. 8, in contrast to the pristine CF, water drops falling on the C18-MWCNT-CF could automatically roll and take away fine sand, demonstrating the remarkable self-cleaning property. The robustness of medical clothing is required to fulfill the practical application of superhydrophobic interfacial materials. Therefore, the mechanical stability of C18-MWCNT-CF was explored to evaluate its durability by means of utilizing extreme mechanical force. As presented in Fig. 9a, the C18-MWCNT-CF was subjected to rubbing and scratching process under external force. After 20 cycles, C18-MWCNT-CF still possessed superhydrophobicity with a WCA approaching 150° verifying its mechanical durability (Fig. 9b). Additionally, the C18-MWCNT-CF remained the hydrophobicity with the WCA approximately 148° after being stretched in case of severe axial tensile force (Fig. 9c). The chemically bonded octadecanoyl groups endowed C18-MWCNT-CF with excessive abrasion resistance (Wang et al. 2019). Further, the amino and carboxyl groups of SNFs can interact with hydroxyl groups on the surface of CF, which facilitated the strong adhesion of MWCNTs towards CF. The robust superhydrophobicity of C18-MWCNT-CF are capable of strong repellency to water and effectively prevent water penetration, which efficiently avoid performance deterioration. These results reflected that the microstructure and surface composition of C18-MWCNT-CF fiber were...
not damaged during mechanical drawing and thus the mechanical wear stability and long-term durability of superhydrophobic fiber was realized consequently.

**Electrical conductivity**

The variation in the loading capacity of MWCNT on pure CF (mg/g) under incremental dipping-drying cycles directly affect the conductivity of the C18-MWCNT-CF. The loading capacity of MWCNT as a function of dipping-drying cycle was shown in Fig. 10a. The loading capacity of MWCNT gradually growing with the increase number of dipping-drying cycle and reached the maximum content of 259.2 mg/g after 4 dipping-drying cycles. As could be observed in Fig. 10b, the sheet resistivity of MWCNT-CF-n and C18-MWCNT-CF exhibited similar downward trends at incremental dipping-drying cycles. The sheet resistivity of MWCNT-CF-1 decreased dramatically with the LC of 115.3 mg/g (580 Ω/sq) in comparison with that of pristine CF (2 × 10^{10} Ω/sq). With the dipping-drying cycles increasing to 2 and 3, the surface resistivity of MWCNT-CF-2 was 187 Ω/sq containing MWCNTs of 203.8 mg/g and MWCNT-CF-3 was 40 Ω/sq containing MWCNTs of 247.5 mg/g. But the loading of MWCNTs seemed to be saturated at 3 dipping-drying cycles, as further increase cycle of 4, the sheet resistivity increased slightly with fluctuation around 40 Ω/sq. Therefore, the dipping-drying cycles of CF samples in subsequent studies were 1, 2, 3. The surface resistivity of MWCNT-CF-n is slightly higher than that of C18-MWCNT-CF, which may be due to the fact that the adsorbed MWCNTs fell off a little after being stirred in the solvent for 1 d and washed several times during MWCNT-CF was modified with stearoyl chloride. The mild decrease in WCA of MWCNTs deposited CF was ascribed to the certain hydrophilicity of the functionalized MWCNTs, but the superhydrophobicity of the CF was not affected.

Furthermore, a test of a bulb lighting experiment was carried out, as shown in Fig. 11. Compared with the pure CF (Fig. 11a), MWCNT-CF exhibited excellent electrical conductivity and was conducive to lighting the LED at 1.5 V power supply (Fig. 11b). The strengthened conductivity was originated from the three-dimension electrical paths that were formed by direct contact of MWCNTs.

**Thermal stability**

The variation of thermal decomposition and pyrolysis behavior of pristine CF, MWCNT-CF-n, and C18-MWCNT-CF samples with temperature in air atmosphere by TGA analysis were presented in Fig. 12. The $T_{5wt\%}$ and $T_{\text{max}}$ of MWCNT-CF-n and C18-MWCNT-CF moved towards lower temperature compared with that of pristine CF due to the decomposition of SNFs, which confirmed that SNFs stabilized MWCNTs were deposited on CF. Particularly, carbon residue of CF was significantly increased from 4.957% (pristine CF) to 10.076, 13.327, 13.842,
and 17.609% of MWCNT-CF-1, MWCNT-CF-2, MWCNT-CF-3, and C18-MWCNT-CF at 600 °C, respectively. The results of carbon residue were consistent with the increasing LC of MWCNTs on CF, which was conductive to the formation of residue and did not affect the thermal stability. After that, weight loss rate became slower as the remainder was mainly the relatively stable MWCNTs carbon skeleton (Su et al. 2020).

**Mechanical properties**

The impact of chemical treatments on the mechanical properties of CF samples were investigated by monitoring the variation of tensile strength and elongation at break (Fig. 13). Compared with pristine CF, the loading of the MWCNTs layer slightly strengthened tensile strength and elongation at break of MWCNT-CF-n and C18-MWCNT-CF. This is because the chemical treatment mainly enhanced the combination of MWCNTs and stearoyl chloride on the CF surface, while the core structure of CF (which is mainly responsible for showing mechanical strength) has changed modestly (Bhattacharjee et al. 2020).

**Microwave absorption performance**

Because of its light weight, nanocarbon-based absorbing materials can absorb electromagnetic energy maximally in a wide frequency range, which has gradually become the focus of attention in the field of absorbing waves in the new era (Qi et al. 2020; Zhang et al. 2021). The microwave absorption performance in case of various thickness were characterized by calculating RL values (Fig. 14). Compared with pristine MWCNTs, SNFs-MWCNTs has a relatively greater absorption performance, the RL_{min} of SNFs-MWCNTs is -22.33 dB as thick as 2.5 mm, while its average RL is only -6.57 dB (Fig. 14a). As shown in Fig. 14b, the RL_{min} of SNFs-MWCNTs were larger than -20 dB covering the testing thicknesses from 2.5 to 3.0 mm. Generally speaking, RL values under -10 dB indicates > 90% microwave absorption (Mu et al. 2018) and > 99% microwave were absorbed when RL is below -20 dB (Qi et al. 2016). Obviously, as expected, SNFs-MWCNTs showed the optimum enhanced microwave absorption with the RL_{min} for -36.08 dB at 9.28 GHz with 2.7 mm
thickness, when the filling amount of MWCNTs was merely 0.78%. The applicable bandwidth of presents the absorption frequency range, which is the critical property for an absorber. The corresponding effective bandwidths over -10 dB of SNFs-MWCNTs from 2.5 to 3.0 mm thickness were calculated to be 3.72 (7.48–11.20), 3.90 (7.16–11.06), 4.00 (6.96–10.86), 3.88 (6.81–10.69), 3.88 (6.67–10.55), and 4.16 GHz (6.47–10.63 GHz), respectively. Therefore, SNFs-MWCNTs provided multiple microwave reflection access to obtain advanced microwave absorption performance (Liu et al. 2015), which could be adjusted by facile controlling LC of MWCNTs in the targeted CF composites.

Performance evaluation

In order to highlight the superiority of as-prepared C18-MWCNT-CF, a comparison of the C18-MWCNT-CF in current study with the state-of-the-art of multifunctional textiles reported in the literature. Compared with the following five similar materials, the greatly enhanced conductivity and superhydrophobicity of C18-MWCNT-CF were contributed to the efficient SNFs-stabilized MWCNTs and tethered octadecanoyl groups. SNFs can not only disperse MWCNTs effectively, but also have the superiority of chemical bonding with CF at high temperature (the amino and carboxyl groups of SNFs can interact with hydroxyl groups on the surface of CF, which facilitated the strong adhesion of MWCNTs towards CF), further providing active sites for subsequent hydrophobic treatment. As shown in Table 1, C18-MWCNT-CF displayed the outstanding comprehensive performance that promises an ideal application prospect in the field of smart textile and wearable electronic devices.

Conclusions

To sum up, superhydrophobic, conductive and microwave-absorbing CF was successfully prepared based on a dip-coating method and surface hydrophobic treatment by depositing SNFs-stabilized MWCNTs and tethering octadecanoyl chain onto CF surface. The aggregated MWCNTs were successfully de-bundled into individually dispersed nanotubes by taking advantages of the high π-π interactions and electrostatic repulsive interactions between MWCNTs and SNFs. The LC of MWCNTs loaded on CF achieved 247.5 mg/g with a WCA of 151° for 3 dipping-drying cycles as the increased surface roughness of the cotton fiber. This approach was superior to most dispersant-assisted dispersion processes reported to date, the C18-MWCNT-CF obtained in the process exhibited fewer defects, remarkable conductivity (40 Ω/sq), impervious mechanical property and beneficial fastness even after 20 scratching cycles as compared to pristine CF. The microwave absorption performance reached above -36.08 dB with the loading content of MWCNT of only 0.78%. Considering the cost, abundant silk, the inexpensive equipment, and absence of organic or toxic solvents and chemicals, SNFs as a stabilizer provided a promising route for large-scale production of MWCNTs dispersion. The multifunctional CF could create intelligent articles with far-ranging applications in sports and work clothing, medical care and strain sensors.

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| Materials | Conductivity (Ω/sq) | Superhydrophobicity (°) | Microwave absorption (dB) | References |
|-----------|----------------------|------------------------|--------------------------|------------|
| C18-MWCNT-CF | 40.0 | 154 | −36.08 | This work |
| MTMS-MWCNT | 4.0 × 10⁴ | 146 | − | Nasirizadeh et al. (2015) |
| C-PDA-CNT | 51.8 | − | − | Sadi et al. (2019) |
| (bPEI/CNTs) n /APP/PDMS | 113.3 | 151 | − | Xue et al. (2020) |
| CCNT/cotton composites | 2.1 × 10³ | − | − | Li et al. (2017) |
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Declaration

Conflict of interest  The authors declare no competing financial interest.

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