Fabrication of MnO2 nanowires@Ag/cellulose laminated membrane with unidirectional liquid penetration for personal thermal management applications

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Abstract

Controllable and reliable fabrication of wearable materials with tunable structures and integrated functionalities are urgently required for personal thermal management. Herein, this highlight presents the fabrication of MnO$_2$ nanowires@Ag/cellulose laminated membrane with infrared insulation, antibacterial and unidirectional liquid penetration properties via orderly vacuum filtration of hydrophobic cellulose, hydrophilic cellulose and ultra-long MnO$_2$ nanowires coated with silver (MnO$_2$ nanowires@Ag). To do this, hydrophobic sugarcane cellulose was obtained by surface modification with silane coupling agent (A151), while hydrophilic sugarcane cellulose was obtained by HNO$_3$ treatment. Silver coated MnO$_2$ nanowires, as the building blocks of laminated membranes, were prepared by magnetron sputtering of silver nanoparticles onto the surfaces of MnO$_2$ nanowires. The characterizations indicated that silver nano coating with high infrared radiation reflectivity and excellent electrical conductivity were successfully fabricated onto MnO$_2$ nanowires surfaces, resulting in infrared insulation properties of the laminated cellulose membranes. In addition, the laminated membranes exhibit excellent unidirectional liquid penetration properties that can enhance the wearing comfort for the laminated cellulose membranes. In the antibacterial tests against Escherichia coli and Staphylococcus aureus, the laminated membranes exhibit large diameters of inhibition zones, revealing the high antibacterial activity. Moreover, excellent electrical conductivity of silver coating grants the superior Joule heating, generating rapid thermal response and uniform electrical heating at low supply voltage for extra warmth. These results indicate a promising potential of the laminated cellulose membranes for tackling personal thermal management issues related to wearable applications.

Introduction

Nowadays, fossil fuels shortages have led industries to seek alternative strategies due to the non-renewability of petroleum, metal mineral, coal and natural gas et al (Li et al. 2020). The high energy demand in modern industry has led to an increase in the use of renewable energy, such as wind energy (Zhou et al. 2012), tidal energy (Douziech, Hellweg, and Verones 2016), solar energy (Phan et al. 2018), biomass energy (Lee et al. 2010; Zhang et al. 2019) and geothermal energy (Alper et al. 2020), because they are not restricted by distribution and content of fossil fuels, without exhaust gases and environmentally friendly procedure. However, these energies have the disadvantages of high operation cost, low efficiency, and large fluctuations by climate and environmental conditions. Currently, reducing energy consumption or making full use of energy is the main means to solve the energy issue. For instance, energy-saving appliances and industrial energy-saving equipment are promoted to reduce the fossil fuel consumption (Huang et al. 2020; Dong et al. 2008; Guan et al. 2021). However, considerable amounts of energy are consumed in the maintenance of the temperature of empty space and inanimate objects inside the building for using thermal management equipment. Human body heat loss has three forms: heat convection, heat conduction and heat radiation. In the outdoor 50% heat is dissipated through infrared radiation (Hazarika et al. 2018), human thermal management is to reduce heat radiation so as to achieve the effect of insulation (Hsu et al. 2017). The heat from the human body can be easily
released through infrared by using ordinary clothing, which is not conducive to human thermal management. Therefore, an ideal thermal management technology with precise thermal regulation is urgently needed.

Wearable material with thermal management properties is a portable material that can be worn directly on the body or integrated with clothes for enhancing human thermal comfort (Gu, Liang, et al. 2020; Gu et al. 2019). Recently, a variety of wearable material with different microstructures and chemical compositions have been reported as good candidates for human thermal management, including cellulose materials, graphene membrane (Qiao et al. 2019), Mxene membrane (Ma et al. 2020), metal nanowires (Gu, He, et al. 2020) and other materials. According to Kirchhoff’s law, the intensities of heat radiation are determined by temperature and infrared emissivity of materials. Therefore, a very useful strategy for human thermal management control is to regulate the surface emissivity or reflectivity of wearable materials. For instance, Yang et al. fabricated the laminated nanofiber/Ag/nanoporous polyethylene (fiber/Ag/nanoPE) with high IR reflectance by transferring nylon-6 nanofibers onto Ag-coated nanoPE substrate. It is demonstrated that the laminated fiber/Ag/nanoPE shows a high IR reflectance (87.0%) and can be used for warming purposes (Yang et al. 2017). Zhou et al. prepared flexible copper coated melamine sponge (Cu-MES) via deposition of copper nanoparticles on the MES surfaces for personal thermal management applications (Zhou et al. 2019). The low infrared emissivity metal coating results in infrared insulation properties of the Cu-MES. In addition, the electric heating of wearable materials has proven to be a useful method for personal thermal management, which can adjust body temperature to a thermally comfort state. Currently, various conductive fiber materials are used for temperature control, including carbon nanotubes (Xu and Buehler 2009), metal nanowire (Zhou et al. 2015) and carbon fibers (Qian et al. 2013). These materials can effectively achieve electrothermal conversion and quickly convert electrical energy into Joule heat. Thermal radiation and electric heating of wearable materials are important for its useful application and, thus, providing thermal management materials with both thermal radiation and electric heating properties is of great importance.

Cellulose as the most abundant polysaccharide material on earth, is widely used as building blocks for fabrics or wearable materials due to the advantages of low price, high chemical stabilities and good mechanical properties (Liu et al. 2018). The controlled fabrication of cellulose-based wearable materials has attracted considerable attention for last decades, not only in terms of function integration, such as anti-ultraviolet radiation (Zhang et al. 2020), flame retardant (Farooq et al. 2018), anti-static (Wei et al. 2020) and self-cleaning (Bedford and Steckl 2010), but also due to their possible applications in textile industry, defense, medical and environmental protection. In this regard, Emam et al. reported the laundering durability textiles to enhance the anti-ultraviolet radiation (UVR) of textiles for secure their skin from several diseases (Emam and Abdelhameed 2017). Shi et al. developed a wet-spinning method to prepare PANI-cellulose composite filament fibers, which displayed excellent good antistatic properties and mechanical strength for the antistatic textile and military industries (Shi et al. 2014). Wei et al. reported an antifouling nanocellulose membrane that by subtle adjustment of surface charge led to self-cleaning property (Wei et al. 2018). Despite these successes, the fabrication of wearable cellulose material with human thermal management properties still remains a great challenge in various extreme and complex
environments. For example, sweat should be able to drain out of clothing to achieve wearing comfort. Recently, Yu et al. reported the highly thermoconductive breathable superhydrophobic nanofibrous membranes to enhance the thermal management of textiles for personal cooling (Yue et al. 2020). Due to the spread of COVID-19, there is a growing and urgent need to develop wearable cellulose material with antibacterial properties. Therefore, the development of a wearable material that is both breathable and antibacterial will be of great interest.

In this work, MnO$_2$ nanowires@Ag/cellulose laminated membrane with infrared insulation, antibacterial and unidirectional liquid penetration properties were fabricated via orderly vacuum filtration of hydrophobic cellulose, hydrophilic cellulose and MnO$_2$ nanowires coated with silver. The silver coating with excellent electrical conductivity not only harvests heat from Joule heating but also prevent body heat loss. In addition, the laminated membranes exhibit high antibacterial activity and excellent unidirectional liquid penetration properties, which can enhance the wearing comfort for personal thermal management application. Based on the above properties, this study not only provides a potential strategy for design wearable thermal management materials, but also may provide new insights for thermal control via infrared insulation and Joule heating.

**Experimental Section**

**Materials**

Hydrochloric acid (HCl), potassium sulfate (K$_2$SO$_4$), potassium persulfate (K$_2$S$_2$O$_8$), manganese sulfate monohydrate (MnSO$_4$·H$_2$O), acetic acid (CH$_3$COOH), nitric acid (HNO$_3$) and ethanol (C$_2$H$_5$OH) were purchased from Sinopharm Chemical Regent Co., Ltd (Shanghai, China). High purity silver (99.99%, Ag 11433), as Ag target, was bought from Zhongnuo New Material Technology Co., Ltd. (Beijing, China). Acetic acid (CH$_3$COOH, 36%), hydrochloric acid (HCl, 36–38%), sodium chlorite (NaClO$_2$) were obtained from Shanghai reagent company. Silane coupling agent (A151) and sodium hydroxide (NaOH) were supplied from Aladdin reagent (Shanghai) Co., Ltd. Staphylococcus aureus and Escherichia coli were purchased from Shanghai Luwei Technology Co., Ltd. Distilled water was used to prepare all solutions throughout the experiment.

**Preparation of MnO$_2$ nanowires**

The MnO$_2$ nanowires were obtained by a hydrothermal process described by Yuan and co-workers with some modifications (Yuan et al. 2008). Briefly, 6 g of K$_2$SO$_4$, 18.6 g of K$_2$S$_2$O$_8$ and 5.8 g of MnSO$_4$·H$_2$O was dissolved into 60 mL of distilled water. Then, the mixture solution was poured into a Teflon-lined stainless-steel autoclave at 250 °C for 5 days. After that, the obtained product was washed thoroughly with distilled water to remove the residual inorganic salt. Finally, to obtain dispersed MnO$_2$ nanowires suspension, 10 g of MnO$_2$ nanowires was dispersed in 250 mL of distilled water under vigorous stirring for 36 h.
Fabrication of MnO$_2$ nanowires@Ag/cellulose laminated membrane

The MnO$_2$ nanowires/cellulose laminated membrane was fabricated sequential deposition of hydrophobic cellulose, hydrophilic cellulose and MnO$_2$ nanowires. Before laminated membrane fabrication, sugarcane cellulose was obtained from sugarcane via alkali treatment and bleaching as described in our earlier work (Yue et al. 2018). The hydrophilic cellulose suspension was obtained by surface oxidation of cellulose by HNO$_3$. Then, pure cellulose membrane was prepared by vacuum filtration of sugarcane cellulose suspension. After drying, the pure cellulose membrane was soaked in a mixture solution of water and ethanol (v/v, 1:1) containing 1 wt % A151 for 3 hours to obtain hydrophobic surfaces. Subsequently, the hydrophilic cellulose suspension was vacuum filtered on the surface of the hydrophobic cellulose membrane sequentially to form laminated cellulose membrane.

The MnO$_2$ nanowires@Ag/cellulose laminated membrane was formed by using magnetron sputtering to uniformly coat silver nanoparticles on the surface of MnO$_2$ nanowires. In a typical experiment, 20 mL of above MnO$_2$ nanowires suspension was filtered onto the surfaces of laminated hybrid cellulose membrane. Thereafter, in a DC mode at the following parameters: the target material, chemically pure (99.99%) silver (Ag); the atmosphere, dry 99.99% nitrogen (N$_2$); the power discharge, 30W; and the Deposition times, 3 min. Finally, the Ag disk with 5 cm diameter is eroded by the impinging energetic ions via energy transfer and the ejected silver nanoparticles are collected on the MnO$_2$ nanowires to obtain MnO$_2$ nanowires@Ag/cellulose laminated membrane. The fabrication process of MnO$_2$ nanowires@Ag/cellulose laminated membrane is shown in Figure 1.

Characterization

Scanning electron microscopy (SEM, S-4800, Hitachi) and Fourier transform infrared spectroscopy (FT-IR, Nicolet Nexus 470) were used to measure the morphologies and functional groups of building blocks and laminated membrane. The infrared emissivity and transmittance of laminated membranes and pure cellulose membrane at the wavelength of 2.5-25 μm were measured by integrating sphere infrared spectroscopy. The general structure and atomic valency states of samples were measured by X-ray diffraction (XRD-6100Lab) and X-ray photoelectron spectroscopy (XPS, Ulvac-PHI, INC, Japan) a K-Alpha spectrometer using Al Kα radiation (1486.6 eV). The tensile strength of MnO$_2$ nanowires@Ag/cellulose laminated membrane was tested by a computer-controlled electronic universal testing machine (CMT6103). The water contact angles (WAC) were measured on a contact angle goniometer (Contact Angle System KSV CM200) at ambient temperature. The contact angle measurements of the hydrophobic side of the laminated membrane by applying 1 μL of distilled water and the WCA values were the average of at least three measurements of a water droplet at different positions. In addition, the WCA values were recorded by the various time to investigate the unidirectional liquid penetration process.

Thermal management properties
In order to study the Joule heating performance of the material, the laminated membrane was cut into 2 cm × 2 cm, and attached with copper tapes for electrical contacts. The laminated membrane and the power are connected by wires to form a closed loop. The power was supplied by a direct power source (WYK-30100), and the temperature was monitored by a thermocouple.

The laminated membrane with low infrared emissivity and high infrared reflectivity can achieve the effect of heat insulation. To further evaluate the thermal management properties, the infrared emissivity and reflectance of the laminated membrane were detected by Fourier transform infrared spectroscopy equipped with an integrating sphere. In addition, the infrared camera was used to take infrared images to further analyze its thermal management properties. In a typical experiment, laminated membrane and pure cellulose membrane are cut into 2 × 2 cm² squares, and placed on the back of the hand. The infrared image was taken with an infrared camera.

Antibacterial activity

Nutrient agar medium was prepared by mixing 5 g of peptone, 2.5 g of yeast extract, and 5 g of NaCl in 500 ml of distilled water and the pH was adjusted to 7. Then, 5 g of agar was added to the liquid medium in the Erlenmeyer flask. The conical flask and all other items related to this experiment were sterilized in an autoclave for 25 min to avoid interference from other bacteria in the environment. The mixture was then transferred to a sterile petri dish in a laminar flow chamber. Then 5 μL of Escherichia coli and Staphylococcus aureus were inoculated into the solid medium, and the laminated membrane and pure cellulose membrane were put into the same medium. Incubate for 12 hours in a 37 °C incubator, observe the status of bacteria in the sterile petri dish and whether there is a zone of inhibition.

Results And Discussion

Characterization

The thermal management properties of laminated membrane generally depend on the surface microstructure and chemical composition. Therefore, the surface morphology and chemical composition were analyzed by SEM and energy dispersive X-ray spectroscopy (EDS), and the results are shown in the Figure 2, Figure S1 and S2. The structure schematic diagram of the laminated membrane is shown in the Figure 2A. Laminated membrane is composed of hydrophobic cellulose, hydrophilic cellulose and silvery coated manganese dioxide nanowires. In this laminated system, the unidirectional liquid penetration can be reached via asymmetric wettability of laminated cellulose membrane, while the MnO₂ nanowires@Ag side can provide the thermal management properties. The sandwich structures were obtained by SEM image of laminated membrane cross-section (Figure 2B), indicating the successful fabrication of MnO₂ nanowires@Ag/cellulose laminated membrane. It can cleanly see from Figure S1 that MnO₂ nanowires with a length up to tens of microns and a width of only a few hundred nanometers. Compared with bare MnO₂ nanowires, the diameters of MnO₂ nanowires@Ag (Figure 2C) were slightly increased, implying that silver is uniformly loaded on the surface of MnO₂ nanowires. In addition, it can be seen in Figure S1D
that MnO$_2$ nanowires@Ag exhibits a smooth surface, which may result in high infrared reflectivity. From the Figure S1A-B, there was no obvious fibrous substance existing in pure cellulose and hydrophilic cellulose due to the alkali treatment of bagasse cellulose. As can be seen Figure 2D, the surface of the cellulose membrane was covered with a layer of stearic acid, forming the hydrophobic interfaces.

In order to better prove the chemical composition of the laminated membrane, EDS was used to analyze the element distribution of the cross-sectional of the laminated, the corresponding EDX results were shown in Figure S2. As indicated, the elements, including C, O, Mn, and Ag elements were distributed uniformly on the cross-sectional of laminated membrane, further confirming the formation of laminated membrane.

In order to study the surface properties of laminated membrane, the surface compositions and chemical states of both sides of the laminated membrane were measured by XPS, and the results are presented in Figure 3. The predominant peaks at, 531, 368, 284, and 102.5 eV of the XPS survey spectrum are attributed to O 1s, Ag 3d C 1s, and Si 2p (Figure 3A), which are in good agreement with EDS results. It can be noted from Figure 3A that there are no obvious characteristic peaks of Mn elements, indicating that silver nanoparticles are well coated on the surface of MnO$_2$ nanowires. Detailing XPS surveys on the region of Si 2p, Ag 3d and C 1s are presented in Figure 3B-D. It can be seen that the characteristic peak at 102.4 eV was assigned to Si 2p, indicating that silane coupling agent was successfully grafted onto cellulose surface to form the hydrophobic interface. The typical high-resolution C1s XPS spectra (Figure 3C) of samples can be deconvoluted into three peaks corresponding to C-C, C-O, and C=O with binding energies of 284.48, 284.78 and 286.53 eV. The presence characteristic peaks of C=O on the hydrophobic side of the laminated membrane indicates that A151 is grafted on the surface of the cellulose, reducing -OH on the surface of cellulose to achieve the hydrophobic effect. In Figure 3D, the peaks of the Ag3d binding energy at about 373.63 eV and 367.58 eV are assigned to Ag 3d$_{3/2}$ and Ag 3d$_{1/2}$. Obviously, the successful deposition of silver coating onto laminated membrane can reduce the emissivity of the MnO$_2$ nanowires, resulting in infrared insulation effect.

To further determine the components and structural characteristics of the laminated membrane, the samples were characterized by XRD diffraction analysis and the XRD results are shown in Figure 4. The XRD diffraction patterns of cellulose before and after surface treatment are displayed in Figure 4A. The characteristic peaks of celluloses at 2$\theta$ of 16.56° and 22.28° were indexed to the (020) and (110) planes of cellulose I (JCPDS no. 50-2241). Compared with pure cellulose, the characteristic diffractions of hydrophilic cellulose were slight decreased due to the structural damage of cellulose during nitric acid oxidation. It can be seen from Figure 4B the XRD pattern of MnO$_2$ nanowires were well indexed to tetragonal phase of $\alpha$-MnO$_2$ (JCPDS card no. 44-0141). No peak for other types MnO$_2$ was observed, implying the high purity and well crystallinity of the MnO$_2$ nanowires. After deposition of silver coating, there are four typical diffraction peaks of Ag crystallized in the MnO$_2$ nanowires@Ag corresponding to (111), (200), (220) and (311) reflections of crystal planes of face-centered-cubic silver crystals (JCPDS 04-0783). The peak intensities of MnO$_2$ nanowires were reduced by deposition of silver coating,
indicating that the silver coating was uniformly loaded on the surface of MnO$_2$ nanowires/cellulose laminated membrane. However, the XRD pattern of MnO$_2$ nanowires@Ag side of laminated membrane showed the characteristic peaks of cellulose and silver coating, only small MnO$_2$ characteristic diffractions were detected.

To investigate the surface properties evolution, FT-IR analysis was used to detect the surface functional groups of building blocks and laminated membrane. The resultant FT-IR spectra of different processed cellulose membrane are displayed in Figure S3A. The characteristic peaks of pure cellulose nearby at 3339 cm$^{-1}$, 2888 cm$^{-1}$, 1646 cm$^{-1}$, 1441 cm$^{-1}$, and 1025 cm$^{-1}$ were attributed to the stretching vibration of O–H, deformation vibration of C-H bond, deformation mode of O–H group, CH$_3$ bending mode, and symmetric stretching vibration of C-O. Compared with pure cellulose, Hydrophobic cellulose exhibits a small peak centered at 1646 cm$^{-1}$ and 1165cm$^{-1}$, which are ascribed to the -C=C- and Si-O, respectively. This may testify that silane coupling agent was successfully grafted onto cellulose surface to form hydrophobic layer. The hydrophilic cellulose exhibited the similar characteristic peaks as pure cellulose. However, the peak strength of hydrophilic cellulose was enhanced, implying the increased hydrophilic functional groups on the surface of cellulose. Asymmetric wettability of laminated cellulose membrane was favorable for droplet transport from hydrophobic interface to superhydrophilic interface. The resultant FT-IR spectra of MnO$_2$ nanowires@Ag side of laminated membrane are displayed in Figure S3B.

The two main characteristic peaks of MnO$_2$ nanowires around at 506 cm$^{-1}$ and 709 cm$^{-1}$ are consistent with Mn-O stretching vibrations. The MnO$_2$ nanowires@Ag have strong absorption peaks nearby at 414 cm$^{-1}$, 496 cm$^{-1}$ and 684 cm$^{-1}$ indicate the presence of silver coating consistent with XPS results. In addition, it can be noticed that the absorption peaks of MnO$_2$ nanowires were inhibited by metal layer. High infrared reflectance of MnO$_2$ nanowires@Ag layer can play a good infrared insulation effect.

Unidirectional permeability of liquid

Unidirectional liquid penetration is to make the wearer more comfortable. If the hydrophobic side close to the skin has a good hydrophobic effect, sweat is not easy to drain, which is easy to breed bacteria and has poor comfort. If close to the inner side of the skin is hydrophilic, wearable material remains wet state will lead to wearer discomfort. To enhance the wearing comfort, the unidirectional liquid permeability of the laminated membrane was investigated via water droplets permeability from the surface to the inside of cellulose via driving force between hydrophobic interfaces to hydrophilic interfaces. The static WAC of pure cellulose, hydrophobic cellulose and hydrophilic cellulose are showed in Figure S4. The results show that water contact angles of cellulose increased from 61.6° to 128.6° via surface grafting of hydrophobic functional groups. However, the nitric acid treated cellulose displayed extremely high hydrophilicity with water contact angle of 22.4°. Therefore, the permeation effect of laminated membrane can be achieved through asymmetric surface tension. Figure 5 shows the evolution of contact angle with time onto hydrophobic side of the laminated membrane. As can be seen in Figure 5 that water droplets could be rapidly absorbed by laminated membrane within 1021.1 s, showing the excellent unidirectional liquid
permeability. Significantly, the water contact angle decreased from 79.1° to 18.6° accompanied by liquid penetration. This commendable feature shows the potential for wearable applications.

Thermal management properties

To study the thermal management properties, the optical properties of the laminated membrane were studied by FT-IR spectrometer equipped with a diffuse gold integrating sphere and infrared images. The thermal management of human body mainly achieves the thermal comfort effect of outdoor environment through solar radiation and human radiation. In the case of low solar radiation, the thermal insulation effect can be achieved by reducing human radiation. However, ordinary clothing has low infrared reflectance and low thermal insulation effect is difficult to achieve in cold environment. In contrast, wearable materials with low infrared emissivity and high infrared reflectivity can achieve good thermal insulation effect. Figure 6A displays infrared reflectance of laminated membrane and pure cellulose. The silver coating of the laminated membrane has a higher infrared emissivity of about 65%, which can achieve thermal insulation effect. Furthermore, the infrared image is used to further explore the thermal management performance of the laminated membrane, and the result is shown in Figure 6B. The images were taken with an infrared camera in an enclosed space at 25°C. The surface temperature of pure cellulose was 22.4°C, while the surface temperature of lamination was 28.8°C, indicating that the laminated membrane has a good insulation effect, and can achieve precise thermal management. Compared with pure cellulose material, the laminated membrane surface has a high reflectivity of silver coating, which can reflect most of the human body’s external radiation heat to the human body to reduce heat loss, achieving a certain heat preservation effect.

In addition to infrared heat insulation, additional heating of wearable materials is an effective way to improve thermal management. The electric heating properties of laminated membrane were investigated under voltage of 3V. The temperature profiles of laminated membrane plotted against heating time are shown in Figure 7A, indicating that laminated membrane can be heated quickly due to good electrical conductivity of MnO$_2$ nanowires and silver coating. The results revealed that the surface temperatures of laminated membrane were increased from 15°C to 42°C within 10 seconds, confirming the excellent electrical heating properties. Specially, for wearable materials, the human body safety voltage of 3V can meet the normal requirement of the human body. Infrared digital photos were taken at room temperature of 25°C and the results were shown in Figure 7B-E. As can be seen, the surface temperature of laminated membrane was heated from room temperature to human desired temperature in just 10 s. Combination of infrared heat and electric properties, it is believed that the laminated membrane may be an ideal wearable material and have potential in broad applications in human thermal management.

Antimicrobial activity

Due to the existence of Ag nanoparticles in outer layer of laminated membrane, the antibacterial property of MnO$_2$ nanowires@Ag/cellulose laminated membrane was evaluated by Escherichia coli and Staphylococcus aureus. The contact of silver nanoparticles with bacteria increases the permeability of
bacterial cell membrane, and changes the pH value of bacterial culture medium and its living environment. The permeability of bacterial cells changed, and the silver nanoparticles entered the bacteria to accelerate the inactivation of the bacteria. Before the experiment began, all the objects used in the antibacterial experiment were treated with antibacterial treatment to ensure that there was no interference from other bacteria during the experiment. **Figure 8A** shows the results of pure cellulose membrane and this material in *Staphylococcus aureus* culture medium. It can be seen that there is a 11.7 mm bacteriostatic circle around laminated membrane, while the edge of pure cellulose membrane has no bacteriostatic circle. **Figure 8B** is the antibacterial experiment results of pure cellulose membrane and this material in *Escherichia coli* culture medium. As can be seen from **Figure 8B** that there is an antibacterial circle with a width of 17.2 mm around laminated membrane, while the pure cellulose membrane has no antibacterial circle, indicating the excellent antibacterial property against *Staphylococcus aureus* and *Escherichia coli*. Bacteria and viruses are widespread in daily life. Hence, in the context of the epidemic COVID-19, the laminated membranes have potential applications in protective clothing or wearable fabrics to keep human health.

**Flexibility and breathability**

As a wearable material applied to the human body, flexibility and breathability are essential. To investigate the mechanical characteristics of laminated membranes, the tensile test was performed by using the microcomputer universal testing machine. The tensile stress–strain curves of the laminated membranes and pure cellulose membrane are shown in **Figure 9A**. Owing to the cross-linked structures of fibers, the laminated membranes showed highly stretchable behavior by delivering a break strain of 7.61% with a tensile stress of 110.52 MPa, while the elongation at break of the pure cellulose membrane was 6.47 % with a tensile stress of 104.7 MPa. The photograph in insets of **Figure 9A** illustrates the flexibility of the laminated membranes, indicating that the laminated membranes can be bended without cracking. The excellent flexibility attributed to the fiber structures of building blocks and interface stability of laminated membranes. Hence, the laminated membrane can work as an efficient and durable wearable material for human thermal management application. In addition, the permeability evaluated by weighing method and the results were depicted in **Figure S5 and Figure 9B**. It is indicated that the permeability of the laminated membrane was close to that of ordinary cotton fabric. In short, laminated membrane displayed unidirectional liquid penetration, excellent antibacterial properties, good mechanical properties and high air permeability, guaranteeing its promising application in human thermal management.

**Conclusions**

In this work, *MnO$_2$* nanowires@Ag/cellulose laminated membrane with tunable structures and integrated functionalities was fabricated via orderly vacuum filtration of hydrophobic cellulose, hydrophilic cellulose and *MnO$_2$* nanowires coated with silver for personal thermal management application. For cellulose side, the laminated membrane exhibits the asymmetric wettability, which was favorable for droplet transport from hydrophobic interface to hydrophilic interface. Compared with pure cellulose membrane, the silver coating side of laminated membrane exhibits the low infrared emissivity and high infrared emissivity,
which can achieve thermal insulation effect. The results revealed that the surface temperatures of laminated membrane were increased from 15°C to 42°C within 10 s due to good electrical conductivity of MnO$_2$ nanowires and silver coating, confirming the excellent electrical heating properties. In the antibacterial tests against Escherichia coli and Staphylococcus aureus, the laminated membrane exhibits large diameters of inhibition zones and low minimum inhibitory concentrations, revealing the high antibacterial activity. Besides, laminated membrane displays excellent flexibility, highly stretchable behavior and high air permeability, guaranteeing its promising application in human thermal management. Therefore, in the context of the epidemic COVID-19, the MnO$_2$ nanowires@Ag/cellulose laminated membrane reported here could be used in the wearable application.

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**Competing Interests**

No conflict of interest exits in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been submitted previously.

**Figures**
Figure 1

Schematic illustration of preparation process of laminated membrane

Figure 3
XPS survey spectrums of two surfaces of MnO2 nanowires@Ag/cellulose laminated membrane (A); high resolution XPS spectra of Si 2p (B), C 1s (C), and Ag 3d (D), respectively. Ag side of laminated membrane (a), Hydrophobic side of laminated membrane (b)

Figure 4

XRD spectra of pure cellulose membrane, hydrophilic membrane, and hydrophobic side of laminated membrane (A). XRD spectra of MnO2 nanowires, MnO2 nanowires@Ag, and Ag side of laminated membrane (B)
Figure 5

WCA on the hydrophobic side of cellulose laminated membrane at time of 0 s (A), 121.1 s (B), 621.1 s (C), and 1021.1 s (D).

Figure 6

[Graph showing infrared reflectivity against wavelength]
Infrared reflectance of laminated membrane and pure cellulose (A), thermal imaging of hand covered with laminated membranes and pure cellulose (B)

Figure 7

Temperature-dependence of time in laminated membrane (A). Infrared images of laminated membrane applied a voltage of 3 V (B-E)

Figure 8

Antibacterial activity against Staphylococcus aureus (A) and Escherichia coli bacteria (B)
Figure 9

(A) tensile stress–strain curves of the laminated membrane and pure cellulose membrane, and the flexibility of laminated membrane. (B) the air permeability comparison between laminated membrane and ordinary cotton

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