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Generation of zinc ion-rich surface via in situ growth of ZIF-8 particle: Microorganism immobilization onto fabric surface for prohibit hospital-acquired infection

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ABSTRACT

Viruses/bacteria outbreaks have motivated us to develop a fabric that will inhibit their transmission with high potency and long-term stability. By creating a metal-ion-rich surface onto polyester (PET) fabric, a method is found to inhibit hospital-acquired infections by immobilizing microorganisms on its surface. ZIF-8 and APTES are utilized to overcome the limitations associated with non-uniform distribution, weak biomolecule interaction, and ion leaching on surfaces. Modified surfaces employing APTES enhance ZIF-8 nucleation by generating a monolayer of self-assembled amine molecules. An in-situ growth approach is then used to produce evenly distributed ZIF-8 throughout it. In comparison with pristine fabric, this large amount of zinc obtained from the modification of the fabric has a higher affinity for interacting with membranes of microorganisms, leading to a 4.55-fold increase in coronavirus spike-glycoprotein immobilization. A series of binding ability stability tests on the surface demonstrate high efficiency of immobilization, >90%, of viruses and model proteins. The immobilization capacity of the modification fabric stayed unchanged after durability testing, demonstrating its durability and stability. It has also been found that this fabric surface modification approach has maintained air/vapor transmittance and air permeability levels comparable to pristine fabrics. These results strongly advocate this developed fabric has the potential for use as an outer layer of face masks or as a medical gown to prevent hospital-acquired infections.

1. Introduction

During the past few years, the number of patients acquiring hospital-acquired infections has increased. One example is an antibiotic resistant bacterium that can result in severe and potentially lethal infections [1]. As in the case of the coronavirus outbreak, hospital-acquired infections are widespread and 17.6% of patients with the COVID-19 virus became infected after admission to the hospital [2]. Consequently, the development of surfaces with antiviral properties as well as those that have protein adsorption applications has attracted a lot of interest. Various types of materials and methods have been employed in the creation of antibacterial and antifouling surfaces in order to prevent bacterial growth and biofilm formation [3-6]. For instance, the self-assembly method of forming polysilsesquioxane (PSQ) structures, the generating of zwitterionic polymer, nitric oxide release structure, and the synthesis of metal nanoparticle such as gold, silver, copper, and zinc [7-10]. According to multiple studies on surface modification literature, metal-ion containing surfaces have gained considerable interest since they exhibit excellent antiviral/bacterial properties by inducing oxidative stress from metal-redox species, which consequently damages microorganism components [10-12].

Regarding protein adsorption, literature reports it to be primarily determined by the properties of the substrate and proteins. Surface energy, polarity, charge, and morphology are important parameters to consider. In general, proteins tend to adhere more strongly to nonpolar than to polar, to high than to low surface tension, and to charged than to uncharged surfaces [13]. A nonpolar surface destabilizes proteins, encouraging conformational reorientations, which result in strong interactions between proteins-protein and proteins-substrate. In most cases, the affinity of proteins for hydrophobic surfaces increases while

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the affinity for hydrophilic surfaces decreases [14]. The use of metal nanoparticles as protein adsorbents has been studied extensively. Copper phosphate nanoflowers have been used to improve DNA adsorption efficiency. It was reported that the maximum absorption capacity rose from 25.3 mg/g to 845.8 mg/g due to the addition of Fe(III) ion [15]. Influenza virus membrane protein (M2e) can stably conjugate with gold nanoparticles via the thiol-gold interaction from the cysteine residue and resulting in the 29% improvement of immobilization efficiency [16]. Moreover, polysaccharides, proteins, and lipids found in bacterial and fungal cell walls contain functional groups that can bind with metal ions [17]. Due to the diverse affinity for membrane proteins, metal ions can immobilize proteins very efficiently. These include interactions such as chelation, H-bonding, hydrophobic, electrostatic, and Van Der Waals interactions [18–20].

2.2. APTES functionalization to the fabric surface

To fabricate the metal ion-rich surface, several approaches are developed to achieve a high metal-containing amount such as direct binding of metal nanoparticles [22,23], blending with polymer matrix and coating [24], ion infusion [25], layer-by-layer assembly between metal nanoparticles and polymer [26], and in situ growth of nanoparticles onto the target surface [11]. However, these techniques still have limitations and drawbacks. Both the ion infusion and the mixture of polymer and metal nanoparticles demonstrate non-distribution and agglomeration of particles [27–29]. Additionally, metal particles are embedded within the polymer matrix, preventing them from binding to protein at the surface. Metal nanoparticles are located at the outermost layer when using in-situ growth and direct binding methods, where they are directly in contact with the surrounding environment. In contrast, the non-uniform coverage, instability, and shedding of metal nanoparticles are limitations of this technique, resulting in a lower level of immobilization efficiency [30,31]. To overcome the limitations and create a surface that prevents hospital-acquired infections from occurring, in situ growth of zinc imidazolate framework-8 (ZIF-8) onto polyester fabric (PET) is performed. A surface that prevents biocontamination transmission by utilizing metal ions-rich surfaces has been developed that has the following advantages: (1) a larger surface area for entrapment of microorganisms due to its porous structure: 4-times higher than pristine fabric. (2) promoting surface hydrophobicity, which enhances the adsorption capacity. (3) The presence of metal ions and uncoordinated N atoms in the imidazolate ring enhances H-bonding, hydrophobic interactions, as well as chelation between metal atoms at the fabric surface and the membrane-protein of the virus. Accordingly, the modified fabric possesses a 4.55-fold increase in virus immobilization capabilities over the pristine fabric and effectively prohibits transmission (>90%).

2. Materials and methods

2.1. Chemicals

The PET nonwoven fabric is a commercial product. 3-Aminopropyl triethoxysilane (APTES, 99%) and zinc acetate dihydrate (ZnAc) were purchased from Sigma-Aldrich; 2-methylimidazole (mM) from Alfa Aesar; biotinylated SARS-CoV-2 S-protein (D614G), His,Avitag™, super stable trimer (MALS verified) from Acrobiosystems; albumin from bovine serum (BSA); FITC conjugate and Streptavidin-FITC from Invitrogen; 99.5% ethyl alcohol and methyl alcohol were purchased from Daejung.

2.2. APTES functionalization to the fabric surface

The APTES surface functionalization procedure in this study is modified from Kong et al. (2015) and Zhang et al. (2018) [32,33]. In order to remove dirt from the fiber surface of the PET fabric, it is soaked in ethanol for 1 h. The fabric is then dried using an air gun until it is completely dry. Following this, a solution of 2% v/v APTES solution is prepared in ethanol using 1 M HCl as a catalyst. Fabric is pretreated with O2 plasma (CUTE-1B, Femto Science, Yongin, Korea) for 2 min, and then immersed in the APTES solution with stirring for 4 h. The excess solution is blown out with the air gun and dried at room temperature. This sample is designated F-A. Upon completion of the drying process, ZIF-8 was generated on the fabric.

2.3. Generation of ZIF-8 on the surface

ZIF-8 precursors are prepared in methanol separately. Initially, the F-A fabric is soaked in 80 mM ZnAc for 10 min. After that, mlin 320 mM is added to the previous solution and incubated for 12 h in a rotary shaker at 60 rpm. Afterward, the non-reacting solution is washed twice with methanol and dried at room temperature. This sample is known as F-A-Z. Comparatively, ZIF-8 is generated on the fabric surface without APTES functionalization. After the cleaning process, the fabric is exposed to O2 plasma for two minutes. Then, the pretreated fabric is transferred to the ZnAc solution with the same protocol as that used for the F-A-Z fabric, which was called F-Z.

2.4. Fabric characterisation

To determine the period of time at which the maximum APTES adsorption occurs on the fiber surface, Fourier-transform infrared spectroscopy (FTIR-4700, Jasco) was employed. The fabric was dried at 50 °C overnight before measurement. Then, the sample was investigated in the range of 500 to 4000 cm−1. A field-emission scanning electron microscope, model JEOL JSM-IT500HR FE-SEM, was used to observe changes in fiber surface morphology, ZIF-8 generation, and fabric surface uniformity. Based on the JEOL-7610F-Plus FESEM model, we obtained the atomic percent using element mapping from Energy Dispersive Spectrometry (FlatQuad, AURIGA, Carl Zeiss). The crystallinity of ZIF-8 that generated on the fabric surface has been observed using a high-resolution X-ray diffractometer (HR-XRD, Rigaku-SmartLab), using a scan rate of 5 •min−1 and Cu Ka radiation (λ = 1.54 Å).

2.5. Water contact angle of the fabric

A contact angle goniometer (Smart Drop Standard, Femto Biomed, South Korea) is used to measure the dynamic contact angles of the coatings on the substrates in order to determine the fabric’s water resistance. Each sample is contacted with a 20 µg droplet of protein solution (20 µg•ml-1) and five randomly selected points at random are included in the statistical analysis. Further, the time-dependent contact angle is also examined at 10, 20, and 30 min.

2.6. Water vapor transmittance rate, air permeability, and aerosol protection

The air permeability levels of the bare, F-A, F-A-Z, and F-Z fabrics are monitored with an air permeability tester (TQD-G1, Labthink Instruments Co., Ltd., Jinan, China) at a pressure of 15 Mpa. The WVTs of the bare, F-A, F-A-Z, and F-Z and commercial spunbond fabrics are evaluated using a water vapor permeability tester (W3/031, Labthink Instruments Co., Ltd., Jinan, China) at a temperature of 38 °C and relative humidity of 90%. Aerosol protection: Aerosols containing 100 nm polystyrene particles are generated with an Aerosol Generator (Model 3073, TSI, US) at 4.5 L.min−1. The generated aerosols are treated with a soft X-ray ionizer (SXC-10 T, SUNJE electronics, Korea) to clean them. The number of 100 nm PS particles in an aerosol is counted using a condensation particle counter (Model 3750, TSI, US).
2.7. Protein entrapment ability

For virus entrapment of the ZIF-8 modified fabric samples, two different molecular weight proteins are used: bovine serum albumin (66 kDa) and SARS-CoV-2 S-protein (139.7 kDa). Each protein is dissolved in 1x PBS and the concentration is adjusted to 20 µg·mL⁻¹. In the case of S-protein, photoluminescence is achieved as a result of the interaction between S-protein-biotin and Streptavidin-FITC affinity. After that, 1 cm² of the fabric is soaked in each protein solution for 30 min. A wipe is used to remove the excess solution from the surface of the fabric. Using a photoluminescent spectrometer (FP-8300, Jasco), the amount of protein adsorbed on five different points on fabric is measured. The fabric with adsorbent protein is located between two cylinders; ten milliliters of DI water are poured into the upper cylinder and passed through to the lower cylinder to simulate protein washout. The amount of protein remaining on the fabric after washing 1, 5, and 10 times are examined in order to confirm the protein immobilization ability.

2.8. Observation of protein adsorption using confocal microscope

Confocal microscopy (LSM 980, Carl Zeiss) is used to investigate protein adsorption on the fabric. For preparing the sample, the fabric is soaking into the protein-FITC solution (20 µg·mL⁻¹) for 30 min, followed by washing two times with DI water. Then, the sample is placed on a glass slide and covered with a cover glass. The image is obtained at an excitation/emission wavelength of 488/525 nm.

2.9. Confirmation of the binding interaction using XPS

X-ray photoelectron spectroscopy (XPS, Thermo Scientific) is used to characterize the surface chemical composition using an Al Kα excitation source. To prepare the sample, the fabric is soaked into a protein solution for 30 min, followed by washing two times with DI water to remove the residual protein. Then, protein-adsorbed fabric is dried under room temperature before measuring XPS.

2.10. Sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE)

To prepare the solution for SDS-PAGE, 1 × 1 cm² of the protein adsorbed fabric was placed into a 1.5 mL microtube that contained 0.5 mL of 1x PBS. Then, the microtube containing protein-adsorbed fabric was shaken using a micro-shaker at 500 rpm. The solution was kept every 1 h to observe the detachment of the entrapped protein on the fiber surface. SDS-PAGE was used to investigate whether the sample maintained the S-protein residues. A running buffer solution for SDS-PAGE was prepared by mixing 100 mL of 10x Tris/Glycine/SDS buffer (Bio-Rad, Hercules, CA) with 900 mL distilled water. S-protein, a positive control, and washing solution from each fabric samples 12 µL were mixed with 4x SDS sample buffer (Merck, Darmstadt, Germany) 3 µL. The mixtures were heated at 95 °C for 5 min. All the samples were loaded on an Any kD™ Mini-PROTEAN® TGX Stain-Free™ Protein Gel (Bio-Rad). Precision Plus Protein™ Dual Color Standards (Bio-Rad) was used as a protein ladder standard. Electrophoresis was performed for 60 min using the Tris/Glycine/SDS buffer at a constant voltage of 100 V. Imaging was performed after transferring the gel to Gel Doc™ EZ Imager (Bio-Rad). Image analysis of the stain-free gel was performed using the Image Lab software (Version 6.1.0, Bio-Rad).

2.11. Durability test

Physical and chemical damage were performed in order to study the fabric’s durability. During the experiment, the fabrics were twisted and bent 100 times in an attempt to mimic the action of human movement and laundry which caused physical damage to the fabrics. The fabrics were then blotted to remove the ZIF-8 or APTES that might crack from the fabric using an air gun before measuring the contact angle was conducted. Fabrics were soaked in 70% ethanol for ten minutes to replicate a common disinfection procedure in the case of chemical damage. The fabric was immersed in ethanol three times before its contact angle was examined. In the final step, the ability of modification fabric to immobilize proteins was assessed using the same procedure described in section 2.7.

3. Results and discussion

3.1. Characterization of the modified fabric

In order to prepare Zn(II) ion-rich surfaces on PET fabrics and overcome the limitations found in previous literature, ZIF-8 is directly generated on a fabric (namely F-Z) for comparison with the sample generated according to APTES surface modification. Fig. 1a shows the generation of ZIF-8 nanoparticles using two different approaches. Pathway 1 involved direct generation onto a fabric surface, and pathway 2 described the modification method to achieve maximum ZIF-8 generation on the surface. In the case of F-Z, fabric is treated with oxygen plasma to create hydroxyl groups on the surface that interact with the Zn(II) ion by electrostatic interactions. Following the addition of 2-methylimidazole, ZIF-8 is generated by the interaction between imidazolate and anchored Zn(II) on the fiber surface. Pathway 2 involves the pretreatment of fabric surfaces with APTES (F-A) and subsequent generation of ZIF-8 on the F-A surface (F-A-Z). To obtain maximum adsorption on the surface, the APTES modification time was examined. FTIR spectra (Figure S1) indicated that saturated adsorption of APTES on the fiber occurred after four hours, but adsorption lasting longer than four hours had no significant effect. The F-A fabric was then immersed in a mixture of zinc acetate and 2-methylimidazole solution to generate ZIF-8 on its surface. SEM images of fabric from both pathways are shown in Fig. 1b (SEM images of all fabric samples are shown in Figure S2). There is a difference between ZIF-8 amounts as a result of the favorable nucleation sites of the two surfaces. In the case of F-A-Z, a self-assembled monolayer with its amine group that extended away from the interface of APTES was formed. Siloxane bonds were formed by the covalent bonding of the fabric to the APTES, thus resulting in strong adsorption of APTES onto the surface [34]. Fig. 1c illustrates the nucleation site provided by the amine termination from APTES, which promotes the generation of ZIF-8 by the complexation between Zn(II) ions and N atoms [35-37].

By using EDS mapping analysis, it was confirmed that APTES had adsorption on fibers and that ZIF-8 is present, as shown in Fig. 2. It is shown in Fig. 2a that the zinc mass percent of F-A-Z increases dramatically and is 9.22 times greater than that of F-Z. Furthermore, due to the presence of APTES and organic linkers in ZIF-8, the nitrogen atom also shows a higher mass percent (8.8-times) than that of F-Z. The N and Zn elements in Fig. 2b inset represent the core elements that can be used to identify ZIF-8. This study confirms that the APTES-functionalized surface is more favorable to the growth of ZIF-8 compared to a pristine PET fabric surface. Additionally, the high adsorption via covalent interaction between APTES and the fiber surface enhances the stability of ZIF-8 on the fabric. Figure S2–6 and Table S1 provide additional details about the mapping result and the atomic percent, respectively. FTIR spectra and XRD patterns are used to confirm the formation of ZIF-8 on the fiber surface. The characteristic peak from the FTIR spectrum of ZIF-8 generation on the fabric surface can be seen in figure S7.

According to the XRD pattern in Fig. 2d, both F-Z and F-A-Z samples demonstrate clear diffraction peak locations at 2θ = 7.30, 10.35, and 12.70, which indicate characteristic peaks, including 011, 002, and 112, are consistent with those of pure ZIF-8 [38,39]. In the case of ZIF-8 nanoparticles, XRD patterns are shown in Figure S8. The surface area of each fabric is determined using the porosimeter shown in Fig. 2e. In comparison to pristine PET fabric, surface areas of the F-A, F-Z, and F-A-Z samples are 2.8, 3, and 4 times greater, respectively. The increased surface area is affected by ZIF-8 generation. These results confirm our
success in creating Zn(II) ion-rich surface using APTES and ZIF-8 as the modified layer.

3.2. Microorganism immobilization efficiency

To verify the ability to prevent the transmission of microorganisms, bovine serum albumin (BSA) and SARS-CoV-2 S-protein were used to investigate the immobilization ability. In the previous literature, it is reported that the carboxylate oxygen and nitrogen of amino acids can bind to the metal atom. This interaction results in the formation of three-point bonds between amino acid and metal surfaces [40]. According to this literature, we hypothesized that ZIF-8, which contains a metal ion core and unsaturated nitrogen from an organic linker has the ability to bind to protein or other components of microorganism cell walls in a similar form to amino acids molecules. First, the possibility of macromolecule protein binding to the fabric surface is observed. In order to measure the BSA immobilization efficiency onto the fabric, each fabric sample is submerged into a solution containing 20 µg•ml$^{-1}$ of BSA-FITC for 30 min. Then, the excess amount of protein solution on the surface was removed using a wipe. Photoluminescence spectroscopy is used to evaluate the intensity of BSA-FITC. At this point, the intensity comes from both physical trap protein by the fiber entanglement and protein that have an interaction with fabric surface. Then, the physical trap BSA-FITC is removed by simply washing. The intensity of the BSA-FITC that interacts with the fabric is measured again, and the results can be seen in figure S9. The weaker binding BSA can be removed with water while the

**Fig. 1.** a) Schematic illustration of the expected reaction of ZIF-8 generation on the fiber surface with two different methods. b) SEM image of ZIF-8 generation from pathways 1 (left) and 2 (right). c) Possibility of the zinc ion interaction with ligands to form the zinc-ligand complex.
stronger binding BSA can be maintained by generating interactions with ZIF-8. After remove the physical trap protein, the fabric with ZIF-8 on its surface retained a greater percentage of binding stability than other fabrics (>90%). According to Figure S9b, in the case of pristine fabric and F-A, most of the intensity comes from the physical traps, and little BSA remains on their surfaces upon washing (approximately 10–30%). The highest intensity of binding 93% is observed in fabric F-A-Z, which has the greatest amount of ZIF-8 on its surface, supporting hypothesis that ZIF-8 could bind to amino acid residues within BSA. For pristine, F-A, F-Z, and F-A-Z, the mass percentage of zinc atoms as determined by EDX is 0, 0, 2.4, and 22.13%, respectively. The stability of the BSA binding on the fabric surface is also investigated, as indicated in figure S9c. Through a combination of gravity and the mass of the water that passes through the fabric, water is poured from the top towards the bottom of the fabric, in order to generate the force to pull BSA out. After ten times of testing, the percentage of BSA immobilization is maintained at 90% in F-A-Z fabric. It is observed that after the first testing showed a decrease in percent immobilization due to the physical trap that binds loosely to the surface. Pristine, F-A, F-Z, and F-A-Z demonstrate decreasing immobilization capabilities for 90, 80, 40, and 10%, respectively. The immobilization ability did not change significantly from 5 or 10 tests since all physical traps were removed and the high stability of BSA immobilization using ZIF-8 is confirmed. As a consequence of the BSA immobilization results, it can be assumed that ZIF-8 modified fabric has 90% capability to prevent microorganism transmission, as BSA is similar to virus outer membrane components. Based on their structure, viruses were categorized into two categories: enveloped and non-enveloped. In both types, DNA/RNA and capsid protein make up the two most important components [41]. The literatures clearly indicate that protein is the predominant component of the virus surface, suggesting that the virus might interact with ZIF-8 in a similar manner to BSA.

SARS-CoV-2 S-protein (139.7 kDa) is used in this study as a model for virus immobilization to confirm our hypothesis. An interaction between
Biotin and streptavidin is used to conjugate S-protein to the fluorescent dye (FITC). Each fabric sample is then immersed in the S-protein/FITC solution (2 \( \mu \)g•mL\(^{-1} \)) and its luminescence intensity is measured as described in the BSA procedure. F-A-Z possesses the highest amount of S-proteins adsorption, as shown in Fig. 3a. Similar to the BSA result, adsorption of S-proteins is the result of both interactions between proteins and ZIF-8 as well as the physical trapping produced by the entanglement of fibers. A simple washing procedure removed the S-proteins in the physical trap, but the binding of S-proteins to ZIF-8 was not altered. Approximately 90% for F-A-Z fabric and 69% for F-Z fabric captured the S-protein via interactions with ZIF-8. In contrast, both pristine fabric and F-A fabric show a similar amount of protein binding between S-protein-ZIF-8 interaction and physical trap as shown in Fig. 3b. Fig. 3c illustrates an examination of the membrane protein-fabric stability using the same procedure as BSA. During the first test, the S-protein adsorption amount on the fabric decreased dramatically, especially in fabrics without ZIF-8. >90% of the trapped liquid is removed from the pristine PET fabric after only one testing, indicating that the protein adsorption is due to physical entrapment. The amount of S-protein that is removed from F-Z and F-A-Z fabrics, respectively. Ten times of binding stability testing demonstrated that S-protein remained on the fabric surface for as much as 76 and 91% on F-Z and F-A-Z fabrics, respectively. Figure S11 illustrates the confocal image of the protein that remains after the protein binding stability test was conducted. After the stability test, less than 30% of the protein remains in the F-A fabric. According to confocal images, 30% of the remaining protein may be trapped by the rough surface of the APTES layer. F-Z and F-A-Z fabrics both display the ability to immobilize S-protein because of the presence of ZIF-8 growing on their surfaces, but their ability to immobilize the protein varies depending on how much ZIF-8 they have on their surfaces. In the case of F-A-Z, a great amount of ZIF-8 was generated on the APTES-functionalized fabric that resulted in a high number of protein immobilization sites, resulting in an increase of fabric surface area, as discussed previously. Figure S11 shows a confocal image that confirms the ability of protein binding while simultaneously including ZIF-8 distribution onto the fabric fiber. It is evident that the results of the binding of protein to ZIF-8 in F-A-Z fabric produce a strong and uniform intensity of fluorescence. After the physical trap protein is removed, SDS-PAGE is used to determine whether the desorbed protein is in the washing solution. The results demonstrate that no protein is detectable (Figure S10) which confirms the ability to prohibit virus transmission from the ZIF-8 modifying fabric surface, especially in F-A-Z (>90%).

The FTIR and XPS spectra in Fig. 4 demonstrate the interaction between the S-protein and ZIF-8. The FTIR spectra of the fabric samples without the protein adsorption can be seen in Figure S12. In Fig. 4 a and b, the spectra are obtained following the immobilization of S-protein on each fabric sample. The dramatic increase in N–H peak intensity at 3260 cm\(^{-1} \) and the C=O peak at 1645 cm\(^{-1} \) from F-Z and F-A-Z reflected considerable protein adsorption on the surface. In addition, vibrations at 3200–3600 cm\(^{-1} \) are also reflected in the formation of coordination bonds between nitrogen atoms and zinc(II) ions by means of the offer of their electron pairs as well as the replacement of the N–H hydrogen bonds with N\( \cdot \)Zn(II) bonds \[44\]. Moreover, it has been shown that the vibration band at 1645 cm\(^{-1} \) can also indicate the involvement of the carbonyl group in the chelation of Zn(II) ions \[45\]. These peaks increase when ZIF-8 amounts are increased on the surface, indicating ZIF-8 is effectively immobilizing S-proteins.

Fig. 3. Investigation of the efficiency of S-protein to interact with the fabric. a) The total intensity obtained from photoluminescence spectroscopy. b) Percent of interaction that can occur on each fabric sample. c) The stability of S-protein and fabric surface interaction. and d) Durability test in terms of protein immobilization efficiency. The result is obtained after applying physical and chemical damages.
XPS techniques are used in this section to further investigate the possible mechanisms of adsorption in F-Z and F-A-Z fabric. In Fig. 4c, the O1s spectrum shows a shift towards lower binding energies for each of the –OH peaks, from 530.123 to 529.825 eV for F-Z, and from 530.745 to 530.165 eV for F-A-Z. In terms of area under the peak of –OH peak of F-Z, it increased from 1.1 to $1.6 \times 10^3$, while the F-A-Z increased from 5.4 to $9.6 \times 10^3$. This indicates that peptidic oxygen of protein is present in both of the fabric samples [46]. F-Z presents a downshift in the binding energy of N-Zn N1s peak from 398.046 to 397.944 eV. The area under the peak increased from 1.1 to $3.9 \times 10^3$, whereas F-A-Z increased from 0 to $5.8 \times 10^3$, as shown in Fig. 4d. Due to the electron-donating and electron-accepting capabilities of metal ions, a decrease in the binding energy of the –OH and N-Zn peaks are attributed to their coordination to Zn(II) [18]. Furthermore, atoms from amine groups share electrons with Zn and consequently have a low electron density [47]. The decrease in –OH and N-Zn binding energy, as well as an increase in its intensity after protein adsorption, indicate that this site participates actively in the coordination to zinc ions. The Cls and Zn2p scan was shown in figure S13. Zn2p3/2 peak in Zn2p spectrum from F-Z shifts from 1044.68 to 1044.58 eV, while F-A-Z shifts from 1044.78 to 1044.46 eV. The shift to a low energy phase indicates a strong affinity between zinc and s-protein. According to FTIR and XPS results, the carboxyl oxygen atoms and amino nitrogen atoms on S-protein form a primary bond with the zinc ion from ZIF-8. Horie et. al., reported the metal compound of Ti, Ce and Zn exerted strong protein adsorption [48]. E.A. Vogler (2012) reported that Lewis acid/base and hydrophobic surfaces are capable of adsorbing protein in three dimensions [49]. The hydrophobic property of the substrate destabilizes proteins, which causes them to reorient themselves, resulting in strong interactions between proteins-proteins and proteins-substrate [14]. In the F-A-Z fabric, Lewis’ acid at the Zn(II) atom of ZIF-8, combined with a hydrophobicity results in a high interaction between the S-protein and the fabric surface. Moreover, there have been reports of interactions between the metal ion and amino acids, such as intramolecular aromatic stacking to produce ternary metal complexes. Additionally, the authors reported that the histidine group within the protein structure acts as a metal-binding site, especially for Cu(II) and Zn(II) [21]. Hence, these bonds created a binding between ZIF-8 and virus membrane protein and provide excellent prohibition of virus transmission from the surfaces (>90%).

The previous literature reported that ZIF-8 is unstable and degraded under phosphate buffer saline solution (PBS). For the purpose of confirming the degradation of ZIF-8 on F-A-Z fabric after protein adsorption, both soaking and spraying conditions were investigated. Microdroplet conditions were used as a method of simulating the
environment of a real application, and microdroplets were generated via an aerosol generator. Additionally, FTIR spectra were analyzed in order to determine whether zinc phosphate was formed due to the decomposition of ZIF-8. The result was compared to the previous literature and revealed that there is no zinc phosphate occurring on the F-A-Z fabric, Figure S14 [38]. Moreover, the conditions of ZIF-8 decomposition in this study are different from those previously described. In F-A-Z fabrics, the ZIF-8 layer tends to pack densely, thereby resulting in a smaller area of ZIF-8 that is exposed to the environment. As a result, ZIF-8 residing on F-A-Z fabric will degrade more slowly than particles directly dispersed in PBS. ZIF-8 degradation is not only influenced by the decreasing amount of surface that is exposed to the solution, but also by the amount of solution that is micron size. Microdroplet amounts that adsorb onto the fabric are significantly smaller than the amounts absorbed in the solution, therefore, the degradation in this study is not comparable to previous studies. As can be seen from the SEM image in Figure S15, ZIF-8 is not degraded following aerosol adsorption. All data suggests that ZIF-8 that is decorated onto F-A-Z fabric can withstand the condition of protein adsorption without decomposing.

3.3. Durability and reusability of the fabric sample

In this section, the durability of ZIF-8 is examined after physical damage and chemical treatment as well as its binding capability to fabrics or F-A surfaces. The most common method of decontamination is rinsing or soaking materials in 60–80% ethanol, an agent that is powerfully virucidal against viruses [50]. However, in recent studies, it has been reported that N95 respirator performance decreases by as much as 40% upon immersion in a solution of 70–75% alcohol. Hence, the durability of the fabric under ethanol soaking is investigated [51]. The durability of ZIF-8 on the fabric is demonstrated by the changes in contact angle and the ability to immobilize proteins in Figures S9d, S14, and 3d. After bending and squeezing the fabric 100 times or soaking in ethanol, the fabric’s contact angle decreased slightly, Figure A14a. Nevertheless, the decrease in the contact angle is not significant when one-way ANOVA is performed. In the case of protein immobilization ability, both BSA and S-protein are unaffected, as shown in Fig. 3d and S9. Furthermore, a variety of laundering cycles are used for F-A-Z fabrics, including 10, 20, 50, and 100 cycles. To determine this fabric’s durability, contact angle and scanning electron microscopy are used. After 100 cycles of laundering, the result in Figure S14b shows no significant change in the water contact angle, and the SEM image in Figure S15 shows that ZIF-8 is slightly decreasing on the fabric surface. From all durability tests, there is no change in the hydrophobicity of the surface and the immobilization properties of proteins have remained unchanged. This indicates that the F-A-Z fabric is durable and can maintain protein immobilization ability. The durability of ZIF-8 on the fabric is directly impacted by the APTES pre-treatment, as described in the preceding section. As a result of the durability test, the F-A-Z fabric could be a viable choice for reuse due to its resistance to physical bending, chemical soaking, and laundering.

3.4. Comfortability test of the fabric

Comfort is one of the most important factors when it comes to clothing. However, the PPE used today has the disadvantage of low thermal exchange and low air/vapor transmission. A water/vapor transmission rate (WVTR) and an air permeability test are used in the study to examine the fabric’s comfortability. A schematic illustration of the improvement in macroscopic properties of the fabric is shown in

Fig. 5. a) Schematic illustration of the sample fabric shows the repelling of bulk water ability while maintaining air–vapor permeability through the pores between the fibers. b) Water contact angle measurement after dropping the water 30 min. The data were measured at 10 points in each fabric sample. The modified fabric maintained an excellent comfort index of the pristine PET nonwoven fabric and the results were demonstrated in c) water vapor transmittance rates and d) air permeability of the sample fabrics which indicates high airflow.
Because of its highly porous structure and loose texture, PET nonwoven fabric was used as a substrate for ZIF-8 formation. Although the surface of the pristine PET fabric is hydrophobic, the large pores in its structure allow water to penetrate into the fabric within 3 to 5 s due to the gravitational force; therefore, the water contact angle of the pristine PET fabric becomes zero. The roughness generated by the ZIF-8 nanoparticles causes a subsequent increase in hydrophobicity. Fig. 5b illustrates that the modified fabric exhibited a contact angle of 150°, however, the pristine fabric had a contact angle of 0°. The contact angles for different time points are shown in Table S2. Results indicated that the hydrophobicity of the surface decreased somewhat after 30 min. Fig. 5c and d illustrate the WVTR and air permeability of the fabric sample. The findings indicated that the modified surface technique we used can maintain the WVTR and air permeability of pristine PET fabric. In comparison to the previous report from Behera et al., Table S3, a very high work rate was retained (>4140 g/m²•day) [52]. Moreover, the WVTR of modification fabric in this study is 1.75 times higher than that of the commercial spunbond fabric. In terms of comfort, this fabric provides high vaporization (4430 g/m²•day) along with good airflow (19.9 L/min). Aerosol protection, which is different from water resistance, also refers to the ability to protect against micro- to nanodroplets. As indicated in Supporting Information, Figure S16, the aerosol protection ability of pristine, F-A, F-Z, and F-A-Z samples are also examined. After a whole modification process, the fabric macrostructure does not change, so there is no difference in its aerosol protection ability. With a single layer of fabric, 50% of aerosols can be blocked, however, a double layer of the fabric increases protection to 80%. Based on the results of this study, F-A-Z is also suitable for use as an outer layer for a personal protective equipment. Due to the fact that both the outermost layer of the medical gown and the face mask can act as surfaces on which viruses can attach and spread. Consequently, the development of fabrics that prevent the transmission of viruses is necessary to decrease the risk of hospital-acquired infections and self-contamination.

3.5. Safety test of the fabric

In order to assure that fabric is safe to use, it is evaluated for biocompatibility, antibacterial activity, as well as antifilm activity. The antibiotic-resistant P. Aeruginosa and S. Aureus were used to examine biofilm formation and bacterial activity on pristine and ZIF-8 modified fabric (F-A-Z). Using SEM, the biofilm formation on the fabric was investigated after bacterial culture was performed, the data was shown in figure S17. The SEM image shows that F-A-Z has lower biofilm formation compared to pristine fabric. Furthermore, the antibacterial activity from ZIF-8 on the fabric surface was confirmed by the distortion of the bacterial morphology. Quantitative results were obtained based on the optical density. Both bacteria exhibited a substantial reduction in numbers of >50% (figure S18). As a result, we hypothesized that microorganisms adsorbing onto fabric surfaces would lose their biological activity and die when time passed. A similar report from the previous literature reported that Zinc ions can induce cell deformation, rupture of the cell wall causing leakage of the cytoplasm, creation of an alkaline microenvironment, all of which led to the growth inhibition or death of the bacterium [39,53].

Figure S19, a human dermal fibroblast (HDF) and human umbilical vein endothelial (HUVEC) cell line were used to investigate the toxicity of ZIF-8 to human cells. Cells were treated with ZIF-8, 200 nm in size, at concentration ranges of 500, 200, 100, 50, 20, and 10 μm/mL. A cytotoxicity assay was conducted after one and three days of treatment. The result in Figure S18 indicates that 50 and 100 μg/mL are the biocompatible thresholds for HUVEC and HDF cells, respectively. In the ranges above these, the cytotoxicity is shown to be due to the action of Zinc ions on the production of reactive oxygen species by mitochondria. As a consequence of this adverse effect, the cell cycle is arrested at the G2/M phase due to irreversible DNA damage, ultimately leading to cellular apoptosis [54]. Nevertheless, it should be noted that the modification fabric we developed was intended for use as a medical gown. Because there was no direct contact between the modification fabric and the human body, we did not conduct a biocompatibility test for this study. Furthermore, due to the metal chelating complexes between ZIF-8 and APTES, there is almost no likelihood of ZIF-8 becoming detached from the fabric during use. As a consequence, ZIF-8 toxicity associated with high doses above 50 mg/ml is extremely rare.

4. Conclusions

In this study, a Zn-ion-rich fabric was explored as a potential surface that can render a hospital-acquired infection prohibitive. The > 90% immobilization of microorganisms is accomplished through the formation of a large amount of nucleation of ZIF-8 on the APTES surface that facilitates the coordination between the Zn(II) ion and the N atom of the silane ligand. As a result, a large amount of ZIF-8 nucleation occurs across the entire fabric surface and plays a role in the immobilization of microorganisms such as BSA, bacteria, and COVID-19 spike glycoprotein on the fabric surface. The covalent bonding between the fabric and the APTES provides a stable platform for the growth of ZIF-8, resulting in the formation of a durable layer of nanoparticles on the fabric surface. The ZIF-8 offers a significantly high surface area and provides a variety of interactions with model microorganisms, such as H-bonding, hydrophobic interaction, and chelation. By interacting in this manner, microorganisms are effectively immobilized, limiting transmission and possibly deactivating bacterial/viruses at the same time. In addition, nano-roughness of nanoparticles promotes hydrophobicity on the surface, thus increasing the efficiency of immobilization of proteins since the surface is more suitable for protein adsorption. Taking these advantages into consideration, it demonstrates the excellence of this modification fabric against microorganism spreading and its capability to serve as a medical gown or as an outer layer on a face mask.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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