Cotton Fabric Coated With Graphene-based Silver Nanoparticles: Synthesis, Modification, and Antibacterial Activity

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Abstract

In this study, silver immobilizing onto graphene oxide (Ag/GO) was synthesized by the in-situ method. Subsequently, silver immobilizing reduced graphene oxide cotton fabric (Ag/rGO/cotton) was made by the dip-coating method in Ag/GO suspension followed by the chemical reduction with the presence of vitamin C as an environmentally friendly reducing agent. The characteristics of Ag/GO, Ag/GO/cotton, and Ag/rGO/cotton were investigated by Fourier transform infrared spectroscopy, X-ray diffraction, Raman spectroscopy, transmission electron microscopy, scanning electron microscope, and energy-dispersive X-ray spectroscopy. The results showed that AgNPs were uniformly distributed on the surface of GO sheets with an average size of 10–15 nm. Regarding Ag/rGO/cotton, the fiber surface was evenly covered by Ag/rGO materials. Besides, there was no significant difference between the two samples of Ag/GO/cotton and Ag/rGO/cotton, indicating the reduction reaction possessed no effect on the cotton structure. Moreover, the Ag/rGO/cotton also exhibited effective hydrophobicity with a wetting angle of 103.85 ± 0.75°. The antibacterial performance of Ag/GO, Ag/GO/cotton, and Ag/rGO/cotton against the Gram-positive (Staphylococcus aureus-S. aureus) and Gram-negative (Pseudomonas aeruginosa-P. aeruginosa) bacteria were determined via the diameter zone of inhibition. The results indicated that the appropriate reducing agent is L-ascorbic acid-vitamin C (VC) with the conditions: the VC:Ag/GO mass ratio of 1:1, the reducing temperature of 140°C, and the reducing time of 120 min showed the highest antibacterial effect against two types of bacteria. All results of the study confirmed that Ag/rGO/cotton possesses significant potential for several antibacterial applications such as protective equipment.

1. Introduction

Cotton is a natural cellulosic fiber with structures consisting of a cellulose polymer with repeated cellobiose units that make cool, soft, and biodegradable properties, making it useful in many industries [1, 2]. Thanks to a hydrophilic structure, they show a superior adsorption capacity of 24–27 times their mass [3]. However, the hydrophilic property of cotton fabric can generate a humid environment and promote the growth of bacteria that cause unpleasant odours, allergies, and infections for consumers [4]. These drawbacks of the cotton fabric have been studied to resolve and ensure the best safety for the users. Moreover, the manufacturing development leads to an increasingly polluted environment with the strong growth of pathogenic organisms present in the soil, water, air, or on the surface of any tools, equipment. These cause many progressive diseases such as infections, respiratory infections, and skin diseases. The user's health may be threatened if the cotton layer is not bacterial resistant [5, 6]. Microbes or germs growing on the face have a harmful influence not only on the materials but also on the user. As a result, the use of antibacterial materials is deemed significant attention in the medical area to reduce bacterial population and lessen pathogenic illnesses produced by face mask textile materials since its bacterial resistance boosts product quality and durability [5, 6]. Therefore, antibacterial materials have been studied and developed, which are confirmed to be the essential applications in various fields such as food storage, clothes, wastewater treatment, medical devices, etc [7].
In nanotechnology, silver nanoparticles (AgNPs) have been widely used, especially in the antibacterial field, to reduce the usage of antibiotics as not being necessary. Nevertheless, AgNPs have many disadvantages such as agglomeration due to the high surface energy, which adversely affects the antibacterial activity [8]. Furthermore, AgNPs can cause several health problems for humans such as organ toxicity, argyria, neurological symptoms, etc [9]. Therefore, stabilizer agents are needed to control the size, shape, and cytotoxicity of AgNPs. On the other hand, graphene oxide (GO) has been known as a potential material for the combination with AgNPs to synthesize stable nanocomposite without compromising the antibacterial property. Thanks to the presence of many oxygen-functionalized groups, GO can be easily dispersed in water and forms different functional groups on fabric surfaces simultaneously [10]. Therefore, the synthesized silver immobilizing onto graphene oxide (Ag/GO) was reported to overcome the disadvantages of both AgNPs and GO, which can prevent agglomeration and enhance antibacterial resistance as opposed to pre-materials. Previous researches coated Ag/GO onto cotton fabric (Ag/GO/cotton) to prevent bacteria growth [11]. However, Ag/GO/cotton is hydrophilic, which endows favourable conditions for the growth of bacteria. Besides, Ag/GO/cotton can stick to wounds during treatment, so they would destroy newly formed cells and create long-healing wounds [12, 13].

Nowadays, there have been many methods for cotton surface modification such as chemical vapour deposition, sol-gel, and coating methods, which possess toxicity, use toxic chemicals pathway and also affect Ag/GO antibacterial activity [14, 15]. Thus, the use of a chemical reduction method (usually with D-glucose, vitamin C, etc.) for treating the Ag/GO is necessary, affirming the simple and low–cost performance due to the direct reduction of the existing substrate without any toxic [16]. As a result, the cotton can be treated with silver immobilizing reduced graphene oxide (Ag/rGO) with a moderate hydrophobic property. This can make the bacteria come into contact with cotton surfaces to proceed with the material antibacterial function. Thus, the modification of cotton fabric to overcome the disadvantage of conventional cotton fabric and increase the antibacterial activity is becoming necessary.

In this study, Ag/GO was synthesized by in-situ method with glucose as a reducing agent before using for the dip-coating process to form Ag/GO/cotton and chemically reducing to Ag/rGO/cotton by vitamin C (VC). The effect of reduction conditions including VC:Ag/GO mass ratio, reducing temperature, and reducing time on the antibacterial activity of the cotton was also investigated in this study. The antibacterial activity of the material was studied by agar disk diffusion test against the Gram-positive (Staphylococcus aureus-S. aureus) and Gram-negative (Pseudomonas aeruginosa-P. aeruginosa) bacteria which are pathogenic causing several health problems. The durability of the cotton was also investigated under different conditions such as colourfastness to washing with at 40 °C, colourfastness to alkaline, acidic of perspiration, and hot pressing at 150 °C.

2. Experimental

2.1. Materials and chemicals
Graphite (particle size < 20 µm), poly(vinyl pyrrolidone) (PVP, \((C_6H_9NO)_n\)), and silver nitrate (AgNO₃) were purchased from Sigma-Aldrich Co. Ltd., USA. Potassium permanganate (KMnO₄), sulfuric acid (H₂SO₄), phosphoric acid (H₃PO₄), hydrogen peroxide (H₂O₂), D-glucose (C₆H₁₂O₆), L-ascorbic acid – vitamin C (VC, C₆H₈O₆), ethanol anhydrous (C₂H₆O), sodium hydroxide (NaOH), and ammonium hydroxide (NH₄OH) were purchased from Xilong Scientific Co. Ltd., China. Note that all mentioned chemicals were used without further purification. Bacteria \(S.\) aureus ATCC 25923 and \(P.\) aeruginosa ATCC 27853 were purchased from Pasteur Institute in Ho Chi Minh City, Vietnam. Nutrient broth and nutrient agar were purchased from Titan Biotech Ltd., India. Cotton fabrics were obtained from Tan Binh market, Ward 6, Tan Binh District, Ho Chi Minh City.

2.2. Synthesis of Ag/GO

GO was prepared via an improved Hummers’ method [17]. Ag/GO was synthesized by an \textit{in-situ} method with D-glucose as a reducing agent. 0.5 g of GO was dispersed in 100 mL of distilled water to obtain solution A. Then, the preparation of solution B was carried out by dissolving 0.5 g of AgNO₃ in 80 mL of distilled water, as well NH₄OH was added slowly to the solution until a dark brown precipitate was disappeared and obtained a clear solution. After that, solution B was added to solution A and the mixture was ultrasonicated for about 10 min. Then, 20 mL D-glucose was added to the prepared mixture and stirred for 1 h at 60 °C. After that, this mixture was cooled down to room temperature and rinsed with distilled water. Finally, Ag/GO was collected after drying at 50 °C.

2.3. Fabrication of antibacterial cotton

2.3.1. Fabrication of Ag/GO/cotton

Ag/GO/cotton was produced by the dip-coating method [11]. First, the cotton fabric (40x40 cm²) was cleaned with 50 ml NaOH 1 M solution and sonicated for 30 min. It was then rinsed with the distilled water until pH 7 and dried until constant weight. Finally, the cotton was dipped quickly into Ag/GO solution at room temperature (25 °C) as shown in Fig. 1. The concentrations of GO suspension were varied to 160, 280, 400, 520, and 640 mg/L. For each concentration, the number of dips was changed to 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 times, respectively.

2.3.2. Fabrication of Ag/rGO/cotton

The obtained Ag/GO/cotton was reduced by the chemical reduction method with eco-friendly reducing agent VC to synthesize Ag/rGO/cotton as shown in Fig. 1. Different VC:Ag/GO mass ratios were sealed in autoclave with survey temperature and time. Finally, the Ag/rGO/cotton was washed and dried at 60 °C. The reducing conditions were analyzed such as: VC:Ag/GO mass ratios (1:0, 1:1, 1:2, 1:3, 1:4, and 1:5), reducing temperature (100, 120, 140, 160, 180, and 200 °C), and reducing time (20, 40, 60, 80, 100, and 120 min).

2.4. Characterization
Fourier-transform infrared spectroscopy (FTIR) (Alpha-E, Bruker Optik GmbH, Ettlingen, Germany) was used for determining functional groups on the surface of Ag/GO at wavenumber in the range of 4000 to 500 cm\(^{-1}\). X-ray diffraction (XRD) was used to observe the structure of Ag/GO by CuK\(_\alpha\) radiation (\(\lambda = 0.154 \text{ nm}\) in the scope of 5~80° (D2 Phaser, Brucker, Germany). Raman spectra were performed using a LabRam micro-Raman spectrometer with a wavelength of 632 nm (He-Ne-laser). Transmission electron microscopy (TEM) (S-4800, Hitachi, Japan) was determined at an accelerating voltage of 100kV. A scanning electron microscope (SEM) (Hitachi S-4800, Japan) was used to reflect the observation of surface structures of GO, Ag/GO, Ag/GO/cotton, and Ag/rGO/cotton. Energy-dispersive X-ray spectroscopy (EDS) (Jeol-JMS 6490, Japan) was also used to investigate the composition of elements C, O, and Ag in Ag/GO, Ag/GO/cotton, and Ag/rGO/cotton. Static water contact angle (OCA-20, DataPhysics-Germany, scale 0.7-4.5) was used for investigating the water wettability of Ag/rGO/cotton.

2.5. Antibacterial activity

The antibacterial activity of Ag/GO, Ag/GO/cotton, Ag/rGO/cotton, and the cotton were determined via the diameter zone of inhibition. Two strains of Gram-positive (S. aureus) and Gram-negative (P. aeruginosa) bacteria were selected to evaluate their antibacterial ability. First, bacteria were cultivated and proliferated in the Mueller-Hinton Agar medium. Then, the Ag/GO/cotton and Ag/rGO/cotton (1x1 cm\(^2\)) were placed on the surface of the jelly discs and incubated at 37°C. After 24 h, the antibacterial ability of the cotton is evaluated by measuring the inhibition zone diameter zone [18].

2.6. Durability tests of Ag/GO/cotton and Ag/rGO/cotton

The durability of the fabric (Ag/GO/cotton and Ag/rGO/cotton) was assessed under various conditions such as colourfastness to washing with at 40 °C, colourfastness to alkaline, acidic of perspiration, and hot pressing at 150 °C. The samples were sent for testing and analysis at the Branch of Vietnam Textile Research Institute-Joint Stock Company in Ho Chi Minh city (VTRSI) Textile Testing Center (TTC). Evaluation of the colour change of the cotton samples was compared to the corresponding grayscale and afterwards, the samples had been conditioned for 4 h in the standard conditions to examine the colourfastness of the cotton.

3. Results And Discussion

3.1. Characterization of Ag/GO

The functional groups of GO and Ag/GO were identified through FTIR spectra as shown in Fig. 2(a). Particularly, an adsorption band was distributed at 3427 cm\(^{-1}\) due to the stretching of the carboxylic acid of absorbed water. The representation of other bands at 2913 and 2848, 2354, 1730, and 1372 cm\(^{-1}\), corresponding to symmetric and asymmetric –CH\(_2\), O=C=O, C=O, and C–O–C stretching vibrations, respectively. In addition, the 1637 cm\(^{-1}\) peak was attributed to aromatic bending vibration of unsaturated C=C of the non–oxidized graphitic domain [19]. As for Ag/GO, it had a similar pattern of FTIR spectrum to GO but the intensities of diffraction peaks declined due to the linkage between AgNPs and GO sheets [20].
Fig. 2(b) shows the XRD pattern of the Ag/GO. Accordingly, four 2θ values of Ag/GO were observed at 38, 44, 64, and 77°, representing characteristic diffraction peaks of AgNPs and well-matched with standard peaks in JCPDS file No. 04–0783 [21,22]. The diffraction peak at 2θ = 9.5° was recorded, which reflects (002) plane of GO [23]. In Ag/GO, this peak disappeared due to the AgNPs formulated on the GO surface, preventing the restacking of GO sheets.

As shown in Fig. 2(c), Raman spectra of GO and Ag/GO are characterized by two bands: D and G, which were observed at approximately 1330 and 1595 cm⁻¹, respectively. The D band is assigned to the breathing mode of K-point phonons with A₁g symmetry, and the G band is ascribed to the tangential stretching mode of E₂g phonon of sp² carbon atoms corresponding to the defects in the graphitic structure and sp² bonding carbon in GO structure [24]. After anchoring AgNPs onto the GO surface, the D and G band values increase as a result of chemical bonds formation and intercalation of GO surface and AgNPs [25].

The TEM image were used to analyze the morphologies of Ag/GO as shown in Fig 3(a). The results demonstrated that spherical-like AgNPs were uniformly distributed on the GO nanosheets-dark thin films with an average size of 10–15 nm. The results suggested that the addition of GO as a stability agent, was vitally crucial as it played an important role in stabilizing the formation of AgNPs onto GO, preventing the agglomeration of those particles.

According to the EDS spectrum in Fig. 3(b), the results indicated that C and O of the material were 23.06 and 23.40 w.t%, respectively, while the percentage of Ag was 54.54 w.t.%. This result did not change too much compared to the precursor ratio (1:1 AgNO₃:GO mass ratio). There were peaks of Ag at 2 to 4 keV indicating the presence of Ag, and two small impurities peaks at 1 and 2.1 keV possibly corresponded to Na and Au in analyzed equipment, respectively [26]. Besides, the SEM images were used to investigate the morphological surface of Ag/GO as shown in Fig. 3(c-d). It is indicated that, on the surface of Ag/GO, there are many folds with rougher surfaces due to AgNPs evenly distributed on the GO sheets. The images revealed the presence of an ultrafine layer, which forms a wavelike structure when they are stacked together [27]. Consequently, the results affirm the uniform presence of Ag on the GO structure.

### 3.2. Characterization and antibacterial activity of Ag/GO/cotton

The influence of concentration and number of dips on the mass % of Ag/GO is shown in Fig. 4(a). The test results showed that when the Ag/GO concentration increased, the amount of material attached to the cotton increased. After 10 dip coatings, the amount of material adhering to the cotton still tended to increase in the concentration range of 160 to 400 mg/L. Meanwhile, the mass of cotton fabric virtually remained the same after 6 times of dipping coating at a concentration of 520 mg/L, indicating that raising the concentration of Ag/GO suspension would reduce the number of dips, thereby decreasing the period of fabrication time. When the Ag/GO concentration was raised to 640 mg/L, the quantity of Ag/GO clinging to the fabric began to develop slowly by the third dip coating, and by the fifth dip, the amount of Ag/GO clinging to the cotton had increased insignificantly. Based on the foregoing findings, 640 mg/L was the
appropriate concentration for the Ag/GO dip-coating procedure on cloth. To determine the best number of dip-coating, Fig. 4 (b, c) presents the comparison of antibacterial activity on Ag/GO/cotton samples fabricated after dip-coated 10, 5, and 3 times. Test results revealed that the antibacterial capacity of all samples after different dip coatings times was identical. This could be explained by the fact that the quantity of Ag/GO in samples after a dip-coated 10, 5, and 3 times was not substantially different. Therefore, the number of suitable dip coating was determined to be 3 times at an Ag/GO suspension concentration of 640 mg/L.

The surface morphology of the Ag/GO/cotton samples was analyzed by SEM images. Before Ag/GO dip-coating, the surface of the fabric had an interlocking fiber structure (Fig. 5 (a, b)) and the surface of the fibers was smooth (Fig. 5(c)). When dipped with Ag/GO material, the surface of the fabrics still maintained the original fiber structure, suggesting dip-coating with Ag/GO did not affect the fabric structure (Fig. 5(d, e)). However, it is interesting to observe that the surface of each fabric changed significantly. The fiber surface became rougher due to being covered by Ag/GO sheets. More importantly, the presence of small white spots is uniformly distributed on the surface of the fabric fibers, indicating the presence of AgNPs, as shown in Fig. 5(f).

The effect of reducing conditions on the antibacterial activity of Ag/rGO/cotton is depicted in Fig. 6. When increasing the reaction temperature from 100 to 200 ºC, the % mass loss gradually increased. The cotton samples after being fabricated at 100 and 120 ºC, with the % mass loss increased by 5.20 and 5.89 %, respectively. It could be seen that 140 ºC was the appropriate temperature for GO to be reduced to rGO with the % mass loss when performing the reaction at this temperature of 7.08 %. However, the cotton samples after reduction at a temperature of 160 ºC onwards appeared material peeling on the cotton surface with the % mass loss also increasing, corresponding to the values of 7.32, 9.47, and 12.77 %, respectively. When the reaction temperature was higher than 200 ºC, the cotton sample began to show signs of decomposition. It is worth noticing that not only GO was reduced to rGO, but the cotton was also decomposed leading to an increase in the % mass loss of the cotton at high temperatures. Besides, the antibacterial results against two types of bacteria on the Ag/rGO/cotton samples at the reaction temperature investigation in Fig. 6(a) showed that in both agar plates, samples reduced at 140 ºC exhibited the best antibacterial ability. Although the inhibitory zone of the samples reduced at 160, 180, and 200 ºC did not change significantly, there was material peeling on the cotton surface of these samples. Therefore, the cotton fabric reduced to 140 ºC was suitable and had higher antibacterial ability than the remaining samples.

The effect of the VC:Ag/GO ratio on the % mass loss in the reduction process was investigated and illustrated in Fig. 6(b). The results revealed that the % mass loss went up rapidly when the ratio between Ag/GO on the fabric surface and reducing agent increased. When increasing the mass ratio of VC:Ag/GO from 1:0 to 1:1, the % mass loss increased sharply with values of 5.49 and 6.76 %, respectively. When the mass ratio of VC:Ag/GO increased from 1:2 to 1:5, the % of mass loss increased insignificantly with values of 6.81, 6.99, 6.92, and 7.06 %, respectively. According to the results of the above study, the ratio 1:1 was exactly adequate for reducing GO to rGO; however, if the VC:Ag/GO mass ratio continued to rise,
the % mass loss would not change significantly and the amount of excess residual chemical, at the same
time, would increase the cost of the synthesis process. Therefore, the mass ratio of VC:Ag/GO 1:1 was
chosen to conduct the following experiments. The antibacterial results against two bacteria strains of the
Ag/rGO/cotton samples for reducing agent ratio investigation in Fig. 6(b) showed that in both agar plates,
the samples were reduced in the condition of reducing agent ratio 1:1 to 1:5 exhibited a minor antibacterial
zone difference and were larger than the sample reduced at 1:0 ratio.

The results of investigating the influence of reaction time on the % mass lost in the reduction process are
shown in Fig. 6(c). When the reaction time increased from 20 to 40 min, the % mass loss increased with
values of 6.23 and 7.08 %, respectively. When the reaction time increased from 60 to 100 min, % mass loss
reached 7.62, 7.80, and 7.93 %, respectively, these values increased but did not differ significantly.
However, when the reaction time was 120 min, the % mass loss peaked at 8.45%. As a result, even after
100 min, it was inadequate to convert all GO to rGO, thus the reaction time had to be increased. The results
of antibacterial activity against two strains of bacteria of Ag/rGO/cotton samples with different reducing
times in Fig. 6(c) showed that in all two agar plates, the sample, which was reduced for 120 min, has the
largest inhibition zone out of others. Therefore, this sample had the highest antibacterial ability of the
other samples.

After evaluating the antibacterial capacity of Ag/rGO/cotton at different reduction conditions, the sample
with the highest antibacterial ability was reduced at a temperature of 140 ºC, VC:Ag/GO mass ratio of 1:1,
and reaction time of 120 min. Besides, Ag/rGO/cotton showed somewhat greater bactericidal activity than
Ag/GO/cotton, albeit the difference was not significant. This could be explained by the fact that when in
direct cell contact, highly conductive rGO mediated stronger oxidative stress than lower conductive GO
[28,29]. Although rGO was not as well dispersed in water as GO, in this study Ag/rGO/cotton was only
partially reduced, so Ag/rGO clinging to the fabric surface did not completely lose the water absorption
properties of cotton fabrics, thereby allowing to contact with bacteria to cause physical damage to cell
membranes and oxidative stress. The results of this antibacterial evaluation were also in good agreement
with the results of a previous study published on the antibacterial effectiveness of fabric dipped in the
following order: rGO – Ag > Ag > GO > Ag – GO [30]. The SEM images of Ag/GO/cotton and
Ag/rGO/cotton are illustrated in Fig. 7. The results showed that there were no significant differences
between the two samples of Ag/GO/cotton and Ag/rGO/cotton, indicating over the reduction process did
not affect the fabric structure or surface.

The distribution of C, O, and Ag elements of the Ag/rGO/cotton sample after surface modification was
presented in Fig. 8 (a-d). The results showed that the material was still evenly distributed on the surface of
the cotton fabric and did not affect by the reduction process. After reduction, the % mass of elements
altered, with the % O decreasing from 37.65 to 35.22 %, proving the oxygen-containing functional groups
in the structure of GO had been successfully reduced as shown in Fig. 8(e). While the % Ag did not change
significantly, which could be explained by the fact that the Ag/rGO has bonded strongly with the fabric
surface, hence there was less Ag loss during the reduction process.
The result of measuring the contact angle of the best Ag/rGO/cotton sample was shown in Fig. 9 with the left and right contact angles being: 103.1 and 104.6 °, respectively. The cotton sample after being reduced has a contact angle of less than 150 ° showing a strong hydrophobicity of the synthesized cotton. It can be seen that the modification of the Ag/GO/cotton surface to become hydrophobic did not significantly affect the initial antibacterial effect of Ag/GO/cotton.

3.4. Durability evaluation

The adhesion of Ag/GO and Ag/rGO sheets to the cotton was evaluated by determining the colourfastness of the cotton under different conditions, as shown in Table 1. The analysis results showed that under acidic, alkaline, and high-temperature conditions, the adhesion of Ag/GO and Ag/rGO to the cotton was quite high. When hot washing with soap, the adhesion of Ag/GO and Ag/rGO to the cotton decreased, but still managed to reach the level of 2–3 on the scale of 1–5. However, the hydrophobic character of Ag/rGO/cotton, which reduces interaction with water molecules and so helps to prevent washout throughout the process, may account for the much greater strength of Ag/rGO/cotton. These findings demonstrate that increasing the hydrophobicity of the outer cotton also supports enhancing the adhesion strength of Ag/rGO to the cloth.

Table 1: Survey results on the adhesion of Ag/GO and Ag/rGO on cotton fabric
| No. | Target                                                                 | Standard                  | Condition                                                                 | Test results (*) |
|-----|------------------------------------------------------------------------|---------------------------|---------------------------------------------------------------------------|-------------------|
|     |                                                                        |                           | 30 min machine wash at 40 °C in 4 g ECE phosphate reference detergent per  | Ag/GO/cotton      |
|     |                                                                        |                           | litre of water with 10 steel balls                                        | Ag/rGO/cotton     |
|     |                                                                        |                           |                                                                            | Color staining/cotton |
| 1   | Colour fastness to washing at 40 °C                                    | ISO 105 C06 A1S–2010     |                                                                            | 2–3               |
|     |                                                                        |                           |                                                                            | 3                 |
|     |                                                                        |                           |                                                                            | 4–5               |
| 2   | Colour fastness to acid perspiration                                    | ISO 105 E04–2013         |                                                                            | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
|     |                                                                        |                           |                                                                            | 3                 |
| 3   | Colour fastness to alkaline perspiration                                | ISO 105 E04–2013         |                                                                            | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
|     |                                                                        |                           |                                                                            | 2–3               |
| 4   | Colour fastness to hot pressing at 150 °C                               | ISO 105 X04–1994         | **Dry**                                                                   |                   |
|     |                                                                        |                           |                                                                            |                   |
|     |                                                                        |                           | Immediately                                                               | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
|     |                                                                        |                           | After 4 hours                                                             | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
|     |                                                                        |                           | **Damp**                                                                  |                   |
|     |                                                                        |                           |                                                                            |                   |
|     |                                                                        |                           | Immediately                                                               | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
|     |                                                                        |                           | After 4 hours                                                             | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
|     |                                                                        |                           | **Wet**                                                                   |                   |
|     |                                                                        |                           |                                                                            |                   |
|     |                                                                        |                           | Immediately                                                               | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
|     |                                                                        |                           | After 4 hours                                                             | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
| 5   | Colour fastness to dry heat                                             | AATCC 117–2009           |                                                                            | 4                 |
|     |                                                                        |                           |                                                                            | 4                 |
|     |                                                                        |                           |                                                                            | 4–5               |

(*) Greyscale rating is based on the 5 step scale of 1–5; where 1 is bad and 5 is good.

**3.5. Fabrication and antibacterial mechanism of Ag/rGO/cotton**
Ag/rGO/cotton was produced by dipping cotton with Ag/GO suspension. Then, the oxygen-containing functional groups on the GO surface were reduced to rGO by chemical means. In particular, VC was used as a non-toxic and environmentally friendly reducing agent. This method gave the product a relatively high-water resistance and the cotton after modification retained its antibacterial effect. In GO there was a conjugate system p–p, p–p from the O of the –OH group and –C=O, making the H of the OH group attached to the double-bonded C very mobile. The mechanism of Ag/GO reduction by VC is shown in Fig. 10. First, the five-ring electron recovery chain of VC increased the acidity of the β and γ-hydroxyl groups, leading to the dissociation of the two protons to form an anion (HOAO−). Then, the anion underwent reactivation on the epoxy and diol groups of GO, yielding the intermediate product. The intermediate was reduced and the VC was oxidized to dehydroascorbic acid [31].

The Ag/rGO nanocomposite material was evenly coated on the stable cotton fabric, increasing the chance of bonding between the bacterial cell and the rGO sheet with silver attached to it. The sharp rGO plate cut the cell wall by physical interaction. At the same time, AgNPs release Ag+ ions, which attached strongly with thiol groups (–SH) of enzymes and proteins on the cell surface by electrostatic attraction, destroying the function of cell membranes and cell walls in selective permeation of intracellular and extracellular substances. Inside the bacterial cell, AgNPs and Ag+ ions played a role in the formation of reactive oxygen species (ROS) due to oxygen imbalance. In addition, Ag+ bound to the DNA of microbial cells and inhibited the replication function, stopped and prevented the growth of bacteria. To get further insights into the bactericidal mechanism of Ag/rGO nanocomposite material, the interaction process is illustrated in Fig. 11 and divided into four stages: (1) rGO plates with the large specific surface area helped to capture bacteria; (2) Formation of ROS free radicals, inhibiting and destroying bacterial cell membranes; (3) The sharp edges of rGO penetrated the membrane, damaging and cutting the cell membrane for Ag+ to enter the cell; (4) Ag+ ions bound to DNA, the enzyme inhibited replication, disrupted metabolism inside cells, killed bacteria.

4. Conclusions

In this study, Ag/rGO/cotton was successfully prepared by dip-coating in Ag/GO solution followed by green chemical reduction. The results showed that the 1:1 VC:Ag/GO mass ratio, the reducing temperature of 140 °C, and the reducing time of 120 min also showed the higher antibacterial effect against two types of bacteria *S. aureus* and *P. aeruginona* for the reduction proceed of the Ag/GO/cotton. The Ag/rGO/cotton also exhibited effective hydrophobicity with a wetting angle of 103.85±0.75 °, and the material remained unchanged after reduction. Therefore, the Ag/rGO/cotton can be extended into antibacterial cotton with high resistance, overcoming the weaknesses of the normal cotton. In addition, given the relevance of technology and personal protective equipment, the current research provides a realistic, practical, and potential method for device development for medical applications.

Declarations
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Figures

Figure 1

<p>Preparation of Ag/GO/cotton and Ag/rGO/cotton</p>
Figure 2

(a) FTIR spectra, (b) XRD patterns, and (c) Raman spectra of GO and Ag/GO
Figure 3

TEM image of (a) Ag/GO; (b) EDS of Ag/GO; SEM images of (c, d) Ag/GO
Figure 4

(a) Effect of concentration and number of dips on the amount of Ag/GO on the fabric; the antibacterial ability against (b) *P. aeruginosa* and (c) *S. aureus* of Ag/GO/cotton in dip-coating times 0, 3, 5, and 10.
Figure 5

<_p>SEM images of (a-c) cotton and (d-f) Ag/GO/cotton</p>
Figure 6

Effect of (a) reducing temperature (100–200 °C), (b) VC:Ag/GO mass ratio (1:0–1:5), and (c) reducing time (20–120 min) on % mass loss and antibacterial activity of Ag/rGO/cotton. (Sample 0 is the unmodified Ag/GO/cotton which was utilized as a control sample in all three conditions investigation)
Figure 7

SEM images of (a-c) Ag/GO/cotton and (d-f) Ag/rGO/cotton
Figure 8

<p>(a-d) X-ray mapping images of Ag/rGO/cotton; (e) EDS spectra of Ag/GO/cotton and Ag/rGO/cotton</p>

Figure 9

<p>The contact angle measurement results (a) Ag/GO/cotton and (b) Ag/rGO/cotton was reduced at the reaction temperature of 140 °C, the ratio VC:Ag/GO of 1:1 for 120 min</p>

Figure 10

<p>Ag/rGO/cotton formation mechanism</p>
Figure 11

<p>Antibacterial mechanism of Ag/rGO/cotton</p>