Antibacterial Electroconductive Composite Coating of Cotton Fabric

Tomasz Makowski¹,*, Mariia Svyntkivska¹, Ewa Piorkowska¹,*, Urszula Mizerska¹, Witold Fortuniak¹, Dorota Kowalczyk², Stefan Brzezinski² and Dorota Kregiel³

¹ Centre of Molecular and Macromolecular Studies Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland; mariias@cbmm.lodz.pl (M.S.); mizerska@cbmm.lodz.pl (U.M.); wfortuni@cbmm.lodz.pl (W.F.)
² Łukasiewicz Research Network, Textile Research Institute, Brzezinska 5/15, 92-103 Lodz, Poland; dorota.kowalczyk@tw.lukasiewicz.gov.pl (D.K.); awbrzezi@toya.net.pl (S.B.)
³ Department of Environmental Biotechnology, Faculty of Biotechnology and Food Sciences, Lodz University of Technology, Wolczanska 171/173, 90-924 Lodz, Poland; dorota.kregiel@p.lodz.pl

* Correspondence: tomekmak@cbmm.lodz.pl (T.M.); epiorkow@cbmm.lodz.pl (E.P.); Tel.: +48-42-6803-228 (T.M.)

Abstract: Graphene oxide (GO) was deposited on a cotton fabric and then thermally reduced to reduced graphene oxide (rGO) with the assistance of L-ascorbic acid. The GO reduction imparted electrical conductivity to the fabric and allowed for electrochemical deposition of Ag° particles using cyclic voltammetry. Only the Ag°/rGO composite coating imparted antibacterial properties to the fabric against Escherichia coli and Staphylococcus aureus. Ag°/rGO-modified fibers were free of bacterial film, and bacterial growth inhibition zones around the material specimens were found. Moreover, Ag°/rGO-modified fabric became superhydrophobic with WCA of 161°.

Keywords: electroconductive cotton; graphene oxide; electrochemical functionalization; antibacterial activity

1. Introduction

Electroconductive textiles draw increasing attention because of their numerous potential applications including sensors, solar cells, and supercapacitors [1–4]. Electroconductivity can be achieved through coating of textiles with carbon nanoparticles, such as carbon nanotubes or graphene materials (GM), including graphene or reduced graphene oxide (rGO), which form conductive networks on fiber surfaces [3,5–8]. Despite the outstanding properties of graphene [3], its use for modification of textiles is limited by difficulty of obtaining stable aqueous dispersions applicable to hydrophilic natural fibers. In turn, functional groups of graphene oxide (GO) facilitate its dispersion in water but adversely influence its electrical conductivity, hence GO has to be reduced chemically or thermally to rGO. Chemical reduction of GO often requires elevated temperature, 80–100 °C, and a relatively long time, even several hours or days, whereas thermal reduction usually demands even higher temperature and oxygen-free conditions [9–11].

In our previous studies, cotton fabric was made electroconductive by coating with GO and its reduction at 220 °C, assisted with L-ascorbic acid or commercial antioxidants used in the plastic industry, resulting in hydrophilicity or hydrophobicity of the fabric, respectively [12,13]. It is worth mentioning that the decomposition of cotton occurs above 240–250 °C [14].

Presently, there is a growing demand for smart and intelligent garments, including cotton cloth, that are electroconductive and able to store energy or communicate. In such applications, antimicrobial activity can eliminate microbial colonization and reduce the possibility of infection. GM particles exhibit antibacterial activity, dependent on their...
dispersibility, adsorption ability, number of corners and sharp edges [15], hence strongly
influenced by the lateral size, shape, number of layers, surface modification, agglomeration,
and dispersion. Three main mechanisms, recently postulated, include the action of sharp
edges, oxidative stress, and wrapping or trapping of bacteria due to the flexible thin-film
structure of GM. The action of the sharp edges, also called nanoknives, nanoblades, or
cutters, is believed to be crucial. The edges, acting as cutters, can mechanically disrupt
the cellular membranes and cause their integrity loss, e.g., [16–18], although it requires the
direct contact of the bacteria with GM sheets. Recently, to obtain an antibacterial material,
Han et al. [19] functionalized GO with hydrophilic polymers and used it as a vector for
silver (Ag) nanoparticles and sulfadiazine. Deposition of Ag particles on carbon nanotube-
coated fibrous materials, including cotton fabric, made them antibacterial [6,20,21], as
such particles act against bacteria and fungi, and are also antiviral [22,23]. Metal-based
nanoparticles are effective against a wide variety of microorganisms as their bonds to
biomolecules are non-specific [23–27].

However, only a few articles described modification of cotton fabric through chemical
reduction of GO and deposition of Ag [28–30]. It improved hydrophobicity and electrical
conductivity, but antibacterial activity was not reported. Recently, GO-coated linen and
cotton fabrics were made antibacterial through simultaneous chemical reduction of GO
and deposition of Ag [21]. The antibacterial properties of the fabric modified solely with
rGO were not examined.

In the present study, to make it electroconductive, cotton fabric was GO-coated and
then GO was reduced thermally to rGO. Ag° particles were deposited electrochemi-
cally on rGO-coated fabric with cyclic voltammetry, which allowed to monitor the re-
dox reactions. The composite Ag°/rGO coating imparted antibacterial activity to the
fabric against the tested bacterial strains, *Escherichia coli* and *Staphylococcus aureus*, and
also superhydrophobicity.

2. Experimental Section

For further modification, white plain weave cotton fabric with 205 threads/10 cm and
295 threads/10 cm in the warp and weft direction, respectively, was used. It was 0.36 mm
thick, with a surface density of 145 g/m². The fabric was cleaned by extraction [5].

To coat the fabric, 0.6 wt.% aqueous dispersion of GO was used from Graphene
Laboratories, Inc. (Calverton, NY, USA) (single layer > 80%, flake size of 0.5–5 µm).

Thermal reduction of GO on the fabric was assisted with L-ascorbic acid (C₆H₈O₆),
(POCH, Poland, 98%). Silver nitrate (AgNO₃) and trisodium citrate (Na₃C₆H₅O₇) (Avantor,
Poland, ≥99%) were used for electrochemical deposition of Ag° particles.

The aqueous dispersion of GO was diluted with water to decrease GO concentration
to 0.1 wt.% and was homogenized for 20–30 min at room temperature (RT) using ultrasonic
homogenizer HielserchUP 200S (Teltow, Germany). The dispersion was deposited on the
fibers by the padding method using a laboratory double-roll padding machine (BENZ,
Switzerland) with horizontally set squeezing rollers. The details of the padding procedure
are described elsewhere [12].

Before the reduction, GO-coated fabric was four times dipped in 0.1 wt.% aqueous
solution of L-ascorbic acid and next dried at RT. The reduction was carried out in a Mettler
Toledo Hot Stage FP82 (Greifensee, Switzerland) equipped with an FP90 temperature
controller. As previously described [12], GO-coated specimens, placed between microscope
glasses, were heated from RT to 220 °C at 10 °C/min, annealed for 1 min, and cooled
down to RT at 10 °C/min. In this way, rGO-coated fabric was obtained. The influence
of such thermal treatment on mechanical properties of the fabric was examined by us
previously [12,13].

Silver particles (Ag°) were deposited on rGO-coated fabric with cyclic voltamme-
try using BioLogic SP-150 (Bio-Logic Science Instruments SAS, Clai, France) potenti-
stat/galvanostat, during five cycles in a mixture of aqueous solutions of sodium citrate and
silver nitrate, with a platinum (Pt°) electrode and a silver chloride electrode (Ag | AgCl), as
the counter and reference electrodes, respectively. The process was controlled and monitored with EC-Lab Electrochemistry v11.32 software. The reduction of Ag⁺ ions occurred in the voltage range of ±1.0 V vs. Ag/AgCl [20]. To remove Ag⁺ ions and salts formed during the reaction, after the process the Ag⁺/rGO-coated fabric was rinsed in distilled water three times and dried at RT.

The Ag content was determined by thermogravimetric analysis (TGA), using TA Instruments TGA 5500 (New Castle, DE, USA) during heating at 20 °C/min in air.

Surface electrical resistivity (R) of the fabric was measured using the four-wire method with Keithley 2400C SourceMeter (Tektronix, Beaverton, OR, USA). Copper electrodes were attached to the surface with silver-containing paste Dotite D-550 (Fujikura Kasei, Tokyo, Japan), 1 cm apart. The measurements were repeated at least three times to obtain average values of R.

The fabric samples were vacuum sputtered with a 10 nm gold layer using Quorum EMS150R ES (Quorum Technologies, Laughton, UK), and then analyzed using a scanning electron microscope (SEM), and also SEM with energy dispersive spectroscopy (EDS), JEOL 6010LA (Tokyo, Japan), at an accelerating voltage of 10 kV.

To determine water wettability, 5 µL distilled water droplets were placed on the examined surfaces and water contact angles (WCA) were measured at 25 °C by means of a RameHart NRL Goniometer 100-00-230 (Succasunna, NJ, USA) coupled to a camera and optical system, using Drop Analysis program. The measurements were repeated five times to obtain average WCA values.

Antibacterial properties of the fabric samples against Gram-positive Staphylococcus aureus ATCC 6538 and Gram-negative Escherichia coli ATCC 8739 were tested using Antibacterial Activity Assessment of Textile Materials: Agar Diffusion Test (ISO20645:2004) [31]. 15 mL of nutritive agar medium, Tripticase Soy Agar from Merck (Darmstadt, Germany), were poured on Petri dishes. Inoculums of microbial cultures of 1–5 × 10⁸ CFU/mL (0.2 mL) were then poured on the agar media. Disk specimens, with 5 mm diameter, were placed on the agar surface. After 48 h incubation at 37 °C, the contact zones under the tested specimens were analyzed visually, and then the inhibition zones, if present, were measured. The fibers were also analyzed by SEM, to evaluate the bacterial colonization.

3. Results and Discussion

The reduction of GO deposited on the fabric made the fabric electrically conductive. When the temperature of the hot stage approached 220 °C, R diminished significantly but at 220 °C it leveled off within 1 min at the value of 0.1 MΩ/sq. During cooling and further storage at RT, R increased but finally stabilized after 24 h. Such behavior was observed by us previously [12,13,32] due to partial reversibility of the reduction. Nevertheless, R of 5.4 MΩ/sq was achieved, showing the presence of conducting 3D-network of rGO on fiber surfaces.

SEM micrographs of GO and rGO-coated fibers are shown in Figure 1. Small thickness and very good adhesion to fiber surfaces make the particles hardly visible on the fibers [13]. However, the areas without typical morphology of cotton fibers are discernible, shown in the insets, which are suggestive of GO or rGO thin layers.

Reduction of Ag⁺ ions occurred on the rGO-coated surfaces, combined with nucleation and growth of Ag⁰ particles, which are visible in SEM micrographs in Figure 2a,b. EDS analysis confirmed the presence of Ag⁰ particles on rGO-coated surface, as shown in Figure 2c. Reaction of silver nitrate with sodium citrate resulted in the formation of silver citrate complex stabilized by carboxyl groups of citric acid, which prevented aggregation of Ag⁰ particles and enabled development of particles immobilized on the surface [33]. The most effective complexing occurs when [citrate]/[Ag⁺] >> 1 [34]. Others [35] studied GO electrochemistry and found that the reduction reactions occurred on edges of GO plates. Thus, we postulate that the reduction of the complex and the formation of Ag⁰ particles, through nucleation and growth, could occur on edges or defects of rGO plates.
Reduction of Ag+ ions occurred on the rGO-coated surfaces, combined with nucleation and growth of Ag° particles, which are visible in SEM micrographs in Figure 2a,b. EDS analysis confirmed the presence of Ag° particles on rGO-coated surface, as shown in Figure 2c. Reaction of silver nitrate with sodium citrate resulted in the formation of silver citrate complex stabilized by carboxyl groups of citric acid, which prevented aggregation of Ag° particles and enabled development of particles immobilized on the surface [33].

The most effective complexing occurs when \([\text{citrate}] / [\text{Ag}^+] \gg 1\) [34]. Others [35] studied GO electrochemistry and found that the reduction reactions occurred on edges of GO plates. Thus, we postulate that the reduction of the complex and the formation of Ag° particles, through nucleation and growth, could occur on edges or defects of rGO plates.

The voltammetry profile during the first and the second cycle, shown in Figure 2d, exhibits one redox weak peak at \(-0.12\) V attributed by others to reduction of hydroxyl groups [36]. Most probably, it was related to residual hydroxyl groups of rGO, remaining
due to its incomplete thermal reduction. Further reactions postulated in [36] were not observed due to a small number of other functional groups on rGO surface and competitive reactions involving Ag$^+$ ions. During the next three cycles, a peak at $-0.44$ V evidenced the reduction of Ag$^+$ ions. The proposed mechanism of the formation of the Ag° particles is shown in Scheme 1.

Scheme 1. Proposed mechanism of Ag° formation on rGO deposited on cotton fiber surfaces.

Based on the results of TGA experiments, by taking into account the residue weight at 900 °C of Ag°/rGO-modified fabric and rGO-modified fabric, the Ag content of 0.4 wt.% was determined. The successful deposition of Ag° particles confirmed the formation of the electroconductive rGO network on fiber surfaces and indicated that rGO-coated fabrics can serve as electrodes in cyclic voltammetry. R of the fabric did not change after the electrochemical modification and was equal to 5.35 MΩ/sq because Ag° was deposited on the rGO as separate particles, which did not form any continuous network. However, the Ag°/rGO-modified fabric became superhydrophobic with WCA of 161°, due to the presence of hydrophobic Ag° particles on the surface, causing the lotus effect.

As seen in Figure 3, no bacterial growth inhibition zone was found around GO-coated or rGO-coated fabric specimens. The growth inhibition zones of about 9 mm and 12 mm for Gram-positive Staphylococcus aureus and Gram-negative Escherichia coli, respectively, were only observed around the specimens of Ag°/rGO-coated fabric.

Ag° particles exhibit non-specific bacterial toxicity that impedes the bacteria resistance development and also broadens the spectrum of antibacterial activity [37]. The main activity mechanisms of metal nanoparticles or ions include attraction to bacterial cell walls, disruption of the cell walls increasing their permeability, and disruption of cell functions [23–25,37,38].

The absence of bacterial growth inhibition zones around specimens does not exclude their antibacterial activity in direct contact with microorganisms. Therefore, SEM was used to analyze the bottom surfaces of the tested fabric specimens. SEM micrographs of bottom surfaces of cotton fabric specimens in Figure 4, modified and unmodified, show that not only the neat fibers but also GO and rGO-coated fibers were inhabited by both tested bacterial strains.
To achieve electroconductivity, a sufficient amount of GO particles had to be deposited on the fiber surfaces to form a 3D-network, which was then made electroconductive by GO coating with GO or rGO platelets. The uncovered areas, without coating, were prone to bacteria colonization. In turn, the activity of Ag° particles is well known and includes the release of Ag+ through oxidative dissolution, in which atmospheric O2 dissolved in water plays a role of oxidizer [38]. Due to the diffusion of thus formed ions, the antibacterial activity of Ag° is influenced by the release of Ag+ in the environment. The absence of bacterial growth inhibition zones around specimens does not exclude the activity of Ag° particles in the surrounding environment, which is reflected in the bacterial growth inhibition zones around the specimens in Figure 3.

Figure 3. Disk specimens of cotton fabric on bacteria inoculated agar after 48 h incubation: E. coli (a) GO-coated, (b) rGO-coated, (c) Ag°/rGO-coated; S. aureus, (d) GO-coated, (e) rGO-coated, (f) Ag°/rGO-coated.

Figure 4. SEM micrographs of bottom surfaces of cotton fabric specimens removed from agar after 48 h incubation: E. coli (a) neat fabric, (b) GO-coated, (c) rGO-coated, (d) Ag°/rGO-coated, S.aureus (e) neat fabric, (f) GO-coated, (g) rGO-coated, (h) Ag°/rGO-coated.

According to the literature, there are three basic mechanisms of antibacterial activity of GO. The first one, the most commonly observed, is the effect of sharp edges, known as nanoblade effect. The nanoblades cut cell membranes causing their damage leading to the death of bacteria [16–18]. The second one is oxidative stress caused by reactive oxygen species, leading to bacteria DNA damage and mitochondrial dysfunction [39]. The third mechanism reported, observed rather in solutions than in coatings, is wrapping or trapping of bacteria by GO flakes, which causes their isolation from the environment [40]. The main mechanisms of antibacterial activity of rGO are related to the nanoblade effect and oxidative stress [15]. In the current study, GO or rGO flakes adhering to cotton fibers and lying flat on them did not expose sharp edges, and no wrapping or trapping of bacteria was observed by SEM. Therefore, their antibacterial activity was greatly limited. To achieve electroconductivity, a sufficient amount of GO particles had to be deposited on
the fiber surfaces to form a 3D-network, which was then made electroconductive by GO reduction. However, the formation of 3D-network did not require full coverage of fibers with GO or rGO platelets. The uncovered areas, without coating, were prone to bacteria colonization. In turn, the activity of Ag⁺ particles is well known and includes the release of Ag⁺ through oxidative dissolution, in which atmospheric O₂ dissolved in water plays a role of oxidizer [38]. Due to the diffusion of thus formed ions, the antibacterial activity of Ag⁺ modified surface does not require a close contact with microorganisms, which is reflected in the bacterial growth inhibition zones around the specimens in Figure 3.

4. Conclusions

The cotton fabric was coated with GO dispersion using the padding method, and then GO was reduced thermally to rGO with the assistance of L-ascorbic acid. Then, on the electroconductive rGO network, Ag⁺ particles were electrochemically deposited with cyclic voltammetry, which enabled monitoring the redox reactions. Antibacterial activity of the modified cotton fabric against Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* bacteria was tested using a disk diffusion method. Neither before nor after the GO reduction the coated fabric exhibited antibacterial activity. This was reflected in the colonization of the fibers by the bacteria, as shown by SEM, and the absence of the bacterial growth inhibition zones around the fabric specimens. Only the Ag⁺/rGO coating imparted antibacterial properties to the fabric reflected in bacterial inhibition growth zones around the tested specimens and the absence of bacterial films on the fibers. Moreover, Ag⁺/rGO-modified fabric became superhydrophobic with WCA of 161°. The obtained results on composite Ag⁺/rGO coating of the fabric seem to be promising for obtaining novel antibacterial materials.

Author Contributions: T.M.: conceptualization, data curation, investigation, writing—original draft; M.S.: data curation, investigation, writing—original draft; E.P.: funding acquisition, conceptualization, formal analysis, writing—original draft, supervision; U.M.: investigation; W.F.: investigation; D.K. (Dorota Kowalczyk): investigation; S.B.: formal analysis; D.K. (Dorota Kregiel): investigation. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Science Centre (Narodowe Centrum Nauki), Poland, grant no. 2014/15/B/ST8/04286.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data are available on request from the corresponding author.

Acknowledgments: Financial support from National Science Centre (Narodowe Centrum Nauki), Poland, grant no. 2014/15/B/ST8/04286, is acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

Ethics Approval: Not applicable.

References

1. Islam, G.M.N.; Ali, M.A.; Collie, S. Textile sensors for wearable applications: A comprehensive review. *Cellulose* 2020, 27, 6103–6131. [CrossRef]

2. Maity, S.; Chatterjee, A. Conductive polymer-based electro-conductive textile composites for electromagnetic interference shielding: A review. *J. Ind. Text.* 2016, 47, 2228–2252. [CrossRef]

3. Molina, J. Graphene-based fabrics and their applications: A review. *RSC Adv.* 2016, 6, 68261–68291. [CrossRef]

4. Stoppa, M.; Chiolerio, A. Wearable Electronics and Smart Textiles: A Critical Review. *Sensors* 2014, 14, 11957–11992. [CrossRef] [PubMed]

5. Makowski, T.; Kowalczyk, D.; Fortuniak, W.; Jezierska, D.; Brzezinski, S.; Tracz, A. Superhydrophobic properties of cotton woven fabrics with conducting 3D networks of multiwall carbon nanotubes, MWCNTs. *Cellulose* 2014, 21, 4659–4670. [CrossRef]

6. Makowski, T.; Zhang, C.; Olah, A.; Piorkowska, E.; Baer, E.; Kregiel, D. Modification of dual-component fibrous materials with carbon nanotubes and methyltrichlorosilane. *Mater. Des.* 2018, 162, 219–228. [CrossRef]

7. Sahito, I.A.; Sun, K.C.; Arbab, A.A.; Qadir, M.B.; Choi, Y.S.; Jeong, S.H. Flexible and conductive cotton fabric counter electrode coated with graphene nanosheets for high efficiency dye sensitized solar cell. *J. Power Sources* 2016, 319, 90–98. [CrossRef]
8. Shateri-Khalilabad, M.; Yazdanshenas, M.E. Fabricating electroconductive cotton textiles using graphene. Carbohydr. Polym. 2013, 96, 190–195. [CrossRef]

9. Chua, C.K.; Pumera, M. Chemical reduction of graphene oxide: A synthetic chemistry viewpoint. Chem. Soc. Rev. 2014, 43, 291–312. [CrossRef]

10. Pei, S.E.; Cheng, H.M. The reduction of graphene oxide. Carbon 2012, 50, 3210–3228. [CrossRef]

11. Huh, S.H. Thermal Reduction of Graphene Oxide. In Physics and Applications of Graphene—Experiments; Mikhailov, S., Ed.; Intech Europe: Rijeka, Croatia, 2011; pp. 73–90.

12. Makowski, T.; Svyntkivska, M.; Piorkowska, E.; Kowalczyk, D.; Brzezinski, S. Conductive and super-hydrophobic cotton fabric through pentaerythritol tetras(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) assisted thermal reduction of graphene oxide and modification with methyltrichlorosilane. Cellulose 2018, 25, 5377–5388. [CrossRef]

13. Jedrzejczyk, M.; Makowski, T.; Svyntkivska, M.; Piorkowska, E.; Kowalczyk, D.; Brzezinski, S. Conductive cotton fabric through thermal reduction of graphene oxide enhanced by commercial antioxidants used in the plastics industry. Cellulose 2019, 26, 2191–2199. [CrossRef]

14. Poletto, M.; Pistor, V.; Zattera, A. Structural Characteristics and Thermal Properties of Native Cellulose. In Cellulose—Fundamental Aspects; Van De Ven, T.; Godbout, L., Eds.; Intech Europe: Rijeka, Croatia, 2013; pp. 45–68.

15. Cao, G.H.; Yan, J.H.; Ning, X.X.; Zhang, Q.; Wu, Q.; Bi, L.; Zhang, Y.M.; Han, Y.S.; Guo, J.B. Antibacterial and antibiofilm properties of graphene and its derivatives. Colloids Surf. B Biointerfaces 2021, 200, 111588. [CrossRef] [PubMed]

16. Nasirzadeh, N.; Azari, M.R.; Rasoulzadeh, Y.; Mohammadian, Y. An assessment of the cytotoxic effects of graphene nanoparticles on the epithelial cells of the human lung. Toxicol. Ind. Health 2019, 35, 79–87. [CrossRef] [PubMed]

17. Pulingam, T.; Thong, K.L.; Appaturi, J.N.; Nordin, N.I.; Dinshaw, J.I.; Lai, C.W.; Leo, B.F. Synergistic antibacterial actions of graphene oxide and antibiotics against bacteria and the toxicological effects of graphene oxide on human epidermal keratinocytes. Eur. J. Pharm. Sci. 2019, 142, 105087. [CrossRef] [PubMed]

18. Zainal-Abidin, M.H.; Hayyan, M.; Ngoh, G.C.; Wong, W.F. From nanoengineering to nanomedicine: A facile route to enhance biocompatibility of graphene as a potential nano-carrier for targeted drug delivery using natural deep eutectic solvents. Chem. Eng. Sci. 2019, 195, 95–106. [CrossRef]

19. Han, F.; Lv, S.; Li, Z.; Jin, L.; Fan, B.; Zhang, J.; Zhang, X.; Han, L.; Li, J. Triple-synergistic 2D material-based dual-delivery antibiotic platform. NPG Asia Mater. 2020, 12, 15. [CrossRef]

20. Makowski, T.; Kowalczyk, D.; Fortuniak, W.; Brzezinski, S.; Kregiel, D. Electrochemical deposition of silver nanoparticle and polymerization of pyrrole on fabrics via conducting multiwall carbon nanotubes. Cellulose 2015, 22, 3063–3075. [CrossRef]

21. Farouk, A.; El-Sayed Saeed, S.; Sharaf, S.; Abd El-Hady, M.M. Photocatalytic activity and antibacterial properties of linen fabric using reduced graphene oxide/silver nanocomposite. RSC Adv. 2020, 10, 41600–41611. [CrossRef]

22. Galdiero, S.; Falanga, A.; Vitiello, M.; Cantisani, M.; Marra, V.; Galdiero, M. Silver Nanoparticles as Potential Antiviral Agents. Molecules 2011, 16, 8894–8918. [CrossRef]

23. Sánchez-López, E.; Gomes, D.; Estéruelas, G.; Bonilla, L.; Lopez-Machado, A.L.; Galindo, R.; Cano, A.; Espina, M.; Etcheto, M.; Camins, A.; et al. Metal-Based Nanoparticles as Antimicrobial Agents: An Overview. Nanomaterials 2020, 10, 292. [CrossRef] [PubMed]

24. Anuj, S.A.; Gajera, H.; Hirpara, D.G.; Golakiya, B.A. Bacterial membrane destabilization with cationic particles of nano-silver to combat efflux-mediated antibiotic resistance in Gram-negative bacteria. Life Sci. 2019, 230, 178–187. [CrossRef] [PubMed]

25. Anuj, S.A.; Gajera, H.P.; Hirpara, D.G.; Golakiya, B.A. Interruption in membrane permeability of drug-resistant Staphylococcus aureus with cationic particles of nano-silver. Eur. J. Pharm. Sci. 2019, 127, 208–216. [CrossRef] [PubMed]

26. Qin, Z.J.; Zheng, Y.K.; Wang, Y.H.; Du, T.Y.; Li, C.M.; Wang, X.M.; Jiang, H. Versatile roles of silver in Ag-based nanoalloys for antibacterial applications. Coord. Chem. Rev. 2021, 449, 214218. [CrossRef]

27. Ul Hoque, M.I.; Chowdhury, A.-N.; Islam, M.T.; Firoz, S.H.; Luba, U.; Alowasheer, A.; Rahman, M.M.; Rehman, A.U.; Ahmad, S.H.A.; Holze, R.; et al. Fabrication of highly and poorly oxidized silver oxide/silver/tin(IV) oxide nanocomposites and their comparative anti-pathogenic properties towards hazardous food pathogens. J. Hazard. Mater. 2021, 408, 124896. [CrossRef] [PubMed]

28. Wang, C.; Guo, R.H.; Lan, J.W.; Jiang, S.X.; Zhang, Z.Y. Microwave-assisted synthesis of silver/reduced graphene oxide on cotton fabric. Cellulose 2017, 24, 4045–4055. [CrossRef]

29. Karami, Z.; Youssefi, M.; Raiesi, K.; Zhiani, M. An efficient textile-based electrode utilizing silver nanoparticles/reduced graphene oxide/cotton fabric composite for high-performance wearable supercapacitors. Electrochim. Acta 2021, 368, 137647. [CrossRef]

30. Bhattacharjee, S.; Macintyre, C.R.; Wen, X.Y.; Bahl, P.; Kumar, U.; Chughtai, A.A.; Joshi, R. Nanoparticles incorporated graphene-based durable cotton fabrics. Carbon 2020, 166, 148–163. [CrossRef]

31. Pinho, E.; Magalhães, L.; Henriques, M.; Oliveira, R. Antimicrobial activity assessment of textiles: Standard methods comparison. Ann. Microbiol. 2011, 61, 493–498. [CrossRef]

32. Mizierska, U.; Fortuniak, W.; Makowski, T.; Svyntkivska, M.; Pumera, M.; Piorkowska, E.; Kowalczyk, D.; Brzezinski, S. Electrically conductive and hydrophobic rGO-containing organosilicon coating of cotton fabric. Prog. Org. Coat. 2019, 137, 105312. [CrossRef]

33. Karadeniz, H.; Erdem, A.; Caliskan, A.; Pereira, C.M.; Pereira, E.M.; Ribeiro, J.A. Electrochemical sensing of silver tags labelled DNA immobilized onto disposable graphite electrodes. Electrocatal. Chem. 2007, 9, 2167–2173. [CrossRef]
34. Patra, S.; Pandey, A.K.; Sen, D.; Ramagiri, S.V.; Bellare, J.R.; Mazumder, S.; Goswami, A. Redox Decomposition of Silver Citrate Complex in Nanoscale Confinement: An Unusual Mechanism of Formation and Growth of Silver Nanoparticles. *Langmuir* **2014**, *30*, 2460–2469. [CrossRef] [PubMed]

35. Brownson, D.A.C.; Smith, G.C.; Banks, C.E. Graphene oxide electrochemistry: The electrochemistry of graphene oxide modified electrodes reveals coverage dependent beneficial electrocatalysis. *R. Soc. Open Sci.* **2017**, *4*, 171128. [CrossRef]

36. Bao, Q.L.; Bao, S.J.; Li, C.M.; Qi, X.; Pan, C.X.; Zang, J.F.; Lu, Z.S.; Li, Y.B.; Tang, D.Y.; Zhang, S.; et al. Supercapacitance of Solid Carbon Nanofibers Made from Ethanol Flames. *J. Phys. Chem. C* **2008**, *112*, 3612–3618. [CrossRef]

37. Stensberg, M.C.; Wei, Q.S.; McLamore, E.S.; Porterfield, D.M.; Wei, A.; Sepúlveda, M.S. Toxicological studies on silver nanoparticles: Challenges and opportunities in assessment, monitoring and imaging. *Nanomedicine* **2011**, *6*, 879–898. [CrossRef] [PubMed]

38. Le Ouay, B.; Stellacci, F. Antibacterial activity of silver nanoparticles: A surface science insight. *Nano Today* **2015**, *10*, 339–354. [CrossRef]

39. Khan, B.; Adeleye, A.S.; Burgess, R.M.; Russo, S.M.; Ho, K.T. Effects of graphene oxide nanomaterial exposures on the marine bivalve, *Crassostrea virginica*. *Aquat. Toxicol.* **2019**, *216*, 105297. [CrossRef]

40. Akhavan, O.; Ghaderi, E.; Esfandiar, A. Wrapping Bacteria by Graphene Nanosheets for Isolation from Environment, Reactivation by Sonication, and Inactivation by Near-Infrared Irradiation. *J. Phys. Chem. B* **2011**, *115*, 6279–6288. [CrossRef]