Hybrid Antibacterial Fabrics with Extremely High Aspect Ratio Ag/AgTCNQ Nanowires

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This study reports the synthesis of extremely high aspect ratios (>3000) organic semiconductor nanowires of Ag–tetracyanoquinodimethane (AgTCNQ) on the surface of a flexible Ag fabric for the first time. These one-dimensional (1D) hybrid Ag/AgTCNQ nanostructures are attained by a facile, solution-based spontaneous reaction involving immersion of Ag fabrics in an acetonitrile solution of TCNQ. Further, it is discovered that these AgTCNQ nanowires show outstanding antibacterial performance against both Gram negative and Gram positive bacteria, which outperforms that of pristine Ag. The outcomes of this study also reflect upon a fundamentally important aspect that the antimicrobial performance of Ag-based nanomaterials may not necessarily be solely due to the amount of Ag^+ ions leached from these nanomaterials, but that the nanomaterial itself may also play a direct role in the antimicrobial action. Notably, the applications of metal-organic semiconducting charge transfer complexes of metal-7,7,8,8-tetracyanoquinodimethane (TCNQ) have been predominantly restricted to electronic applications, except from our recent reports on their (photo)catalytic potential and the current case on antimicrobial prospects. This report on growth of these metal-TCNQ complexes on a fabric not only widens the window of these interesting materials for new biological applications, it also opens the possibilities for developing large-area flexible electronic devices by growing a range of metal-organic semiconducting materials directly on a fabric surface.

1. Introduction

The development of antimicrobial fabrics is an increasingly important field of research with applications ranging from odor-free textiles to self-cleaning surfaces, wound healing dressings and maintenance of an infection-free environment in healthcare settings.[1] Various methods incorporating different types of fibers and antibacterial agents have been reported to develop antimicrobial fabrics. Antibacterial substances may either be introduced during fiber production,[1] or fabrics may be coated with antibacterial materials post-fabrication.[1–3] In the latter case, antibacterial fabrics can be prepared by either simple soaking techniques such as layer by layer assembly of the antibacterial agent on to the fabric through non-specific electrostatic interactions[3] or via functionalization of the fabric surface followed by covalent bonding of an antibacterial agent to the fabric.[2] A range of materials such as antibacterial peptides,[4] L-cysteine,[5] oxidizing agents (chlorine, chloramines, iodine),[6] phenolic compounds,[7] chitosan,[8] and nanoparticles of Ag,[9,10] TiO_2,[10] ZnO,[10] and CuO[11] have been explored as active antibacterial agents within a fabric environment.

Among different inorganic materials, silver is by far the most widely used antimicrobial agent in general textiles as well as in wound dressings due to its broad-spectrum antibacterial performance and relatively lower toxicity to human cells than that to microbial cells.[12] It is recognized that although Ag^+ ions are highly effective against infectious agents, the high leachability of ionic silver from the fabric not only results in fast depletion of antimicrobial activity, it may also cause metal ion toxicity issues in the wound fluid. Ag nanoparticle-functionalized fabrics may overcome some of these issues by allowing continuous slow release of Ag^+ ions through oxidation of Ag nanoparticles in the presence of wound fluids.[9,13–15] However, one of the major limitations associated with Ag nanoparticles is that they are mostly active against Gram negative bacteria, with significantly lower performance against Gram positive bacteria. Therefore, realizing the importance of silver-based nanomaterials towards developing antimicrobial fabrics, and the potential of new materials to further improve the antimicrobial performance of silver-based fabrics, we have for the first time, investigated silver 7,7,8,8-tetracyanoquinodimethane (AgTCNQ), a metal-organic

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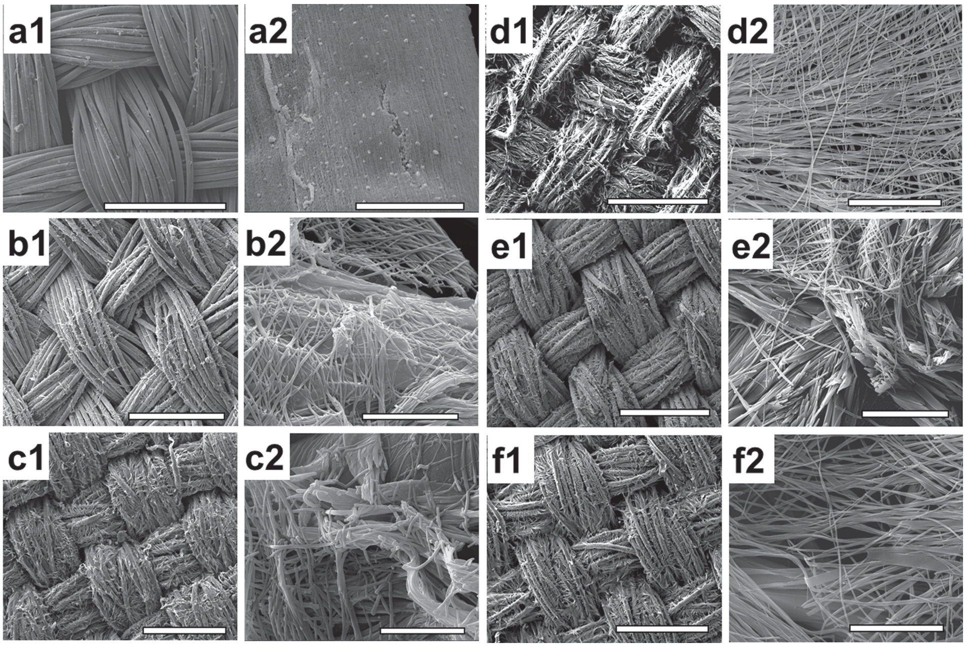

Figure 1. SEM images of Ag fabric (a) before and (b-f) after its reaction with TCNQ for (b) 1, (c) 5, (d) 10, (e) 30, and (f) 60 min. Scale bars in a1–f1 correspond to 500 µm, and those in a2–f2 correspond to 100 µm.

semiconductor charge transfer complex as an alternative candidate for the production of antibacterial fabrics.

Notably, M-TCNQ complexes (where M is a transition metal) have received considerable attention over the past 40 years with a particular resurgence in interest in the past few years through the work of Dunbar et al., Bond et al., and Miller et al.[16–18] This is because of their interesting magnetic,[19] optical,[20] electronic,[21] and field emission properties,[22] which make them promising candidates for molecular electronics through the development of memory and switching devices. However, the application of these materials had been restricted to the field of electronics until very recently when we discovered that CuTCNQ can also offer promising photocatalytic properties.[23–25] In the current study, we report high antibacterial performance of these metal-organic semiconductor complexes, by growing AgTCNQ nanowires on a silver fabric in a time-dependent manner, and systematically studying the performance of these hybrid metal/metal-organic semiconductor fabrics against both Gram negative (*Escherichia coli*) and Gram positive (*Staphylococcus albus*) bacteria.

2. Results and Discussion

AgTCNQ can be prepared by different routes including organic vapor-solid-phase reaction,[22] electrocrystallization[26] or by simply dipping a silver film into acetonitrile saturated with TCNQ.[20] To create AgTCNQ nanowire-decorated fabrics, we employed a facile approach, wherein initially Ag-coated fabric was woven in an open weave geometry from silver-coated Nylon (Shieldex 117/17 using 2 ply conductive silver yarns), which was followed by immersing these Ag fabrics in acetonitrile solutions of TCNQ in a time-dependent manner (for experimental details, please refer to supplementary information).[20] Pristine TCNQ, a yellow/green coloured crystalline solid acid, which is an excellent electron acceptor, underwent spontaneous one electron reduction at room temperature upon interaction with the electron donor Ag^0 to form a blue coloured material indicative of AgTCNQ,[27] as described by the following:

$$Ag^0 + TCNQ^0 \rightarrow Ag^+ + TCNQ^- \tag{1}$$

Ag^+ and $TCNQ^-$ ions thereafter undergo a corrosion-crystallization process through a multistep mechanism analogous to that proposed previously,[28] leading to formation of a crystalline AgTCNQ complex on the Ag fabric surface:

$$Ag^+ + TCNQ^- \rightarrow AgTCNQ \tag{2}$$

After reaction with TCNQ, the greyish-silver colour Ag fabric changed to a dense blue colour indicating the formation of AgTCNQ. Illustrated in **Figure 1** are the representative scanning electron microscopy (SEM) images of AgTCNQ nanostructures on the Ag fabric surface (hereafter referred to as Ag/AgTCNQ fabric) that were spontaneously formed through reaction of metallic Ag with a solution of 10 mM TCNQ in acetonitrile at different reaction times. It is evident that the reaction is extremely fast and within one minute, the textile surface is uniformly decorated with AgTCNQ nanowires of 50–300 nm diameter and hundreds of microns in length. As the reaction progresses in time, a dense coverage of the textile surface with AgTCNQ nanowires that do not change in their diameter is observed, however their length extends to sub-millimetre dimensions within 10 min of reaction, leading to an extremely high aspect ratio of over 3000. No further significant change in either the AgTCNQ nanostructure dimensions or their coverage was observed beyond 10 min of reaction. The higher magnification SEM images are shown in Figure S1. Notably, although the solution-based synthesis of AgTCNQ nanowire particles has been previously achieved, the length of the nanowires is typically restricted to 10–20 μm.[29] It is also noteworthy that during the time-dependant conversion of Ag to AgTCNQ, no precipitation in the reaction solution is observed, indicating that these extremely high aspect ratio AgTCNQ nanowires are rigidly adhered to the surface of Ag fabric.

Raman spectroscopy was employed to validate the formation of AgTCNQ, as $TCNQ^0$ and $TCNQ^-$ have distinctive Raman signatures. It is evident from **Figure 2**a that the spectral positions in the background corrected[30] Raman spectra of Ag/AgTCNQ fabrics at different reaction times do not change, and their spectra are distinct from the pristine TCNQ powder. The Raman spectrum of pristine TCNQ powder shows characteristic vibrational modes at 1200 cm^{-1} (C=CH bending), 1450 cm^{-1} (C–CN wing stretching) and 1600 cm^{-1} (C=C ring stretching) modes that correlate well with the literature.[31] In all the Ag/AgTCNQ fabrics, the C–CN wing stretching vibrational mode shifts from 1450 cm^{-1} to 1380 cm^{-1}, verifying the formation of $TCNQ^-$ (AgTCNQ) nanowires on the fabric surface.[24,32]

Formation of AgTCNQ was further validated using FTIR spectroscopy (Figure 2b), which showed characteristic AgTCNQ modes at 2197, 2184 and 2160 cm^{-1} for $v(C \equiv N)$ stretching, 1505 cm^{-1} for $\pi(C = C)$ wing stretching, and 823 cm^{-1} for $\delta(C - H)$ bending vibrations that corroborate well with the literature.[31,33] Among these vibrational modes, the shift of 862 cm^{-1} vibrational mode in $TCNQ^0$ to 823 cm^{-1} in AgTCNQ is particularly important, as the presence of this peak in the latter is consistent with $TCNQ^-$, and not $TCNQ^0$ or $TCNQ^{2-}$ or their mixed valence states, because these vibrational modes are highly sensitive to the subtle changes in the oxidation states.[22]

Since Raman and FTIR spectroscopy do not provide information about the fate of fabric-bound metallic silver after its conversion to AgTCNQ, X-ray photoelectron spectroscopy (XPS) spectroscopy was employed as a highly sensitive technique capable of probing the oxidation states of different elements within a sample. XPS analysis was performed by background correcting the raw data using Shirley algorithm, aligning the elemental binding energies (BEs) to the adventitious C 1s BE of 285 eV, and deconvoluting the spectral components using a Gaussian-Lorentzian function involving least square fitting procedure.[34] Comparison of the Ag 3d core level XPS spectra of Ag and Ag/AgTCNQ fabrics revealed the presence of characteristic metallic Ag^0 $3d_{5/2}$ binding energy (BE) signature at 368.2 eV,[35] which was present both in the Ag and Ag/AgTCNQ fabrics (Figure 2c), thereby indicating the presence of residual Ag in Ag/AgTCNQ fabrics. The latter also showed an additional significant Ag $3d_{5/2}$ BE component at 369.4 eV that corresponds to Ag^+ ions complexed with $TCNQ^-$,[22] further confirming the formation of Ag/AgTCNQ fabrics. Additionally, the change in the nature of TCNQ molecules was probed by investigating the N 1s core levels (Figure 2d) that in the case of pristine TCNQ, showed a major BE feature at 399.2 eV along with a shake-up feature at 2.4 eV higher BE.[36] After formation of AgTCNQ, the major N1s BE component shifted to 398.3 eV along with a similar shake-up signature, validating the formation of a $TCNQ^-$ species, without the formation of any other TCNQ species.[37–39] An additional N 1s peak was observed in AgTCNQ fabric at 400 eV, which was at the same location as that observed in Ag fabric before its reaction with TCNQ, and can be assigned to the original nylon fabric, which consists of polyamides.

XRD analysis was performed to investigate the kinetics of AgTCNQ nanowire synthesis and Ag metal consumption during the growth process while confirming the crystal structure of the resulting material (Figure 2e and f). Pristine TCNQ powder showed characteristic TCNQ signatures with major peaks at 18.6°, 24.2°, 26°, 27.5°, 28.5° and 30.1° 2θ.[20,32] The conversion of Ag to AgTCNQ occurs within one min of reaction, which is evident from the presence of characteristic AgTCNQ XRD signatures[20] in all the fabrics reacted with TCNQ at different time points (curves 3–7, Figure 2e). Notably, as the reaction progresses with time, there appears to be a concomitant increase in the intensity of the AgTCNQ peak at 28° 2θ with a simultaneous reduction in the Ag peak at 38° 2θ. When the ratios of the intensities of these characteristic AgTCNQ and Ag peak are plotted as a function of reaction time, it reveals that over 90% of the reaction takes place within the initial 10 min, leading to near-linear burst growth of AgTCNQ nanowires on the fabric surface, after which the formation of AgTCNQ at the cost of Ag remains minimal (Figure 2f). These results support SEM observations, wherein a dense coverage of fabric surface with AgTCNQ nanowires was observed within 10 min of reaction, following which no significant change in the nanostructure morphology and/or dimensions was observed.

As previously indicated, the applicability of AgTCNQ and other similar metal-TCNQ based organic semiconductors had been restricted to the field of electronics until recently when our group started showing the potential of such materials for photocatalysis applications.[23,24,32] In the current study, we have not only investigated the potential of these materials for antimicrobial applications, but also have employed a high surface area textile as the test material, which brings this concept closer to practical applicability. As evident from **Figure 3**, all the fabrics, whether pristine Ag fabric, or the Ag/AgTCNQ fabrics formed after reaction of TCNQ with Ag fabric at different reaction times show antimicrobial activity against both Gram negative bacteria *E. coli* and Gram positive bacteria *S. albus*. In general, the observed antibacterial activity was found stronger against the Gram negative bacteria (Figure 3a) in comparison to the Gram positive bacteria (Figure 3b). This is a feature commonly observed in most of the inorganic antimicrobial agents, wherein most of the nanomaterials show antimicrobial activity against Gram negative bacteria, while only selected few show antimicrobial performance against Gram positive bacteria.[40] It is notable that the antimicrobial potential of Ag/AgTCNQ fabrics is improved over Ag fabrics both in the case of Gram negative and Gram positive bacteria, as the reaction between Ag fabric and TCNQ continues in time, with the highest antimicrobial activity achieved with Ag/AgTCNQ fabrics formed after 10 min of reaction. After 10 min, the antimicrobial activity of Ag/AgTCNQ fabrics does not seem to increase further as the reaction progresses in time. Additionally, the exposure time of bacteria to the fabrics also plays a role in controlling the antimicrobial profile of these fabrics, with 60 min of exposure showing significantly higher activity over 10 min exposure. The quantitative

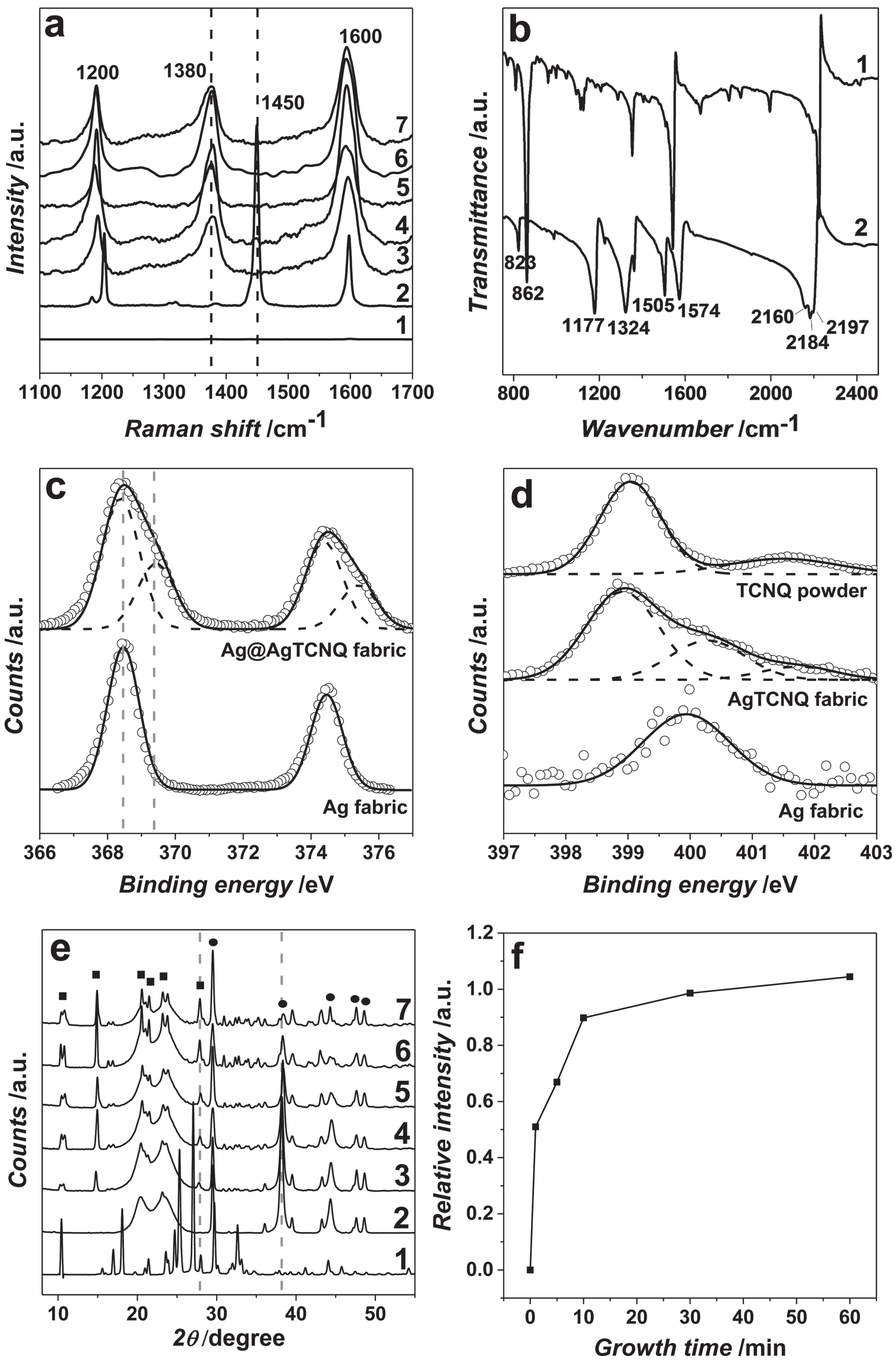

Figure 2. (a) Raman spectra of 1) Ag fabric, 2) TCNQ powder and 3–7) Ag/AgTCNQ fabric at reaction times of 1, 5, 10, 30, and 60 min; (b) FTIR spectra of 1) TCNQ powder and 2) Ag/AgTCNQ fabric formed after 60 min; (c, d) XPS spectra of different materials showing (c) Ag 3d and (d) N 1s core levels; (e) XRD patterns corresponding to 1) pristine TCNQ, 2) Ag fabric and 3–7) Ag/AgTCNQ fabrics formed after 1, 5, 10, 30, and 60 min of reaction, respectively, wherein the peaks denoted with cubes signify AgTCNQ signatures while those denoted with spheres correspond to metallic Ag; (f) relative intensity of AgTCNQ to Ag peaks at chosen 2θ values of 27.8° and 38.3°. The peaks chosen for plotting relative intensity in panel (f) are highlighted with dashed lines in panel (e).

comparison of the best antimicrobial performance of the tested fabrics show that at 60 min of bacteria-fabric exposure, while pristine Ag fabric can cause only 60% *E. coli* death, Ag/AgTCNQ fabric formed at 10 min of reaction lead to over 90% cell death (Figure 3a). In comparison, these fabrics cause 30% and 70% cell deaths, respectively, in the case of *S. albus* (Figure 3b).

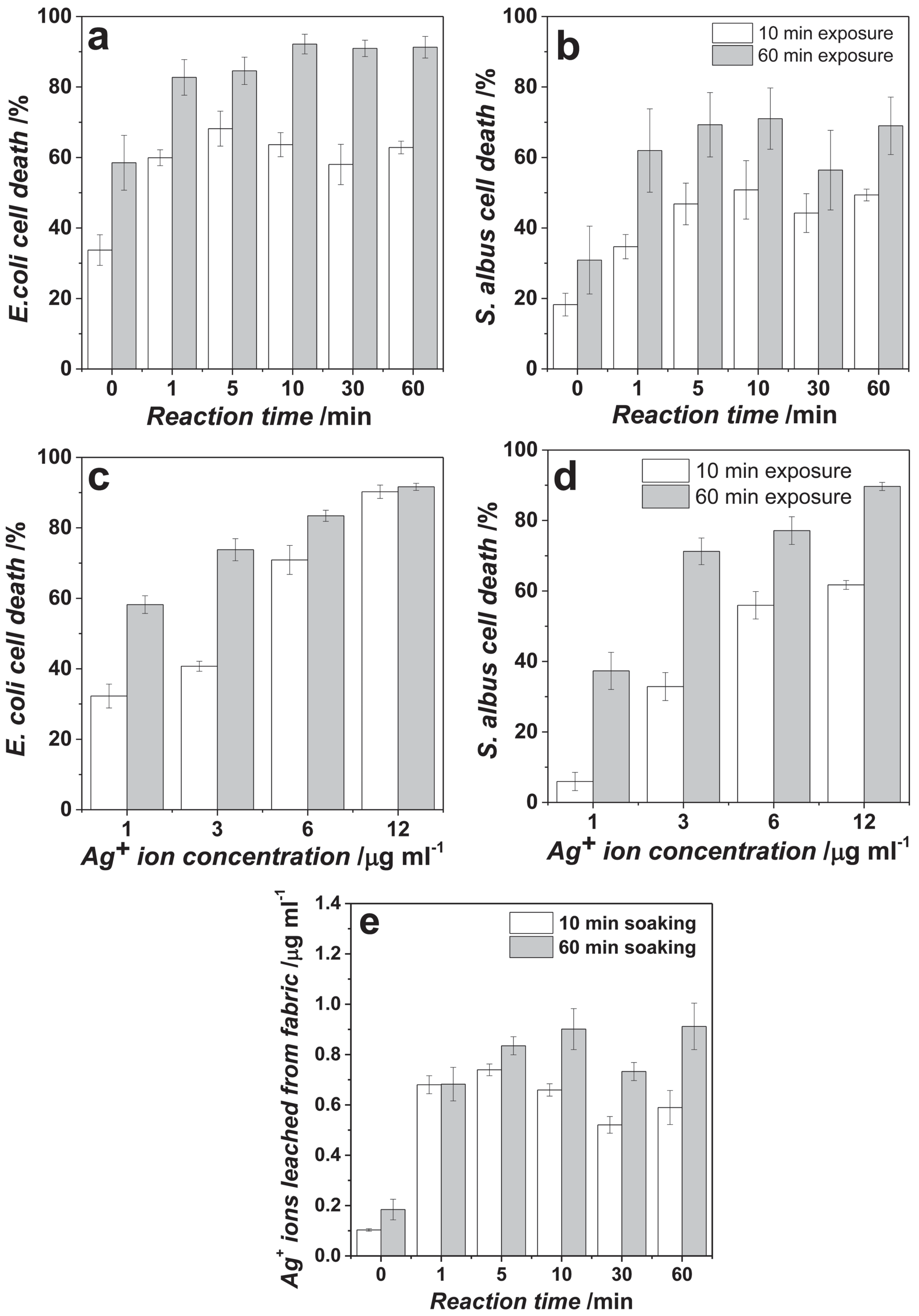

Figure 3. Antimicrobial profile of Ag fabrics against (a) *E. coli* and (b) *S. albus* before ($t = 0$) and after its reaction with TCNQ for different reaction times ($t = 1$, 5, 10, 30, and 60 min), while exposing these fabrics to bacteria for either 10 min or 60 min. Panels (c) and (d) show antimicrobial profile of different concentrations of Ag^+ ions after their exposure to *E. coli* and *S. albus*, respectively for 10 and 60 min. Panel (e) shows the amount of Ag^+ ions leached from 10 mg of Ag fabric prepared before and after reaction with TCNQ at different reaction time, while exposing to bacteria-free biological media for 10 and 60 min.

Although the higher activity of Ag/AgTCNQ fabric over pristine Ag fabric suggests that AgTCNQ has antibacterial properties, further control experiments were performed to ascertain the antibacterial activity of pristine AgTCNQ nanowires. Figure S2 shows the outcomes of zone inhibition assays, wherein it is cleary observed that the discs prepared from pristine AgTCNQ nanowires are able to efficiently suppress the growth of both *E. coli* and *S. albus* around the regions where these materials were applied.

It is an issue of ongoing debate in the current literature whether the nanomaterial toxicity observed from Ag-based nanomaterials arises from the leaching of Ag^+ ions as a result of Ag nanoparticle (Ag^0) oxidation, or the Ag^0 form of the nanoparticle is itself inherently toxic to bacteria.[40,41] Therefore, to elucidate the mode of action of these nanomaterials on the antimicrobial performance, atomic absorption spectroscopy (AAS) was performed on the bacterial media exposed to Ag and Ag/AgTCNQ fabrics for 10 and 60 min (Figure 3e). AAS results show that a maximum of 0.2 μg/mL and 0.9 μg/mL of Ag^+ ions are leached out of the Ag and Ag/AgTCNQ fabrics, respectively, after their exposure to the bacterial growth media for 60 min (Figure 3e). Antimicrobial tests show that while the Ag fabrics cause a maximum of 60% and 32% cell death in case of *E. coli* and *S. albus*, respectively, the Ag/AgTCNQ fabrics lead to 90% and 70% cell death, respectively, on a 60 min exposure (Figure 3a,b). The higher antimicrobial activity of Ag/AgTCNQ fabrics over Ag fabrics may initially be assigned to the higher leachability of Ag^+ ions from Ag/AgTCNQ fabrics over Ag fabrics. However, it is also noted from a control experiment involving Ag^+ ions from $AgNO_3$ that a similar 60 min exposure of bacteria to 1 μg/mL concentration of Ag^+ ions cause only 60% *E. coli* cell death (Figure 3c) and 40% *S. albus* cell death (Figure 3d). Considering that 1 μg/mL concentration of Ag^+ ions in the control experiment is 500% and 110% higher than Ag^+ ion leached from Ag and Ag/AgTCNQ fabrics, respectively under same conditions, it may be argued that the observed antimicrobial performance of the nanomaterials, at least in the current case of Ag and AgTCNQ, is not entirely due to the leached Ag^+ ions. In fact, the antibacterial activity of all the fabrics in regards to the release of Ag^+ ions by these fabrics is found to be higher than the direct addition of the equivalent amount of Ag^+ ions to the bacterial cultures. In a recent interesting report, after accounting for the equivalent amounts of released Ag^+ ions, the role of higher number of surface defects present on Ag nanoplates in comparison to that in Ag spheres and wires was assigned for the high "surface reactivity" of Ag nanoplates against aquatic organisms.[41] The relatively few recent reports in the literature and our consistent observations with all the fabric-based systems point to the strong likelihood that the observed antimicrobial performance of the Ag-based nanomaterials is not entirely due to the leached Ag^+ ions and it is highly likely that the nanomaterial component of the Ag and AgTCNQ fabrics plays a direct role in causing antimicrobial activity, both in the case of Gram negative *E. coli* and Gram positive *S. albus*. It should however be noted that although all the antibacterial experiments were performed under constant stirring conditions to allow uniform Ag^+ ion concentration in the bacterial growth media, the concentration of Ag^+ ions in the stagnant boundary layer near the fabric surface might be higher than the bulk solution. These additional Ag^+ ions in the stagnant boundary layer are likely to play an additional role in compensating for the higher antibacterial activity observed from Ag-based nanomaterials that cannot be explained solely on the basis of leached Ag^+ ions.

3. Conclusion

A facile fabrication route towards the synthesis of novel nanostructured textiles decorated with one-dimensional AgTCNQ organic semiconductor nanowires has been demonstrated for the first time. Considering that the applicability of TCNQ-based metal-organic charge transfer complexes has not hitherto been investigated for antimicrobial applications, a detailed investigation of the potential of Ag/AgTCNQ fabrics as an antimicrobial fabric was performed, which showed a significantly improved performance over Ag fabric. These Ag/AgTCNQ fabrics showed high antimicrobial performance against both Gram positive and Gram negative bacteria. The outcomes of this study also strongly suggest that the antimicrobial performance of Ag-based nanomaterials may not necessarily be due to the amount of Ag^+ ions released from these nanomaterials, and in fact the nanomaterial may also play direct role in causing antimicrobial activity. Moreover, considering that less than 1 μg (0.8%) of Ag^+ ions are leached out of 10 mg Ag fabric consisting of 0.127 mg equivalent of Ag in one hour, the Ag/AgTCNQ fabrics reported here are likely to show antibacterial performance at least for over five days (127 h). Notably, such a high predicted longevity of Ag/AgTCNQ fabrics is based on the assumption that Ag^+ ions will continue to leach out of the fabric, which is not likely to be the case, as Ag^+ ion leaching may stabilize over extended exposure periods due to equilibrium restrictions. It is likely that other metal-TCNQ organic semiconductors might also show antimicrobial performance, an aspect that we are currently investigating in our group. Due to the well-known low solubility of AgTCNQ and other metal-TCNQ in aqueous solutions, such TCNQ-decorated fabrics may provide a controlled release mechanism and long life reservoir for continuous Ag^+ ion release over long periods and thus be a potential candidate for production of wound band aids and gauzes. Also, considering that this is the first report on the growth of a AgTCNQ-based metal organic semiconductor on a flexible textile surface, and since metal-TCNQ complexes have demonstrated electronic applications, this report is likely to fuel significant interest in the development of TCNQ-based flexible electronic devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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