

# High Speed Water Sterilization Using One-Dimensional Nanostructures

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**ABSTRACT** The removal of bacteria and other organisms from water is an extremely important process, not only for drinking and sanitation but also industrially as biofouling is a commonplace and serious problem. We here present a textile based multiscale device for the high speed electrical sterilization of water using silver nanowires, carbon nanotubes, and cotton. This approach, which combines several materials spanning three very different length scales with simple dyeing based fabrication, makes a gravity fed device operating at 100000 L/(h m<sup>2</sup>) which can inactivate >98% of bacteria with only several seconds of total incubation time. This excellent performance is enabled by the use of an electrical mechanism rather than size exclusion, while the very high surface area of the device coupled with large electric field concentrations near the silver nanowire tips allows for effective bacterial inactivation.

**KEYWORDS** Nanowires, nanotubes, environmental applications, multiscale, textile

One-dimensional nanostructures have been extensively explored for a variety of applications in electronics,<sup>1,2</sup> energy,<sup>3–8</sup> and photonics.<sup>9</sup> Most of these applications involve coating or growing the nanostructures on flat substrates with architectures inspired by thin film devices. It is possible, however, to make complicated three-dimensional mats and coatings of metallic and semiconducting nanowires, as has been recently demonstrated in the cases of superwetting nanowire membranes<sup>10</sup> and carbon nanotube (CNT) treated textiles<sup>11,12</sup> and filters.<sup>13–15</sup> We present an exciting new strategy for taking advantage of silver nanowires' (AgNWs) and CNTs' unique ability to form complex multiscale coatings on cotton to produce an electrically conducting and high surface area device for the active, high-throughput inactivation of bacteria in water. Notably, unlike previous membrane-based approaches to this problem, our device does not function by the size exclusion of bacteria, requiring a high pressure drop and leading inevitably to clogging, but instead combines three components spanning several length scales into an active nanoscale architecture which inactivates bacteria as they pass through. This leads to a gravity fed, biofouling resistant device that can inactivate bacteria at faster flow rates than conventional filters while consuming less energy.

Our proposed structure, illustrated in Figure 1A, consists of fibers spanning three length scales, each providing a different functionality. The backbone of our material, cotton, was chosen since it is cheap, widely available, and chemically and mechanically robust. These considerations are extremely important for making filters of practical impor-

tance and are a challenge for many other technologies, including electrospun nanofibrous filters.<sup>10</sup> The pores between fibers in cotton are in the range of tens to hundreds of micrometers, much larger than the length scale of bacteria, which prevents the device from mechanically clogging during use.

The next component of the structure is AgNWs grown by a previously developed technique,<sup>16</sup> with diameters from 40 to 100 nm and lengths up to 10  $\mu\text{m}$ . These provide a secondary mesh as seen from SEM images in Figure 1e–g. Silver is chosen since it is a very well-known bactericidal agent, and recently a large amount of interest has been spurred by the discovery that silver nanoparticles work extremely well at killing bacteria and can be attached to various surfaces with chemical techniques.<sup>17–20</sup> AgNWs afford advantages over Ag nanoparticles in previous studies: First, a NW can have multiple binding points with cotton fibers for strong physical adhesion. Second, AgNWs can form an efficient electrical transport network in filters since they reduce significantly the number of electron hopping times as compared to nanoparticles. This is an important advantage. Noble metal electrodes are known to exhibit antibacterial action under moderate currents,<sup>21</sup> and the enhancement of a sheet of silver nanorods' antibacterial action when placed in an electric field has recently been observed.<sup>22</sup> Due to the interconnected nature of the silver nanowire coating, we can take advantage of this phenomenon for very effective bacterial inactivation.

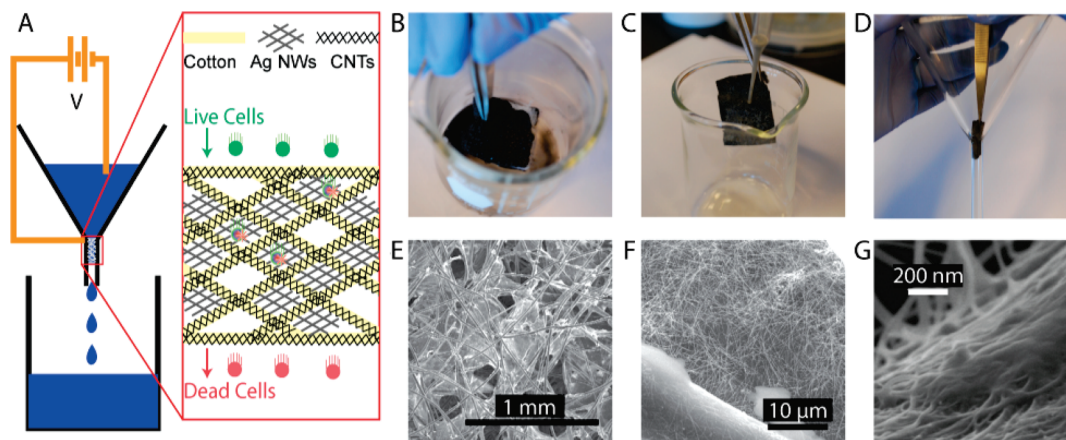
The final component of the proposed device is CNTs, which have been well developed as a means to provide conformal conductive coatings on a wide variety of substrates, especially for transparent conducting coatings for solar cells<sup>23</sup> and recently for the facile coating of textiles including cotton.<sup>24</sup> This component of the system ensures good electrical conductivity over the entire active area of the

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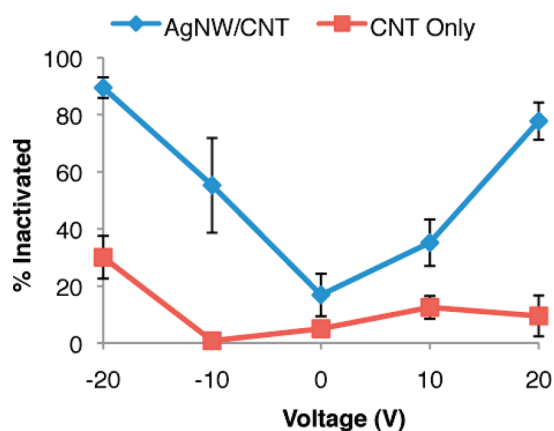
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**FIGURE 1.** Schematic, fabrication, and structure of cotton, AgNW/CNT device. (A) Schematic of active membrane device proposed. (B) Treatment of cotton with carbon nanotubes (CNTs). (C) Treatment of device with silver nanowires (AgNWs). (D) Integration of treated cotton into funnel. (E) SEM image showing large scale structure of cotton fibers. (F) SEM image showing AgNWs. (G) SEM image showing CNTs on cotton fibers.

device so it can be placed at a controlled electric potential and used in solution as a porous electrode.

AgNWs were synthesized by first reducing 25 mg of AgCl in 330 mg of poly(vinylpyridine) in 20 mL of ethylene glycol at 170 °C under vigorous stirring, followed by dropwise addition of 110 mg of AgNO<sub>3</sub> dissolved in 10 mL of ethylene glycol over 10 min.<sup>16</sup> After growth the AgNWs were transferred into methanol by two steps of centrifugation at 6000 rpm for 20 min each. The CNT ink was prepared by dispersing 1.6 mg/mL laser ablation CNTs in water with 10 mg/mL sodium dodecylbenzenesulfonate (SDBS) as surfactant.<sup>25</sup> The fabrication of the device is illustrated in panels B–D of Figure 1. Cotton textiles can be coated easily with CNTs by submerging them in the aqueous CNT ink (Figure 1b). Remarkably, a single dip renders the devices conducting, with a measured low sheet resistance of ~100 Ω/□. The cotton is then rinsed well in distilled water to remove excess surfactant. AgNWs can be easily added to the conductive cotton by pipetting them directly from a methanol solution (Figure 1C) followed by drying on a hot plate at 95 °C for 30 min and copious rinsing to remove any excess solvent and surfactant. The final material is mechanically robust, with a lower sheet resistance of approximately 1 Ω/□. It can be mechanically manipulated for integration into the final filtering system, in our case a simple glass funnel (Figure 1d). Figure 2 illustrates the performance of a filter 4 mm in diameter and 2.5 cm long, running under gravity feed at a flow rate of 1 L/h (or 80000 L/(h m<sup>2</sup>) when adjusted for filter size), compared to a typical value of around 1 L/(h m<sup>2</sup>) for a nanofibrous size exclusion membrane operated at 130 psi.<sup>26</sup> The efficacy of the device for inactivating bacteria is assessed by dispersing treated solution onto an agar plate, a substrate which includes nutrients and attachment sites for the bacteria. After dispersal, the plates are incubated at 37 °C overnight. Each healthy cell in the plated solution multiplies and generates a colony of bacteria after incubation: these colonies can be easily seen by eye and so the number of



**FIGURE 2.** Inactivation efficiency at five biases for AgNW/CNT cotton as well as CNT-only cotton. Total error bar dimension represents 1 standard deviation over three samples for the AgNW/CNT curve and four samples for the CNT only curve.

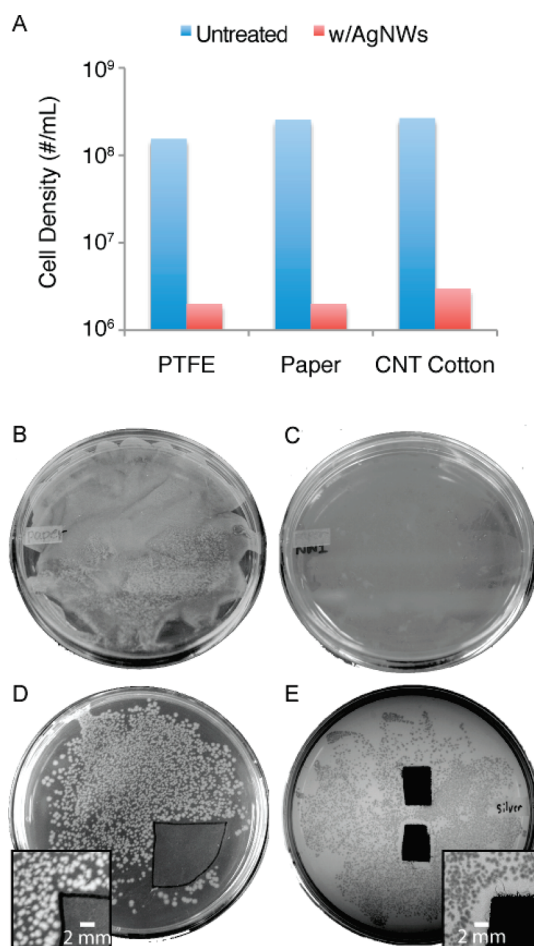
healthy bacteria in the initial solution are counted and compared to that of an untreated sample of the same solution. For each measurement 100 mL of solution with nominal *Escherichia coli* density of 10<sup>7</sup>/mL was flowed through the device. Treated solution was diluted 1000 times and 100 μL were plated. The device was operated at five separate biases from –20 to +20 V, and a Cu mesh counterelectrode held at ground was present in the solution separated approximately 1 cm from the filter. The results with the AgNW/CNT cotton are compared to that of CNT-only cotton (Figure 2a). At 0 potential, neither filter effectively removes bacteria. However, at –20 V the AgNW/CNT cotton inactivates 89% of the bacteria, while at +20 V it inactivates 77%. The CNT-only cotton shows much less activity at all voltages tested, indicating the importance of the AgNWs for effective bacterial inactivation. Over the scale of volumes studied here, the performance of the device remains robust (Supplementary Figure 1A in Supporting Information). Bacterial inactivation at 80–90% may not be

enough for most applications; however the device shows similar performance over a wide range of bacteria concentrations, from  $10^7$  to at least as low as  $10^4$  bacteria/mL (Supplementary Figure 1B in Supporting Information), and three stage serial application of this process may be used to effectively reach inactivation efficiencies  $>98\%$  (Supplementary Figure 2 in Supporting Information).

In addition to enabling electrical inactivation of bacteria, Ag NWs also impart a passive resistance to biofouling, and they can be easily integrated into a variety of filters without the need for chemical strategies to attach them to interior surfaces. Filters of the relevant scale for bacteria filtration are small enough that the AgNWs become easily mechanically entangled by filtering a AgNW solution through the filter. In addition to CNT-coated cotton, two different filters were so treated, one a simple ashless paper filter (Whatman 42) with a pore size of  $2.5\ \mu\text{m}$  and the other a  $5\ \mu\text{m}$  tortuous PTFE filter (Millipore). In order to test the antibacterial effectiveness of the included AgNWs, each filter was inoculated with bacteria by passing a bacterial solution through and then placed in media overnight at  $37\ ^\circ\text{C}$  after which the optical density at  $600\ \text{nm}$  was measured to assess bacterial concentration. The results clearly show that filters not treated with silver, including CNT-only cotton, showed a robust growth of bacteria, while the bacteria concentration in the solutions incubated with AgNW-treated material was reduced to the detection limit of the absorbance system used, at least a 2 to 3 order of magnitude reduction (Figure 3A). Representative plates were prepared from undiluted solutions for the paper filters without (Figure 3B) and with (Figure 3C) AgNWs. No cells at all were observed for the AgNW-treated filters, so the actual order of magnitude reduction in bacteria concentration may be as large as 7 orders of magnitude.

In order to investigate the intrinsic chemical antibacterial strength of the AgNWs, a standard Kirby–Bauer approach was used. Agar plates were prepared and inoculated with *E. coli*, then a film of AgNWs was applied to the plate using a AgNW treated PTFE filter as a mechanical stamp, Figure 3D. If the AgNWs dissolve and release  $\text{Ag}^+$ , one would expect to see a region near the AgNW film in which no bacteria can grow. In these studies, bacteria grew all the way up to the AgNW-treated area (marked by a dark outline in Figure 3D), but not inside, indicating that there is very little dissolution from the AgNW film. In Figure 3E, a AgNW/CNT cotton sample has also been tested, and a very small bacteria-free zone,  $\sim 2\ \text{mm}$ , can be observed, indicating that some small amount of silver dissolution may occur. This result is consistent with a similar test previously published on silver nanoparticle treated ceramic filters.<sup>19</sup>

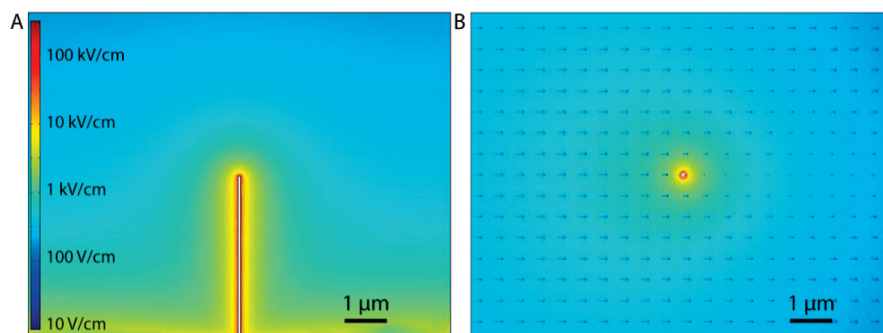
The local environment around the AgNWs during electrical device operation was investigated with finite element simulations using experimentally measured currents and voltages. At  $20\ \text{V}$  the device draws  $3\ \text{mA}$  of current, representing a power consumption of only  $60\ \text{mW}$ , or  $200\ \text{J/L}$  at



**FIGURE 3.** AgNW antibacterial and antifouling testing. (A) Optical density measurements of solutions incubated with various treated and untreated substrates after inoculation with *E. coli* and overnight incubation.  $10^6$  cells/mL is the detection limit of the system. (B) Agar plate inoculated with bacteria solution incubated overnight with standard ashless filter paper; the light color is from a high density of cell colonies, the gray areas are agar without colonies. (C) Agar plate inoculated with bacteria solution incubated overnight with filter paper treated with AgNWs; no colonies are visible. (D) Kirby–Bauer (KB) antibiotic strength measurement for a mat of AgNWs stamped from a PTFE filter, showing no inhibition zone; the light color is from the cell colonies, the darker area is agar without colonies. (E) KB result for AgNW/CNT cotton showing a small  $2\ \text{mm}$  inhibition zone. The contrast in this image is reversed; the cell colonies are darker and the agar without colonies is lighter.

our measured flow rate. For comparison, a typical ultrafiltration membrane running at  $130\ \text{psi}$  and a flow rate of  $1\ \text{L/h}$  will consume around  $250\ \text{mW}$  and  $1\ \text{kJ/L}$ . A simulation of the electric field around a NW protruding perpendicularly from a flat surface in  $1\ \text{mM}$  NaCl solution is shown in Figure 4A. A counterelectrode has been placed in solution  $2\ \text{cm}$  from the NW and a  $20\ \text{V}$  potential difference has been applied. Transient simulations using the Nernst–Planck equations with electroneutrality were carried out. The anodic evolution of  $\text{O}_2$  is simulated at the NW and the surface from which it protrudes. More detailed parameters are given in the Supporting Information. As can be seen in the simulation, the electric field concentration along the edges of the





**FIGURE 4.** Simulation of e-field near NW surface in solution. log plot of the electric field near a NW in solution at experimental anodic conditions with (A) no flow and (B) a flow rate of 1 L/h, as calculated in a 2D geometry using finite element software solving the Nernst–Planck equations with electroneutrality. The scale for both panels is shown on the left side of panel A. The blue arrows in panel B show the direction and relative magnitude of convective  $\text{Na}^+$  flux to illustrate the applied flow condition.

NW is extremely high,  $>100$  kV/cm. Figure 4B shows the results of a similar simulation, but now a flow rate of 1 L/h in the positive  $x$  direction has been imposed on the solution. In order to accurately account for ionic flow around the NW, the simulation geometry has been changed so the NW extends in the  $\pm z$  direction, outside of the simulation. The electric field intensity more than 5 nm from the NW surface is not affected by the applied flow condition; however, the maximum intensity at the NW surface is increased in excess of 1000 kV/cm. The pH in the vicinity of this surface is significantly altered at this very large applied voltage, dropping to as low as 3, which could also have an impact on the bacterial viability. Experimentally the bulk pH of the solution is unchanged after filtration.

The most exciting phenomenon observed here is high throughput inactivation of bacteria during flow through a highly porous material treated with CNTs and AgNWs placed at a moderate voltage. Considering the flow rate of 1 L/h, a cross sectional area of  $12.5 \text{ mm}^2$ , and a length of 2.5 cm, the average incubation time of the solution with the device is just over 1 s, which is small compared to that needed for other commonly used techniques. The physical processes at work may be quite complicated, as there are several components of the system that can be hostile to bacteria. First, silver itself is a well-known bactericide, and silver nanomaterials have been investigated extensively as treatments and coatings to impart antibacterial properties to otherwise biocompatible substrates.<sup>17</sup> Second, electric fields exceeding  $10^5$  V/cm are also known to adversely effect cell viability by breaking down cell membrane in a process known as electroporation.<sup>27</sup> Third and finally, changes to the solution chemistry during current flow, including pH changes as well as in situ production of chemicals like chlorine have also been investigated as a route to sterilizing fluids.<sup>28</sup> It is also quite possible that two or more of these processes may work in concert to inactivate the bacteria.

The bacteria inactivation is almost certainly caused at least in part by the inherent antibacterial action of silver. There are two hypotheses for the antibacterial action of silver nanomaterials. The first is that nanomaterials are slowly

oxidized, releasing  $\text{Ag}^+$  ions which cause damage to proteins and genetic material in a wide array of single cellular organisms leading to cell death or inhibited growth.<sup>17</sup> However, cell killing by silver nanoparticles has also been observed without the telltale signs of  $\text{Ag}^+$  poisoning and in these cases a membrane damage mechanism has been proposed.<sup>29</sup>

Nonetheless, the effect of silver cannot alone account for the dramatic improvement of killing efficiency observed when the AgNWs are placed at relatively moderate biases of 20 V. One possibility is the electrically enhanced generation of  $\text{Ag}^+$  ions; however, the effect appears to be insensitive to the sign of the applied bias suggesting this is not the dominant mechanism. Another well-known mechanism by which cells can be killed by electric fields in solution is electroporation. In electroporation, electric fields are applied so that the potential drop across the cell membranes in solution exceeds their breakdown potential of around 400 mV, or 800 kV/cm for a 5 nm membrane.<sup>27</sup> When oscillating fields are used, less intense electric fields are required. Fields of only 100 V/cm at frequencies of 100 kHz are commonly used to open tiny pores in cell membranes for DNA transfection.<sup>27</sup> The effect has also been studied for food and water sterilization, referred to as the pulsed electric field technique (PEF),<sup>30</sup> where oscillating voltages in excess of at least several kilovolts with microsecond square pulses are required to reach appreciable efficiency.<sup>30</sup> The finite element simulations clearly show that such high electric fields,  $\sim 1000$  kV/cm, may be present inside the filters under the applied conditions, making electroporation a possible mechanism.

An important concern whenever nanoscale material is used is the potential for unanticipated health effects.<sup>31</sup> Although the flow conditions studied here do not result in mass material release over the time scales reported, it can be expected that at least trace amounts of both CNTs and AgNWs will be present in the effluent. Accurately quantifying the amount of material released is an important topic of future investigation. A considerable amount of work has gone into characterizing the health effects of CNT inhalation,<sup>32</sup> although it is widely recognized that multiwall CNTs

are a common byproduct of methane combustion and are therefore ubiquitous in the environment.<sup>32</sup> Should further investigation reveal that even trace release of CNTs into processed water is unacceptable, the cotton-coated CNT substrate used here could be replaced by some other conductive textile substrate, such as carbon cloth. Although the CNT treatment does significantly improve device performance, bacterial inactivation of 87% can be achieved with a three-stage serial use of cotton treated only with AgNWs (Supplementary Figure 2 in Supporting Information), compared to >98% for the composite filter.

In conclusion, we here report a novel approach to killing highly concentrated bacteria in a high throughput gravity fed device raised to a moderate bias of 20 V. The ultimate impact of this technology may be direct implementation as a cheap point-of-use water filter for deactivating pathogens in water, or perhaps more probably as a new component to be integrated into existing filtration systems to kill microorganisms which cause biofouling in downstream filters. Such technology could dramatically lower the cost of a wide array of filtration technologies for water as well as food, air, and pharmaceuticals, where the need to frequently replace filters is a large cost and difficult challenge. This study has only demonstrated the efficacy of this technology in killing *E. coli*, so the next most obvious step is to determine the efficacy versus a wider array of microorganisms; however, silver is known to be an extremely general agent so it can be expected that this device will also work over a wide array of organisms. This study also highlights a volumetric device made possible by some of the unique advantages of bottom up fabrication on an unusual substrate for nanomaterials, cotton. Such work, distinct from architectures and technologies based on thin film approaches, offers a new way forward for nanotechnology.

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**Supporting Information Available.** Results of the filtration performance as a function of time and bacteria concentration, as well as the performance of several alternative composite structures, detailed information on the COMSOL simulation, including a table of physical parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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