

Development of Nanowire-Modified Electrodes Applied in the Locally Enhanced Electric Field Treatment (LEEFT) for Water Disinfection

Journal:	Journal of Materials Chemistry A
Manuscript ID	TA-PER-04-2020-003750.R2
Article Type:	Perspective
Date Submitted by the Author:	28-May-2020
Complete List of Authors:	Zhou, Jianfeng; Georgia Tech, Yu, Cecilia; Georgia Institute of Technology, Civil and Environmental Engineering Wang, Ting; Georgia Institute of Technology, Civil and Environmental Engineering Xie, Xing; Georgia Institute of Technology, Civil and Environmental Engineering; Georgia Institute of Technology



Development of Nanowire-Modified Electrodes Applied in the Locally Enhanced Electric Field Treatment (LEEFT) for Water Disinfection

Jianfeng Zhou**, Cecilia Yu**, Ting Wang, and Xing Xie*

School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta,

Georgia 30332, United States.

* Corresponding author. Phone number: (404)894-9723. E-mail: xing.xie@ce.gatech.edu.

** These authors contributed equally.

Abstract:

Locally enhanced electric field treatment (LEEFT) is introduced as a nanowire-enabled physical water disinfection method with the advantages of low energy consumption, wide spectrum effectivity, and the absence of disinfection by-product (DBP)-forming chemical additives. The electrodes used for LEEFT are modified with nanowires, which enhance the electric field near the nanowire tips significantly. Even with a very low external applied voltage (usually <10 V), the local electric field strength is high enough to enable irreversible electroporation, thus causing microbial inactivation. Here, the development of nanowire-modified LEEFT electrodes is reviewed in terms of their reasoning of material selection, synthesis, characterization, and disinfection performance. Subsequently, we summarize the desired properties of the LEEFT electrodes (*e.g.*, high conductivity, appropriate nanowire morphology, high durability, and low to no toxicity to humans and the environment), point out the strategies of developing new electrodes for the LEEFT, and propose a guideline on how to evaluate electrodes developed in the future. In the end, the challenges and opportunities of LEEFT electrodes for practical application are also discussed.

1. Introduction

Disinfection has long been a crucial and significant process in water treatment. Regardless of whether it is conducted as the final step in a water treatment plant or at a household level, disinfection inactivates waterborne pathogens that have the potential to harm our communities. Indeed, the implementation of chlorination has greatly assisted improvements in public health, contributing to the reduction of almost half of the total mortality rate and 75% of the infant mortality rates in major US cities.^{1, 2} The drawbacks of chlorination, however, have remained difficult to remedy; these include its ineffectiveness against chlorine-resistant pathogens such as *Legionella* and *Cryptosporidium*,^{3,4} undesirable odors or taste in post-treatment water, and perhaps most importantly, the numerous disinfection by-products (DBPs) that form when free chlorine contacts naturally-occurring organic matter.^{5,6} Alternatives to chlorination such as chloramination, ozonation, and UV irradiation have been explored, but these techniques either generate alternative DBPs, suffer from microbial regrowth, and/or expend high energy (**Table 1**).⁷⁻⁹ Ideally, new water purification methods should minimize the use of chemicals and impact on the environment, while at the same time, consume lower energy. Thus, locally enhanced electric field treatment (LEEFT) has been introduced as a viable physical disinfection technology (Figures 1a & b) that retains high microbicidal performance even at low energy and economic cost.

LEEFT can be considered as a refined form of pulsed electric field treatment (PEFT), which has been studied for decades in liquid food pasteurization, clinical therapy, and water disinfection.¹⁰⁻¹⁵ During PEFT, microorganisms exposed to strong electric field pulses (typically >10 kV/cm) with a short duration (typically <100 μ s) are inactivated by irreversible electroporation.^{16, 17} Previously used mainly for biomedical studies, electroporation itself is a sublethal phenomenon that is applied for the introduction of drugs or genetic materials into living cells.^{18, 19} Under an applied electric field, the water molecules within and without a cell begin to polarize, and a transmembrane potential is built up across the cell membrane.^{20, 21} Once this transmembrane potential has surpassed a certain value, the molecules of the lipid bilayer will reorient to form pores, and materials across the cell barrier begin to exchange. The threshold potential for pore formation varies for different microorganisms and is also affected by the applied pulse parameters and the cell's orientation in the electric field. Generation of the large electric pulses necessary for permanent and lethal electroporation has unfortunately corresponded with unfavorably high energy consumption and also operational safety hazards due to the potential arcing of the circuit. Thus, the use of PEFT for practical purposes and treatments has remained limited.^{11, 12}

LEEFT has aimed to address these issues by developing an electrode structure utilizing the unique properties of nanomaterials. When a 1-dimensional nanostructure (*i.e.*, nanowires) experiences an external electric field, the lightning-rod effect causes the electric field strength to become enhanced manifold at the tip of the nanostructure, as much as 5 orders of magnitude (**Figure 1c**).^{22, 23} Employing this phenomenon, researchers have found that nanowire-modified electrodes can achieve irreversible electroporation even at low voltage conditions due to the localized strengthening of the electric field. Thus, high performance can be achieved even at safer operational conditions. As a refined form of PEFT, LEEFT should be considered as a physical disinfection technique that does not rely on chemical toxicity to kill cells, and potentially neither adds nor generates DBPs.^{10, 24} Furthermore, it is expected to be effective against a broad spectrum of human pathogens, including bacteria, protozoa, and viruses.^{11, 25-28}

Till now, multiple nanowire-modified electrodes and reactors have been developed for LEEFT disinfection (**Figures 1d**). High bacterial and viral inactivation efficiencies have been achieved,

and despite limited studies on the underlying mechanism, the results indicate a successful combination of low cost and high efficiency.^{26, 29} Indeed, LEEFT has demonstrated the potential for outstanding disinfection performance (>6-log inactivation for bacteria) with as low as just 1 V applied voltage. With achieving a >6-log inactivation as a prerequisite, the specific energy consumption of current-generation LEEFT devices has dropped from 200 J/L to only 1.2 J/L in lab-scale disinfections.^{30, 31} This value is significantly less than that of the conventional PEFT (typically >100 kJ/L), as well as other contemporary methods, such as UV disinfection (20-60 J/L) or membrane filtration (500-1000 J/L).^{9, 32} Thus, LEEFT has shown great promise as a competitive and even potentially advantageous technology in water disinfection.

In this perspective, existing nanowire-modified LEEFT electrodes are firstly summarized, followed by the four major desired properties of the electrodes, including high conductivity, appropriate nanowire morphology, high mechanical and electrochemical durability, and low toxicity. Based on these desired properties, the strategies to develop future LEEFT electrodes are discussed, followed by a guideline of the procedures to evaluate those electrodes.

2. Development of the LEEFT Electrodes

Electrode design is a core component of LEEFT disinfection since the sufficient enhancement of the electric field near the nanowire tips is crucial for microbial inactivation. Two primary requirements exist for LEEFT electrodes according to the theory of electroporation and the lightning-rod effect: (1) Nanowires and their attached substrates should be conductive, and (2) nanowire tips should be exposed to allow microorganisms to readily approach the regions with the strong electric field. Nanowire-modified electrodes that meet the above criteria should be able to inactivate microorganisms even with a low applied voltage. In this section, existing LEEFT electrodes are reviewed in terms of the reasoning behind their material selection, synthesis, characterization, and disinfection performance. In particular, parameters of LEEFT disinfection are summarized in **Table 2** including the log inactivation efficiency and lifespan of the electrodes as the two most important parameters at the current stage of LEEFT.

2.1 Silver nanowire (AgNW)-modified electrodes

Silver nanowires (AgNWs) were initially selected for LEEFT disinfection because of their high conductivity and intrinsically microbicidal properties. The AgNW-modified electrode consisted of three parts: a substrate "backbone" that provided a network of support, a carbon nanotube (CNT)-coating on the substrate to make it conductive, and the AgNWs for electric field enhancement.^{23, 26} Cotton and polyurethane sponges were selected as the backbone due to their large porous structure, low price, and chemical and mechanical durability. The pore size of the substrate was large enough (tens to hundreds of micrometers compared with the typically less than a few micrometers for microorganisms) to enable high water flux and prevent biofouling or physical screening.

The coating of CNTs onto the substrate was achieved by submersion in an aqueous CNT ink (**Figure 2a**). Notably, the coating provided a conformal conductive network (~100 Ω ·cm) with a single dip. Then, AgNWs suspended in a methanol solution were pipetted onto the textile to form a secondary mesh structure (**Figures 2b & c**). After drying and rinsing, the final material was ready to use with a further decreased electrical resistance of ~1 Ω ·cm. At this stage, the orientation of the AgNWs was not yet fully perpendicular, and the nanowires were also not very uniformly

distributed. The disinfection performance was evaluated using log inactivation efficiency (η , η =-log₁₀(C_{eff}/C_{in}), where C_{eff} and C_{in} are the effluent and influent microbial concentration), and the bacterial and viral concentrations were measured by a standard plating technique and plaque assay, respectively (**Figures 2d & e**). The AgNW-modified electrodes achieved an efficient inactivation of bacteria (>6 logs, for both gram-positive and negative bacteria) and virus (>2 logs) (**Figures 2f-h**). The applied voltage was 10-20 V and the energy consumption was about 100 J/L.²⁶

2.2 Copper oxide nanowire (CuONW)-modified electrodes

Copper oxide nanowires (CuONWs) were chosen for LEEFT disinfection because of the low cost of Cu and the easy fabrication process. The authors heated Cu substrates (meshes or foams, **Figures 3a & b**) in the air at 400-500 °C, and CuO nanowires grew vertically to the electrode surface, as shown in **Figure 3c**.³⁰ The Cu mesh served as both the supportive backbone and the precursor for the CuONWs. After the oxidation process, the mesh turned black due to the formation of CuONWs. The fabricated nanowires uniformly covered the electrode surface, and more tips were exposed as compared to the AgNW-modified electrodes (**Figure 3c**).

A measurement of the nanowire size was performed with the assistance of scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (**Figures 3c & d**), and the nanowire diameters were found to be mostly <30 nm. A monoclinic structure was observed by the electron diffraction pattern using high-resolution TEM (HR-TEM), which confirmed the nanowire material to be CuO instead of Cu₂O (**Figure 3e**). A high inactivation efficiency was achieved with a much lower applied voltage (1 V for >6-log inactivation of *E. coli*) during the subsequent LEEFT disinfection experiments. In addition to artificial water samples, secondary effluents from

wastewater treatment plants were also used as the water matrix to test the proficiency of LEEFT in real-world applications, and a promising >4-log inactivation was achieved (**Figure 3f**). Nevertheless, a short lifespan of the CuONW-modified electrodes was observed: after only ~10 min operation, the nanowires were mostly washed out, which caused disinfection failure. A resulting Cu concentration of ~500 μ g/L in the effluent was detected, indicating the fragile nature of the CuONWs grown on the electrodes. Thus, developing more durable LEEFT electrodes became a primary research objective for LEEFT disinfection.

2.3 Copper phosphide nanowire (Cu₃PNW)-modified electrodes

To enhance the durability of the electrodes, more durable materials were chosen to form the nanowires. A copper phosphide nanowire (Cu₃PNW)-modified electrode was next developed on a Cu substrate for LEEFT disinfection. The fabrication of Cu₃PNW-modified electrodes followed two steps. First, the Cu mesh was electrochemically anodized in a NaOH solution to grow copper hydroxide nanowires (Cu(OH)₂NWs). Then, the Cu(OH)₂NW-modified electrode was heated in Argon (Ar) downwind of sodium hypophosphite at 100 °C for 2 hours. The color of the electrode also changed from reddish-brown to blue to black during these two steps (**Figure 4a**). During this phosphidation process, the Cu(OH)₂NWs were gradually converted to Cu₃PNWs of approximately ~10 μ m length and ~500 nm diameter (**Figure 4b**).³¹

The successful fabrication of Cu₃PNWs was evaluated by several methods. Elemental analysis by energy dispersive X-ray (EDX) and inductively coupled plasma - optical emission spectrometry (ICP-OES) showed an atomic ratio of 3:1 for Cu and P, respectively, and well-resolved lattice fringes with an interplanar distance of 0.200 nm corresponding to the (300) plane of the Cu₃P

phase were observed via HR-TEM imaging (**Figure 4c**). The electrochemical durability of both the Cu(OH)₂NW- and Cu₃PNW-modified electrodes was also characterized by cyclic voltammetry (CV). A much lower current response was observed on Cu₃PNW-modified electrodes, which indicated an elevated electrochemical durability (**Figure 4d**). Uniform distribution of Cu and P on the nanowires was confirmed by scanning TEM (STEM) and the corresponding EDX mapping (**Figure 4e**).With such electrodes equipped in a LEEFT device, the inactivation efficiency remained high (>6 logs) for 12 hours, and no bacteria were detected on the agar plates throughout the prolonged operation time. The Cu release was reduced to $<50 \mu g/L$, but shortened nanowires were still observed by SEM after 12 hours of continuous operation.

2.4 Protective coating layer to enhance durability

Another method to enhance the durability of the electrodes was also explored: coating the nanowire-modified electrodes with a protective layer. Poly-dopamine (PDA) was selected as the coating material because of its high mechanical strength, good adhesive force, and facile fabrication process. The fabrication of the CuONW/Cu₃PNW-modified electrodes followed the previous studies, after which the electrode was immersed in a dopamine solution at 40 °C for a certain number of hours.³³ Dopamine molecules then self-polymerized onto the surface of the electrode, forming a uniform protective layer (**Figure 5a**).^{33, 34} After the coating, the substrate remained porous, and the nanowire tips were still exposed, as indicated by SEM and TEM images (**Figures 5b-d**). The thickness of the PDA layer was tunable and increased (from 25 to 100 nm) with a longer coating time (from 4 to 24 hours) (**Figure 5e**). Uniform, smooth coating layers and clear nanowire-polymer interfaces were observed under TEM imaging (**Figure 5f**). The presence of a successful coating also was confirmed with elemental mapping by EDX and element peak

signals by X-ray photoelectron spectroscopy (XPS) (**Figure 5g**). In terms of the electrode durability, the PDA-coated CuONW-modified electrode was continuously used for 16 hours at a relatively low flux, and >6-log inactivation of *E. coli* was achieved during this operation time. The lifespan of the PDA-coated electrode was thus almost 100 times longer than that of the bare CuONW-modified electrode. Notably, for the PDA-coated Cu₃PNW-modified electrodes, an alternating current (AC) was applied instead of a direct current (DC) to power the disinfection. An AC voltage with a sufficiently high frequency (usually >10⁴ Hz) was theorized to effectively reduce electrochemical reactions, which would greatly extend the lifespan of the electrode. With only 1 V AC applied, the LEEFT cell was successfully operated for 15 days, again at a relatively low flux and high bacterial inactivation efficiency (> 6 logs) (**Figure 5h**). This lifespan of 15 days remains the best record thus far for LEEFT disinfection. The effluent Cu concentration also remained at a very low level throughout the operation time (<10 µg/L) (**Figure 5i**), indicating a minimum loss of electrode material, and thus elevated durability. Such a low Cu concentration poses negligible toxicity to humans and is suitable for safe consumption.

2.5 Other nanowire-modified electrodes

The development of nanowire-modified electrodes for pathogen inactivation has already attracted some global research interest. Some works studied the synergetic effects of LEEFT and other disinfection methods (*e.g.*, metal nanoparticles, reactive oxygen species (ROS), and joule heating), while others aimed for the inactivation of airborne pathogens or antimicrobial surfaces rather than water disinfection. Regardless, the presence of the nanowires on these electrodes remains central to their good disinfection performance, giving insights into the potential developments of future LEEFT electrodes for water disinfection.

An electrode modified with branched CuONWs and zinc oxide nanowires (ZnONWs) has been demonstrated to give effective bacterial inactivation (>2 logs) in water.³⁵ The CuONWs were first synthesized on a Cu foam via a wet chemical process, followed by a hydrothermal method for ZnONW growth (**Figure 6a**). The CuONWs were covered with ZnONW branches, forming CuO–ZnONW hierarchical nanostructures (**Figures 6b & c**). This hybrid electrode demonstrated a better inactivation efficiency than the CuONW electrode alone for both grampositive and negative bacteria due to the larger number of active sites. Other hybrid electrodes have been made by embedding silver nanoparticles (AgNPs) on either ZnONWs or CuONWs (**Figures 6d & e**) using different loading methods, such as a wet chemical process, electroplating, and a light irradiation method.³⁶ For example, a cuprous oxide nanowire (Cu₂ONW)-modified electrode was synthesized by an *in-situ* chemical oxidation process, followed by immersed in an AgNO₃ solution for AgNP loading. A high disinfection efficiency for *S. aureus* and *E. coli* was achieved by the synergetic effects of Ag, electroporation, and electrochemically generated ROS (**Figure 6f**).³⁷

Using a synthesis method similar to the CuONW-modified electrodes, iron oxide nanowire (IONW)-modified electrodes have been developed for the inactivation of airborne pathogens. After heating, the strong mechanical strength of the iron substrate was retained, while the length and diameter of the vertically grown nanowires were about 13 μ m and 120 nm, respectively (**Figures 6g & h**). A high air-borne bacterial inactivation (~8 logs for *S. epidermidis*) was achieved with 4.5 V applied voltage and 30 s contact time (**Figure 6i**).³⁸ In another interesting study, gold-coated tellurium nanowires (Au-TeNWs) were synthesized on carbon fiber fabrics to enhance the antimicrobial effect of shoe soles (**Figures 6j-I**).³⁹ Notably, the Au-TeNW-modified

electrodes showed an elevated conductivity (~90 S/cm) over the bare TeNW-modified electrodes, which made them more suitable for building up the strong electric field.

3. Discussion about the Desired Properties of the LEEFT Electrodes

Since an abundance of potential electrode materials exists, rational design should be applied to the development of future LEEFT electrodes. According to the experience gained from previously developed electrodes, we believe the desired LEEFT electrodes should possess the following four properties: high conductivity, appropriate nanowire morphology, high durability, and low toxicity to humans and the environment. In this section, these desired properties are discussed in terms of the reasoning, theoretical explanation, and examples.

3.1 Conductivity

It is essential for the nanowire-modified electrode, including both the nanowires and the substrate, to have a high electrical conductivity with no upper limit. Low conductivity, *i.e.*, high resistance, may result in significant voltage drops at the electrode, thus weakening the electric field that can be built up near the tips of the nanowires. Highly conductive substrates made of metal or graphite, such as those that have been commonly used in various electrochemical systems, are preferred. Dielectric materials with desirable properties (*e.g.*, porous polyurethane sponges) may still be used as the substrate, but a coating of conductive materials (*e.g.*, CNTs and/or graphene) must be applied. For the nanowires, metallic materials (*e.g.*, AgNW) with little electric resistance will be preferred, while some semiconducting materials (*e.g.*, CuO and Cu₃P) can also be sufficient to enable effective disinfection. Theoretically, the conductivity of the nanowires (*e.g.*, $\sim 10^2$ S/cm

for CuONWs) should be significantly higher than that of the water matrix being treated (*e.g.*, 5×10^{-5} - 2×10^{-3} S/cm for natural fresh waters) in order to exhibit the lightning-rod effect discussed before.

3.2 Morphology of nanowires

The aspect ratio (length to diameter ratio) and density of the nanowires are two critical morphological parameters for LEEFT electrodes. The lightning-rod effect, which causes a strong electric field enhancement at the tip of a nanowire, is essential for inactivating microorganisms with a lower voltage. The aspect ratio of the nanowires directly affects the electric field enhancement factor (K), and the enhancement factor of a single, straight nanowire can be estimated by Equation (1):

$$K = \frac{E}{E_0} = \alpha_{\overline{D}}^L \tag{1}$$

where *E* and *E*₀ are the electric field at the nanowire tip and in the background, respectively, α is a constant, and *L* and *D* are the length and diameter of the nanowire, respectively.²² Thus, nanowires with higher aspect ratios should have a higher enhancement factor, which can reduce the necessary applied voltage. Nevertheless, previous results indicate that a minimum applied voltage exists for LEEFT disinfection, since the threshold of transmembrane potential (usually around 1 V) should be met no matter how significant the enhancement factor is.¹⁶ Therefore, it is probably not necessary to have nanowires with extremely high aspect ratios (*e.g.*, more than a few thousand). Nanowires with very high aspect ratios (*e.g.*, CNTs and TiO₂) are also typically more flexible, making it difficult to stand them up straight on the electrode surface and expose the tips (**Figures 7a & b**).^{40, 41} Furthermore, an extremely high aspect ratio may make the nanowires fragile and reduce their durability in the water, which will be discussed further in Section 3.3. Besides the aspect ratio, the density of the nanowires grown on the electrode surface also affects the LEEFT disinfection performance and should be limited to an appropriate range. A significant number of nanowires with exposed tips on the electrode surface are required to ensure the treatment capacity. However, if the nanowires are too densely packed, the distribution of the electric field strength will be affected and the enhancement factor (*K*) at the tips will be reduced. An extreme example is the vertically grown carbon nanotube (CNT) forest synthesized by alcohol chemical vapor deposition (CVD) (**Figures 7c & d**).⁴² Thus, even though CNTs possess the advantages of high aspect ratio and high conductivity, the tips of this particular nanomaterial are not exposed individually to allow for the full electric field enhancement effect.

3.3 Durability

The durability of a LEEFT electrode can be measured by the time it effectively operates or the volume of water it can treat while maintaining a high inactivation efficiency. Needless to say, the electrode is preferred to be as durable as possible to reduce the overall cost of the LEEFT. For the nanowire-modified electrodes, it is necessary for not only the nanowires and the substrate themselves to be durable, but also the junction between them. The overall durability is mostly determined by the electrode material and also affected by experimental conditions such as the applied voltage and flux. As the most durable electrodes for LEEFT to date, the PDA-coated Cu₃PNW-modified electrodes can operate for as long as 15 days at a flux of 2 m³/(h·m²), a voltage of 1 V, and an effective inactivation of *E. coli* (>6 logs), resulting in a total water treatment capacity of more than 25 L for electrodes with an area of just 1 cm² each.

The durability of the LEEFT electrode is affected by both its mechanical and electrochemical properties. Flow-through or flow-by devices are typically used for LEEFT disinfection, so the nanowires are subjected to the sheer force of the traveling water. Loss of nanowires due to their detachment from the substrate and the resulting debris in the effluent have been observed in previous studies.^{30, 33} Nanowires with a high aspect ratio will suffer from such mechanical erosion and be ruptured rapidly. On the other hand, undesirable electrochemical reactions may occur when a voltage is applied between the two electrodes. Surface acidification on the positive electrode can cause the dissolution of metal ions (*e.g.*, Cu ions from CuONW), weakening the nanowire. For those LEEFT electrodes with metal components, direct electrochemical oxidation introduces these ions into the effluent (*e.g.*, Ag ions from AgNW or Cu ions from Cu substrates). Poor durability in the water can thus lead to secondary contamination of the effluent with excess metal concentration as well as electrode failure.

3.4 Toxicity

As the current LEEFT is targeted towards water disinfection, the materials used should be nontoxic and pose as little threat as a possible to humans and the environment. Ideal electrodes would have minimum solubility in water, regardless of the applied electric potential. If molecules or ions do dissolve from the electrode, then they should be at levels which do not jeopardize people's health. For example, silicon nanowires (SiNWs) may be a good candidate for LEEFT electrode modification due to their very low solubility.⁴³ Some electrodes may release molecules or ions to the water at higher levels, either with or without an electrical potential, but the toxicity of the released substances is manageable, and they are thus considered acceptable for water treatment, *e.g.*, previously developed AgNW- and CuNW-modified electrodes release Ag and Cu ions which can be toxic to humans above certain levels.^{26, 30, 44} For these LEEFT electrodes, careful examination of the potential hazardous substances in the effluent should be conducted to make sure the concentrations are in the range below the recommended levels. For example, the maximum contaminant level goal (MCLG) of Cu and Ag are 1300 and 100 µg/L, respectively, as regulated by U.S. Environmental Protection Agency (EPA).^{44, 45} Lastly, highly toxic materials should not be used for LEEFT electrodes, even though they can be synthesized to nanowires that meet the other criteria. For example, the MCLG of lead (Pb) is zero, which means Pb should never be used to fabricate LEEFT electrodes for water disinfection.⁴⁴

4. Strategies and Future Directions for Developing New LEEFT electrodes

To date, the nanowire-modified electrodes for LEEFT have been prepared by two different strategies. In one strategy, the nanowires (*e.g.*, AgNWs) are first prepared through solution-based methods (*e.g.*, catalyzed solution-liquid-solid (SLS) growth), made into a well-dispersed suspension, and then applied to a conducting matrix by dip-coating or drop-casting.⁴⁶⁻⁴⁸ The advantage of this strategy is that high quality nanowires with high crystallinity and conductivity can be prepared by a variety of existing methods.⁴⁹⁻⁵³ Many studies for controlling the morphology (*e.g.*, length and diameter) of the nanowires have been reported and can readily be adapted to realize the desired aspect ratios of the nanowires for LEEFT electrodes. However, preparing a well-dispersed suspension of the nanowires as well as maintaining the suspension during storage can be challenging. Another challenge specific to this strategy also exists; when modifying the electrodes with these pre-synthesized nanowires, it is difficult to orient the nanowires vertically rather than letting them lie down on the electrode surface. After assembly, only the tips of the standing nanowires can be utilized most effectively for the LEEFT. The previous CNT-coated

Journal of Materials Chemistry A

sponge could achieve a functioning attachment for the LEEFT fairly well because the CNT coating provided an electrode surface with many microscale pores that the Ag NWs could be inserted into.²⁶

In the other strategy, the nanowires (*e.g.*, CuO, Cu(OH)₂, and IONWs) are directly grown from a conductive substrate using an oxidation method (*e.g.*, thermal or hydrothermal).^{30, 31, 54} Some post-synthesis treatments (*e.g.*, annealing or CVD) can be applied to further tune the composition of the nanowires for better performance (*e.g.*, phosphidation of the Cu(OH)₂NWs to more stable Cu₃PNWs).^{31, 55} In addition to being relatively simple and scalable, the major advantage of this strategy is that the nanowires are naturally rooted on the electrode surface in a perpendicular direction, and are thus favorable for the LEEFT. However, there are also several limitations. First, this strategy is typically not applicable to metal nanowires that can achieve a higher conductivity. Second, the types of nanowires that can be synthesized and the synthesis methods that can be used are heavily restricted by the properties of the available substrates. And last but not least, the methods to control the morphology (*e.g.*, length, diameter, and density) of these nanowires on the electrode surface are still not fully understood.⁵¹⁻⁵³

Notably, for both strategies, it is vital to keep the nanowires attached to the electrode "backbone" with a sturdy junction that is also electrically conducting. Adding a protective coating layer (*e.g.*, PDA) may serve to protect this junction as well as the nanowire body, reducing the undesirable release of constituents (*e.g.*, Cu) and extending the electrode lifespan.^{33, 56} However, the application of such a protective coating may affect the conductivity and performance of the LEEFT electrode for microbial inactivation and potentially introduce secondary contaminants as well. More studies are needed to explore different coating materials and the application procedures to achieve both significant enhancement of the electrode durability and minimum impact on the

LEEFT efficiency. We believe that the future development of LEEFT electrodes will still primarily rely on these two preparation strategies, but variations on the specific synthesis, assembly, and/or coating methods are to be expected.

In addition to the Ag- and Cu-modified NWs demonstrated in previous LEEFT electrodes, future developments may adopt other materials. For small scale applications, employing NWs made of noble metals (e.g., Pt and Au) may be affordable and even preferable as they are expected to be more durable and not readily ionized with a positive potential, i.e., under oxidation conditions.⁵⁷ Such nanowires could be fabricated by a template-based anodic aluminum oxide (AAO) method.^{49, 58} Silicon (Si) NWs are chemically inert with controllable morphology, and can be much cheaper and promising for large scale applications.⁵⁹ One major concern, however, is their lower conductivity compared with metal NWs to build up the electric filed. Such a problem may be alleviated by various doping methods.^{60, 61} Carbon-based and conductive polymer NWs are also alternatives for LEEFT electrodes.^{62, 63} Nevertheless, as mentioned in Section 3.2, the fabrication of the desired morphology using these two categories of materials is a major obstacle. Many opportunities and challenges for creative fabrication of nanowires exist, and other than nanowires, 2D materials with available sharp edges may also be employed for LEEFT disinfection, including nanorods, nanostraws, nanocones, nanoflakes, and nanoblades.⁶⁴⁻⁷¹

5. A General Guideline to Evaluate LEEFT Electrodes

More LEEFT electrodes are being developed, but a standard protocol to evaluate these electrodes is still lacking, making it difficult for researchers to compare electrodes on an equivalent basis. In this section, a general guideline to evaluate LEEFT electrodes is proposed and divided

into three aspects: the electrode characterization, electrode durability, and disinfection performance. Notably, the evaluation methods for LEEFT electrodes are not limited to the methods stated here.

5.1 Electrode characterization

The morphology and structure of the electrodes can be studied using common material characterization tools including SEM, TEM, and XRD. Typical results are shown in **Figures 5b-g**. Using high resolution SEM or TEM images, the diameters and lengths of the nanowires can be measured and their aspect ratios calculated.^{30, 31} EDX can be performed in conjunction with these high magnification techniques to analyze the elemental composition of the electrode (**Figure 4e**), and XPS can be applied to study the surface composition (**Figure 5g**). With some maneuvering, the mechanical properties of nanowires can also be measured. Specifically, an atomic force microscope (AFM) can be used to determine the elasticity, strength, and toughness of individual nanowires by pinning them at one end and measuring the bending force needed for nanowire displacement and fracture (**Figure 8a**).⁷²

The conductivity of nanowires is usually measured by isolating single nanowires and connecting each end to structures that can be probed for electrical resistance (i.e. conducting silver paint or vapor deposited metal contacts). Liu et al applied a two-probe method to measure the conductivity of a single CuONW that was removed from a LEEFT electrode (**Figure 8b**).²⁹ This standard two-probe method is useful for nanowires with greater resistivity or restricted geometry, while a four-probe method that separates the current and voltage probes can be used to obtain more sensitive readings.^{53, 73} The resistivity of very thin nanowires may be affected by their size because

of quantum confinement; the conductivities of Bi, GaN and Si nanowires measured via the twoprobe method were found to transition from metallic to semiconducting at specific diameters.^{60, 74, 75} More recently, Akin et al developed a less restrictive, contactless method to determine the conductivity of individual nanowires by suspending them in solution and then measuring the change in their orientation under fluctuating AC electric fields (**Figure 8c**).⁷⁶

The conductivity of the whole electrode can be measured via electrochemical characterization. For this method, a potentiostat equipped with an electrochemical impedance spectroscopy (EIS) board is required. A three-electrode setup should be applied with the developed LEEFT electrode as the working electrode (WE), a counter electrode (CE, *e.g.*, Pt or Ti), and a reference electrode (RE, *e.g.*, Ag/AgCl). The results of EIS measurements can be reported as Nyquist plots, from which the resistance or conductivity of the whole electrode can be determined (**Figure 8d**).^{37, 77} Cyclic voltammetry (CV) sweeps can also be performed using this setup to illustrate the electrochemical reactions taking place within a certain potential window (e.g., **Figure 4d**), giving insights into the electrochemical stability of the electrode.³¹

5.2 Durability test of the electrodes under different conditions

Previous studies have observed the loss and degradation of the nanowires on LEEFT electrodes followed by the failure of microbial inactivation, which suggests that the insufficient durability of the electrodes is a critical challenge.^{31, 33} Nevertheless, a systematic durability test for LEEFT electrodes has not been done. Such a test should aim to evaluate both the chemical durability of the electrode under different electrochemical conditions and the mechanical durability under different hydraulic conditions. Specifically, electrodes can be tested as the working electrode in a

three-electrode setup in an electrochemical cell. Different electrochemical conditions controlled by a potentiostat can be applied. The electrodes should be tested in different electrolytes, such as phosphate buffer solutions with various concentrations and various pH values, to study the effect of ion strength and pH on the electrode durability. The electrolyte can also contain different organic matters at various concentrations to investigate the impact of naturally-occurring organic matter. There should be no mixing during these tests to avoid the loss of nanowires caused by hydraulic scouring. To test the mechanical durability of the new electrodes under different hydraulic conditions, water can be continuously circulated through the electrodes at different flow velocities. In order to simulate real environmental water with suspended solids, the tested water samples can be dosed with different sizes of particles (*e.g.*, silicon dioxide) at different concentrations.

The morphological and structural changes in the electrodes after being applied for disinfection treatment can be characterized using SEM and TEM at different times (**Figures 3c, 8e**). The weight of the electrodes before and after the operation can be measured using a precision microbalance. The release of the electrode materials into the effluent should be quantified. The released metals (*e.g.*, Cu or Ag) can be measured by atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS), while organic release can be determined by total organic carbon (TOC) analysis. To differentiate the two types of release, *i.e.*, dissolved or detached, the samples can be pretreated by acid digestion, filtration, and/or centrifugation (**Figure 5i**).^{31, 33} With all these results obtained, the major mechanisms (*e.g.*, electrochemical corrosion and mechanical erosion) that cause the degradation of the electrodes can be investigated, and the findings can then suggest how to further improve the durability of the electrodes.

5.3 Disinfection performance

The evaluation of the water disinfection performance of a LEEFT device equipped with the nanowire-modified electrodes is essential if the electrodes are to be improved. It is acceptable to test the disinfection efficiency with model bacteria (preferably including both gram-negative and gram-positive strains) in a controlled matrix (*e.g.*, synthetic water samples) to demonstrate the proof-of-concept of high inactivation efficiency at the initial stage of electrode development. The impact of the operation conditions (*e.g.*, applied voltage and flux) on the disinfection performance should be evaluated to find out the minimum applied voltage and/or maximum flux that allows for a certain high level (*e.g.*, 4, 5, or 6-log) of microbial inactivation. Long-term disinfection tests are suggested to determine the maximum lifespan of the electrode. Notably, the scale and design of the LEEFT reactor can significantly affect the disinfection performance. The majority of previous electrodes were evaluated in a flow-through parallel reactor, and it may be better to establish such a device as a standardized LEEFT reactor that can be applied for general evaluation and facile electrode comparisons in the future.^{30, 31, 33}

6. Challenges and Opportunities

Previously, most of the disinfection experiments for LEEFT were carried out in a controlled environment with known model bacteria.^{30, 31} Although a lifespan of 15 days has been achieved with a total volume of 25 L of treated water, there is still a long way to go before the current laboratory outcomes can be translated to real-world results. This is in part because of the limited options for synthesis methods that are feasible for the required unique morphology (*i.e.*, vertically-grown nanowires on a substrate) of LEEFT electrodes. Previously used dip-coating methods suffered from the difficulty of solution storage and unregulated nanowire orientation, while the oxidation methods highly rely on and are thus constrained by the properties of available substrates. The selection of

electrode materials is also constrained by the requirement of less or non-toxic substances for the substrate and nanowires, as the application of LEEFT in water treatment should have minimal impacts on human health. This excludes a broad range of metallic or metal oxide nanowires (*e.g.*, Pb nanowires) because of their easy dissolution in water under an applied electrical potential. Therefore, developing effective LEEFT electrodes with new materials or through novel fabrication approaches is particularly intriguing and opens a great opportunity for material scientists. On the basis of the existing LEEFT electrodes, future research is expected to further improve their properties (*e.g.*, the aspect ratio of the nanowire and durability). For small scale applications, another direction is to develop low-cost sacrificing LEEFT electrodes, which can be rationally designed to dissolve during the LEEFT to enhance the treatment performance.

Significant improvements of the treatment capacity still need to be made before bench-scale LEEFT devices can be scaled up for large applications (*e.g.*, centralized water treatment plants). The increase of treatment capacity (*i.e.*, flux) can be achieved by either increasing the applied voltage, reducing the pore size of the substrate, or improving the engineering design. Meanwhile, the electrodes should be durable enough to minimize the maintenance. An increased voltage can indeed enhance the disinfection performance and volume, but it inevitably introduces more electrochemical reactions. Thus, the LEEFT electrodes would be more potential to become corroded, and theoretically require an even higher electrochemical durability to withstand erosion. A porous substrate (*e.g.*, a foam) is currently used for nanowire growth; reducing the pore size of the substrate can decrease the time needed for the pathogens to travel to the regions of high-electric field, and thus increase the inactivation efficiency. Of course, an overly small pore size could lead to clogging and biofiltration rather than successful LEEFT disinfection. Lastly, the process of LEEFT disinfection can be optimized from an engineering perspective. For example, baffles can be added into the reactor to

adjust the flow pattern and enhance mixing. This may be beneficial to facilitate microorganism transport to the vicinity of the electrode surface. In general, when a higher flux is enabled, regardless of the method, more attention should be placed on the mechanical durability of the electrodes, since each individual electrode will need to endure higher flux (*i.e.*, higher sheer force).

Another critical issue for LEEFT is the unpredictable disinfection performance and electrode durability in complex water matrixes. The bulk of previous studies tested the inactivation efficiency using synthetic (DI water or saline solution) or filtered natural water samples.^{30, 56} In reality, however, the existence of natural organic matters, ions, and suspended particulates may greatly lower the disinfection efficiency. Previous studies have tried to tackle this problem by investigating the influence of pH, ionic strength, ion type, and organic matters.⁷⁸ Nevertheless, a systematic and detailed understanding of the effects of water quality parameters on the electrode durability and the mechanisms behind is still required. For example, it is worth investigating the fouling of the LEEFT electrodes when natural organic matters (of different concentrations, molecular weight, functional groups, and solubility) exist in the water. The influence of the water conductivity on the rate of electrode erosion should also be studied, since a higher conductivity leads to more electrochemical reactions with a constant voltage operation, and thus higher potential of the dissolution of metal/metal oxide electrodes. Long-term monitoring of the water quality during LEEFT disinfection is also suggested to be included in the future research. On the other hand, more studies using natural water samples are needed to evaluate the true disinfection performance and electrode durability of LEEFT technology. Investigations of the disinfection process in different water matrixes will surely promote the development of real-world applications of LEEFT.

The development of existing LEEFT electrodes has taken the technology into an exciting and competitive sphere, and despite challenges in the synthesis and selection of electrode materials,

nanowire-enabled LEEFT has shown great potential as an alternative disinfection technique to traditional chlorine-based water treatment. An immature understanding of the underlying mechanisms and impacts of real-world conditions must be overcome; however, the success of LEEFT remains impressive. After all, only 1 V of applied voltage is necessary for the complete (>6-log) inactivation of bacteria that can be accomplished within seconds. The continued growth and advancement of this technology are to be expected, and future efforts for the development of new electrodes will likely lead to an even more polished electrode durability and disinfection performance. Currently, LEEFT technology has mainly been applied for water disinfection. As the COVID-19 pandemic is currently posing enormous threats to public health and the global economy, it would be intriguing to extend the applications of LEEFT to the disinfection of bioaerosols and contaminated surfaces. Overall, LEEFT technology promises great returns in the form of extraordinarily fast, low cost, easily operated, environmentally-friendly, and chemical-free drinking water disinfection that is effective against a broad spectrum of human pathogens.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgements

This study is supported by the National Science Foundation via Grant CBET 1845354. The authors acknowledge the technical assistance from Ms. Wensi Chen (Georgia Tech School of Civil & Environmental Engineering).

References:

- 1. Centers for Disease Control and Prevention, *Morb Mortal Wkly Rep*, 1999, **48**, 621-629.
- 2. D. Cutler and G. Miller, *Demography*, 2005, **42**, 1-22.
- 3. S. Cervero-Aragó, S. Rodríguez-Martínez, A. Puertas-Bennasar and R. M. Araujo, *PLOS ONE*, 2015, **10**, e0134726.
- 4. I. R. Cooper and G. W. Hanlon, *Journal of Hospital Infection*, 2010, **74**, 152-159.
- 5. M. Deborde and U. Von Gunten, *Water research*, 2008, **42**, 13-51.
- 6. R. D. Morris, A. M. Audet, I. F. Angelillo, T. C. Chalmers and F. Mosteller, *American Journal of Public Health*, 1992, **82**, 955-963.
- 7. M. Guo, J. Huang, H. Hu, W. Liu and J. Yang, *Water Res*, 2012, **46**, 4031-4036.
- 8. D. L. Sedlak and U. von Gunten, *Science*, 2011, **331**, 42.
- 9. Y. Chang, D. J. Reardon, P. Kwan, G. Boyd, J. Brant, K. L. Rakness and D. Furukawa, AWWA Research Foundation & California Energy Commission, Denver, 2008.
- 10. C. Gusbeth, W. Frey, H. Volkmann, T. Schwartz and H. Bluhm, *Chemosphere*, 2009, **75**, 228-233.
- 11. T. Kotnik, W. Frey, M. Sack, S. Haberl Meglič, M. Peterka and D. Miklavčič, *Trends in Biotechnology*, 2015, **33**, 480-488.
- 12. G. Saldaña, I. Álvarez, S. Condón and J. Raso, *Critical Reviews in Food Science and Nutrition*, 2014, **54**, 1415-1426.
- 13. F. J. Barba, O. Parniakov, S. A. Pereira, A. Wiktor, N. Grimi, N. Boussetta, J. A. Saraiva, J. Raso, O. Martin-Belloso, D. Witrowa-Rajchert, N. Lebovka and E. Vorobiev, *Food Research International*, 2015, **77**, 773-798.
- 14. C. Jiang, R. V. Davalos and J. C. Bischof, *IEEE Transactions on Biomedical Engineering*, 2015, **62**, 4-20.
- 15. J. F. Edd, L. Horowitz, R. V. Davalos, L. M. Mir and B. Rubinsky, *IEEE Transactions on Biomedical Engineering*, 2006, **53**, 1409-1415.
- 16. R. Pethig and G. H. Markx, *Trends in Biotechnology*, 1997, **15**, 426-432.
- 17. T. Wang, H. Chen, C. Yu and X. Xie, *Environment international*, 2019, **132**, 105040.
- 18. J. Gehl, Acta Physiologica Scandinavica, 2003, **177**, 437-447.
- 19. M. P. Stewart, R. Langer and K. F. Jensen, *Chemical Reviews*, 2018, **118**, 7409-7531.
- 20. T. Kotnik, F. Bobanović and D. Miklavc^{*}ic^{*}, *Bioelectrochemistry and Bioenergetics*, 1997, **43**, 285-291.
- 21. D. P. Tieleman, H. Leontiadou, A. E. Mark and S.-J. Marrink, *Journal of the American Chemical Society*, 2003, **125**, 6382-6383.
- 22. J. A. Rojas-Chapana, M. A. Correa-Duarte, Z. Ren, K. Kempa and M. Giersig, *Nano Letters*, 2004, **4**, 985-988.
- 23. D. T. Schoen, A. P. Schoen, L. Hu, H. S. Kim, S. C. Heilshorn and Y. Cui, *Nano letters*, 2010, **10**, 3628-3632.
- 24. J. C. Weaver and Y. A. Chizmadzhev, *Bioelectrochemistry and bioenergetics*, 1996, **41**, 135-160.
- 25. C. Haas and D. Aturaliye, *Journal of applied microbiology*, 1999, **86**, 899-905.
- 26. C. Liu, X. Xie, W. Zhao, N. Liu, P. A. Maraccini, L. M. Sassoubre, A. B. Boehm and Y. Cui, *Nano Letters*, 2013, **13**, 4288-4293.
- 27. A. Mizuno, T. Inoue, S. Yamaguchi, K.-I. Sakamoto, T. Saeki, Y. Matsumoto and K. Minamiyama, 1990.
- 28. S. Spilimbergo, F. Dehghani, A. Bertucco and N. R. Foster, *Biotechnology and bioengineering*, 2003, **82**, 118-125.
- 29. C. Liu, X. Xie, W. Zhao, J. Yao, D. Kong, A. B. Boehm and Y. Cui, *Nano letters*, 2014, **14**, 5603-5608.

- 30. Z.-Y. Huo, X. Xie, T. Yu, Y. Lu, C. Feng and H.-Y. Hu, *Environmental science & technology*, 2016, **50**, 7641-7649.
- 31. Z.-Y. Huo, J.-F. Zhou, Y. Wu, Y.-H. Wu, H. Liu, N. Liu, H.-Y. Hu and X. Xie, *Journal of Materials Chemistry A*, 2018, DOI: 10.1039/C8TA06304D.
- 32. K. Reineke, F. Schottroff, N. Meneses and D. Knorr, *Frontiers in microbiology*, 2015, **6**, 400.
- 33. Z.-Y. Huo, H. Liu, C. Yu, Y.-H. Wu, H.-Y. Hu and X. Xie, *Chemical Engineering Journal*, 2019.
- 34. Z.-Y. Huo, H. Liu, W.-L. Wang, Y.-H. Wang, Y.-H. Wu, X. Xie and H.-Y. Hu, *Journal of Materials Chemistry A*, 2019, **7**, 7347-7354.
- 35. J. Tian, H. Feng, L. Yan, M. Yu, H. Ouyang, H. Li, W. Jiang, Y. Jin, G. Zhu, Z. Li and Z. L. Wang, *Nano Energy*, 2017, **36**, 241-249.
- 36. L. Yue, S. Chen, S. Wang, C. Wang, X. Hao and Y. F. Cheng, *Environmental Science: Nano*, 2019, **6**, 2801-2809.
- 37. S. Wang, W. Wang, L. Yue, S. Cui, H. Wang, C. Wang and S. Chen, *Chemical Engineering Journal*, 2020, **382**, 122855.
- 38. D. Wang, B. Zhu, X. He, Z. Zhu, G. Hutchins, P. Xu and W.-N. Wang, *Environ Sci Nano*, 2018, **5**, 1096-1106.
- 39. C.-M. Chiu, Y.-Y. Ke, T.-M. Chou, Y.-J. Lin, P.-K. Yang, C.-C. Wu and Z.-H. Lin, *Nano energy*, 2018, **53**, 1-10.
- 40. S. Masahito, Y. Kashiwagi, Y. Li, K. Arstila, O. Richard, D. J. Cott, M. Heyns, S. De Gendt, G. Groeseneken and P. M. Vereecken, *Nanotechnology*, 2011, **22**, 085302.
- 41. L. Liu, Z. Liu, H. Bai and D. D. Sun, *Water research*, 2012, **46**, 1101-1112.
- 42. J. I. Sohn, S. Lee, Y.-H. Song, S.-Y. Choi, K.-I. Cho and K.-S. Nam, *Applied physics letters*, 2001, **78**, 901-903.
- 43. G. B. Alexander, W. Heston and R. K. Iler, *The Journal of Physical Chemistry*, 1954, **58**, 453-455.
- 44. U. S. E. P. A. (USEPA), National Primary Drinking Water Regulations, <u>https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-</u> <u>regulations</u>, (accessed June 28, 2018).
- 45. J. Zhou, T. Wang and X. Xie, *Environment international*, 2019, **128**, 30-36.
- 46. I. Gonzalez-Valls and M. Lira-Cantu, *Energy & Environmental Science*, 2009, **2**, 19-34.
- 47. H. Wang, Q. Feng, F. Gong, Y. Li, G. Zhou and Z.-S. Wang, *Journal of Materials Chemistry A*, 2013, **1**, 97-104.
- 48. J. Liu, H. Bai, Y. Wang, Z. Liu, X. Zhang and D. D. Sun, *Advanced Functional Materials*, 2010, **20**, 4175-4181.
- 49. G. Cao and D. Liu, *Advances in Colloid and Interface Science*, 2008, **136**, 45-64.
- 50. F. Wang, A. Dong, J. Sun, R. Tang, H. Yu and W. E. Buhro, *Inorganic Chemistry*, 2006, **45**, 7511-7521.
- 51. N. Wang, Y. Cai and R. Q. Zhang, *Materials Science and Engineering: R: Reports*, 2008, **60**, 1-51.
- 52. Y. Xia, J. A. Rogers, K. E. Paul and G. M. Whitesides, *Chemical Reviews*, 1999, **99**, 1823-1848.
- 53. Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Advanced Materials*, 2003, **15**, 353-389.
- 54. D. Wang, B. Zhu, X. He, Z. Zhu, G. Hutchins, P. Xu and W.-N. Wang, *Environmental Science: Nano*, 2018, **5**, 1096-1106.
- 55. P.-C. Chang, Z. Fan, D. Wang, W.-Y. Tseng, W.-A. Chiou, J. Hong and J. G. Lu, *Chemistry of materials*, 2004, **16**, 5133-5137.
- 56. J. Zhou, T. Wang, W. Chen, B. Lin and X. Xie, *Environmental Science: Nano*, 2020.
- 57. Z. Li, F. Gao and Z. Gu, Sensors and Actuators B: Chemical, 2017, 243, 1092-1101.
- 58. Y. Zhong, C.-L. Xu, L.-B. Kong and H.-L. Li, *Applied Surface Science*, 2008, **255**, 3388-3393.
- 59. H. Park and K. B. Crozier, *Acs Photonics*, 2015, **2**, 544-549.

- 60. S.-W. Chung, J.-Y. Yu and J. R. Heath, *Applied Physics Letters*, 2000, **76**, 2068-2070.
- 61. M.-V. Fernández-Serra, C. Adessi and X. Blase, *Nano letters*, 2006, **6**, 2674-2678.
- 62. K. Wang, H. Wu, Y. Meng and Z. Wei, *Small*, 2014, **10**, 14-31.
- 63. K. Wang, D. Loftus, T. Leng, J. Harris and H. Fishman, *Investigative Ophthalmology & Visual Science*, 2003, **44**, 5054-5054.
- 64. X. Xie, A. M. Xu, S. Leal-Ortiz, Y. Cao, C. C. Garner and N. A. Melosh, *ACS nano*, 2013, **7**, 4351-4358.
- 65. Y. Zhang, Y. Wu, H. Ding, Y. Yan, Z. Zhou, Y. Ding and N. Liu, *Nano Energy*, 2018, **53**, 666-674.
- 66. Z. Tsakadze, I. Levchenko, K. Ostrikov and S. Xu, *Carbon*, 2007, **45**, 2022-2030.
- 67. J. M. Kontio, J. Simonen, J. Tommila and M. Pessa, *Microelectronic engineering*, 2010, **87**, 1711-1715.
- 68. P. Liu, Y. Huang, J. Yan, Y. Yang and Y. Zhao, ACS applied materials & interfaces, 2016, 8, 5536-5546.
- 69. Q. Chen, J. Li, B. Zhou, M. Long, H. Chen, Y. Liu, W. Cai and W. Shangguan, *Electrochemistry communications*, 2012, **20**, 153-156.
- 70. N. Lin, P. Berton, C. Moraes, R. D. Rogers and N. Tufenkji, *Advances in colloid and interface science*, 2018, **252**, 55-68.
- 71. S.-S. Yun, S. Y. Yoon, M.-K. Song, S.-H. Im, S. Kim, J.-H. Lee and S. Yang, *Lab on a Chip*, 2010, **10**, 1442-1446.
- 72. E. W. Wong, P. E. Sheehan and C. M. Lieber, *Science*, 1997, **277**, 1971.
- 73. M. Heaney, 2003, pp. 7-1 to 7.
- 74. S. H. Choi, K. L. Wang, M. S. Leung, G. W. Stupian, N. Presser, B. A. Morgan, R. E. Robertson, M. Abraham, E. E. King, M. B. Tueling, S. W. Chung, J. R. Heath, S. L. Cho and J. B. Ketterson, *Journal of Vacuum Science & Technology A*, 2000, **18**, 1326-1328.
- 75. Y. Huang, X. Duan, Y. Cui and C. M. Lieber, *Nano Letters*, 2002, **2**, 101-104.
- 76. C. Akin, J. Yi, L. C. Feldman, C. Durand, S. M. Hus, A.-P. Li, M. A. Filler and J. W. Shan, *ACS Nano*, 2015, **9**, 5405-5412.
- 77. B.-Y. Chang and S.-M. Park, Annual Review of Analytical Chemistry, 2010, **3**, 207-229.
- 78. Z.-Y. Huo, G.-Q. Li, T. Yu, Y. Lu, H. Sun, Y.-H. Wu, C. Yu, X. Xie and H.-Y. Hu, *Environmental Science: Water Research & Technology*, 2018, **4**, 872-881.
- 79. C. Wang, L. Yue, S. Wang, Y. Pu, X. Zhang, X. Hao, W. Wang and S. Chen, *The Journal of Physical Chemistry C*, 2018, **122**, 26454-26463.
- 80. J. C. Crittenden and B. M. W. Harza, *Water treatment: principles and design*, Wiley, 2005.
- 81. N. Ngwenya, E. J. Ncube and J. Parsons, in *Reviews of environmental contamination and toxicology*, Springer, 2013, pp. 111-170.
- 82. S.-L. Loo, A. G. Fane, W. B. Krantz and T.-T. Lim, *Water research*, 2012, **46**, 3125-3151.
- 83. C. A. Martínez-Huitle and E. Brillas, *Angewandte Chemie International Edition*, 2008, **47**, 1998-2005.
- 84. A. Kraft, *Platinum metals review*, 2008, **52**, 177-185.
- 85. C. Zhang, Y. Li, D. Shuai, Y. Shen and D. Wang, *Chemical Engineering Journal*, 2019, **355**, 399-415.
- 86. O. K. Dalrymple, E. Stefanakos, M. A. Trotz and D. Y. Goswami, *Applied Catalysis B: Environmental*, 2010, **98**, 27-38.
- 87. J. Chen, S. Loeb and J.-H. Kim, *Environmental Science: Water Research & Technology*, 2017, **3**, 188-202.
- 88. S. Madaeni, *Water Research*, 1999, **33**, 301-308.
- 89. S. Loeb, C. Li and J.-H. Kim, *Environmental science & technology*, 2017, **52**, 205-213.
- 90. Z.-Y. Huo, Y. Du, Z. Chen, Y.-H. Wu and H.-Y. Hu, *Water Research*, 2020, 115581.



Figure 1. Introduction to locally enhanced electric field treatment (LEEFT). (**a**) Schematic of water carrying bacteria through porous electrodes for LEEFT inactivation. (**b-c**) Schematic (**b**) and COMSOL simulation (**c**), respectively, of lightning-rod effect at the nanowire tip, which enhances the external electric field. (**d**) Optical image of a LEEFT device equipped with the nanowire-modified electrodes.⁵⁶



Figure 2. Highlights of the AgNW-modified electrodes. (**a**) Synthesis method of AgNWmodified electrodes showing the substrate before coating, after CNTs coating, & after AgNWs coating. (**b** & c) SEM images of post-synthesis AgNW electrodes (**b** for polyeurathane sponge and **c** for cotton textile), with inset in (**b**) of high-magnification SEM image showing individual AgNWs. The sponge substrate provides a more continuous framework, increasing the uniformity of the AgNWs coating as compared to the cotton substrate. (**d** & **e**) Schematic of disinfection experiment procedures for bacteria (**d**) and viruses (**e**), respectively. (**f-h**) Log inactivation efficiency of LEEFT for *Escherichia coli, Bacillus subtilis*, & bacteriophage MS2, respectively, at

different voltages. The error bars in **h** represent the standard deviations of each triplicate measurement.^{23, 26}



Figure 3. Highlights of the CuONW-modified electrodes. (**a** & **b**) CuONW grown on mesh (**a**) or foam (**b**) substrates via heating in air. (**c**) SEM image of CuONWs grown vertically to the electrode surface. (**d**) TEM image providing accurate diameter measurement. (**e**) Crystal structure verification (CuO not Cu₂O) by HR-TEM. (**f**) Log removal efficiencies of LEEFT for *Bacillus subtilis*, *Enterococcus faecalis*, and total bacteria analyzed by heterotrophic plate count (HPC) in

secondary effluents from wastewater treatment plants (WWTPs). Dashed lines indicate all bacteria were inactivated and no live bacteria could be detected.^{29, 30}



Figure 4. Highlights of the Cu3PNW-modified electrodes. (**a**) Optical images of the Cu (substrate), Cu(OH)₂NW-modified Cu (intermediate), and Cu₃PNW-modified Cu (product) meshes. (**b**) SEM images showing Cu₃PNWs have a diameter of ~500 nm and length of 10 μ m, standing vertical to electrode surface. (**c**) High resolution TEM of the Cu₃PNW crystal structure.

(d) Better electrochemical stability of Cu_3PNW than $Cu(OH)_2NW$ indicated by CV test with a sweeping rate of 10 mV/s. (e) STEM images with EDX elemental mapping of a single Cu_3PNW nanowire.³¹



Figure 5. Highlights of the PDA-coated electrodes. (a) PDA synthesis method and schematic with PDA-coated CuONW as an example. (b-d) SEM images of the PDA-coated CuONW-modified electrode showing that the PDA coating does not affect the substrate microstructure or cover the tip of nanowires. (e) TEM images showing that the thickness of the coating layer is well controlled by the coating times, from 4, 12, 16, to 24 h (I, II, III, and IV, respectively). (f) HR-TEM image showing a clear interface between CuO and PDA. (g) Element confirmation of the PDA-coated CuONW-modified electrode by XPS. (h) Disinfection performance of LEEFT with an AC voltage (1 V). The lifetime of 15 days is the best record for LEEFT electrodes so far. (i) Effluent Cu concentration during the disinfection experiment in h. The concentrations for the PDA-coated Cu₃PNW-modified electrode are under 5 μ g/L indicating high electrode durability and trivial toxicity to humans.^{33, 34}



Figure 6. Highlights of other nanowire-modified electrodes. (**a**) Synthesis schematic for CuO-Zn hybrid nanowires. (**b & c**) SEM images of the CuO-ZnO hybrid nanowires & hierarchical nanostructures. (**d**) SEM image of the AgNP-doped Cu₂O nanowires and (**e**) TEM image of the AgNP-embedded CuO electrodes. (**f**) Schematic of electroporation working in synergy with ROS and AgNPs for water disinfection. (**g & h**) Optical and SEM image of IONWs. (**i**) Disinfection performance of IONWs for airborne *Staphylococcus epidermidis*. (**j**) Schematic diagram of a

wearable fiber-based electroporation device. (k & l) SEM images showing the TeNWs and Au-

TeNWs coated on carbon fiber fabrics.^{35-37, 39, 54, 79}



Figure 7. Unfavorable nanowire morphology for LEEFT electrodes. (**a** & **b**) SEM images of pure TiO₂ (**a**) and Ag/TiO₂ (**b**) nanofibers. (**c** & **d**) SEM images showing vertically well-aligned CNTs over a large area (**c**), and in an enlarged and perpendicular view (**d**).^{41, 42}



Figure 8. Selected nanowire characterization methods. (a) Nanowires pinned down at one end with a deposited SiO₂ pad (schematic in **I**, optical image in **II**, AFM image in **III**) can be bent by an AFM tip to measure the mechanical strength as a function of displacement (schematic in **IV**). (b) Conductivity measurement for a single CuONW using two-probe method. (c) Schematic of the contactless measurement of nanowire conductivity using solution-based electro-orientation spectroscopy. (d) Example Nyquist plots for the C/Cu₂O-AgNPs electrodes. (e) SEM images comparing PDA-coated Cu₃PNWs and their tips before and after LEEFT treatment as negative electrode.^{29, 37, 72, 76, 77}

Table 1. Summary of water disinfection methods with the associated mechanism, advantages, and disadvantages.

	Methods	Examples	Mechanism	Advantages	Disadvantages	Ref
Chemical	Chemical disinfectants	Chlorine, Chloramines, Chlorine Dioxide, ozone, and Peracetic acid (PAA)	Oxidation of pathogenic components (e.g., proteins, nucleic acids, lipids, and enzymes) through the application of chemical oxidants	Easy to operate, cost- effective, fast and effective disinfection (strong oxidants), residual antimicrobial power (weak oxidants)	DBP formation, chemical storage and transportation, unfavorable taste and odor, poor inactivation of protozoa and endospores (chlorination)	80-82
	Electro- chemical	Electro-chlorination, silver-copper ionization (SCI), and boron doped diamond (BDD) electrodes	Electrochemical production of disinfectants in-situ, either oxidants or toxic heavy metals	Easy to operate, low-to- medium cost, broad spectrum pathogenic inactivation, medium maintenance required	Expensive electrodes (BDD), introduction of secondary contaminants (heavy metal ions)	83, 84
	Photo- catalysis	Example catalysts: TiO ₂ , WO ₃ , WS ₂ , and CdS	Oxidation through reactive oxygen species (ROS) generated by catalysts exposed to irradiation	No DBP formation, no need for complex equipment and chemicals, economically friendly and nontoxic (TiO ₂)	Low overall efficiency, further decreased efficiency in high turbidity water, low throughput	85, 86
Physical	Ultraviolet (UV)	Mercury vapor-filled UV lamps, UV-LED, and solar disinfection (SODIS)	Disruption of DNA and destruction of culturability by shortwave irradiation	No DBP formation, rapid process and high throughput, diverse wavelengths (UV-LED)	Pathogen self-repair and regrowth after treatment, poor inactivation of certain viruses, decreased efficiency in high turbidity water	81, 82, 87
	Membrane filtration	Ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO)	Physical screening of pathogens with controlled pore size driven by pressure, or temperature difference	No DBP formation, high efficiency, modular design, can remove other contaminants simultaneously	Pathogens are not inactivated, high cost, high maintenance, flux decrease due to membrane fouling	81, 82, 88
	Thermal	Boiling, photothermal, SODIS	Heat-induced irreversible denaturation and breakdown of proteins and genomes	Easy to operate, sustainable, cost-effective (SODIS)	Long treatment time, labor intensive, low throughput	82, 89

Electric field treatment	Pulsed electric field treatment (PEFT)	Electric-field-induced irreversible electroporation damages the bacterial cell membrane by a high external voltage	No DBP formation, broad- spectrum pathogenic inactivation, no chemical requirement	Electrode erosion, high energy consumption, operational safety hazards	10, 27, 90
	Locally enhanced electric field treatment (LEEFT)	Nanowire-modified electrodes enhance the electric field locally to achieve irreversible electroporation, which thus reduces the external voltage	No DBP formation, broad- spectrum pathogenic inactivation, no chemical requirement, low energy consumption, safe operation	Electrode erosion, decreased efficiency in complex water matrixes, potential complex fabrication, and potential for health risks from exposure to nanomaterials	31, 56, 90

Table 2. Summary of key parameters of previous LEEFT electrodes.

Material	Morphological parameters		LEEFT disinfection parameters							
	Length (µm)	Diameter (nm)	Aspec t ratio*	Minimum voltage	Capacity ^{**} (m ³ /(hm ²)	Energy consumption* * (J/L)	Effluent metal concentration	Durability	Model pathogens***	Ref
AgNW- modified electrodes	5-20	<100**** *	50- 200	10 V DC	15	100	~70 µg/L Ag	N.R.****	E. coli (-), Salmonella enterica (-), Bacillus subtilis (+), Enterococcus faecalis (+), and MS2	26
CuONW- modified electrodes	>10	<30	~333	1 V DC	2.5****	25	~800 µg/L Cu	10 min	E. coli (-), Salmonella enterica (-), Bacillus subtilis (+), Enterococcus faecalis (+), and MS2	29, 30
Cu ₃ PNW- modified electrodes	~10	~500	~20	1 V DC	2	1.2	< 30 μg/L Cu	12 h	E. coli (-), Enterobacter hormaechei (-), Enterococcus durans (+), and Bacillus subtilis (+)	31
PDA- CuONW- modified electrodes	~5	30-130	38- 167	1V DC	1.8	4	~25 µg/L Cu	16 h	E. coli (-), Enterobacter hormaechei (-), Bacillus subtilis (+), and staphylococcus epidermidis (+)	33, 56
PDA- Cu ₃ PNW- modified electrodes	~10	520-590	~20	1 V AC	2	N.R.	<5 μg/L Cu	15 days	E. coli (-), Enterobacter hormaechei (-), Enterococcus durans (+), Bacillus subtilis (+), and MS2	34

* The aspect ratio is calculated from dividing the average length by the average diameter of the nanowires.

** The capacity, energy consumption, and effluent metal concentration summarized in this table are the conditions where 6-log of *E*. *coli* was achieved by the minimum applied voltage.

*** The gram-negative and gram-positive bacteria are denoted as "(-)" and "(+)", respectively. No denotation indicates a model virus (MS2).

**** N.R. stands for "not reported" in the origin literature.

***** The value was not reported in the origin literature, but measured/ calculated in this work.