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H$_2$O$_2$ generation enhancement by ultrasonic nebulisation with a zinc layer for spray disinfection

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A B S T R A C T

With the outbreak of COVID-19, microbial pollution has gained increasing attention as a threat to human health. Consequently, many research efforts are being devoted to the development of efficient disinfection methods. In this context, hydrogen peroxide (H$_2$O$_2$) stands out as a green and broad-spectrum disinfectant, which can be produced and sprayed in the air directly by cavitation in ultrasonic nebulisation. However, the yield of H$_2$O$_2$ obtained by ultrasonic nebulisation is too low to satisfy the requirements for disinfection by spraying and needs to be improved to achieve efficient disinfection of the air and objects. Herein, we report the introduction of a zinc layer into an ultrasonic nebuliser to improve the production of H$_2$O$_2$ and generate additional Zn$^{2+}$ by self-corrosion, achieving good disinfecting performance. Specifically, a zinc layer was assembled on the oscillator plate of a commercial ultrasonic nebuliser, resulting in a 21-fold increase in the yield of H$_2$O$_2$ and the production of 4.75 μg/ml Zn$^{2+}$ in the spraying droplets. When the generated water mist was used to treat a bottle polluted with Escherichia coli for 30 min, the sterilisation rate reached 93.53%. This ultrasonic nebulisation using a functional zinc layer successfully enhanced the production of H$_2$O$_2$ while generating Zn$^{2+}$, providing a platform for the development of new methodologies of spray disinfection.

1. Introduction

Amongst the numerous microorganisms that are suspended in the air or adsorbed on the surface of objects, pathogenic microorganisms can cause damage to human tissues and organs upon entering the human body through inhalation or via contact with skin and mucous membranes, thus posing a threat to human health [1–3]. To prevent infection by microorganisms, ultraviolet radiation and ozone are the most commonly used air disinfection techniques; however, they can only be used in the absence of people due to their potential biological toxicity [1,2].

Nebulisation is also a common air disinfection method in which a disinfectant such as ethanol, sodium hypochlorite or peroxyacetic acid, is nebulised [4,5]. Most chemical disinfectants are highly toxic and pose a risk of generating persistent residues [6]. In contrast, hydrogen peroxide (H$_2$O$_2$) is known as a green oxidant because its degradation products are only oxygen and water and is relatively safe and environmentally friendly compared with other disinfectants. Moreover, it is a broad-spectrum disinfectant that indiscriminately kills all types of pathogens [7]. Therefore, it is widely employed in air and surface disinfection [7]. Choi et al. demonstrated that an aerosolised peroxyce-based sanitiser at a concentration of 0.5% can effectively remove pathogens from environmental surfaces [8]. Many studies reported that masks used in the COVID-19 epidemic can be effectively and safely disinfected using vapourised H$_2$O$_2$ [9,10].

Ultrasonic nebulisation can produce H$_2$O$_2$ vapour at ambient temperatures. Furthermore, the safety, stability and low energy consumption of ultrasonic nebulisation renders it suitable for frequent air purification. Wood et al. evaluated the use of relatively low levels of H$_2$O$_2$ vapour for the inactivation of pathogens in an indoor environment. The H$_2$O$_2$ vapour was generated using humidifiers with an H$_2$O$_2$ solution. The results showed that exposure to low levels of H$_2$O$_2$ vapour for four to seven days (average air concentrations of approximately 5–10 ppm) effectively inactivated B. anthracis spores on multiple materials [11]. However, the risk of storage, transportation and use of large amounts of H$_2$O$_2$ limits the practical application of this method. An
alternative method for H\textsubscript{2}O\textsubscript{2} production is cavitation in ultrasonic nebulisation, which can produce H\textsubscript{2}O\textsubscript{2} directly during use in a green and efficient manner [12]. Unfortunately, the amount of H\textsubscript{2}O\textsubscript{2} produced in the process is too small for disinfecting the surroundings. Therefore, the H\textsubscript{2}O\textsubscript{2} production by cavitation reactions in ultrasonic nebulisation requires further improvement.

Silver, copper and zinc have been widely used as inorganic metal anti-bacterial agents in liquid or air environments because of their high efficiency and bio-friendliness [13,14]. These inorganic metal anti-bacterial agents exert their anti-bacterial effect mainly through direct contact, ion dissolution and catalytic oxidation [15,16]. Mosci et al. demonstrated an automated room disinfection system using stabilised H\textsubscript{2}O\textsubscript{2} (<8\%) and silver ions that reduced effectively the microbial presence in health facilities with minimal environmental impact [17]. Matsula et al. proposed a new non-alcoholic disinfectant consisting mainly of three types of metal ions (iron, zinc and nickel) for environmental surface disinfection, which quickly inactivated a variety of microorganisms and was safe to human skin, showing no cytotoxicity [18]. In addition, these metal ions possess the advantages of good stability and long duration.

The process of metal zinc self-corrosion in H\textsubscript{2}O produces Zn\textsuperscript{2+}, H\textsubscript{2}O\textsubscript{2} and other reactive oxygen species [19], amongst which H\textsubscript{2}O\textsubscript{2} and Zn\textsuperscript{2+} are effective and stable anti-bacterial ingredients. Thus, we envisioned that introduction of a zinc layer into an ultrasonic nebulisation system could improve the production of H\textsubscript{2}O\textsubscript{2} and generate additional Zn\textsuperscript{2+} by self-corrosion for use as a spray disinfectant. In this study, a spray disinfectant device was developed by assembling a zinc layer on a commercial ultrasonic nebuliser. The ability of the zinc layer to increase the H\textsubscript{2}O\textsubscript{2} production and generate Zn\textsuperscript{2+} in aqueous solution under ultrasonication was evaluated, and the reaction process and mechanism were explored. Then, the sterilisation performance of the device was tested using a plate counting method, and a sterilisation ratio of 93.53\% for Escherichia coli (E. coli) after 30 min treatment was obtained. This spraying method proved suitable for disinfecting the surrounding environment and the surface of objects and offers the advantages of low toxicity, low energy consumption and simple operation and storage.

2. Materials and methods

2.1. Materials

The main materials used were commercial zinc sheets, zinc foam and oscillating plates. The zinc foam was purchased from Kunshan Luchuang Electronic, China. The main chemicals used were 3,3′,5,5′-tetrachloroethylbenzidine (TMB), horseradish peroxidase (HRP), benzoquinone (BQ), isopropyl alcohol (IPA), nitrotetrazolium blue chloride (NBT), hydrochloric acid, zinc nitrate, Luria Broth (LB) liquid medium, agar medium, glutaraldehyde and anhydrous ethanol. E. coli (ATCC25922) was acquired from Wenzhou Kont Biotechnology, China. The concentration after full growth was about 1 \times 10^8 cfu (colony forming unit)/mL. All materials and chemicals were used without any treatment.

2.2. H\textsubscript{2}O\textsubscript{2} production and free radicals trapping test

A chromogenic reaction was conducted to detect the yield of H\textsubscript{2}O\textsubscript{2} using TMB as a chromogenic agent. H\textsubscript{2}O\textsubscript{2} can oxidise TMB to produce a blue oxidative product under HRP catalysis [20–22]. In detail, 0 cm\textsuperscript{2} (Zn0), 1 cm\textsuperscript{2} (Zn1), 3 cm\textsuperscript{2} (Zn3), or 5 cm\textsuperscript{2} (Zn5) were added into 100 mL of pure water for ultrasonic irradiation in an ultrasonic cleaner (KQ5200DE, 160 W). Every hour, 500 mL of the ultrasonicated solution was mixed with 100 mL of a 10 mg/mL HRP solution in dimethylsulfoxide and 1.8 mL of acetic acid/sodium acetate buffer (pH 3.6), and then 20 mL of a 100 μg/mL HRP solution was added. After 60 min, the yield of H\textsubscript{2}O\textsubscript{2} was determined by measuring the absorbance at 652 nm on an ultraviolet–visible (UV–vis) spectrophotometer (UV-7600). In the free-radical trapping test, 1 mM BQ and 1 mM IPA were used to capture superoxide (‘O\textsubscript{2}-) and hydroxyl (‘OH) radicals, respectively [23]. Other operations were conducted as above.

2.3. Superoxide radical detection and Zn\textsuperscript{2+} concentration test

The amount of O2\textsuperscript{•-} was determined by monitoring the change in an NBT concentration upon the reaction of NBT with O2\textsuperscript{•-} in a molar ratio of 1:4, which produced insoluble purple formazan, leading to a decrease in the characteristic UV absorption peak of NBT at 259 nm [24–26]. Zinc sheets were added into 10 mL of a 0.025 mM NBT solution for ultrasonic irradiation. At every 30 min interval, approximately 3 mL of solution was taken to the UV–vis spectrophotometer. In addition, the Zn\textsuperscript{2+} concentration was determined using inductively coupled plasma (ICP) spectrometry (Thermo scientific iCAP7600). In detail, 3 mL of the reacted solution was filtered to remove insoluble substances, and the filtrate was acidified with hydrochloric acid. In addition, a 100 μg/mL zinc nitrate solution was diluted to prepare a series of standard solutions with different concentrations.

2.4. Characterisation

The surface morphology of zinc sheets and zinc foam was observed by Scanning electron microscopy (SEM, ZEISS Gemini 300). X-ray diffraction (XRD, Ultima IV) was used to obtain the phase structure of zinc sheets. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha with Al K\textalpha radiation.

2.5. Electrochemical tests

The open circuit potential and Tafel curves of the zinc sheets were obtained under ultrasonic and non-ultrasonic conditions using a computer-controlled electrochemical workstation (CHI 760E) in 5 wt\% NaCl at ambient temperature. These experiments were performed in a three-electrode cell composed of a graphite electrode as a counter electrode, zinc sheets (0.5 cm × 0.5 cm) as a working electrode and a silver/silver chloride (Ag/AgCl, 3 M KCl) electrode as a reference electrode.

2.6. Bacteria inactivation test

The sterilisation performance of the device was evaluated according to the plate counting method [27,28]. E. coli was selected as the target bacteria, which was reactivated in LB liquid medium prepared and sterilised at high temperature and pressure. Briefly, 2.5 mL of the bacterial solution was taken from the purchased E. coli freezing medium and diluted to 1.25 mL (1:500) with the prepared LB liquid medium, followed by shaking overnight at 37 °C and 200 rpm. Next, all items used in the experiment were strictly sterilised. For the bacteria inactivation test, deionised distilled (DDI) water sterilised at high temperature and pressure was used. The device was set up on a sterile workbench, with 10 mL of sterile DDI water added into a sterile dish, and then the device was started. A bacteria solution (2.5 μL) was added to the collection bottles of the control group (without zinc foam) and the experimental group (with zinc foam), and 2.5 mL of nebulisation solution was collected after 30 min. Then, 2.5 μL of the treated bacteria solution was put into a sterile culture dish, and an appropriate amount of LB solid medium was added and evenly mixed. Three parallel samples were prepared in each group. The changes in the number of bacterial colonies were observed after 24 h of incubation at 37 °C.

The sterilising rate of the device was calculated as follows: [27]

\[ E_a = \frac{N_0 - N_a}{N_0} \times 100\% \]

where \( N_0 \) and \( N_a \) represent the number of live colonies on the control plate and the experimental plate, respectively.
2.7. Morphology observation of live/dead bacteria

The above bacteria solution was dropped onto a silica substrate. After air drying, 2.5% glutaraldehyde solution was added to fix the bacteria for 3 h. The samples were washed with 10%, 30%, 50%, 70%, 90% and 100% ethanol for 3 min and then frozen overnight. SEM observations were conducted after drying in a freeze dryer for 6 h [28,29].

3. Results and discussion

3.1. Evaluation of the performance of the \( \text{H}_2\text{O}_2 \) and \( \text{Zn}^{2+} \) production using zinc sheets under ultrasonication

To facilitate the analysis of the sterilisation performance of the ultrasonic nebulisation system using a zinc layer, the generation of \( \text{H}_2\text{O}_2 \), free radicals and \( \text{Zn}^{2+} \) was detected by performing the same cavitation process as that employed in the ultrasonic nebulisation, that is, using an ultrasonic cleaner (160 W) in water. First, the production of \( \text{H}_2\text{O}_2 \) using the zinc sheets under ultrasonic vibration was tested on the basis of the chromogenic reaction of TMB. As shown in Fig. 1(a), the \( \text{H}_2\text{O}_2 \) quantity generated by the zinc sheets under ultrasonic conditions was calculated according to the linear fitting spectra of the \( \text{H}_2\text{O}_2 \) concentration with the UV–vis absorption intensity (Supporting Fig. S1). The \( \text{H}_2\text{O}_2 \) concentration was directly proportional to the ultrasonication time and the number of zinc sheets. For \( \text{Zn}^0 \) under ultrasonication, the production of \( \text{H}_2\text{O}_2 \) was approximately 1.23 \( \mu \text{M/h} \), whereas the \( \text{H}_2\text{O}_2 \) concentration reached 7.20 \( \mu \text{M/h} \) using \( \text{Zn}1 \). The highest \( \text{H}_2\text{O}_2 \) concentration of 59.67 \( \mu \text{M} \) was achieved when the number of zinc sheets was five (\( \text{Zn}5 \)). The results demonstrated that the addition of zinc sheets greatly increased the cavitation to generate more \( \text{H}_2\text{O}_2 \) than in the absence of zinc sheets, and the yield of \( \text{H}_2\text{O}_2 \) positively correlated with the zinc content and reaction time.

In addition, as shown in Fig. 1b, for \( \text{Zn}5 \), the concentration of \( \text{H}_2\text{O}_2 \) in the absence of ultrasound was 55.08 \( \mu \text{M} \) after 4 h, whereas it reached 238.68 \( \mu \text{M} \) with ultrasound. Without ultrasound treatment, the zinc sheets produced \( \text{H}_2\text{O}_2 \) in water due to the corrosion of zinc, while the ultrasound greatly improved the \( \text{H}_2\text{O}_2 \) production performance. The application of ultrasound is considered to improve the zinc corrosion, providing additional sites for the cavitation reaction.

To explore the reaction pathway of the \( \text{H}_2\text{O}_2 \) production with zinc sheets, IPA and BQ were used to capture ‘OH and ‘O₂⁻ radicals. As shown in Fig. 1c, the capture of ‘OH had almost no effect on the \( \text{H}_2\text{O}_2 \) production, whereas the capture of ‘O₂⁻ decreased the concentration of \( \text{H}_2\text{O}_2 \) obviously. These results indicated that ‘O₂⁻ played a decisive role in the generation of \( \text{H}_2\text{O}_2 \), whereas the role of ‘OH was negligible. Furthermore, the yield of ‘O₂⁻ was quantitatively calculated according to the reaction with NBT (Supporting Fig. S2a). A solution of soluble colourless NBT was converted into insoluble purple formazan in the presence of zinc sheets under ultrasound, as shown in Supporting Fig. S2b. For \( \text{Zn}1 \) under ultrasonication, the concentration of ‘O₂⁻ was calculated to be 29.62 \( \mu \text{M} \) after 60 min (Fig. 1e). The continued decrease in the NBT concentration with time shown in Fig. 1d proves the continuous production of ‘O₂⁻ induced by the zinc sheets. In conclusion, the production of \( \text{H}_2\text{O}_2 \) using zinc sheets depended mainly on the generation of ‘O₂⁻ under ultrasound. According to previous reports, ultrasonic cavitation only produces a small amount of ‘O₂⁻ [12]. Thus, the ‘O₂⁻ radicals produced by zinc under ultrasonication stemmed mainly from zinc corrosion [30], which was enhanced significantly by ultrasonication, enabling the generation of significant amounts of \( \text{H}_2\text{O}_2 \).

In addition, after the ultrasonic reaction, \( \text{Zn}^{2+} \) were detected in the solution as a result of zinc corrosion. As shown in Fig. 1f, for \( \text{Zn}1 \), the \( \text{Zn}^{2+} \) concentration increased with time until reaching approximately 4.04 \( \mu \text{g/mL} \) after 4 h. The related data of \( \text{Zn}5 \) is shown in Supporting Table S1. The concentration of \( \text{Zn}^{2+} \) is directly proportional to the ultrasonic time and the number of zinc sheets, which is consistent with the change of hydrogen peroxide concentration (Fig. 1a). Therefore, to investigate in more detail the corrosion of zinc, the morphology, structure and composition of the zinc sheets were evaluated before and after ultrasonic irradiation, as discussed in the next section.

3.2. Characterisation and electrochemical tests of ultrasonic-facilitated corrosion of zinc sheets

The corresponding SEM images of zinc sheets before and after 4 h ultrasound treatment are shown in Fig. 2a and b. Many cracks and loose structures on the surface of the zinc sheets can be seen before ultrasound irradiation, as shown in Fig. 2c and d. These observations were conducted after drying in a freeze dryer for 6 h [28,29].
ultrasonic irradiation. (f) Tafel curves of zinc sheets under ultrasonic (120 W or 240 W) and non-ultrasonic conditions (0 W). before and after 4 h of ultrasonic irradiation. X-ray photoelectron spectra of the zinc sheets for high resolution (d) O 1s and (e) Zn 2p region before and after 4 h of ultrasonication. The surface of the zinc sheets after ultrasonication. Most importantly, octahedral-like crystals appear. Moreover, clusters of needle-like particles were clearly seen on the surface of the zinc sheets after ultrasonication. The octahedral-like particles are Zn(OH)$_2$ [31], which was confirmed by XRD and XPS analyses.

The XRD pattern of zinc sheets before and after 4 h ultrasound treatment is shown in Fig. 2c. The diffractogram for zinc sheets before ultrasonication corresponds exactly to the ICDD card number 04-0831 of zinc. For zinc sheets after ultrasonication, besides the peaks corresponding to zinc, two new diffraction peaks appear in the diffractogram. As the illustration in Fig. 2c shows, these two new peaks were consistent with the characteristic peaks on the (1 1 0) and (1 0 1) surfaces of Zn(OH)$_2$ (ICDD card number 38-0385) [31,32]. In addition, before ultrasound treatment, a very low and wide peak at 22.88° shown in XRD patterns proves the amorphous Zn(OH)$_2$ (Illustration (A) in Fig. S3). As shown in Illustration (B) of Supporting Fig. S3, a narrower and higher peak appeared at 22.96° after ultrasound treatment, which is attributed to the increase in the amount of Zn(OH)$_2$. Meanwhile, a small peak of amorphous ZnO at 34.22° (Illustration (B)) appeared after ultrasound treatment due to the increased ZnO content (ICDD card number 36-1451), but there is no ZnO peak in XRD before ultrasound treatment (Illustration (A)), because the content of ZnO is too little to be detected by XRD but by XPS.

The chemical composition of the surface and the state of the zinc sheets before and after 4 h of ultrasound treatment was studied using XPS. The binding energies of the O 1s and Zn 2p peaks were calibrated using the carbon C 1s peak (284.8 eV). As shown in Fig. 2d, the O 1s region of the spectra of the zinc sheets before and after ultrasonication are divided into O-Zn and OH-Zn [33]. In the zinc sheets before ultrasound treatment, amorphous ZnO and Zn(OH)$_2$ were formed upon natural oxidation of the zinc sheets in air [34], which is in accord with the XRD results. And the proportion of the O-Zn and OH-Zn peaks was 0.26, whereas it decreased to 0.11 after ultrasound treatment, indicating that the Zn(OH)$_2$ content increased, which is consistent with the appearance of octahedral-like particles in the SEM images. Additionally, the Zn 2p region of the zinc sheets before and after ultrasound irradiation is shown in Fig. 2e. The binding energies of the Zn 2p$_{1/2}$ and 2p$_{3/2}$ peaks for the original Zn sheets and those subjected to ultrasound treatment were close (difference ~ 0.10 eV). In the spectrum of the latter, both Zn peaks were shifted to slightly lower energy compared with those in the spectrum of the original Zn sheets. However, this shift is very small, indicating that the main composition of the zinc sheet surface did not change significantly after ultrasonic irradiation. This tiny shift in the bonding energy peaks can be attributed to the increase of ZnO and Zn(OH)$_2$ and the enrichment of excess electrons at the zinc surfaces [19,34–36]. The above characterisations confirmed that ultrasonic irradiation accelerates the corrosion of the zinc sheets. Considering the detected increase in the concentration of H$_2$O$_2$, Zn$^{2+}$ and Zn(OH)$_2$ after ultrasound treatment, the corrosion of zinc in pure water can be attributed to the dissolution of zinc and the generation of H$_2$O$_2$ according to the following chemical reaction equations [19,30]:

$$\text{Zn} - 2e^- \rightarrow \text{Zn}^{2+}$$ (1)

$$e^- + \text{O}_2 \rightarrow \text{O}_2^-$$ (2)

$$e^- + \text{O}_2^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2$$ (3)

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2$$ (4)

The ultrasonic-facilitated corrosion of zinc sheets was further studied by performing electrochemical tests. The corrosion potential and corrosion current density are important parameters to measure the corrosion resistance of materials. As shown in the Tafel curves depicted in Fig. 2f, the value of the corrosion potential equalled the open circuit potential. The corrosion current density of zinc sheets was obtained according to the extrapolation of the Tafel curves. The corrosion potential and current density of the zinc sheets under different ultrasonic intensities are summarised in Supporting Table S2. It was found that under 120 W ultrasound treatment, the corrosion potential of the zinc sheets decreased and the corrosion current density increased compared with those of the original zinc sheets. This result indicates that the zinc sheets are more susceptible to corrosion and the corrosion rate increases.
increasing the ultrasonic power. Thus, when the ultrasonic power was under ultrasound [37,38]. This trend becomes more obvious with increasing the ultrasonic power. Thus, when the ultrasonic power was 240 W, the corrosion potential decreased by 63 mV and the corrosion current increased by 55.52 μA compared with the zinc sheets without ultrasound treatment. This result demonstrates that ultrasonic irradiation can accelerate the corrosion of the zinc sheets.

3.3. The mechanism of enhancement for H$_2$O$_2$ generation

As mentioned above, the increase in the corrosion of the zinc sheets induced by ultrasonic irradiation and cavitation can be envisaged as the main reason for the enhancement in the H$_2$O$_2$ generation. As shown in Fig. 3, compared with the cavitation in a homogeneous liquid phase, the surface defects present on the zinc sheets, such as cracks, provide more nucleation sites for the generation of cavitation bubbles to improve the cavitation effect. In turn, the micro-jet formed by the collapse of the cavitation bubbles continuously impacts and grinds the zinc sheets, which further increases the number of surface defects (cracks, holes, surface roughness, etc.), thus exposing more active sites. As a result, the corrosion of the zinc sheets and, therefore, the cavitation and generation of H$_2$O$_2$, is accelerated [12,39-41]. Additionally, ultrasonic mechanical cleaning and peeling removes the passivation layer on the surface of the zinc sheets, which contributes to the improvement of the corrosion reaction [40,42].

3.4. Spray disinfection based on ultrasonic nebulisation with zinc foam

Cavitation creates a water mist via the ultrasonic nebulisation process shown in Fig. 4a. The key component of the ultrasonic nebulisation device is the oscillator plate, which consists of a piezoelectric lead zirconate titanate ceramic (PZT) and a micropore steel piece (Fig. 4b and e). The electrical signal from the driven circuit board can be transformed into a high-frequency oscillatory signal through the oscillator plate to realise water nebulisation. Using this device, the H$_2$O$_2$ production and sterilisation performance of the ultrasonic nebulisation system was studied.

To promote the sterilisation performance of the zinc layer, a zinc foam employed as a functional layer was loaded on the oscillator plate for the following tests. The XRD pattern of the zinc foam is shown in Supporting Fig. S4. The Zn foam was mainly composed of metallic zinc, together with a small amount of metallic nickel and trace amounts of zinc oxide. However, the impurities had little effect on the ion-composition in the nebulisation solution. As shown in Supporting Table S3, after 30 min, the concentration of zinc ion in the nebulisation solution was about 200 times that of nickel ion. Therefore, the ions in the nebulisation solution were almost zinc ions. As presented in Supporting Fig. S5, the porous structure of zinc foam is beneficial for its reactivity. Fig. 4c shows a photograph of the assembly of the zinc foam on the concave surface of the oscillator plate. Fig. 4d reveals the porous structure of the zinc foam, which exhibits macropores of 200 μm in diameter. Additionally, Fig. 4e shows a detailed structural diagram of the assembly of the zinc foam and the oscillator plate. The sterilisation performance was evaluated using the device shown in Fig. 4f. The bacteria solution was coated on the inside surface of the collecting bottle and then treated with the nebulisation solution for 30 min. The nebulisation solution in the bottle was collected for bacterial culturing to evaluate the ability of the spray disinfection.

3.5. Sterilization performance based on a spray disinfection device

The sterilisation performance of the ultrasonic nebulisation enhanced with zinc foam was investigated using E. coli as the target bacteria. As shown in Fig. 5a and b, the number of colonies was significantly reduced in the presence of zinc foam (b) compared with the assembly without zinc foam (a). As shown in Supporting Fig. S6 and Table S4, the sterilisation rate was calculated to be 93.53%, which demonstrates the good potential of this device for spray disinfection. In addition, as shown in Fig. 5c and d, the morphologies of the bacteria treated with ultrasonic nebulisation without zinc foam (c) and with zinc foam (d) were analysed. In the presence of zinc foam (d), the bacterial morphology was wrinkled and holes appeared on the surface of the bacterial cell walls. Such a remarkable sterilization effect is believed to arise from the production of H$_2$O$_2$ and Zn$^{2+}$. As shown in Fig. 5e and f, the concentrations of H$_2$O$_2$ and Zn$^{2+}$ generated on the device were 121.25 μM and 4.75 μg/mL, respectively, after 30 min. For the production of H$_2$O$_2$, the zinc foam enabled a 21-fold enhancement compared with the device without zinc enhancer (5.71 μM) within 30 min. Due to the low concentration of H$_2$O$_2$ and Zn$^{2+}$ under such a low power supply, this ultrasonic nebulisation is useful for spray disinfection and exhibits low toxicity to the human body [11,43].

The disinfection mechanism can be divided into three stages, as shown in Fig. 6. Firstly, H$_2$O$_2$ and Zn$^{2+}$ are produced by the cavitation and corrosion with zinc foam during ultrasonic nebulisation. The water mist containing H$_2$O$_2$ and Zn$^{2+}$ is then dispersed in the air and comes into full contact with the bacteria. Finally, the positively charged Zn$^{2+}$ are adsorbed on the negatively charged cell wall of E. coli, resulting in the destruction of the cell wall and membrane upon interaction with proteins [14-16]. Additionally, H$_2$O$_2$ directly crosses the cell membrane [14,44] and increases the level of reactive oxygen species in the cytoplasm, which leads to a series of oxidative stress reactions such as lipid peroxidation, protein denaturation and DNA damage [45-47].

Considering the cost of the zinc layer for real application, the service life of the ultrasonic nebuliser with the zinc layer was evaluated. The corresponding results on the changes in mass, morphology and composition of the zinc sheets and foam are presented in Supporting Table S5 and S6 and Figs. S8-11. After 48 h of ultrasound exposure, the amount of ZnO and Zn(OH)$_2$ corrosion products increased a little, whereas the mass of the zinc sheets and the zinc foam did not decrease.
and the main component of both is metallic zinc. Considering the low price of the zinc sheets and foam, which is 0.02 $/cm² and 0.39 $/cm², respectively, the corrosion rate seems to satisfy the cost requirements of an effective disinfection device for daily life use.

Taken together, the presented results demonstrate that the ultrasonic nebulisation enhanced by a zinc layer achieves the desired sterilisation performance, which stems from the increased production of H₂O₂ and Zn²⁺. This method requires a low power consumption of 2 W and makes full use of the mechanical energy during the humidifying process. In such a low-powered system, the concentration of Zn²⁺ and H₂O₂ is low, reducing toxicity to humans. However, to further improve the sterilisation performance, the ultrasonic nebulisation process would require...
higher power, and the potential toxicity to humans should be carefully evaluated. Although there are some problems concerning security, stability and service life that need to be addressed, this method provides good disinfection performance by ultrasonic nebulisation based on commercial devices. The zinc layer could be easily loaded in any commercial ultrasonic nebuliser, providing extra functionality for the sterilisation of air or other objects, which has great application potential.

4. Conclusions

In this paper, we have made full use of ultrasonic nebulisation to achieve excellent spray disinfection performance, which is enhanced by incorporating a zinc layer into the device. When the zinc layer is subjected to ultrasound, the corrosion and cavitation processes are accelerated, producing a significant amount of \( \text{H}_2\text{O}_2 \) and \( \text{Zn}^{2+} \). The reaction pathway concerning the \( \text{H}_2\text{O}_2 \) production is mostly dependent on the generation of \( \cdot \text{O}_2 \), as evidenced by radical capture experiments. Furthermore, ultrasonic-facilitated corrosion of zinc sheets was demonstrated by surface defects, more \( \text{Zn}^{2+} \) and \( \text{Zn(OH)}_2 \) production and increased corrosion current density. Finally, the sterilization performance of the ultrasonic nebulisation process, enhanced by the zinc layer, was analyzed. After 30 min, 121.25 \( \mu \text{M} \) \( \text{H}_2\text{O}_2 \) and 4.75 \( \mu \text{g/mL} \) \( \text{Zn}^{2+} \) were produced, and a sterilization ratio of 93.53% for \( E. \text{coli} \) was obtained. This proved that the antibacterial ingredients were produced and dispersed in the air by a commercial ultrasonic nebulizer. With the aid of a zinc layer, this ultrasonic nebulisation system provides a green, convenient and energy saving method for air or object disinfection.

Conflicts of interest

The authors declare no conflict of interest.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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