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# Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

# Chemical warfare agents decontamination via air mircoplasma excited by a triboelectric nanogenerator

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#### ARTICLE INFO

Keywords: Triboelectric nanogenerator Microplasma 2-chloroethylethyl sulfide Oxidation product Chemical warfare agents

#### ABSTRACT

Low-temperature air plasma, as an emerging green and efficient technology, has great potential to do chemical warfare agents (CWAs) decontamination. However, conventional plasma devices are bulky, costly and inconvenient. More importantly, their practical application is limited by the power grid and battery capacity. Here, A double layer paper-strip rotary triboelectric nanogenerator (dps-rTENG) is fabricated to serve as a self-powered high-voltage device to induce microplasma in air for CWAs decontamination. The degradation efficiency of 2-chloroethylethyl sulfide (2-CEES), a surrogate for the sulfur mustard (HD), reaches more than 99% within 2 min of microplasma treatment, and the energy utilization efficiency ( $E_e$ ) of the dps-rTENG is calculated to be 0.520 µg/J, which is one order of magnitude higher than those of the commercial power supplies. Further study confirms that the degradation process of the dps-rTENG induced microplasma is well controllable to avoid the formation of large amounts of 2-chloroethyl ethyl sulfone (2-CEESO<sub>2</sub>), a toxic excessive oxidation product. Triboelectric microplasma provides a new approach for self-powered, easily portable decontamination system for CWAs in future.

## 1. Introduction

In the twentieth century, Chemical Warfare Agents (CWAs) were widely used on the battlefield [1,2]. Even now, they are often used by criminals to threat public safety. According to physiological effects, they can be classified into vesicants (blistering agents), nerve agents, blood agents (cyanogenic agent), riot-control agents (tear gases), choking agents (pulmonary agents), psychotomimetic agents and toxins [3]. Among them, sulfur mustard (HD) is a widely used CWA, due to its high

toxicity, simple preparation, and low manufacturing cost [4]. The oily nature of HD makes it persistent on the surfaces it contacts and it is often used via aerosol exposure. Despite the prohibition of Chemical Weapons Convention (CWC) for its production, storage and transport, HD still represents a great threat to global health [5].

Conventional CWAs decontamination methods include pyrolysis [6], hydrolysis [7,8], oxidation [6], physical adsorption or chemical adsorption via materials [9–16]. However, there are still some problems unsolved, for example, low degradation efficiency, secondary

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https://doi.org/10.1016/j.nanoen.2022.106992

Received 14 December 2021; Received in revised form 19 January 2022; Accepted 25 January 2022 Available online 29 January 2022 2211-2855/© 2022 Elsevier Ltd. All rights reserved.





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environmental pollution, and high material cost. An efficient, environment-friendly and low-cost decontamination method is still highly demanded.

In recent years, plasma technology as a high-efficient method for CWAs degradation has caught researchers' attentions. Atmospheric pressure plasma has been proven an efficient degradation method for HD, or its surrogate (2-Chloroethyl ethyl sulfide (2-CEES) or 2-chloroethyl phenyl sulfide (2-CEPS), which contains the same CH<sub>3</sub>-Cl functional group as HD). Different plasma configurations including plasma jet, corona discharge and coaxial arranged dielectric barrier discharge (DBD) have been reported. For example, Herrmann et al. used plasma jet to degrade 1.9 mg/cm<sup>2</sup> HD over the aluminum coupons (1.27 cm diameter), and the degradation rate reached 99.9% within 2 min [17]. Li et al. successfully degraded 20 mg/m<sup>2</sup> 2-CEPS via plasma jet within 2 min over the aluminum coupons (10 mm diameter) [18]. Li et al. reported that using pulsed corona plasma for 2-CEES gas decontamination with the gas flow rate of 2 m<sup>3</sup>/h [19]. 2-CEES with initial concentration of 212.6 mg/m<sup>3</sup> was decontaminated to 0.09 mg/m<sup>3</sup> within 14.1 s. However, due to the high excitation energy required for their plasma discharge, their work suffered from the problems of large-sized devices, low energy efficiency and dependence on the electric power supply. These problems limit the actual applications of plasma degradation of CWAs, especially in battle field [20]. Heesso et al. first reported wearable atmospheric pressure plasma fabrics produced by knitting flexible wire electrodes for CWAs decontamination [21]. HD with 0.905 mg was almost completely decontaminated within 25 min plasma treatment. However, the plasma device still needed a commercial electric power to get energy.

The triboelectric nanogenerator (TENG) as a novel type of energy harvesting device can convert mechanical energy in the environment into electrical energy, which can get rid of the dependence on commercial electric power [22-25]. It has many advantages, including self-powered feature, simple structure, easy construction, low cost, and high conversion efficiency. More importantly, it is capable to output voltages up to thousands of volts with an easily portable device size, which may address the problem of traditional plasma energy supply. In 2018, four classical types of microplasma were excited via TENG successfully by Wang's group [26]. Afterwards, Liu et al. conducted a systematic analysis of DBD through experiments and simulations in 2019 [27]. Moreover, the plasma excited by TENG show a wide range of applications in many fields such as CO<sub>2</sub> gas sensing [28], ammonia synthesis [29,30], bacterial sterilization [31], and performance optimization of ZnO nanowire sensor [32]. The microplasma powered by TENG will be an ideal candidate to develop a self-powered CWAs decontamination system.

Herein, a double layer paper-strip rotary triboelectric nanogenerator (dps-rTENG) is fabricated to excite microplasma in air for the decontamination of 2-CEES. The double layer structure successfully doubles the short circuit current, and the open circuit voltage of dps-rTENG exceeds 3 kV. Three modes of discharge are used to induce microplasma in air for 2-CEES decontamination. Then decontamination of 2-CEES and the discharge details of the air microplasma are systematically investigated. Experimental results show that the microplasma excited by the dps-rTENG can effectively decontaminate 2-CEES with a much higher energy efficiency, which is very promising for practical decontamination of more CWAs treatment.

#### 2. Experimental section

# 2.1. Fabrication of the dps-rTENG and electric characteristics

The dps-rTENG consists of three parts: two stators, a rotator, and a series of paper strips. Acrylic sheet (3 mm thick) are cut into disks with a diameter of 26 cm by a laser cutting machine, which serve as the substrate of the stator and rotor. Aluminum foil is cut into 12 sectors and attached to the stator acrylic disk to work as pairs of electrodes, and they are electrically connected every other one. The gap between each sector is 3 mm. Two poly tetra fluoroethylene (PTFE) tapes are cut into 6 sectors and fixed on both sides of rotator, respectively. Here, the PTFE acts as negative triboelectric layer, and the aluminum electrodes as induction layer. Paper strips ( $2 \text{ cm} \times 13 \text{ cm}$ ) are folded along the long axis to form a ridge shape, and evenly taped between the Al electrodes as the charge supplementary source, contacting continuously with PTFE during operation. The rotator is fixed on the shaft of a rotary motor. The upper and lower stators are fixed with screws. The open circuit voltage is measured using an oscilloscope (Teledyne LeCroy HD 4096). The short circuit current and transfer charge quantity is measured using an electrometer (Keithley 6517). A variable resistance box is used for voltage and current measurement in needle-plate circuits.

#### 2.2. Fabrication of plasma chamber

An aluminum crucible ( $\emptyset = 6.7$  mm, height = 6 mm, thickness = 0.2 mm) as the container of 2-CEES is placed on the bottom of a glass jar ( $\emptyset$  mouth = 39 mm,  $\emptyset$  bottom = 66 mm, height = 138 mm). The aluminum crucible and a tungsten needle electrode (curvature radius of needle tip = 0.22 mm, length = 180 mm) are connected to the two electrodes of the dps-rTENG, respectively. The tungsten needle is placed 1 mm above the liquid level of 2-CEES.

# 2.3. Construction of three discharge modes

The rectifier bridge is composed of four voltage-resistant diodes (R5000, DO-1). In AC mode, the electrodes of dps-rTENG are connected directly to the tungsten needle and the aluminum crucible. In the negative DC mode, the negative electrode after rectification is connected to the tungsten needle. In the positive DC mode, the negative electrode after rectification is connected to the aluminum crucible.

#### 2.4. Processing steps of 2-CEES

(i) Before the experiment, air is blown into and out of the jar with an air pump, removing any decontamination products and pollutant; (ii) Add 40  $\mu$ L acetonitrile to the aluminum crucible, and wipe the crucible with a cotton swab to remove any surface chemicals and contaminants; (iii) Add 40  $\mu$ L 2-CEES to the aluminum crucible and start the degradation; (iv) Collect the remaining liquid into a sampling bottle; (v) Add 40  $\mu$ L dichloromethane into the aluminum crucible for elution, and collect the eluent into the same sampling bottle; (vi) Add another 70  $\mu$ L dichloromethane into the sampling bottle to adjust to the appropriate volume; (vii) Measure the concentration of 2-CEES with gas chromatography-mass spectrometry (GC-MS). Repeat the above steps (i-vi) for each sample.

#### 2.5. Liquid and gaseous 2-CEES detection with GC-MS

The 2-CEES samples are analyzed using Thermo Scientific Trace GC Ultra. An oil pump and auto-sampler are connected to a quadrupole mass spectrometer DSQ II (Thermo Scientific). The DB-5MS(5%-phenyl-methypolysiloxane) GC column (30 m  $\times$  0.25 mm  $\times$  0.25 µm)) is applied, which is obtained from Agilent Technologies (Palo Alto, CA, USA). The instrument parameters are set as follows: spitless injection model with a time of 0.7 min, and injector temperature of 250 °C; carrier gas (He) flow rate of 1.0 mL/min; gaseous 2-CEES injection volume of 1 mL, and liquid 2-CEES injection volume of 1 µL. During the auto-injection process, dichloromethane and methanol are applied as the dichloromethane solvent. The GC temperature control program starts from 50 °C and is maintained for 2.0 min, ramps at 10 °C/min to 170 °C, then increases at 40 °C/min, and finally is maintained at 250 °C for 3 min to clean the column.

# 2.6. Spectral acquisition

Add 2-CEES on the surface of the plate electrode. The spectrometer probe is placed close to the generated plasma. The excited species are analyzed using the optical emission spectroscopy (Shanghai Fuxiang Optical Co., LTD, FX2000L+RD) with an integration time of 100 ms.

#### 2.7. Ozone detection

Pump suction ozone  $(O_3)$  detector (Shenzhen Pulitong Electronic Technology Co., Ltd, XLA-BX-O3) is used for  $O_3$  detection. The  $O_3$  detector needs to be warmed up for 60 s after it is turned on, then open the chamber and put the inspiratory mouth of detector into the chamber. Leave it for a certain time and record the highest value.

# 2.8. Statistical analysis

The data are statistically analyzed using single factor analysis of variance. The data are shown as mean  $\pm$  s.d. (SD, n = 3) in the figures.

# 2.9. Simulations

The details of the simulation setup and electric field intensity distribution is given in the Supplementary materials, the Methods and Materials part, Table S1 and Fig. S1.

# 3. Results and discussion

# 3.1. Electrical characterization of dps-rTENG and microplasma

The decontamination system consists of a dps-rTENG and a needleplate discharge chamber, as demonstrated in Fig. 1a. The working mechanism of the dps-rTENG is illustrated in Fig. 1b. PTFE inclines to be negatively charged, while paper tends to be positively charged in the triboelectric series. In this device, before the PTFE layer on the rotator contacts with the paper strips on the stator, there are small amount of negative charges on the surface of PTFE. After the PTFE layer makes slight frictions with the paper strip, it gets much more negative charges. Furthermore, the negative charges on the PTFE induce an equal amount of positive charges on the corresponding Al electrode on the stator, which generates a potential difference between pairs of Al electrodes. To increase the output, one more identical layer of PTFE and stator with paper strips and Al electrodes are added at the other side of the rotator. The Al electrodes on the upper and lower stators are parallel connected.

In this device, the paper strips have two functions. First, they work as the charge supplement source, which constantly make frictions with PTFE and result in charge accumulation on PTFE, reducing charge dissipation. Second, the soft paper can maintain soft contact with PTFE, which avoids the direct and hard contact of PTFE and metal electrodes, and enables a long-term high performance of our device.

As shown in Fig. 2a-c, the open circuit voltage and short circuit current of dps-rTENG are 3 kV and  $171 \mu$ A, respectively, and the transferred charge is 465 nC at a rotation speed of 600 rpm. Compared with the single layer paper-strip rTENG (ps-rTENG), the open circuit voltage of dps-rTENG is the same, but the short circuit current and the transferred charge are doubled, as demonstrated in Fig. 2d-f. The paper strip based charge supplementary structure is derived from our previous work. After adding one paper strip, the voltage of the rTENG is triplicated, and the current and charge are quintupled, respectively [31]. To promote the performance of our device even further, in this study, we design a double layer structure on the basis of our previous device. Another identical stator layer with Al electrodes is fabricated and fixed at the back of the PTFE rotor. Meanwhile, a new PTFE layer is symmetrically attached to the back of the original PTFE rotor. In addition, 4 paper strips are used instead of 1 paper strip for each layer to ensure full and balanced contact between the paper strips and the PTFE films. Due to this double layer design, the short circuit current and the transferred charges are doubled compared with the single-layer ps-rTENG. Because TENG has the feature of high voltage and low current, this simple structure design that doubles the current output is very helpful to induce



Fig. 1. Experimental setup. (a) The schematic diagram of the 2-CEES decontamination system based on the dps-rTENG; (b) The working mechanism of the dps-rTENG.



Fig. 2. Characteristics of the dps-TENG. Output of the dps-rTENG (a-c) and the single layer ps-TENG (d-f); (g) Variation of the current and voltage curves under the different external loads; (h) Average power curve under the different external loads.

microplasma.

The voltage, current and average power under various external loads are illustrated in Fig. 2g, the voltage and current don't change significantly before 0.1 M $\Omega$ . After the external load exceeded 1 M $\Omega$ , the voltage rises and the current falls rapidly with the increase of the external loads until 100 M $\Omega$ . The average power first increases and then decreases with external load, reaching a maximum of 60.9 mW at 16 M $\Omega$ , as presented in Fig. 2h.

In order to avoid the highly hazardous handlings associated with HD, 2-CEES with a similar chemical structure is used as HD surrogate in the experiments. The molecular structures of HD and 2-CEES are shown in Fig. 3a. A needle-plate discharge chamber is constructed for 2-CEES decontamination, as shown in Fig. 3b. It consists of a tungsten needle and an aluminum crucible in a jar. The discharge characteristics under different spacing of needle and plate are shown in Supplementary material Fig. S2. The dps-rTENG can successfully excite plasma even at a needle-plate spacing of 1.5 mm. In consideration of an appropriate spacing to maximize the energy utilization of plasma while avoiding contact of the needle tip with 2-CEES, a spacing of 1 mm is chosen for the later experiment. A purple corona is clearly observable at the tip of the needle in Fig. 3c. The voltage and current drops and rise sharply when the discharge occurs. The discharge voltage is close to 3 kV and the discharge current reaches 410  $\mu$ A, as shown in Fig. 3d. The discharge current is much larger than the displacement current. This is due to the formation of a conductive path between the needle and plate during the discharge, which causes the change of resistance of the gas environment [33]. In addition, the microplasma induction system can be enlarged to degrade larger amount of CWAs. Plasma is successfully excited with four needles with dps-rTENG excitation, as shown as Video S1 in the Supplementary Materials.

Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2022.106992.

To investigate the degradation dependency on the discharge modes, three different electric modes (AC, negative DC, positive DC) are compared for 2-CEES degradation efficiency. The different modes are adjusted by the rectifier bridge. Fig. 3e shows the circuit diagrams (i-iii) of the three modes. Experimental details are described in Experimental Section. The relative videos are displayed in the Supplementary



**Fig. 3.** Characteristics of the microplasma. (a) Chemical structure of HD and 2-CEES; (b) Schematic diagram of needle-plate discharge device; (c) Photograph of the corona discharge; (d) The current and voltage curves of the dps-rTENG with a needle-plate space of 1 mm; (e) The circuit diagrams of AC (i), negative DC (ii), positive DC (iii); (f) Current and voltage curves of three modes with acetonitrile as dielectric layer.

materials Video S2–4. The negative DC and AC have better discharge stability, and in Fig. 3f, they also have higher discharge frequency. Therefore, in terms of electrical properties, negative DC and AC are better than positive DC, which may have better 2-CEES decontamination effect. The further results are shown below.

Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2022.106992.

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#### 3.2. Decontamination of 2-CEES

2-CEES is placed between the electrodes to be treated by the microplasma directly, as illustrated in Fig. 3b. 40  $\mu$ L 2-CEES with different concentrations (50 mg/L, 100 mg/L and 150 mg/L) are used in the experiment. The decontamination of 2-CEES is studied using GC-MS. The retention time for the analytes C<sub>4</sub>H<sub>9</sub>CIS (2-CEES) is 6.64 min

First, the degradation efficiency of different concentrations of 2-CEES in AC mode is investigated. Fig. 4a demonstrates that the degradation rates gradually increase with time. 2-CEES with concentration of 50 mg/L, 100 mg/L and 150 mg/L are almost completely degraded at 80 s, 160 s and 200 s, and the decontamination rates reach 99.52%, 99.75% and 99.72%, respectively. Subsequently, 100 mg/L 2-CEES is used in later experiments. To verify the role of 2-CEES volatilization in



Fig. 4. Decontamination of 2-CEES. (a) Decontamination rates of 50 mg/L, 100 mg/L, and 150 mg/L 2-CEES after AC microplasma treatment; (b) Decontamination rates of 100 mg/L 2-CEES after AC, positive DC, and negative DC microplasma treatment.

the decontamination process, 100 mg/L 2-CEES without microplasma treatment is set as the control group. Compared with experimental groups, the peak area of 2-CEES (indicating the concentration of 2-CEES) in control group exhibits only a slight change after 240 s air exposure (Fig. S3). Contrarily, experimental group exhibits obvious drop in the peak areas, indicating that the microplasma treatment is the main reason for 2-CEES reduction. To further confirm the impact of volatilization, the gas in the chamber of the control group is collected with a gas bag and measured by GC-MS. However, no 2-CEES signal is detected.

Second, three discharge modes are investigated for degradation optimization. Fig. 4c-e show the chromatograms of 2-CEES in the AC, negative DC, and positive DC mode at different treatment time. The 2-CEES peaks disappear faster in the AC and negative DC modes. Fig. 4b summarizes the decontamination rates in the three modes. The negative DC and AC modes have similar degradation effects, which reach 99.87% and 96.56% at 120 s, respectively. The decontamination rate of the positive DC mode at 120 s, however, is significantly lower (78.91%). The decontamination rate of the positive DC mode is also significantly lower than the other two at 160 s, and doesn't reach 99.41% until 240 s. The p-values between each group is shown in Fig. S4. Therefore, among the three modes, the negative DC and AC have higher decontamination efficiency than the positive DC.

#### 3.3. Decontamination products of 2-CEES

The 2-CEES peaks gradually decrease, as shown in the chromatograms in Fig. 4c-e, indicating that 2-CEES is degraded and converted to other substances. In this section, the decontamination products are analyzed. Fig. 5a-f are the chromatograms of products in different modes. With the increase of treatment time, two new peaks appear at 11.54 min and 11.87 min, representing 2-chloroethyl ethyl sulfoxide (2-CEESO) and 2-chloroethyl ethyl sulfone (2-CEESO<sub>2</sub>), respectively (Fig. S5). Here, 2-CEESO is the oxidation product of 2-CEES with little toxicity, which is a desired product for 2-CEES degradation [34]. Overoxidation to 2-CEESO<sub>2</sub> is not wanted because sulfone is also highly toxic [35]. The oxidation process is shown in Fig. 5g. Their formation is due to the action of oxidizing substances, adding one or two oxygen to the S atom of 2-CEES. The toxicity of sulfur mustard is allied to the electrophilic character owing to the anchimeric assistance of S atom, and their neutralization is realized by the deactivation of this electronic assistance [36].

Fig. 6a-d show the change of the concentration of 2-CEESO and 2-CEESO<sub>2</sub> during the decontamination process. In the early stage of degradation process, the 2-CEESO concentration is proportional to the microplasma treatment time, indicating that 2-CEES is gradually converted into 2-CEESO. As shown in Fig. 6a, it needs shorter time to reach the maximum 2-CEESO content in the negative DC and AC mode (120 s) than in the positive DC mode (240 s), which are consistent with the result of 2-CEES reduction (Fig. 4). After 120 s, the 2-CEESO content in the negative DC and AC mode decrease slightly. Fig. 6b shows that 2-CEESO<sub>2</sub> is neither detected before 80 s in the negative DC and AC mode, nor before 120 s in the positive DC mode, which is a satisfying situation. After that, the 2-CEESO<sub>2</sub> signal appears. These results suggest that the plasma treatment time is not the longer the better, otherwise large amount of unwanted 2-CEESO2 will be produced. Luckily, a proper time window does exist when 2-CEES are mostly converted to 2-CEESO but not 2-CEESO<sub>2</sub>. In all, the negative DC and AC mode performs better than the positive DC mode, which is consistent with the degradation rate.

To better clarify the oxidation path of 2-CEES under our microplasma treatment, 150 mg/L 2-CEES in AC mode is treated for a longer period to



Fig. 5. Chromatograms of the degradation products. (a-c) Chromatograms of 2-CEESO after AC, positive DC, and negative DC microplasma treatment; (d-f) Chromatograms of 2-CEESO<sub>2</sub> after AC, positive DC, and negative DC microplasma treatment; (g) Oxidation path of 2-CEES.

observe the conversion of 2-CEESO to 2-CEESO<sub>2</sub>, as shown in Fig. 6c and Fig. 6d. The relevant chromatograms are shown in Fig. S6. At 200 s of the microplasma treatment in the AC mode, the decontamination rate reaches more than 99% (Fig. 4a), and the 2-CEESO reaches its maximum concentration (Fig. 6c). During this period, the 2-CEESO<sub>2</sub> concentration increases slowly and keeps at a low level (Fig. 6d). After 200 s, the concentration of 2-CEESO begins to decrease, while the 2-CEESO<sub>2</sub> concentration starts to increase rapidly. The above results demonstrates that 2-CEES has been completely converted to 2-CEESO at 200 s, with minor amount of 2-CEESO<sub>2</sub> generated, which is the most wanted result for 2-CEES decontamination. Therefore, the generation of toxic 2-CEESO<sub>2</sub> can be effectively avoided by controlling the microplasma treatment time to achieve the desired degradation result.

#### 3.4. Ozone concentration and spectroscopic characterization

2-CEES can be oxidized by the plasma due to its rich free radicals and active species. To further elucidate the degradation results, the emission spectra of our air microplasma and O<sub>3</sub> concentration are performed. Fig. 7a illustrates the results of microplasma spectrum acquisition in three modes. In all spectra, OH ( $A^2\Sigma^+ \rightarrow X^2\Pi$ ) emission at 306–309 nm, N<sub>2</sub> second positive system N<sub>2</sub> ( $C^3\Pi_u \rightarrow B^3\Pi_g$ ) at 330–420 nm, N<sub>2</sub><sup>+</sup> first negative system N<sub>2</sub><sup>+</sup> ( $A^2\Pi_u \rightarrow X^2\Sigma_g^+$ ) at 390–420 nm and H- $\alpha$  emission at 656.3 nm are observed. The main formation reactions of OH, N<sub>2</sub> ( $A^3\Sigma^+_u$ ), O (<sup>1</sup>D), and H etc. active species in microplasmas are given as

follows [37-39]:

$$v + O_2 \rightarrow O^- + O$$
  $1.2 \times 10^{-12} \ cm^3 s^{-1}$  (1)

$$e + O_2 \rightarrow e + O + O(^1D)$$
  $3.2 \times 10^{-11} \ cm^3 s^{-1}$  (2)

$$e + O_2 \rightarrow O^+ + O + 2e$$
  $4.6 \times 10^{-16} \ cm^3 s^{-1}$  (3)

$$O(^{1}D) + H_{2}O \rightarrow 2OH$$
  $2.3 \times 10^{-10} \ cm^{3}s^{-1}$  (4)

$$e + H_2 O \rightarrow e + H + OH$$
  $2.6 \times 10^{-12} cm^3 s^{-1}$  (5)

$$e + N_2 \rightarrow e + N_2 \left( A \sum_{u}^{+} \right)$$
  $1.1 \times 10^{-10} \ cm^3 s^{-1}$  (6)

Reactions (1)-(3) can produce a lot of O atoms and O ( $^{1}$ D), and it has been reported that OH formation is mainly due to the interaction of O ( $^{1}$ D) and H<sub>2</sub>O in reaction (4) in a humid air [40]. The negative DC and AC have similar N<sub>2</sub> emission intensity, which are much higher than that of the positive DC (Fig. 7a). Related reports have proven that negative DC can generate more energetic electrons, so more electrons participated in reaction (6), causing a higher N<sub>2</sub> emission intensity in the negative DC mode compared to positive DC mode [41]. This is consistent with the result that the negative DC and AC have better degradation effect than the positive DC.

Besides short reactive species, long-life species such as the O3



Fig. 6. Curves of the degradation products. (a) 2-CEESO curve in the three modes microplasma treatment; (b) 2-CEESO<sub>2</sub> curve in the three modes microplasma treatment; (c) 2-CEESO curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEESO<sub>2</sub>); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-CEESO<sub>2</sub> curve in the AC microplasma treatment (150 mg/L 2-CEES); (d) 2-



Fig. 7. Emission spectra and O<sub>3</sub> concentration. (a) Emission spectra of corona discharge with 2-CEES in different modes; (b) O<sub>3</sub> concentration of the three modes at 0–320 s.

generated in the discharge process also have strong oxidizing ability. An  $O_3$  detector is used to measure the  $O_3$  concentration in three modes at different discharge time. It can be seen from Fig. 7b that the  $O_3$  concentration has a good linear relationship with the discharge time in three modes. Negative DC and AC discharge produced similar  $O_3$  concentrations. However, the  $O_3$  concentration of positive DC is only 6.23 ppm at 320 s, much lower than those of negative DC (10.93 ppm) and AC (9.37 ppm). The formation of  $O_3$  is main due to the addition of O atoms

to O2 molecules:

$$O + O_2 + M \to O_3 + M, M = O, O_2, O_3 N_2$$
(7)

$$O(^{1}D) + O_{2} \rightarrow O_{3} \tag{8}$$

O<sub>3</sub> can also be formed by ions:

$$O_2^- + O \rightarrow O_3 + e \tag{9}$$

Both of the O and O (<sup>1</sup>D) are involved in the reactions (7)-(9). In the reaction (1)-(3), the more electrons participate, the more O and O (<sup>1</sup>D) generated, which are used to form  $O_3$ .

### 3.5. Calculation of electron density by simulation

Electrons in the plasma are essential for 2-CEES degradation, either by direct cracking or reactive species oxidation. The discharge processes in air applied by three different discharge modes are simulated via COMSOL. Simulation details are given in the Supplementary materials.

Fig. 8a-d show the simulation results of electron density distribution in the three modes. The maximum electron density reaches  $1 \times 10^{21}$ /m<sup>3</sup>, which is consistent with previous reports [26,42]. Fig. 8a (i-iii) and Fig. 8b (i-iii) are the electron density distribution maps of the negative half cycle and positive half cycle of the AC mode, respectively. At one-quarter (Fig. 8a (iii)) and three-quarter cycle (Fig. 8b (iii)), the average electron density are  $2.76 \times 10^{16}$  /m<sup>3</sup> and  $1.81 \times 10^{16}$  /m<sup>3</sup>, respectively. Fig. 8c (i-iii) and Fig. 8d (i-iii) are the negative DC and positive DC electron density distribution maps. The electron density distribution in the negative DC mode is roughly the same as the negative half cycle of AC. This is due to the fact that the potential of plate electrode is higher than that of needle electrode in both of negative DC and AC modes. But the average electron density is  $1.01 \times 10^{18}$  /m<sup>3</sup> at 120 ns in the negative DC mode, which is higher than that of AC, even though the frequency is 100 kHz. Similarly, the electron density distribution of positive DC is roughly the same as the positive half cycle of AC, but the average electron density is  $2.5 \times 10^{17}/m^3$  at 120 ns, which is lower than that of negative DC, but still higher than AC.

To further explain the difference in electron density, the electric field intensity distribution of the negative DC and positive DC are compared, as shown in Fig. S7a (i-iii) and Fig. S7b (i-iii). Whether positive DC or negative DC, a horizontal electric field is formed on the dielectric layer surface due to the interfacial charges accumulation [43]. Different from negative DC, due to the positive charges accumulation on the dielectric layer surface, the positive DC also forms a vertical electric field opposite to the applied electric field direction, which weakens the applied electric field. Therefore, the average electric field strength of positive DC (3.49  $\times 10^5$  V/m) is lower than that of negative DC ( $-3.54 \times 10^5$  V/m) at 90 ns, which explains the higher electron density in the negative DC mode.

The number of electrons that reach the dielectric layer surface is very important. The electron density in the negative DC and positive DC modes are compared at a distance of 0.01 mm, 1 mm, and 4 mm from the dielectric layer surface at  $3 \mu s$  as shown in Fig. 8e. The electron density in the negative DC mode is significantly higher than that in the positive DC mode at all distances. Meanwhile, due to the existence of



**Fig. 8.** Electron density distribution. The negative half cycle (a) and positive half cycle (b) of the AC mode at 1.2 µs (i), 1.5 µs (ii), and 2.5 µs (iii). The negative DC (c) and positive DC (d) mode at 0.06 µs (i), 0.09 µs (ii), and 0.12 µs (iii). The electron density distribution curves (e) and electric field distribution curves (f) of the negative DC and positive DC mode at different distances from the dielectric layer surface at 3 µs.

vertical electric field, there is extremely low electron density at a radial distance of - 0.6–0.6 mm, which is consistent with the lower degradation rate. To illustrate the formation of vertical electric field in the positive DC mode, Fig. 8f compares the electric field strength between positive DC and negative DC at different positions in the vertical direction. In positive DC mode, an extremely high electric field is observed near the dielectric surface. However, in negative DC mode, the electric field intensity hardly changes with distance and remains at a low value. In summary, the simulation results prove that negative DC produces more energetic electrons, which is consistent with the results of optical spectra, O<sub>3</sub> concentration, and 2-CEES degradation rate.

Finally, the energy utilization efficiency ( $E_e$ ) of dps-TENG driven microplasma is calculated and compared with literatures. The  $E_e$  of different power sources to degrade CWAs is summarized in Supplementary material Table S2. The  $E_e$  was obtained according the following formula:

$$E_e = \frac{(M_0 - M_t)}{P_t} \tag{10}$$

where  $M_0$  is the 2-CEES initial amount,  $M_t$  is the residual 2-CEES amount after plasma treatment for *t* seconds, *t* is the plasma treatment time, and *P* is the average discharge power. The discharge voltage and current in negative DC mode are adopted for the calculation of the  $E_e$  of TENG [44], and the average discharge power is 0.064 W. The  $E_e$  of the dps-rTENG is calculated to be 0.520 µg/J, which is one order of magnitude higher than that of commercial power supply. Therefore, the dps-rTENG consumes much less energy to degrade the same amounts of CWAs.

#### 3.6. Demonstration of self-powered dps-rTENG

Except for driven by a motor, the dps-rTENG can also be driven by human motions with the help of multi-stage gears, as shown in Fig. 9a-c. The multi-stage gears can convert 1 Hz input frequency to 22 Hz output. Driven by a slow hand swing, the output voltage and current of the multi-stage gear dps-rTENG reach 3 kV and 120  $\mu$ A, respectively; and the frequency is 55 Hz. The demonstration video is displayed as Video S5 in the Supplementary materials. This output is adequate to induce air microplasma in our study. The multi-stage gears structure provides possibility to do real self-powered CWAs degradation for individual combat in future.

Supplementary material related to this article can be found online at doi:10.1016/j.nanoen.2022.106992.

# 4. Conclusion

In this work, we present a microplasma decontamination system for 2-CEES based on a dps-rTENG. The output voltage of the dps-rTENG reaches up to 3 kV, which successfully excites microplasma in air. The dps-rTENG is applied to decontaminate 2-CEES in AC, negative DC, and positive DC modes. The degradation rate of 2-CEES (40 µL; 100 mg/L) reaches more than 99% within 2 min, and the  $E_e$  of dps-rTENG reaches  $0.520 \,\mu g/J$ , which is one order of magnitude higher than those of the reported commercial power supplies. Meanwhile, after analyzing the different discharge and degradation process among the three modes, the results show that the negative DC and AC modes produce more energetic electrons and active species in the air plasma, which lead to better degradation effect. In addition, by controlling the microplasma treatment time, this system can effectively avoid the generation of toxic 2-CEESO<sub>2</sub>, which is critical to solve the problem of over-oxidation. Finally, a manually driven dps-rTENG is demonstrated which can generate adequate output for microplasma induction. This system has the advantages of self-power, simple structure, easy portability, and low cost, providing a new approach to decontaminate 2-CEES or other CWAs. This work not only extends the application of TENG, but also has great significance for the degradation of CWAs in individual combat.

# CRediT authorship contribution statement

Yuan Bai: Methodology, Visualization, Writing – original draft, Shubin Chen: Methodology, Visualization, Writing – original draft, Huiyan Wang: Methodology, Engui Wang: Methodology, Xianghao Kong: Methodology, Yansong Gai: Methodology, Xuecheng Qu: Methodology, Qi Li: Methodology, Shuang Xue: Methodology, Peiwen Guo: Methodology, Ruixue Wang: Conceptualization, Writing – review & editing, Funding acquisition, Hongqing Feng: Conceptualization, Writing – review & editing, Funding acquisition, Zhou Li: Conceptualization, Writing – review & editing, Funding acquisition.



Fig. 9. The dps-rTENG is driven manually after adopting multi-stage gears. (a) Photograph of the dps-rTENG driven by a human hand. (b-c) The front and back sides of the manually driven dps-rTENG. (d-f) The voltage, current and the multi-stage gears of the dps-rTENG.

# **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.

#### Acknowledgments

This work is supported by the National Natural Science Foundation of China (81971770, T2125003, 61875015, 51877205, 61875015 and 52011530191), Beijing Natural Science Foundation (JQ20038 and L212010), the Fundamental Research Funds for the Central Universities (BUCTRC201906 and BUCTZY2022), Key Project of Beijing University of Chemical Technology (XK1803-06), National Key Research and Development Program of China (2018YFA0903000 and 2020YFA0712102), and Funds for First-class Discipline Construction (XK1805), State Key Laboratory of NBC Protection for Civilian (SKLNBC2021-0X) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA16021101).

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2022.106992.

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