

Effect of Humidity on Plasma Discharge, Reaction Species Generation and Indoor Air Purification

5.1 Introduction

In recent decades, atmospheric pressure plasma discharges have been extensively studied for indoor air purification [Timmermann et al., 2018] [Asilevi et al., 2021; Xia et al., 2019a; Zhao et al., 2019]. This method is recognized for its efficiency, energy savings, and environmental benefits in removing contaminants [24, 25]. In these plasma systems, high-energy electrons (HEEs) collide with gaseous molecules, leading to their ionization and excitation, which generates electrons, radicals, ions, and excited molecules [Ahlawat et al., 2024a] [Pandey et al., 2023]. However, unlike controlled laboratory environments, indoor air purification is significantly influenced by environmental conditions, particularly relative humidity (RH) [Ki et al., 2019] [Liu et al., 2022]. RH plays a vital role in characterizing plasma because it is an environmental parameter that fluctuates continuously. RH influences multiple parameters like electrical parameters, i.e. discharge current and power, the generation of different reactive species (N , N_2^* , $\bullet OH$, O_3 , etc.), and the antimicrobial disinfection efficiency of APP [Zhang et al., 2018].

In this context, Lukes et al. [Lukes et al., 2012] demonstrated how reactive species like $\bullet OH$, H_2O_2 and O_3 were produced by an electrical discharge plasma at the gas-liquid interface, which has a potent effect on microorganisms. Ki et al. [Ki et al., 2019] investigated the effect of RH on the discharge plasma in a chamber measuring 0.175 m^3 . They showed that the concentration of $\bullet OH$ and H_2O_2 increased two-fold in the HH condition compared to the LH condition. In contrast, the concentration of O_3 was reduced to halve. Timmermann et al. [Timmermann et al., 2018] showed that humidity is one of the critical, influential parameters for the surface DBD; it affects the discharge characteristics and the generation of reactive species. Due to their powerful redox properties, the reactive species produced during the plasma discharge process play a major role in the removal of various microorganisms. A primary focus of this study is to understand the action mechanism of reactive species on naturally occurring airborne microorganisms (TBCs and TFCs). This is because the elimination process needs to be better understood, especially in HH conditions.

In this chapter, a DBD-APP source has been developed to see the effect of low humidity (20% – 40%) and high humidity (70% – 90%) on the electrical and optical properties, the generation of different active species and their effect on the removal of TBCs and TFCs in an enclosed environment [Jangra et al., 2024]. Moreover, the investigation of the plasma-generated species has been carried out in the LH and HH environments. The indoor air disinfection has been examined in lab conditions.

The following are the key elements of originality in this research:

1. By coating one of the electrodes of the DBD-APP source with TiO_2 NPs, it has been shown that plasma-produced HEEs have sufficient energy to activate the catalyst.
2. The O_3 production by the DBD-APP source has been found to be below 150 ppb, which is the allowable concentration for indoor environments.
3. To check the disinfection in larger and actual indoor environments with a short time duration, a typical office room with a volume of approx. 28 m^3 has been used.

4. The study on naturally occurring microorganisms (such as TBCs and TFCs) is special since most of the previous studies used lab-cultured microorganisms.
5. The role and mechanism of the active air ions and reactive species generated from the TiO₂-coated outer electrode in the disinfection process are highlighted.

5.2 DBD-APP Source and Experimental Setup

An already described plasma source in Figure 2.3 of chapter 2 (named in this chapter as DBD-APP source) has been used for the detailed analysis. The DBD-APP source is housed in a rectangular stainless-steel box for further experimentation. A DC motorized fan is installed at the end of the box to circulate the ionized air (active air ions and reactive species) in the enclosed space. All experiments are performed using a bipolar microsecond pulsed power source. The initial value of RH in the indoor environment was $50 \pm 5\%$, which has been adjusted using a commercial humidifier/dehumidifier, and the values are measured using a Hygro-thermometer probe (ELTH-2, Elinco Innovations, India). Because of the difficulties associated to precisely measure indoor environment RH, this study has been focused on only two distinct RH ranges. The schematic representation of the experimental setup for indoor air disinfection by the DBD-APP source is described in Figure 5.1. The developed DBD-APP source is then used for the elimination of naturally occurring microorganisms from the indoor environment.

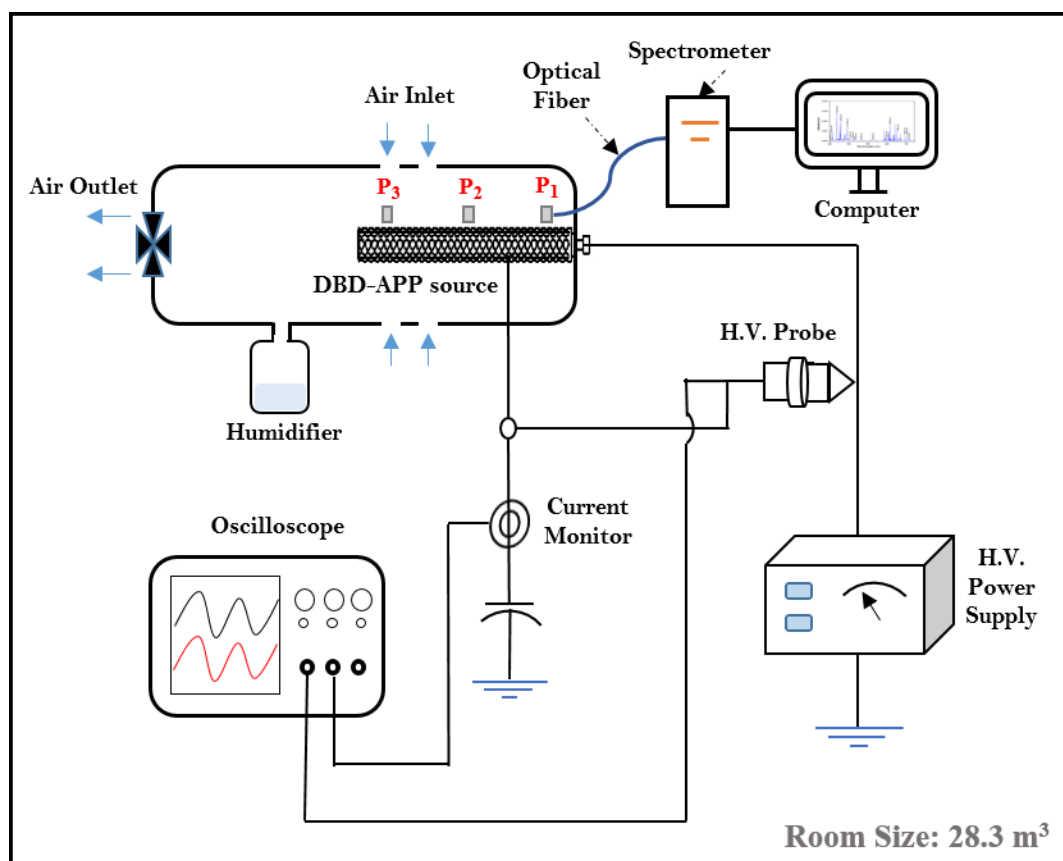


Figure 5.1: Schematic diagram of the complete experimental setup for indoor air purification by DBD-APP source.

5.3 Experimental Analysis and Discussion

5.3.1 Discharge Characteristics of DBD-APP Device

The voltage-current (VI) characteristics of the plasma discharge at different RH conditions are shown in Figures 5.2 (a) and 5.2 (b) at the same input parameters (4 kV/20 kHz). These are for the low humidity (LH: 20% – 40%) and high humidity (HH: 70% – 90%) cases, respectively. For the same input parameters (4 kV/20 kHz), in the LH case, the discharge current is ~ 185 mA, and the estimated discharge power is ~ 7.7 W. But for the HH case, the discharge current decreased to ~ 145 mA, and consequently, the discharge power ~ 5.6 W. A similar effect has been seen by Ki et al. [Ki et al., 2019], they found that the increase in RH caused a decrease in the power consumed in a surface DBD reactor operated at the same applied voltage. This is due to the fact that water vapour in a barrier discharge decreases the surface resistance of the dielectric and reduces the discharge current. Abdelaziz et al. [Abdelaziz et al., 2018] investigated the effect of humidity on the surface DBD for naphthalene decomposition and observed that humidity does not affect the discharge mode (filamentary), but it significantly impacts the properties, especially the amplitude of the discharge current.

In the LH case, the minimum discharge power obtained is 3.75 W at the breakdown voltage of 2.5 kV, as shown in Table 5.1. The discharge power increases with the applied voltage, reaching up to 26.55 W at 5.5 kV. In contrast, for the HH case, the breakdown voltage to ignite the discharge is 3.5 kV, but the minimum discharge power obtained is 3.81 W (nearly equal to the LH case for 2.5 kV). However, when the voltage is increased further after the breakdown, the power obtained in the HH is lesser as compared to the LH case, and the main reason for this behavior is the contraction of the discharge current [(see Figure 5.2)]. It can also be observed that the breakdown voltage under the HH discharge condition is higher as compared to the LH discharge condition despite having the same discharge power. This is due to the presence of more water vapors (in HH case), which is electronegative in nature (i.e., water vapors have an affinity of electrons). Thus, free electrons in the gap are attracted to these vapors, causing a delay in the ionization process, which in turn increases the breakdown voltage. As the change in RH affects the amount of power used to generate plasma, it can also influence the generation of different reactive species during plasma discharge.

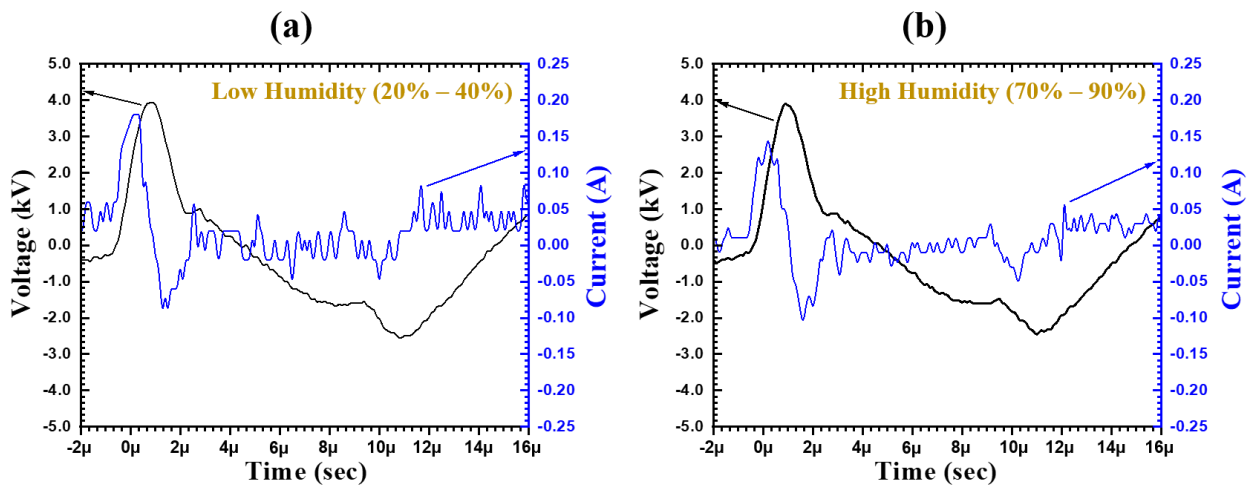


Figure 5.2: Typical VI characteristics of DBD-APP source in (a) LH and (b) HH conditions.

Table 5.1: The discharge power as a function of different applied voltages.

Voltage (kV)/Discharge Power (W)	2.5	3.0	3.5	4.0	4.5	5.0	5.5	6.0
LH	3.75	4.15	4.95	7.74	10.15	13.84	26.55	32.74
HH	-	-	3.81	5.63	7.68	9.88	18.65	24.31

5.3.2 Optical Emission Spectroscopy of DBD-APP Source

The emission spectrum were taken at both central (P_2) and edge discharge locations (P_1 and P_3) in order to examine the spatial distribution of plasma parameters over the discharge regime, as depicted in Figure 5.1. Figure 5.3 shows the OES for the gas-phase characterization of the excited species under LH and HH conditions at centralized position (P_2). The recorded spectra at other discharge locations (P_1 and P_3) are similar to the centralized position, which confirm the spatial distribution of plasma discharge. The spectra are dominated by the peaks related to N_2 second positive system (SPS, $C^3\Pi_u \rightarrow B^3\Pi_g$) emissions at 316.3, 337.1, 353.5, 357.6, 376.0, and 380.4 nm wavelengths and the peaks at 391.4, 399.9, and 405.3 nm are ascribed to the first negative system of N_2^* (FNS, $C^2\Sigma_u^+ \rightarrow B^3\Sigma_g^+$), accompanying with the generation of electronically excited N_2 ($A^3\Sigma_u^+$) and ionized nitrogen species generated during the discharge process [Nikiforov et al., 2011]. The reason for this is the very high concentrations of molecular nitrogen (N_2) in the atmosphere and their direct and step-wise electron impact excitations from the molecular ground state and the first metastable state [Misra et al., 2015]. The decrease in the emission intensity of N ($2D \rightarrow 4S$, 746.8 nm) and O ($^5S_0 \rightarrow ^5P$, 777.1 nm) can also be observed with the increase in RH. This is due to the fact that the presence of heavy species (H_2O) might influence the efficiency of energy transfer, through various mechanisms, including inelastic collisions, vibrational and rotational excitations, electronic excitations, and ionisation processes, leading to a decrease in the electron temperature [Nikiforov et al., 2011].

As Ye et al. [Ye et al., 2017] have also noted, it is challenging to identify the emission of OH(A-X) at 308 nm in air discharges. It was probably because the quenching of excited OH radicals by O_2 , N_2 and H_2O molecules is much faster than the de-excitation processes to the ground state [Yao et al., 2016], making it very difficult to observe OH in the spectra. Nonetheless, it is undeniable that air plasma discharge contains $\bullet OH$ as a weak emission signal from the $\bullet OH$ is apparent between 306 and 309 nm. The $\bullet OH$ production mainly involves dissociation (equation 5.1) and collision reaction (equation 5.2). The OES also reveal that the emission intensity of $\bullet OH$ is higher in the case of HH conditions compared to LH conditions. In the HH conditions, the increase in H_2O concentration causes more collisions between electrons and H_2O molecules, producing more $\bullet OH$ (equation 5.1). Meanwhile, more H_2O molecules can gain $O(1D)$ to generate $\bullet OH$ and restrict O_3 production (equation 5.2), which otherwise reacts with O_2 and forms O_3 (equation 5.3).

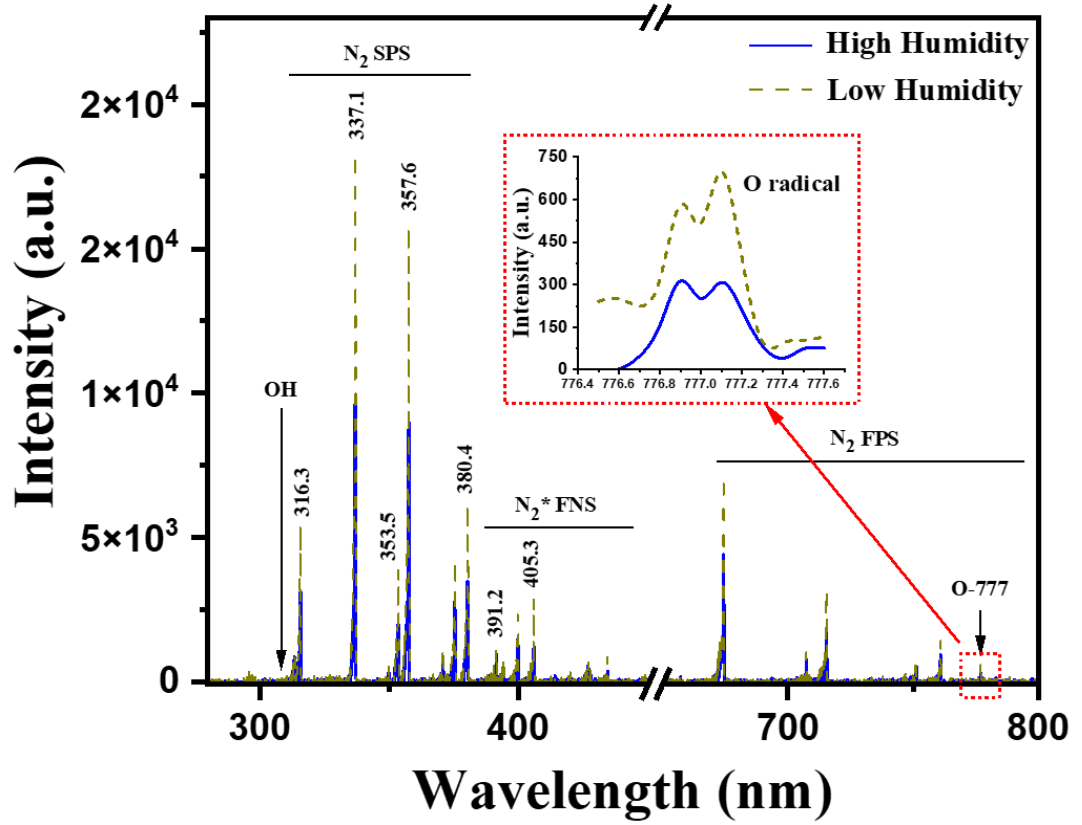


Figure 5.3: Optical emission spectrum of DBD-APP source under LH and HH conditions (inset shows the comparison of emission intensity of atomic oxygen at 777.1 nm).

The presence of $O(1D)$ can also be verified by a prominent peak at 777.1 nm (see inset of Figure 5.3) in the emission spectra, which is attributed to excited oxygen atoms [Misra et al., 2015]. It has been observed that the peak at 777.1 nm has been decreased in the HH case, as also mentioned by Zhou et al. [Zhou et al., 2021].



Due to the quick depopulation of excited atomic oxygen in the air DBD plasma, the atomic oxygen emission in this study is found modest. Also, due to the interaction with water molecules, the peak of atomic oxygen in the OES is reduced in the HH environments (equation 5.2). Using the OES investigations, it is not possible to identify and quantify the O_3 formation. Detecting O_3 directly using OES is challenging because O_3 does not have strong or characteristic optical emission lines in the spectral range typically accessible by standard OES setups. O_3 formation in DBD plasma involves the reaction of atomic oxygen (O) with O_2 . Monitoring the emission lines of atomic oxygen, particularly the $O(1D)$ lines at 777.1 nm, can provide indirect evidence of O_3 formation [Rezaei et al., 2014]. OES investigations provide an idea about the formation of $\bullet OH$, but the quantification of $\bullet OH$ needs to be done further. An analysis of these aspects was conducted through the use of an O_3 analyzer and a chemical probe method. The findings from these techniques are presented in detail in the following sections.

5.3.3 Estimation of Electron and Gas Temperature

The optical emission spectroscopic analysis is a useful technique to determine the plasma parameters, particularly, electron temperature (T_e) [Isola et al., 2010]. The method that depends on the relative intensities of two spectral lines that belong to the same atomic species is preferred over other methods for calculating the electron temperature using OES because it eliminates the need to know the number density of the atomic species. In this study, using the intensities of two spectral lines (380.4 nm and 391.2 nm) of excited nitrogen molecules, the electron temperature of the DBD air plasma has been estimated. The total emission intensity corresponding to two spectral lines are shown in Table 5.2.

Table 5.2: The effect of applied voltage and relative humidity on the emission intensity of N₂ (380.4 nm and 391.2 nm) atomic lines.

Voltage (kV)/Spectral Line (nm)	Low Humidity		High Humidity	
	Total Intensity (a. u.)			
	380.4	391.2	380.4	391.2
3.5	2257	615	1582	489
4.0	2857	783	2208	532
4.5	3152	1060	3158	987
5.0	3535	1289	3617	1312
5.5	4163	1842	3954	1687

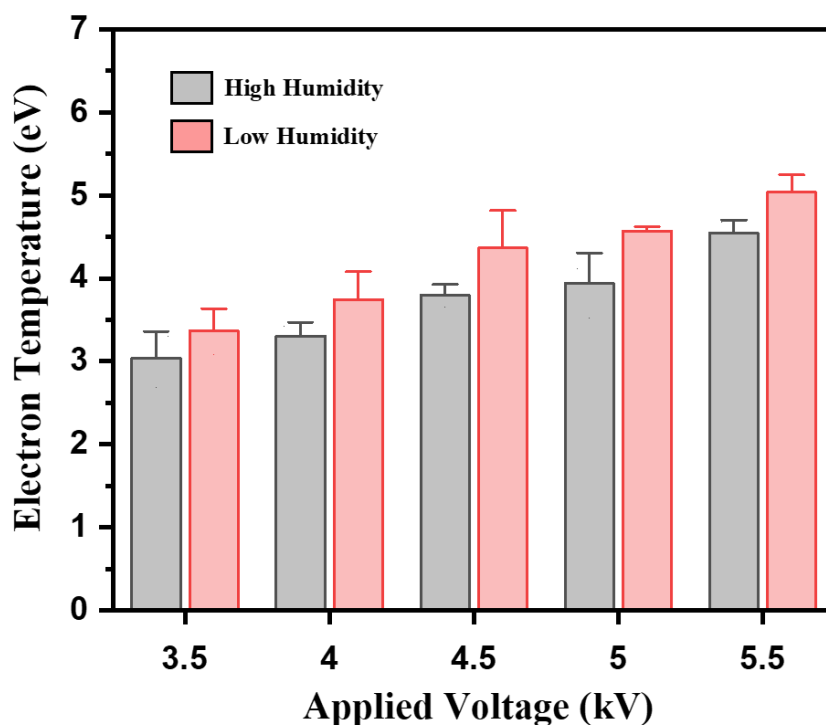


Figure 5.4: Variation of electron temperature at different applied voltages (3.5 – 5.5 kV) and at a fixed pulse repetition rate of 20 kHz with varying humidity.

At different RH, the electron temperature of air DBD plasma at different applied voltage keeping pulse repetition frequency fixed (i.e., 20 kHz) is shown in Figure 5.4. The electron temperature in the HH condition is somewhat lower than in LH. This is because the presence of

heavy species (H_2O) alters the efficiency of energy transfer. It is important to note that the electron energy is high enough (> 3.2 eV) to activate the TiO_2 catalysts, which produce electron-hole pairs and various other species.

The emission spectra of N_2 (C-B) are also used to determine the rotational temperature (T_{rot}) or gas temperature of the SPS of N_2 by fitting the experimental spectra with the simulated ones using LIFBASE software [Van Surksum et al., 2018]. The peak correlation, which is basically a term used for defining the best fit between the measured and simulated spectra was in the range of 0.794 ($\sim 79.4\%$). Under the experimental condition 4 kV/20 kHz, the rotational/gas temperature obtained by fitting is 450 K, which can be converted to 176.85 °C. Meanwhile, the reactor surface temperature is only 30 – 40 °C. Therefore, it can help prove that the excitation of N_2 and H_2O molecules is due to the high energetic electrons produced by the DBD-APP source, which in turn heats the surrounding molecules.

5.4 TiO_2 Characterization and Impact on Reactive Species Generation

The optical bandgap (E_g) energy of the synthesized TiO_2 NPs has been determined using the Tauc equation and Kubelka-Munk method [Makula et al., 2018]. A linear plot of the straight-line proportion of photon energy ($h\nu$) versus ($\alpha h\nu^{\frac{1}{2}}$) is extrapolated to determine the precise values of the indirect band gap of NPs. The indirect band gap of the synthesized TiO_2 NPs is found to be 3.21 eV (in the anatase phase), as can be seen from Figure 5.5 (a). XRD has been performed to investigate the crystal phase of the synthesized TiO_2 NPs and the obtained patterns are shown in Figure 5.5 (b). The XRD pattern exhibited peaks at 25.31°, 36.02°, 37.89°, 48.02°, 53.96°, 55.09°, 62.73°, 68.81°, 70.29° and 75.11°. These peaks are corresponding to the crystal planes of (101), (103), (004), (200), (105), (211), (204), (106), (220) and (215), respectively. The XRD pattern is well-matched to the pattern of anatase TiO_2 according to the reference JCPDS card 21-1272 [Chen et al., 2022] [Wei et al., 2013].

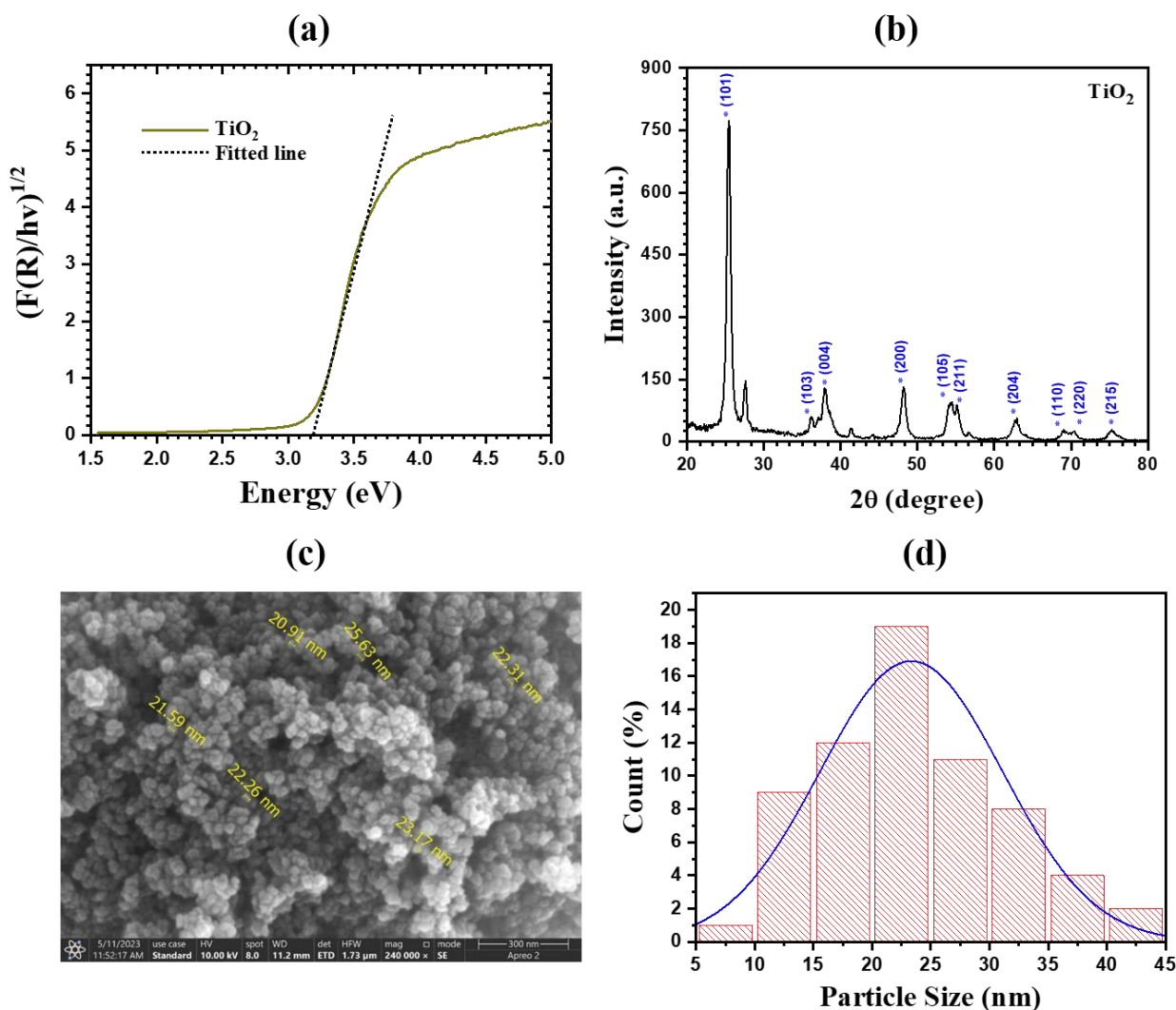


Figure 5.5: (a) Optical band gap calculation, (b) XRD patterns and (c) FE-SEM image of synthesized TiO₂ NPs annealed at 450 °C, (d) particle size distribution histogram with Gaussian fitting.

The surface morphology of synthesized TiO₂ NPs is examined by the FE-SEM micrograph and is shown in Figure 5.5 (c). The FE-SEM images revealed that the NPs exhibit a homogeneous distribution, whereas their size displays non-uniformity. The average particle size has been determined by fitting the particle size distribution function as described by Jalili et al. [Jalili et al., 2019] and shown in Figure 5.5 (d). The average particle size and standard deviation are estimated using a particle size distribution histogram via ImageJ software (version 2.0). The calculated average particle size is 22 nm with a standard deviation of 1.6 nm, which confirms the formation of TiO₂ NPs. A scotch tape test was conducted to evaluate the coating's adhesiveness, revealing that it remains stable and does not degrade over time.

As already discussed in previous chapter, it is well known that TiO₂ can be activated when sufficiently strong photonic energy ($h\nu > 3.2 \text{ eV}$) is used to bridge the band gap between the VB and the CB, leading to the generation of electron-hole pairs [Etacheri et al., 2015]. The dominant N₂ (C-B) peaks (between 300 – 400 nm, see Figure 5.3) in the emission spectra confirm that the plasma discharges can produce UV light. However, due to its lower intensity than conventional UV lamps, the UV light generated by plasma sources is not necessarily the key factor in activating photocatalysts [Mei et al., 2016b]. Whitehead [Wallis et al., 2007] suggested that in the plasma catalysis systems, electron-hole pairs can be formed by the electron impact on the surface of catalysts, typically possessing a mean energy of $> 3.2 \text{ eV}$, in a manner analogous to UV photons. So, the main activation factor of TiO₂ photocatalysts could be the presence of HEEs generated by the plasma discharge.

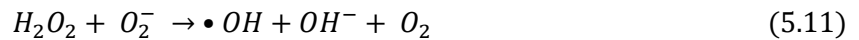
Moreover, the surface property and the change in the chemical states of the TiO₂ NPs were assessed using XPS analysis. Figure 5.6 shows the XPS spectrum recorded for the synthesized TiO₂. There are two spectra observed: one is for O1s and the other for Ti2p. In Figure 5.6 (a), the peak observed at 529.52 eV is mainly observed for TiO₂. Another peak observed at 531.20 eV is possibly attributed to the adsorbed hydroxyl and oxygen ion; a broad peak of this suggests that they are weakly bound [Bharti et al., 2016]. Figure 5.6 (b) represents the spectrum of Ti2p, in which two doublet peaks are observed, Ti2p_{3/2} and Ti2p_{1/2}, at binding energy 458.32 eV and 463.98 eV, respectively. This observed doublet is because of the spin-orbit coupling interaction [Cottre et al., 2021]. Other than *Ti* and *O*, there is no other peak observed, which suggests the phase purity of the synthesized TiO₂.

Also, the XPS data for TiO₂ after plasma exposure is recorded and shown in Figure 5.6 (c) and 5.6 (d). From the data, it is found that there is an increment of binding energy value 0.02 eV in O1s and a decrease in binding energy 0.25 eV in the (O, OH) peak. Similarly, the binding energy of Ti2p_{3/2} is also decreased by 0.02 eV, and the binding energy of Ti2p_{1/2} is increased by 0.01 eV. The density of the charge increases or decreases depending on whether there is an increase in binding energy or a decrease in binding energy. There is no significant change observed for Ti2p, which is also consistent with the previously reported results [Krishnan et al., 2017]. A significant increment in the binding energy suggests that there is a decrement in the charge carrier [Wang et al., 2021b]. From XPS spectra of O1s, it is further observed that the change in binding energy before and after plasma exposure (for O, OH) has significantly decreased by 0.25 eV, this might be due to the fact that during plasma exposure TiO₂ release hydroxyl ions, result in decrement of the hydroxyl ion charge carrier. These releases of hydroxyl ions can significantly enhance the active ions and reactive species generation of the DBD-APP source [Simonsen et al., 2009].

These HEEs, generated from the DBD-APP source, along with the electron-hole pairs generated by the TiO₂ NPs, further can react with the water vapors present in the air as,



Further, there are a set of reactions from which the generation of $\bullet OH$ can take place [Zhang et al., 2018].



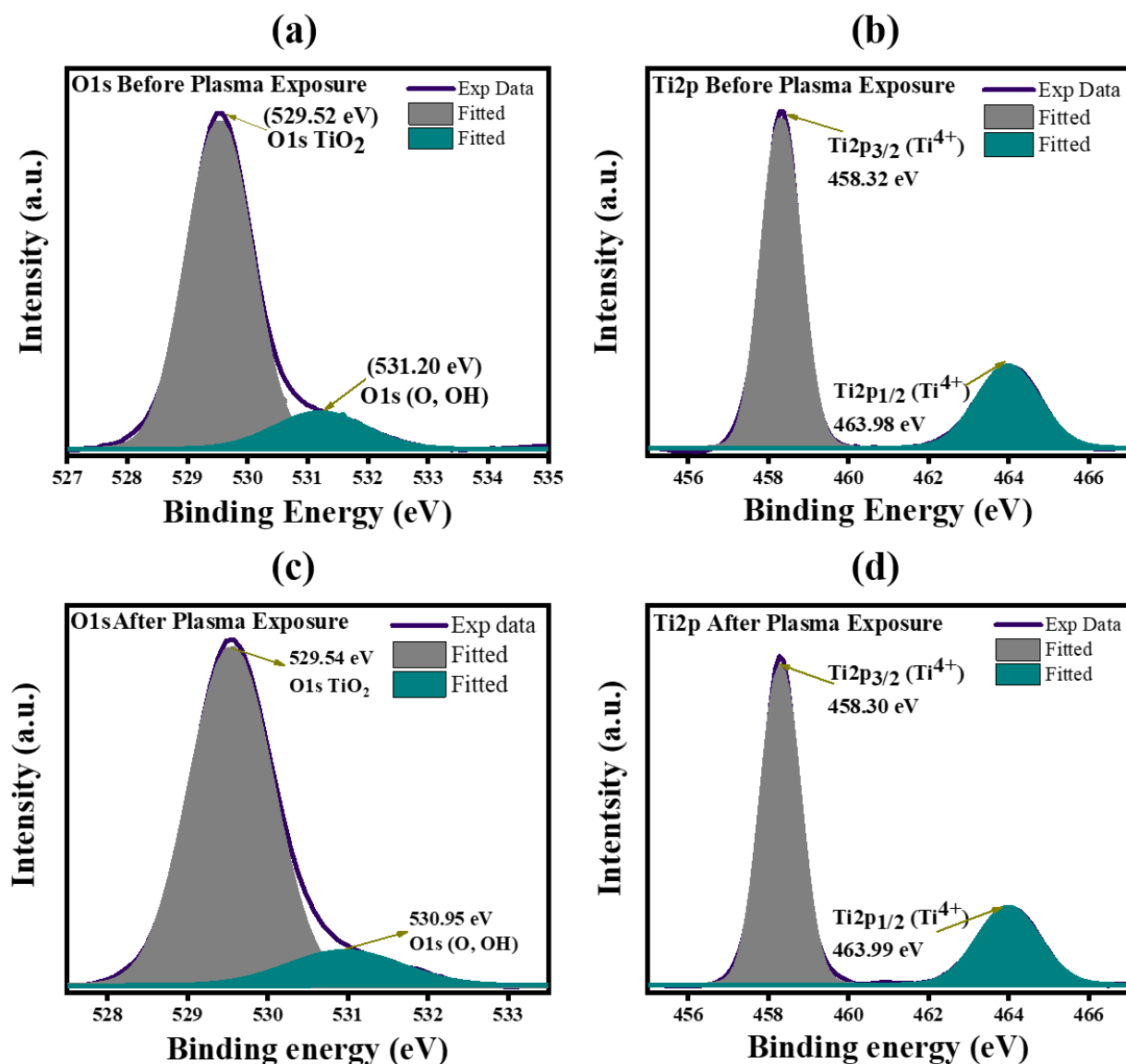


Figure 5.6: High resolution XPS spectra of Ti2p and O1s in TiO₂ NPs (a, b) before plasma exposure (c, d) after plasma exposure.

5.5 Effect of Humidity on Reactive Species Generation

As depicted in above equations (5.4 – 5.11), when TiO₂ generated electrons and holes collide with different molecules they will lead to generation of negative air ions (NAI) and positive air ions (PAI). The concentrations of NAI and PAI are accordingly quantified under different parameters and RH conditions, which have varied between $500 - 1.2 \times 10^5$ ions/cm³ and $500 - 1.5 \times 10^5$ ions/cm³, respectively. The concentration of NAI and PAI as a function of applied voltages in LH and HH environments can be seen from Figure 5.7 (a) and 5.7 (b), respectively. It has been observed that the concentration of NAI and PAI produced by the DBD-APP source is affected by the humidity levels. In the HH environments, the excessive water molecules collide with the air ions and facilitate the recombination of positive and negative ions, leading to a reduction in the overall ion concentration. This is well supported by the OES study, where the relative intensity of molecular nitrogen species is decreased with increase in the RH (see Figure 5.3).

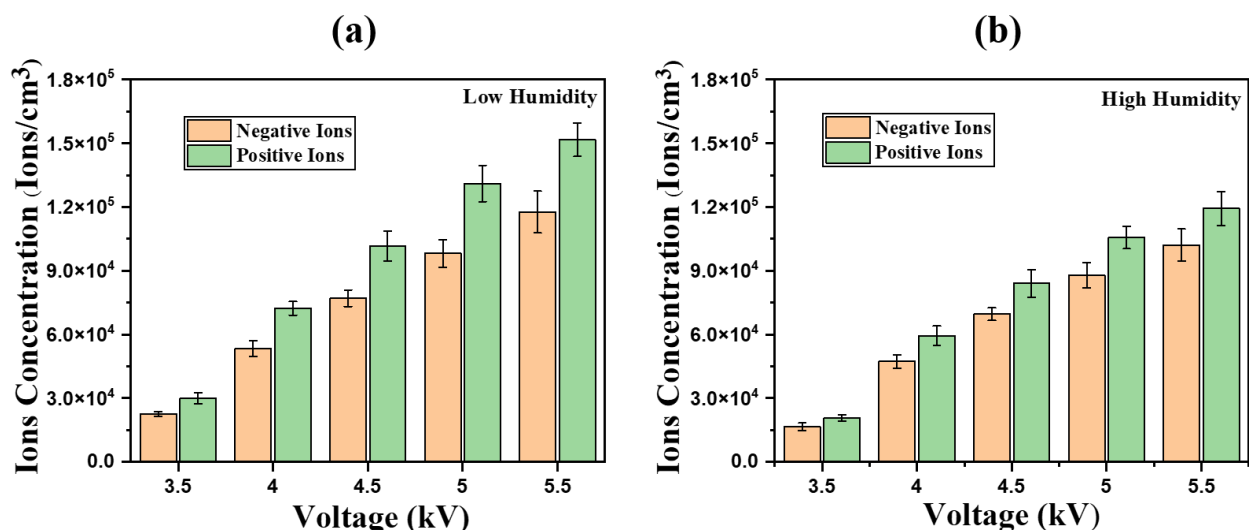


Figure 5.7: Concentration of negative and positive air ions as a function of applied voltages (a) in LH and (b) in HH environments.

These active air ions further react with water vapors and produces the $\bullet\text{OH}$ at the site of contamination. As reported by Jiang et al., [Jiang et al., 2018] the lifetime of these NAIs was found to be 100 seconds to several minutes, and they can travel up to some distances in the indoor environment. Luts and Salm [A. Luts and J. Salm, 1994] identified that O_2^- are the primarily negatively charged ions and is more stable than other NAIs and when O_2^- react with water to form $\bullet\text{OH}$ and H_2O_2 . We measured the concentration of $\bullet\text{OH}$ at various input parameters under both LH and HH conditions because voltage and frequency offer the more suitable input parameters for subsequent research. Figure 5.8 (a) shows the concentration of $\bullet\text{OH}$ at different applied voltages (3.5 – 5.5 kV) and at a fixed pulse repetition rate of 20 kHz, under LH and HH conditions.

The rate of formation of $\bullet\text{OH}$ under LH and HH conditions at 4 kV/20 kHz (after 20 minutes of treatment time) are 15.2×10^{-8} M/s and 25.6×10^{-8} M/s, respectively. By changing the humidity from LH to HH, a double-fold increase in the concentration of $\bullet\text{OH}$ has occurred at the same input voltage. The same trend has followed for 5.5 kV under LH and HH conditions, and the rate of formation of $\bullet\text{OH}$ obtained are 22.5×10^{-8} M/s and 38.7×10^{-8} M/s, respectively. It can be seen that the rate of formation of $\bullet\text{OH}$ is higher in the HH case due to the presence of more water vapors. Figure 5.8 (b) shows the concentration of $\bullet\text{OH}$ generated from the DBD-APP discharge with respect to plasma treatment time at 4.0 kV/20 kHz. Under the LH condition, the concentration of $\bullet\text{OH}$ was around 134.71 μM after 15 minutes and continued to increase to 287.25 μM after 30 minutes of treatment. Under the HH conditions, the concentration of $\bullet\text{OH}$ was around 221.28 μM after 15 minutes and continued to increase up to 524.12 μM after 30 minutes of treatment time. Nakagawa et al. [Nakagawa et al., 2014] also investigated that in a coaxial cylinder DBD increase in RH from 20% to 100%, increases the concentration of $\bullet\text{OH}$ up to two fold.

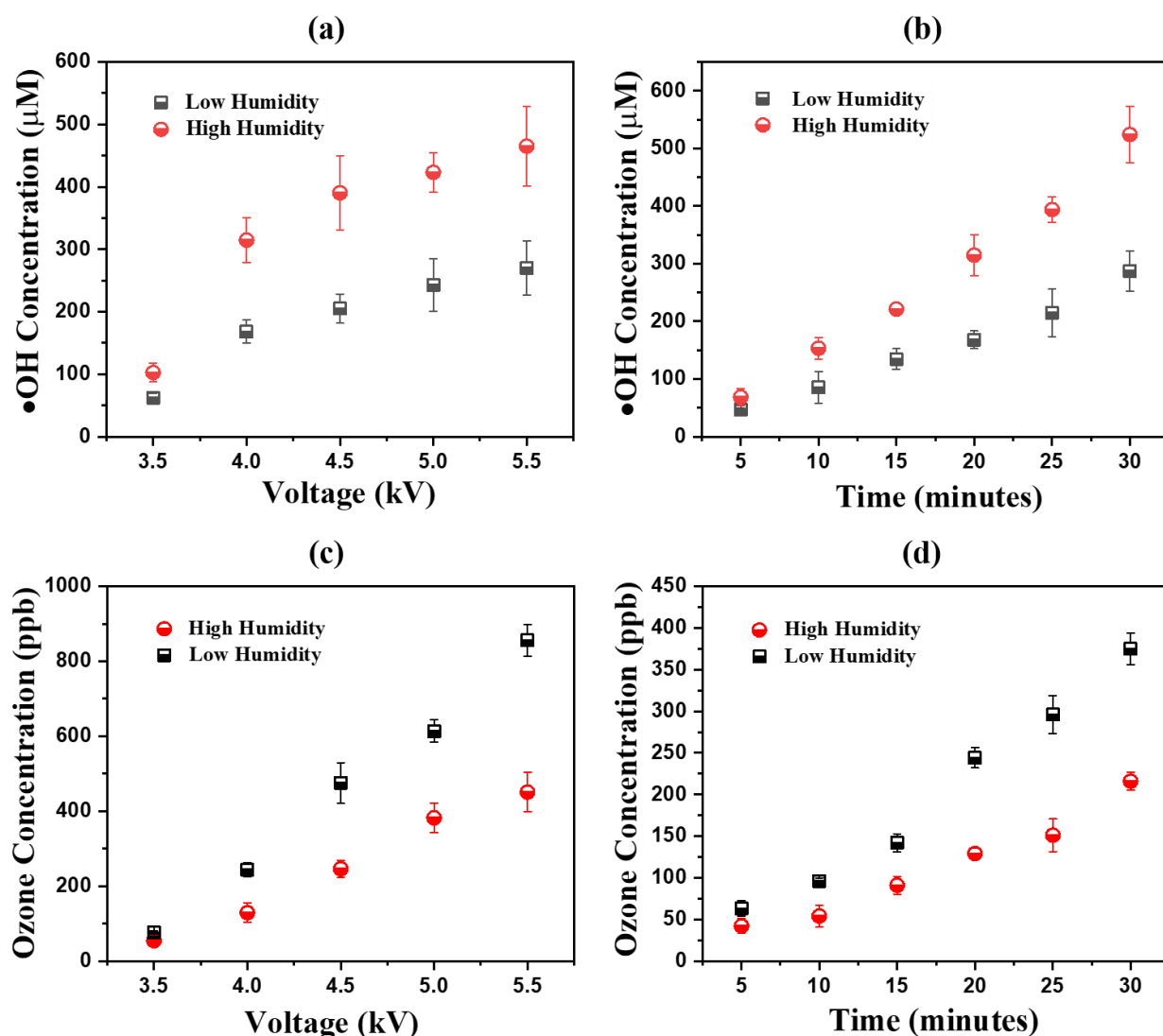


Figure 5.8: (a) Variation in the concentration of •OH under the influence of applied voltage and RH with a fixed frequency of 20 kHz, (b) Effect of RH on •OH concentration at a fixed parameter of 4 kV/ 20 kHz with varying time, (c) Variation in the concentration of O₃ under the influence of applied voltage and RH with a fixed frequency of 20 kHz, and (d) Effect of RH on O₃ concentration at a fixed parameter of 4 kV/ 20 kHz with varying time.

On the other hand, the O₃ concentration showed the opposite trend as shown in Figure 5.8 (c). In the HH conditions, water molecules tend to consume atomic O via the following reaction: $O + H_2O \rightarrow OH + OH$, leading to a reduction of the atomic O as can also be seen from OES. It is well known that, in the DBDs, atomic O was primarily responsible for O₃ generation: $O + O_2 + M \rightarrow O_3 + M$, hence, the generation of O₃ has been inhibited by water [Yao et al., 2015]. The concentration of O₃ is measured at different applied voltages (3.5 – 5.5 kV) and at a fixed pulse repetition rate of 20 kHz to set a voltage parameter for microbial analysis. In the LH condition, the concentration of O₃ recorded is 244 ppb and 856 ppb at 4.0 kV and 5.5 kV of applied voltage, respectively. But in the HH condition, the concentration of O₃ decreases to 129 ppb and 451 ppb at 4.0 kV and 5.5 kV of applied voltage, respectively [see Figure 5.8 (c)]. That means the HH case favors restricting the O₃ concentration within the permissible range for the enclosed environment. Figure 5.8 (d) shows the concentration of O₃ generated from the DBD-APP discharge with respect to plasma treatment time at 4.0 kV/20 kHz. The O₃ concentration in the HH condition is below 150 ppb after 20 minutes of continuous operation of the source, which is within the permissible limit. Highly reactive •OH and O₃ are in general used for a variety of sterilization processes. However, since O₃ is a contaminant of the environment and might have negative health effects, it is frequently thought that plasma devices in enclosed spaces should remove the O₃ generation [Lippmann, 1989].

As $\bullet\text{OH}$, a similar trend has been observed for H_2O_2 as shown in Figure 5.9 (a) and 5.9 (b). After 20 minutes of plasma exposure, the H_2O_2 concentration was 0.14 mg/L in the LH case and 0.31 mg/L in the HH case at 4 kV/20 kHz. The same trend has followed for 5.5 kV under LH and HH conditions, and the H_2O_2 concentrations obtained are 0.51 mg/L and 0.83 mg/L, respectively. The obtained concentration of H_2O_2 is very low because of the air DBD plasma [Judée et al., 2018] [Yayci et al., 2020], but it might be participating in the microbial inactivation. Table 5.3 presents the variation in the concentration of $\bullet\text{OH}$, O_3 and H_2O_2 under the influence of input energy and RH with a fixed frequency of 20 kHz.

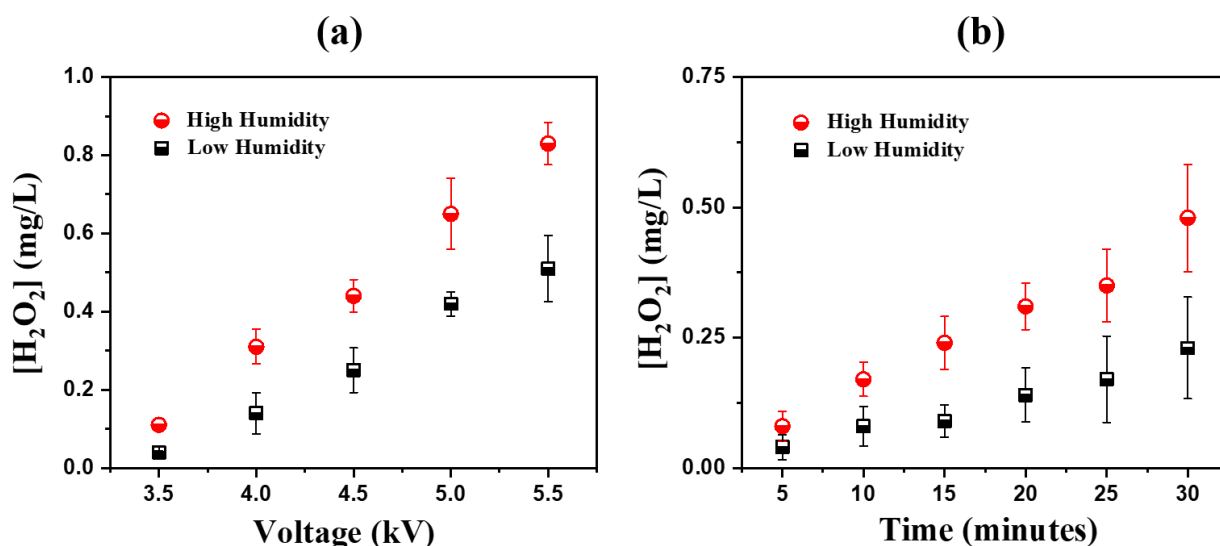


Figure 5.9: (a) Variation in the concentration of H_2O_2 under the influence of applied voltage and RH with a fixed frequency of 20 kHz and (b) Effect of RH on H_2O_2 concentration at a fixed parameter of 4 kV/ 20 kHz with varying time.

Table 5.3: Variation in the concentration of $\bullet\text{OH}$, O_3 and H_2O_2 under the influence of input energy and RH with a fixed frequency of 20 kHz.

Input Energy (W)	Hydroxyl Radicals ($\bullet\text{OH}$) (μM)		Ozone (O_3) (ppb)		Hydrogen Peroxide (H_2O_2) (mg/L)	
	LH	HH	LH	HH	LH	HH
2.18	62.3	102.6	76	54	0.04	0.11
3.31	168	314.73	244	129	0.14	0.31
5.02	205.2	390.5	475	246	0.25	0.44
9.75	242.6	423.2	614	382	0.42	0.65
13.2	270.1	465.1	856	451	0.51	0.83

The other reactive species including $\bullet\text{OH}$ and H_2O_2 have been demonstrated in numerous studies to be crucial in the inactivation of microorganisms [Kvam et al., 2012] [Sakudo et al., 2019]. Due to the fact that, $\bullet\text{OH}$ has a strong oxidation potential of 2.8 eV, greater than the oxidation potential of other reactive species [Kanazawa et al., 2012], the $\bullet\text{OH}$ can act directly with the microorganisms present in the air; therefore, they play an important role in room air disinfection. One such recent study using NTP was conducted by Ki et al. [Ki et al., 2019], in which they

employed a chamber with an area of 0.175 m³ to examine the influence of LH and HH conditions on generating different reactive species. They reported a twofold increase in the generation of reactive •OH and H₂O₂ under HH conditions, along with a halving of O₃ levels. However, the O₃ concentration they observed exceeded permissible limits for indoor environments. For the real space experiment, they utilized a chamber with an area of 2.43 m³ to examine the disinfecting power of the reactive species generated under HH conditions and observed a 97% reduction in bacteria after 30 minutes. In our study, we utilized an actual office room measuring 28 m³ to assess the impact of reactive species in the air. The obtained O₃ concentration at the optimized parameters remained well below 150 ppb, which is within permissible limits for indoor environments. However, in this study, the rate of •OH formation is 25.83×10⁻⁸ M/s, approximately three times higher than the reported rate of 8.31×10⁻⁸ M/s under HH conditions [Ki et al., 2019]. The primary cause of this discrepancy could be due to the addition of TiO₂ NPs catalyst to the outer electrode of the DBD-APP discharge system that is providing opportunities for the higher •OH generation.

5.6 Room Air Disinfection

To see the effect of active air ions and reactive species generated by DBD-APP source on indoor air disinfection, a room of approximately 28.3 m³ has been selected. The experiments are undertaken under LH and HH conditions. Figure 5.10 (a) and 5.10 (b) show the reduction of TBCs and TFCs as a function of treatment time, respectively. The initial number of TBCs and TFCs were 260 CFU/m³ and 80 CFU/m³, respectively. After that, the room air is exposed to atmospheric plasma-generated reactive species for 5, 10, 15, and 20 minutes. Most of the reduction in TBCs and TFCs is observed within 5 minutes of plasma exposure (see Figure 5.10 and Table 5.3). Under LH condition, after 5 minutes of treatment, TBCs and TFCs are reduced to 128 CFU/m³ and 36 CFU/m³, corresponding to inactivation efficiency of 50.77% and 55%, respectively. But in HH condition, after 5 minutes of treatment, TBCs and TFCs were reduced to 46 CFU/m³ and 19 CFU/m³, corresponding to inactivation efficiency of 82.81% and 76.25%. When the treatment time is increased up to 20 minutes, the inactivation efficiency of TBCs and TFCs were further enhanced to 95.77% and 98.75%, respectively. The CFU test showed that TBCs and TFCs reduction occurs in all cases, but compared to LH conditions, the reduction is significantly higher under HH conditions. This results from an increased concentration of •OH and H₂O₂ under HH circumstances while maintaining the same input parameters. The measured concentration of O₃ in low and high humidity environments is very low (< 200 ppb) for microbial disinfection. For example, Westover et al. [Westover et al., 2023] employed a substantially high O₃ concentration of 20 ppm (or 20000 ppb) to eliminate *E. coli* bacteria. To evaluate the influence of the natural decay of microorganisms in the indoor environment, a blank test is also conducted without the use of a DBD-APP source. The results show that natural decay has no discernible effect on the inactivation efficiency of TBCs and TFCs. Table 5.4 presents the load of microorganisms (for a maximum of 20 minutes) in the confined space of the room, both with and without the DBD-APP source operating at varying humidity levels.

The possible mechanism for microorganism's deactivation using DBD-APP source is described as:

1. The electric field can disrupt the lipid matrix of microorganisms, increasing trans-membrane conductivity and diffuse permeability. Consequently, the formation of aqueous pores in the membrane can take place, which may change the electrical potential across the membrane and cause cell lysis [Trainito et al., 2015].
2. The on-site produced •OH may rupture the outer cell wall of bacteria because of the presence of chains of proteins and acids that are vulnerable to oxidation. These irreversible damages can kill and deactivate the bacteria because the oxidative processes

- penetrate the bacterium's membranes, changing their morphological structure (eliminating the membranes) until they reach their genetic material [Das et al., 2024].
3. When a balanced concentration of positive and negative air ions is produced in the air, the electron pulsation will receive a certain amount of energy. The energy that is transferred after the collision of electrons and bacteria will be the same as or comparable to the chemical bond energy; as a result, the bond will be ruptured, and bacteria can no longer breed/reproduce [Lunov et al., 2016] [Dobrynin et al., 2009].

Table 5.4: Colony Counts of airborne microorganisms with and without the operation of the DBD-APP source.

Exposure Time (minutes)	Natural Decay		Low Humidity		High Humidity	
	TBCs	TFCs	TBCs	TFCs	TBCs	TFCs
0	260	80	260	80	260	80
5	252	78	128	36	46	19
10	254	76	106	21	36	9
15	249	78	84	15	30	3
20	254	77	55	10	11	1

*TBCs and TFCs are in CFU/m³

#Values are shown as mean of three readings

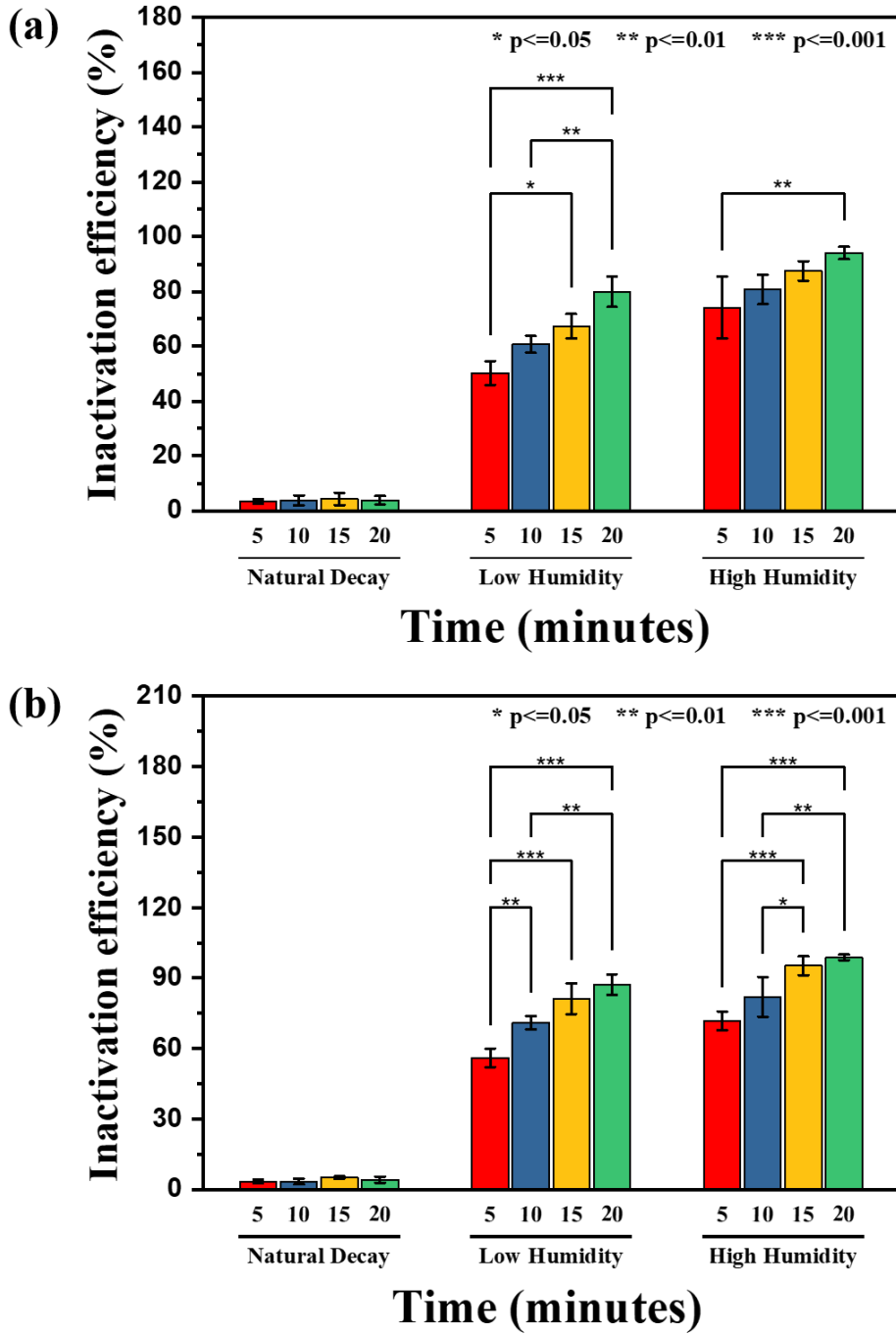


Figure 5.10: Inactivation of (a) TBCs and (b) TFCs as a function of the treatment time under LH and HH conditions. The statistical significance (*, **, and *** denote $P \leq 0.05$, $P \leq 0.01$ and $P \leq 0.001$, respectively) was determined between the various treatment times/RH conditions and the error bars show the mean $\pm$ SD of samples.

5.7 Conclusion

This study examines and analyzes the effects of RH on the properties of DBD-based atmospheric pressure plasma discharge, as well as its effects on the production of ROS, and consequently reduction of airborne TBCs and TFCs in the indoor environment. The following inferences serve as a summary of the work's primary findings:

- 1) Under the same applied voltage, the electric characteristics – discharge current and power show decreasing trends as RH rises.
- 2) Water molecules had a significant impact on the O, N, N_2^* species present in the discharge; as a result, the dissociation of the water causes the concentration of $\bullet\text{OH}$ to double under the HH condition. Concurrently, the amount of O_3 that produced was repressed by half.

- 3) The XPS analysis of TiO_2 before and after the plasma exposure reveals that the plasma-produced HEEs activate the TiO_2 catalysts for the production of electron-hole pairs and, as a result, produce different reactive species.
- 4) The increase in the concentration of on-site produced $\bullet\text{OH}$ is also verified by using a chemical probe. The rate of formation of $\bullet\text{OH}$ is found to be $9.3 \times 10^{-8} \text{ M/s}$ and $17.5 \times 10^{-8} \text{ M/s}$ in the LH and HH conditions, respectively.
- 5) Room disinfection by having TBC and TFC elimination efficiencies of $\sim 95.8\%$ and $\sim 98.7\%$, respectively, has been accomplished by the developed DBD-APP source in just 20 minutes of continuous operation.

These findings indicate that the DBD-APP source may efficiently eliminate airborne microorganisms that are naturally present indoors while using a very small amount of average power (i.e., $\sim 5.6 \text{ W}$ in our case). These will be advantageous for future industrial applications of DBD plasma technology for indoor air cleansing. Additional research is needed to examine the impact of humidity on several airborne viruses, including SARS-CoV-2 and the MS2 phage, in order to establish this as useful technology for pandemics.