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ABSTRACT
Dielectric barrier discharge (DBD) is an effective method for treating volatile organic compounds (VOCs). In the presence of a photocatalyst, photocatalytic technology can be used to generate a variety of reactive oxygen species (ROS). Numerous experiments have demonstrated that DBD–photocatalyst synergism is superior to the use of either approach individually. In this study, the degradation mechanism of VOCs under the DBD–photocatalyst system was investigated via the ReaxFF reaction molecular dynamics method. Acetaldehyde, toluene, 1,2,4-trimethylbenzene, cresol, and phenol were selected as representative VOCs and ⋅O and ⋅OH were chosen as representative ROS to construct the DBD and DBD–photocatalyst reaction systems. A concentration control group and a component control group were established. Comparison of the various ROS revealed that ⋅O and ⋅OH possess higher activities and are more conducive to cracking VOC molecules. Among the various VOCs, the reaction rate was faster for highly reductive reactants. The carbon conversion rate was only dependent on the molecular complexity and was higher for simpler structures. To simulate the DBD–photocatalyst synergistic conditions, we established concentration control simulation systems. When ⋅OH is used as the ROS, a large number of oxidative adsorption and hydrogen abstraction processes can occur. Increasing the ⋅OH concentration promotes the VOC removal reactions to afford complete cracking of the VOCs into the small-molecule product CO₂.

I. INTRODUCTION
In recent years, atmospheric-pressure low-temperature plasma has been widely applied in numerous scientific fields. In particular, it has become an important topic in the field of air cleaning technologies as it provides an effective method for generating reactive oxygen species (ROS). Volatile organic compounds (VOCs) are one of the major causes of air pollution. This large class of compounds includes aromatic hydrocarbons, alkanes, phenols, aldehydes, etc., among which benzene and toluene have attracted particular attention from scholars owing to their high volatility and concentration. Many experiments have also been conducted with phenols and aldehydes because of the serious pollution associated with these compounds. The use of dielectric barrier discharge (DBD) to generate low-temperature plasma is an ideal solution for removing low concentrations of VOCs from large volumes of air at a high flow rate.

DBD is extensively used in exhaust gas treatment owing to its simple device construction, low energy consumption, and high processing efficiency. DBD can be used to produce low-temperature plasma over a large area, and the ROS contained therein can play a vital role in the decomposition of VOCs. The diversity and high concentration of ROS in plasma are the key features underlying the application of plasma in the biological and environmental fields. Previous research into the mechanism of DBD sterilization and treatment of waste gases and water has focused on the behavior of ROS in plasma. Nani et al. compared the production of active species (OH radicals, hydrogen peroxide, and ozone) and the removal of the herbicide metolachlor in direct current (both positive and negative polarity) and DBD systems. This study also
demonstrated the key role of ROS in the treatment of this herbicide. The catalytic method utilizes the photocatalytic performance of TiO$_2$ to generate large quantities of ·OH radicals in an optical cavity under the action of ultraviolet (UV) light and high-energy particles.\textsuperscript{19–22} The introduction of an appropriate catalyst to a DBD system greatly improves the performance of VOC treatment owing to the synergistic effects of high-energy electrons, strongly oxidizing free radicals, high-energy active species such as ozone, and UV photocatalysis.\textsuperscript{21–25}

Numerous experiments have demonstrated that dielectric barrier discharge–photocatalyst (DBD-P) synergy can improve the treatment performance and efficiency.\textsuperscript{22–23} Previous studies into DBD-P technology have mainly focused on two aspects, namely, the factors influencing the reaction and the reaction mechanism. Thevenet \textit{et al.} used low-temperature plasma photocatalytic technology to degrade acetylene and found that DBD-P technology could completely acetylate acetylene and greatly improve CO$_2$ selectivity.\textsuperscript{26} Assadi \textit{et al.} experimentally studied the removal of iso-valeraldehyde from air via DBD, DBD-P, and photocatalytic methods and found that the formation of ·OH in the presence of water vapor promoted degradation in the photocatalytic reactor.\textsuperscript{3}

Kim \textit{et al.} investigated the degradation of benzene using both plasma and TiO$_2$–based photocatalysts and found that the carbon balance and CO$_2$ selectivity were improved after loading the TiO$_2$ with Ag or Pt.\textsuperscript{37} Owing to the limitations of experimental methods, it is challenging to explore the reaction mechanism of the DBD treatment of VOCs experimentally. Moreover, the mechanism of action of the various ROS during processing remains unclear. In addition, the experimental approach is not suitable for exploring the nature of the bonding between the molecules or the nanoscale mechanism of the DBD-P treatment of VOCs. Consequently, the mechanism of DBD-P treatment of VOCs is yet to be elucidated. Therefore, molecular dynamics provide a promising alternative for exploring the reaction mechanism.

With the development of computational chemistry, molecular simulations can be exploited to examine the reaction pathways, transition states, reaction mechanisms, and other aspects of chemical reactions that are difficult to investigate experimentally.\textsuperscript{48,49} This approach has been extensively used in materials and biology research.\textsuperscript{35–37} For example, Cui \textit{et al.} used molecular dynamics to study the mechanism of the destruction of \textit{Staphylococcus aureus} dextran by ROS in plasma and found that the hydrogen evolution reaction between the ROS and the dextran structure led to the cleavage of chemical bonds and cell wall destruction.\textsuperscript{36}

On the basis of the above considerations, in this work, molecular dynamics simulations were used to analyze the removal of VOCs by ROS. First, acetaldehyde was selected as a simple molecule containing methyl and aldehyde groups and its reactions with various ROS (·O, ·OH, HO$_2$, and H$_2$O$_2$) were compared. Owing to the good results obtained for ·O, this species was selected for further analysis and its reactions with a variety of VOCs (toluene, 1,2,4-trimethylbenzene, acetaldehyde, phenol, and cresol) were examined. First-principles calculations were applied to analyze the energy band structure of the photocatalyst (TiO$_2$), and the important factors for processing VOCs under DBD-P conditions were explored.

The findings of this study are helpful for understanding the DBD-P treatment of VOCs at the nanoscale level of chemical reactions. The approach adopted in this study overcomes the limitations of conventional experimental methods and provides a theoretical basis for the further improvement of exhaust gas treatment technology and photocatalysts.

II. COMPUTATIONAL METHODS AND SIMULATION DETAILS

A. Overview of ReaxFF molecular dynamics simulations

ReaxFF uses a general relationship between the bond distance and bond order, on the one hand, and between the bond order and bond energy, on the other hand, that leads to the proper dissociation of bonds to separated atoms. Other valence terms present in the force field (angle and torsion) are defined in terms of the same bond orders such that all of these terms go to zero smoothly as bonds break. In addition, ReaxFF uses Coulomb and Morse (van der Waals) potentials to describe nonbond interactions between all atoms.\textsuperscript{40} The resulting force field can be used to simulate the chemical reactions of millions of atoms and condensed phases. The time scale is only nanoseconds, which has considerable advantages for the simulation of chemical reactions.

Similar to a traditional force field, ReaxFF divides the total energy in a molecule into the sum of various parts. The energy of each part is a function of the key level. The total energy expression for the system is given in the following equation:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conf}} + E_{\text{vdW}} + E_{\text{Coulomb}},$$

(1)

where $E_{\text{bond}}$ is the bond energy term, $E_{\text{over}}$ and $E_{\text{under}}$ are the overcoordination energy and undercoordination penalty, respectively, $E_{\text{val}}$ and $E_{\text{pen}}$ are valence energy terms describing the bond angle, $E_{\text{tors}}$ and $E_{\text{conf}}$ are four-body conjugate terms that describe the four-atom connection when processing the dihedral angle, $E_{\text{vdW}}$ is the van der Waals interaction described for short-range Pauli repulsion, and $E_{\text{Coulomb}}$ is the nonbond Coulombic energies.

According to the interaction energy $E_{\text{system}}$ between atoms, the distance $r_{ij}$ between two atoms in the following moment can be calculated. When the distance between two atoms changes, the ReaxFF force field instantaneously calculates the current atomic charge, calculates the bond order $BO_{ij}$ and judges the connection between the atoms, and simulates the bond cleavage and formation in the reaction, thus describing the evolution of the chemical bond.\textsuperscript{42}

B. Construction of the simulation system

1. Selection of VOCs and ROS

Compared with other VOCs, benzene and toluene have been the focus of researchers owing to their high volatility and concentration. Other benzene derivatives have also been detected at high concentrations in the atmosphere.\textsuperscript{42–44}

For the benzene derivatives, we selected toluene, which has the simplest structure, and 1,2,4-trimethylbenzene, which has a high atmospheric concentration and a relatively complex structure. In addition, the treatment of phenols and aldehydes is important for environmental management and the decomposition of aldehydes has also been the focus of experimental research. Therefore, five representative volatile gases were selected and used in the simulations,
the density of the ROS components decreased in the following order: active barrier particles in DBD.

nation of active species.

H \cdot \text{ing} \text{ toluene in plasma are } \cdot \text{O} \text{, } \cdot \text{OH}, \text{HO}_2, \text{and } \text{H}_2\text{O}_2 \text{ are generated mainly through the dissociation and recombination of active species.}^{39,40} \text{ Liu et al. simulated the composition of active barrier particles in DBD.}^{41} \text{ As the discharge time lengthened, the density of the ROS components decreased in the following order: } \text{O}_3 \text{ > } \text{H}_2\text{O}_2 \text{ > } \text{HO}_2 \text{ > } \cdot \text{O} \text{ > } \cdot \text{OH}. \text{ In low-temperature plasma, } \text{O}_3 \text{ is a weak oxidant with a reactivity that is much lower than that of } \cdot \text{OH. Van Durme et al. reported that the species capable of degrad-}

ing toluene in plasma are } \cdot \text{O} \text{, } \cdot \text{OH}, \text{and } \text{O}_3, \text{ although the reaction rate of } \text{O}_3 \text{ is very low and this species can be neglected when considering the oxidation kinetics of toluene.}^{42} \text{ On the basis of the above considerations, } \cdot \text{O}, \cdot \text{OH}, \text{HO}_2, \text{ and } \text{H}_2\text{O}_2 \text{ were selected as representative ROS.}

2. System construction and relaxation

In this study, the simulation software Material Studio inte-
grated with multiple functional modules was used to construct the simulation systems for the reactions between four ROS and acetaldehyde, as depicted in Fig. 1. The system density was fixed at 0.5 g/cm^3. The Forcite module was adopted to enable fast energy calculations and reliable geometric optimization, and the GULP module was applied to perform the molecular dynamics calculations, including multiple potential energy functions, such as the ReaxFF force field.\text{\textsuperscript{54,55}}

The constructed initial models of the systems were in high energy states that may differ considerably from the actual conformations. To ensure the validity of the simulation results, the initial models were relaxed and kinetically optimized.

This energy minimization process was applied to the initial models until the total system energy became stable. Experiments have shown that the ambient temperature has little effect on the cracking performance.\text{\textsuperscript{36,37}} We also performed a time-varying sim-
ulation to confirm that increasing the temperature only slightly accelerated the reaction progress and did not exert a large effect on the cracking performance. To simulate the reactions at normal temperature and pressure, the NPT isothermal–isobaric ensemble was used with kinetic optimization for 50 ps. The set temperature was 298 K, and the air pressure was standard atmospheric pressure. The simulations were performed using HE.ff force fields containing three elements, namely, C, H, and O. This treatment afforded more reasonable molecular conformations of the systems.

C. Simulation details

The reaction systems were studied under three sets of condi-
tions. As the reactant concentration used in the simulations exceeds that in reality, the reaction time was greatly shortened, and the general simulation time was on the order of picoseconds.\text{\textsuperscript{36}} The step size and reaction time for each reaction system were set to 0.1 and 200 ps, respectively, and we simulated the basic reaction 20 times to ensure data reliability. Owing to the synergistic effects of multi-
ple ROS during actual DBD treatment, the ROS concentration can be appropriately increased in simulations of a single ROS.\text{\textsuperscript{32}} The parameters of reaction systems were set as follows:

(1) The effects of various ROS (\cdot \text{O}, \cdot \text{OH}, \text{HO}_2, \text{and } \text{H}_2\text{O}_2) on the molecular cleavage of acetaldehyde were studied. The type of ROS was the only variable, and systems with VOC:ROS = 8:20 were used.

(2) To study the cracking characteristics of various VOCs, reaction systems composed of \cdot \text{O} and one of the five VOCs, including toluene, 1,2,4-trimethylbenzene, acetalde-
hyde, phenol, and cresol, were examined. After considering the results for various concentrations, reaction systems with VOC:ROS = 30:80 were selected for the main analysis.

(3) The energy band structure of the photocatalyst TiO\textsubscript{2} was ana-
lyzed via first-principles calculations, and the main crystal structures of TiO\textsubscript{2}, namely, anatase and rutile, were exam-
ined. The energy and self-consistent field convergence ac-
curacy (SCF tolerance) in the calculation process were both 2 × 10\textsuperscript{-6} eV/atom. A nonspin polarization treatment was employed.

(4) To simulate the DBD-P processing of VOCs, acetaldehyde was selected as a representative VOC. The reaction results were analyzed at concentrations of VOC:ROS = 10:5, 10:10,
10:20, 10:40, 10:60, 10:80, and 10:90. As the concentration was increased, the process of increasing the activity of photogenerated holes in the DBD-P system was simulated, that is, the increased production of ⋅OH.

III. RESULTS AND DISCUSSION

A. Analysis of simulation results of acetaldehyde treatment with ⋅O, ⋅OH, HO₂, and H₂O₂

In their simulations of the ROS treatment of yeast dextran, Cui et al. found that O and ⋅OH were the most active species. Furthermore, in their analysis of active species in plasma, Liu et al. found that H₂O₂ and HO₂ were long-lived particles with a prolonged duration of action. In this study, H₂O₂, HO₂, ⋅O, and ⋅OH were selected as representative ROS to form a reaction system with acetaldehyde.

The reaction between ⋅O and acetaldehyde can mainly be divided into two parts, namely, the binding of ⋅O and the abstraction of hydrogen by ⋅O, as depicted in Fig. 2. In acetaldehyde, oxidation is highly likely to occur at the unsaturated C=O bond of the aldehyde moiety. Therefore, the aldehyde moiety is much more reductive than the methyl group. Consequently, most of the ⋅O first binds to the aldehyde C atom, and then a second ⋅O captures the aldehyde H atom. As the C atom now connects two O atoms, it can no longer form additional bonds to ⋅O. Following binding of ⋅O to the methyl C atom, the C–C bond is cleaved to form CO₂.

The simulation results revealed that the hydrogen abstraction reaction is the key reaction responsible for inactivating ⋅O. A single ⋅O can mediate two hydrogen abstraction reactions to form H₂O, corresponding to an activity of 2. H₂O possesses low reactivity and exerts little effect on the cleavage of VOCs.

In the reaction of ⋅OH with acetaldehyde, ⋅OH also initially binds to the aldehyde group and then engages in a hydrogen abstraction reaction, as shown in Fig. 3.

The hydrogen abstraction reactions in the reaction between the aldehyde group and ⋅OH can be divided into two parts: a second molecule of ⋅OH first captures the H atom from the ⋅OH introduced into the aldehyde group and a third molecule of ⋅OH then captures the H atom originally present in the aldehyde group.

The hydrogen abstraction reactions convert the acetaldehyde to an unstable structure, CH₃CO₂, as depicted in Fig. 3, which then undergoes C–C bond cleavage due to the oxidative electron-withdrawing reaction of ⋅OH to form the final product CO₂. The C atoms in the generated CO₂ molecules are mostly derived from the aldehyde groups. The activity of ⋅OH is 1, H₂O is formed after the hydrogen abstraction reaction, and no addition or hydrogen abstraction reaction occurs.

The binding and hydrogen abstraction reactions of HO₂ are depicted in Figs. 4 and 5, respectively. It can be seen that both the
The degradation of acetaldehyde by H$_2$O$_2$, HO$_2$, ·O, and ·OH mainly involves attachment to C atoms, C–C bond cleavage, and C–H bond cleavage by O atoms. The numbers of cleaved C–C and C–H bonds were statistically analyzed for the four reaction systems to analyze the effects of the various ROS.

According to the data presented in Table I, the total number of broken bonds is highest in the reaction between ·O and acetaldehyde, and this reaction is the most thorough. The second highest number of broken bonds occurs for ·OH, which is much higher than that for H$_2$O$_2$ and HO$_2$. Owing to their higher reactivity and less self-reaction, ·O and ·OH play major roles in the cleavage of VOCs. These two systems are, therefore, the most relevant for explaining the effects of DBD on VOCs and were selected for further examination. The numbers of broken bonds caused by H$_2$O$_2$ and HO$_2$ are small, indicating the relatively low reactivity of these species. Therefore, although H$_2$O$_2$ and HO$_2$ have a longer duration of action, it is difficult for these species to mediate the cleavage of acetaldehyde owing to their low reaction rate. In addition, H$_2$O$_2$ and HO$_2$ undergo a large degree of self-reaction to form H$_2$O during the reaction, which makes these simulation results not ideal.

### B. Analysis of reaction of ·O with five VOCs

Owing to its high reactivity, ·O was selected as an important ROS to examine its reactions with five representative VOCs, namely, toluene, 1,2,4-trimethylbenzene, phenol, cresol, and acetaldehyde. Following on from the analysis of the acetaldehyde cracking mechanism presented above, a detailed analysis of the remaining four VOCs is presented here. From the atomic-level analysis, the cracking mechanisms of these four reactants are as follows.

#### 1. Toluene degradation mechanism

The effect of the methylation of the benzene ring is reflected in the activation of the ortho-position and the passivation of the meta-position. The C1, C2, and C4 atoms of toluene are more reactive, whereas the C3 atom does not easily react. Therefore, during the treatment of toluene with ·O, the C1–C2 bond is most easily cleaved, as depicted in Fig. 6.

The results of charge-density calculations for the process of ·O addition to the C atoms are presented in Fig. 7. The oxidation by ·O reduces the charge of the connected C atoms and molecular bonds, rendering the C–C bond extremely weak and breaking the original stable structure of the benzene ring.

As shown in Fig. 8, the cracking of toluene mainly involves the following three cases: C1–C2 bond cleavage (① → ②), C2–C3 bond cleavage (① → ③), and C3–C4 bond cleavage (① → ④).

| ROS  | O addition on C | C–C bond cleavage | C–H bond cleavage | Total number of broken bonds |
|------|----------------|-------------------|-------------------|-----------------------------|
| ·O   | 24             | 3.25              | 39.75             | 43                          |
| ·OH  | 16.5           | 2.75              | 17.5              | 20.25                       |
| HO$_2$ | 6.5           | 1.5               | 8.25              | 9.75                        |
| H$_2$O$_2$ | 11.25       | 2.5               | 12.5              | 15                          |
FIG. 6. Cracking of toluene: (a) \( \cdot O \) addition to C1 and (b) \( \cdot O \) addition to C2 and cleavage of the benzene ring.

We used the Materials Studio software package to calculate the reaction energy via density functional theory, and the obtained reaction energies are listed in Table II.

As reported in Table II, the energy required for C1–C2 bond cleavage is significantly lower than those of the other two pathways. This energy is mainly provided by \( \cdot O \). Therefore, it is easier for \( \cdot O \) to break the C1–C2 bond, and consequently, this is the main pathway of ring cleavage. This result is consistent with the findings of the molecular dynamics simulations.

After cleavage of the benzene ring, \( \cdot O \) continues to react with the carbon chain of the molecule. Owing to the electron capture of \( \cdot O \), when \( \cdot O \) attaches to two adjacent C atoms in the carbon chain, the corresponding C–C bond will break. This results in the formation of the unstable compound CHO₂. Next, \( \cdot O \) continues to engage in hydrogen abstraction, removing H from CHO₂ to form the final product CO₂. This process is depicted in Fig. 9. The CO formation process is similar to that of CO₂, except for the number of O atoms connected to the terminal carbon. The reaction of toluene with \( \cdot O \) to form CO is depicted in Fig. 10.

2. 1,2,4-trimethylbenzene degradation mechanism

The presence of the three methyl groups makes the activity of each of the carbon sites of 1,2,4-trimethylbenzene similar such that \( \cdot O \) addition to the C atoms is relatively random.

In this process, \( \cdot O \) attaches to two adjacent C atoms of the benzene ring to mediate ring cleavage, as depicted in Fig. 11. During the cleavage of 1,2,4-trimethylbenzene, the C atoms that are ultimately dehydrogenated to form CO₂ are mostly those that were not initially linked to a methyl group. Only two C–C bonds need to be broken to detach the C atoms not attached to a methyl group, whereas it is necessary to cleave three C–C bonds to detach the C atoms linked to a methyl group. This process requires the attachment of more \( \cdot O \) radicals, which is difficult to achieve. The formation processes of the small molecules are similar to those described for toluene.

3. Phenol degradation mechanism

The phenolic hydroxyl group activates the ortho and para positions of the benzene ring such that the C1, C2, and C4 atoms of phenol are relatively reactive and easily combine with \( \cdot O \). In addition, the phenolic hydroxyl group itself is easily oxidized. In the reaction between phenol and \( \cdot O \), the phenomenon of \( \cdot O \) abstracting the H atom of the phenolic hydroxyl group occurred many times, as depicted in Fig. 12.

| Number | Bond cleavage position | \( \Delta E \) (kJ/mol) |
|--------|------------------------|-----------------------|
| 1 \( \rightarrow \) 2 | C1–C2                  | 596.41                |
| 1 \( \rightarrow \) 3 | C2–C3                  | 648.58                |
| 1 \( \rightarrow \) 4 | C3–C4                  | 630.33                |

FIG. 7. Charge-density calculation results for \( \cdot O \) addition to toluene.

FIG. 8. Pathways for the cleavage of toluene.
The structure with a single O atom connected to C1 is not stable, but it is not a C=O bond structure formed by ·O gaining electrons. Therefore, the C−O bond structure formed by C1 gaining hydrogen has little effect on the degradation of the benzene ring. Thus, there is not a large degree of C1−C2 bond cleavage in this reaction. Tracking the C atoms in the final product revealed the existence of various cleavage modes for the benzene ring. One of these modes involves cleavage of the C1−C2 bond, as depicted in Fig. 13.

By tracking the products, it was determined that the main pathway to the final products involves the detachment of C2. The CO2 generation process is presented in Fig. 14.

4. Cresol degradation mechanism

The reducibility of the phenolic hydroxyl group causes the H atom of this moiety to be readily captured by ·O, as depicted in Fig. 15. It can be seen from the simulation results that substitution with other groups does not affect the activity of the phenolic hydroxyl group.

As the methyl and phenolic hydroxyl groups exert an activating effect on the α-para-position of the benzene ring, the C2 and C4 atoms of cresol are more reactive, and the addition rate is higher than that of the other substrates. As the C2 and C4 positions are not directly connected, the addition to any pair of adjacent C atoms is random. Therefore, it was observed in the simulations of the treatment of cresol with ·O that the initial cleavage position of phenol is randomly distributed among multiple C−C bonds. The processes of CO2 and CO formation are the same as those described above.

C. Statistical data analysis for the ·O treatment of five VOCs

Numerous experiments have demonstrated that the low-temperature plasma treatment of VOCs is very rapid. In an experimental study of the DBD treatment of VOCs, Yue et al. reported that the residual mass concentration of VOCs decreased rapidly during the first 3 h of treatment and then gradually stabilized.48 In accordance with these experimental findings, the simulation results also showed that the degradation of VOCs by ·O is very fast and the five VOCs were rapidly cracked within 1 ps of simulation time.

The variation of the number of VOC molecules in each system over time during the reaction is presented in Fig. 16.

The consumption rates of cresol and phenol were significantly higher than those of the other VOCs, as the presence of the phenolic hydroxyl group makes cresol and phenol easily oxidized. The reaction of ·O capturing the phenolic H atom is more favorable than the attachment and capture of the H atoms from other locations, resulting in a sharp decrease in the number of reactant molecules. After 10 ps, the number of reactant molecules remained essentially unchanged. Almost all of the reactant molecules in the cresol, phenol, and acetaldehyde systems participated in the reaction, whereas some reactant molecules remained in the toluene and 1,2,4-trimethylbenzene systems.

The variation of the number of ·O radicals in each system over time is presented in Fig. 17. The ·O radicals in each system can participate in all of the reactions, and the reaction rates were not substantially different. However, the ·O consumption rates in the cresol and phenol systems were still faster than those in the other systems.

The relative reaction rate $\nu$ can be defined as follows:

$$\nu = \frac{\Delta N}{t},$$  \hspace{1cm} (2)

where $\Delta N$ is the number of VOC molecules consumed and $t$ is the reaction time (picoseconds). To compare the relative initial reaction rates of the various reaction systems, $\Delta N$ was taken as a half-molecule number, which has a fixed value of 15. The value of $t$ was taken as the time at which half of the VOC molecules had been cleaved.

The times at which the five reactants had undergone initial cleavage and the relative reaction rates are listed in Table III. Although acetaldehyde possesses the simplest molecular structure and a reducing aldehyde group, this aldehyde group has poorer reducibility compared with the hydroxyl group such that the reaction rate of acetaldehyde was far less than that of phenol. When VOCs are treated with ·O, the reaction rate is directly related to the reducibility of the reactants.

For VOCs containing benzene rings, when a C−C bond in the benzene ring is broken, the molecule becomes a long carbon chain that is susceptible to oxidation by ·O. Multicarbon molecules undergo cleavage of multiple chemical bonds and are gradually degraded into small-molecule compounds.
The final products are CO₂ and CO. The degree of degradation of different VOCs can be compared by studying the carbon contents of the final products and starting reactants. The carbon conversion rate $C_{\text{conv}}$ can be defined as follows:

$$C_{\text{conv}} = \frac{C_0}{C} \times 100\%,$$  

(3)

where $C$ is the total number of C atoms in the VOC molecules involved in the reaction and $C_0$ is the total number of C atoms in CO₂ and CO after the reaction.

Owing to the limited sample data in these systems, the carbon conversion rate was used solely for qualitative analysis. The obtained carbon conversion rates for the various VOCs are listed in Table IV.

Comparison of the carbon conversion rates for the five VOCs revealed that the value was significantly higher for acetaldehyde than for the other reactants, while the carbon conversion rates for VOCs containing benzene ring structures were not significantly different. This latter finding was attributed to the necessity of benzene ring cracking and long-chain carbon cleavage to produce the final products of CO₂ and CO.

However, the degradation of acetaldehyde requires the cleavage of only a single C−C bond. In addition, it was found that although the phenolic reactants exhibit a high reaction rate, the reaction is not thorough. Because a large amount of ·O reacts with the phenolic hydroxyl group, there are insufficient ·O radicals to participate in further degradation.

In summary, the initial cracking rate is related to the chemical properties of the VOC, while the carbon conversion rate is
independent of the reducibility of the reactant. A simpler molecular structure of the VOC leads to a higher carbon conversion rate and more comprehensive degradation.

D. Analysis of photocatalytic principle of TiO$_2$

The use of plasma treatment alone is still associated with problems such as an unsatisfactory product distribution and incomplete exhaust gas degradation.\textsuperscript{11,56,57} Numerous experiments have demonstrated that if a photocatalyst is added to the plasma discharge region, DBD can be used to improve the efficiency of exhaust gas treatment and realize complementary advantages.\textsuperscript{24–28}

Among the numerous oxide and sulfide semiconductor catalysts, TiO$_2$ has attracted a great deal of attention in photocatalysis owing to its strong oxidizability, chemical stability, and high catalytic efficiency.\textsuperscript{58} The energy band of TiO$_2$ semiconductor materials is not continuous, and the principle of processing VOCs is presented in Fig. 18.

The forbidden band is located between the valence band (VB) and conduction band (CB). High-energy electrons and high-energy particles generated in the plasma field can activate the photocatalyst. When the energy of high-energy electrons, photons, or other active particles in the plasma field is greater than the bandgap, the electrons on the VB can be excited into the CB to generate many strongly oxidative photogenerated holes ($h^+$) on the VB and strongly reductive photoreactive electrons ($e^-$) on the CB. This generation of electron–hole pairs is the key to catalytic oxidation by TiO$_2$. The mobility of its electronic structure allows TiO$_2$ to generate chemically active ·OH radicals.\textsuperscript{59} The reduction reaction can occur only when the CB bottom energy exceeds the reduction potential energy. The corresponding oxidation reaction occurs when the VB bottom energy is lower than the oxidation potential energy.

Materials Studio was used to construct structural models of anatase TiO$_2$ and rutile TiO$_2$. The anatase structure is composed of TiO$_6$ octahedra formed by coedges, whereas the rutile structure is composed of TiO$_6$ octahedra sharing vertices and coedges. The structural differences between anatase and rutile endow these polymorphs with different densities and electronic band structures.

| VOC                 | Initial cracking time $t_0$ | Initial relative reaction rate $v_0$ |
|---------------------|-----------------------------|-------------------------------------|
| Toluene             | 2.66                        | 5.64                                |
| 1,2,4-trimethylbenzene | 5.68                       | 2.64                                |
| Acetaldehyde        | 2.38                        | 6.30                                |
| Phenol              | 0.52                        | 28.85                               |
| Cresol              | 0.51                        | 29.41                               |

TABLE III. Initial cracking times and reaction rates for the VOCs.
### TABLE IV. Carbon conversion rates for the five VOCs.

| VOC          | Initial number of C atoms | Number of CO2 generated | Number of CO generated | Total number of final products | Carbon conversion rate (%) |
|--------------|---------------------------|--------------------------|------------------------|-------------------------------|---------------------------|
| Toluene      | 30 × 7                    | 3.75                     | 1.5                    | 5.25                          | 2.50                      |
| 1,2,4-trimethylbenzene | 30 × 9                  | 5.50                     | 0.1                    | 5.60                          | 2.07                      |
| Acetaldehyde | 30 × 2                    | 10.25                    | 0                      | 10.25                         | 17.08                     |
| Phenol       | 30 × 6                    | 2.75                     | 0.25                   | 3.00                          | 1.67                      |
| Cresol       | 30 × 7                    | 0.5                      | 0.1                    | 0.6                           | 0.29                      |

First-principles calculations based on density functional theory were performed in this study. The Generalized gradient approximation (GGA) exchange correlation functional PW91 was used, the plane wave truncation energy was set to 300 eV, the K-point value of the Brillouin region was $6 \times 6 \times 6$, the self-consistent accuracy was $2.0 \times 10^{-5}$ eV/atom, the force acting on each atom was less than 0.05 eV/Å, and the internal stress was less than 0.1 GPa.

The CASTEP module can be used to study the energy band and density of states of crystalline materials and is a common module for first-principles research. Montanari and Harrison used the CASTEP module to perform density functional theory calculations of rutile TiO$_2$ and calculated the equilibrium geometry, bulk modulus, and gamma-point phonons. In addition, Vajeeston et al. used this module to calculate the phase stability of the CaB$_2$H$_2$ phase at ambient and high pressures.

The energy band structures for anatase and rutile TiO$_2$ calculated in this study are presented in Figs. 19 and 20, respectively. As calculated from these structures, the bandgaps for anatase and rutile TiO$_2$ were 2.255 and 1.918 eV, respectively.

Sun et al. found that the weakest C−H bond dissociation enthalpy of a VOC is the key to determine the catalytic effect during the catalytic dissociation of VOCs. The weakest C−H bond dissociation enthalpies of the common VOCs of toluene, benzene, and acetaldehyde are 373.3 kJ/mol (3.88 eV), 472.4 kJ/mol (4.91 eV), and 394.6 kJ/mol (4.1 eV), respectively. The weakest C−H bond dissociation enthalpy of VOCs is generally above 370 kJ/mol (3.85 eV), which is not in the TiO$_2$ forbidden band. The O−H bond dissociation energy in H$_2$O is approximately 20 kJ/mol (0.21 eV), which is located in the forbidden band of TiO$_2$ and this bond can, therefore, be catalytically cleaved to form -OH.

Therefore, the influence of the photocatalytic treatment of VOCs actually originates not from the catalytic degradation of the VOC itself but rather the continuous production of -OH. Xu et al. investigated the reaction of TiO$_2$ nanopowders with surface-adsorbed H$_2$O to form -OH. Electron spin resonance spectroscopy was applied to detect the strong -OH signal of the TiO$_2$ nanopowder upon exposure to UV irradiation.

O$_3$ is produced when VOCs are subjected to DBD treatment alone, which can act as a long-lived species in plasma. The removal of...
O$_2$ is the key point of photocatalysis synergy. The decomposition of O$_2$ is related to the conductivity of the catalyst. The bond energy of the O$\cdots$O$_2$ bond in ozone is 106.62 kJ/mol (1.11 eV), which is located in the forbidden band of TiO$_2$. O$_2$ adsorbs to the surface of TiO$_2$ and undergoes cleavage to form active oxygen species such as ·O and O$_2$·. The decomposition of O$_3$ further increases the concentration of ROS, thereby promoting the further cleavage of VOCs.

### E. Analysis of ·OH treatment of acetaldehyde

Wallis et al. studied the treatment of Freon with plasma and a photocatalyst. The degradation rate under photocatalytic synergy was 125% higher than that obtained using plasma treatment alone. Both surface reactions and gas-phase reactions can degrade VOCs during DBD-P. Surface reactions can proceed via two pathways. On the one hand, catalytic cracking can be directly carried out by adsorbing VOCs, although this pathway has limited effect as previously discussed. On the other hand, VOC molecules can adsorb on the surface of TiO$_2$ and cracked by ·OH. The essence of this method is also the role of ·OH. Therefore, to simplify the calculations, the gas-phase reaction is mainly discussed here. The improvement in the VOC degradation rate under DBD-P was verified via molecular dynamics simulations.

In the simulated DBD-P treatment of the VOCs, the concentration of ·OH in the system was increased. Acetaldehyde was used as the reactant, and multiple sets of concentration gradients were simulated. The simulations were repeated 20 times for each group. The reaction results are presented in Fig. 21. Owing to the limited number of samples, the data were used only for qualitative analysis.

The results at low ·OH concentrations simulate the lower concentration of free radicals in the absence of a photocatalyst, whereas those at higher ·OH concentrations simulate the synergistic action of DBD-P treatment and the subsequent adsorption of ·OH by photocatalytic holes. As the concentration of ·OH increases, the amount of remaining acetaldehyde molecules decreases continuously until stabilizing. This result demonstrates the improved treatment of acetaldehyde using DBD-P.

As shown in Fig. 21, H$_2$O generation initially increased and then leveled off with increasing ·OH concentration. Water molecules can be formed in two ways. The first way involves the combination of ·OH and ·H when ·OH undergoes a hydrogen abstraction reaction, and the second way involves the collision of ·OH radicals with each other, which can also generate active particles such as H$_2$O$_2$ that exhibit oxidative properties in both experiments and simulations. That is, the product formed by the combination of hydroxyl radicals is still active. When the ·OH concentration is continuously increased, almost all of the acetaldehyde molecules are adsorbed. In addition, the water molecules produced by the first method are almost saturated. As the first method is the main origin of water molecules, the number of water molecules generated does not change significantly with increasing ·OH concentration.

When the concentration of CH$_3$CHO·OH is 10:40, acetaldehyde cleavage is difficult. Although there is a high adsorption rate, the two C atoms are not cleaved such that there is no CO$_2$ generation. Therefore, the treatment of VOCs does not reach completion under DBD treatment alone. As the concentration of ·OH increases, such as when CH$_3$CHO·OH is 10:90, photocatalysis becomes increasingly important. Corresponding to the photocatalytic reaction, ·OH is generated by continuous adsorption of holes under discharge conditions. Under oxidation by ·OH, the acetaldehyde reaction is more extensive and thus tends to afford the final product.

### IV. CONCLUSIONS

In this study, the ReaxFF force field was used to simulate the reaction between ROS and VOC molecules and first-principles calculations were applied to explore the energy band structure of TiO$_2$ to analyze the mechanism underlying the photocatalytic treatment of VOCs. The results revealed that different ROS have distinct effects on VOCs and different VOCs undergo cleavage via distinct mechanisms. The DBD-P method can significantly improve the performance of exhaust gas treatment.

1. The simulation results revealed that ·O has the highest activity among the four ROS, followed by ·OH, whereas HO$_2$ and H$_2$O$_2$ are less efficient in the simulated cracking of VOCs owing to their self-decomposition and depletion reactions.
2. The ·O radical was selected as a representative ROS and its reactions with five representative VOCs were simulated to examine the cleavage reactions occurring under DBD conditions. The oxidation reactions of VOC molecules with ·O are based on an electron-grabbing adsorption process from the C atoms in VOC molecules by ·O. The attachment of ·O radicals to adjacent C atoms results in cleavage of the C–C bond, thereby degrading the reactant into the final products of CO$_2$ and CO.
3. The details of the reactions between the five VOCs and ·O are not identical. Owing to the reducibility of cresol and phenol, at the beginning of the reaction, the oxidation effect of ·O on these molecules is very strong, leading to higher reaction rates compared with those of the other VOCs. Judging from the final products, the carbon conversion rate of each reaction was found to be dependent only on the complexity of the molecular structure. A simpler molecular structure afforded a higher carbon conversion rate.
REFERENCES

1. M. Bahri and F. Haghighat, CLEAN-Sol土 Water Air. 42, 1667 (2014).
2. A. Indarto, D. R. Yang, and C. H. Azhari, Chem. Eng. J. 131, 337 (2007).
3. K. W. Kim, S. Kim, and H. J. Kim, Hazard Mater. 177, 90 (2010).
4. A. Bouzzaa, C. Vallet, and A. Laplancher, J. Photoch. Photobio. A. 177, 212 (2006).
5. U. Roland, F. Holzer, and F. D. Kopinke, Catal. Today 73, 315 (2002).
6. O. Karatum and M. A. Deshusses, Chem. Eng. J. 294, 308 (2016).
7. C. Subrahmanyam, A. Renken, and L. Kiwi-Minsker, Chem. Eng. J. 134, 78 (2007).
8. D. Kim, Y. Shim, and J. Park, Jpn. J. Appl. Phys. 55, 040302 (2016).
9. B. R. Raju, E. L. Reddy, and J. Karuppiah, J. Chem. Sci. 125, 673 (2013).
10. M. F. Mustafa, X. Fu, and Y. Liu, J. Hazard Mater. 347, 317 (2018).
11. Y. S. Mok, Plasma Sci. Technol. 8, 207 (2006).
12. I. Nani, J. Phys. D: Appl. Phys. 51, 274002 (2018).
13. D. Dobrynin, Plasma Med. 7, 2 (2012).
14. N. Mastanahia, Plasma Process. Polym. 10, 1120 (2013).
15. R. Atkinson, Chem. Rev. 86, 69 (1986).
16. E. S. C. Kwock and R. Atkinson, Atmos. Environ. 29, 1685 (1995).
17. J. M. Andino, J. Phys. Chem. 100, 10967 (1996).
18. T. D. Pham and B. K. Lee, Chem. Eng. J. 307, 63 (2017).
19. F. Moulis and J. Krysa, Catal. Today 209, 153 (2013).
20. H. B. Huang, Plasma Chem. Plasma Process. 27, 577 (2007).
21. W. R. Chen, Environ. Sci. Technol. 40, 2734 (2006).
22. P. Sano, N. Negishi, and E. Sakai, J. Mol. Catal. A: Chem. 245, 235 (2006).
23. F. Hammer, Plasma Sources Sci. Technol. 11, 196 (2002).
24. P. D. Sullivan, M. J. Rood, and K. D. Dombrowski, J. Environ. Eng. 130, 258 (2004).
25. Q. H. Trinh and Y. S. Mok, Korean J. Chem. Eng. 33, 735 (2016).
26. F. Thevenet, O. Guaitella, and E. Puzenat, Catal. Today 122, 186 (2007).
27. A. Assadi, A. Bouzzaa, and C. Vallet, Chem. Eng. J. 254, 124 (2014).
28. H. H. Kim, H. Kobara, and A. Ogata, IEEE Trans. Ind. Appl. 41, 206 (2005).
29. H. H. Kim, Catal. Commun. 4, 347 (2003).
30. M. Kim, S. Harrad, and R. M. Harrison, Environ. Sci. Technol. 35, 997 (2001).
31. A. Mercado-Cabrera, Plasma Sci. Technol. 19, 075501 (2017).
32. J. Chen, Chem. Eng. J. 284, 166 (2016).
33. H. C. Pham and K. S. Kim, Ind. Eng. Chem. Res. 52, 5296 (2013).
34. W. F. Van Gunsteren, X. Daura, and N. Hansen, Angew. Chem. 57, 884 (2018).
35. J. Zhao, T. Li, and Z. Xin, Eng. Fuel. 32, 2156 (2018).
36. X. Cui, T. Zhao, and L. Zou, J. Appl. Phys. 51, 355401 (2018).
37. Y. Li, X. Zhang, and S. Xiao, Ind. Eng. Chem. Res. 57, 5173 (2018).
38. F. Gesteira, L. Pol-Fachin, and C. T. V. Jane, PLoS ONE 8, e70880 (2013).
39. H. I. Petracek, D. M. Zuckerman, and J. N. Sachs, Langmuir 18, 1340 (2002).
40. A. C. T. Van Duin, S. Daugupta, and F. Lorant, J. Phys. Chem. A 105, 9396 (2001).
41. T. Zhao, L. Shi, and Y. T. Zhang, Proc. CSEE 37, 4548 (2017).
42. R. Atkinson, Atmos. Environ. 34, 2063 (2000).
43. S. C. Kim and W. G. Shim, Appl. Catal. B: Environ. 98, 180 (2010).
44. C. Ao, S. Lee, and C. Mak, Appl. Catal. B: Environ. 42, 119 (2003).
45. A. A. Amine, L. Sivachandiran, and T. P. Nguyen, J. Hazard. Mater. 357, 305 (2018).
46. C. Subrahmanyam, A. Renken, and L. Kiwi-Minsker, Appl. Catal. B: Environ. 65, 157 (2006).
47. X. M. Tian, X. He, and X. M. Wang, Adm. Tech. Environ. Monit. 18, 11 (2006).
48. X. G. Yue, High Voltage Eng. 41, 3523 (2015).
49. B. Atkinson, Atmos. Chem. Phys. 4, 1461 (2004).
50. A. Galano, J. Phys. Chem. 106, 9520 (2002).
51. T. Gierczak, J. Phys. Chem. 103, 877 (1999).
52. D. X. Liu, J. F. Li, and Z. Z. Ma, High Voltage Eng. 42, 421 (2016).
53. J. V. Durme, J. Dewulf, and W. Sysmans, Chemosphere 68, 1821 (2007).
54. K. Chenoweth, A. C. T. Van Duin, and W. A. Goddard, J. Phys. Chem. A 112, 1040 (2008).
55. O. Rahaman, A. C. T. Van Duin, and W. A. Goddard, J. Phys. Chem. B 115, 249 (2011).
56. M. Palau, A. A. Assadi, and J. M. Penya-Roja, J. Photoch. Photobio. A 299, 110 (2015).
57. J. Yan, H. I. Kim, and S. J. Choung, Korean J. Chem. Eng. 25, 780 (2008).
58. R. K. Ou, L. Chen, and Z. C. Yan, Environ. Sci. Technol. 34, 79 (2011).
59. L. Feigelson, L. Muszkat, and L. Bir, Water Sci. Technol. 42, 275 (2000).
60. B. Montanari and N. M. Harrison, Chem. Phys. Lett. 364, 528 (2002).
61. P. Vajeeston, P. Ravindran, and B. C. Hauback, Int. J. Hydrogen Energy 36, 10149 (2011).
62. Z. Sun, Chin. J. Environ. Eng. 8, 1683 (2010).
63. R. F. Xu, L. F. Qi, and X. X. Hu, New Chem. Mater. 33, 63 (2005).
64. F. Shigera, Catal. Today 89, 89 (2004).
65. A. E. Wallis, J. C. Whitehead, and K. Zhang, Catal. Lett. 113, 29 (2007).