RESEARCH ARTICLE

Preparation of graphene-based catalysts and combined DBD reactor for VOC degradation

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Abstract

The objective of this study was to compare the transformation of by-products between single dielectric barrier discharge (SDBD) and double dielectric barrier discharge (DDBD), to optimize the preparation of graphene-based catalysts and apply them in combination with DBD for volatile organic compound degradation. We compared the degradation performance of SDBD and DDBD, prepared, and characterized graphene-based catalysts. SEM, BET, XRD, and FTIR analyses showed that the morphologies and internal structures of the three catalysts were the best when 0.25 mL of [BMIM]PF6 was added. When MnOx/rGO, FeOx/rGO, and TiOx/rGO were used in combination with DDBD, the degradation rates of benzene were found to be 83.5%, 77.2%, and 63.8%, respectively, whereas the O3 transformation rates were 60%, 79%, and 40%, respectively. Moreover, the NO2 transformation rates were 70%, 55%, and 42.5%, respectively, whereas the NO transformation rates were 69%, 39%, and 33.5%, respectively. The CO2 selectivity was 62%, 51%, and 49%, respectively. MnOx/rGO exhibited superior performance in the degradation of benzene series, NO transformation, NO2 transformation, CO2 selectivity, and energy efficiency. On the other hand, FeOx/rGO exhibited superior performance for O3 transformation. Based upon the XPS analysis, it was found that Mn3O4 and Fe3O4 played a leading role in promoting the degradation of benzene series and the transformation of by-products.

Keywords DDBD · Graphene · Transition metal catalysts · Benzene series · By-products

Introduction

Volatile organic compounds (VOCs) include non-methane hydrocarbons, oxygenated volatile organic compounds, and organochlorine compounds (Park et al. 2013). The emissions of these substances to natural environments harm human health and the ecological environment (Ehn et al. 2014). In most parts of China, the emissions of VOCs are dominated by aromatic hydrocarbons, which are high in concentration and difficult to be removed (An et al. 2014; Zhu and Liu. 2014; Fang et al. 2018; Li et al. 2018; Luo et al. 2020). Benzene series chemicals such as benzene and toluene are the main harmful substances for human body and the environment (Zhang et al. 2017; Ran et al. 2018). Benzene and toluene are the typical and most common benzene series, which are very harmful and exist in a large number of industrial activities, and are the pollutants in urgent need of degradation (Kalbande et al. 2021). Low-temperature plasma technology can rapidly degrade VOCs and has a wide range of applications (Assadi et al. 2015, 2016). Dielectric barrier discharge (DBD) technology makes the discharge evenly distributed on the surface of the dielectric through extreme insertion of high voltage (Costa et al. 2017). Based upon the structure, DBD is classified as single dielectric barrier discharge (SDBD) and double dielectric barrier discharge (DDBD). Liang et al. (2015) used toluene as a typical VOC and DBD technology to study its peak voltage, gas flow, initial toluene concentration, discharge frequency, and working cycle. Mustafa et al. (2018) studied the relationship...
between medium spacing and degradation efficiency in an experimental study using DDBD. Zhang et al. (2014) studied and optimized various parameters such as applied voltage and discharge length by comparing the performance of SDBD and DDBD in degrading styrene, and detected and discussed the by-products of O3 and NOx. The by-product transformation and mechanism of SDBD and DDBD in the degradation of VOCs by DBD are still unclear.

Increasing the DBD energy can improve the removal efficiency of VOCs, which is inconsistent with the principles of energy-savings and removal efficiency, and can produce harmful by-products (such as O3 and NOx). In order to cover the shortages of low-temperature plasma technology, the catalytic technology, which can further enhance the removal efficiency and reduce by-products, is combined with the low-temperature plasma technology (Yao et al. 2018, 2019). Transition metals are often used as catalytic materials for synergistic low-temperature plasma due to their low cost and high performance. Yao et al. (2019) studied the degradation of toluene using NB-Mn/McM-41 in a DBD reactor and confirmed that the metal was highly dispersed on the surface of McM-41. Huang et al. (2011) studied how to improve the removal efficiency of mixed VOCs and control by-products in the emission process. According to different types of pollutants, the coordination between the transition metal catalyst types and DBD is also different (Herrera et al. 2019; Alqahtani et al. 2020). The supporting materials can improve the catalytic performance, reduce the amount of catalyst required, increase the catalytic activity, and include materials such as activated carbon, molecular sieves, and graphene. Graphene is an emerging material and has a huge specific surface area and strong plasticity and ductility, which can solve the problems of agglomeration and low activity in catalyst loading. The preparation methods of graphene oxide (GO) and reduced graphene oxide (rGO) composite catalysts include oxidation reduction method, vapor deposition method, blending method, and hydrothermal method (Tseng et al. 2010; Mishra et al. 2013; Hao and Ji. 2012; Yukimura et al. 2005). Lian et al. synthesized GO and rGO using an improved Hummers’ method (IHM). The method can effectively produce GO and reduce GO from graphene. The layer spacing of the prepared GO was higher than that of rGO, and the specific surface area of rGO (292.6 m\(^2\)/g) was larger than that of GO (236.4 m\(^2\)/g) (Yu et al. 2017).

Since most researchers have focused on preparing catalysts and optimizing plasma, only a few studies have used graphene as a catalyst carrier for the DBD reactor. In addition, the performances of SDBD and DDBD for the degradation of benzene series and its by-products are unknown. In the present study, the optimal experimental conditions were obtained by comparing the degradation rate of benzene series, the transformation rate of by-products, energy efficiency, and other indicators. Based on IHM and different methods to add KMnO\(_4\), the preparation conditions of GO were optimized using cheap flake graphite (FG) as the raw material. In order to explore the performance of Mn, Fe, and Ti in the degradation of benzene series, graphene-based catalytic materials were prepared using ionic liquid-assisted hydrothermal method. The effect of the addition of ionic liquid on the catalyst was studied. The synthesized catalyst and the optimal reactor conditions were used to discuss the degradation of benzene series and the formation of by-products and CO\(_2\). The results from the study provide theoretical guidance for the plasma synergistic catalyst technology.

**Experimental**

**Experimental setup**

Figure 1 shows the combination of DBD reactor and the catalyst system. The airflow controller (Chengdu Times Hongyu Testing Instrument Co., Ltd., Chengdu, China) was used to control the initial flow. DBD (Nanjing Suman Plasma Co., Ltd., Nanjing, China) was connected to the regulator (Zhejiang Chint Electric Appliance Co., Ltd., Hangzhou, China), and its initial voltage was adjustable. The DBD reactor was connected with the oscilloscope (UTD2102cex) to observe the variation in waveform of the reactor. The tail gas was analyzed using the O3 detector (Zhejiang Healthy Photon Co., Ltd., Hangzhou, China) and GS-MS (Chongqing Chuanyi Ninth Factory, Chongqing, China) system. Figure 1 shows the structural differences between the SDBD and DDBD systems. The catalyst was loaded in a transparent tube with high-temperature resistance, and a dense stainless steel mesh carried the catalyst at the bottom. Table S1 shows SDBD and DDBD residence times.

**Electrical parameters**

The main electrical parameters were the initial voltage (IV), output voltage (OV), discharge power (DP), specific energy density (SED), and energy efficiency (EE). The oscilloscope was used to connect the two channels (CH1 and CH2) to the discharge host’s IC detection port and the U detection port of the dielectric barrier device, respectively. The corresponding voltage (VM, VO) and capacitance were obtained by series measurements. The discharge power is calculated using Eq. (1).

\[
P(w) = f CM \int VdVM \tag{1}
\]

where \(P\) is the power (W), \(f\) is the frequency (Hz), \(CM\) is the reactor capacitance (F), and \(VM\) is the reactor voltage (V).
SED refers to the electric energy obtained when the gas enters the device (J/L) and is calculated using Eq. (2).

\[ SED(J/L) = \frac{P}{Q} \]  

(2)

where \( P \) is the power (W), and \( Q \) is the airflow (L/s).

EE is an important indicator of energy consumption for treating VOCs (Ji et al. 2021) and directly reflects the energy consumption of the device. In this paper, the EE is defined as the energy consumed to remove a unit mass of VOCs (g/kWh) and is given by Eq. (3).

\[ EE(g/Kwh) = \frac{C_{in} - C_{out}}{SED} \times 3.6 \]  

(3)

where \( C_{in} \) is the initial gas concentration (ppm), \( C_{out} \) is the outlet gas concentration (ppm), and 3.6 is the ratio between 3600 s and 1000L.

**Data processing**

The components of VOCs were benzene and toluene. The standard curve was obtained using the chromatographic column (wax) combined with GC–MS (Chongqing Chuanyi Ninth Factory). The \( O_3 \) transformation rate is calculated using Eq. (4), the NO and NO\textsubscript{2} transformation rate are calculated using Eqs. (5)–(6), the mineralization of benzene and toluene is calculated using Eqs. (7)–(8).

\[ O_3 \text{ transformation rate (\%)} = \frac{c_{O_3} - c_{O_3\text{out}}}{c_{O_3\text{in}}} \times 100\% \]  

(4)

where \( c_{O_3\text{in}} \) is the initial \( O_3 \) concentration (ppm), and \( c_{O_3\text{out}} \) is the outlet \( O_3 \) concentration (ppm).

\[ NO \text{ transformation rate (\%)} = \frac{c_{NO} - c_{NO\text{out}}}{c_{NO\text{in}}} \times 100\% \]  

(5)
where $c_{\text{NO}_2\text{in}}$ is the initial NO concentration (ppm), and $C_{\text{out}}$ is the outlet NO concentration (ppm).

\[
NO_2\text{ transformation rate} = \frac{C_{\text{NO}_2\text{in}} - C_{\text{NO}_2\text{out}}}{C_{\text{NO}_2\text{in}}} \times 100\%
\]

where $c_{\text{NO}_2\text{in}}$ is the initial NO concentration (ppm), and $C_{\text{out}}$ is the outlet NO concentration (ppm).

Mineralization (toluene)\(\%\) = \[
\frac{c_{\text{CO}_2}}{6(c_{\text{Toluene}}\text{in}) - c_{\text{Toluene}}\text{out})} \times 100\% \tag{7}
\]

where $c_{\text{CO}_2}$ is the outlet CO\(_2\) concentration (ppm), $c_{\text{Toluene}}\text{in}$ is the inlet toluene concentration (ppm), $c_{\text{Toluene}}\text{out}$ is the outlet toluene concentration (ppm), and 7 is the number of carbon in toluene.

Mineralization (benzene)\(\%\) = \[
\frac{c_{\text{CO}_2}}{6(c_{\text{Benzene}}\text{in}) - c_{\text{Benzene}}\text{out})} \times 100\% \tag{8}
\]

where $c_{\text{CO}_2}$ is the outlet CO\(_2\) concentration (ppm), $c_{\text{Benzene}}\text{in}$ is the inlet toluene concentration (ppm), $c_{\text{Benzene}}\text{out}$ is the outlet toluene concentration (ppm), and 6 is the number of carbon in benzene.

**Preparation of materials**

**GO preparation**

The principle of IHM is that graphite is oxidized to graphite oxide by the oxidant, which is then ultrasonically exfoliated into GO with fewer layers or monolayers. First, 150 mL of concentrated H\(_2\)SO\(_4\) and 45 mL H\(_3\)PO\(_4\) were taken and mixed carefully and slowly. Then, 4 g of FG was added to the above solution, mixed uniformly by stirring the solution. Then, 20 g of KMnO\(_4\) was taken under ice bath conditions and slowly added to the mixture during stirring (the first solution was added with 10 g KMnO\(_4\) twice at an interval of 30 min. The second solution was added with 5 g KMnO\(_4\) four times with an interval of 10 min.). The resultant GO solutions were called GO1 and GO2. The reaction temperature was controlled at no more than 5 °C, and the ice water bath was removed after stirring for 30 min. The temperature was controlled at about 50 °C and stirred for 2 h. Bubbles were generated (brown-green thick) and slowly added to deionized water. The temperature increased to 100 °C and maintained for 15 min. The mixture was yellowish-brown. An appropriate amount of H\(_2\)O\(_2\) (30 wt.%) was added until the solution became bright yellow. The yellowish-brown solid was obtained after hot filtration, which was washed successively with HCl (10%) solution and distilled water until no SO\(_4^2-\) (BaCl\(_2\) solution identification) was detected. The obtained yellowish-brown precipitate was the graphite oxide. To form a brown solution, an appropriate amount of deionized water was added, and the mixture was ultrasonically treated for 2 h. Finally, the obtained mixed solution was centrifuged, dried at 80 °C, and stored.

**rGO-based catalyst preparation**

GO solution (500 mg/L) was ultrasonically treated for 1 h and mixed with the loaded Mn\(_\text{Ox}\), Fe\(_\text{Ox}\), and Ti\(_\text{Ox}\) (manganous acetate, ferric nitrate nonahydrate, and tetrabutyl titanate; 15 wt.%) for 10 min. Then, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF\(_6\)) was quantitatively dropped into the mixed system. Moreover, 150 mg of Vitamin C was added, and pH was adjusted to 10 using concentrated ammonia. The solution was stirred for 50 min at room temperature. Subsequently, the polytetrafluoroethylene-coated vessel was immediately incorporated, and the hydrothermal reaction was carried out at 200 °C for 10 h. After the reaction, it was dried in a vacuum drying oven at 60 °C and stored after calcination.

**Catalyst characterization**

An FEI Inspect F50 (FSEM) electric field emission scanning electron microscope was used. The working voltage was set to be 10 kV. Moreover, a DX-2700 X-ray diffractometer was used for XRD analysis. The voltage was 40 kV, and the diffraction angle lied within the range of 20–80°. The scanning speed was 8°/min. Furthermore, 0.1 g of sample was degassed at 100 °C for 1 h and then further degassed at 350 °C for 4 h. After degassing, N\(_2\) was used as adsorbate at −196 °C. BET method was used to calculate the specific surface area of the sample, whereas BJH method was used to calculate the pore volume and pore size. X-ray photoelectron spectroscopy (XPS, Thermoscientific Co., Ltd., Waltham, USA) was used to explore the valence state and the form of metal compounds. The composition and valence state of the compounds can be determined by determining the peak position of the scanned curve and measuring the peak spacing. The prepared catalyst materials were crushed and fully mixed in KBr for FTIR analysis. The mixture was pressed on the work-table for scanning electron microscope observations. The range of infrared spectrum was 4000–400 cm\(^{-1}\), and the scanning resolution was higher than 0.09 cm\(^{-1}\).

**Results and discussion**

**SDBD and DDBD treatment of benzene series**

**Discharge parameters and air tube analysis**

Discharge parameters are an essential aspect for the performance of DBD reactor. Through different output voltages, different discharge powers of SDBD and DDBD were obtained (Fig. S1). The discharge power of DDBD was
higher than that of SDBD under different output voltages. With the increase in voltage, the difference in the discharge power increased gradually, reaching the value of 15.5 W. Figure 2 showed the relationship between SED, airflow, and output voltage. For a certain voltage, with the increase of flow rate, the reactor’s SED decreased gradually, whereas SDBD attenuated faster than the DDBD. For a constant airflow, the SED increased gradually with the increase of output voltage. Compared with the DDBD, the SED of SDBD increased slightly. It can be seen that, in the DBD, the SED was positively correlated with the output voltage and negatively correlated with the airflow. The preservation capability of SDBD for SED was weaker than that of DDBD.

**Effect of initial concentration on the degradation rate and by-products**

The degradation efficiencies of SDBD and DDBD for benzene and toluene mixture decreased gradually with the increase of initial concentration, and the degradation rate decreased from the highest value of 78% to the lowest value of 3% (Fig. 3). When the energy density was kept constant, the high-energy electrons and active particles were limited with the increase of pollutant concentration. The removal rate decreased with the increase of initial concentration. The removal rate of VOCs in DDBD was higher than that of SDBD because the SED of DDBD was higher than that of SDBD and released more electricity. The degradation rate of toluene was significantly higher than that of benzene (about 11–21% higher), which was due to the fact that toluene has one more methyl entity than benzene that is easier to fall off (Wu et al. 2013; Liu et al. 2017; Najafpoor et al. 2018; Dang et al. 2016). The EEs of the two reactors for the VOCs’ mixture were different from each other. The EE of DDBD was slightly higher than that of SDBD by 0.1–0.25 g/kWh (Fig. 3), indicating that the EEs of the two reactors for benzene and toluene treatment were not significantly different because the SED of the two reactors was constant. The SED and degradation efficiency of DDBD for toluene and benzene were higher than those of SDBD. From the perspective of the reactor structure, the discharge breakdown of a single medium was relatively easy. The two layers of the medium increased the thickness of barrier, which led to increased energy consumption and reduced EE. With the increase in the initial concentrations of benzene and toluene, the overall EE first increased, became flat, and then, decreased. In the case of constant SED, the electric energy generated by the device was constant, and the active substances in the device were constant. With the increase in the concentration of benzene series, the increased by-products consumed more electricity, which degraded the pollutants. However, when the increase in the initial concentration reached to a certain
extent, the need for electric energy was limited, which interfered with the by-products. Therefore, the degradation efficiency and energy utilization rate decreased for the process.

In the air tube (Fig. S2) with the output voltage of 12 kV and flow rate of 275 L/h, O₃ concentration produced by SDBD was about 3787.43 ppm, and that produced by DDBD was about 2144.47 ppm. For the constant SED, the transformation rate of O₃ increased with the buildup of output voltage (Fig. 4a), indicating that part of O₃ generated by the plasma device was involved in the degradation of VOCs, while some part of O₃ got transformed and degraded (Mao et al. 2017; Chen et al. 2018). The higher the benzene series concentration, the more O₃ consumption. When the concentration increased to about 100 ppm, the consumption rate of O₃ was slower than in the previous stage. The concentration of NO₂ in SDBD was 196.54 ppm, whereas that in DDBD was 73.21 ppm. Figure 4b showed that, when the initial concentration was 20–80 ppm, NO₂ in SDBD was slightly higher than that in DDBD. After 80 ppm, the transformation rate of NO₂ in DDBD was higher than that in SDBD, which may be due to the presence of minor ·O and other substances in SDBD compared to DDBD. With the increase of concentration, limited ·O preferentially participated in the degradation of VOCs and intermediates, which reduced the transformation of NO₂ in SDBD. The fluctuation in the rate of transformation of NO₂ in SDBD was unstable, which may have been caused by the instability of SDBD.

The concentration of NO was 13.25 ppm in SDBD and 0.981 ppm in DDBD. As the initial concentration of VOCs increased, the transformation rate of NO in SDBD increased significantly (Fig. 4c), which was due to the reason that there were more substances such as ·O in SDBD than in DDBD that contributed to the transformation of NO into NO₂. Figure 4d shows the relationship between the CO₂ selectivity and the degradation of benzene and toluene in the two reactors. The mineralization of SDBD was slightly lower than that of DDBD during the degradation of benzene. The mineralization of the two reactors gradually decreased with the increase of initial concentration. The reason why the mineralization of SDBD was lower than that of DDBD was that the discharge of DDBD was stable, and more active substances were produced in stable states. Furthermore, more active substances were involved in the process of ring-opening of benzene and toluene, which effectively degraded the VOCs and converted them into CO₂. The efficiency was higher, so the CO₂ selectivity of DDBD was higher than that of SDBD. For the phenomenon that the degree of mineralization decreased with the increase in the concentration of VOCs. This could be due to the reason that the SED was constant, and the total amount of active substances were also constant. When the concentration of VOCs increased, the limited active substances were not sufficient to transform VOCs into CO₂, resulting in an increase in the intermediate products, which led to a decrease in the selectivity of CO₂. The second reason is that, with the increase in the concentration of VOCs, the intermediate products increased, which increased the consumption of electricity and led to a decrease in the degree of mineralization. In addition, the
selectivity of CO₂ in SDBD was relatively unstable, which was caused by the unstable discharge of electric energy and the unstable amount of intermediate products.

**Effect of output voltage on the degradation rate and by-products**

As the output voltage increased, the degradation rate of VOCs became larger (Fig. S3), which was due to the increase in the electric field’s intensity and more active substances, thus improving the efficiency of the degradation of VOCs. For the same output voltage, the degradation efficiency of VOCs of SDBD was lower than that of DDBD because the DDBD was more stable and produced more effective active substances, thereby improving the degradation efficiency of VOCs. The output voltage was positively correlated with the EE (Fig. S3). As the SED increased, the electric field intensity increased, and the active substances increased the species involved in the degradation of VOCs, which in turn increased the energy efficiency. Beyond the voltage of 13 kV, the energy efficiency could not be increased. Although the active substances produced by the reactor increased, the concentration of the degraded target pollutants became limited, and therefore, the EE became limited.

When the concentration of VOCs, flowrate, and output voltage had values of 110 ppm, 275 L/h, and 10–13 kV, the transformation rate of O₃ increased with the increase of voltage (Fig. S4a). Due to the increase of SED, although the generated O₃ increased, the active substances increased as well. Most of the O₃ transformed into active substances and participated in the degradation reactions of VOCs. When the
output voltage lied within the range of 13–16 kV, with the increase of voltage, the O$_3$ transformation rate decreased. Moreover, the O$_3$ concentration generated at this stage increased sharply, and the concentration of VOCs was limited. The excess O$_3$ cannot participate in the transformation, so the transformation rate decreased. Within the output voltage range, the difference of O$_3$ transformation between the two reactors was not obvious. The transformation rate of NO$_2$ in SDBD was higher than that in DDBD after the output voltage of 10 kV (Fig. S4b). When the concentration and flow rate of VOCs were constant, the buildup of voltage led to the increase of active substances and the consumption of more -O, which reduced the formation of NO$_2$ and increased the number of intermediate products. The generated NO was involved in the degradation of intermediate products, which also reduced NO$_2$. In addition, the increase of O$_3$ concentration also promoted the transformation of NO$_2$. The transformation rates of NO and NO$_2$ in SDBD were also higher than those in DDBD (Fig. S4c).

The degree of mineralization of SDBD in benzene degradation was significantly lower than that of DDBD (Fig. S4d). DDBD generated electrical energy more stably than SDBD, which in turn generated more active substances consistently. More active substances were involved in the ring-opening process of benzene and toluene (Han et al. 2020), which improved the degradation efficiency of VOCs into CO$_2$. Therefore, DDBD had higher CO$_2$ selectivity than the SDBD. Similarly, the mineralization of DDBD was higher than that of SDBD. Beyond the output voltage of 12–13 kV, the selectivity of CO$_2$ tended to stabilize. When the intermediate product increased to the maximum, it gradually degraded into CO$_2$ and reached a certain degree of stability. Even if the active substance increased, the mineralization did not change, and the selectivity of CO$_2$ tended to stabilize.

**Effect of airflow on the degradation rate and by-products**

Residence time is calculated from reactors volume and airflow (Table S1). The degradation efficiency of VOCs by SDBD and DDBD decreased with the increase of flow rate (Fig. S5). Due to the decrease of residence time, the contact time between the VOCs and active substances decreased. The energy efficiency of SDBD was higher than that of DDBD (Fig. S5). With the increase in the flow rate, the energy efficiency increased. When the concentration of VOCs and the output voltage were constant, SED decreased, and the degradation rate of VOCs exhibited little change, which led to an increase in energy efficiency. However, due to the limitation of residence time, the energy efficiency increased slightly.

With the change in the gas flow rate, the transformation rate of O$_3$ fluctuated significantly (Fig. S6a) because the formation and transformation of O$_3$ were greatly affected by the residence time. Another reason was that the flow had a significant impact on SED. The overall performance of DDBD for O$_3$ transformation was better than SDBD because DDBD discharge was more stable. Furthermore, its SED was less affected by flow than that of SDBD, and therefore, it would produce more active substances to promote the transformation of O$_3$. The transformation rates of NO$_2$ and NO both decreased with the increase of airflow (Fig. S6b). There was little difference between the SDBD and DDBD for the transformation of NO$_2$. The transformation of NO in SDBD was higher than that in DDBD (Fig. S6c). This could be due to two reasons. The first was the shorter residence time and the shorter contact reaction time for NO$_2$ and active substances. The second was that the SED decreased with the increase in the flow rate, and the amount of active substance produced decreased.

With the increase in the flow rate, the mineralization of SDBD and DDBD gradually decreased, which was also consistent for the degradation of toluene (Fig. S6d). This could be due to the reason that both the SED and the number of active substances decreased. The limited active substances were not sufficient to degrade benzene and toluene to CO$_2$, resulting in an increase in the intermediate products and a decrease in the selectivity of CO$_2$. The second reason was that the residence time decreased, due to which, the contact

![Fig. 5](image-url) (a) SEM characterization of FG, (b) SEM characterization of GO1, (c) SEM characterization of GO2

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time between the intermediate products and the active substances decreased, thus decreasing the degree of mineralization. SDBD was slightly less mineralized than DDBD during the degradation of benzene.

**Preparation of rGO-based catalyst**

**Preparation of GO**

The FG morphology was stacked. The layers were closely connected, while the edges were clearly defined and compact (Fig. 5a). Both the GO1 and GO2, prepared using different methods (Fig. 5b,c), were significantly different from flake graphite in morphology after the IHM and ultrasonic exfoliation. For GO1, although the layer spacing increased, the morphology and appearance were not ideal. The degree of oxidation stripping was also not high. On the other hand, by adding KMnO₄ in multiple batches, GO2 was intercalated by orderly oxidation. GO2 was complete and orderly than GO1.

BET surface area ($S_{BET}$), total pore volume ($V_{total}$), and average pore diameter ($d_{pore}$) of the flake graphite were low, and the two kinds had significant differences compared with the FG (Table S2). The physical performance was significantly improved, and the preparation of GO from the flake graphite was relatively complete. Furthermore, $S_{BET}$ of GO2 increased by about 11% compared with GO1; however, $V_{total}$ and $d_{pore}$ did not increase significantly.

XRD characterization (Fig. 6a) showed that the FG had a characteristic graphite peak at 26.5°, whereas both the GO1 and GO2 had a characteristic peak of GO at 10.6°, and 42.5°. According to Bragg’s law, the layer spacing of GO2 was nearly three times larger than that of FG, indicating that introduction of KMnO₄ in batch mode can effectively increase the layer spacing of GO.

Figure 6b showed no peak of FG, indicating that there was no functional group. A series of characteristic peaks appeared in GO2, indicating that the polar groups increased sharply, and O–H appeared at 3375 cm⁻¹. The absorption peak at 1621 cm⁻¹ belonged to the unoxidized vibration peak of C=C, whereas the absorption peak at 1261 cm⁻¹ was ascribed to the C–H stretching vibration (Kizil et al. 2002; Almasian et al. 2010). The absorption peak at 1135 cm⁻¹ was ascribed to C–O–C. These polar functional groups all indicated that GO introduced more hydrophilic groups, which is also the reason for GO’s hydrophilic solid properties.

**Preparation of catalyst using ion-assisted hydrothermal method**

In the absence of [BMIM]PF6, the nanocrystals showed irregular morphology and local dispersion, whereas most of them had severe agglomeration (Fig. 7a). The manganese catalyst was effectively dispersed on the rGO after the addition of [BMIM]PF6. The addition of [BMIM]PF6 could effectively improve the degree of dispersion and reduce the degree of agglomeration (Fig. 7b). The excessive addition of [BMIM]PF6 made the nanocrystals exhibit irregular morphology, and the agglomeration phenomenon occurred locally (Fig. 7c).

When [BMIM]PF6 was not added, the formation of crystals was incomplete, and the layer edge was crimped, which is not conducive to the presence of nucleation center

![Fig. 6](image-url) (a) XRD characterization of FG, GO1, and GO2, (b) FTIR characterization of FG and GO2
of the catalyst (Fig. 7d). When the dosage of [BMIM]PF6 was 0.25 mL, the morphology and structural characteristics of the prepared FeOx/rGO catalyst were apparent. The crystal dispersion was a little high (Fig. 7e). When the dosage of [BMIM]PF6 was 0.5 mL, the crystal dispersion was not too high (Fig. 7f). The TiOx/rGO catalyst prepared with the addition of 0.25 mL of [BMIM]PF6 had good structural morphology (Fig. 7g). The crystal formation of 0 mL (Fig. 7h) and 0.5 mL (Fig. 7i) was not complete, and the lamellar edges were crimped, which was not conducive to nucleation.

Within the 0–0.25-mL range, the $S_{\text{BET}}$ and $V_{\text{total}}$ of the three catalysts increased, whereas $d_{\text{pore}}$ decreased. Within the range of the added amount of 0.25–0.5 mL, excessive addition led to poor dispersion performance of the catalyst, agglomeration, and other phenomena, which all resulted in smaller specific surface areas (Table S3). When the dosage of [BMIM]PF6 was 0.25–0.5 mL, $S_{\text{BET}}$, $V_{\text{total}}$, and $d_{\text{pore}}$ of the three catalysts showed little change.

In the absence of [BMIM]PF6, the characteristic peaks of MnOx/rGO with different intensities appeared. When 0.25 mL [BMIM]PF6 was added, some characteristic peaks of Mn$_3$O$_4$ appeared (Fig. 8a). When there was no [BMIM]PF6, there were two characteristic peaks of FeOx/rGO at 27.3° and 42.5°, both of which belonged to Fe$_3$O$_4$ (JDPDF 26–1136). When 0.5 mL of [BMIM]PF6 was added, the characteristic peak at 27.3° was weaker than that when there was no [BMIM]PF6, while the
characteristic peak at 42.5° became narrower and sharper. Compared with the characteristic diffraction peak when 0.5 mL of [BMIM]PF6 was added, the characteristic peak at 0.25 mL was sharper, narrower, and higher in intensity, indicating that better crystals were formed due to relatively intact lattices and a higher degree of crystallization under the condition of 0.25 mL of ion-assisted solution (Fig. 8b). All diffraction peaks of TiOx/rGO catalyst belonged to TiO2 (JDPDF 21–1272). With the increase in the dosage of [BMIM]PF6, the diffraction peak of C=O gradually weakened (Fig. 8c).

Figure S7a shows the FTIR characteristics of three catalysts prepared with different additives. The MnOx/rGO prepared without [BMIM]PF6 had an O–H vibration stretching peak at 3487 cm⁻¹, while the addition of 0.25 mL [BMIM]PF6 significantly weakened its peak intensity and introduced some new groups (O–H group, H2O group, and C–O–H group). Moreover, the addition of 0.5 mL [BMIM]PF6 had no prominent characteristic peak compared with the first two, which may be due to the addition of too much ionic liquid that resulted in incomplete hydrothermal reduction reaction and crystallization of [BMIM]PF6 without introducing more new groups. For FeOx/rGO, when [BMIM]PF6 dosage was 0–0.25 mL, there was an O–H stretching vibration peak at 3487 cm⁻¹, whereas the peak intensity decreased for the added amount of 0.5 mL (Fig. S7b). The more substantial characteristic peak (O–H group) at 3487 cm⁻¹ was of the 0.5 mL [BMIM]PF6 dosage spectrum. In contrast, the characteristic peak intensity of [BMIM]PF6 for 0 mL and 0.25 mL was slightly weaker (Fig. S7c). For the three dosage conditions of the ionic liquid, the preparation results of the catalyst were ideal when the [BMIM]PF6 dosage was 0.25 mL. The crystal had enhanced physical properties, many active centers for the nucleation of catalyst, and its internal structure and functional groups were excellent.

DDBD combined with the three catalysts

Degradation of benzene series using MnOx/rGO, FeOx/rGO, TiOx/rGO combined with DDBD system

The degradation rate of MnOx/rGO + DDBD was the highest among the four combinations of benzene and toluene degradation (Fig. 9a), with the value for benzene reaching to around 82% and that for toluene 86%. Compared to the DDBD device without a catalyst system, the degradation rate increased by 20–43%. The degradation efficiency of FeOx/rGO + DDBD was second only to MnOx/rGO + DDBD, which was determined by the properties of Mn and Fe catalysts (Qin et al. 2021). In other words, O3 produced by plasma can have a synergistic effect with catalyst (Saoud et al. 2019), VOCs and active substances induced a redox reaction on the surface of the catalyst (Abidi et al. 2019; 2020), and its degradation capability was closely related to the redox capability of the catalyst itself. Mn has a stronger catalytic capacity and higher redox capacity (Durán et al. 2009). The degradation efficiency of TiOx/rGO + DDBD was lower than the first two, among which TiOx/rGO mainly relied on the ultraviolet (UV) light generated by plasma to trigger the catalytic effect (De Souza et al. 2006; Zhao et al. 2015; Brückner et al. 2021). However, this system consisted of a series device. The UV light generated by DBD was relatively weak on the catalyst at the tail end, due to which, its catalytic effect was not very ideal. The EE of MnOx/rGO + DDBD was the highest (Fig. 9b), which was 31–54% higher than that of DDBD without a catalytic system. The EE was related to the SED and degradation efficiency. The degradation efficiency of the MnOx/rGO + DDBD system was the highest, and its energy efficiency was also the highest.

The O3 transformation rate of FeOx/rGO + DDBD was the highest (Fig. 9c), reaching the value of about 80%. Compared with the DDBD without a catalyst system, the
O$_3$ transformation rate of FeO$_x$/rGO + DDBD increased by about 43.5% because the introduced FeO$_x$/rGO transformed the excess O$_3$ into active substances, such as superoxide free radicals. The NO transformation of MnO$_x$/rGO + DDBD was about 71%, and the NO$_2$ transformation was about 73%, which was about 47% higher than a single DDBD processing unit. The MnO$_x$/rGO + DDBD system had the highest degree of mineralization (Fig. 9d). The reaction of active substances with manganese-based catalysts resulted in more VOCs being effectively degraded and more intermediate products transformed into CO$_2$.

XPS characterization of the three catalysts

The most obvious atomic content was that of C, followed by O (Table S4). Catalysts were combined with graphene to produce –COOH. The surface of the catalyst adsorption caused –OH/CO$_3$$^{2-}$. Moreover, O$^{2-}$ was combined with the three transition metal lattice oxygen. The oxygen content of the three transition metal catalysts included adsorbed water (–COOH), adsorbed oxygen on the surface of the catalyst (–OH/CO$_3$$^{2-}$), and lattice oxygen (O$^{2-}$) (Huang et al. 2012; Kara et al. 2014; He et al. 2019; Zeng et al. 2019). Overall, the proportion of each catalyst was not much different from the theoretical value (Fig. 10a). MnO$_x$/rGO catalyst contained the highest content of lattice oxygen, whereas TiO$_x$/rGO catalyst had the most surface adsorbed oxygen. Moreover, FeO$_x$/rGO lied in between the two (Fig. 10b). Generally speaking, lattice oxygen and surface adsorbed oxygen often determine the excellent catalytic performance. Therefore, all the three transition metals had a high catalytic capability.

In the high-resolution spectra, manganese mainly existed in the form of Mn$_{2p1}$ and Mn$_{2p3}$, whereas iron mainly existed in the form of Fe$_{2p1}$. Furthermore, titanium mainly existed in the form of Ti$_{2p3}$. The high-resolution O$_{1s}$
spectrum was assigned to –COOH at 532.1 eV, to –OH/CO$_3^{2−}$ at 531.4 eV, and to O$_2^{−}$ at 530.9 eV. For the high-resolution spectral image of Mn$_{2p}$ (Fig. 10c), a prominent characteristic peak near 653.8 eV belonged to Mn$_{2p1}$. At the binding energy of 642.1 eV, its characteristic peak belonged to Mn$_{2p3}$. According to the comparison of XPS binding energies and spacing, MnO$_x$/rGO catalyst mainly existed as Mn$_3$O$_4$. For Fe$_{2p}$ high-resolution spectrograph (Fig. 10d), the characteristic peak was not apparent at 724.7 eV, which should belong to Fe$_{2p1}$. The characteristic peak of Fe$_{2p3}$ (710.3 eV) was more potent than that of Fe$_{2p3}$. According to the XPS binding energy (B.E.) results and the binding energy spacing, FeO$_x$/rGO catalyst mainly existed in the form of Fe$_3$O$_4$. In the Ti$_{2p}$ spectrum (Fig. 10e), the characteristic peak at the binding energy of 464.9 eV belonged to Ti$_{2p1}$, whereas the characteristic peak at the binding energy of 1458.2 eV belonged to Ti$_{2p3}$. According to the XPS B.E. results and spacing, the TiO$_x$/rGO catalyst mainly existed as TiO$_2$.

**Conclusion**

The degradation rate of DDBD to benzene series was higher than that of SDBD, and EE of DDBD and SDBD were close. The NO$_2$ transformation rate of DDBD was higher than that of SDBD. Although the NO transformation rate of SDBD was higher than that of DDBD, the NO concentration was very low and can be ignored. There was little difference between SDBD and DDBD in the O$_3$ transformation performance, and the mineralization of DDBD was higher than SDBD. The best preparation method of GO was when KMnO$_4$ solution was added four times, and the interval was less than 10 min. The morphology and internal structure of MnO$_x$/rGO and FeO$_x$/rGO were the best in dosages of 0.25 mL [BMIM]PF$_6$. For TiO$_x$/rGO catalyst, the dosages of 0.25 mL and 0.5 mL [BMIM]PF$_6$ had no significant difference.

The results showed that rGO/MnO$_x$ + DDBD had the best performance in the degradation of benzene series, NO$_2$.
transformation rate, NO transformation rate, and mineralization. The rGO/FeO₃ has the highest transformation performance for O₃. Combined with the experimental performance and the XPS characterization results, Mn₃O₄ exhibited high performance in the degradation of benzene series, NO transformation, CO₂ selectivity, and EE. FeO₃ showed high performance in the degradation of benzene series and O₃ transformation.

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**Author contribution** ZL did research experiments and analyzed the data; YW, GZ, and JY did the other experiments; ZL, along with SL, led the writing of the manuscript.

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**Data availability** All data generated or analyzed during this study are included in this published article.

**Declarations**

**Ethics approval** There are no ethical issues in this article.

**Consent to participate** All the authors agree to participate in this paper.

**Consent for publication** All the authors agree to the publication of this paper.

**Competing interests** The authors declare no competing interests.

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