Vehicle Exhaust Gas Clearance by Low Temperature Plasma-Driven Nano-Titanium Dioxide Film Prepared by Radiofrequency Magnetron Sputtering

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Abstract

A novel plasma-driven catalysis (PDC) reactor with special structure was proposed to remove vehicle exhaust gas. The PDC reactor which consisted of three quartz tubes and two copper electrodes was a coaxial dielectric barrier discharge (DBD) reactor. The inner and outer electrodes firmly surrounded the outer surface of the corresponding dielectric barrier layer in a spiral way, respectively. Nano-titanium dioxide (TiO2) film prepared by radiofrequency (RF) magnetron sputtering was coated on the outer wall of the middle quartz tube, separating the catalyst from the high voltage electrode. The spiral electrodes were designed to avoid overheating of microdischarges inside the PDC reactor. Continuous operation tests indicated that stable performance without deterioration of catalytic activity could last for more than 25 h. To verify the effectiveness of the PDC reactor, a non-thermal plasma (NTP) reactor was employed, which has the same structure as the PDC reactor but without the catalyst. The real vehicle exhaust gas was introduced into the PDC reactor and NTP reactor, respectively. After the treatment, compared with the result from NTP, the concentration of HC in the vehicle exhaust gas treated by PDC reactor reduced far more obviously while that of NO decreased only a little. Moreover, this result was explained through optical emission spectrum. The O emission lines can be observed between 870 nm and 960 nm for wavelength in PDC reactor. Together with previous studies, it could be hypothesized that O derived from catalytically O3 destruction by catalyst might make a significant contribution to the much higher HC removal efficiency by PDC reactor. A series of complex chemical reactions caused by the multi-components mixture in real vehicle exhaust reduced NO removal efficiency. A controllable system with a real-time feedback module for the PDC reactor was proposed to further improve the ability of removing real vehicle exhaust gas.

Introduction

Vehicle exhaust gas contains hydrocarbons, nitrogen oxides, carbon dioxide, carbon monoxide, sulphur dioxide, carbon particles, fine particulate matter and small amounts of aromatic hydrocarbons (benzene) and dioxins. Among these pollutants, hydrocarbons are a major contributor to smog, especially in urban areas. Prolonged exposure to hydrocarbons can cause asthma, liver disease, lung disease and cancer. Carbon monoxide reduces the ability to carry oxygen, and overexposure to carbon monoxide poisoning can be fatal. Nitrogen oxides(NOx), which is a mixture of NO, N2O, and NO2, is generated when nitrogen in the air reacts with oxygen at the high temperature and pressure inside the engine. NOx is a precursor to smog and acid rain.

In the past few decades, non-thermal plasma (NTP) has been widely used to remove volatile organic compounds (VOC) and NOx [1–2]. However, the application of NTP has been greatly restricted by its low energy efficiency and poor CO2 selectivity. Besides, undesirable byproducts (such as ozone), need to be further treated. Recently, these problems were solved to some extent by a combination of non-thermal plasma with catalyst, so called plasma-driven catalysis. As a promising technology, this technique integrates the advantages of high selectivity from catalysis and fast ignition from plasma, which maintained high energy efficiency and mineralization rate with low by-product formation [3–4].

Plasma-driven catalysis (PDC) is a physical and chemical reaction. The reactive species from plasma, such as ions, electrons, excited atomics, molecules and radicals, generate considerable micro-discharge on the surface of the dielectric. These reactive species, especially high energy electrons, contain a large amount of energy, which will activate nearby catalyst and lower the activation energy of the reaction. Internal transition of high-energy particles will generate ultraviolet radiation [5–6]. If absorbed energy is greater than the band gap, the electron inside the semiconductor will be excited with a transition from the valence band to the conduction band, which will form electron-hole pairs and induce a series of further redox reactions. Photo-excited holes have a strong ability to obtain electrons, resulting in reacting with the hydroxide ions together with water adsorbed on the catalyst surface and then generating hydroxyl radicals, which leads to a further oxidation of...
pollutants. Compared with common catalysts, plasma-driven catalysts have many unique advantages, such as high distribution of reactive species, decreased energy consumption, enhanced catalytic activity and selectivity as well as the reduction of the sensitivity to poison [7–8].

Compared with non-thermal plasma, the addition of catalysts could significantly enhance the VOC removal efficiency with increased CO₂ selectivity and carbon balance, while the byproducts, such as O₃ and organic compounds were dramatically reduced, which was mainly due to increased amount of O formed from O₃ destruction [9]. Besides, plasma-driven catalysis has also been used in NO₃ removal. It was reported that plasma-generated ozone, hydroxyl radicals and atomic oxygen played important roles in the oxidation of NO to NO₂ [10]. Many efforts have been made to purify VOC or NOx gas by using plasma-driven catalysis [11–13]. However, those studies focused on only one specific polluted gas or some simulated gases, which were quite different from real vehicle exhaust gas from a launched car. In fact, complex components in the exhaust interacted with each other. For example, according to the molecular dynamics theory, NO removal efficiency depends heavily on the content of HC and other. For instance, the complex components in the exhaust interacted with each other. In this study, the experiment included exhaust gas source collection, treatment and components detection. The real exhaust gas was acquired from a jeep (Charokee-type Beijing Jeep 2500, made in China in 1999), in which the engine with inline four-cylinder was fed by #93 gasoline, in the condition of

Employed to treat the real vehicle exhaust. In order to explain the result, a simple and intuitive method-optical emission spectroscopy was conducted, which was different from chemical kinetics analysis in previous studies. This study also analyzed the practical problems for the application of PDC technique in real vehicle exhaust and proposed some solutions.

Materials and Methods

The PDC Reactor

As shown in Fig. 1, the proposed PDC reactor was a coaxial DBD reactor with three quartz tubes as dielectric barrier layers and two copper electrodes. The inner electrode attached to the inner quartz tube with a spiral rotation, of which the helix width and the pitch were 6 mm and 2 mm, respectively, while the outer electrode attached to the outer quartz tube in the same way as the helix width of 9 mm and the pitch of 4 mm. The nano-titanium dioxide film prepared by radio frequency magnetron sputtering (JGP450 High vacuum magnetron sputtering, China) was coated on the outer surface of middle quartz tube. During the process of coating TiO₂ film, the Ti target was set at the bottom of the vacuum chamber to avoid a large amount of impurities groups into TiO₂ film, and the inner quartz rotated by a constant angular velocity of 0.15 r/s, guaranteeing a well-distributed film on the same circle of the reactor. The proportion of oxygen and argon was about 1:1 with the power of 150W at 1 Pa pressure. The XRD detection given in Fig. 2 indicates that the titanium dioxide has an approximate composition of 85% anatase and 15% rutile forms of TiO₂. The discharge of the whole PDC reactor was shown in Fig. 3, with the excited voltage of 7.78 kV and the power of 2.75W. In order to know the surface features of the TiO₂, AFM detection was conducted on three points on the middle quartz tube with different distances of 20 mm, 50 mm, 90 mm from the same side, respectively. It was worth mentioning that the tube rotated at a certain speed of 0.15 r/s, which would help to form the uniform film in the same circle. Fig. 4 shows the AFM photograph of the uniform surface of the TiO₂. The length of the whole PDC reactor was 180 mm, and the outside diameter of the outer quartz tube was 18 mm, which constituted a compact reactor.

Clearance System

In this study, the experiment included exhaust gas source collection, treatment and components detection. The real exhaust gas was acquired from a jeep (Charokee-type Beijing Jeep 2500, made in China in 1999), in which the engine with inline four-cylinder was fed by #93 gasoline, in the condition of

Figure 1. A schematic diagram of plasma-driven catalysis reactor. The PDC reactor was a coaxial DBD reactor with three quartz tubes as dielectric barrier layers and two copper electrodes. The outer and inner electrodes attached to the surfaces of the corresponding quartz tubes in a spiral rotation, respectively. The length of the whole reactor was 180 mm. The outside diameters of the quartz tubes were 18 mm, 10 mm and 6 mm, respectively.

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temperature/humidity 90°C/60% (monitored by MINGLE Hygrometer TH101B, China). The contents of components in the vehicle exhaust before and after treatment with the PDC reactor were detected by an exhaust gas analyzer (CV-5Q, Tianjin Shengwei Inc. Tianjin, China), which serves officially as a standard exhaust analysis in Beijing, China.

Clearance Process

At the beginning of each experiment, the jeep was started to let the vehicle exhaust gas steadily emit while the exhaust gas analyzer was turned on for detection. Then the exhaust was induced into the PDC reactor, which was excited for low temperature plasma later at the voltage of 8–10 kV. As shown by the detected spectrum in Fig. 5, many significant peaks can be observed in spectrum scope of working plasma inside the PDC reactor ranged from 250 nm to 520 nm, which satisfies the required wavelengths of TiO₂ catalysis.

We then conducted experimental comparisons among three different groups, including a control group without any plasma treatment, a PDC group with TiO₂, and a NTP group which had an identical structure to the PDC reactor but without the catalyst TiO₂. Five tests were conducted for each group. In each test, after engine reaching steady state, the concentrations of different components of the vehicle exhaust were recorded sequentially at an interval of 20 s within 3 minutes for three groups. Then plasma was excited in both PDC and NTP reactors which the vehicle exhaust gas was lead into. The concentrations of different components were recorded at an interval of 20 s within another 9 minutes for these two groups.

Electrical Measurement

The PDC reactors were ignited by an AC high voltage power supply equipped with a transformer, which controlled the input power of the plasma generator (CTP-2000K). AC high frequency high voltage exported from the generator was applied to the PDC reactor, providing excitation power for the reactor. The excitation power was measured through the output voltage and current detection in the generator. Applied high voltage (V) was measured with a 1000:1 high voltage probe (TEKtronix, P6015A). V–Q Lissajous method was used to determine the discharge power in the PDC reactor. The charge Q was determined by measuring the voltage across the capacitor of 0.47 μF connected in series to the ground line of the PDC reactor. The voltage across this capacitor is proportional to the charge. The signals of applied voltage and charge were recorded with a digitizing oscilloscope (Tektronix, MSO2024) by averaging 62.5 k scans. The discharge power (Pdis) was evaluated from the area of V–Q parallelogram by multiplying the frequency. Specific input energy (SIE), which is defined as the energy input per unit gas-flow rate, can be obtained as follows:

$$SIE (J/L) = \frac{P_{dis} (watt)}{gas \ flow \ rate (L/min)} \times 60 \quad (1)$$

In this study, both the minimum excited state and steady state of working PDC reactor were measured according to the method above.
Optical Emission Spectroscopy

Optical emission spectroscopy (OES) is one of the most widely used diagnostic methods for low-temperature plasmas [20]. Optical emission spectrometry involves applying electrical energy in the form of spark generated between an electrode and a metal sample, whereby the vaporized atoms are brought to a high energy state within a so-called “discharge plasma”. These excited atoms and ions in the discharge plasma create a unique emission spectrum specific to each element. Thus, a single element generates numerous characteristic emission spectral lines. Therefore, the light generated by the discharge can be said to be a collection of the spectral lines generated by the elements in the sample. This light is split by a diffraction grating to extract the emission spectrum for the target elements. The intensity of each emission spectrum depends on the concentration of the element in the sample. Detectors (photomultiplier tubes) measure the presence or absence of the spectrum extracted for each element and the intensity of the spectrum to perform qualitative and quantitative analysis of the elements [21,22]. The vehicle exhaust gas was induced into the PDC and NTP reactors, respectively. And the plasmas in the two reactors were excited with the same voltage and power. The probe was put at the same point of each reactor. Then the spectrums were obtained.

Results

Vehicle Exhaust Clearance

Figure 6(a) and (b) show that both of the two reactors have a positive effect on the reduction of HC and NO. Moreover, the removal efficiency of PDC reactor was significantly higher than that of NTP reactor. The vehicle exhaust removal efficiency $\eta$ was estimated as follow:

$$\eta(\%) = \frac{c_{in} - c_{out}}{c_{in}} \times 100\%$$  

where $c_{in}, c_{out}$ are inlet and outlet concentration of the certain component, respectively.

According to Eq.1, the removal efficiency in the PDC reactor for HC and NO are as follows:

$\eta_{\text{NO}} = 64.5\% \pm 1.8\%$, and $\eta_{\text{HC}} = 32.1\% \pm 1.3\%$. 

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Figure 4. AFM photograph of prepared TiO$_2$ film. AFM detections on three points on the middle quartz tube with different distances of (a) 20 mm, (b) 50 mm and (c) 90 mm from the same side.

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Figure 5. Spectrum of the discharge by PDC and NTP reactor. The appearance of O spectrum can be observed between 870 nm and 960 nm for wavelength in PDC reactor.

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Electrical Measurement

Experimental data indicated that our vehicle exhaust flow rate was about 590 sccm. The voltage and current of the PDC reactor were measured through capacitor sampling and resistance sampling, respectively. The V-Q Lissajous method was used to determine the discharge power. Both of the minimum excited state and steady state of PDC reactor were measured. All the electrical measurement results were shown in Fig. 7. At the minimum excited state, the effective voltage and current were 7.78 kV and 0.35 mA. Specific input energy was about 279.66 J/L. At the steady state, the effective voltage and current were 8.06 kV and 0.33 mA. Specific input energy was about 289.83 J/L.

Optical Emission Spectrum

The optical emission spectrum result was shown in Fig. 5. The OH, NO and N emission lines are visible. The appearance of O emission lines can be observed between 870 nm and 960 nm for wavelength in PDC reactor [23,24,25,26]. Considering the facts that the removal efficiency of HC treated by PDC was much higher than that of NTP, while the removal efficiency of NO by
PDC was only a little higher than that of NTP, we hypothesized that O might have made a significant contribution to the much higher HC and NO removal efficiencies.

**Discussion**

First of all, in this study, the proposed PDC reactor was designed with three quartz tubes as dielectric layers. The outer and middle quartz tubes were both dielectric barrier layers. The middle one could separate the catalyst from the high voltage electrode, which could prevent high voltage electrode from being oxidized by oxygen during the reactions. On the other hand, the middle quartz tube could increase the area for depositing more TiO2 film compared with a bare electrode. Furthermore, the addition of middle quartz tube could provide more chances to generate microdischarges [27], which would increase catalyst surface temperature [28], enhance the dispersion of active catalytic components [29,30] and influence the stability with catalytic activity of the exposed catalyst material [31]. All above would promote catalytic VOC removal efficiency. However, hot spots can be formed in PDC reactors as a result of localizing heating by intense microdischarges, which might lead to the damage to the high voltage electrode and catalyst [32]. In order to avoid too many hot spots, each electrode surrounded the outer surfaces of corresponding dielectric barrier in a spiral way. The method of preparing TiO2 film was RF magnetron sputtering without any toxic or organic gas evaporating into the air. Continuous operation tests indicated that stable performance without deterioration of catalytic activity could last for more than 25 h.

Secondly, the removal efficiency result was further explained through the optical emission spectrum approach, a simple and intuitive method different from chemical kinetics analysis in previous studies. The optical emission spectrum result showed that the appearance of O emission lines can be observed between 870 nm and 960 nm for wavelength in PDC reactor. It is our suggestion that the enhanced performance of hydrocarbon destruction was mainly due to a great amounts of atomic oxygen (O) formed, primarily from catalytically O3 decomposition. Compared with NTP reactor, TiO2 film acting as a semiconductor oxide catalyst provided a large number of free electron-hole pairs and consequently promoted the oxidation-reduction reaction.

The emission of O3 from the NTP reactor was harmful to both human health and global environment. The addition of catalyst could significantly enhance the HC destruction with an increased O formation while the byproducts O3 from the plasma were dramatically reduced [9]. Basically, O3 formation in the NTP reactor proceeded via a two-step process [33]: formation of atomic oxygen and recombination of atomic oxygen with oxygen molecule (Eqs. (3)-(5));

\[
O_2 + \text{electron} \rightarrow O(1 D) + O(3 P) \quad (3)
\]

\[
O(1 D) + M \rightarrow O(3 P) + M (M = O_2 \text{or N}_2) \quad (4)
\]

\[
O(3 P) + O_2 + M \rightarrow O_3 + M \quad (5)
\]

where O(1D) and O(3P) represent the excited and ground state oxygen atom, respectively.

It has been also reported that O3 can be decomposed by catalysts into molecular oxygen via atomic oxygen and peroxides (Eqs. (6)-(8)) [34], where * denotes an active site on the catalyst surface:

\[
O_3 + \ast \rightarrow O \ast + O_2 \quad (6)
\]

\[
O \ast + O_3 \rightarrow O_2 + O_2 \ast \quad (7)
\]

\[
O_2 \ast \rightarrow O_2 + \ast \quad (8)
\]

In general, atomic oxygen, which is highly active and involved in HC oxidation, is also imposed positive effect on NO destruction [9].

Thirdly, in the presence of catalyst TiO2 film, when there is a faster rate of oxidation of hydrocarbons (Fig. 6b) there is not a significant increasing reduction of NO (Fig. 6a) correspondingly. Since the gas employed in this study was real vehicle exhaust gas containing many different kinds of compositions, there would be some reactions that did not occur in only one specific gas or some simulated gases. Actually, those complex components in the vehicle exhaust interacted with each other during the PDC process, which would remarkably influence the removal efficiency of NO and HC. It is worth mentioning that there exists a dynamic equilibrium between NO and HC, that HC decomposition will lead to the formation of NO [14]. Besides, it is known that both •OH and O3 play an important role in NO removal. However, since O3 is an •OH scavenger, partial O3 and •OH will react with each other as follow [35]:

\[
•OH + O_3 \rightarrow O_2 + H_2O \quad (9)
\]

Thus both contents of O3 and •OH will decrease with an increased O2 content. It has been reported in a previous literature that high O level will definitely lead to a conversion back to NO, and decrease the the removal efficiency of NO [36]. Although several studies have indicated that plasma-driven catalysis technique was quite effective in removing NO or hydrocarbon [37,38,39,40,41], according to our results and analysis above, the clearance rate of NO would be reduced if mixed with HC as well as other gas components.

The complex chemical reactions among gas compositions in the vehicle exhaust gas are briefly illustrated in Fig. 8. For example, higher NO removal efficiency is under the condition of lower content of HC or decreased O3 content [14], meanwhile, NO can be removed by the formation of NO2 through the reaction with partially oxidized hydrocarbons and peroxy radicals (RO2) [10]. Thus, the removal efficiency of HC could not be as high as that of NO in our experiment. Besides, many fundamental components from working plasma, including ozone, hydroxyl radicals and atomic oxygen also play an important role in the oxidation of NO to NO2 [10]. When hydrocarbon was treated by the plasma discharge, partially oxidized hydrocarbons (CxHyOz) and peroxy radicals (RO2) reacting with NO will be generated and strongly influenced NO2 formation rate. Meanwhile, NO2 reacted with the catalyst TiO2 film, while partially oxidized hydrocarbons were consumed during selective catalytic reduction, producing CO2, N2, and H2O, which are environment-friendly products [42]. Finally, •OH radicals can convert the formed NO2 into HNO3 [10] with the existence of H2O [9]:
Based on the complex chemical reactions mentioned above, the removal efficiency of NO and HC should have been much higher if the PDC reactor was used to remove only NO or HC at the same amount of electricity consumption.

Besides, there were some other factors affecting the removal efficiency of NO and HC by using the proposed PDC reactor. On one hand, water vapor existing in the vehicle exhaust would reduce the vehicle exhaust removal efficiency. Although the drying modules had been assembled in our experiments, water vapor could not be removed completely and it would generate a considerable number of \( \cdot \text{OH} \), leading to enhancement of NO conversion but decrease of HC removal efficiency with an increased incompletely oxidizing byproducts [10]. Meanwhile, water vapor can make catalyst deactivate through poisoning its active sites, annihilating high energetic electrons and depress the HC destruction through competing to be absorbed by the catalyst [43]. It has been reported that the highest carbon balance and \( \text{CO}_2 \) selectivity were obtained with water vapor content between 0.5 and 1.5% [17]. In further study, water vapor could be well controlled to further improve the exhaust removal efficiency.

On the other hand, similar to the presence of water vapor, the oxygen content in the vehicle exhaust that affects significantly the discharge performance plays a key role in the occurring chemical reactions. It has been mentioned that the optimal oxygen ranges between 1% and 5% for VOC with NTP [44], while NO\(_x\) decomposition by plasma was known to be possible only if the oxygen content was less than about 4% [45,46]. In this study, the oxygen content in the exhaust ranged roughly from 3.5% to 4.2% all the time as shown in Fig. 9, which could benefit the PDC reactor for HC removal. However, the oxygen content above could have also benefited the PDC reactor for NO removal efficiency, but it was unreal for the exhaust gas containing VOC [14]. The effect of oxygen content on the NO and HC removal efficiency in this study was obviously reflected in the removal result as shown in Fig. 6.

In order to enhance the ability of the application of PDC reactor in vehicle exhaust gas, a reliable automatic control system will be expected. Based on the measured proportion of HC and NO in real-time, vehicle exhaust can be further removed effectively by the feedback control system that adaptively induces the air outside into PDC reactor. Particularly, the oxygen in air can be used to modulate the appropriate proportions among HC, NO and \( \text{O}_2 \) while the nitrogen in air can help keep the high removal efficiency of NO [45].

\[ e + H_2O \rightarrow e + \cdot \text{OH} + H \quad (10) \]

\[ O(1\text{D}) + H_2O \rightarrow e + 2\cdot \text{OH}. \quad (11) \]

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**Author Contributions**

Organized and helped with the design of the research: JZ, JF. Conceived and designed the experiments: JZ. Performed the experiments: SY YL SS KZ. Analyzed the data: SY YL. Contributed reagents/materials/analysis tools: SY JF KZ. Wrote the paper: SY JZ.
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