

## Oxidation Mechanism of Diesel Particulate Matter in Plasma Discharges

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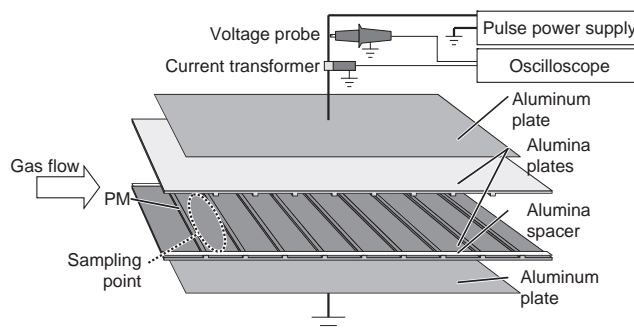
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The oxidation mechanism of diesel particulate matter (PM, carbon is the main component) in plasma discharges is investigated by using X-ray photoelectron spectroscopy (XPS) and thermogravimetry. XPS analysis results showed that the ratio of  $sp^2$  carbon decreased and the ratio of  $sp^3$  carbon increased after plasma discharge; while the ratio of  $sp^2$  carbon increased and the ratio of  $sp^3$  carbon decreased after reacting in  $O_3$  atmosphere without plasma discharge.

Diesel vehicles emit particulate matter (PM). As PM has been associated with lung cancer and asthma,<sup>1</sup> it must be removed from exhaust gases. The main components of PM are soot, soluble organic fraction (SOF) and inorganic particles. Soot is mainly composed of graphitic or fullerenic carbon compounds, and SOF is composed of incompletely combusted fuel or lubricant oil. Soot particles aggregate and combine with SOF to form PM with a size range of 10–500 nm.<sup>2</sup> Diesel particulate filters (DPFs) have been developed for PM removal from diesel vehicles. The DPFs have an advantage of a high PM removal ratio; however, the pressure loss on the DPFs because of PM deposition in the DPFs and DPF regeneration create fuel penalties.<sup>3</sup> Carbon materials such as carbon black or activated carbon can be partially or completely oxidized by plasma discharges in oxygen-containing atmosphere.<sup>4,5</sup> We also have developed a plasma PM removal system of a low fuel penalty.<sup>6</sup>  $O_2$ ,  $H_2O$ , and  $NO$  in diesel exhaust gases can be activated to  $O$ ,  $OH$ ,  $O_3$ , and  $NO_2$  by plasma discharges. PM is oxidized by these active oxygen species to yield gaseous products of  $CO$  and  $CO_2$ . However, the influence of plasma discharges on carbon bonding of PM surface is still unknown. In this study, the mechanism of PM oxidation has been investigated by analyzing changes in carbon bonding after PM oxidation using thermogravimetry (TG) and X-ray photoelectron spectroscopy (XPS).

The PM oxidation by plasma discharges was carried out using a dielectric barrier discharge (DBD) model reactor with a discharge gap fed with a gas mixture of 15% oxygen (nitrogen balanced) at a flow rate of 5 L/min. The DBD model reactor consists of two alumina plates grooved on their one side ( $75 \times 75 \times 1 \text{ mm}^3$ ) and two flat aluminum plates ( $55 \times 55 \times 0.5 \text{ mm}^3$ ). Two alumina spacers ( $75 \times 10 \times 0.3 \text{ mm}^3$ ) were placed between the alumina plates to form a discharge gap (Figure 1). A pulse power supply (DP-15K03, PEEC) was used to supply a pulse voltage (peak value: 8.5 kV) to the DBD model reactor at a pulse repetition (100 Hz). The discharge voltage and current were measured using a voltage probe (P6015A, Tektronix), a current transformer (P6021, Tektronix) and a digital phosphor oscilloscope (WaveSurfer 44Xs, LeCroy). 1.4 W of discharge energy was injected into the DBD model reactor.

PM samples used in this study were collected from the exhaust gas of a diesel engine (as untreated-PM) and DBD reactor described in our previous work (as treated-PM).<sup>6</sup> The composi-



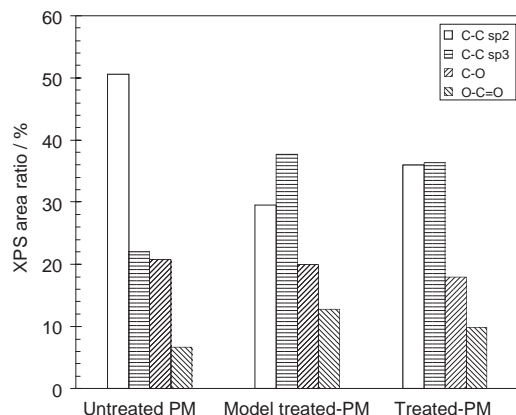
**Figure 1.** Basic structure of the DBD model reactor.

tion of the exhaust gas was estimated to be  $N_2$  77%,  $O_2$  16%,  $H_2O$  4%, and  $CO_2$  3% from diesel fuel supply rate and engine rotation speed. The untreated-PM sample was treated with plasma discharges using the DBD model reactor as follows: 1) a suspension (3.5 mL) of 10 mg of untreated-PM sample in acetone was painted on one side of the grooved surface of the alumina plate to form a thin film of PM. 2) The alumina plate with PM thin film was dried at  $60^\circ C$  in air for 30 min. 3) Pulse voltages were applied to the DBD model reactor in order to oxidize PM thin film on the aluminum plate for 30 min at  $200^\circ C$ . 4) A portion of PM sample remaining on the alumina plate (about 2 cm down stream from the gas inlet of the DBD model reactor) was collected. This PM sample was defined as model treated-PM.

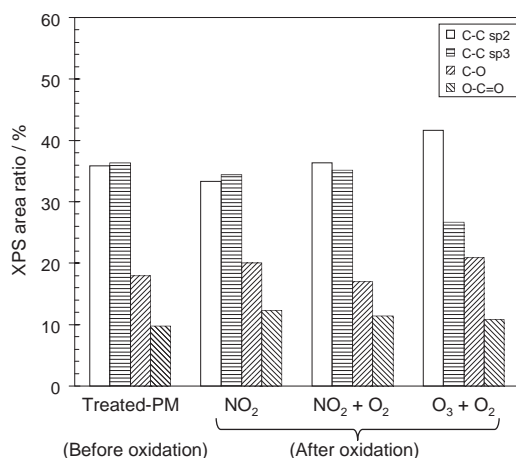
The weight decrease due to the treated-PM oxidation in active oxygen species atmosphere (100 ppm  $NO_2$ , 100 ppm  $NO_2 + 10\% O_2$ , or 100 ppm  $O_3 + 10\% O_2$ , helium balanced) was measured using TG (TG-8120, Rigaku) at  $200^\circ C$  for two hours.

Before and after the plasma discharges and oxidation with active species, the PM samples were analyzed using XPS (ESCA-3200, Shimadzu). The manipulation of XPS spectra was performed using computer software (XPSPEAK Ver. 4.1, Raymond Kwok). The  $C1s$  XPS spectra were fitted to four line shapes with binding energies at 284.4, 285.2, 286.4, and 288.9 eV. These peaks were assigned to C–C  $sp^2$ , C–C  $sp^3$ ,<sup>7</sup> C–O, and O–C=O,<sup>8</sup> respectively. XPS area ratio for each carbon bond was calculated from their area.

Figure 2 shows the area ratio of each carbon bond before and after plasma discharges using the DBD reactor and DBD model reactor. The ratio of  $sp^2$  carbon in treated-PM and model treated-PM decreased, and that of  $sp^3$  carbon increased after plasma discharges. This finding implied that the graphitic  $sp^2$  carbon was attacked and broken by active species ( $O$ ,  $OH$ , electrons, etc.) generated in plasma discharges to yield  $sp^3$  carbon. The weight decreases due to the oxidation of the treated-PM samples in 100 ppm  $NO_2$ , 100 ppm  $NO_2 + 10\% O_2$ , and 100 ppm  $O_3 + 10\% O_2$  were 5.3%, 7.0%, and 11.5%, respectively. The results show that  $O_3$  is most effective for treated-PM oxidation.



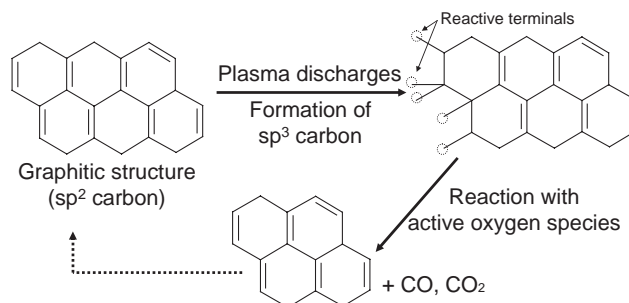
**Figure 2.** XPS area ratios of each carbon bond before and after plasma discharges.



**Figure 3.** XPS area ratios of each carbon bond before and after oxidation of treated-PM in different gas atmosphere.

Figure 3 shows area ratios of each carbon bond before and after the treated-PM oxidation using TG. The area ratios of  $sp^2$  and  $sp^3$  hybridized carbons were not significantly changed except after oxidation with  $O_3$ . The ratio of  $sp^3$  carbon decreased while the  $sp^2$  carbon increased, and weight of the sample decreased after oxidation with  $O_3$ . These results suggested that  $O_3$  can oxidize  $sp^3$  carbon to CO and  $CO_2$  more effectively than  $NO_2$ . As to  $O_3$  oxidation of carbon materials, Banerjee and Wong reported that contaminant material of single-walled carbon nanotubes such as amorphous carbon can be removed even by solution-phase ozonolysis.<sup>9</sup>

The findings in Figures 2 and 3 suggested that the plasma-generated active oxygen species (O and OH) react with the graphitic carbon to yield  $sp^3$  carbon including reactive terminals. The active oxygen species, such as  $O_3$ , react with the  $sp^3$  carbon



**Figure 4.** Mechanism of PM oxidation with active oxygen species generated by plasma discharges.

to give  $CO_2$  and CO. The mechanism of PM oxidation in plasma discharges is illustrated in Figure 4.

PM oxidation with active oxygen species generated by plasma discharge was investigated using XPS and TG. The ratio of  $sp^2$  carbon decreased while the ratio of  $sp^3$  carbon increased after plasma discharge. After reaction with  $O_3$ , the PM weight decreased and the ratio of  $sp^2$  carbon increased while the ratio of  $sp^3$  carbon decreased. It was suggested that the active oxygen species generated by plasma discharges reacted with the  $sp^2$  carbon to form  $sp^3$  carbon that can be further oxidized to CO and  $CO_2$ .

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