

Article

Experimental Study on the Effect of Partial Oxidation on the Microscopic Morphology of Soot Particles

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Abstract: Diesel engine exhaust pipes are in a high-temperature and high-oxygen environment; the carbon soot formed by fuel combustion will be partially oxidized, and its physicochemical properties will change significantly after oxidation. In order to study the effect law of partial oxidation on carbon soot particles emitted from automobiles, commercial carbon black samples (Printex-U carbon) were selected to replace actual carbon soot particles in this paper, and experiments were conducted on a fixed-bed catalytic oxidation device to obtain carbon soot particles with four oxidation rates by varying the time duration of oxygen introduction. Subsequently, the microstructure images of the corresponding carbon soot particles were obtained using TEM and measured after image processing with ImageJ software. The results showed that the average particle size, particle layer spacing, and distortion of carbon soot particles gradually decreased with the increase in oxidation rate. Moreover, the basic particle edge structure of carbon soot particles gradually blurred, the disordered structure inside the carbon soot particles increased, and the structure was destroyed or oxidized away with the gradual oxidation of the outer layer. Lastly, the density degree inside the particles gradually increased, the outer carbon layer arrangement became more regular, and the graphitization degree gradually became larger. The oxidation of carbon soot particles followed the contraction model and the internal oxidation model.

Keywords: carbon soot particles; fixed-bed reactor; microscopic morphology; TEM; oxidation rate



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1. Introduction

Diesel engines are widely used in many fields because of their good power and fuel economy. However, the particulate matter emissions from diesel engines have always been a major problem due to their dilute combustion and high temperature and pressure during the combustion process [1]. The particulate matter in diesel engine emissions is formed in a very complex process, which includes many physical and chemical reactions. Under the conditions of high temperature and oxygen deprivation, fuel molecules undergo thermal cracking and oxidation to produce small molecules with fewer carbon molecules. Through a reaction, these small molecules gradually form carbon nuclei, which continuously adsorb organic matter to grow into larger particulate matter [2–5]. In order to solve the problem of environmental pollution caused by particulate matter in diesel engine emissions, a diesel particulate filter (DPF) needs to be installed in the exhaust system to collect and oxidize the high-temperature exhaust. Therefore, it is necessary to clarify the mechanism of soot formation under the condition of partial oxidation in DPF. This article provides a theoretical reference for an in-depth study of the oxidation mode, oxidation mechanism, oxidation regeneration, and catalytic oxidation of diesel engine exhaust particles. Studying microscopic morphology and physical and chemical properties of carbon black particles

after oxidation is the key to refining the formation mechanism of carbon black. This has great significance for the elimination of subsequent particles.

The study of the microscopic morphological properties and physicochemical properties of carbon soot particles after oxidation is critical to refine the formation mechanism of carbon soot and is significant for the subsequent elimination of particulate matter [6,7]. Microscopic morphological properties include characteristic parameters such as microcrystal size, layer spacing, and distortion of carbon soot, while oxidation activity is an important property of carbon soot itself, which represents the oxidation reaction ability of the particles under specific conditions [8]. According to the literature [9] on the morphological characteristics of carbon soot, the carbon layer spacing is the average distance between adjacent carbon layer planes, and the distortion is a measure of the undulation of the carbon layer, indicating the ratio of the actual carbon layer profile length to the straight-line distance between the ends of the carbon segments.

In recent years, many researchers have investigated the law of the effect of oxidation treatment on the microscopic morphology of carbon soot particles. Meng et al. investigated the effect of thermal aging on the oxidation properties of carbon soot particles under different conditions of temperature, time, and oxygen volume fraction, and the results showed that the diameter and inner core region of the basic carbon particles became smaller at higher aging temperatures, longer aging durations, and increased aging oxygen volume fraction [10]. Raj et al. studied the influence of the structural differences of the polycyclic aromatic hydrocarbons made using dust particles on the reactivity of O₂ through experiments and calculations, and they conducted a quantitative analysis [11]. Toth et al. studied the effect of oxidative pressure above atmospheric pressure on the balance of soot nanostructures. It was found that higher pressures produced structures composed of larger graphene layers. Increasing the oxidation pressure could also reduce the spacing between graphene sheets. Pressure significantly affected the symmetry of soot nanostructures [12]. Ishiguro et al. found that the microcrystalline layers within the soot particles grew and arranged in planes sequentially, forming a turbo-layered structure [13]. In the final stage of oxidation, the size of the microcrystalline layer planes in carbon soot particles did not become smaller, but the outermost microcrystals of carbon soot particles flaked off, thus reducing the size of the particles. Fang et al. showed that, as the aging temperature, time, and oxygen mass fraction decreased, the shell structure of the basic carbon particles became more ordered, with a relatively high degree of graphitization and low oxidation activity [14].

To further refine the effect of oxidation treatment on the micromorphology of carbon soot particles emitted from diesel engines, experiments were conducted in this paper using commercial carbon soot (Printex-U carbon) on a fixed-bed catalytic oxidation unit. Because the microscopic morphology of carbon soot particles belongs to the nanoscale range, it is difficult to directly obtain the parameters of the morphology. In order to further study the microscopic morphology of carbon soot, transmission electron microscopy (TEM) was performed to observe the morphology of carbon soot particles, and ImageJ software was used to observe, process, count, and analyze the microstructure of the particles to study the influence of the morphology of carbon soot particles under different oxidation levels [15].

2. Materials and Methods

2.1. Experimental Materials

Engines are often operated under variable operating conditions, which can lead to variable engine performance indicators, and the composition of the soot particles generated by the engine is related to the engine characteristics; therefore, it is difficult to collect carbon soot particles with constant properties. In addition, the physical and chemical properties of commercial soot are similar to engine soot. Using commercial soot as the experimental object can also achieve the same research purpose. Therefore, commercial carbon black samples (Printex-U carbon) were selected for the experiments to replace the actual carbon soot particles. Printex-U carbon, as a replacement carbon soot with high elemental carbon content, is also used in most experiments. Boger comparatively

showed that Printex-U carbon was indeed a reasonable replacement. Conditions which enable the oxidation of soot under normal driving operation were identified [16]. Atribak selected three real diesel soot samples to compare with Printex-U carbon. Then, through structural characterization, he found that the structure of Printex-U carbon is similar to the other carbon soot samples in terms of morphology and microstructure, with no obvious difference shown [17]. Setiabudi studied the role of NO_2 and O_2 in soot combustion by analyzing the combustion characteristics of soot and the drift spectrum of surface oxygen complex (SOC) as an intermediate product of soot oxidation. Furthermore, he confirmed that Printex-U carbon was a reliable carbon soot model that can be used for exploratory probes [18]. Therefore, selection of Printex-U carbon is viable for experimental studies. Oxygen and nitrogen cylinders were used in this experiment, both of which were 99.99% pure (see Table 1).

Table 1. Experimental materials.

Material	Element	Composition/Concentration
Printex-U carbon	C	Carbon
O_2	O	99.99%
N_2	N	99.99%

2.2. Experimental Rig and Sample Observation

In laboratory-scale studies, the oxidation activity of carbon soot is usually achieved using a fixed-bed type of programmed warming oxidation technique. It is a good choice to use a fixed-bed test bench to research the effect of oxygen on the microscopic morphology of soot particles. It can also eliminate the interference of other components in engine exhaust. In typical experimental tests, an appropriate amount of commercial carbon soot alternative for actual carbon soot is uniformly placed in a tubular quartz reactor and heated by programmed warming in an appropriate amount of reaction gas. The experiment was based on the experimental rig shown in Figure 1a, and the whole rig consisted of nitrogen and oxygen reaction gas cylinders, a mass flow rate apparatus, a gas mixing tank, a programmed warming reactor, and an exhaust gas treatment device.

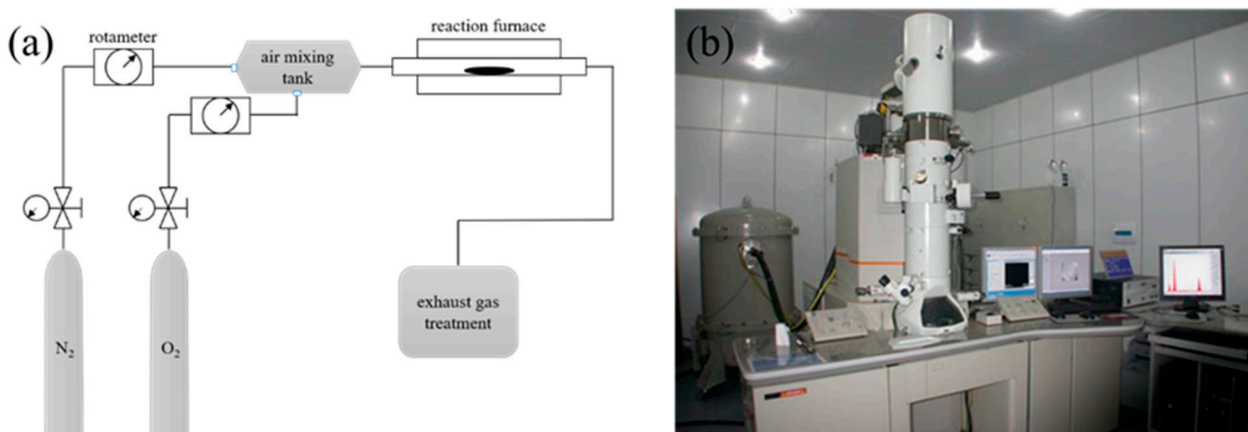


Figure 1. (a) Schematic diagram of fixed-bed catalytic oxidation device. (b) Field-emission high-resolution transmission electron microscope (JEM-2100F).

The experimentally obtained samples were observed for morphological characteristics using a field emission high-resolution transmission electron microscope (JEM-2100F, as shown in Figure 1b, produced by the Japan Electron Corporation). The main technical specifications of the transmission electron microscope were an acceleration voltage of 200 KV, point resolution of 0.23 nm, lattice resolution of 0.102 nm, scanning transmission image lattice resolution of 0.20 nm, minimum electron beam spot of 0.5 nm, and magnification of 0.5–1.1 million times. For sample preparation for TEM analysis, a tiny amount of sample

was dissolved in absolute ethanol and then sonicated for 10–15 min. A piece of facial tissue with filter paper was placed on a clean table, and the carrier screen was placed face up in the center of the filter paper. A dropper was used to apply sample onto the carrier net, which was observed after drying.

2.3. Experimental Procedure

Firstly, a 0.1 g sample of carbon black was placed evenly and flatly in a quartz boat, which was placed in a tubular heating furnace reactor, and N_2 was passed into the reactor at a gas flow rate of 50 mL/min to remove the remaining impurities in the furnace. Subsequently, a programmed temperature increase was applied to heat the sample from room temperature to 300 °C at a rate of 10 °C/min, and the temperature was maintained at 300 °C for 20 min to remove the adsorbed water, as well as some soluble organic from the sample. According to the thermogravimetric analysis, it was found that the conversion rate of carbon soot was maximum at 530 °C. Therefore, the reaction furnace was continuously heated to 530 °C, and, when the temperature reached 530 °C, N_2 was stopped, and O_2 was passed at a gas flow rate of 50 mL/min. The experiment was carried out in four groups: the first control group did not involve the passing of O_2 after heating to 530 °C; the second group involved the passing of O_2 for 15 min when the furnace was heated to 530 °C; the third group involved the passing of O_2 for 20 min when the furnace was heated to 530 °C; the fourth group involved the passing of O_2 for 30 min when the furnace was heated to 530 °C. The carbon soot particles were collected and observed by TEM, and the measured data were compared and analyzed.

3. Results and Discussion

At the end of the experiment, the mass m_x after weighing (x represents the number of groups) in the first group was $m_0 = 0.1$ g, while that at the end of the experiment was $m_1 = 0.0954$ g, but it did not undergo an oxidation reaction. The mass change was due to the mass of adsorbed water and the volatilization of some soluble organic matter. The same soot used in the subsequent groups of experiments was tested, and the impurity quality was the same. The oxidation rate is represented by P_x , and the experimental change mass is represented by $M_x = m_1 - m_x$; thus, the oxidation rate of each group is $P = M_x/m_0$. After calculation, the first group of soot samples was not oxidized, and P_1 was 0%; after the reaction of the second group of 0.1 g soot samples, M_2 was 0.0439 g, and P_2 was 56.1%; after the third group of 0.1 g soot samples reacted, M_3 was 0.0288 g, and P_3 was 71.2%; the M_4 of the fourth group of 0.1 g soot samples after the reaction was 0.0106 g, and P_4 was 89.4%.

The collected carbon soot particles were magnified using transmission electron microscopy, and the overall shape and structure of the carbon soot particles could be observed. Small and densely clustered particles presented short and curved lamellae, showing the trend of fullerene nanostructures. The lamellae were not tightly packed and showed little stacking order. It is obvious from Figure 2a–d that the microstructure of the basic carbon particles was formed by microcrystalline carbon layers arranged in a certain form on the outside, while the inner layer was a large amount of amorphous carbon randomly oriented, i.e., the carbon soot particles all showed a “shell-core” structure. It can also be seen from Figure 2a–d that the basic carbon fume particles under different oxidation levels showed different microscopic morphology, and the edges of carbon fume particles tended to be gradually blurred as the oxidation level increased, while amorphous regions were found inside the carbon fume particles.

However, more information could not be perceived about the morphology of carbon soot particles from a qualitative comparison of images; thus, it was necessary to further process and analyze the TEM images. Combined with the image post-processing software, important information such as the average particle size and number of particles could be obtained. In order to compare the morphological characteristics of four groups of carbon soot oxidation degree, the particle size, carbon layer spacing, and carbon layer distortion were analyzed to obtain detailed information on the carbon soot particle samples. When

counting the particle size of the basic carbon particles, the “cross method” [19] was used to count the basic carbon particles with obvious contours in the electron micrographs. As shown in Figure 3, two crosses were selected for each elementary carbon particle, and the average of the two diameters was taken to represent the particle size of the carbon fume particle; finally, the average of all the counted particle sizes was taken as the average particle size of carbon fume particles in an oxidized state.

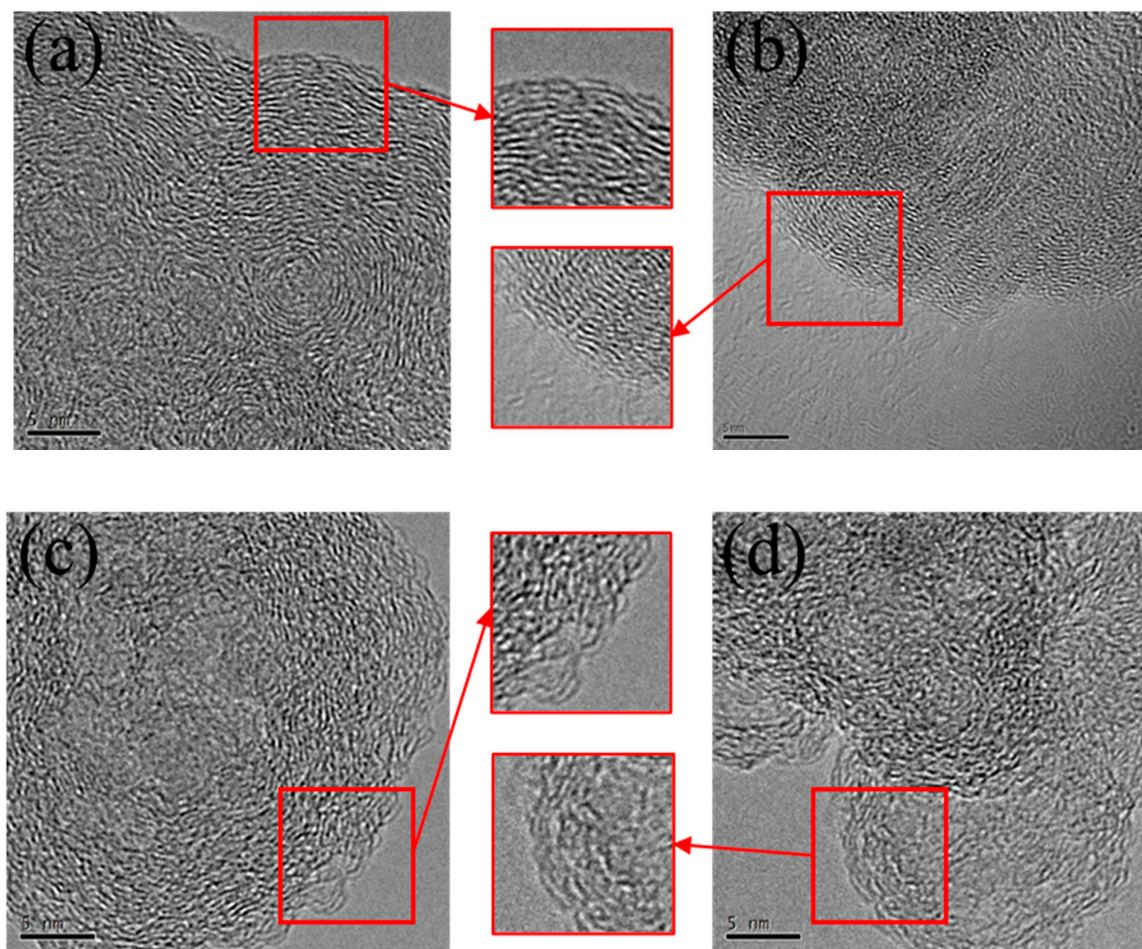


Figure 2. Microstructure comparison of soot particles with different oxidation rates of (a) 0%, (b) 56.1%, (c) 71.2%, and (d) 89.4% at 5 nm scale.

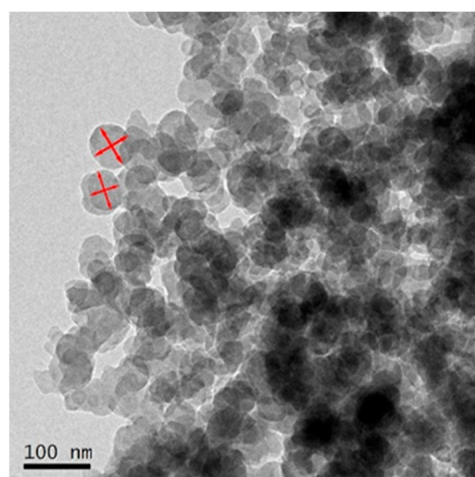


Figure 3. “Cross method” measurement method.

In order to more accurately describe the changes in the microstructure of carbon soot particles, high-resolution images of carbon soot particles were measured using the image processing software ImageJ. The microstructural characteristic parameters of carbon soot particles were obtained in order to quantitatively compare the thermal aging of carbon soot particles with different oxidation rates. The images were first set to scale, followed by Fourier variation, filtering, Fourier inverse variation, image binarization, and image skeletonization [20]. After processing the image through the above steps, each carbon layer became a line with a width of only 1 pixel. The carbon layer spacing refers to the spacing between two adjacent carbon layers, as shown in Figure 4. Carbon layer spacings (d_n) were measured, and the measured results were then divided by the number of carbon layers n to obtain the average carbon layer spacing (D). D was used to represent the carbon layer spacing of carbon soot particles to reduce the error caused by the measurement. The distortion (T) of the carbon layer cannot be directly measured; it is the ratio of the length (La) of the carbon layer and the distance s between the two endpoints of the carbon layer. The carbon soot particles consist of the accumulation of basic carbon particles; as basic carbon particles are more subjected to particle size statistics, the results become more accurate. Thus, more than 400 data were measured for each oxidation state of the carbon soot particle images.

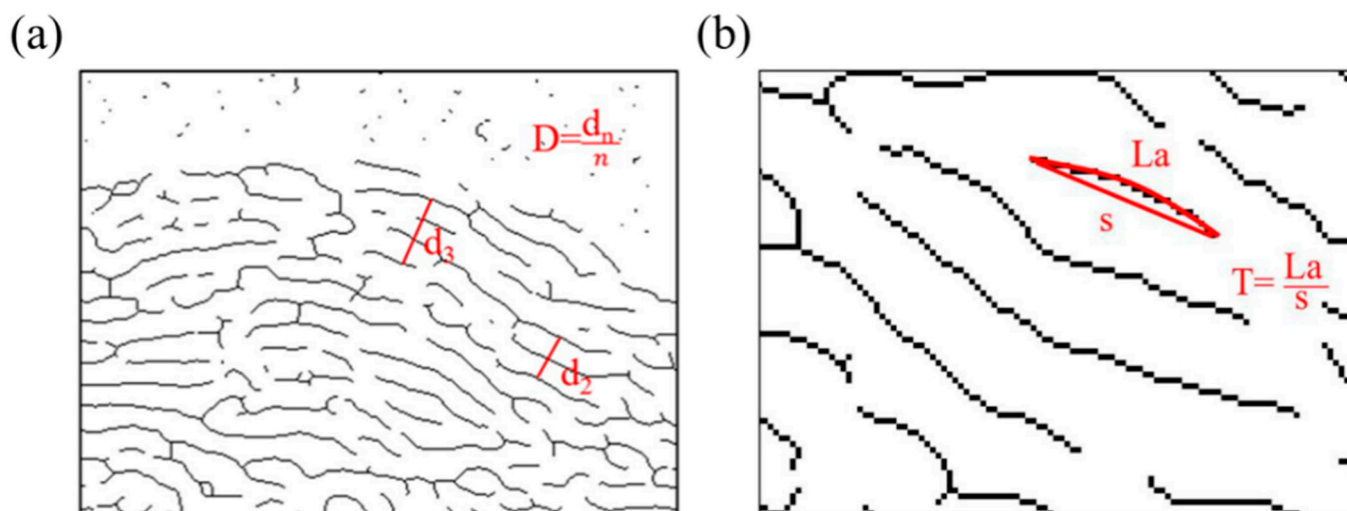


Figure 4. Schematic diagram of carbon layer spacing (a) and distortion (b).

3.1. Particle Size Analysis

The soot images after each group of reactions were selected, as shown in Figure 5(I–IV). The TEM image was taken at a scale of 100 nm, and the soot particle size was calculated using the “cross method”. After the measured data were counted and organized, we analyzed the particle size of carbon soot in each oxidation state. As can be seen in Figure 6, the basic particle size distributions of the experimental carbon soot at 0%, 56.1%, 71.2%, and 89.4% oxidation levels were between 0 and 65 nm, but the particle size peaks were in different intervals for different oxidation levels.

In the first group of carbon soot with 0% oxidation (in Figure 5a), the peak particle size appeared in the range of 30–35 nm, and the percentage of particles in the range of 30–35 nm was 23.29%. In the first group with an oxidation rate of 0%, 60.27% of carbon soot particles were distributed in the interval of 25–40 nm, and their average particle size was calculated as 36.438 nm.

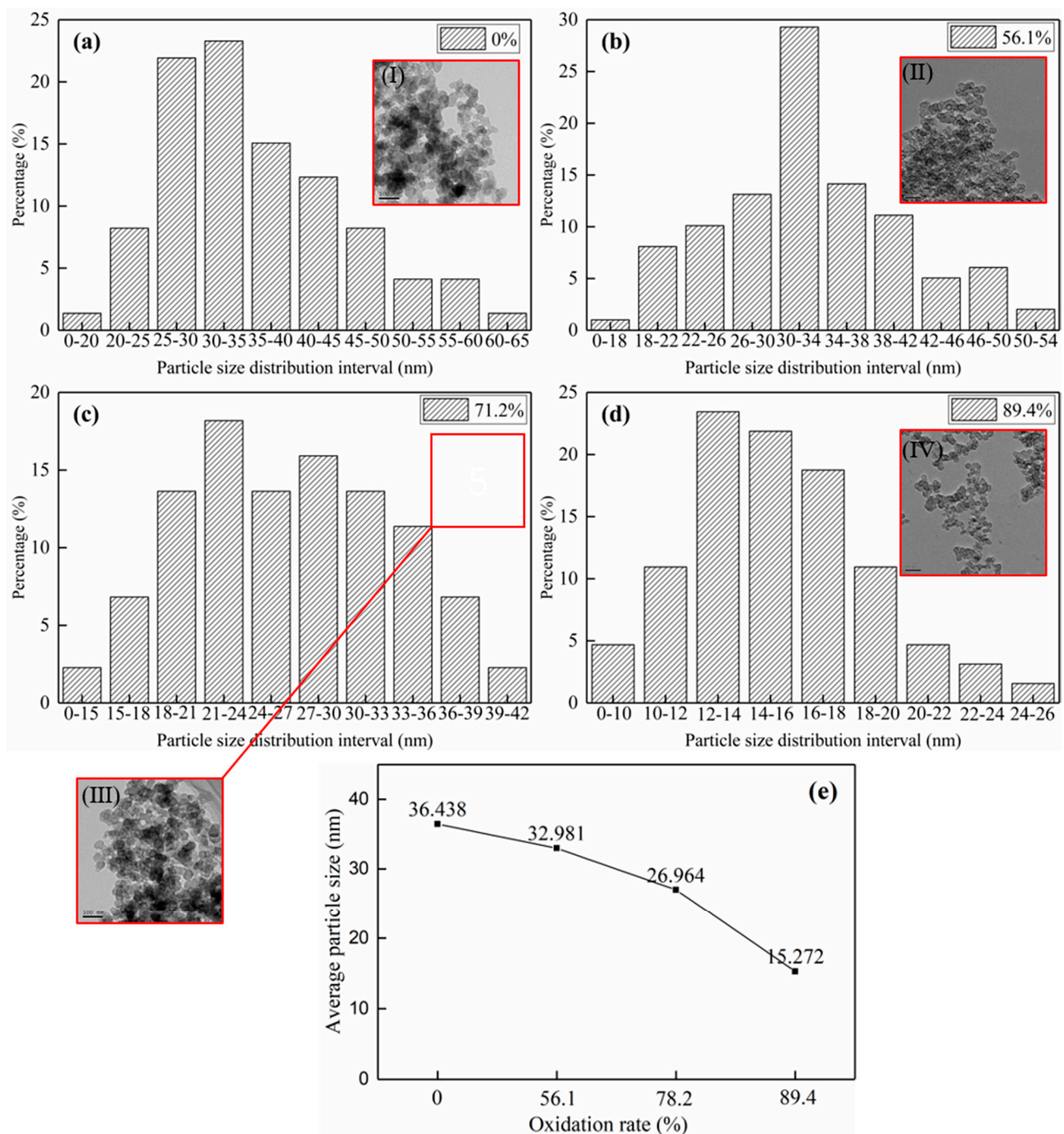


Figure 5. Particle size distribution and average particle size for different soot oxidation rates: (a) 0%, (b) 56.1%, (c) 71.2%, (d) 89.4%, (e) average particle size.

In the second group of carbon soot with 56.1% oxidation (Figure 5b), the peak particle size appeared in the range of 30–34 nm, and the percentage of particles in the range of 30–34 nm was 29.29%. More than half of the carbon soot particles were distributed in the range of 26–38 nm, and the average particle size was calculated as 32.981 nm.

In the third group of carbon soot with 71.2% oxidation (Figure 5c), the peak particle size appeared in the range of 21–24 nm, and the percentages of particles in the ranges of 21–24 nm, 24–27 nm, and 27–30 nm were 18.18%, 13.64%, and 15.91%, respectively. Nearly half of the carbon soot was distributed in the range of 21–30 nm. The average particle size of the carbon soot particles in the second group was 26.964 nm.

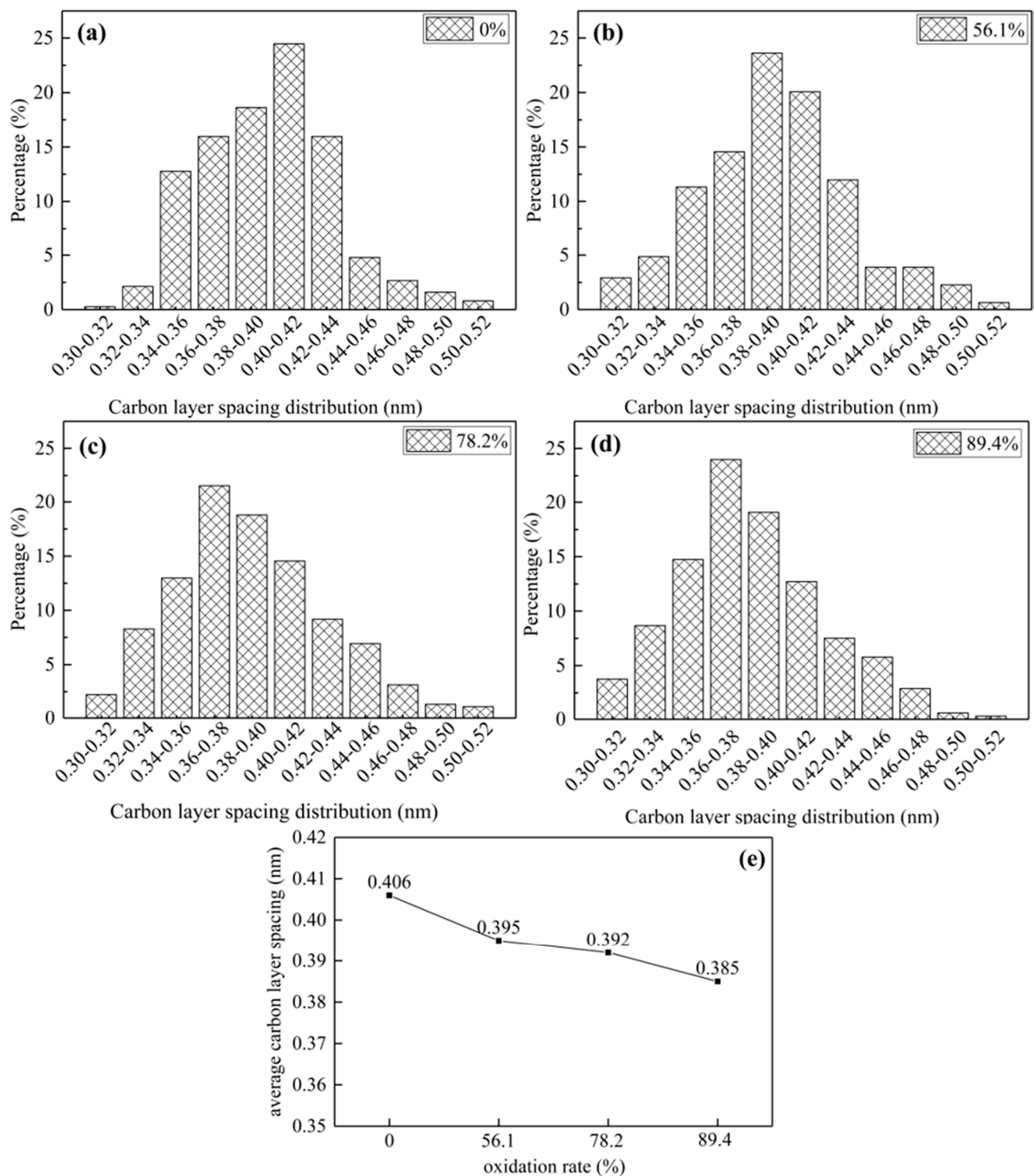


Figure 6. Carbon layer spacing distribution and average interlayer spacing for different soot oxidation rates: (a) 0%, (b) 56.1%, (c) 71.2%, (d) 89.4%, (e) average carbon layer spacing.

In the fourth group of carbon soot with 89.4% oxidation (Figure 5d), the peak particle size appeared in the range of 12–14 nm, and the percentages of particles in the ranges of 12–14 nm, 14–16 nm, and 16–18 nm were 23.43%, 21.88%, and 18.75%. More than 60% of carbon soot particles were in the range of 12–18 nm, and the average particle size was 15.272 nm.

Soot particles are mainly composed of spherical or nearly spherical basic carbon particles, with a particle size of 20–40 nm. According to the comparison of these four sets of experimental data, the distribution range of their peaks became smaller and smaller; the average particle size of carbon soot obtained from the four sets of experiments was 36.438 nm, 32.981 nm, 26.964 nm, and 15.272 nm. It can be concluded that, with the increase in oxidation rate, the particle size of carbon soot particles decreased. Comparing Figure 5(I–IV), it can also be seen that the particle size of soot particles continued to decrease, the basic particle edge structure of soot particles was gradually blurred, and the disordered structure inside the soot particles increased, indicating that the oxidation of soot particles started from the outer layer. As the outer layer was gradually oxidized, the inner carbon layer became exposed. The number of carbon atoms at the edge of the carbon layer increased, and the oxidation reaction of the carbon layer caused the structure to be destroyed or oxidized, leading to a gradual decrease in particle diameter.

3.2. Carbon Layer Spacing Analysis

Figure 6 shows the distribution of the carbon layer spacing. Under different oxidation levels, the carbon layer spacing of carbon soot particles was distributed between 0.30 and 0.52 nm, showing a single-peak distribution. At a 0% oxidation level, the peak of carbon layer spacing distribution was in the range of 0.40–0.42 nm, with the highest percentage of 24.47%. At a 56.1% oxidation level, the peak of carbon layer spacing distribution was in the range of 0.38–0.40 nm, with the highest percentage of 23.62%. At a 78.2% oxidation level, the peak of carbon layer spacing distribution was in the range of 0.36–0.38 nm, with the highest percentage of 21.62%. The peak of carbon layer spacing distribution was found in the interval of 0.36–0.38 nm at a 78.2% oxidation level, with a percentage of 21.48%. The peak of carbon layer spacing distribution was found in the interval of 0.36–0.38 nm at an 89.4% oxidation level, with the highest percentage of 23.99%.

Comparing the four groups of carbon layer spacing distribution maps, it can be seen that the distribution of carbon layer spacing gradually moved to smaller spacing as the oxidation rate increased. In particular, when the oxidation rate increased from 0% to 78.2%, the peak of carbon layer spacing decreased from being in the 0.40–0.42 nm interval to being in the 0.36–0.38 nm interval. It can also be deduced from the calculation that the average carbon layer spacing was 0.406 nm for a 0% oxidation rate of carbon soot, 0.395 nm for a 56.1% oxidation rate, 0.392 nm for a 78.2% oxidation rate, and 0.385 nm for an 89.4% oxidation rate, while the average value of carbon layer spacing tended to decrease with the increase in oxidation rate. The standard deviation of each oxidation rate could also be calculated. The four standard deviations of oxidation rate from 0% to 89.4% were $x_1 = 14.5$, $x_2 = 12.25$, $x_3 = 8.67$, and $x_4 = 5.27$. Thus, as the oxidation rate increased, the fluctuation of the sample data gradually decreased.

Since the interlayer spacing mainly reflects the distance between two adjacent microcrystalline layers of the basic carbon particles, a smaller interlayer spacing indicates a more compact microstructure of the basic carbon particles, thereby increasing the degree of graphitization of the soot particles. A smaller soot particle layer spacing resulted in a smaller contact space with oxygen and a lower oxygen concentration, which prevented oxygen from entering the edge of the microcrystalline carbon layers on both sides. The proportion of activated carbon atoms in the microcrystalline carbon layer decreased, thereby reducing the activity of the edge carbon atoms. Therefore, as the oxidation rate increased, the oxidation activity also decreased.

The layer spacing describes the relative arrangement direction between the microcrystalline carbon layers, which is close to the distance between the microcrystalline carbon layers. As the soot particles were oxidized, their oxidation activity was constantly weakened. The reduced activity of the carbon atoms at the edges of the carbon layer inhibited the oxygen components from entering the microcrystalline carbon layer, thus causing a decrease in the oxygen concentration and the contact space between the carbon layer and

oxygen. Moreover, the distance between the carbon layers decreased with the increasing degree of oxidation.

3.3. Carbon Layer Distortion Analysis

As can be seen in Figure 7, the distribution of carbon layer distortion for the four oxidation states also showed a single-peak distribution, with distortion peaks of carbon soot particles with different oxidation rates located at different intervals. For the carbon soot particles with a 0% oxidation rate, the most prevalent interval of carbon layer distortion was 1.12–1.16, followed by 1.08–1.12, and the least distributed interval was 1.32–1.36; the mean value of carbon layer distortion was calculated to be 1.143. For the carbon soot particles with a 56.1% oxidation rate, the most prevalent interval of carbon layer distortion was 1.08–1.12. For carbon soot particles with a 71.2% oxidation rate, the distribution was similar to that for a 56.1% oxidation rate, but with a reduced range of distribution; the most prevalent interval of carbon layer distortion was 1.08–1.12, and the average value of carbon layer distortion was calculated as 1.135. For the carbon soot particles with an oxidation rate of 89.4%, the distribution range of carbon layer distortion was 1.08–1.12, and the mean value of carbon layer distortion was calculated as 1.118. On the basis of the decreasing distribution range and mean value of carbon layer distortion, it can be concluded that the carbon layer distortion of carbon soot particles decreased with the increase in oxidation degree.

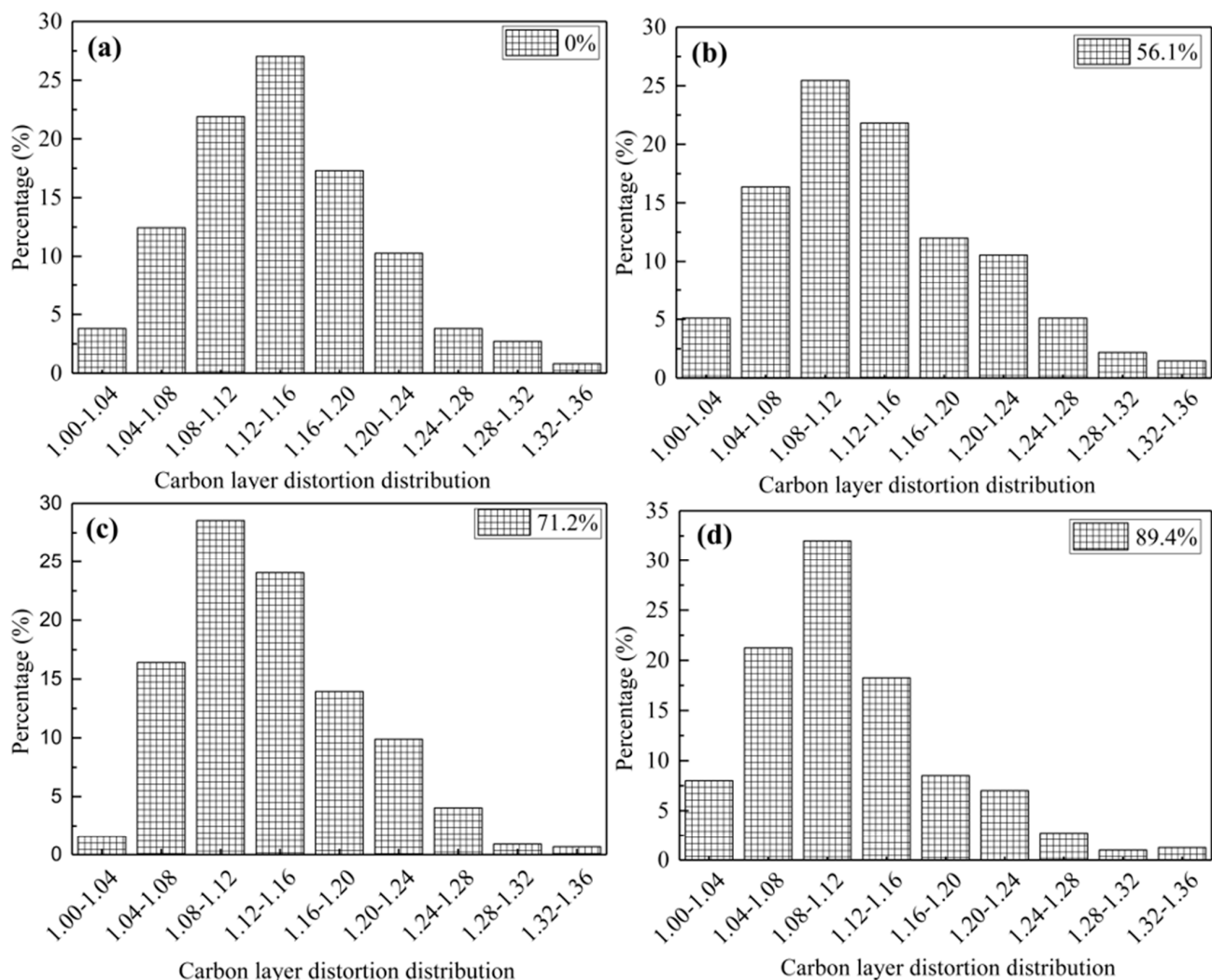


Figure 7. Cont.

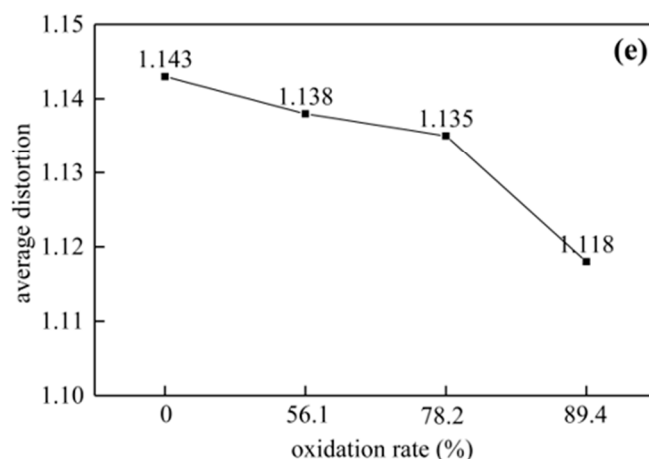


Figure 7. Carbon layer distortion distribution and average tortuosity for different soot oxidation rates: (a) 0%, (b) 56.1%, (c) 71.2%, (d) 89.4%, (e) average distortion.

The size of the crystallite curvature can directly reflect the proportion of odd-numbered carbon rings in polycyclic aromatic hydrocarbons. A decrease in the distortion indicates that the number of odd carbon rings is decreasing, while the increase in internal dehydrocarbonization of the soot particles results in a more regular microstructure and a greater degree of graphitization. At the same time, the decrease in the degree of distortion causes a reduction in the force of chemical bonds in the internal structure, as well as in the repulsive force between adjacent carbon layers, while the microcrystalline carbon layer is promoted to reach the minimum energy state. The activation energy of the corresponding soot particles increases, and the oxidation activity decreases. As with the law of decrease in the interlayer spacing of adjacent carbon layers, thus reflects the reduction in oxidation activity of the soot particles.

3.4. Analysis of Oxidation Patterns

Oxidation models provide the necessary information to describe the transformations during the oxidation of carbon soot. Chang et al. introduced three classical oxidation models [21]: (1) the shrinkage nucleation model (SCM), as shown in Figure 8(a1), which always maintains an unreacted nucleus as the reaction process proceeds; (2) the homogeneous reaction model, which maintains a constant particle size and decreases in density as oxidation proceeds; (3) the internal oxidation model (IOM), as shown in Figure 8(a2), where carbon soot produces a hollow structure during the oxidation process.

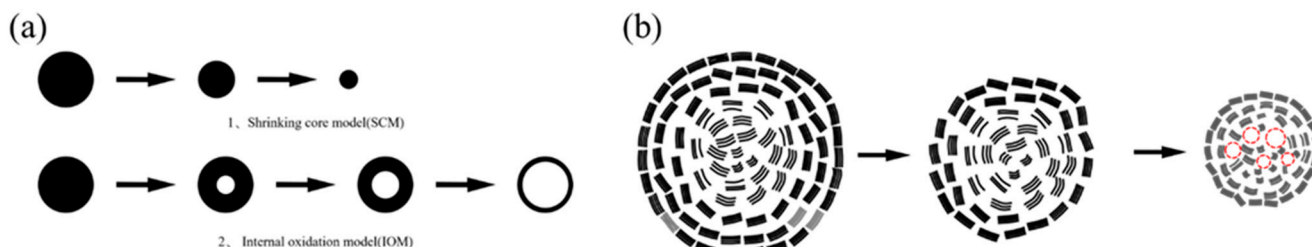


Figure 8. (a) Schematic diagram of oxidation model; (b) diagram of soot oxidation model. Developed from [21].

According to the particle size analysis of the particles, with the increase in oxidation rate, there was a decreasing trend of particle diameter. The average particle size of carbon soot particles ranged from 36.438 nm at a 0% oxidation rate to 15.272 nm at an 89.4% oxidation rate. A continuous decrease in particle size and oxidation of the outer region of the particles occurred ahead of the inner region, as observed in the TEM pictures,

indicating that the carbon soot oxidation process followed the shrinkage nucleus model oxidation mode.

The oxidation of carbon soot also followed the internal oxidation model during the carbon soot particle oxidation process. In Figure 9b, it can be found that the TEM image for a carbon soot oxidation rate of 56.1% gradually became blurred at the edges of the carbon soot compared with the unoxidized carbon soot, and disorder gradually appeared among the particles. As the oxidation rate increased, the ordered crystalline structure eventually transformed into amorphous carbon. Due to the surface reaction, the surface of carbon soot particles gradually became rough. With the oxidation proceeding, it can be observed in Figure 9c,d that carbon soot was oxidized to form multiple cavities inside the carbon soot when the oxidation rate reached 71.2%.

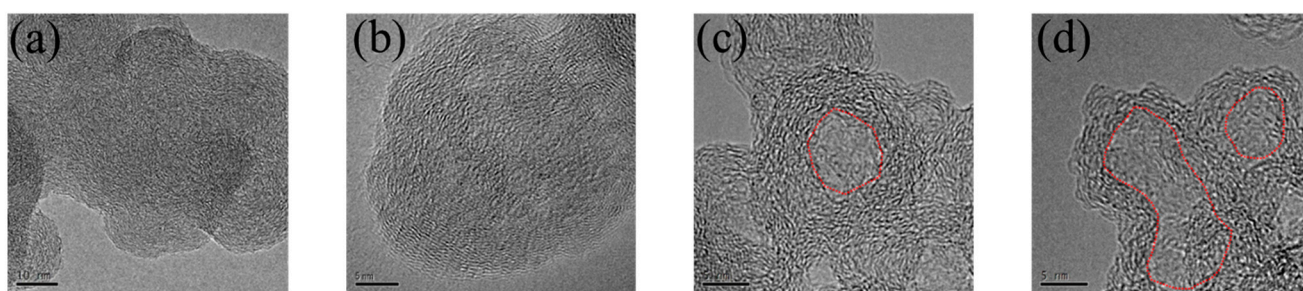


Figure 9. Microstructure of soot particles with different oxidation rates of (a) 0%, (b) 56.1%, (c) 71.2%, (d) 89.4%.

It was found experimentally that the carbon soot carbon layer spacing gradually decreased as the oxidation process increased, while the density inside the particles gradually increased. In addition, by comparison, the carbon layer length of carbon soot gradually became shorter with the increase in oxidation degree during the oxidation process. In summary, the oxidation model of carbon soot is modeled in Figure 9b, following the pattern of contraction nucleation and internal oxidation.

4. Conclusions

- (1) With the increase in oxidation rate, the average particle size of carbon soot particles decreased. The basic particle edge structure of carbon soot particles gradually became blurred, and the disordered structure inside the smoke particles increased, indicating that the oxidation of carbon soot particles started from the outer layer. With the gradual oxidation of the outer layer, the structure was destroyed or oxidized away, which led to a gradual decline in the diameter of the particles.
- (2) As the oxidation rate increased, the carbon layer spacing of carbon soot particles decreased, indicating that the microstructure of the basic carbon particles became more compact and orderly, which led to an increase in the graphitization of carbon soot particles and a decrease in oxidation activity.
- (3) With the increase in oxidation rate, the carbon layer distortion of carbon soot particles decreased, indicating a more ordered structure of the generated carbon soot particles, a more regular and graphitized microstructure, and a smaller repulsive force between adjacent carbon layers. This promoted the microcrystalline carbon layer to reach the minimum energy state, and the oxidation activity of carbon soot particles decreased.
- (4) During the oxidation of carbon soot particles, their size decreased continuously, and they maintained an unreacted inner core. In addition, the internal oxidation of carbon soot resulted in the formation of multiple cavities with a hollow interior and an irregular shell. The oxidation of carbon soot particles followed the contraction model and the internal oxidation model.

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Conflicts of Interest: The authors declare no conflict of interest.

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