



공학박사 학위논문

# 미세먼지 제거를 위한 환원 그래핀 옥사이드 필터

A reduced graphene oxide filter for particulate matter removal

2021년 2월

서울대학교 대학원

기계항공공학부 정원지

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이 논문을 공학박사 학위논문으로 제출함

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#### Abstract

# A reduced graphene oxide filter for particulate matter removal

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Air pollution is one of the most serious problems facing mankind because of its impact on ecosystems and human beings. In particular, particulate matter less than 2.5 micrometers in diameter  $(PM_{2.5})$  is the biggest problem that threatens human health. Here, it is firstly presented a filter that removes the PM<sub>2.5</sub> at a high efficiency with a low pressure-drop. A high surface area afforded by a two-dimensional nanomaterial of reduced graphene oxide (rGO) and a highly porous structure provided by an rGO foam render the filter efficient PM removing and enable low pressure drop operation. Repeated regeneration and reuse with little loss of efficiency demonstrates the robustness of the filter. Additionally, its quality factor which represents overall efficiency was almost twice the best ever reported in the literature. The copper- based reduced graphene oxide (C-rGO) filter with the rGO foam formed on both sides of a copper mesh plays role of removing the outdoor PM and at the same time purifying the indoor PM efficiently. Moreover, this

thesis introduces a filter system that removes both filterable PM (FPM) and condensable PM (CPM) from pollution source with high efficiency. The system which is consisted of two nichrome-based reduced graphene oxide (NrGO) filters and a condenser between them can remove the usual FPM and at the same time CPM-induced dust particle that typically leaves the pollution source unabated. The filters, quite effective in removing the PM with their three-dimensional structure, retain the removal capability even at high temperature and in acidic condition that prevail at the pollution source. With advantages such as simple fabrication, easy scaling-up, bidirectionality, and low pressure drop, the filter presented here would exemplify the desirable set of characteristics for the PM removal filters. And the proposed filter system could provide a solution for removal of both FPM and CPM from the pollution source.

**Keywords**: air pollution, particulate matter removal filter, reduced graphene oxide, indoor PM purification, condensable PM, thermal stability and acid resistance, pollution source.

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#### **Chapter 1. Introduction**

Poor air quality can have adverse effects on human health, climate, and ecosystems.[1, 2] An average adult breathes in approximately 15 m<sup>3</sup> of air a day through 20,000 times of respiration.[2, 3] Therefore, the air pollution caused by rapid industrialization of the world is one of the most serious problems facing mankind.[4-6] Various substances causing air pollution include CO<sub>x</sub>, NO<sub>x</sub>, SO<sub>x</sub>, organic matters, and particulate matter. Among these, the particulate matter that has an aerodynamic equivalent diameter of less than 2.5 micro-meters  $(PM_{2.5})$  is the most controversial factor threatening human health. This microscopic solid or liquid substance penetrates into the alveoli during respiration and can cause fatal problems such as cardiopulmonary disease and trachea cancer.[3, 7-11] Besides, direct blocking of sunlight by the particles has a bad influence on ecosystem. [12, 13] PM<sub>2.5</sub> is released into the atmosphere mainly by industrial exhausts, secondary inorganic aerosol, soil dust, and coal combustion.[14] Because of the seriousness, the PM has become an environmental problem that has attracted much attention not only from developing countries such as China and India but also from the United States, Europe, and the world.[15-17]

Many conventional filter systems have been utilized to remove  $PM_{2.5}$  by size exclusion. Most of them, however, suffer from high power consumption,

large pressure drop, and large filter volume. To resolve these problems, a new class of PM removal filters has been advanced using nanomaterials[11, 18] that is based on adsorption rather than size exclusion. Various polar polymer nanofiber networks formed through electrospinning, for instance, were introduced to produce high-efficiency transparent PM removal filters.[1] Various metal-organic-framework materials were utilized to form a large area PM removal filter through a roll-to-roll technique.[19] In addition, silver nanowires were used to advance a reusable, active PM removal filter.[11]

Electrospun polymer nanofiber



Figure 1-1  $PM_{2.5}$  removal filter research

Metal-organic framework coated mesh



Nanofiber Sponge



For any adsorption-based filters, a high surface area is highly desirable. When the particulate matters are removed by adsorption onto the filter surface, more such matter would be captured if the surface area were larger. In general, a porous structure made of two-dimensional material has a larger surface area per weight inherently than porous structure made of one-dimensional material. The filters developed so far, however, are made of nanoparticles or nanofibers.

In this thesis, it is firstly explored that graphene oxide (GO), a 2-D material, in designing a filter for removing PM<sub>2.5</sub>. GO is a carbonaceous material that has excellent oxidation resistance, and good electrical conductivity[20, 21] when converted to reduced graphene oxide (rGO). GO nanoplates were assembled into a porous network using an self-assembly method on copper or nichrome mesh and then turn it into an rGO porous structure by thermal reduction.[22] Each filters named as C-rGO (copperbased reduced graphene oxide) filter and N-rGO (nichrome-based reduced graphene oxide filter) filter. This 3-D rGO assembled filter is quite porous with large pores, requiring little pressure drop for flow of air. High surface area and little pressure drop render the filter very efficient in PM<sub>2.5</sub> removing. And rGO structure forms on both sides of a copper mesh. Therefore, the side of the filter facing the outside can remove PM<sub>2.5</sub> from the air ventilated into a house, and at the same time the other side facing inward can filter household  $PM_{2.5}$ . This bidirectional nature of the filter makes it valuable in light of the

fact that a long-term exposure to just 10 micrograms of PM<sub>2.5</sub> in the indoor, which could be generated by cooking and other human activities, has an adverse effect on human health.[23, 24]. Therefore, it is firstly confirmed that a porous structure which was fabricated by conductive rGO, has fine dust removal performance.

And then, this thesis explores a filter system that effectively removes both filterable PM and condensable PM at the pollution source for the first time in the world. It was found that the reduced graphene oxide filter to be efficient in removing both PM under the conditions prevailing at the pollution source. Nichrome mesh was used as a substrate instead of copper, which is weak to heat and oxidation.[25-28] The improved thermal stability and chemical resistance of the filter made it suitable for the filter installation directly at the pollution sources unlike other PM removal filters made of polymer nanofiber. It was verified that an oil heater and a condenser can be used to generate both types of PM through a method inspired by the US EPA (Environmental Protection Agency) method 202, and demonstrate that rGO filter system removes PM efficiently. In addition, the feasibility of the filter was checked in harsh PM generation environment.

## Chapter 2. Particulate matter (PM) removal using copper-based reduced graphene oxide (C-rGO) filter

In this chapter, it is confirmed that the applicability of copper-based reduced graphene oxide (C-rGO) as a PM<sub>2.5</sub> removal filter. After forming a threedimensional structure by graphene oxide (GO), electrical conductivity is given through a reduction process. The filter removes  $PM_{2.5}$  with high efficiency (> 99.9%). Various chemical analysis is conducted to support this. Reusability and durability of C-rGO filter is also found. Moreover, it can purify indoor  $PM_{2.5}$  simultaneously due to the bidirectional characteristic.

#### 2.1 Preparation of C-rGO filter

#### 2.1.1 Graphene oxide solution

Graphene oxide (GO) solution were prepared by a modified Hummer's method as shown in Figure 2-1. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 99%), potassium permanganate (KMnO<sub>4</sub>, 99.3%), and graphitic powder were mixed in a beaker and the mixture was stirred at 45 degrees for 6h. It was neutralized by deionized water and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%). By filtering the solution using a membrane filter (47mm diameter, 0.45  $\mu$ m pore size), the GO buckypaper was obtained. Annealing at 60 degrees for 24h leads to GO powders. Finally, the GO solution was made by dispersing the GO powders in deionized water in concentrations of 2 mg/ml.[22] Figure 2-2 is Atom force microscopy(AFM) image of fabricated graphene oxide.



Figure 2-1. Preparation of graphene oxide solution



Figure 2-2. Atom force microscopy image of fabricated graphene oxide

#### 2.1.2 Fabrication of C-rGO filter

#### 2.1.2.1 Self-assembled rGO structure

For the fabrication of C-rGO filter, the self-assembly method was used. The prepared GO solution was placed in a customized bottle. Copper mesh (300 µm opening) and copper plate (99.9%) were rinsed with DI water and sonicator for 30 min. For this process, they were then immersed into the GO solution (2 mg/mL), 1 cm apart. Using the copper mesh as an anode, 5V of DC voltage was applied between the copper mesh and the copper plate. The GO nanoplates are attracted by the electrostatic force at the anode and adhere to the surface. The cupric ions acting as electron carriers bond with the surrounding GO nanoplates, leading to a hydrogel structure. In the case of copper, the condition in which cupric ions melt when voltage is applied in a two-electrode system is not complicated. Therefore, copper was used as metal because it was easy to fabricate the structure and the price was relatively inexpensive. Consequently, the copper-based GO (C-GO) structure forms on the copper mesh, which was dried in a vacuum chamber at room temperature for 3h. Finally, it was annealed under vacuum at 220 degrees for 5 h to remove residual water and functional groups. The annealing reduces GO to rGO structure, which was used for PM removal filter[22] and named it as C-rGO filter. Figure 2-3(a) illustrates this self-assembly method of coating 3-D

porous GO onto the copper mesh. This filter can easily be scaled up by increasing the size of the copper mesh.[29] (see Figure. 2-4)

#### 2.1.2.2 Spectroscopy of C-rGO filter

The pores of the C-GO aerogel are several tens of microns in size as seen in the typical Scanning Electron Microscope (SEM) image in Figure 2-3(a). These large pores permit easy air flow through the foam. The optical images of the initial C-GO hydrogel and the C-rGO structure resulting from a thermal reduction are shown in Figure 2-3(b) and (c), respectively. Because of the reduction, color of GO changes from brown to black. The 3-D C-rGO structure formed on copper mesh (C-rGO filter) is used as the PM removal filter.



Figure 2-3. C-GO fabrication process, and structure: (a) Illustration of C-GO fabrication process. Scanning Electron Microscope (SEM) image shows the GO coated surface (Scale bar is 50  $\mu$ m). (b) Optical image of copper mesh right after C-GO fabrication process. (c) Optical image of C-rGO coated copper mesh right after thermal reduction process (C-rGO filter)



Figure 2-4. The optical image of large C-rGO filter

#### 2.1.3 Characteristics of C-rGO filter

As shown in Figure 2-5, the C-rGO structure consists of pores with various diameters with an average pore size of 7.3 µm. The electrical conductivity of the C-rGO formed on the metal mesh was 1700 S/cm, which is comparable to the value reported for rGO structures[30], enabling it to remove PM by electrostatic attraction force. It is used two point probes measurements to obtain electrical conductivity of material.[31] First, sample material was prepared as close to the cuboid as possible. Then, current and voltage drop across the material were measured by DC powers supplier (IT6720, Itech electronics, South Korea). Using this, the resistance was calculated and then resistivity was also obtained by sample's cross sectional area, length, and resistance. Finally, find the inverse value of the resistivity to calculate the electrical conductivity.[32]

For comparative purposes, air filters were purchased, polypropylene (Com #1, Cleanairtech Co., South Korea) and polyethylene terephthalate filter (Com #2, Haniltech Co., South Korea), which are commonly used commercial filters, to analyze their electrical conductivities.[1, 33-35] (These commercial filters will also be used in later comparative experiments) The commercial filters have no electrical conductivity, implying that they are not suitable for electrostatic precipitation



Figure 2-5. Pore diameter distribution of rGO structure

#### 2.2 PM removal performance of C-rGO filter

#### 2.2.1 Method

Particulate matter of high density was generated by burning the incense. It consists of high density PM with various diameters that are mostly less than 2  $\mu$ m.[11] A power supplier (IT6720) was used to supply voltage to the filter. Ion discharger (TFB-YD1249, Trump Electronics International Group Co, China) was used as a negative ionizer that provides negative charge to PM. The concentration of PM<sub>2.5</sub> was measured by Laser particle sensor module (PM2005, Wuhan Cubic Optoelectronics Co, China). PM counter has a measurement range up to 2000  $\mu$ g/m<sup>3</sup>. PM was continuously injected to the inlet side (left cell in Figure 2-6) and the concentration of PM at both inlet and outlet sides (right cell in Figure 2-6) was measured in real time for the determination of PM filtering efficiency.

A schematic diagram of the experimental setup to test the  $PM_{2.5}$  removal performance of C-rGO filter is illustrated in Figure 2-6. The filter was placed between two separate cells. PM was injected into the inlet side by burning incense and the concentration of  $PM_{2.5}$  was measured in real time using a counter. At the same time, a negative ionizer was installed to charge the PM from incense. When a voltage of 12V was applied to the ionizer, a current of 0.005A occurred. The concentration of PM in the outlet side, was also measured simultaneously. Positive voltage (5 V) was applied to the filter so that the rGO plates on C-rGO filter were charged. An optical image of the experimental setup is shown in Figure 2-7. The experiment was carried out by constantly burning incense to inject  $PM_{2.5}$  continuously into the inlet side.



Figure 2-6. Schematic experimental setup for PM removal with C-rGO filter



Figure 2-7. Optical image of actual experimental setup for PM removal with C-rGO filter

#### 2.2.2 PM removal demonstration

#### 2.2.2.1 PM removal using C-rGO filter

Figure 2-8 shows the result of control sample for which a bare copper mesh (300 µm opening) was placed between the two cells instead of C-rGO filter. As the smoke from the incense was introduced into the inlet side, the concentration of  $PM_{2.5}$  immediately soared to 2000 µg/m<sup>3</sup>. The outlet side PM concentration followed suit in a jagged way after a minute delay, clearly indicating that the bare copper mesh did not collect PM. When the proposed C-rGO filter was placed between the two cells, on the other hand, the outlet PM concentration tapers downed immediately to a negligible level as shown in Figure 2-9 despite the persistently high level of PM concentration introduced at the inlet side at 2000  $\mu$ g/m<sup>3</sup>. From this result, the dust removal efficiency of C-rGO filter was calculated to be higher than 99.9%. The optical image in the inset of Figure 2-9 shows the tissue paper rubbed against the inlet side wall and the outlet. The tissue rubbed against the inlet side is stained by the PM accumulated whereas the one at the outlet is clear. The PM particle collection could be ascribed to the electrostatic attraction force between the negative charge of PM and the positive charge of the filter.[11] As can be seen in the Figure 2-10, PM was removed only when both postive voltage and ionizer were activated. In Figure 2-11, it was obvious that the diffusion of fine dust was not restricted because of blocking the air flow by an electric field.


Figure 2-8. Experimental PM removal result with bare copper mesh



Figure 2-9. Experimental PM removal result with C-rGO filter



Figure 2-10. The result of investigation for role of ionizer and positive voltage



Figure 2-11. (a) Air flow velocity data across C-rGO filter between inlet and outlet side during PM removal experiment. (b) PM removal result in (a) experiment

#### 2.2.2.2 PM removal using rGO coated filter

It is also compared that the removal performance of rGO-coated copper mesh and that of C-rGO foam to investigate the effect of rGO surface and surface area. The ambient air dry after self-assembly process made a thin rGO film on individual copper wires constituting the mesh instead of porous rGO structure (Figure 2-12). When rGO-coated copper mesh was placed between two cells of experimental setup, PM concentration of outlet side increased to  $2000 \ \mu g/m^3$  for about 400 secs with the exposure to the incense (Figure 2-13). Comparing Figure 2-8 and Figure 2-13, rGO surface seems to help the adsorption of PM on the mesh. However, rGO-coated copper mesh does not sufficiently collect PM<sub>2.5</sub>, implying that the removal performance of C-rGO foam presumably comes from its high surface area and suitable pore size.



Figure 2-12. SEM image of rGO coated mesh (Scale bar is 300 µm)



Figure 2-13. Experimental PM removal result with rGO-coated mesh and C-rGO foam

## 2.2.3 Microscopy for verification

#### 2.2.3.1 Scanning electron microscope (SEM)

To examine the adsorption capacity, SEM images were taken and chemical analyses were conducted. The surface morphology of the sample was obtained by using a field-emission electron microscope (Hitachi S-4800) at an acceleration voltage of 15 keV. Figure 2-14(a) and (b) show the typical SEM images of the filter before and after PM removal test, respectively. A considerable amount of dust particles is seen to be accumulated on C-rGO nanoplates as seen in Figure 2-14(b) (red region), compared to Figure 2-14(a) for fresh filter. The typical shape of the particles collected on conventional filters is spherical, with the sphere forming on one dimensional nanowire or nanofiber. In contrast, the particles adsorbed on the C-rGO filter form a surface, covering the surface like snow. For further examination, crosssectional SEMs were also taken. Figure 2-15(a) and (b) show the middle and the bottom part of the cross section of the filter, respectively. Figure 2-15(a) clearly indicates that the PM particles penetrate to the middle section and adhere to the rGO plates as they do in the bottom part (Figure 2-15(b)).



Figure 2-14. (a) SEM images of C-rGO filter before PM removal (Scale bar is  $10 \ \mu m$ ). (b) SEM images of C-rGO filter after PM removal (Scale bar is  $10 \ \mu m$ ). Dust particles were accumulated on rGO nanoplates (red region)



Figure 2-15 Cross sectional SEM image of C-rGO filter after  $PM_{2.5}$  removal test: (a) The middle part of cross section (Scale bar is 20  $\mu$ m). (b) The bottom part of cross section (Scale bar is 20  $\mu$ m)

## 2.2.3.2 Effective surface area of C-rGO filter

It is known that the surface area of self-assembled rGO structure is calculated to be 144.5 m<sup>2</sup>/g.[22] At the same time, the average density of rGO structure was measured to be 12.3 mg/cm<sup>3</sup>. Considering that the thickness of the filter is 600  $\mu$ m (see Figure 2-30), it can be estimated that C-rGO filter has a surface area of 1066 cm<sup>2</sup> per apparent area of 1 cm<sup>2</sup>. The apparent area of the filter in the experimental set-up was a circular shape with a diameter of 1.5 cm. Consequently, filter has effective surface area of 1883 cm<sup>2</sup> during removal test. Thus, large surface area afforded by the 3-D foam structure consisting of 2-D plates help maximize the electrostatic attraction effect effect.[11, 22, 36] would be the reason for such a broad surface coverage.

## 2.2.4 Spectroscopy for verification

## 2.2.4.1 Energy-dispersive X-ray spectroscopy (EDX)

The species collected on the filter were investigated by chemical analyses. The chemical composition of the sample was obtained by energy-dispersive X-ray (EDX) spectroscopy using an energy dispersive X-ray detector (Oxford Instruments, X-MaxN). Figure 2-16(a) and (b), respectively, provide EDX data for the C-rGO filter before and after the PM removal test. As given in Figure 2-16(a), the as-fabricated C-rGO filter consists of C, O, S and Cu, which is identical with existing work.[37] On the other hand, Figure 2-16(b) shows that the filter contains inorganic elements such as chlorine, potassium, and silicon in addition to the original components. Since these are ingredients of PM, it can be concluded that these dust particles are adsorbed on C-rGO filter surface.[14, 38] The EDX mapping images in Figure 2-17 reveal the existence of these components throughout the surface, indicating that the dust particles are uniformly adsorbed on the rGO plates and that the large surface area is utilized very effectively.



Figure 2-16 Energy-Dispersive X-ray (EDX) analysis result of C-rGO filter:

(a) before and (b) after  $PM_{2.5}$  removal test



Figure 2-17 EDX mapping analysis result of C-rGO filter after PM<sub>2.5</sub> removal test: Mapping result for (a) chloride, (b) silicon, and (c) potassium

## 2.2.4.2 X-ray photoelectron spectroscopy (XPS)

To probe the chemical binding characteristics of the filter before and after the PM removal test, X-ray photoelectron spectroscopy (XPS) was carried out. The chemical properties of the sample were investigated by an XPS spectrometer (Kratos, AXIS-HSi). As shown in Figure 2-18(a), the fresh C-rGO filter has strong C-C, C-O, and C-O-C bonds at 284.6 eV, 285.7 eV, and 286.7 eV, respectively. It also has very weak C=O and O=C-O bonds at 287.9 eV and 289.1 eV.[39-41] After the PM removal, the filter has a C-Cl bond at 287.2 eV.[42](Figure 2-18(b) and Figure 2-19) This result is consistent with the EDX data because both of the them suggest presence of chloride. These analysis results confirm that the PM<sub>2.5</sub> species are adsorbed on C-rGO filter.



Figure 2-18 Results of X-ray photoelectron spectroscopy (XPS) analysis of C-rGO filter before (a) and after (b) PM removal



Figure 2-19 Partial results of XPS analysis of C-rGO filter after PM removal (excerpt from Figure 2-18(b)): Enlarged graph of the binding energy from 286 eV to 288.5 eV

# 2.2.5 Performance of C-rGO filter under harsh condition

#### 2.2.5.1 Pressure drop of C-rGO filter

A quantity of interest in air purification by filtration, including PM removal filter, is the pressure difference across the filter, which is a measure of how easily the air can pass through the filter. To evaluate PM removal performance under flow condition, an electric fan and anemometer (Ane3, DAIHAN) were utilized. A differential pressure gauge (testo 510, Testo, Germany) was used to measure pressure drop after filter.[1] At a flow rate of 0.5 m/s of air, the pressure drop was zero when the filter was a bare copper mesh, which increased to just 5 Pa when it was replaced with the C-rGO filter. It was also found that the pressure drop value increases linearly with the air flow rate. (Figure 2-20). Because the pressure drop is proportional to the power of the maintain system pump, it is obvious that C-rGO filter is optimized for low energy consumption.[11]



Figure 2-20 Optical image of pressure drop test result: (a) Pressure drop test result of control sample. (b) Pressure drop test result of C-rGO filter. Air flow rate is 0.5 m/s for both cases. (c) The result of time-dependent pressure drop test of C-rGO filter. (d) Pressure drop test result against air flow rate

## 2.2.5.2 PM removal under air flow and humid condition

In this context, experiment was conducted to confirm whether it is possible to remove a PM flowing with air. As presented in Figure 2-21(a), an electric fan was used to make an air flow and measured the flow rate just ahead C-rGO filter. Burning the incense to inject PM, the removal performance of the filter was checked and the results are shown in Figure 2-21(b). The filter shows a 95% removal efficiency even at a 1.1 m/s flow rate and 98.5% at 0.2m/s flow rate. For confirming whether dust particles were adsorbed by the electrostatic attraction force even in the presence of flow velocity, SEM analysis was carried out. In Figure 2-21(c) and (d), it is obvious that particles were attached to the rGO. From this, it can be concluded that C-rGO filter effectively removes PM even in the air flow.

Because most of the atmosphere contains moisture, PM removal filter have to maintain its performance even in a humid environment. As can be seen in Figure 2-22, C-rGO filter showed 98% and 95% fine dust removal performance even in a condition of 60% and 90% relative humidity, respectively. Therefore, it was proved that there is no obstacle in applying the filter even in haze weather.



Figure 2-21.  $PM_{2.5}$  removal test under the air flow: (a) Optical image of experimental setup and anemometer. (b) Result of PM removal performance according to air flow rate. (c) SEM image of the filter surface after PM removal (Scale bar is 20  $\mu$ m). (d) More magnified SEM image of the filter surface after PM removal (Scale bar is 5  $\mu$ m)



Figure 2-22. PM<sub>2.5</sub> removal test under humid condition

## 2.2.6 Reusability and durability of C-rGO filter

#### 2.2.6.1 Analysis to confirm reusability

Dust particles adsorbed on the filter by the electrostatic attraction force can be removed by the polarity of a solvent.[11] Therefore, C-rGO filter was immersed after PM removal in deionized water, which has a dipole moment of 1.85.[43] The beaker in the left hand side of Figure 2-23 remains transparent after 3 hours of soaking of a pristine C-rGO filter. On the other hand, the water in the right hand side beaker turned brown when a PM-laden C-rGO was placed in the water for 3 hours for cleaning. The SEM images in Figure 2-24 show that the adsorbed dust particles were almost removed and the original porous structure was also maintained without too much deformation.

Possible changes in chemical bonding states of the filter due to the cleaning were probed by Fourier Transform Infrared (FT-IR) spectroscopy. (Thermo Scientific, Nicolet 6700). The spectra of pristine C-rGO filter in Figure 2-25 (black curve) have C=O, O=C-O, and C-O functional groups at 1730 cm<sup>-1</sup>, 1560 cm<sup>-1</sup>, and 1100 cm<sup>-1</sup>, respectively, that are typical of thermally reduced GO structure.[44-46] In contrast, peaks due to C-N and C-Si group appear at 1210 cm<sup>-1</sup> and 840 cm<sup>-1</sup> in the case of spent C-rGO filter(blue curve). In addition, a broad peak around 3300 cm<sup>-1</sup> indicates

existence of O-H group.[1, 47, 48] This finding is consistent with previous chemical bond analysis results. The spectra of cleaned C-rGO (red curve) are almost identical with the pristine filter with the peaks for O-H, C-N and C-Si group vanished, indicating reusability of the cleaned filter.



Figure 2-23. Optical images of DI water color after 3hrs of immersion of pristine C-rGO filter (left beaker) and used C-rGO filter (right beaker) in the water, respectively



Figure 2-24. SEM image of C-rGO filter after cleaning process: (a) SEM image of the surface of the filter. (Scale bar is  $10 \ \mu m$ ). (b) SEM image of the cross section of the filter. (Scale bar is  $20 \ \mu m$ )



Figure 2-25. Fourier Transform Infrared (FT-IR) spectroscopy results of pristine, PM adsorbed, and rinsed C-rGO filter

## 2.2.6.2 Cycle performance of C-rGO filter

The reusability of the filter was tested by repeatedly cleaning and reusing the same filter five times. The results of the repeated PM<sub>2.5</sub> removal experiments are shown in Figure 2-26 that were conducted under the same conditions as in the previous PM removal experiment. Removal efficiency higher than 99% was maintained all throughout the five cycles of cleaning followed by reuse, demonstrating excellent reusability of C-rGO filter fabricated in this thesis.



Figure 2-26.  $PM_{2.5}$  removal experiment results of C-rGO filter for 5 repeated cycles of regeneration and reuse of the filter

## 2.2.6.3 Long-term PM removal of C-rGO filter

Long-term PM removal test was conducted to further investigate the durability and feasibility of C-rGO filter. Figure 2-27 shows the results of a month-long PM removal test using the filter. Since the experiment was performed outdoors, the data of the inlet side represents outdoor PM concentrations for the measurement period. On the contrary, the concentration of the outlet side was kept close to zero throughout the period due to the C-rGO filter, showing long-term purification capability of the filter.



Figure 2-27 Experimental results of long-term PM removal test with the filter

## 2.2.7 Quality factor of C-rGO filter

The quality factor (QF) introduced earlier is a measure of comprehensive efficiency of PM removal filter, given by

$$Q_F = \frac{-\ln\left(1 - E\%\right)}{\Delta P + V_{ionizer} \times I_{ionizer}} \tag{1}$$

where E,  $\triangle P$ , V and I are the PM removal efficiency, the pressure drop, voltage of ionizer and current of ionizer respectively.[49] For a comparison, data was collected and plotted the quality factor calculable from literature[1, 11, 15, 19, 50-56] along with C-rGO filter in Figure 2-28 with the inverse of the pressure drop as the abscissa. For studies not using an ionizer, only the pressure drop was considered. As can be seen in figure, C-rGO filter has the highest QF value among the PM removal filters. The unusually high quality factor of the filter can be ascribed to the 3-D structure composed of 2-D material fabricated by the self-assembly method, thereby affording large surface area and high porosity unlike the conventional methods of stacking nanofibers or wires on a mesh.



Figure 2-28 Filtration efficiency comparison in terms of quality factor vs. inverse of pressure drop

## 2.3 Indoor air purification

### 2.3.1 Bidirectionality of C-rGo filter

## 2.3.1.1 Indoor air pollution

Figure 2-29 shows the PM concentration both inside and outside of a building in Seoul, South Korea, on January 17, 2018. The outdoor measurements (black) were made outside the building and the indoor measurements (red) inside a room with the windows closed. Surprisingly, there was not much difference between the two measurements, the indoor concentration even exceeding the outdoor concentration at times. These measurements are an indication that the PM in the indoor space cannot be controlled simply by closing windows because of the dust generated by human activities, illuminating the importance of indoor air purification.



Figure 2-29 Indoor and outdoor concentrations of  $PM_{2.5}$  at a location in Seoul, South Korea, on January 17, 2018

#### 2.3.1.2 Indoor PM adsorption of C-rGO filter

Figure 2-30 is a typical SEM image showing a cross-section of a C-rGO filter with a thickness of 600 µm made by self-assembly method (2 mg/mL GO solution, 5V applied). The cylindrical and spherical shapes in the figure represent the cross sections of copper wires constituting the copper mesh. Unlike the filters typically used for PM removal, both sides of the filter, and not one side, are filters, the filter foam fully covering the mesh on both sides, which is a feature unique to C-rGO filter. This feature allows the filter to perform dual roles of not only filtering the outdoor air but also purifying the indoor air at the same time. This bidirectionality investigation was the first attempt in a PM removal researh.

Figure 2-31 gives a schematic illustration of indoor and outdoor PM removal filter. As explained shortly, both sides of the copper mesh are coated with the rGO foam. Therefore, the outdoor PM is removed when the outside air passes through the filter. At the same time, the indoor PM is also captured by the inside part of the filter, purifying the indoor air. This filter is unique in that the PM filters so far has the sole purpose of removing only the PM carried in by the outside air or only the PM inside.



Figure 2-30 Cross sectional SEM image of the C-rGO filter (Scale bar is  $250 \ \mu m$ )



Figure 2-31 Schematic illustration of indoor and outdoor PM removal by CrGO filter through electrostatic attraction force

#### 2.3.2 Indoor PM removal using C-rGO filter

To demonstrate that it filters the indoor air, a series of experiments were conducted. When the PM generated by burning incense was introduced to a cell and then the cell was closed, the PM concentration in the closed cell was high and invariant with time (Figure 2-32), as one would expect. Thereafter, five pulses of PM were introduced to the cell intermittently but this time the filter was installed one side facing inward. The PM measurements shown in Figure 2-33 clearly demonstrate that the inward side of the filter is fully functional in purifying the indoor air.



Figure 2-32 PM injection test result of the perfectly sealed cell without C-rGO filter



Figure 2-33 PM injection test result with C-rGO filter

#### 2.3.3 Indoor and outdoor PM removal test

Indoor and outdoor air purificaion was also demonstrated under real environment. As shown in Figure 2-34, two cells separated by the filter were placed on a windowsill with the windows open. The left-hand side cell, named outdoor cell, is completely open to the atmosphere whereas the other cell, named indoor cell, is not open to the outside. Given in black in Figure 2-35 is the PM concentration in the outdoor cell or the atmosphere. Given in red in the figure is the PM concentration in the indoor cell. In a series of experiments, one side of the indoor cell was opened approximately for one minute and then closed every hour and the resulting indoor cell concentration was continuously measured for 10 hours (see Figure 2-36). As shown by the red spike every hour in the figure, the PM concentration in the indoor cell jumped up when the cell was opened and then gradually decreased to almost zero when the cell was closed after one minute. Details on the concentration change are shown in the inset of the figure. This result is an indication that the filter can remove the indoor PM effectively. The PM concentration in the indoor cell remains almost zero, except when the PM is introduced intentionally to the cell, in spite of the air passing through the filter at all times from the PM-laden outdoor cell. In this experiment, PM was removed without negative ionizer because they could be polar naturally. This result shows that the filter also removes the PM from the outdoor since otherwise the PM

carried over into the indoor cell would cause the concentration to increase, which demonstrates the dual nature of the filter. Typical SEM images of the filter before and after the experiments are given in Figure 2-37.



Figure 2-34 Optical image of experimental setup for simulation of real environment



Figure 2-35  $PM_{2.5}$  removal experiment results of C-rGO filter in simulation test. The inset image is the enlarged version of one of sharp red peaks. The dotted line indicates the time at which the cell was completely sealed



Outdoor PM is removed by left side of C-rGO filter (continuously)



Outdoor PM is removed by left side of C-rGO filter (continuously)



Outdoor PM is removed by left side of C-rGO filter (continuously)

Figure 2-36. Schematic illustration of intermittent PM injection experiment. Indoor cell was opened approximately for one minute and then closed


Figure 2-37. SEM image of C-rGO filter after indoor air purification experiment that simulating the real environment: (a) and (b) SEM image of surface that adjacent to the outdoor cell air (Scale bar is 50  $\mu$ m). (c) SEM image of surface adjacent to the indoor cell air (Scale bar is 10  $\mu$ m). (d) More magnified SEM image of surface adjacent to the indoor cell air (Scale bar is 5  $\mu$ m)

# Chapter 3. Nichrome-based reduced graphene oxide (N-rGO) filter for removing PM from the source

In this chapter, nichrome-based reduced graphene oxide (N-rGO) was used as a PM removal filter for pollution source. Filterable PM (FPM) and condensable PM (CPM) which are the main cause of air pollution was removed by introduced filter system for the first time in the world. The system includes N-rGO filter for adsorbing PM and the condenser for cooling the precursor of CPM. A large surface area of N-rGO structure give the filter efficient adsorption capacity. Thermal stability and acid resistance of N-rGO filter were also investigated that suggest applicability of the filter to pollution source which has harsh condition. Various chemical analysis and experiment verify the PM removal efficiency and the robustness of the filter.

# 3.1 PM emission source

### 3.1.1 Filterable PM (FPM) and condensable PM (CPM)

PM is contained in the exhaust gas generated from the combustion reaction of fossil fuels and biomass used in automobiles, plants, and incinerators.[14, 57-59] Fossil fuel combustion which accounts for more than 80% of global energy consumption is the prime pollution source of PM.[60, 61] In general, PM is classified into filterable particulate matter (FPM) and condensable particulate matter (CPM). FPM refers to the soot that is discharged from the exhaust gas in the form of particles. CPM refers to the dust that exists in the gas phase at the exhaust gas temperature but is condensed into dust particles after cooling and dilution by atmosphere. All CPMs have been found to be PM<sub>2.5</sub> with diameter less than 2.5 micrometers, and these particles can easily penetrate and accumulate in the human body.[62, 63] Typical precursors of CPM are volatile organic compounds (VOC), nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>) etc.[64] In other words, FPM is the PM contained in the exhaust gas in the form of particles from the beginning, and CPM is the PM that is generated by condensation of the precursor in the exhaust gas after exiting the stack.[65, 66]

At present, the regulations related to PM are focused only on FPM. The United States, Europe, and China have created regulations to curtail FPM emissions from fossil fuel combustion to a level below a certain limit and this effort has significantly reduced the concentration of FPM.[65, 67, 68] However, the regulation on the CPM is also essential. Figure 3-1 shows the ratio of FPM and CPM from various types of combustion stationary pollution sources.[69, 70] Some sources emitted FPM and CPM at about the same rate while others produced CPM much more than FPM. There is also a report that 76% and 50% of PM generated from coal boilers and oil boilers, respectively, is CPM.[71] All CPM is ultra-fine PM with a diameter of 2.5 micrometers or less and they must be removed as well as FPM.[72] Unfortunately, the generation and elimination of CPM has not been addressed so far. So we tried to reduce the emission of both FPM and CPM in this research for the first time.



Figure 3-1. Component ratio of filterable particulate matter (FPM) and condensable particulate matter (CPM) of various pollution sources[69, 70]

#### 3.1.2 High temperature and acidic gas

Preventing PM from being released into the air is the most effective way to reduce the particulate matters.[14] As shown in Figure 3-2, the emission gas temperature of the major sources, such as coal plants and industrial incinerators, ranges from 50 °C to 250 °C [73-85] and thus, the filter material for the pollution source must have a good thermal stability. Therefore, a filter made of polyimide nanofiber or yttria-stabilized ZrO<sub>2</sub>, which has a relatively high thermal stability, has been utilized. However, they showed quite high pressure drop and could not prove reusability.[14, 86] Various polymer nanofiber filters, such as polyacrylonitrile (PAN), polyethylene terephthalate (PET), and polyurethane (PU), have also been studied for the PM removal. However, the filters are not available in high temperature environments.[87-89] To make matters worse, the exhaust gas from fossil fuel combustion also contains harmful acidic gases such as NO<sub>x</sub> and SO<sub>x</sub>, which promote the degradation of polymer.[90-93] Therefore, additional research is needed for the PM removal filter that can withstand both high temperature and acids and has low pressure drop.



Figure 3-2. Temperature range of flue gas flowing the exhaust pipe (black dots and lines) and the exhaust gas flowing the smokestack (blue dots and lines) of various pollution sources[73-85]

# 3.2 Preparation of experiment

#### 3.2.1 Fabrication of N-rGO filter

In this part, Nichrome mesh was used as a metal mesh instead of copper, which is weak to heat and oxidation because FPM and CPM are contained in the high-temperature exhaust gas with acidic gas [25-28] Graphene oxide (GO) was synthesized by a modified Hummer's method. In order to fabricate a 3-D porous filter, graphene oxide hydrogel was coated on the nichrome mesh through the self-assembly process. A Nichrome mesh with a 300 µm opening and a nichrome foil (Wire mesh koera Inc, South Korea), 1 cm apart, were connected to both electrodes of a DC power supply and they were immersed in the GO solution in a custom-made container at a concentration of 2 mg/mL. The mesh was rinsed thoroughly by sonication before fabrication. When a 5 V DC voltage was applied between the two electrodes, nichromebased GO (N-GO) hydrogel formed on the mesh connected to the anode. Immediately, the hydrogel was freeze-dried for 3 hours in vacuum, which turns it into a 3-D N-GO aerogel structure. Finally, by removing the functional group attached to the GO through a heat treatment at 220 °C for 5 hours, the N-rGO structure was produced.[29] This N-rGO structure on nichrome mesh was used as N-rGO filter for PM removal. A brief illustration of the selfassembly process used for making N-rGO filter is presented in Figure 3-3. As

shown in Figure 3-4, the rGO structure covered the entire filter surface of the nichrome mesh without apparent defects. The as-fabricated N-rGO filter surface is shown in the SEM image in **Figure 3-5** and **3-6** It can be seen that the three-dimensional porous structure is formed.



Figure 3-3. Illustration of filter fabrication on nichrome mesh



Figure 3-4. Optical image of fresh N-rGO filter right after thermal reduction process



Figure 3-5. SEM image of pristine N-rGO filter surface (scale bar is  $40 \ \mu m$ )



Figure 3-6. Magnified SEM image of pristine N-rGO filter (scale bar is 20  $\mu m)$ 

#### 3.2.2 FPM and CPM generation and removal system

FPM and CPM were generated by a kerosene (Daejungchem) oil heater (Alpaca TS-77, Taeseo electric co, South Korea). Graham condenser (Lklab korea, South Korea) was used to cool the gaseous CPM precursors in the exhaust gas, which transformed it into solid dust particles.

A dedicated system was organized to demonstrate that the filterable PM and the condensable PM can be removed at the same time. Figure 3-7 illustrates how N-rGO filter system works in removing FPM and CPM. The stationary pollution source in the figure has two stacks for comparison: the left stack with one PM removal filter and the right stack with two PM removal filters and a condenser. In the left stack, the exhaust gas enters the stack and FPM is removed by the filter. However, as the FPM-free exhaust gas approaches the stack outlet, it is cooled and condensed by the ambient air and CPM precursor changes to particle phase. Therefore, CPM cannot be removed from the exhaust gas and the CPM-induced particles are all emitted to atmosphere. In the right stack, the exhaust gas is cooled through the condenser after the FPM removal. That is, cooling the exhaust gas prior to emission is a prerequisite for filter system. Then, the CPM-induced dust particle is removed by the second PM removal filter. The stack finally discharges the exhaust gas from which both FPM and CPM are removed. Consequently, if two filters and one condenser are installed in series rather than just one PM removal filter, it is possible to remove both FPM and CPM from the stationary source. Studies on removing PM have merely focused on discharging FPM-removed exhaust gas, and have not considered generation of CPM by cooling.

Figure 3-8 shows a schematic diagram of the N-rGO filter system and experimental setup for a study on FPM and CPM. This system was configured by modifying the US EPA Method 202 designed to measure the concentration of CPM on a laboratory scale.[71] An oil heater was chosen as the pollution source since it is known to generate both FPM and CPM.[94] The exhaust gas from the heater flows through a pipe to the inlet side of the first membrane chamber, in which a holder containing the N-rGO filter separates the inlet from the outlet of the chamber. The details on the chamber configuration are given in Figure 3-9. A PM counter was installed in each side to monitor the change of PM concentration in real time. A negative ionizer was installed in the inlet side to negatively charge the injected PM. Applying a positive voltage of 5 V was sufficient for the PM to be adsorbed onto the rGO sheets by electrostatic attraction force.[11] The FPM filtered gas was then passed through a condenser to generate CPM from the CPM precursor in the gas, which in turn was captured in the second N-rGO filter in the second membrane chamber.



Figure 3-7. Schematic illustration of removal of both FPM and CPM at the source



Figure 3-8. Schematic diagram of FPM and CPM removal experiment setup using N-rGO filter and condenser



Figure 3-9. Schematic diagram of experimental setup for membrane chamber with N-rGO filter

# 3.3 FPM and CPM removal performance of N-rGO filter

#### 3.3.1 FPM removal using N-rGO filter

Since the porous structure of rGO on metal mesh is electrically conductive, it could adsorb all dust particles charged by a negative ionizer using electrostatic attraction force when a positive voltage is applied to the N-rGO filter.[11, 95] As stated in the literatures, the condensed CPM is the same as FPM except for its smaller average diameter. Both of them exist in the solid or liquid phase and contain water-soluble ions that make PM particles polar.[96-101] Therefore, all dust particle consisting of CPM and FPM could be captured through this mechanism by the N-rGO filter.

Figure 3-10 provides the results of the FPM generation and removal experiments. When an oil heater using kerosene as fuel is operated with plenty of oxygen, the exhaust gas contains a considerable amount of FPM. Since the exhaust gas was directly injected into the inlet side of the membrane chamber 1, a high PM concentration of  $2000 \ \mu g/m^3$  was measured at point 1 (see Figure 3-8). As the 99.9% of PM was removed while passing through the N-rGO filter installed in the membrane chamber 1, the PM concentration was dramatically decreased at point 2 (see Figure 3-8). The SEM image of N-rGO filter used in this experiment is shown in Figure 3-11. A substantial amount of PM was adsorbed on the rGO sheets (red region) by the electrostatic

attraction force, and it was distinctly different from the pristine filter surface (Figure 3-5 and 3-6) before the removal test. Although the FPM was effectively removed by the filter, the exhaust gas from which the FPM was removed still contains the CPM precursor in the gas phase.



Figure 3-10. FPM removal experiment result by the filter in membrane chamber 1 (maximum measurement value of PM counter is 2000  $\mu$ g/m<sup>3</sup>)



Figure 3-11. SEM image of N-rGO filter used in membrane chamber 1 after PM removal experiment (scale bar is 10  $\mu$ m). Red region represents accumulated dust particles

#### 3.3.2 CPM removal using N-rGO filter

# 3.3.2.1 CPM generation verification

To verify the generation of new dust particle from CPM after the removal of FPM from the exhaust gas, the gas was cooled by a condenser after it passed through the first membrane chamber according to the configuration in Figure 3-8. In theory, the CPM precursors that were emitted in the gaseous state are transformed to dust particle when condensed.[64] This transformation of CPM is checked in Figure 3-12. The cooling temperature was set at 20°C according to the method 202 initially with isopropyl alcohol (IPA) circulated through the condenser.[102] The temperature was also set at 5°C to have a more dramatic condensation effect. Shown in the figure are the concentration of PM detected at the point 3 (see Figure 3-8) in the second membrane chamber at 20°C (orange line in Figure 3-12) and 5°C (red line in Figure 3-12). The results clearly show appearance of PM or generation of PM after condensation, when in fact the exhaust gas was cleared of PM when leaving the first membrane chamber, and PM reappeared after condensation. A higher amount of PM formed at a lower temperature. If the PM removal process had ended at membrane chamber 1, the amount of PM detected at point 3 would have been released into the atmosphere.

# 3.3.2.2 CPM removal performance of N-rGO filter

PM concentration was recorded in the outlet side (point 4, see Figure 3-8) of the membrane chamber 2 in real-time (blue line in Figure 3-12) with the condenser at 5 °C to examine the efficiency of the N-rGO filter in removing the generated PM. As can be seen in Figure 3-12, it is clear that a significantly lower concentration of PM was detected than at point 3 (red line). The SEM image of Figure 3-13 shows the N-rGO filter surface after the second PM removal experiment. Not as many particles as in Figure 3-11 can be observed because there were not many PM particles compared to the FPM particles directly generated from the oil heater, but a clear difference could be observed when compared with a pristine filter (red circles). The efficiency of removing the newly generated PM by the filter was measured to be 93%, which was lower than the efficiency of removing FPM.

According to the literatures, ultra-fine dust particles generated by condensation have a diameter less than 2.5 microns, which is smaller than FPM.[71, 103, 104] For charged particles, the electrostatic attraction force  $(F_E)$  is given by:

$$F_E = \frac{K_E \times q^2}{x^2} \tag{2}$$

where  $K_E$  is a constant number, q is the charge on the particle and x is the particle diameter. In this equation,  $F_E$  is proportional to the square of particle diameter because equilibrium charge q is proportional to the square of particle diameter.[105, 106] In addition, there was also a study demonstrating that the driving force of electrostatic precipitator is proportional to the total charge of particle which is proportional to the square of the particle radius.[107] Thus, less CPM was removed by the filter than FPM.



Figure 3-12. CPM removal experiment result of the filter in membrane chamber 2



Figure 3-13. SEM image of N-rGO filter used in membrane chamber 2 after CPM removal experiment (scale bar is  $10 \ \mu m$ ). Red circles represent captured CPM

# 3.3.3 Spectroscopy for verification

The most important issue is that the condensed dust particle removed through membrane chamber 2 was not FPM but CPM. Although it is assumed that all FPMs have been removed through membrane chamber 1, additional analysis was needed to assert that CPM had removed. First, EDX analysis was performed to analyze the components of the N-rGO filter of membrane chamber 2 before and after the condensed PM removal test (Figure 3-14(a) and (b)). The N-rGO filter was composed of 6 components of Carbon (C), Oxide (O), Sulfur (S), Chrome (Cr), Iron (Fe) and Nickel (Ni) before removal experiment as shown in Figure 3-14. The conventional reduced graphene oxide prepared by hummer's method consisted of C, O, and S.[37] And Cr, Fe, and Ni were component of nichrome which act as mediators of binding between rGO sheets in 3-D network structures.[108, 109] As can be seen in Figure 3-14(b), after the removal test, N-rGO filter was composed of the same components with different weight percent (wt%). In particular, the ratio of S and Ni increased by almost two-fold. So, it was checked whether the increase in S and Ni was due to the removed PM.

In this context, an EDX mapping image was obtained for the N-rGO filter before and after the PM removal experiment. Figure 3-15 gives an image of the rGO sheet of the filter before PM removal. It was obvious that C, S,

and Ni are uniformly distributed without any special shape. However, in Figure 3-16, the result of the rGO sheet with adsorbed particle after the PM removal test was completely different. The distribution of carbon was homogeneous throughout the sheet as shown in Figure 3-16(b) because the element is the main component of both CPM and reduced graphene oxide. Therefore, it is not reasonable to say that the detected carbon came from captured CPM. In contrast, S and Ni were dispersed with high density in the shape of the dust particles and were also distributed in the entire rGO sheet (Figure 3-16(c) and (d)). In addition, In Figure 3-17(a), EDX analysis data for cropped region of rGO sheet and condensed particle (red rectangle) showed higher S and Ni composition ratios than those of the general N-rGO filter analysis results (Figure 3-14(a)). Also, it was confirmed that no component other than C, O was detected in the component analysis of FPM captured at point 1 of the first membrane chamber (Figure 3-17(b)). So, it is obvious that the increase in S and Ni was due to the removed PM that was generated by cooling. It had been known that S and Ni are constituents of CPM originating from pollution source.[70] After all, the increase of S and Ni in the N-rGO filter placed on the membrane chamber 2 could be due to the removal of CPM.

To summarize, through N-rGO filter system, FPM was removed by the first membrane, and CPM was produced and eliminated by the condenser and second membrane. N-rGO filter has a moderate pore size and electrical conductivity unlike other PM removal filters, making it an outstanding electrostatic precipitator, effectively removing the CPM with a diameter of 2.5 microns or less.[50, 110-118] (see Table. 1) Thus, both CPM and FPM were removed from the pollution source simultaneously.



Figure 3-14. Result of EDX analysis of N-rGO filter (a) before and (b) after CPM removal test (scale bar is  $20 \ \mu m$ )



Figure 3-15. (a) SEM image of N-rGO filter used in EDX analysis (scale bar is 2  $\mu$ m). EDX mapping analysis result for (b) Carbon, (c) Sulfur, and (d) Nickel



Figure 3-16. (a) SEM image used in EDX analysis which composed of N-rGO filter after PM removal experiments (used in membrane chamber 2) and dust particles (scale bar is 2  $\mu$ m). EDX mapping analysis result of red rectangle region for (b) Carbon, (c) Sulfur, and (d) Nickel



Element	Wt%
С	50.23
0	38.28
S	3.22
Cr	0.4
Fe	0.08
Ni	7.79

Element	Wt%
С	95.89
0	4.11

Figure 3-17. EDX analysis result of (a) cropped region of the image of Figure

3-16. (scale bar is 1  $\mu$ m) and (b) collected FPM (scale bar is 2  $\mu$ m)

Filter type	Pore size ranges (µm)	Electrical Conductivity (S/cm)	Ref. #
Polyimide nanofiber membrane/carbon woven fabric	0.1-4.1	No statement	49
PVDF/PAN fibrous membrane	1.8-5.5	2.6 x 10 <sup>-8</sup>	106
PSU, PVB, and PVDF fibrous membranes	5-30	No statement	107
PTFE microfiber membrane	2.1-3.3	No statement	108
PAN fibrous membranes	5-8	1.8 x 10 <sup>-8</sup>	109
Polyester fiberous membrane	35-85	No statement	110
PTFE hollow fiber membranes	1-5	No statement	111
Amino acid salt fiber membranes	22-599	No statement	112
Porous alumina	29-54	No statement	113

ceramics			
Carbon woven fabric	20-236	588	114
Reduced graphene oxide filter	0.15-89	1700	This work

Table. 1. Pore size and electrical conductivity of other PM removal filters.

# 3.3.4 Reusability of N-rGO filter

Reusability of N-rGO filter was figured out. From this part, burning incense was used to generate PM. After the PM removal, the filter was immersed in deionized water to induce dust particles to be separated from the N-rGO surface by the polarity of the water.[11] As shown in inserted SEM image of Figure 3-18, the treatment restores the 3-D porous rGO structure to the same shape as the pristine filter. Also, it was obvious that N-rGO filter maintained similar performance during the five successive experiments with a single filter which was rinsed after every cycle (graph of Figure 3-18). These results verified the reusability of the filter.



Figure 3-18. Result of PM removal test with a single filter. (Inserted image: SEM image of rinsed N-rGO filter surface (scale bar is 20 μm))

# 3.3.5 Performance of N-rGO filer under air flow condition

The mechanical strength of N-rGO filter was evaluated to confirm its usability. Given filter system is designed to directly remove PM at the pollution source, N-rGO filter has to be able to operate in air flow condition. Therefore, it is investigated that the efficiency of PM removal of the filter in an air stream with a speed of 2.5 m/s which is a typical test velocity for ANSI/ASHRAE Standard 52.2.[119, 120] As shown in Figure 3-19, it was found that the performance of the filter was maintained without significant change in five repeated experiments. The result confirms that it has sufficient mechanical strength for use at the pollution source.



Figure 3-19. PM removal efficiency of N-rGO filter in air flow (2.5 m/s) condition

# 3.3.6 PM removal rate of N-rGO filter

Air purification efficiency of the filter per unit time was measured in this part. Figure 3-20 shows the result of the PM concentration after the injection of dust into the closed cell without and with the N-rGO filter. In the case of cell without N-rGO filter, the concentration of PM decreased due to sinking or sticking to the wall, but it took about 1 hour to go back to its original state (black line). On the other hand, in the presence of the N-rGO filter, the PM concentration was reduced to its original value in about 400 seconds in three consecutive experiments (red line). On the basis of the volume of the closed cell and the effective area of the filter, the average rate of the dust particle removal was calculated to be  $11.34 \text{ }\mu\text{g}/\text{m}^2 \cdot \text{s}$ .


Figure 3-20. PM concentration data of closed cell test without N-rGO filter and with the filter

## 3.4 Thermal stability of N-rGO filter

#### 3.4.1 Characteristics of filter after exposure to high temperature

The exhaust gas generated from the PM pollution source is at a high temperature. Most of the conventional PM removal filters electro-spun with a polymer are inevitably vulnerable to heat. Therefore, viability of the filter at the high temperature is an issue to be resolved for any filter.[14, 34, 86] Most organic materials are known to be oxidized by atmospheric oxygen at high temperature.[121-123]

To test the viability, N-rGO filter was annealed under atmospheric condition at 350 °C for 10 hours to confirm whether oxidation occurred or not. Figure 3-21 shows XPS analysis results before and after the annealing, revealing that no change has occurred in the process of annealing. The asfabricated N-rGO filter showed peaks due to C-C, C-O, and C=O bonds, which have been identified in conventional reduced graphene oxide, at 284.6 eV, 286 eV, and 288.2 eV, respectively.[124-126] The fraction of the peak area was 0.7 for C-O peak / C-C peak and 0.63 for C = O peak / C-C peak. After annealing, the fraction of the peak area was 0.77 for C-O peak / C-C peak. After annealing, the fraction of the peak area was 0.77 for C-O peak / C-C peak and 0.69 for C = O peak / C-C peak. Although there was a slight rise in both peak fractions, no significant difference was found. Chemical bonding state of the filter before and after annealing was also confirmed by FT-IR spectroscopy

(Figure 3-22). The pristine filter had split peak of 2920 cm<sup>-1</sup> 2850 cm<sup>-1</sup> because of the CH<sub>2</sub> bond, and C=O, C=C and C-C bond were observed at 1730 cm<sup>-1</sup> 1580 cm<sup>-1</sup>, and 1225 cm<sup>-1</sup>, respectively. These peaks were consistent with previous chemical binding analysis result and many existing studies which have analyzed graphene oxide and carbon materials.[44, 127-129] The FT-IR analysis also shows that no significant change occurred due to the annealing. The SEM image of the N-rGO filter after annealing (Figure 3-23) is similar to that of the pristine filter (Figure 3-5 and 3-6), maintaining the porous 3-D network structure consisting of 2-D reduced graphene oxide sheets.

Figure 3-24 shows thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of the filter. Moisture and volatile compounds were removed up to 150°C, and then oxygen functional groups which were not removed in the reduction process were removed. After 400°C, the weight of filter decreased rapidly due to decomposing of the carbonyl group. Therefore, the filter was sufficient to maintain performance up to 350 °C.[130, 131]



Figure 3-21. XPS analysis of N-rGO filter before and after annealing



Figure 3-22. FT-IR spectroscopy of N-rGO filter before and after annealing



Figure 3-23. SEM image of N-rGO filter after annealing process (scale bar is  $20 \ \mu m$ )



Figure 3-24. Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves of N-rGO filter in air condition

#### 3.4.2 PM removal under high temperature condition

To demonstrate the ability of the N-rGO filter to properly remove PM even under high temperature environment, the membrane chambers in Figure 3-9 were wrapped around with heating mantles to provide a high temperature environment, as illustrated in Figure 3-25. In this test, incense was burned to generate a large amount of PM with various diameters, and the temperature of the heaters was set to 350 °C.[11] Because the exhaust gas of pollution source that generates a large amount of PM is emitted within a temperature range between 50 and 250 °C, temperature was set at 350 °C.[73-85] In order to ensure the effect of the high temperature, the filter was annealed at such environment for 3 hours before removal test. The concentration of PM in the inlet side increased and remained at 2000  $\mu$ g/m<sup>3</sup> right after the burning. As a result of filtering by the N-rGO filter, the concentration in the outlet side was maintained at a low value (Figure 3-26). The SEM image of the filter used in this experiment can be seen in Figure 3-27. As in the FPM removal filter, PM was adsorbed extensively on the rGO sheet by electrostatic attraction force. Existing high-temperature filter studies have shown stability to temperatures between 200 and 750 °C. Considering that the commercial high-temperature filter can be used at temperatures between 200-400 °C, it can be concluded that N-rGO filter has adequate thermal stability.[132]



Figure 3-25. Schematic diagram of experimental setup



Figure 3-26. Result of PM removal test under high temperature condition (maximum measurement value of PM counter is 2000  $\mu$ g/m<sup>3</sup>)



Figure 3-27. SEM image of N-rGO filter after PM removal test in high temperature condition (scale bar is  $20 \ \mu m$ )

## 3.4.3 Control experiment result of commercial filter

Polypropylene, (Com #1, Cleanairtech Co., South Korea) polyethylene terephthalate filter (Com #2, Haniltech Co., South Korea) and glass microfiber filter (Com #3, Sterlitech Co., USA) were used for control experiment. As can be seen in Figure 3-28(a), (b) and (c), before annealing, commercial filters showed a tangled fiber morphology. Structures of polymeric filter were completely collapsed after annealing (Figure 3-28(d) and (e)). However, glass fiber filter which has good thermal stability maintained an original morphology (Figure 3-28(f)).

Then, comparative experiments were conducted to prove the suitability of N-rGO filter for high temperature condition. Figure 3-29 and 3-30 shows the results of experiments on the removal of PM at room and high temperature of three commercial filters. All Commercial filters have good PM removal ability at room temperature (RT). However, polymeric commercial filters have proven ineffective in the high temperature (HT) condition. The concentration in the outlet side with the commercial filters eventually reached the same level of PM concentration in the inlet side. This might be attributed to the loss of the original structure at high temperatures, as shown in the SEM image. Glass fiber filter, on the other hand, have proven effective in the HT condition because it has good thermal stability. Therefore, it was found that the N-rGO filter has better thermal stability than the commercial polymeric filters and has equivalent thermal stability to commercial filter used for high temperatures.



Figure 3-28. SEM image of (a) Com #1 and (b) Com #2 (c) Com #3 before annealing. SEM image of (d) Com #1 and (e) Com #2 (f) Com #3 after annealing. Scale bar of (a) and (d) is 200  $\mu$ m. Scale bar of (b) and (e) is 600  $\mu$ m. Scale bar of (c) and (f) is 25  $\mu$ m



Figure 3-29. Result of PM removal test in room and high temperature condition of (a) Com #1 and (b) Com #2



Figure 3-30. Result of PM removal test in room and high temperature condition of Com #3

## 3.4.4 PM removal under air flow condition

The performance of the N-rGO filter in the presence of air flow, omnipresent around a pollution source, was also evaluated in the high temperature environment. The change in the concentration of PM detected at the inlet side and outlet side with a steady air flow of 0.2 m/s is shown in Figure 3-31. At the inlet side, the PM concentration was detected at 2000  $\mu$ g/m<sup>3</sup> since the beginning of experiment. The outlet side PM concentration detected was negligible. The PM removal efficiency of the N-rGO filter under the air flow was 99%.

The pressure drop is also one of the important factors that determines the efficiency and energy consumption of the filter.[11] As can be seen in Figure 3-32, the pressure drop results of N-rGO filter under the high temperature condition was similar those of C-rGO filter. This suggests that the filter does not lose its porous structure even in such high temperature environment. The results so far do demonstrate its ability to remove PM even under high temperature environment. The ability is unaffected by the air flow typically present around a pollution source and the pressure drop across the N-rGO filter is minimal.



Figure 3-31. Result of PM removal test in high temperature with air flow (0.2m/s) condition



Figure 3-32 Pressure drop test result of N-rGO filter against air flow rate

## 3.5 Acid resistance of N-rGO filter

#### 3.5.1 Characteristics of filter after exposure to acidic oxide

Exhaust gas including PM is not only at a high temperature but also contains acidic gases such as  $NO_x$  and  $SO_x$ .[91, 133] These acidic gases react with organic materials and accelerate their degradation, especially at the nanoscale.[134, 135] Therefore, the stability of the PM filter against these acidic gases is essential as much as the durability against high temperature.[14, 86] The acid resistance of the filters of previous research has not been confirmed, and therefore its application to the pollution source was not certain.

To examine the acid resistance of the N-rGO filter, ionization solutions of nitric and sulfuric oxide were prepared. The NO<sub>x</sub> solution was prepared by dissolving sodium nitrite (NaNO<sub>2</sub>) and sodium nitrate (NaNO<sub>3</sub>) both at a concentration of 6000 mg/L. The SO<sub>x</sub> solution was an aqueous solution of sodium sulphate anhydrous (Na<sub>2</sub>SO<sub>4</sub>) with the same concentration. This method using the ionization solution of nitric and sulfuric oxide has been utilized to test the corrosion rate of materials exposed to NO<sub>x</sub> and SO<sub>x</sub> gases.[136] The N-rGO filter was immersed in each solution for 24 hours to conduct the chemical analysis and PM removal experiment for testing the acid resistance of the filter.[86](Figure 3-33)

Figure 3-34 shows the results of XPS analyses of the N-rGO filters after

the exposure to  $NO_x$  and  $SO_x$  solution, respectively. Both exposed filters had peaks at 284.6 eV, 286 eV and 288.2 eV and these peaks are exactly the same as the data for pristine filter before the exposure (Figure 3-21). For the  $NO_x$ exposed filter, the fraction of the peak area was 0.71 for C-O peak / C-C peak and 0.69 for C = O peak / C-C peak. After the SO<sub>x</sub> exposure, the fraction of the peak area was 0.77 for C-O peak / C-C peak and 0.69 for C = O peak / C-C peak. Compared with the pristine filter, there were only slight changes in the fractions. FT-IR analyses of the two N-rGO filters exposed to the solutions also conducted. Figure 3-35 gives FT-IR analysis results of as-fabricated NrGO filter and the filters immersed in the solution for 24 hours. All the filters had absorption peak at 2920 cm<sup>-1</sup>, 2850 cm<sup>-1</sup>, 1730 cm<sup>-1</sup>, 1580 cm<sup>-1</sup>, and 1225 cm<sup>-1</sup>. These peaks are also identical to the fresh N-rGO filter presented in the previous analysis (Figure 3-22). The SEM images of the filters after exposure to each solution, shown in Figure 3-36 and 3-37, reveal that the surface morphology of the N-rGO filter is the same as that of the fresh filter. The well maintained porous structure suggests the filter effectively removed the PM. These results showed that the N-rGO filter does maintain its integrity even after exposure to the  $NO_x$  and  $SO_x$  for 24 hours.



Figure 3-33. Optical image of acid resistance test setup of the N-rGO filter



Figure 3-34. XPS analyses data of  $NO_x$  exposed and  $SO_x$  exposed N-rGO filter



Figure 3-35. FT-IR spectroscopy result of pristine,  $NO_x$  exposed and  $SO_x$  exposed N-rGO filter



Figure 3-36. SEM image of N-rGO filter after NOx exposed. Scale bar is 20  $\mu m$ 



Figure 3-37. SEM image of N-rGO filter after  $SO_x$  exposed. Scale bar is 20

μm

## 3.5.2 PM removal of N-rGO filter after exposure to acidic oxide

Figure 3-38 shows PM removal test results of NO<sub>x</sub> exposed and SO<sub>x</sub> exposed N-rGO filter. Experiments were carried out by placing NO<sub>x</sub> or SO<sub>x</sub> exposed filter into a membrane chamber to determine how effectively it can remove the PM generated by incense burning. The concentration of PM in the outlet side in both cases was negligible, indicating good performance of adsorbing and removing PM even after exposure to acidic solutions. The SEM images in Figure 3-39 and 3-40 show that rGO sheets of N-rGO filter were covered thick with dirt, forming blackish soot. Overall, N-rGO filter retained chemical bonding, surface morphology, and PM removal efficiency after prolonged exposure to NO<sub>x</sub> and SO<sub>x</sub>. Therefore, N-rGO filter can be applied to a PM pollution source that emits exhaust gas containing toxic substances at a high temperature.



Figure 3-38. Result of PM removal experiment of  $NO_x$  exposed and  $SO_x$  exposed N-rGO filter (maximum measurement value of PM counter is 2000  $\mu$ g/m<sup>3</sup>)



Figure 3-39. SEM image of  $NO_x$  exposed N-rGO filter after PM removal experiment. Scale bar is 20  $\mu$ m



Figure 3-40. SEM image of  $SO_x$  exposed N-rGO filter after PM removal experiment. Scale bar is 20  $\mu$ m

## **Chapter 4. Conclusion**

In this thesis, a reduced graphene oxide, a material of high surface area per weight, has firstly investigated as a filter for removing PM<sub>2.5</sub> as opposed to the conventional way of utilizing nanowires or nanofibers for the adsorption filter. The rGO nanoplatelets have self-assembled into a highly porous foam formed on a copper mesh (C-rGO filter) for it to be used as an adsorption filter for the PM removal. The highly porous and void nature of the filter allows air to pass through the filter at a high rate with minimal pressure drop and the high surface area provides sufficient sites for PM to adsorb for the desired level of removal. Better than 99% PM removal achieved by the filter even after 5 consecutive cycles of cleaning and reuse demonstrates the robustness of the filter. Some experiment verified its long-term operation capability. The high surface area and the large void space render the filter highly efficient, its quality factor being almost twice the best ever reported in the literature. The foam assembled on both sides of the copper mesh provides a unique feature of accomplishing role of filtering not only the air ventilated into a room but also the air inside.

The generation of CPM and the ability of the proposed filter to remove both FPM and CPM from the pollution source have also shown in this thesis. The 3-D porous filter made with reduced graphene oxide and nichrome mesh (N-rGO filter) possessed the capability to remove PM by electrostatic attraction force. A filter system consisting of two filters and a condenser have suppressed PM emissions from the pollution source to the atmosphere. The usual FPM in emission gas is directly removed by the first filter with an efficiency of 99.9%. The gas phase CPM precursor contained in the exhaust gas is cooled by the condenser to covert CPM, which is then removed by the second filter with an efficiency of 93%. In addition, reusability of the N-rGO filter has investigated. The filter has been demonstrated to have excellent chemical and structural stability even after exposure to high temperature and toxic acids.

Strengths such as simple fabrication, easy scaling-up, bidirectionality, and low power consumption stem from low pressure drop demonstrated here lay the groundwork for high efficiency  $PM_{2.5}$  removal filter. Not only that, the integrated PM removal system could be installed directly on pollution source, which would dramatically reduce both CPM and FPM emission.

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초 록

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대기 오염은 생태계에 미치는 영향이 막대함에 따라 인류가 직면 한 가장 심각한 문제 중 하나이다. 특히 직경 2.5 마이크로 미터 미만의 입자상 물질은 인체 건강을 직접적으로 위협하는 오염원이 다. 이 논문에서는 낮은 압력 강하의 고효율 미세먼지 제거 필터 를 소개한다. 2차원 나노 물질인 환원 그래핀 옥사이드로 구성된 다공성 필터는 높은 표면적을 이용한 효율적인 미세먼지의 제거가 가능하였으며, 낮은 압력 강하에서도 작동하였다. 뿐만 아니라 효 율성 손실이 거의 없는 반복 재생 및 필터의 재사용이 가능하였다. 이에 따라 필터의 전반적인 효율성을 나타내는 성능지수에서 기존 의 최고 값보다 월등히 높은 값을 나타내었다. 또한 구리 메쉬 양 면에 환원 그래핀 옥사이드 구조체가 형성된, 구리 기반의 환원 그래핀 옥사이드 필터는 실외 미세먼지를 제거하는 동시에 실내 미세먼지를 효율적으로 정화하는 역할을 하였다. 이와 더불어 본 논문에서는, 미세먼지 발생원에서 여과성 미세먼지와 응축성 미세 먼지를 모두 제거하는 필터 시스템을 소개한다. 니크롬 기반의 환 원 그래핀 옥사이드 필터2개와 그 사이에 위치한 콘텐서로 구성된 시스템은 여과성 미세먼지를 제거하는 동시에 일반적으로 발생원 에서 정화되지 않고 대기중으로 배출되는 응축성 미세먼지 입자를 제거 할 수 있었다. 3차원 구조로 미세먼지 제거에 매우 효과적인 이 필터는 대부분의 발생원 환경과 유사한 고온 및 산성 조건에서 도 효율을 유지하였다. 결론적으로 간단한 제조, 손쉬운 대면적화. 양방향성 및 낮은 압력 강하 등의 장점을 가진 환원 그래핀 옥사 이드 필터는 미세먼지 제거에 최적화된 특성들을 갖추고 있었다. 또한 제시된 필터 시스템은 오염원에서 여과성 미세먼지와 응축성 미세먼지를 모두 제거하는 해결책을 제공하였다.

**주요어:** 대기 오염, 미세먼지 제거 필터, 환원 그래핀 옥사이드, 실 내 미세먼지 정화, 응축성 미세먼지, 내열성과 내산성, 오염원

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