**Antibacterial and antviral filter with high adhesion copper film on filter fibers using linear ion beam treatment.**

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**1. Introduction**

Filters are essential products used in masks and air purifiers to prevent harmful factors in the air such as find dusts and pathogens. Among the various types of filters, the polymer membrane filter has a shape in which thin polymer microfibers are randomly arranged in a two-dimensional plane, which physically prevents harmful factors in the air from passing through. Recently, the use of masks has increased rapidly due to the COVID-19 pandemic issue, and filters are a key material for masks. Wearing a mask is known to prevent airborne droplets from penetrating into the lungs very effectively, so it is very effective in preventing infectious diseases (Leung, Chu et al. 2020, Xi, Si et al. 2020).

Various methods exist to remove harmful factors, and a representative method is to utilize active devices using electricity such as plasma and ultraviolet rays. However, these methods have a disadvantage in that an additional system is required because electricity is essential.

In this study, to develop an antibacterial/antiviral filter, and for this purpose, copper coating was used. Copper is a representative antibacterial/antiviral material known for a long time. However, if copper falls off the filter and is inhaled, there is a human toxicity issue, so it is necessary to strongly adhere the copper to the filter surface. In order to coat copper with high adhesion on the filter, our research team performed surface modification through an ion beam, and then was able to form copper with high adhesion through copper sputtering. At this time, through the control of the process conditions, it was confirmed that the fine filter fiber was not damaged, and the differential pressure/filtering performance of the filter was hardly changed. This process was able to proceed with a roll-to-roll process through a linear ion beam and sputtering process, so it was possible to secure mass production.

**2. Materials and Methods**

2.1. Materials

A polyethylene terephthalate (PET, Airo Co., Ltd.) filter with an average diameter of 30 μm and 70 g/m2 of density was used.

2.2. Ion Beam Treatment and Copper Sputtering Deposition

Fig. 1a shows the schematics of the processes of ion beam treatment and copper sputtering. Oxygen ion beams were generated from linear ion beams source, which is the same as used in our group previous studies(reference). The process was performed by changing the applied power to 100, 150, 200 W by controls of applied voltage and gas flow rate, and the samples were moved at a fixed speed of 10 millimeter per seconds. The aforementioned process conditions were named as Ion Beam 1, Ion Beam 2, and Ion Beam 3, respectively. After ion treatments, copper was deposited using a direct current magnetron sputtering system with the purity more than 99.99% copper sputtering target. The working pressure was 1.0 mTorr with argon gas, and the sputtering power was 300 W. The thickness of copper film was 30 nm.

2.3. Adhesion Test of Deposited Copper Thin Film

Three kinds of adhesive tape with different adhesive force (3M Scotch® MagicTM Tape 810, with 2.5 N/cm of peel strength, 3M Scotch® Filament Tape 8959 with 9.0 N/cm of peel strength and 3M VHBTM 4910 Tape with 26 N/cm of peel strength) were used to evaluate the adhesion force between the sputtered copper film and filter fiber. After attaching a 20 mm wide tape to a length of 100 mm, it was released through a 90° peeling tester to measure adhesion. This process is shown in Fig. 1b.

2.4. Observing Surface of Filter and Tapes

The optical microscope and field-emission scanning electron microscopy (FE-SEM; JSM 6700F, JEOL, Tokyo, Japan) was used for observing the surface of filter and detached tape.

2.5. Preparations of SARS-CoV-2 elimination performance evaluation

The antibacterial properties were evaluated using *Staphylocuccus aureus* ATCC 6538, *Klebsiella pneumoniae* ATCC 4352, *Escherichia coli* ATCC 25922 and *Pseudomonas aeruginosa* ATCC 27853, according to KS K 0693:2016 test method. The reduction rate was calculated by following equation,

… Equation 2

where A is the colony-forming unit(CFU) per milliliter of control group, and B is the CFU/mL of the experimental group.

2.6. Preparations of SARS-CoV-2 elimination performance evaluation

Figure 1C shows the schematic of the test system of SARS-CoV-2 elimination performance evaluation. For the aerosol test, closed cylindrical chamber was produced with vibrating nebulizer (HL100A; Health & Life Co., Ltd., New Taipei City, Taiwan). The 50 nm thickness of copper coated filter with 70 mm of dimeter is installed in the chamber, and bioaerosols with SARS-CoV-2 viruses were sprayed on the filter with a flow rate of 320 μL/min for 300 s. For comparison, the same process was repeated using a non-copper-coated filter.

2.6. SARS-CoV-2 plaque assay

Plaque assay, the gold standard for the direct quantification of infectious virus (Baer & Kehn-Hall, 2014), for SARS-CoV-2 was performed referring to previous study (Mendoza et al., 2020). Vero76 cells were seeded into 6-well tissue culture plates 24 h before infection with 10-fold serial diluted virus in DMEM containing 2% FBS for 1 h. The infected cells were washed with phosphate buffered saline for 3 times and cultured with 1% low-melting point agarose and 2% FBS-containing cell culture media in 5% CO2 incubator at 37℃ for 72 h. After solid overlay aspirate from each well, the cells were fixed by 4% paraformaldehyde for 1 h at room temperature and stained with 0.5% crystal violet solution for 15 min (S2 Fig). The plaque was observed using a white-light transilluminator. The number of plaques was expressed as log PFU/cm2 filter.

2.7. Fabrications of HEPA filter

HEPA filter were fabricated using a copper-deposited filter. This filter was used as the outermost material of the HEPA filter, and the melt-blown filter was combined to complete the HEPA filter production.

2.8 Evaluations of HEPA filter air conditioning performance

Floating microorganisms and virus removal tests of the manufactured HEPA filter were performed, respectively. *Klebsiella pneumoniae ATCC 4352* was used as the microorganism test bacteria, and *Bacteriophage MS2 ATCC 15597-B1* (host bacteria *Escherichia coli ATCC 15597*) was used as the test virus. A commercial air purifier (Atomy) and the copper coated HEPA filter were installed in the center of the 30 m3 closed chamber, and the aerosols were sprayed into the chamber. MAS-100 NT (MERCK) was used to measure the concentration of airborne bacteria before the operation of the air purifier, and the concentration of airborne bacteria was checked after operating the product for one hour. For comparison of removal performance, the same test was performed without operation of the product. The initial concentration when the air purifier was not operated (C) and the concentration after 1 hour (D), the initial concentration when the air purifier was operated (E) and the concentration after 1 hour operation (F) were measured, respectively. The reduction rate was calculated using the equation 2.

… Equation 2

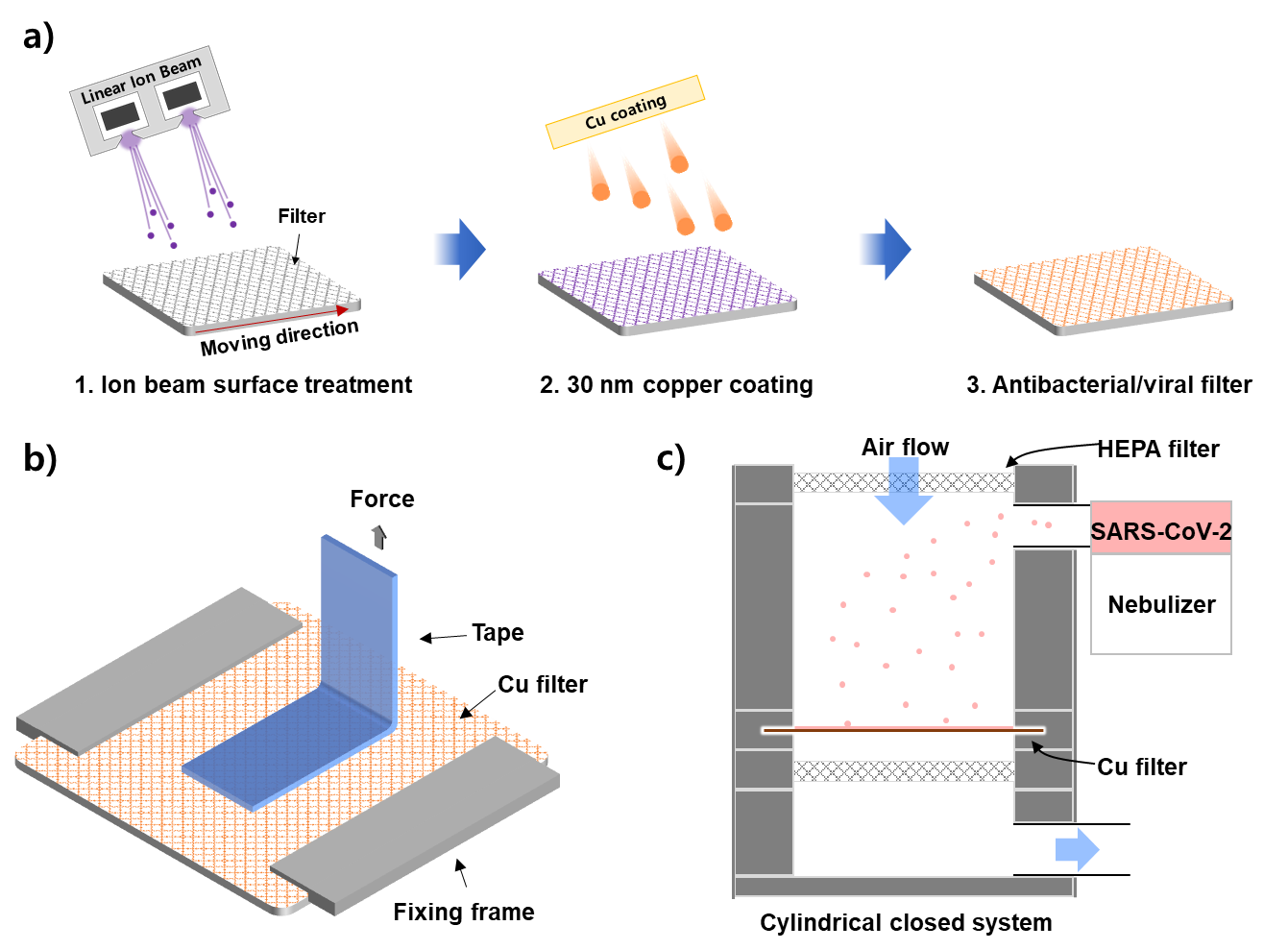
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Figure 1. Schematic diagrams of a) ion beam treatment and cu sputtering, b) 90o peeling test, and c) a closed system for evaluation of aerosol filters

**3. Results and Discussion**

After the oxygen ion beam treatment was completed, observation using the naked eye and optical microscope was performed to check the degree of damage to the filter. As a result of visual observation of the fabricated sample with a size of 100 by 100 mm, it showed a contraction as the ion beam process power increased. Ion Beam 1 was 0.5% and Ion Beam 2 was 0.7%, and the dimensions did not change, but the ion beam of the strongest power showed a contraction of more than 5% in the Ion Beam 3 sample. When macroscopic temperature change is measured, it shows a change of up to 50oC or less under all conditions, but there is a difference in the thermal energy generated by actually colliding with the fiber for each sample. The Stopping and Range of Ions in Materials (SRIM) calculation method is a calculation method based on an inert monoatomic gas, and although it does not match this process using an oxygen ion beam, it can roughly estimate the amount of thermal energy applied to the ions. As a result of this calculation, it can be seen that if the applied energy is 10 or more, there is a possibility of shrinkage, which is directly related to damage to the fibers constituting the filter. If you look at Fig. 2d, you can observe the fiber agglomeration at the bottom of the figure, and it can be inferred that this was caused by heat. When the fibers are agglomerated in this way, the pressure loss of the filter increases, making it difficult to obtain the desired filter efficiency.

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Figure 2. Optical microscopes images under dark field according to ion beam treatment conditions.

Strong adhesion between the filter fiber and deposited copper film ensures durability and user safety because detachment of copper nanoparticles from the mask surfaces may pose a toxicity threat. The adhesion of the copper film deposited on the filter fiber was evaluated using a tape test (Figure 1b). As a result of performing a 90-degree peeling evaluation using tapes with various adhesive strengths, it was confirmed that the peeling strength of the oxygen ion beam-treated specimen was higher than that of the untreated specimen. All untreated specimens showed adhesion of 1 N/cm or less, whereas ion beam-treated specimens showed adhesion of 5 N/cm or more in all tapes.

The figure shows the results of microscopic observation of the surface of the filter and tape after peeling. It was confirmed that the copper thin film was detached from the specimen not treated with the ion beam, while the filter fiber was removed from the specimen treated with the ion beam. This means that the adhesion between the copper thin film and the filter fiber is 5 N/cm or more, and it can be seen that it has a higher adhesion than the strength of the filter fiber itself.

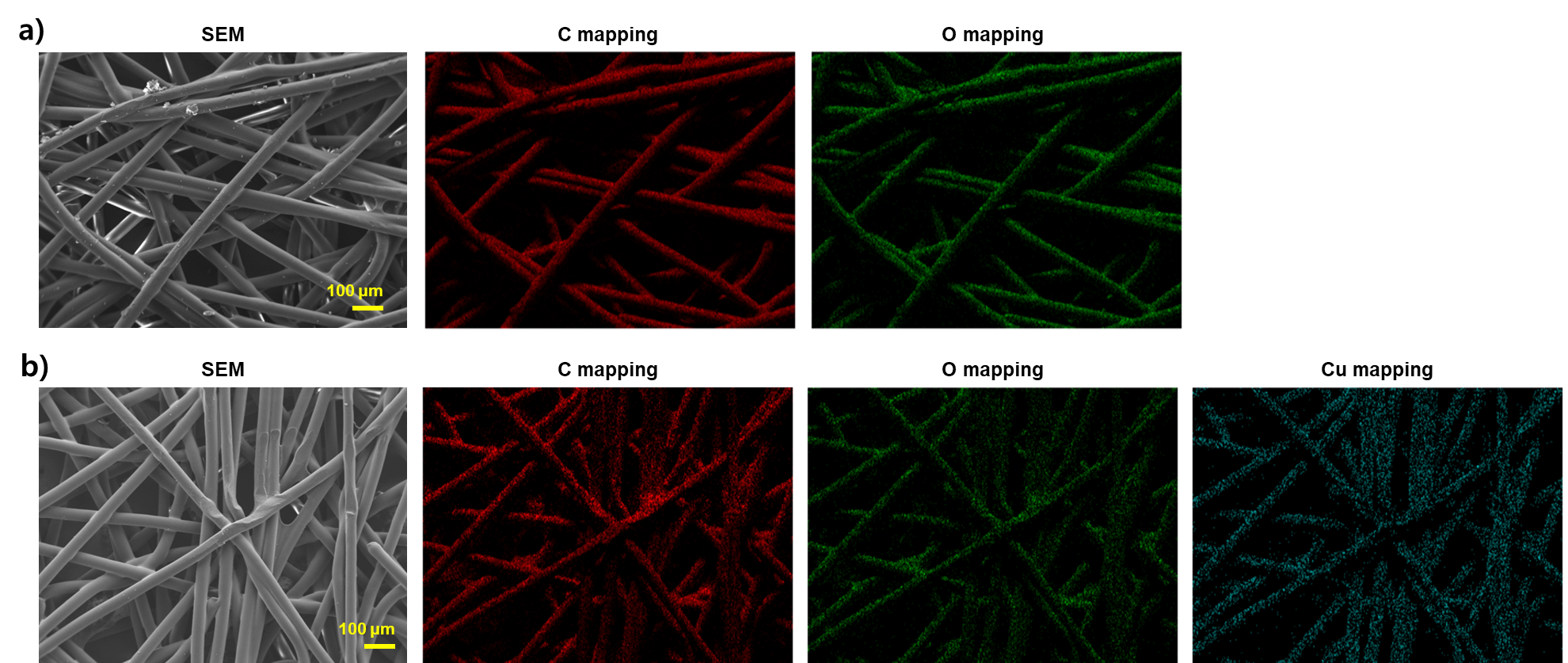


Figure S1. SEM and EDS mapping images of a) bare filter, and b) cu coated filter

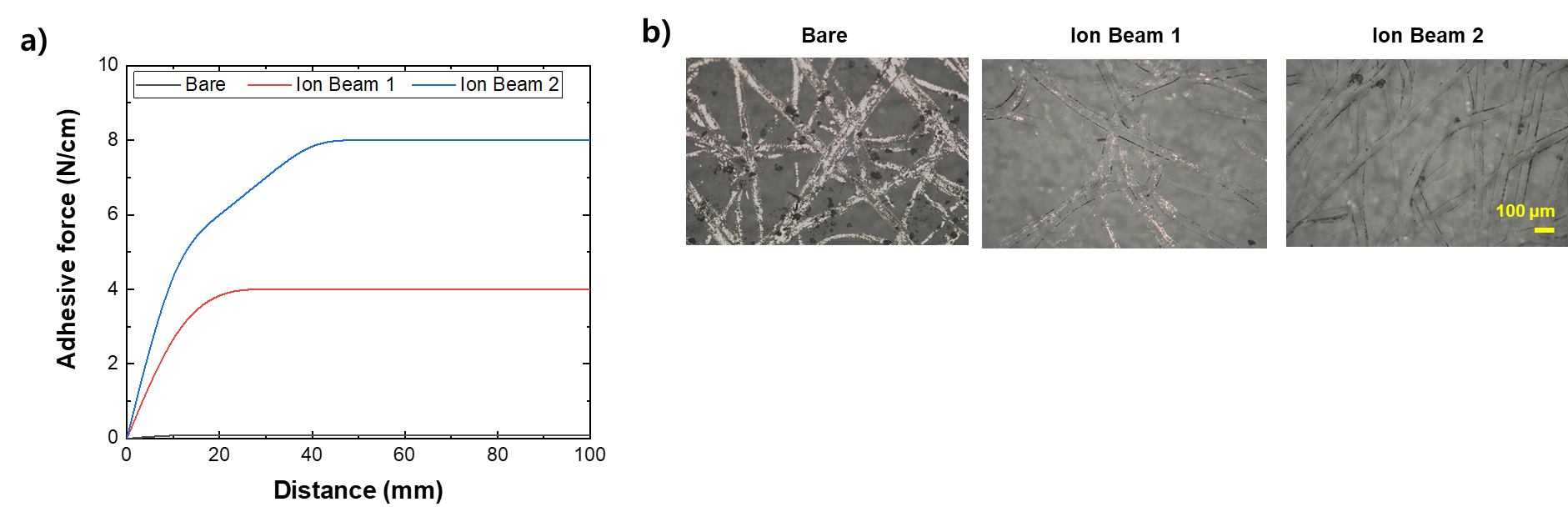


Figure 3. Adhesive strength result of 90o peeling test and optical microscope images of tape surface after release

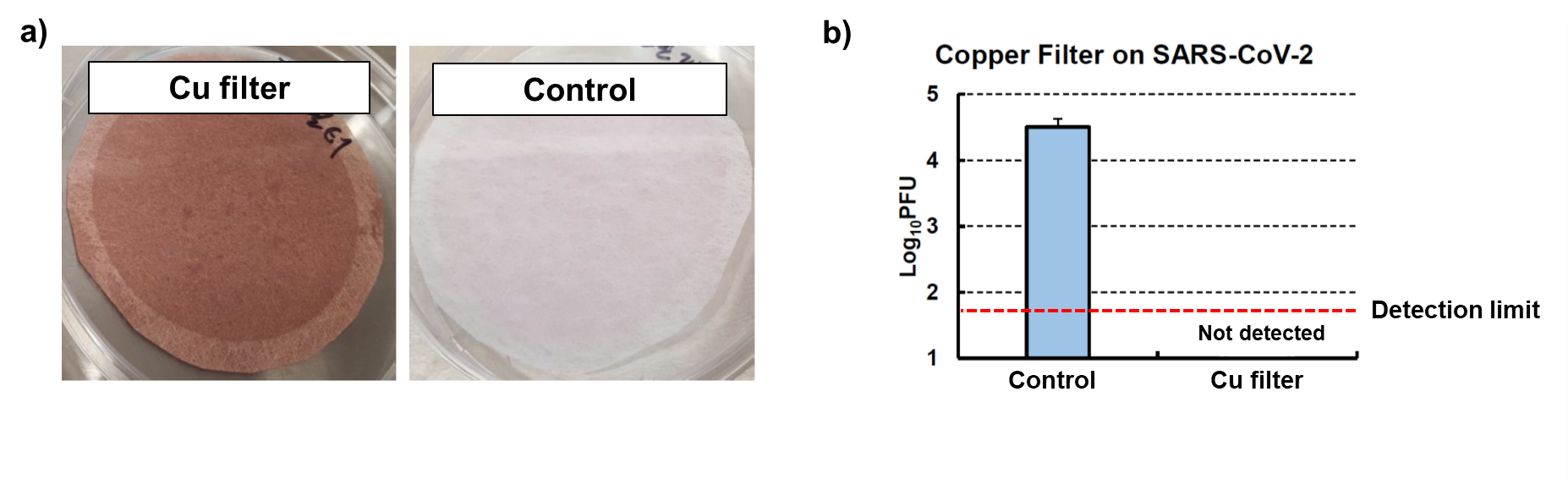
Figure 4 shows the results of the evaluation of the antibacterial properties of the copper deposition filter against 4 types of strains. It was confirmed that the bacterial reduction rate of more than 99.99% for all the bacteria inoculated on the copper filter. This is because of the antibacterial properties of copper formed on the filter fiber surface, bacteria are removed.

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Figure 4. Adhesive strength result of 90o peeling test and optical microscope images of tape surface after release

The SARS-CoV-2 virus evaluation result of a copper deposition filter using a cylindrical device is shown in the figure 4. The copper deposited filter was found to induce inactivation of SARS-CoV-2 aerosols by more than 99.8% compared with the control group (Fig. 5b), reaching an undetectable level (detection limit: 1.699 log PFU/cm2 filter). It was found that all SARS-CoV-2 viruses on the surface of the copper-deposited filter were inactivated.

 Figure 5. a) images of copper coated filter and non-copper coated filter after spraying SARS-CoV-2 aerosol, b) inactivation of SARS-CoV-2

As a result of the airborne microorganism and virus test, it was confirmed that there was almost no difference in filter performance between the case in which the HEPA filter manufactured using the copper filter was used and the case where it was not. This means that the physical properties of the filter developed through this study are hardly changed.

**4. Conclusions**

It was found that the copper-coated filter was very effective in removing SARS-CoV-2. In this study, an ion beam surface treatment technique was used to strongly attach copper to the filter fiber. As a result of surface treatment using oxygen ion beam, it was confirmed that the filter fiber and the copper-coated thin film had a strong adhesion of 5 N/cm or more. A HEPA filter was manufactured using a copper-coated filter, and as a result of applying it to an air purifier, it was possible to confirm the filter performance results similar to that when a non-copper-coated filter was used.

The copper coating filter developed through this study can remove viruses remaining on the filter surface. This can minimize the risk of secondary infection that may occur in situations where a person has to deal with a filter, such as exchange and disposal of filters. Moreover, copper, which is known to have the effect of removing most bacteria and viruses, will be available not only for SARS-CoV-2 viruses but also for unknown viruses that may occur in the future.

**5. References**

Leung, N. H. L., et al. (2020). "Respiratory virus shedding in exhaled breath and efficacy of face masks." Nat Med **26**(5): 676-680.

We identified seasonal human coronaviruses, influenza viruses and rhinoviruses in exhaled breath and coughs of children and adults with acute respiratory illness. Surgical face masks significantly reduced detection of influenza virus RNA in respiratory droplets and coronavirus RNA in aerosols, with a trend toward reduced detection of coronavirus RNA in respiratory droplets. Our results indicate that surgical face masks could prevent transmission of human coronaviruses and influenza viruses from symptomatic individuals.

Xi, J., et al. (2020). "Effects of mask-wearing on the inhalability and deposition of airborne SARS-CoV-2 aerosols in human upper airway." Phys Fluids (1994) **32**(12): 123312.

Even though face masks are well accepted as tools useful in reducing COVID-19 transmissions, their effectiveness in reducing viral loads in the respiratory tract is unclear. Wearing a mask will significantly alter the airflow and particle dynamics near the face, which can change the inhalability of ambient particles. The objective of this study is to investigate the effects of wearing a surgical mask on inspiratory airflow and dosimetry of airborne, virus-laden aerosols on the face and in the respiratory tract. A computational model was developed that comprised a pleated surgical mask, a face model, and an image-based upper airway geometry. The viral load in the nose was particularly examined with and without a mask. Results show that when breathing without a mask, air enters the mouth and nose through specific paths. When wearing a mask, however, air enters the mouth and nose through the entire surface of the mask at lower speeds, which favors the inhalation of ambient aerosols into the nose. With a 65% filtration efficiency (FE) typical for a three-layer surgical mask, wearing a mask reduces dosimetry for all micrometer particles except those of size 1 microm-3 microm, for which equivalent dosimetry with and without a mask in the upper airway was predicted. Wearing a mask reduces particle penetration into the lungs, regardless of the FE of the mask. The results also show that mask-wearing protects the upper airway (particularly the nose and larynx) best from particles larger than 10 microm while protecting the lungs best from particles smaller than 10 microm.