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Inorganic Additives Induce More Small-Sized Microplastics Releasing from Medical Face Masks

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a simulated Raman scattering (SRS). We also pioneered a three-dimensional imaging (3D imaging) method for investigating the internal aging of plastic using SRS, which clearly revealed the link between inorganic additives inside polymers and photoaging. We found that inorganic additives substantially accelerate the photoaging of the plastic materials through multiple pathways and induce more small-sized microplastics. Follow-up radical quenching experiments confirmed carbonate radicals as the main cause of this phenomenon. Our research exposes the hazardous potential of inorganic additives in masks to amplify the emission of microplastics.

KEYWORDS: surface-enhanced Raman spectroscopy, micro- and nanoplastics, medical face masks, stimulated Raman scattering, inorganic additives

1. INTRODUCTION

Microplastics (less than 5 mm in size)¹ are usually produced by mechanical friction² and aging degradation of plastic products. Due to the widespread use of plastic products, microplastics are almost ubiquitous in the natural environment. More and more studies confirm that they come from a wide range of sources, such as baby products,^{3,4} plastic lunch boxes,^{5–8} and mineral water bottles.^{7,9–12} A large amount of microplastics have been detected in the diseased tissues of lung cancer patients¹³ and cardiac surgery patients,¹⁴ confirming the potential harm of microplastics to the human body.

During the COVID-19 pandemic, medical face masks (MFMs), owing to their accessibility and affordability compared to other medical supplies, were extensively used. Reportedly, an unimaginable number of MFMs, exceeding 200 million each day, were used during the COVID-19 outbreak.¹⁵ Many researchers^{15–22} have reported the release of microplastics from MFMs, mainly focusing on the quantity of microplastics released from MFMs,^{16,18,23} the leaching of additives,^{23–31} as well as toxicological analysis of microplastics from MFMs.^{32–37} However, the effect of inorganic additives on the release of micro- and nanoplastics from MFMs has still not been studied. 60% of masks on the market contain calcium carbonate (CaCO₃) additives³⁸ and are widely used by

consumers. $CaCO_3$ has been reported to accelerate the photodegradation of pollutants^{39–41} as well as the photoaging of plastics.⁴² So, there is an urgent need to understand the impact of CaCO₃ additives on the release of micro- and nanoplastics from MFMs.

In this study, we characterize and quantify micro- and nanoplastics (<5 μ m) released from the best-selling MFMs using surface-enhanced Raman spectroscopy (SERS) method, bridging the gap in existing scholarly research on the release of small-sized microplastics from MFMs. The aging properties of plastic fibers were also characterized for the first time in three dimensions (3D) by stimulated Raman scattering (SRS) to visually analyze the internal aging. Combining the analysis of the aging process of MFM fibers, screening for the role of free radicals, and the release of microplastics, we revealed the influence of inorganic additives on the release of microplastics

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2. EXPERIMENTAL SECTION

2.1. Sample Preparation and Instruments. Commercial pure polypropylene (PP) particles without inorganic additives were purchased from SINOPLAST Co., Ltd. (Guangzhou, China). These particles have irregular shapes and sizes. Customized plastic raw materials for MFMs with and without 30% CaCO₃ were purchased from Liyuan Materials Co., Ltd. (Dongguan, China). Regular 1 μ m microplastics (particle size distribution is shown in Figure S1) were purchased from Hugebio Co., Ltd. (Shanghai, China). 200 nm pore size filter membrane and 1 μ m pore size filter membrane were purchased from Longjin Membrane Technology Co., Ltd. (Taian, China). MFMs were selected based on their market performance on Taobao, China's leading e-commerce platform, where all chosen samples ranked among the top-selling products in terms of both sales volume and consumer ratings. Specific information is shown in Table S2. MFM-As (A1, A2, A3, A4, and A5) are MFMs without CaCO₂ additives, and MFM-Bs (B1, B2, B3, B4, and B5) are MFMs with CaCO₃ additives. Furfuryl alcohol, triethylenediamine, butylated hydroxytoluene , benzophenone, 2,4-Di-tert-butylphenol, 2,5-Di-tert-butylhydroquinone, 3-tert-butylphenol, and 2,4,6-Tri-tert-butylphenol were purchased from Sinopharm Co., Ltd. (Beijing, China).

2.1.1. Raman Microspectroscopy and SERS. Raman spectroscopy was performed with an XploRA Plus confocal Raman spectrometer (Jobin Yvon, HORIBA Gr, France) coupled to a (x100) microscope objective (Olympus, 0.90 numerical aperture). Surface enhanced Raman spectroscopic detection of the micro- and nanoplastics was achieved by Klarite substrates. 532 nm laser power of 25% was used with an acquisition time of 10 s and 5 accumulations. Since the 532 nm laser is more sensitive to the C-H signal (~3000 cm^{-1}) than the 785 nm laser, which helps us to carry out the judgment of polymers, and Shi et al.⁴³ realized the identification of PP nanoplastics by Klarite with the 532 nm laser. Moreover, our group's previous FDTD simulations⁴⁴ showed that the 532 nm laser produces a more accessible hot spot for nanoplastics (>800 nm) in the Klarite substrate compared to the 785 nm laser. Therefore, we selected the 532 nm laser wavelength for our study.

2.1.2. Stimulated Raman Scattering. In the SRS microscopy system, two laser beams were used, respectively, the tunable pump beam (680-1300 nm) and the fixed Stokes beam (1040 nm). A commercial optical parametric oscillator (OPO) laser (Insight DS+, Newport, CA) generated two beams of the corresponding wavelengths, and SF57 glass rods chirped them into picoseconds, respectively, to gain high spectral resolution. The Stokes beam was intensity-modulated by an electrooptical modulator (EOM) before it was combined with the pump beam and sent into a laser scanning microscope (FV 1200, Olympus). A 60× immersion objective lens (Olympus, UPLSAPO 60XWIR, NA 1.2 water) focused the combined light into the sample, and the transmission light was filtered (CARS ET890/220, Chroma) and detected with a photodiode (PD). After being demodulated with a lock-in amplifier (LIA) (HF2LI, Zurich Instruments), the stimulated Raman loss (SRL) signal was finally obtained for each pixel of an image. A typical SRS image takes about 1 s (512×512 pixels and 2 μ s pixel dwell time). To obtain the SRS spectra, a

motorized translation stage (M-ILS250CC, Newport) served as the delay scanner for the two beams.

2.2. Photoaging Experiment. For Raman and PY-GC/ MS quantification experiments, whole MFMs were placed in clean quartz Petri dishes and received 7 days of simulated daylight exposure (Text S2). For SRS imaging, a fiber was taken from the inner layer (the layer closest to the wearer's face) of each of two MFMs (MFM-A1 and MFM-B1) with tweezers. The ends were secured with tape to a clean slide, the fibers were submerged with drops of water, and the slides were sealed with a coverslip and double-sided tape. After each experiment, the coverslip and double-sided tape were removed and the fibers were aged with simulated light for 14 days, and then the SRS experiment was repeated.

2.3. Identification and Quantification. 2.3.1. Raman. MFM was transferred to a beaker, and 300 mL of deionized water was slowly added. MFM was gently pressed with a clean glass rod to expel trapped air bubbles and achieve complete immersion. Once fully wetted, the mask remained submerged for the duration of the experiment. After 1 h, 100 μ L of the solution were sampled with a glass pipette (Nichiryo), dropped onto the Klarite substrate, and allowed to dry naturally for the next step of Raman analysis. Before each experiment, the Raman peak positions were calibrated using clean silicon wafers. Standard Raman spectra were obtained from purchased standard samples of PP, and it will be recorded as PP-particle and counted when the Raman spectra of the detected particle agrees with the standard spectra. The counting method was referred to Tsering et al.⁴⁵ as shown in Text S1. After spectral acquisition for individual particles, the particle will be located through the Klarite pit indexing method and immediately transferred to SEM for characterization.⁴⁶ The pits on the Klarite substrate are arranged in a regular pattern. By referencing the positions of the pits (for example, counting from left to right and top to bottom), the target particles can be accurately located.

2.3.2. PY-GC/MS. MFM was placed in 300 mL of deionized water for 1 h to extract micro- and nanoplastics. To prevent the concentration from falling below the limit of quantification, micro- and nanoplastics were collected cumulatively from ten MFMs per experiment. Then MFMs were removed, and the solution was filtered through a 1 μ m pore size filter membrane. The inside of the sample beaker was rinsed several times with deionized water, and the rinsed water was filtered together with the solution. At the end of the process, the filtrate solution was filtered through a 200 nm pore size filter membrane along with deionized water from multiple rinses of the filter flask. Five random area samples⁴⁷ were taken from the 200 nm pore size filter membrane using a sampler and transferred to the injector for subsequent analysis. The accuracy of area counting on filter membranes has been well established.⁴⁸ Each experiment was independently repeated six times.

Furthermore, a block sample $(1 \text{ cm} \times 1 \text{ cm})$ was cut from the inner layer of MFM-B1 and glued to a silicon wafer for scanning electron microscopy (SEM, TESCAN Co., Ltd., Czech Republic) and energy-dispersive X-ray spectroscopy (EDS) testing.

2.4. Exploration of Aging Mechanisms. After 14 days of photoaging experiments, characterizations of two groups of samples before and after photoaging were done by Fourier transform infrared spectroscopy (FTIR) to obtain the carbonyl index (details in Text S4): plastic raw materials for MFMs with



Figure 1. a, Raman spectra of commercial pure PP particles of different sizes. **b**, Raman spectra of nanoplastics released from MFM-A. **c-g**, SEM of micro- and nanoplastics corresponding to Raman spectra in **a** and **b**. To avoid signal interference by Raman peaks of the substrate, the silicon peak $(\sim 1000 \text{ cm}^{-1})$ has been removed.

and without CaCO₃ additives; MFM-B1, B2, B3, B4, B5 with and without inhibition of $CO_3^{\bullet-}$ (details in Text S5).

2.5. Analysis of Other Factors That May Affect Photoaging of MFMs. Pieces $(1 \text{ cm} \times 1 \text{ cm})$ were cut from each MFM and separated into three layers. The morphology was observed and recorded under a 5× microscope to determine if there were any visible notches or fractures on the surface of fibers.

Representative antioxidants and anti-UV additives (butylated hydroxytoluene, benzophenone, 2,4-Di-*tert*-butylphenol, 2,5-Di-*tert*-butylphenol, details in Table S6) were selected for HPLC-MS analysis. Ten independent MFMs were collected from each MFM brand, with approximately 1.5 g taken from each MFM. These were placed into separate glass bottles, to which 30 mL of acetonitrile was added. Ultrasonic extraction was performed for 1 h, after which 1 mL of extract from each bottle was pooled into a single centrifuge tube and nitrogenblown to near dryness. Subsequently, 1 mL of methanol was added, and the samples were sonicated for an additional 30 min before being prepared for HPLC-MS analysis (details in Text S4).

2.6. Quality Assurance and Quality Control. Experiments were carried out in a high cleanliness laboratory with latex gloves and plastic-free fiber lab coats worn throughout to avoid potential microplastic pollution outside the experiment. Pipette tips are made of glass (Nichiryo) and all glass instruments are cleaned with deionized water (Direct-Q). All samples were processed on a clean bench. The glass supplies used were treated using a muffle oven at 450 °C for 4 h to

ensure no microplastic interference, after which they were wrapped in clean aluminum foil.

2.7. Data Analysis. Raman spectra were analyzed by using LabSpec 6 software. SRS data were processed by ImageJ and AMIRA. Details are shown in Text S3. Software R version 4.4.1 was used for statistical analysis. Details of the analysis can be found in Table S8. The p < 0.05 indicated statistical significance, and * indicated p < 0.05, ** indicated p < 0.01, *** indicated p < 0.001.

3. RESULTS AND DISCUSSION

3.1. Detection of Micro- and Nanoplastics Released from MFMs. The inverted pyramid-shaped pit of Klarite has a significant enhancement of the Raman signal of micro- and nanoparticles, enhancement factors (the ratio of SERS signal intensity to normal Raman signal intensity, indicating the degree of signal amplification) for nanoplastics on Klarite were found to reach 2 orders of magnitude. 43,46 Based on our previous study,⁴⁶ nanoplastics with sizes as low as 360 nm can be detected using Klarite. We first examined the SERS detection of PP on Klarite by using standard PP powder. In Figure 1a,c, the microplastic (~5 μ m) has an obvious Raman spectrum and can be easily identified as PP. We found that the PP particle with the size down to ~ 800 nm (nanoplastic 1 and nanoplastic 2 in Figure 1a,d,e) can be well identified on Klarite. In real sample, as can be seen in Figure 1b, Raman spectroscopy confirms the presence of PP nanoplastics (nanoplastic A and B in Figure 1b,f,g) released from MFM-A. We found a few Raman characteristic peaks consistent with standard PP, including those between 808 and 840 cm⁻¹



Figure 2. Characterization of CaCO₃ in MFM-B. **a**, Raman signatures of CaCO₃ in MFM-B. **b**, 3D SRS imaging of CaCO₃ particles (~1086 cm⁻¹) inside the MFM-B fiber (~2880 cm⁻¹). SEM (c) and EDS of the MFM-B: carbon (d), calcium (e), and oxygen (f).

 $(-CH_2)^{49}$ and ~1150 cm⁻¹ (-CH₃ and C-C),⁵⁰ around 1460 cm⁻¹ (-CH₃).⁵¹⁻⁵⁵

It is worth mentioning that the use of Klarite substrate revealed a particular advantage in identifying potential microplastics. The substrate's deep inverted pyramid-shaped pits offered exceptional visibility of transparent microplastic specimens under the microscope, a feature absent in flat substrates. Beyond this, the deep inverted pyramidal pits exhibit a remarkable suppression effect on the visual distortion, known as coffee rings. Thus, we can conduct a primary visual screening of the potential microplastic population with greater ease, saving identification time.

The Raman spectrum of the released particles from MFM-B is similar to that of MFM-A. However, as shown in Figure 2a, it has three additional peaks corresponding to CaCO₃. The peaks for CaCO₃ appear primarily at 278, 715, and 1086 cm⁻¹, with the most notable peak at 1086 cm⁻¹ resulting from the symmetric stretching vibration of the internal carbonate ion.⁵⁶ SRS was performed to obtain 3D chemical imaging of the fiber $(CaCO_3: 1086 \text{ cm}^{-1}, \text{PP}: 2880 \text{ cm}^{-1})$, and a large number of CaCO₃ particles are clearly visible in the fibers (Figure 2b). Except for some agglomerates, particles are uniformly dispersed in the fiber, with about 20 particles ranging in size from 600 nm to 5 μ m³⁸ in a 10- μ m fiber. Zhang et al.⁵⁷ mentioned in their study that the addition of CaCO₃ to PVC plastics suffers from an inability to stabilize the dispersion, with a relatively concentrated distribution. This aligns with our findings, but our 3D SRS imaging characterizes this phenomenon more clearly and on a smaller scale. Moreover, as shown in the EDS analysis of MFM-B in Figure 2(d-f), we found that, in addition to carbon (C), calcium (Ca) and oxygen (O) are also present, indicating the presence of $CaCO_3$

in MFM-B. These all demonstrate the presence of CaCO₃ as inorganic additive in fibers.

3.2. Quantification. The forms of microplastics released from MFMs include particles,²³ fragments,¹⁶ and fibers,^{58–60} with larger-sized microplastics dominated by fragments and fibers. When abandoned in the environment and subjected to aging factors including light exposure, MFMs can exhibit striking microplastic release kinetics.^{16,61} Given the study on release of small-sized microplastics from MFMs remains inadequate, and the potential environmental hazards are more serious compared to larger-sized microplastics.⁶² This research centered on a detailed examination of particles (<5 μ m). We performed background control experiments (Figure S2) on the whole process, and there was no obvious microplastic interference in the detection area. In addition, with the complete procedure of Raman measurements, the recovery rate of nanoplastics was 77.5% (Table S1 and Figure S3). As shown in Figure 3a,b, the number of micro- and nanoplastics released from MFM-Bs was significantly higher than that from MFM-As after photoaging (p < 0.01). Furthermore, the increase in the number of micro- and nanoplastics released from MFM-Bs due to photoaging was significantly greater than that from MFM-As (p < 0.01)(Figure 3d). In addition to the number concentration of micro- and nanoplastics released from all MFMs, we specifically conducted size distribution statistics for microand nanoplastics released from MFM-A1 and MFM-B1, as shown in Figure 3c. Here, MFM-A1 and MFM-B1 were selected as representatives of two MFMs with and without CaCO₃, respectively. It can be observed that the size distribution of MFM-A1 is shifted toward larger sizes compared to MFM-B1 overall, which suggests that the original MFM-B1 can release smaller micro- and nanoplastics



Figure 3. a, Quantification of micro- and nanoplastics released from MFMs (MFM-As: A1, A2, A3, A4, and A5 are MFMs without CaCO₃ additives, MFM-Bs: B1, B2, B3, B4, and B5 are MFMs with CaCO₃ additives) by Raman. Data points above the bars indicate individual replicate measurements. The data are presented as the mean \pm sd (*n* = 6). b, Comparison of the number concentrations of micro- and nanoplastics released from MFM-As and MFM-Bs after photoaging. Each data point corresponds to the mean of the number of microplastics obtained from six replicate experiments for each MFM brand type. The data are presented as the mean \pm sd (n = 5). ** indicated p < 0.01. c, size distribution of the micro- and nanoplastics and e, proportion of micro- and nanoplastics (<2.5 μ m) released from MFM-A1 and MFM-B1. d, Increasing trend in the amount of microand nanoplastics released from MFM-As and MFM-Bs before and after photoaging, calculated by dividing the number concentration of micro- and nanoplastics after photoaging by that before photoaging. Data points above the bars indicate the mean of increasing trends of six replicate experiments for each MFM brand type. The data are presented as the mean \pm sd (n = 5). ** indicated p < 0.01.

compared to MFM-A1. By comparing the particle size distribution of microplastics between the original and photoaging groups, we found that the main body of the distribution in the photoaging group shifted toward smaller sizes compared to the original group, both for MFM-A1 and MFM-B1. This indicates that both MFM-A1 and MFM-B1 were photoaged under light exposure. However, MFM-B1 suffers from a more pronounced tendency toward photoaging. A more intuitive size proportion chart is shown in Figure 3e, we paid special attention to the proportion of micro- and nanoplastics with a size less than 2.5 μ m. Both the original MFM-B1 group (proportion of MPs < 2.5 μ m is 70.6%) and the aged group (proportion of MPs < 2.5 μ m is 86.8%) were higher than

MFM-A1 (proportion of MPs < 2.5 μ m is 58.7–71.6%), respectively. While conducting the number concentration measurements, we also analyzed the mass concentration of nanoplastics released from MFM-A1 and MFM-B1 using PY-GC/MS. As shown in Figure S4, after photoaging, the mass concentration of nanoplastics released from MFM-B1 increased significantly, far exceeding that from MFM-A1 (p< 0.01), which is consistent with the results presented in Figure 3. These results show that the photoaging process causes more obvious damage to MFM-Bs, leading to the release of more small-sized microplastics.

3.3. Aging Characterization. By comparing the changes in the number of particles released and the size distribution before and after photoaging, we found that the CaCO₃ additive appears to enhance the photoaging process. To test this conjecture, we have selected two of these MFMs (MFM-A1 and MFM-B1) to conduct further 14-day photoaging experiments. After photoaging over 14 days, as shown in Figure S5, the MFMs underwent many changes that were visible to the naked eye. The MFM-A1 shows little change, with only minor damage observed, but it would tear more easily than the original MFM when touched. In contrast, MFM-B1 is much more severe, with the fibers clearly visible in a shredded state and a large amount of powder and debris when touched. The microscopic counterpart is the change in the internal structural characterization of the fibers.

The highest intensity C-H signal was imaged in 3D by SRS to compare the two groups of MFMs before and after aging. As seen in Figure S6a,b,c,d, they are longitudinal cross sections inside the fibers (in the same position before and after aging), one part of the 3D imaging in Movies S1-S4. We found that there are two modes of MFM-aging damage, one as shown in Figure S6a,b, where a huge irregular bulge appears on the surface of the fibers and then detaches from the body with external stress. The other, as shown in Figure S6cd, is the destruction of the apparent tensile structure (Figure S6c) of the fibers during the aging process, which may be due to thermal expansion or the breakage and change of chemical bonds leading to structural instability, which ultimately results in the transformation into round cavities (Figure S6d) with no angle and then peeling off from the body with the ensuing external stresses from the environment. The former studies^{49,50,63} alluded to a method of

determining the aging of PP by using the I_{841/808} (ratio of the peaks 841 and 808 cm⁻¹), with the higher $I_{841/808}$, the higher the degree of aging. We found that this method seems to be affected by the orientation of the material itself, it is dependent on the polarization state of light, so we controlled the polarizations to be in parallel to the fiber axis and chose to carry out in situ aging experiments with the same experimental parameters at the same position of the same fiber in our experiments in order to minimize the influence of other factors on the experiments. And, due to the presence of noise and background of SRS imaging, the 3D mapping plot obtained by dividing the two peak intensities at 841 and 808 cm⁻¹ will show many outliers. So, we made some changes based on this method, using green and blue to represent the distribution of peak intensities at 808 and 841 cm⁻¹, respectively, across the entire fiber. By analyzing the relative intensities of these two colors in the image, we can characterize the difference between the two peaks and, consequently, determine the degree of aging. In Li et al.'s study,⁴⁹ they performed surface aging mapping and we added in-house aging characterization to



Figure 4. a, Carbonyl index: comparison of MFMs aging before and after inhibition of $CO_3^{\bullet-}$ generation (n = 6). ** indicated p < 0.01. b, Underlying mechanism of CaCO₃ to promote MFMs photoaging. c, Cross-sectional SRS view of the inside of an MFM-B1 fiber. d, Schematic: effect of CaCO₃ in fibers on light. e, SRS imaging of microplastics and 3D imaging of individual microplastics.

achieve 3D aging characterization of fibers in Movies S5-S8, so as to better study the aging effect of additives on the interior of the plastic fiber. The final experimental results are shown in Figure S7; the results are consistent with the aging trend. The highlight area of MFM-A in Figure S7a,b is mainly concentrated on the surface. The highlighted regions in Figure S7b correspond to the bulges produced by aging.

3.4. Analysis of the Effect of CaCO₃ Additives. To investigate the role played by CaCO₃ additives in the internal aging process of fibers, we aged the MFM fibers for a short period of time (5 days) in the expectation that CaCO₃ would be observed in the more intact fibers. In 2D imaging, I_{841/808} is desirable for characterizing the aging of fibers. As shown in Figure S8, we obtained a visual characterization of the aging and CaCO₃ distribution inside the fibers. Brighter regions indicate higher aging, and interestingly, CaCO₃ almost exactly overlaps with the aging regions. This suggests that there is indeed a very clear link between CaCO₃ and fiber aging during photoaging. Furthermore, as we analyzed in Figure 2b, the proportion of CaCO₃ additives in the fibers is appreciably high. Consequently, it is anticipated that this will significantly promote the photoaging of polypropylene.

After characterizing the relationship between $CaCO_3$ additives and the degree of aging in MFMs through in situ SRS imaging, we aimed to further visually demonstrate the role of $CaCO_3$ additives in promoting the photoaging of MFMs. To achieve this, we customized two types of plastic raw materials typically used in MFM nonwoven processing, with the only difference being the presence or absence of 30% $CaCO_3$ additives. The carbonyl index, a widely used parameter in numerous studies,^{5,49,64,65} was employed to compare the degree of photoaging of the plastics, as it is a key indicator of plastic aging. As shown in Figure S9, prior to photoaging, the carbonyl indexes were nearly identical for both materials, indicating that there was little difference in the degree of aging between the two samples. However, after photoaging, the carbonyl index for the raw material containing CaCO₃ increased significantly (p < 0.05), suggesting that CaCO₃ additives substantially enhanced the photoaging of MFMs. Corresponding to the results we observed, Li et al.⁴² have experimented with the photoaging of PP-CaCO₃ composite materials from a materials science perspective and found that CaCO₃ additives promote the photoaging of PP significantly.

While directly demonstrating the contribution of CaCO₃ to the photoaging and breakage of MFMs, we also made efforts to eliminate the influence of other factors. Ten brands of MFMs were screened for the presence of antioxidants and anti-UV additives (Section 2.5), and their raw forms were compared. These factors are known to affect the photoaging of MFMs, as fibers with inherent structural weaknesses may be more susceptible to deterioration during the photoaging process. Additionally, antioxidants and anti-UV additives can mitigate the effects of photoaging. Additives such as butylated hydroxytoluene (Table S6), which have been reported as representative antioxidants and anti-UV additives in MFMs,^{23,66} were selected as the primary screening targets. As shown in Table S2, all ten MFMs have intact fibers with no visible damage on the surface except the inner damage caused by CaCO₃. Furthermore, the content of most antioxidants and anti-UV additives in MFM-As did not significantly exceed that in MFM-Bs (p > 0.05), and even the content of individual antioxidants was lower in MFM-As than in MFM-Bs (p < 0.05) (Figure S10). Therefore, we conclude that these factors are unlikely to be the primary contributors to the substantial differences observed in photoaging and microplastic release.

An additional experiment was conducted on MFM-Bs to rule out the possibility of $CO_3^{\bullet-}$ involvement in the photoaging process by quenching $CO_3^{\bullet-}$ using triethylenediamine, a known quencher of both 1O_2 and $CO_3^{\bullet-67}$. Quencher experiments with 1O_2 (Figure S11) showed no significant

promotion of photoaging in the MFMs (p > 0.5). However, when CO3^{•-} was quenched, the aging of MFMs was significantly suppressed compared to the control groups (p <(0.01) (Figure 4a). Previous studies have reported that CaCO₃ synergizes with photoactive substances to enhance oxidizability,⁶⁸⁻⁷⁰ which is consistent with our findings. Based on these results, we propose a potential reaction mechanism. We referred to Zhu et al.'s study, which indicated that the initial stage of the photochemical process in the MFM polymer is initiated by photoexcitation of the initiator, a common photoaging pathway for microplastics.^{71–74} As shown in Figure 4b, two possible subsequent pathways can be considered: one is that the excited triplet state of an initiator transfers electrons directly to the carbonate, resulting in the formation of $CO_3^{\bullet-.75}$ The other pathway is that the excited triplet state of an initiator reacts first with contacted water molecule to generate hydroxyl radicals, which then interact with carbonate to produce $CO_3^{\bullet-.75,76}$

In summary, we have confirmed that the primary reason CaCO₃ promotes photoaging and degradation of MFMs is the generation of CO₃^{•-} during the photochemical process. The long-lived CO3^{•-} creates a high steady-state concentration within the fibers and fully reacts with the PP structure, exacerbating the photoaging of the MFMs. Additionally, the disruption of the internal structure by $CaCO_3$ (Figure 4c) when incorporated into fibers,⁷⁷ along with the uneven enrichment of CaCO₃ (Figure 4d) upon light exposure, are likely contributing factors to its promotion of MFM photoaging.³⁹ Also, it is noteworthy that functional groups (absorbed hydroxyl groups) on the surface of CaCO₃ may catalyze the photo-oxidation reaction of PP.^{39,42} Compared to this surface aging process of MFM-A1, the simultaneous aging inside and outside of the MFM-B1 fibers leads to the release of more and smaller microplastics. In addition, we highlight the need for studies that investigate microplastic release in the full-size segment of a wider range of MFM brands, materials, and manufacturing processes and simulated conditions that better match real environmental conditions to gain a more comprehensive understanding of the factors influencing microplastic release.

Based on the aforementioned results, $CaCO_3$ additives can increase the release of microplastics from MFMs. This can be further confirmed by performing SRS imaging of released microplastics in an attempt to find the corresponding clues. From Figure 4e, we can find that most of the tiny particles released are a combination of PP and $CaCO_3$, which suggests that most of microplastics are not simply polymer fragments. Most of them are attached or wrapped unions, which can still be firmly combined even after several processes such as sample preparation, indicating that these microplastic particles are most likely to come from the plastic shedding near the CaCO₃. This again suggests a strong link between increased microplastic release after photoaging and the CaCO₃ particles.

4. ENVIRONMENTAL IMPLICATIONS

An increasing number of studies^{16,19,20,78,79} are presently concentrating their efforts on investigating micro- and nanoplastics released from MFMs. However, prevailing detection methodologies⁷⁹ primarily target particles in the tens of micrometers range and above. Moreover, direct quantification^{16,78} of particles smaller than 5 μ m without identification in some studies results in an inaccurate estimation of the quantity of microplastics discharged from MFMs. To address the knowledge gap, our research successfully achieved the identification of nanoparticles released from MFMs using SERS substrates, thereby enhancing our understanding of the release of nanoplastics from respiratory protection devices.

Moreover, our innovative application of SRS microscopy has enabled us to achieve the 3D imaging of microplastics, revealing that these particles are complex mixtures of polymers and additives rather than pure polymer monomers. This highdefinition 3D visualization of microplastics on a micrometer scale marks a significant advancement in the field with potential implications for the use of SRS in characterizing microplastic additives in various environments. MFMs, particularly those containing $CaCO_3$, have emerged as a significant source of microplastics. These are further released into the environment through processes such as light-induced aging.

The application of SERS with Klarite substrates and 3D SRS imaging to study the release of microplastics from MFMs and the aging of PP fibers has revealed the significant impact of $CaCO_3$ additives on the formation of smaller and more abundant plastic particles. This innovative use of established techniques highlights the value of applying advanced methods to new research questions in environmental science. The identification of $CO_3^{\bullet-}$ as the primary driver of MFMs degradation and subsequent microplastic formation underscores the critical role that inorganic additives and their associated radical chemistry play in the environmental transformation of plastic products into microplastics.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.5c01717.

- 3D SRS characterization of the degree of MFM-B aging after aging(AVI)
- 3D SRS characterization of MFM-A morphology after aging(AVI)
- 3D SRS characterization of MFM-B morphology before $\operatorname{aging}(\operatorname{AVI})$
- 3D SRS characterization of MFM-B morphology after aging(AVI)

3D SRS characterization of the degree of MFM-A aging before aging(AVI)

3D SRS characterization of the degree of MFM-A aging after aging(AVI)

3D SRS characterization of the degree of MFM-B aging before aging(AVI)

3D SRS characterization of the degree of MFM-B aging after aging(AVI)

Details on quantitative methods; information on light aging apparatus; details on data analysis methods; information on other experimental equipment; free radical burst experimental methods; details on quality control experimental methods and results; PY-GC/MS quantitative results; changes in the appearance of the MFMs before and after aging, changes in SRS imaging; results of other antioxidant and UV-resistant agent screenings; changes in the carbonyl index; imaging of CaCO in fibers; experimental flowchart (PDF)

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