Water-repellent TiO_2-Organic dye-based Air Filters for Efficient Visible-light-activated Photochemical Inactivation against Bioaerosols

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Abstract

Recently, bioaerosols, including the 2019 novel coronavirus, pose a serious threat to global public health. Herein, we introduce a visible-light-activated (VLA) antimicrobial air filter functionalized with titanium dioxide (TiO_2)–crystal violet (CV) nanocomposites facilitating abandoned visible light from sunlight or indoor lights. The TiO_2–CV based VLA antimicrobial air filters exhibit a potent inactivation rate of ~99.98% and filtration efficiency of ~99.9% against various bioaerosols. Under visible-light, the CV is involved in overall inactivation by inducing reactive oxygen species production both directly (CV itself) and indirectly (in combination with TiO_2). Moreover, the susceptibility of the CV to humidity was significantly improved by forming a hydrophobic molecular layer on the TiO_2 surface, highlighting its potential applicability in real environments such as exhaled or humid air. We believe this work can open a new avenue for designing and realizing practical antimicrobial technology using ubiquitous visible-light energy against the threat of infectious bioaerosols.

Keywords

Visible light, TiO_2/dye nanocomposites, Photocatalytic disinfection, Bioaerosols, Functional filter

Global public health depends on preparedness to suppress threats against emerging airborne microorganisms (called bioaerosols).[1] Bioaerosol threats have occurred in various forms, including the COVID-19, the emergence of MERS-CoV in 2012, the H1N1 influenza pandemic of 2009, and the SARS epidemic.[2–6] Airborne transmission of bacterial pathogens, such as *Bordetella pertussis*, *Bacillus anthracis*, *Mycobacterium tuberculosis*, *Corynebacterium diphtheriae*, and *Neisseria meningitides*, is also associated with the collapse of the respiratory system and neurological abnormalities.[7–9] These infectious diseases are highly lethal respiratory diseases, resulting in high mortality rates worldwide.[10] Bioaerosols disperse in the form of droplets produced during talking and sneezing, as well as airborne particles developed by the evaporation of these droplets.[11,12] Bioaerosols can be breathed through the nose or mouth during respiratory activities and can proliferate and spread as they attach to dust to derive their nutrients.[13,14]

To limit the spread of airborne microorganisms, the general public code of conduct for prevention is to wear facepiece masks as the first respiratory protective device.[15] Wearing masks is the most important public health measure to prevent the transmission of bioaerosols.[16] However, incorrect use of masks may increase the spread of disease.[17] Long-term mask use can result in infection due to rubbing of the nose or eyes after first touching the mask, causing secondary bioaerosol spread.[18] This is because microorganisms captured on the filter surface remain viable.[19–22] Therefore, it is necessary to kill the microorganisms completely. Over the last several decades, various strategies for incorporating antimicrobial organic/inorganic materials into filter fibers have been developed to deactivate bioaerosols.[23,24] However, as these

filters effectively eliminate only microorganisms that are directly in contact with antimicrobial substances, the antimicrobial activity progressively diminishes due to the accumulation of dust that covers the functional particles. Other techniques using thermal energy and UV irradiation have also been suggested; however, these methods are less compatible with commercial masks, as they require additional devices and energy consumption.[25–27]

As visible-light photocatalytic technologies have recently been introduced, inactivation of bioaerosols using visible-light-activated (VLA) sterilization has been highlighted.[28,29] VLA photocatalytic inactivation is a green technology capable of utilizing either natural sunlight or indoor lights accessible anytime and anywhere without the use of additional devices.[30–33] Reactive oxygen species (ROS) induced by photocatalytic reactions facilitate the inactivation of microorganisms; the generated ROS acts as a strong germicidal agent, damaging cell membranes and DNA.[34] Most VLA inactivation studies have focused on the hybridization of titanium dioxide (TiO_2) nanoparticles (NPs) with metal atoms or other low band-gap semiconductors.[35,36] However, these approaches have several disadvantages, such as doping of expensive noble metals, use of toxic materials, and difficult synthesis.[37] Researches applying the antimicrobial potential of metal-organic frameworks (MOF) on facepiece mask filters are ongoing.[28,29,38] However, MOF filters have some limitations in terms of their cost and complicated fabrication processes. VLA dye sensitization is a useful tool to induce visible light photocatalysis on the surface of TiO_2 being active under ultraviolet (UV) light.[39] Organic dyes are considered a promising photoactive antimicrobial material due to their low cost and high efficiency.[40] However, the main drawback of these dyes

is weak moisture stability; dyes are leached out from the TiO_2 surface when they are exposed to moisture because of their strong affinity for water.[41,42] Thus, the resistance of dyes to humidity is an issue when considering their potential use in facepiece masks.

Herein, we introduce a water-repellent VLA antimicrobial nanostructure for use as an effective and practical antimicrobial air filter that completely kills airborne microorganisms. The VLA antimicrobial activity results from combining photocatalytic TiO_2 NPs with hydrophobic molecules of 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES) and a visible-light sensitizer of crystal violet (CV) organic dye (denoted as TiO_2@PFOTES-CV NPs). Figure 1a shows the synthesis of TiO_2@PFOTES-CV NPs for preparation of a VLA antimicrobial filter. The triethoxy-silane group of PFOTES was covalently bonded to TiO_2 (Fig. S1).[43] Then, the incorporation of CV dye into TiO_2 NPs enhances the photocatalytic reaction of TiO_2 to visible light.[44] As a result, TiO_2@PFOTES-CV has potent antimicrobial activity against various bacterial bioaerosols under visible light. The UV-Vis absorbance spectra of TiO_2, TiO_2@PFOTES, CV, and TiO_2@PFOTES-CV were measured over a wavelength range of 400–700 nm (Fig. 1b). The TiO_2 and TiO_2@PFOTES solution did not show primary absorption, whereas the TiO_2@PFOTES-CV solution showed significant absorption at 584 nm with a shoulder peak at 549 nm. The primary absorbance of TiO_2@PFOTES-CV was similar to that of the CV dye.

VLA antimicrobial air filters were prepared via aerosol deposition of TiO_2@PFOTES-CV NPs, as depicted in Figs. 1c and S2. The size distribution of the nebulized NPs was a monomodal curve with a peak diameter of 29.4 nm (Fig. 1d). The VLA NPs coated on the surface of the commercial mask filter were easily visible to the naked

eye, as the color of the filter changed from white to violet (Fig. 1e). As the particle deposition time increased, the weight of the deposited NPs increased linearly from 0.5 to 3.7 μg/mm^2 (y = 0.51x, r^2 = 0.9825), indicating stable generation of aerosol NPs (Fig. S3). The scanning electron microscopy (SEM) images in Fig. 1f show that the control filter had a smooth and clear surface (top image), whereas the coated filter had a relatively rough surface and a complex three-dimensional (3D) structure of NPs (bottom). The shape of TiO_2@PFOTES-CV NPs on the filter fibers was identified as the spherical and polydisperse. Submicronic particles were deposited in a dendritic structure, increasing the reactive surface area. Consequently, this structure leads to enhanced filtration and bacterial inactivation performances.

Figure 2a shows the antimicrobial activity of the air filters in visible light (The test procedure is depicted in Fig. S4). The bactericidal performance of the TiO_2@PFOTES-CV filters against *Staphylococcus epidermidis* was greatest after 4 h of exposure to a visible light source, which resulted in a 3.75 log reduction, compared to 0.92, 0.22, and 2.00 log reductions for the TiO_2, PFOTES, and CV filters, respectively. This result corresponds with previous findings of synergistic enhancement in the antimicrobial performance with CV and photocatalyst materials, such as TiO_2 and ZnO.[44,45] Thus, the VLA antimicrobial activity of TiO_2@PFOTES-CV filters is predominantly affected by the interaction of TiO_2 and CV dye.

To determine the synergistic enhancement mechanisms in inactivation of the TiO_2-CV nanocomposites, we examined their band offset alignment. To determine the band offset of CV and TiO_2, X-ray photoelectron spectroscopy (XPS) and UV-Vis spectroscopy were employed (Fig. S5). The adventitious C1s peak at 284.8 eV was

used as a reference in the XPS analysis. The band gap energies of CV and TiO_2 were 1.98 eV and 3.09 eV, respectively, and the HOMO band maximum energy (E^{HBM}) of CV and valance band maximum energy (E^{VBM}) of TiO_2 were 1.98 eV and 3.09 eV, respectively. The offset of the core level was determined from an XPS spectrum of CV and TiO_2.[46] The difference in binding energy between N1s and Ti2p core levels was investigated in CV and TiO_2 (Fig. S6).[46] As shown in Fig. 2b, the difference in binding energy between the N1s core level and E^{HBM} was 398.78 eV for CV, and the difference between Ti2p and E^{VBM} was 456.28 eV for TiO_2. The E^{HBM} of CV was 1.4 eV higher than the E^{VBM} of TiO_2, and the LUMO band maximum energy (E^{LBM}) of CV was 0.29 eV higher than the conduction band maximum energy (E^{CBM}) of TiO_2, indicating formation of a staggered (type I) band alignment at the interface between CV and TiO_2.[47,48] These results suggest that upon visible-light irradiation, photogenerated electrons can flow from CV to TiO_2, resulting in electron accumulation in TiO_2. The excessive electron accumulation in TiO_2 will encourage electron transfer to the environment, resulting in a redox reaction.

To determine the ROS responsible for the inactivation effect of TiO_2@PFOTES-CV filters, ROS scavenger quenching assays were performed. The relative change in concentration of each scavenger, the number of *S. epidermidis* was compared. As shown in Fig. 2c, superoxide radical (O_2^-), hydrogen peroxide (H_2O_2), and hydroxyl radical (•OH) are generated by the filter; •OH is the main contributor to the death of bacteria. As shown in Fig. 2d, we suggest that photoexcited electrons in the CV dye molecules flow into TiO_2 NPs, which produces a redox reaction (type I) through interaction with moisture (water molecule),[49,50] oxygen,[51,52] hydrogen[28] in air, resulting

in generation of O_2^-, H_2O_2, and •OH. On visible light irradiation,[53] CV molecule itself without contact with TiO_2 induce $^1O_2$ generation through energy transfer (type II). The generation of $^1O_2$, O_2^-, H_2O_2, and •OH produces a multi-site attack against bacteria that results in their death. These results indicate that the potent antimicrobial activity of TiO_2@PFOTES-CV filters can be attributed to a synergistic effect between CV and TiO_2.

To scrutinize the outstanding VLA inactivation of TiO_2@PFOTES-CV NPs, further studies were conducted under various reaction conditions. We demonstrated that antimicrobial performance was dependent mostly on the amount of TiO_2@PFOTES-CV NPs (Fig. 2e). The antimicrobial performance of the TiO_2@PFOTES-CV filter gradually increased in proportion to the deposition weight in the dark. The rough 3D surface formed by aerosol deposition prevents close contact with the relatively rigid cell wall.[54] The nano-rough surface interferes with the preliminary adhesion step of bacteria, resulting in apoptosis.[55] For these reasons, TiO_2@PFOTES-CV filters have some intrinsic antimicrobial performance even in the dark, but the effect is much smaller compared with the performance associated with visible-light photochemical inactivation. After the 4 h exposure to the indoor light at 2.9 mW/cm^2, antimicrobial activity under visible-light exponentially improved up to ~99.98% as the amount of TiO_2@PFOTES-CV NPs increased to 3.7 μg/cm^2, indicating almost complete inactivation.

We also confirmed that the antimicrobial efficiency was largely affected by the exposure time and light intensity. Figure 2f shows the relative changes in the number of viable *S. epidermidis* at different light exposure times and intensities. C_o and C are

the number concentrations obtained from the control and TiO_2@PFOTES-CV filter, respectively. The intensity was controlled by varying the distance between the filter surface and the light source (Figs. S7 and S8). Under low-irradiation conditions, although VLA antimicrobial activity increased slightly, no relationship between VLA antimicrobial activity and irradiation time was observed (p-value > 0.05). However, as the intensity of the light source increases, the VLA antimicrobial performance increased with irradiation time. After 4h of exposure to the indoor light, VLA antimicrobial performance of TiO_2@PFOTES-CV filter was up to ~99.9% at 2.9 mW/cm^2 and ~99.98% at 6.9 mW/cm^2, respectively. In addition, the VLA antimicrobial performance of the filters was maintained for the average daily duration of facepiece mask total use (Fig. S9). However, to confirm the more stability of their use, further studies are necessary.

In addition, we confirmed VLA antimicrobial performance of TiO_2@PFOTES-CV filter under the exposure of natural sunlight condition (Fig. S10). Antimicrobial performance with natural sunlight reached ~93.20% in after 30 min and up to ~ 99.98% in just 1 h (Fig. S11). This enhancement of antimicrobial performance by sunlight is due to greater light intensity of natural sunlight (18~21 mW/cm^2). In addition, sunlight provides a wide spectrum areas containing UV to facilitate TiO_2 photocatalytic reaction, and thus enhancing the antimicrobial performance of TiO_2@PFOTES-CV filter. These results demonstrated the feasibility of the VLA antimicrobial air filters, which can be easily used indoors and outdoors without additional devices.

Figure 2g shows the antimicrobial activity of the antimicrobial air filter against several bacteria, including *S*. *epidermidis*, *Bacillus subtilis*, *Escherichia coli*, and

Enterobacter aerogenes. The TiO_2@PFOTES-CV filter exposed to visible light for 4 h exhibited almost complete inactivation of bacteria (antimicrobial efficiency of > 99.9%). These results highlight the excellent photobactericidal activity of TiO_2@PFOTES-CV NPs against various bacteria.

The 3D nanostructures of TiO_2@PFOTES-CV have a positive effect on filtration performance. The complex 3D structure formed on fibers produces abrupt changes in streamline curvature, which increases the mechanical filtration efficiency. The particle filtration performance was tested using *S. epidermidis* bioaerosols (Fig. S12). Figure 3a shows the size distribution of *S. epidermidis* bioaerosols as a function of size. The test concentration of bacterial bioaerosols was ~278 particles/cm^3. The peak particle diameter of the tested bioaerosols was clearly recognized at 0.90 μm. The filtration efficiency against *S. epidermidis* bioaerosols was significantly augmented after deposition of TiO_2@PFOTES-CV NPs (Figs. 3b and 3c), indicating that the complex 3D structure of the NPs enhanced the collision probability of bacteria in the vicinity of the fibers (Fig. S13). The overall filtration performance of the other bioaerosols did not differ greatly from that of *S. epidermidis* due to their similar physical size (Fig. S14). However, the pressure drop across the filter rose linearly from 24.3 to 103.1 Pa as the NPs accumulated further (Figs. 3c and S15). The high pressure drop of the filter causes discomfort in breathing when wearing a facepiece mask. Thus, optimization of TiO_2@PFOTES-CV deposition is required for practical feasibility and antimicrobial filtration effectiveness. The efficiency of filter decreased at a deposition weight > 2.2 μg/cm^2, because the pressure drop increased while the filtration performance has peaked. Thus, deposition weight of 2.2 μg/cm^2 is substantially optimal in terms of

antimicrobial filtration effectiveness (Fig. S16). These results demonstrated the feasibility of the VLA antimicrobial facepiece mask that can effectively filter harmful airborne particles.

Since filters are commonly exposed to highly humid conditions such as exhaled or damp air, haze, or rain, their humidity resistance is important. Figure 4a shows the mechanism of the humidity resistance of the air filters. PFOTES forms a hydrophobic barrier that prevents direct contact between water and TiO_2@CV. The hydrophobic barrier plays an essential role in the durability of TiO_2@PFOTES-CV nanostructures by preventing filter wetting and particle effusion. To confirm the humidity resistance of TiO_2@PFOTES-CV filters, the water contact angles of the air filters with or without PFOTES were evaluated. As shown in Fig. 4b, the water contact angle of TiO_2@CV was hardly measurable owing to its hydrophilic nature. However, TiO_2@PFOTES-CV NPs gave water contact angles > 140° because of the highly hydrophobic character of PFOTES. To further verify the water repellency, water was dropped continuously on the samples. In the absence of PFOTES, the water droplets fully wetted the filter surface, whereas the water droplets did not spread on the surface of the TiO_2@PFOTES-CV filter and instead rolled down (Fig. 4c). The water infiltrated the PFOTES-free filter more easily than the TiO_2@PFOTES-CV filter; thus, a lot of NPs on the PFOTES-free fibers were swept away by the water (Figs. 4c and 4d). In addition, if the concentration of PFOTES was too low, the dye would not be protected from leaching, indicating that PFOTES concentration is important for protecting dye molecules against water. These results emphasize the function of PFOTES in the water stability of the filter by forming a hydrophobic barrier at the TiO_2 surface.

In addition, the mechanical robustness of the TiO_2@PFOTES-CV nanostructure was examined under airflows similar to human breathing conditions (Fig. S17). We were not able to monitor notable particles detaching from the fibers. The stable adhesion against airflow seemed to be attributed to Van der Waals forces acting among individual NPs as well as between the NPs and the fiber surface (Table S1). Their robust durability to water and wind makes transmission of the NPs and dyes improbable, reducing the possibility of subsequent adverse effects.

To summarize, we present a practical antimicrobial air filter with TiO_2@PFOTES-CV NPs that are photochemically reactive to ubiquitous visible-light. To form 3D nanostructures with a large specific surface area, TiO_2@PFOTES-CV NPs were coated onto fibers using a simple aerosol deposition method. VLA antimicrobial air filters deactivate various bacteria with exceptional efficiency due to the ROS produced by the synergy of TiO_2 and CV activated by visible-light. We confirmed the feasibility of the VLA photochemical reaction through the band offset results of the TiO_2-CV NPs. The filtration performance was dramatically strengthened by the rough surface of the 3D nanostructure formed by the NPs. The humidity resistance of the TiO_2@PFOTES-CV nanostructure remained stable in the presence of water droplets due to the hydrophobic barrier by PFOTES, indicating potential use in real environments such as exhaled or damp air, haze, or rain. Although the TiO_2@PFOTES-CV filter shows an outstanding antimicrobial performance against various bacteria, the TiO_2@PFOTES-CV filter may not be effective against all microorganisms. Therefore, a future study is needed to confirm antimicrobial performance against various bioaerosols (e.g., virus and fungi).

Supporting Information

This material is available free of charge via the internet at https://pubs.acs.org/doi.

Additional figures, table, and experimental details.

Author contribution

J.H.J. conceived the concept. J.H.J. organized the study. K.J.H., S.B.J., H.S.K., and J.H.J. designed and implemented the experiments. K.J.H. and D.Y.C. analyzed the data and created the figures. J.S. and G.B.H. conducted the ROS scavenger quenching assay. K.J.H., D.Y.C., S.B.J., and J.H.J. co-wrote the paper with contribution of G.B.H., H.S.K., and Y.K. All authors discussed the results and assisted during manuscript preparation.

Notes

The authors declare no competing interests.

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filtration efficiency (blue circle) and pressure drop (red triangle) plotted against the TiO_2@PFOTES-CV deposition weight.

Figure 4. Humidity resistance of the VLA TiO_2@PFOTES-CV filters. (a) Schematic illustrating the principle of the humidity resistance of the TiO_2@PFOTES-CV filter forming the hydrophobic barrier of PFOTES molecules. (b) Measurement of the water contact angle. Top images represent the results of sessile drop tests for the TiO_2@CV filter (left) and TiO_2@PFOTES-CV filter (right), and bottom images correspond to the tilted top view of each filter. (c) Water-repellent behavior of the TiO_2@CV filter (left) and TiO_2@PFOTES-CV filter (right), and (d) UV-Vis spectra of the solutions effused from each filter for analysis of the leaching degree of NPs according to PFOTES concentration.