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Photocatalytic inactivation of airborne bacteria in a polyurethane foam reactor loaded with a hybrid of MXene and anatase TiO\textsubscript{2} exposing {001} facets

Siyi Lu, Ge Meng, Can Wang*, Hong Chen

School of Environmental Science and Engineering, Tianjin University, Tianjin 300350, PR China
Tianjin Key Lab of Indoor Air Environmental Quality Control, Tianjin 300350, PR China

HIGHLIGHTS

- Photocatalyst based on monolayer Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} and TiO\textsubscript{2} exposing {001} facets was synthesized.
- A continuous flow-through reactor was established for photocatalytic aerosol disinfection.
- Photo reactivation and dark repair of bacteria after UV and photocatalysis was observed.

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ABSTRACT

A hybrid of TiO\textsubscript{2} exposing {001} facets and monolayer Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} nanosheet (MXene) was synthesized, characterized and used as a photocatalyst in this study. The introduction of MXene (3.4 wt\%) helped to reduce the recombination of photo-induced electrons and holes, and thus enhanced the photocatalytic activity by 30%. A continuous flow-through reactor loaded with the as-prepared photocatalyst coated onto polyurethane foam was developed to inactivate airborne bacteria. The photocatalytic inactivation efficiency of airborne Escherichia coli (E. coli) achieved 3.4 lg order under ultraviolet (UV) irradiation at 254 (UV254), which was superior to that using UV254-only treatment with 2.5 lg order under the same operating condition (95% relative humidity and retention time of 4.27 s). The effect of humidity and bacteria species on inactivation performance was also investigated. The thick cell membrane could protect bacteria from photocatalytic oxidation while high humidity increased the photocatalytic inactivation efficiency by generating more reactive oxygen species. The phenomena of photo reactivation and dark repair of airborne E. coli using UV254-only treatment was observed. However, no reactivation occurred after UV photocatalytic inactivation, and even a continuous decline under visible light. These results suggested a different inactivation mechanism between UV irradiation and UV photocatalysis that the former inactivated bacteria by damaging their DNA, whereas photocatalysis physically damaged their cell structure.

1. Introduction

Bioaerosols are airborne microbial cells with fragments and particulate matter of biological origin, such as virus, bacteria, and fungal spores [1,2]. These small particles cause infectious diseases, acute toxic reactions, and allergies and thus affect human health [3]. Outbreaks of severe acute respiratory syndrome (SARS) and influenza H1N1 viral infections across the globe have attracted worldwide attention for airborne microbial prevention and control measures [4].

Ultraviolet (UV) irradiation, especially UVC, has been recommended to inactivate various infectious organisms due to its ability to inactivate airborne organism by effectively damaging their DNA [5–7]. However, other studies have reported that the “dead” state of bacteria caused by exposure to UVC irradiation may not be permanent. Inactivated bacteria may be reactivated after a period of time; thus, the survival of bacteria and the risk must be re-assessed [8,9]. Photocatalysis has been applied in previous studies and turns out to be a promising purification technique for water disinfection [10], statistic surface sterilization [11,12], and antimicrobial materials development [13]. However, the research in the field of dynamic bioaerosols...
disinfection within a flow-through device is very limited [13,14]. Therefore, this study aimed to establish a continuous flow-through reactor to inactivate airborne bacteria dynamically under UV photocatalysis.

Catalyst is an important part of the photocatalytic reactor [15–17]. Titanium dioxide (TiO2), especially commercial Degussa P25, has been widely used as a photocatalyst since Matsunaga [18] and his coworkers first applied photocatalyst to inactivate microorganism. Reviews [19] have shown that the photocatalytic reactivity of TiO2 can be further improved by metal/nonmetal doping and crystal facet regulation. Both theoretical and experimental evidence show that (001) facets are much more reactive than the thermodynamically stable (101) facets due to their higher surface energy. Anatase TiO2 nanosheets with reactive (001) facets exhibited a superior photocatalytic activity to that of P25 [20]. Furthermore, Sun et al. [21] discovered that introducing a two-dimensional material could enhance the electron transfer yield and thus improving the photocatalytic performance of TiO2.

A new family of two-dimensional early transition metal carbides and/or nitrides (MXenes) has attracted intense interest since they were synthesized [22]. Most studied nanosheet among MXenes is Ti3C2Tx (T = OH, F or O) [23]. Density functional theory (DFT) calculations were characterized, and the function of monolayer Ti3C2Tx was investigated. The obtained multilayered Ti3C2Tx suspension was centrifuged at 9000 rpm for 20 min, and a dark colloidal Ti3C2Tx nanosheets dispersed successively in ethanol and deionized water by ultrasonication. Next, the precipitate was redispersed in dimethyl sulfoxide (DMSO) for intercalation. Finally, the mixed solution was placed in a Teflon autoclave, and the vessel was sealed and heated at 180 °C for 12 h. After hydrothermal treatment, the reaction system was cooled to room temperature and washed several times with absolute ethanol and deionized water. The sample was collected under vacuum drying at 60 °C for 24 h. The samples were named as (001)TiOx, (001)TiOx/MXene (0.9%), (001)TiOx/MXene (3.4%), and (001)TiOx/MXene (7.2%) according to their MXene contents (weight percentage).

2.1. Preparation of MXene

2.1.1. Preparation of MXene

Ti3AlC2 (purchased from 11 technology Co., Ltd, Jilin, China) was used as the raw material to prepare multilayered Ti3C2Tx. Ti3C2Tx was produced by immersing 2 g of Ti3AlC2 in 40 mL of hydrochloric acid solution containing 2 g of LiF and 9 M of HCl for 24 h at 35 °C [34]. During this process, Al species in Ti3AlC2 were selectively etched by HF. The obtained multilayered Ti3C2Tx suspension was centrifuged at 3500 rpm for 10 min and washed with deionized water until the pH of the solution was higher than 6. Then the precipitate was dispersed in dimethyl sulfoxide (DMSO) for intercalation. Next, the precipitate was dispersed successively in ethanol and deionized water by ultrasonication (500 W) for 1 h with ice bath. The suspension was then centrifuged at 9000 rpm for 20 min, and a dark colloidal Ti3C2Tx nanosheets (MXene) solution was obtained [35].

2.1.2. Synthesis of (001)TiOx/MXene

Anatase TiO2 nanoparticles with exposed (001) facets were incorporated with MXene through the one-step hydrothermal method [20]. A certain amount (0.9 wt%, 3.4 wt%, and 7.2 wt%) of MXene was dissolved in isopropyl alcohol by sonication to obtain a solution of MXene nanosheets. Then, tetraethyl titanate (TBT) was added, and the mixture was sonicated to form a uniform solution. Next, fluoric acid (40 wt%) was dropped into the solution under continuous stirring to tune the growth mode of the nanocrystals and the exposure of (001) facets during synthesis. Finally, the mixed solution was placed in a Teflon autoclave, and the vessel was sealed and heated at 180 °C for 12 h. After hydrothermal treatment, the reaction system was cooled to room temperature and washed several times with absolute ethanol and deionized water. The sample was collected under vacuum drying at 60 °C for 24 h. The samples were named as (001)TiOx, (001)TiOx/MXene (0.9%), (001)TiOx/MXene (3.4%), and (001)TiOx/MXene (7.2%) according to their MXene contents (weight percentage).

2.1.3. Characterization

The crystallographic structure of the catalysts was characterized by X-ray diffraction (XRD) analysis using Cu-Kα radiation (Bruker D8 Focus, Germany) with a 2-theta range of 5°–80°. The morphology of the samples was obtained by field emission scanning electron microscopy (SEM) at an accelerating voltage of 5 kV (Hitachi S-4800, Japan) and by transmission electron microscopy (TEM) at an accelerating voltage of 200 kV (JEM-2010FEF, USA), followed by energy dispersion spectroscopy (EDS) to detect the elements content in the samples. The light absorption spectra were recorded by UV–Vis diffuse reflectance spectrophotometer (UV–Vis DRS) at wavelength range of 200–800 nm (UV-2600, Shimadzu, Japan). BaSO4 was used as reflectance reference for the UV–Vis spectrophotometer. The band gap energy of the sample was determined by plotting [F(R)]∞2 against the photon energy. X-ray photoelectron spectroscopy (XPS) was analyzed by a Thermo ESCALAB 250Xi spectrometer at a spot size of 500 μm, using an Al Kα source with a resolution of 0.05 eV. Photoluminescence (PL) spectra were obtained using a fluorescence spectrometer (F-4600, Hitachi, Japan). The excitation wavelength was set at 254 nm.

2.1.4. Other analytical methods

Photocatalytic reactivity was evaluated through the degradation of methylene blue (MB) under UV radiation. Detailed information can be found in supplementary material (Text S1 and Fig. S1, SI). For the analysis of different oxidation pathways in the photocatalytic process, trapping tests for radicals and holes were carried out, in which 0.1 M of tert-butanol (t-BuOH) and 0.1 M of EDTA-2Na were used as scavengers of hydroxyl radical (HO·) and holes (h+), respectively.

The as-prepared (001)TiOx/MXene catalyst was loaded onto the PU foam by dipping in a 1% ethanol base catalyst solution for 10 min, dried in vacuum at 55 °C for 8 h, and fabricated to develop a quartz reactor for bacteria inactivation in bioaerosols. The preparation and coating process mentioned above is presented in Fig. 1.

2.2. Photocatalysis experiments

2.2.1. Bioaerosol generation and collection

E. coli (Gram-negative, G−) and B. subtilis (Gram-positive, G+) and its spore were used to evaluate the photocatalytic inactivation efficiency. The bacterial suspension was aerosolized by an aerosol generator (Topas, ATM226, Germany, Fig. S3) to a particle size of 1–5 μm to produce bacteria-containing bioaerosols. The number of bacteria in effluent bioaerosols was detected through the plate counting method using a 0.1-mL sample of the 30-mL bacteria solution collected by an AGI-30 impinger (Qingdao Junray Intelligent Instrument Co., Ltd., China) at a flow rate of 12.5 L/min for 10 min. The nutrient agar plates
were then incubated for 24 h at 37 °C. The number of colony-forming units (CFUs) on each nutrient agar plate was manually counted. Each experiment was conducted in duplicate.

2.2.2. Photoreactor setup

A schematic representation of the experimental setup for inactivating airborne bacteria is shown in Fig. S2 in SI. The photoreactor is a cylinder-shaped double-layer quartz casing with dimensions of 7 cm diameter × 35 cm length. PU foam was used as a catalyst carrier to support the as-prepared photocatalyst to increase the contact area with which the reactor was packed up. To test the filtration of PU foam and the inactivation of UV irradiation, experiments were also conducted under PU foam-only and UV-only conditions. The bioaerosols containing bacteria passed through the photoreactor from bottom to top, and were subsequently collected and measured. Other parameters are listed in Table S1 in SI.

The inactivation performance was measured by log inactivation efficiency (E), which is defined as the logarithmic order of bacteria concentration decrease after inactivation [36]:

\[
E = \log\left(\frac{N_0}{N_t}\right)
\]

where \(N_0\) and \(N_t\) are the specific bacteria concentration (CFU/m\(^3\)) in bioaerosols before and after inactivation treatment, respectively.

The electrical efficiency per log order (EE/O) in the process of UV/photocatalytic inactivation was applied to evaluate the energy consumption. EE/O is defined as the electrical energy (kW-h) required to reduce the concentration of microbes by one order of magnitude in 1 m\(^3\) air using the following equation [37]. In this study, only the energy consumed by UV lamps was considered and the other consumption was not included.

\[
EE/O (\text{kW-h/m}^3) = \frac{P \times t}{V \times \log\left(\frac{N_0}{N_t}\right)}
\]

where \(P\) is the lamp power output. Only the lamp power was considered, and the UV lamp with a wavelength of 365 nm (UV365) is 8 W, while the UV lamp with wavelength of 254 nm (UV254) is 15 W. \(V\) is the reactor volume. \(t\) is the retention time.

2.2.3. Photo reactivation and dark repair

Reports indicate that the bacteria after UV treatment might not be really “dead” and can be reactivated after a period time of repair under certain circumstances [38,39]. The method of repair and cultivation was applied to determine the resuscitation potential of the E. coli inactivated by UV irradiation and the photocatalytic treatment to an unculturable state. The absorbent containing bacteria after treatment was placed under visible light (40 W, 400–750 nm) or in the dark. The samples were taken and plate-cultured at durations of 0, 24, 48, 72, and 96 h. The sampling and culture conditions are the same as those described in Section 2.2.1.

3. Results and discussion

3.1. Structure and properties of Ti\(_3\)C\(_2\)T\(_x\) and \{(001)\}TiO\(_2\)

Fig. 2(a) shows the morphology of multilayered Ti\(_3\)C\(_2\)T\(_x\), indicating that the Al element in Ti\(_3\)AlC\(_2\) was removed after LiF/HCl etching and therefore exhibited an accordion-like shape [Fig. 2(b)]. The removal of Al was also verified by EDS [Fig. S4], indicating that the content decreased to 3%. The Ti\(_3\)C\(_2\)T\(_x\) nanosheet (MXene) was prepared after the DMSO intercalation and ultrasound delamination of the multilayered Ti\(_3\)C\(_2\)T\(_x\), as shown in Fig. 2(c). The TEM images clearly demonstrated the morphology and size of MXene. The low contrast indicates few atomic layers and uniform lamellae, with a nanosheet size of approximately 100 nm. The MXene film was prepared by the self-assembly Ti\(_3\)C\(_2\)T\(_x\) nanosheets under vacuum filtration (Fig. S5), after which they were separated from the colloidal solution. In this study, the monolayer Ti\(_3\)C\(_2\) nanosheets were verified by the HRTEM images (Fig. S6). The flexible MXene film has a smooth surface. Fig. 2(d) shows the XRD pattern of Ti\(_3\)AlC\(_2\), multilayer Ti\(_3\)C\(_2\)T\(_x\), and MXene. Meanwhile, the production of MXene is verified by (002) peak at around 10° (2θ), where the peak shifted to a lower angle after Ti\(_3\)C\(_2\)T\(_x\) delamination [32,40,41].

Anatase TiO\(_2\) samples with exposed (001) facets were synthesized by hydrothermal methods, namely, \((001)\)TiO\(_2\), \((001)\)TiO\(_2\)/0.9% MXene, \((001)\)TiO\(_2\)/3.4% MXene and \((001)\)TiO\(_2\)/7.2% MXene. The SEM, TEM, and HRTEM observations of (001) TiO\(_2\)/MXene (Fig. 3) show that the average nanoparticle size is 20–30 nm × 3 nm, and the
lattice spacing of {001} facet is 0.23 nm, agreeing well with the anatase TiO2 crystallite exposing a large proportion of {001} facets.

3.2. Performance and mechanism of {001} TiO2/MXene hybrid as photocatalyst

The crystal phases of the samples were investigated by XRD, as shown in Fig. 4(a). After hydrothermal oxidation, the anatase TiO2 (JCPDS No. 21–1272) phase emerged, and the sharp diffraction peak indicates good crystallinity. A (002) reflection of Ti3C2Tx at 7.5° can be observed, suggesting the existence of MXene, although its intensity is weak due to the low contents.

As shown in Fig. 4(b), the optical absorption properties of the photocatalysts with different MXene contents were investigated using a UV–Vis diffuse reflectance spectrometer. Intense ultraviolet characteristic absorptions were observed from 200 to 400 nm and are consistent with the range of the anatase TiO2 absorptions [42]. Clearly, the absorption intensity was significantly strengthened by the addition of 3.4% and 7.2% MXene, suggesting the enhancement of the anatase TiO2 catalytic ability by introducing MXene. The bandgap energy of the photocatalysts was determined by plotting \([F(R_\infty)hv]^2\) against the photon energy in Fig. 4(c). The bandgap of TiO2 obtained by the transverse intercept of the extension line of the straight part is 3.5 eV, which is higher than the theoretical value (3.2 eV). The corresponding band gap value of {001} TiO2/MXene samples was approximately 3.5 ~ 3.65 eV. A slight increase of TiO2/MXene band gap was observed compared with that of pure TiO2. However, this change could be ignored considering that Tauc plot is an empirical equation, and MXene was considered to serve as co-catalyst in this experiment [42–44].

The photocatalytic activity of the catalysts with different MXene contents in anatase TiO2 is shown in Fig. 4(d). A rather low activity was found in the absence of UV irradiation, indicating that the effect of adsorption by the catalyst can be neglected. Approximately 85% of the
MB was photodegraded by the (001)TiO2 catalyst after 180 min reaction. Photocatalytic activity was improved by adding MXene, and the highest degradation efficiency was observed when the (001)TiO2/3.4% MXene catalyst was used, which was 30% higher than that using the (001)TiO2 catalyst. Su et al. [44] also observed much better property of monolayer Ti3C2Tx than multilayer Ti3C2Tx as a co-catalyst. Interestingly, with the increase of MXene content in the (001)TiO2 catalyst to 7.2%, a slight decrease of MB photodegradation efficiency was observed compared with that in the (001)TiO2/3.4% MXene catalyst. This phenomenon might be explained by the excellent electrical conductivity of MXene, facilitating the transfer of the charge carrier from the semiconductor to MXene and thus reduce the electron-hole recombination rate and improve the photocatalytic activity [45,46]. However, overloading MXene in (001)TiO2 catalyst may cause the reduction of photocatalytic active sites and then reduce the degradation efficiency. Therefore, (001)TiO2/MXene with the MXene content of 3.4% can achieve optimum activity.

In addition, the sample of (001)TiO2/MXene(3.4%) was tested by XPS spectra, and the results are shown in Fig. 5. Two main peaks at the binding energy of 458.9 eV (Ti 2p3/2) and 464.6 eV (Ti 2p1/2) can be found in the high-resolution XPS of Ti 2p [Fig. 5(b)], which were originated from TiO2. Two small Ti (I, II, or III) peaks (at 457.3 eV and 463.4 eV) can also be observed in the Ti 2p scanned spectra, suggesting the presence of MXene in (001)TiO2/MXene (3.4%) [44]. Fig. 5(c) and (d) show high-resolution XPS spectra of O 1 s and C 1 s, respectively. A clear peak of Ti-O bond structures suggests the presence of TiOx species in the sample. However, C-Ti peak is hard to be observed in C 1 s spectra because of the high content of TiO2 [47,48].

PL spectra of the TiO2/MXene and pure TiO2 are tested and shown in Fig. S7. The recombination of photo-induced electrons and holes lead to the release of photons and heat, resulting in PL [49]. The PL intensity decreases after loading with MXene, compared with that of the pure (001)TiO2. These results suggested that the monolayer MXene in (001)TiO2 improved electrons transport between the contacting surfaces, and thus inhibiting the recombination of photo-induced electrons and holes [20].

Fig. 6 shows the possible mechanism of improved photocatalytic activity achieved by (001)TiO2/MXene. The photocatalysts absorbed light and then the photogenerated electrons (e−) were excited to the conduction band (CB), while holes (h+) were left in the valence band (VB). Instead of recombining with h+ again, the excited charge carriers were transferred to MXene [31,49,50], with high electrical conductivity and two-dimensional structure, at the interface. Therefore e− and h+ were more likely to react to produce OH·, or other free radicals, that can be utilized for degradation of organics, thus leading to the enhancement of photocatalytic activity [27,44].

### 3.3. Photocatalytic inactivation of airborne bacteria

Inactivation experiments on UV irradiation, filtration, and photocatalysis were conducted. The inactivation efficiency and EE/O performance are presented in Fig. 7.

Inactivation efficiency caused by UV365-alone was approximately 0.4 logarithmic (lg) order, while that of UV254-alone was 2.5 lg order. The inactivation efficiency increased by 0.3 lg order when the filtration of PU foam was added. Notably, the photocatalyst-coated PU foam had a high inactivation efficiency of 3.4 and 2.5 lg order under UV254 and UV365, respectively.

Rasool and Yury [32] reported the antimicrobial activity of Ti3C2 MXene to waterborne bacteria. However, no obvious antimicrobial activity to airborne bacteria was observed in our previous study. In this study, (001)TiO2/MXene (3.4%) showed good photocatalytic activity in inactivating bacteria under both UV365 and UV254. The enhancement of inactivation efficiency from 3.0 lg to 3.4 lg order under UV254,
or from 0.6 to 2.5 under UV365 (Fig. 7) was attributed to the addition of the (001)TiO$_2$/MXene catalyst. In other words, the presence of photocatalysis significantly improved the inactivation performance, especially for UV365. Therefore, the inactivation performance obtained under UV365/photocatalysis can be considered a photocatalysis-dominated damage, whereas that obtained under UV254/photocatalysis was the sum of photocatalytic oxidation and UV photolysis.

As for EE/O under UV irradiation and photocatalysis, Fig. 7(b)

Fig. 5. XPS spectra of (001)TiO$_2$/MXene (3.4%) (a) fully scan (b) high-resolution deconvolution of Ti 2p peak (c) O 1s peak (d) C 1s peak.

Fig. 6. Possible mechanism of improved photocatalytic activity.
shows that the addition of a photocatalyst remarkably reduced the energy consumption for inactivating E. coli compared with the condition of UV365-only inactivation. The EE/O using UV365 fell by half when the PU foam was added, because the inactivation efficiency (UV365/foam) increased by double due to PU filtration effects, while the energy consumption stayed unchanged. Interestingly, the electrical efficiencies of UV/photocatalysis under UV254 and UV365 were nearly the same, indicating that photocatalytic inactivation under UV365 is also an economical and efficiently method.

To investigate the influence of bacteria species, inactivation experiments for E. coli and B. subtilis and its spore were conducted (Fig. 8(a)), which were representative of gram-negative bacteria, gram-positive bacteria, and bacteria in a dormant state, respectively. Results show that the degree of difficulty of photocatalytic inactivation followed the order E. coli < B. subtilis < spore of B. subtilis regardless of the UV source adopted. A widely recognized theory is that photocatalysis inactivates microorganisms by reactive oxygen species (ROS), which first compromises the cell membrane or cell wall, and then penetrates to reach the internal cellular component and eventually causes cell death [51]. Generally, gram-positive bacteria have a dense peptigosaccharide layer in their cell membrane of 20–80 nm in thickness, while gram-negative bacteria have a much thinner membrane of ~10 nm with a loose peptigosaccharide layer. Endospore, as gram-positive bacteria in dormant state, has another thick cell wall in addition to the original dense peptigosaccharide layer. Therefore, the phenomenon of different photocatalytic inactivation efficiency might be explained by the much thicker bacterial wall of B. subtilis and its spore than that of E. coli.

![Fig. 7. (a) Inactivation performance and (b) EE/O of E. coli under UV irradiation and photocatalysis (Relative humidity = 95%; initial bacteria concentration: ~10^8 CFU/m^3; retention time: 4.27 s).](image)

![Fig. 8. Effect of (a, c) bacteria species (relative humidity = 30%) and (b, d) humidity (spore of B. subtilis) on inactivation performance and EE/O (retention time: 4.27 s; irradiation intensity: 10 mW/cm^2).](image)
Moreover, the effect of relative humidity was also studied [Fig. 8(b)]. The log inactivation efficiency improved with the increasing relative humidity from 30% to 95%. Most of the other studies showed that ROS was responsible for the photocatalytic inactivation of microbes and hydroxyl radical (·OH) is dominant [51,52]. Furthermore, trapping tests [seen from SI] and results indicate that indirect and direct oxidation account for 30% and 70% of the photocatalytic degradation, respectively, where the indirect pathway includes oxidation by ROS, primarily by the ·OH. The generation of ·OH is dependent on the moisture content in aerosols:

\[ \text{H}_2\text{O} + h^+ \rightarrow \cdot\text{OH} + \text{H}^+ \]

Sansotera et al.'s study [53] revealed that the increase in atmospheric humidity progressively increased the photodegradation rates of VOCs given that water vapors can be adsorbed on the TiO$_2$ active sites as resources for ·OH, and therefore the enhancement of inactivation performance may result from the promoted generation of ·OH under high humidity [54]. Fig. 8(c) and (d) show that the EE/O required for spore of B. subtilis significantly increased compared with that for E. coli and B. subtilis and it decreased with the increasing humidity.

The EE/O performance in this work and other previous studies are presented in Fig. 9. Most studies explored the photocatalytic inactivation efficiency of TiO$_2$ or modified TiO$_2$ with metal doping. The inactivation efficiency ranged from 0.3 to 2.6 log order, but the EE/O in different studies varied by nearly tens of times, which is dependent on the treatment volume and retention time. The EE/O in our study is apparently lower than those in other studies, which may be attributed to two reasons. On the one hand, the photocatalytic activity of TiO$_2$ was promoted due to the addition of MXene. The DFT calculations predict that MXenes exhibit metallic conductivity, which is favorable to electron–hole separation and charge transfer. On the other hand, the adoption of a new flow-through reactor was adopted, thus increasing the contact area and shortening the retention time to only a few seconds.

### 3.4. Photo reactivation and dark repair

The performance of photo reactivation and dark repair after UV254, UV365, UV254/photocatalysis and UV254/photocatalysis treatment, respectively, are shown in Fig. 10. Detailed pictures of culture plates are shown in Fig. S8. Fig. 10(a) and (b) indicate that after UV254 irradiation treatment, the culturable cell counts of E. coli decreased from 10$^6$ CFU/mL to 10$^3$ CFU/mL according to the plate cultivation, and then reached approximately 10$^3.7$, 10$^5$, and 10$^5.5$ CFU/mL at 48, 72, and 96 h, respectively, under visible light. Repair still occurred in the dark but was lower and slower than that in photo reactivation. A similar
reactivation was also observed when UV365 irradiation treatment was used. However, no reactivation was observed after UV photocatalytic inactivation, and a continuous decline was even observed under visible light, as shown in Fig. 10(c) and (d). These reactivation results may raise a re-evaluation of the inactivation performance and health risk.

Zhang et al. [62] reported that many pathogens can enter the viable-but-nonculturable (VBNC) state in response to environmental stresses, such as UV irradiation, chloramine, and free radical. The resuscitation of VBNC cells induced by chloramine was not observed, but resuscitation was observed when UV254 was used in their study. A similar phenomenon was also found in our study, and Fig. 11 presents a diagram of the inactivation mechanism of UV irradiation and UV photocatalysis. UV irradiation inactivates bacteria by damaging their DNA, especially the pyrimidine dimer in it, which can be repaired under certain circumstances, such as under visible light. However, UV photocatalysis disinfects microorganisms by ROS oxidation and causes physical damage to their outer membrane [63], and the membrane cannot be rebuilt without nutrition. Therefore, UV photocatalytic inactivation can be considered a more thorough disinfection approach than UV irradiation.

4. Conclusion

In summary, this study prepared a hybrid of MXene and TiO2 exposing {001} facets as photocatalysts. The introduction of MXene can help to reduce the recombination of photo-induced electrons and holes, and thus improved the photocatalytic activity. A novel continuous flow-through reactor loaded with the as-prepared photocatalyst coated onto polyurethane foam was developed to inactivate airborne bacteria. The inactivation efficiency of airborne E. coli under UV254/photocatalysis was superior to that using UV254-only treatment under the same operating condition. The effect of humidity and bacteria species on inactivation performance was also investigated. The thick cell membrane could protect bacteria from photocatalytic oxidation while high humidity increased the photocatalytic inactivation efficiency by generating more ROS.

The photo reactivation and dark repair performance of the after-inactivated microbe were also investigated in this study. The bacteria after photocatalytic oxidation were difficult to reanimate, whereas those after UV-only treatment can be repaired and become culturable again. These results suggested a different inactivation mechanism between UV irradiation and UV photocatalysis that the former inactivated bacteria by damaging their DNA, whereas photocatalysis physically damaged their cell structure. Therefore, photocatalytic inactivation is considered as a more thorough disinfection technology compared with single UV inactivation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/jcej.2020.126526.

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