New strategy for photocatalytic antibacterial concrete: in situ fluoride-modified negatively charged interfaces

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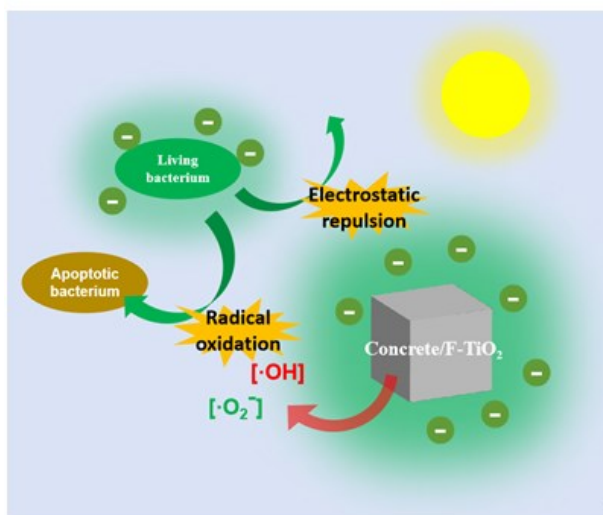
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Graphical abstract

Abstract

In natural long-termuse microbes from rainwater can adhere to and proliferate on these concrete surfaces, potentially accelerating material corrosion and posing health risks. To combat this, our study introduces a straightforward and effective antimicrobial surface strategy. We applied a fluorine-modified titanium dioxide photocatalyst coating to permeable foam concrete surfaces. The fluorine regulation enhances electron transfer to the titanium dioxide, creating a negatively charged interface. This charge repels negatively charged microbes electrostatically and curbs microbial growth through the oxidative properties of photogenerated radicals. Tested under 50 mW/cm^2 of simulated sunlight, the bacterial count at the negatively charged interface was just 35.7% of that at a positively charged interface, with the coating retaining about 90% of its antibacterial efficacy even in highly contaminated conditions. This research offers a cost-effective and efficient method for developing antimicrobial coatings for building materials.

Keywords: photocatalytic antibacterial, concrete, F-TiO$_2$, electrostatic repulsion, electronegative interface

1. Introduction

Rainwater runoff can transport numerous microbes and nutrients, potentially leading to microbial colonization and biofilm formation on these materials, which may block their pores (Newman *et al.* 2006). Additionally, microbial activity can hasten the degradation and aging of building materials (Grengg *et al.* 2018), compromising their longevity. Consequently, the development of antimicrobial building materials has emerged as a critical area of research (Kirthika *et al.* 2023).

Rather than incorporating antibacterial agents directly into building materials, applying antibacterial surface coatings offers a more cost-effective alternative, drawing significant research interest (Cloutier *et al.* 2015). While metals like copper, silver, and gold have proven effective and durable in these applications (Bharadishettar *et al.* 2021; Knetsch *et al.* 2011; Rai *et al.* 2010), their high cost and potential for heavy metal pollution pose challenges, particularly where preserving rainwater quality is crucial (Yin *et al.* 2021). Non-heavy metal semiconductor photocatalysts, such as titanium dioxide, offer a greener solution by using light to activate antimicrobial species (Mahy *et al.* 2019). Nevertheless, the high microbial load in natural rainwater can impede these photocatalysts' effectiveness, necessitating improvements in their performance and microbial resistance at the surface (Salleh *et al.* 2024).

This study explores the use of titanium dioxide, a common photocatalyst in pollution control for concrete, enhanced with a simple fluorine-based surface modification technique (Castro-Hoyos *et al.* 2022; Dozzi *et al.* 2013). By manipulating fluorine charge transfer, we not only boost the generation of photo-induced radicals but also create a negatively charged surface that repels microbes, enhancing the antimicrobial properties of the coating. Traditionally, fluorine-modified materials are synthesized in lab settings through complex methods, limiting their scalability (Liu *et al.* 2012). Our approach utilizes a straightforward spraying technique for in-situ fluorination on concrete, simplifying the application process and

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potentially facilitating widespread use, thus offering a practical solution for deploying antimicrobial concrete materials on a large scale.

2. Experiment

2.1. Materials and reagents

This experiment uses foamed concrete, which has low density and good permeability, commonly used in building exteriors. The shape is a 2cm cube, purchased from Taobao (https://m.tb.cn/h.5xuaiLVug0AgxDE?tk=Idx8WM0Y8sz). The experiment involves coating preparation and chemical reagents such as tetrabutyl titanate, hydrofluoric acid, anhydrous ethanol, and sodium chloride, all of analytical grade, purchased from China National Pharmaceutical Group Chemical Reagent Company. Reagents preparation and dilution use ultrapure water (resistivity ≥18.2 MΩ·cm).

2.2. Preparation of modified concrete

First, prepare a solution of ethanol containing 10% by volume of tetrabutyl titanate, spray it evenly over the entire surface of the concrete block using a spraying method. Then dry it in an oven at 60°C, place the sample in a muffle furnace, heat it to 400°C and keep it warm for 2 hours to obtain concrete/TiO_2 samples. Next, prepare a 1% by volume hydrofluoric acid aqueous solution, spray it evenly on the surface of concrete/TiO_2, ensure it is wetted, then dry it in a fume hood to obtain concrete/F-TiO_2 samples.

To facilitate the testing of the photocatalyst properties, TiO_2 and F-TiO_2 powders were also synthesized. Dry the ethanol solution containing 10% by volume of tetrabutyl titanate in a container, collect the resulting powder, place it in a quartz boat, then heat it in a muffle furnace at 400°C and keep it warm for 2 hours to obtain TiO_2 powder. Immerse this powder in a 1% by volume hydrofluoric acid aqueous solution for 20 minutes, dry it after filtration, and finally obtain F-TiO_2 powder.

2.3. Culture and Enumeration of Microorganisms

In this study, we used Escherichia coli (ATCC25922) as the indicator strain. Before the experiment, bacterial suspensions were retrieved from the -80°C freezer and activated in liquid LB medium for two generations. The specific steps are as follows: first, the frozen strain was thawed in a water bath, then 0.5 mL of the bacterial suspension was inoculated into the liquid LB medium and cultured at 37°C for 20 hours. Afterwards, 1 mL of the activated bacterial suspension was inoculated into fresh liquid LB medium and continued to be cultured at 37°C for another 10 hours. Once activation was complete, the bacterial suspension was centrifuged at 4°C and 4500 rpm for 10 minutes, the supernatant was discarded, and the bacteria were resuspended in saline to prepare the strain stock solution.

To determine the total number of E. coli colonies in the samples, we used the plate count method. First, the sample was thoroughly shaken and serially diluted, then 1 mL of the water sample was used to prepare plates using the pour plate method. After incubating at 37°C for 20 hours, colony counts were performed to determine the total number of colonies and calculate the sterilization rate.

2.4. Experimental Methods

Photocatalytic antibacterial experiment: under the illumination of a xenon lamp at 50mW/cm^2, a concrete/F-TiO_2 sample is added to 50 mL of a solution containing about 10^4 CFU/mL of E. coli. Samples of 3 mL are taken every half hour for a duration of 2 hours. It is particularly important to cover the top of the beaker with a 1mm thick transparent organic plastic sheet to prevent the trace amounts of short-wave ultraviolet light from the xenon lamp from affecting the antibacterial simulation experiment.

Laser confocal microscopy staining experiment: 5 µmol/L of SYTO-9 is used to stain live bacteria with green fluorescence, and 2 µg/mL of PI solution is used to stain dying bacteria with red fluorescence. 500 µL of the staining solution is gently dropped onto the sample surface, stained in the dark at 37°C for 15 minutes, then gently rinsed off with saline. The stained sample is then ready for imaging.

2.5. Characterisation of samples

In this study, the results from Scanning Electron Microscope (SEM), Energy Dispersive Spectroscopy (EDS), Transmission Electron Microscope (TEM), X-ray Diffraction (XRD), ZETA potential, Ultraviolet-visible Absorption Spectroscopy (UV-vis), X-ray Photoelectron Spectroscopy (XPS), and Electron Paramagnetic Resonance (EPR) were provided by the third-party testing agency Baice (https://www.zkbaice.cn/). The Laser Scanning Confocal Microscope (LSCM) results were provided by the third-party testing agency Scientific Compass (https://www.shiyanjia.com/). Detailed information about the specific instrument models and related parameters can be obtained from the aforementioned websites. Additionally, due to the excessive hardness of the concrete samples, the samples were mainly obtained by breaking them into flat, small pieces.

3. Results and discussions

3.1. Morphological structure of antimicrobial concrete

This study utilized the impregnation-cauterization technique to apply a titanium dioxide coating to concrete surfaces, subsequently modifying it with fluorine through hydrofluoric acid treatment. Initially, the untreated concrete appeared as a grayish-white cube (**Figure 1a**). Post-application of the titanium dioxide and fluorine, no noticeable change in appearance was observed, likely due to the minimal titanium dioxide used. This suggests that the hydrofluoric acid treatment preserved the integral structure of the concrete, confirming its appropriateness for surface treatments. X-ray diffraction (XRD) analysis revealed the formation of an anatase type titanium dioxide coating on the concrete (**Figure 1b**). The diffraction patterns for Concrete/TiO_2 and Concrete/F-TiO_2 displayed similar peak positions and intensities,

indicating that the fluorine modification did not affect the phase structure of the concrete or titanium dioxide. X-ray photoelectron spectroscopy further demonstrated the presence of an additional fluorine peak in F-TiO$_2$ compared to TiO$_2$ (**Figure 1c**), verifying the effective incorporation of fluorine.
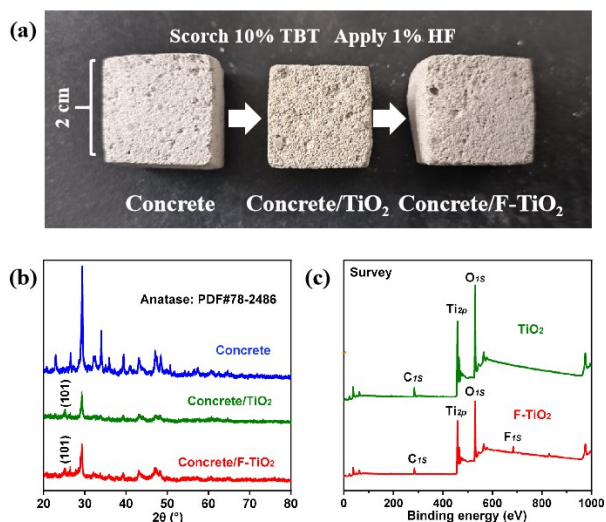

Figure 1. (a) Actual morphology of concrete samples, (b) XRD pattern of concrete samples, (c) XPS pattern of TiO$_2$ coating.

Scanning electron microscopy (SEM) offers a detailed view of the microstructures of the materials analyzed. The analysis reveals that the concrete surface contains numerous pores ranging from 200 μm to 1mm (**Figure 2a**), providing a large surface area for the titanium dioxide coating. Moreover, the presence of many micropores on its surface (**Figure 2b**) contributes significantly to the concrete's high permeability. **Figure 2c** demonstrates that the titanium dioxide coating does not fully cover the micropore-rich surface layer of the concrete, ensuring that the Concrete/TiO$_2$ retains excellent water permeability. Energy spectrum analysis effectively displays the elemental distribution, indicating a significant overlap between titanium and oxygen areas, which distinctly do not coincide with the calcium regions in the concrete (**Figures 2d1-2d3**), verifying the application of titanium dioxide on the concrete surface. Examination of the surface morphology of Concrete/F-TiO$_2$ (**Figure 2e**) shows that the titanium dioxide surface transitions from smooth to rough due to etching by hydrofluoric acid. The pronounced overlap of titanium (**Figure 2f1**) and fluorine (**Figure 2f1**) in the energy spectrum analysis substantiates the significant incorporation of fluorine, aligning with the findings presented in **Figure 1c**. Consequently, this study successfully develops a catalyst coating on the concrete surface.
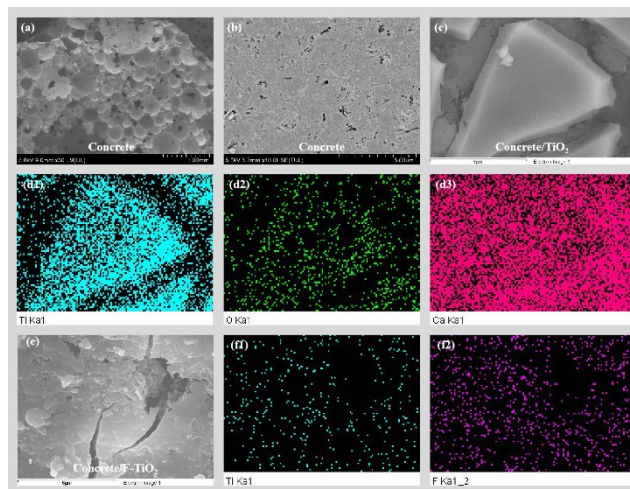

Figure 2. SEM morphology of Concrete surface with (a) macropores and (b) micropores. (c) SEM morphology of Concrete/TiO$_2$ and its (d1) titanium, (d2) oxygen and (d3) calcium element distribution images. (e) SEM morphology of Concrete/F-TiO$_2$ and its (f1) titanium and (f2) oxygen distribution images.
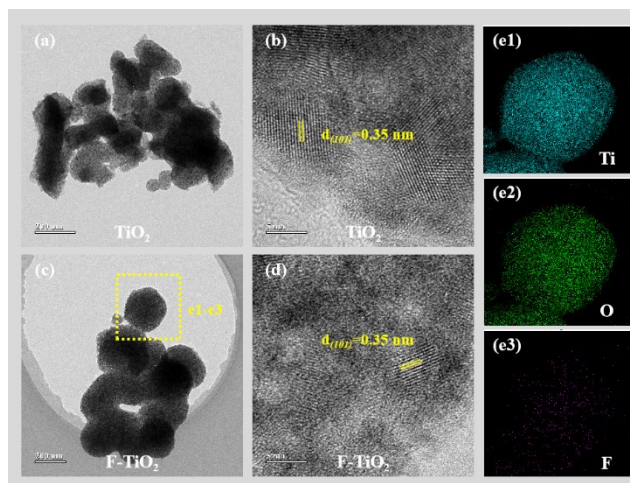

Figure 3. (a) TEM and (b) HRTEM images of TiO$_2$. (c) TEM and (d) HRTEM images of F-TiO$_2$ and its (e1) titanium, (e2) oxygen and (e3) fluorine elemental distribution images.

The changes in the titanium dioxide coating before and after fluorine modification were further analyzed using a transmission electron microscope (TEM). The results indicate that the titanium dioxide coating on the concrete surface mainly consists of elliptical particles with diameters of several hundred nanometers (**Figure 3a**), which are highly crystalline with a lattice fringe spacing of 0.35 nm (**Figure 3b**). This spacing corresponds to the (101) orientation of the anatase phase of titanium dioxide, aligning with the findings in **Figure 1b**. The treated F-TiO$_2$ displays uniform spherical shapes with a diameter of about 200nm (**Figure 3c**), possibly due to the etching effect. However, the lattice fringe spacing of F-TiO$_2$ remains at 0.35 nm (**Figure 3d**), suggesting that the addition of fluorine elements did not significantly alter the crystal phase of titanium dioxide. Energy spectrum tests under TEM mode reveal that the distributions of titanium (**Figure 3e1**), oxygen (**Figure 3e2**), and fluorine (**Figure 3e3**) elements completely overlap. Alongside the widespread distribution of fluorine elements in **Figures**

2f1 and 2f2, this confirms that fluorine elements were uniformly introduced on every particle in the antibacterial coating in this study, indicating successful and comprehensive fluorine modification of titanium dioxide nanoparticles.

3.2. Photocatalytic disinfection properties of antimicrobial concrete

This study utilized Escherichia coli to evaluate the photocatalytic disinfection capabilities of antibacterial concrete when exposed to light. The findings indicated that light exposure significantly reduced the E. coli levels to 6750 CFU/mL (**Figure 4a**). Incorporating concrete decreased the E. coli count further to 5250 CFU/mL, primarily due to the adsorptive properties of the concrete's large pores. When titanium dioxide was applied to the concrete surface, the disinfection efficiency of the Concrete/TiO$_2$ improved, lowering the bacterial count to 2840 CFU/mL. This suggests that a photocatalyst coating is an effective antibacterial approach. With fluorine modification, the disinfection efficiency of Concrete/F-TiO$_2$ increased further, dropping the bacterial count to 1005 CFU/mL, which shows that fluorine significantly boosts the photocatalytic performance of titanium dioxide. To thoroughly assess the antibacterial effect of Concrete/F-TiO$_2$, it was immersed in a high-concentration E. coli solution for one day before testing its photocatalytic disinfection capabilities. The results indicated that while the concrete absorbed bacteria (**Figure 4b**), it did not effectively prevent their growth. In contrast, the photocatalytic disinfection efficiency of Concrete/TiO$_2$ was approximately 60%, demonstrating that high microbial concentrations impacted the disinfection outcome. Nevertheless, even with significant bacterial contamination, Concrete/F-TiO$_2$ maintained a disinfection efficiency of about 80%, proving that fluorine-modified titanium dioxide coating could effectively counteract high microbial loads and retain about 90% of its catalytic activity. Scanning electron microscopy showed that few E. coli were present on the surface of Concrete/F-TiO$_2$, and the bacteria were visibly shriveled and cracked, highlighting strong antibacterial properties. These findings confirm that the concrete material developed in this study successfully achieves its antibacterial objectives by inactivating microbes under light exposure.

To more effectively assess the antibacterial properties of the materials, we utilized a Laser Scanning Confocal Microscope (LSCM) to examine microbial survival on the material surfaces. Green fluorescence indicates live bacteria, while red fluorescence signifies dead bacteria. The observations showed a high number of live bacteria on the concrete surface (**Figure 5a**) and a lower count of dead bacteria (**Figure 5d**), suggesting that while concrete can adsorb E. coli, it lacks the capability to deactivate them, as also indicated in **Figure 4c.** On the Concrete/TiO$_2$ surface, there was a significant reduction in live bacteria (**Figure 5c**) and a substantial increase in dead bacteria (**Figure 5e**), demonstrating that the titanium dioxide coating effectively deactivates the attached microbes.

However, prolonged or high concentration microbial exposure might result in an excessive bacterial buildup, potentially impacting the generation and transfer of photoactive species. Notably, on the Concrete/F-TiO$_2$ surface, there were virtually no live bacteria (**Figure 5c**) and fewer dead bacteria (**Figure 5f**), highlighting the benefits of fluorine-modified titanium dioxide in minimizing bacterial attachment and activity, thus significantly reducing microbial pollution on the concrete surface, consistent with findings in **Figure 4d**. Consequently, the Concrete/F-TiO$_2$ developed in this study presents a more promising application potential than Concrete/TiO$_2$.
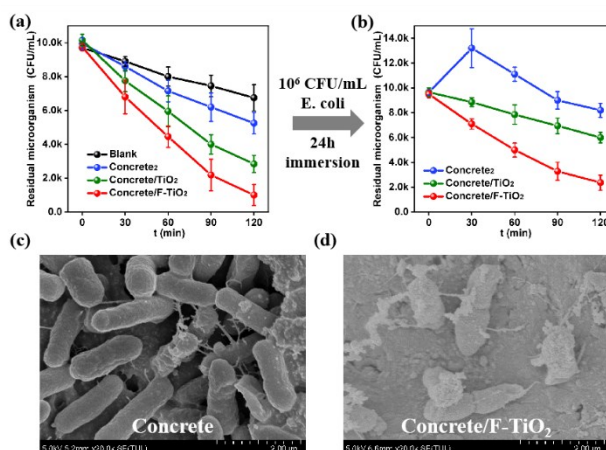

Figure 4. (a) Photocatalytic disinfection effect of Concrete material. (b) Photocatalytic disinfection effect of concrete material after high concentration of microbial contamination, and (c) SEM morphology images of the surface of Concrete sample and (d) the surface of Concrete/F-TiO$_2$ sample.
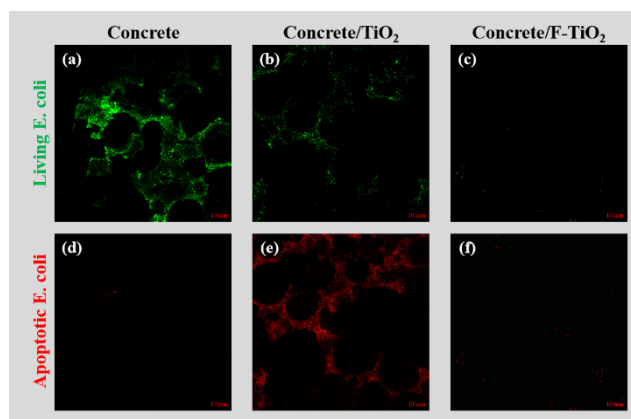

Figure 5. Fluorescence distribution of surviving E. coli on the surface of each sample under laser confocal microscopy: (a) Concrete, (b) Concrete/TiO$_2$, (c) Concrete/F-TiO$_2$. Apoptotic E. coli fluorescence distribution: (d) Concrete, (e) Concrete/TiO$_2$, (f) Concrete/F-TiO$_2$.

3.3. Photocatalytic Disinfection Mechanism of Antimicrobial Concrete

To investigate the superior antibacterial properties of fluorine-modified titanium dioxide coatings, this study examined the changes in characteristics before and after modification, focusing on photoactive species and charge dynamics. We employed DMPO as a trapping agent and electron paramagnetic resonance (EPR) technology to

assess the generation of active species under light exposure. The findings indicated that fluorine-modified F-TiO₂ produced significantly more hydroxyl radicals (**Figure 6a**) and superoxide radicals (**Figure 6b**), effectively inactivating microbes in water and demonstrating strong photocatalytic disinfection capabilities, as shown in Concrete/F-TiO₂ in **Figure 4a**. ZETA potential testing was used to analyze the charge properties of the catalyst surface. It revealed that in neutral aqueous solutions, both the fluorine-modified titanium dioxide and E. coli cell surfaces are negatively charged, reducing bacterial adhesion on the Concrete/F-TiO₂ surface through electrostatic repulsion. In contrast, concrete and titanium dioxide surfaces are positively charged, which hinders the reduction of microbial contamination on surfaces, as observed in **Figures 5c and 5f**. Further exploration of F-TiO₂'s optimal photocatalytic performance involved ultraviolet-visible absorption spectroscopy (UV-vis) and X-ray photoelectron spectroscopy valence band spectra (XPS-VB). The study found a narrowing of the titanium dioxide bandgap from 3.07 eV to 2.98 eV after fluorine modification (**Figure 6d**), enhancing photon absorption and electron-hole pair generation. The valence band spectra indicated valence band tops of 2.66 eV for TiO₂ and 2.87 eV for F-TiO₂ (**Figure 6e**), suggesting a higher valence band top and a lower conduction band position for F-TiO₂, which facilitates electron migration from TiO₂ to F-TiO₂ and reverse hole migration under illumination. The fine spectra of titanium elements showed a shift to lower binding energy in F-TiO₂ (**Figure 6f**), suggesting increased electron cloud density around titanium atoms and confirming electron migration from TiO₂ to F-TiO₂. The introduction of fluorine creates a Type II heterojunction, enhancing the effective separation of electron-hole pairs, providing the material basis for the higher radical generation by F-TiO₂, and explaining the negative charge on the F-TiO₂ surface.
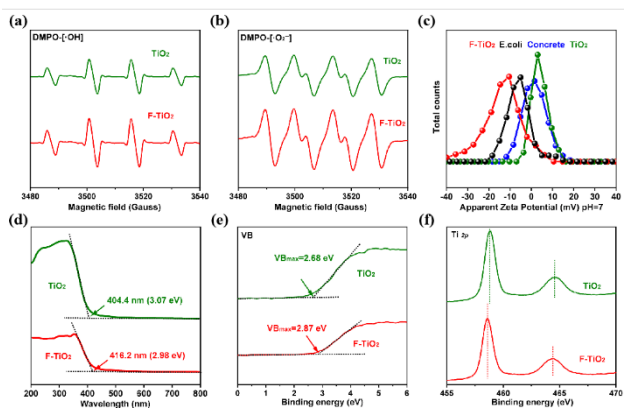

Figure 6. Photo-radical generation of TiO₂ and F-TiO₂: (a) hydroxyl radicals and (b) superoxide radicals. (c) Zeta potential test of E. coli and concrete materials.(d) UV-vis spectra, (e) XPS-VB spectra and (f) XPS-Ti spectra of TiO₂ and F-TiO₂.

In summary, this research developed a photocatalytic antibacterial technology for concrete that minimizes bacterial adhesion via electrostatic repulsion and produces numerous free radicals to deactivate bacteria (refer to **Figure 7**). The operational principle involves the creation of a TiO₂/F-TiO₂ heterostructure within a fluorine-modified titanium dioxide coating. Upon exposure to light, electrons transfer from TiO₂ to F-TiO₂, forming superoxide radicals, while holes transfer from F-TiO₂ to TiO₂, creating hydroxyl radicals, thereby effecting disinfection through this radical mechanism. Furthermore, the fluorine modification is achieved through an impregnation method, resulting in a catalyst coating on Concrete/F-TiO₂ with an external layer of fluorine-containing F-TiO₂ and an internal layer of fluorine-free TiO₂. This configuration imparts additional photoelectrons and negative charges to the surface layer, thus endowing the Concrete/F-TiO₂ with a negatively charged surface that aids in reducing bacterial adhesion via electrostatic repulsion.
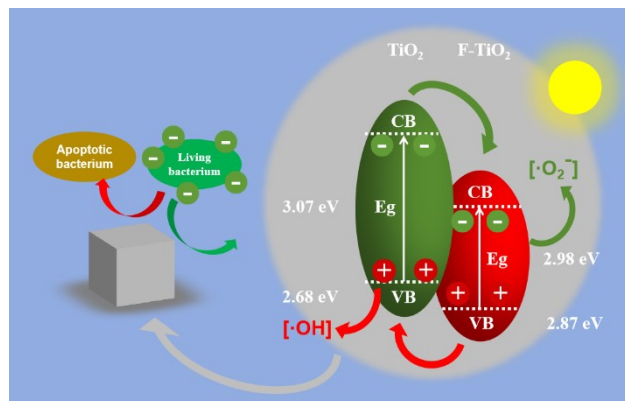

Figure 7. Schematic diagram of photocatalytic antimicrobial mechanism of Concrete/F-TiO₂

4. Conclusion

Overall, this study has successfully developed an effective photocatalytic antibacterial coating technology for concrete and has reached the following conclusions:

1) By employing a method of impregnation, calcination, and etching, we have in-situ constructed a photocatalytic coating on the concrete surface. This method, compared to the traditional approach of applying powder prepared ex-situ, is more suitable for convenient on-site application.

2) With fluorine modification, the titanium dioxide-based photocatalytic coating formed a heterojunction structure, which accelerated the separation of photogenerated electrons and holes, enhancing the generation of photo-induced free radicals and significantly boosting the photocatalytic microbial inactivation capability.

3) The addition of fluorine groups gave the photocatalytic antibacterial coating a negatively charged surface. Due to the electrostatic repulsion of the negatively charged surface against negatively charged bacteria, the coated concrete surface can effectively resist microbial intrusion.

This research provides a reliable method for modifying foamed concrete, ensuring long-term antimicrobial properties of building materials, and has significant reference value for promoting sustainable sponge city construction.

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