

# Photocatalytic Nanomaterials for the Abatement of Microorganisms

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The global spread of pathogenic microorganisms, including bacteria, viruses, and fungi, poses a serious threat to public health and the global economy, as evidenced by the severe and widespread impact of the COVID-19 pandemic. Traditional disinfection methods are commonly used, such as chemical disinfectants or heat treatments, but they often incur high costs, have toxicity issues, and are unable to completely inactivate microorganisms under all environmental conditions. These limitations have contributed to a gradually increasing rate of resistance due to phenotypic adaptation. Additionally, the rising incidence of antibiotic-resistant bacteria has led to the intensification of the search for effective antimicrobial agents [1].

In this context, following the devastating impact of the COVID-19 pandemic, researchers have focused on managing the abatement of SARS-CoV-2 and exploring new alternatives for pathogen removal [2–4]. Within these options, photoactive nanomaterials have attracted considerable research interest due to their small size, which facilitates numerous unique properties. These materials can generate reactive oxygen species (ROS) under irradiation, which have biocidal effects on pathogens without releasing toxic by-products. Nanomaterials are versatile tools that can be applied in various fields, including diagnostics, biomedicine, environmental remediation, and water treatment; therefore, they have sparked significant public interest.

In general, the photocatalytic process, carried out using materials such as titanium dioxide (TiO<sub>2</sub>)-based semiconductors [5–7], is activated by light and relies on the generation of electron–hole pairs upon band gap photoexcitation, which subsequently induce the production of hydroxyl radicals in water. The overall catalytic efficiency of such a system is determined by the competition between the recombination and trapping of charge carriers, as well as between the recombination of trapped carriers and the interfacial charge transfer [8]. Ultimately, the biocidal activity of nanoparticle (NP)-based materials is largely dependent on their photocatalytic performance, which is significantly influenced by several intrinsic factors, including the NP's morphology, size, chemistry, crystalline phase, structure, and precursor, along with potential modifications involving metals, other semiconductors, and organic compounds [9].

This Special Issue, “*Photocatalytic Nanomaterials for Abatement of Microorganisms*”, aims to collect original research papers and reviews regarding new or previously known photocatalytic nanomaterials and their synthesis, characterization, and application in light-driven microbial inactivation (of bacteria, viruses, and fungi). Of the eight articles in this Special Issue, seven papers concern the use of innovative photocatalysts and their applications in the field of antimicrobials, and one paper is a review that highlights the causes of COVID-19 transmission, and consequently provides a roadmap for controlling the spread of the disease.

In Contribution 1, Alebrahim et al. reported on the antiviral performances of thermally sprayed TiO<sub>2</sub> coatings under UVA irradiation, ambient light, and dark conditions against



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human coronavirus, HCoV-229E. Furthermore, to improve the mechanical properties and antiviral activity of these TiO<sub>2</sub> coatings, the authors combined TiO<sub>2</sub> composites with other oxides, such as Cu<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub>, using several different methods (suspension plasma spray, atmospheric plasma spray, and suspension high-velocity oxygen fuel techniques). The thermally sprayed coatings demonstrated antiviral activity that was comparable to or slightly better than that of copper. Indeed, the highest level of antiviral activity observed was approximately 20% to 50% higher than that of a pure copper plate. The antiviral performance of the coatings was influenced by a combination of factors, including the photocatalytic activity of TiO<sub>2</sub>, the direct contact of Cu<sub>2</sub>O components, and the surface properties of the coatings, such as porosity and roughness.

A preliminary study by Al Hallak et al. (Contribution 2) investigated and compared the efficiencies of pure photocatalysts (TiO<sub>2</sub>, ZnO, Au/ZnO), without any interfering material (such as organic binders, surfactants, etc.), in preventing microbial contamination and inhibiting the growth of microorganisms such as *Escherichia coli* (*E. coli*) and *Aspergillus niger* (*A. niger*) on surfaces of indoor building materials. The results highlighted the bactericidal activities of TiO<sub>2</sub>, ZnO, and Au/ZnO against *E. coli* and revealed the variation in their efficiencies based on factors such as concentration, contact duration, light/dark conditions, and especially the type of microorganism. Notably, spores of *A. niger* were more resistant than *E. coli* cells. Furthermore, ZnO nanoparticles exhibited stronger biocide activity than undoped ZnO NPs, supporting the use of Au doped ZnO in paints, coatings, and other applications under indoor light conditions.

Selishchev et al. (Contribution 4) focused their research on TiO<sub>2</sub> nanoparticles deposited via the impregnation method onto cotton-rich fabrics and investigated their photoactive properties as self-cleaning textiles, both with and without UV radiation. TiO<sub>2</sub>-functionalized cotton fabric was tested against influenza virus A/PR/8/34 (H1N1). Virus inactivation and degradation were tested using 50% tissue culture infective dose (TCID<sub>50</sub>) and polymer chain reaction (PCR) techniques, respectively. The TCID<sub>50</sub> method confirmed the inactivation of the influenza virus when the contaminated photoactive fabric was irradiated with UV light in the A region. Long-term irradiation (for 3–6 h) led to the destruction of all virion structures, including the RNA molecules.

In addition to its excellent potential for decontaminating surfaces, TiO<sub>2</sub>-based materials were further investigated in Contribution 5 by Uppal et al. The authors demonstrated the antiviral potential of the MACOMA™ photocatalytic disinfection system in the presence of the HCoV-OC43 strain (a human coronavirus belonging to the family of *Betacoronaviruses*, which also includes SARS-CoV-2), under UVA light conditions. This system provides a rapid, eco-friendly, and reliable disinfection method that enhances virus inactivation on surfaces. The UVA–TiO<sub>2</sub> coupled disinfection system completely reduced the virus expression to background levels within 60 min under experimental conditions, where virus droplets were positioned approximately 1.2 feet from the light source.

Furthermore, in Contribution 6, Kisand et al. presented an interesting study on SaniTise™ glass, a product marketed by Pilkington. In particular, the photocatalytic and antibacterial properties of SaniTise™ under indoor-like conditions were investigated and compared to the commercially advertised photocatalytic BIOCLEAR® (Saint Gobain) and non-photocatalytic PLANICLEAR® (Saint Gobain) glass surfaces. Antibacterial assays were carried out against *E. coli* and *Staphylococcus aureus* (*S. aureus*) under testing conditions that resembled real-life glass usage. The authors employed antibacterial tests in a liquid environment, as suggested in the ISO 27447 protocol (ISO 27447; Fine Ceramics (Advanced Ceramics, Advanced Technical Ceramics)—Test Method for Antibacterial Activity of Semiconducting Photocatalytic Materials. International Organization for Standardization: Geneva, Switzerland, 2019.), and a “dry droplet method”. BIOCLEAR® had no

effect on *E. coli* after 4 h under UVA conditions in a liquid environment; however, after following the dry droplet method at a 90% relative humidity (RH), *S. aureus* exhibited almost complete inhibition on the BIOCLEAR<sup>®</sup> surface. Furthermore, the dry droplet method combined with  $RH \leq 50\%$  also resulted in complete bacterial inactivation on the control surface of PLANICLEAR<sup>®</sup>.

Suner et al. (Contribution 3) and Widyastuti et al. (Contribution 7) investigated the antibacterial activity of non-TiO<sub>2</sub> nanomaterials, namely nitrogen-doped arginine carbon dots (Arg CDs) and Ti<sub>3</sub>O<sub>x</sub> thin film, respectively.

In Contribution 3, Suner et al. prepared Arg CDs using a microwave-assisted method, aiming to enhance their antibacterial properties by modifying them with different amine sources, including ethyleneimine (EDA), pentaethylenhexamine (PEHA), and polyethyleneimine (PEI). The Arg CDs' antibacterial properties, against both Gram-negative (*E. coli*) and Gram-positive bacteria (*S. aureus*), were determined using a microtiter broth dilution method under UV light exposure. The researchers also determined the minimum inhibitory concentration (MIC) values. The results showed that photoexcited EDA-modified Arg CDs at a concentration of 5 mg/mL were able to inhibit approximately  $49 \pm 7\%$  of pathogenic bacteria, such as *E. coli*, after 5 min of UV light exposure. Additionally, the biocompatibility of both bare and modified Arg CDs was evaluated through blood compatibility tests on L929 fibroblast cells, including hemolysis, blood clotting assays, and cytotoxicity analysis.

Widyastuti et al. (Contribution 7) used a pure Ti target in an Ar/O<sub>2</sub> gas mixture to synthesize Ti<sub>3</sub>O<sub>x</sub> thin film on a glass substrate, by using reactive high-power impulse magnetron sputtering (HiPIMS) under different sputtering powers (2 and 2.5 kW) and without post-thermal annealing. The study investigated how different sputtering powers influenced various properties of the thin films, including their structure, morphology, chemical composition, optical characteristics, and photocatalytic and antibacterial properties. The Ti<sub>3</sub>O<sub>x</sub> films deposited at 2.5 kW showed good photocatalytic activity under UV light irradiation, with a higher MB dye degradation rate than TiO<sub>2</sub> thin films. Moreover, the antibacterial analysis revealed that Ti<sub>3</sub>O<sub>x</sub> films exhibited a high inhibition rate against both *E. coli* and *S. aureus*, highlighting the potential of Ti<sub>3</sub>O<sub>x</sub> films for photocatalytic and antibacterial applications.

To conclude this Special Issue, Mohite et al. (Contribution 8) presented a review on the causes of the global spread of COVID-19 and the reasons for its persistent presence over time compared to other diseases. The authors proposed a roadmap for controlling the spread of the virus. It has previously been well established that the transmission of the SARS-CoV-2 virus primarily occurs through contact with contaminated surfaces, such as doorknobs, packaging, and handrails. In addition, COVID-19's ability to survive for longer periods on high-touch surfaces has also been an important contributor to its spread. The focus of the review was to suggest an innovative approach to coating surfaces in public places exposed to visible light using photocatalytic nanocomposite paints, which are self-sterilizing against the spread of communicable diseases. Therefore, the review describes formulations of different nanoparticle-engineered photocatalytic paints, demonstrating their effectiveness in destroying pathogens under visible light exposure, and includes field trials to showcase their practical application.

Undoubtedly, the timing of the opening of this Special Issue and its overlap with the tail end of the COVID-19 pandemic has led researchers to find alternative ways to combat the spread of pathogenic microorganisms for the promotion of public health. In addition, some authors have highlighted how the current methods used to test levels of antimicrobial activity are often not relevant for the contexts in which photocatalytic nanomaterials are used. This Special Issue has allowed us to answer the following questions: *Does the*

photocatalytic nanomaterial have a broad-spectrum action on different types of microorganisms (bacteria, viruses, and fungi)? Can nanomaterials really be used by studying their antimicrobial activity through an application under real condition? All the contributions to this Special Issue have aided in answering the first question, and Contributions 4, 5, and 6 have answered the second question.

We recognize that many other questions still need to be answered, such as whether these nanomaterials are harmful to humans. Only Contribution 3 by Suner et al. answers this question, as they studied the cytotoxic effects of a specific material in their paper. Overall, however, this Special Issue allows us to affirm that a multi-technique approach helps us to understand the mechanisms of action of photocatalytic nanomaterials.

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