

A Comprehensive Review on the Structure and Visible-Light-Driven Antimicrobial Properties of $\text{WO}_3/\text{TiO}_2/\text{CuO}$ Nanocomposites

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Abstract—The $\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites exhibit potent and broad-spectrum antimicrobial activity under visible light, primarily due to synergistic mechanism involving the generating of reactive oxygen species (ROS) and the release of Cu^{2+} ions. Under light exposure, the heterojunction structure promotes efficient interaction at the nanoscale, leading to the production of ROS such as hydroxyl radicals ($\cdot\text{OH}$) and super oxide anions ($\cdot\text{O}_2^-$). These reactive species damage microbial cell membranes, protein, and nucleic acids, inducing oxidation stress that ultimately result in microbial cell death. Additionally, the sustained release of Cu^{2+} ions enhances the antimicrobial efficacy by disrupting cellular processes and increasing membrane permeability. Simultaneously Cu^{2+} ions interact with microbial cells by disrupting membrane integrity, denaturing proteins and interfering with DNA replication and enzymatic pathways. This dual mode mechanism effectively inactivation both Gram-negative and Gram-positive bacterial (Eg: *E.coli*, *S. aureus*) as well as fungal strains (Eg: *Candida albicans*, *Aspergillus niger*) demonstrating the nanocomposites potential as a powerful antimicrobial agent for diverse application, including disinfection, biofilm control and environmental purification.

Index Terms— $\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites; antimicrobial activity; reactive oxygen species; Cu^{2+} ions; membrane disruption; bacterial and fungal strains; visible light.

1. INTRODUCTION

$\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites have garnered significant attention in recent years as highly efficient multifunctional materials, primarily due to the synergistic integration of their advanced antimicrobial properties. Among the constituent

components, titanium dioxide (TiO_2) stands out as widely explored n-type semiconductor, known for its strong oxidative capability under ultraviolet (UV) light irradiation. This property enables TiO_2 to effectively inactivate a broad spectrum of bacterial and fungal pathogens through the production of reactive oxygen species (ROS), such as hydroxyl radicals ($\cdot\text{OH}$) and super oxide anions ($\cdot\text{O}_2^-$) which damage vital cellular structural including membranes, proteins, and DNA. However, the antimicrobial effect of pure TiO_2 is limited visible light due to its wide band gap (3.2 eV for rutile), which hinder its responsiveness to common lighting condition [1].

To enhance performance under ambient or visible light, tungsten trioxide (WO_3) has been incorporated into the TiO_2 matrix. With a narrower band gap (2.8 eV), WO_3 enables broader light absorption and adds significant structural and oxidation stability, especially in moist chemically reactive environments [2]. It contributes to the formation of heterojunction that facilities efficient charge carrier dynamics, allowing for prolonged ROS lifetimes which enhances the material sterilizing effectiveness.

The integration of copper oxide (CuO) introduces a highly valuable antimicrobial dimension to the nanocomposites. As a p-type semiconductor with a narrow bandgap (1.2-1.7 eV), CuO enhances performance not just under visible light, but more importantly, through its intrinsic biological properties [3]. CuO continuously release Cu^{+} ions which have been shown to disrupt microbial membranes, increase cellular permeability and lead to cytoplasmic leakage. These ions also interface with key metabolic enzymes and protein, leading to irreversible oxidative damage and cellular function. The antimicrobial activity of

CuO is effective even in the absence of light making it a critical component for application in low- light or dark environmental [4]. Additionally, Cu²⁺ ions can bind to intercellular proteins and enzymes, disturbing their normal function and causing oxidation stress through intercellular ROS accumulation. This dual - mode antimicrobial mechanism highly effective against wide range of pathogenic microorganisms, including Gram-positive and Gram- negative bacteria as well as various fungal strains.

The strategic integration of these semiconducting oxides results in a ternary hetero structure that leverages the unique properties of each component to achieve superior functionality. The heterojunction interfaces formed between TiO₂, WO₃, and CuO facilities directional charge flow and z- scheme or step- scheme charge transfer pathways, depending on the alignment of their conduction and valence bands. This optimized charge separation significantly minimizes electron - holes recombination losses, thereby enhancing the photocatalytic generation of ROS.

Collectively, these reactive oxygen species- particularly hydroxyl radical and super oxide ions- are known to attacks the lipids membranes, proteins, and DNA Of microbes, ultimately leading to cellular dysfunction and death [5,6] As result WO₃/TiO₂/CuO nanocomposites are emerging as promising candidates for use in antimicrobial application, where both environment and biological decontamination are critical for antimicrobial activity. The review aims to comprehensively explore the synthesis strategies, structural and optical characteristics and antimicrobial mechanism of WO₃/TiO₂/CuO nanocomposites with an emphasis on their effectiveness under- light irradiation.

2. CHARACTERIZATION TECHNIQUES

2.1 X-ray Diffraction (XRD)

X-Ray Diffraction (XRD) analysis is fundamental technique used to investigate the crystalline structure, phase composition, and crystallite size of nanomaterials. For the WO₃/TiO₂/CuO nanocomposites, XRD patterns typically exhibit distinct peaks corresponding to the rutile TiO₂, notably at 2θ value of 27.3°, which is assigned to the (101) reflection plane. Additional peaks are observed

for monoclinic WO₃ at 2θ values around 23.1°, 23.6° and 24.4° indicating the successful incorporation of tungsten oxide into the composite's matrix. Peaks around 35.5° and 40.7° further confirm the presence of monoclinic phase CuO, attributes to its (002) and (111) planes respectively [7]. The retention of these well- defined crystalline phases within the composites without the formation of undesirable secondary phases or peaks shift, demonstrates that the co- synthesis process effectively preserves the structural identity of each component. This is critical because maintaining the individual crystallinity features of TiO₂, WO₃, and CuO allow for synergistic interactions especially in charge transport and antimicrobial performances, which are pivotal for the nanocomposites multi functionality [8-9].

2.2 Ultraviolet (UV-Vis) Spectroscopy

Ultraviolet - visible spectroscopy (UV-Vis) is used to evaluate the optical properties and bang gap energies of semiconductor - based nanocomposites. In the case of WO₃/TiO₂/CuO, the spectra, reveals a red- shift in the absorption edge when compared to pristine TiO₂ whose absorption is largely confined to the ultraviolet region due to its wide band gap of 3.2 eV. The addition of WO₃(band gap 2.6eV) and CuO (band gap 1.2-1.7 eV) enable the nanocomposites to absorb light across a broader spectrum, particularly in the visible range between 400 and 700 nm [10]. This extended absorption range is vital for application under solar irradiation or indoor lighting condition as it enhances light utilization. The broader and intensified absorption not only boosts the material potential for generating reactive species but also increase the effectiveness activity under ambient light exposure [11].

2.2 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is employed to identify the chemical bonds, surface functionalities, and molecular interactions within the nanocomposites. In the FTIR spectrum of WO₃/TiO₂/CuO, characteristic absorption bands are observed that corresponds to specific metal-oxygen bonds. For instance, strong stretching vibrations in the region of 500-700 cm⁻¹ are indicative of Ti-O-Ti linkages in TiO₂. A prominent peak around 800 cm⁻¹ can be attributed to W-O bonds within the WO₃ structure, while Cu-O stretching vibrations typically

appear near 600 cm^{-1} [12]. Additionally, broader bands around 3400 cm^{-1} and 1600 cm^{-1} are associated with O-H stretching and H-O-H bending modes of surface-absorbed water molecules. These hydroxyl groups are particularly important, as they actively participate in the antimicrobial reaction by forming hydroxyl radicals ($\cdot\text{OH}$) upon light irradiation, which contribute significantly to microbial inactivation [13]. The presence of these functional groups confirms the nanocomposites potential for ROS generation and subsequent antimicrobial activity.

2.3 High-Resolution Scanning Electron Microscopy (HRSEM)

High-Resolution Scanning Electron Microscopy (HRSEM) provides detailed morphological and topographical insights into the surface architecture of the nanocomposites. HRSEM images typically reveal that the TiO_2 particles form a relatively uniform and spherical matrix, which serves as a scaffold for the integration of smaller CuO and WO_3 nanoparticles. These secondary particles are finely dispersed on the TiO_2 surface, creating a heterogeneous yet homogeneously distributed ternary structure [14]. The micrographs often show a porous and interconnected network, which is beneficial for maximizing surface area and enhancing the number of reactive and antimicrobial sites available on the material. This kind of morphology is essential for effective interactions with microbial cells, as it promotes better pathology and proximity, thereby increasing the probability of ROS contact and Cu^{2+} ion uptake by microbes [15]. Moreover, the

nanoscale roughness and porosity of the composite enhance its ability to trap and destroy pathogens through both chemical and physical mechanism, underscoring the materials superior antimicrobial potential [16].

4.5 Antimicrobial activity

The antimicrobial mechanism of the $\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites is driven by a visible-light activated bacterial and fungal process. In Figure 1, under light exposure electrons (e^-) in the nanocomposites are excited from the valence band to the conduction band leaving behind holes (h^+). These photogenerated charge carriers trigger redox reaction, wherein electrons reduce molecular oxygen (O_2) to produce superoxide radicals ($\text{O}_2\cdot$) while holes oxidize water (H_2O) to generate hydroxyl radicals ($\cdot\text{OH}$) [21]. These reactive oxygen species (ROS) aggressively target microbial cells by damaging lipids membrane, denaturing essential proteins and fragmenting nucleic acids leading to cellular dysfunction and death. Concurrently, Cu^{2+} ions released from CuO further enhance antimicrobial efficacy by penetrating microbial cells binding to sulfhydryl (-SH) groups in enzymes and interacting with DNA thereby inhibiting replication, enzyme function and respiration [29]. This synergistic mechanism-combination ROS induced oxidative stress with Cu^{2+} mediated biochemical disruption ensures highly effective antimicrobial activity even against biofilms-forming and drug-resistance bacterial strains as well as resilient spore forming fungal pathogens [30,31,32].

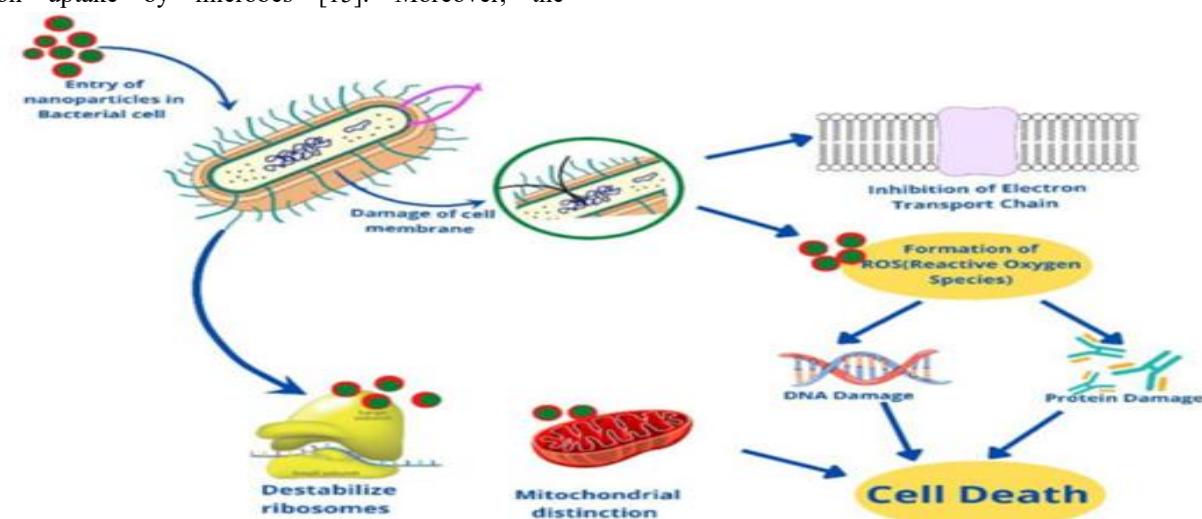


Figure 1: Schematic illustration of the antibacterial mechanism of nanocomposites

3. ANTIBACTERIAL ASSAY

This article evaluates the light- activated antibacterial potential of $\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites, motivated by the growing challenge of antimicrobial resistance and my interest in nanomaterials.

The $\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposite demonstrates broad-spectrum antibacterial activity against both Gram- negative and Gram- positive bacterial strains under light irradiation, attributed to the synergistic action of reactive oxygen species (ROS) and copper ion release.

As Figure 2, nanoparticles exert multiple antimicrobial effect, including membrane disruption inhibition of protein and enzyme activity, interference with DNA and RNA processes and the suppression of biofilm formation. The ROS generated upon light exposure (e.g. $\cdot\text{OH}$, $\text{O}_2\cdot$, H_2O_2) in combination with Cu^{2+} ions, amplify this mechanism, making $\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites potent antibacterial agents.

3.1 *Escherichia coli* (E. coli)

A Gram -negative bacterium characterized by its protective outer membrane and intrinsic resistance to many antibiotics, its efficiently inactivated by the nanocomposites. The reactive oxygen species (ROS) generated under light exposure, along with Cu^{2+} ions released from CuO , synergistic ally damage the bacterial cell membrane, disrupt intra cellular proteins, and fragment DNA, resulting in cell death [16].

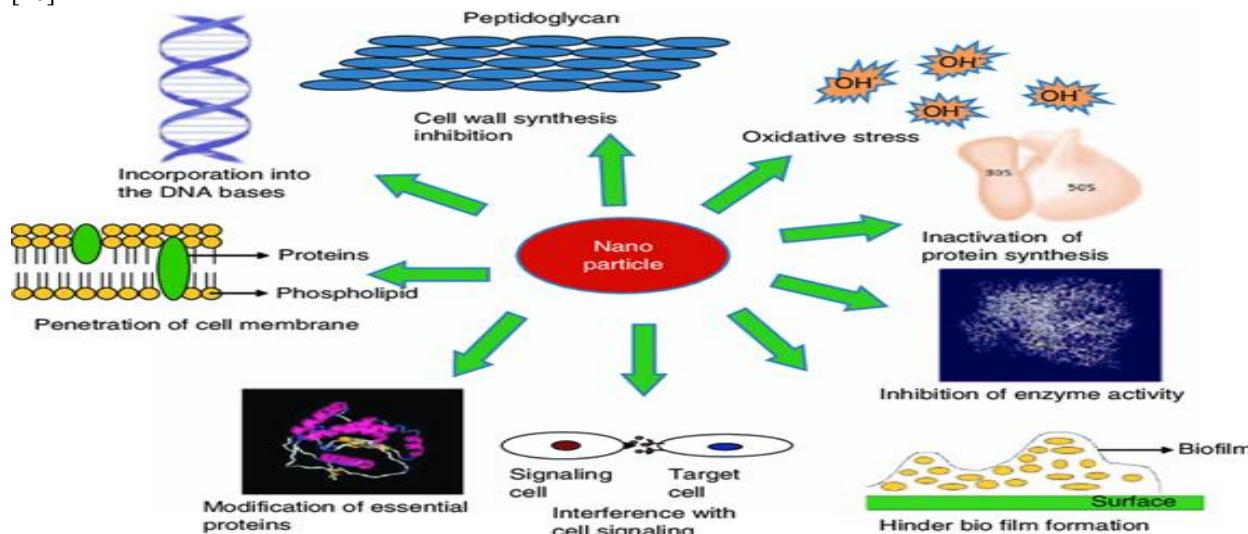


Figure 2: Antibacterial activity for nanoparticles

3.2 *Staphylococcus aureus*

A gram-positive bacterium with a thick peptidoglycan cell wall, susceptible to the oxidative stress generated by the nanocomposite. The ROS disrupt metabolic pathways and cellular structures, leading to inhibited growth and eventual bacterial inactivation [18].

3.3 *Pseudomonas aeruginosa*

Pseudomonas aeruginosa known for its robust multi-drug resistance and biofilm forming capabilities, is effectively neutralized through the dual action of ROS and Cu^{2+} ions. ROS penetrate and dismantle the extracellular polymeric substances (EPS) of the biofilm, while Cu^{2+} interferes with bacterial efflux pump systems and disrupts intracellular homeostasis [19].

3.4 *Salmonella typhi*

A major food-borne pathogen, is also susceptible to the nanocomposite treatment. Upon exposure, oxidative stress leads to membrane lipid peroxidation, intercellular leakage and completed cellular destruction [20].

3.4 *Bacillus Subtilis*

A spore- forming Gram-positive bacterium known for its high resistance to environmental stress, shows measurable susceptibility to prolonged ROS exposure. Although more resilient than non-sporulating strain *B.subtilis* is eventually deactivated due to cumulative oxidative damage [21].

4. ANTIFUNGAL ASSAY

Although antifungal investigation involving $\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites are still in their early stages growing experimental evidence underscore their remarkable potential in suppressing the growth of various pathogens fungi. Comparative studies using structurally related system such as $\text{TiO}_2/\text{CU}_2(\text{OH})_2\text{CO}_3$ have demonstrated robust antifungal activity under visible light, particularly against *Fusarium graminearum* a widespread and economically significant plant pathogen.

The underlying mechanism of action involves the photo activation of the nanocomposites which leads to the production of ROS such as hydroxyl radicals ($\cdot\text{OH}$) super oxide anions ($\text{O}_2\cdot\cdot$) and hydrogen peroxide (H_2O_2). These ROS molecules aggressively attack the fungal cell wall, compromising its structural integrity, followed by spore membrane rupture and leakage of cytoplasmic contents ultimately resulting in fungal cell death [22, 23]. As illustrated in Figure 3, ROS- mediated oxidative stress and the action of Cu^{2+} ions contribute to membrane disruption, leakage of cell components, and compete fungal cell inactivation. This inclusion of CuO adds an additionally antifungal pathways through the release of copper ions, which bind to proteins and inhibit enzymatic function essential for fungal survival, thereby synergistically enhancing the antifungal efficacy of the nanocomposites systems.[24].

4.1 *Candida albicans*

A clinically important opportunistic yeast responsible for wide range of mucous and system infection in humans has been shown to be highly vulnerable to the action of the $\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites,. When exposed to visible light, the antimicrobial activity to generated ROS compromises the yeast's plasma membrane, leading to increased permeability and structural breakdown. Simultaneously Cu^{2+} ions infiltrate the cell, targeting mitochondria and

disrupting the respiratory chain, which result in reduced ATP production, energy starvation and eventual cell lysis [25].

4.2 *Aspergillus niger*

Aspergillus niger a common filamental fungal well-known for its robust spore forming capacity and resistance to environmental stressors is also susceptible to the nanocomposites under visible-light activation. The oxidative environment generated by ROS induce structural and functional damage to the fungal spores, rendering the, non-visible and incapable of germination. The high oxidative stress disrupts key bio molecular structures such as protein, lipids, and nucleic acids, leading to irreversible loss of cellular function and death [26].

4.3 *Fusarium graminearum*

A destructive plant pathogen associated with grains crop contamination and mycotoxin production shows marked sensitivity to the composite. Upon treatment with the nanocomposites ROS- induced degradation of the fungal cell wall polysaccharides and plasma membrane lipids occurs. This oxidative assault is further intensified by Cu^{2+} ions which enter the cytoplasm and denature structural and metabolic proteins thereby accelerating the cell breakdown and functional collapse [27].

4.4 *Penicillium chrysogenum*

A Fungal commonly implicated in food spoilage and allergic reaction also demonstrate pronounced sensitivity to the nanocomposites. Upon visible- light exposure the dual action of oxidative and ionic stress inhibits its ability to form spores, a critical aspect of its reproductive cycle and environmental persistence. The ROS degrade membrane bound organelles and nucleic acids, while Cu^{2+} ions interfere with enzymatic system involved in spore maturation, leading to marked reduction in fungal viability and propagation [28].

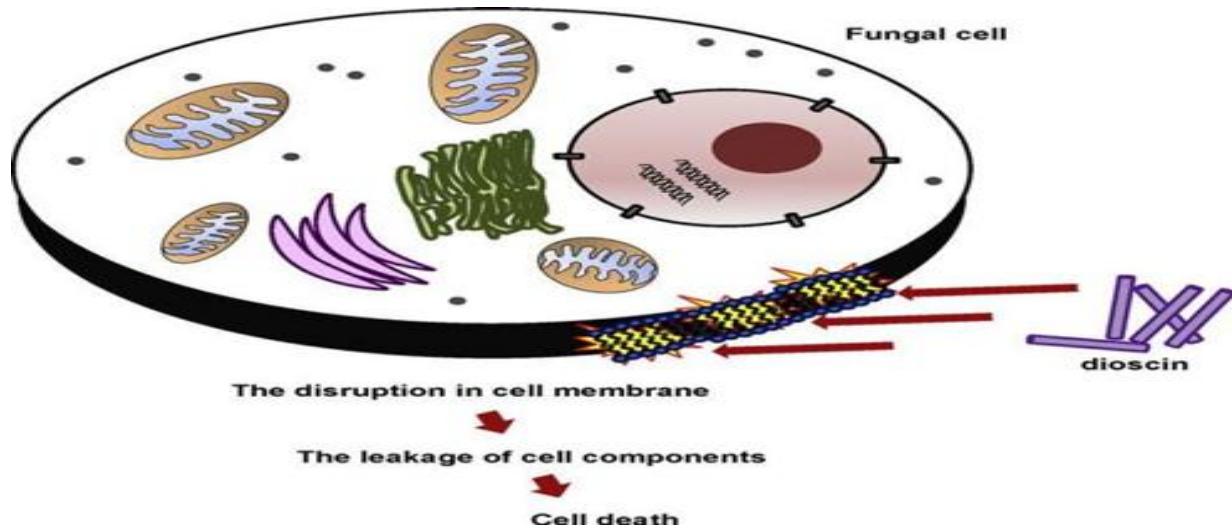


Figure 3: Schematic representation of the antifungal activity

5. CONCLUSION

$\text{WO}_3/\text{TiO}_2/\text{CuO}$ nanocomposites exhibit strong antimicrobial activity under visible light due to their efficient generation of reactive oxygen species (ROS) and release of Cu^{2+} ions. These features enable effective inactivation of both Gram- negative (*E.coli*, *P. aeruginosa*, *S. typhi*) and Gram- positive (*S.aureus*, *B.subtilis*) bacteria through membrane disruption DNA damage and enzymatic inhibition. Similarly fungal pathogens such as *candida Albicans*, *Aspergillus niger*, *Fusarium grammarian* and *penicillium chrysogenum* are neutralized via oxidative damage and interference with mitochondrial function. The composites structural integrity visible light activation and dual action antimicrobial mechanism make it a promising material for broad- spectrum microbial control.

REFERENCES

- [1] Fujishima, A., Rao, T. N., & Tryk, D. A. (2000). Titanium dioxide photocatalysis. *Nature*, 37(7), 10–15.
- [2] Zhang, J., Xu, Q., Feng, Z., Li, M., & Li, C. (2008). Importance of the relationship between surface phases and photocatalytic activity of TiO_2 . *Journal of Physical Chemistry C*, 112(26), 10325–10334.
- [3] Azizi, R., Sayadi, M. H., & Shekari, H. (2021). Synthesis and photocatalytic degradation performance of WO_3/TiO_2 nanocomposite for dye removal under visible light. *Optik*, 241, 166981.
- [4] Warsi, A.-Z., Sultan, M., Rehman, S., et al. (2022). Green synthesis and characterization of TiO_2 -based nanomaterials with enhanced photocatalytic and antimicrobial activity. *Nanomaterials*, 12(4), 713.
- [5] Barakat, M. A., Schaeffer, H., & Hayes, G. (2010). Photocatalytic degradation of methylene blue using Fe-doped TiO_2 nanoparticles. *Chemosphere*, 78(5), 567–571.
- [6] Gnanaprakasam, A., Sivakumar, V. M., Thirumurugan, M. (2021). A review on hybrid nanocomposite photocatalysts for environmental applications. *Environmental Chemistry Letters*, 19(5), 4135–4162.
- [7] Gao, Y., Ma, D., Li, Y., et al. (2017). Hydrothermal synthesis and enhanced visible-light-driven photocatalytic activity of WO_3/TiO_2 heterostructures. *Ceramics International*, 43(1), 633–640.
- [8] Azizi, R., Sayadi, M. H., & Shekari, H. (2021). Structural and photocatalytic properties of WO_3/TiO_2 heterostructures synthesized via co-precipitation. *Journal of Materials Science: Materials in Electronics*, 32, 11346–11356.
- [9] Xu, J., Han, Y., & Liu, H. (2022). Synergistic photocatalytic and antibacterial performance of ternary $\text{TiO}_2/\text{WO}_3/\text{CuO}$ heterojunction nanocomposites. *Materials Chemistry and Physics*, 280, 125754.

[10] Wang, Y., Wang, L., Peng, S., & Zhang, H. (2018). Visible-light-driven photocatalysis and enhanced antibacterial activity of CuO–WO₃–TiO₂ ternary nanocomposites. *Ceramics International*, 44(5), 5275–5282.

[11] Yang, X., Zhao, F., Shi, W., et al. (2020). Fabrication of CuO/TiO₂ nanocomposite with enhanced photocatalytic activity. *Materials Science in Semiconductor Processing*, 114, 105086.

[12] Sakar, M., Hassan, M. M., & Sharma, A. (2022). Structural, optical and antimicrobial studies of CuO-TiO₂ nanocomposites. *Materials Chemistry and Physics*, 285, 126102.

[13] Zhao, W., Ma, W., Chen, C., Zhao, J., & Shuai, Z. (2009). Efficient degradation of toxic organic pollutants with Ni₂O₃/TiO₂ under visible irradiation. *Journal of Hazardous Materials*, 170(2–3), 729–734.

[14] Bai, Y., Mora-Sero, I., De Angelis, F., Bisquert, J., & Wang, P. (2016). Titanium dioxide nanomaterials for photovoltaic and photocatalytic applications. *Applied Catalysis B: Environmental*, 200, 558–565.

[15] Patil, S. S., Jadhav, V., & Salunkhe, R. R. (2022). Antimicrobial photocatalytic nanomaterials for water disinfection. *Materials Today Communications*, 30, 103022.

[16] Tang, W., Zhang, H., Zhang, Y., & Zhang, X. (2015). Enhanced visible light photocatalytic activity of CuO/TiO₂ nanocomposites. *Applied Surface Science*, 347, 1–7.

[17] Nguyen, V. H., Nguyen, L. T., Nguyen, T. M., et al. (2022). Recent advances in heterojunction photocatalysts for solar water purification. *Catalysts*, 8(9), 352.

[18] He, Y., Duan, X., Chen, S., et al. (2023). Engineering visible-light-active WO₃-based heterojunctions for environmental remediation. *ACS Applied Materials & Interfaces*, 15(2), 2217–2227.

[19] Tamboli, D. P., & Lee, D. S. (2013). Mechanistic antimicrobial approach of inorganic metal oxide nanoparticles. *Colloids and Surfaces B: Biointerfaces*, 102, 221–226.

[20] Padmavathy, N., & Vijayaraghavan, R. (2008). Enhanced bioactivity of ZnO nanoparticles—an antimicrobial study. *Science and Technology of Advanced Materials*, 9(3), 035004.

[21] Damm, C., Münstedt, H., & Rösch, A. (2006). The antimicrobial efficacy of polyamide 6/silver-nano- and microcomposites. *International Journal of Antimicrobial Agents*, 26(6), 586–590.

[22] Li, Q., Mahendra, S., Lyon, D. Y., et al. (2014). Antimicrobial nanomaterials for water disinfection and microbial control. *RSC Advances*, 4(101), 58160–58165.

[23] Siddiqi, K. S., Husen, A., & Rao, R. A. K. (2018). A review on biosynthesis of silver nanoparticles and their biocidal properties. *Journal of Nanobiotechnology*, 16, 14.

[24] Hajipour, M. J., Fromm, K. M., Ashkarraan, A. A., et al. (2012). Antibacterial properties of nanoparticles. *Trends in Biotechnology*, 30(10), 499–511.

[25] Hu, H., Liu, Z., & Randrianantoandro, N. (2019). Antifungal activity of copper-based nanocomposites against *Candida albicans*. *International Journal of Nanomedicine*, 14, 6277–6290.

[26] Santos, D. M., Santos, J. L., & Costa, M. C. (2019). Copper oxide nanostructures as antimicrobial agents: Effect against *Aspergillus niger*. *Science of the Total Environment*, 650, 2036–2046.

[27] Wani, T. A., Alhazmi, H. A., & Ahmad, A. (2020). Green synthesized CuO nanoparticles for control of fungal plant pathogens. *Journal of Environmental Chemical Engineering*, 8(1), 103558.

[28] Guo, M., Liu, Q., Li, C., et al. (2017). Synthesis and antifungal activity of metal oxide nanocomposites against food spoilage molds. *Materials Science and Engineering: C*, 74, 19–25.

[29] Zhang, Y., Wu, X., & Liu, Y. (2013). Reactive oxygen species induced antifungal activity of silver nanoparticles against *Penicillium chrysogenum*. *Journal of Biomedical Nanotechnology*, 9(7), 1126–1135.

[30] Wang, Y., Tang, L., Li, J., et al. (2020). Multifunctional antimicrobial photocatalytic nanocomposites for sterilization under visible light. *Journal of Hazardous Materials*, 393, 122466.

[31] Li, X., Xu, H., Chen, Z., et al. (2017). Synergistic antibacterial effects of mixed metal oxide nanoparticles. *Chemosphere*, 173, 689–698.

[32] Singh, J., Dutta, T., Kim, K. H., et al. (2018).

Multifunctional metal oxide-based nanocomposites for microbial control. International Journal of Nanomedicine, 13, 7587–7600.