UNIVERSITAT
JAUME I

INORGANIC SEMICONDUCTORS AS BIOCIDAL MATERIALS

Chemistry Degree Final Project

-AUTHOR: VICENTE RAMÓN SALVADOR PAULO
-TUTOR: JUAN MANUEL ANDRES BORT
-DATE: 09/24/2021

Table of contents

Abstract

A class of material that has great interest is the inorganic semiconductors that are defined as inorganic solids capable of changing their conductivity, passing from an insulator to a conductor. Inorganic semiconductors figure prominently in many current technologies, and they will play an important role in enabling a host of future applications. In this context, metal oxides as semiconductors are an important area of research because almost all contemporary electronic technologies involve the use of these materials. They have attracted huge attention due to their unique material properties and their practical applications in chemistry, physics, materials science, biology, and medicine.

This TFG addresses recent investigations performed on different metal oxide semiconductors to find a relationship between the material properties (photocatalytic and biocide activities). In particular, the most representative metal oxides as well as metal oxides composed of Ag have been presented as photocatalytic and biocide-based materials. An understanding of the corresponding mechanisms is obtained based on the presence of reactive oxygen species (ROS). ROS are the significant players, generated from the electron transfer process involving O_2 and the bond making/breaking processes associated to H_2O, in the development and function of photocatalytic and biocide materials. As case example the representative ZnO metal oxide has been selected.

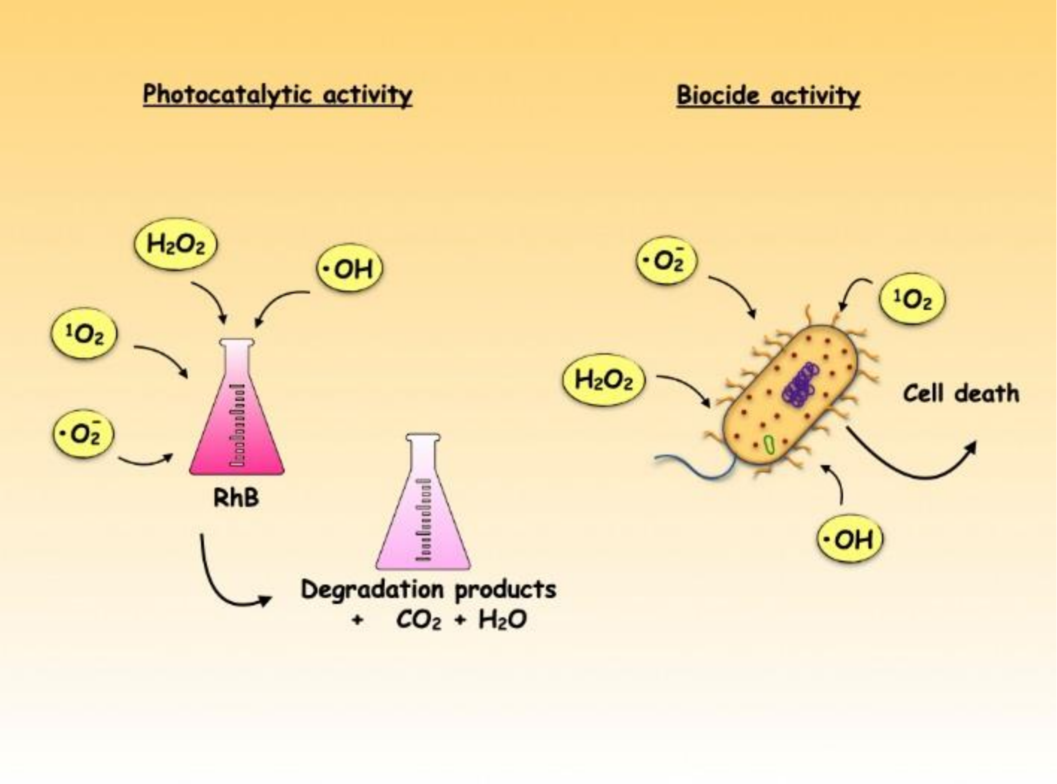


Figure 1. A schematic representation of how inorganic semiconductors produce ROS, which are responsible for the degradation process of RhB (photocatalytic activity) and the death of the cell membrane (biocide activity).

1. Introduction

Today, environmental pollution and public health are one of the most important issues for our human beings. Many industrial activities such as the textile, pulp, dyes and bleaching industries introduce a wide variety of persistent organic pollutants into natural waters if lack of proper treatment, and thus destroying the environmental sustainability and also causing high toxicity and damaging to human beings and other creatures in the ecosystem. Photocatalysis has been recognized as useful owing to the prominent functions of environmental cleaning such as water purification [1] and it is a promising advanced oxidation processes are often used in the degradation of organic pollutants due to their high efficiency, simplicity, good reproducibility, and easy handling [2].

The semiconductor photocatalysts are used for several decades in the past, called green technology, having received great attention, and shows an excellent ability for degrading contaminant by utilizing sunlight without causing any pollution. Metal oxides can act as semiconductors and from the perspective of photochemistry, it is clear that the role of photocatalysis is to trigger or accelerate oxidation-reduction reactions in the presence of a semiconductor. With the fast development of science and technology, developing materials with the features like “lighter”, “higher” and “stronger” becomes the primary goals of materials scientists. That has prompted engineering of metal oxides to become one of the most promising technologies involving in the photocatalytic degradation of organic pollutants and in treatment of bacterial diseases.

Apart from the abovementioned applications, another advantageous opportunity provided by metal oxides in support of environmental remediation constitutes its biocide activity, along with its biological compatibility. Microorganisms (including bacteria, fungi and viruses) are one of the main causes of disease in the world [3]. The public health outbreaks caused by emerging COVID-19 infectious diseases constitute the forefront of current global safety concerns and a significant burden on global economies [4]. While there is an urgent need for the effective treatment of these outbreaks based on antiviral and vaccines, it is essential to explore any other effective intervention strategies that may reduce the mortality and morbidity rates of the disease. The development of innovative materials able to prevent not only the transmission, spread, and entry of virus (such as COVID-19) but also bacteria, fungi into the human body is currently in the spotlight.

2. Main goals.

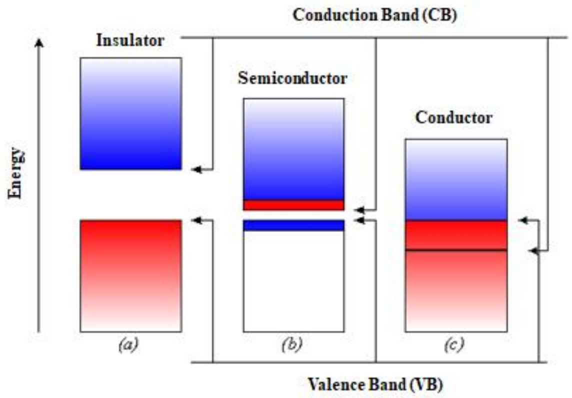
The main aims of present TFG can be summarized as follows: (i) To propose a mechanism for understanding the photocatalytic and biocide activities of inorganic semiconductors, and (ii) Explain these functionalities based on the presence of reactive oxygen species (ROS). The organization of tis TFG can be summarized as follows. In section 3 the definition of a semiconductor and how it work is provided. Section 4 discusses the photocatalytic activity of inorganic semiconductors.

Then, section 5 shows the mechanism of photodegradation of organic dyes. Section 6 explains how the highly reactive species generated are by the semiconductors, and they are involved in the photocatalytic reduction and oxidation steps. An understanding of the biocidal activity and their possible effects of inorganic semiconductors is presented in Section 7. Finally, conclusions and outlook of this TFG are summarized.

3. ¿What is a semiconductor and how does it work?

Semiconductors are compounds that selectively act as conductors or insulators, depending on the external conditions to which they are subjected, such as temperature, pressure, radiation and magnetic or electric fields. The preparation of these novel semiconductors has always been the goal of chemistry and material scientists because almost all contemporary electronic technologies involve the use of semiconductors. The study of these materials constitutes an active research topic due to their excellent performance. They are often encountered in science and engineering disciplines, and figure prominently in many current technologies, and they will play an important role in enabling a host of future applications, ranging from the degradation of pollutants (such as various organic dyes, poisonous molecules/ions, etc.), energy conversion, and biocidal activity, among others. [5-7].

The semiconductor photocatalysts are used for several decades in the past, called green technology, having received great attention, and shows an excellent ability for degrading contaminant by utilizing sunlight without causing any pollution. They also offer high versatility since it is possible to tune the band gap by modifying the geometrical and electronic structure. The achievable rapid fabrication of these materials allows the control of physical and chemical properties, allowing the control of the macroscopic properties of particle assemblies through contacts at the nanoscale. An ideal semiconductor needs to fulfill the following: it should be chemically and biologically inert, stable, photochemically active, and cheap. Nowadays, semiconductors play a central role in acing new global environment- and energy-related issues [8]. In fact, this research field is broad, not only for promoting the solar into chemical energy conversion through thermodynamically up-hill reactions producing fuels, such as H_2 evolution from H_2O [9-12], but also the obtention of CH_4 and CH_3OH from CO_2 [13-14].



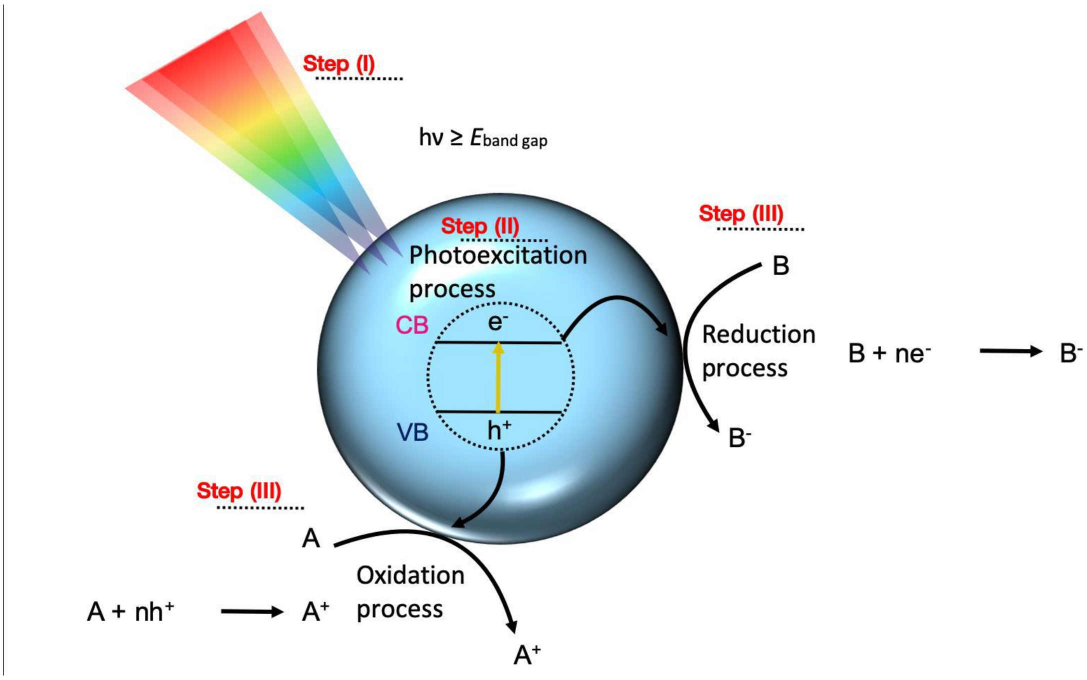
1

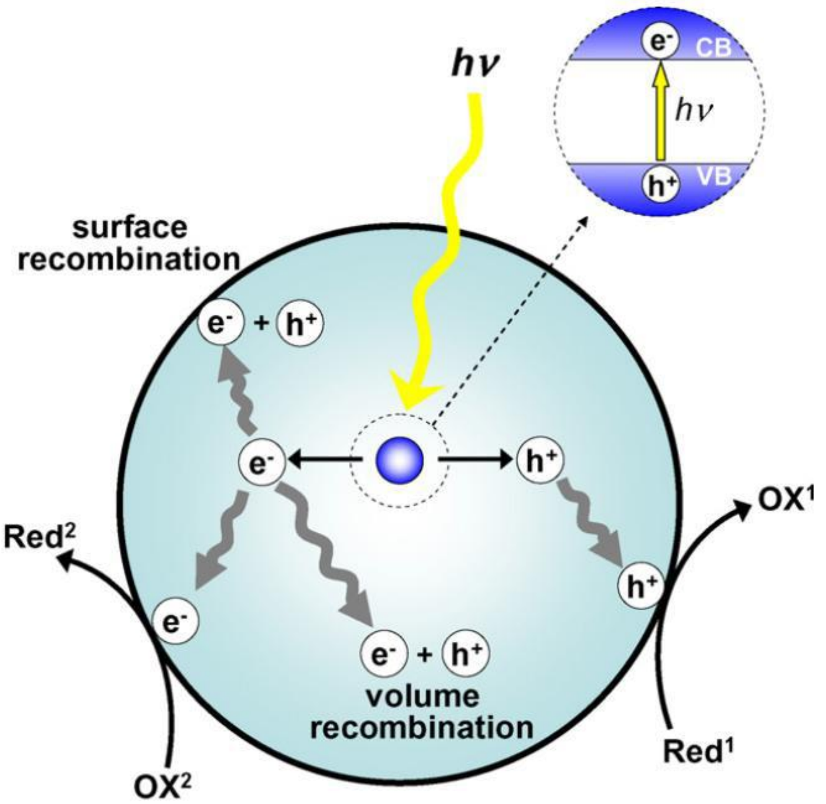
Figure 2. A schematic representation of the CB and VB at an insulator, semiconductor and conductor.

The increase in the electrical conductivity is directly related to the presence of a forbidden region separating the valence band (VB) and the conduction band (CB), called band gap region. As a result, when some energy is supplied to the solid, electrons (e^-) are excited from the VB to the CB gaining some mobility in the system. The strong point of the inorganic semiconductors is the fact that electrical conductivity can be altered by external and internal stimuli. They are the basis of advanced multifunctional materials, such as photocatalysis, i.e. the direct conversion of sunlight into chemical energy, electrocatalysts and fuel cell components, chemical power source insertion cathodes, high temperature superconductors, multiferrous materials, magnetic and magnetoresistive materials, solar cell energy materials and photoluminescence [15].

Semiconductor photocatalysts are irradiated with light, hv, with photon energy greater than their bandgap energy (Egap), the e^- in the VB) will be excited in the CB, leaving positive holes (h^+) in the VB, and creating an e^--h^+ pair. In this way, an electron and a hole are produced and rapidly thermalized in the CB and the excess energy (hv-Egap) is lost as heat. If the excess energy is enough, it can in principle be used to generate additional charge carriers by carrier multiplication.

The photocatalytic reactions that occur in the photoactivated semiconductor particle are presented in Figures 1 and 2. The three key processes of photocatalysis are: first the absorption of light, followed by the photoexcitation process in which the electron is excited and passes from the VB to the CB, and finally the reduction or oxidation process of the compound.





Figures 3 and 4. Schematic representation of the key steps in the photocatalytic process in a semiconductor. From reference [16].

4. *Photocatalytic activity of inorganic semiconductors*

In order to verify if the inorganic semiconductor is capable of splitting the H_2O molecule to generate the hydroxyl radicals (•OH) and/or reduce the O_2 to superoxide radical ($•O_2^-$), it is possible to compare the position of the valence band (VB) and the CB with the potential of $H_2O/•OH$ and $O_2/•O_2^-$ at different pH, such as 0 and 7.

Figure 5 displays the calculated VB and CB values of some Ag-based semiconductors.

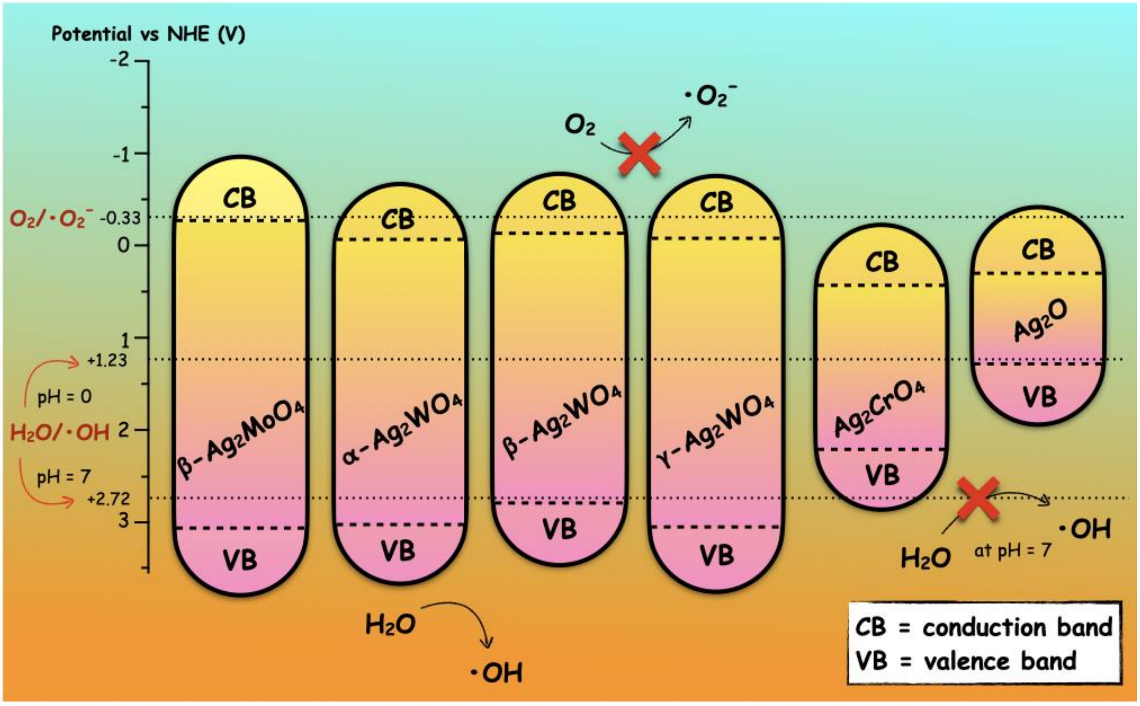


Figure 5. Scheme for the band structure of some Ag-based semiconductors and the potentials of radical generation in pH = 0 and 7.

A particular substrate can undergo chemical reactions on the semiconductor photocatalysts depending on the relative positions between its redox potentials and the band edges of semiconductor photocatalyst.

There are four possibilities, as follows:

(1) If the redox potential of the substrate is lower than the CB edge of the semiconductor photocatalyst, then the substrate can undergo reductive reactions.

(2) If the redox potential of the substrate is higher than the VB edge of the semiconductor photocatalyst, then, the substrate can undergo oxidative reactions.

(3) If the redox potential of the substrate is higher than the CB edge or lower than the VB of the semiconductor photocatalyst, then the substrate can undergo neither reductive nor oxidative reactions.

(4) If the redox potential of the substrate is lower than the CB edge and higher than the VB of the semiconductor photocatalyst, then the substrate can undergo either reductive or oxidative reactions.

According to **Figure 5**, the position of VB of β-Ag_2MoO_4, α-Ag_2WO_4, β-Ag_2WO_4, and γ-Ag_2WO_4 renders that they can be used as photocatalysts due to the strong oxidation ability. The activations of both molecular oxygen, O_2, and water, H_2O, are the fundamental steps in almost all photocatalytic oxidation/reduction reactions. In terms of thermodynamic conditions, the estimated VB positions of β-Ag_2MoO_4, α-Ag_2WO_4, β-Ag_2WO_4, and γ-Ag_2WO_4 are more positive than the redox potential +2.72 V for $\bullet OH/H_2O^-$ versus NHE [17], leading to the oxidation of H_2O to form $\bullet OH$, as a strong oxidant species for dye degradation. However, these Ag-based semiconductors are energetically unfavorable to carry out the reduction reactions, i.e., because they do not fit the redox potentials -0.33 V to carry out the reduction reaction to transform O_2 to $\bullet O_2^-$.

Since photocatalytic processes respond to chemical reactions taking place on the surface of the photocatalysts, free charge carriers first need to diffuse into the active sites on the surface of the photocatalysts before they can induce photocatalytic reactions. For example, in the degradation of organic dyes, light-generated holes (h^+) can readily react with H_2O molecules attached to the surface to produce $\bullet OH$ radicals, while light-generated e^- can react with O_2 to produce $\bullet O_2^-$. Due to the high oxidation capacity of both $\bullet OH$ and $\bullet O_2^-$, organic dyes decompose.

5. Mechanism for Photodegradation of Organic Dyes

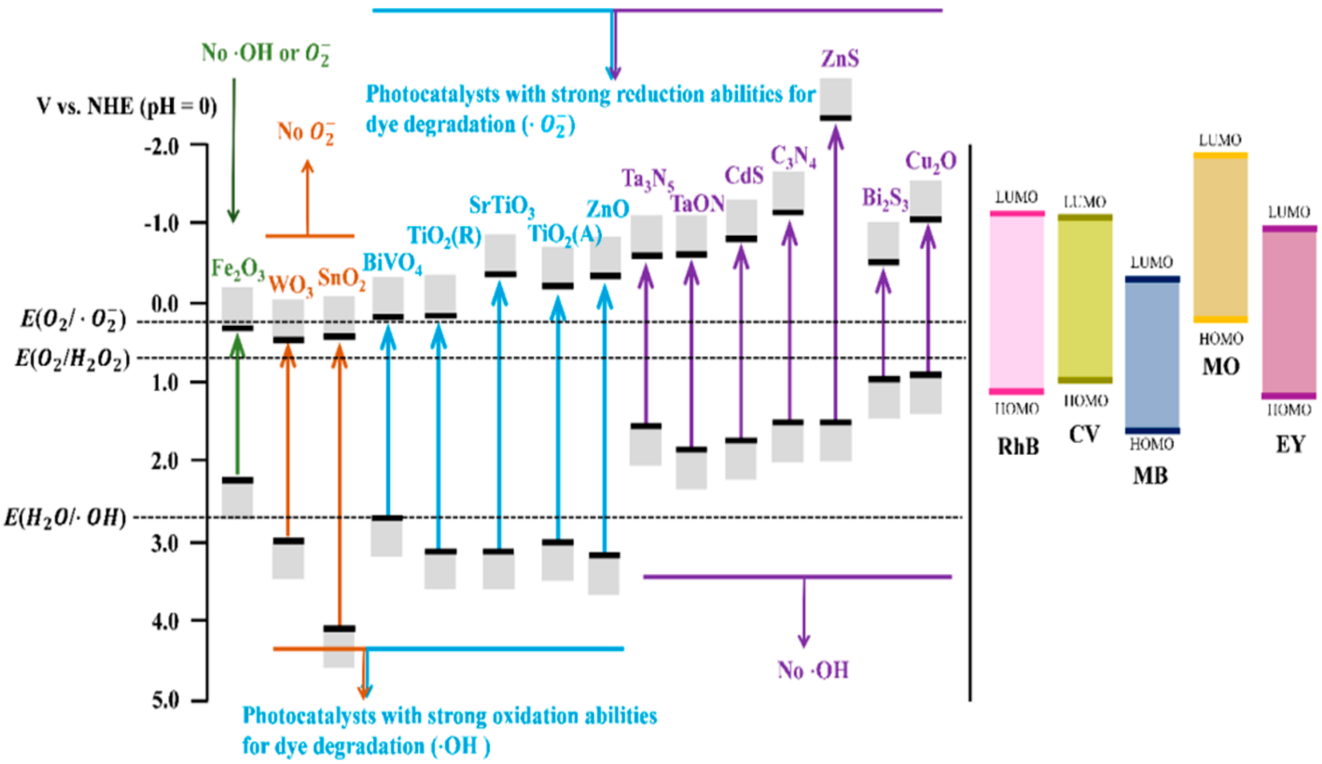


Figure 6. Scheme for the band structures of common photocatalysts, and potentials of the radical generation and HOMO and LUMO levels of five representative dye molecules. From reference [18].

In **Figure 6.** we can see for the band structures of common inorganic semiconductor, including the most representative metal oxides, acting as photocatalysts, and potentials of the radical generation and HOMO and LUMO levels of five representative dye molecules. Based on their band positions, the generation of ROS in semiconductor photocatalysts can directly degrade dye molecules (RhB, Rhodamine B, CV, crystal violet, MB, methylene blue, MO, Methyl orange, YE, Eosin Yellow).

The direct photodegradation of dye molecules involves the excitation of semiconductor photocatalysts under light irradiation, leading to the scavenging of photoexcited e^- by dissolved O_2 in the solution, as the CB of the photocatalyst is more negative than the reduction potential E^0 (O_2/$\bullet O_2^-$). Meanwhile, the photoexcited h^+ can oxidize the adsorbed H_20 to generate $\bullet OH^-$, as the VB of photocatalysts are more positive than the oxidation potential E^0 (H_2O/$\bullet OH$). These highly reactive $\bullet O_2^-$ and $\bullet OH$ can oxidize or degrade the adsorbed dye molecules. In addition, the photoexcited e^- and h^+ which are essentially active may also attack the dye molecules to complete the photodegradation process. In this figure the photocatalysts with strong oxidation and reduction abilities for dye degradation, through the use of $\bullet OH$ and $\bullet O_2^-$ are highlighted in blue color. The semiconductors no able to generate $\bullet O_2^-$ (WO_3 and SnO_2) and $\bullet OH$ are marked in orange and purple color, respectively. Fe_2O_3 (in green color) is not capable to generate $\bullet OH$ or $\bullet O_2^-$.

6. Semiconductor as a generator of highly reactive species.

The energy absorbed by a photocatalyst comprises the range of ultraviolet and/or visible light, even natural sunlight. As it was commented, when a semiconductor absorbs light, if the energy of the photons is enough to excite the e^- in the VB, they migrate to a higher energy level in the CB of the material, with creation of h^+ in the VB. This phenomenon generates the charge carriers known as e^-/h^+ pairs. The photocatalytic effects are exerted by the redox reactions caused by photoinduced e^- and h^+ generated on the heterogeneous solid surfaces of photocatalysts. Several reactive species are are formed through the reactions with the e^- and h^+, which are involved in the actual oxidative and reductive reactions in photocatalysis. Because photocatalysts are practically used under aerobic conditions, the presence of oxygen, O_2, and water, H_2O, as reaction species is fundamental to generate the reactive oxygen species (ROS). They are the reactive molecules and free radicals of oxygen generated as the by-products of aerobic respiration.

The species to which oxygen converts with high reactivity are generally called reactive oxygen species (ROS). Four major ROS are recognized, comprising superoxide anion radical ($\bullet O_2^-$), hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), and hydroxyl radical ($\bullet OH$). In photocatalysis, the efficiency of the photoinduced degradation varies over a wide range depending on the kinds of semiconductors (photocatalysts) used and the solution conditions employed. ROS are also important for advance oxidation processes in which, for example, organic pollutants in the wastewater are removed. Since ROS are primary intermediates of photocatalytic reactions, the identification, the quantification, and the kinetics evaluation of ROS are necessary for a complete understanding the photodegradation mechanisms, improving the degradation efficiency, and utilizing the various technologies developed for practical applications [18].

Figure 7. shows the ROS generated in the photocatalytic reduction and oxidation steps of O_2 and H_2O.

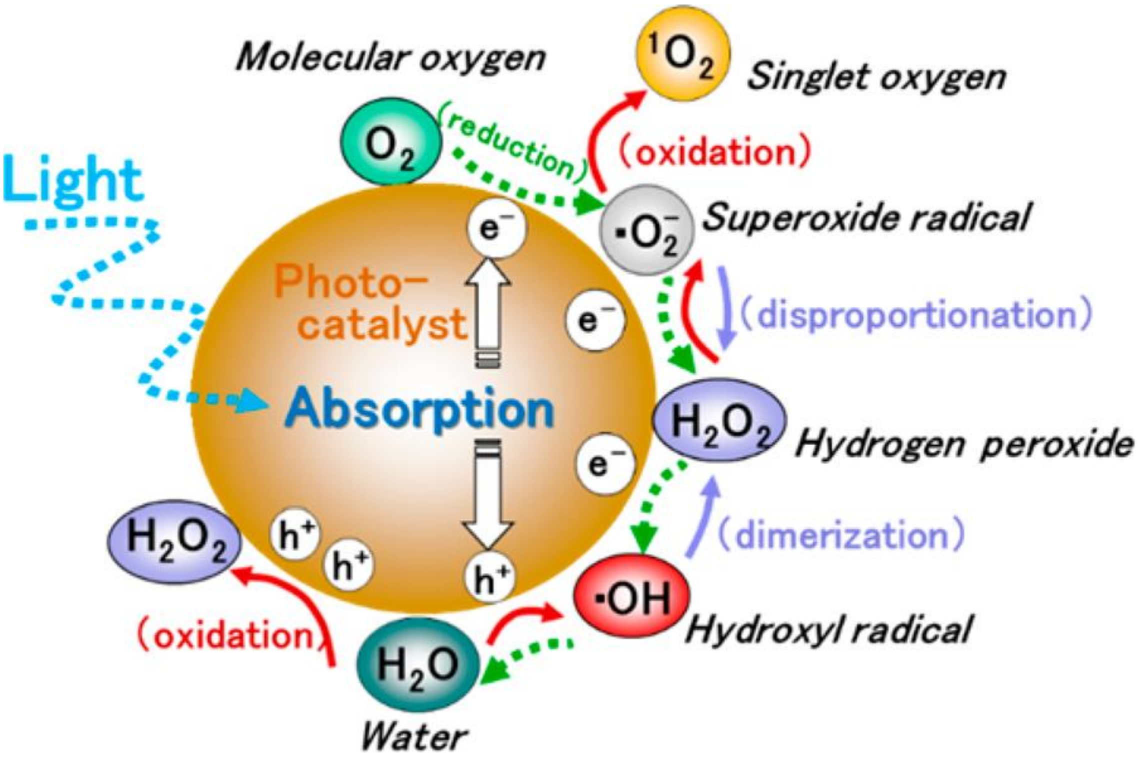


Figure 7. Reactive oxygen species (ROS) generated in the photocatalytic reduction and oxidation steps of O_2 and H_2O respectively. From Reference [19].

Activation of both O_2 and H_2O is one of the most important chemical processes of enormous interest and practical importance. In a semiconductor, the photogenerated h^+ at the VB can migrate to the surface of the material and react with H_2O molecules to produce •OH and proton (H^+), while the photoexcited e^- in the CB can react with the adsorbed molecular O_2 to produce $\bullet O_2^-$. Besides, through further reactions, $\bullet O_2^-$ and •OH species can transform into other highly oxidative species: singlet oxygen ($^1O_2$), perhydroxyl radical ($\bullet HO_2$), or hydrogen peroxide (H_2O_2), as illustrated in **Figure 7**. The ROS are the key signaling molecules in both photocatalytic and physiological processes and play an important role in the development and function of photocatalytic and biocide material.

An illustrated diagram of ROS generation is shown in the following **Figure 8**.

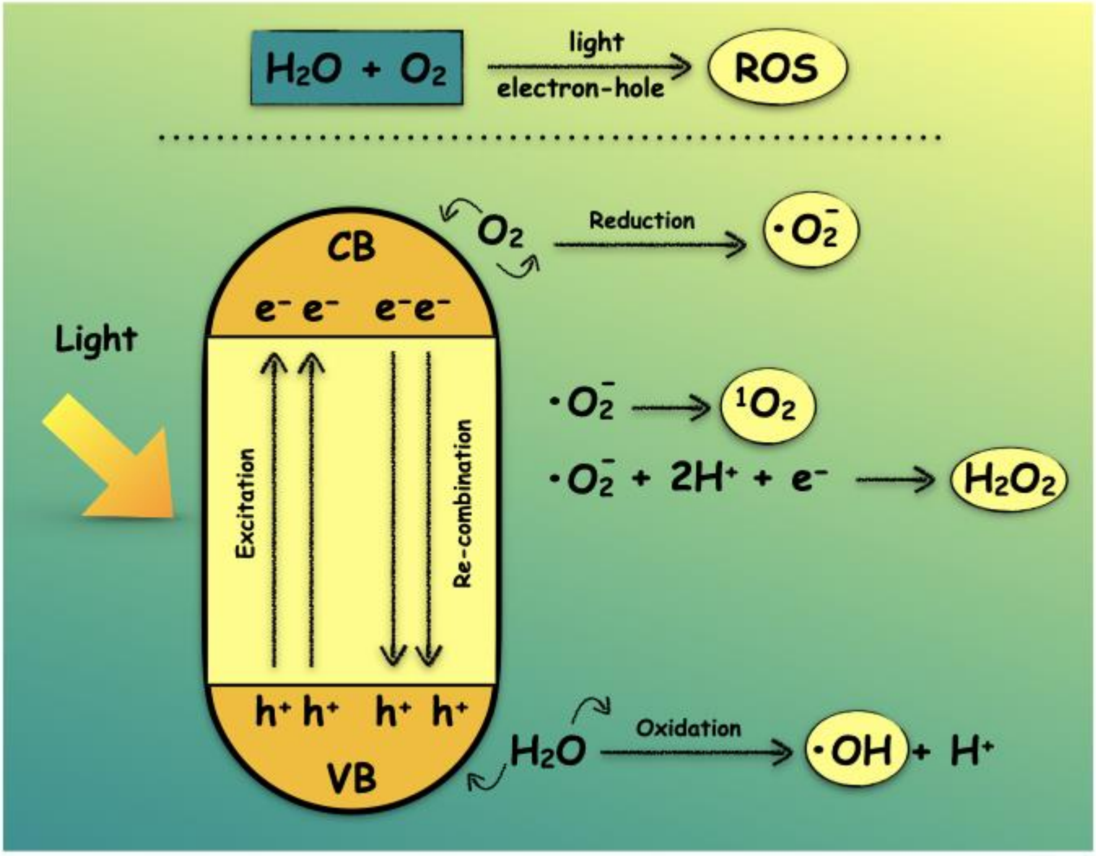


Figure 8. A schematic representation for the generation of ROS by a semiconductor.

The generation of ROS due to e^-/h^+ pairs is based on the following reactions [20-21]:

(1) $O_2 + e^- \longrightarrow \bullet O_2^-$

(2) $\bullet O_2^- + H^+ \longrightarrow \bullet O_2H$

(3) $\bullet O_2H + H^+ \longrightarrow H_2O_2$

(4) $H_2O_2 + e^- \longrightarrow \bullet OH + OH^-$

(5) $H_2O + h^+ \longrightarrow \bullet OH + H^+$

(6) $OH^- + h^+ \longrightarrow \bullet OH$

(7) $\bullet OH + \bullet OH \longrightarrow H_2O_2$

Furthermore, some electronic states can appear in the forbidden gap to undergo an ionization process to form electronic defects, i.e., quasi-free e^- and h^+ [22, 23]. In addition, it was demonstrated that the recombination of e^-/h^+ pairs is probable at bulk sites while surface defects improve the reactivity by promoting the adsorption of O_2 and H_2O. Then, exposed surfaces with a difference in charge density (due to the dipole moment) bind the adsorbates strongly and drive the photocatalytic reactions [24, 25]. The ability to control these properties at the nanoscale has allowed correlations to be made between nanocrystal structure and their optical, magnetic, and electronic properties, which has implicated these materials in various applications ranging from biomarkers to photocatalysts [26-27].

Another way to explain the regeneration of ROS is based on the analysis of molecular orbitals of O_2 and the e^- transfer processes. O_2 molecule has 16 electrons and the electrons having the highest energy control their reactivity. Figure 9 shows the electron spins at the highest occupied molecular orbitals for O_2. Their ground state is triplet with two unpaired electrons on each of the two antibonding π orbitals (π_x* and π_y*). $\bullet O_2^-$ is formed by reducing O_2, via an e^- transfer process, while the singlet oxygen molecules, $^1O_2$, is formed by oxidation of O_2, other electron transfer process. H_2O_2 are formed successively by reducing O_2 or by filling the two π* orbitals with an electron, followed by the protonation to each orbital. Then, the high reactive species O_2^{2-}, $^{\cdot}O_2H$, and HO_2^- are formed along the different steps.

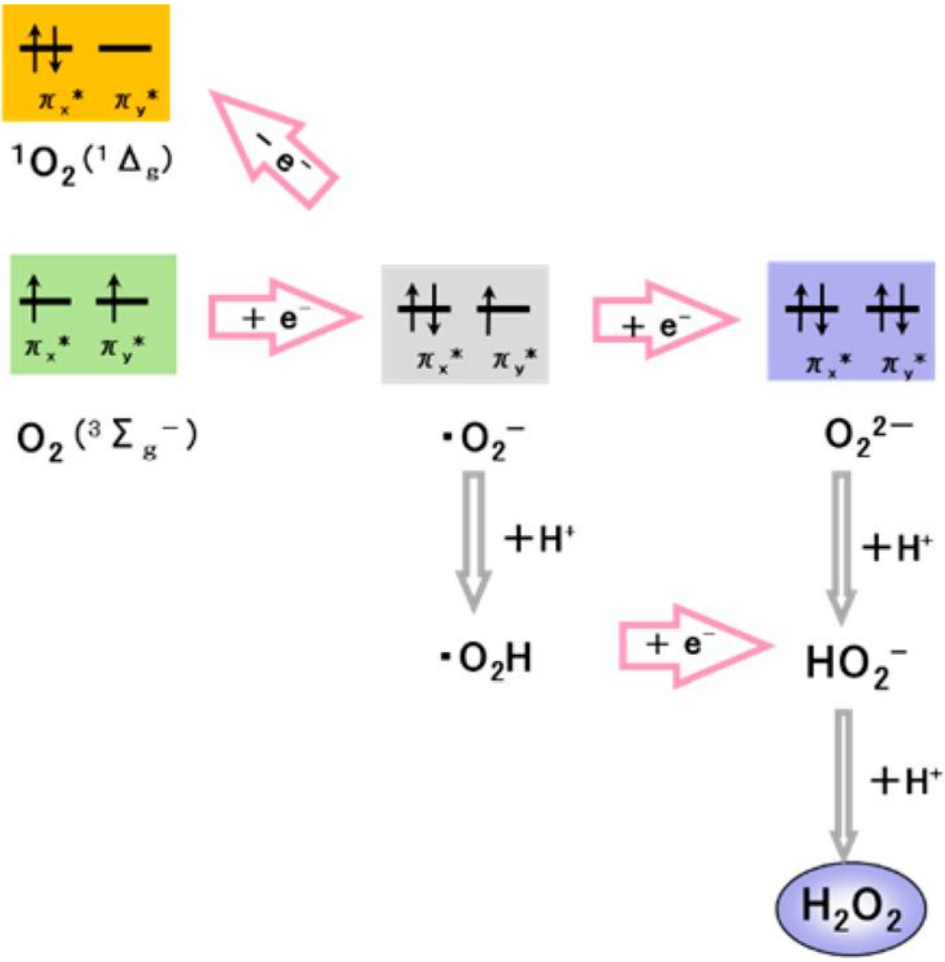


Figure 9. An explanation for the generation of ROS from O_2, based on the antibonding π orbitals (π_x* and π_y*). These pathways involve electron transfer and protonation processes. From Reference [19]

7. Biocide activity of inorganic semiconductors.

ROS are generated in cellular metabolism and are essential for cellular signalling networks and physiological functions. However, the functions of ROS are 'double-edged swords' to living systems that have a fragile redox balance between ROS generation and elimination. A modest increase of ROS leads to enhanced cell proliferation, survival and benign immune responses, whereas ROS stress that overwhelms the cellular antioxidant capacity can damage nucleic acids, proteins and lipids, resulting in oncogenic mutations and cell death. ROS are therefore involved in many pathological conditions. This TFG summarizes the roles of ROS under pathological conditions.

ROS are biologically active molecules formed inside the mitochondria of living cells during cellular respiration [28]. ROS are linked with the deleterious effects on cells and play an important role in natural defense by the immune system against microbes [29]. Normal physiology of cells is maintained when the ROS level is balanced with the neutralizing molecules known as antioxidants. Whenever this balance shifts toward the ROS, the cell is considered under oxidative stress. Then, an increase in ROS concentration in lipids, proteins, and DNA could be damaged by ROS [30], provoke oxidative stress linking to uncountable pathologies [31]. ROS can still inhibit the replication activities of DNA/plasmid and some proteins enzymes, due to its interaction with phosphate/sulfate groups or even due to genetic changes. [28,29] All of these results, added to the permeability of ROS under the cell membrane, can affect the expression of proteins essential for the correct functioning of microorganisms, as well as their replication. It has also been observed that coatings based on copper oxides eliminate copies of SARS-CoV-2, responsible for the current pandemic, upon contact with these surfaces, due to the production of ROS that degrade the constituent proteins and membranes of these microorganisms. [30–35]

ZnO is a n-type semiconductor with a band-gap of 3.37eV, and a significantly large free exciton binding energy of 60 meV allows for efficient exciton emission at room temperature. Due to these photoelectric features, it has potential applications as a photocatalytic degrading agent and bacteriostatic agent under visible light and becomes one of the most important semiconductors in this field. Actually, ZnO has been widely used in the treatment of varieties of contaminants in wastewater such as completely degradation of organic matter (or chlorine) and controlling the spread and infection of various strains. And these successful applications are largely benefit from the high specific surface area, excellent hydrophobicity and oxidizing ability of ZnO. At the same time, ZnO can be adsorbed on the surface of bacteria and thus effectively inhibit the growth of microorganisms in the process of wastewater treatment and purification. When ZnO particles are reduced to nanoscale size, they are toxic to most bacteria and can kill them rapidly. While they are not toxic to human body and can be biocompatible with human's cells. Therefore, we can select as an example ZnO as a semiconductor material because promising results have also been obtained to be used as a biocidal material (against the propagation of viruses, bacteria, fungi). [33]

In comparison to the photocatalytic activity, the antibacterial activity of ZnO depends on factors such as size, particle morphology and concentration of nanoparticles or also on the chemical equilibrium of the solution (concentration, pH, chemical composition, reagent temperature...etc). The addition of impurities to modulate its electrical properties (doping) native to the semiconductor due to oxygen vacancies or zinc interstitials.

It is reported that the biocide activity of ZnO was due to the membrane lipid peroxidation caused by the oxidation of ROS produced by the interaction of ZnO resulting in cell wall dysfunction [34]. The presence of •OH and/or $•O_2^-$**,** as well as H_2O_2 [35], cause the damages of DNA and cellular proteins, and even lead to the death of molecules. The proposes mechanism is as follows:

- **Step 1** $\mathbf{ZnO + hv \longrightarrow e^-_{CB} + h^+_{VB}}$
- **Step 2** $\mathbf{h^+_{VB} + H_2O \longrightarrow •OH^- + H^+}$
- **Step 3** $\mathbf{e^-_{CB} + O_2 \longrightarrow •O_2^-}$
- **Step 4** $\mathbf{O_2^- + H^+ \longrightarrow •HO_2}$
- **Step 5** $\mathbf{•HO_2 + H^+ + e^-_{CB} \longrightarrow H_2O_2}$

Under ultraviolet light, the e^- in the VB of ZnO are excited to the CB, forming free-moving negatively charged e^- and positively charged h^+ **(step 1)**. The h^+ decompose the H_2O molecules into •OH and H^+ in the ZnO suspension **(Step 2)**. Dissolved O_2 molecules converted into $•O_2^-$ **(Step 3)** and reacted with H^+ to form $•HO_2$ radicals **(Step 4)**. At last, H_2O_2 molecules were produced when $•HO_2$ is collided with e^- and H^+ **(Step 5)**.

As we can see in the picture when the energy absorbed by the ZnO particles is higher than bandgap, highly oxidizing radicals will be generated on the surface through the irradiation of light and photocatalytic reactions would occur. As shown in **(Figure 9.)**, the vacancy of zinc near the VB captures the hole, while the oxygen vacancy near the CB captures the electron. Photogenerated e^- are lifted from the VB to the CB, forming positively charged h^+ and negatively charged e^- on the surface of ZnO.

In the following **Figure** we can see a schematic representation of the photocatalytic mechanism of the ZnO.

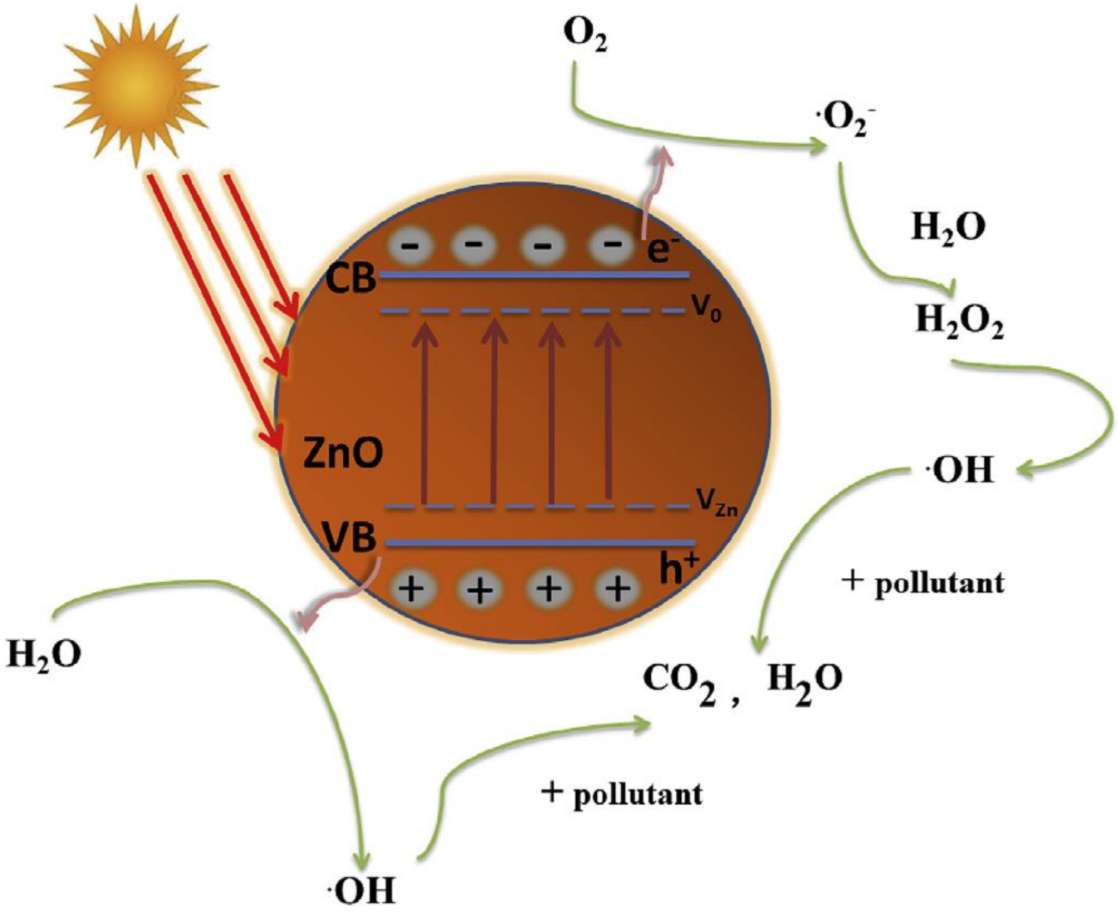


Figure 10. Photocatalytic mechanism of ZnO. From Reference [36].

•OH and $\bullet O_2^-$ are negatively charged particles, which could not seep into the cytomembrane to maintain immediate contact with the outside surface of the bacteria. However, H_2O_2 could infiltrate into the cells and kill bacteria [32]. The production of H_2O_2 largely lies on the surface grain of ZnO, which results in a large number of oxygen species on the surface and smaller nanoparticles have higher antibacterial activity [36]. As highlighted, ZnO exhibits excellent and generally greatest antimicrobial activity than other antimicrobial-derived metals. In addition, ZnO safety and its compatibility with human skin justify its widespread use as an antibacterial agent and make it a suitable additive for textiles and surfaces that get in contact with the human body. In the last years, the attention was focused on nanostructured zinc oxide with the development of several physical, chemical, and eco-friendly ("green chemistry") approaches to obtain ZnO with different morphologies that show significant growth inhibition of a wide spectrum of bacterial species. When applied in well-defined sizes, crystalline structure and concentrations, these materials have been shown to be very effective inhibitors against a wide range of bacteria. The exact mechanisms of action of ZnO are not completely clear yet, but several models are conceived. In addition, One of the proposed mechanisms is based on the electrostatic interactions between ZnO and cell walls resulting in destroying bacterial cell integrity, with the delivery of antimicrobial Zn^{2+} cations, their accumulation into bacteria cells, and ROS formation effectiveness is closely related with concentration and surface area; higher concentrations and larger surface area displayed better antibacterial activity.

In the next **Figure 11.** as schematic representation of the antibacterial mechanism of ZnO is displayed. The whole antibacterial process and the related mechanism might be attributed to the same mechanism of the photocatalysis activity associated to the generation of ROS.

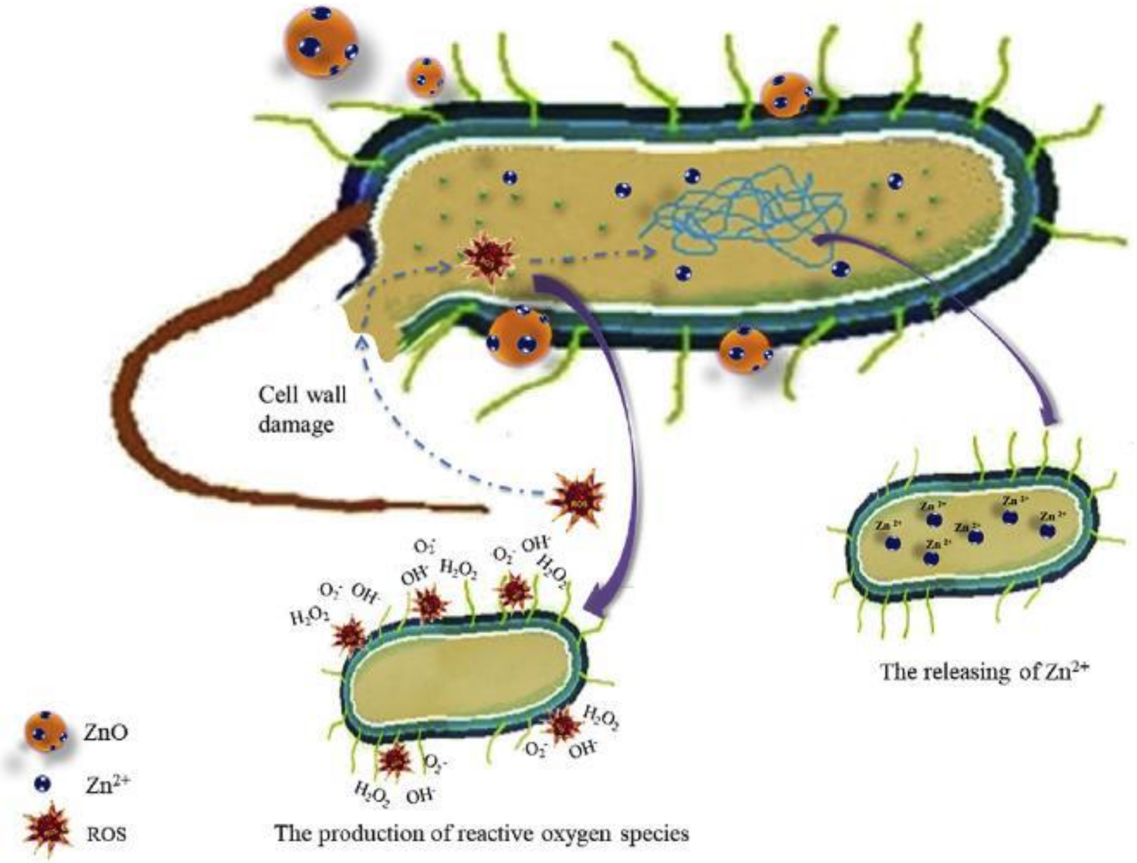


Figure 11. Antibacterial mechanisms of ZnO. From Reference [36]

8. Conclusions and outlook

Inorganic materials that have inherently exceptional physicochemical properties (*e.g.*, catalytic, optical, thermal, electrical, or magnetic performance) that can provide desirable functionality and technological applications. In particular, inorganic semiconductors are an interesting class of materials for the fight against biocide infections as they can produce microorganism-killing radicals to prevent their transmission. In particular, materials based on inorganic semiconductors are known to have the ability to release ROS. These in turn, when in contact with microorganisms, are responsible for membrane damage, which lead them to death. Specifically in microorganism and proteins are affected by the rapid rates of reaction with ROS.

Our goal in this TFG should help in understanding the properties of inorganic semiconductors as biocide materials. It is well known that generated ROS can be regarded as potential biocide agents because of the rapid oxidation of various biomacromolecules in cells. Although a low level of ROS has a significant effect on supporting the cellular life cycle, excessive ROS could generate oxidative stress, giving rise to oxidative damage to the cellular constituents. Through this property, ROS act as strong oxidants to destroy microorganisms and contribute to sterilization. In this TFG we provide a strategy to understand how ROS are generated in inorganic semiconductors, showing how photoenhanced catalytic and biocide activities and the related mechanism are similar.

Finally, it is important to remark that it is necessary to gain more insight in the mechanism of action, at atomic level, of generated ROS: How they destroy and damage the microorganisms´ cells?; how we discover the type of ROS responsible of the biocide activity?; how we can accelerate o retard your presence along the corresponding molecular mechanism?. We believe that this timely work will stimulate and guide additional in-depth studies in the area of inorganic semiconductors, with unique properties and functionality. We expect future prospects and opportunities in this rapidly growing biomedical field

REFERENCES

1. J. Schneider, D. Bahnemann, J. Ye, G. L. Puma, Photocatalysis: Fundamentals and Perspectives; Dionysiou, D. D., Eds.; Royal Society of Chemistry: Cambridge, 2016.
2. T. Dandan Zhua, Qixing Zhoua; Environmental Nanotechnology Monitoring & Management, 12, (2019), 1002552.
3. JJ Steffan, JA Derby, EC. Brevik; Curr Opin Environ Sci Heal, 17, (2020), 35.
4. E. Shadmi, Y. Chen, I. Dourado, I. Faran-Perach, J. Furler, P. Hangoma, P. Hanvoravongchai, C. Obando, V. Petrosyan, K. D Rao, A. L. Ruano, L. Shi, L. Eugenio de Souza, S. Spitzer-Shohat, E. Sturgiss, R. Suphanchaimat, M. V. Uribe, S. Willems; Health equity and COVID-19: global perspectives, 19, (2020), 104.
5. Y.B. Wang, T.H. Wu, J. Barbaud, W.Y. Kong, D.Y. Cui, H. Chen, X.D. Yang, and L.Y. Han; Science, 365, (2019), 687.
6. L.P. Zhang, J.R. Ran, S.Z. Qiao, and M. Jaroniec; Chem. Soc. Rev., 48, (2019), 5184.
7. C. Kranz and M. Wachtler; Chem. Soc. Rev., 50, (2021), 1407.
8. F.E. Osterloh; ACS Energy Lett., 2, (2017), 445.
9. J. Cai, J. Shen, X. Zhang, Y. Hau Ng, J. Huang, W. Guo, C. Lin, Y. Lai; Small methods Rev., 3, (2019),

1800184.

10. F. Pellegrino, F. Sordello, M. Minella, C. Minero, and V. Maurino; Catalysts, 9, (2019), 32.

11. Y.O. Wang, H. Suzuki, J.J. Xie, O. Tomita, D.J. Martin, M. Higashi, D. Kong, R. Abe, and J.W. Tang; Chem. Rev., 118, (2018), 5201.
12. Z. Wang, C. Li, and K. Domen; Chem. Soc. Rev., 48, (2019), 2109.
13. P. Prabhu, V. Jose, and J.M. Lee, Adv. Funct. Mater., 30, (2020), 1910768.
14. S.Z. Xu and E.A. Carter, Chem. Rev., 119, (2019), 6631.
15. J. Singh, Electronic and Optoelectronic Properties of Semiconductor Structures. New York,Cambridge University,2003.
16. Y. Shiraishi; T. Hirai, Photochem.Photobiol.C9, (2008), 157.
17. ES H.A. Schwarz and R.W. Dodson; J. Phys. Chem., 88, (1984), 3643.
18. Y.H. Chiu, T. F. Mark Chang, Y. C. Chen, M. Sone and Y. J. Hsu, Catalysts Rev., 9, (2019), 430.
19. Y. Nosaka and A.Y. Nosaka; Chem. Rev. 117, (2017), 11302.
20. Y. Li, W. Zhang, J.F. Niu, and Y.S. Chen; ACS Nano, 6, (2012), 5164.
21. C.E. Tsai, S.M. Yeh, C.H. Chen, and H.N. Lin; Nanoscale Res. Lett., 14, (2019).
22. J. Xiong, J. Di, J.X. Xia, W.S. Zhu, and H.M. Li; Adv. Funct. Mater.,28, (2018).
23. J. Nowotny, M.A. Alim, T. Bak, M.A. Idris, M. Ionescu, K. Prince, M.Z. Sahdan, K. Sopian, M.A.M. Teridi, and W. Sigmund; Chem. Soc. Rev., 44, (2015), 8424.
24. T. Hisatomi and K. Domen;Nat. Catal.; 2, (2019), 387.
25. B. Mei, K. Han, and G.D. Mul, ACS Catal. 8, (2018), 9154.

26. M. Assis, C.C. de Foggi, V. Teodoro, J.P.D. da Costa, C.E. Silva, T. Robeldo, P.F. Caperucci, C.E. Vergani, R.C. Borra, I. Sorribes, A.F. Gouveia, M.A. San-Miguel, J. Andres, and E. Longo, Appl. Surf. Sci. 545, (2021), 148964.

27. M. Assis, R.A.P. Ribeiro, M.H.C. Costa, M.M. Teixeira, Y.G. Gobato, G.A. Mendonca, L. de Boni, A.J.A. de Oliveira, J. Bettini, J. Andres, and E. Longo; ACS Omega, 5, (2020), 10052.

28. J. Lee, N. Koo, D.B. Min; Compr. Rev. Food Sci. Food Saf., 3, (2004), 21.

29. M. Mittal, M.R.Siddiqui, K.Tran, S.P. Reddy; A.B. Malik, Antioxid. Redox Signaling., 20, (2014), 1126-1167.

30. K. Dasuri, L. Zhang, Keller;Free Radical Biol.Med.; 62, (2013), 170−185.

31. M. Schieber, Chandel;Curr. Biol., 24, (2014), R453−R462.

32. S. Behzadinasab, A. Chin, M. Hosseini, L. Poon, and W. A. Ducker; ACS Appl. Mater. Interfaces, 12, (2020), 34723.

33. R.K. Dutta, B.P. Nenavathu, M.K. Gangishetty, A.V. Reddy; Colloids Surf. B 94, (2012),143.

34. A. Kędziora, M. Speruda, E. Krzyżewska, J. Rybka, A. Łukowiak, G. Bugla-Płoskońska; Int. J. Mol. Sci. 19, (2018), 444.

35. N. Padmavathy, R. Vijayaraghavan; Sci. Technol. Adv. Mater. 9, (2008), 1-7.

36. J. Liu, Y. Wang, J. Ma, P. Yi, W. Aiqin; ELSEVIER, Journal of Alloys and Compounds, 783, (2019), 898.

37. L.S. Reddy, M.M. Nisha, M. Joice, P.N. Shilpa; Pharm. Biol., 52, (2014), 1388-1397.