ZnO nanostructured materials for surface and biological applications

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ABSTRACT

Currently, the design of nanostructured materials has exceptional features for developing surfaces and structures to beat many challenges facing numerous daily life technologies. Nanostructured surface coatings have been developed as a result of nanotechnology progress. Zinc oxide (ZnO) has sparked widespread interdisciplinary attention as a fascinating nanostructured material for building sustainable and protective nanocomposite surfaces. Owing to their outstanding physico-mechanical and biomedical capabilities of ZnO-based materials, many applications and materials associated with ceramics, flame retardants, pigments, rubber, cosmetics, batteries, fouling resistance, and coatings have been engineered using various nanostructured ZnO additives. This chapter presents a variety of polymer nanocomposites with ZnO nanostructured materials as reinforcements that have excellent properties for antibacterial, antifouling, and anticorrosion applications. Well-dispersed ZnO nanofillers within the polymer resin can enhance antifouling, water-repellency, and corrosion protection to offer a long-lasting and sustainable surface material. In this regards, the use of innovative ZnO/polymer hybrids was highlighted as a recent advancement in hydrophobic biological surfaces for various applications. Coatings containing nano-ZnO as a filler can be made by using several ways to embed ZnO nanoparticles into various polymeric resins. Hybrid design of polymer and inorganic ZnO-based materials is receiving prominent attention in hybrid materials due to its versatility and unique features. Ggraphene/ZnO nanocomposites show fruitful properties in developing protective surfaces and producing robust superhydrophobic coatings featuring surface topography with controllable microstructures, micro/nano roughness, water-repellency, and anticorrosion properties. Moreover, the synthesized ZnO-based polymeric nanocomposites for surface and biological applications is highlighted in this chapter. It discusses methods for regulating the size and shape of nano-ZnO to prevent marine fouling and steel corrosion. Engineering eco-friendly durable ZnO nanocomposites requires a high level of stability and long-term durability. This work discusses the antibacterial and antifouling properties of ZnO nanostructures. Recent breakthroughs and current researches on ZnO nanocomposites for protective coating applications are also highlighted. Last but not least, this work will consolidate and conclude a number of active perspectives on the difficulties and future developments that are at the forefront of this research platform. Simplicity, safety, environmental consequences, benignancy, economic feasibility, sustainability, and potential applications are among the advantages of the developed nano-coatings. It concludes with a discussion of the field's current and future advancements. This chapter is planned to serve as a modern research portal for the creation of a future sustainable and long-lasting coating.

Keywords: *Nanostructured surface, coatings, protective nanocomposite, ZnO nanofillers, graphene, antifouling materials.*

1. Introduction:

Nanomaterials researches play an important role in solving problems and improving our lives in every aspect of technology. In this context, a lot of research endeavors have been devoted to provide several promising strategies to manufacturing surfaces and coatings based on nanostructured materials to enhance structural properties of surfaces as well as physical and chemical properties [Idumah et al., 2020; Xavier et al., 2020; Arukalam et al., 2016; Hu et al., 2021]. As is notable, the design of nanostructured thin-layer films, surfaces and coatings occupies a privileged position in numerous applications associated with the environmental, energy, and biological applications [Panwar et al., 2022; Behera et al., 2022; Idumah et al., 2021; Karki et al., 2022; El-Safty et al., 2020a; El-Safty et al., 2020b].

Interest in polymer composite systems research has been rapidly expanding in recent years because to their numerous potential applications [Ponnamma et al., 2017; Goutham et al., 2017], dielectrics [Deshmukh et al., 2017], biological field [Stodolak et al., 2009; Reda et al., 2021; Shenashen et al., 2022], food packaging [Maizurah et al., 2007], bioplastics [Domenek et al., 2004], extraction and water treatment [Gomaa et al., 2018; 2021; Awual et al 214], and coatings [Selim et al., 2017a; 2015a; 2015b; 2019a]. Adding inorganic nanofillers to polymers increases polymer properties that are radically different from standard polymer properties, according to the researchers [Nagaraj et al., 2018; Selim et al., 2017b; 2020a; 2018a; 2018b; Sadasivuni et al., 2013]. Nanoparticles (NPs) have been found to have a significant impact on the characteristics of basic polymers when used to produce nanocomposite [Selim et al., 2019b; Mazrouaa et al., 2019; Ponnamma et al., 2014]. A multicomponent structure having microscopic fillers (less than 100 nm in at least one dimension) is referred to as a polymeric nanocomposite [Selim et al., 2017c; 2019b; Kafy et al., 2015]. Because of their high aspect ratio and enormous surface area, nanofillers behave as intelligent improver in the polymeric resins. As a hot spot at the moment, nanofillers with controlled size and morphology are desirable reinforcing materials for polymers [Selim et al., 2022]. Moreover, various organic-inorganic hybrid nanocomposite materials have been designed for various applications [Khairy et al., 2013; Soliman et al., 2017; Azzam et al., 2017; El-Sewify et al., 2017]. In this regards, diverse nano-inorganic dopants including SiO_2, Al_2O_3, TiO_2, SiO_2, ZnO, and other nano-metal oxide are commonly utilized as nano-dopants in the polymeric resins [Wang et al., 2001; Hirvikorpi et al., 2011; Selim et al., 2020b; Khalifa et al., 2020]. In this context, this study will focus on studying the features of ZnO nanofillers to develop new structural surfaces with advanced properties. ZnO can adopt many various nanomaterials including NPs, nanowires (NWs), and nanorods (NRs). ZnO has a broad-band gap (3.4 eV) and is an n-type (II-V) semiconductor with several functions.

Even in the presence of sunlight, water, and air, it possesses excellent chemical stability, UV absorbance, and binding energy (60 meV) [Janotti and Van de Walle, 2009]. ZnO can be used in biomedical applications because it is non-toxic and safe for the environment [Hezam et al., 2018]. ZnO NPs have unique features that allow them to exist in both an anti-electrostatic and conductive form, as well as having excellent chemical, optical, magnetic, electrical features. Polymer coatings, semiconductors, photochemical, UV-shielding materials, piezoelectric devices, optical waveguides, antibacterial agents, UV-laser emitters, cosmetics, solar cells, self-purification, and gas sensors materials (Figure 1) [Parangusan et al., 2018; Seo et al., 2013; Li et al., 2002; Yi et al., 2005] have a lot of potential. ZnO exhibits bactericidal activity in the absence of light and at pH 7–8 [Tam et al., 2008]. Additionally, visible fluorescence is detected in ZnO NPs, especially when synthesized by sol-gel, but hydrothermal synthesis renders them ideal for usage in UV emitters. Traditional metal oxides, such as ZnO, are combined with polymers in certain structural layouts to achieve the desired performance [Goutham et al., 2017], which is a commonly utilised major method for producing ZnO/polymer nanocomposite.

The components' characteristics, the filler's large surface area, polymer-nanofiller interfacial bondings and nanofiller's well-distribution within the resins are all thought to contribute to the improvement in attributes. This can be fulfilled by tailoring the characteristics of nanofillers, polymers, and the hybrid nanocomposite to achieve outstanding features. In the required application, selecting an appropriate polymeric resin is crucial. Chemical and heat resistance, mechanical durability, biological activity, and friction coefficient can all be improved by incorporating ZnO into a polymer matrix [Thangamani et al., 2017]. The benefits of ZnO NPs are shown in Figure 2.

In general, controlling the structure of the ZnO/polymer composite well contributes to the improvement of the desired properties of the final structure, so many efforts have emerged regarding the adaptability and management of the filler particle interactions with the polymer matrix. Studying the ZnO nanofillers' structure-property relationship is inevitable to develop newly structured surfaces with advanced properties. It takes into account the impacts of functionalization, surface area to volume ratio of nanofillers, the antifouling effect, sustainability, and multifunctionality. Controlled ZnO nanostructures aid in the creation of a rough morphology and the generation of extra functionalities for the superhydrophobic surface. The influences of dispersing nano-ZnO within different polymeric resins is investigated in depth in this chapter, which covers production, processing, characterisation methods, and a wide range of applications. Our research focuses on ZnO effects on modulating polymer nanocomposites' surface, mechanical, photo-induced, antifouling, and antibacterial characteristics. Incorporation of nano-ZnO structure within various polymeric resins is an excellent technique for generating better performance even at low nanofillers loading percentages; thus producing feasible and applied nanocomposite surface materials.

2. Synthesis methodologies of nanostructured ZnO particles and polymer composites

A variety of methods are used to synthesize ZnO NPs with different morphologies from distinct precursor materials. The most widely used methods are solid-state reactions [Suwanboon et al., 2013], pyrolysis via flame spray [Lee et al., 2012], chemical, sonochemical, microwave, sol-gel, hydrothermal, and solvothermal methodologies [Stanković et al., 2011; Sharma et al., 2011; Kazeminezhad et al., 2013; Ba-Abbad et al., 2013; Aneesh et al., 2007]. ZnO NPs are made via the co-precipitation technique. Two important concerns in all of these synthesis processes are the homogeneity of the ZnO particle dispersion and the low reaction temperature. Nanostructures, on the other hand, contain impurities and metal ions that need be removed to optimize NP formation. Some of the many nano-ZnO shapes such as NPs, NRs, nanorings, nanotubes, flower-like, and nanobelts. These nanostructures can be dispersed in a wide range of liquids and polymeric resins. ZnO NPs cluster like other NPs, compromising their uniform distribution in the polymer medium. Inorganic particles or polymers can be grafted onto the ZnO surface to alleviate this problem [Wang et al., 2008].

This would improve the distribution and interfacial bonding of nano-ZnO within the polymeric resin to produce improved nanocomposite materials. Such desired composite performance is influenced by the size of the nanofillers as well as the polymer matrix's properties. This is often accomplished by selecting appropriate chemical and physical mixing procedures to reinforce the polymeric resin. Chemical reactions create chemical connections between polymers and fillers, unlike physical procedures that involve polymer/nanofillers mixing within a suitable solvent. Chemical synthesis yields composites that are multi-structured and stable, with stronger polymer/nanofiller connections. On the other hand, physical methods create polymer/nanofillers static connections, such as Lewis acid/base and/or van der Waals force interactions. Chemical-grafting of polymers onto ZnO surfaces yields homogenous, clear products that are easily removed separated from the system of reaction [Xiong et al., 2007]. The breakdown temperatures of such composites are usually higher than those of ordinary polymers, and there is no significant phase separation. This assures that the system's polymer-ZnO linkages are strong, and that the stronger the contact, the more stable the nanocomposites will be and can be applied for various industrial applications.

3. Surface and biological applications of ZnO nanostructures

In every field of technology, ZnO Nanomaterials help to solve problems and make our lives easier. There is an urgent need to develop innovative nanomaterials with improved properties to meet the demand for improvement [Shenashen et al., 2014; Shenashen et al., 2017]. If new structured nanomaterials with enhanced properties are to be produced, the investigation of the structure-property relationship is a necessary. Engineering applications for ZnO-based surfaces include self-cleaning, anti-biofouling, anti-icing, anticorrosion, and textiles. To make superhydrophobic nano-surfaces, researchers employed a straightforward method of NP's distribution within the polymer resin and then coating water-repellent polymeric nanocomposite film on a suitable substrate [Dong et al., 2011]. Controlled NP structures help create a rough morphology and provide additional characteristics for a superhydrophobic surface.

3.1. Self-cleaning surfaces

Superhydrophobic nanostructured surfaces have piqued attention in a variety of industrial applications around the globe. Biomimetic [Salta et al., 2020] is an engineering architectures with a hierarchy, tectonics of materials, nano-surfaces, and machineries model based on the function and structure of biological systems. Biological systems could develp superhydrophobic coating materials. The development of biomimetic surfaces with micro and nanostructures is used to reduce fouling in the maritime environment. As a result, it's vital to clarify the process and precision for constructing bio-replicated multiscale structures [Sharma et al., 2018]. Many natural surfaces are superhydrophobic and self-cleaning, such as butterfly wings as well as cabbage leaves [Barthlott and Neinhuis, 1997]. The term *"Lotus Effect"* was named after the Lotus plant leaves *(Nelumbo nucifera)* [Mohamed et al., 2015], represent a well-known water-repellent example. Electron microscopy revealed projecting nubs 20–40 µm apart on the surface of lotus leaves were covered by a waxy-rough crystalloid surface. WCAs ≥ 150 ° and low contact angle hysteresis, are all characteristics of so-called superhydrophobic surfaces. Micro/nano binary roughness in combination with a low surface free energy (SFE) can facilitate such operations [Martines et al., 2005].

Since the initial synthetic ultra-hydrophobic coating was conducted in 1996 [Onda et al., 1996], there have been a slew of new ways to create surface roughness that displays superhydrophobicity. Superhydrophobicity is a technique for ensuring important surface qualities are protected. Creating a hierarchical, rough morphology with low energy molecules is required for the fabrication of superhydrophobicity surfaces [Selim et al., 2017d]. A simple method of dispersing NPs in a hydrophobic polymer matrix followed by surface coating the hydrophobic polymer/NP composite dispersion on a suitable substrate [Ding et al., 2021] was used to fabricate superhydrophobic nano-surfaces in addition to etching, lithography, biomimetic, and stamping processes. Controlled NP structures contribute in the formation of a rough morphology and the establishment of extra superhydrophobic surface capabilities [Gao and Guo, 2017].

Surface roughness and hydrophobicity can be increased not only by increasing the solid–liquid contact, but also by trapping air between the surface and the liquid droplet on a rough surface. The surface water-repellency will be enhanced by trapping of air as it has a WCA of 180° [Ma et al., 2005]). A hierarchical micro-nano structured surface with a low SFE is responsible for superhydrophobicity [Yang and Guo, 2015]. ZnO nanostructures in zero dimensional (0D), 1-dimensional (1D), 2-dimensional (2D), as well as 3-dimensional (3D) dimensions have been described in the literature. Zero-dimension NPs are virtually spherical NPs. Using ZnO particles manufactured by a hydrothermal process, Gao et al. [Gao and Jia, 2015] constructed ultrahydrophobicity on a hierarchical nano-surface by dropping on glass substrates for a thorough experimental technique. To minimize surface energy and roughness, this method used a functional fluoroethylene-vinylether polymer with inorganic ZnO particles. The WCA can range from 135 ° ± 4 ° to 145 ° ± 3 ° and even 152 ° ± 2 ° depending on the reaction medium composition, and the ZnO particles can be formed in various shapes by adjusting reaction medium composition.

Furthermore, "chestnut" ZnO particles were more flexible than 1D nano-ZnO rods, that proved useful large-area grounding. The most prevalent 1D structures include NRs, nano-needles, nanotubes, NWs, and nanocombs. Based on the lotus leaves' chemical nanostructures of lotus leaves. Chakradhar et al. [Chakradhar et al., 2011] used a 155° WCA to make ultrahydrophobic PDMS/nano-ZnO composite surfaces. To produce ZnO nanowires over tin oxide substrate doped with flourine, Pauporte et al. [Pauporte et al., 2011] used a one-step electrochemical technique. The temperature at which ZnO NWs are deposited has been discovered to be a key factor in defining their morphology and structure. The surface non-wettability of a surface treated with stearic acid was changed from hydrophilicity to hydrophobicity (WCA of 168.3°). An in-situ photo-reduction approach can prepare rGO/ZnO nanocomposite for self-cleaning and pollution-removal characteristics were studied [Mandal et al., 2019; Kumbhakar et al, 2018; Wang et al., 2012] (Figure 3). Kumbhakar et al., [Kumbhakar et al, 2018] reported a green fabrication method to produce 2D rGO-ZnO nanocomposites using from zinc acetate and Apple juice for self-cleaning and photocatalytic applications (Figure 3B). The results shows the photo-degradation of methylene blue dye (~91%) within 1h.

The 2D architectures of ZnO including nanosheets, nanoplates, and nanopellets [Chiu et al., 2010]. Li and co-workers [Li et al., 2015] created nano-ZnO sheets on the bamboo-like substrate after utilizing chemical vapour deposition to alter the surface with fluoroalkyl silane. In the acidic rains pH = 3, UV radiation for this newly formed structure displayed good water repellency and superhydrophobicity stability.

Snowflakes, Flower-like, and dandelion, formations and other 3D morphologies of ZnO have been discovered [Polshettiwar et al., 2009; Bitenc and Orel, 2009]. Dai et al. [Dai et al., 2013] developed a 3D hierarchical ZnO film with variable wettability and lotus leaf-like micro/nano patterns. This superhydrophobic surface was created using ZnO micro pillars with a homogenous ZnO coating, which was then followed by the formation of ZnO NRs on the micropillars structure. The highest contact angle after 24 hours of growth is 160 °. Developing ZnO hierarchical micro/nano structures with customizable morphology and surface topologies, as well as programmable wettability, remains a major challenge, despite the fact that there are multiple approaches for creating diverse morphologies of ZnO. The mean length and diameter size of nano-ZnO pillars can be changed in a hydrothermal reaction system by altering the solution concentration, growth time, and reaction temperature, according to Hao et al. [Hao et al., 2015]. Anchored graphene materials are well-defined photo-catalysts that can be used to make outstanding superhydrophobic, self-cleaning, and photocatalytic surface materials. He [He, 2015] developed a low-cost photocatalytic self-cleaning rGO/ZnO nanocomposite film. A trendy and environmentally sustainable trend is to use graphenic nanocomposite as strong fouling-release (FR) surface (Figure 4).

3.2. Antifouling coating surface

In the maritime industry, biofouling is a fast-moving and complex problem [Grant et al., 2022]. Shipping is responsible for over 90% of all global trade. When the friction drag caused by fouling layers rises, the ship's velocity drops. As a result, significant feasting of fuel is required for attaining the desired velocity, resulting in increased travel costs as well as the release of destructive substances into the environment [Jin et al., 2022]. Biofouling has typically been avoided by using leachant anti-fouling coatings, which release toxicants into the maritime environment, killing non-target creatures such as fish and dolphins. As global embargoes and constraints have grown, the usage of biocidal antifouling technologies has spurred the development of environmentally benign alternatives, such as FR technology. Silicone FR paints employ a method that prevents fouling attachments which decrease coating-fouling adhesion strength and improve the fouling-resistance.

PDMS has many advantages over tin-free antifouling paints including non-stick, eco-friendly, non-leaching and a CH_3 group, including ultra-smooth topology, extremely mobile surface, and reduced surface tension [Selim et al., 2018c]. Thermally stable, anti-oxidant, anti-ozone, and UV resistant, PDMS is a great choice for a variety of applications. Although silicone paints already have good FR capabilities, inorganic boosting nano-additives are now required for better mechanical and FR performance. Inorganic–organic interactions can boost FR surface self-cleaning capabilities and performance by developing ultra-water-repellent surfaces with low SFE. Because of its remarkable chemical, optical, electrical, mechanical, and surface characteristics, metal oxide-based materials have been used in a variety of applications, including superhydrophobic FR coatings [Selim et al., 2018d; 2018e].

The latest trend in eco-friendly, self-cleaning coatings is non-toxic FR nanocomposite coatings for vessel bottoms and the shipping sector. Biocompatibility, economics, corrosion resistance, and environmental safety are all exceptional features of graphene materials. Droplets of water pick up and eliminate dust, viruses, and bacteria as they come into contact with a surface. Self-cleaning is the term for this process. Superhydrophobic characteristics in marine coatings are advantageous for better antibacterial and anti-biofouling performance [Bressy et al., 2022].

The surface's weakness, which can be mechanically abraded, removes the coating's self-cleaning properties due to roughness degradation and layer removal, is a major challenge. PDMS is often used to make superhydrophobic coatings. The introduction of various surface textures on PDMS with different textured materials, such as porous, hierarchical structure, or microsized repetitive pillars, creates an ideal blend of chemical functionality and topological homogeneity to prepare superhydrophobic surfaces. When expressing superhydrophobicity and self-cleaning properties, many FR techniques yield good results, but their scalability, robustness, or cost limit their industrial application potential. In this case, it is possible to build long-lasting, low-cost superhydrophobic FR and protective coatings. A superhydrophobic coating on multiple substrates was designed using PDMS to modify the synthesized MWCNTs/ZnO nanocomposites prepared via the sol-gel method (Figure 5A) [Barthwal et al., 2020]. The engineered PDMS-MWCNTs/ZnO nanocomposite has superior superhydrophobic features with a water contact angle of 156°. The PDMS-MWCNTs/ZnO nanocomposite coating provides excellent anti-fouling and self-cleaning properties, as well as the ability to separate oil-water mixtures through a copper mesh coated with the prepared nanocomposite.

Mechanical stability, FR self-cleaning, and barrier qualities useful for maritime coatings were predicted in organic/inorganic hybrid concept materials with dual-scale roughness [Padmavathi et al., 2021]. A composite material for FR coatings with low free energy and superhydrophobicity based on PDMS loaded with ZnO NRs was reported (Figure 5B) [Selim et al., 2019d]. The filmed surface was applied on steel surface for micro/nanostructured non-wettable (WCA 158°) by dispersing 0.5 wt.% of ZnO NR fillers. The nanofillers exhibit stable surface at different pH values. Field experiments have shown that the silicone enriched with 0.5 wt.% ZnO NRs exhibits a high FR effectiveness when compared to the virgin silicone surface [Selim et al., 2019d]. The findings were confirmed during a 180-day field test in seawater. To generate an increased ultrahydrophobic nano-surface, scientists employed a nanocomposite of PDMS with vinyl terminals and Fe_3O_4 nanospheres. A series of efficient PDMS/ZnO@SiO_2 hybrid composite was developed via the in-situ method for maritime navigation [Selim et al., 2017e] (Figure 6).

3.3. anticorrosion surfaces

The severe environmental and economic consequences of metallic corrosion prompted the development of anticorrosion materials [Ammar et al., 2017; Shaban et al., 2021]. Superhydrophobic nanostructured coatings could be used for a number of anticorrosion applications. Because of their wide-range of applications, steel surface protection during service operations is inevitable.

Anticorroion performance of organic/inorganic nanocomposite coatings can extend the protect steel constructions for long times. Surface roughness and reduced free energy are characteristics of anticorrosion PDMS-based nano-coatings with surface superhydrophobicity (WCA >150° and CA hysteresis <10 [Qing et al., 2015; Arukalam et al., 2018]. By providing corrosion resistance and preventing adhesive failure, PDMS functions as a corrosion-resistant layer. It prevents blisters from forming and creates a barrier for corrosive ions. It has a higher electrical resistance and acts as a corrosion inhibitor by restricting the flow of external current between the anodes and cathodes [Yilgör and Yilgör, 2014].

Surface stability is a problem with most thin organic corrosion prevention coatings [Ejenstam et al., 2015]. Corrosion-resistance and water-repellent surfaces can be developed using organic–inorganic nanocomposite [Selim et al., 2019e]. It is advantageous to build corrosion-resistant coatings using nano-ZnO fillers. Coatings with exceptional barrier qualities can be made using a graphene nanosheet-like structure [Othman et al., 2019]. To avoid closely packed GO structures, GO nanosheets can be decorated with nano-metal oxide particles [McAllister et al., 2007; Gutierrez-Gonzalez et al., 2015]. 1D metal oxide NPs, notably NRs, have been used to anchor graphene materials by researchers [Selim et al., 2019e]. Water-repellency of PDMS/GO-TiO_2-diatomaceous earth hybrid nanocomposite surface achieved surface durability and 96.7% corrosion inhibition [Nine et al., 2015]. NRs of ZnO exhibit large surface area as well as water-repellent characteristics [Wang et al., 2019]. A ternary composite of silicone resin filled with GO-ZnO exhibited corrosion-protection and ultrahydrophobic surface [Selim et al., 2021] (Figure 7). To create GO nanosheets with a thickness of 2 nm, a modified Hummers' method was employed.

Nano-ZnO rods with 40 nm mean diameter and a prominent exposed crystal facet of [0001] were manufactured using a controlled hydrothermal methodology. A chemical bath deposition process was used to make a GO-ZnO hybrid nanofiller with precise size and morphology. To analyze such nanocomposites' corrosion barrier characteristics, they were exposed to a 3.5% NaCl solution on the surface. According to Tafel polarization and EIS investigations, the addition of the nanofiller improved the coating's corrosion protection. The maximum impedance value is found in the ternary nanocomposite coating of silicone resin enriched with 1 wt.% of GO-ZnO fillers. The PDMS coating system has been improved by 1 wt.%. The anticorrosion of GO-ZnO hybrid fillers were also demonstrated. The exceptional corrosion resistance was attributed to the efficient dispersion of the graphene-based nanocomposite.

3.4. Perovskite Solar Cells (PSCs)

PSCs research has advanced significantly in the previous decade [Green et al., 2014; Nogay et al., 2019]. PSCs are divided into two categories, depending on the device architecture meso-superstructured and planar heterojunction solar cells [Ball et al., 2013]. TCO/hole transport layer/perovskite absorber/PC61BM/cathode inverted structure revealed great commercialization prospects for planar PSCs [You et al., 2014]. This is due to the low-temperature processing, ease of use, high PCE, and large-scale manufacturing capacity. Their electrical properties are greatly influenced by charge injection and extraction at the cathode contact [Elseman et al., 2020]. When a barrier still remains between the interfacial contact between the Fermi level of certain electrode metals and the lowest unoccupied molecular orbital of organic material (PCBM) in organic optoelectronic devices, however, electron injection and extraction are poorer [Yip et al. 2008]. The interfacial contact between PCBM layer and metal electrode can reduce electronic extraction and injection.

PSCs can be made more efficient using interfacial materials. The interfacial engineering of PSCs has received more attention as a result of this paradigm. PSC interfacial engineering has gotten a lot more attention as a result of this methodology. Because of its wide band gap semiconductor and high electron mobility, ZnO is widely used as a hole blocking layer and electron transport in modern photovoltaics [Wang et al., 2018]. Nano-ZnO is a suitable option for interfacial engineering as a CBL [Liang et al., 2012] because of its exceptional material stability and charge carrier extraction efficiency.

In terms of nanostructures, shape, modification of surface, and composite hybrid, the performance of ZnO (employed as CBLs in polymeric resin and organic solar cells) has been investigated [Liang et al., 2013]. The influences of ZnO geometric structures on the solar cells' photovoltaic efficiency has been investigated. The NR shape of ZnO is an excellent morphology for making photovoltaic instrument because it increases the active area of the solar cell while lowering electrical losses. Nano-ZnO seed layer serves as a hole barrier, preventing recombination at the cathode, while ZnO-NRs facilitate electron collection and transmission [Wang et al., 2010]. Changes in the crystallinity of the seed layer have no effect on ZnO-NR growth since it happens exclusively in the [002] plane. The NR shape, [002] orientation, reduced size, and enhanced solar cell hole blocking layer are all benefits of the NR form.

Jia et al. [Jia et al., 2016] reported a ZnO-based solar cell surface device using (poly[(9,9-bis(3′-(N,N-dimethylamion)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyl)-fluorene)-alt-2,7-(9,9-diocty). The device's efficiency was considerably increased as a result of more selective electron extraction. Between the PCBM layer and Ag electrode, Zhu et al. [Zhu et al., 2019] employed a ZnO/TIPD film to improve inverted PSCs. In the ambient atmosphere, PCBM/ZnO/TIPD PSCs have a PCE and stability of 13.7%, which is greater than ZnO:TIPD or bare PCBM-based PSCs. For inverted PSCs with excellent power conversion efficiency (PCE), advanced cathode buffer layers (CBLs) based on ZnO [Selim et al., 2020c] were developed (Figure 8). After combining with bathocuproine (BCP), a controlled hydrothermal technique can be used to produce nano-ZnO rods with a mean diameter of 40 nm. Planar PSCs (p − i − n) with a device structure of (indium tin oxide /PEDOT:PSS/CH3NH3PbI3xClx/PC61BM/CBLs/Ag) were fabricated using the produced composite ZnO-NRs/BCP as a basis. The produced PSC composite exhibited 18.13% PCE and longer term stability as compared with single-layer BCP (15.17%) or NRs of ZnO (16.55%) devices. The Narayanan group [Narayanan and Annamalai, 2016] created ZnO-NRs on microslide glass substrates with 150-450 nm mean size.

3.5. Antibacterial active agents

Controlled NPs hold a lot of promise in biological and health-related domains because of their non-toxicity and biocompatibility [Hatamie et al., 2015]. NPs of ZnO, in particular, are antimicrobial and can deform and destroy bacterial cell membranes, causing intracellular material leaks and, eventually, bacterial cell passing. ZnO NPs could be used to preserve crops and food, according to these studies [Liu et al., 2009].

The antibacterial effectiveness of ZnO NPs in controlling *Rothia secludes* in biofilm formation was established in biofilm growth experiments on polystyrene plates [Khan et al., 2014]. The ciprofloxacin's bacterial resistance could be improved by enriching with ZnO NPs against *S. aureus E. coli.* The notion that the particles interfere with NorA protein pumping could explain the enhanced activity of *S. aureus* in the presence of ZnO NPs [Banoee et al., 2010]. ZnO's antibacterial mobility may be influenced by the size and closeness of regular white light. Preliminary research found that the smaller the molecule size, the more effective it is at preventing microbial growth. Furthermore, the author speculated that ZnO surface coatings exhibit high antibacterial activity against different microoragisms [Jones et al., 2008]. ZnO sensitivity was higher in gram-positive bacteria than in gram-negative bacteria. Manufactured ZnO was also tested for antibacterial action against a variety of pathogens, including foodborne illnesses. The antibacterial activity of the synthesized ZnO toward *S. aureus* and Salmonella typhimurium [Tayel et al., 2011].

ZnO NPs can also be used in antibacterial coating materials to prevent microorganisms from forming biofilms by connecting, colonising, diffusing, and shaping them. A comparable study between the antibacterial actions of ZnO NRs and SiC NWs with varied diameter sizes, crystal orientation, and topological surface was investigated by Askar et al. [Askar et al.,2021]. Both materials have high aspect ratio, surface area, and active centers to microbes. ZnO NRs had better antibacterial performance than SiC NWs based on MIC, immunomodulatory effect, and inhibitory zone. ZnO NRs outperformed SiC NWs in killing pathogenic bacteria, morphological disorder, and cellular membrane damage, as revealed by scanning microscopic and confocal laser captures. Electrostatic interaction between the negative bacterial surfaces and positive Zn^{+2} ions causes ZnO NRs to have a strong bacterial-resistance capability (Figure 9). Gram-positive bacterial strains are more susceptible to ZnO NRs-induced microbial suppression than Gram-negative organisms because of their outer membrane proteins which protect them from cytotoxicity. ZnO NRs-based fabrics were also used to demonstrate wearable detection and antibacterial control without the use of an antiperspirant [Hatamie et al., 2015].

3.5.1. ZnO with other metals.

Bacterial-resistant inorganic nanomaterials are widely used against various microbial strains for various biological applications. When ZnO is coupled with other metals, it has antibacterial properties (Table 1). Inorganic antibiotic NPs are useful for a variety of antibacterial industrial fields. Mg/ZnO and Sb/ZnO nanocrystals have been shown to have antibacterial action toward *S. aureus*, *E. coli,* and *Aspergillus niger*. The antibacterial performance of ZnO doped with other NPs was previously reported. After irradiation, ZnO doped with Sb increased from 12% in the dark to 93.4 percent after irradiation. Mg and Sb impregnated NPs demonstrated good bactericidal potencies at a 1:10 ratio, particularly against *S. aureu and E. coli* making them ideal antimicrobial nano-agent [Zhang et al., 2011]. The antibacterial activities of ZnO paired with Mn ions produce a stable and long-term performance [Jones et al., 2008; Ravichandran et al., 2014]. Undoped and Mn-doped ZnO NPs, as well as fluorine doped ZnO exhibited high antibacterial activity against *P. aeruginosa* [Rajendar et al., 2016; Ravichandran et al., 2015]. Also, ZnO doped with Pd (5 mol%) composites showed enhanced the antibacterial activity (64.07%) aaginst *E. coli*. On the other hand, while low Pd concentration of 1 mol% demonstrated the highest antibacterial activity (76.43%) toward *P. aeruginosa* [Cruz-Reyes et al., 2015]. Nano-ZnO doped with Ag are effective anti-infection agents and can be employed to manufacture biomedical devices. Also, polymer-Ag-ZnO nanostructured composite represents high antibacterial action for biomedical applications [Michael et al., 2014]. Also, Nd-doped ZnO nanomaterial exhibited high antimicrobial performance [Vijayaprasath et al., 2015].

3.5.2. Synthetic polymer/ZnO composite

Despite the fact that synthetic polymers are widely used in the pharmaceutical, culinary, textile, and other industries, they lack antibacterial characteristics. Polymer composites incorporating ZnO must be researched because materials with antibacterial characteristics on the exterior are needed for improved applications. Antibacterial characteristics of ZnO/polymer composites are summarized in Table 2. Because ZnO NPs operate as nucleating agents, and increasing their loading enhances crystallization temperature and crystallinity, the resulting composite exhibits superior crystalline behavior when combined with poly (phenylene sulphide). They also demonstrated dynamic suppression of various bacterial strains as the ZnO concentration increased. The ZnO nanostructured composites have the potential to be used in medicine and dentistry as lightweight, high-performance materials.

The inclusion of excellent-distributed ZnO NPs within a sunflower oil (SFO)-derived highly branched alkyd matrix has been shown to improve the cellular cytotoxicity and anticorrosive characteristics of composites for surface coatings [Selim et al., 2017f] (Figure 10). The cellular toxicity of mouse L929 fibroblast and MG-63 human osteoblast cells was assessed using the MTT test after 24 hours. Even at greater fillers' percentages, the MTT assay revealed that the nanocomposites generated are non-toxic to cell lines.

In polymer composites for surface coating, ZnO has been proposed as effective antibacterial active materials [Schwartz et al., 2012]. Hyperbranched polyurethane urea–ZnO hybrid coatings also increased antifungal capabilities (*Aspergillus flavus*) [Jena et al., 2012]. High density polyethylene/ZnO composite exhibited high antibacterial performance against *E. coli* and *S. aureus* [Li et al., 2010]. Poly(ether ether ketone) enriched with ZnO NPs (0.5 wt.%) exhibited dynamic improvement, flame-retardant capability, and antibacterial performance. toward *S. aureus and E. coli* bacterial strains [Frederickson et al., 2005]. Doumbia et al. [Doumbia et al., 2015] exhibited a high antibacterial activity of polylactide resin filled with ZnO (3 wt.%) fillers.

Polylactide/ZnO/copper chlorophyll acid exhibits a 99.9% antibacterial activity against *E. coli*, with no noticeable loss in antibacterial efficacy during tolylene diisocyanate growth. This shows that the polylactide/ZnO/copper chlorophyll acid /tolylene diisocyanate combination kills *E. coli* 99% of the time [Fan et al., 2015]. The biocidal effect of ZnO-polyvinyl alcohol has been linked to particle size variations in pure ZnO. Polyvinyl chloride/ZnO composite exhibited high antibacterial activity against *S. aureus* and *E. coli* and growth [Li et al., 2009]. Low density polyethyelene/Ag/ZnO exhibited high antibacterial performance for food packaging applications [Emamifar et al., 2012]. The biological activity of Ag-based compounds has been shown to be extended by ZnO. In both the presence and absence of light, the hydroxyapatite/ZnO hybrid nanocomposite demonstrated good bioactivity and high antibacterial performance against 95.65% for *E. coli* (95.65%) and with *S. aureus* (99.45%) [Zhou et al., 2008]. A nanocomposite of hydroxyapatite/ZnO [Saha et al., 2020] induces a shift in microorganisms' static/bactericidal property. The calcium phosphate additive to the previous nanocomposite could alter the hardness and break toughness slightly when compared to pure Hydroxyapatite. According to the study, a hyperbranched-ZnO composite containing 5 weight percent ZnO was able to attain extreme densification and hardness.

4. Conclusions

Due to their unique structure and physicochemical properties, ZnO nanomaterials have shown considerable promise in surface and biological applications. Recent studies reported that the majority of research on metal oxide-based polymeric nanostructured composites exhibited various surface and biological applications. ZnO NPs' dispersion in the polymer resin improve the chemical, physical, and antibacterial properties. ZnO added to a variety of polymer matrices would boost modulus and strength considerably. ZnO has emerged as a new green broad-spectrum antibacterial agent with low bacterial resistance and sustained release properties. The fundamental functions of size- and shape-controlled hybrid nanocomposites have been introduced for various ZnO applications. In addition, ZnO's chemical variety provides the polymer with distinct characteristics. Surface, electrical, physico-mechanical, thermal, sensing, energy storage, and fuel cell features of ZnO/polymer composites are improved by well-distribution of ZnO nanofillers. Nanotechnology as a whole will be transformed by these prospective nanocomposites, which will have uses in electrical, mechanical, and chemical fields. Each example also contains remedies/proposals for overcoming hurdles and suturing extremely efficient ZnO nanocomposites. The final features are strongly influenced by the polymer/ZnO interfacial contact which can improve the mechanical, physical, and biological characteristics. ZnO nanofillers' distribution is controlled during the manufacturing process, which affects reinforcing and, as a result, material properties. The cytotoxic effect on mammalian cells has also been investigated in recent years. Electrostatic interaction with the bacterial cells, oxidative stress, and cell entrapment are all well-known mechanisms for ZnO bacterial resistance. The necessary processes must be followed when using the appropriate reaction media, dissolution medium, polymer molecular weight, ZnO architecture, and desired output. The effect of structurally folded ZnO nanoagents tectonics, polymer nanocomposites, and building blocks on the production of exceptional antibacterial surface coatings is discussed in this chapter. Because of the functional groups in ZnO, the surface charge can be decreased even at low concentrations. This improves filler-polymer compatibility, resulting in composites with outstanding dielectric properties. The surface and biological percolation concentration displays efficient distribution of ZnO NPs with non-toxic and light-weight structure in various industry. As a result, many additional studies must be conducted in order to industrialize ZnO/polymer nanocomposites for human applications. This chapter will provide many inspirations to the researchers in the field of material science, chemistry, physics, biology, and engineering. It will promote both academic and industrial research on various ZnO applications.

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Figures

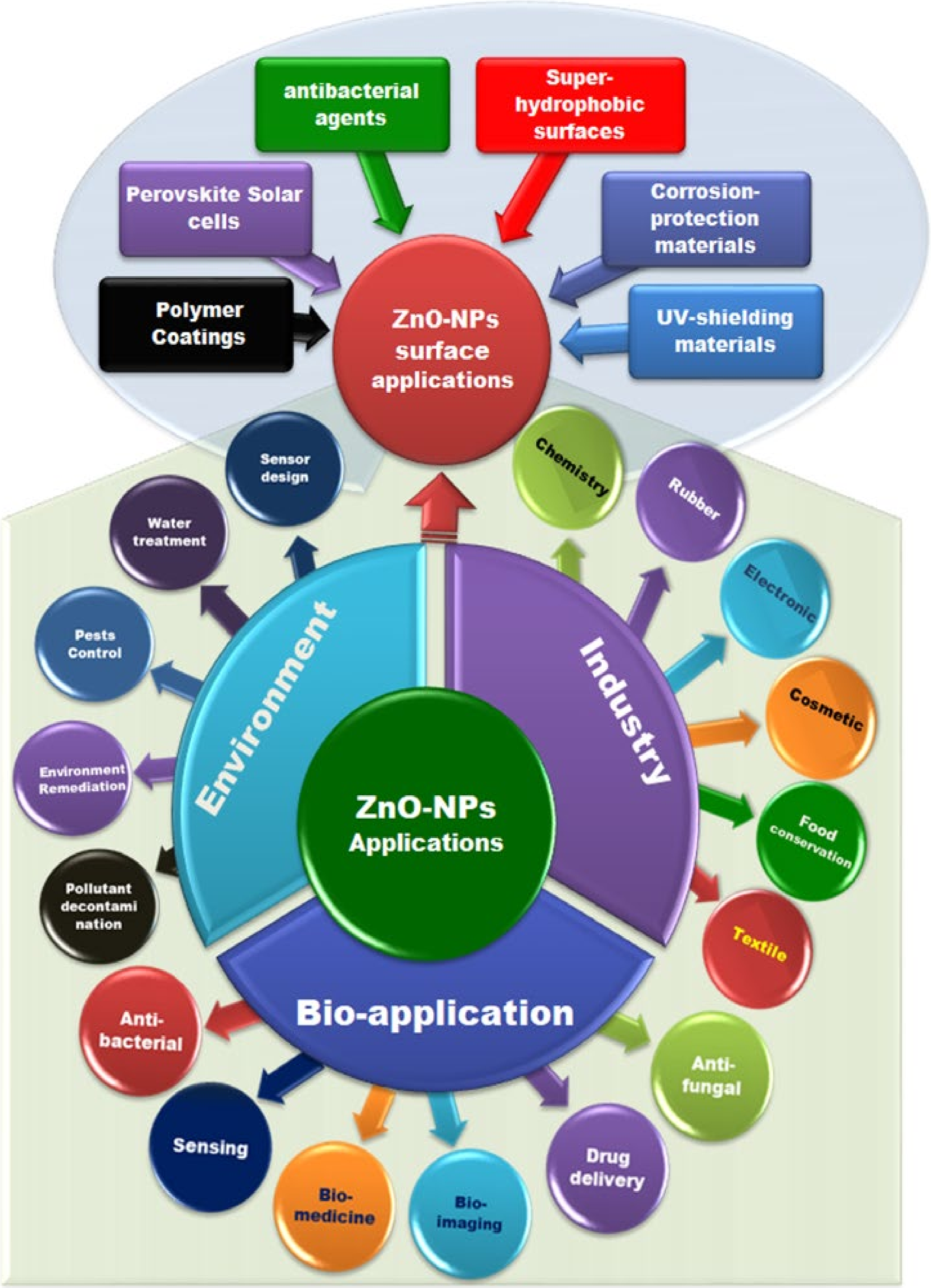

Figure 1: ZnO NPs in various applications including environment, industry and bioapplications, as well as specific use of ZnO-NPs the surface fields.

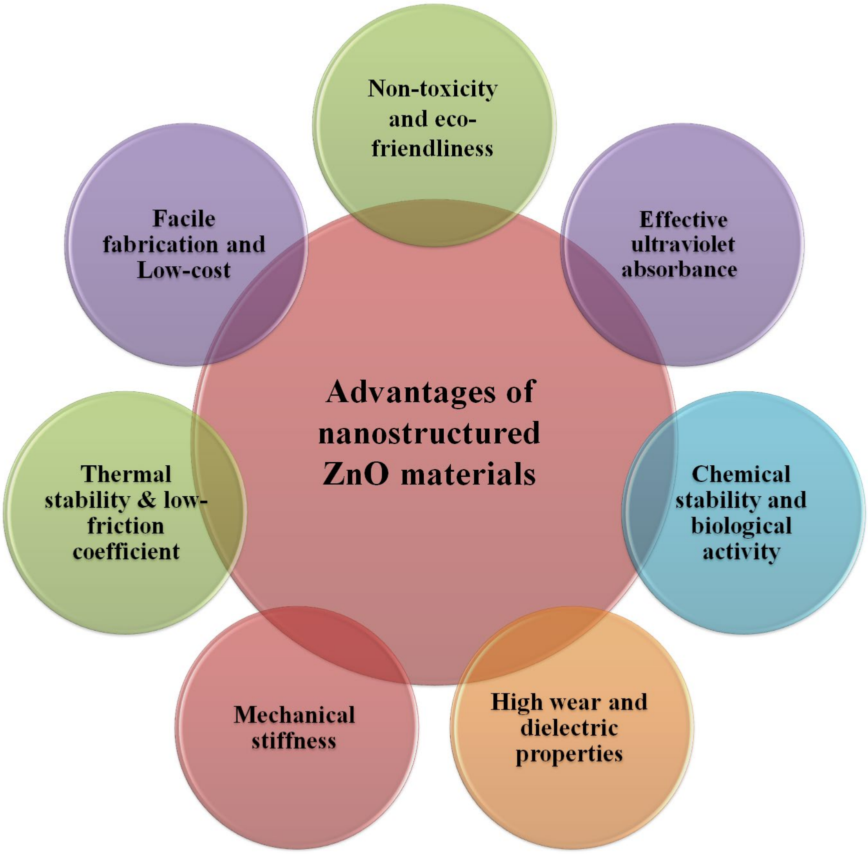

Figure 2: Chemical, Physical, and biological advantages of the ZnO nanostructured materials.

Figure 3: Self-assembly and photocatalytic production of rGO/ZnO hybrid nanocomposite for dye removal. (A) photocatalytic ZnO/rGO nanocomposite for toxic dyes degradation [Mandal et al., 2012]; Copyright © 2018 Elsevier B.V. All rights reserved, (B) photocatalytic degradation of Rhodamine B [Wang et al., 2012]; Copyright 2012, with ACS permission, and (C) rGO/ZnO hybrid photocatalyst nanocomposite synthesized from zinc acetate and Apple juice for self-cleaning and photo-degradation of methylene blue dye [Kumbhakar et al, 2018] Copyright © 2018 Elsevier B.V. All rights reserved.

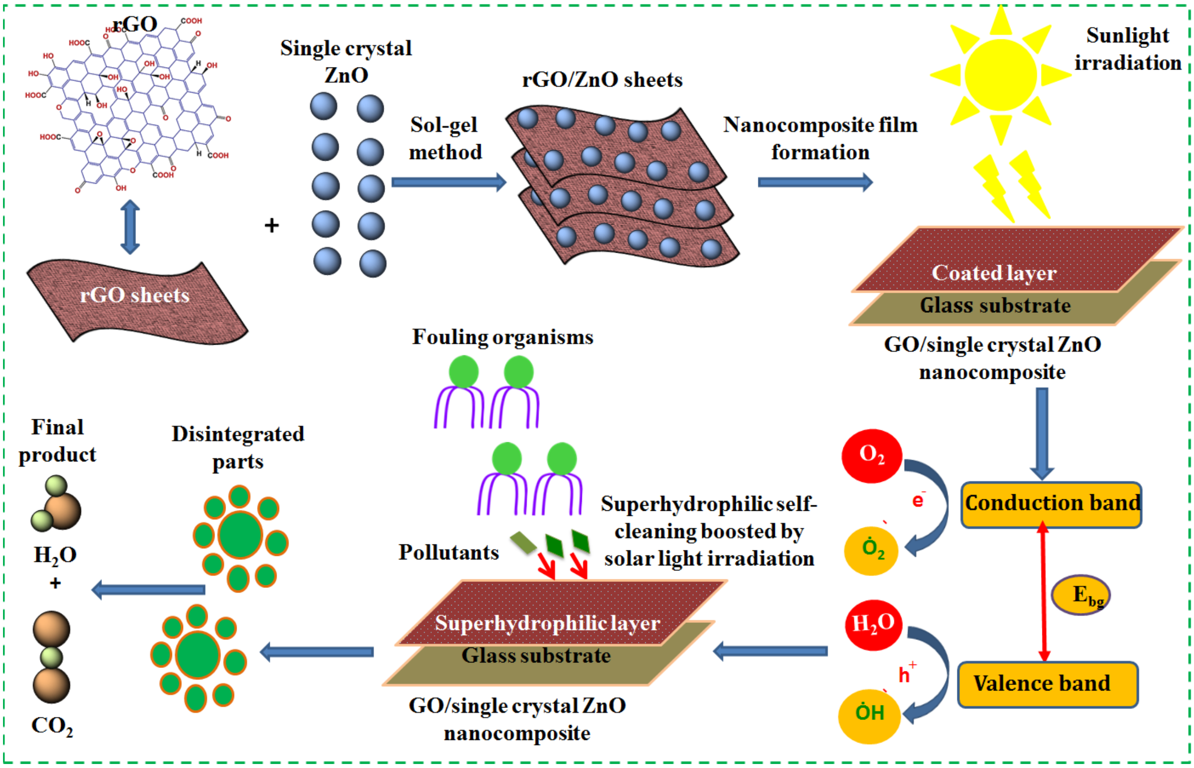

Figure 4: A single-phase method was employed to develop rGO/ZnO hybrid composite coated on a glassy surface and subjected to UV-Vis irradiation for photocatalytic self-cleaning application. It produced a pollutant-repellant and FR nanosurface. Solar light may fragment soil, which can then be transformed to CO_2 and H_2O [He, 2015]. In 2015, the copyright was granted by Elsevier Ltd.

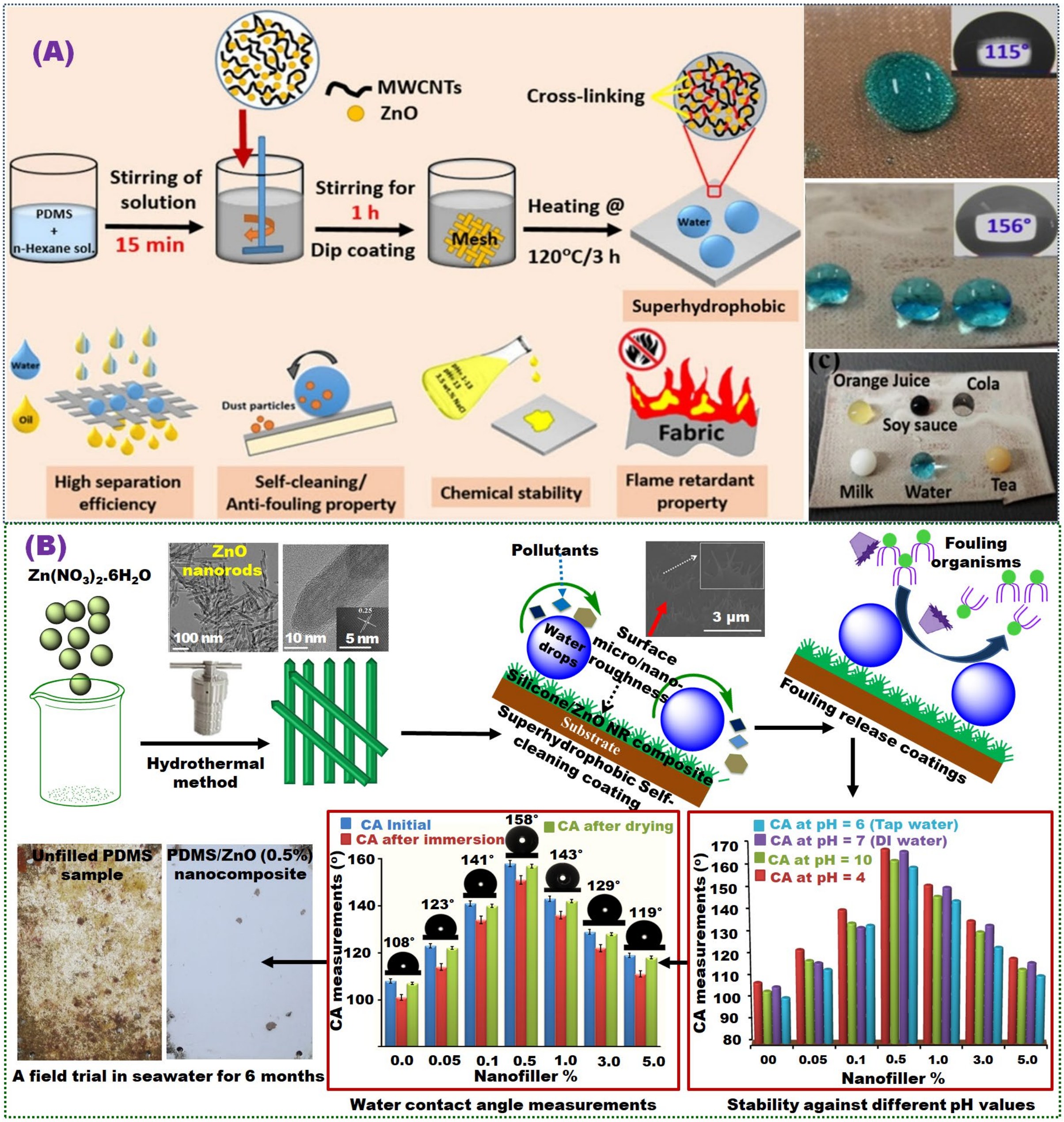

Figure 5: (A) A superhydrophobic coating of PDMS modified MWCNTs/ZnO nanocomposites designed on different substrates for various applications [Barthwal et al., 2020]; Copyright © 2020 Elsevier B.V. All rights reserved. PDMS/ZnO NR composite (B) Schematic design of PDMS/ZnO nano-composite surface manufactured using a hydrothermal and annealing technique for marine FR coating tested at different pH values and nanofiller content [Selim et al., 2019d]; Copyright 2019, produced after Elsevier Ltd permission.

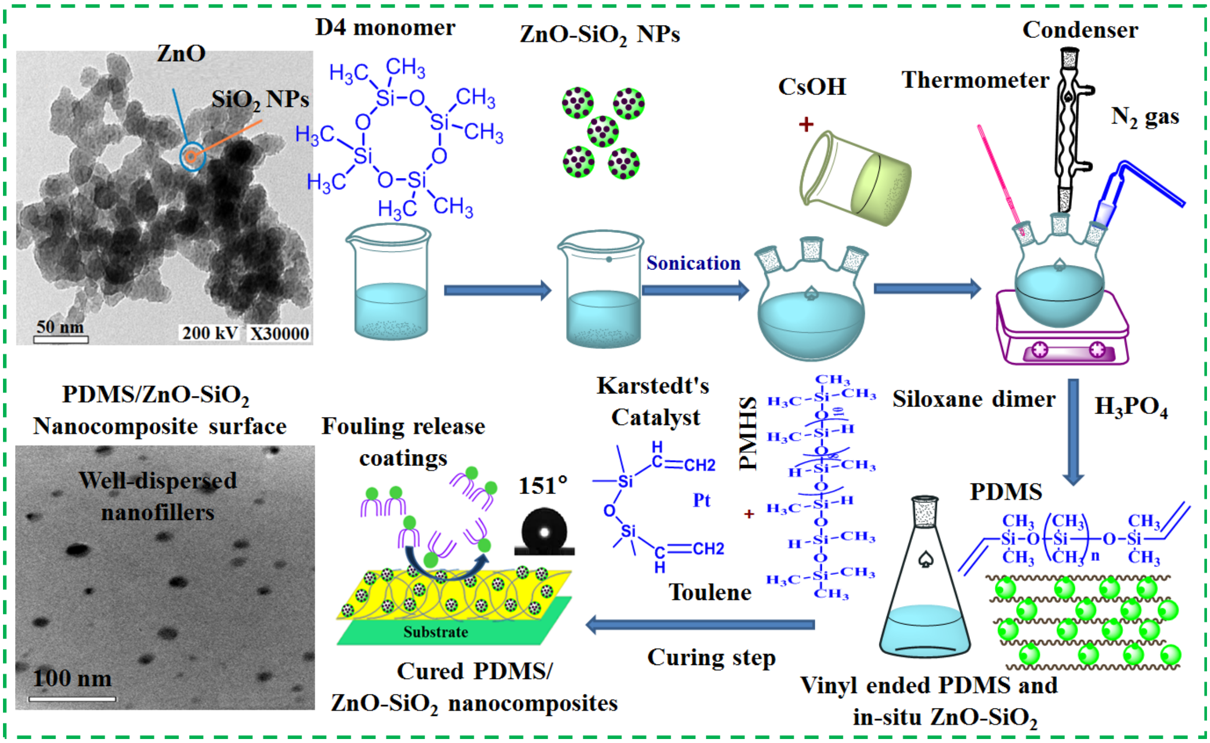

Figure 6: Engineering of silicone/ZnO-SiO_2 composite film via in-situ method and hydrosilation curing technique. The TEM image of ZnO-SiO_2 nanofiller and SEM of silicone resin enriched with this nanofillers were illustrated [Selim et al., 2017e]. Copyright 2017; reprinted with Elsevier's permission.

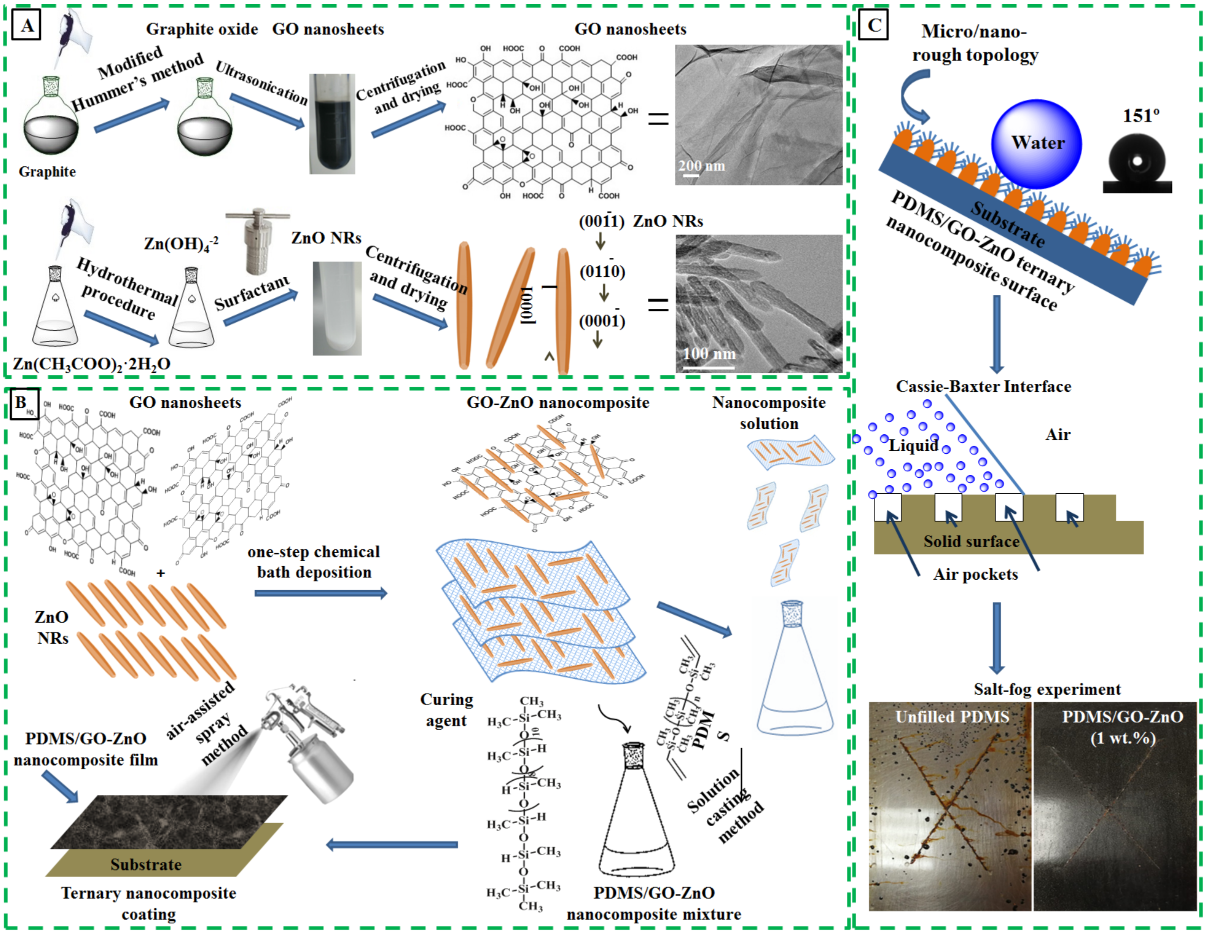

Figure 7: (A) A modified Hummers' procedure and a surfactant-assisted hydrothermal method are used to synthesise GO nanosheets and ZnO NRs. (B) Chemical bath deposition methodology to prepare GO-ZnO nanofillers which were dispersed in the silicone matrix to produce ternary surface which is explained by the Cassie-Baxter approach for water-repellency [Selim et al., 2021]. Copyright 2021, reprinted with Elsevier's permission.

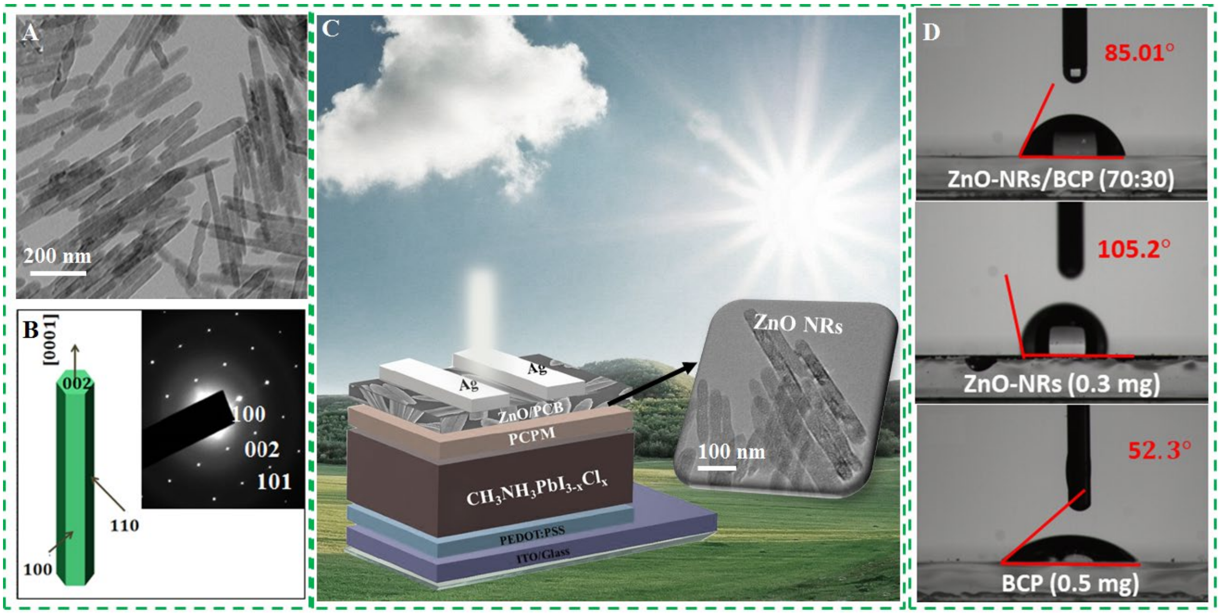

Figure 8: (A) ZnO NRs' TEM capture; (B) schematic illustration as well as SAED results for ZnO-NRs; (C) schematic illustration of ITO/PEDOT:PSS/$CH_3NH_3PbI_3xClx/PC_{61}BM$/CBLs/Ag surface. (D) represents WCAs of ZnO NRs/BCP, ZnO NRs as well as BCP thin-films [Selim et al., 2020c]. Copyright 2020, with permission from the ACS.

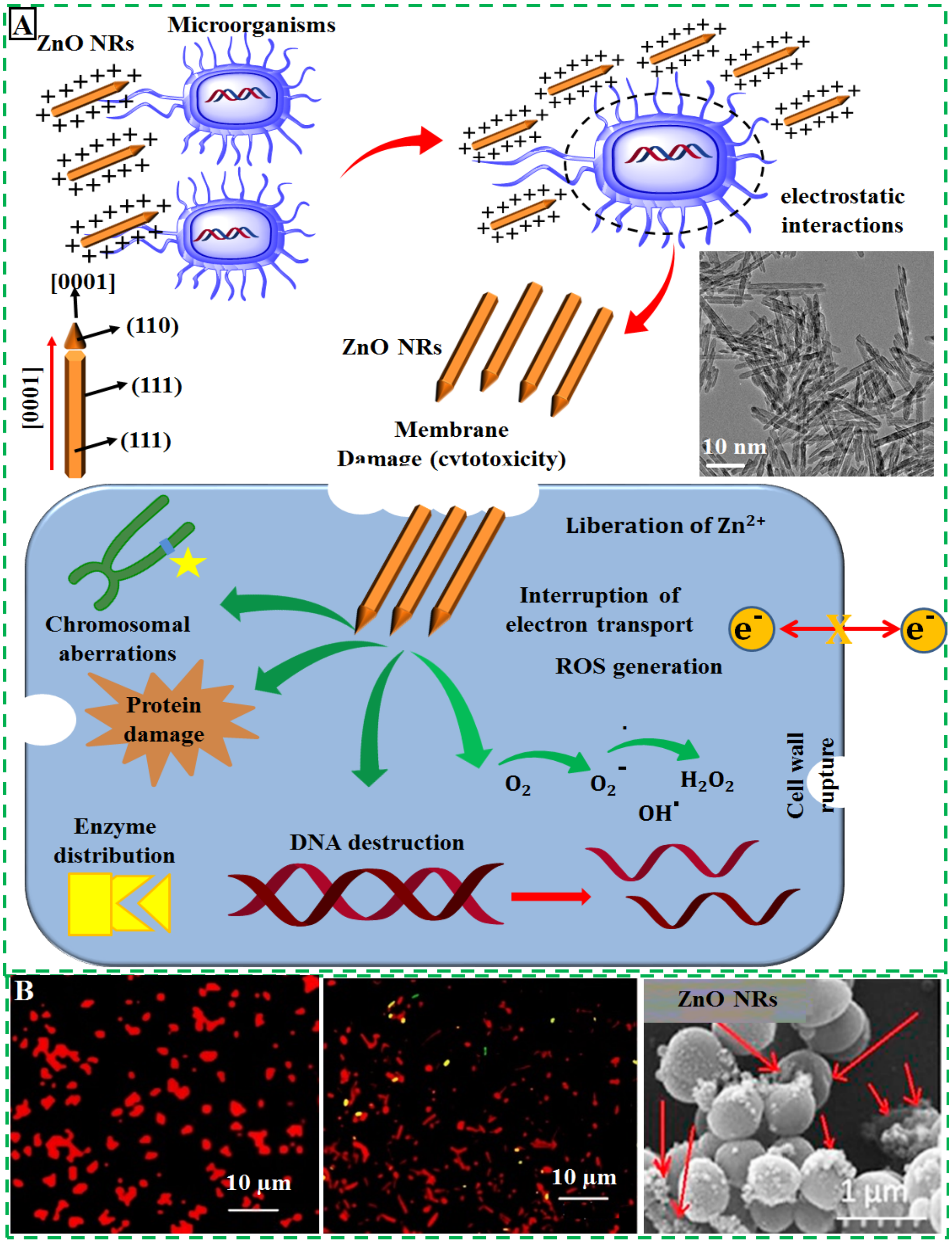

Figure 9: (A) Illustration of ZnO NRs' antibacterial mechanism against diverse bacterial organisms, showing the interaction between bacterial surface and ZnO NRs. This can destroy DNA and cause cellular-wall destruction, cell cytotoxicity, and microbial death. ZnO NRs' TEM pictures is included herein. (B) ZnO NRs confocal images versus S. aureus and E. coli specimens and SEM of S. aureus after treatment with NRs [Askar et al., 2021]. Copyright 2021, produced with Elsevier's permission.

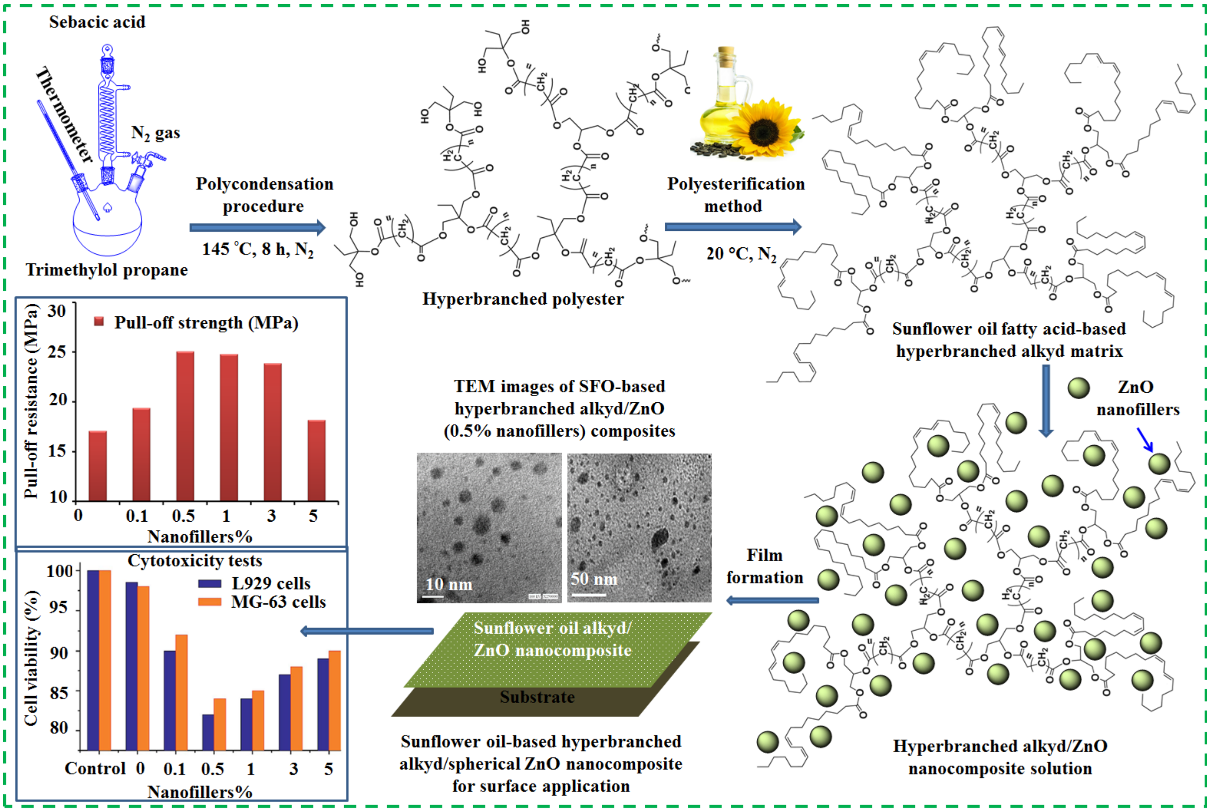

Figure 10: (A) representation of SFO-derived highly branched alkyd synthesized using A2+B3 technique from prepared polyester and SFO; (B) schematic of the hydroxyl-terminated hyperbranched polyester synthesised using the A2+B3 methodology. At a low concentration, (G) and (H) Alkyd/ZnO nanocomposite's TEM picture with well-distributed nanofillers. L929 and MG-63 cells were used in an MTT assay to assess the Cellular toxicity. Mechanical durability was assessed using a pull-off test for virgin and alkyd/ZnO nanocomposites [Selim et al., 2017f]. Copyright 2017, produced with Elsevier's permission.

Tables:

Table 13: ZnO's antibacterial properties when combined with other metals.

Materials	Applications	Microorganisms	References
NRs of ZnO	Food safety and agriculture	*E. coli*	Li et al., 2009
NRs of ZnO	Formation of anti-biofilm	*R. dentocariosa* and *R. mucilaginosa*	Khan et al., 2014
Ciprofloxacin with ZnO	Resistance to antibiotics	*E. coli* and S. aureus	Banoee et al., 2010
NRs of ZnO	Diseases that are contagious	*S. aureus*	Jones et al., 2008
ZnO NPs	Food preservation	*S. typhimurium* and S. aureus	Tayel et al., 2011
ZnO	Applications in textiles	*E. coli*	Hatamie et al., 2015
Mg-doped ZnO	Several uses	*E. coli*, *S. aureus*, *Saccharomyces* and *Aspergillus niger*	Zhang et al., 2011
ZnO:Mn	Biomedicine	*P. aeruginosa* and *E. coli*	Ravichandran et al., 2014; Rajendar et al., 2016
ZnO:Mn:F	Biomedicine	*B. subtilis*	Ravichandran et al., 2015
Pd doped ZnO	Healthcare establishments	*P. aeruginosa* and *E. coli*	Cruz-Reyes et al., 2015
Ag doped ZnO	Biomedical equipment	*S. aureus and E. coli*	Michael et al., 2014
Nd doped ZnO	Biomedicine	*Pseudomonas aeruginosa* and *Streptococcus mutans*	Vijayaprasath et al., 2015

Table 2: ZnO's antibacterial properties when combined with polymers.

Materials	Applications	**Microorganisms**	**Ref.**
Poly(N - isopropylacrylamide) /ZnO composite	Implants in the Orthopaedics	*Staphylococcus epidermidis and S. aureus*	Selim et al., 2017f
ZnO/Hyperbranched polyurethane-urea	Antimicrobial substances	*E. coli* and *S. aureus*	Schwartz et al., 2012
High-density polyethylene/ZnO composite	Materials for photodegradation	*E. coli* and *S. aureus*	Jena et al., 2012
Poly(ether ether ketone/ZnO composite	*Spina, Trauma, and orthopedics, and*	*E. coli* and *S. aureus*	Li et al., 2020
Poly(lactic acid)/ZnO/copper chlorophyll acid	Applications in textiles	*E. coli*	Doumbia et al., 2015
ZnO coated polyvinylchloride surface	Packaging of food	*E. coli, S. aureus, Penicillium citrinum, Aspergillus flavus*	Fan et al., 2015
Low-density polyethylene/Ag/ZnO film	Materials for packing	*Food pathogens*	Li et al., 2009
Nanohydroxyapatite/ZnO complex	Applications in food packaging	*E. coli* and *S. aureus*	Emamifar et al., 2012
Hydroxyapatite/ZnO composite	Implantation of bone	*E. coli, S. aureus, and S. epidermidis*	Zhou et al., 2008
Ethylene diamine tetra acetic acid/sulfated β-cyclodextrin/cotton fabric/ZnO composite	Implantation of bone	*S. aureus* and *E. coli*	Saha et al., 2010
ZnO- incorporated NR latex foam	Applications in textiles	*S. aureus* and *E. coli*	Rathnayake et al. 2014
Brown seaweed Padina tetrastromatica- ZnO	Materials that are antibacterial	*S. aureus* and *E. coli*	Pandimurugan et al., 2014
ZnO and bacterial cellulose composites	Applications in food packaging	*S. aureus* and *E. coli*	Janpetch et al., 2016