UNIQUE POLYMER POLY(N-ISOPROPYLACRYLAMIDE) AND RARE EARTH METAL IONS WITH ZINC OXIDE AND SILVER NANOPARTICLES -SYNERGIC EFFECTS

Basil Baby[1], Maya Devi.S[2], R. Ganesh[3],R.Sivakumar[4]

[1]Research scholar, Research and Development Center, Bharathiar University, Coimbatore-641046.

[2]Assistant Professor, Department of Chemistry, NSS College of Engineering, Palakkad- 678008, Kerala, Mail: mayadevi968@gmail.com,

[3] Assistant Professor Department Computer Science and Engineering - Artificial intelligence and Machine learning, Institute of Aeronautical Engineering (IARE) ,Dundigal, Hydrabad -500043, Telangana, India

[4] Professor, Computer Science and Engineering, Ahalia School of Engineering, Palakkad-678557

Abstract

Poly(N-isopropylacrylamide) (PNIPAM) is a temperature-responsive polymer that has garnered significant interest in various biomedical and industrial applications. This review focuses on the synergistic effects of incorporating zinc oxide (ZnO) and silver nanoparticles (AgNPs), with PNIPAM.Rare earth metal ions (such as Gd, Ce, La, Nd, Dy, and Eu) along withzinc oxide (ZnO) and silver nanoparticles (AgNPs),to enhance the biological and chemical properties of the resulting composites.

Introduction

A few of the many terminologies that are frequently used in the scientific community are nanoscience, nanotechnology, nanomaterials, and nanostructure. The current advancement of research, the growth of knowledge, and the enhancement of living standards in our society all depend on nanoscience and nanotechnology [1]. We have contributed to the overall growth of "nanomaterials" in material science over the past ten years. At systematic lengthening of up to 100 nanometers, nanotechnology covers applications in the physical, chemical, and biological sciences. It is now possible to see objects at the nanoscale, modify their structure, make nanomaterials, and carry out a wide range of other operations thanks to the development of advanced measurement instruments [2]. In the twenty-first century, nanotechnology has a significant impact on our economy and society, just like information technology, molecular biology, and semiconductor technology. The field of nanotechnology is expected to advance industry, energy, healthcare, information technology, biotechnology, and national security [3, 4]

1. Preparation Techniques

It has become highly crucial to have exact control over the size, shape, and crystalline structure of nanoparticles in many of the businesses that make use of nanotechnology. Some examples of these industries are medicine, electronics, and catalysis. The two most common types of synthesis processes for nanoparticles are referred to as "bottom-up" and "top-down" approaches, respectively.

There are many different bottom-up methods that can be used to synthesize metal oxide nanoparticles. Some examples of these methods include sol-gel processing [5], combustion synthesis [6], and gas-phase methods,[7], the co-precipitation method [8], the microwave synthesis, and the hydrothermal synthesis [9]. When it comes to the production of considerable quantities of doped and co-doped ZnO nanoparticles, the co-precipitation and sol-gel procedures are regarded as being among the simplest and most cost-efficient of these methods. As a consequence of this, the explanation of the sol-gel method will be given a great deal of attention in this chapter because the materials that will be synthesized in the chapters that follow were prepared using this particular approach.

2. Nanomaterials' characteristic

Characterizations used in our present study. Characterization includes powder X-ray diffraction (XRD) measurements, Energy dispersive X-ray absorption (EDS) analysis, Field Emission Scanning Electron Microscopy (FESEM) measurements, Photocatalytic measurements, Antibacterial activity, HR-TEM analysis, X-ray PhotoelectronScanning (XPS) spectroscopy, UV-Vis, FTIRspectra analysis, Wound healing ability, biocompatibility.

3. Use of nanoparticles

Nanomaterials can be applied in a variety of ways because they have special, advantageous chemical, physical, and mechanical properties. These include, but are not limited to, the following applications:Energy from fuel cell, Microelectronics ,high-resolution sensorsFor High-Definition TV, phosphors ,Battery power batteries , Medicine ,Implants for medicationsAeronautical parts,ToxinsPhotocatalysis

3.1 Photocatalysis

Photocatalysts are nano catalytic materials that become active when exposed to light (UV or visible). As a result, a photocatalyst may take in the light that creates the electron-hole pairs that enable the reactant molecules to go through chemical changes. The catalytic material's original chemical makeup is restored after the conclusion of the reaction [10]. More extensive uses for nano photocatalysts in environmental remediation include energy conversion, the breakdown of organic compounds, and the removal of hazardous organic and inorganic pollutants from industrial wastewater [11].

In general, photocatalytic degradation comprises many phases, including chemical reaction [12], adsorption-desorption [13], and recombination of charge carriers [14]. When light strikes a semiconducting substance, the incident energy must be larger than the substance's bandgap or forbidden gap. In order to make holes (h+) in the valance band, the electrons can be excited from the valance band (VB) and promoted to the conduction band (CB). The CB's excited electrons can swiftly dissipate their energy in the form of heat before returning to the VB and recombining with its holes. The name of this procedure is electron-hole recombination. Doping with non-metals, transition metals, and rare earth metals as well as creating composites with other semiconductor materials can prevent it [15]. In these circumstances, the electrons and holes travel to the photocatalyst's surface where they engage in redox reactions with molecules that have been adsorbed. Fig. 5 depicts the photocatalysis procedure. The photocatalytic activity was conducted in an aqueous solution, with the catalyst's surface in continual contact with water molecules. After being exposed to light, the holes in the VB can oxidize water molecules to produce hydroxide (OH) free radicals, while the excited electron in the CB can do the same with oxygen molecules to produce superoxide (O2) free radicals. The primary species involved in the photodegradation of dyes into inert by-products such H2O, CO2, and mineral acids are these OH and O2 radicals [16]. The mechanism for the photoinduced formation of electron-hole pairs in a photocatalyst and the corresponding reduction and oxidation reactions are shown in Figure2.A superior photocatalyst must have key properties like being non-toxic, chemically and thermally stable, having high bandgap energy, being economical, and more.

Doping is the process of adding trace amounts of an impurity to the semiconductor metal oxide's crystal lattice in order to alter certain characteristics. When modified to make visible or ultraviolet regions photoactive, the bandgap plays a crucial part in the photocatalytic activity. It enhances photocatalytic activity and reduces charge carrier recombination [17, 18].

3.2 Photocatalyst in ZnO

A special semiconductor photocatalyst that effectively absorbs visible light must be created. ZnO semiconductor nanomaterial possesses favorable energy bandgap (2.4–3 eV) in the visible range, wide surface area, high surface energy, and tiny size. It makes ZnO the best substance for the photocatalytic degradation of dyes driven by visible light. The outstanding characteristics of nanostructured ZnO make it an essential component of photocatalytic dye degradation [19]. The electron can readily recombine with photogenerated holes in ZnO due to its positive conduction band potential (ECB) and reduced valance band potential (EVB), which affects the photocatalytic activity. Rapid electron-hole pair recombination, which would reduce photocatalytic efficacy, is one of ZnO's drawbacks. Therefore, one of the best solutions to this issue is to modify ZnO nanomaterial by doping with appropriate metal ions. As an electron, RE3+ ions function.

Numerous nanoparticles are thought to have special chemico-physical characteristics and high surface area to volume ratios that support efficient antimicrobial activity. The study also showed that normally occurring bacteria do not become resistant to antimicrobial agents when exposed to metal nanoparticles. Nanomaterials have several antimicrobial properties, including the ability to compromise bacterial cell walls and membranes, produce reactive oxygen species (ROS) through photocatalysis, disrupt energy transfer, and inhibit the synthesis of DNA and enzymes. Since ancient times, people have been aware of silver's ability to fight microorganisms. Silver, in the forms of metallic silver, silver nitrate, and silver sulfadiazine, has been used for treating burn wounds, dental procedures, catheters, and the management of bacterial infections The clinical use of silver (such as in wound dressings) is reviewed in light of the recent advent of bacteria that are resistant to antibiotics and the limited efficacy of antibiotics [20]. Among the numerous varieties of metal and metallic

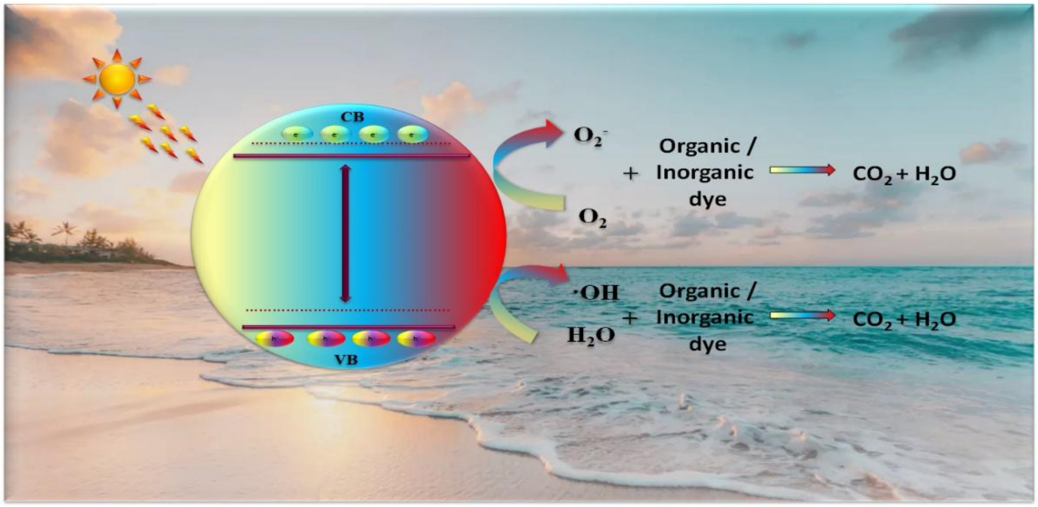

Figure 1: Photocatalysis Decomposition mechanism

ZnO nanoparticles are the most efficient against bacteria, viruses, and other microorganisms.

and many eukaryotic bacteria. The ZnO NPs release silver ions at the same time as attacking the respiratory chain and cell division, which ultimately results in cell death. Size and shape have an inverse relationship with ZnO NPs' antibacterial activity [21]. Antimicrobial activities against Gram-positive and Gram-negative bacteria (such as E. coli and S. aureus) were improved and synergistic when ZnO NPs were used in combination with medicines such penicillin G, amoxicillin, erythromycin, and vancomycin. Wound dressings, coating for medical devices and surgical masks, impregnated textile fabrics, nanogels, and nanolotions are just a few of the numerous uses for ZnO NPs. Long-term contact with substances containing soluble silver can result in irreversible skin and eye pigmentation (argyrosis). Along with other hazardous consequences, they include blood cell count alterations, organ damage (such as liver and kidney), irritability (such as eyes, skin, respiratory, and digestive tract), and organ irritation. However, while some studies suggest that ZnO NPs are non-toxic and metallic silver appears to pose little risk to health [22], other studies have found concentration-dependent negative effects of ZnO NPs on mitochondrial activity. Therefore, a thorough and comprehensive explanation of their possible toxicity is necessary given the emergence of ZnO NPs as promising antibacterial nanomaterials.

ZnO demonstrates potent antibacterial properties across a wide spectrum [23]. ZnO's ability to take in ultraviolet (UV) or visible light causes a separation of charges, which in turn causes the generation of electron-hole pairs, which in turn causes antibacterial activity. There is also the chance that positively charged ZnO particles could kill bacteria when they come into close contact with them. It has been discovered that ZnO possesses bactericidal capabilities even when light is not present [24]. It is the food additive that is utilized the most frequently in the process of increasing cereal-based foods. ZnO is coated into the linings of food cans in packages for meat, fish, maize, and peas, in order to preserve colors and to prevent food deterioration [25]. This is done because of the antibacterial qualities that ZnO possesses. Because of their high surface-to-volume ratio, nano-sized particles of zinc oxide have stronger antibacterial properties than bulk materials do. This is because they are able to interact with bacteria more effectively. Recent research has demonstrated that these nanoparticles are playing an essential part in the elimination of microorganisms found within human cells. At the same time, it has a rather minor impact on human cells [26].

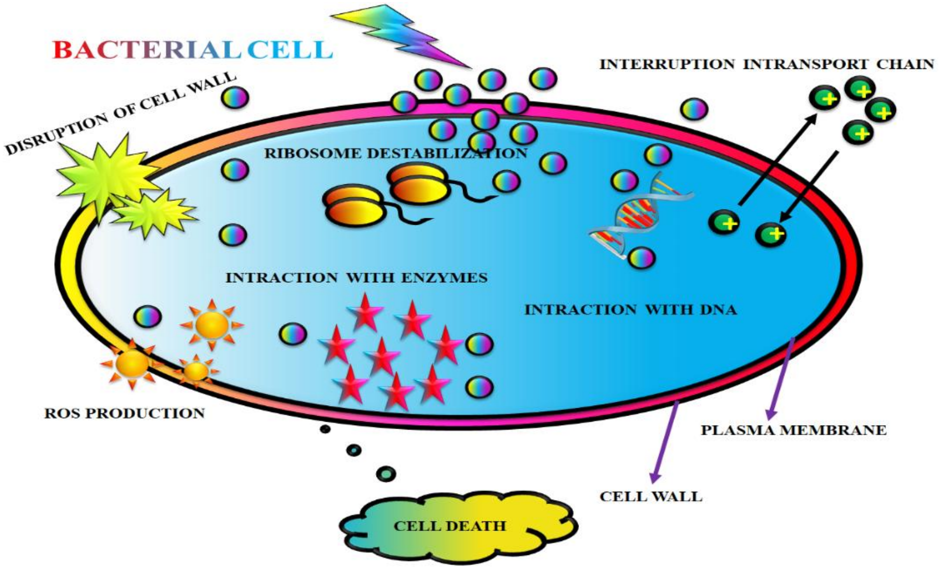

Figure 2: Antibacterial mechanism

4. Poly(N-isopropylacrylamide)-Based Hydrogels

Poly(N-isopropylacrylamide) (PNIPAM) is a thermosensitive polymer that exhibits a negative temperature response. This means that it gets more soluble as the temperature falls, which leads to a volume phase change that is promoted by hydrogen bonding. PNIPAM is a prominent thermosensitive polymer. This singular attribute of PNIPAM has generated a substantial amount of interest from the scientific community. Because of its prominent thermoresponsivebehavior at a lower critical solution temperature (LCST), smart hydrogels based on PNIPAM are extremely ideal for a wide variety of biomedical applications, such as wound dressings, drug delivery, and tissue engineering. Smart hydrogels also have the potential to be used in the treatment of burns.

4.1 Unique Properties of PNIPAM

There are several different methods that can be used to create hydrogels that are physically crosslinked, such as the development of ionic and hydrogen bonds, the forces of Van der Waals, hydrophobic interactions, and crystalline structures [28]. Strong hydrogen bonding between polymer chains in the hydrogel can have an effect on drug release, which can be further controlled by parameters such as the kind of solvent used, the degree of sonication, the temperature of the solution, and the polymer content when the hydrogel is being formulated [29]. In order to circumvent the physicochemical and mechanical limits of biomaterials, crosslinking, which involves the formation of robust linkages between the molecules that are reacting, is one of the methods that is frequently used. It is also possible to use ionic interactions at room temperature and at a physiological pH in order to circumvent these constraints. Many different methods, including condensation polymerization, irradiation with high-energy ionizing radiation (such as electron beams, gamma rays, or X-rays), and chain-growth polymerization [30], are used to generate hydrogels, and bifunctional crosslinking agents are frequently used in this process.

In the realm of biomedical science, PNIPAM-based hydrogels can be used for a wide variety of applications, including the effective delivery of medicinal molecules. This is accomplished by controlling the movement of substances inside a medium and modifying the dimensions in a thermo-controlled manner. In aqueous conditions, the lower critical solution temperature (LCST) of PNIPAM is around 32 degrees Celsius. This property is distinguished by the isopropyl and amide moieties that it possesses. The formation of PNIPAM hydrogels is possible through the process of crosslinking PNIPAM itself or its derivatives in Figure 5, which results in a reversible and considerable volume phase transition toward the LCST through the processes of swelling and shrinking [31].

Because AgO NPs and Ag-based compounds are extremely poisonous to a variety of bacteria, they represent intriguing prospects for a variety of uses in the medical industry. In light of this, the current research involved the synthesis of nanoparticles of zinc and silver, which were then conjugated with the chemical molecule N-isopropylacrylamide (NIPAM). We tested the NPs and NP–NIPAM conjugates for their ability to limit the growth of bacteria.

SUMMARY AND CONCLUSIONS

The misuse of antibiotics has led to the proliferation of drug-resistant bacteria, necessitating the development of new antimicrobials. Nanomaterials hold great potential in medicine, and in an experiment, zinc and silver nanoparticles were synthesized and conjugated with N-isopropylacrylamide (NIPAM) to enhance their activity and stability. Testing these nanoparticles and conjugates against various pathogens revealed significant inhibition of bacterial growth, particularly against Enterococcus faecium and Staphylococcus aureus. The composites demonstrated larger inhibitory zones compared to individual nanoparticles. Moreover, fabrics coated with these composites showed protective effects against drug-resistant bacteria. The synergistic mode of action observed in nanoparticle-NIPAM conjugates suggests their potential as viable and effective alternatives to traditional antibiotics for compacting drug resistant bacteria, wound healing with high biocompatibility

The different rare earth metal ions, including Gd, Ce, La, Nd, Dy, and Eu, can change the characteristics of the photocatalyst, leading to high photocatalytic efficiency. Excellent optical characteristics of the metal oxide doped with rare metal ions enhance photocatalytic activity. The bandgap energy value of the rare metal-doped metal oxide is smaller than that of the pure form. By occupying an empty shell, rare metal ions behave as electron trappers, capturing the excited electron in CB. The recombination of photogenerated charge carriers should be decreased as a result of this procedure . The breakdown of organic dyes by photocatalysis is caused by this efficient charge separation.

Reference

1. G KassegnWeldegebrieal. “Synthesis method, antibacterial and photocatalytic activity of ZnO nanoparticles for azo dyes in wastewater treatment: a review”. In: Inorganic Chemistry Communications 108140 (2020).
2. R Bakkiyaraj et al. “Facile synthesis, structural characterization, photocatalytic and antimicrobial activities of Zr doped CeO2 nanoparticles”. In: Journal of Alloys and Compounds 724 (2017), pp. 555–564.

3. Akshkumar Verma and Ashish Verma. “Synthesis, characterization, mechanoluminescence, thermoluminescence, and antibacterial properties of SrMgAl10O17: Eu phosphor”. In: Journal of Alloys and Compounds 802 (2019), pp. 394–408.
4. Manoj Kumar, Ganesh Singh, and MS Chauhan. “Europium (Eu3+)- doped ZnO nanostructures: Synthesis, characterization, and photocatalytic, chemical sensing and preliminary assessment of magnetic properties”. In: Ceramics International 47.12 (2021), pp. 17023–17033.
5. Song Ge et al. “Facile hydrothermal synthesis of iron oxide nanoparticles with tunable magnetic properties”. In: The Journal of Physical Chemistry C 113.31 (2009), pp. 13593–13599
6. Yasuaki Kitamura et al. “Combustion synthesis of TiO2 nanoparticles as photocatalyst”. In: Powder Technology 176.2-3 (2007), pp. 93–98.
7. Wei-Ning Wang et al. “One-step synthesis of titanium oxide nanoparticles by spray pyrolysis of organic precursors”. In: Materials Science and Engineering: B 123.3 (2005), pp. 194–202.
8. L. M. ; Chen Tian et al. “Gold Nanorods as Plasmonic Nanotransducers: Distance-Dependent Refractive Index Sensitivity”. In: Langmuir 2012 28 (2012).
9. Ranjbar A et al. Effects of silver nanoparticle (Ag NP) on oxidative stress biomarkers in rat. Nanomedicine Journal, 2014.
10. A. Phuruangrat et al. “‘Synthesis and characterization of europium-doped zinc oxide photocatalyst’”. In: J 2014 (2014)
11. T. Ghrib et al. “‘Effect of europium doping on the microstructural, optical and photocatalytic properties of ZnOnanopowders’”. In: Arab J. Basic Appl. Sci., vol. 29, no 29.1 (2022), pp. 138–149.
12. J. C. Sin et al. “‘Sunlight photocatalytic activity enhancement and mechanism of novel europium-doped ZnO hierarchical micro/nanospheres for degradation of phenol’”. In: Appl. Catal 148–149 (2014), pp. 258–268.
13. A. R. Khataee et al. “‘Europium-doped ZnO as a visible light responsive nanocatalyst: Sonochemical synthesis, characterization and response surface modeling of photocatalytic process’”. In: Appl. Catal 488 (2014), pp. 160–170
14. C. Shivakumara et al. “‘Photoluminescence and photocatalytic properties of Eu3+-doped ZnO nanoparticles synthesized by the nitrate-citrate gel combustion method’”. In: Eur. Phys. J. Plus, vol. 132, no 132.1 (2017

15. L. V. Trandafilović et al. "'Enhanced photocatalytic degradation of methylene blue and methyl orange by ZnO:Eu nanoparticles'". In: Appl. Catal 203 (2017), pp. 740–752.
16. D. Dash, N. R. Panda, and D. Sahu. "'Photoluminescence and photocatalytic properties of europium doped ZnO nanoparticles'". In: Appl. Surf 494 (2019), pp. 666–674.
17. Raffi M et al. Studies of the growth parameters for silver nanoparticle synthesis by inert gas condensation. Journal of Materials Research, 2007.
18. O. Bechambi et al. Photocatalytic activity of ZnO doped with Ag on the degradation of endocrine disrupting under UV irradiation and the investigation of its antibacterial activity. Elsevier B, 2015.
19. K. Szyszka et al. "'Structural modification of nanohydroxyapatite Ca10(PO4) 6(OH) 2 related to Eu3+ and Sr2+ ions doping and its spectroscopic and antimicrobial properties'". In: J. Inorg 203 (June 2020), p. 110884.
20. Noor Akbar et al. "and Naveed Ahmed Khan Zinc oxide nanoparticles conjugated with clinically-approved medicines as potential antibacterial molecules". In: AMB Express. 2021; 11 (2021), p. 104
21. C. Shi et al. "'Ultra-trace silver-doped hydroxyapatite with non-cytotoxicity and effective antibacterial activity'". In: Mater. Sci. Eng 55 (2015), pp. 497–505
22. B. Shao et al. "'Eu3+-doped layered gadolinium hydroxides as drug carriers and their bactericidal behavior'". In: Mater. Sci. Eng 127 (2021), p. 112213.
23. Agarwal H. "Shanmugam V A review on anti-inflammatory activity of green synthesized zinc oxide nanoparticle: mechanism-based approach". In: Bioorg Chem 94 (2020), p. 103423.
24. M. T. Elsayed et al. "khalaf Ahmed, and K". In: R. Shoueir, 'Morphological, antibacterial, and cell attachment of cellulose acetate nanofibers containing modified hydroxyapatite for wound healing utilizations', J. Mater. Res. Technol., vol. 9, no 9.6 (2020), pp. 13927–13936.
25. A. Sharma et al. "'Methods of preparation of metal-doped and hybrid tungsten oxide nanoparticles for anticancer, antibacterial, and biosensing applications', Surfaces and Interfaces". In: 28 (Nov. 2022), p. 101641.
26. S. Sathishkumar et al. "'Smart flower like MgO/Tb,Eu-substituted hydroxyapatite dual layer coating on 316L SS for enhanced corrosion resistance, antibacterial activity and osteocompatibility'". In: J. Sci. Adv. Mater. Devices, vol. 5, no 5.4 (2020), pp. 545–553.
27. S. M. Saleh. "ZnO nanospheres based simple hydrothermal route for photocatalytic degradation of azo dye". In: Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 211 (2018).

28. A. ;Seremeta Sosnik and K. P. “Polymeric hydrogels as technology platform for drug delivery applications”. In: Gels 2017 3.52. (2017)
29. Silver S, Phung LT, and Silver G. Silver as biocides in burn and wound dressings and bacterial resistance to silver compounds. Journal of Industrial Microbiology and Biotechnology, 2006
30. N. ; Reddy Reddy, R. ; Jiang, and Q. “Crosslinking biopolymers for biomedical applications”. In: Trends Biotechnol. 2015 33 (2015).
31. L. ; Wang Tang et al. “Poly(N-isopropylacrylamide) -based smart hydrogels: Design, properties and applications”. In: Prog. Mater. Sci. 2021 115 (2021), p. 100702.