

Chapter I

CHAPTER I

INTRODUCTION

Nanotechnology refers to the utilization of technology on a minuscule scale, ranging from 1 to 100 nanometers, enabling the manipulation of matter at this level to create innovative materials and devices with exceptional properties. These advancements find practical applications in various fields, including medicine, electronics, energy, and the environment, leading to significant benefits for society. This rapidly emerging megatrend empowers scientists and engineers to employ individual atoms and molecules, forming functional structures that have the potential to revolutionize numerous industries ¹.

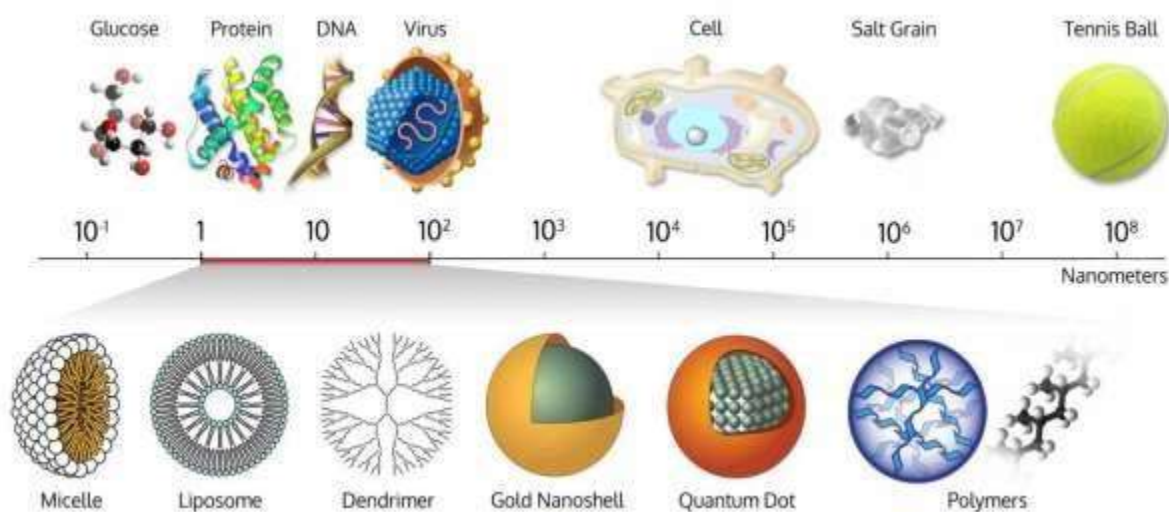


Figure 1.1 *Bio nanoparticles in nanometer scale*

1.1 HISTORY OF NANOTECHNOLOGY

During an international conference on industrial production held in Tokyo in 1974, N. Taniguchi introduced the term "nanotechnology." This term described the precise manipulation of materials with nanometer precision and the study of nano-sized mechanisms. The concept of nanotechnological strategy originated with Feynman and was further expanded upon by E. Drexler in his book "Engines of Creation: The Coming Era of Nanotechnology," published in 1986. Subsequent to that period, from the late 1980s to the early 1990s, several significant discoveries and inventions greatly influenced the advancement of nanotechnology. This led to a substantial increase in nanotechnological

research and designs, resulting in a surge of publications on the subject and an expansion of practical applications. Consequently, there was a significant increase in project financing and numerous organizations and countries became involved ².

In 1991, the United States launched its inaugural nanotechnological program under the National Scientific Fund. Later, in 2001, the National Nanotechnological Initiative (NNI) was established with the primary goal of fostering collaboration among federal departments to prioritize nanotechnology development. The objective was to make nanotechnology the foundation for the USA's economy and national security in the first half of the 21st century ³.

The term "nanometer" was first introduced by Richard Zsigmondy, who was awarded the Nobel Prize in chemistry in 1925. He used a microscope ingeniously to measure the size of particles like gold colloids, coining the term "nanometer" for particle size characterization. In the 20th century, Richard Feynman, the Nobel Prize Laureate in physics in 1965, emerged as a visionary force. During the 1959 American Physical Society conference at Caltech, Feynman delivered a groundbreaking speech titled "There's Plenty of Room at the Bottom." In this speech, he presented the idea of manipulating matter at the atomic level, which laid the foundation for modern nanotechnology and opened up possibilities for technological advancements at the nanoscale ².



Figure 1.2 History of Nanotechnology

1.2 PROPERTIES OF NANOMATERIALS

Nanomaterials, also known as materials containing nanostructures, exist in various dimensions for their structural components. These dimensions range from zero dimensions, encompassing nanoparticles, nanoclusters, and quantum dots, to one dimension represented by nanorods and nanotubes, two dimensions in the form of nano-thin films, and three dimensions as nanomaterials themselves. All these variations fall within the size range of 1-100 nm. When combined with polymers, biomolecules, or other nanostructured materials, these nanomaterials create nanocomposites, often leading to particle sizes larger than 100 nm. The exceptional physical and chemical characteristics of nanomaterials, such as solubility, toxicity, strength, magnetism, diffusivity, optics, color, and thermodynamics, arise from their high surface-to-volume ratio ⁴.

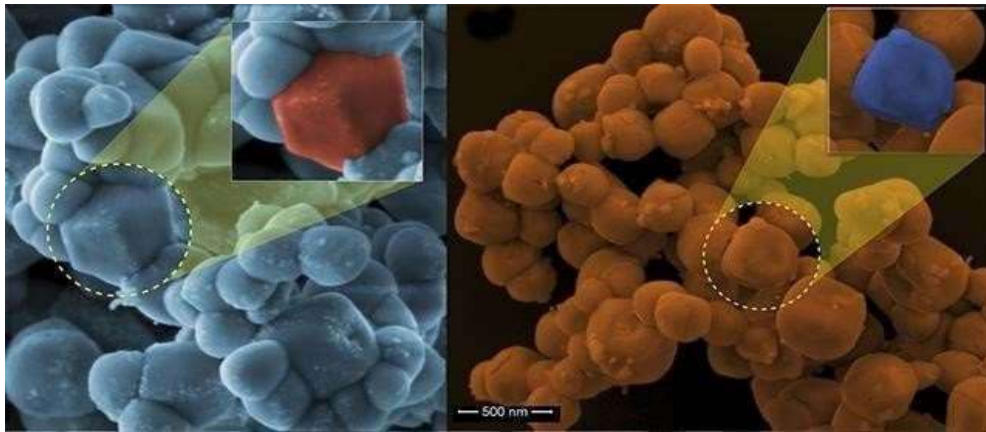


Figure 1.3 *Shape influences in properties of nanomaterials*

Nanotechnology's revolutionary potential is evident as it captures global interest from developed and developing nations alike, spurring increased investments. This cutting-edge technology presents diverse opportunities in agriculture, food, medicine, and beyond. Researchers, driven by rising consumer concerns about food quality and health, are exploring nanotechnology's capacity to enhance food without compromising nutrition. Manipulating matter at the atomic level opens doors to innovative materials with extraordinary properties. Operating on a mind-bogglingly small scale, nanotechnology measures one nanometer as a billionth of a meter (10^{-9} meters). It merges biology, physics, chemistry, medicine, and engineering to tailor materials between 1–100 nm [10^{-9} meters], all rooted in the principles of quantum mechanics. Within this transformative field, gas

sensors play a crucial role, finding applications in medicine, air quality monitoring, environmental science, the automotive industry, and the military, primarily classified as chemical detectors.

1.3 NANOMEDICINE IN THE 21st CENTURY

Several researchers have recently examined and verified that over 50 nanomedicine formulations have been approved for clinical usage. These formulations are currently employed in the treatment of cancer, iron-replacement therapies, anesthetics, fungal treatments, macular degeneration, and rare genetic diseases. Noteworthy contributions to these advancements have been made by nano/microparticle imaging agents. Among the most widely accepted categories are liposomes, iron colloids, protein-based nanoparticles, nano-emulsions, nanocrystals, and metal oxide nanoparticles. It is worth mentioning that recent formulations have seen a consistent rise in approvals, underscoring the emergence of advanced nanomedicine generations in the market.

1.4 NANOCOMPOSITES

Nanocomposites represent a cutting-edge class of materials that involve the dispersion of nanofillers within a matrix, finding applications across chemistry, physics, biology, and material science. Nanotubes, with their high surface area-to-volume ratio, are particularly suited for ablative and reinforcement purposes. By incorporating nanoparticles into a polymer matrix, the ablative and mechanical properties are further enhanced, making these materials well-suited for thermal protection in rocket nozzles, space vehicles, and combustion chambers. They provide resilience to high temperatures, thrust, and impact, all while being lightweight and capable of forming intricate shapes.

The unique properties of nanocomposites depend on the characteristics of the parent molecules, their morphology, and the interfacial features, resulting in fascinating materials with exceptional qualities. In nanocomposite research, a wide range of popular polymers is used, including polyamides, polypropylene, polyethylene, styrene, vinyl, polycarbonates, epoxies, acrylics, polybutylene terephthalate, polyurethanes, and various engineering resins.

Nanocomposites cover an extensive spectrum of organic and inorganic materials, spanning from three-dimensional metal matrix composites to two-dimensional lamellar composites and even one-dimensional to zero-dimensional core shells of nanowires, offering a diverse array of mixed layered materials. One particularly noteworthy material in this context is Montmorillonite, also known as nano clay or bentonite, which has garnered significant interest. It is a natural clay formed through the in-situ alteration of volcanic ash or the hydrothermal alteration of volcanic rocks. The widespread availability and relatively low cost of Montmorillonite make it a popular choice in nanocomposite applications.

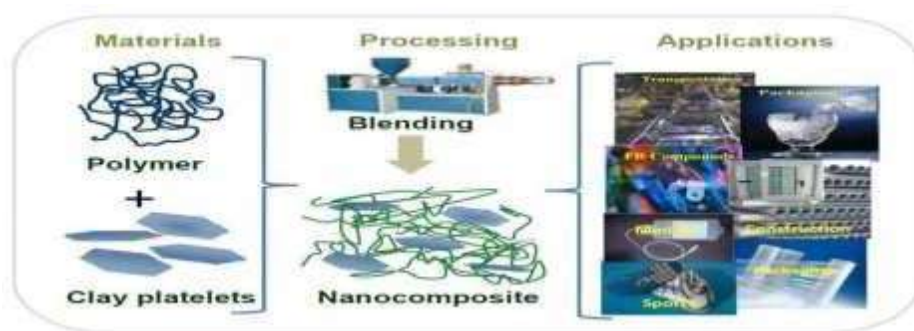


Figure 1.4 *Nanocomposites Applications*

1.5 NANOCOMPOSITES TYPES

As per Azonano's report in 2009, nanocomposites are materials with a nanoscale arrangement that enhances the overall properties of products. These composites typically incorporate substances like clay, carbon, polymer, or a combination of these, along with nanoparticles such as zeolites, clays, metal oxides, metal phosphates, chalcogenides, chains, and clusters like $(Mo_3Se_3)^{n-}$. Numerous experimental studies consistently demonstrate that nanocomposites exhibit novel and improved characteristics compared to traditional macro composites, making them highly valuable for diverse applications, including mechanically reinforced lightweight components, non-linear optics, battery cathodes, Ionics, nanowires, sensors, and more.

In the fields of bioceramics and biomineralization, both organic and inorganic nanocomposites play a significant role. These materials involve the in-situ growth and polymerization of biopolymers and inorganic matrices. Another type is lamellar nanocomposites, which boost interactions at the interface between two phases. As far back

as 1979, Theng categorized nanocomposites into two groups: multilayer structures and inorganic or organic composites. Multilayer structures are formed through gas phase deposition or the self-assembly of monolayers. On the other hand, inorganic or organic composites can be created using sol-gel techniques, linking clusters together, or coating nanoparticles within polymer layers ⁵.

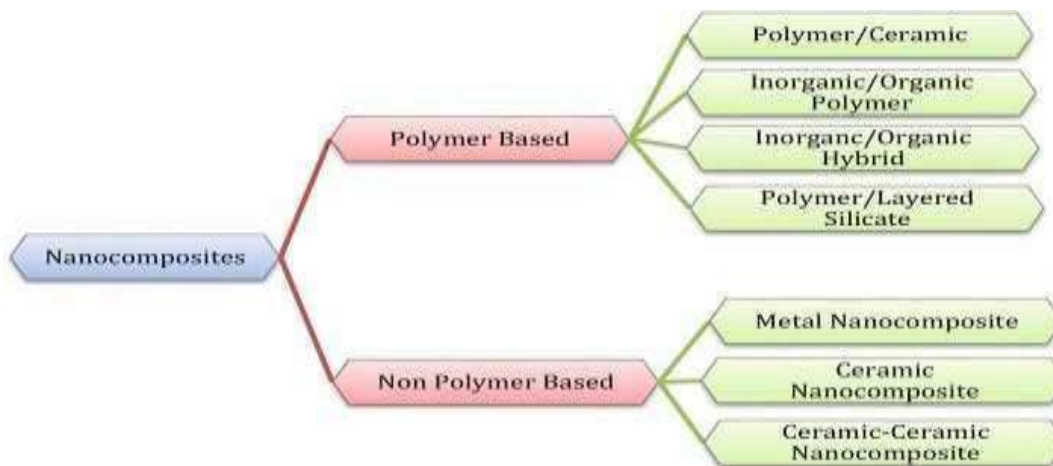


Figure 1.5 *Types of Nanocomposites*

1.6 APPLICATION OF COMPOSITES IN VARIOUS FIELDS

1.6.1 Drug Delivery Applications

Drug delivery systems are vital for precise drug targeting, especially when using nanocomposites with renewable elements. An intriguing nanocomposite, hydroxyapatite (HA)/collagen alginate, shows promise for both bone filling and drug delivery, especially when combined with growth factors. Additionally, porous HA/collagen scaffolds facilitate the controlled release of fibroblast growth factor-2. Another application involves HA/CH nanocomposites for accurate vitamin delivery, utilizing anionic polysaccharides like alginate, carrageenan, and pectin, influencing molecule transfer in biomedical settings. The coprecipitation method successfully creates safe CHHA composites implantable in the bone marrow without inflammation. Moreover, alginate-HA nanocomposites support bone regeneration in tissue engineering scaffolds. These advancements hold significant potential for biomedical applications ⁶.

1.6.2 Antimicrobial Applications

Designers are utilizing bio-renewable resources to create nanocomposites with antimicrobial properties. These nanocomposites primarily consist of polysaccharides and proteins as matrix elements. Additionally, inorganic metals or metal oxides like Au, Ag, or TiO₂, along with antibacterial organic compounds such as essential oils, are employed as antibacterial agents (**Figure 1.6**). A prime example of such nanocomposites is the Zein protein-based antibacterial food packaging, derived from corn gluten meal, which is rich in zein and widely acknowledged for its beneficial properties ⁷.

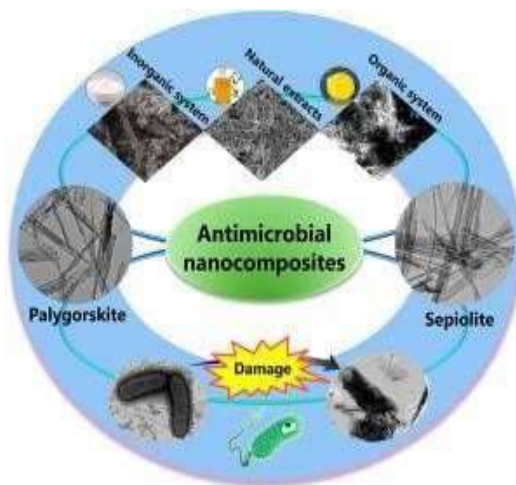


Figure 1.6 *Antimicrobial nanocomposites*

1.7 AMINO GUANIDINE

Aminoguanidine is a hydrazine derivative and a bifunctional molecule, and the salts prepared from aminoguanidine are anticipated to resemble the hydrazine moiety. The nitrogen constituent and asymmetric bifunctional nature of aminoguanidine are responsible for its enhanced thermal and chemical reactivity. Thus, its salts are employed to prepare metal complexes with important physical properties such as ferroelectricity (pyroelectricity and piezoelectricity) and second harmonic generation. It is also an excellent chelating ligand and forms monodentate or bidentate complexes with metal ions. Due to the presence of carbon with four nitrogen atoms, aminoguanidine acts as an outstanding starting material in cyclization processes. In particular, the four nitrogen atoms in aminoguanidine undergo coordination in various modes to form different types of complexes. However, in the free state, aminoguanidine is unstable, while in the solid state,

it exists as a mono (+1) or di (+2) cation. In the solid form, its extreme nitrogen atom has hydrazine moiety in the sp^3 hybridized state and the extra non-hydrogen atoms are in the sp^2 hybridized state⁸⁻¹¹.

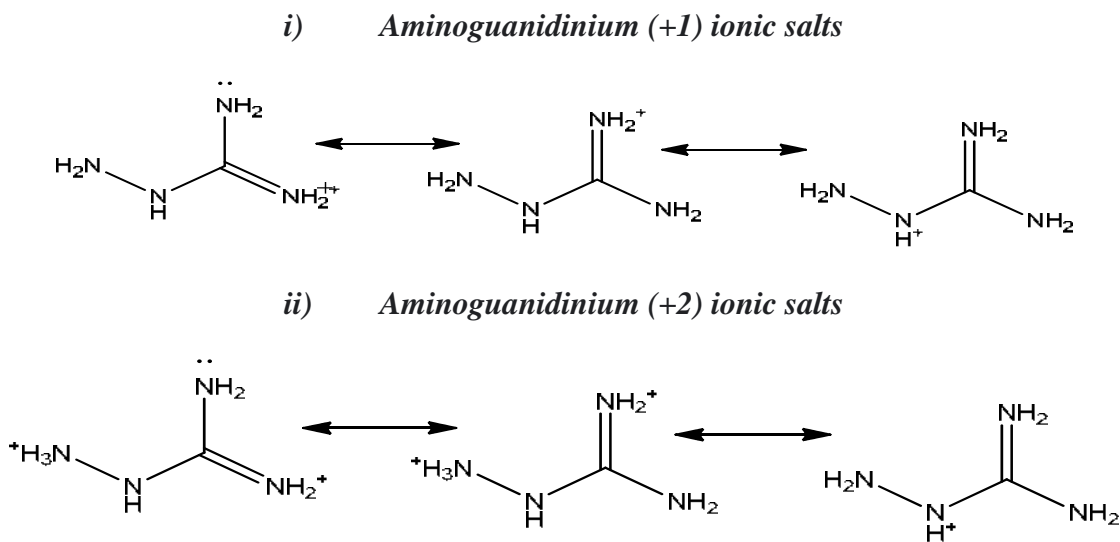


Figure 1.7 Configuration of [aminoguanidinium (+1)] and [aminoguanidinium (+2)] salts

1.8 GUANIDINE

Guanidine is a high-alkalinity crystalline compound formed by guanine oxidation. It is an essential molecule containing a 'CN3' - core with a wide range of interesting properties. It was first synthesized by degradation of an aromatic neutral product guanine, by Strecker in 1861. It is a neutral, nitrogen-containing compound extensively used as a strong bases in organic chemistry. Guanidine is a set of compounds with great chemical and biological importance and the hydrophilic nature of guanidine plays a significant role in the stabilization of protein conformations via hydrogen bonding. The main functionalities of the guanidine salts were broadly found in natural products, pharmaceutically active compounds, and the molecules employed for supramolecular study. Guanidinium salts have been briefly studied for their structural properties and the nature of hydrogen bonding. There are various structural phase transformations of the coordinating composites made up of guanidinium cation using different inorganic acids or salts, some being ferroelectric substances. Guanidine is considered a versatile ligand that is capable of bonding to the metal centers in a variety of coordination modes. It is most commonly known neutral donor ligand or as a monoanion. Earlier studies on new metal

complexes using guanidine with acetic, trichloroacetic, and trifluoroacetic acids were reported by Drozd. There was a report on the Gold complexes of guanidine. Guanidines are found as counterions, as chelate guanidine, and as neutral guanidine ligands with various metals in coordination chemistry¹²⁻¹⁷.

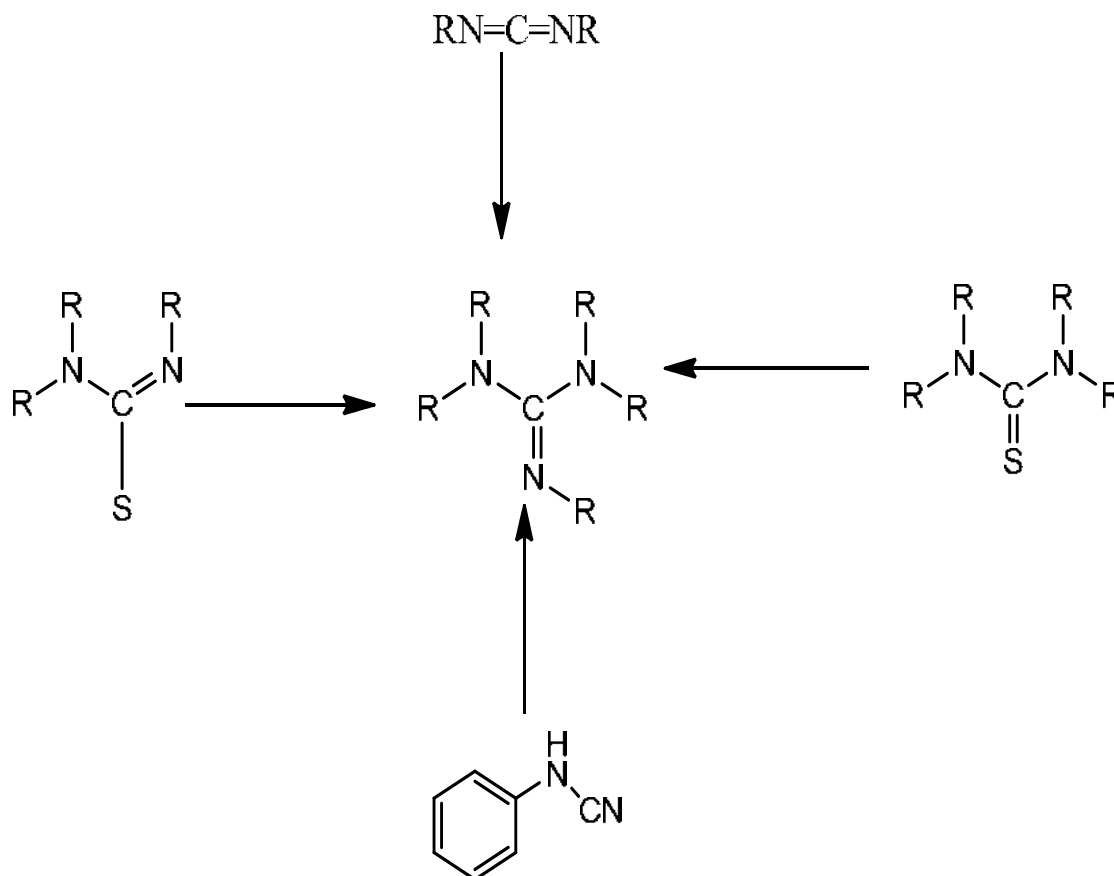


Figure 1.8 *Synthesizing guanidine derivatives.*

1.9 1-NAPHTHOIC ACID

1-naphthoic acid (1-naphthalene carboxylic acid) and its derivatives have attracted great attention from researchers because they possess an extensive range of biological and chemical applications in medicine, photo chemicals, organic pigments, pesticides, photosensitive materials, dyes, cosmetic preparations, etc. Complexes of naphthalene derivatives have been examined since the 1960s when 1-naphthoic acid was compiled from a planar dimer unit. It was mainly used to synthesize highly economical and effective herbicides, and it also acts as a plant growth regulator, thermal testimony material, and photosensitive object. Some materials prepared from 1-naphthoic acid have the resistivity

of plasticizers and solvents, and these significant features led to the detailed spectral examination of 1-naphthoic acid, where one of the best examples is a naphthalene derivative, which is often used as a chelating agent ¹⁸.

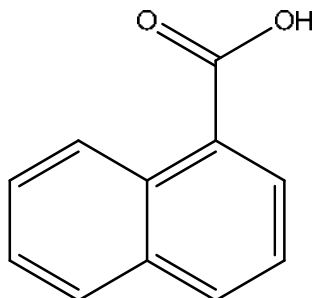


Figure 1.9 Structure of 1-naphthoic acid.

1.10 2-NAPHTHOIC ACID

2-naphthoic acid has great coordination ability of -COOH groups with metal and supports complex formation. It is a hydrazide derivative highly used in many biological activities. The Kolbe - Schmitt reaction is generally used for producing naphthoic acid. It acts as an important intermediate for the synthesis of dyes, medicine, and organic pigments. It has a naphthalene-based color intermediate, so it is used in paint, waterproofing agents, and photosensitive materials and they are frequently used in chelating agents. Hydroxy naphthoic acids develop coloured chelates when react with metal ions. Derivatives of naphthoic acid show significant anti-microbial activity against *Bacillus thuringiensis*, *Escherichia coli*, *Bacillus cereus*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Candida albicans*. In the medical field, much clinical evidence clearly shows that naphthoic acid decreases stress in the liver and resists insulin in liver tissues ^{19,20}.

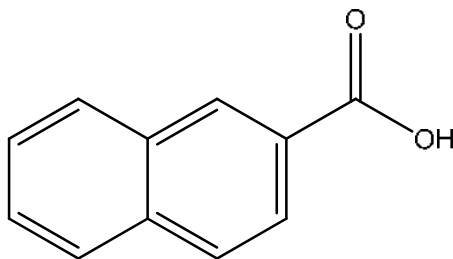


Figure 1.10 Structure of 2-naphthoic acid.

1.11 APPLICATIONS

i) Anti-corrosion

To achieve sustainable development goals, researchers are focused on developing sustainable environmental protection and management methods. To achieve this, metal and mixed metal oxides have gained much attention due to their promising properties that make them suitable for various applications, namely anticorrosion, energy storage devices, sensors, and biosensors.

Further, to achieve the objective of sustainable development, the grave concern of corrosion must be dealt with urgently, because when metals are corroded, they lose their original strength. Thus, the metal item has to be replaced, which requires the consumption of natural resources, resulting in devastating environmental degradation. Consequently, metal corrosion should be avoided by designing anti-corrosion materials to achieve sustainability^{20,21}.

ii) Organic Light Emitting Diodes (OLEDs)

Transition metal complex as a phosphor in light emitting diode because the challenging factor is to match its electronic structure. The given chemical surroundings will enforce the weak ligand field on transition metals rather than alkali metals since these metals have weak spatial interaction with ligand orbitals. Subsequently, metal complexes with half-filled 3d orbitals and ligands with hetero atoms have a bunch of electrons in excited states; in turn, they are actively near to one another in both the ground state and excited state.

In the lowest excited state of the metal complexes, the transition from metal-to-ligand charge transfer (MLCT) and ligand-to-metal charge transfer (LMCT) generally has more impact on photophysical and photochemical properties and has more practical applications. Similarly, ligand-to-ligand charge transfer (LLCT), where the electron is transferred from one ligand to another, is also helpful in synthesizing WLEDs^{22,23}

iii) Hydrogen Evolution Reactions

Transition to hydrogen production to evade harmful universal ecological effects triggered by the extreme and rapid growth in hydrocarbons and coal. The expansion of fuel manufacture based on the protection of sustainability is most recommended for

forthcoming generations. Presently accessible hydrogen-based ignition cells need it in its paramount purity. Adversely, the existing low-cost technique available in the industrial market releases CO₂ and depletes fossil fuels for the production of energy sources.

To avoid these shortcomings, several other approaches for hydrogen production, such as photochemical generation, thermochemical process, photoelectrochemical water splitting using sunlight, acid-hydrolysis, and electrochemical water splitting, are being exhaustively examined and utilized. Amid these, electrochemical water splitting is considered a quick and more accessible technique for manufacturing hydrogen with 99.999% purity.

So, hydrogen was considered an excellent energy source and a user-friendly approach to defeating the energy crises and environmental problems. An efficient and cost-effective method to synthesize high-purity hydrogen was electrochemical water splitting. It is hard to fabricate effective and long-lasting electrocatalysts to decrease the overpotential of the process and to achieve high expertise in water splitting.

Recent studies specify that incorporating heteroatoms like N, S, and O with advanced electronegativity into the surface of the catalysts is a persuasive technique for nurturing hydrogen production. For example, the d-band, electron density, and nitrogen inclusion can modify the HER activity with excellent efficiency and stability. In the presence of hetero atoms, the course of water assimilation and dissimilation and hydrogen adsorption/desorption behavior take place quickly. Furthermore, stable electronegative heteroatoms inserted at anionic locations successfully modify the catalyst's electrical characteristics and reduce the communication among metals and negative groups. Ultimately it will anchor the hydrogen behaviour on the catalyst's membrane thereby enhancing the effectiveness of the HER. Incorporating heteroatoms with higher electronegativity into the crystal lattice would be a promising way to obtain effective and stable HER activity^{24,25}.

REFERENCES

1. Adya, A. K. & Canetta, E. Nanotechnology and Its Applications to Animal Biotechnology. *Anim. Biotechnol. Model. Discov. Transl.* 247–263 (2014).
2. Bayda, S., Adeel, M., Tuccinardi, T., Cordani, M. & Rizzolio, F. The History of Nanoscience and Nanotechnology: From Chemical–Physical Applications to Nanomedicine. *Molecules* **25**, 112 (2020).
3. Roco, M. C. The long view of nanotechnology development: The National Nanotechnology Initiative at 10 years. *J. Nanoparticle Res.* **13**, 427–445 (2011).
4. Baig, N., Kammakakam, I., Falath, W. & Kammakakam, I. Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges. *Mater. Adv.* **2**, 1821–1871 (2021).
5. Carrier, M. & Nordmann, A. Science in the Context of Application: Methodological Change, Conceptual Transformation, Cultural Reorientation. *Bost. Stud. Philos. Hist. Sci.* **274**, 1–7 (2011).
6. Farokhzad, O. C. & Langer, R. Impact of nanotechnology on drug delivery. *ACS Nano* **3**, 16–20 (2009).
7. Li, X., Zuo, S., Wang, B., Zhang, K. & Wang, Y. Antimicrobial Mechanisms and Clinical Application Prospects of Antimicrobial Peptides. *Molecules* **27**, (2022).
8. Bryden, J. H. The crystal structure of aminoguanidine hydrochloride. *Acta Crystallogr.* **10**, 677–680 (1957).
9. Adams, J. M. & IUCr. The crystal structure of aminoguanidinium dihydrogen orthophosphate. *urn:issn:0567-7408* **33**, 1513–1515 (1977).
10. Naidu, S. R., Prabhakaran, K. V., Bhide, N. M. & Kurian, E. M. Thermal and Spectroscopic Studies on the Decomposition of Some Aminoguanidine Nitrates. *J. Therm. Anal. Calorim.* 2000 613 **61**, 861–871 (2000).
11. Murugavel, S., Ganesh, G., Subbiah Pandi, A., Govindarajan, S. & Selvakumar, R. Amino-guanidinium hydrogen fumarate. *Acta Crystallogr. Sect. E Struct. Reports Online* **65**, o548–o548 (2009).

12. Göbel, M. & Klapötke, T. M. First structural characterization of guanidine, $\text{HN}=\text{C}(\text{NH}_2)_2$. *Chem. Commun.* 3180–3182 (2007) doi:10.1039/B705100J.
13. Sapse, A. M., Snyder, G. & Santoro, A. V. Ab initioSCF study of guanidine and substituted guanidines. *Int. J. Quantum Chem.* **20**, 755–762 (1981).
14. Tan, C. H. & Coles, M. The chemistry of guanidine, guanidinium, and guanidinate compounds. *Aust. J. Chem.* **67**, 963–964 (2014).
15. Drozdov, F. V. & Kotov, V. M. Guanidine: a Simple Molecule With Great Potential: From Catalysts To Biocides and Molecular Glues. *Ineos Open* (2021) doi:10.32931/io2030r.
16. Khalaf, M. *et al.* Guanidine group: Definition and pharmaceutical applications. *Res. J. Pharm. Biol. Chem. Sci.* **7**, 1026–1031 (2016).
17. Powell, D. A., Ramsden, P. D. & Batey, R. A. Phase-transfer-catalyzed alkylation of guanidines by alkyl halides under biphasic conditions: A convenient protocol for the synthesis of highly functionalized guanidines. *J. Org. Chem.* **68**, 2300–2309 (2003).
18. Fan, B., Li, Q., Li, Y., Song, X. & Yin, J. Solubility measurement and correlation for 1-naphthoic acid in nine pure and binary mixed solvents from $T = (293.15 \text{ to } 333.15) \text{ K}$. *J. Mol. Liq.* **273**, 58–67 (2019).
19. Kumar, V. 2-Naphthoic acid prototropism within ionic liquid based media. *J. Mol. Liq.* **339**, 116831 (2021).
20. Abdel-Kader, N. S., Abdel-Latif, S. A., El-Ansary, A. L. & Sayed, A. G. Combined experimental, DFT theoretical calculations and biological activity of sulfaclozine azo dye with 1-hydroxy-2-naphthoic acid and its complexes with some metal ions. *New J. Chem.* **43**, 17466–17485 (2019).
21. Swathika, M. *et al.* Design and synergistic effect of nano-sized epoxy-NiCo₂O₄ nanocomposites for anticorrosion applications. *RSC Adv.* **12**, 14888–14901 (2022).
22. Okpara, E. C., Olatunde, O. C., Wojuola, O. B. & Onwudiwe, D. C. Applications of Transition Metal Oxides and Chalcogenides and their Composites in Water Treatment. *Environ. Adv.* **11**, 100341 (2023).

23. Ravaro, L. P., Zandoni, K. P. S. & de Camargo, A. S. S. Luminescent Copper(I) complexes as promising materials for the next generation of energy-saving OLED devices. *Energy Reports* **6**, 37–45 (2020).
24. Vesborg, P. C. K., Seger, B. & Chorkendorff, I. Recent development in hydrogen evolution reaction catalysts and their practical implementation. *J. Phys. Chem. Lett.* **6**, 951–957 (2015).
25. Wang, X., Xiao, H., Zhang, M., Lin, H. & Liu, G. Four luminescent metal-organic chain compounds based on semi-rigid N-donor ligands and 3-hydroxy-2-naphthoic acid for recognition of Fe^{3+} and $\text{Cr}_2\text{O}_7^{2-}$ ions. *Polyhedron* **179**, (2020).