

ISBN: 978-93-88901-83-3

# RESEARCH TRENDS IN MATERIAL SCIENCE

**EDITORS:**

**DR. ALOKE VERMA**

**DR. PAYAL GOSWAMI**

**DR. VEERABHADRAYYA M**

**DR. R. G. VAIDYA**

BHUMI PUBLISHING, INDIA



FIRST EDITION: SEPTEMBER 2023

# Research Trends in Material Science

(ISBN: 978-93-88901-83-3)

## Editors

**Dr. Alope Verma**

Department of Physics,  
Kalinga University,  
Naya Raipur (CG)

**Dr. Payal Goswami**

Department of Mathematics,  
Govt. Pt. J. L. N. PG Arts & Science  
College, Bemetara (CG)

**Dr. Veerabhadrayya M**

Department of Physics,  
University College of Science,  
Tumkur University, Tumkur, Karnataka

**Dr. R. G. Vaidya**

Department of Physics,  
University College of Science,  
Tumkur University, Tumkur, Karnataka



*Bhumi Publishing*

**September 2023**

***First Edition: September, 2023***

***ISBN: 978-93-88901-83-3***



**© Copyright reserved by the Editor**

Publication, Distribution and Promotion Rights reserved by Bhumi Publishing, Nigave Khalasa, Kolhapur

Despite every effort, there may still be chances for some errors and omissions to have crept in inadvertently.

No part of this publication may be reproduced in any form or by any means, electronically, mechanically, by photocopying, recording or otherwise, without the prior permission of the publishers.

The views and results expressed in various articles are those of the authors and not of editors or publisher of the book.

Published by:

Bhumi Publishing,

Nigave Khalasa, Kolhapur 416207, Maharashtra, India

Website: [www.bhumipublishing.com](http://www.bhumipublishing.com)

E-mail: [bhumipublishing@gmail.com](mailto:bhumipublishing@gmail.com)

Book Available online at:

<https://www.bhumipublishing.com/book/>



## **PREFACE**

*In the vast landscape of scientific inquiry, the realm of Material Science stands as a dynamic crucible where innovation and discovery converge. As we embark on this journey through the pages of "Research Trends in Material Science," we find ourselves at the crossroads of tradition and cutting-edge exploration.*

*This preface serves as a portal, inviting you to traverse the ever-evolving terrain of materials research—a discipline that has ceaselessly pushed the boundaries of human understanding. From the elemental building blocks to the intricacies of nanomaterials, this book encapsulates the diverse facets of material science that have captured the imaginations of researchers and engineers alike.*

*As we delve into the chapters that follow, you'll witness the seamless interplay between theory and experimentation, where scientists unravel the secrets held within the molecular tapestry of materials. From the inception of innovative synthesis techniques to the application of advanced characterization methods, each page unfolds a narrative of progress and possibility.*

*The landscape of material science is not merely confined to laboratories and academic institutions; it extends its tendrils into industries and everyday applications. The discoveries documented here bear the potential to revolutionize fields as diverse as electronics, healthcare, energy, and beyond.*

*In the spirit of collaborative exploration, this compilation not only outlines current research trends but also beckons researchers, students, and enthusiasts to join the ongoing conversation. As we stand on the precipice of new breakthroughs, the collective pursuit of knowledge is paramount.*

*May this book serve as both a testament to the achievements of the past and a compass guiding us toward the uncharted territories of tomorrow. Welcome to the forefront of Research Trends in Material Science, where curiosity knows no bounds, and the journey is as exhilarating as the destination.*

**Editors**

## TABLE OF CONTENT

<b>Sr. No.</b>	<b>Book Chapter and Author(s)</b>	<b>Page No.</b>
1.	<b>SELF-ASSEMBLY OF CYCLIC PEPTIDES: FORMATION OF SUPRAMOLECULAR CYCLIC PEPTIDE NANOTUBES (SCPNs)</b> Krishnananda Samanta	1 – 15
2.	<b>SOLID WASTE MANAGEMENT PRACTICES: A CASE STUDY OF KERALA, INDIA</b> Rincy A and Anila George	16 – 25
3.	<b>A REVIEW ON CADMIUM SULPHIDE (CdS) THIN FILMS SYNTHESIS AND ITS APPLICATIONS</b> Y. A. Chaudhari	26 – 30
4.	<b>RECENT ADVANCEMENTS IN METAMATERIALS</b> Kailash Nemade	31 – 36
5.	<b>NANOTECHNOLOGY: ENVIRONMENTAL, HEALTH AND SAFETY ISSUE</b> M. S. Bisen, A. V. Bagde and Y. S. Bopche	37 – 49
6.	<b>A CONDUCTING POLYANILINE AND ITS APPLICATIONS</b> Sandip V. Patil	50 – 55
7.	<b>BIOREMEDIATION OF HEAVY METAL CONTAMINATED SOILS</b> R. Jayashree and V. Bhagyasree	56 – 66
8.	<b>INTRODUCTION AND APPLICATIONS OF III-V SEMICONDUCTOR COMPOUNDS AND ALLOYS</b> Uttam Paliwal	67 – 74
9.	<b>A REVIEW ON DIFFERENT TECHNIQUES FOR ENHANCEMENT OF EFFICIENCY OF SNS BASED SOLAR CELL</b> A. M. Kute and S. R. Takpire	75 – 80
10.	<b>A BRIEF REVIEW ON SYNTHESIS METHODS OF FERROELECTRIC MATERIALS</b> Parshuram B. Abhange, Vijay S. Raykar and Vivek A. Rane	81 – 88



## SELF-ASSEMBLY OF CYCLIC PEPTIDES: FORMATION OF SUPRAMOLECULAR CYCLIC PEPTIDE NANOTUBES (SCPNS)

Krishnananda Samanta

Department of Chemistry,

Balurghat College, University of Gour-banga, 733101, West Bengal, India

Corresponding author E-mail: [krishnanandasamanta5@gmail.com](mailto:krishnanandasamanta5@gmail.com)

### Abstract:

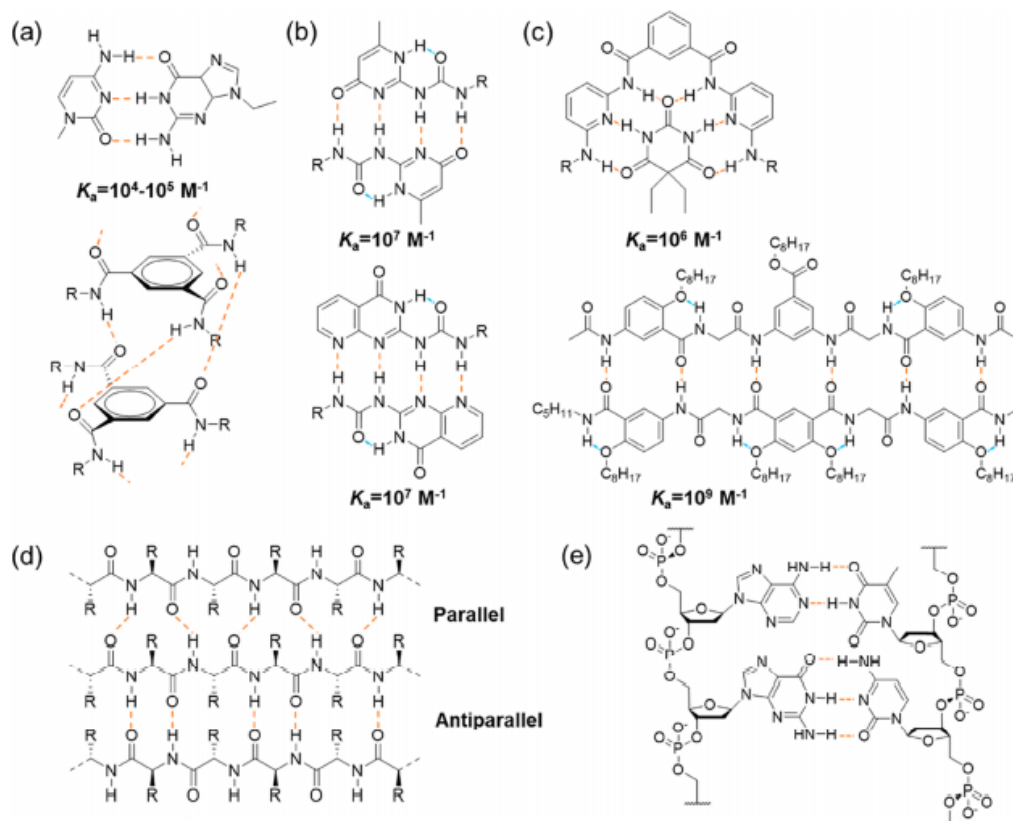
The development of cyclic peptide which self-assembled through supramolecular interactions into tubular structures to form supramolecular cyclic peptide nanotubes (SCPNS) is the current area of research interest. A range of cyclic peptides have been identified to have such properties, including  $\alpha$ -peptides,  $\beta$ -peptides,  $\alpha,\gamma$ -peptides, and peptides based on  $\delta$ - and  $\epsilon$ -amino acids. Furthermore, functionalization of these cyclic peptides through their conjugation to polymer chains produced cyclic peptide– polymer conjugates nanostructures.

**Keywords:** Self-assembly, cyclic peptides, nanostructures

### Introduction:

Supramolecular chemistry deals with the area of chemistry focusing on spatial chemical systems with spatially organized molecules *via* noncovalent interactions [Lehn *et al.*, 2002]. Among, these interactions, hydrogen bonding, metal coordination, hydrophobic interactions, van der Waals interactions,  $\pi$ – $\pi$  interactions, and electrostatic interactions are widely being used in the supramolecular chemistry. The formation of large hydrogen bonding networks drive the formation of ordered supramolecular structures. However, polarity of the medium plays a vital role in this regard. Because hydrogen bonding is drastically weakened in the presence of hydrogen bonding competitors or in very polar media [Jorgensen *et al.*, 1990], it is challenging to transfer these hydrogen bonding motifs in aqueous environment [Murray *et al.*, 1992]. Delicate molecular design by means of hydrophobic shielding is typically required for the construction of supramolecular structures in water [Krieg *et al.*, 2016]. Nature has already been widely used hydrogen bonding arrays such as the formation of  $\alpha$ -helix and  $\beta$ -sheet secondary structures of proteins. Furthermore, the formation of double helix structure of DNA is one of the most important examples by nature. The secondary structures of protein are held in shape by hydrogen bonds between the carbonyl and amide groups of the corresponding amino acid. While the

formation of complementary hydrogen bonds between the nucleotides is the driving force to form the double helix structure of DNA. These examples inspired supramolecular chemist to adapt these biobased building blocks to construct functional nanostructures through supramolecular assemblies (Figure 1) [Sato *et al.*, 2018], McLaughlin *et al.*, 2011].



**Figure 1: Examples of multiple-hydrogen-bonding arrays: (a) triple-hydrogen-bonding, (b) quadruple-hydrogen-bonding, (c) sextuple-hydrogenbonding, (d)  $\beta$ -Sheet structure of a protein, and (e) double helix structure of DNA (the dashed lines in orange represent intermolecular hydrogen bonds, while the dashed lines in blue represent intramolecular hydrogen bonds) (Perrier *et al.*, 2021)**

Self-assembling cyclic peptides (CPs) are bioinspired supramolecular building blocks, which stack into supramolecular cyclic peptide nanotubes (SCPNS), driven by  $\beta$ -sheet-like hydrogen bonding. Considering the rare supramolecular strategies of fabricating nanotubes, they offer a versatile route toward the construction of a diverse range of nanotubes [Shimizu *et al.*, 2020]. More interestingly, the hydrophobic side chains of the cyclic peptides can effectively shield the hydrogen bonds from the access of water molecules when forming nanotubular structures, which enhanced the extraordinary stability of SCPNS in water.

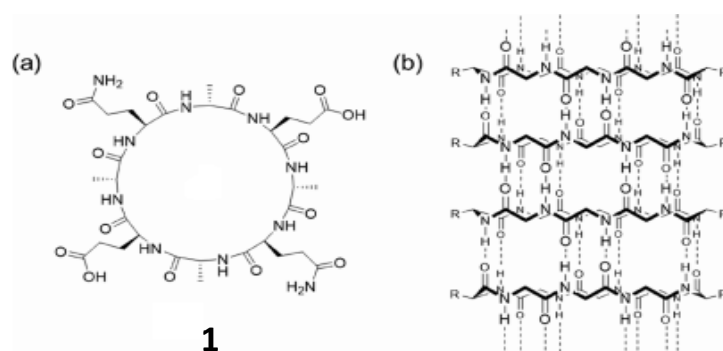


## 1. Tubular Ensembles of Cyclic Peptides

There are several types of cyclic peptides reported to date that are able to stack into SCPNs, which can be mainly categorized as cyclic  $\alpha$ -alt(D,L)-peptides, cyclic  $\beta$ -peptides, cyclic  $\alpha,\gamma$ -peptides, and cyclic peptides containing  $\delta$  or  $\epsilon$ -amino acids on the basis of their composition. The ability to form  $\beta$ -sheet-type hydrogen bonds between the adjacent peptide subunits on both sides of the ring structures leads to the formation of SCPNs.

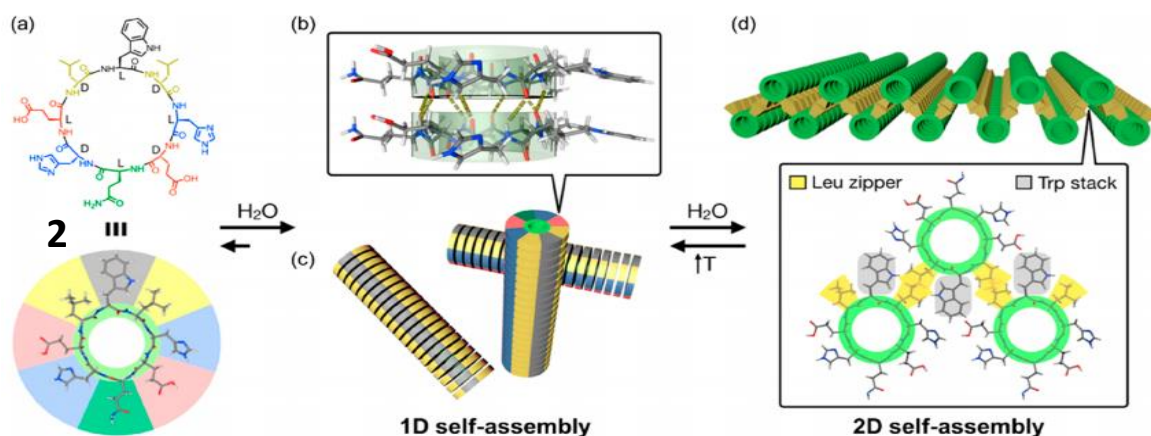
### 1.1 Tubular Ensembles of Cyclic $\alpha$ -alt(D,L)-Peptides:

Ghadiri *et al.* [1993] reported for the first time a well-characterized peptide nanotube formed by a cyclic  $\alpha$ -alt(D,L)-peptide. An octapeptide **1** with the sequence of cyclo-[(L-Gln-D-Ala-L-Glu-D-Ala)<sub>2</sub>] was designed and synthesized (Figure 2). Two glutamic acids were introduced to prevent subunit association through Coulombic repulsion in a basic aqueous solution. The formation of rod-shaped crystals was triggered by the controlled acidification of the alkaline cyclic peptide solution. The resulting peptide assembly was fully characterized by transmission electron microscopy (TEM), electron diffraction (ED), Fourier-transform infrared (FT-IR) spectroscopy, and molecular modeling. These results clearly indicated the formation of ordered tubular structures with internal diameters of 7.5 Å and distances between ring-shaped subunits of 4.73 Å with an antiparallel orientation through the backbone-backbone intermolecular hydrogen bonding interactions. During the simulation, 10 cyclic peptide subunits in water were shown to form a stable tubular structure, with average intersubunit distances between 4.75 and 4.80 Å, in good agreement with the experimental results. More interestingly, the behavior of water molecules was studied. The average number of water molecules inside the 10-peptide tube was found to be 32.8, clearly showing the hydrophilic nature of the internal cavity.



**Figure 2: (a) Chemical structure of the cyclic  $\alpha$ -alt(D,L)-peptide **1**. (b) Schematic representation of the SCPN emphasizing the antiparallel stacking and the extensive network of intermolecular hydrogen-bonding interactions (Ghadiri *et al.*, 1993)**

Montenegro *et al.* [2020] reported a cyclic peptide capable of undergoing sequential 1D-to-2D self-assembly in an aqueous medium. As indicated in Figure 3, an asymmetric cyclic peptide 9 with the sequence of cyclo-[D-Leu-L-Trp-D-Leu-L-His-D-Glu-L-Gln-DHis-L-Glu-] was designed to have four distinct domains: (i) a hydrophobic tripeptide domain of Leu-Trp-Leu, (ii) two hydrophilic ionizable domains on either side of the peptide ring comprising pH-sensitive Glu and His, and (iii) a neutral hydrophilic domain of Gln opposite to the hydrophobic domain. In solution, an amphiphilic nanotube is expected to form based on the multiple hydrogen bonding interactions between the peptide rings, which could subsequently assemble into a nanotubular bilayer to bury its hydrophobic face from the aqueous environment. Meanwhile, at physiological pH, the surface of the tubular ensemble will have a highly anionic character due to the deprotonated glutamate residues ( $pK_a \approx 4.2$ ) and the neutral histidine residues ( $pK_a \approx 6.0$ ) [Nelson *et al.*, 2008]. The aggregation of the individual layers is prevented by the strongly anionic surface, leading to the formation of large and flat nanosheets with lateral dimensions in the high micrometer range (e.g.,  $260 \mu\text{m} \times 50 \mu\text{m}$ ). At the same time, the thickness is only 3.2 nm. The formed nanosheets are highly dynamic and can reversibly transform into 1D nanotubes under the stimuli of pH or temperature.

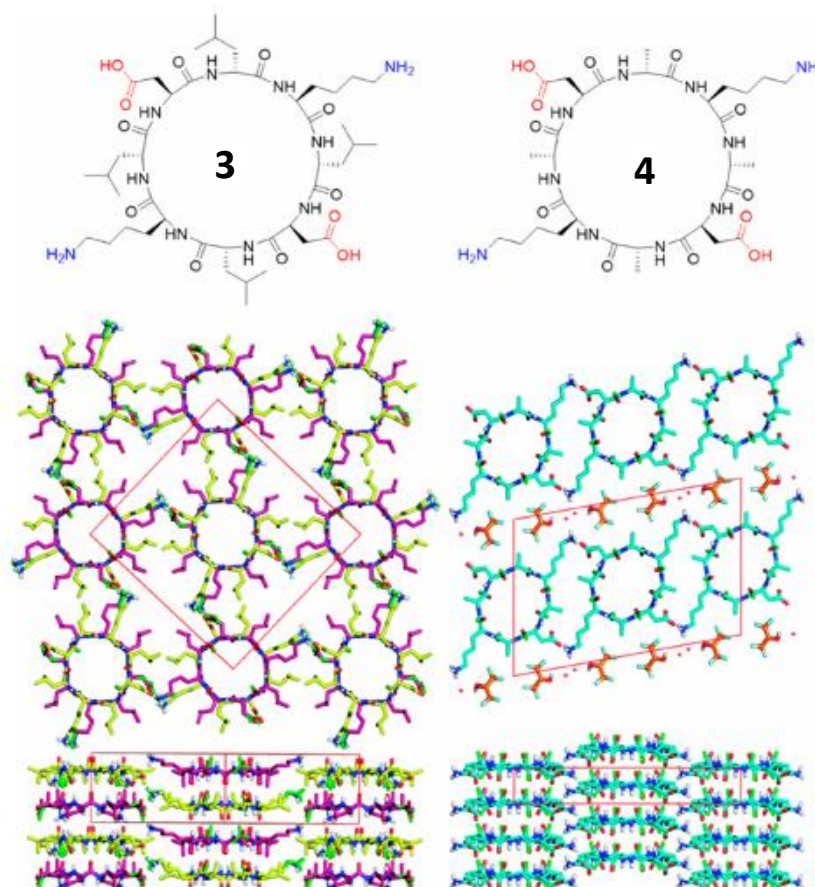


**Figure 3: Proposed model for the sequential 1D-to-2D self-assembly of cyclic peptide 2. (a) Chemical structure of cyclic peptide 2. (b) Formation of amphiphilic nanotubes based on the multiple hydrogen-bonding interactions between the peptide rings. (c) Formation of 2D nanosheet assembly by the amphiphilic nanotubes (Montenegro *et al.*, 2020)**

A systematic structural modification at key positions of the original 2D sheet-forming cyclic peptide was carried out to assess their effect on 2D nanosheet assembly. It was found that the mutation of the central hydrophobic residue Trp in the original peptide was well

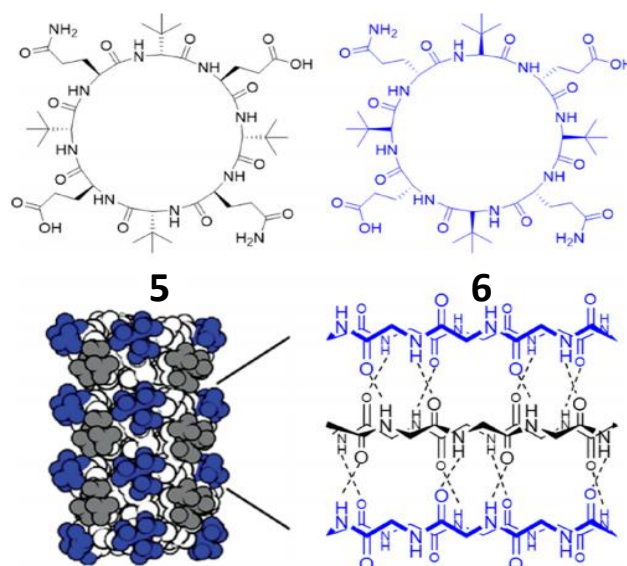
tolerated; 2D nanosheets could be observed when replacing Trp with Ala, Leu, or Phe. Similarly, the two Leu moieties could also be substituted with Phe moieties.

Chalmers *et al.* [2017], reported the first two crystal structures of cyclic  $\alpha$ -alt(D,L)-peptides. Two water-soluble cyclic peptides with the sequences of cyclo[-(L-Asp-D-Leu-L-Lys-D-Leu)<sub>2</sub>] (**3**) and cyclo[-(L-Asp-D-Ala-L-Lys-D-Ala)<sub>2</sub>] (**4**) were used to grow crystals in aqueous media (Figure 4). The crystal structure of **10** shows that the peptide rings arrange in continuous  $\beta$ -sheet-like nanotubes with extensive hydrogen-bonding interactions with two adjacent peptides. Within each nanotube, the peptides are assembled in an antiparallel fashion with like residues aligned along the nanotubes. Two conformations of **10** are present within the unit cell, differing slightly in backbone conformation and side-chain rotamers. Some disorder is observed in the amide carbonyls of the Asp residues as well as the side chains of Asp and Lys. The positively charged Lys side chains of each nanotube form a continuous network through ionic interactions with the negatively charged Asp side chains of an adjacent tube. Adjacent nanotubes run antiparallel to one another. Unlike peptide **3**, the crystal structure of peptide **4** shows the peptides are stacked in parallel and separated by layers of hexafluoroisopropanol (HFIP). Along the nanotube, each peptide is in alignment with its neighboring peptides. Although the CO and NH groups of the peptides interact through hydrogen bonds that are slightly offset, the CO...HN distances are similar to those found in the antiparallel crystal structure [Vijayaraj *et al.*, 2010]. The short Ala side chains allow the SCPNs to pack closely together, and each peptide forms two ionic interactions with its neighboring peptides. In the meantime, the less bulky Ala residues in **4** increase the flexibility of the peptide backbone, which is evident in the disorder of all backbone amide carbonyl groups, and the more oval pore shape than for **3**. These findings of both antiparallel and parallel stacking in cyclic peptides with similar sequences show that, contrary to the assumptions that have been made to date, cyclic  $\alpha$ -alt(D,L)-peptides do not necessarily adopt an antiparallel arrangement in the solid state. This implies that the steric hindrance caused by the side chains of amino acids also plays an important role in directing the stacking behaviors of the cyclic peptides.



**Figure 4: Chemical structures of cyclic peptides 3 and 4 and crystal structures of their SCNPs (Chalmers *et al.*, 2017)**

Svensson *et al.* [2004] designed a new cyclic peptide **5** with a sequence of cyclo-[(L-Gln-D-Tle-L-Glu-D-Tle)<sub>2</sub>] by replacing the D-Leu amino acids of the nanotube-forming cyclic peptide cyclo-[(L-Gln-D-Leu-L-Glu-D-Leu)<sub>2</sub>] with a bulkier amino acid tert-leucine (Tle) (Figure 5). It fails to assemble into nanotubes either by the formation of parallel or antiparallel hydrogen bonds. This is attributed to the steric clashes between near-neighboring homochiral residues of Tle. However, nanotubes are found to form when mixing **5** with its enantiomer cyclo-[(D-Gln-L-Tle-D-Glu-L-Tle)<sub>2</sub>] **6** through close antiparallel hydrogen bonding. The bulky tert-butyl side chains are positioned above the homochiral Gln and Glu residues of the enantiomeric peptide to overcome the steric hindrance, leading to the formation of a repetitive layered pattern of enantiomers. The presence of Tle residues in every second position can also be expected to shield the hydrogen bonds between peptide backbones in a nanotube from interaction with water, something that will result in increased stability in aqueous solution.

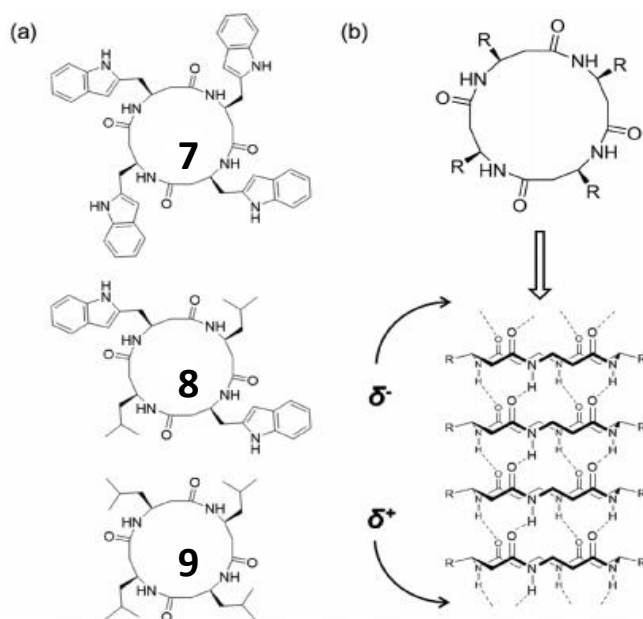


**Figure 5: Chemical structures of cyclic peptides 5 and 6 and the proposed layered structure of enantiomers (Svensson *et al.*, 2004)**

### 1.2 Tubular Ensembles of Cyclic $\beta$ -Peptides:

Cyclic  $\beta$ -peptides, consisting of a certain number of  $\beta$ -amino acids, are proved to be capable of forming SCPNs similar to cyclic  $\alpha$ -alt(D,L)-peptides. Despite the possible difficulty related to the synthesis of unnatural amino acids, the ability of  $\beta$ -peptides to resist enzymatic degradation and their favorable conformational properties emphasize their potential advantages over cyclic  $\alpha$ -alt(D,L)-peptides.

Ghadiri *et al.* [1998] explored the ion transport activities of the channel-forming cyclic  $\beta$ -peptides using three homochiral cyclic  $\beta$ -tetrapeptides, cyclo[-( $\beta^3$ -HTrp) $_4$ ] (**7**), cyclo[-( $\beta^3$ -HTrp- $\beta$ -HLeu) $_2$ ] (**8**), and cyclo[-( $\beta$ -HLeu) $_4$ ] (**9**) (Figure 6). Different from the  $C_2$  symmetrical conformation in which the central hole of the peptide ring is collapsed reported by [Seebach *et al.*, 1997] they proposed that the cyclic  $\beta$ -tetrapeptides will adopt an alternative  $C_4$  symmetrical conformation which gives an internal diameter of 2.6–2.7 Å in a lipid membrane environment. As a result, cyclic peptide **7** exhibited an ion transport rate of  $1.9 \times 10^7$  ions  $s^{-1}$  for  $K^+$  ion, which is comparable with the  $K^+$  transport rate of the previously reported cyclic  $\alpha$ -alt(D,L)-peptide, cyclo-[(L-Trp-D-Leu) $_3$ -L-GlnD-Leu-]. Considering the significantly smaller internal diameter of the nanotube formed by **7** compared to its cyclic  $\alpha$ -alt(D,L)-peptide counterpart (7–8 Å), the result might emphasize the importance of the existing macrodipole. However, a direct comparison using cyclic  $\beta$ -peptide and cyclic  $\alpha$ -alt(D,L)-peptide with similar chemical structure and the internal diameter is necessary to draw a firm conclusion.



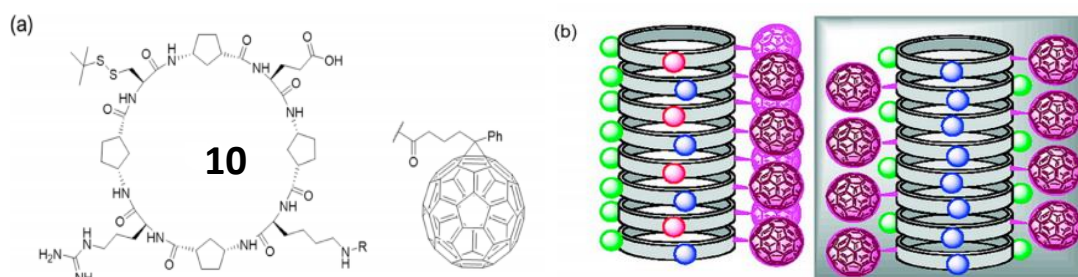
**Figure 6: (a) Chemical structures of the three cyclic  $\beta$ -tetrapeptides 7–9. (b) Predicted tubular structure with a parallel arrangement, showing a macrodipole along the nanotube (Ghadiri *et al.*, 1998)**

### 1.3 Tubular Ensembles of Cyclic $\alpha,\gamma$ -Peptides:

A new type of self-assembling cyclic peptides with novel structural and internal cavity properties was proposed and developed by [Castedo *et al.*, 2003]. These peptides are composed of an even number of alternating  $\alpha$ -amino acids and cyclic  $\gamma$ -amino acids. Planar ring conformations similar to cyclic  $\alpha$ -alt(D,L)-peptides and cyclic  $\beta$ -peptides lead to the formation of nanotubes driven by intermolecular hydrogen bonding interactions.

The nanotube structure of cyclic  $\alpha,\gamma$ -peptides was experimental confirmed by Granja *et al.* [2009]. As shown in Figure 7, a cyclic octapeptide **10** with the sequence of cyclo-[D $\gamma$ -Acp-L-Cys-D- $\gamma$ -Acp-L-Arg-D- $\gamma$ -Acp-L-Lys-D- $\gamma$ -Acp-L-Glu-] was designed and synthesized. Hydrophilic residues were introduced, aiming to increase the water solubility of the cyclic peptide and, at the same time, induce the self-assembly process under appropriate and controlled conditions. Moreover, the positively charged Arg residue and negatively charged Glu residue were expected to form complementary interstrand saltbridge interactions, which might induce the predominant formation of only one  $\beta$ -sheet pattern in the nanotube and also stabilize the nanotube. As a result, long fibrous structures were visualized by atomic force microscopy (AFM), which consisting of several nanotubes packed in a parallel manner. In the meantime, shorter needle-shaped structures with 2.5–3.0 nm in height were also observed, corresponding to the expected single-nanotubes. Furthermore, a fullerene moiety

was then attached to the cyclic peptide to aid in the characterization. TEM revealed the presence of long filaments ( $\sim 200$  nm) that were  $\sim 2.5$  nm in width, consistent with the width of the nanotubes. Combining the results obtained by TEM and scanning tunneling microscope (STM), it is concluded that the cyclic peptides are able to align the  $C_{60}$  moieties to form 1D fullerene arrangements in which the fullerenes point outward from the nanotube on both sides of the nanotubes. In other words, guided by the cyclic peptides, the fullerenes form two parallel wires separated by the peptide nanotube, which opens up opportunities for 1D alignment of functional materials.



**Figure 7: (a) Chemical structure of the cyclic octapeptide 10.**  
**(b) Two possible structures of the SCNP (Granja *et al.*, 2009)**

Pizzi *et al.* [2019] reported a cyclic hexapeptide **11** containing three pyridyl moieties connected to its backbone forms a hydrogen-bonded dimer, which tightly encapsulates a single xenon atom, like a pearl in its shell (Figure 8). The dimers of N-alkylated cyclic  $\alpha,\gamma$ -peptides process cavities with tunable properties, which could be used as molecular capsules to entrap guest molecules. Single-crystal X-ray diffraction shows the drum-shaped dimer has an approximate van der Waals internal equatorial diameter of  $5.4$  Å and a height appropriate for hosting a sphere with a maximum diameter of  $4.5$  Å, which fits well with the size of a single xenon atom ( $4.3$  Å). The two flat rings self-assemble in an antiparallel  $\beta$ -sheet like arrangement through six hydrogen bonds involving the amide moieties and the amidic  $C=O$  ( $N\cdots O$  distances of  $2.83$ - $2.98$  Å. The body-centred structure of the crystal forms tubular channels by stacking the dimers along the crystallographic  $c$  axis. Each dimer interacts with the next neighbour by a series of weak  $C\cdots O$  contacts ( $C\cdots O$  distances of  $3.06$  -  $3.22$  Å) between the amidic oxygens and the linker chains (both  $-CH_2$  and acetylenic carbons) connecting the pyridine moieties. Additional van der Waals contacts involving the Leu side chains further stabilize the tubular channels. The tubular channels show parallel packing, stabilized by short contacts involving the pyridine moieties of nearby rings. Further stabilization of the lateral self assembly is provided by the interactions between the pyridine

residues and the peptide backbone of adjacent tubes. It is highly anticipated that by rational designing the N-alkylated cyclic  $\alpha,\gamma$ -peptides, the resulting dimeric motifs with desired cavity properties could be used as supramolecular hosts, which bind with guest molecules with high affinity and selectivity.



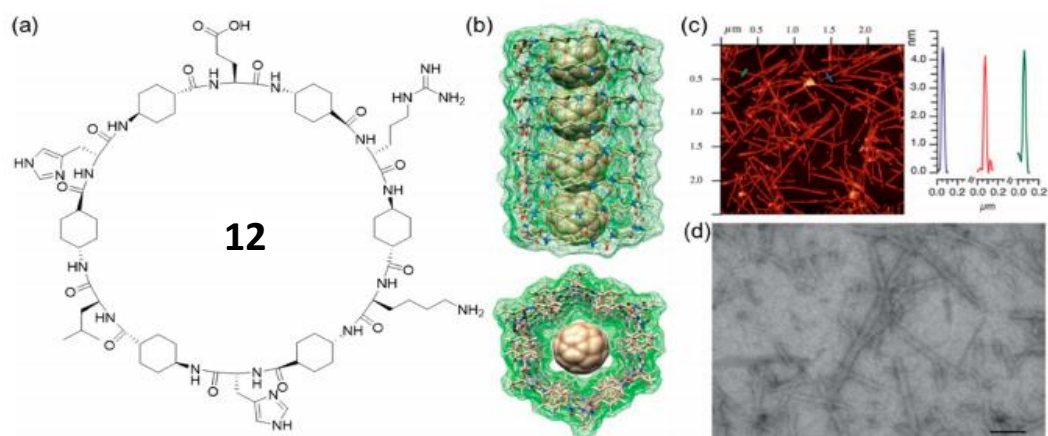
**Figure 8: (a) Chemical structures of the cyclic hexapeptide 11 and the corresponding dimer. (b) Crystal structures of the dimeric ensemble containing a Xe atom in the intradimer cavity (Pizzi *et al.*, 2019)**

#### 1.4. Tubular Ensembles of Cyclic Peptides Containing $\delta$ - or $\epsilon$ -Amino Acids:

The introduction of  $\delta$ - or  $\epsilon$ -amino acids will further allow the design of new cyclic peptides with various self-assembling structures and properties. However, to retain the necessary rigid shape of the cyclic peptide rings to facilitate intermolecular hydrogen bonding,  $\delta$ - or  $\epsilon$ -amino acids with more rigid conformation need to be used.

Lamas *et al.* [2018] reported that 4-aminocyclohexanecarboxylic acid is a rigid stretcher building block for the preparation of cyclic peptides that self-assemble to form peptide nanotubes with large diameter and hydrophobic pore. First, confirmed the assembling properties of the cyclic (D,L)  $\alpha,\delta$ -peptides with dimeric models then, the studies were extended to the formation of nanotubes. A cyclic dodecapeptide **12** was designed, with the incorporation of Glu, Lys, and His residues to improve solubility in aqueous media and provide control over the assembling process (Figure 9). With the help of Arg residue to facilitate the deposition of the nanotube on an anionic mica surface, fibrous structures with lengths of a few  $\mu\text{m}$  and average heights of 3.3–3.9 nm were observed using AFM by drop-casting the aqueous solution on mica, proving the formation of nanotubes. Moreover, the nanotubes with hydrophobic, large internal cavities were further used for the efficient encapsulation of fullerene  $\text{C}_{60}$  to form peptide nanopeapod-type structures. It is, thus, anticipated that these new nanotubes with large internal diameters and hydrophobic properties will function as efficient platforms such as nanocarriers and nanochannels.



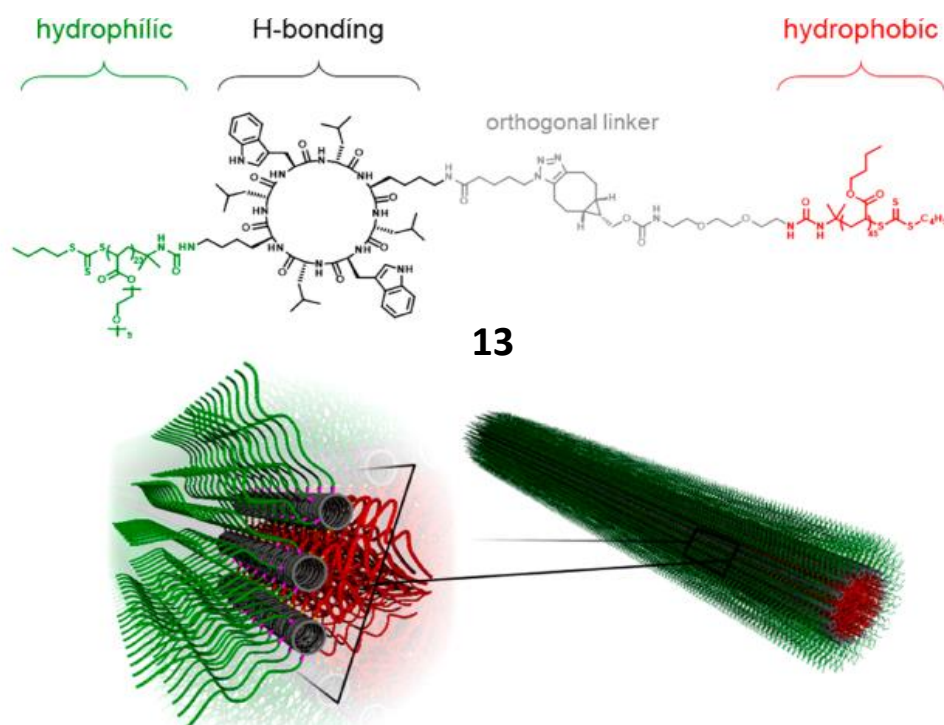


**Figure 9: (a) Chemical structure of the cyclic D,L- $\alpha,\delta$ -peptide 12. (b) Side and top views of a computer-assisted model of C<sub>60</sub> encapsulated in the inner cavity of SCPN. (c) AFM topography micrographs from aqueous solutions of cyclic peptide 50 and C<sub>60</sub> deposited over mica and AFM height profiles along the transects. (d) STEM image of an aqueous solution of cyclic peptide 50 and C<sub>60</sub> after deposition on a holey carbon grid (scale bar 100 nm) (Lamas *et al.*, 2018)**

## 2. Cyclic Peptide–Polymer Conjugates:

One of the major drawbacks of self-assembling cyclic peptide nanotubes is their poor solubility in solvents and the propensity to laterally aggregate in large bundles. Inspired by the concept of synthetic polymer–biomolecule conjugates initially proposed by Ringsdorf, polymers have been attached to cyclic peptides, resulting in cyclic peptide–polymer conjugates. The introduction of polymers onto the periphery of cyclic peptide cores not only improve the solubility of these cyclic peptide nanotubes but provide the steric hindrance to avoid their lateral aggregation.

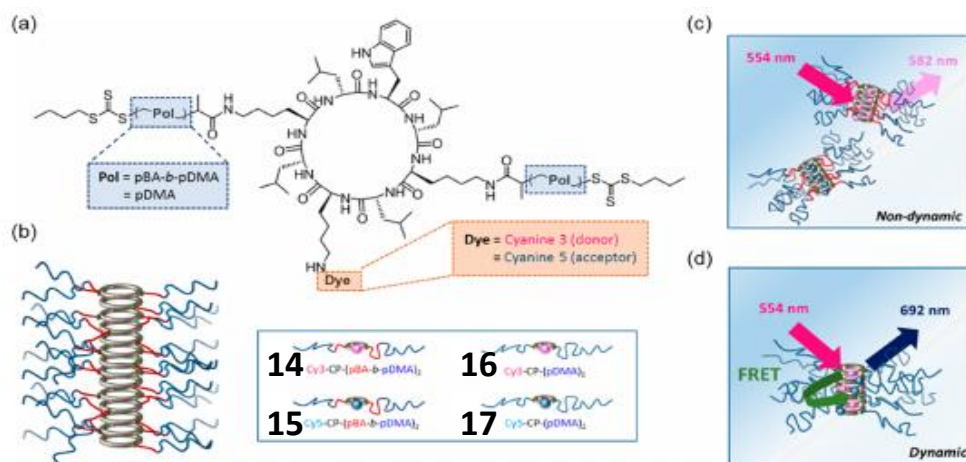
Brendel *et al.* [2019] designed an asymmetric cyclic peptide–polymer conjugate, pBA-CP-pPEGA (**13**), bearing one hydrophobic polymer pBA and one hydrophilic polymer pPEGA (Figure 10). The conjugate assembles into amphiphilic Janus nanotubes, which is expected to self-assemble further into a more complex core–shell cylindrical assembly in aqueous solution, named tubisome. The core of the tubisome consists of the hydrophobic pBA, while the hydrophilic pPEGA forms the shell. The tubisome structure is proved by SANS. The core diameter of these cylindrical structures was around 15 nm, much larger than the internal diameter of a single nanotube (0.75 nm). Such a large diameter confirmed these structures were composed of several nanotubes. The tubisome structure is driven by both the intermolecular hydrogen bonding interaction between peptide rings and the hydrophobic effect of amphiphilic polymers in water.



**Figure 10: Chemical structure of the asymmetric cyclic peptide–polymer conjugate pBA-CP-pPEGA 78 and its self-assembled tubisome structure in water (Brendel *et al.*, 2019)**

Rho *et al.* [2019] synthesized a cyclic peptide in which, the periphery of the CP was conjugated with an amphiphilic diblock co-polymer (Figure 11). This cyclic peptides self-assemble to form peptide nanotubes which are highly dynamic in nature, i.e., they disassemble and re-assemble readily, they form progressively mixed nanotubes. The dynamic nature of these nanotubes was probed via FRET using conjugates attached with Cyanine (Cy) 3 (FRET donor) and Cy5 (FRET acceptor) (**14– 17**) to detect the mixing of cyclic peptide conjugate unimers between nanotubes. If the Cy3 and Cy5 dyes are in close in proximity to one another, upon excitation of the donor dye, we should observe the emission of the acceptor dye due to energy transfer between the FRET pair. This proximity-dependent energy transfer can only take place when two different dye conjugates are assembled together in the same nanotube (each cyclic peptide is around 7.5 Å in diameter and the distance between the two peptides is 4.5 Å; the FRET range is between 10 to 100 Å). The change in FRET ratio over time was observed to be extremely slow, while in the control conjugate system, the increase in FRET ratio was very fast, and the plateau was reached within 60 min. Moreover, the mixing degree of the diblock conjugates was only 41% even after 7 days, which was far lower than that of the control conjugate (89%). The results confirm that the introduction of hydrophobic segments effectively stabilizes the hydrogen-

bonded cyclic peptide ensemble, affording a much less dynamic system (Figure 34). This process should eventually lead to a statistically mixed nanotube where the Cy3 and Cy5 modified peptide should be randomly distributed throughout the aggregate and a constant final FRET ratio is reached.



**Figure 11: (a) Chemical structures of dye-functionalized cyclic peptide–diblock polymer conjugates 14 and 15. (b) Structure of the SPCPN formed by the cyclic peptide–diblock polymer conjugate. (c) Scheme showing no FRET occurring in a stable nondynamic system. (d) Scheme showing FRET occurring in a dynamic system (Rho *et al.*, 2019)**

### Conclusion:

In this chapter, the design of CPs as scaffolds for the self-assembly of nanotubes with controllable internal diameter, pore chemistry, and exterior functionality, as well as the use of dimers of cyclic peptides, accessed via N-alkylation, to study the relative strength of the stacking interaction was discussed. By modification of the peptide structure through the introduction of different  $\alpha$ -,  $\beta$ -, or  $\gamma$ -residues, nanotubes have been designed for a wide range of applications from ion channels, to encapsulation. The cyclic peptide motif is a powerful one for the formation of functional nanotubes because the hydrogen-bonding interactions are strong enough to direct the assembly of large molecules such as fullerenes, and polymers, providing a synthetically facile route to form complex nanostructures that are otherwise very challenging to prepare. Not only can these molecules be used to functionalise the periphery of the tube, opening up a range of new applications, such as membranes controllable on the sub-nanometer size range, but they can also be used to control the nanotube length and sterically stabilise individual tubes in solution.

**References:**

1. Lehn, J.-M. (2002). Supramolecular Polymer Chemistry-Scope and Perspectives. *Polym. Int.*, 51(10), 825–839.
2. Jorgensen, W. L., & Pranata, J. (1990). Importance of Secondary Interactions in Triply Hydrogen Bonded Complexes: Guanine-Cytosine vs Uracil 2,6-Diaminopyridine. *J. Am. Chem. Soc.*, 112(5), 2008–2010.
3. Murray, T. J., & Zimmerman, S. C. (1992). New Triply Hydrogen Bonded Complexes with Highly Variable Stabilities. *J. Am. Chem. Soc.*, 114(10), 4010–4011.
4. Krieg, E., Bastings, M. M. C., Besenius, P., & Rybtchinski, B. (2016). Supramolecular Polymers in Aqueous Media. *Chem. Rev.*, 116 (4), 2414–2477.
5. Sato, K., Hendricks, M. P., Palmer, L. C., & Stupp, S. I. (2018). Peptide Supramolecular Materials for Therapeutics. *Chem. Soc. Rev.*, 47, 7539–7551.
6. McLaughlin, C. K., Hamblin, G. D., & Sleiman, H. F. (2011). Supramolecular DNA Assembly. *Chem. Soc. Rev.*, 40, 5647–5656.
7. Song, Q., Cheng, Z., Kariuki, M., Hall, S. C. L., Hill, S. K., Rho, J. Y., & Perrier, S. (2021). Molecular Self-Assembly and Supramolecular Chemistry of Cyclic Peptides, *Chem. Rev.*, 121 (22), 13936-13995.
8. Shimizu, T., Ding, W., & Kameta, N. (2020). Soft-Matter Nanotubes: A Platform for Diverse Functions and Applications. *Chem. Rev.*, 120, 2347–2407.
9. Ghadiri, M. R., Granja, J. R., Milligan, R. A., McRee, D. E., & Khazanovich, N. (1993). Self-assembling Organic Nanotubes Based on a Cyclic Peptide Architecture. *Nature*, 366 (6453), 324–327.
10. Insua, I., & Montenegro, J. (2020). 1D to 2D Self Assembly of Cyclic Peptides. *J. Am. Chem. Soc.*, 142 (1), 300–307.
11. Nelson, D. L., Cox, M. M., & Cox, M. M. (2008). *Lehninger principles of biochemistry*, 5th ed. W H Freeman & Company: New York.
12. Silk, M. R., Newman, J., Ratcliffe, J. C., White, J. F., CaradocDavies, T., Price, J. R., Perrier, S., Thompson, P. E., Chalmers, D. K. (2017). Parallel and Antiparallel Cyclic D/L Peptide Nanotubes. *Chem. Commun.*, 53, 6613–6616.
13. Vijayaraj, R., Raman, S. S., Kumar, R. M., & Subramanian, V. (2010). *J Phys Chem B*, 114, 16574-16583.

14. Rosenthal-Aizman, K., Svensson, G., & Undén, A. (2004). Self-Assembling Peptide Nanotubes from Enantiomeric Pairs of Cyclic Peptides with Alternating D and L Amino Acid Residues. *J. Am. Chem. Soc.*, 126 (11), 3372–3373.
15. Clark, T. D., Buehler, L. K., & Ghadiri, M. R. (1998). Self-Assembling Cyclic  $\beta$ 3 -Peptide Nanotubes as Artificial Transmembrane Ion Channels. *J. Am. Chem. Soc.*, 120, 651–656.
16. Seebach, D., Matthews, J. L., Meden, A., Wessels, T., Baerlocher, C., McCusker, L. B. (1997). Cyclo- $\beta$ -Peptides: Structure and Tubular Stacking of Cyclic Tetramers of 3-Aminobutanoic Acid as Determined from Powder Diffraction Data. *Helv. Chim. Acta*, 80, 173–182.
17. Amorín, M., Castedo, L., & Granja, J. R. (2003). New Cyclic Peptide Assemblies with Hydrophobic Cavities: The Structural and Thermodynamic Basis of a New Class of Peptide Nanotubes. *J. Am. Chem. Soc.*, 125 (10), 2844–2845.
18. Reiriz, C., Brea, R. J., Arranz, R., Carrascosa, J. L., Garibotti, A., Manning, B., Valpuesta, J. M., Eritja, R., Castedo, L., Granja, J. R. (2009).  $\alpha,\gamma$ Peptide Nanotube Templating of One-Dimensional Parallel Fullerene Arrangements. *J. Am. Chem. Soc.*, 131 (32), 11335–11337.
19. Pizzi, A., Ozores, H. L., Calvelo, M., García-Fandiño, R., Amorín, M., Demitri, N., Terraneo, G., Bracco, S., Comotti, A., Sozzani, P., Bezuidenhout, C. X., Metrangolo, P., Granja, J. R. (2019). Tight Xenon Confinement in a Crystalline Sandwich-like Hydrogen-Bonded Dimeric Capsule of a Cyclic Peptide. *Angew. Chem., Int. Ed.*, 58, 14472–14476.
20. Lamas, A., Guerra, A., Amorín, M., & Granja, J. R. (2018). New Self-Assembling Peptide Nanotubes of Large Diameter Using  $\delta$ -Amino Acids. *Chem. Sci.*, 9, 8228–8233.
21. Brendel, J. C., Catrouillet, S., Sanchis, J., Jolliffe, K. A., & Perrier, S. (2019). Shaping Block Copolymer Micelles by Supramolecular Polymerization: Making ‘Tubisomes’. *Polym. Chem.*, 10, 2616–2625.
22. Schneider, T. L., Mathew, R. S., Rice, K. P., Tamaki, K., Wood, J. L., Schepartz, A. (2005). Increasing the Kinase Specificity of K252a by Protein Surface Recognition, *Org. Lett.*, 7, 1695-1698.

## **SOLID WASTE MANAGEMENT PRACTICES: A CASE STUDY OF KERALA, INDIA**

**Rincy A and Anila George\***

PG and Research Department of Environmental Science,

St. John's College Anchal, Kollam, Kerala, 691306

Corresponding author E-mail: [anila.george44@gmail.com](mailto:anila.george44@gmail.com)

### **Abstract:**

The preservation of our environment and the promotion of sustainable development axis upon the proficient management of solid waste. This overview provides a comprehensive examination of key aspects of solid waste management, underscoring its importance, challenges, and potential solutions. Vital to mitigating adverse environmental impacts and enhancing public health, effective solid waste management encompasses the meticulous collection, efficient transportation, proper disposal, and recycling of waste materials. Within this realm, challenges arise from the escalating volume of waste, improper disposal practices, and insufficient resources allocated to waste infrastructure. Addressing these issues necessitates the adoption of state-of-the-art technologies, the promotion of waste reduction, and active engagement of communities. These elements compose the bedrock of sustainable solutions. This abstract highlight the pressing need to tackle solid waste management urgently, fostering communities that are not only cleaner and healthier but also inherently sustainable.

**Keywords:** Solid Waste Management, Waste to Energy, Kerala

### **Introduction:**

Most human actions inevitably result in waste, which is a given alongside mortality and change in our lives. Even though we cannot stop these events, we can improve our preparedness by improving management (Agarwal *et al.*, 2015). Solid waste is made up of materials that are undesirable or pointless that are generated from a variety of sources, including residential, industrial, and commercial activity in a given area. Based on its source (domestic, industrial, commercial, construction, or institutional), content (organic materials, glass, metal, plastic, paper, etc.), or possibility for reuse, solid waste can be divided into many categories. Food scraps, paper, plastic, metals, glass, textiles, rubber, leather, and demolition and building debris all make up solid waste. Additionally, a lot of packaging waste is produced, including paper, plastic, and other materials. These substances are normally solid

or semi-solid, and people typically get rid of them by throwing them away or burning them. Municipal solid waste is described as waste created by homes and companies, as opposed to industrial waste, which is defined as waste produced by manufacturers or businesses. (Yusof *et al.* (2004). The degree of commercial activity, population density, economic standing, cultural standards, and the specific city or region all have an effect on the amount of waste produced (Kumar *et al.*, 2017).

In today's world, a lot of ordinary goods are made for single use and eventual disposal. The consumption patterns of many people can be characterized by the proliferation of disposable products and single-use packaging. The difficulty of getting rid of these waste products has grown because disposables are now more widely available. Waste is a by-product produced in almost every human activity, including healthcare, agriculture, marketplaces, crafts, food processing, and more (Abah and Ohimain, 2011).



Several reasons, including the following, contribute to the rise in solid waste generation:

**Population Growth:** The amount of waste produced rises proportionally as the world's population continues to expand. More people produce more waste, including household waste and other consumables.

**Increase in Industrial Manufacturing:** The expansion of industrial activities leads to the production of goods and products on a larger scale. This, in turn, generates more waste in the form of manufacturing by products, packaging materials, and industrial waste.

**Urbanization:** People move from rural areas to cities as a result of rapid urbanization. In urban environments, consumption patterns change, and there is typically more packaging and disposable items, contributing to an upsurge in solid waste production.

**Modernization:** As societies modernize, they tend to adopt convenience-oriented lifestyles, which often involve the use of single-use items and technology. This results in a higher volume of waste, particularly electronic waste (e-waste) from outdated gadgets and appliances.

**Automobile Exhaust:** Automobiles emit pollutants and particulate matter into the atmosphere, contributing to air pollution. While not directly related to solid waste generation, this pollution can indirectly impact the environment and human health by affecting waste disposal sites and ecosystems.

A complex issue that is driven by societal, economic, and demographic variables is the rise in solid waste. To effectively manage trash and promote sustainable practices, it is imperative to comprehend these factors (Thompson, 2009).

According to data from the World Bank, 2.01 billion tonnes of MSW are produced annually around the world, and of this trash, around one-third is handled and disposed of in a way that doesn't harm the environment. The majority of developed nations use techniques that are safe for the environment. According to Joseph *et al.* (2018), the composition of MSW changes depending on a number of factors, such as geography, source site of collection, and lifestyle habitats. Municipal Solid Waste (MSW) is created in around 1.3 billion tons annually, and by 2025, it is expected to increase to 2.2 billion tons globally.

### **Solid waste generation in India**

The Central Pollution Control Board's annual report for the fiscal year 2020–21 states that India produced a total of 160,038.9 Tonnes Per Day (TPD) of solid trash. Out of this, 152,749.5 TPD, which accounts for 95.4 percent, was successfully collected. According to the same data, 29,427.2 TPD (18.4%) of the waste was dumped in landfills, while 79,956.3 TPD (50 percent) underwent waste treatment. It should be noted that a sizeable percentage of 50,655.4 TPD, or 31.7 percent of the total trash produced, is still unaccounted for. The amount of solid waste processed has increased over the last five years, rising from 19% in 2015–16 to almost 50% in 2020–21. In contrast, less solid waste is being dumped in landfills,



from 54% in 2015–16 to 18.4% in 2020–21. It's interesting to note that between 2015–16 and 2020–21, the amount of solid trash produced per person (measured in grams per day) stayed the same. (The Energy and Resources Institute (TERI) and the International Centre for Environment Audit and Sustainable Development (ICED) of Jaipur, India,

### **Solid waste generation in Kerala**

Kerala is a tropical peninsular state in western India, making up 38,863 Km<sup>2</sup> of the nation's total land area, or 1.2%. The area is bounded by the Eastern longitudes of 74°.27'47" and 77°.37'.12" E and the Northern latitudes of 8°.17'.30" and 12°.47'.40". The state is bordered by water on one side and by land on three others. The state is bordered on the west by the Arabian Sea (Lakshadweep Sea), on the south by Tamil Nadu and the Indian Ocean, on the north and north-east by the states of Karnataka, and on the east by the state of Tamil Nadu. About 560 kilometers of shoreline are present in the State. According to the Census of India 2011, Kerala had 3,34,06,061 residents, or 2.76 percent of all Indians. 52 percent of the people in the state are women, and 48 percent are men. Kerala had the lowest decadal population growth rate of all the Indian States at 4.9 percent. At 450 grams per person per day, the total trash produced in the State amounts to almost 15000 tons per day. The centre and northern regions of the State are anticipated to produce more waste in the future than the southern region. The state of Kerala produces around 11,449 tonnes of solid trash every day, with 3,452 tonnes coming from urban regions and 7,997 tonnes coming from rural ones, according to the Kerala State Environment Plan 2022. Kerala produces 3.7 million tonnes of solid trash per year.

### **Solid waste management**

Municipal solid waste management (MSWM) is a systematic process that includes resource recovery in addition to the collection, processing, and disposal of solid waste. Management of municipal solid waste is crucial because, if not handled effectively, it has negative effects on society's aesthetics, ecology, and health (Abhirami, 2021). Waste management procedures vary across established and developing countries, between urban and rural areas, and between producers in the residential and industrial sectors. There is a possible risk to public health as a result of improper waste management, treatment, and disposal systems (Tom and Kamal, 2020). A comprehensive Solid Waste Management Strategy encompasses a range of activities aimed at minimizing environmental impact, ensuring public health and safety, and optimizing resource recovery through proper

handling, segregation, collection, transportation, storage, recycling, disposal, and treatment of solid waste. Each activity plays a vital role in the overall waste management process.

Inadequate Municipal Solid Waste (MSW) disposal and management give rise to various forms of pollution, affecting the air, soil, and water. The reckless dumping of waste leads to the contamination of both surface and groundwater sources. MSW builds up in drains in metropolitan areas, creating stagnant water that serves as an insect breeding ground and causes floods during rainy seasons. Furthermore, unregulated incineration and the improper burning of MSW are major contributors to urban air pollution. The decomposition of organic waste in landfills releases greenhouse gases, and the untreated leachate from these dumps contaminates the nearby soil and water sources. Additionally, improper MSW management poses health and safety concerns. Waste attracts rats and insects, which could transmit diseases like cholera and dengue fever (Alam and Ahmade, 2013).

Kerala's waste management landscape comprises 6 Municipal Corporations, 87 municipalities, 77 Taluks, 14 District Panchayats, 152 Block Panchayats, and 941 Grama Panchayats. Annually, the state generates a total of 3.7 million tons of solid waste, with a breakdown of 69% being biodegradable waste and 31% non-biodegradable waste. Among the biodegradable waste, there is an approximate moisture content of 70%. In the non-biodegradable waste category, the waste can be further categorized into combustible (79.2%) and non-combustible (20.8%) fractions. Kerala's municipalities produce an average of 0.28 kg of waste per person every day. According to estimates by the World Bank's Urban Development Section, the amount of garbage produced per person is expected to increase at an annual rate of 1.41%, which is an exponential growth rate. As a result, it can be said that each person currently produces 0.343 kilograms of MSW each day, for a daily average of 7056 tonnes of MSW production (Varma, 2006). Kerala is thought to produce around 8000 tons of garbage every day, of which 7% is plastic waste. As a result, due to a lack of disposal options, every town and community in the state is currently attempting to manage the solid waste that keeps accumulating (Harikrishnan, 2014).

Kerala grapples with the daunting challenge of managing a daily waste output exceeding 8000 tons, with plastic waste constituting 7% of this total. This predicament has left every town and city in the state struggling to cope with the mounting piles of solid waste, as disposal options remain limited. As one traverses from the northern to the southern regions of Kerala, it becomes evident that the landscape is marred by numerous garbage

hotspots. These hotspots include places like Kelugudde, Seethangoli, and Kollangana in Kasargod; Pettippalam and Chelora in Kannur; Njeliyaparamba in Kozhikode; Pirivusala in Palakkad; Lalur in Thrissur; Chakkukandam in Guruvayur; Brahmapuram in Ernakulam; Vadavathur in Kottayam. As a result of Kerala's unrelenting march toward urbanization, local resistance movements have developed to protest the indiscriminate disposal of solid waste, especially plastic and technological garbage (Harikrishnan, 2014).

In Kerala, waste management is usually done by incineration, landfilling, composting, reuse, and recycling (Varma *et al.*, 2006). The Kerala State Pollution Control Board produces various rules for the implementation of waste management in Kerala. Kerala consists of various waste management programs like Suchitwa mission, Haritha Kerala Mission, Kudumbha Sree for Haritha Karma Sena, Kerala Solid Waste Management Project (KSWMP) and Clean Kerala Limited. The problems faced by the Kerala waste management is the overloaded waste dumping beyond the capacity that led to a major health problem in Kerala which is particularly due to the less land availability, dense population, and increasing quantities. Some key features of Kerala's waste management system include:

**Segregation at Source:** Kerala urges locals to separate garbage into categories like hazardous, non-hazardous, and biodegradable at the source.

**Door-to-Door Collection:** Door-to-door waste collection services have been developed by the state to guarantee the proper disposal of separated waste.

**Biodegradable Waste Composting:** Kerala promotes composting of biodegradable waste through community composting units and decentralized composting facilities.

**Non-Biodegradable Waste Recycling:** Recycling facilities are set up to manage non-biodegradable waste materials like plastics, paper, and metals.

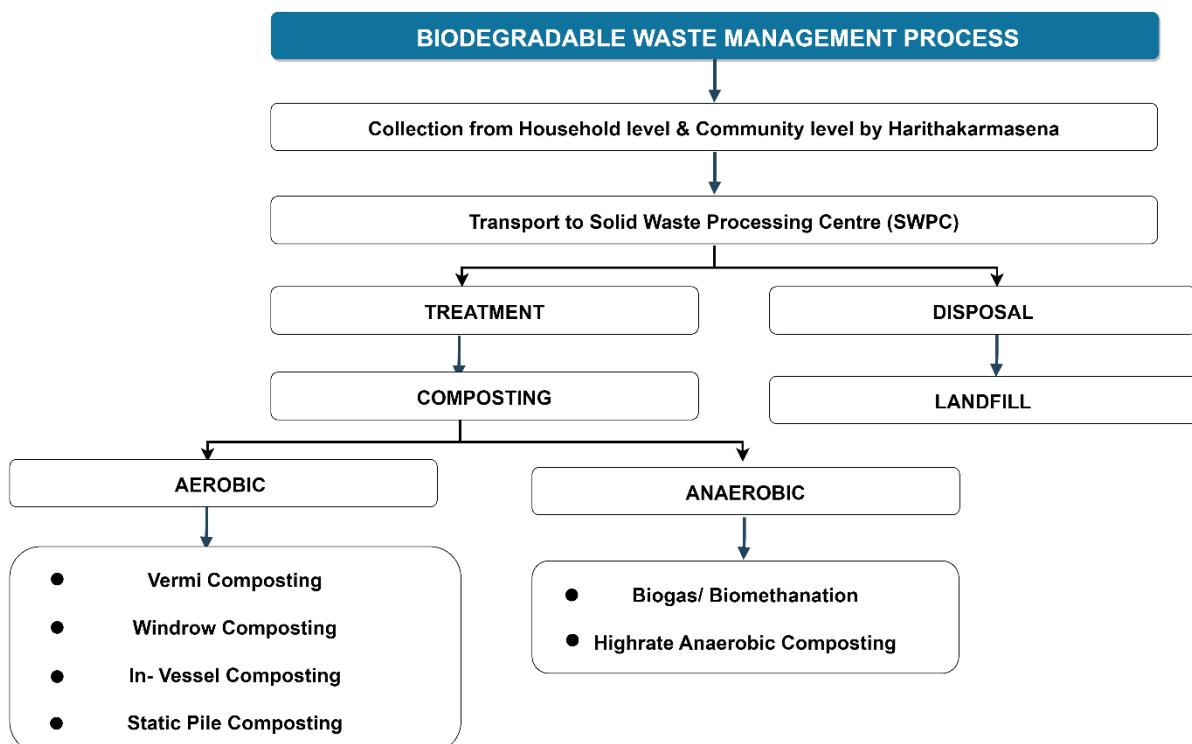
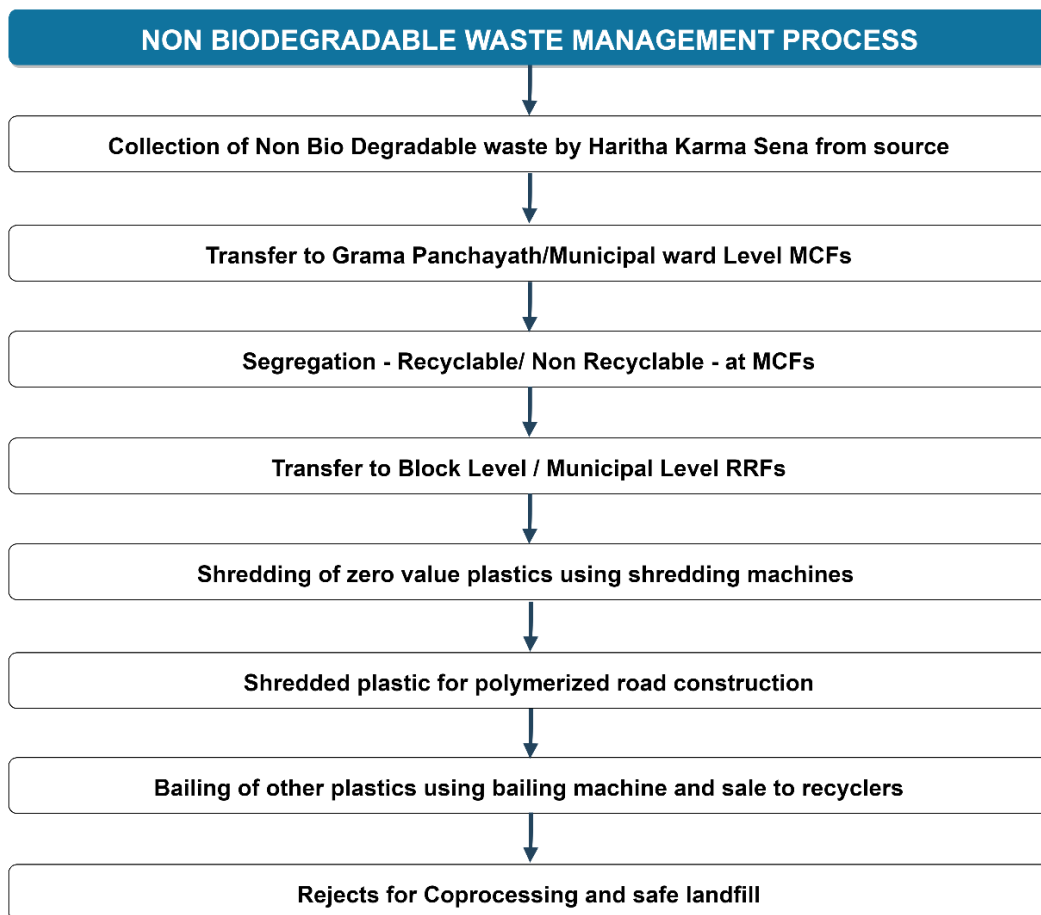
**Hazardous Waste Management:** Hazardous waste is processed and disposed of in accordance with environmental rules by industries and healthcare facilities.

**Waste-to-Energy Plants:** Kerala has investigated waste-to-energy systems to create energy from non-recyclable garbage.

**Awareness and Education:** Public awareness campaigns and educational programs are conducted to encourage responsible waste disposal and reduce littering.

**Legal Framework:** The state has enacted laws and regulations to govern waste management practices and ensure compliance.

**Green Initiatives:** Some cities in Kerala have implemented initiatives like "clean and green" campaigns to beautify public spaces while promoting cleanliness.



Kerala's waste management system reflects its commitment to sustainable development and environmental conservation. However, the effectiveness of these initiatives may vary across different regions of the state. Effective solid waste management attempts to lessen or eliminate negative effects on the environment, human health, and economic growth while fostering a higher standard of living. Monitoring, collecting, transportation, processing, recycling, and disposal are just a few of the critical procedures involved in managing municipal garbage (Manoj, 2017). The fundamental principles of waste management include three objectives:

1. management of urban solid waste management used to protect the health of the urban population especially the health of the low and middle income groups.
2. should be to protect the environment by controlling water and soil pollution it should also ensure the sustainable management.
3. By offering effective waste management services and guaranteeing the effective use and conservation of movable materials and resources, to assist urban economic development.

Managing solid waste is a difficult problem everywhere in the world, and the main causes are a lack of social responsibility and knowledge, as well as a lack of creative solutions. It has been noted that the waste generation rate rises in tandem with rising income, or globally. More garbage is produced as a result of urbanization (Kaza *et al.*, 2018). Over the last three decades, the weight of producing industrial and hazardous waste has shifted more to emerging nations. A rise in the garbage generated by emerging cities is also increased by factors such as population, migration to surrounding cities, growing city populations, and the creation of new cities, countries.

To uphold environmental sustainability and public health, effective solid waste management is indispensable. Communities can mitigate the detrimental impact of waste on the environment and conserve resources by implementing comprehensive waste reduction, recycling, and disposal programs. It is imperative for governments, businesses, and individuals to collaborate, fostering innovative solutions and reducing overall waste production. This collective effort will lead to a more sustainable and responsible approach to managing solid waste, ensuring a cleaner, healthier future for all.

#### **References:**

1. Abah, O., & Ohimain, E. I. (2011). Health care waste management in Nigeria: A case study. *Journal of Public Health and Epidemiology*, 3(3), 99-110.

2. Abhirami, K. S., Kunnel, A. P., Archa, R., & Latheef, A. (2021). Assessment of municipal solid waste management in Kochi city. *International Journal of Engineering Research & Technology (IJERT)*, ISSN: 2278-0181.
3. Agarwal, R., & Rajashree. (2015). Waste management initiatives in India for human wellbeing. *European Scientific Journal*, June 2015/SPECIAL/edition,
4. Alam, P., & Ahmade, K. (2013). Impact of solid waste on health and the environment. *Special Issue of International Journal of Sustainable Development and Green Economics (IJS DGE)*, ISSN No.: 2315-4721, 2(1).
5. Harikrishnan, G. (2014). Humanities Solid Waste Management: a comparative study between Kerala and Tamil Nadu. *International Journal of Research in Social Sciences and Humanities (IJRSSH)*, 4(4), ISSN: 2249-4642, 29.
6. International Centre for Environment Audit and Sustainable Development (iCED), Jaipur, India in Collaboration with The Energy and Resources Institute (TERI), New Delhi. (2022).
7. Joseph, K., Rajendran, S., Shenthilnandan, R., & Rakesh, M. (2012). Integrated approach to solid waste management in Chennai: An Indian Metro City. *Journal of Material Cycle and Waste Management*, 14(2).
8. Kaza, S., & Bhada T. P. (2018). Decision maker's guides for solid waste management technologies. *Urban Development series Knowledge Papers*, The International Bank for Reconstruction and Development/THE WORLD BANK 1818 H Street, N.W. Washington, D.C. 20433, U.S.A., pp,1-44.
9. Kumar, S., Smith, S. R., Fowler, G., Velis, C., Kumar, S. J., Arya, S., Kumar, R. R., & Cheeseman, C. (2017). Challenges and opportunities associated with waste management in India. *Royal Society of Open Science*, <https://doi.org/10.1098/rsos.160764>.
10. La Grega, G., Buckingham, M. D. P. L., & Evans, J. C. (2001). *Hazardous Waste Management*, 2<sup>nd</sup> Edition, Mc-Graw Hill publications.
11. Manoj, K. (2022). Solid Waste Management. *Riet Greater Noida, Journal of Construction and Building Materials Engineering*, 3(2).
12. Moeller, D. W. (2005). *Environmental Health* (3<sup>rd</sup> ed.). Cambridge, MA: Harvard University Press.
13. Thompson, A. (2009). *Land: Open Dumping and its effects on our environment*. Oklahoma Department of Environment Quality.

14. Tom, T., & Kamal, R. C. H. (2020). A Study on Waste Management of Household with Special Reference to Uzhavoor Panchayat-Kottayam District, Kerala. *Alochana Chakra Journal*, IX(5): 2533-2543.
15. Varma, A. (2006). A Technical report on the status of Municipal Solid Waste in Kerala.
16. Yusof A., Inane, B., & Hassan, M. N. (2004). Overview of waste disposal and landfills/dumps in Asian countries. *Material Cycles and Waste Management*, 16, 104–110.
17. <https://document.kerala.gov.in/documents/generalreports/general2909202215:09:15.pdf>

# A REVIEW ON CADMIUM SULPHIDE (CdS) THIN FILMS SYNTHESIS AND ITS APPLICATIONS

Y. A. Chaudhari

Department of Physics,

Shri Pancham Khemraj Mahavidyalaya, Sawantwadi, Dist. – Sindhudurg (M.S.)

Corresponding author E-mail: [drtusharphysics@gmail.com](mailto:drtusharphysics@gmail.com)

## Abstract:

Cadmium sulphide (CdS) is a type of semiconductor material used for different applications. The present article describes the review on preparation of CdS thin films using chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) techniques. This review article also presents the different applications of CdS thin films.

**Keywords:** CdS, thin films, CBD, SILAR, applications

## Introduction:

The n-type semiconductor CdS, which has a straight band gap of 2.4 eV, has been thoroughly studied as a thin film. The cadmium sulphide (CdS) thin films are a highly stable as well as economical material in photovoltaic sector [1]. The CdS thin films have number of potential applications in various fields such as electrochemical cells, thin film solar cells [2], photosensor, photoconductor, photocatalyst [3], Light emitting diodes [4], optical detector [5], field effect transistor (FET) [6], piezoelectric transducer [7].

## Synthesis of Cadmium sulphide (CdS) thin films:

The CdS thin films have been prepared by using different synthesis route such as chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) route.

### 1. Chemical Bath Deposition (CBD):

It is a solution phase technique in which the compound semiconductors are obtained from the aqueous solution using chemical bath deposition [8].

Producing large-area thin films for solar energy related applications can be achieved using the chemical bath deposition technique [9].

Toma *et al.* [10] reported the synthesis of CdS thin films via chemical bath deposition method.



A. Fernandez Perez *et al.* [11] reported the preparation of doped and undoped CdS thin films over a different substrate such as glass, copper and bronze via chemical bath deposition (CBD) route.

Rondiya *et al.* [12] reported the formulation of cadmium sulfide (CdS) thin films through a chemical bath deposition (CBD) route.

Fouad Ouachtari *et al.* [13] reported the formulation of CdS thin films using a chemical bath deposition (CBD) technique on a glass substrate.

R. John Xavier *et al.* [14] reported the thin film formulation of Cadmium sulfide material using chemical bath deposition on a glass substrate.

D Kathirvel *et al.* [15] reported the synthesis of CdS thin film through chemical bath deposition route.

R. Sahraei *et al.* [16] reported the thin film formulation of Cadmium sulfide (CdS) material using new chemical bath deposition method.

O. Okorie *et al.* [17] reported the thin film preparation of CdS material by applying a chemical bath deposition route.

Mahesh Kamble *et al.* [18] reported the formulation of CdS thin films via chemical bath deposition technique.

N.T. Shimpi *et al.* [19] reported the thin film formulation of CdS material through chemical bath deposition route.

## **2. Successive ionic layer adsorption and reaction (SILAR):**

The successive ionic layer adsorption and reaction (SILAR) method, often known as a modified variant of chemical bath deposition, is one of the most recent technique for the deposition of thin films [20].

K. M. Garadkar *et al.* [21] reported the formulation of CdS thin films via SILAR route. Sankapal *et al.* [22] reported the thin film formulation of cadmium sulfide material through successive ionic layer adsorption and reaction technique.

Mukherjee *et al.* [23] reported the formulation of CdS thin film through SILAR route.

Phasook *et al.* [24] reported formulation of Mn incorporated CdS thin films via successive ionic layer adsorption and reaction technique.

Pradhabhan *et al.* [25] reported the synthesis of thin films of Cu incorporated CdS material through Successive Ionic Layer Adsorption and Reaction route.

Pradhabhan *et al.* [26] reported the formulation of cadmium sulphide (CdS) thin films through SILAR technique.

Manikandan *et al.* [27] reported the formulation of CdS thin films via successive ionic layer adsorption and reaction (SILAR) route.

Desale *et al.* [28] reported the formulation of CdS thin films through SILAR technique.

### **Conclusions:**

In this article, we have reviewed the synthesis techniques of CdS thin films by chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) routes as well as the applications of CdS thin films.

### **References:**

1. Lalwani Rajesh, Brijlata Sharma, R. Das. (2015). Synthesis and photoconductivity studies of CdS thin films prepared by chemical bath deposition method. *International Journal of Advanced Engineering Research and Studies*, 4(2), 278-279.
2. Pushpalatha H. L., S. Bellappa, R. Ganesh. (2014). Structural and morphological studies of CdS thin films grown by photochemical deposition. *International Journal of ChemTech Research*, 6(3), 1998-2001.
3. Nikam C. P., S. R. Gosavi. (2014). Characterization of nanocrystalline CdS thin films deposited on FTO by CBD for photosensor applications. *Advances in Applied Science Research*, 5(5), 267-272.
4. Razaw Dindar Hussein, Adeeb Omer Jafer. (2022). A review on Physical Properties of CdS Thin Film. *Journal of Physical Chemistry and Functional Materials*, 5(1), 40-50.
5. Ratana Devi I., L. Raghmani Singh. (2020). Study of Optical Properties of CdS and Cu doped CdS Thin Films Fabricated by Chemical Bath Deposition Technique. *International Journal For Innovative Research In Multidisciplinary Field*, 6(3), 210-215.
6. Rajpal S., V. Bandyopadhyay. (2013). Structural and Optical Properties of CdS Thin Film Grown by Chemical Bath Deposition. *Journal of Nano and Electronic Physics*, 5(3), 03021-1 – 03021-3.
7. Maske Dilip (2016). Growth and Characterization of CdS Thin Films by Chemical Bath Deposition. *International Journal of Scientific and Research Publications*, 6(6), 264-266.
8. Kathalingam A., N. Ambika, M. R. Kim, J. Elanchezhiyan, Y. S. Chae, J. K. Rhee. (2010). Chemical bath deposition and characterization of nanocrystalline ZnO thin films. *Materials Science-Poland*, 28(2), 513-522.
9. Nair P. K., M. T. S. Nair, V. M. Garcia, O. L. Arenas, Y. Pena, A. Castillo, I. T. Ayala, O. Gomezdaza, A. Sanchez, J. Campos, H. Hu, R. Suarez, M. E. Rincon. (1998).

- Semiconductor thin films by chemical bath deposition for solar energy-related applications. *Solar Energy Materials and Solar Cells*, 52, 313-344.
10. Toma F. T. Z., K. M. A. Hussain, M. S. Rahman, Syed Ahmed. (2021). Preparation and characterization of CdS thin film using chemical bath deposition (CBD) technique for solar cell application. *World Journal of Advanced Research and Reviews*, 12(03), 629–633.
  11. Fernandez Perez A., M. G. Sandoval-Paz. (2016). Synthesis and characterization of chemically deposited CdS thin films without toxic precursors. *Journal of Physics: Conference Series*, 720, 012029.
  12. Rondiya Sachin, Avinash Rokade, Bharat Gabhale, Subhash Pandharkar, Madhavi Chaudhari, Abhijit Date, Minakshi Chaudhary, Habib Pathan, Sandesh Jadkar. (2017). Effect of bath temperature on optical and morphology properties of CdS thin films grown by chemical bath deposition. *Energy Procedia*, 110, 202 – 209.
  13. Ouachtari Fouad, Ahmed Rmili, Sidi El Bachir Elidrissi, Ahmed Bouaoud, Hassan Erguig, Philippe Elies. (2011). Influence of Bath Temperature, Deposition Time, and [S]/[Cd] Ratio on the Structure, Surface Morphology, Chemical Composition and Optical Properties of CdS Thin Films Elaborated by Chemical Bath Deposition. *Journal of Modern Physics*, 2, 1073-1082.
  14. John Xavier R., A. Angelin Prema, P. Arockia Sahayaraj, C. Pragathiswaran, V. Dharmalingam. (2016). The properties of chemical bath deposited cadmium sulfide thin films with the effect of ammonia salt concentration. *Advances in Applied Science Research*, 7(2), 178-182.
  15. Kathirvel D, N Suriyanarayanan, S Prabakar, S Srikanth. (2019). Electrical properties of chemical bath deposited CdS thin films. *International Journal of Physics Research and Development (IJPRD)*, 1(1), 19-25.
  16. Sahraei R., S. Shahriyar, M. H. Majles Ara, A. Daneshfar, N. Shokri. (2010). Preparation of Nanocrystalline CdS Thin Films by a New Chemical Bath Deposition Route for Application in Solar Cells as Antireflection Coatings. *Prog. Color Colorants Coat.*, 3, 82-90.
  17. Okorie O., A. D. A. Buba. (2017). Optical and Dielectric Properties of Cadmium Sulphide Thin Film Grown Using Chemical Bath Deposition Technique. *IOSR Journal of Applied Physics (IOSR-JAP)*, 9(5), 82-89.
  18. Kamble Mahesh, Bharat Bade, Sachin Rondiya, Subhash Pandharkar, Adinath Funde, Sandesh Jadkar. (2019). Synthesis, characterization, and study of cadmium sulphide

- (CdS) films fabricated using chemical bath deposition method. *Journal of Emerging Technologies and Innovative Research (JETIR)*, 6(5), 74-78.
19. Shimpi N.T., M. S. Shinde, P.B. Ahirrao. (2019). Characterization of Nanocrystalline CdS thin films deposited on ITO by chemical bath deposition for photo sensor applications, 6(5), 2630-2637.
  20. Pathan H. M., C. D. Lokhande. (2004). Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method. *Bull. Mater. Sci.*, 27(2), 85-111.
  21. Garadkar K. M., A. A. Patil, P. V. Korake, P. P. Hankare. (2010). Characterization of CdS thin films synthesized by SILAR method at room temperature. *Archives of Applied Science Research*, 2(5), 429-437.
  22. Sankapal B. R., R. S. Mane, C. D. Lokhande. (2000). Deposition of CdS thin films by the successive ionic layer adsorption and reaction (SILAR) method. *Materials Research Bulletin*, 35(2), 177-184.
  23. Mukherjee A., B. Satpati, S. R. Bhattacharyya, R. Ghosh, P. Mitra. (2015). Synthesis of nanocrystalline CdS thin film by SILAR and their characterization. *Physica E: Low-dimensional Systems and Nanostructures*, 65, 51-55.
  24. Phasook N., S. Kamoldirok, W. Yindeesuk. (2018). Optical properties of Mn-doped CdS thin films grown by the SILAR method. *IOP Conf. Series: Journal of Physics: Conf. Series*, 1144, 012009.
  25. Pradhabhan D., Dr. A. Sakthivelu. (2019). Optical, Structural and Electrical Properties of Cu Doped CdS Thin Films Fabricated by SILAR Method. *International Journal of Engineering Research & Technology (IJERT)*, 8(7), 623-627.
  26. Pradhabhan D., Dr. A. Sakthivelu. (2017). Effect Of Deposition Cycles on Optical, Structural And Electrical Characterizations of SILAR Deposited Cadmium Sulphide Thin Films. *International Journal of Advanced Trends in Engineering and Technology (IJATET)*, 2(2), 23-28.
  27. Manikandan K., C. Surendra Dilip, P. Mani, J. Joseph Prince. (2015). Deposition and Characterization of CdS Nano Thin Film with Complexing Agent Triethanolamine. *American Journal of Engineering and Applied Sciences*, 8(3), 318-327.
  28. Desale Dipalee J., Shaeed Shaikh, Farha Siddiqui, Arindam Ghosh, Ravikiran Birajdar, Anil Ghule, Ramphal Sharma. (2011). Effect of annealing on structural and optoelectronic properties of CdS thin film by SILAR method. *Advances in Applied Science Research*, 2(4), 417-425.

## **RECENT ADVANCEMENTS IN METAMATERIALS**

**Kailash Nemade**

Department of Physics,

Indira Mahavidyalaya, Kalamb Dist. Yavatmal 445401, Maharashtra, India

Corresponding author E-mail: [krnemade@gmail.com](mailto:krnemade@gmail.com)

### **Abstract:**

This chapter presents a comprehensive review of the latest breakthroughs in metamaterial science and technology. We explore developments in various metamaterial applications, including invisibility cloaks, super lenses, acoustic manipulation, and quantum metamaterials. Additionally, we delve into emerging frontiers such as topological metamaterials and smart, adaptive structures. This chapter addresses the key challenges of metamaterial manufacturing, efficiency optimization, and integration into real-world systems. The implications of these advancements are far-reaching, offering prospects for revolutionizing fields ranging from telecommunications and quantum computing to energy efficiency and healthcare. In addition to this chapter highlights the remarkable progress in metamaterials and underscores their transformative potential in shaping the technological landscape of the future.

**Keywords:** Metamaterials; Negative Refractive index; Acoustic Metamaterials

### **Introduction:**

Metamaterials represent a groundbreaking and interdisciplinary field of materials science that has gained immense attention and significance in recent years. These synthetic materials are meticulously engineered at the nanoscale to possess unique properties and capabilities that defy the natural constraints of conventional materials. Metamaterials owe their name to their inherent ability to manipulate and metamorphose the behaviour of waves, be they electromagnetic, acoustic, or thermal, in ways that were once considered purely theoretical. The concept of metamaterials originated from the pursuit of extending the boundaries of material science, particularly in the domain of wave manipulation. This innovative approach capitalizes on the idea that by structuring materials at scales much smaller than the wavelength of the waves they interact with, we can control and tailor their properties with unparalleled precision. One of the most striking features of metamaterials is their ability to achieve a negative refractive index. Unlike natural materials, which always refract light or other waves in a positive direction, metamaterials can bend waves in a

direction opposite. This unique property has led to revolutionary developments in the field of optics, enabling the creation of superlenses capable of imaging objects at resolutions well beyond the diffraction limit, a feat once thought impossible [1].

Beyond optics, metamaterials have found application in a wide range of domains. They have played a pivotal role in the development of cloaking devices, where they can render objects invisible to certain wavelengths of light or even sound. In telecommunications, metamaterials have enabled the miniaturization of antennas and improved signal processing, leading to faster and more efficient communication systems. In the realm of medical imaging, these materials have offered the potential for groundbreaking advancements in early disease detection and non-invasive diagnostic tools.

Metamaterials have also shown promise in energy management and thermodynamics by manipulating the flow of heat in ways that challenge traditional principles of thermal conductivity. In the ever-evolving field of acoustics, metamaterials are used to design novel materials that can control sound waves, leading to the creation of sound barriers, acoustic cloaks, and innovative noise-cancelling technologies.

This introduction merely scratches the surface of the immense potential and impact of metamaterials. As we delve deeper into this field, we will explore the underlying principles, fabrication techniques, and an array of applications that continue to emerge, revolutionizing industries and reshaping our understanding of the interaction between matter and waves in the modern world [2].

### **Advancements in Metamaterials:**

Metamaterials, a cutting-edge field at the intersection of materials science and physics, have witnessed remarkable advancements in recent years. These synthetic materials, meticulously designed at the nanoscale, have broken new ground in the manipulation of electromagnetic waves, sound, and thermal energy. Below are some noteworthy recent developments in the field of metamaterials [3].

**Cloaking Devices:** Metamaterials have progressed beyond theoretical concepts to practical applications, including cloaking devices. Researchers have developed metamaterials that can bend electromagnetic waves around an object, rendering it invisible to certain frequencies of light. This breakthrough has implications for military stealth technology and advanced optics.

**Hyperbolic Metamaterials:** Hyperbolic metamaterials, characterized by extreme anisotropy, have opened new possibilities for subwavelength imaging and focusing. Recent

advances in this area have led to the creation of hyperlenses capable of capturing images with unprecedented detail, surpassing the limits of traditional optical systems.

**Acoustic Metamaterials:** In the realm of acoustics, researchers have made significant strides in designing metamaterials that control and manipulate sound waves. Applications include soundproofing materials, acoustic cloaks that divert sound waves around objects, and innovative noise-cancelling technologies with potential use in various industries.

**Metamaterials for 5G and Beyond:** Metamaterial-based antennas and components have emerged as key enablers of high-speed wireless communication. These materials have enabled the development of compact and efficient 5G antennas, paving the way for the rapid deployment of next-generation wireless networks.

**Metamaterials for Sensing and Imaging:** Metamaterials have found applications in sensing and imaging technologies, including medical imaging and environmental monitoring. By tailoring metamaterial structures, researchers have improved the sensitivity and resolution of sensors and imaging devices.

**Topological Metamaterials:** Recent work in topological metamaterials has explored unique electronic and photonic properties. These materials exhibit robust topological properties that make them highly resilient to defects and imperfections, promising advancements in quantum computing and photonic devices.

**Flexible and Reconfigurable Metamaterials:** Advancements in flexible and reconfigurable metamaterials have led to adaptive materials that can change their properties on-demand. These materials are finding applications in dynamic optical systems and flexible electronics.

The field of metamaterials continues to evolve rapidly, driven by interdisciplinary collaborations among scientists and engineers. These recent advancements are not only expanding our understanding of fundamental physics but also paving the way for transformative technologies across a wide range of industries, from telecommunications and imaging to defence and energy management. As researchers push the boundaries of metamaterial design and fabrication, we can anticipate even more groundbreaking developments soon.

### **Application of Metamaterials**

Metamaterials, with their ability to manipulate electromagnetic waves, acoustic waves, and thermal energy in unprecedented ways, have found a wide range of applications across various industries. Here are some notable applications of metamaterials [4]:

**Super Lenses:** Metamaterial-based super lenses can overcome the diffraction limit, allowing for subwavelength imaging in fields like microscopy and medical imaging. This technology enables imaging with unprecedented detail.

**Antennas and Wireless Communication:** Metamaterial antennas and components have revolutionized wireless communication. They enable compact and efficient antennas for applications like 5G networks, satellite communication, and radar systems.

**Energy Harvesting and Solar Cells:** Metamaterials can enhance the absorption and trapping of electromagnetic radiation, making them valuable in the development of more efficient solar cells and energy harvesting devices.

**Thermal Management:** Thermal metamaterials can control the flow of heat, leading to applications in thermal cloaking, improved insulation, and more efficient heat exchangers.

**Sensors and Imaging:** Metamaterial-based sensors offer enhanced sensitivity and resolution, making them valuable in medical imaging, environmental monitoring, and security screening.

**Quantum Optics:** Metamaterials are being explored in quantum optics for the manipulation of quantum states of light and the development of quantum computing components.

**Space Exploration:** Metamaterials can be used to create lightweight, radiation-resistant materials for spacecraft and space-based instruments.

These applications highlight the versatility and potential of metamaterials to revolutionize industries and solve complex challenges. As research in metamaterials continues to advance, it is likely that new and innovative applications will emerge, further expanding their impact across various fields of science and technology.

### **Future Scope and Challenges**

Metamaterials have already demonstrated remarkable capabilities and found applications in various domains, but their journey is far from over. The future holds exciting opportunities and challenges for the field of metamaterials [5]:

#### **1. Future Scope:**

**Quantum Metamaterials:** Exploring metamaterials in the realm of quantum mechanics holds promise for quantum computing, quantum communication, and quantum sensing. Quantum metamaterials can manipulate quantum states of light and matter, enabling novel devices and technologies.



**Topological Metamaterials:** Advancements in topological metamaterials may lead to robust and defect-tolerant materials with applications in quantum information processing, fault-tolerant computing, and topologically protected quantum states.

**Smart Metamaterials:** Developing metamaterials with adaptive, tunable properties could revolutionize various industries, from telecommunications and medical devices to aerospace and energy harvesting.

## **2. Challenges:**

**Manufacturability:** Fabricating metamaterials at scales required for practical applications remains a challenge. Scalable, cost-effective manufacturing processes need to be developed.

**Frequency Bandwidth:** Many metamaterials are designed for specific frequencies or limited bandwidths. Expanding the operational bandwidth of metamaterials is essential for versatile applications.

**Regulatory Challenges:** Some metamaterial applications may face regulatory hurdles, particularly in areas like telecommunications and healthcare, requiring careful navigation of legal and safety considerations.

**Interdisciplinary Collaboration:** Metamaterial research often requires collaboration between physicists, engineers, material scientists, and other specialists. Effective interdisciplinary communication and cooperation are essential.

## **Conclusions:**

In conclusion, metamaterials stand at the forefront of materials science, offering a captivating journey into the realm of engineered matter. These synthetic materials, with their unique abilities to control and manipulate waves of various forms, have already ushered in a wave of innovation across a multitude of fields. From invisibility cloaks to super lenses, from quantum realms to energy-efficient solutions, the scope of metamaterials is vast and inspiring. Looking ahead, the future of metamaterials promises even greater breakthroughs. Quantum metamaterials, topological designs, and smart, adaptive structures hold the potential to revolutionize quantum computing, communications, and various industries. The challenges of manufacturing, efficiency, and integration are hurdles that researchers and engineers are diligently working to overcome.

## **Acknowledgements:**

Author is very much thankful to Principal, Indira College, Kalamb Dist. Yavatmal for providing all necessary academic assistance during this work.

**References:**

1. Fu, X., & Cui, T. J. (2019). Recent progress on metamaterials: From effective medium model to real-time information processing system. *Progress in Quantum Electronics*, 67, 100223.
2. Kumar, R., Kumar, M., Chohan, J. S., & Kumar, S. (2022). Overview on metamaterial: History, types and applications. *Materials Today: Proceedings*, 56, 3016-3024.
3. Fan, J., Zhang, L., Wei, S., & Zhang, Z. (2021). A review of additive manufacturing of metamaterials and developing trends. *Materials Today*, 50, 303-328.
4. Liu, R., Ji, C., Zhao, Z., & Zhou, T. (2015). *Metamaterials: Reshape and Rethink*, 1, 179-184.
5. Montgomery, S. M., Kuang, X., Armstrong, C. D., & Qi, H. J. (2020). Recent advances in additive manufacturing of active mechanical metamaterials. *Current Opinion in Solid State and Materials Science*, 24, 100869.

## NANOTECHNOLOGY: ENVIRONMENTAL, HEALTH AND SAFETY ISSUE

M. S. Bisen\*<sup>1</sup>, A. V. Bagde<sup>2</sup> and Y. S. Bopche<sup>3</sup>

<sup>1</sup>Department of Physics, Yashwantrao Chauhan Arts, Commerce and Science College,  
Lakhandur, Maharashtra 441803

<sup>2</sup>Department Of Physics, Chintamani College of Science, Pombhurna, Maharashtra 442918

<sup>3</sup>Department of Physics, Dhote Bandhu Science College, Gondia, Maharashtra 441614

Corresponding author E-mail: [msbisen26@gmail.com](mailto:msbisen26@gmail.com)

### Abstract:

Application of nanotechnology has seen a tremendous expansion for several years. A lot of nanotechnology driven products are seen to be used in society. Despite all the wonderful benefits of nanotechnology the impact of widespread use of these materials on environment, health and safety should be the issue of concern, as these concerns are not clearly understood or defined. This chapter surveys the impact of development of nanotechnology on the environmental, health and safety issues. This information could be helpful to the scientist, authorities or policymakers to realize the risk involved and the necessary steps taken for the sustainable development.

### Introduction:

Nanosized materials or particles have at least one dimension less than 100 nm. According to the National Nanotechnology Initiative, a program established in 2001 to coordinate federal nanotechnology research and development, nanotechnology is the “the understanding and control of matter at the nanoscale, at dimensions between approximately 1 and 100 nanometres, where unique phenomena enable novel applications and Matter can exhibit unusual physical, chemical, and biological properties at the nanoscale, differing in important ways from the properties of bulk materials, single atoms, and molecules. It encompasses nanoscale science, engineering and technology in fields such as chemistry, biology, physics, materials science and engineering” (« About Nanotechnology | National Nanotechnology Initiative », s. d.). Nanotechnology has brought radical transformation in almost every area or subject we know. It is seen to represent a new industrial revolution in the fields of medicine, physics, chemistry, biology, telecommunications, electronics and energy (Juanola-Feliu *et al.*, 2012).

Applications of nanotechnology that directly benefit the environment are nanotechnologies for site remediation and wastewater treatment (Watlington, 2005),

nanomaterial-based solar cells for improved energy efficiency, the use of nanocatalysts for air purification (Sinha *et al.*, 2007), and nanostructured filters or nanoreactive membranes for water purification (Theron *et al.*, 2008). Evidently, the science of the very small has become very big in a brief course of time.

In spite of all the wonderful benefits of nanotechnology, there could still be some unintended environmental and health risks accompanying with the extensive use of nanomaterials which might not have yet been fully understood (Upreti *et al.*, 2015). To better understand the potential hazard associated with it, we need a risk assessment of life-cycle of nanomaterial. Alternative green manufacturing methods are needed to be adopted that are less troublesome to environment and health. The emergence of nanotechnology and their applications has brought great concern over adverse impacts on the environment, health, and safety. Man-made nanomaterials, known as engineered nanomaterials such as ultrafine particles refer to airborne particulates of less than 100nm in aerodynamic diameter, generated through the use of nanotechnology, diesel exhaust particles, products of cooking, heating and wood burning in indoor environments (Li *et al.*, 2016). Nanoparticles may be released into the environment with the possibility of human or ecosystem exposure at various stages in their life cycles. It is proposed that nanoparticles may enter the body and accumulate in organs, such as lung, liver, spleen, kidneys, or brain, potentially causing harm or death to humans and animals, and the release of nanoparticles into the environment might harm the ecological system (Chen & Chen, 2017).

Nanotechnology is evolving to become a leading industry. However, there is a great deal of uncertainty surrounding the potential health effects of nanomaterials and its components. This study focuses on the hazards and risks that nanomaterials pose to physical and environmental health together with the risks posed during their manufacture and research. We need various strategies to minimize the risk of human exposure to nanotechnologies both within and outside the manufacturing enterprise.

### **Impact of Nanotechnology on Environmental, Health and Safety Issue:**

Understanding the potential effects of nanoparticles on environment, health and safety is essential to ensure safe and responsible development and application of nanotechnology, as well as to build public trust and support for this emerging technology.

As nanotechnology has advanced, the release of nanomaterials into the environment has become a growing concern. These materials can accumulate in the environment and potentially harm ecosystems and human health. Studies have shown that nanoparticles can

affect soil organisms, aquatic organisms, and even mammals (Roco *et al.*, 2011). The manufacture and use of nanomaterials can require significant amounts of energy, which can contribute to greenhouse gas emissions and other environmental impacts (Savolainen *et al.*, 2013). Some nanotechnology applications, such as water treatment, may require significant amounts of water. As water becomes an increasingly scarce resource in many parts of the world, this could become a significant environmental concern (Council, 2013). Nanomaterials used in agriculture, such as nano-fertilizers, could potentially contribute to eutrophication of water bodies, which can harm aquatic ecosystems (Klaine *et al.*, 2008). The monitoring of the environmental impacts of nanotechnology will be critical in minimizing its negative effects while maximizing its benefits.

The health impacts of nanomaterials depend on a variety of factors, including their size, shape, surface area, and chemical composition. Inhalation of nanomaterials has been shown to cause inflammation, oxidative stress, and pulmonary fibrosis. The small size of nanomaterials allows them to penetrate deep into the lungs, where they can cause damage to the respiratory system. A study by Shvedova *et al.* (2005) (Shvedova *et al.*, 2005) showed that carbon nanotubes caused pulmonary inflammation and fibrosis in mice. Some nanomaterials have been found to be toxic to cells and can cause damage to DNA and other cellular structures. This can lead to cell death and tissue damage. For example, silver nanoparticles have been shown to be toxic to human lung cells *in vitro* (E. J. Park *et al.*, 2010). Nanoparticles have also been shown to have immunological effects. A study published in the journal *Nature Materials* found that exposure to gold nanoparticles caused an immune response in mice, including the activation of T cells and the production of inflammatory cytokines (Dykman & Khlebtsov, 2017). Some studies have suggested that nanomaterials may increase the risk of infection. For example, a study found that exposure to silver nanoparticles increased the risk of bacterial infection in mice (Kubyshevkin *et al.*, 2016). However, more research is needed to fully understand the potential health risks associated with the use of nanomaterials in medicine and healthcare.

While nanotechnology has the potential to revolutionize many fields, it also raises concerns about potential risks and safety issues associated with the production and use of nanomaterials. Some nanomaterials may pose a fire or explosion hazard due to their high surface area and reactivity (Kestens *et al.*, 2016). To address these safety concerns, researchers are developing new methods for producing and handling nanomaterials safely. For example, researchers are exploring ways to encapsulate nanoparticles to reduce their

toxicity and improve their stability. They are also investigating ways to prevent nanoparticles from being released into the environment during manufacturing and use. Therefore, detail understanding of their sources, release interaction with environment, and possible risk assessment would provide a basis for safer use of engineered nanoparticles with minimal or no hazardous impact on environment (Bhatt & Tripathi, 2011).

### **Concerns of some important Nanoparticles:**

#### **1. Carbon Nanotubes (CNT's):**

Due to their superior mechanical, electrical, and magnetic properties, CNTs have a very broad commercial application. Therefore, much of the concern associated with nanotechnology derives from the potential risks of CNTs. CNTs are basically long and thin cylinders of carbon having diameter in the range of few nanometres. It can be a single walled or multiple walled carbon nanotubes. They have a needle-like shape and are strong and tough in character.

It has been a matter of great concern that if such fine particles like enter the working environment as suspended particulate matter (PM) of respirable sizes could pose an occupational inhalation exposure hazard. The size and shape of CNTs make them more likely to penetrate deep into the lungs, leading to inflammation and damage. Recently, multi walled CNTs and other carbonaceous nanoparticles in fine (<2.5  $\mu\text{m}$ ) PM aggregates were found in combustion streams of methane, propane, and natural-gas flames of typical stoves (Lam *et al.*, 2008). If CNTs production would surge and prices drop, then issue of occupational inhalation exposures could arise. Extensive use of CNTs in industrial products, household commodities, automobiles and other products that could be subject to deterioration could generate fine particulate matter that may contribute to environmental pollution.

CNTs with its exceptional adsorption capability and high adsorption efficiency for various organic pollutants have found application in water treatment. But there is risk of CNTs to escape from treatment system and enter into the product water as residual CNTs that may pose the concern to human health (Das *et al.*, 2018; Simate *et al.*, 2012).

Studies shown that redox cycling and DNA damage induced by iron-containing carbon nanomaterials (Kolosnjaj *et al.*, 2007). Also, Lam *et al.* (Lam *et al.*, 2004) have shown that, for the test conditions, carbon nanotubes penetrating to the lungs can be much more toxic than carbon black and quartz, which is considered a serious occupational health hazard in chronic inhalation exposures.

## 2. Silver Nanoparticles

Silver nanoparticles are particles of silver having size in the range of 1 to 100 nm that are commonly used in various applications such as medical devices, cosmetics, textiles, and food packaging due to their antimicrobial properties. While they have numerous benefits, their widespread use also has raised concerns to both the environment and human health.

Silver nanoparticles can enter the environment through the release of products containing them or from their disposal in waste streams. Once released, silver nanoparticles can interact with different components of the environment, such as water, soil, and air. Silver nanoparticles can be toxic to aquatic organisms such as fish, algae, and other marine life, causing long-term damage to aquatic ecosystems (Fabrega *et al.*, 2011). These nanoparticles can enter the soil through waste disposal and agricultural practices, leading to soil contamination and decreased soil quality (Ihtisham *et al.*, 2021). It can accumulate in the food chain, leading to biomagnification and increased toxicity in higher organisms (Yoo-iam *et al.*, 2015). Silver nanoparticles can also change the composition of microbial communities, including those that play important roles in soil fertility, nutrient cycling, and decomposition (Chavan & Nadanathangam, 2019).

Silver nanoparticles can enter the body through inhalation, ingestion, and dermal exposure, leading to cellular damage, inflammation, and potential DNA damage (Genotoxicity)(Kim *et al.*, 2010; M. V. D. Z. Park *et al.*, 2011).

Silver nanoparticles can trigger allergic reactions in some individuals, leading to skin irritation, asthma, and other respiratory symptoms (Chuang *et al.*, 2013). Overuse of silver nanoparticles can lead to the development of antibiotic-resistant bacteria, making it difficult to treat infections in the future (Panáček *et al.*, 2017). The long-term effects of exposure to silver nanoparticles are still unknown, and further research is needed to understand their potential impact on human health.

## 3. Zinc Oxide Nanoparticles

Zinc oxide nanoparticles are tiny particles of zinc oxide that are typically less than 100 nanometres in size. Due to their small size, they possess unique physical and chemical properties compared to their bulk counterparts. Zinc oxide nanoparticles are increasingly being used in a wide range of consumer products including as UV filters in sunscreen, in electronics and optoelectronics, as well as in biomedicine and food packaging etc. due to their unique properties, such as high UV protection and antimicrobial activity (Nath *et al.*, 2018). However, their release into the environment through various sources, including

industrial and domestic waste, has raised concerns about their potential adverse effects on the environment. The environmental effects of ZnO nanoparticles depend on various factors such as their concentration, size, surface coating, and exposure time (M. Baek *et al.*, 2011). ZnO nanoparticles can accumulate in aquatic organisms and affect their growth and reproduction. Studies have shown that it can cause mortality and growth inhibition in fish, algae, and other aquatic organisms (Sibiya *et al.*, 2022). ZnO nanoparticles can leach into soil and affect soil quality. They can also affect the growth and development of plants by altering the nutrient content of soil. Inhalation of ZnO nanoparticles can cause respiratory problems such as lung inflammation and fibrosis.

Studies have also shown that ZnO nanoparticles can enter the bloodstream and accumulate in organs such as the liver, kidneys, and brain, potentially leading to toxic effects (Miri Baek *et al.*, 2012; Rajput *et al.*, 2018). ZnO nanoparticles can have antimicrobial properties and can affect the diversity and composition of microbial communities in soil and water (Jain *et al.*, 2020). ZnO nanoparticles can also have direct toxic effects on wildlife and aquatic organisms, leading to changes in population dynamics and ecosystem functioning (Hazeem, 2022). Inhalation of high concentrations of zinc oxide nanoparticles may cause respiratory irritation, lung inflammation and damage, and oxidative stress (Fukui *et al.*, 2012). Skin exposure to zinc oxide nanoparticles has been shown to cause oxidative stress (Surekha *et al.*, 2012), cell damage, and inflammation, which may increase the risk of skin cancer (Tu *et al.*, 2013). However, the risk of skin cancer from topical application of zinc oxide nanoparticles in sunscreen is considered to be very low due to their low penetration into the skin (Mohammed *et al.*, 2019).

## **Solutions:**

### **1. Green Alternatives**

*Green chemistry*, also known as *sustainable chemistry*, is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Michael Berger of *Nanowerk LLC* (Berger, 2008) has suggested the following principles of green chemistry, as outlined by the US Environmental Protection Agency (EPA) on their “Green Chemistry” website, to nanomanufacturing processes.

1. Design chemical syntheses leaving no waste to treat or clean up
2. Design safer chemicals and products
3. Design less-hazardous chemical syntheses with little or no toxicity to humans and the environment.



4. Use raw materials and feedstocks that are renewable
5. Use catalysts, not stoichiometric reagents to minimise waste
6. Avoid chemical derivatives
7. Maximize atom economy by designing syntheses so that there should be few, if any, wasted atoms.
8. Use safer solvents and reaction conditions
9. Increase energy efficiency by running chemical reactions at ambient temperature and pressure whenever possible.
10. Design chemicals and products to degrade after use
11. Analyse in real time to prevent pollution using real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. Minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

## **2. Life Cycle and Risk Assessment**

As with any new technology, it is important to evaluate the potential risks associated with nanomaterials throughout their life cycle, from production to disposal and that demands the need for the life cycle assessment of nanomaterials. The life cycle of nanomaterials typically includes different stages such as production of nanomaterial, transportation, handling and storage, its use and finally disposal at the end of their life cycle. However, the Life cycle assessment methodology used currently have limitations, since it has no means of distinguishing nanoparticles from bulk materials. Life cycle assessment methodology determine human health and environmental impacts are calculated using formulas based upon quantities of pollutants discharged to air, water, and land. Life-Cycle Assessment, therefore, can essentially only conclude that impact of nanomaterials is less significant than bulk materials which can be misleading (Matthews *et al.*, 2002).

Risk assessment helps us better understand the potential risk associated with human health and environment from exposure to toxic substances and other contaminants (Wang *et al.*, 2021). The process involves identifying potential hazards and evaluating the likelihood and severity of any adverse effects. Factors that may be considered in a risk assessment include the physicochemical properties of the nanomaterial, the route of exposure, and the potential for accumulation or persistence in the environment (Oomen *et al.*, 2013). In order to minimize risks associated with nanomaterials, it is important to implement appropriate safety measures and to continue to monitor and evaluate potential hazards throughout the

life cycle of the material. Regulatory agencies around the world have developed guidelines and standards for the safe use and handling of nanomaterials, and it is important for individuals and organizations involved in nanotechnology to stay up to date with these regulations and best practices.

### **3. Use safe-by-design Approaches**

Incorporating safe-by-design approaches into the development of nanomaterials can help minimize Environment, health and safety risks. These approaches involve designing nanomaterials having inherently low toxicity and to be less likely to release particles into the environment. For example, in nanotechnology there are two key nanoscale manufacturing techniques: the top-down and the bottom-up approach. The top-down approach involves miniaturization from bulk level to nanoscale dimensions through carving or grinding methods, that is lithography, etching, or milling. In the bottom-up approach process begin at the atomic or molecular level and growth take place through nucleation and/or growth from liquid, solid, or gas precursors via chemical reactions or physical processes, that is, through techniques like sol-gel or epitaxy. The top-down approach dominates over the bottom-up approach, but it is believed to produce more waste. It has been suggested to prioritize the bottom-up approach in order to minimize the unwanted waste for sustainable development (Khan, 2020).

### **4. Public awareness**

Increasing public awareness of the potential Environmental, health and safety impacts of nanotechnology can help ensure that appropriate safety measures are put in place. This includes communicating the risks and benefits of nanotechnology to the public and engaging with stakeholders.

### **Conclusion:**

It is beyond doubt that nanotechnology holds immense capacity for various applications, including medicine, electronics, and energy. However, it is important to also recognize that there are potential environmental, health, and safety risks associated with the production, use, and disposal of nanomaterials that should be addressed. The risks associated with nanotechnology are complex and multifaceted, and that more research is needed to fully understand their impacts on human health and the environment. It is crucial that regulatory agencies and policymakers take a precautionary approach to manage these risks to ensure that the benefits of nanotechnology can be realized without compromising human health and the environment, particularly given the uncertainty surrounding some of

the potential hazards. Addressing these environmental, health, and safety issues of nanotechnology will require collaboration between scientists, regulators, industry, and other stakeholders with the goal of achieving the safe and responsible development of nanotechnology and enabling its continued growth and innovation.

#### References:

1. National Nanotechnology Initiative. (s. d.). About Nanotechnology. Consulté 2 mars 2023, à l'adresse <https://www.nano.gov/about-nanotechnology>
2. Baek, M., Kim, M. K., Cho, H. J., Lee, J. A., Yu, J., Chung, H. E., & Choi, S. J. (2011). Factors influencing the cytotoxicity of zinc oxide nanoparticles: Particle size and surface charge. *Journal of Physics: Conference Series*, 304(1).
3. Baek, Miri, Chung, H. E., Yu, J., Lee, J. A., Kim, T. H., Oh, J. M., Lee, W. J., Paek, S. M., Lee, J. K., Jeong, J., Choy, J. H., & Choi, S. J. (2012). Pharmacokinetics, tissue distribution, and excretion of zinc oxide nanoparticles. *International Journal of Nanomedicine*, 7, 3081-3097.
4. Berger, M. (2008). Nanotechnology - not that green? Consulté 4 mars 2023, à l'adresse <https://www.nanowerk.com/spotlight/spotid=7853.php>
5. Bhatt, I., & Tripathi, B. N. (2011). Interaction of engineered nanoparticles with various components of the environment and possible strategies for their risk assessment. *Chemosphere*, 82(3), 308-317.
6. Chavan, S., & Nandanatham, V. (2019). Effects of Nanoparticles on Plant Growth-Promoting Bacteria in Indian Agricultural Soil. *Agronomy*, 9(3).
7. Chen, R., & Chen, C. (2017). Environment, health and safety issues in nanotechnology. In: *Springer Handbooks*, p. 1559-1586. Springer.
8. Chuang, H. C., Hsiao, T. C., Wu, C. K., Chang, H. H., Lee, C. H., Chang, C. C., & Cheng, T. J. (2013). Allergenicity and toxicology of inhaled silver nanoparticles in allergen-provocation mice models. *International Journal of Nanomedicine*, 8, 4495.
9. Council N. R. (2013). Triennial Review of the National Nanotechnology Initiative. *National Academies Press*.
10. Das, R., Leo, B. F., & Murphy, F. (2018). The Toxic Truth About Carbon Nanotubes in Water Purification: a Perspective View. *Nanoscale Research Letters*, 13(1), 1-10.
11. Dykman, L. A., & Khlebtsov, N. G. (2017). Immunological properties of gold nanoparticles. *Chemical Science*, 8(3), 1719-1735.

12. Fabrega, J., Luoma, S. N., Tyler, C. R., Galloway, T. S., & Lead, J. R. (2011). Silver nanoparticles: Behaviour and effects in the aquatic environment. *Environment International*, 37(2), 517-531.
13. Fukui, H., Horie, M., Endoh, S., Kato, H., Fujita, K., Nishio, K., Komaba, L. K., Maru, J., Miyauhi, A., Nakamura, A., Kinugasa, S., Yoshida, Y., Hagihara, Y., & Iwahashi, H. (2012). Association of zinc ion release and oxidative stress induced by intratracheal instillation of ZnO nanoparticles to rat lung. *Chemico-biological interactions*, 198(1-3), 29-37.
14. Hazeem, L. (2022). Single and Combined Toxicity Effects of Zinc Oxide Nanoparticles: Uptake and Accumulation in Marine Microalgae, Toxicity Mechanisms, and Their Fate in the Marine Environment. *Water* 2022, Vol. 14, Page 2669, 14(17), 2669.
15. Ihtisham, M., Noori, A., Yadav, S., Sarraf, M., Kumari, P., Brestic, M., Imran, M., Jiang, F., Yan, X., & Rastogi, A. (2021). Silver Nanoparticle's Toxicological Effects and Phytoremediation. *Nanomaterials*, 11(9), 2164.
16. Jain, D., Shivani, Bhojiya, A. A., Singh, H., Daima, H. K., Singh, M., Mohanty, S. R., Stephen, B. J., & Singh, A. (2020). Microbial Fabrication of Zinc Oxide Nanoparticles and Evaluation of Their Antimicrobial and Photocatalytic Properties. *Frontiers in Chemistry*, 8, 778.
17. Juanola-Feliu, E., Colomer-Farrarons, J., Miribel-Català, P., Samitier, J., & Valls-Pasola, J. (2012). Market challenges facing academic research in commercializing nano-enabled implantable devices for in-vivo biomedical analysis. *Technovation*, 32(3-4), 193-204.
18. Kestens, V., Roebben, G., Herrmann, J., Jämting, Å., Coleman, V., Minelli, C., Clifford, C., De Temmerman, P. J., Mast, J., Junjie, L., Babick, F., Cölfen, H., & Emons, H. (2016). Challenges in the size analysis of a silica nanoparticle mixture as candidate certified reference material. *Journal of Nanoparticle Research*, 18(6), 1-22.
19. Khan, S. H. (2020). Green Nanotechnology for the Environment and Sustainable Development. In: *Green Materials for Wastewater Treatment*, Environmental Chemistry for a Sustainable World. Vol. 38, p. 13-46. Springer, Cham.
20. Kim, Y. J., Yang, S. I., & Ryu, J. C. (2010). Cytotoxicity and genotoxicity of nano-silver in mammalian cell lines. *Molecular and Cellular Toxicology*, 6(2), 119-125.
21. Klaine, S. J., Alvarez, P. J. J., Batley, G. E., Fernandes, T. F., Handy, R. D., Lyon, D. Y., Mahendra, S., McLaughlin, M. J., & Lead, J. R. (2008). Nanomaterials in the environment: Behavior, fate, bioavailability, and effects. *Environmental Toxicology and Chemistry*, 27(9), 1825-1851.

22. Kolosnjaj, J., Szwarc, H., & Moussa, F. (2007). Toxicity studies of carbon nanotubes. *Advances in experimental medicine and biology*, 620, 181-204.
23. Kubyshkin, A., Chegodar, D., Katsev, A., Petrosyan, A., Krivorutchenko, Y., & Postnikova, O. (2016). Antimicrobial Effects of Silver Nanoparticles Stabilized in Solution by Sodium Alginate. *Biochemistry & Molecular Biology Journal*, 2(2), 13.
24. Lam, C. W., James, J. T., McCluskey, R., Arepalli, S., & Hunter, R. L. (2008). A Review of Carbon Nanotube Toxicity and Assessment of Potential Occupational and Environmental Health Risks. *Critical Reviews in Toxicology*, 36(3), 189-217.
25. Lam, C. W., James, J. T., McCluskey, R., & Hunter, R. L. (2004). Pulmonary toxicity of single-wall carbon nanotubes in mice 7 and 90 days after intratracheal instillation. *Toxicological sciences: an official journal of the Society of Toxicology*, 77(1), 126-134.
26. Li, N., Georas, S., Alexis, N., Fritz, P., Xia, T., Williams, M. A., Horner, E., & Nel, A. (2016). A work group report on ultrafine particles (American Academy of Allergy, Asthma & Immunology): Why ambient ultrafine and engineered nanoparticles should receive special attention for possible adverse health outcomes in human subjects. *The Journal of allergy and clinical immunology*, 138(2), 386-396.
27. Matthews, H. S., Lave, L., & MacLean, H. (2002). Life Cycle Impact Assessment: A Challenge for Risk Analysts. *Risk Analysis*, 22(5), 853-860.
28. Mohammed, Y. H., Holmes, A., Haridass, I. N., Sanchez, W. Y., Studier, H., Grice, J. E., Benson, H. A. E., & Roberts, M. S. (2019). Support for the Safe Use of Zinc Oxide Nanoparticle Sunscreens: Lack of Skin Penetration or Cellular Toxicity after Repeated Application in Volunteers. *Journal of Investigative Dermatology*, 139(2), 308-315.
29. Nath, M. R., Ahmed, A. N., Gafur, M. A., Miah, M. Y., & Bhattacharjee, S. (2018). ZnO nanoparticles preparation from spent zinc-carbon dry cell batteries: studies on structural, morphological and optical properties. *Journal of Asian Ceramic Societies*, 6(3), 262-270.
30. Oomen, A. G., Bos, P. M. J., Fernandes, T. F., Hund-Rinke, K., Boraschi, D., Byrne, H. J., Aschberger, K., Gottardo, S., Von Der Kammer, F., Kühnel, D., Hristozov, D., Marcomini, A., Migliore, L., Scott-Fordsmand, J., Wick, P., & Landsiedel, R. (2013). Concern-driven integrated approaches to nanomaterial testing and assessment – report of the NanoSafety Cluster Working Group 10. <http://dx.doi.org/10.3109/17435390.2013.802387>, 8(3), 334-348.

31. Panáček, A., Kvítek, L., Smékalová, M., Večeřová, R., Kolář, M., Röderová, M., Dyčka, F., Šebela, M., Prucek, R., Tomanec, O., & Zbořil, R. (2017). Bacterial resistance to silver nanoparticles and how to overcome it. *Nature Nanotechnology*, 13(1), 65-71.
32. Park, E. J., Yi, J., Kim, Y., Choi, K., & Park, K. (2010). Silver nanoparticles induce cytotoxicity by a Trojan-horse type mechanism. *Toxicology in Vitro*, 24(3), 872-878.
33. Park, M. V. D. Z., Neigh, A. M., Vermeulen, J. P., de la Fonteyne, L. J. J., Verharen, H. W., Briedé, J. J., van Loveren, H., & de Jong, W. H. (2011). The effect of particle size on the cytotoxicity, inflammation, developmental toxicity and genotoxicity of silver nanoparticles. *Biomaterials*, 32(36), 9810-9817.
34. Rajput, V. D., Minkina, T. M., Behal, A., Sushkova, S. N., Mandzhieva, S., Singh, R., Gorovtsov, A., Tsitsuashvili, V. S., Purvis, W. O., Ghazaryan, K. A., & Movsesyan, H. S. (2018). Effects of zinc-oxide nanoparticles on soil, plants, animals and soil organisms: A review. *Environmental Nanotechnology, Monitoring & Management*, 9, 76-84.
35. Roco, M. C., Hersam, M. C., & Mirkin, C. A. (2011). Nanotechnology Research Directions for Societal Needs in 2020. *Springer Netherlands*.
36. Savolainen, K., Backman, U., Brouwer, D., Fadeel, B., Fernandes, T., Kuhlbusch, T., & Landsiedel, R. (2013). Nanosafety in Europe 2015-2025: Towards Safe and Sustainable Nanomaterials and Nanotechnology Innovations. Consulté à l'adresse [www.ttl.fi/en/publications/electronic\\_publications/pages/default.aspx](http://www.ttl.fi/en/publications/electronic_publications/pages/default.aspx)
37. Shvedova, A. A., Kisin, E. R., Mercer, R., Murray, A. R., Johnson, V. J., Potapovich, A. I., Tyurina, Y. Y., Gorelik, O., Arepalli, S., Schwegler-Berry, D., Hubbs, A. F., Antonini, J., Evans, D. E., Ku, B. K., Ramsey, D., Maynard, A., Kagan, V. E., Castranova, V., & Baron, P. (2005). Unusual inflammatory and fibrogenic pulmonary responses to single-walled carbon nanotubes in mice. *American Journal of Physiology - Lung Cellular and Molecular Physiology*, 289(5-33-5), 698-708.
38. Sibiya, A., Jeyavani, J., Santhanam, P., Preetham, E., Freitas, R., & Vaseeharan, B. (2022). Comparative evaluation on the toxic effect of silver (Ag) and zinc oxide (ZnO) nanoparticles on different trophic levels in aquatic ecosystems: A review. *Journal of Applied Toxicology*, 42(12), 1890-1900.
39. Simate, G. S., Iyuke, S. E., Ndlovu, S., Heydenrych, M., & Walubita, L. F. (2012). Human health effects of residual carbon nanotubes and traditional water treatment chemicals in drinking water. *Environment International*, 39(1), 38-49.

40. Sinha, A. K., Suzuki, K., Takahara, M., Azuma, H., Nonaka, T., & Fukumoto, K. (2007). Mesostructured Manganese Oxide/Gold Nanoparticle Composites for Extensive Air Purification. *Angewandte Chemie*, 119(16), 2949-2952.
41. Surekha, P., Kishore, A. S., Srinivas, A., Selvam, G., Goparaju, A., Reddy, P. N., & Murthy, P. B. (2012). Repeated dose dermal toxicity study of nano zinc oxide with Sprague-Dawley rats. *Cutaneous and Ocular Toxicology*, 31(1), 26-32.
42. Theron, J., Walker, J. A., & Cloete, T. E. (2008). Nanotechnology and water treatment: applications and emerging opportunities. *Critical reviews in microbiology*, 34(1), 43-69.
43. Tu, M., Abbood, H. A., Zhu, Z., Li, H., & Gao, Z. (2013). Investigation of the photocatalytic effect of zinc oxide nanoparticles in the presence of nitrite. *Journal of hazardous materials*, 244-245, 311-321.
44. Upreti, G., Dhingra, R., Naidu, S., Atuahene, I., & Sawhney, R. (2015). Life cycle assessment of nanomaterials. *Green Processes for Nanotechnology: From Inorganic to Bioinspired Nanomaterials*, 393-408.
45. Wang, L., Wu, W. M., Bolan, N. S., Tsang, D. C. W., Li, Y., Qin, M., & Hou, D. (2021). Environmental fate, toxicity and risk management strategies of nanoplastics in the environment: Current status and future perspectives. *Journal of Hazardous Materials*, 401, 123415.
46. Watlington, K. (2005). Emerging Nanotechnologies for Site Remediation and Wastewater Treatment. *Washington DC: Environmental Protection Agency*.
47. Yoo-iam, M., Chaichana, R., & Satapanajaru, T. (2015). Toxicity, bioaccumulation and biomagnification of silver nanoparticles in green algae (*Chlorella* sp.), water flea (*Moina macrocopa*), blood worm (*Chironomus* spp.) and silver barb (*Barbonymus gonionotus*). *Chemical Speciation & Bioavailability*, 26(4), 257-265.

## **A CONDUCTING POLYANILINE AND ITS APPLICATIONS**

**Sandip V. Patil**

Shri Pancham Khemraj Mahavidyalaya, Sawantwadi

Corresponding author E-mail: [spkphysics.svp@gmail.com](mailto:spkphysics.svp@gmail.com)

### **Abstract:**

Nowadays, conducting polymers are very popular for many applications. These include polyaniline and polypyrrole, which are still the focus of ongoing research in a variety of areas including electronics, energy storage, chemical sensing, etc. Among conducting polymers, polyaniline stands out for its extensive range of electrical, electrochemical, and optical properties as well as its high stability. This book chapter deals with structure, properties and possible applications of conducting polyaniline.

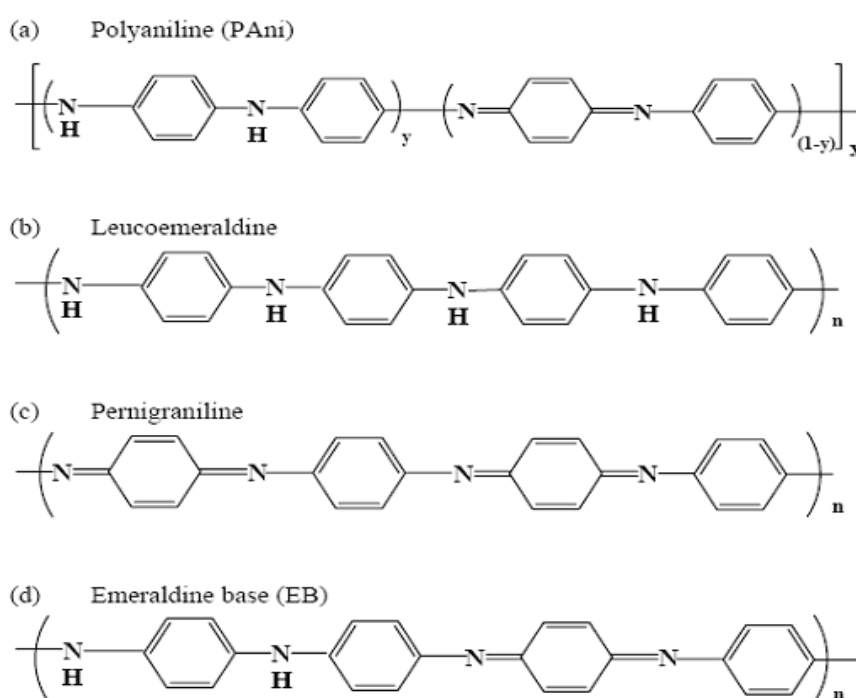
### **Introduction:**

The repeated addition of numerous tiny molecules results in polymers, which are large molecules. The Greek words "poly" (meaning many) and "meres" (meaning units) are the origin of the word polymer. Monomers are the tiny molecules that are used to create polymers. Polymerization describes the process of creating polymers. These polymers are insulators because electricity cannot pass through them. The term conducting polymers is used to describe polymers that permit electric current to flow through them. It refers to both electronically and ionically conducting polymers since electrical conductivity can be either ionic or electronic in nature. Conjugated conducting polymers are among the electronically conducting polymers, whereas ionically conducting polymers are frequently referred to as polymer electrolytes. The flexibility and processability of polymers, along with the electrical and optical capabilities of metals and inorganic semiconductors, are crucial characteristics of conducting polymers. In 1971, the first intrinsic conducting polymer named polyacetylene was reported by Shirakawa et al. [1]. A conducting polymer other than polyacetylene was immediately added to the concept of conductivity and electroactivity. There are four major types of semiconducting polymers that have been developed so far. They are conjugated conducting polymers, charge transfer polymers, ionically conducting polymers and conductively filled polymer. In this book chapter, the structure, properties and possible applications of Polyaniline and polypyrrole are discussed in detail.



## Polyaniline

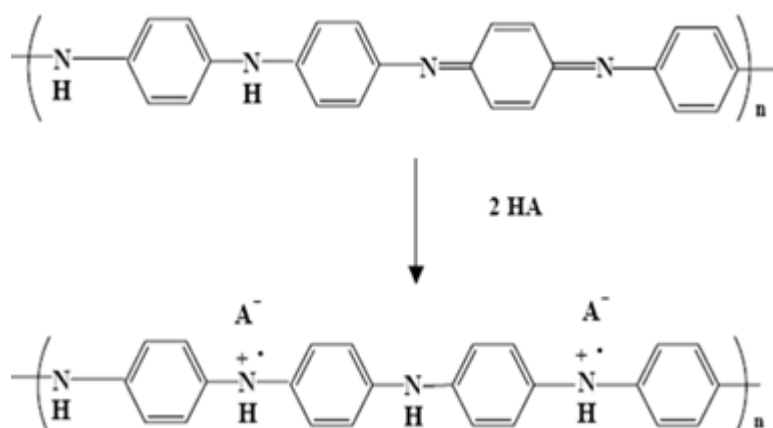
Letheby [2] achieved a dark-green precipitate with a platinum electrode while anodizing aniline in a sulphuric acid solution in 1862, the year when the first report on the creation of "aniline black" was published. This powdered green substance quickly gained the name "aniline black." Since "aniline black" was a material that powdered and was difficult to work with, interest in it remained mostly academic for more than a century. The first organic synthesis of intermediary compounds in the "aniline black" formation was carried out by Green and Woodhead [3], and three distinct aniline octamers were found and given the names leucoemeraldine, pernigraniline, and emeraldine base. These names are still used, indicating various oxidation states of Polyaniline (Fig. 1.1).



**Figure 1.1: Various states of oxidation and protonation of polyaniline**

A typical phenylene-based polymer is polyaniline, which has a phenylene ring on either side of its chemically flexible —NH group in a polymer chain. It is a unique polymer because it can exist in a variety of structures depending on the value of  $(1-y)$  in the general formula of the polymer shown in Figure 1.1 (a) [4-5]. Both protonation and redox doping have the potential to reversibly alter the electrical characteristics of polyaniline. As a result, polyaniline could be represented as a mixed oxidation state polymer made up of repeat units that are reduced ( $-\text{NH}-\text{B}-\text{NH}-$ ) and oxidised ( $-\text{N}=\text{Q}=\text{N}-$ ), where  $-\text{B}-$  and  $=\text{Q}=\text{N}-$  stand for benzenoid and quinoid units, respectively, and together form the polymer chain. (Figure 1.1

(a)), the average oxidation state is given by  $1-y$ . Polyaniline can take on a variety of configurations in a variety of oxidation states, starting from the totally reduced leucoemeraldine base state (LEB), depending on the oxidation state of nitrogen atoms that occur in amine or imine configuration. (Figure 1.1 (b)),  $y-1 = 0$ , to the fully oxidized pernigraniline base state (PNB) (Figure 1.1 (c)), where  $1-y = 1$ . The "half" oxidized ( $1-y = 0.5$ ) emeraldine base state (EB) (Figure 1.1 (d)) is a semiconductor and is composed of an alternating sequence of two benzenoid units and a quinoid unit. The protonated form is the conducting emeraldine salt (ES). The electronic structure and excitations of these three insulating forms (LEB, PNB, EB) are contrasted. When doped with acids, the EB intermediate forms of polyaniline can become non-redox, producing the conductive emeraldine salt state of polyaniline. as demonstrated in Figure 1.2. Among inherently conducting polymers, polyaniline is exceptional in that it may be doped with a proton donor, often by adding an organic acid. The "protonic acid doping" provides the structure a positive charge and multiplies the conductivity of polyaniline when compared to the undoped form. The electrical characteristics of polyaniline can be easily adjusted, and it is stable in air. [6-7].



**Figure 1.2: Protonic acid doping of polyaniline (emeraldine base) to polyaniline (emeraldine salt)**

### Synthesis of Polyaniline

Polyaniline can be synthesized by different methods in different forms. Electrochemically polyaniline can be synthesized either by potentiostatic, galvanostatic or cyclic voltammetric techniques [8]. Films deposited potentiostatically and galvanostatically produces uniform deposit but not adherent to the substrate. Many reports are available on different modes of electrodeposition for polyaniline thin films. They can be synthesized by other routes such as Chemical bath deposition, Successive Ionic Layer Adsorption and Reaction Method and other types of polymerization techniques. A. Aynaou [9] investigated

the deposition mechanism, electrochemical stability, and electrochemical performance of the elaborated polyaniline films prepared by cyclic voltammetry and chronoamperometry. Zhou *et al.* [10] used pulse galvanostatic method to synthesize polyaniline in HNO<sub>3</sub> solution and studied relationship between preparation conditions, morphology and electrochemical properties of polyaniline. Polyaniline nanoparticle films were deposited electrophoretically on the surface of copper sheet electrode by M. Fuseini *et al.* [11]. in the presence of formic acid and acetonitrile as electrolyte.

### **Properties of Polyaniline**

The three forms of Polyaniline each have different physical characteristics, and these forms exhibit various colours depending on their chemistry. If the polymer type is leucoemeraldine, polyaniline appears white/clear or colourless; if it is pernigraniline, it produces blue to violet colour; and if it is emeraldine, it produces blue colour, if it is green colour it is in emeraldine salt form. Only the emeraldine salt form of polyaniline has substantial electrical conductivity, and the other forms do not. The electropolymerization process produces extremely porous emeraldine salts with subpar mechanical characteristics. Due to polyaniline's excellent electrical conductivity in its emeraldine salt form, it is a popular conductive polymer in the electrical industry.

### **Applications of conducting Polyaniline**

#### **1. Gas sensing**

A sensor is a device that can display various environmental changes and detect the presence of other objects. Conducting polyaniline has been employed as a sensing substance for a variety of vapors, including methanol, ethanol, acetone, and benzene, as well as for a variety of gases, including NH<sub>3</sub> and hydrogen [12, 13].

Since polyaniline thin films have excellent processing capabilities, they are frequently utilized in gas sensors. Recently, based on device architecture and sensing mechanisms, polyaniline based bio/chemical sensors, such as chemi-resistive sensors, electrochemical sensors, and transistor-based sensors, are explained by D. Yang *et al.* [14]. Polyaniline-chemically coated the electrode of quartz-crystal microbalance has been developed by Ayad *et al.* [15] to detected phosphoric acid in the liquid phase and also as a pH sensors. Huang *et al.* [16] tested different volatile organic compounds including methanol, ethanol and acetone with polyaniline/ZnO organic-inorganic hybrids at low temperature of 90 °C. polyaniline-coated fabric was used by K. Liu *et al.* [17] as the active material to construct high

performance, flexible, all fabric pressure sensors with a bottom interdigitated textile electrode.

## 2. Supercapacitor

Supercapacitors, often referred to as electrochemical capacitors, use electrode materials with a high surface area to produce capacitances that are many orders of magnitude higher than those of normal capacitors. Due to highly porous nature polyaniline electrode can be used for supercapacitors. Dhawale *et al.* [18] synthesized hydrophilic polyaniline nanofiber electrode for electrochemical supercapacitor. The polyaniline electrode showed highest specific capacitance of  $861 \text{ F g}^{-1}$  at the voltage scan rate of  $10 \text{ mV/s}$ . W. Mahfoz *et al.* [19] developed a symmetric supercapacitor device using polyaniline electrodeposited on steel mesh. Fabricated supercapacitor has a high specific capacitance of  $\sim 353 \text{ mF cm}^{-2}$ .

### Conclusion:

All conduction polymers, polyaniline in its conducting emeraldine salt form can be synthesized by electrochemical polymerizations. The deposited polyaniline in thin film form shows the fascinating properties such as electrical conductivity, high surface area, porosity. The favorable properties of polyaniline showed wide applications in gas sensor and supercapacitor field. So polyaniline is a potential candidate in many applications and easy to synthesize.

### References:

1. Shirakawa, H., & Ikeda, S. (1971). Infrared Spectra of Poly(acetylene). *Polymer Journal*, 2(3).
2. Letheby, H. (1862). XXIX.—On the production of a blue substance by the electrolysis of sulphate of aniline. *J. Chem. Soc.*, 15, 161.
3. Green, G., & Woodhead, A. E. (1910). CXVII.—Aniline-black and allied compounds. Part II. *J. Chem. Soc., Trans.*, 97, 2388.
4. Epstein, A. J. (1999). In *Conductive Polymers and Plastics in Industrial Applications*. Norwich, New York: Plastics Design Library.
5. Trivedi, D. C. (1997). In *Handbook of Organic Conductive Molecules and Polymers* (H. S. Nalwa, Ed.), 505. Chichester: John Wiley & Sons.
6. Matsuguchi, M., & Asahi, T. (2011). *Sens. Actuators B*, 160, 999.
7. Ziadan, K. M., & Saadon, W. T. (2012). *Energy Procedia*, 19, 71.

8. Sowmya, Sudhakar, Y., & Selvakumar, M. (2016). Supercapacitor studies of electrochemically synthesized multi-layered polyaniline on stainless steel substrate. *Ionics*, 22, 1729–1739.
9. Aynaou, A., Youbi, B., Ait Himi, M., Lghazi, Y., Bahar, J., El Haimer, C., Ouedrhiri, A., & Bimaghra, I. (2022). Electropolymerization investigation of polyaniline films on ITO substrate. *Materials Today: Proceedings*, 66(1), 335.
10. Zhou, H. H., Jiao, S. Q., Chen, J. H., Wei, W. Z., & Kuang, Y. F. (2004). Relationship between preparation conditions, morphology and electrochemical properties of polyaniline prepared by pulse galvanostatic method (PGM). *Thin Solid Films*, 450(2), 233.
11. Fuseini, M., Zaghoul, M. M. Y., Elkady, M. F., & El-Shazly, A. H. (2022). Evaluation of synthesized polyaniline nanofibres as corrosion protection film coating on copper substrate by electrophoretic deposition. *J Mater Sci*, 57, 6085.
12. Tanguy, N. R., Thompson, M., & Yan, N. (2018). A review on advances in application of polyaniline for ammonia detection. *Sensors and Actuators B: Chemical*, 257, 1044.
13. Ayad, M. M., El-Hefnawey, G., Torad, N. L., (2009). A sensor of alcohol vapours based on thin polyaniline base film and quartz crystal microbalance. *Journal of Hazardous Materials*, 168(1), 85.
14. Yang, D., Wang, J., Cao, Y., Tong, X., Hua, T., Qin, R., & Shao, Y. (2023). Polyaniline-Based Biological and Chemical Sensors: Sensing Mechanism, Configuration Design, and Perspective. *ACS Applied Electronic Materials*, 5(2), 593.
15. Ayad, M. M., Salahuddin, N. A., & Alghaysh, M. O. (2010). Phosphoric acid and pH sensors based on polyaniline films. *Current Applied Physics*, 10(1), 235.
16. Huang, J., Yang, T., Yanfei, K., Wang, Y., & Wang, S. (2011). Gas sensing performance of polyaniline/ZnO organic-inorganic hybrids for detecting VOCs at low temperature. *Journal of Natural Gas Chemistry*, 20, 515.
17. Liu, K., Zhou, Z., Yan, X., Meng, X., Tang, H., Qu, K., Gao, Y., Li, Y., & Yu, J. (2019). Polyaniline Nanofiber Wrapped Fabric for High-Performance Flexible Pressure Sensors. *Polymers*, 11(7), 1120.
18. Dhawale, D. S., Salunkhe, R. R., Jamadade, V. S., Dubal, D. P., Pawar, S. M., & Lokhande, C. D. (2010). Hydrophilic polyaniline nanofibrous architecture using electrosynthesis method for supercapacitor application. *Current Applied Physics*, 10(3), 904.
19. Mahfoz, W., Das, H. T., Shah, S. S., Sanhoob, M., Anjum, A., Al-Betar, A., & Aziz, M. A. (2023). Designing High-Performing Symmetric Supercapacitor by Engineering Polyaniline on Steel Mesh Surface via Electrodeposition. *Chem. Asian J.*, 18(4), e202201223.

## BIOREMEDIATION OF HEAVY METAL CONTAMINATED SOILS

R. Jayashree\* and V. Bhagyasree

Department of Environmental Sciences,  
Tamil Nadu Agricultural University, Coimbatore 641 003

\*Corresponding author E-mail: [jayashree.r@tnau.ac.in](mailto:jayashree.r@tnau.ac.in)

### Abstract:

The rational use and protection of water resources and supplying human kind with adequate clean fresh water, or, to be concise, “water problems” are among today’s most acute and complex scientific and technical problems. Utilization of sewage wastewater for irrigating agricultural crops is associated with several non-biological risk factors; perhaps the most significant being heavy metal contamination. Reclamation of sewage irrigated agricultural soils using different microbial consortium is necessary to rehabilitate the soil without any risk of biomagnification of heavy metals through crop produce to human being. Detoxification and rehabilitation of contaminated soil with the use of microbes has emerged as the most safe, easy and effective technology. Native soil microorganisms have been explored and harnessed for their ability to remove or detoxify toxic products released due to human activities in the environment.

### Introduction:

Mankind is currently confronted with one of the greatest challenges in its history: how to adequately use its limited freshwater resources. The challenge implicates the use of water for drinking, agriculture, and the preservation of fragile freshwater ecosystems. The rational use and protection of water resources and supplying human kind with adequate clean fresh water or, to be concise, “water problems” are among today’s most acute and complex scientific and technical problems.

Under arid and semi-arid environmental conditions, in which irrigation is a pre-requisite for agricultural development, the importance of effluent as a source of irrigation water is as great as the need for its disposal. Effluent becomes exceptionally valuable where other sources of water are scarce, and its utilization for irrigation frees high quality water for other uses (Feigin *et al.*, 2012).

According to the estimates of International Water Management Institute, the volume of treated and untreated municipal wastewater generated is 11,787 and 26,467 million litres per day (Amerasinghe *et al.*, 2013) from Class I and II cities in India. For a country like India

whose economy is agriculture-based, use of this voluminous, nutrient loaded treated wastewater for agricultural irrigation helps in facing chronic shortage of water supply. The increasing agricultural reuse of treated effluent serves goals such as promoting sustainable agriculture, preserving scarce water resources, and maintaining environmental quality and also significantly relieves pressure on water resources. Despite the obvious benefits of treated wastewater irrigation like high nutritive value, increased productivity rate from poor soils, reduced fertilizer application rates, increased soil organic matter and other essential nutrients for plant growth and development; the human and environmental health implications of this process have opened a new controversial front in the public debate.

Irrigation of agricultural crops with recycled wastewater is associated with several non-biological risk factors; perhaps the most significant being heavy metal contamination. In this context, different studies have shown the accumulation of heavy metals such as cadmium (Cd), nickel (Ni), chromium (Cr), lead, and other elements in soil and plants under wastewater irrigation regimen (Gatica and Cytryn, 2013). Rattan *et al.* (2005) reported the buildup of DTPA- extractable Zn (208%), Cu (170%), Fe (170%), Ni (63%) and Pb (29%) in soils irrigated with sewage for 20 years.

In a study by Rani *et al.* (2014) on long term effect of sewage irrigated fields, the heavy metals Cd, Ni and Pb levels in sub-surface soils were found to be 2.60, 4.88 and 72.47 mg kg<sup>-1</sup>. Similarly, sewage- irrigated land recorded significantly higher concentrations of heavy metals (Cr, Ni, Pb and Cd) than bore well water- irrigated land due to gradual accumulation of heavy metals in sewage- irrigated soils (Salakinkop and Hunshal, 2014).

Irrespective of their sources in the soil, accumulation of heavy metals can degrade soil quality, reduce crop yield and the quality of agricultural products, and thus negatively impact the health of human, animals and the ecosystem. The ability of heavy metals bioaccumulation to cause toxicity in biological systems-human, animals, microorganisms and plants- is an important issue for environmental health and safety.

The threat of heavy metal pollution to public health and wildlife has led to an increased interest in developing systems that can remove or neutralise its toxic effects in soil, sediments and wastewater. Unlike organic contaminants, which can be degraded to harmless chemical species, heavy metals cannot be destroyed. Remediating the pollution they cause can therefore only be envisioned as their immobilisation in a non-bioavailable form, or their re-speciation into less toxic forms. While these approaches do not solve the

problem altogether, they do help to protect afflicted sites from noxious effects and isolate the contaminants as a contained and sometimes recyclable residue.

Microorganisms have been successfully exploited to deal with heavy metal pollution in a variety of schemes. Emerging technologies in this area rely on enhancing the biosorption of metals into biomass, or the precipitation of ions by exploiting some metal-related facet of bacterial metabolism.

The goal of microbial remediation of heavy metal contaminated soils and sediments are to immobilize the metal in situ to reduce metal bioavailability and mobility or to remove the metal from the soil. Low cost and higher efficiency at low metal

The adequate protection and restoration of soil ecosystems contaminated with heavy metals require characterization and remediation. Remediation of heavy metal contaminated soils would entail knowledge of the source of contamination, basic chemistry and environmental fate and associated health effects (risks) of the heavy metals. Synergistic use of plants (phytoremediation) and microbes (bioremediation) for remediating heavy metal contaminated soils are getting increased reception due to their cost- effectiveness and eco-friendly services. Bioremediation is an innovative and promising technology available for removal of heavy metals.

### Bioremediation of heavy metals in contaminated soils:

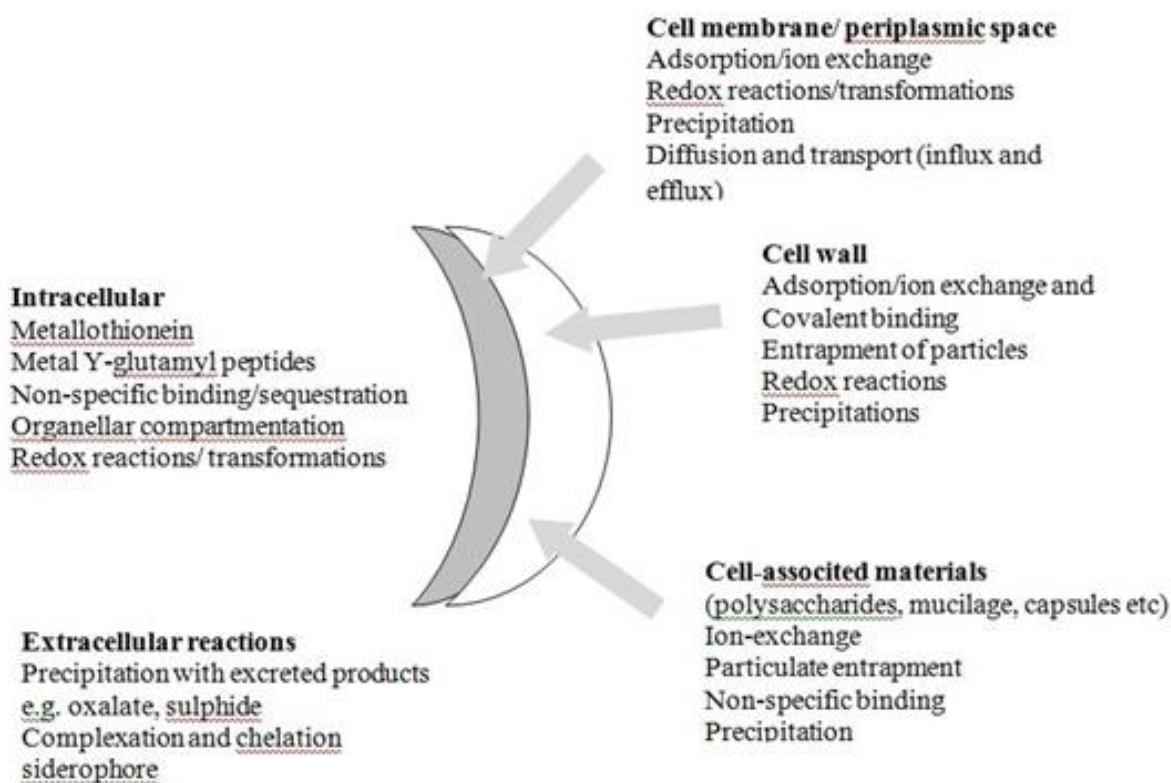


Figure 1: The microbial uptake and detoxification of toxic metals



Conventional physicochemical techniques for metal remediation such as filtration, acid leaching, electrochemical processes or ion exchange are expensive and may not be very effective. Bioremediation based on microorganisms, plants or other biological systems offers a cost-effective and environment friendly method for metal clean-up (Haferburg *et al.*, 2010).

The possible mechanisms of microbial uptake and detoxification of toxic metals in soil matrix is presented in Fig. 1.

### **Factors affecting bioremediation of heavy metals**

#### **pH:**

Soil properties affect metal availability in diverse ways. Harter (1983) reported that soil pH is the major factor affecting metal availability in soil. Availability of Cd and Zn to the roots of *Thlaspi caerulescens* decreased with increase in soil pH. Das *et al.* (2014) studied the major environmental factors that affect the biosorption processes and were found to be (i) initial metal ion concentration, (ii) ambient pH, (iii) biomass, and (iv) presence of other toxic metals. Calvino and Baath (2016) determined bacterial and fungal growth in response to Cu additions to the soil with varying pH. At higher pH, it was hypothesized that the toxic effect of Cu would decrease. High pH thus mitigated the toxic effect of Cu indicating that pH is an important parameter for toxicity determinations. At a pH range of 3-7, 50.2–78.4% of Cr, 63.7–74.1% of Cu, 74.9–88.2% of Zn and 15.5–38.6% of Ni leached out from the sludge, whereas at a pH of 7, only 1.5% of Cr, 1.7% of Cu, 15.3% of Zn and 15.5% of Ni was solubilized.

#### **Moisture:**

Significant positive correlations have been recorded between heavy metals and some soil physical properties such as moisture content and water holding capacity (Sharma *et al.*, 2013). A moderate correlation was noticed between water holding capacity (WHC) and chromium (Cr) with r values 0.651.

#### **Organic Carbon:**

Soil organic matter plays a key role in reduction of Cr(VI) to Cr(III). Under aerobic, field moist conditions, organic matter rich soil (amended with 50 tons ha<sup>-1</sup> organic matter) was reported to reduce 96% of added Cr(VI), whereas sterile soils receiving the same amendments reduced only 75% of the original Cr(VI), demonstrating the importance of the presence of soil microorganisms in conjunction with a readily available carbon source in heavy metal detoxification (Sharma *et al.*, 2013).

### **Bioremediation of heavy metals by microorganisms:**

Studies on bacterial prevalence in heavy metal contaminated sites have demonstrated a high number of microorganisms. They are indigenous organisms that have not only adapted to the new environments but have also flourished under them. Microorganisms possess a variety of mechanisms to deal with high concentrations of heavy metals and often are specific to one or a few metals. Microbes have developed mechanisms to tolerate the metals either by presence of heavy metals through efflux, complexation, or reduction of metal ions or to use them as terminal electron acceptors in anaerobic respiration (Haferburg *et al.*, 2010).

Although some heavy metals are important as essential trace elements, at higher concentrations, they are found to be toxic to microbes. A number of interactions between microbes and metals have important environmental and health implications. Some implications are useful, such as the use of bacteria to clean up metal-contaminated sites. Other implications are not as beneficial as the presence of metal tolerance mechanisms may contribute to the increase in antibiotic resistance.

Heavy metals cannot be degraded during bioremediation but can only be transformed from one organic complex or oxidation state to another. Due to a change in their oxidation state, heavy metals can be transformed to become either less toxic, easily volatilized, more water soluble (and thus can be removed through leaching), less water soluble (which allows them to precipitate and become easily removed from the environment) or less bioavailable.

Detoxification and rehabilitation of contaminated soil with the use of microbes has emerged as the most safe, easy and effective technology. Native soil microorganisms have been explored and harnessed for their ability to remove or detoxify toxic products released due to human activities in the environment.

Microorganisms have co-existed with metals since early history. This is reflected in the wide range of divalent or transition metals at the active centres of many enzymes. The requirement of living systems to both acquire and reject metals has led to the selection of a whole repertoire of mechanisms of interaction which ensure the adaptation of microorganisms to a changing and frequently hostile environment (Sharmistha *et al.*, 2010).

The heavy metal-resistant bacterial strain SJ-10 from fly ash contaminated soil identified as *Bacillus sp* absorb the Ni. The adsorption isotherms revealed the absolute adsorption capacity ( $Q_{\infty}$ ) of 244 mg Ni g<sup>-1</sup> dry cell mass vis-a-vis 161 mg Ni g<sup>-1</sup> synthetic resin (Amberlite IR-120). The higher relative adsorption capacity (KF) of 7.37, and the intensity of

adsorption ( $1/n$ ) of 0.58 with dry cell biomass suggested higher affinity of *Bacillus* cells towards nickel ions. The total Ni bioaccumulation capacity of isolate SJ-101 was 1.44 mM Ni g<sup>-1</sup> cells representing 39.4% extracellular and 45.4% intracellular accumulation. Higher Ni tolerance and sorption capacity of *Bacillus sp.* SJ-101, explicitly signifies its implications in Ni bioremediation process.

The effect of bacterial inoculants on Ni uptake by Ni hyperaccumulating *Alyssum murale* plants from low, moderate and high Ni soils was studied. Nine bacterial strains, originally isolated from the rhizosphere of *A. murale* grown in serpentine Ni-rich soil, were examined for their ability to solubilize Ni in different soils and for their effect on Ni uptake into *Alyssum*. *M. oxydans* AY509223 significantly increased Ni extraction by 10 mM Sr (NO<sub>3</sub>)<sub>2</sub> from the high and medium soils and had no effect on Ni extraction from the low Ni soils. The other eight bacterial isolates significantly increased Ni extraction from all soils. *M. oxydans* AY509223 significantly increased Ni uptake of *A. murale* grown in the low, medium, and high soils by 36.1%, 39.3%, and 27.7%, respectively, compared with uninoculated seeds. *M. oxydans* AY509223 increased foliar Ni from the same soils from 82.9, 261.3 and 2829.3 mg kg<sup>-1</sup> to 129.7, 430.7, and 3914.3 mg kg<sup>-1</sup>, respectively, compared with uninoculated controls. Clearly, this result showed that, despite the fact that *Alyssum* hyper accumulates Ni even without rhizobacteria inoculation; bacteria can appreciably increase the accumulation of Ni for hyper accumulation from soils with a high proportion of non-soluble Ni. This study indicates that bacteria facilitated the release of Ni from the non-soluble phases in the soil, thus enhancing the availability of Ni to *A. murale*. A possible explanation might be acid, siderophore production and phosphate solubilization.

The biosorption potential of *Bacillus subtilis* from aqueous solution was assessed. The maximum biosorption of Pb was 97.68% within 48 h of incubation time with optimum pH 4.5 and optimum temperature 40° C for 700 ppm of initial loading. According to the results of Vivas study on Nickel-tolerant *Brevibacillus brevis* and arbuscular mycorrhizal fungus to reduce metal acquisition and nickel toxicity effects in plants growing in nickel supplemented soil, selected bacterial inoculation improved the mycorrhizal benefit in nutrients uptake and in decreasing Ni toxicity. The growth of clover (*Trifolium repens*) and its uptake of N, P and Ni were studied and following inoculation of soil with *Rhizobium trifolii*, and combinations of two Ni-adapted indigenous bacterial isolates (one of them was *Brevibacillus brevis*) and an arbuscular mycorrhizal (AM) fungus (*Glomus mosseae*). Coinoculation of *G. mosseae* and the Ni-tolerant bacterial strain (*B. brevis*) achieved the highest plant dry biomass (shoot and

root) and N and P content and the lowest Ni shoot concentration. Dual inoculation with the most Ni-tolerant autochthonous microorganisms (*B. brevis* and *G. mosseae*) increased shoot and root plant biomass and substantially reduced the specific absorption rate (defined as the amount of metal absorbed per unit of root biomass) for nickel in comparison with plants grown in soil inoculated only with *G. mosseae* (Girma *et al.*, 2015)

Rhizosphere microorganisms harboring nickel hyperaccumulators, *Rinorea bengalensis* (Wall.) O. K. and *Dichapetalum gelonioides* sp. *andamanicum* (King) Leenh. endemic to serpentine outcrops of Andaman Islands, India, were screened for their tolerance and accumulation of Ni. Viable cells of selected Ni-tolerant bacterial isolates (MIC = 13.6–28.9 mM Ni) belonging to *Pseudomonas*, *Bacillus* and *Cupriavidus* were capable of accumulating nickel (209.5–224.0  $\mu\text{M Ni g}^{-1}$  protein) from aqueous solution. Kinetics of nickel uptake in *C. pauculus* KPS 201 followed a linearized Lineweaver-Burk plot. The  $K_m$  and  $V_{max}$  for nickel uptake by minimal medium grown-cells approximated 1.5 mM Ni and 636.9  $\mu\text{M Ni g}^{-1}$  protein, respectively. The Ni-hyperaccumulators in combination with these Ni-resistant bacteria could be an ideal tool for nickel bioremediation.

Aerobic batch biosorption experiments were carried out for removal of Cr (VI), Fe (III) and Cu (II) ions from aqueous metal solutions by Samarth *et al.* (2012). Per cent removal efficiency for iron, chromium and copper ions was 95, 52 and 32 (w/v) after 48 hrs at 120 rpm. Optimum pH was found to be 3.5 for Fe (III) and Cr (VI) whereas for Cu (II) it was 2.5. Optimum incubation temperature was found to be 28 °C. Metal tolerance studies were also carried out using aqueous metal solutions of these metals individually and in combination.

The use of sulfate-reducing bacteria (SRB) in passive treatments of acidic effluents containing heavy metals has become an attractive alternative biotechnology. Barbosa *et al.* (2014) aimed to cultivate a mixed culture of SRB using different lactate concentrations at pH 7.0 in the presence of Ni, Mn and Cu. Different concentrations of metals were added to the system at neutral pH conditions. The presence of metals interfered in the sulfate biological removal however the concentration of sulfide produced was high enough to remove over 90 % of the metals in the environment. The molecular characterization of the bacterial consortium based on *dsrB* gene sequencing indicated the presence of *Desulfovibrio desulfuricans*, *Desulfomonas pigra* and *Desulfobulbus* sp. The results of this study reinforce the potential of using mixed SRB cultures instead of pure cultures for the removal of sulfate

and metals in batch systems, suggesting new possibilities for the treatment of sulfate-rich industrial wastewater and/or mine drainages.

It was inferred from the study of Husain *et al.* (2013) that bacterial biosorbents can be used for heavy metal removal. Highest nickel uptake upto 1000ppm concentration was recorded when *Pseudomonas fluorescence* cells were subjected for bioremoval of nickel ions. Similarly, Naz *et al.* (2015) studied the biosorption of heavy metals by *Pseudomonas sp.* and arrived at the results that it reduced 37% Pb, 32% Ni, 32% Cr. Thus it can contribute to an enhanced remediation of contaminated environment.

In a study by Basha and Rajaganesh (2014) four microbial strains namely *Escherichia coli*, *Salmonella typhi*, *Bacillus licheniformis* and *Pseudomonas fluorescence* reduced maximum of 98.34% of cadmium, 94.83% of lead and 96.14% of zinc from the effluent samples.

Bioleaching of heavy metal-contaminated soils using *Burkholderia sp.* Z-90 isolated from cafeteria sewer sludge and its capability for removing Zn, Pb, Mn, Cd, Cu, and As was investigated by Yang *et al.* (2016). The removal efficiency was 44.0% for Zn, 32.5% for Pb, 52.2% for Mn, 37.7% for Cd, 24.1% for Cu and 31.6% for As, respectively.

Bioremediation with *Brevibacteria sp.* is found effective in removal of micro-units of Zn, Cu and Mg from domestic sewage. The treatment efficiency is of the order Cu > Zn > Mg and with respective removal percentages of 77, 63 and 55% (Ojoawo *et al.*, 2016).

Heavy metal removal by bacterial consortium from acid mine drainage through bioleaching processes were investigated by Shi *et al.* (2015). The findings show that Cu, Zn and Cd bioleaching efficiencies (12 days) were 81–91, 87–93 and 81–89 %, respectively, which were significantly higher than those of Fe–S control ( $P < 0.05$ ) and blank control ( $P < 0.01$ ).

Gheethi *et al.* (2014) studied the biosorption of heavy metals by bacteria isolated from secondary effluents from sewage plants. The biosorption process was found to be efficient in removing heavy metals: 87.63 % of cadmium, 74.61 % of copper, 58.32 % of nickel, 61.9 % of lead and 94.26 % of zinc, respectively.

#### **Effect of organic amendments on heavy metal bioremediation:**

Addition of organic amendments has often been shown to increase the CEC of soils, thereby resulting in increased metal adsorption. Beesley *et al.* (2010) studied the effects of biochar and green waste compost amendment on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi- element polluted soil. After adding both amendments, it was observed that there was a significant increase in dissolved organic

carbon, pH content whereas there was a 10-fold decrease in Zn and Cd contents. Biochar was most effective, resulting in a 10-fold decrease of Cd in pore water and a resultant reduction in phytotoxicity.

Inyang *et al.* (2012) examined the ability of two biochars converted from anaerobically digested biomass (DAWC (digested dairy waste biochar) and DWSBC (digested whole sugar beet biochar)) to sorb heavy metals using a range of laboratory sorption and characterization experiments. Both biochars were effective in removing a mixture of four heavy metals ( $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$  and  $Cd^{2+}$ ) from aqueous solutions.

Similarly, Angelova *et al.* (2013) studied the effect of organic amendments on soilchemical characteristics and inferred that soil application of compost and vermicompost decreased DTPA-extractable levels of heavy metals in the soil. Compost and vermicompost treatments had significant effect on soil physical and chemical properties like EC, pH, organic matter, macro and micronutrients content. Compared with the unamended soil, soil treated with organic amendments showed apparent increases of organic matter, total N, pH, EC and available macro elements (P, K, Ca and Mg).

The effect of vermicompost on biotransformation and bioavailability of hexavalent chromium in soil was studied by Rangasamy *et al.* (2013). The vermicompost and microbial cultures (*Pseudomonas fluorescens* and *Trichoderma viride*) were used for chromium detoxification studies. The chromium (VI) reduction was observed in best treatment like vermicompost alone reduced the chromium up to 85 per cent and vermicompost along with *Pseudomonas fluorescens* reduced the hexavalent chromium upto 84.6 per cent. The large amount of hexavalent chromium was detoxified due to application of vermicompost.

A number of amendments are used either to mobilize or immobilize heavy metals in soils. Different kinds of organic amendments that have been used for the treatment of contaminated soil include manures, biosolids, sawdust, wood-ash, composts obtained from different source materials, sewage sludge, bark chips and woodchips (Gul *et al.*, 2015). Concentrations make biotechnological processes very attractive in comparison to physiochemical methods for heavy metal removal. Metal remediation strategies using microorganisms can minimize bioavailability and biotoxicity of heavy metals.

There are a number of microorganisms that can be used to remove metal from the environment, such as bacteria, fungi, yeast and algae. Because of the adaptability of microbes and other biological systems, these can be used to degrade or remediate environmental hazards. The main requirements are an energy and a carbon source. Some of the microorganisms that play great role in bioremediation of heavy metals are *Pseudomonas*

spp., *Alcaligenes* spp., *Arthrobacter* spp., *Bacillus* spp., *Corynebacterium* spp., *Flavobacterium* spp., *Azotobacter* spp., *Rhodococcus* spp., *Mycobacterium* spp., *Nocardia* spp., *Methosinus* spp., *Methanogens*, *Aspergillus niger*, *Pleurotus ostreatus*, *Rhizopus arrhizus*, *Stereum hirsutum*, *Phormidium valderium* and *Ganoderma applanatum* (Girma, 2015).

Husain *et al.* (2013) showed that bacterial biosorbents can be used for heavy metal removal. 95% nickel uptake upto 1000ppm concentration was recorded when *Pseudomonas fluorescense* cells were subjected for bioremoval of nickel ions. In a study by Basha and Rajaganesh (2014) four microbial strains namely *Escherichia coli*, *Salmonella typhi*, *Bacillus licheniformis* and *Pseudomonas fluorescense* reduced maximum of 98.34% of cadmium, 94.83% of lead and 96.14% of zinc from the effluent samples.

### References:

1. Amerasinghe, P., Bhardwaj, R. M., Scott, C., Jella, K., & Marshall, F. (2013). Urban wastewater and agricultural reuse challenges in India. In: Colombo, Sri Lanka, IWMI, pp. 36.
2. Angelova, V. R., Akova, V. I., Arnitova, S., & Ivanov, K. I. (2013). The effect of organic amendments on soil chemical characteristics. *Bulg. J. Agric. Sci.*, 19(5), 958-971.
3. Basha, S. A., & Rajaganesh, K. (2014). Microbial Bioremediation of heavy metals from textile industry dye effluents using isolated bacterial strains. *Int. J. Curr. Microbiol. App. Sci.*, 3(5), 785-794.
4. Barbosa, L. P., Costa, P. F., Bertolino, S. M., Silva, J. C. C., Guerra-Sa, R., Leao, V. A., & Teixeira, M. C. (2014). Nickel, manganese and copper removal by a mixed consortium of sulfate reducing bacteria at a high COD/sulfate ratio. *World J. Microbiol. Biotechnol.*, 30, 2171-2180.
5. Calvino, D. F., & Baath, E. (2016). Interaction between pH and Cu toxicity on fungal and bacterial performance in soil. *Soil Biol. Biochem.*, 96, 20-29.
6. Das, P., Sinha, S., & Mukherjee, S. K. (2014). Nickel Bioremediation Potential of *Bacillus thuringiensis* KUNi1 and Some Environmental Factors in Nickel Removal. *Biorem. J.*, 18(2), 169-177.
7. Feigin, A., Ravina, I., & Shalhevet, J. (2012). Irrigation with Treated Sewage Effluent: Management for Environmental Protection. In: Springer Science & Business Media Technology & Engineering.
8. Girma, G. (2015). Microbial bioremediation of some heavy metals in soils: An updated review. *Indian J. Sci. Res.*, 6(1), 147-161.

9. Gul, S., Naz, A., Fareed, I., & Irshad, M. (2015). Reducing heavy metals extraction from contaminated soils using organic and inorganic Amendments- a review. *Pol. J. Environ. Stud.*, 24(3), 1423-1426.
10. Haferburg, G., & Kothe, E. (2010). Metallomics: lessons for metaliferous soil remediation. *Appl. Microbiol. Biotechnol.*, 87, 1271–1280.
11. Husain, R. S. A., Thatheyus, A. J., & Ramya, D. (2013). Bioremoval of nickel using *Pseudomonas fluorescens*. *Am. J. Microbiol. Res.*, 1(3), 48-52.
12. Inyang, M., Gao, B., Yao, Y., Xue, Y., Zimmerman, A. R., Pullammanappallil, P., & Cao, X. (2012). Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass. *Biores. Technol.*, 110, 50-56.
13. Naz, T., Khan, M. D., Ahmed, I., Rehman, S. U., Rha, E. S., Malook, I., & Jamil, M. (2015). Biosorption of heavy metals by *Pseudomonas* species isolated from sugar industry. *Toxicol. Ind. Health*, 2, 134-140.
14. Ojoawo, S. O., Rao, C. V., & Goveas, L. C. (2016). Bioremediation of Zn, Cu, Mg and Pb in Fresh Domestic Sewage by *Brevibacterium* sp. *Int. J. Environ. Res.*, 10(1), 139-148.
15. Rani, K. U., Sharma, K. L., Nagasri, K., Chandrika, D. S., Savithri, V. L., & Lal, M. (2014). Effect of long-term sewage water irrigation on micronutrient and heavy metal content in soil and plants under Musi river basin in Hyderabad. *J. Indus. Pollut. Cont.*, 30(1), 7-22.
16. Salakinkop, S. R., & Hunshal, C. S. (2014). Domestic sewage irrigation on dynamics of nutrients and heavy metals in soil and wheat (*Triticum aestivum* L.) production. *Int. J. Recyc. Org. Waste Agric.*, 3, 64.
17. Samarth, D. P., Chandekar, C. J., & Bhadekar, R. K. (2012). Biosorption of heavy metals from aqueous solution using *Bacillus licheiformis*. *Int. J. Pure Appl. Sci. Technol.*, 10(2), 12-19.
18. Sharma, R. M. S., & Raju, N. S. (2013). Correlation of heavy metal contamination with soil properties of industrial areas of Mysore, Karnataka, India by cluster analysis. *Intl. Res. J. Env. Sci.*, 2(10), 22– 27.
19. Shi, C., Zhu, N., Shang, R., Kang, N., & Wu, P. (2015). Simultaneous heavy metals removal and municipal sewage sludge dewaterability improvement in bioleaching processes by various inoculums. *World J. Microbiol. Biotechnol.*, 31(11), 1719-1728.



## **INTRODUCTION AND APPLICATIONS OF III-V SEMICONDUCTOR COMPOUNDS AND ALLOYS**

**Uttam Paliwal**

Department of Physics,

Jai Narain Vyas University, Jodhpur-342001

Corresponding author E-mail: [uttamphy@gmail.com](mailto:uttamphy@gmail.com)

### **Abstract:**

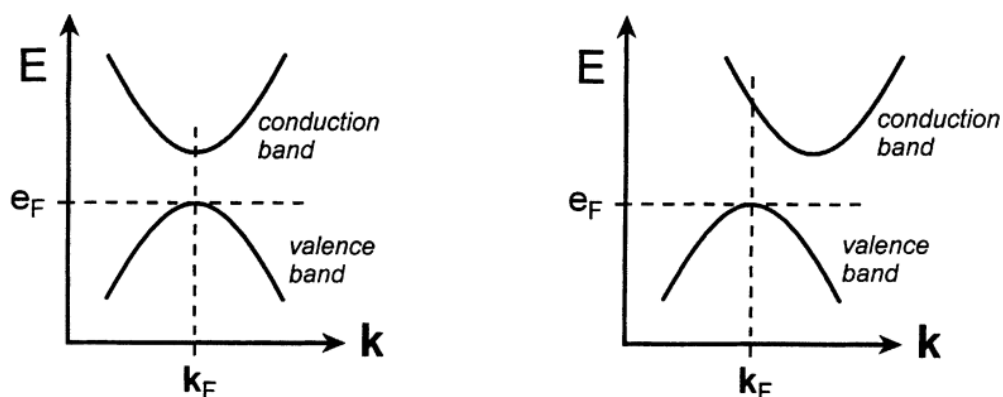
In this chapter the introduction and applications of semiconducting compounds and alloys formed by combining group III and V is presented. The brief introduction about various aspects of group III-V semiconductor compounds in electronic, optoelectronic and other technologically important devices are discussed. The applications of semiconductor alloys formed by mixing the III-V materials i.e. Among III-V compounds the InP, InAs, InSb, GaN, GaP, GaAs, GaSb, AlN, AlP, AlAs, AlSb are presented and discussed here.

### **Introduction:**

Semiconductors are the fundamental building block of many useful applications in our daily life e.g. diodes, transistors, integrated circuits, and opto-electronic devices such as laser diodes, photo-diodes, photo-detectors, ultra-violet lasers, infrared sensors, and optical fibres etc. The limitation of any semiconducting compound is that it has a defined or constant value of bandgap. This limitation can be removed by fabricating the mixed semiconductor compounds or semiconductor alloys. These alloys are a mixture of two or more semiconductor compounds. By creating mixed compounds or semiconductor alloys from the right binary compounds, the bandgap can be adjusted. The binary semiconductors can be used to create the mixed compounds as ternary or quaternary alloy. Thus, a material functioning at a desired bandgap can be prepared in advance. The physical properties like bandgap, refractive index, thermal conductivity of thus prepared ternary and quaternary semiconductor alloys depend upon the composition of the compounds and it may vary linearly or non linearly with the composition [1-3].

The bandgap and its characteristics are the essential quantity that makes semiconductors usable. A semiconductor's bandgap is unique to that material and defines it. The bandgap is defined as the difference between the maximum value of the valence band and minimum value of the conduction band. In the direct bandgap material, the maxima of the valence band coincide with the minimum value of the conduction band while in the

indirect bandgap material these two does not coincide to each other. A symbolic band diagram of the direct or indirect bandgap is drawn in the Figure 1 given below-



**Figure 1: Direct and indirect bandgap [4]**

When a photon of energy  $h\nu$  falls on the semiconductor the absorption of photon in the semiconductor device depends on the photon energy and band-gap energy  $E_g$  of the semiconductor. If  $h\nu < E_g$  then the photon will not be absorbed and it will be transmitted through the material so that the material becomes transparent. But if  $h\nu > E_g$  then the photon will interact with the material and it will make transition of electron from valence band to conduction band thus creating a hole [4].

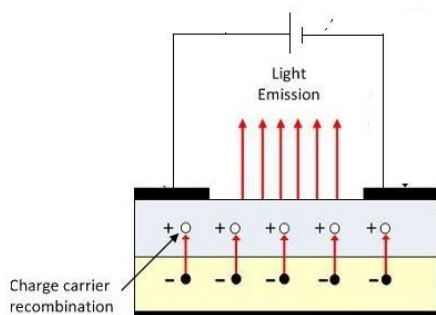
#### **Application of semiconductors in optoelectronic devices:**

The optoelectronic devices are the instruments in which the optical energy is emitted, modified, or converted to the electronic energy or vice-versa. The photodiodes or photo detectors, light emitting diodes, laser diodes are examples of optoelectronic devices. The development of various optoelectronic devices is possible only after the discovery of semiconducting materials. Now a brief discussion of some optoelectronic devices is presented here.

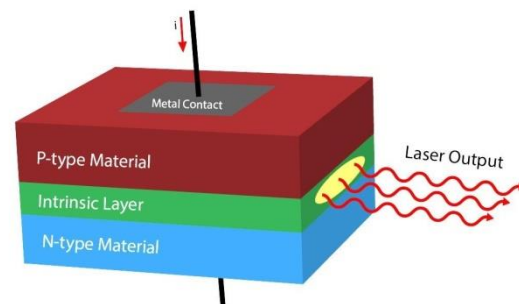
The photo detector is a device that converts the incoming optical light or signal into an electrical energy. The photo detectors, also known as photodiodes are used in optical communication systems because of their small size, fast detection speed, and high detection efficiency. A photodiode is operated in reverse bias used for digital imaging and optical communication [5]. The purpose of a photodiode is to convert the light energy into electric energy by absorbing the photons at the surface of a semiconductor. The most common

structure of a photodiode is PIN structure in which an intrinsic layer sandwiched between the p- and n-type layers, and that is why a semiconductor photodetector is also known as a PIN diode.

The light emitting diode (LED) is a PN-junction diode that transforms electric energy into light energy. When an electric current flows through it in the forward direction, the LED emits light. Based on the recombination of electrons and holes, which occurs when the electrons from the N type combine with the holes from the P-type portion, an LED emits light. A schematic diagram of a LED is given [6] in the Figure 2.



**Figure 2: Schematic diagram of a LED**



**Figure 3: Schematic diagram of a Laser Diode**

A laser diode is a semiconductor device that produces stimulating emission to emit coherent light thus a laser diodes emits highly focused coherent light beam or laser. A laser diode is essentially a p-n semiconductor junction diode with a forward bias voltage supplied to initiate a current through the junction. Narrow-band coherent photons are released as a result of the semiconductor material's population inversion. The dopants in the semiconductor determine the laser's frequency. Numerous industries, including telecommunications, material processing, and medical treatments, employ laser diodes extensively [7].

### **III-V semiconductor compounds:**

The III-V semiconductor compounds are formed by the cation of group Group III and anions from group V. These materials generally crystallize in the cubic zincblende crystal structure and hexagonal type wurtzite crystal structure. The binary semiconductors GaAs, InAs, InP, GaN, AlSb, etc. are examples of III-V compounds. The coordination numbers of the atoms in cubic zinc-blende and hexagonal wurtzite structures is 4. The zinc-blende type structure is more common than rest two as in this structure the  $sp^3$  hybridization take place

which leads to a strong bonding between the III and V group atoms. The III-V semiconductor compounds are very useful in fabrication of various types of opto-electronic devices as these materials possess a direct bandgap that allows for the efficient absorption and emission of light [8]. In following table the lattice constants and bandgaps of some III-V semiconductors are given [1,3].

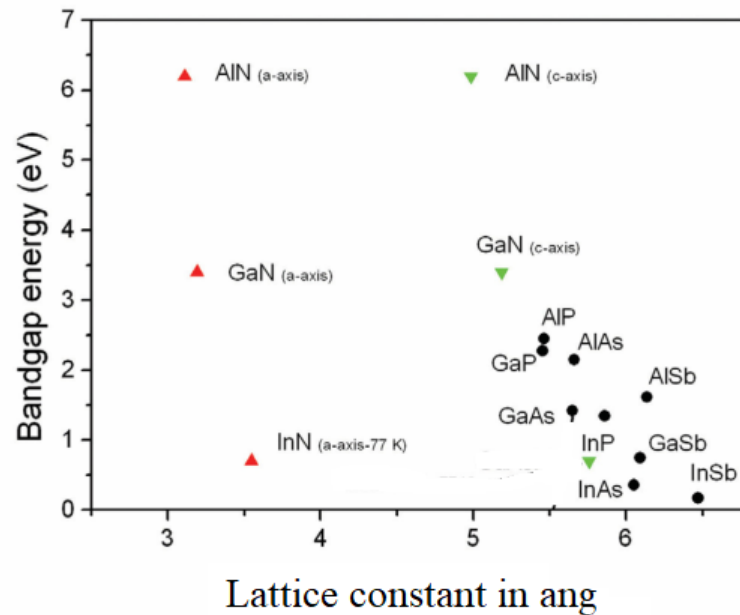
**Table 1: The experimentally reported lattice constants and bandgaps of some III-V semiconducting compounds [1, 3]**

Compound	zinc-blende	wurtzite		Bandgap $E_g$ (eV)	
	$a$ (Å)	$a$ (Å)	$c$ (Å)	direct	indirect
BN	3.62	---	---	--	6.2
BP	4.54	---	---	--	2.1
AlP	5.46	---	---	3.6	2.5
AlAs	5.66	---	---	3.1	2.2
AlSb	6.14	---	---	2.3	1.6
$\alpha$ -GaN	---	3.19	5.19	3.5	--
$\beta$ -GaN	4.52	---	---	3.2	--
GaP	5.45	---	---	--	2.3
GaAs	5.65	---	---	1.5	--
GaSb	6.096	---	---	0.8	--
InN	---	3.55	5.76	1.9	--
InP	5.87	---	---	1.4	--
InAs	6.06	---	---	0.4	--
InSb	6.48	---	---	0.2	--

The main advantage of III-V group semiconductor is the availability of distinct materials and device applications. Consequently, the development of a variety of various materials, growth, and device fabrication technologies took place. The most used fabrication technologies are molecular beam epitaxy, metalorganic vapour phase epitaxy, liquid phase epitaxy and vapour phase epitaxy [9]. The III-V compounds offer the advantage of combining bandgap variations and heterojunction effects together with the small lattice mismatch avoiding the extensive formation of interface states [9].

Furthermore, the III-V group semiconductor also exhibit excellent thermal conductivity due to which it is possible to rapid dissipation of heat within a semiconductor

device formed by these materials. This enhances their use in high power applications and broadens the range of performance [8].



**Figure 4: The bandgap versus lattice constants for some III-V semiconductors [10]**

The bandgaps versus the lattice constants of some III-V semiconductor compounds is depicted in the figure 4 which show the possibility of lattice matching of these materials while forming the alloys. The lattice matched hetero-structures exhibits an advantageous relative alignment of both the conduction and valence band which is desired across the interfaces of the hetero-structures [8]. For example the  $\text{In}_x\text{Ga}_{1-x}\text{As}$  that is grown on the InP substrate and have important technological applications in area of infrared emitters and detectors and high speed transistors for microwave applications [8].

### III-V Semiconductor Ternary Alloys:

Semiconductor alloys provide a way to tune the magnitude of the forbidden gap and other material parameters to widen the application of semiconductor devices in new technologies such as quantum wells, quantum dots and other superlattices. The effects of alloy composition, size, doping and lattice strain can be combined to achieve maximum applications [12]. The Semiconducting materials with bandgap throughout a desired and extended range are required to expand the application scope of any material. The bandgap may be direct or indirect in the nature and it may or may not vary linearly. The state-of-art technology enables to control impurity level at high precision. The bandgap engineering has opened new opportunities for various optoelectronic device technologies. The doping of

impurity in multinary alloys allows altering properties of electronic devices. The doping modifies various critical properties of materials. Doping and processing techniques produce semiconductors of desired technical specifications. One can tune bandgap and other properties according to the above equations and design materials of interest.

An alloy can be defined as a solid solution of two or more binary compounds and a alloy crystal is a mixed crystal. The III-V compounds offer to form anionic or cationic type of ternary and quaternary alloys. In usual notations the cationic ternary alloys are denoted as  $A_xB_{1-x}C$  (A and B are cations from III group and C is anion from V group). Similarly the anionic alloy is represented as  $AB_xC_{1-x}$  (A is anion of III group, B and C are anions of V group). In the cationic alloy, ratio of compounds AC and BC is  $\frac{x}{1-x}$  while in the anionic alloy the ratio of AB and AC is  $\frac{x}{1-x}$ . The bonding between the AC and BC cannot be defined adequately while this is possible in compounds.

The ternary alloy parameter T (T may be bandgap, lattice constant, refractive index or any other physical quantity) for  $AB_xC_{1-x}$  type alloy can be given as [2,11] –

$$T_{A_xB_{1-x}C} = xB_{AC} + (1-x)B_{BC} \quad (1)$$

Here  $B_{AC}$  and  $B_{BC}$  are corresponding parameter for binary compounds AC and BC. The above relation holds true for only a linear variation which may be not valid for most of the alloys. So if the variation is non linear then the following quadratic expression may be given as [2,11]-

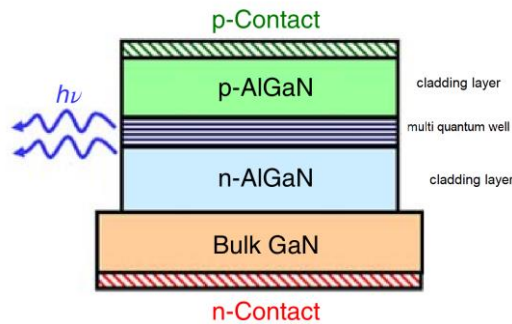
$$T_{A_xB_{1-x}C} = xB_{AC} + (1-x)B_{BC} + C_{A-B}x(1-x) \quad (2)$$

Here  $C_{A-B}$  is sometimes known as the bowing parameter.

### **Applications of III-V semiconductor compounds and alloys:**

Now a brief discussion about the applications of III-V semiconductor compounds and alloys is presented. Due to the high electron mobility of III-V materials these are useful in fabricating the majority carrier active devices like field effect transistors. The nitride semiconductors (GaN, AlGa<sub>n</sub>N, InAlN, InGa<sub>n</sub>N, InAlGa<sub>n</sub>N, AlN, etc.) based optoelectronic devices like LED and LD are much studied and developed on various substrates in search of enhanced efficiency and better stability due to high melting point and low decomposition temperature. So they have vital applications in high-voltage, high-power, and high-temperature electronics, in comparison of traditional materials like SiC. These materials are also used in power electronics due to reduction of the electric power consumption [12]. A laser diode

fabricated using GaN and AlGaN is shown in following figure in which the light is confined between the cladding layers of p type and n type AlGaN [12]-



**Figure 5: The edge emitting laser diode [12]**

The GaInAs and GaAlAs are grown on the GaAs substrate to develop the high mobility field effect transistors [9]. AlGaAs is the most important and the most studied III-V semiconductor alloy due to the fact that GaAs is a direct-gap material while AlAs is an indirect material [13]. The InGaAs alloy is an important material in fabricating the high-speed electronic devices and long-wavelength quantum cascade lasers. It shows direct bandgap for entire composition range [13]. InGaAsN and InAsN alloys with the energy band gap in mid-infra red emission region can be lattice matched to GaAs and InP substrates and the emission wavelength of this type of heterostructure can cover the full mid-IR region from 2 to 5  $\mu\text{m}$  [14].

GaAlSb is an important III-V antimonide material having applications in various optoelectronic devices. The interplay of direct band gap in GaSb and indirect band gap in AlSb as well as inter-subband transitions in these random alloys are of high importance to propose promising materials for the cutting edge technological applications in detectors and lasers. InGaSb serves as the hole quantum well material in type-II infrared lasers and photodetectors with strain-balanced active regions [13]. The mid-infra red quantum dot lasers are also fabricated using InAlAs, InGaAs, InAsP, InAsSb, InSb and InAs [14]. The AlInSb alloy provides a less strained barrier material for mid-infra red interband cascade lasers and other antimonide device structures [13].

### **Summary:**

The III-V semiconducting compounds and alloys are very useful in fabrication of various electronic and optoelectronic devices like high-electron-mobility, bipolar transistors, diode lasers, light-emitting diodes, photodetectors, mid infra red sensors, electro-optic modulators, frequency-mixing components. The III-V alloys formed by mixing

of two or more binary compounds provide a way to tune the magnitude of the forbidden gap and other material parameters to widen the application of semiconductor devices in which the effects of alloy composition, size, doping and lattice strain can be combined to achieve maximum applications. The spectral range of these devices is very broad covering almost complete visible spectra.

#### References:

1. Adachi, S. (2005). *Properties of Group IV, III-V and II-VI Semiconductor*. John-Wiley & Sons: England.
2. Adachi, S. (2005). *Properties of Group-IV, III-V and II-VI Semiconductor Alloys: Group IV, III-V and II-VI Semiconductors*. John Wiley & Sons: West Sussex, England.
3. Madelung, O. (2005). *Semiconductor Data Handbook, III edition*. Springer-Verlag: Berlin.
4. Abedin, M. (2015). *A Self-Adjusting Lin-Log Active Pixel For Wide Dynamic Range CMOS Image Sensor*. <http://dx.doi.org/10.13140/RG.2.1.3871.8965>.
5. Hui, R. (2020). *Introduction to Fiber-Optic Communications*. Academic Press.
6. Circuit Globe. (2023). <https://circuitglobe.com>.
7. Xometry. (2023). <https://www.xometry.com>.
8. Kuech, T.F. (2016). *III-V compound semiconductors: Growth and structures. Progress in Crystal Growth and Characterization of Materials, 62, 352–370*.
9. Malik, R.J. (Ed.). (1989). *III-V Semiconductor Materials and Devices*. Elsevier Science Publishing.
10. Mokkaṭpati, S., & Jagadish, C. (2009). *III-V compound SC for optoelectronic devices. Materials Today, 12, 22*.
11. Kasap, S., & Capper, P. (Eds.). (2017). *Springer Handbook of Electronic and Photonic Materials*. Springer.
12. Jaros, M. (1985). *Electronic properties of semiconductor alloy systems. Rep. Prog. Phys., 48, 1091-1154*.
13. Vurgaftman, I., Meyer, J.R., & Ram-Mohan, L.R. (2001). *Appl. Phys. Rev., 89, 5815*.
14. Yin, Z., & Tang, X. (2007). *A review of energy bandgap engineering in III-V semiconductor alloys for mid-infrared laser applications. Solid-State Electronics, 51, 6–15*.



## **A REVIEW ON DIFFERENT TECHNIQUES FOR ENHANCEMENT OF EFFICIENCY OF SNS BASED SOLAR CELL**

**A. M. Kute\*<sup>1</sup> and S. R. Takpire<sup>2</sup>**

<sup>1</sup>Department of Physics,

Ghulam Nabi Azad Art's, Commerce and Science College, Barshitakli, Akola, India

<sup>2</sup>Department of Physics,

Mahatma Jyotiba Fule Commerce, Science and Vitthalrao Raut Art's College,

Bhatukali, Dist- Amaravati

Corresponding author E-mail: [ashitkute@gmail.com](mailto:ashitkute@gmail.com)

### **Abstract:**

Due to its exceptional absorption coefficient, capacity to moderate environmental impacts, and simplified manufacturing costs, SnS is quickly becoming recognized as a viable material for the development of solar technology. However, SnS crystallizes in an orthorhombic structure, which results in a highly anisotropic charge transport behavior. Tailoring the crystallographic orientation of the SnS absorber layer plays a critical role in the enhancement of the transfer of charge carriers and the power conversion efficiency (PCE). However, interface losses continue to be a constraint on the efficiency of SnS-based solar cells. Thus, this research provides a creative avenue. The results of this study provide important new information for improving and increasing the efficiency of SnS-based solar cells.

**Keywords:** SNS Based Solar Cells, Efficiency Enhancement Technique,

### **Introduction:**

Nowadays, photovoltaic technology plays a crucial role in the world transition towards exploring clean renewable energy resources. Solar energy has emerged as a key player in the clean energy revolution [1, 2]. With the continuous and accelerated global development of the technology of the solar cell to assure it as a fundamental clean and efficient alternative energy resource, researchers have focused their efforts on developing new materials with high optical absorption over a broad spectral range and high stability to be exploited in the thin film photovoltaic cells [3, 4, 5]. Thin-film solar cells (TFSCs) are regarded as one of the most competitive photovoltaic technologies due to their high module efficiency and low cost of mass manufacture [6, 7]. With power conversion efficiencies (PCEs) more than 20%, the advent of chalcogenide solar cell technologies based on CdTe and CIGS has created new opportunities for the development of TFSCs [8, 9]. Furthermore, many

design approaches, including the selection of suitable electron and hole transport layers (HTL, ETL), plasmonic effects, graded band gap aspect, and optimum elaboration circumstances, have made significant improvements in photovoltaic performances possible [10]. Despite these exceptional qualities, the mass production of CdTe- and CIGS-based TFSCs was constrained by the need for critical raw materials (CRM) and high toxicity components [11, 12]. In contrast, a great deal of research has been done on CZTS and  $Sb_2Se_3$ , which are promising compounds for TFSC applications that are non-toxic, earth-abundant, and free of CRM. Although there are encouraging photovoltaic performances in this situation, the measured PCE values are substantially below expectations, and reaching the related theoretical limits is still challenging [13]. This is mostly because to a number of flaws brought on by a number of phenomena, such as recombination losses, dependability concerns, undesirable band-alignment, and poor bulk quality as a result of developing homogeneously dispersed single-phase quaternary material-related problems. By considering these obstacles, research efforts are now concentrated on finding substitute binary semiconducting materials that present excellent opportunities for bridging the gap between high conversion efficiency, reasonably priced, and ecologically friendly TFSCs [14].

Recently, research has focused on solar cells based on thin-sulfide alloys (SnS). This is primarily because of the exceptional optical and electrical characteristics of the SnS compound, which include high carrier mobility, an adjustable direct band gap (1.1 eV), excellent absorption capabilities, and low recombination velocity [15]. Furthermore, SnS thin-film is thought to be a cheap, non-toxic, and CRM-free earth-abundant material, making it an excellent choice for TFSC applications [16]. It is anticipated that these intriguing characteristics will cover the way for the development of high-efficiency TFSCs with a theoretical maximum limit of 25%. As a result, a lot of researchers focused more on SnS TFSCs as a potential substitute for CdTe in binary absorber materials.

Even though SnS material has enormous potential for photovoltaic applications, developed CdS/SnS-based TFSCs typically have recorded PCEs of less than 4.0%. This extremely low value is coupled with valence, conduction band offsets, and lattice mismatching effects in heterostructured devices, among other consequences. Furthermore, the performance of solar cells is invariably impacted by significant recombination effects resulting from high defects density caused by poor crystallinity and secondary phase development [17]. Furthermore, it appears difficult to achieve high absorption properties while retaining an effective carrier extraction capability due to the SnS absorber thickness's incompatibility with the corresponding carrier diffusion length. A number of buffer-based metal oxides, including ZnO, Zn (O, S),  $SnO_2$ , and  $TiO_2$ , were employed to improve the SnS

TFSC photovoltaic capabilities in order to overcome these problems [18]. As a result, the PCE value is enhanced to 4.8%, although further work is needed to perhaps attain its maximum value. Ferheti *et al.* [19] identified that controlling the band offsets by selecting appropriate junction partner, while improving the light-scattering effects in the SnS absorber remains a considerable challenge owing to an absence of design pathway, mitigating the main loss mechanisms associated with SnS TFSCs. He proposes a new SnS TFSC structure based on combining strained-SnO<sub>2</sub> buffer layer and back grooves texture to bridge the gap between high absorption and improved carrier transport characteristics. It is found that the proposed Zn(O,S)/strained-SnO<sub>2</sub>/SnS structure with back grooves opens up the route to overcome the optical losses and promotes enhanced carrier transport mechanisms, making it a suitable candidate for thin-film photovoltaic applications.

The surface plasmonic resonance behavior, or SPR, of nanostructured noble metals, particularly silver and gold, is an effective and successful method for enhancing the absorption features of the deposited active layer and consequently increasing the cell's J<sub>sc</sub> and PCE without the need to increase the film's thickness in order to avoid the e-h recombinations. This method is worth mentioning despite all the exhausting efforts. Through the trapping of incident light in the active layer and the facilitation of charge carrier separation through the effect of near field enhancement due to the plasmonic structured particles yielding a high photoelectrical efficiency, the localized surface plasmon oscillations coupled with the incident electromagnetic field improve the absorption cross-section. This strategy achieved significant theoretical and experimental improvements in the performance efficiency of many solar cells either organic or inorganic. Silver and gold nanoparticles are the most common elements utilized in the plasmonic enhanced optoelectronics and solar cell devices owing to the positioning of their tunable SPR plasmonic absorption in the visible spectrum in addition to their oxide-free nature which may deteriorate the plasmonic features.

Gohari *et al.* [20] closely examined the deposition angle of the SnS layer and its effects on the bandgap properties of SnS solar cell. The findings of the investigation offer valuable insights for enhancing the design of SnS-based solar cells and making them more efficient. He reported that by altering the deposition angle, the efficiency is enhanced from 7.83 % to 12.17 %. Additionally, to further boost the efficiency of the SnS solar cell, the thickness and doping concentration of the CZTSSe layer are also being important. The final efficiency of 14.02 % has been achieved with the open circuit voltage of 0.68 V for the SnS solar cell.

El-Mahalawy *et al.* [21] discussed the approach to boost the photovoltaic performance of the thermally evaporated CdS/SnS heterojunction solar cells by utilizing a spin-coated

layer of silver and gold nanostructured particles on the surface of the implemented CdS/SnS heterojunction. The decoration process of the heterojunction by Ag-NPs and Au-NPs achieved marvelous enhancements in the cell's conversion efficiency. The photovoltaic enhancement is interpreted in the light of the impact of NPs on the measured structural, morphological, electronic, and optical properties of the heterojunction. Thi-Thang Ho et al. [22] reported that by controlling the substrate tilting angle and temperature ramp\_rate in vapor transport deposition, the crystal growth orientation was tuned to a preferred direction which significantly suppressed the unfavorable crystallographic plane. Through the combination of these two approaches, the PCE could be increased from 0.11% to 2%.

In solar cells based on p-type tin monosulfide, SnS, absorber layers paired with n-type zinc oxysulfide, Zn(O,S) layers that selectively transmit electrons but block holes [23]. methodically explored the loss process and mitigated. Annealing the SnS films in H<sub>2</sub>S results in bigger grains with fewer grain boundaries, which reduces recombination at grain boundaries. A few monolayers of SnO<sub>2</sub> are inserted between these layers to decrease recombination close to the p-SnS/n-Zn(O,S) junction. Recombination at the junction is further decreased by nitrogen doping the Zn(O,S) to lower its free electron concentration and by modifying the conduction band offset. Over 4.4% of the cells that are produced are efficient.

### **Result and Discussion:**

Recent developments in SnS research for solar cells have demonstrated that, controlling the band offsets by selecting appropriate junction partner, while improving the light-scattering effects in the SnS absorber reflects encouraging outcomes. However, the decoration process of the heterojunction by Ag-NPs and Au-NPs achieved marvelous enhancements in the cell's conversion efficiency. In this study the deposition angle of the SnS layer and its effects on the bandgap properties of SnS solar cell closely examined in view of enhancement of efficiency in the device's short-term development.

### **References:**

1. Soliu, O. Ganiyu A., & Carlos A. (2020). Renewable energies driven electrochemical wastewater/soil decontamination technologies: A critical review of fundamental concepts and applications. *Applied Catalysis B: Environmental*, 270, 118857.
2. Kleber Costa Corrêa, Mauricio Uriona-Maldonado, & Caroline Rodrigues. (2022). The evolution, consolidation and future challenges of wind energy in Uruguay. *Energy Policy*, 161, 112758.

3. Choudhary, P., & Srivastava, R. (2019). Sustainability perspectives- a review for solar photovoltaic trends and growth opportunities. *Journal of Cleaner Production*, 227, 589-612.
4. Pandiyan, A., Veeramuthu, L., Yan, Z., & Lin, Y. (2023). A comprehensive review on perovskite and its functional composites in smart textiles: Progress, challenges, opportunities, and future directions. *Progress in Materials Science*, 140, 101206.
5. Cramer, C., Ionescu, E., Nelson, A., & Kato, Y. (2022). Additive manufacturing of ceramic materials for energy applications: Road map and opportunities. *Journal of the European Ceramic Society*, 42, 3049-3088.
6. Amin, N., Shahahmadi, S., Chelvanathan, P., Rahman, K., & Akhtaruzzaman, M. (2017). Solar Photovoltaic Technologies: From Inception Toward the Most Reliable Energy Resource. *Encyclopedia of Sustainable Technologies*, 11-26.
7. Islam, M., Pandey, A., Hasanuzzaman, M., & Rahim, N. (2016). Recent progresses and achievements in photovoltaic-phase change material technology: A review with special treatment on photovoltaic thermal-phase change material systems. *Energy Conversion and Management*, 126, 177-204.
8. Bae, S., Zhao, H., Hsieh, Y., Zuo, L., & Marco, N. (2016). Printable Solar Cells from Advanced Solution-Processible Materials. *Chem*, 1, 197-219.
9. Nattestad, A., Perera, I., & Spiccia, L. (2016) Developments in and prospects for photocathodic and tandem dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 28, 44-71.
10. Kanatzidis, M., Poeppelmeier, K., Guloy, A., & Lattner, S. (2008) Report from the third workshop on future directions of solid-state chemistry: The status of solid-state chemistry and its impact in the physical sciences. *Progress in Solid State Chemistry*, 36, 1-133.
11. Chee, A. (2023). On current technology for light absorber materials used in highly efficient industrial solar cells. *Renewable and Sustainable Energy Reviews*, 173, 113027.
12. Sharaf, O., & Orhan, M. (2015) Concentrated photovoltaic thermal (CPVT) solar collector systems: Part I – Fundamentals, design considerations and current technologies. *Renewable and Sustainable Energy Reviews*, 50, 1500-1565.
13. Hayat, A., Sohail, M., Raza, S., Ali, H., Ajmal, Z., & Zada, A. (2023) Recent advances, properties, fabrication and opportunities in two-dimensional materials for their potential sustainable applications. *Energy Storage Materials*, 59, 102780.

14. Khan, S., Mahmood, A., Ali Shah, A., Rahman, G., & Ullah, N. (2022) Challenges and innovative strategies related to synthesis and electrocatalytic/energy storage applications of metal sulfides and its derivatives. *Journal of Electroanalytical Chemistry*, 923, 116760.
15. Wang, P., Lan, Y., Huan, C., Luo, J., Cai, W., Fan, J., & Huang, Z. (2023) Recent progress on performance-enhancing strategies in flexible photodetectors: From structural engineering to flexible integration. *Materials Science and Engineering: R: Reports*, 156, 100659.
16. Khan, S., Mahmood, A., Ali Shah, A., Rahman, G., & Khan, A. (2022) Challenges and innovative strategies related to synthesis and electrocatalytic/energy storage applications of metal sulfides and its derivatives. *Journal of Electroanalytical Chemistry*, 923, 116760.
17. Wu, P., Wang, S., Li, X., & Zhang, F. (2022) Beyond efficiency fever: Preventing lead leakage for perovskite solar cells. *Matter*, 5, 1137-1161.
18. Tang, G., & Yan, F. (2021) Recent progress of flexible perovskite solar cells. *Nano Today*, 39, 101155.
19. Ferhati, P., Djeflal, F., & AbdelMalek, F. (2023) Towards improved efficiency of SnS solar cells using back grooves and strained-SnO<sub>2</sub> buffer layer: FDTD and DFT calculations. *Journal of Physics and Chemistry of Solids*, 178, 111353.
20. Gohri, S., Madan, J., & Pandey, R. (2023) Enhancing the efficiency of SnS-based solar cells using a GLAD technique and CZTSSe layer. *Solid State Communications*, 377, 115380.
21. El-Mahalawy, A., Amin, F., Wassel, A., & El Salam, M. (2022) Overcoming the poor performance of n-CdS/p-SnS solar cells by plasmonic effect of gold and silver nanoparticles. *Journal of Alloys and Compounds*, 923, 166484.
22. Thi-Thong, H., Jokar, E., Quadir, S., Rueil-San, C., Liu, F., Chen, C., & Chen, K. (2022) Enhancing the photovoltaic properties of SnS-Based solar cells by crystallographic orientation engineering. *Solar Energy Materials and Solar Cells*, 236, 111499.
23. Sinsersuksakul, P., Sun, L., & Lee, S. (2014) Overcoming the Efficiency Limitations of SnS Based Solar Cell. *Adv. Energy Mater*, 1400496.

## **A BRIEF REVIEW ON SYNTHESIS METHODS OF FERROELECTRIC MATERIALS**

**Parshuram B. Abhange\*, Vijay S. Raykar and Vivek A. Rane**

Department of Physics,

G. M. Vedak College of Science, Tala, Raigad-402111, India.

\*Corresponding author E-mail: [pbabhange@gmail.com](mailto:pbabhange@gmail.com)

### **Abstract:**

As we are known that the chemistry of material has many aspects, such as structure of materials, reactions of materials and synthesis of materials. In the previous years it was considered that the synthesis of material is more empirical than the structure and reactions of materials. But now a days the synthesis has become more systemized and conceptually grounded. In the history of material synthesis Alchemy has given the concept of modern chemistry by improving the experimental techniques like refluxing and distillation. The modern concept of synthesis was evolved with the atomic theory in middle of 19<sup>th</sup> century. In 1858 the scientist Kekule and Couper proposed a valence theory. The Russian chemist Aleksandr Butlerov later supported this theory and declared that one and only one chemical formula was to correspond to one compound and atoms in the molecule were bounded with each other in accordance with valence theory. He used the term chemical structure in 1961 and synthesized t-butyl alcohol (CH<sub>3</sub>)<sub>3</sub>COH, which became the first synthesized material. The synthesis of many organic materials was carried by many laboratories and today we have not only the synthesis of organic materials but peoples are also synthesizing the inorganic materials, drugs, chemicals etc. These material syntheses are planned on the basis of their use and properties. Since the discovery of ferroelectricity in Rochelle salt nearly a century ago, ferroelectrics have transitioned from an academic curiosity to serious contenders in the fields of nonvolatile memory devices, actuators for microelectromechanical systems (MEMS) devices, mechanical energy conversion, and many other applications at the forefront of modern science [1–3].

**Keywords:** Structure of materials, refluxing, distillation, chemical formula, ferroelectricity.

### **Introduction:**

Many properties of dielectric ceramics are mainly dependent on defect equilibrium, microstructural features of material such as grain size, porosity etc. which plays very important role in determining the final properties. Both of these aspects are heavily

dependent upon the processing techniques of the dielectric ceramics and also on their physical dimensions and appearance i.e. whether they are in bulk form or thin film form.

The major difference between the bulk processes and thin films process is that, the bulk processes are treated as equilibrium processes while thin films processes are generally non-equilibrium processes and thereby altering the kinetics of phase formation. The bulk processing requires high temperatures for complete phase formation and densification, while thin films can be made at much lower temperatures for achieving the desired phase as well as structural perfection.

Thus, in this chapter, we will focus on a brief review of most common synthesis methods for tailoring the properties of material in general and electro-ceramic properties in particular.

### **Types of material synthesis:**

The last decade has witnessed the rapid development of new synthetic pathways to low-dimensional ferroelectric nanomaterials, and these synthetic developments have both transformed our understanding of the fundamental physics of nanoscale ferroelectricity and spawned tantalizing new applications in solar energy conversion,[4] biosensing,[5] and many other areas. The materials can be synthesized by many ways depending upon their use and nature. These can be generally classified as bellow.

#### **1. Physical synthesis:**

The physical synthesis is further classified into mechanical and vapour. Mechanical synthesis includes high energy ball milling and melt mixing. The high energy ball milling is the simplest method to synthesize nanoparticles of some metals and alloys in the form of powder. Different types of mills are there such as vibratory, planetary, tumbler, rod etc. In ball milling method the temperature can be varied from 100°C to 1100°C. Using this method the materials like W, Co, Cr, Al-Fe, Ni-Ti and Ag-Fe are made nanocrystalline in a short time of few minutes to few hours.

In melt mixing process the liquid is cooled below certain temperature to form either crystalline or amorphous solid (glass). Along with temperature, the rate of cooling and tendency to nucleate also decide whether the melt can be cooled as crystalline solid or glass with long range order. The homogeneous or inhomogeneous nucleation takes place and nuclei are formed spontaneously which can grow to form ordered, crystalline solid. Generally, the metals form crystalline solids, but they can form amorphous solids if cooled at very high rate ( $\sim 10^5$ - $10^6$  K/s). With this method the nanoparticles are also formed by mixing



the molten streams of metals at high velocity with turbulence. For example, a molten stream of Ti and molten stream of Cu-B form nanoparticles TiB<sub>2</sub>. The last three decades have featured an explosion in the development of both zero and one-dimensional nanostructures [6, 7].

Vapour synthesis includes the methods based on evaporating the materials on substrates to form nanostructures and these are physical vapour deposition, laser ablation, sputter deposition, electric arc etc. Usually, the materials to be evaporated are electrically heated using suitable filament, crucible or boat. In case of deposition by evaporation the number of atoms leaving the surface of solid or liquid must be greater than the number of atoms returning to the surface. In case of synthesis by evaporation the material which is to be evaporated creates a pressure of  $\sim 10^{-1}$  Pa or more to achieve required vapour pressure for synthesis.

In physical vapour deposition with consolidation the materials are used as sources of evaporation. The inert gas or reactive gas is used for collisions with material vapour. The clusters or nanoparticles condense on cold finger. The whole process takes place in vacuum chamber and therefore products of desired purity can be obtained. During evaporation the atoms of the source material collide with gas molecules and form bigger particles, which condense on cold finger. When the reactive gases like H<sub>2</sub>, O<sub>2</sub> and NH<sub>3</sub> are used then the evaporated material interact with these gases and forms hydride, oxide or nitride particles. The gas pressure in the deposition chamber decides the size, shape and also the phase of evaporated material.

The laser ablation or vaporization is a technique in which the vaporization of the material is affected using pulses of high-power laser beam. The set up consists the ultra-high or high vacuum system, inert or reactive gas introduction facility, laser beam, solid target and cooled substrate etc. Generally, the laser which operate in UV range is used because other wavelengths (IR or visible) are often reflect from surfaces of some metals. The atoms of solid source are evaporated with powerful beam of laser. These atoms collide with the atoms of inert or reactive gases, cool on them forming clusters and finally condense on the cooled substrate. This method is also used to form alloys or compounds by simultaneous evaporation and mixing of two materials in inert gas.

The sputter deposition technique is used for deposition of stoichiometric thin films from target material. The target material used may be some alloy, ceramic or compound. The sputter deposition is also a very good method for deposition of multilayer films for mirrors

or magnetic films. In this technique, some inert gas ions like  $Ae^+$  are incident on target at a high energy. The ion-target interaction is a complex phenomenon which depends on the energy of ions and ratio of ion mass to that of target atoms mass. The sputter deposition may be carried out using Radio Frequency sputtering, Direct Current sputtering or magnetron sputtering.

## **2. Chemical synthesis:**

It is a very simple technique to synthesize the nanomaterials. Also, it is inexpensive, requires less instrumentation as compared to many physical methods and can be carried at low temperature. Using chemical synthesis, the materials of different sizes and shapes can be obtained. Usually, the materials are obtained in liquid form but they can be easily converted into dry powder or thin films. The chemical synthesis includes colloids, sol-gel, L-B films, inverse micelles etc.

Colloids are the materials having two or more phases (solid, liquid or gas) of same or different materials in which one of the phases must having the dimensions less than micrometer. The sub-class of colloids having dimensions in the nanometer range is called nanomaterials. Thus, the colloids are the phase separated sub-micrometer particles of various shapes and sizes like rods, tubes, plates etc. The metal and semiconductor nanoparticles can be synthesized using colloidal route. The metal nanoparticles are synthesized by reduction of some metal salt or acid while semiconductor nanoparticles can be synthesized by wet chemical route using appropriate salts.

The L-B method (developed by Langmuir and Blodgett) is used to transfer organic overlayers at air-liquid interface onto solid substrates. In this method the amphiphilic long chain molecules which have hydrophilic group at one end and a hydrophobic group at the other end can be used. These molecules spread over the surface of water when they are put in the water. Then their hydrophilic ends called 'heads' are immersed in water while their hydrophobic ends called 'tails' remain in air. These molecules can be compressed using movable barrier to form a 'monolayer' and align the tails. Then these monolayers can transfer onto a suitable solid substrate like glass, silicon etc. by dipping the substrate in the liquid in which such monolayers are formed. The ordered multilayers of molecules can be obtained by dipping and pulling the substrate in liquid several times keeping constant pressure on the molecules. Using L-B method it is possible to obtain nanoparticles.

Inverse micelles or a micro-emulsion is a widely used method to synthesize nanoparticles. The biocompatibility (useful in novel application like drug delivery of

nanomaterials) and biodegradability (useful to avoid environmental pollution) are the advantages of this method. When the two immiscible liquids are stirred together, they form the 'emulsion' having droplet size larger than 100 nm up to even few millimetres. The class of immiscible transparent liquids having droplet size  $\sim 1$  to 100 nm is known as microemulsions. Using inverse micelles or microemulsions nanoparticles of copper, cobalt, BaSO<sub>4</sub>, CaCO<sub>3</sub>, CdS or ZnS can be synthesized.

### **3. Biological synthesis:**

The micro-organisms, animals and plants in nature synthesize different materials. Synthesis of materials in laboratories using these micro-organisms, animals and plants can be carried out on large scale which is called eco-friendly or green synthesis. In biological systems the synthesis of nanoparticles is carried out by using biological ingredients like micro-organisms, enzymes, DNA and membranes.

The organisms which can be seen using microscope are called micro-organisms e.g. bacteria, fungi or yeasts. These micro-organisms when interact through their cells with metals which comes in contact with them form nanoparticles. Synthesis of metal, semiconductor or insulator nanoparticles using micro-organisms is possible.

The metal nanoparticles can be obtained using various fungi e.g. Fusarium oxysporum is used to produce gold or silver nanoparticles. Using microbial routes, the semiconductor nanoparticles like ZnS, CdS, PbS and others can be produced. The Klebsilla pneumoniae bacteria are used to synthesize the nanoparticles of Cds with size ranging from 5-200 nm.

Synthesis of nanoparticles with plants is also possible. E.g. nanoparticles of gold can be synthesized with leaves of geranium plant or live alfalfa plants. Also, nanoparticles can be synthesized using DNA and membranes. Adding cadmium acetate, sodium chloride and DNA with proper concentration, the nanoparticles of CdS can be obtained.

### **4. Hybrid synthesis:**

Hybrid synthesis includes particle arresting in glass or zeolites or polymers, electrochemical, chemical vapour deposition, micro emulsion-zeolite etc.

Some of the methods of the type mentioned above are discussed briefly as follows.

#### **Solid state reaction method:**

This method can be used to prepare wide range of materials including mixed metal oxides, sulfides, nitrides, aluminosilicates, etc. For solid state reaction method the temperature required is very high (ranging from 500-2000°C), because to overcome the

lattice energy significant amount of energy is needed, so a cation or anion can diffuse into a different site.

In this method the solid materials are not raised to their melting point, so reactions take place in the solid state (subsolidus). The starting raw materials were weighted in stoichiometric proportion and grinded in agate mortar to achieve the required homogenous mixture of reactants. The prepared mixture will be pre-sintered at high temperatures for few hours. After pre-sintering the mixture will be again grinded into fine powders.

These powders were then pressed into compact pellets with the help of hydraulic press. These prepared pellets were again kept into the furnace for final sintering at high temperature. After final sintering these samples will be used for characterization.

### **Sol-gel method:**

This is a method to prepare metal oxide glasses and ceramics by hydrolyzing a chemical precursor to form a solution (sol) by dispersal or hydrolysis. A sol is a colloidal solution of reactants with the particles of different size (~1-100 nm diameters). The dispersal is the stage in which oxides or hydroxides are mixed in water having specific pH. So that the solid particles remain in suspension instead of formation of the precipitate.

The hydrolysis is the process in which the metal alkoxides were added to water, which are then hydrolyze to give the oxide as a colloidal product. The sol will be converted into gel by dehydrating or polymerizing, which on drying (evaporation) and pyrolysis gives an amorphous oxide. In sol-gel method the time and temperature will be reduced as compared to the conventional methods.

### **Co-precipitation and precursor methods:**

In these methods the precursors such as nitrates and carbonates can be used as starting materials instead of oxides. In co-precipitation method the soluble salts of metal were weighted in stoichiometric proportion and mixed together to form precipitate as hydroxides, citrates, oxalates, or formats by decomposing on heating. Then the precipitate is filtered and dried to give the final product. In precursor method the homogeneous single phase precursor materials were mixed with proper stoichiometry. On heating the precursor materials decompose to give desired product.

### **Hydrothermal synthesis:**

In hydrothermal method the reactants are heated in water/steam at high pressures and temperatures in a closed vessel which is called as autoclave constructed with stainless

steel. It is fitted with safety valves and typically lined with a non-reactive material such as teflon. The water used functions both as a solvent and as pressure transmitting medium.

The hydrothermal process also takes place in nature due to which many minerals are formed e.g. zeolites, emeralds, etc.

### **Combustion synthesis:**

This is a high temperature self-propagating synthetic method. The reactions in combustion synthesis are highly exothermic ( $\Delta H < -170$  kJ/mol) and even explosive which is needed to maintain a self-propagating high reaction temperature. In combustion synthesis the reactants were mixed together, pelletized and then ignited (with electric arc, laser, heating coil) at high temperature.

After ignition, the reaction propagates as a synthesis wave. Also, it is necessary that, the reaction must lose less heat than it generates. For faster reaction the temperatures up to 3000 K are maintained. This method can be used to prepare many refractory materials including oxides, intermetallics, nitrides, borides, silicides, and ceramics.

### **Thin films:**

To prepare thin films the starting material were heated to form vapors. Then at suitable temperature they are mixed together and transported to the substrate by carrier gas. The starting materials generally include hydrides, halides, and organometallic compounds, since these tend to be volatile.

Different types of thin films e. g. Microcrystalline Monolayer, multilayer, Crystalline, Amorphous, superlattice, junctions Free-standing, supported Epitaxial (commensurate), incommensurate can be prepared. The film properties generally include thickness, texture (single crystal, microcrystalline, domains, and orientation), surface roughness, form (supported or unsupported), nature of substrate etc.

Different methods can be employed for the preparation of thin film like Chemical vapor deposition (CVD), Metal organic chemical vapor deposition (MOCVD), Cathodic deposition, Anodic deposition, nitridation, Molecular beam epitaxy, Supersonic cluster beams, Electroless deposition, Thermal oxidation, Aerosol deposition, Liquid phase epitaxy, Self-assembly, Surface anchoring, Microwave Laser ablation, Cathode sputtering, Vacuum evaporation etc.

### **Microwave synthesis:**

It is well known that the microwave ovens are generally used for heating or cooking food. Around 1986 some scientists showed that the domestic microwave ovens can be used

in scientific laboratories for large scale, rapid and uniform synthesis of materials. But for controlled chemical synthesis, the kitchen microwave ovens are not used because they don't have good control on stirring, temperature or power. However, in association with the equipment which controls the various parameters it can be used for microwave synthesis.

Microwaves with very long wavelength and frequencies in the range of  $\sim 300$  to  $300,000$  MHz are the part of electromagnetic spectrum. But only certain frequencies are used for domestic and other equipment while rest of them is used for communication purpose. The oscillating electric and magnetic fields are associated with microwave which produces nodes and antinodes. This consequently produces hot and cold spots in vessel with non-uniformities. Due to this only a single mode in which length of cavity (or reaction vessel) is equal to single wave only is used. Heating in microwave apparatus takes place due to the orientation of dipoles of molecules in solution. These dipoles try to align themselves in the direction of electric field. In doing so these dipoles also vibrates and produces heat, therefore external energy is not needed to heat the vessel. Using this method different types of oxide, sulphide and other nanoparticles have been synthesized to obtain the products of uniform shape and size.

#### References:

1. Scott, J.F. (2007). Applications of modern ferroelectrics. *Science*, 315(954).
2. Scott, J.F., & Paz de Araujo, C.A. (1989). Ferroelectric memories. *Science*, 246(4936).
3. Wang, Z.L. (2008). Self-powered nanotech. *Scientific American*, 82(82).
4. Yang, S.Y., Seidel, J., Byrnes, S.J., Shafer, P., Yang, C.-H., Rossell, M.D., Yu, P., Chu, Y.-H., Scott, J.F., Ager III, J.W., & Martin, L.W. (2010). Above-bandgap voltages from ferroelectric photovoltaic devices. *Nature Nanotechnology*, 5(143).
5. Nguyen, T.D., Deshmukh, N., Nagaraj, J.M., Kramer, T., Purohit, P.K., Berry, M.J., & McAlpine, M.C. (2012). Piezoelectric nanoribbons for monitoring cellular deformations. *Nature Nanotechnology*, 7(587).
6. Murray, C.B., Kagan, C.R., & Bawendi, M.G. (2000). Synthesis and characterization of monodisperse nanocrystals and close-packed nanocrystal assemblies. *Annual Review of Materials Science*, 30(545).
7. Law, M., Goldberger, J., & Yang, P. (2004). Semiconductor nanowires and nanotubes. *Annual Review of Materials Research*, 34(83).

## **About Editors**



Dr. Alope Verma is the Head of the Physics Department at Kalinga University, Naya Raipur (CG). He has over 13 years of excellent teaching and academic experience. He earned his PhD in Physics. He has over 40 research papers, four books, and seven book chapters published in national and international journals. In national and international conferences and seminars, he has presented over 50 research papers. He has attended over 100 workshops, FDPs, and webinars. Several students successfully completed dissertation work under the supervision of Verma. He has received numerous teaching and academic awards.



Dr. Payal Goswami working as Guest Lecturer in the Department of Mathematics at Govt. Pt. J. L. N. PG Arts & Science College, Bemetara (CG). She has a decade of exemplary teaching experience and scholarly knowledge. In the field of mathematics, she earned a Doctor of Philosophy degree. She is the author of ten research papers and two book chapters that have appeared in national and international academic journals. She has presented 10 research papers at a national and international level. She has participated in over twenty workshops, faculty development programs (FDPs), and webinars. Under the supervision and guidance of Goswami, a number of students have successfully completed their dissertation. She has received numerous teaching and academic distinctions.



Dr. Veerabhadrayya M is presently serving as Assistant Professor of Physics at University College of Science, a constituent college of Tumkur University, Tumkur, Karnataka. He obtained his Master's degree in Physics from Karnatak University, Dharwad in 1997 and M. Phil. Degree from Annamalai University in 2007. He cleared SLET in 1998 and CSIR-NET in 2011. He is awarded with Ph.D. degree from Tumkur University, Tumkur in 2021. He has published 3 research articles in international journals and 8 research articles in international and National conference proceedings. He is interested in material science, XRD analysis, sensors and electronics. He has written two book chapters. He has 25 years of teaching experience at UG and PG level. He worked as a Coordinator of Department of studies and research in Physics (PG) at University College of Science, Tumkur. He is involved in academic activities of Tumkur University and other Universities. He is the life member of Indian Science Congress Association and Swadeshi Vignana Andolan.



Dr. R. G. Vaidya, is currently working as Assistant Professor in the Department of Physics, University College of Science, Tumkur University, Tumakuru, Karnataka. He has more than ten years teaching and research experience. He has published research papers in peer reviewed international journals. He has attended and presented his research work in various national and international level conferences, workshops, seminars, etc.

