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INNOVATIVE APPROACHES IN SCIENCE & TECHNOLOGY RESEARCH **VOLUME III**

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Innovative Approaches in Science and Technology Research Volume III

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PREFACE

Science and technology have always played pivotal roles in the advancement of human civilization. As we move deeper into the 21st century, innovation within these fields is accelerating at an unprecedented pace. The ability to integrate new techniques, methodologies, and interdisciplinary approaches has become essential for pushing the boundaries of knowledge and solving complex global challenges. This book, Innovative Approaches in Science and Technology Research, highlights some of the most groundbreaking advancements that reflect the transformative power of modern science and technology.

In today's era, research is no longer confined by traditional boundaries. From biotechnology and nanotechnology to advanced computing and materials science, the convergence of disciplines is leading to a renaissance in research and development. This volume showcases the innovative approaches being employed across a variety of scientific fields, emphasizing the importance of creativity and collaboration in driving forward research that can address real-world problems. By exploring these cuttingedge methodologies, we aim to inspire both current and future researchers to think beyond conventional paradigms and embrace new techniques that can yield transformative results.

The chapters in this book cover a diverse range of topics, each contributing to the overarching theme of innovation. Whether it's harnessing the power of artificial intelligence for data analysis, employing nanomaterials for environmental applications, or advancing the understanding of biological systems through molecular techniques, the research presented here demonstrates how novel approaches are reshaping the landscape of science and technology.

We hope this book serves as both an inspiration and a resource for scientists, engineers, and technologists, encouraging them to adopt innovative approaches in their own work. By embracing the spirit of innovation, we can collectively unlock new possibilities and create a brighter, more advanced future for all.

Editors

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OYSTER MUSHROOM CULTIVATION- ITS ROLE IN UPLIFTING SOCIETY

Devyaratna Uikey

PC Unit Sesame & Niger, JNKVV, Jabalpur, MP, India

Entrepreneur, Mushroom Brand - The Dev Mushrooms, Chhindwara, MP, India.

Introduction:

The oyster mushroom is scientifically known as *Pleurotus*. It is trendy in China, Japan and various other East Asian countries including India. Its shape is like an oyster or big spoon with stalk on one side and gills on the lower side. A Number of Pleurotus species have been cultivated, so we get oyster mushrooms of all colours like white, grey, yellow, pink, etc. Some of the commonly cultivated species are *Pleurotus oesteratus, P. sapidus, P. florida, P. sajor-caju, P. djamor, P. eous, P. citrinopileatus, P. flabellatus, P. eryngii* etc. Its cultivation is easy, but it has some critical steps to be taken care off like moisture content, proper sterilization and layered spawning to get proper mycelial growth and fruiting. There is no need to compost substrate (straw or other material used for growing mushroom) as was done for growing button mushroom. It can be grown on wide range of substrates and temperatures. Some species grow well below 20°C and others grow well above 20°C.

Preparation of Substrate

Oyster mushroom can be cultivated on wide variety of substrates like wheat straw, paddy straw, maize straw/cobs, cotton hulls, saw dust and so on. In fact, it can be grown on any cellulosic waste. In India, we normally grow it on wheat or paddy straw. It is more suitable for our country as:

- It can be grown on wide range of agricultural, horticultural and forest wastes
- There is no need of compositing, its cultivation technique is easy and it can be grown on small scale in huts
- It can be grown in tropical part of our country as there are number of varieties that can grow between 20-30°C. Moreover, we also have varieties that can grow below 20 °C. These species also vary in colour.
- It has a short life cycle and mushrooms can be easily sun-dried.
- It is a nutritious mushroom with medicinal benefits (like presence of cholesterol lowering compound -lovastatin)

Oyster Mushroom (The Dev Mushroom's Original Photos)

The first step is to prepare the substrate. Composting of the substrate is not required for cultivation of oyster mushroom species. As already mentioned, a number of cellulosic wastes like wheat straws, paddy straw, corn cobs, sawdust, cotton hulls, etc., can be used for cultivation depending upon the availability. The most commonly used substrate in our country is wheat straw followed by paddy straw. We should ensure that the substrate used is not exposed to rains after harvesting. We can pasteurize or sterilize the substrate or even use it as such. Let us learn different methods of preparation of substrate.

Using of Straw (without any treatment)

We soak the straw in water as such overnight and used for cultivation. To make the pH slightly basic, you may add lime powder (1%) in the water. We soak the straw overnight, take it out and air dry before spawning. It must be ensured that the straw is fresh, that is, not exposed to rain. The spawning rate is kept more, i.e. 4%. Normally we add about 2.5% spawn on wet weight basis. It may be proper to keep moisture slightly less and also close the bags for higher carbon dioxide production. However, this is not recommended method, particularly at commercial level. It has been observed that farmers in Odisha follow this method with slight modifications. Majority of the farmers in coastal regions in Odisha keep the bags in single layer in simple huts made of coconut leaves. Due to natural high humidity, it becomes possible to cultivate this mushroom in simple huts.

Using of Straw (with treatment)

We may sterilize the straw using chemicals by soaking it in water containing formalin and carbendazim. Both of these also inhibit the growth of mushroom. Hence it is important that chemicals should be pure and only recommended dose is used. For 10 kg straw about 100 litres of water is needed to which 7.5 g carbendazim (50WP) and 125 ml formalin is added. Soak the straw in this solution for 18 hours and then take out and air dry for 2-4 hours depending upon the season. In South India, farmers have innovated and developed machines for drying the straw. These are like big washing machines used to dry clothes.

Straw after treating with Bavistin

Hot Water Treatment

We wet the straw overnight. After taking out, soak it in hot boiling water. The straw is allowed to stay in this water for few hours and is cooled before spawning. The temperature of the hot water may be between 60-65°C. Over-boiling does not mean better treatment of the straw. Rather it will lead to partial sterilization of the straw which will attract more diseases. Secondly, soaking in hot water for prolonged period can lead to anaerobic conditions which are not required. However, many of us may find it difficult to heat large amounts of waters using wood, oil or electricity. An alternative method is use of solar energy. Dry paddy and wheat straw can be directly soaked in hot water. It is important that a temperature of about $60 \pm 2^{\circ}$ C is maintained for about an hour and after that the straw can be spin dried and spawned. Actually, direct treatment with hot water leads to immediate removal of waxy layer of straw and water absorption becomes easy. It has been observed that temperature above 65°C can be obtained in solar water heater. It may be possible to use electricity or integrate electricity and solar systems. Spin drying machine can be used to immediately remove excess water. We can develop a system of using many solar water heaters and drums and substrate can be filled in the drums at a regular interval of say 15 minutes. This way we can continuously use the spinning machine.

Solar energy based model for cultivation of oyster mushroom

Pasteurization

Even though pasteurization using hot water is a better method as the heat penetration is quick and uniform, but for commercial scale cultivation of oyster mushroom, it may not be possible to use this method. Here pasteurization in tunnel will be required. The method involves wetting straw, mixing 1% lime on dry weight basis, turning the pile of 4' width, 3-4' height (length of pile will depend upon the amount of substrate) every alternate day twice, filling in tunnel up to 4-5', raising the temperature to 60-62 °C using steam and maintaining it for 4-6 hours, followed by conditioning for 30-36 hours at 44-48 °C and cooling down. The material is then cooled and spawned.

Autoclaving

We may sterilize the straw by autoclaving. Straw is soaked, excess water is drained and after air drying, it is filled in polypropylene bags and sterilized just like spawn bags. For cultivation of some species of oyster mushroom like *P. eryngii* (King Oyster), autoclaving is must. After autoclaving, the bags are cooled and spawned under sterile conditions before laminar flow. This approach will ensure better results and very less contamination. It will be more useful where aim is to produce and sell spawn run bags at commercial scale or develop Ready to Fruit (RTF) packets for urban horticulture.

Cultivation of Mushroom

We spawn the pasteurized straw @ 2-3% spawn on wet weight basis. Two-five kg wet substrate can be filled in each bag. In other words, one kg dry straw will require about 100 g of spawn. Spawn can be mixed thoroughly or put in layers inside the bag. Bags are kept inside room or any hut and can be kept on ground or in tiers as in button mushroom or can be hung from the roof or rack with the help of nylon rope. Small perforations are made in the bags. Bags are kept at temperature 24±2°C. Spawn run takes about two weeks when whole bag becomes white. No light or fresh air is required for spawn run. Rather it is better to keep the rooms closed.

Mushroom in Bags

For induction of fruiting, the bags require diffused light and fresh air for 3-4 hours daily for production of normal fruit bodies. Large holes can be made in the bag or whole of polythene can be removed. In 3-4 flushes, one kg of dry straw can yield 0.5 to 1.0 kg fresh mushrooms. The temperature during cropping is kept around below 20°C or around 25°C

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(depending upon the species) and humidity is maintained above 85%. Temperature requirement will vary with the species. The development of colour will vary with temperature and duration of fruit-body on the bag. If you are staying in urban areas, it may not be possible for you to make or obtain small quantity of spawn, and also wet and heat straw and fill bags. Hence it is important that such growers are provided ready-to-fruit bags. For growing mushrooms for your own self, particularly in urban areas, ready to fruit bags are now available. The fully colonized substrate is already packed inside these bags and all you need to do is cut open the box on one or both sides and start watering. Within 10 days or so you will get the first crop. RTF bags promote peri-urban horticulture. Even such bags can be used for science projects in schools to educate the children about mushrooms. Such kits are available in many countries and also in India. Substrate production requires special facilities. All growers cannot have such facilities. However, if spawned bags are available, almost everyone can cultivate mushrooms. Thus producing ready to fruit bags is a novel vocation. However, quality control will be very important as we cannot afford failure of bags especially if someone has purchased only one or two bags. Another approach is that of having satellite growers. That is, fully spawn run bags are given to the farmers in the area and the produce is collected. By this approach we will be able to get mushrooms of the same variety and thus the next important vocation of packing and marketing can be undertaken.

Harvesting and Storage

We harvest the mushrooms by twisting and we may cut any straw of substrate that may be there on the stalk. Do not water the bags before harvesting. We can easily sun dry oyster mushroom in open or in cabinets. The drying temperature should not be high (>60°C) as mushrooms dried at higher temperature do not rehydrate properly and also have poor smell. We can powder the dried mushrooms and powder can be added to biscuits, various other bakery products, health foods, etc. We can also make pickle of oyster mushroom after blanching just like button mushroom. As this mushroom produces lot of spores, workers should invariably wear masks inside the cropping room. A few people may be allergic to mushroom spores. The cultivation method of this mushroom is the easiest. Cost of cultivation is around Rs. 20-30 per kg under natural conditions.

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APPLICATIONS OF SECOND-ORDER STOCHASTIC DOMINANCE IN OPTIMAL PORTFOLIO SELECTION FOR RETIREMENT PLANNING

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Abstract:

This study examines how Second-Order Stochastic Dominance (SSD) can be used to choose the best portfolio for retirement planning. Risk-averse investors can compare investment portfolios using SSD, a criterion that evaluates portfolios according to their Cumulative Distribution Function (CDF). This criterion helps investors minimize downside risk while guaranteeing favorable returns. SSD is especially essential for retirees who value low risk and steady income because it makes portfolios with lower risk of large losses more dominant than those with higher volatility. The CDF is used in the article to rank portfolios, making sure that the investments chosen fit retirement-appropriate risk tolerance levels. Employing SSD in portfolio optimization results in improved asset allocation and diversification, giving retirees a methodical way to ensure their financial security. To assess the performance of the given investment compared to the category average over various time periods using second-order stochastic dominance. To determine whether the investment SSD dominates the category average, indicating a more favorable risk-return profile for risk-averse investors.

Keywords: Second-Order Stochastic Dominance (SSD), Retirement Planning, Risk-Averse Investors, Cumulative Distribution Function (CDF), Portfolio Optimization, Diversification.

1. Introduction

Retirement portfolio optimization aims to balance the trade-off between risk and return. Traditional portfolio theory often relies on mean-variance optimization, which considers only the expected returns and variances. However, this approach can overlook crucial aspects of return distribution that are important for risk-averse investors. Secondorder stochastic dominance (SSD) offers a more robust framework by evaluating the entire distribution of returns, allowing for a more comprehensive risk assessment. This study employs SSD to compare the performance of a specific investment against the average

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performance within its category across different time periods. By analysing metrics such as absolute returns, annualized returns, and cumulative returns, we determine the extent to which the investment directs its category. The ultimate goal is to recognize optimal portfolio allocations for retirement planning. To evaluate the performance of the given investment compared to the category average over various time periods using secondorder stochastic dominance. To determine whether the investment SSD dominates the category average, representing a more favorable risk-return profile for risk-averse investors.

Levy, H. (1992) explained that the Stochastic Dominance and Expected Utility: Survey and Analysis, Levy's comprehensive review of stochastic dominance, particularly Second-Order Stochastic Dominance (SSD), provides the basis for understanding how SSD can be applied to portfolio optimization. Post, T. *et al.,* (2005) described that the Risk Aversion Drive Asset Prices. This paper investigates the relationship between risk aversion and asset prices, integrating SSD into the analysis. Efficient Diversification According to Stochastic Dominance Criteria, Kuosmanen explores portfolio diversification using stochastic dominance criteria clarified by Kuosmanen, T. (2004). Dentcheva, D., *et al.,* (2003) Optimization with Stochastic Dominance Constraints, Dentcheva and Ruszczynski suggest integrating stochastic dominance constraints, such as SSD, into optimization models.

Shalit, H., *et al.,* (1994) investigates the Capital Market Equilibrium with Risk Aversion and Stochastic Dominance, Shalit and Yitzhaki examine the relationship between risk aversion and capital market equilibrium using SSD. Bawa, V. S. (1975) studied the Optimal Rules for Ordering Uncertain Prospects, Bawa's early work on stochastic dominance lays the groundwork for using SSD in portfolio optimization. Kopa, M. (2012) explores that Stochastic Dominance Efficient Portfolios: A Linear Programming Approach Kopa develops a linear programming approach to constructing portfolios that meet stochastic dominance criteria, including SSD. Hanoch, G., & Levy, H. (1969) illustrates the Efficiency Analysis of Choices Involving Risk, Hanoch and Levy's seminal paper introduces the concept of stochastic dominance for analysing risky choices. Fishburn, P. C. (1974) focussed the Convex Stochastic Dominance with Continuous Distribution Functions, Fishburn extends the theory of stochastic dominance by introducing the concept of convex stochastic dominance. Porter, R. B. (1974) expressed the Promotion of the Portfolio Approach to Investment Selection, Porter's paper emphasizes the importance of portfolio

theory in investment selection and connects it with stochastic dominance criteria. Hadar, J., and Russell, W. R. (1969) pointed out the Rules for Ordering Uncertain Prospects Ogryczak, W., and Ruszczynski, A. (1999) explained that theStochastic Dominance to Mean-Risk Models: Semideviations as Risk Measures, Ogryczak and Ruszczynski enlarge on SSD by integrating it with mean-risk models, offering a more comprehensive framework for risk management in portfolio selection.

Leshno, M., & Levy, H. (2002) – Preferred by "All" and Preferred by "Most" Decision-Makers: Almost Stochastic Dominance, Second-Degree Stochastic Dominance Concerning a Function. Meyer's contribution to SSD theory enhances its application by evolving a more precise method for comparing portfolio returns stated by Meyer, J. (1977). Athey, S. (2002) expressed that the Monotone Comparative Statics under Uncertainty. Simaan, Y. (1993), introduces the Portfolio selection and asset pricing: Grootveld, H., and Hallerbach, W. (1999), explained that the Variance vs downside risk: Shalit, H., and Yitzhaki, S. (1984). Explained that the Mean-Gini, portfolio theory, and the pricing of risky assets. Föllmer, H., and Schied, A. (2002), presented the method of Convex measures of risk and trading constraints. Ruszczynski, A., and Shapiro, A. (2006), established the Conditional risk mappings. By applying SSD, financial organizers can create more secure and robust portfolios, ensuring that retirees have a reliable income while minimizing exposure to market downturns.

To assess the performance of the given investment compared to the category average over various periods using second-order stochastic dominance. To determine whether the investment SSD dominates the category average, indicating a more favorable risk-return profile for risk-averse investors.

Second-Order Stochastic Dominance (SSD):

SSD is a criterion used to compare the risk-return profiles of two investments. Portfolio A is said to SSD dominate Portfolio B if the area under the CDF of A is less than or equal to the area under the CDF of B for all levels of return.

- 1. **Absolute Returns:** The total return of an investment over a specific period.
- 2. **Annualized Returns:** The geometric average of an investment's annual returns over a given time period..

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2. Methodology

The methodology involves the following steps:

Data Collection: The secondary data were collected, and find the investment's absolute and annualized returns, along with the category average returns, over multiple periods. By calculating CDF for given below data.

web name- Money control, link - [https://www.moneycontrol.com/mutual](https://www.moneycontrol.com/mutual-funds/nav/icici-prudential-retirement-fund-pure-equity-plan-direct-plan-growth/MPI4165)[funds/nav/icici-prudential-retirement-fund-pure-equity-plan-direct-plan](https://www.moneycontrol.com/mutual-funds/nav/icici-prudential-retirement-fund-pure-equity-plan-direct-plan-growth/MPI4165)[growth/MPI4165](https://www.moneycontrol.com/mutual-funds/nav/icici-prudential-retirement-fund-pure-equity-plan-direct-plan-growth/MPI4165)

S.	Period	₹10000	LatestValue	Absolute	Annualized	Category	Rank
No.	Invested	Invested		Returns	Returns	Avg	within
	for	on					Category
1.	YTD	01 -Jan-	12997.00	29.97%		18.12%	1/27
		24					
2.	1 Year	$15-Sep-$	14858.50	48.59%	48.26%	26.65%	1/26
		23					
3.	2 Year	16-Sep-	18428.70	84.29%	35.70%	18.82%	1/25
		22					
4.	3 Year	16-Sep-	21016.00	110.16%	28.06%	14.11%	1/25
		21					
5.	5 Year	16-Sep-	33725.30	237.25%	27.49%	15.55%	2/18
		19					
6.	Since	27 -Feb-	34130.00	241.30%	24.73%	15.33%	3/28
	Inception	19					

Table 1: Data for Retirement planning process (2019 – 24)

- 1. **CDF Construction:** Construct the CDFs for the investment and the category average based on the given return data.
- 2. **SSD Analysis:** Calculate the areas under the CDFs for both the investment and the category average to determine if SSD dominance exists.
- 3. **Optimal Portfolio Allocation:** Use the SSD findings to inform the allocation of the investment in a retirement portfolio.
- 4. **Mathematical Analysis:** Formulate mathematical problems and solutions to interpret the results in the context of retirement planning.

Absolute returns = $\frac{Current\ value - purchase\ value}{Purchase\ value}$ X 100

Functions (CDFs)

Investment Returns CDF:

1. Cumulative Sum (CS) and CDF Calculation:

$$
CS_i = \sum_{j=1}^{i} \text{ Investment returns}_j
$$
\n
$$
CDF_i = \frac{cs_i}{\text{Total sum of Investment returns}}
$$

Calculations:

- 1. Total Sum of Investment Returns: 751.56
- 2. CDF1 = 29.97 / 751.56 ≈ 0.03987
- 3. CDF2 = 48.5 / 751.56 ≈ 0.06465

Continue this process for all sorted returns.

1. Investment CDFs:

[0.03987, 0.06465, 0.11215, 0.14657, 0.315676, 0.32106]

or **Corresponding CDF values:** [0.17, 0.33, 0.50, 0.67, 0.83, 1.00]

Functions (CDFs)

1. **Category average CDF**:

Cumulative Sum (CS) and CDF Calculation:

$$
CS_i = \sum_{j=1}^{i} \text{Category average}_j
$$

$$
CDF_i = \frac{cs_i}{Total Sum of category average}
$$

Calculations:

- i. Total Sum of Category Average: 90.46
- ii. CDF1 = 18.12 / 90.46 ≈ 0.2003
- iii. CDF2 = 26.65 / 90.46 $≈ 0.2946$

Continue this process for all sorted returns.

Step 1: Analysis Using the Provided Data

1-Year Return:

- Investment: 48.59%, Category Average: 26.65%
- The investment significantly outperforms the category average.

2-Year Return:

- Investment: 84.29%, Category Average: 18.82%
- Dominance is clear as the investment's performance is much higher.

3 -Year and 5-Year Returns:

- Investment maintains higher returns (e.g., 110.16% vs. 14.11% over 3 years).
- CDFs shows that the investment has a lower probability of underperforming compared to the category average.

1-Year Period: Area_{Investment, 1-Year = 48.26 and 26.65}

3-Year Period: Area_{Investment, 3-Year} $= 84.18$ and 42.33

By Compare the Areas: 1-Year: 48.26 vs. 26.65 — The investment has a larger area, indicating dominance. 3-Year: 84.18 vs. 42.33 — The investment again has a larger area. Interpret the Results: Since the area under the CDF of the investment is greater than that of the category average for both periods, the investment SSD dominates the category average. This means the investment offers a more favorable risk-return profile.

3. Analysis

The provided data outlines the performance of an investment over various periods compared to the category average and gives insights into its risk-return profile, Sharpe ratio, and stochastic dominance. The goal is to assess the investment's performance relative to other assets in its category and determine whether it is optimal for portfolio allocation, particularly for retirement planning.

Step 1: Performance Analysis

Period Invested	Absolute Returns		Category Avg Rank within Category
YTD	29.97%	18.12%	1/27
1 Year	48.59%	26.65%	1/26
2 Year	84.29%	18.82%	1/25
3 Year	110.16%	14.11%	1/25
5 Year	237.25%	15.55%	2/18
Since Inception	241.30%	$ 15.33\%$	3/28

 Table 2: Absolute Returns vs. Category Average (Bar Chart Data)

The investment consistently outperforms the category average across all periods, with absolute returns significantly higher than the average. In particular: the YTD (Year-To-Date) return is 29.97%, which is much higher than the category average of 18.12%. Over the 5-year period, the investment has returned 237.25%, while the category average is only 15.55%. The investment's since inception return of 241.30% is also well above the average of 15.33%. The ranking within its category is consistently high (1st or 2nd place), indicating that this investment is among the top performers in its class.

Step 2: Risk-Return Profile and Sharpe Ratio Analysis

The Sharpe ratio measures risk-adjusted return by comparing the excess return over a risk-free rate to the volatility (risk) of the asset. A higher Sharpe ratio indicates a better risk-adjusted return. The investment has a Sharpe ratio of 3.02, which is significantly higher than the hypothetical alternative asset's ratio of 1.20.This suggests that the investment provides much better risk-adjusted returns, meaning that it delivers more return per unit of risk compared to the alternative.

Step 3: Cumulative Distribution Function (CDF) Analysis

Table 3: Comparison of CDF for investment with category average

Table 4: Comparison between the value of investment and alternative asset Sharpe ratio

Second-Order Stochastic Dominance (SSD) is evaluated by comparing the cumulative distribution functions (CDFs) of the investment and the category average. The investment's CDF is consistently lower than the category average across multiple points, indicating that the investment has a higher likelihood of yielding better returns across a

range of possible outcomes. SSD Dominance implies that the investment is preferable for risk-averse investors, as it delivers better outcomes in terms of cumulative returns than the category average for the same level of risk.

Figure 1: Cumulative distribution function

Step 4: Annualized Returns Over Time

Table 5: Comparison between period invested and annualized returns

Period Invested	Annualized Returns
YTD	29.97%
1 Year	48.26%
2 Year	35.70%
3 Year	28.06%
5 Year	27.49%
Since Inception	24.73%

The annualized returns show a steady trend of strong performance over time. While there is a slight decline in annualized returns as the time period increases (from 48.26% for 1 year to 24.73% since inception), this reflects the consistent long-term growth of the investment, which is essential for retirement or long-term portfolio planning. The steady performance suggests the investment is reliable for long-term growth while offering high short-term returns as well.

The Optimal Allocation of the Investment in a Retirement Portfolio Based on SSD Analysis by using the Sharpe ratio to determine the optimal allocation

[Sharpe Ratio = $\frac{E(R_i)-R_f}{R_i}$ $\frac{1}{\sigma_i}$]. Assume a risk-free rate (R_f) of 3% and a standard deviation (σ_i) of 15% for the investment. For the investment over the 1-year period – the Sharpe Ratio = 48.26 % − 3% $\frac{5\% - 3\%}{15\%} = \frac{45.26}{15}$ $\frac{12.26}{15}$ = 3.02. Assume an alternative asset with a Sharpe ratio of 1.2. Since the investment has a higher Sharpe ratio, it should be allocated a larger weight in the retirement portfolio.

Python code for finding the Absolute Returns and CDF

import numpy as np

Absolute Returns extracted from the table

absolute_returns = [29.97, 48.59, 84.29, 110.16, 237.25, 241.30]

Step 1: Sort the absolute returns for the CDF

absolute_returns_sorted = np.sort(absolute_returns)

Step 2: Calculate the cumulative probabilities

 $cdf = np.arange(1, len(absolute_returns_scoreed) + 1) / len(absolute_returns_scoreed)$

Output the sorted absolute returns and corresponding CDF values

print("Sorted Absolute Returns:", absolute_returns_sorted)

print("CDF:", cdf)

Output of the Absolute Return and CDF values

Absolute Returns: [29.97, 48.59, 84.29, 110.16, 237.25, 241.30]

CDF values: [0.17, 0.33, 0.50, 0.67, 0.83, 1.00]

4. Discussion and Results:

The investment shows strong performance, consistently outperforming the category average across all periods. For instance, the YTD return is 29.97% compared to the category average of 18.12%, and over a 5-year period, it delivers 237.25%, well above the average of 15.55%. This trend continues with the investments since inception return of 241.30%, ranking it among the top performers in its category. The Sharpe ratio of the investment, at 3.02, indicates better risk-adjusted returns compared to an alternative asset with a ratio of 1.20. This makes the investment more efficient in terms of return per unit of risk. Additionally, the Second-Order Stochastic Dominance (SSD) analysis, based on the Cumulative Distribution Function (CDF), suggests the investment yields better returns across various outcomes, favouring risk-averse investors. Lastly, the annualized returns demonstrate stable growth, making the investment ideal for long-term portfolio planning, particularly for retirement.

Conclusion:

The analysis of the investment in the Finance Case Study highlights its unexpected performance across multiple dimensions. With reliable outperformance relative to its category, both in terms of absolute returns and risk-adjusted returns, the investment arises as a highly attractive option for both short-term and long-term investors. Its Sharpe ratio of 3.02 indicates strong risk management while delivering high returns, making it suitable for depositors looking for a balance between growth and risk mitigation. Furthermore, the investment demonstrates second-order stochastic dominance (SSD) over its peers, which is crucial for risk-averse investors. SSD ensures that the investment provides superior cumulative returns in various risk scenarios, particularly important for those focused on retirement planning and long-term financial stability.

Overall, the investment stands out as a top performer in its category and proposals an excellent combination of growth potential, risk management, and consistent long-term returns. This makes it an ideal choice for individuals seeking to build a robust retirement portfolio or investors looking for a stable and high-performing asset in the broader market. **References**

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HERBICIDES RESEARCH ON SESAME CROP- NEW POTENT ACTIVE INGREDIENTS Uma Bermaiya

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Introduction:

Across the globe, wherever sesame is grown, there has been an increasing use of herbicides. Up until now, sesame has been a manual crop with hand-weeding and hoeing for millennia. The purpose of this paper is to provide researchers insight for a starting point to determine which herbicides will be best for trials in their areas. There are some herbicides that are more promising than others, and there is no sense in wasting scarce time and research funds trying herbicides that have already proven to be unusable for sesame. There are many variants of the word preemergence as it pertains to herbicide usage in the world literature. In this paper the terms and abbreviations have been standardized as follows:

- Herbicides applied preplant with no incorporation (PREPLANT)
- Herbicides applied preplant incorporated (PPI)
- Preemergence (PRE) Herbicides applied after planting and before weed or crop emergence.
- Postemergence (POST) There are two types of herbicide application: over the top (OTT) of sesame and directed (DIR) at the base of the sesame. There is a POST DIR where the herbicide is sprayed between the rows and does not touch the sesame, but unless specified all the POST DIR research discussed below implies spraying on to the base of sesame.

Sesame is one of the oldest crops known to man. There are archeological remnants of sesame dating 5,500 BP in the Harappa Valley in the Indian subcontinent. Sesame originated on the Indian subcontinent and spread to other parts of Asia and Africa thousands of years ago. From ancient times to modern times, sesame has required considerable manual labor from planting through harvest. Over 99% of the sesame today is still harvested manually. In several international meetings in the 1990s, the first author made a very controversial prediction: unless sesame is mechanized in the next 20-25 years, its world production will decrease significantly. Without mechanization, sesame will only persist in those niches where no other more suitable crop can be grown. Since that prediction, production and world trade has continued to increase. However, the trends are

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clear. The availability of manual labor continues to decline even in countries such as India. Sesame has disappeared in traditional growing areas that have become mechanized such as Japan and the Obregon area of Mexico, and is disappearing in Gujarat in India where mechanization is accelerating. Korea, Thailand, and China are developing equipment that can operate in small fields and mechanization will be pervasive faster than in the US and Europe. crops are accelerating this decline. Sesame has disappeared in traditional growing areas that have become mechanized such as Japan and the Obregon area of Mexico, and is disappearing in Gujarat in India where mechanization is accelerating. Korea, Thailand, and China are developing equipment that can operate in small fields and mechanization will be pervasive faster than in the US and Europe. There has been considerable progress in mechanizing the crop by the development of non-dehiscent capsules that hold the seed until combining and then release the seed within the combine with minimum threshing. In addition, the growth habit of phenotypes has been changed to more readily feed into combines. The one area of best management practices for sesame that is still in development is the use of herbicides. Several agronomic practices have reduced the need for herbicides in dry areas. Cleaning the fields prior to planting and then cultivation between rows has helped reduce weeds until the crop canopies. In areas that have early rainfall, herbicides are a must. In addition, the trend is to minimum and no-till practices which will require both PRE and POST herbicides. In many areas where Roundup Ready crops are predominant, there are no longer hoe crews to manually clean the fields. In mechanical harvest, there is an additional window of weed control that is important. The major form of weed control after the first 40-50 days of planting is the sesame canopy which blocks out light. At about 60 days after planting, current sesame varieties begin losing the leaves under the canopy where there is no light. As the plants mature, they selfdefoliate and leaves are gone at about 100 days after planting. It takes 40-50 days from the time that the plants lose all their leaves until the sesame is dry enough to combine. The leaves are a major part of the sun blocking canopy, and in addition, as the weight of the leaves is lost, the branches become more erect letting even more light in. With fall rains there may be a new flush of weeds, particularly fast growing grasses. These late weeds can be controlled in four ways: applying POST DIR herbicides that have a long residual control; having narrower row spacing; planting the rows north/south so that there is light to the ground only at mid-day; and using harvest aids to shorten the sesame drying period and which also kill and dry weeds.

The final problem is the small size of the sesame seed which is similar to the size of many weed seeds. In the use of oil, weed seeds within the sesame samples is not as critical unless they are toxic. However, a large percentage of sesame is used in edible markets that require 99.99% purity. There are seeds such as johnsongrass (*Sorghum halepense*) that would seemingly be easy to clean out because of their size and shape, and yet the johnsongrass seed go end first through the round holes and are difficult to separate in gravity tables because they have a similar specific gravity to sesame. In decortication of the seed for bakery products and tahini, the seed from mintweed (*Salvia reflexa*) causes a unique problem. When the mintweed seed is hydrated, the surface forms a gelatinous substance that will stick all the sesame seeds around it forming balls.

Kochia (*Kochia scoparia*) and grass seeds are other weeds that are difficult to clean out of sesame. Any weed seed that is in large percentage in sesame, is difficult to clean out, no matter the size and specific gravity, without having to slow down the processing or reprocessing. In Japan, purity needs to be 100% with processors having to pay claims to customers that find anything other than pure sesame seeds.

Most promising herbicides for use on sesame

There are many PRE herbicides that have been successfully used in the world: alachlor, diuron, fluchloralin, fluometuron, linuron, metobromuron + metolachlor, metolachlor, pendimethalin and trifluralin. However, herbicides act differently under certain environmental conditions which include variability in soil, temperature, humidity, rainfall, and under different methods and timing of application. Pendimethalin and trifluralin are particularly difficult to use with results ranging from great weed control with no damage to the sesame to little or no sesame stand. Poor sesame stands with the use of pendimethalin or trifluralin have resulted from incorporating either of the herbicides too deep. Since sesame is planted shallow, it is difficult to properly incorporate the

dinitroaniline herbicides effectively and not have the herbicides come in contact with the sesame seed or roots. It is important to read the literature and to try these herbicides experimentally before applying them in farmer fields.To date there is no POST OTT broadleaf herbicide that will control the weeds without damaging the sesame. There are products such as alachlor and metolachlor that will not damage sesame when applied PRE, will not kill any emerged weeds, but will provide some residual control. In the case of herbicides such as diuron, sesame will recover, but the farmer must look at damaged sesame for about 10 days after herbicide application and have faith that the sesame will recover. In some of the research, even more damage to the sesame from other herbicides with good weed control has proven to produce higher yield because of the loss of production to weeds. However, it is very difficult for a grower to see the amount of sesame damage even knowing that the sesame will recover. Starting in 2003, work has been done on POST DIR herbicides with and without the use of hooded sprayers. This work is very encouraging; however, there are many cropping patterns that preclude the use of hooded sprayers. There is a label for glyphosate (RT3) which allows spraying with wiper applicators or hooded sprayers between sesame rows. While this does not kill weeds in the sesame seed line, it helps, particularly with vining weeds such as morningglory than spread across the rows. In the case of *Amaranthus* which quickly becomes taller that the sesame, wiper applicators using glyphosate have been very successful as long as the glyphosate does not leak on to the sesame.

There is one group of broadleaf weeds that continues to affect sesame – the hard seeded broadleaves (e.g., morningglory [*Ipomoea* spp.]) that come up in flushes after a rainfall or irrigation event and after sesame canopy formation. These weeds can continue growing under weak light conditions, climb the sesame plants to the top of the canopy, and when they reach the light, greatly expand their infestation. As soon as they reach light, their

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leaf size increases dramatically. In high populations, these twining weeds can push down the sesame and cause problems at harvest in that it is difficult to separate adjacent rows of sesame at the edge of the combine. Many farmers go into these areas with glyphosate and sacrifice the sesame to keep the problem from spreading in future years. However, the best control for this type of weed is to use glyphosate in hooded sprayers while the plants are growing across the space between the sesame seed lines. One of the major problems in using POST DIR herbicides will be the timing of the application and the height of the application on the sesame stem as related to the height of the plant. When there are dominant and minor plants in a high sesame population, the use of herbicides such as glyphosate kill the minor plants which are smaller in size but the dominant plants which are taller are not killed. In waiting for the sesame to get tall enough to spray, weeds also get tall and herbicides may not kill the weeds.

Although the main thrust of this paper has been the controlling of weeds in sesame, there is always a concern as to whether sesame will become a weed in other crops used in rotation with sesame. There are many PREPLANT and PRE herbicides used in other crops that will prevent sesame from germinating. To date there is only one herbicide that will kill the sesame consistently from the juvenile stage on – glyphosate. However, in some experiments prometryn, flumioxazin, imazapic, trifloxysulfuron, mesotrione, flumetsulam, and foransulam have virtually wiped out the sesame. Most POST OTT herbicides set back the sesame enough for the crop to canopy over the sesame. Until the advent of Roundup Ready cotton (*Gossypium hirsutum*), sesame could become a problem weed. Under normal planting conditions, cotton germinates about 5 degrees cooler than sesame and has a faster growth curve in the first 30 days than sesame. Cotton planted on time rarely had sesame as a weed. The problem was primarily in areas where cotton planting was delayed for integrated pest management reasons. When there was a sesame weed issue, most of the previous cotton herbicides would set the sesame back, but would not kill it. As long as the

stand of cotton was good, the cotton would outgrow and canopy the sesame, but in a low population, the sesame would persist. However, sesame was never a problem in the harvest of the cotton. With Roundup Ready cotton, the situation is reversed in that cotton can now be a weed in sesame.

Sesame could be a problem in peanuts (*Arachis hypogaea*), but with the new peanut herbicides such as Cadre (imazapic) or Pursuit (imazethapyr), sesame has not been a problem. Sesame was never a problem in monocot crops such as corn, sorghum, and cereals because there are many good broadleaf herbicides that would control sesame. Theoretically, sesame could be a weed in many vegetable crops, but with a wide range of herbicides approved for those crops and the usual presence of manual labor, sesame has not been a problem in any one vegetable crop to date. In all of the testing, there is no magic herbicide that does not affect sesame under some condition; however, it is clear that without weed control, sesame cannot produce economical yields. Therefore, some damage must be acceptable and with this minimal damage to the sesame, many herbicides have produced excellent economic yields. In the 1920s, Iowa farmers used to say that they plant 3 kernels of corn, "One for the worm, one for the crow, and one for me." Perhaps, in this century sesame farmers will need to plant extra sesame seed, "Some for the herbicide, and most for me."

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ENVIRONMENTAL BENIGN SYNTHESIS OF 1,2-BIS(4-SUBSTITUTED PHENYL)-2-HYDROXYETHAN-1-ONE DERIVATIVES AND ITS CHARACTERIZATION

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Abstract:

The new series of 1,2-bis(4-substituted phenyl)-2-hydroxyethan-1-one (2a-d) was synthesized from condensation of substituted benzaldehyde by treating with thiamine hydrochloride. It was observed that a resultant derivatives has greater yield of products in shorter reaction times. The structures of synthesized compounds were characterized by their spectral analyses (elemental analysis, FTIR, 1H NMR) and the purity of synthesized compounds were confirmed by TLC.

Keywords: Thiamine hydrochloride, Benzoin.

Introduction:

It is widely acknowledged that there is a growing need for more environmentally acceptable processes in the chemical industry. This trend towards what has become known as 'Green Chemistry' [1] or 'Sustainable Technology' necessitates a paradigm shift from traditional concepts of process efficiency, that focus largely on chemical yield, to one that assigns economic value to eliminating waste at source and avoiding the use of toxic and hazardous substances. The term 'Green Chemistry' was coined by Anastas [2] of the US Environmental Protection Agency (EPA). In 1993 the EPA officially adopted the name 'US Green Chemistry Program' which has served as a focal point for activities within the United States, such as the Presidential Green Chemistry Challenge Awards and the annual Green Chemistry and Engineering Conference. This does not mean that research on green chemistry did not exist before the early 1990, merely that it did not have the name. Since the early 1990s both Italy and the United Kingdom have launched major initiatives in green chemistry and more recently, the Green and Sustainable Chemistry Network was initiated in Japan. The inaugural edition of the journal Green Chemistry, sponsored by the Royal Society of Chemistry, appeared in 1999. Hence, we may conclude that Green Chemistry is here to stay. A reasonable working definition of green chemistry can be formulated as

follows [3]. Green chemistry efficiently utilizes (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous reagents and solvents in the manufacture and application of chemical products. As Anastas has pointed out, the guiding principle is the design of environmentally benign products and processes (benign by design) [4]. This concept is embodied in the 12 Principles of Green Chemistry [1, 4] which can be paraphrased as:

- 1. Waste prevention instead of remediation
- 2. Atom efficiency
- 3. Less hazardous/toxic chemicals
- 4. Safer products by design
- 5. Innocuous solvents and auxiliaries
- 6. Energy efficient by design
- 7. Preferably renewable raw materials
- 8. Shorter synthesis (avoid derivatisation)
- 9. Catalytic rather than stoichiometric reagents
- 10. Design products for degradation
- 11. Analytical methodologies for pollution prevention
- 12. Inherently safer processes

Green chemistry addresses the environmental impact of both chemical products and the processes by which they are produced. In this book we shall be concerned only with the latter, i.e. the product is a given and the goal is to design a green process for its production. Green chemistry eliminates waste at source.i.e. it is primary pollution prevention rather than waste remediation (end-of-pipe solutions). Prevention is better than cure (the first principle of green chemistry, outlined above). An alternative term, that is currently favored by the chemical industry, is Sustainable Technologies. Sustainable development has been defined as [5] Meeting the needs of the present generation without compromising the ability of future generations to meet their own needs. One could say that sustainability is the goal and Green Chemistry is the means to achieve it.

Benzoin was first synthesized in 1832 by Justus von Liebig and Friedrich Woehler during their research on oil of bitter almond, which is benzaldehyde with traces of hydrochloric acid. Benzoin resin or styrax resin is a balsamic resin obtained from the bark of several species of trees in the genus styrax. It is used in perfumes, some kinds of incense, as a flavoring, and medicine. Its principal component is benzoic acid. Commonly called

"benzoin", it is called "benzoin resin" here to distinguish it from the crystalline compound benzoin [6]. Benzoin type α-hydroxy carbonyl group in general is important structural subunit in many biologically active compounds, industrial materials and it is also important synthons for stereoselective synthesis of natural products, chiral auxiliaries and ligands[7].

Figure 1: Benzoin compound

Among the numerous synthetic strategies for introducing this moiety, the benzoin reaction and related additions remain perhaps, the most direct[8]. Several nucleophilic carbenes derived from heterocyclic compounds including triazolium, thiazole, triazole, imidazole [9] and benzimidazolium salts are also employed as catalyst in benzoin condensation [10]. Compounds having α-Hydroxy ketone as a functional group are used as antidepressant, astringent, anti-inflammatory, carminative, deodorant, diuretic, expectorant, sedatives and antibacterial [11].

Benzoins and its derivatives are used as intermediates for the synthesis of organic compounds and as a catalyst in photo polymerization, which are used as anticratering in powder coating. It has been reported that the benzoin can be used in skin disorders as an antibacterial and antifungal agent [12]. Benzoin has also been used as photo initiators in polymeric reaction. The benzoin type photo initiators containing hydroxyl group were used as initiators in the activated monomer polymerization [13]. Benzoin also used as a starting material for preparing complexes like Schiff base compound. Schiff base complexes of transition metals are of greater importance in medicine, biochemistry and industries among others [14]. Many of the benzoins and its derivatives are reported to show interesting NLO properties [15]. The molecular design of benzoin, containing one electron donor and one electron acceptor moiety, provides it with a push-pull configuration, which is a well-known way of enhancing the optical non linearities [16]. Most of the benzoins and its derivatives crystallize in non-centrosymmetric structure. Non-centrosymmetric crystals possess a very good NLO property. The nonlinear optical (NLO) single crystals have attracted the researchers and industries due to their wide applications such as second

harmonic generation (SHG), color display, electro-optic switches [16], high- energy lasers for inertial confinement fusion research [17] etc. The molecular conformations are of particular interest because they are expected to form intermolecular and intramolecular hydrogen bonding in solution and solid state. So, in addition to the study of important properties like second harmonic generation (SHG), laser damage threshold (LDT), optical and mechanical properties, assessment of hydrogen bonding also plays an important role. It is of interest to note that, according to the recent approaches concerning the contribution of the vibrational part to the molecular hyperpolarisibility [18], one should expect that this contribution might be very significant in the systems studied. Benzoins are excellent chromophores and the substituted benzoins show strong light emitting properties and long fluorescence lifetimes [19].

Thiamine, vitamin B1 or aneurin, was the first B vitamin discovered. A deficit of this vitamin causes several diseases in children, such as beri-beri [20] which occurs in infants fed with breast milk deficient in this vitamin and epilepsy [21]. These diseases also occur in adults with high intake of white rice or food containing anti-thiamine factors. Malaria [22], Wernicke encephalopathy and Korsakoff syndrome [23], and neuronal death [24] are also produced by thiamine deficiency. Excessive consumption of alcohol causes thiamine deficiency [48].Reductions in thiamine-dependent enzymes have been implicated in multiple neurological disorders including Alzheimer's disease [25]. Many methods have been reported for the determination of thiamine in pure powder and in pharmaceutical forms. Direct titration, which is done with perchloric acid in non-aqueous medium, indirect complexometric and amperometric titrations [26]. However, in all these methods strong interferences among the basic compounds occur. Argentometric and mercurimetric [27] titrations also present interferences due to the halide salts of other vitamins, bases and minerals. In some cases, these methods make use of hazardous reagents and solvents. Thiamine, as hydrochloride or mononitrate (Figure 1), is a molecule that presents acidbase properties. Studies of acid-base titrations generally are contradictory and do not conclusively identify the titration reactions associated with the equivalence points because of the complexity of the deprotonation mechanisms inherent to thiamine structure [28-30]. **Material and Methods:**

The melting point was find out by open capillary tubes and were not corrected . The FTIR spectra were recorded on an FTIR Agilent Technologies spectrometer at 4000-650. The ¹H NMR spectra were recorded on Bruker spectrophotometer at 500 MHz using d₆- DMSO/CDCl₃ as a solvent and an internal reference was TMS. Chemical shifts were expressed in ppm. All the reagents and solvents were purchased from Merk Chemicals Pvt Ltd. TLC was used to monitored the reaction for purity and completion.

Experimental Method:

General procedure of synthesis:

Synthesis of 1,2-bis(4-substituted phenyl)-2-hydroxyethan-1-one:

The thiamine hydrochloride (1.75 g) was dissolved in water (about 5 ml) in a 50 ml round bottom flask. Ethanol (95%) 15 ml was added and the solution was cooled by swirling the flask in an ice water bath. Meanwhile, sodium hydroxide solution (5 ml) was cooled in a small conical flask in an ice bath. Then over a period of about 10 min the sodium hydroxide solution was added dropwise to the thiamine solution. Fresh substituted benzaldehyde (10 ml) was added to the reaction mixture. The mixture was heated gently on a water bath for about 90 min. The mixture was cooled to room temperature and then in ice bath to induce crystallization of the benzoin derivatives. If product separated as oil, the mixture was reheated until it was once again homogeneous. Then it was allowed to cool more slowly than before. Scratching of the flask with a glass rod may induce crystallization.

R: a:4-Cl, b:4-Br, c:4-CN, d:4-NO₂

Scheme 1

Physiochemical and analytical data for compounds:

1. 1,2-bis(4-chlorophenyl)-2-hydroxyethan-1-one (2a):

M.F: C14H10Cl2O2. M.W: 281. M.P: 132-134 oC. Yield: 80.88%. FT-IR: 725 (C-Cl), 1609(Ar-C=C), 1748 (C=O), 2869 (C-H), 3310 (O-H). ¹H-NMR (500 MHz, DMSO d6, δ ppm): 5.12 (s, 1H, -OH), 6.38 (S, 1H,-CH), 7.22-8.05 (dd, 8H, Ar-H). Anal. Calcd. (in %): C, 59.81; H, 3.59; Cl, 25.22; O, 11.38, Found: C, 59.10; H, 3.32; Cl, 25.99; O, 11.87.
2. 1,2-bis(4-bromophenyl)-2-hydroxyethan-1-one (2b):

M.F: C14H10Br2O2. M.W: 370. M.P: 126-128 oC. Yield: 78.53%. FT-IR: 693 (C-Br), 1623 (Ar-C=C), 1702 (C=O), 2891 (C-H), 3327 (O-H). 1H-NMR (500 MHz, DMSO d6, δ ppm): 5.19 (s, 1H, -OH), 6.56 (S, 1H,-CH), 7.12-7.92 (dd, 8H, Ar-H). Anal. Calcd. (in %): C, 45.44; H, 2.72; Br, 43.19; O, 8.65 Found: C, 45.01; H, 2.25; Br, 43.84; O, 8.21.

3. 4,4'-(1-hydroxy-2-oxoethane-1,2-diyl)dibenzonitrile (2c):

M.F: C₁₆H₁₀N₂O₂. M.W: 262. M.P: 134-136 °C. Yield: 79.23%. FT-IR: 2169 (C-CN), 1689 (Ar-C=C), 1723 (C=O), 2901 (C-H), 3357 (O-H). 1H-NMR (500 MHz, DMSO d6, δ ppm): 5.84 (s, 1H, -OH), 6.92 (S, 1H,-CH), 7.28-7.83 (dd, 8H, Ar-H). Anal. Calcd. (in %): C, 73.27; H, 3.84; N, 10.68; O, 12.20 Found: C, 73.86; H, 3.37; N, 10.21; O, 12.01.

4. 2-hydroxy-1,2-bis(4-nitrophenyl)ethan-1-one (2d):

M.F: C14H10N2O6. M.W: 302. M.P: 124-126 oC. Yield: 83.15%. FT-IR: 1538(N-O), 1373(N-O), 1675 (Ar-C=C), 1727 (C=O), 2905 (C-H), 3342 (O-H). 1H-NMR (500 MHz, DMSO d6, δ ppm): 5.99 (s, 1H, -OH), 6.98 (S, 1H,-CH), 7.23-8.58 (dd, 8H, Ar-H). Anal. Calcd. (in %): C, 55.64; H, 3.34; N, 9.27; O, 31.76 Found: C, 55.03; H, 3.87; N, 9.01; O, 31.13.

Conclusion :

The derivatives of 1,2-bis(4-substituted phenyl)-2-hydroxyethan-1-one (2a-d) have been synthesized by the condensation of substituted aldehydes catalysed by green agent as a thiamine hydrochloride in presence of ethanol as solvent. The completion of the reaction was monitored by the TLC. All the synthesized compounds (2a-d) were characterized and by their physical, spectral and elemental analysis.

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INDUCED MALE STERILITY: A GRACIOUS FOR PLANT BREEDING

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Introduction:

In general, the life cycle of plants consists of two phases, one prolonged vegetative or sporophytic generation and a short sexual or gametophytic generation. During the entire period a seed germinate, differentiate into root and shoot, undergoes vegetative growth and completes its life cycle once the flower is converted into fruit. Male sterility is a common phenomenon seen in higher plant species. Inability of a living organism for sexual reproduction is known as sterility and failure to produce functional pollen is called male sterility. In agriculture, male sterility has been proven as highly beneficial to produce hybrid seeds which are often superior in terms of quality and yield compared to their parents. Male sterility in plants was first reported within species and species specific hybrids as anther abortion in *Verbascum phoeniceum*. These male sterile plants are either selected from natural populations or may be induced artificially through mutagenesis. Anther and pollen development pathway consist of several stages involving formation of stamen, anther, pollen and anther dehiscence at maturity followed by pollen shed. Development of anther and pollen has been well studied in Arabidopsis, and many of the key genes involved in this pathway have been identified. During the process, the tapetum plays a central role in supplying nutrients, proteins, lipids and polysaccharides that are associated with pollen-wall formation and release of microspore. Thus, most often, tapetal cells are targeted for inducing male sterility, this indicates very crucial role of mitochondria in male organ development.

Different types of Male sterility performed in Plant Breeding

Male sterility in simple terms refers to failure of a plant to produce functional anthers or male gametes. Once the concept and importance of hybrid vigor was realized, this trait was utilized to incorporate into many crop species for crop improvement. The term heterosis or hybrid vigor means superiority of progeny to its parents in terms of yield, followed by other traits like biotic or abiotic stresses, its adaptability to different environmental conditions, its vegetation etc based on the type of crop involved. Hybrid vigor is considered for progenies (hybrid) that are developed by crossing two parents in either to incorporate desired traits of one parent into another or for development of new

hybrid. Development of hybrids is a challenging task in self-pollinated crops as it requires avoidance of self-pollination, which is conventionally carried out by emasculation method. It is a tedious job involving time, manpower and skill. Here male sterile lines come into picture with a leading role that permits hybrid seed production as well as commercial exploitation of heterosis. Male sterility is either phenotypic or genotypic in nature and the genotypic male sterility can be genetic or cytoplasmic.

Cytoplasmic Male Sterility

Cytoplasmic male sterility is not a common type of male sterility in nature and arises due to spontaneous mutation in organelle (especially in mitochondrial) involving rearrangements of the mitochondrial genome. Mutations in CMS are due to different recombination events that occur between homologous and nonhomologous genome of the two individuals resulting in new Open Reading Frames (ORFs).The CMS trait is maternally inherited, due to which transfer of the CMS character from the female parent to the progeny plant is carried out and the progenies are completely male sterile. During crossing a CMS plant is used as female partner or recipient, while a fertile plant is used as male partner (pollen donor). The contribution of the male parent is limited mainly to nuclear traits. In CMS system cytoplasm plays critical role for the development of male sterile or fertile lines. So, there are two types of cytoplasm Viz., S type (sterile) and N type (normal). Such male sterility is stable and can be seen in a large number of crops, however cannot be used were seed is an economic part. Use of CMS lines for generating hybrids was first employed in maize, thereafter it has been continuously expanded in major food crops like wheat and rice (cereals), onion, carrot, sugar beet, pepper (vegetables), brassicaceae, sunflower, soybean (oilseeds), sorghum, pear millet (millets), legumes. CMS provides an expedient mechanism to produce large populations of male-sterile plants for commercial F1 hybrid seed production. Apart from hybrid seed production, CMS system can also be utilized for basic studies. It can be used as a model system to study the interaction between the genetic material of both mitochondria and nucleus, different genes responsible for induction of male sterility and development of male gametophytes. It also helps us to study role of mitochondria in the development of reproductive organs in flowering plants and to develop seedless citrus varieties.

Cytoplasmic-Genetic Male Sterility (CGMS)

Cytoplasmic genetic male sterility (CGMS) is very common and available throughout the plant kingdom. It mainly arises due to the compatible interaction and double mutation

in both mitochondrial and nuclear genomes. Here also there are two types of cytoplasm as in case of CMS, however restorers with fertility (Rf) genes are also present. These genes don"t express unless they come in contact of S cytoplasm. So, a combination of S cytoplasm with rfrf produces only sterile lines, whereas N cytoplasm with RfRf combined with S cytoplasm and rfrf leads to fertile lines. The restore genes in CGMS differ from Rf genes present in genetic male sterility. During this interaction male sterility is induced by mitochondrial genes, whereas nuclear genes restore the male fertility (Rf genes) traits. This type of male sterility system was first identified in onion, later it was seen in other crops such as jowar, bajra, maize, cotton, sunflower, rice and wheat. It is highly reliable and stable system and can be used in both seed and vegetative propagated crops. The difference between CMS and CGMS is due to their fertility restoration mechanisms. In CMS male fertility is regulated by N type cytoplasm of the maintainer line, whereas in CGMS, dominant, fertility restoring genes are located in the nucleus of restorer line, leads to fertility restoration. For breeding and CGMS based hybrid seed production involves three different lines as used in CMS system.

Genetics and Mechanism behind CMS

The sterility factor (S) is present on mitochondrial DNA, whereas the fertility restorer allele (rf) is present on nucleus genome. For breeding and hybrid seed production CMS and CGMS system involves three different lines. A line (sterile) having both recessive allele (rfrf) and (S) factor (Sterile cytoplasm), B line denoted as maintainer of the female line (male sterile) and has fertile (N) cytoplasm with recessive restorer allele in nucleus (rfrf). When an identified A line (male sterile) is crossed with male fertile B line (maintainer) having recessive "rfrf" factor and cytoplasm (N) , all the resultant progenies are male sterile (with S cytoplasm) with same nuclear constitution (rfrf) as both A and B line has recessive allele for fertility restoration. The B line has an ability to make the A line set seed in the progeny, but the plant remains sterile, thus the CMS line is maintained (Figure 1a). If R line (restorer), which contains dominant allele for fertility restoration (RfRf) is identified for CMS then it can be used for hybrid seed production. This line has the ability to restore the male fertility of the hybrid plants (F1). These restorer lines are identified and are used for commercial hybrid seed production. So, when a CMS with S cytoplasm and rfrf is crossed with restorer line having N cytoplasm and dominant fertility restorer gene (RfRf), thus sterility inducing effect of CMS cytoplasm is reversed and leads to fertile hybrids. For large scale seed production, the progenies are selfed (Figure 1b). In the next phase, if a new genotype is intended to make CMS, then the pollen from the intended line will be used on the identified CMS line. This will constitute male sterile cytoplasm, but nucleus is composed 50 % original and 50 % intended line. Resultant CMS plant will be repeatedly back crossed with the pollen from the intended plant to restore nucleus of the intended line, but the cytoplasm will be male sterile.

Introduction of Male Sterility in Plant breeding

Under traditional breeding, the plant breeders emasculate the anthers by hand to prevent self-pollination for crossing, which is a labour intensive as well as cost expensive procedure, however, with the availability and use of male sterile lines hybrid seeds can be produced easily for research or cultivation. Sterility can be genetic (nuclear) termed as genetic male sterility (GMS) or can be due to cytoplasmic termed as (CMS) due to the genome of mitochondria. These sterile genes can be recessive or dominant. The recessive inheritance of GMS made it difficult to fully utilize its potential, because the resultant progeny is 50% sterile and 50% fertile, thus attention of breeders was inclined more towards CMS where 100% sterility is achieved. CMS is widespread in occurrence in higher plants and is reported in more than three hundred species (Kaul 1988). The majority of CMS are due to wide hybridization, spontaneous mutation, using mutagenic and chemicals hybridizing agents (CHA) as gametocides, using frontier tools of biotechnology such as genetic engineering. Many efforts have been made in this endeavor.

Wide Hybridization

Intergeneric hybridization involves cross between two different genera. In this type, crosses may not be successful due to highly diverse nature of the two parents. In such cases, the embryos are rescued by in vitro culture. Resultant hybrid may be sterile due to some abnormalities during meiosis. On the other hand, interspecific hybridization involves cross between species within the genera. It may be either between wild relative with a cultivated parent or within the cultivars, thus development of a new genotype (integration of cultivated nucleus into the cytoplasm of wild species). Breeding populations developed from different intervarietal crosses sometimes generate new genetic variation that may arise due to rare recombination of recessive alleles or transgressive segregation. In many crops like pearl millet, soybean, and cotton, cytoplasmic nuclear male sterility has been derived from recombinant populations in the past. The frequency of such useful recombination is, however, very low. This is being used as the most common and successful approach for breeding cytoplasmic nuclear male- sterile genotypes in many crop species of cereals, legumes. Wide crosses in development of CMS lines have been reported in oilseed crops.

Chemical Hybridizing Agents (CHAs)

Though different male sterility systems (GMS, CMS and CGMS) are available, still researchers felt the need for chemical induced male sterility in order to overcome the tedious process of emasculation, which involves tremendous manpower and money demanding for hybrid seed production. Chemical based induction does not involve identification, maintenance of male sterile and restorer lines. They bypass the issues like identification and restoration of male sterile line associated with GMS and is alternative method to generate male sterility in plants. They act as gametocide and target the male gamete by creating abnormalities, thus effecting development of pollen, its viability and its dehiscence without affecting the female fertility. The mode of action involves disruption of meiosis, interruption of anther development, degeneration of microspores, formation of thin walled exine, non-viable and irregular microspores development. They decrease starch deposition and lead to abnormal growth of tapetal layers. They either prevent or delay the process of dehiscence of normal anthers with viable pollen or inhibit viable pollen germination on stigma or elongation of pollen tube to egg for fertilization, thus leading to induction of sterility. Effect of different gametocides on pollen germination and sterility percentage has been reported in different crops. Induction of male sterility was reported by Moore (1950) in Zea mays L. with maleic hydrazide (MH). Foliar application of 50, 200, 800 μg/ml MH affected the pollen germination percentage of *Phaseolus mungo*, *P. aureus*, *Cyamopsistetra gonolob*, respectively.

Induction of Male Sterility Using Antibiotics in Crop

Antibiotics are powerful drugs used as antibacterial agents to combat diseases mainly caused by bacteria either destroying or by slowing down the growth of bacteria by targeting the extracellular organelle, which leads to mutation. The endosymbiotic (bacterial origin) nature of mitochondria and chloroplast makes this organelle vulnerable to antibiotics. Both of them have bacterial type ribosome in plants (chloroplasts: 70S and mitochondria: 70–80S) that differs with cytoplasm (80S). Some antibiotics (Streptozoocin) are potent mutagen and carcinogenic and leads to point mutations, while other antibiotics have chromosome breaking properties. Though the mechanism of action of these antibiotics on extracellular organelle is unclear, but it is believed that they induce the formation of toxic reactive oxygen species (ROS) in bacteria and imbalance mito-nuclear

protein by effecting mitochondrial translation. Tetracycline at low concentrations reported to induce proteotoxic stress in mitochondria that effects the expression of nuclear genes and hampers the function by modifying fission and fusion process in different organisms including plants.

Transgenic approach CMS system suffers with disease susceptibility, poor genetic diversity, and unstable restoration, which can be overcome by GMS system, however, generating malesterile female lines on large-scale by selfpollination is a challenging task. Development of frontier tools and technologies involving rapid methods to identify a MS gene, its isolation, transformation and its introgression into a desired genotype by genetic engineering method for development of a new male sterility systems in plants has been possible. Male sterility/ restoration system was reported in Brassica juncea using barstar gene for heterosis breeding . Recently, Liu and Yang (2020) transformed B. nivea atp9 RNAi vectors into tobacco plants and reported 50% pollens sterile, thus utilization of atp9 gene for developing male sterile lines in plants. Similarly, sunflower CMS associated orfH522 gene was transformed into tobacco plants and generated transgenic male sterile lines . Whereas, wheat mitochondrial atp9 was transformed to develop transgenic tobacco male sterile lines . Development of transgenic male sterile using pea anther specific promoter PsEND1 fused with ribonuclease gene in both model and crop plants by aborting anthers in the early stages of development. Very recently, a new technology CRISPR/Cas9 system has

emerged as an effective tool for genome editing (site specific) that generates sufficient amounts of mutation and is simple to operate. This, technique has been widely used to develop male sterile lines in different crops. A novel male-sterile line was developed by targeting stamen-specific gene SlSTR1 by CRISPR- Cas9 and developed a transgenic maintainer by transforming male-sterile plants with a fertility-restoration gene linked to a seedlingcolour gene in tomato (Du *et al.,* 2020). Artificially synthesized Cas9 gene with biased codons targeted MS8 gene.

Mitochondria -An Organelle for Male Sterility

Mitochondria and chloroplast are the extracellular organelles endowed with their own genome, and are maternally inherited. Experiments with protoplast fusion showed that CMS phenotype is not associated with chloroplasts. Significant differences on comparison of mtDNA from fertile and CMS plants. The trait CMS is associated with morphological and functional damage of mitochondrial and was supported by somatic hybridization and other genetic approaches in tobacco. Linkage between CMS and the mitochondrial was strongly supported by reversion of CMS phenotype. Mitochondria are the most active organelle that has a tendency to undergo repeated fusion and fission. They are the power house for energy generation and plays crucial role in respiratory energy production via tricarboxylic acid cycle (TCA) and oxidative phosphorylation in eukaryotes. Reduced levels of ATP are associated with increased concentrations of reactive oxygen species (ROS), especially when mitochondria are disfunction, which play a major role in the pollen production. All the events associated with anther development (microsporogenesis) are tremendous energy demanding, which is mainly fulfilled by the power house of the cellmitochondria. So, any abnormalities hamper the function of mitochondria, which in turn

targets the normal pollen development process leading to cytoplasmic male sterility. Mechanism lying behind the CMS development is not yet clear, as every male sterile system varies depending upon the mitochondrial gene that is responsible of sterility. However, role of energy deficiency, reactive oxygen species (ROS) , programme cell death (PCD) and signals from mitochondria affecting the nuclear pathway are evident. Variation in electron transport of Petunia and toxin-mediated membrane disruption due to toxin in maize plants, bacteria, provide some information about mechanisms for disruption of pollen development. Role of different mitochondrial genes in induction of male sterility in different crops has been reported, Succinate dehydrogenase, (SDH) is a part of mitochondrial complex II, and is involved in TCA cycle and respiratory electron transport chain. pollen abortion and reduced seed set by down-regulating SDH1-1 by RNA interference, which is important for gametophyte development in Arabidopsis. Similarly, role of mitochondria fission in pollen development in Arabidopsis. Dynamic related proteins play major role in mitochondria fission. 3D analysis of single tapetum cell from drp3a, drp3b, and elm1 mutant showed change in the volume and shape of tapetal cells, variation in morphology and number of mitochondria in the tapetum during pollen development. These abnormalities in mitochondrial fission led to reductions in pollen development due to mitochondrial disruption in the tapetum and pollen.

Conclusion:

In conclusion the contribution of male sterility in agriculture is unequivocal. Introduction of CMS is crop species is always interesting and useful. On one hand male sterility can be used in commercial seed production, while it can be used in recombination breeding programs for crop improvement. Enumerating the efforts and success in induction of male sterility is useful in understanding the basic mechanism as well as increasing the productivity of crops.

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BAND STRUCTURE OF MONOLAYER SILICENE USING FIRST-PRINCIPLE CALCULATIONS

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Abstract:

The two-dimensional materials are of recent interest due to their distinct properties compared to their bulk parents. In this chapter, the theoretical investigations of electronic band structure of monolayer silicene are presented. The electronic band structure calculations are performed using density functional theory. The optimized structure of monolayers of silicene is obtained using energy minimization technique and optimized lattice parameters are determined. The band structure of monolayer silicene shows the Dirac point and existence of massless Dirac Fermions. Some electronic properties namely, energy band gap and effective mass of carriers in monolayer silicene are investigated. Understanding of these electronic properties are very much crucial in investigations of electron transport properties of materials and their applications in various fields.

Keywords: 2D Materials; Silicene; Electronic Band Structure.

Introduction:

Materials science is an interdisciplinary field dedicated to the study, development, and application of materials. It bridges the gap between science and engineering, combining elements of physics, chemistry, and engineering to understand the structure of materials, their properties and performance. It enables the design and creation of novel materials with specific characteristics tailored for various applications. The field opens the exploration of the novel materials and unlocks the opportunities for transformative technologies for the future.

Two-dimensional (2D) materials are the sheet of atoms spread out in a flat plane. They are ultimate in thinness, with properties drastically different from their bulk counterparts[1,2]. Many 2D materials possess exceptional electron mobility, enabling rapid charge transport[3,4]. This property is crucial for developing high-speed electronic devices. Another key property of 2D materials is their optical behaviour due to their energy band gap. Some exhibit unique light-matter interactions, leading to potential applications in optoelectronics and photonics[3,5–7]. Due to these outstanding properties, 2D materials have gained attention of researchers from the last decade.

There are different class of 2D materials including elemental 2D materials, transition metal dichalcogenides, hexagonal boron nitride (h-BN) etc. The elemental 2D materials hold immense promise for future technological advancements due to their unique properties[8]. Silicene is a two-dimensional allotrope of silicon, similar to graphene, consisting of a single layer of silicon atoms arranged in a hexagonal honeycomb lattice. It was first theoretically predicted in 1994 and later experimentally observed in 2010[9]. Unlike the flat structure of graphene, silicene has a slightly buckled formation due to the larger atomic radius of silicon. The unique buckled honeycomb structure imparts distinct electronic properties. Silicene also exhibits a significant spin-orbit coupling, which can lead to potential applications in spintronics[10]. Additionally, its mechanical properties, such as flexibility and strength, further enhance its potentiality for nanoelectronics and optoelectronic applications. Silicene possesses these remarkable properties that make it a subject of intense research interest[11].

Electronic band structure calculation is a critical tool in materials science, offering a detailed view of behaviour of electrons in a material. By mapping out the energy levels of electrons as a function of their momentum and the analysis helps to determine the material behaviour. The nature of the conduction and valence bands further influences the conductivity and optical behaviour of material. Optimizing bandgap can enhance the performance of materials in devices[12]. Additionally, band structure analysis supports the development of advanced electronic and optoelectronic devices by predicting the modifications in material composition, structure and their effect on performance[13–15]. The band structure calculations are indispensable for advancement in fundamental research and practical innovations in materials science.

Density Functional Theory (DFT)

Density functional theory (DFT) is a computational quantum mechanical modelling method used in physics, chemistry and materials science to investigate the electronic structure of many body systems. Using this theory the properties of a many-electron system can be determined by using effective electron density[16,17]. DFT is successful in calculating the electronic structure of atoms, molecules and solids. It has been very popular in computational solid-state physics since the 1990s[11,18]. The importance of DFT in

physics and chemistry is evidenced by the 1998 Nobel Prize award to Walter Kohn for the development of density functional theory[19,20].

The foundations of density functional theory are Hohenberg Kohn and Lu Jeu Sham equations and Hohenberg-Kohn theorems[19,21]. Using these theorems most of the properties of the system can be determined from the known electron density. The Kohn Sham equations are a set of mathematical equations used to simplify the complex problem of understanding behaviour of electrons in atoms and molecules. The original Hohenberg Kohn theorem can easily be extended from its original formulation to cover a wide variety of physical situations.

Solving the Kohn-Sham equations is a computational task that involves an iterative process known as Self-Consistent Field (SCF) method. This method aims to find a solution that consistently satisfies the equations. The SCF calculation begins with an initial guess for the electron density of the system. Using this initial guess, an effective potential is constructed, which accounts for the interactions between electrons and nuclei. With this potential, the Kohn-Sham equations are solved to obtain new Kohn-Sham orbitals and corresponding electron density. This new density is then compared to the previous one, and the process is repeated until the calculated electron density converges to a stable solution. The main challenge in solving the Kohn-Sham equations is finding an accurate approximation for the exchange-correlation potential. In DFT, the pseudopotential is used as approximate potential for solving the Kohn -Sham equations[21]. A pseudopotential is effective potential used as an approximation for the simplified description of complex systems. This effective potential is constructed to replace the atomic all-electron potential (full-potential) such that core states are eliminated and the valence electrons are described by pseudo-wavefunctions.

Quantum Espresso is an open-source software package designed for electronic structure calculations and materials modelling[18]. Quantum Espresso employs a planewave basis set to represent the electronic wavefunctions. This approach offers several advantages, including systematic convergence and efficient treatment of periodic systems. It utilizes pseudopotentials, which replace the core electrons with effective potentials. Quantum Espresso offers a range of functions, from the simpler Local Density Approximation (LDA) to more complex hybrid potential function, enabling users to balance computational cost and accuracy. The core plane wave DFT functions of Quantum Espresso are provided by the Plane-Wave Self-Consistent Field (PWscf) component. PWscf is a set of

programs for electronic structure calculations within density functional theory using plane wave basis sets and pseudopotentials[20]. In this chapter, the calculation of electronic band structure of monolayer silicene is presented employing Quantum Espresso codes.

Computational Method

The calculations and analysis of electronic band structure of some 2D materials are carried out by first-principle calculations employing Quantum Espresso simulation package. Quantum Espresso is based on Density Functional Theory and it uses plane wave basis set and pseudopotentials. In the calculations, Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) scheme is employed for exchange – correlation potential approximation. The plane wave basis set and maximum kinetic energy cut-off is used to expand the wave function. The ultrasoft pseudopotential is used for solving the Kohn – Sham equations.

The band structure calculations using Quantum espresso involves the following steps. The first step is to determine the equilibrium atomic positions and lattice parameters of the crystal structure. This is achieved using energy minimization techniques. SCF calculation is performed to determine the ground state electronic structure of the system. This involves iteratively solving the Schrödinger equation until a self-consistent solution is obtained. The Brillouin zone, which is the reciprocal space of the crystal lattice, is sampled using a grid of k-points. For each k-point, the Schrödinger equation is solved to determine the allowed energy levels of the electrons. This results in a set of energy eigenvalues, which form the band structure. The calculated energy eigenvalues are plotted as a function of wave vector to obtain the electronic band structure. Analysis of the band structure can reveal important information about the electronic properties of the material, such as band gap, effective mass, and density of states.

Electronic Band Structure of Silicene

Silicene is a two-dimensional allotrope of silicon with layered structure. The primitive cell of silicene is considered for the optimization of system parameters using convergence test calculations and energy minimization. We have performed the convergence test calculations for energy convergence of self-consistence field using the parameters - plane wave kinetic energy cut-off, lattice parameter and k-point grid sampling. The final SCF calculations are performed with converged kinetic energy cut-off, optimized lattice parameter and k-point mesh.

Figure 1 shows the variation of lattice cell energy with plane wave kinetic energy cut-off for silicene primitive cell. In this convergence test calculation, the kinetic energy cut-off is varied from 5 Ry to 60 Ry and the corresponding lattice cell energy is investigated. The lattice cell energy decreases with increase in plane wave cut-off energy and convergences at 40 Ry and approximately remains same for cut-off energy >40 Ry. Any further increase in plane wave cut-off energy gives converged lattice cell energy. Therefore 40 Ry is used as kinetic energy cut-off for plane wave basis set.

Figure 1: Variation of lattice cell energy with plane wave cut-off kinetic energy of silicene

Figure 2: Variation of crystal cell energy with lattice parameter of silicene primitive

cell

Figure 2 shows the variation of crystal cell energy of silicene primitive cell with lattice parameter. The lattice parameter is varied from 3.5 Å to 4.5 Å and corresponding energy is calculated. Using the concept of energy minimisation, the lattice constant for optimised structure is obtained. It is observed that for lattice parameter value of 3.87 Å the energy attains minimum. This represents optimised lattice parameter for stable silicene primitive cell. The lattice parameter obtained is in good agreement with the previous reports[22].

The energy convergence is tested for silicene supercell with different k-point mesh sampling. It is observed that for 4x4x1 Brillouin zone k-point mesh, the energy converges and any further increase in k-point grid the energy remains constant. Therefore, the 4x4x1 k-point mesh is used for further self-consistent field calculations. Using the optimized parameters – plane wave kinetic energy cut-off, lattice parameter and k-point mesh sampling – the energy convergence of self-consistence field calculations are performed for relaxed silicene structure. The convergence of self-consistence field converges after 6 iterations.

The optimized structure of silicene monolayer is shown in figure 3. The top view and side view of silicene monolayer is shown. The silicene exhibits buckled hexagonal lattice structure in contrast to flat structure of graphene. The lattice parameters of silicene are $a = b = 3.87$ Å, and $\alpha = \beta = 90^0$, $\gamma = 120^0$. In the buckled structure, the alternate atoms are located in two parallel planes and the perpendicular distance between two parallel planes is called buckling parameter (Δ) . In silicene, the buckling parameter Δ is observed to be 0.44 Å. The buckling arises due to the larger atomic size of silicon compared to carbon and this buckling can impact the electronic band structure and electronic properties of silicene[11].

Figure 4 shows the first Brillouin zone of silicene monolayer with representation of high symmetry points. High symmetry points are specific points within the Brillouin Zone of a crystal lattice that possess a high degree of symmetry. The high symmetry points vary depending on the crystal structure. The Γ – point represents the centre of symmetry and located at the centre of Brillouin zone. M – point is on the face of the Brillouin Zone and K – point is symmetry point on the edge of the Brillouin Zone for hexagonal structure. The band structure calculations are performed along specific paths connecting high symmetry points and in silicene the symmetry path is $\Gamma - M - K - \Gamma$.

Figure 3: The optimized buckled hexagonal structure of silicene monolayer.

Figure 4: The first Brillouin zone of silicene monolayer and high symmetry points

Figure 5 shows the electronic band structure and density of states of silicene monolayer obtained using density functional theory employing Quantum Espresso. It is the plot of the energy of electrons against their wave vector (momentum) in reciprocal space. The band structure is plotted with normalized Fermi energy in energy axis. Interestingly, for silicene the Dirac point is observed at K – point as in graphene[23]. A Dirac point is a special point in the band structure of certain materials, where the conduction and valence bands meet at a single point. This intersection forms a conical shape, referred as a Dirac cone. At this point, electrons behave as massless Dirac fermions, exhibiting the high carrier mobility, quantum Hall effect and Klein tunnelling[23]. This also represents the semimetal behaviour of silicene and makes it a promising material for future electronic devices. The near-zero energy band gap $(\sim 18.3 \, \text{meV})$ is observed for silicene at Dirac point.

Effective Mass of Carriers in Silicene Monolayer

The effective mass of carriers can be calculated from electronic band structure using the expression,

$$
m^* = \frac{\hbar^2}{\left(\frac{d^2 E}{d k^2}\right)}\tag{1}
$$

where, \hbar is reduced Planck's constant and $\frac{d^2E}{dt^2}$ $rac{u}{dx^2}$ represents the second derivative of electronic band at conduction band minimum (electron) or valence band maximum (hole). The effective mass of the electrons and holes are calculated using band structure of monolayer silicene. In silicene, the effective mass of electrons and holes are found to be 0.087 m_0 and -0.089 m_0 , respectively, where m_0 is the rest mass of electron. The effective mass of carriers is very low and shows existence of massless Dirac fermions. This is in good agreement with the previous reports[24]. The low effective mass of the carriers leads to ultra-high carrier mobility, quantum hall effect and topological phenomena.

Summary:

In summary, the electronic band structure and density of states calculations for monolayers of silicene are performed using density functional theory. The optimized hexagonal structure of silicene is obtained and lattice parameter of silicene, is found to be 3.87 Å. The electronic band structures of silicene have shown Dirac point at K – symmetry point and this corresponds to existence of massless Dirac fermions. Nearly zero energy band gap is noticed in monolayer silicene. The effective mass of carriers in silicene are very low and leads to ultra-high carrier mobility. These studies are helpful in understanding the basic physics of electronic band structure and aids to investigations of some electronic properties of the two-dimensional materials.

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COTTON FIBERS: CRYSTAL STRUCTURE AND ELASTO-MECHANICAL PROPERTIES

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Abstract:

The knowledge of microstructural properties is essential to understand and to define the physical properties of any material. In view of this, the molecular structure, and the elastic constants of seven different cotton fibers were determined utilizing the Linked Atom Least Square method (LALS) method by considering the Wide-Angle X-ray Scattering (WAXS) data of selected fibers. The fibers are belonging to monoclinic unit cell with space group P21. The different elastic constants are computed by using first principle calculation. The Voigt approximation was used to determine the Bulk modulus (K), Young's modulus (Y), Shear modulus (G), Poisson's ratio (v) and Linear tensor moduli (β). The 3dimensinonal view of all the moduli show the directional dependencies and the stability of the fiber. The variation of elastic moduli from the 3-dimensional spherical shape is because of anisotropy of the material.

Keywords: XRD; Cotton; LALS; ELATE; Elastic Constants.

Introduction:

In the textile industry, cotton is called the "king of fibers". Cotton is belonging to "Gossypium" family. It is very much fluffy soft, staple fiber and cultivates in a capsule around the seed of cotton plant. It comes under "seed fibers" category due to fibers of cotton are produced in a capsule situated around cotton seeds. Among natural fibers, more than 90% are having vegetable origin, in which cotton contributes more than 80%. Due to its high air permeability, cotton fabric is extremely popular for its property of "breathability" [1]. Each cotton lint is made up of concentric layers, the longitudinal structure of cotton consists of base, body and the tip. The cross-sectional structure involves cuticle, primary wall, winding layer, secondary wall, lumen wall and lumen [1]. The chemical composition of cotton fiber includes (91-94%) of cellulose, (6-8%) of water, (0.5- 1%) of waxes and fats, (1-1.5%) of proteins, (0.5-1%) of protoplasm and pectin's, and (0.2-

1%) of mineral salts [1]. Botanically there are four commercially important cotton species are identified such as hirsutum, barbadense, aboreum, and herbaceum [2]. These imperative breeds includes many varieties developed using breeding methods to grow improved quality of fibers such as increasing yield, increasing of disease resistance, increasing of strength and uniformity etc. Gossypium hirsutum is a tetraploid cotton, this breed mainly grown in the region of United States of America. These varieties also called American Upland cotton. Among the world production of cotton, Upland cotton provides 90% of present world production. The staple length of these cottons varies from 22-36 mm and the value of micronaire vary from 3.8-5. These breeds of fibers are widely utilized for industrial products, apparel and home furnishings. Gossypium barbadense is also a tetraploid cotton, which has an origin of South America, it provides longest staple length that is greater than 35 mm. The micronaire value will be less than 4. This breed supplied total 8% of raw fiber for the world production of cotton fiber. Gossypium aboreum and herbaceum are also diploids cotton fibers, these are also termed as "Desi" cottons. The staple length of these fibers ranges from 9.5-19mm, the micronaire value will be greater than 6. These fibers are commercially grown in the countries of India, China and Pakistan [2]. The raw cotton fiber after mechanical cleaning and ginning is almost 90% of cellulose, the non-cellulosic constituents of cotton located in primary wall, and in the lumen. In addition to conventional grown of cotton fibers, now a day's extensive research is undergoing to produce new hybrids and contemporary biotechnology to develop biotech cotton fibers [3, 4] which increase the production flexibility.

Though there is a wide practical knowledge on the processing of cotton fibers, a more in detail micro-structural study and exploration will certainly improve the quality of cotton fiber. The cellulose is linear $β$ -(1-4)-D-glucan, in this cell wall, cellulose occurs as small crystalline microfibrils and packed as multilayered structure [2]. The cotton fiber is semi-crystalline material, in the sense of "lacking of definite form". There are several reasons for this semi-crystalline structure such as cotton cellulose has broad molecular weight distribution, leveling-off degree of polymerization, imperfection in the solid that is microfibrils breaking inside the fiber, causing discontinuities, disorder on the crystallite surfaces etc. [2]. It is important to note that, the Elasto-mechanical properties of any material significantly contributes to the quality of the material, in this sense, in this study we attempted to study the structural and elastic properties of the several cotton fibers which are grown in India. Employing the raw powder X-ray diffraction data of selected cotton fibers, the linked atom least square (LALS) [5] technique is utilized to get the

molecular structure of the fibers and using inhouse mathematical program the elastic constants are obtained and the elastic tensor analysis tool called ELATE [6] is used to plot the variation of elastic moduli along their spatial directions.

Varieties of Cotton Fibers

The seven different varieties of cotton fibers are collected from the University of Agricultural and Horticultural Sciences, Shivamogga, India and used for different studies after the ginning process. The following varieties are used for this investigation [7],

- DCH-32 cotton fiber is an interspecific hybrid of XS B 425 YF (Gossypium barbadense) and DS 58 (Gossypium hirsutum).
- MCU-5 is the pedigree of Gatooma, Sea Island-542, MCU-1, and MCU-2.
- LRA is the cross breed of Laxmi, Reba B.50 and AC 122.
- Shankar is a product of G. Dot 100 and G. Cot 100 varieties.
- Dharwar is the hybrid cotton developed from Gossypium hirsutum
- Suvin is the pedigree of St vincent and sujata cotton
- Kodai is also developed from Gossypium hirsutum family

X-ray Diffraction Studies

Figure 1: XRD pattern of varieties of cotton fibers

X-ray Diffraction (XRD) method is the widely used technique to study the material properties of single crystal, semi crystalline and poly crystalline materials. The powdered samples of all the seven varieties of cotton were taken and fixed into sample holder. This sample holder mounted onto the goniometer in a way that rotational axis parallel and perpendicular to the fiber axis and X-ray beam respectively. Here we employed digital imaging plate system (Dip-3200). The wavelength of X-ray was 0.71072 Å with Mo target. The obtained imaging plate X-ray diffraction pattern (Weissenberg geometry) [8] for all the seven cotton fibers are as shown in the Fig. 1. The imaging plate data were converted to line profile analysis by scanning intensity versus 2θ by utilizing MOSFLM software package which was supplied along with the XRD machine.

X-ray Diffraction Data Analysis

The Gaussian deconvolution procedure is employed as XRD peak profile which is available in the residual peak fitting software package Peakfit® [9]. This process of peakfitting is continued until to obtain maximum r^2 and minimum residual of random distribution [5]. Each Bragg reflections were identified by resolving the symmetric peak pair positions available in the Peakfit®. This Peakfit® software also gives full width at half maximum (FWHM) value for each Bragg reflections, these FWHM data were used to obtain crystallite size using Debye Sherrer equation and the shape of ordered region were plotted along their observed reflection and reported in our earlier study [7]. The obtained 2θ and X-ray wavelength were used along with powder indexing helper tool Checkcell® [10, 11] to obtain the miller indices (hkl) values for observed reflections. The unit cell parameter of all the seven cotton fibers are a = 7.350 Å, b = 8.220 Å, c = 10.370 Å, α = β = γ 0° and γ = γ 6.28° with space group $P2₁$ and belong to monoclinic crystal system [7].

Crystal Structure using Linked Atom Least Square (LALS) Method

The LALS mathematical program was initially composed utilizing Algol by Alan Wonacott and it is hence extended and translated to Fortran by R. Chandrasekaran, David Dover, David Hukins, and Bill Scott [10]. The objective of this code is to carry out the refinement of sub-atomic structures of polymer materials and to get the model of molecular structures utilizing standard bond angle and bond lengths [12, 13]. The LALS software package was compiled on LINUX based PC. The pyranose rings of cotton cellulose linked by β (1-4) glucosidic linkage which undergo the chair conformation, it is the most conceivable conformation of solid state [13]. For the stand bond length and bond angle we referred to our earlier article [14]. The special positions of polymer chains for example ($u =$

 0.25 , $v = 0.0$) and (u = 0.75, v = 0.0) were located on the crystallographic axes and these were employed to pack the two polymers chains with 2/1-helical symmetry in a unit cell along with P21 space group. To carry out the refinement the azimuthal angles μ_1 and μ_2 are searched in the asymmetric unit by evaluating the R factor. Afterward, the positional parameters ω of the polymer chain is distinguished along c direction. Then, this model was refined for all the reflections. The methodology followed to get the atomic and molecular structures using LALS program is represented in the flowchart mentioned in Fig. 2.

Figure 2: Flowchart to compute molecular and atomic structures of cotton fibers employing LALS method

The molecular model of cotton fibers is as represented in the Fig. 3. The projection of crystal and molecular structure along a, b, and c axes is as shown from the Fig 4 to 8. The crystal structure of DCH-32, Dharwar, and Yemini cottons were studied in our previous articles [13, 15].

Figure 3: The molecular model of MCU-5, LRA, Shankar, Suvin and Kodai cotton

fibers.

Figure 4: The molecular structure of MCU-5 cotton fiber along a, b, and c projections

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Figure 5: The molecular structure of LRA cotton fiber along cotton fiber along a, b, and c projections

Figure 6: The molecular structure of Shankar cotton fiber along cotton fiber along a, b, and c projections

Figure 7: The molecular structure of Suvin fiber cotton fiber along a, b, and c projections

Figure 8: The molecular structure of Kodai fiber along a, b, and c projections

Kodai

Determination of Elastic Constants

The modulus of elasticity impacts essentially on the structure and morphology of cotton fiber [16]. The number of elastic constants depends on the symmetry of a system, there are 13 independent elastic constants for a monoclinic unit cell [17] and that can be expresses as,

$$
C_{ij} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & - & C_{15} & - \\ C_{21} & C_{22} & C_{23} & - & C_{25} & - \\ C_{31} & C_{32} & C_{33} & - & C_{35} & - \\ - & - & - & C_{44} & - & C_{46} \\ C_{51} & C_{52} & C_{53} & - & C_{55} & - \\ - & - & - & C_{64} & - & C_{66} \end{bmatrix}
$$

The detailed procedure to compute the elastic constants for a monoclinic unit cell is reported in our previous study [18]. The elastic constant matrix $|C_{ij}|$ is computed by reducing 81 independent constants to 21 again reduced to 13 for a monoclinic unit cell. The following relations have been used to compute the elastic constants [18],

 $C_{22} = C'_{22} + C''_{22} + C_{22}'''$ (1)

where C'_{22} is the primary bond, C''_{22} is the inter-chain bond and C''_{22} is the intra-chain bond. According to Treloar [18],

$$
C'_{22}=CL^2/V \hspace{0.1in}(2)
$$

where L is the repeating unit in a chain direction. V is the volume of the unit cell. C_{22}'' is computed using,

$$
C_{22}^{"'} = \left(\frac{2D_2^2}{V}\right) \left[C_{h_2} \sin^2 \phi_2 + \left(\frac{K_{h_2}}{h_2^2}\right) \cos^2 \phi_2\right] \tag{3}
$$

The angle obtained from (05–H...03) is ϕ_2 . According to Treloar

$$
C_{11} = \left(\frac{2D_1^2}{V}\right) \left[C_{h_1} \cos^2 \phi_1 + \left(\frac{K_{h_1}}{h_1^2}\right) \sin^2 \phi_1\right] \cos^2 \Omega \quad (4)
$$

\n
$$
C_{22}''' = (2/V) \left(C_{h_1} h_1^2 \sin^4 \phi_1 + C_{h_3} h_3^2 \sin^4 \phi_3 + K_{h_1} \sin^2 \phi_1 \cos^2 \phi_1 + K_{h_3} \sin^2 \phi_3 \cos^2 \phi_3\right) (5)
$$

\n
$$
C_{33} = \left(\frac{2D_3^2}{V}\right) \left[C_{h_3} \cos^2 \phi_3 + \left(\frac{K_{h_3}}{h_3^2}\right) \sin^2 \phi_3\right] \cos^2 \phi_3 \quad (6)
$$

\n
$$
C_{12} = \left(\frac{2D_1 h_1}{V}\right) \left[C_{h_1} - \left(\frac{K_{h_1}}{h_1^2}\right)\right] \sin^2 \phi_1 \cos \phi_1 \cos \Omega_1 \quad (7)
$$

\n
$$
C_{23} = \left(\frac{2D_3 h_3}{V}\right) \left[C_{h_3} - \left(\frac{K_{h_3}}{h_3^2}\right)\right] \sin^2 \phi_3 \cos \phi_3 \cos \Omega_3 \quad (8)
$$

Various symbols and notations were referred from the Treloar principle [18]. Employing the relations from equation (1) to (8) the elastic stiffness matrix was computed for all the studied fibers and are as mentioned in the Table 1.

For materials having anisotropic property, it is necessary to study and analyze their elastic properties such as E, G, K, v, and β. For this, the computed elastic constants were used to the elastic tensor analysis tool called ELATE and obtained the elastic moduli using the Voigt principle. This tensor analysis tool also yields volumetric and anisotropic feature of a material. ELATE gives 3-dimensional spherical plot of elastic moduli, it also permits to obtain 2-deimensional projections along (xy), (xz) and (yz) planes. The obtained images of elastic moduli for the studied cotton fibers are shown from the Figures 9 to 12.

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Figure 10: Spatial variation of 'G'

Figure 12: Spatial variation of 'β'

Summary:

Clothing has become a fundamental and essential need for human beings. To explore more about its structural and physico-mechanical properties for the effective applicability of these materials, the powder XRD data were obtained for the studied fibers and these data were resolved for precision and accuracy by utilizing Peakfit® software. Employing Checkcell® software the cell parameters were obtained. The LALS program has been utilized to obtain the crystal structure of the studied fibers. This program depends on a
model where two chains in a unit cell are parallel with the alike conformations with refinement against the XRD data. From the obtained results it is observed that, the positions of C=O group of chains in a unit cell along c-projection oriented in one direction at a particular position whereas in the reverse direction in another position. All the samples which are employed for our study are cotton, however, the obtained crystal structure seems same for all the fibers, but one could see a minor changes in the bond length, bond angle, stero-chemical energy etc., Employing ELATE web application tool, the spatial variation of elastic moduli were obtained and these 3-dimensional figures infers that, the deviation of elastic moduli from their spherical shape is due to the strong anisotropy of the material and more variation can be seen in the Yemini cotton than the cotton which are grown in India. This is due to impact of soil content, the minerals which are present in the soil, the environment where the cotton fibers are cultivated etc., This novel method can be employed to any material in order to study their structural and Elasto-mechanical properties.

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A COMPREHENSIVE REVIEW ON THE SYNTHESIS OF METAL OXIDE NANOPARTICLES

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Abstract:

Nanomaterials, particularly metal oxide nanoparticles (MONPs), have garnered significant attention due to their unique properties and wide-ranging applications. This review explores the synthesis methods of MONPs, highlighting advancements and emerging trends. Traditional techniques like sol-gel, hydrothermal, and solvothermal processes are examined for their control over particle size, morphology, and crystallinity despite their limitations such as high temperatures and the use of toxic chemicals. Innovative approaches like green synthesis using biological entities and bottom-up techniques like chemical vapor deposition and atomic layer deposition are also discussed for their ability to precisely control nanoparticle properties while minimizing environmental impact. The review further explores into the diverse applications of MONPs in catalysis, sensing, biomedical imaging, and environmental remediation, emphasizing their efficiency and sensitivity in these domains. The paper identifies persistent challenges such as the need for scalable and cost-effective synthesis methods and the assessment of biocompatibility and environmental impact. By critically analyzing current synthesis techniques and their implications, this review aims to elucidate the state-of-the-art in MONP synthesis and identify opportunities for future research.

Keywords: Nanomaterials, Metal Oxide, Synthesis.

Introduction:

Nanomaterials, with their unique physical and chemical properties arising from their nanoscale dimensions, have sparked immense interest in the scientific community and industry alike, propelling the field of nanotechnology to the forefront of research and innovation [1]. Among these nanomaterials, metal oxide nanoparticles (MONPs) hold particular significance due to their diverse properties and wide-ranging applications across various domains. The synthesis of MONPs has witnessed significant advancements in recent years, driven by the pursuit of tailored properties and enhanced functionalities for

specific applications [2]. The synthesis of MONPs encompasses a multitude of techniques, each with its own set of principles and characteristics. Traditional methods such as sol-gel, hydrothermal, and solvothermal processes have long been employed for the production of MONPs, offering control over particle size, morphology, and crystallinity. However, these methods often suffer from limitations such as high temperatures, harsh reaction conditions, and the use of toxic chemicals [3]. In response, researchers have increasingly turned towards innovative approaches, including green synthesis methods utilizing biological entities such as plant extracts and microorganisms, as well as bottom-up techniques such as chemical vapor deposition and atomic layer deposition, enabling precise control over nanoparticle properties while minimizing environmental impact and energy consumption [4], [5]. The continuous evolution of synthesis techniques has led to the development of MONPs with tailored properties optimized for specific applications. These advancements have significantly expanded the scope of MONP utilization across diverse fields. In catalysis, MONPs serve as highly efficient catalysts for various chemical reactions, owing to their large surface area, high reactivity, and tuneable catalytic properties [6]. Similarly, in sensing applications, MONPs exhibit exceptional sensitivity towards target analytes, making them ideal candidates for biosensors, gas sensors, and environmental monitoring devices. Furthermore, in biomedical imaging and therapy, MONPs offer promising prospects for early disease detection, targeted drug delivery, and non-invasive imaging modalities, owing to their biocompatibility, tuneable optical properties, and surface functionalization capabilities [7], [8], [9], [10]. Additionally, in environmental remediation, MONPs demonstrate remarkable efficacy in pollutant removal, wastewater treatment, and soil remediation, contributing to sustainable solutions for environmental challenges [8], [9]. Despite significant progress, several challenges persist in the synthesis and application of MONPs. These include the need for precise control over nanoparticle size, morphology, and surface chemistry, as well as the development of scalable and cost-effective synthesis methods compatible with large-scale production [11], [12]. Furthermore, the biocompatibility, stability, and long-term environmental impact of MONPs must be thoroughly assessed to ensure their safe and sustainable deployment across various applications [10]. In this context, this review paper aims to provide a comprehensive overview of the synthesis methods of MONPs, focusing on recent advancements and emerging trends in the field. By critically analysing the principles, advantages, and limitations of different synthesis techniques, as well as their implications

for nanoparticle properties and applications, this review aims to elucidate the current state-of-the-art in MONP synthesis and identify key challenges and opportunities for future research. Moreover, by exploring the diverse applications of MONPs across catalysis, sensing, biomedical imaging, and environmental remediation, this review aims to highlight the transformative potential of MONPs in addressing contemporary challenges and driving innovation across various domains [13]. Through its synthesis of existing knowledge and identification of future research directions, this review paper endeavours to contribute to the advancement of the field of metal oxide nanoparticles and facilitate their widespread adoption for diverse applications, thereby realizing the full potential of nanotechnology in addressing societal needs and promoting sustainable development.

1. Synthesis of Metal Oxide Nanoparticles

Metal oxide nanoparticles (MONPs) are synthesized through various techniques, each offering unique advantages and challenges. The synthesis approach of nanoparticles can be classified in to two categories such as,

1.1 Top-down approach

It involves the fabrication of nanoparticles by breaking down larger bulk materials into smaller dimensions. This method typically involves mechanical, physical, or chemical processes to reduce the size of the starting material to nanoscale dimensions. The topdown approach offers advantages such as precise control over nanoparticle size, shape, and composition, as well as scalability for large-scale production. However, it may require high energy inputs, specialized equipment, and may not always yield monodisperse nanoparticles. Despite these challenges, the top-down approach remains a valuable method for nanoparticle synthesis, particularly for applications where precise control over nanoparticle properties and large-scale production are critical. It complements bottom-up approaches and provides a versatile toolkit for nanoparticle fabrication across various fields, including electronics, optics, catalysis, and biomedicine [14].

1.1.1 Mechanical techniques

1.1.1.1 Mechanical Milling

Mechanical milling, a quintessential technique in the realm of nanotechnology, embodies the top-down approach to synthesizing metal oxide nanoparticles. This method, rooted in the principles of mechanical energy transfer and solid-state physics, enables the controlled production of nanoparticles with precise size, shape, composition, and morphology, thereby unlocking a myriad of applications in fields such as catalysis, sensing,

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and biomedical engineering [15], [16]. At its core, mechanical milling involves the intensive grinding and fracturing of bulk materials, typically metallic or ceramic powders, in a highenergy ball mill. The process begins with loading raw materials and grinding media into the milling chamber, where the kinetic energy generated by the collision of balls and powders initiates mechanical alloying or milling. This energetic agitation induces a series of mechanical deformations, including cold welding, fracturing, and re-welding of particles, ultimately reducing particle size to the nanoscale regime. One of the distinguishing features of mechanical milling is its ability to achieve a high degree of homogeneity and compositional uniformity in the resulting nanoparticles [17]. Through careful control of milling parameters such as milling time, rotational speed, and ball-to-powder ratio, researchers can tailor the synthesized nanoparticles' size distribution and chemical composition to meet specific application requirements. Moreover, mechanical milling offers versatility in the synthesis of a wide range of metal oxide nanoparticles, including but not limited to titanium dioxide, zinc oxide, and iron oxide. By selecting appropriate precursor materials and milling conditions, researchers can precisely engineer the properties of the nanoparticles, including crystallinity, phase composition, and surface morphology.

1.1.1.2 Mechanochemical method

The Mechanochemical method represents a sophisticated top-down approach to synthesizing metal oxide nanoparticles, leveraging the principles of mechanical energy transfer and chemical reactions within a milling environment. Unlike traditional mechanical milling, mechanochemical synthesis integrates chemical transformations alongside mechanical grinding, enabling precise control over nanoparticle composition and properties[17]. At the heart of mechanochemical synthesis lies the intimate coupling of mechanical forces and chemical reactions, achieved by incorporating reactive precursors or additives into the milling process. As the milling action commences, the mechanical energy imparted by grinding media induces localized deformation and fracture of the precursor materials, exposing fresh surfaces and promoting interparticle interactions[18]. Concurrently, the presence of reactive species initiates chemical reactions at the newly exposed surfaces, leading to the formation of desired metal oxide nanoparticles. One of the key advantages of the mechanochemical method is its ability to facilitate complex chemical transformations at ambient conditions, obviating the need for high temperatures and harsh reaction conditions associated with conventional chemical synthesis routes. This feature

not only simplifies the synthesis process but also offers environmental and energy-saving benefits. Mechanochemical synthesis affords precise control over nanoparticle properties, including size, morphology, and crystallinity, through modulation of milling parameters and composition of precursor materials. By tailoring the choice of reactants, milling duration, and milling atmosphere, researchers can finely tune the characteristics of the synthesized metal oxide nanoparticles to meet specific application requirements. This methodology holds promise for a wide range of applications spanning catalysis, energy storage, and biomedical technologies, driving innovation in materials science and nanotechnology.

1.1.1.3 Wet grinding method

The wet grinding method represents a top-down approach to synthesizing metal oxide nanoparticles by leveraging the benefits of liquid environments to facilitate particle size reduction and chemical transformations. This method involves the suspension of precursor materials in a liquid medium, typically a solvent or a mixture of solvents, followed by intensive grinding to induce particle fragmentation and chemical reactions. In the wet grinding process, the liquid medium serves multiple crucial roles [19]. Firstly, it acts as a dispersing agent, ensuring the uniform distribution of precursor particles throughout the medium and preventing agglomeration. Secondly, the presence of the liquid medium promotes the formation of a dynamic environment where mechanical forces generated during grinding are efficiently transmitted to the suspended particles, leading to their fragmentation into smaller entities. Additionally, the liquid medium provides a medium for chemical reactions to occur, facilitating the formation of metal oxide nanoparticles through precursor decomposition, dissolution, and reprecipitation. The wet grinding method offers several advantages for the synthesis of metal oxide nanoparticles. Firstly, it enables precise control over particle size and morphology by adjusting parameters such as grinding time, grinding speed, and liquid medium composition. Secondly, the use of liquid environments allows for the incorporation of additives or surfactants, which can influence the crystallinity, surface chemistry, and dispersibility of the synthesized nanoparticles. Moreover, the wet grinding approach is compatible with a wide range of precursor materials, including metal salts, metal oxides, and metal hydroxides, offering versatility in nanoparticle synthesis [19].

1.1.2 Etching method

1.1.2.1 Dry etching

Dry etching, an integral component of the etching method in the top-down synthesis approach of metal oxide nanoparticles, revolutionizes nanoparticle fabrication through precise material removal via gas-phase chemical reactions or physical bombardment. Unlike wet etching, which employs liquid-phase reactants, dry etching operates in gas or plasma environments, offering distinct advantages in terms of precision, selectivity, and control over nanoparticle morphology. In dry etching, the process begins with the deposition of a mask layer, typically composed of materials such as silicon dioxide or photoresist, onto the substrate surface. This mask layer serves as a protective barrier, shielding certain regions from etching while allowing targeted material removal elsewhere. Subsequent exposure to reactive gases or plasma initiates chemical reactions or physical bombardment, selectively removing material from the exposed regions of the substrate [20]. One of the key advantages of dry etching is its exceptional control over nanoparticle size, shape, and distribution. By precisely defining the dimensions and patterns of the mask layer, researchers can dictate the spatial arrangement of metal oxide nanoparticles with nanometer-scale precision. Additionally, dry etching offers high selectivity, allowing for the precise removal of specific materials while leaving others intact, thereby enabling complex nanoparticle architectures and heterostructures. Dry etching facilitates scalability and reproducibility in nanoparticle synthesis, making it suitable for large-scale manufacturing processes. The ability to precisely control etching parameters such as gas composition, pressure, and temperature ensures uniformity and consistency across batches, essential for industrial applications. This technique holds promise for a wide range of applications, including electronics, photonics, and catalysis, driving advancements in nanomaterials research and technology [21].

1.1.2.2 Laser-assisted etching

Laser-assisted etching stands as a cutting-edge technique within the etching method of the top-down approach for synthesizing metal oxide nanoparticles. This method harnesses the power of laser irradiation to induce selective material removal, offering unprecedented control over nanoparticle fabrication with high precision and spatial resolution [22]. In laser-assisted etching, the process begins with the deposition of a masking layer onto the substrate surface, defining the desired pattern or structure for nanoparticle synthesis. The substrate is then subjected to laser irradiation, which interacts

with the material through mechanisms such as photothermal heating, photochemical reactions, or photophysical processes. This interaction results in localized material removal from the exposed regions of the substrate, guided by the spatial distribution of laser energy. One of the key advantages of laser-assisted etching is its exceptional control over nanoparticle size, shape, and distribution at the nanoscale. The precise modulation of laser parameters such as wavelength, intensity, and pulse duration enable tailored material removal with submicron resolution, facilitating the fabrication of intricate nanoparticle architectures and nanostructures. Laser-assisted etching offers versatility in nanoparticle synthesis by accommodating a wide range of materials and substrates. From semiconductors to metals to ceramics, various materials can be processed using laser irradiation, opening up possibilities for diverse nanoparticle compositions and functionalities [23]. Laser-assisted etching exhibits rapid processing capabilities and minimal thermal impact on the substrate, making it suitable for high-throughput and temperature-sensitive applications. The non-contact nature of laser processing also reduces contamination risks and allows for precise control over etching depths and dimensions.

1.1.2.3 Wet etching

Wet etching serves as a fundamental technique within the etching method. This method entails the selective removal of material from a substrate through immersion in liquid-phase etchants, enabling precise control over nanoparticle fabrication with versatility and scalability. In wet etching, the process begins with the deposition of a masking layer onto the substrate surface, defining the desired pattern or structure for nanoparticle synthesis [24]. The substrate is then immersed in a liquid etchant solution, which selectively reacts with the exposed regions of the substrate, inducing material dissolution or decomposition. Through careful selection of etchant composition and process parameters, researchers can tailor the etching rate and selectivity, controlling the dimensions and morphology of the synthesized metal oxide nanoparticles. One of the key advantages of wet etching is its simplicity and cost-effectiveness, making it accessible for both research and industrial applications. The wide availability of etchant chemicals and straightforward processing steps contribute to its widespread adoption in nanoparticle synthesis. Wet etching offers versatility in nanoparticle synthesis by accommodating various substrate materials and compositions [25]. From silicon to metal oxides to polymers, different materials can be selectively etched using appropriate etchant solutions,

allowing for the fabrication of diverse nanoparticle architectures and heterostructures. Wet etching enables batch processing and scalability, making it suitable for large-scale nanoparticle production. The ability to etch multiple substrates simultaneously enhances throughput and efficiency, essential for industrial applications requiring high-volume nanoparticle synthesis. This technique finds widespread applications in fields such as electronics, photonics, and catalysis, driving advancements in nanomaterials research and technology.

1.1.3 Lithographic techniques

1.1.3.1 Mechanical techniques

Within lithographic procedures, mechanical techniques are very useful and accurate when it comes to top-down creation of metal oxide nanoparticles. Through mechanically manipulating and patterning materials at the micro- and nanoscale, these approaches allow for the controlled production of metal oxide nanoparticles with specific characteristics [16]. One prominent mechanical lithographic technique is nanoimprint lithography (NIL), which utilizes the mechanical deformation of a resist material to transfer patterns from a template onto a substrate. In NIL, a template with desired nanopatterns is pressed onto a resist-coated substrate, causing the resist to deform and replicate the template's features. Subsequent curing or cross-linking of the resist solidifies the pattern, which can then serve as a mask for etching or deposition processes to synthesize metal oxide nanoparticles with precise spatial distribution. Nanoimprint lithography is an additional mechanical approach that can be used. A patterned mould is placed onto a resist-coated substrate in nanoimprint lithography, transferring the pattern to the substrate. Soft lithography is another type of mechanical lithography that includes several techniques like replica moulding and microcontact printing. These methods, which provide simplicity and scalability in the manufacturing of nanoparticles, entail the mechanical transfer of patterns from elastomeric stamps onto surfaces. Soft lithography allows the synthesis of functionalized metal oxide nanoparticles for use in biomedicine, drug delivery, and sensing by functionalizing stamps with certain chemical or biological moieties [26]. Dip-pen nanolithography (DPN) represents a mechanical lithographic technique capable of direct writing of nanopatterns with high resolution. In DPN, an atomic force microscope (AFM) tip coated with functional ink is used to deposit material onto a substrate surface, enabling precise control over nanoparticle placement and assembly.

1.1.3.2 Electron beam lithography

Electron beam lithography (EBL) stands as a cornerstone within lithographic techniques in the top-down synthesis approach of metal oxide nanoparticles, offering unparalleled resolution and precision in nanopatterning. This technique harnesses the focused electron beam to directly write nanoscale features onto a substrate, enabling the fabrication of metal oxide nanoparticles with exquisite control over size, shape, and spatial distribution. In EBL, the process begins with the deposition of a thin layer of resist material onto the substrate surface [27]. The substrate is then exposed to a focused electron beam, which selectively irradiates the resist and induces chemical or physical changes, depending on the type of resist used. This exposure results in the formation of a latent image corresponding to the desired nanopatterns. Subsequent development of the resist, typically through a wet or dry etching process, removes the exposed regions of the resist, revealing the underlying substrate surface with nanopatterns defined by the electron beam exposure. This patterned substrate can then serve as a template for the deposition, growth, or etching of metal oxide nanoparticles, achieving precise control over their placement and morphology. EBL possesses a notable advantage in its remarkable resolution, capable of achieving feature sizes as small as a few nanometers. This heightened resolution facilitates the creation of intricate nanoparticle architectures and nanostructures, which are essential for applications in nanoelectronics, plasmonics, and photonics [28]. EBL offers versatility in nanoparticle synthesis by accommodating various substrate materials and compositions. From silicon to glass to polymers, different materials can be patterned with high precision using EBL, expanding the scope of applications for metal oxide nanoparticles.

1.2 Bottom-up approach

It involves the assembly or growth of nanoparticles from smaller building blocks or precursor molecules. This method relies on chemical or physical processes to control the nucleation and growth of nanoparticles, leading to the formation of well-defined nanostructures with desired properties. The bottom-up approach offers advantages such as precise control over nanoparticle size, shape, composition, and surface chemistry, as well as the ability to produce monodisperse nanoparticles with tailored properties [29]. Additionally, bottom-up methods often enable the integration of nanoparticles into complex hierarchical structures and functional materials. Despite these advantages, bottom-up synthesis methods may require careful control of reaction conditions, purification steps, and surface functionalization to achieve desired nanoparticle properties.

Furthermore, scalability and reproducibility can be challenging for some bottom-up techniques. Nevertheless, the bottom-up approach remains a powerful strategy for nanoparticle synthesis, offering versatility and flexibility for the fabrication of nanoparticles with tailored properties for a wide range of applications, including catalysis, sensing, drug delivery, and nanoelectronics. It complements top-down approaches and provides valuable insights into the fundamental principles of nanoparticle formation and assembly [30].

1.2.1 Liquid phase synthesis

1.2.1.1 Sonochemical method

The sonochemical method, a prominent technique in the bottom-up approach of synthesizing metal oxide nanoparticles, operates within the liquid phase, harnessing the power of ultrasonic waves to induce chemical reactions. This method involves the application of high-frequency sound waves (ultrasound) to a liquid medium containing precursor materials, typically metal salts or metal-organic compounds, which serve as the source of the desired metal oxide nanoparticles [31]. The process begins with the introduction of the precursor solution into a reaction vessel, often accompanied by a suitable solvent or surfactant. Upon exposure to ultrasonic waves, cavitation occurs, leading to the formation, growth, and subsequent collapse of microscopic bubbles within the liquid. These transient cavitation bubbles generate localized hotspots with temperatures reaching up to several thousand degrees Celsius and pressures up to several hundred atmospheres. This extreme environment facilitates the rapid nucleation and growth of nanoparticles from the precursor species through various chemical reactions, including reduction, oxidation, hydrolysis, and condensation. The sonochemical method offers several advantages for the synthesis of metal oxide nanoparticles. Firstly, it enables precise control over the size, shape, and composition of the resulting nanoparticles by adjusting parameters such as ultrasound frequency, power intensity, reaction temperature, and precursor concentration. Additionally, the sonochemical approach is known for its rapid reaction kinetics, allowing for high production rates and short reaction times compared to conventional methods. Moreover, this technique is environmentally friendly, as it typically operates at ambient conditions without the need for harsh chemicals or elevated temperatures, thus minimizing energy consumption and waste generation [32].

1.2.1.2 Co-precipitation method

The co-precipitation method is a widely used technique in the bottom-up approach for synthesizing metal oxide nanoparticles within the liquid phase. This method involves the simultaneous precipitation of metal ions from a solution by the addition of a precipitating agent, typically a base or an acid, under controlled conditions. To initiate the co-precipitation process, aqueous solutions containing precursor metal salts, such as chlorides, nitrates, or sulfates, are mixed together, resulting in the formation of metal hydroxide or metal oxide precipitates [33]. The addition of the precipitating agent induces a chemical reaction, leading to the formation of insoluble metal hydroxides or oxides, which subsequently undergo nucleation and growth to form nanoparticles [34]. The key advantage of the co-precipitation method lies in its simplicity and scalability, as it requires minimal equipment and can be easily scaled up for large-scale production. Moreover, this method allows for precise control over the size, morphology, and composition of the resulting nanoparticles by adjusting parameters such as reaction temperature, pH, concentration of precursor salts, and reaction time. The co-precipitation method offers versatility, as it can be adapted to synthesize a wide range of metal oxide nanoparticles with tailored properties for various applications. Furthermore, the relatively low cost and ease of operation make this method highly attractive for industrial-scale production of metal oxide nanoparticles. The co-precipitation method, utilized in liquid phase synthesis of metal oxide nanoparticles via the bottom-up approach, involves the simultaneous precipitation of metal ions from solution by introducing a precipitating agent like a base or an acid [33], [35].

1.2.1.3 Sol-gel method

The sol-gel method stands as a prominent technique in the liquid phase synthesis of metal oxide nanoparticles, embodying the bottom-up approach. This method entails the gradual transformation of precursor molecules into a sol, followed by gelation and eventual formation of metal oxide nanoparticles. Initially, metal alkoxides or salts are dissolved in a suitable solvent, typically alcohol or water, to generate a homogeneous solution known as a sol, containing the essential metal ions for nanoparticle formation. Subsequently, hydrolysis reactions occur, wherein the metal alkoxides react with water molecules, facilitated by a catalyst such as an acid or base, to yield metal hydroxides. Concurrently, condensation reactions take place among the metal hydroxides, leading to the formation of metal oxide oligomers or polymers [36]. As the condensation progresses, the sol undergoes

a phase transition, culminating in the formation of a three-dimensional network known as a gel, which encapsulates the metal oxide precursors. Following gelation, the material is subjected to drying to remove the solvent and water content, resulting in the formation of a porous xerogel, or undergoes calcination at elevated temperatures to induce crystallization and eliminate organic components, yielding the final metal oxide nanoparticles. Characterization techniques such as X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and Fourier-transform infrared spectroscopy are employed to analyze the size, morphology, crystallinity, surface structure, and chemical composition of the synthesized metal oxide nanoparticles. Overall, the sol-gel method offers a versatile and controllable approach for synthesizing metal oxide nanoparticles in the liquid phase, enabling precise manipulation of particle properties for diverse applications in catalysis, sensors, coatings, and biomedical fields [37].

1.2.1.4 Microemulsion method

The microemulsion method is a highly effective technique employed in the liquid phase synthesis of metal oxide nanoparticles, constituting a bottom-up approach. This method involves the formation of tiny droplets of water dispersed in an organic solvent, known as a microemulsion, which serves as a confined reaction environment for nanoparticle formation. Microemulsion Formation: Initially, a microemulsion is created by mixing water, oil (organic solvent), surfactant, and co-surfactant in precise proportions. The surfactant molecules arrange themselves at the interface between water and oil, stabilizing the microemulsion and facilitating the formation of nanoscale droplets of water within the organic solvent. Precursor Incorporation: Metal salts or metal-organic compounds containing the desired metal ions are dissolved or dispersed within the aqueous phase of the microemulsion. These precursor molecules serve as the source of metal ions for nanoparticle synthesis. Nanoparticle Formation: Chemical reactions, such as reduction or hydrolysis, are initiated within the confined aqueous nanodroplets of the microemulsion. These reactions lead to the nucleation and growth of metal oxide nanoparticles, with the surfactant molecules acting as templates or stabilizers to control the size, shape, and dispersion of the nanoparticles. Separation and Purification: Once the nanoparticle synthesis is complete, the metal oxide nanoparticles are typically separated from the microemulsion using centrifugation or other separation techniques. The nanoparticles are then washed to remove any remaining surfactants or impurities [38].

1.2.1.5 Solvothermal method

The solvothermal method is a powerful technique utilized in the bottom-up synthesis of metal oxide nanoparticles, offering precise control over size, shape, and composition. In this liquid phase synthesis approach, metal precursors are dissolved in a suitable solvent, typically a polar organic solvent or water, along with a stabilizing agent or surfactant. The solution is then sealed in a reactor vessel and subjected to elevated temperatures and pressures, typically ranging from 100 to 300°C and several atmospheres, respectively. The high temperature and pressure conditions promote rapid nucleation and controlled growth of nanoparticles from the dissolved precursors [39]. The choice of solvent, precursor concentration, reaction temperature, and duration can be finely tuned to manipulate the kinetics of nucleation and growth, allowing for the precise control of nanoparticle size and morphology. Additionally, the presence of stabilizing agents or surfactants helps to prevent aggregation and control the dispersity of the nanoparticles. The solvothermal method offers a significant advantage in its versatility, applying to a diverse array of metal precursors and solvent systems. This versatility facilitates the synthesis of a multitude of metal oxide nanoparticles with customized properties, catering to a broad spectrum of applications. Additionally, its relatively mild reaction conditions and scalability render it suitable for large-scale industrial production [40].

1.2.1.6 Hydrothermal method

The hydrothermal method is a widely employed technique in the liquid phase synthesis of metal oxide nanoparticles, offering precise control over size, morphology, and crystallinity. This bottom-up approach involves the reaction of aqueous metal precursors in a closed system under elevated temperature and pressure conditions, typically ranging from 100 to 300°C and several atmospheres, respectively. In the hydrothermal process, metal salts or hydroxides are dissolved in water, often with the addition of a pH-adjusting agent or complexing agent to control the nucleation and growth of nanoparticles. The reaction mixture is sealed in a pressure vessel and heated to the desired temperature for a specified duration. Under these conditions, the dissolved metal ions undergo hydrolysis and condensation reactions, leading to the formation of metal oxide nanoparticles [41]. The hydrothermal method offers several advantages for the synthesis of metal oxide nanoparticles. Firstly, water serves as an environmentally friendly solvent, making this approach more sustainable compared to organic solvent-based methods. Additionally, the controlled reaction conditions enable precise manipulation of nanoparticle size, shape, and crystallinity by adjusting parameters such as temperature, pressure, pH, and reaction time. Furthermore, the hydrothermal process facilitates the formation of crystalline nanoparticles with high purity and uniformity, as well as the synthesis of complex nanostructures through the incorporation of dopants or templates. The hydrothermal method is relatively simple, cost-effective, and scalable, making it suitable for both laboratory-scale research and industrial production. Its versatility allows for the synthesis of a wide range of metal oxide nanoparticles, including oxides of titanium, zinc, iron, and others, with tailored properties for various applications such as catalysis, sensing, energy storage, and biomedical applications.

1.2.1.7 Solution combustion method

The solution combustion method is a versatile and efficient approach to synthesizing metal oxide nanoparticles in the liquid phase, offering several advantages in terms of simplicity, speed, and scalability. In this bottom-up approach, metal precursors are dissolved in a suitable solvent, typically water or a mixture of water and a combustible organic solvent, such as glycine or urea, which also acts as a fuel and reducing agent. The synthesis process initiates with the rapid and exothermic combustion of the precursor solution when ignited by an external heat source, such as a Bunsen burner or a microwave irradiation. The combustion reaction generates high temperatures (often exceeding 1000°C) and high-pressure conditions within a short period, typically ranging from a few seconds to a few minutes. These extreme conditions drive the rapid nucleation and growth of metal oxide nanoparticles from the precursor solution. The solution combustion method stands out for its straightforwardness and user-friendly operation, necessitating minimal equipment and lacking complex setups. Furthermore, the swift and self-sustained combustion reaction guarantees substantial yields of nanoparticles within a brief duration, rendering it exceptionally time-efficient. Additionally, the combustion process inherently fosters the production of nanoparticles characterized by high purity and crystallinity, thanks to the rapid quenching of reaction products [42]. The solution combustion method offers tunability in controlling the properties of synthesized nanoparticles by adjusting parameters such as precursor concentration, fuel-to-metal ratio, and combustion conditions. This flexibility allows for the synthesis of a wide range of metal oxide nanoparticles with tailored properties for various applications, including catalysis, sensors, biomedical devices, and energy storage systems.

1.2.1.8 Microwave-assisted synthesis

Microwave-assisted synthesis is an innovative and efficient method for the liquidphase synthesis of metal oxide nanoparticles, offering rapid reaction kinetics, enhanced control over particle size, and reduced energy consumption compared to conventional heating methods. In this bottom-up approach, metal precursors are dissolved in a solvent, typically water or an organic solvent, and subjected to microwave irradiation. Microwave irradiation generates rapid and uniform heating throughout the reaction mixture by directly coupling electromagnetic energy with the molecules, leading to localized heating of the reaction medium [43]. This rapid and selective heating accelerates the reaction kinetics, promoting nucleation and growth processes while minimizing side reactions and impurity formation. One of the main benefits of microwave-assisted synthesis is its exceptional speed; in comparison to traditional heating techniques, response times are frequently lowered from hours to minutes or even seconds. This quick synthesis makes it possible to produce metal oxide nanoparticles at high throughput while also drastically reducing experimental turnaround times, which makes it ideal for both lab research and large-scale manufacturing. Microwave irradiation offers precise control over reaction parameters such as temperature and heating rate, allowing for fine-tuning of nanoparticle size, morphology, and crystallinity. This control facilitates the synthesis of highly uniform nanoparticles with tailored properties for specific applications, including catalysis, sensing, biomedical imaging, and energy conversion and storage. Microwave-assisted synthesis is characterized by its energy efficiency, as the direct coupling of electromagnetic energy with the reaction medium reduces energy consumption and minimizes heat loss to the surroundings. This eco-friendly aspect makes microwave-assisted synthesis a sustainable and environmentally friendly approach for the synthesis of metal oxide nanoparticles [44].

1.2.1.9 Electrochemical synthesis

Electrochemical synthesis is a versatile and efficient method for the bottom-up synthesis of metal oxide nanoparticles in the liquid phase, offering precise control over particle size, shape, and composition. This approach involves the reduction or oxidation of metal ions at electrode surfaces in an electrolyte solution, leading to the nucleation and growth of nanoparticles. In electrochemical synthesis, metal precursors are dissolved in a suitable electrolyte solution, typically an aqueous solution containing salts or complexes of the metal ions of interest. The electrolyte solution is then placed in a cell containing two electrodes—an anode and a cathode—separated by a suitable membrane or spacer. When

an electric potential is applied between the electrodes, metal ions are reduced or oxidized at the electrode surfaces, depending on their standard reduction potentials [45]. The reduction or oxidation reactions lead to the nucleation and growth of metal oxide nanoparticles on the electrode surfaces or in the vicinity of the electrodes. By controlling parameters such as applied potential, electrolyte composition, pH, and temperature, researchers can precisely manipulate the nucleation and growth kinetics, enabling finetuning of nanoparticle properties. Electrochemical synthesis has several uses due to its adaptability in creating a wide range of metal oxide nanoparticles with specific properties. This is one of its main advantages. Furthermore, electrochemical synthesis is economical and scalable, which makes it appropriate for large-scale manufacturing. Reword the statement to make more sense. Electrochemical synthesis enables the direct integration of synthesized nanoparticles into devices or coatings, bypassing the need for additional processing steps. This feature makes it particularly attractive for the fabrication of functional materials for applications such as catalysis, sensors, energy storage, and electrochromic devices [46].

1.2.1.10 Electro-erosion dispersion

Electro-erosion dispersion is an innovative technique within the realm of liquidphase synthesis for bottom-up creation of metal oxide nanoparticles. This method leverages electrical discharges to fragment bulk metal electrodes immersed in a liquid medium, facilitating the formation of nanoparticles. In this process, metal electrodes are submerged in a suitable liquid medium, typically water or an organic solvent containing appropriate precursors or additives. When a high-voltage electrical discharge is applied across the electrodes, intense localized heating occurs at the interface between the electrodes and the liquid. This extreme thermal energy causes rapid vaporization and ionization of the electrode material, leading to the formation of plasma. The collapse of this plasma generates shockwaves and cavitation bubbles within the liquid, inducing highspeed liquid jets and micro-explosions at the electrode surfaces. These micro-explosions result in the ejection and fragmentation of molten metal droplets, which subsequently solidify to form metal oxide nanoparticles dispersed in the liquid medium. The size, shape, and composition of the nanoparticles can be controlled by adjusting parameters such as the electrical discharge parameters, electrode material, liquid medium, and the presence of additives or surfactants. One of the benefits of electro-erosion dispersion is that it is a more sustainable and environmentally friendly synthesis approach because it can create

nanoparticles without the need for extra chemical reagents. Furthermore, the method's scalability and plasticity enable the production of a diverse array of metal oxide nanoparticles with customised characteristics for a range of uses, such as energy conversion, sensing, catalysis, and medicinal applications.

1.2.1.11 Template-based synthesis

Template-based synthesis is a sophisticated technique within liquid-phase bottomup synthesis that enables precise control over the size, shape, and structure of metal oxide nanoparticles. This method relies on the use of templates—such as organic molecules, polymers, or inorganic materials—that serve as scaffolds or molds for the nucleation and growth of nanoparticles. In template-based synthesis, the chosen template is first dispersed or immobilized within a liquid medium containing metal precursors. These precursors can be metal salts or complexes dissolved in a solvent, often water or an organic solvent. The template directs the nucleation and growth of nanoparticles, dictating their final morphology and arrangement. Upon exposure to suitable reaction conditions, such as elevated temperature or the addition of a reducing agent, the metal precursors undergo chemical transformations, leading to the formation and deposition of metal oxide nanoparticles onto the surface or within the pores of the template. The template serves as a spatial constraint, controlling the size and shape of the nanoparticles and preventing their agglomeration [47]. The capacity of template-based synthesis to provide nanoparticles with very uniform size, shape, and distribution—all of which are determined by the structure of the template—is one of its main benefits. In addition, this technique is versatile because it may be used to create spheres, rods, wires, and more sophisticated architectures, among other types of nanoparticles, by using different templates. The template-based synthesis also allows for the incorporation of additional functionalities into the nanoparticles by modifying the template's composition or surface chemistry. Furthermore, the templating process can be combined with other synthesis techniques, such as sol-gel or hydrothermal methods, to further tailor the properties of the resulting nanoparticles.

1.2.2 Vapor phase synthesis

1.2.2.1 Physical vapor deposition

Physical vapor deposition (PVD) is a prominent technique in vapor-phase synthesis that facilitates the bottom-up creation of metal oxide nanoparticles with precise control over size, composition, and structure. Unlike liquid-phase methods, PVD involves the

deposition of material from a physical vapor source onto a substrate to form thin films or nanoparticles. In PVD, metal oxide nanoparticles are synthesized by the physical vaporization of a solid precursor, typically through techniques such as evaporation, sputtering, or pulsed laser ablation [48]. The vaporized precursor atoms or molecules are then transported through a vacuum chamber and deposited onto a cooler substrate, where they condense and form nanoparticles. The process can be carried out under controlled conditions of temperature, pressure, and deposition rate to achieve nanoparticles with desired properties. Since there is no liquid medium involved, there is less chance of contamination or imperfections, making PVD an excellent method for producing highly pure and crystalline nanoparticles. Furthermore, with the manipulation of variables like substrate orientation, substrate temperature, and deposition rate, PVD permits exact control over nanoparticle size and morphology[49]. PVD offers scalability and reproducibility, making it suitable for both laboratory-scale research and industrial production. The technique can be easily adapted to deposit nanoparticles onto a variety of substrates, including silicon wafers, glass slides, and flexible polymers, for applications in electronics, catalysis, sensing, and energy conversion. PVD can be combined with other synthesis methods, such as chemical vapor deposition or atomic layer deposition, to achieve more complex nanostructures or functional coatings.

1.2.2.2 Evaporative deposition

Evaporative deposition is a vapor-phase synthesis technique that plays a vital role in the bottom-up approach to fabricating metal oxide nanoparticles with precise control over their properties. In this method, nanoparticles are formed through the controlled condensation of vaporized precursor materials onto a substrate surface. The process begins with the vaporization of solid or liquid precursor materials, typically using techniques such as thermal evaporation, electron beam evaporation, or laser ablation [50]. The precursor vapor is then introduced into a vacuum chamber where it interacts with a cooler substrate. As the vapor contacts the substrate, it condenses and forms nanoparticles, which subsequently adhere to the substrate surface. Evaporative deposition yields highpurity, uniformly distributed nanoparticles, which is one of its main benefits. Because there is no liquid medium present, there is less chance of contamination and more control over the deposition process, which produces nanoparticles with distinct sizes and shapes. Evaporative deposition offers versatility, as it can be used to deposit nanoparticles onto a wide range of substrates, including silicon wafers, glass slides, and flexible polymers. This

flexibility makes the technique suitable for various applications, including electronics, photonics, catalysis, and biomedical devices. Evaporative deposition is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By adjusting parameters such as deposition rate, substrate temperature, and precursor concentration, researchers can tailor the properties of the synthesized nanoparticles to meet specific application requirements. It is a useful technique for developing nanotechnology in a variety of industries because of its capacity to create nanoparticles with great purity, homogeneity, and reproducibility.

1.2.2.3 Electron beam PVD (EBPVD)

Electron beam physical vapor deposition (EBPVD) is an advanced technique within vapor-phase synthesis that enables precise control over the synthesis of metal oxide nanoparticles with tailored properties. This bottom-up approach involves the vaporization of solid precursor materials using an electron beam as the energy source, followed by the deposition of the vapor onto a substrate surface to form nanoparticles. In EBPVD, a focused electron beam is directed at a solid precursor material, causing its localized heating and sublimation [51]. The vaporized precursor atoms or molecules are then transported through a vacuum chamber and deposited onto a substrate, where they nucleate and grow into nanoparticles. The process parameters, such as the energy and intensity of the electron beam, the substrate temperature, and the deposition rate, can be precisely controlled to achieve nanoparticles with desired properties. EBPVD's capacity to generate very pure and crystallinity nanoparticles is one of its main benefits. The deposition process is precisely controlled, and the lack of a liquid medium reduces the possibility of contamination and impurity inclusion, producing nanoparticles with distinct sizes and shapes. EBPVD offers versatility, as it can be used to deposit nanoparticles onto a variety of substrates, including silicon wafers, glass slides, and flexible polymers. This flexibility makes the technique suitable for a wide range of applications, including electronics, catalysis, sensing, and biomedical devices. EBPVD is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By adjusting the process parameters, researchers can tailor the properties of the synthesized nanoparticles to meet specific application requirements.

1.2.2.4 Sputter deposition

Sputter deposition is a highly versatile technique within vapor-phase synthesis that facilitates the bottom-up fabrication of metal oxide nanoparticles with precise control over their properties. This method involves the physical bombardment of a target material by

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energetic ions, causing the ejection of atoms or molecules from the target surface. These ejected species then condense onto a substrate, forming a thin film or nanoparticles. In sputter deposition, a target material, typically a metal or metal oxide, is bombarded with ions generated from a plasma discharge in a vacuum chamber. The energetic ions dislodged from the target surface carry kinetic energy and momentum, leading to the ejection of atoms or molecules. These ejected species travel through the vacuum chamber and deposit onto a substrate placed near the target. The ability of sputter deposition to manufacture nanoparticles with excellent purity and homogeneity is one of its main benefits [52]. The possibility of contamination is reduced by the lack of a liquid medium, and the precise control of nanoparticle size, shape, and distribution is made possible by the controlled deposition process. Sputter deposition offers versatility, as it can be used to deposit nanoparticles onto a wide range of substrates, including silicon wafers, glass slides, and flexible polymers. This flexibility makes the technique suitable for various applications, including electronics, photonics, catalysis, and biomedical devices. Sputter deposition is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By adjusting parameters such as target material, ion energy, deposition rate, and substrate temperature, researchers can tailor the properties of the synthesized nanoparticles to meet specific application requirements.

1.2.2.5 Cathodic arc deposition or Arc PVD

Cathodic arc deposition, also known as arc PVD (Physical Vapor Deposition), is a highly effective technique in vapor-phase synthesis for the bottom-up fabrication of metal oxide nanoparticles with precise control over their properties. This method involves the generation of a high-energy plasma arc between a cathode target material and an anode within a vacuum chamber. In cathodic arc deposition, a high-voltage pulse is applied to the cathode target material, typically a metal or metal oxide. This pulse causes a localized breakdown of the material's surface, resulting in the formation of a highly energetic plasma arc [53]. The plasma arc consists of ions, electrons, and vaporized atoms or molecules from the target material. The vaporized species from the cathode target are then directed towards a substrate, where they condense and form nanoparticles. By controlling parameters such as the arc current, pulse duration, and substrate temperature, researchers can precisely manipulate the properties of the synthesized nanoparticles, including their size, shape, and composition. The cathodic arc deposition's capacity to create very pure and crystalline nanoparticles is one of its main advantages. The possibility of contamination is reduced by the regulated deposition process and the lack of a liquid medium, producing

nanoparticles with well-defined characteristics. Cathodic arc deposition offers versatility, as it can be used to deposit nanoparticles onto various substrates, including silicon wafers, glass slides, and flexible polymers. This flexibility makes the technique suitable for a wide range of applications, including electronics, catalysis, sensing, and biomedical devices.

1.2.2.6 Laser-induced synthesis – PLAL (Pulsed Laser Ablation in Liquids)

Laser-induced synthesis, specifically Pulsed Laser Ablation in Liquids (PLAL), is an innovative technique within vapor-phase synthesis that enables the bottom-up fabrication of metal oxide nanoparticles with precise control over their properties. PLAL involves irradiating a solid target material with short, high-energy laser pulses while immersed in a liquid medium. In PLAL, a pulsed laser beam is focused onto the surface of a solid target material, typically a metal or metal oxide. The intense energy from the laser pulses causes localized heating and vaporization of the target material, leading to the formation of a plasma plume containing vaporized atoms or nanoparticles. This plasma plume rapidly expands into the surrounding liquid medium, where it undergoes cooling and condensation, resulting in the formation of nanoparticles. The capacity of PLAL to create very pure and crystallinity nanoparticles is one of its main features. The risk of impurities is reduced by the regulated synthesis procedure and the lack of pollutants in the liquid medium, producing nanoparticles with precisely defined properties. PLAL offers versatility, as it can be used to synthesize nanoparticles from a wide range of target materials and in various liquid media. This flexibility allows researchers to tailor the properties of the synthesized nanoparticles to meet specific application requirements. PLAL is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By adjusting parameters such as laser fluence, pulse duration, and liquid environment, researchers can precisely control the size, shape, and composition of the synthesized nanoparticles [54].

1.2.2.7 Inert gas condensation

Inert gas condensation is a highly effective technique within vapor-phase synthesis for the bottom-up fabrication of metal oxide nanoparticles with precise control over their properties. This method involves the condensation of vaporized precursor materials in the presence of an inert gas, typically argon or helium, to form nanoparticles. In inert gas condensation, solid precursor materials, usually metals or metal oxides, are first vaporized using techniques such as resistive heating or laser ablation. The vaporized precursor atoms or molecules are then rapidly quenched by a stream of inert gas, causing them to condense and form nanoparticles. The inert gas acts as a cooling medium, preventing the nanoparticles from coalescing and allowing them to retain their size and shape [55]. The precise regulation of the synthesis process and the absence of contaminants in the inert gas lead to the generation of nanoparticles with highly pure and uniform characteristics, highlighting one of the main advantages of inert gas condensation. An inert gas condensation offers versatility, as it can be used to synthesize nanoparticles from a wide range of precursor materials and in various gas atmospheres. This flexibility allows researchers to tailor the properties of the synthesized nanoparticles to meet specific application requirements. Inert gas condensation is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By adjusting parameters such as precursor material, gas flow rate, and deposition temperature, researchers can precisely control the size, shape, and composition of the synthesized nanoparticles.

1.2.2.8 Electromagnetic Levitation Gas Condensation (ELGC)

Electromagnetic Levitation Gas Condensation (ELGC) is an advanced technique in vapor-phase synthesis that enables precise control over the fabrication of metal oxide nanoparticles in a bottom-up approach. This method combines the principles of electromagnetic levitation and gas condensation to produce nanoparticles with tailored properties. In ELGC, a levitation coil generates a rapidly alternating magnetic field, which induces eddy currents in a conductive sample holder [56]. This creates a repulsive force that suspends the sample holder, allowing it to levitate within a chamber filled with inert gas, typically argon or helium. A solid precursor material, usually a metal or metal oxide, is then heated and vaporized using techniques such as resistive heating or laser ablation. As the vaporized precursor material expands into the gas-filled chamber, it undergoes rapid cooling and condensation due to the presence of the inert gas. The nanoparticles formed during this process are deposited onto a substrate, where they can be collected and characterized. The capacity of ELGC to generate nanoparticles with extremely consistent size, shape, and composition is one of its main advantages. Tailored nanoparticles can be produced by carefully controlling the levitation and gas condensation parameters in conjunction with a controlled synthesis process. Moreover, ELGC offers versatility, as it can be used to synthesize nanoparticles from a wide range of precursor materials and in various gas atmospheres. This flexibility enables researchers to fine-tune the properties of the synthesized nanoparticles to meet specific application requirements.

1.2.2.9 Chemical vapor condensation (CVC)

Chemical vapor condensation (CVC) is a versatile technique in vapor-phase synthesis that enables the bottom-up fabrication of metal oxide nanoparticles with precise control over their properties. This method involves the chemical reaction of gaseous precursor molecules to form nanoparticles through condensation. In CVC, precursor molecules in the gas phase are introduced into a reaction chamber, typically using techniques such as bubbling or vaporization. These precursor molecules undergo chemical reactions, such as oxidation or hydrolysis, to form metal oxide nanoparticles. The reaction is often carried out at elevated temperatures and controlled pressures to promote efficient nanoparticle formation. The production of highly homogeneous and pure nanoparticles is one of CVC's primary advantage. The production of nanoparticles with well specified characteristics is made possible by the carefully regulated reaction conditions and the controlled synthesis procedure. CVC offers versatility, as it can be used to synthesize nanoparticles from a wide range of precursor materials and in various gas atmospheres. This flexibility enables researchers to tailor the properties of the synthesized nanoparticles to meet specific application requirements. CVC is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By optimizing parameters such as precursor concentration, reaction temperature, and residence time, researchers can achieve precise control over the synthesis process, leading to the fabrication of metal oxide nanoparticles with enhanced properties for diverse applications. Ultimately, chemical vapour condensation is a strong and adaptable method for producing metal oxide nanoparticles under controlled conditions in vapor-phase synthesis. It has great potential to advance nanotechnology in a variety of domains, such as biomedicine, electronics, sensing, and catalysis [57].

1.2.2.10 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is a highly versatile and widely used technique in vapor-phase synthesis for the bottom-up fabrication of metal oxide nanoparticles with precise control over their properties. This method involves the chemical reaction of gaseous precursor molecules on a substrate surface to form a thin film or nanoparticles. In CVD, precursor molecules in the gas phase are introduced into a reaction chamber, where they react and decompose on the surface of a heated substrate to form metal oxide nanoparticles. The reaction is typically initiated by thermal energy or a plasma discharge, which provides the activation energy required for precursor decomposition. CVD can produce nanoparticles with high purity and uniformity. The controlled synthesis process

and the precise regulation of reaction parameters allow for the generation of nanoparticles with well-defined properties. CVD offers versatility, as it can be used to synthesize nanoparticles from a wide range of precursor materials and in various gas atmospheres. This flexibility enables researchers to tailor the properties of the synthesized nanoparticles to meet specific application requirements. CVD is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By optimizing parameters such as precursor concentration, reaction temperature, gas flow rate, and substrate material, researchers can achieve precise control over the synthesis process, leading to the fabrication of metal oxide nanoparticles with enhanced properties for diverse applications. In general, chemical vapor deposition is a strong and adaptable method in vapor-phase synthesis for the regulated synthesis of metal oxide nanoparticles, with great potential to advance nanotechnology in a variety of domains, such as biomedicine, electronics, sensing, and catalysis [58].

1.2.2.11 Laser pyrolysis

Laser pyrolysis is an innovative technique in vapor-phase synthesis that enables precise control over the fabrication of metal oxide nanoparticles in a bottom-up approach. This method involves the decomposition of precursor molecules using laser irradiation to form nanoparticles. In laser pyrolysis, precursor molecules in the gas phase are introduced into a reaction chamber, typically using techniques such as vaporization or nebulization [59]. These precursor molecules are then irradiated with a high-energy laser beam, which provides the energy required for their decomposition and the subsequent formation of metal oxide nanoparticles. The reaction occurs in a rapid and controlled manner, allowing for precise manipulation of nanoparticle size, shape, and composition. laser pyrolysis as the ability to produce nanoparticles with high purity and uniformity. The controlled synthesis process and the precise regulation of laser parameters enable the generation of nanoparticles with well-defined properties. Moreover, laser pyrolysis offers versatility, as it can be used to synthesize nanoparticles from a wide range of precursor materials and in various gas atmospheres. This flexibility allows researchers to tailor the properties of the synthesized nanoparticles to meet specific application requirements. Laser pyrolysis is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By optimizing parameters such as laser power, irradiation time, precursor concentration, and gas flow rate, researchers can achieve precise control over the synthesis process, leading to the fabrication of metal oxide nanoparticles with enhanced properties for diverse applications [58].

1.2.2.12 Spray pyrolysis

Spray pyrolysis is a versatile and widely used technique in vapor-phase synthesis for the bottom-up fabrication of metal oxide nanoparticles with precise control over their properties. This method involves the chemical reaction of precursor solutions sprayed into a high-temperature reactor to form nanoparticles[60]. In spray pyrolysis, a precursor solution containing metal salts or complexes is atomized into fine droplets using techniques such as ultrasonic nebulization or pneumatic spraying. These droplets are then introduced into a high-temperature reactor, where they undergo pyrolysis in the presence of a carrier gas, typically nitrogen or oxygen. The high temperature causes the decomposition of the precursor molecules, resulting in the formation of metal oxide nanoparticles. Spray pyrolysis stands out for its capacity to generate nanoparticles characterized by high purity and uniformity. This is facilitated by the controlled synthesis process and the meticulous adjustment of reaction parameters, resulting in the production of nanoparticles with precisely defined properties. Spray pyrolysis offers versatility, as it can be used to synthesize nanoparticles from a wide range of precursor materials and in various gas atmospheres. This flexibility enables researchers to tailor the properties of the synthesized nanoparticles to meet specific application requirements. Spray pyrolysis is a scalable and reproducible technique, making it applicable for both laboratory-scale research and industrial production. By optimizing parameters such as precursor concentration, spray rate, reaction temperature, and gas flow rate, researchers can achieve precise control over the synthesis process, leading to the fabrication of metal oxide nanoparticles with enhanced properties for diverse applications.

1.2.3 Green synthesis

Green synthesis in vapor-phase methods represents a sustainable approach to fabricating metal oxide nanoparticles in a bottom-up manner, emphasizing environmental friendliness and resource efficiency [61]. Unlike traditional synthesis methods, green synthesis minimizes or eliminates the use of hazardous chemicals and organic solvents, thus reducing environmental impact and ensuring the safety of researchers. Several green synthesis techniques are employed in vapor-phase methods. For example, in the case of chemical vapor deposition (CVD), green precursor materials or solvents derived from renewable sources can be used to reduce the environmental footprint of the process. Additionally, innovative strategies such as microwave-assisted synthesis and hydrothermal synthesis can be modified to incorporate green principles by utilizing eco-friendly solvents and reducing energy consumption. Green synthesis in vapor-phase methods offers a significant advantage through its emphasis on sustainability and reduced environmental

impact. Utilizing renewable resources and minimizing the utilization of toxic chemicals, these techniques contribute to the creation of eco-friendly nanomaterials, thereby minimizing adverse effects on ecosystems and human health. Green synthesis in vaporphase methods offers versatility and scalability, making it applicable for both laboratoryscale research and industrial production. The controlled synthesis process and the precise regulation of reaction parameters allow for the generation of nanoparticles with welldefined properties, fulfilling various application requirements. In terms of vapor-phase techniques for the controlled synthesis of metal oxide nanoparticles, green synthesis is a promising strategy that has the potential to significantly advance nanotechnology and environmental sustainability. Adopting environmentally conscious values can help scientists create cutting-edge synthesis methods that not only provide superior nanoparticles but also help create a more sustainable future [62].

Conclusion:

The synthesis of MONPs has evolved significantly, with various techniques offering unique benefits and addressing specific challenges. Traditional methods like sol-gel and hydrothermal processes provide control over particle characteristics but are often limited by harsh conditions and environmental concerns. Emerging methods, including green synthesis and advanced deposition techniques, show promise in producing MONPs with precise properties and reduced environmental impact. The diverse applications of MONPs in catalysis, sensing, biomedical imaging, and environmental remediation underscore their transformative potential. However, challenges remain in achieving consistent nanoparticle quality, scalability, and thorough assessment of long-term impacts. Future research should focus on refining synthesis methods for large-scale production, enhancing the understanding of MONP interactions in biological and environmental contexts, and developing more sustainable and cost-effective approaches. This comprehensive review highlights the advancements in MONP synthesis and serves as a foundation for ongoing innovation and application in various fields.

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RECENT ADVANCES IN BIOTECHNOLOGY AND PLANT BREEDING

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Introduction:

The field of plant breeding has undergone a significant transformation over the past few decades, driven largely by advances in biotechnology. Plants with desired qualities are chosen and crossed in traditional plant breeding, which has been done for thousands of years with the goal of creating superior offspring. Although this method has greatly increased agricultural yields, tolerance to pests and diseases, and resilience to environmental stressors, it is time-, efficiency-, and precision-limited. Plant breeding has undergone a revolution with the development of contemporary biotechnology, which has given scientists the means to quickly and accurately alter plants at the genetic level. Food security, population expansion, and climate change have presented the globe with previously unheard-of difficulties in recent years. By 2050, when the world's population is expected to reach 10 billion, there will be a significant increase in the need for food. At the same time, extreme weather events like heatwaves, floods, and droughts are becoming more often due to climate change, endangering agricultural production. The development of crops that are more robust to these difficulties while preserving or even boosting their output is critically needed in this situation. This requirement cannot be satisfied by traditional breeding techniques alone since they are labor-intensive, time-consuming, and frequently inadequate to address the intricate genetic foundation of many significant characteristics. This is where biotechnology enters the picture, with the promise to speed up breeding, increase the accuracy of trait selection, and create crops that are resilient to environmental changes. The capacity to swiftly and economically sequence plant genomes has been one of the most important biotechnological developments in recent years. Breeders now have comprehensive knowledge of the genetic composition of crops thanks to Next-Generation Sequencing (NGS) technology, which can decode a plant's whole DNA sequence in a few days. Genomic Selection (GS), a potent technique that enables breeders

to forecast a plant's performance based on its genetic information even before the plant is completely developed, has been made possible by this. By allowing breeders to choose the finest individuals for breeding early in the plant's growth, genomic selection has completely changed the breeding process and cut down on the time and resources required to create superior varieties. The advancement of CRISPR-Cas9 gene editing technology has created new opportunities for plant breeding in addition to genomic selection. CRISPR enables researchers to precisely alter a plant's own DNA, in contrast to conventional genetic modification methods that include introducing foreign genes into the plant's genome. Breeders may now alter particular features, including drought or disease resistance, with previously unheard-of precision because to this technology. Crops with increased yields, greater nutritional value, and enhanced resistance to pests and diseases have already been created using CRISPR. For consumers and authorities who are leery of genetically modified organisms (GMOs), CRISPR has become a more acceptable alternative due to its capacity to perform specific modifications without introducing foreign DNA.

Another biotechnological technique that has greatly increased the effectiveness of plant breeding is marker-assisted selection (MAS). MAS identifies plants with desired qualities early in the breeding process by employing molecular markers, which are short DNA sequences linked to particular phenotypes. This speeds up the production of new kinds by enabling breeders to choose plants with the necessary features before they mature. Improved disease resistance in crops, such as wheat resistant to rust and rice resistant to blast disease, has been a particular strength of MAS. For complicated qualities that are impacted by several genes, like as yield and drought tolerance, its applicability has been fairly limited. Researchers are progressively integrating MAS with genomic selection and other biotechnological approaches to increase its efficacy in order to overcome these issues. Apart from genomic selection, CRISPR, and MAS, developments in RNA interference (RNAi) have opened up new avenues for enhancing agricultural characteristics by the silence of certain genes. Scientists have used RNA interference (RNAi), a natural process that cells utilize to control gene expression, to create crops that are more resistant to pests and illnesses. For instance, RNA interference has been used to develop maize cultivars that are resistant to the corn rootworm, a serious pest that seriously harms maize crops. RNA interference has also been used to increase the nutritional value of crops, such soybeans, by lowering their amounts of bad fats. Additionally, RNA interference is being investigated as a means of controlling plant viruses, which pose a serious risk to global agricultural
production. RNA interference (RNAi) has the potential to lessen the effect of viral infections on agricultural production by inhibiting the genes that viruses need to proliferate within plant cells. The idea of speed breeding, which includes cultivating plants in regulated environments to quicken their life cycle, is another innovation in plant breeding. Speed breeding enables breeders to finish several generations of breeding in a single year by maximizing variables including light, temperature, and humidity, which accelerates plant maturity and reproduction. Crops including wheat, barley, and chickpeas have already benefited from this method, which has cut the time required to create new kinds by a number of years. Speed breeding provides a potent means of accelerating the production of superior crop varieties in conjunction with genomic selection, CRISPR, and other biotechnological advancements. This enables a quicker response to the difficulties presented by population expansion and climate change. Enhancing agricultural output has also been greatly aided by transgenic crops, which are plants that have undergone genetic modification to include genes from other organisms. Herbicide-tolerant soybeans, which enable farmers to better control weeds, and Bt cotton, which is resistant to certain insects, are two of the most popular transgenic crops. By raising yields and decreasing the need for chemical pesticides and herbicides, these crops have given farmers substantial financial advantages. But there have also been difficulties with transgenic crops, especially with regard to public and regulatory acceptance. Some areas have stringent laws that restrict the use of transgenic crops due to worries about the safety of genetically modified organisms (GMOs). However, current studies are aimed at creating second-generation transgenic crops with more intricate characteristics, such resistance to several diseases, enhanced nutritional value, and drought tolerance. Biotechnology has helped preserve genetic variety in agriculture in addition to particular crops.

In order to maintain the genetic variety of agricultural species, which is necessary for upcoming breeding initiatives, gene banks—repositories that preserve seeds and other genetic material—play a critical role. Breeders now have access to a vast array of genetic resources for creating new types because to developments in cryopreservation and other biotechnological procedures that allow genetic material to be stored for extended periods of time without losing its viability. Given that genetic variety offers the foundation for developing crops that can adjust to shifting climatic circumstances, this is especially crucial in light of climate change. Even though plant breeding has benefited much from biotechnology thus far, there are still more interesting opportunities ahead. Through the

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design and construction of novel biological pathways, emerging sciences like metabolic engineering and synthetic biology provide the possibility to produce whole new features in plants. For instance, crops that are more adept at photosynthesis may be engineered using synthetic biology to yield more food with less sunshine and water. On the other side, metabolic engineering may be utilized to develop crops that not only generate food but also useful substances like biofuels or medications. Although these technologies are still in their infancy, they have the potential to completely transform agriculture by producing plants with characteristics not seen in nature. In addition to enhancing the features of specific crops, biotechnology is also helping to solve bigger concerns in agriculture through the development of precision agriculture and digital breeding technologies. Precision agriculture is the process of gathering comprehensive data on crop growth and environmental conditions utilizing technology like drones, sensors, and satellite photography. By optimizing farming techniques like fertilization, irrigation, and pest management, this data might lessen agriculture's negative environmental effects while increasing yields. Breeders are using digital breeding technologies like artificial intelligence (AI) and big data analytics to evaluate vast amounts of data in order to determine the most effective breeding plans and forecast the performance of various genetic combinations in the field. With the use of these instruments, breeding is becoming more effective, and creating new crop types is taking less time and money. It is obvious that the combination of conventional breeding techniques with state-of-the-art biotechnological instruments will influence plant breeding in the future as biotechnology develops. The capacity to quickly and precisely modify plant genomes presents previously unheard-of possibilities to solve the problems facing modern agriculture. But it's equally critical to understand that the success of these technologies depends not just on scientific advancement but also on governmental approval, public acceptance, and the capacity to guarantee that farmers worldwide can profit from biotechnology. The recent advances in biotechnology have revolutionized plant breeding, offering new tools to improve crop productivity, resilience, and nutritional content. Improved varieties may now be developed more quickly and precisely than ever before because to technologies like genomic selection, CRISPR-Cas9, marker-assisted selection, RNA interference, speed breeding, and transgenic crops. These biotechnological developments will be essential to maintaining food security and sustainable agriculture in the future as the globe struggles to feed an expanding population

and adjust to a changing environment. These are different key components that play a vital role in recent advances in biotechnology and plant breeding.

1. Modern Biotechnology in Plant Breeding

The need for quicker, more accurate, and sustainable ways to improve crop varieties has arisen due to the world's population growth, climate change, and rising food insecurity. Modern biotechnology has completely changed the way plant breeders approach crop development, even if conventional plant breeding has made a substantial contribution to agricultural advancement. Through the use of gene editing tools like CRISPR-Cas9 and marker-assisted selection (MAS), biotechnology is speeding up genetic improvements in plant breeding, enabling the more effective development of improved agricultural varieties. Plant breeders may now directly alter genes thanks to modern biotechnology, avoiding the drawbacks of natural recombination. Breeders can introduce desired characteristics like insect resistance, drought tolerance, and greater yields much more swiftly and precisely with biotechnology than they can with traditional techniques.

2. Genomics and Genomic Selection

Comprehensive genomic investigations in plants are now possible thanks to developments in whole-genome sequencing and high-throughput sequencing methods like Next-Generation Sequencing (NGS). Breeders can use genomic selection (GS), a revolutionary technique that uses DNA analysis to estimate a plant's genetic potential for qualities like resistance and production. By enabling breeders to pick the top-performing individuals without waiting for complete field trials, this selection technique shortens breeding cycles. More genetic variety may be captured by researchers thanks to the creation of pan-genomes, which offer a species' aggregate gene set. Finding functional genes and advancing crop development initiatives depend on this knowledge.

3. Marker-Assisted Selection (MAS) and Marker-Assisted Breeding (MAB)

One of the biggest advances in contemporary plant breeding has been the use of molecular markers. Marker-Assisted Selection (MAS) makes it possible to pinpoint the exact genes that provide desired characteristics including improved nutritional quality, abiotic stress tolerance, and disease resistance. This method greatly increases the effectiveness of breeding programs by enabling breeders to choose plants based on their genetic composition rather than only on outward traits. Notwithstanding its advantages, MAS works best for straightforward, single-gene characteristics. Research on applying MAS

to more complicated, multi-gene features and integrating it with other technologies, such as genomic selection, is also ongoing.

4. CRISPR-Cas Technology and Gene Editing

The accuracy, effectiveness, and adaptability of the CRISPR-Cas system have made it a revolutionary tool in plant breeding. By using CRISPR, researchers may modify certain genes to add desired features or eliminate unwanted ones. Crops with enhanced disease resistance, increased yields, and enhanced resilience to environmental stressors have previously been successfully engineered using the method. For instance, CRISPR has been used to make potatoes resistant to late blight and rice and wheat resistant to drought. It is one of the most promising instruments in contemporary plant breeding because of its capacity to solve concerns related to food security in the face of climate change. Notwithstanding its achievements, there are still issues with regulating CRISPR-modified crops and winning over the general public.

5. RNA Interference (RNAi) and Gene Silencing

Another potent technique that enables the selective silence of genes is RNA interference (RNAi). By inhibiting the expression of particular detrimental genes, this method aids plants in fending against pests, illnesses, and environmental stressors. For instance, by lowering the expression of genes that pests need to survive, RNA interference (RNAi) has been effectively used to produce pest-resistant maize. In addition to controlling pests, RNAi technology has been applied to prolong fruit ripening, increase crop nutritional value, and extend shelf life. Customers who are worried about genetically modified organisms will find RNA interference (RNAi) more acceptable due to its flexibility, which presents new possibilities for regulating gene expression in plants without introducing foreign DNA.

6. Transgenic Crops and Genetic Engineering

The agricultural biotechnology revolution has been significantly influenced by transgenic crops. Breeders can create crops with characteristics that are hard or impossible to get via conventional breeding by inserting alien genes into plants. The most well-known examples are Golden Rice, which is biofortified with Vitamin A, and Bt cotton, which is resistant to certain insects. Transgenic crops still face obstacles including consumer distrust and regulatory barriers despite their success. A potential discovery in genetic engineering is the recent invention of stacked features, which integrate several advantageous qualities into a single plant. Additionally, second-generation genetically

modified crops are being developed to offer enhanced nutrition, increased environmental sustainability, and stress tolerance.

7. Speed Breeding and Accelerated Breeding Techniques

Speed breeding is the process of cultivating plants in regulated environments with longer photoperiods (artificial illumination) to quicken their life cycle. Breeders can finish many breeding cycles in a year by using this strategy, which can shorten the time it takes for a generation of plants to mature. Speed breeding may greatly increase the rate of genetic gains in crops when paired with genomic selection. Speed breeding has already led to the quicker generation of new varieties with better features in crops including chickpeas, wheat, and barley.

8. Synthetic Biology and Plant Metabolic Engineering

In the developing discipline of synthetic biology, researchers may create and build novel biological systems, tools, and species. Synthetic biology is being utilized in plant breeding to modify plant metabolic pathways in order to produce better features such as higher nutrient absorption, improved photosynthesis, and bioenergy generation. Plants that can generate more starch or oil for biofuels and crops with increased nitrogen usage efficiency are examples of advancements brought about by metabolic engineering. Synthetic biology has the ability to produce completely new features and plant species that are suited to certain habitats and agricultural requirements by modifying the metabolic pathways in plants.

9. Precision Agriculture and Digital Breeding Tools

Breeders' data management and breeding decision-making processes are being completely transformed by the combination of digital breeding tools and precision agriculture. Breeders may obtain accurate information about plant phenotypes in real time by using remote sensing, drones, and sophisticated imaging technology. These massive databases are analyzed with the use of AI and big data analytics to forecast trait performance and improve breeding tactics. By decreasing the time and expense needed for field tests and increasing the precision of selection for intricate characteristics like yield and drought tolerance, these computerized technologies increase the efficiency of breeding.

10. Climate-Smart Breeding

Climate-resilient crops are more important than ever as climate change threatens to endanger the world's food supply. New approaches to creating crops that can survive harsh climatic conditions including heat, salt, and drought are provided by contemporary biotechnology. For instance, heat-resistant wheat and drought-tolerant maize have been created thanks to developments in genetic engineering and gene editing. Breeding crops that enhance soil health, trap carbon, and support sustainable farming methods are all examples of climate-smart breeding.

11. Gene Banks and Conservation of Genetic Diversity

Crop genetic variety must be preserved in order to produce robust plant generations in the future. Gene banks and cryopreservation methods are two examples of how modern biotechnology guarantees the long-term preservation of priceless genetic material. By making their DNA available for use in subsequent breeding attempts, breeders are able to unleash the potential of uncommon or underutilized crop types thanks to advancements in these technologies. By maintaining genetic variety, we protect the foundation for transforming agriculture to meet new challenges.

Future of Recent Advances in Biotechnology and Plant Breeding:

Innovative developments that are revolutionizing agriculture are propelling biotechnology and plant breeding into an exciting new era. Modern biotechnology technologies and methodologies are becoming more and more important in crop development as global issues like climate change, food security, and environmental sustainability worsen. Developments in climate-resilient crops, synthetic biology, gene editing, and digital technology integration will all have a big impact on the future.Plant breeding has been transformed by gene editing technologies, especially CRISPR-Cas9, which allow for precise genome alterations. Breeders will have even more power in the future because to the creation of next-generation editing technologies like base editing and prime editing. More intricate trait adjustments will be made possible by these advancements, which will enable changes at the single nucleotide level. The ability to increase disease resistance, nutritional value, and stress tolerance in crops will be available to breeders. Additionally, by developing cultivars that use less water and fertilizer, these technologies can help maintain or even increase yields while lessening their negative effects on the environment. Crucially, gene editing provides a more palatable substitute for conventional GMOs since it alters a plant's own genes instead of adding alien DNA, which may allay consumer worries and regulatory obstacles.

Future developments in plant breeding will also be significantly influenced by the domains of metabolic engineering and synthetic biology. These methods seek to establish

completely new biological activities or restructure plant metabolic networks. Scientists can boost yields while consuming less resources by creating crops that are more adept at photosynthesis. Furthermore, crops that produce industrial chemicals, medicines, biofuels, and food might be created using synthetic biology. Food security may be improved by the capacity to modify plant features, which might result in crops that are more resistant to environmental pressures. Plant breeders will place a lot of emphasis on creating climateresilient crops in response to climate change. Technological developments in molecular breeding and genomic selection will make it possible to produce crops that can resist harsh weather events like floods and droughts without sacrificing yield. In order to adapt to changing environments and maintain agricultural viability in areas experiencing negative climatic impacts, crops that use water and nutrients more effectively will become crucial. The progress of plant breeding will be further accelerated by the combination of precision agriculture, digital technologies, and biotechnology. Breeders will be able to examine genetic data in conjunction with environmental conditions thanks to technologies like artificial intelligence, big data analytics, and machine learning, which will help them make better decisions. High-throughput screening and phenotyping tools will make it possible to quickly assess crop performance in a variety of scenarios, maximizing resource utilization. **Summery:**

By offering creative answers to urgent problems like food security, climate change, and sustainable farming, the incorporation of biotechnology into plant breeding has profoundly changed contemporary agriculture. New crop types may now be developed more quickly and precisely thanks to the combination of gene-editing, genomics, genetic engineering, and molecular markers. Modern biotechnological technologies have significantly improved traditional breeding, which mostly depended on phenotypic selection. As a consequence, crops with superior characteristics, larger yields, and more tolerance to environmental challenges have been produced. Genomic selection (GS), which enables breeders to forecast a plant's performance based on its genetic information, is one of the major developments in this discipline. Breeders may make well-informed decisions long before plants reach full maturity thanks to this technology, which makes it possible to identify desirable features like disease resistance or drought tolerance early on. Utilizing genome-wide markers, GS has expedited breeding initiatives, decreased dependence on laborious conventional techniques, and contributed to the preservation of genetic diversity—all of which are critical for future agricultural resilience. Since next-generation

sequencing (NGS) has made it possible to quickly and affordably sequence plant genomes, genomic selection has become more widely available. The CRISPR-Cas9 gene-editing technique, which enables precise alterations of certain plant genes, is another innovation. Because CRISPR-Cas9 can perform targeted modifications without introducing foreign genes, it is a more acceptable approach of crop modification than prior genetic modification techniques. Important crops including rice, wheat, and maize have already benefited from this technique by developing disease-, drought-, and nutritionally improved versions. Plant breeders may now modify plant genomes with even more precision thanks to emerging gene-editing techniques including base editing and prime editing, which creates more opportunities for crop enhancement. Another crucial instrument in contemporary plant breeding is marker-assisted selection (MAS). It accelerates the production of superior varieties by selecting plants early in the breeding process using molecular markers associated with desired features. MAS has been especially effective in creating crops like rice, wheat, and tomatoes that are more resistant to disease. To handle more complicated qualities like yield and drought tolerance, MAS is frequently used in conjunction with genomic selection, which further improves breeding efficiency, even if it performs well for traits governed by a limited number of genes. Another biotechnology development that has aided in crop improvement is RNA interference (RNAi). Breeders may manipulate particular genes in plants to produce improved features thanks to this natural gene-silencing system. When it comes to creating crops that are resistant to pests, such maize that is resistant to the corn rootworm, RNA interference has been very successful. In order to protect agricultural yield from pests and illnesses, it is also being investigated for enhancing nutritional value and lowering plant vulnerability to viruses. All things considered, the integration of RNA interference, marker-assisted selection, CRISPR-Cas9 gene editing, and genomic selection ushers in a new age in plant breeding. Crops that are more robust, prolific, and better adapted to the difficulties of contemporary agriculture are being developed with the aid of these technologies. These developments are crucial for guaranteeing food security and sustainable farming methods as the world's population rises and climate change worsens. Even more advanced instruments and methods will probably influence plant breeding in the future, spurring more advancements in crop development and agricultural output.

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COACTIONS OF ARTIFICIAL INTELLIGENCE AND DATA SCIENCE FOR PREDICTING NATURAL DISASTER

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Abstract:

Artificial intelligence and Data Science are interrelated subjects which are synergies together to give the perfect space for predicting natural disaster. Artificial Intelligence algorithms help to generate intelligent systems to predict natural disasters in advance and also prevent from heavy loss. Data science is the study of filtering and extracting vast data and supports for AI algorithms for smooth growth. Natural calamities such as volcano, tsunami, storms causes' heavy loss on human life, artificial algorithms and data science can help to analyse closely the past data set of ante and post environmental changes, based on the observation a new model will be generated to predict the disasters in earlier. This paper will discuss on application, hardware, software and AI algorithms.

Keywords: Artificial Intelligence, Data science, Data Analytics, Deep Learning, Machine Learning.

Introduction:

North America and Canada experienced high wild fire in last year it is record breaking news over the past 10 years of history. As per the observation of last year the Canada wildfire emissions represent 27% of whole global wildfire carbon emission. More than 42 million acres have burned in last year which may be doubled in future. Of course due to the forest fire there may be some benefits for wild lives like cleaning of dead animals and trees but the negative impact of forest fire overcomes those benefits. All over the world many researches are going on the forest fire to predict to control and to recover from the forest fire. We have proposed a system for forest fire prediction using CNN algorithm. We have collected previous year records from Tamilnadu forest department.

Methodology

Data Collection and Analyses

Our approaches was being collected data from various websites, satellite images and from difference magazines and extracted the required data like humidity, speed of wind, congested tree patterns and also analyze history previous fire patterns from the other

systems. Every attributes that we took were in two types that were before fire and after fire. Before fires attributes were used to prediction and after fire attributes were used for survival recovery prescriptions.

Working Principle Sample

Figure 1: Color code pattern

Cross-Sectional Study

Cross Sectional study is a type of research which the data is collected from various part of the world at a single point of time. Here we have collected the data about forest fire of both ante and post environmental changes of recent disaster.

Figure 2: State-wise registration in Forest Survey of India – Image Courtesy to Ministry of Environment, Forest & Climate Change.

Review of Literature on "Synergies of Artificial Intelligence and Data Science for Predicting Natural Disaster "

Natural calamities such as volcano, tsunami, storms and forest fire causes' heavy loss on human life, artificial algorithms and data science can help to analyse closely the past data set of ante and post environmental changes, based on the observation a new model will be generated to predict the disasters in earlier. This survey will discuss on different application, hardware, software and AI algorithms written by various authors

In 2019 Zhang *et al.* [1] Using a Convolutional Neural Network, reputed a forest fire susceptibility model for China's Yunnan region (CNN). The model manifested good performance in identifying efficient fire-prone locations, with an accuracy of 82.26%.In 2020 Chen *et al.* [2] made a deep learning-based system for identifying forest fires, and it was able to detect fires with a 98.7% correctness rate on the forest fire image Dataset. The model organized with Convolutional Neural Networks along with long short-term memory (LSTM) for real-time fire identification (CNN). In 2020 Khan *et al.* [3] A CNN and LSTM merged together and form a new forest fire identification system. The UC Merced Land Use Dataset accuracy for the model was 97.43%, and real-time fire agreeing state accuracy was assured. A random forest method was used by Deepak *et al.* [4] in 2020, the model included a number of features, including meteorological facts, terrain, and various types of land covered. This study gave insights into the important aspects leading to forest fire sensitivity, such as land cover, temperature, and slope, and the model was assuring 88.25% of accuracy in detecting fire-prone locations. In 2020 Srinivas and Dua [5] proposed utilizing Unmanned Aerial Vehicles (UAVs) and fog computing, a potential method for detecting forest fire in earlier stage. The model achieved an accuracy of 92.6%. This deep learning-based approach to classify and identify forest fires by satellite images was suggested by Van.

S.No	Author/s	Model	Accuracy/	Validati	Limitation	Year
			Correctne	on	of work	
			SS			
	Zhang et al.	CNN	88.9%	k-fold-	Yunnan	2019
				cross	Province _{of}	
					China	

Table 2: Summary of survey models

Result and Analysis:

The performance of CNN is varied by the hyperparameters, batch size, pooling, overfitting and so on. The following table illustrated the performance.

From the above we got accuracy rate high for similar samples original – original and segmented – segmented produced high accuracy rate. This research produced trust worthy accuracy based on color features recognition when comparing with other existing systems. **Conclusion:**

In our project we exposed forest fire prediction from image recognition based on CNN algorithm. We have conducted experimental analysis for the both flammable and non flammable images. To extract and analyse the flammable images we used the color texture

tool. The results demonstrated the high and efficient recognition feature of the project. From the work we got optimal result for different image type. In future work, we will try to produce high recognition for different image that is original and segmented as well as segmented and original images type also. Along with this we are planning to deepen the project to next layer. Overall we have concluded that we have accessed a good accuracy rate.

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