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Hydrogen as a Catalyst for Sustainability: Decoding the Value Chain of a Low-Carbon Future

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Abstract

The escalating global demand for energy, propelled by rapid economic expansion and population growth, has intensified dependence on fossil fuels, resulting in heightened greenhouse gas emissions and accelerated resource depletion. This pressing scenario underscores the urgent need to transition from conventional energy systems to renewable energy alternatives. Hydrogen (H₂) has emerged as a clean energy fuel to facilitate a shift towards a lower carbon economy. Unlike carbon-based synthetic fuels, H₂ offers the potential for a carbon-neutral or even carbon-negative lifecycle when produced from renewable energy sources. This review provides a comprehensive and systematic analysis of the hydrogen economy, detailing its value chain from production to practical application and elucidating its potential to support decreasing carbon footprint. Herein, we discuss a variety of hydrogen production methodologies, including established techniques such as steam methane reforming and innovative approaches such as electrocatalysis, photocatalysis, biomass conversion, and non-thermal plasma-enhanced dry reforming of methane. Further, it discusses the key concept and governing parameters and emphasises its vital role in decarbonising key sectors. In addition, the review also examines hydrogen storage and transport technologies, including high-pressure compression, cryogenic liquefaction, and chemical carriers such as liquid organic hydrogen carriers (LOHCs) and metal hydrides, evaluating their technical feasibility and scalability. Furthermore, the study explores the applications of hydrogen in industrial processes, transportation, and power generation, highlighting its potential to substitute carbonintensive energy sources. Finally, this review delineates key research and development priorities, underscoring the necessity for interdisciplinary efforts to establish H₂ as a foundational element of a sustainable, low-carbon energy system.

Keywords: Hydrogen, Generation, Storage, Utilization

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1. Introduction

The increase in global population and economic development has led to a significant rise in energy demand, exerting considerable pressure on conventional energy resources. Power generation is essential for industrial growth and is critical in driving economic progress and technological advancements. However, the reliance on fossil fuels to fulfil this demand has resulted in resource depletion, energy security risks, and environmental challenges. Fossil fuels dominate global energy consumption, yet their limited availability and rapid depletion raise longterm sustainability concerns. Additionally, the combustion of fossil fuels contributes to the release of greenhouse gases, exacerbating climate change and underscoring the urgent need for a transition to cleaner energy alternatives. To address these pressing issues effectively, embracing hydrogen-based technologies, enhancing the integration of renewable energy sources, and investing in advanced energy storage systems is imperative. Their crosslinking with each other is vital for ensuring a sustainable and resilient clean energy infrastructure supporting future economic and technological growth. The key drawbacks of consuming these traditional resources (fossil fuels) are CO₂ emissions and increased global warming [1].



Figure 1. Schematic illustration of the hydrogen value chain

Renewable energy resources are the most promising candidates for replacing these conventional resources because of increased environmental problems. Hydrogen, the most abundant element in the universe, is the cornerstone of the global transition to clean energy. Molecular hydrogen gas (H₂) is an attractive fuel. It has the highest gravimetric energy density (142 MJ/kg), and its combustion byproduct is pollution-free water, making it an excellent energy carrier and a potential candidate for future lowcarbon energy systems. Thus, they are considered essential chemicals, but their generation, storage, distribution, and further application, generally called as hydrogen value chain (**Figure 1**), are vital for decarbonising the industry and fulfilling the net zero target. Traditional production methods, such as steam methane reforming (SMR), are carbon-intensive and contribute ~830 Mt of CO₂ emissions annually [2]. Green hydrogen produced via renewable energy-powered electrolysis or novel pathways such as NTP offers a sustainable alternative. Another emerging pathway is photocatalytic hydrogen evolution, which has attracted tremendous interest because it generates green hydrogen based on solar radiation. However, the process is highly complex, as many factors influence photocatalytic hydrogen evolution. At the same time, novel photocatalysts, such as MOFs, perovskites, conjugated polymers, carbon-based materials, quantum dots, and others, face challenges such as stability and scalability.

In contrast, thermo-chemical pyrolysis and gasification are existing approaches in industries and play a dominant role in H₂ production, with costs in the range of 1.34–2.27 \$/kg. Hydrogen storage is a critical aspect of the hydrogen economy, influencing its viability for energy applications. Storage methods include compressed gas, liquid hydrogen, metal hydrides, and chemical carriers such as ammonia and liquid organic hydrogen (LOHCs). Although compressed and liquid hydrogen offer direct storage solutions, they require high pressures (350-700 bar) or cryogenic temperatures (-253°C), leading to energy-intensive processes. Solid-state storage in metal hydrides and chemical carriers provides safer and more compact alternatives but faces challenges related to kinetics and reversibility. Advancements in storage materials and system integration are essential for enhancing efficiency and enabling large-scale hydrogen deployment before efficient hydrogen distribution, essential for the widespread adoption of hydrogen-based energy systems. H₂ can be transported through pipelines, compressed gas or liquid hydrogen tankers, and chemical carriers such as ammonia or liquid organic hydrogen carriers (LOHCs). Pipelines represent the economically efficient option for large-scale distribution. However, retrofitting existing infrastructure presents notable challenges that must be addressed. Cryogenic liquefaction and compression enable long-distance transport but incur high energy costs. Advancements in hydrogen carriers and storage technologies are essential to overcome logistical barriers and ensure a reliable supply chain. As a clean energy carrier, hydrogen can replace fossil fuels in hard-to-abate industries such as steelmaking, cement production, and



Figure 2. Comparison of Energy density (kWh/l) vs. energy per unit mass (kWh/kg) (top) and energy density of carbon and zero-carbon-based fuels (bottom). Image taken from reference [4] with permission

chemical manufacturing, where direct electrification is challenging. In the transport sector, hydrogen fuel cells offer a viable alternative to heavy-duty trucks, maritime shipping, and aviation, reducing reliance on carbon-intensive fuels. In addition, hydrogen can be blended with natural gas or used in dedicated hydrogen turbines for low-carbon power generation. Coupled with carbon capture and storage (CCS) or produced via renewable-powered electrolysis, hydrogen has the potential to enable profound emission reduction across the energy system. However, achieving net zero requires overcoming the challenges related to hydrogen production scalability, cost reduction, infrastructure expansion, and energy efficiency improvements. Strategic policy frameworks, technological

advancements, and international collaborations are essential for unlocking the full potential of hydrogen in a sustainable and decarbonised global economy. Further, India's National Green Hydrogen Mission (NGHM), with its significant ₹19,744 crore investment, is an example of sustainable development efforts to establish hydrogen as a linchpin of decarbonization [3].

2. Hydrogen Properties

Hydrogen has unique physicochemical properties, such as having the highest energy per unit mass of approximately 3.7 kWh/kg (Figure 2 top). Furthermore, it compares other fuels used as automotive fuels and carbon- and non-carbon-based energy densities. However, its volumetric energy density is relatively low, at just 0.089 g/L in gaseous form under standard conditions. This low density necessitates high-pressure compression (350-700 bar) or liquefaction at -253°C for practical storage and transportation. In addition, hydrogen is colourless, odourless, and non-toxic; however, it has a wide flammability range (4-75% in air) and low ignition energy, requiring careful handling. Its high diffusivity allows for rapid dispersion, which reduces the risk of explosion in the open air. Additionally, hydrogen has a low boiling point (-252.9°C) and melting point (-259.2°C), creating cryogenic challenges that impact its applications. These properties significantly influence the use of hydrogen in fuel cells, combustion processes, and hydrogen-based industrial reactions, thereby highlighting the need for advanced storage and distribution technologies.

Another primary concern is hydrogen embrittlement, in which hydrogen diffuses into metal pipelines and storage containers, weakening their structural integrity and increasing the risk of cracking and failure. This issue is particularly critical in high-pressure pipelines and storage systems, where prolonged exposure can accelerate material degradation. As known, H_2 low energy density by volume requires both high-pressure compression and cryogenic liquefaction, which requires substantial energy input and specialised infrastructure. next challenges The associated with H₂ leakage are significant due to its small molecular size, which facilitates its escape through the distribution infrastructure's seals, channels, and microscopic pores. Additionally, the absence of a dedicated H₂ pipeline network, contrast to the well-established in infrastructure for natural gas, restricts the potential for large-scale deployment. To address this limitation, alternative hydrogen transportation methods, including liquid organic hydrogen carriers (LOHCs) and ammonia-based storage solutions, are being explored for their feasibility in long-distance and large-volume hydrogen transport. Addressing these challenges will require advancements in materials science, pipeline coatings, and efficient hydrogen carrier technologies to ensure a safe and costeffective distribution.

3. Hydrogen Production Technologies Hydrogen production can be categorised into two groups based on raw materials: fossil fuels and renewable resources, such as biomass and water. We primarily considered biomass or water when producing hydrogen from renewable sources. Using biomass as feedstock, the processes can be divided into two subcategories: thermochemical and biological [5]. Thermochemical technologies include pyrolysis, gasification, liquefaction, combustion, and plasma catalysis. On the other hand, the main biological processes for hydrogen production are photolysis and fermentation. The second category of renewable technologies focuses on methods that generate hydrogen through water-splitting processes. These methods include electrolysis, thermolysis, photocatalysis, and photoelectrolysis using water as the only input material. Different pathways for hydrogen production are shown in Figure 3. Additionally, hydrogen production methods are commonly classified using a colour

coded system that categorises hydrogen based on its production method.

d) **Turquoise Hydrogen** is generated through methane pyrolysis and natural gas is thermally decomposed into



Figure 3. Schematic Illustration of various hydrogen generation processes.

- a) Gray Hydrogen is primarily produced from natural gas through steam methane reforming (SMR) without carbon capture, producing emissions of approximately 9 to 10 kilograms of CO₂ for every kilogram of hydrogen produced. Although this method of hydrogen production is the most common today, it significantly contributes to carbon emissions.
- b) Blue Hydrogen is derived from steam methane reforming (SMR) or autothermal reforming (ATR) with carbon capture, utilisation, and storage (CCUS). This process can reduce CO₂ emissions by up to 90%. It provides a transitional solution while green hydrogen is being developed, but its effectiveness depends on the efficiency and infrastructure of CCUS.
- c) Green Hydrogen is produced through water electrolysis using renewable energy sources (solar, wind, hydro) with zero direct CO₂ emissions. It is considered the most sustainable option, but its cost remains high (\$3–6 per kg of H₂) because of expensive electrolysers and renewable electricity.

hydrogen and solid carbon. This process avoids CO₂ emissions but requires further development for largescale implementation.

- e) Pink (or Purple) Hydrogen is usually produced through electrolysis powered by nuclear energy; this process offers a low-carbon alternative with stable baseload electricity. However, challenges persist, such as high nuclear infrastructure costs and effective waste management.
- f) Yellow Hydrogen is produced through electrolysis using grid electricity, which has a carbon footprint that varies based on the energy mix. If renewable energy powers the process, it qualifies as green hydrogen; otherwise, it may produce emissions.
- **g)** White Hydrogen is naturally occurring geological hydrogen in underground reservoirs. It is currently in the early exploration stage and has the potential to be a sustainable hydrogen source if the extraction becomes viable.
- h) Black/Brown Hydrogen, produced from coal gasification, emits significant levels of CO₂ and is the most carbon-

intensive form of energy. Owing to environmental concerns, this is an obsolete technology.

One of the emerging pathways is Photocatalytic hydrogen evolution, which uses light energy to initiate a chemical reaction that leads to hydrogen evolution, involves light absorption by semiconductor/ photocatalyst materials, leading to the splitting of water molecules and the formation of hydrogen and oxygen gases via redox reactions at the conduction band (CB) and valance band (VB) region respectively [6]. An effective photocatalyst typically consists of redox properties that expedite the required chemical processes and a lightcollecting antenna for solar energy absorption. Next, photoexcited electrons (e⁻) and holes (h⁺) along the thermodynamic potential of reactions process the redox reaction. The photocatalyst absorbs UV-Vis light from the sun or other illumination sources. The photoexcited electrons go to the conduction band (CB), forming electronhole pairs with holes in the valence band (VB). The energy gap, or band gap, the difference between VB and CB, determines how much light is absorbed or whether the catalyst is photoactive or UV-active. In a photocatalytic water-splitting system, photoexcited electrons and holes move to the surface of the photocatalyst after light illumination and act as reducing and oxidising agents, respectively. Upon contact with water, whether on the surface of the photocatalyst or within the cocatalyst, the ensuing oxidation and reduction processes as described are initiated, in the equation below. In a photocatalyst (PC), the absorption of photons leads to the generation of electron-hole pairs, initiating the process of water splitting (R1).

$$PC + 4hv \rightarrow 4e^- + 4h^+$$
 R1

The oxidation half-reaction occurs at the anode, where water molecules are oxidised to oxygen and protons (R2).

$$2H_2O + 4h^{\scriptscriptstyle +} \rightarrow O_2 + 4H^{\scriptscriptstyle +} \qquad \qquad R2$$

Simultaneously, at the cathode, the reduction half-reaction facilitates hydrogen evolution(R3) as follows: $4H^+ + 4e^- \rightarrow 2H_2$ R3

The overall water-splitting reaction (OWS) (R4) can be represented as:

$$2H_2O + 4e^- + 4h^+ \rightarrow 2H_2(g) + O_2(g)$$
 R4

To proceed, the energy input must overcome the standard Gibbs free energy change (ΔG°) of 237 kJ mol⁻¹, corresponding to an electrochemical potential of 1.23 eV. As a result, the band gap of the photocatalyst must be at least 1.23 eV (approximately 1000 nm) to enable thermodynamically favourable water splitting. However, a band gap closer to the visible range is perceived to harvest 45% of the light falling on the earth's surface. At the same time, most studies focused only on UV light active photocatalyst, which contributes only 5% of the light spectrum. However, nanostructuring efficient photocatalysts for hydrogen (H₂) evolution remains a significant challenge, requiring a balance light between optimal absorption, thermodynamic potential difference, and redox activity [7]. Photocatalytic hydrogen (H₂) production holds significant promise for sustainable energy conversion but encounters several limitations. For Instance, higher band gap, the recombination of electrons and hole pairs. catalyst recyclability, and the prolonged hours of reactions in the presence of cocatalysts and sacrificial reagents for higher yields. Furthermore, the higher thermodynamic potential to proceed with the nonspontaneous reaction, ineffective charge carriers' dynamics, formed gas separation and unfavourable anode-cathode reactions impede overall efficiency. Over the past two decades, various strategies have been investigated to address these obstacles, including band gap engineering, metal/ metal or nonmetal doping, heterojunction formation, surface modification, and the development of core-shell nanostructures. Notably, enhancing charge separation and

catalytic activity by incorporating cocatalysts, defect engineering, and Zscheme or type II configurations has promising demonstrated results in improving performance. Optimising reaction conditions, enhancing catalyst improving design, and reactor configurations are crucial for minimising kinetic losses and enhancing charge transfer dynamics[6]. In addition, advanced lightharvesting strategies, such as elevating plasmonic behaviours, can be leveraged to enhance light-harvesting effects. Nanostructuring with different catalyst combinations for tailoring catalyst properties enhances photocatalytic H₂ evolution that can be further optimised for applications. practical, clean energy Meanwhile, electrocatalysis remains a wellestablished hydrogen production method, with alkaline electrolysis, proton exchange membrane (PEM) electrolysis, and solid oxide electrolysis cells (SOEC) being the most widely deployed technologies[8]. In PEM electrolysers, water oxidation at the anode generates protons (H^{+}) and oxygen(R7), while the protons migrate through the membrane to the cathode, forming hydrogen gas(R8). In contrast, alkaline and SOEC electrolysers introduce water at the cathode, where it is reduced to hydrogen gas and hydroxide ions (OH⁻)(R6), with hydroxide ions migrating to the anode for oxygen evolution(R5). The key reactions for each system are as follows.

Alkaline	and	SOEC	Electr	olysis					
Anode Rea	Anode Reaction								
$40H^{-} \rightarrow 0$	R5								
Cathode R $2H_2O + 2e^{-1}$		R6							
PEM Elect Anode Rea 2H₂O → O	rolysis action 2 + 4H ⁺ -	+ 4e⁻		R7					
Cathode R	eaction								

 $4H^+ + 4e^- \rightarrow 2H_2$

Electrolysis allows the production of highpurity hydrogen directly from water; however, its efficiency and energy consumption vary depending on the technology used. Commercial alkaline electrolysers can achieve annual hydrogen production rates of up to 380,000 kg with a system energy consumption of approximately 53.4 kWh/kg of hydrogen (H₂) and an efficiency of 73%. Solid Oxide Electrolysis Cells (SOEC) differ from alkaline and Proton Exchange Membrane (PEM) electrolysis systems operating at elevated temperatures[9]. This allows for partial replacing electrical energy with thermal energy, resulting in higher efficiency. However, the requirement for high temperatures (typically above 700°C) poses challenges for material durability. Electrolysis is one of the cleanest methods for H₂ production and reducing energy consumption improving and system longevity are critical areas for further research and development. Hydrogen can also be produced from fossil fuels via hydrocarbon reforming and pyrolysis [10,11]. Numerous chemical techniques are employed in hydrocarbon reforming, including steam reforming, partial oxidation, and autothermal steam reforming (as discussed with the reaction equation). Partial oxidation (POx) serves as a traditional method for hydrogen production, which involves the conversion of hydrocarbons, steam, and oxygen into hydrogen and carbon oxides. The catalytic POX process operates at approximately 950°C and can utilise a range of feedstocks, from methane to naphtha. Conversely, the non-catalytic POX process necessitates higher temperatures, specifically between 1150°C and 1315°C, making it suitable for processing heavier hydrocarbons such as heavy oil and coal. Hydrocarbon reforming reaction, usually used in the chemical process plant as a broader category of hydrogen production, facilitates the transformation of hydrocarbon into hydrogen through steam and oxygen as reactants. In the steam reforming (SR)

R8

process, hydrocarbons react with steam to yield hydrogen and carbon monooxides (R10), while partial oxidation entails the reaction of hydrocarbons with oxygen(R9). Next, autothermal reforming integrates both processes, effectively balancing the endothermic and exothermic reactions to enhance overall efficiency. The steam reforming consists of three fundamental steps: generating synthesis gas (syngas), the water-gas shift (WGS) (R11) reaction to produce additional hydrogen, and subsequent purification through methanation (R12) or various gas separation techniques. The raw materials for this process can range from methane, natural gas, and other methane-containing gases to various combinations of light hydrocarbons, including ethane, propane, butane, pentane, and light and heavy naphtha. If the feedstock contains organic sulfur compounds, a desulfurisation step is necessary before the reforming process to prevent poisoning of the reforming catalyst, which is typically nickel-based.

Reforming Reactions

1. Catalytic Reforming:	
$C_nH_m+(n/2)O_2 \rightarrow nCO+(m/2)H_2$	R9

2. Noncatalytic Reforming	
$CH_4 + nH_2O \rightarrow nCO + (m + n) H_2$	R10

Water-Gas Shift (WGS) Reaction
$$CO + H_2O \rightarrow CO_2 + H_2$$
R11

Methanation Reaction	
$\mathrm{CO} + 3\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + \mathrm{H}_2\mathrm{O}$	R12

Thermochemical technologies primarily involve pyrolysis and gasification. Both processes yield various gaseous products, including methane (CH₄) and carbon monoxide (CO), which can be further processed to produce additional H₂ through steam reforming and water-gas shift (WGS) reactions. In addition to these methods, combustion and liquefaction are considered less preferable. Combustion results in low hydrogen production and emits polluting byproducts, whereas liquefaction requires challenging operational conditions, ranging from 5 to 20 MPa, in the absence of air [12].

pyrolysis Biomass is ล thermochemical process that generates liquid oils, solid char, and gaseous compounds by heating biomass to temperatures between 650 K and 800 K at pressures of 0.1 to 0.5 MPa. This process occurs without oxygen, except in cases where partial combustion is permitted to supply the required thermal energy. On the other hand, biological H₂ production operate under ambient processes temperature and pressure, making them inherently energy efficient. These processes utilise renewable energy sources that are virtually inexhaustible and contribute to waste recycling using organic waste as feedstock. The primary biological pathways for H₂ generation include direct and indirect bio-photolysis, photofermentation, dark fermentation, and multistage (sequential) dark and photofermentation processes. Biophotolysis is a biological mechanism that photosynthetic principles leverages observed in plants and algae for H₂ production. Unlike higher plants, which only reduce carbon dioxide (CO_2) owing to the absence of H₂ producing enzymes, certain algae possess hydrogenase and nitrogenase enzymes that can generate molecular hydrogen under specific conditions. For example, green algae, such as Chlamydomonas reinhardtii, can produce hydrogen through direct bio-photolysis, where water molecules are split into protons and oxygen during photosynthesis. The protons are then converted into molecular H₂ by the hydrogenase enzyme. However, hydrogenase is highly sensitive to oxygen and requires strict oxygen control below 0.1% to sustain hydrogen production. Moreover, at full sunlight intensity, nearly 90% of the photons captured by the photosynthetic apparatus (chlorophyll and associated pigments) remain unused, resulting in efficiency limitations. Indirect bio-photolysis, primarily facilitated by cyanobacteria (blue-green algae), occurs in

two stages. In the first stage, photosynthetic activity produces glucose, as shown in the following reaction (R13-14):

$\begin{array}{l} 12H_2O+6CO_2+\{light\ energy\}\rightarrow C_6H_{12}O_6+\\ 6O_2 \end{array}$

In the second stage, glucose is further broken down to yield hydrogen:

This process relies on enzymes hydrogenase and nitrogenase, achieving hydrogen production rates comparable to green algae. However, indirect bio-photolysis is still largely conceptual, with an estimated capital cost of \$135 per square meter and a projected hydrogen production cost of approximately \$10 per gigajoule, or \$1.42 per kilogram of H₂. Despite their potential, biological methods for H₂ production face several challenges including low conversion efficiency, oxygen sensitivity of key enzymes, and scalability constraints. Future advancements in genetic engineering, reactor design, and metabolic optimisation may improve the feasibility of these methods for large-scale hydrogen production.

Plasma catalysis has emerged as a hvdrogen promising approach for production, leveraging non-thermal plasma (NTP) to drive chemical reactions at relatively low bulk temperatures [13,14]. The interaction between the plasmagenerated reactive species and catalytic surfaces facilitates enhanced reaction kinetics, lowers energy barriers, and enables hydrogen generation from diverse feedstocks, including water, hydrocarbons, ammonia, and biomass-derived gases. Plasma catalysis integrates the benefits of plasma-induced radical formation with those of heterogeneous catalysis, creating an efficient route for H₂ production. Depending on the nature of the feedstock, different reaction pathways can be employed:

Plasma-Catalytic Water Splitting

In this process, water molecules undergo dissociation in the plasma environment, leading to the formation of H_2 (R15) and oxygen radicals. These reactive species subsequently interacted with the catalyst, enhancing the reaction selectivity and improving the hydrogen yield (R16).

Overall Reaction
$$2H_2O \rightarrow 2H_2 + O_2$$
R15

Activation Pathway $e^- + H_2O \rightarrow H^+ + OH^- + e^-$ R16

Plasma-Catalytic Methane Reforming (Dry Reforming (R17) & Steam Reforming (R 18))

Dry Reforming:	
$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$	R17

R18

Steam Reforming $CH_4 + H_2O \rightarrow 3H_2 + CO$

The above reactions can be activated from plasma or non-thermal plasma, which reduces the need for high temperatures compared with conventional thermocatalytic reforming. Plasma-catalytic ammonia Decomposition and Plasmaassisted NH₃ decomposition (as shown in reaction R19) allow for efficient hydrogen production at lower temperatures than traditional thermal-based catalytic processes.

$$2NH_3 \rightarrow N_2 + 3H_2$$
 R19

High energy plasma, usually called the 4th state of matter, offers several advantages for hydrogen production. It enables lowtemperature activation, allowing reactions to proceed at reduced temperatures compared to conventional thermal catalytic processes, eventually lowering the energy requirement. high-energy electrons in The nonequilibrium reaction pathways help overcome activation barriers and facilitate alternative reaction mechanisms. In addition, plasma catalysis can integrate into the hydrocarbon processing unit's operation. Their ease of continuous feedstock treatment, such as ammonia and biomassderived gas processing. The interaction between plasma-generated reactive species and catalytic surfaces mainly enhances reaction kinetics, improves selectivity, and boosts overall catalytic performance [15]. Despite these advantages, plasma catalysis needs continuous temperature and pressure control to use plasma efficiently. That may hinder its widespread industrial application. Energy efficiency remains critical because plasma generation requires significant power input at a specific frequency, such as over 50 kHz. Furthermore, catalyst stability under plasma conditions is oxidised or sintered, which affects long-term

Table 1.	Comparison o	of Hydrogen	Production	Processes	with advantages.	disadvantages a	nd TRL levels.
I abic 1.	Comparison c	n nyulogen	1 louuetion	1100005005	with advantages,	aisuavaitages e	

Process	Efficiency (%)	Major Advantages	Major Disadvantages	Technology Readiness
				Level (TRL)
Steam Reforming (SR)	74–85	A 1		9
Partial Oxidation (POx)	60–75	with established	CO ₂ is a byproduct of fossil fuel use.	8–9
Autothermal Reforming (ATR)	60–75			8–9
Methane Pyrolysis	~50	Emission-free, reduced-step procedure.	Carbon byproducts, dependence on fossil fuels.	6–7
Biomass Pyrolysis	35-50	Environmentally	Tar formation,	5-6
Biomass Gasification	4065	friendly, abundant, and affordable raw materials.	varying hydrogen yield, and seasonal changes in feedstock availability.	6–7
Bio-photolysis	10	CO ₂ consumed, O ₂ is the only byproduct and operates under mild conditions.	Requires sunlight, low H ₂ yield, O ₂ sensitivity, and controlled temperature.	3-4
Dark Fermentation	6080	CO ₂ -neutral process effectively aids in waste recycling.	Lower yield and conversion efficiency. require large reactor volume.	4-5
Photofermentation	0.1	CO ₂ -neutral methods can use organic waste and wastewater.	Requires sunlight, low conversion efficiency, O ₂ sensitivity.	3-4
Electrolysis	40-60	No emissions with renewable sources, proven technology, integrates with RES.	Low efficiency, high capital costs.	8–9
Thermolysis	20-45	Clean, sustainable, abundant feedstock, O ₂ as the only byproduct.	Material corrosion, high capital costs.	4-5
Photo-electrolysis	0.06	Emission-free, abundant feedstock, O ₂ as the only byproduct.	Requires sunlight and low apparent quantum yield	3-4

performance. The next challenge is the scalability for higher flow rates, which needs advancements in reactor design and optimisation of plasma discharge catalyst interactions. Addressing these issues requires the development of robust catalysts, improved reactor configurations and enhanced process integration strategies. Nonetheless, Plasma catalysis is a promising pathway for sustainable hydrogen production, particularly in decentralised and renewable energy-integrated systems. Next, in **Table 1**, we compare the various H_2 production processes' efficiency, significant advantages and disadvantages, and the corresponding Technology Readiness Level (TRL). However, continued research and technological advancements are essential to overcoming existing limitations and revamping the full potential of the H₂ economy.

Developing H_2 generation technologies requires a comprehensive approach integrating catalyst and reactor design, simulation-driven optimisation, in situ analytical techniques, techno-economic evaluation, life cycle assessment (LCA), process integration, and regulatory compliance. This development seeks to enhance reaction kinetics, optimise process intensification. and ensure economic feasibility. Developing highly active and durable catalysts, including nanostructured materials, doped metal oxides, and transition metal phosphides, is crucial for enhancing efficiency, catalytic selectivity, and operational stability. Next, an in-depth understanding of plausible reaction mechanisms, such as intermediate formation, charge transfer dynamics, and rate-determining steps, are crucial for enhancing catalytic overall performance. Besides this, theoretical and computational approaches such as density functional theory (DFT) calculations and microkinetic modelling will aid in identifying active sites and adsorption energetics, facilitating the rational design of catalyst facets[16]. Further, process modelling and simulation using tools like ASPEN Plus, COMSOL Multiphysics, and computational fluid dynamics (CFD) also play a key role in optimising reactor operation configurations for elevating energy efficiency[17]. As a result, such techniques improve mass and heat transfer characteristics, enhancing reactor performance in thermochemical, electrochemical, and plasma-assisted hydrogen production systems. Furthermore, techno-economic analysis (TEA) and life Cycle Assessment (LCA) are essential for evaluating the commercial viability of H₂ production, considering factors such as capital expenditure (CAPEX), operational costs (OPEX), and overall economic feasibility study. In general, overall minimization of overall carbon footprint for H₂ generation technologies is desired as indicated in Figure 4 for further development.

Investigation using current state-ofthe-art tools and techniques such as In-situ characterisations of Fourier Transform Infrared spectroscopy (FTIR), Electron Paramagnetic Resonance (EPR), and Near-



Figure 4. Minimisation of overall carbon footprint for hydrogen generation technologies.

Ambient Pressure X-ray Photoelectron Spectroscopy NAP-XPS are also crucial for ensuring operational catalysts stability and optimising H_2 production efficiency. Such analysis helps identify the key parameters and the effect of different available feedstock qualities on the reaction condition. Also, it is important to elucidate the reaction mechanism for hydrocarbons, and biomass-derived ammonia, gas decomposition under the influence of various reaction conditions and correlate with the overall economic viability of hydrogen production. Further, transitioning from laboratory-scale research to pilot-scale validation and industrial deployment requires comprehensive testing of catalyst performance, process stability, and energy efficiency under realistic conditions. By advancing reactor designs, optimising processes, and incorporating sustainability assessments, H₂ production technologies can be scaled into economically viable and environmentally sustainable solutions, supporting the growth of the H₂ economy. After analysis of thermos economic analysis, it desired to process the residue or by-product without impacting the environment. Also. following the environmental constraint set by the Climate Intergovernmental Panel on Change. To ensure sustainability, LCA analysis checked should be for environmental footprint calculations, considering greenhouse gas emissions, consumption, energy and resource utilisation. Reactor design remains pivotal, requiring advancements in structured catalysts, microreactors, and modular systems for decentralised H₂ production. The selection of reactor materials must thermal consider stability. corrosion resistance, and mechanical strength to withstand high-temperature and reactive environments. Energy efficiency is essential for optimising H₂ production, with strategies including waste heat recovery, process intensification through membrane separation, and integration with renewable energy sources. These approaches not only improve H₂ yield but also reduce overall energy consumption, contributing to a more sustainable and cost-effective hydrogen production process.

4. Hydrogen Storage

Recently, the world has turned to H_2 as a promising candidate for several industrial including transportation, applications, electricity generation, and long-term energy storage. However, efficiently storing H₂ presents significant challenges due to its low volumetric energy density and high diffusivity. Traditional storage methods, such as compressed gas tanks and cryogenic liquid H₂ tanks, are commonly used but have limitations. These include concerns about long-term storage, such as embrittlement, energy-intensive liquefaction processes, and potential leakage due to hydrogen's small molecular size. Several advanced H₂ storage methods are being explored, as shown in Figure 5, to address these challenges, categorised into physical, phase, and material-based, which are further classified into different sections. However, emerging options include underground storage, metal and complex hydrides, metal-organic frameworks (MOFs), and liquid organic hydrogen carriers (LOHCs). Underground storage in geological formations, such as salt caverns, provides a viable option for largescale and long-duration H_2 storage[18]. However, significant capital investment, proximity to suitable geological sites, and careful management are required to prevent contamination of the stored gas. Metal and complex hydrides can chemically absorb and release H₂, allowing for high volumetric storage densities of up to 6 wt.% when using compounds like MgCl₂. Nonetheless, their slow-release kinetics and high thermal activation requirements pose practical challenges. Metal hydrides, such as MgH₂ and LaNis, show promising hydrogen capacities of 6-7 wt.%, but the cyclic adsorption and desorption process results in decreased efficiency with each cycle metal-organic [19,20]. Emerging frameworks (MOFs) use exceptionally high surface areas exceeding $10,000 \text{ m}^2/\text{g}$ to physisorption-based enhance storage. prolonged adsorption However, and desorption remain challenging.

While MOFs are recognised for their high surface area and microporous structures that facilitate H_2 adsorption, their practical application is limited by the low operating temperatures needed for effective adsorption and innovative material designs to optimise performance under ambient conditions. Integrating metal hydride (MH) storage into Power-to-Power (P2P) systems offers significant advantages in H₂-based energy storage. The MH tank, positioned between an electrolyser and a fuel cell or hydrogen internal combustion engine, operates at outlet pressures of approximately



Figure 5. Schematic illustration of Hydrogen Storage in various categories.

30 bar, eliminating the need for additional compression. This is a distinct advantage over compressed gaseous hydrogen (CGH₂) storage systems. The desorption pressure associated with metal hydride (MH) storage aligns effectively with the inlet pressure requirements of proton exchange membrane (PEM) fuel cells, which typically range from 3 to 5 bar. This compatibility facilitates the direct supply of hydrogen without excessive pressurisation, thereby enhancing system safety, reducing maintenance requirements, and minimising overall costs by eliminating the need for high-pressure components [21]. Moreover, MH storage is characterised by high volumetric energy density and scalability, making it suitable for smallscale residential energy storage applications and large-scale seasonal hydrogen reserves. Its capacity to retain hydrogen without losses further underscores its viability for medium- to long-term storage applications. In residential energy systems, overall efficiency is of paramount importance. A conventional power-to-gas-to-power (P2P) configuration comprises an electrolyser, a fuel cell, and a hydrogen storage unit, each contributing to efficiency losses at various stages of the energy conversion process. Nonetheless, system efficiency may be optimised by harnessing the reaction heat generated during hydrogen absorption and desorption.

The heat produced during the charging phase (absorption) and waste heat from the electrolyser can be redirected for residential heating or integrated into thermal energy storage systems. Similarly, the waste heat from the fuel cell can be effectively harnessed during the discharging phase (desorption). Despite MH storage exhibiting lower efficiency than battery-based energy storage systems, its scalability and compact design offer advantages for medium- to long-term hydrogen storage applications. While MH storage's slower H₂ release kinetics is generally not a limiting factor for a steady energy supply, a small buffer storage system may be necessary to accommodate peak power demands. Similar considerations apply to off-grid hydrogen storage systems reliant on renewable energy sources, where stability and energy density are key parameters.



Figure 6. Volumetric and gravimetric energy densities of storage systems such as metal hydrides and others. Image taken from [22] with permission.

For backup power applications, seasonal variations of sunlight availability are crucial for energy storage. However, MH storage's inherently slower hydrogen release kinetics presents a challenge. As a result, batteries are more suitable for short-duration backup power applications. A hybrid system that integrates metal hydride (MH) storage with a smaller battery may provide an optimal solution for extended backup durations ranging from several days to weeks. Such configuration prefers MH storage's high volumetric energy density and scalability ensuring immediate while response capabilities. However, addressing regulatory constraints related to large-scale hydrogen storage is desired. The implementation of large-scale metal hydride storage systems is accompanied by the need for extensive administrative and regulatory approvals, therefore increasing the complexity of their deployment [22]. Despite these challenges, hydrogen storage based on metal hydrides remains a promising long-term solution, particularly for decentralised, off-grid, and industrial applications, due to its inherent safety, efficiency, and scalability. Complex metal hydrides are notably advantageous for mobile applications because of their high hydrogen storage capacity and relatively low weight. In addition, concerns are associated with MH toxicity and flammability.

Nonetheless, practical challenges hinder the widespread adoption due to lesser efficiency under actual operating conditions. The reversible hydrogen storage capacity is significantly lower than theoretical predictions, often decreasing each cycle. Moreover, the multi-step dehydrogenation and hydrogenation processes necessitate elevated temperatures and pressures, resulting in slow kinetics and diminished reversibility. Ongoing research efforts are concentrated on developing advanced catalysts and alternative reaction pathways to overcome these limitations. Next, thermal management is critical to MH storage configurations' viability. Efficient heat exchange mechanisms maintain operational stability and enhance hydrogen release and uptake rates. Currently, technologies based complex hydrides are not vet on commercially mature and require further fundamental research and process optimisation to facilitate large-scale implementation. An advantage of lithiumbased metal hydrides is their less abundant raw material and recyclability performance, making them a sustainable alternative to conventional high-pressure H₂ storage in carbon-fibre-reinforced tanks. As industries increasingly adopt circular economy principles and prioritise life-cycle carbon footprint reduction, these attributes could drive broader adoption of MH storage solutions for medium- to long-term H₂ applications. Consequently, greater emphasis should be placed on developing efficient recycling processes and end-of-life studies to enhance the sustainability of metal hydride technologies. Improved recycling methods could also reduce manufacturing costs for MH-based storage tanks, thereby increasing their competitiveness with alternative hydrogen storage technologies and facilitating their commercialisation within the H₂ energy sector.

5. Hydrogen Distribution

Efficient H₂ transport is critical to a sustainable hydrogen economy, necessitating cost-effective, high-capacity,

and safe storage and distribution methods. Among available technologies, Liquid Organic Hydrogen Carriers (LOHCs) provide a promising solution due to their reversible hydrogenation and dehvdrogenation cycles, which enable safe, long-distance transport without the need for cryogenic liquefaction or high-pressure storage (shown in Figure 7). LOHCs chemically bind H₂ under moderate temperature and pressure conditions during and hydrogenation release it via dehydrogenation at the point of use. These processes, however, require significant energy input, which can be minimised through heat integration and catalyst optimisation to improve overall efficiency and economic viability. The feasibility of LOHC-based transport largely depends on hydrogenation and dehydrogenation efficiencies, which are influenced by carrier separation inefficiencies, losses, and catalyst stability. The primary cost drivers in hydrogenation include solvent losses and the energy-intensive separation of accumulated byproducts, while in dehydrogenation, the high cost of noble metal catalysts poses a significant challenge. Advancements in lowhigh-performance catalysts cost, with reduced deactivation rates and lower reaction temperatures are essential to enhance the process efficiency. Optimising heat recovery between exothermic and endothermic dehydrogenation can significantly reduce the overall energy demand and improve the hydrogen yield. LOHCs such as dibenzyl toluene, perhydro-N-ethyl carbazole, and methylcyclohexane exhibit 5-7 wt% H₂ storage capacities, making them competitive with alternative H₂ storage methods. Their low vapour pressure, non-toxic nature, and chemical stability enhance operational safety and compatibility with existing petrochemical infrastructure, facilitating large-scale implementation. For transoceanic transport, LOHCs are advantageous over compressed or liquefied hydrogen, minimising H₂ losses due to boil-off and enabling continuous supply chains for industrial and mobility



Figure 7. Schematic Illustration of LOHC supply chain.

applications. **Table 2** presents LOHC couples discussed in this Perspective, along with their hydrogen storage capacity, standard Gibbs free energy (ΔG°), and standard redox potential (E°)[23].

For transoceanic transport, LOHCs are advantageous over compressed or liquefied hydrogen, minimising H₂ losses due to boil-off and enabling continuous supply chains for industrial and mobility applications. Table 2 presents LOHC couples discussed in this Perspective, along with their hydrogen storage capacity, standard Gibbs free energy (ΔG°), and standard redox potential (E°) [23]. For a comparison of the LOHC couples, the ΔG° per mole of H₂ transferred (ΔG° relative) is also included. An example of an LOHC couple is the dibenzvltoluene/ pair perhydrodibenzyltoluene (H0-DBT/H18-DBT). An example of an LOHC dibenzvltoluene/ couple is the perhydrodibenzyltoluene pair (H0-BT/H18-DBT). The H0-DBT/H18-DBT couple offers a hydrogen storage capacity of 6.24 wt %, making it an efficient system for reversible hydrogenation and dehydrogenation cycles. Another notable advantage of the H0-DBT/H18-DBT couple is its extensive liquid range, characterised by melting points (MPs) below -30 °C and boiling points (BPs) exceeding 350 °C. This property ensures stability and ease of handling across various operating conditions. Nonetheless, a major limitation of the dibenzyl toluene (DBT)-based liquid

organic hydrogen carrier (LOHC) system is its substantial energy requirement during the thermo-chemical dehydrogenation (TCD) process, which adversely impacts the overall efficiency of H₂ storage and release.

No.	LOHC Pair	Reaction		H Loading (wt%)	∆G° (kJ/mol)	∆G° relative (kJ/mol H²)	E° (V vs SHE)
1	Dibenzyltoluene (H0- DBT)/Perhydrodibenzyltoluene (H18-DBT)	$\Box = C_{21}H_{20} + 9H_2 \rightleftharpoons C_{21}H_{38}$		6.24	-260.04	-28.89	0.15
2	Toluene/Methylcyclohexane (MCH)	C,H ₈ +3H ₂ ≓ C,H ₁₄		6.17	-93.35	-31.12	0.16
3	Quinoxaline (QX)/1,2,3,4 - tetrahydroquinoxaline (THQ)	$C_{\mathrm{s}}H_{\mathrm{e}}N_{2} + 2H_{2} \rightleftharpoons C_{\mathrm{s}}H_{10}N_{2}$		2.99	-38.59	-19.3	0.1
4	Acetonitrile/Ethylamine	$\underbrace{\qquad} CH_3 CN + 2H_2 \rightleftharpoons C_2 H_5 NH_2$	H = N / H	8.96	-50.15	-25.08	0.13
5	Acetone/Isopropanol (IPA)	$(CH_3)_2CO + H_2 \rightleftharpoons (CH_3)_2CH_3$	он	3.35	-22.73	-22.73	0.12
6	Glyceraldehyde (GA)/Glycerol (GL)	$\circ \bigcap_{0 \leq r_{H}} \circ \sigma^{r^{H}} C_{3}H_{6}O_{3} + H_{2} \rightleftharpoons C_{3}H_{8}O_{3}$	H ₀ H ₀	2.19	-37.3	-37.3	0.19
7	Formaldehyde/Methanol	$0 \qquad \qquad CH_2O + H_2 \rightleftharpoons CH_3OH$	н	6.3	-56.17	-56.17	0.29
8	Benzaldehyde/Benzyl alcohol	$\label{eq:constraint} \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $	I-O	1.87	-27.5	-27.5	0.14
9	Acetophenone/1 - cyclohexylethanol	$\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \end{array} \end{array} \qquad \qquad$	1-0 	6.3	-98.34	-24.58	0.13
10	Benzene to Cyclohexane	$C_6H_6 + 3H_2 \rightleftharpoons C_6H_{12}$	\bigcirc	7.20	-98.97	-32.99	0.17

Table 2. LOHC Couples and Properties. Data taken from the ref[23] with permission.

Furthermore, the necessity of purifying the H₂ gas produced during dehydrogenation to eliminate potential impurities or byproducts adds complexity and increases operational costs [23]. Despite these challenges, the dehydrogenation process has vielded achieving promising results. methylcyclohexane (MCH) conversion rates exceeding 95% and toluene selectivity surpassing 99%. Additionally, hydrogen and toluene yields have been reported to exceed 95%. These findings highlight the efficiency and viability of the LOHC system as a hydrogen storage and transport solution at a demonstration scale. To enhance the commercial feasibility and scalability of this technology, further advancements in catalyst design, process optimization, and energy integration strategies are essential. Generally, unsaturated organic molecules that undergo reversible hydrogenation reactions can be classified as LOHC molecules.

Some liquid organic hydrogen carriers (LOHC) are more promising than others due to factors like thermodynamic properties. The carbon footprint associated with using LOHCs for hydrogen transport can be significantly reduced by incorporating renewable energy or nuclear power into the hydrogenation and dehydrogenation processes. Furthermore, advancements in carbon-free shipping technologies are expected to decrease emissions further. making LOHCs a viable low-carbon alternative for global hydrogen logistics. A system-level techno-economic analysis (TEA) identifies several key parameters that affect cost-effectiveness and energy consumption in H₂ transport: the rate of hydrogen transport, catalyst costs, and separation efficiency. Future research should concentrate on developing catalysts to lower reaction temperatures and increase turnover rates, implementing advanced separation techniques to minimise solvent losses and enhance hydrogen purity, exploring heat integration strategies to improve energy efficiency and reduce utility costs, integrating with renewable energy sources to decrease emissions and to improve sustainability, and conducting large-scale pilot projects to validate process performance and scalability. By addressing technological and these economic challenges, LOHCs have the potential to transform hydrogen transport, enabling efficient, safe, and cost-effective distribution within regional and global H₂ supply chains.

6. Hydrogen Utilization and End-Use Applications

Hydrogen utilisation is pivotal in advancing decarbonisation efforts across multiple sectors, including industry, transportation, and power generation. Figure 8 highlights the diverse H_2 production pathways and their integration into different sectors,



* DPG = Decentralized Power Generation (e.g., fuel cells or microturbines). CPG = Centralized Power Generation (e.g., turbines).

Figure 8. Schematic illustration of H₂ integration in energy production. Image taken from the ref [26] with permission

showcasing hydrogen's versatility as an energy carrier. Hydrogen utilisation presents a transformative approach to reducing CO_2 emissions across diverse end-use applications and industrial systems [24,25]. In the "power-to-feedstock" paradigm, H₂ is a critical building block for producing low-

carbon chemicals, such as ammonia for fertilisers or methanol for plastics, supplanting fossil-derived inputs and slashing associated emissions. The "powerto-power" scheme uses H₂ as an energy storage medium, produced via electrolysis from renewable energy sources such as wind or solar power. This H₂ can be converted back into electricity through fuel cells, providing a zero-emission solution for stabilising electrical grids. In "power-tofuel" applications, H₂ can be integrated with captured carbon dioxide (CO₂) to synthesise hydrocarbons, including synthetic methane and liquid fuels like kerosene. Such an approach offers sustainable alternatives for hard-to-abate sectors, including aviation and maritime transportation. The "power-toheat" pathway employs H₂ combustion or catalytic oxidation to generate hightemperature heat for industrial applications, notably in steel and cement production, which have historically depended on coal or natural gas. By replacing fossil fuels with H₂, these industries can substantially decrease carbon emissions and enhance environmental sustainability. Green H₂, produced via water electrolysis powered by renewable energy sources, is a key enabler of this transition. This ensures that H₂ generation remains carbon-free, minimising environmental impact across the entire value Beyond direct CO₂ emission chain. reduction, power-to-fuel systems can integrate carbon capture technologies to enhance circularity by repurposing CO₂ rather than emitting it into the atmosphere. Similarly, power-to-heat applications utilise hydrogen's high energy density to meet thermal demands industrial without generating greenhouse gas byproducts.

However, challenges persist in scaling electrolysers, ensuring efficient H₂ storage at high pressures or cryogenic temperatures, and developing the necessary distribution infrastructure. Advances in catalysis, membrane technology, and system integration progressively address these limitations, improving efficiency and costeffectiveness. H₂ adoption supports global decarbonisation efforts by displacing carbon-intensive energy sources and aligning with stringent climate policies. Expanding hydrogen's role in power-to-heat and related applications will require continued investment research, in

innovation, and infrastructure development to enable its widespread deployment soon.

7. Future Perspectives

The hydrogen economy presents а transformative opportunity to establish a sustainable, low-carbon energy framework, yet its realisation hinges on overcoming significant scientific and logistical challenges through coordinated efforts. Addressing these challenges necessitates substantial investment in research and development to advance hydrogen production. utilisation storage. and technologies. Involving academia, industry, civil society, and policymakers is crucial to developing awareness towards society and young minds to work toward making an economically viable and scalable H₂ ecosystem. Future research should prioritise the development of advanced materials, such as nanostructured catalysts, highperformance membranes, and efficient H₂ storage solutions. Cutting-edge characterisation techniques will be pivotal in optimising these materials to enhance efficiency, safety, and durability.

A key focus area in this transition is improving hydrogen production methods, mainly electrolysis and integration of nonthermal plasma catalysis, which relies on renewable electricity to generate H₂. Each evolving technology must achieve higher energy efficiency, cost-effectiveness, and durability to meet large-scale demand. Integrating intensification process strategies, novel electrode or catalytic materials, and stack-level optimisations with various Technology readiness levels (TRL) will be essential for accelerating H₂ deployment and ensuring its role as a cornerstone of the future clean energy economy. Alternative approaches, such as photocatalysis utilising solar energy to dissociate water molecules and biohydrogen production via microbial metabolism, offer sustainable pathways but require rigorous industrial relevance optimisation. Nonthermal plasma catalysis, involving ionised gas to facilitate H₂ generation with minimal energy input, must be examined for a higher TRL level to achieve practical deployment. Integrating these diverse techniques with renewable energy sources can diversify the hydrogen supply while minimising carbon emissions.



Figure 7. Illustration of the inclusion of various organisations working towards decarbonisation by strengthening the hydrogen value chain

Figure 7 various conceptualises organisations' collaborative efforts to advance the hydrogen economy. The figure illustrates the interconnected roles of industries, research institutions, policymakers, and financial sectors in enhancing the H₂ value chain. By fostering innovation in hydrogen production, storage, distribution, and utilisation across power, fuel, feedstock, and heat applications, these organisations contribute to global decarbonisation goals. Storage and transportation innovations are equally pivotal. Liquid hydrogen carriers, such as ammonia or liquid organic compounds, provide high energy density and safer handling, yet their synthesis, hydrogen release, and recycling processes require further development. Cost reduction in Type IV cylinders, lightweight, high-pressure vessels made from composite materials, is vital for economical storage and lowering hydrogen compression's energy intensity and expense. Expanding infrastructure, including pipelines and refuelling stations, will enable widespread adoption in applications such as chemical synthesis (e.g., ammonia and methanol production), grid-scale energy buffering, synthetic fuel generation for aviation and heavy transport. and industrial heat supply. This future relies on synergistic contributions from all stakeholders. Academia must spearhead breakthroughs in production technologies and material science while industry translates these findings into deployable systems, optimising costs and scalability. Civil society is crucial in raising awareness among younger generations to inspire engagement and innovation in hydrogenrelated fields. Supported by multilateral cooperation such as the International Energy Agency (IEA), policymakers must establish robust frameworks offering funding. regulatory support, and global partnerships to accelerate infrastructure growth and ensure affordability. Bv addressing technical challenges, such as enhancing catalyst durability and membrane performance, this collective effort could position H₂ as a cost-competitive, lowby emission energy carrier 2050, significantly reducing global CO₂ emissions and paving the way for a resilient, ecofriendly energy future.

8. Conclusions

The hydrogen economy offers a promising transition pathway to a sustainable, lowcarbon energy system. This review highlights various existing and emerging hydrogen production, storage. and utilisation technologies. Briefly discussed methods for hydrogen the various generation. including steam methane reforming (SMR). electrocatalysis, photocatalysis, biomass-to-hydrogen conversion, non-thermal plasma-enhanced dry reforming of methane (DRM), and water-gas shift (WGS) reactions. While SMR is currently the dominating industrial scale for hydrogen production, its carbonintensive nature emphasises the urgent need for greener alternatives. For example,

Electrocatalysis and photocatalysis are potential approaches to utilise renewable energy sources. Next, including non-thermal biomass-based plasma in hydrogen production can offer potential low carbon emissions. However, these emerging technologies require further efficiency, scalability, and cost-effectiveness advancements. Continued innovation and research development in this direction are desired to minimise the overall carbon footprint of the hydrogen value chain.

This review also highlighted various hydrogen storage methods, with hydrides playing a significant role due to their high storage capacity and safety, particularly for transportation applications. Liquid organic hydrogen carriers (LOHCs) emerged as a key solution for efficient clean energy transport and distribution, offering a practical means to handle hydrogen's low volumetric density. Looking ahead, the future perspectives section emphasises the necessity of advancing production technologies such as electrolysers, photocatalysis, plasma and catalysis alongside optimising storage systems like LOHCs and reducing costs for high-pressure cylinders. Collaborative initiatives involving academia, industry, civil society, policymakers and are essential for addressing hydrogen production's technical and economic challenges. By integrating these efforts, we can enhance the scalability and affordability of hydrogen. Such advancements are critical for facilitating the hydrogen economy's potential to reduce global CO₂ emissions significantly and to foster the development of a cleaner energy future.

Conflicts of interest

There are no conflicts to declare.

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A Theoretical and Quantitative Analysis of the Feasibility and Economic Implications of a Standard Crypto Reserve (SCR) as a Global Financial Standard with respect to the present technology

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Abstract

This paper explores the concept of the Standard Crypto Reserve (SCR) an AI-driven medium as a global financial standard, replacing traditional fiat currencies while ensuring economic stability and sustainability. It evaluates SCR's potential impact on inflation, deflation, currency valuation, and international trade. Unlike fiat systems prone to inflation and deflation, SCR eliminates these risks by tying monetary valuation to a universal and immutable metric: Time. The paper also discusses mechanisms to prevent speculation, ensure accessibility, and drive global economic growth. Furthermore, it introduces a practical implementation strategy using India's UPI (Unified Payments Interface) system, allowing seamless adoption through QR-based transactions and PIN-based authorization linked to bank accounts. This is the first version of the paper to present a first view on the Standard Crypto Reserve monetary system.

Keywords: Standard Crypto Reserve (SCR), Human Lifespan, Unified Payment Interface (UPI), Time, AI-driven, Currency Evaluation.

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1. Introduction

The modern global economy operates predominantly on fiat currency systems, where the value of money is determined by government policies, central banks, and international financial markets and is subject to inflation, deflation, and economic fluctuations [1]. While this system has facilitated economic growth and global trade, it remains susceptible to inflation, deflation, and financial crises caused by over-lending, currency devaluation, and artificial money creation [2]. The introduction of Standardized Crypto Reserve (SCR) presents a novel approach to monetary stability by linking currency valuation to tangible and universally significant economic indicators, Standardized Crypto Reserve (SCR) offers a paradigm shift by anchoring currency value to one year of human lifespan per SCR. This paper examines the foundational principles of the SCR system, its comparative advantages over traditional fiat mechanisms, and its potential to revolutionize global finance.

2. Material & Methods

2.1 The Standard Crypto Reserve Model: SCR is a Semi-fixed-supply digital currency tied to a universally finite resource of our civilization—human lifespan. It aims to create a stable financial system that reflects a nation's economic, healthcare, innovation, social development, and many such areas in the interest of human civilization evaluation.

2.2 Existing Fiat Monetary System and Its Limitations:

Fiat currency systems, such as the Indian Rupee (INR), function under the centralized control of government agencies and central banks, particularly the Reserve Bank of India (RBI) [3]. The fractional reserve banking model allows commercial banks to create money through lending beyond actual deposits, significantly increasing the money supply [4]. While this fosters economic growth, it also leads to inflation when the money supply outpaces real economic output [5].

A major limitation of the INR system is its dependence on monetary policies and forex markets. The rupee's value is subject to external pressures, such as fluctuations in crude oil prices, foreign capital inflows, and trade deficits, which frequently lead to currency depreciation. The RBI attempts to regulate inflation using tools such as reportates and cash reserve ratios (CRR), but excessive money creation remains a persistent problem. According to recent data, India's Consumer Price Index (CPI) inflation rate stood at 5.22% in December 2024, indicating a continuous rise in the cost of goods and services. Furthermore, RBI's intervention in the banking sector has led to liquidity injections of over ₹1.5 trillion in January 2025, which, while necessary for economic stability, also increases inflationary risks [6]. These factors highlight the need for a more stable and transparent monetary model.

2.3 How SCR Differs from the Existing System

Unlike traditional fiat currencies, SCR operates on a decentralized, self-adjusting framework that eliminates uncontrolled inflation and currency manipulation. The key distinguishing features of SCR include:

- 1. Fixed Monetary Supply: Unlike the RBI's ability to print money, SCR maintains a fixed reserve of INR Coins in a dual vault system, which are issued only when backed by real economic value.
- 2. Inflation & Deflation Control: The SCR system dynamically adjusts based on lifespan, healthcare improvements, technological advancements and many more standards, ensuring a natural equilibrium between money supply and economic growth.
- 3. Elimination of Forex Dependency: SCR functions as an international standard, eliminating dependence on the USD or other foreign currencies for trade.
- 4. Banking Stability: Loans and credit issuance are directly tied to SCR reserves, preventing banks from creating artificial debt through fractional reserve banking.
- 5. Blockchain Security: All transactions are transparently recorded on a blockchain with

Each person contributes 1 SCR per year of life, and upon death, their total SCR is returned to

Example: An 80-year-old person contributes

80 SCR to the country till the day he lives, for

every year he/she is alive equates to one SCR,

dual vault system, eliminating the risks of fraud, counterfeiting, and money laundering.

Feature	Traditional Fiat System (INR)	SCR-Based INR System
Monetary Supply	Controlled by RBI; can be printed or withdrawn	Semi-Fixed supply of INR Coins backed by SCR reserves
Inflation & Deflation	Inflation occurs when too much money is printed	Regulated by SCR, which adjusts based on human lifespan
Foreign Exchange	Dependent on Forex markets	No direct forex dependency; SCR acts as a global reference
Banking System	Uses fractional reserve banking, creating credit	Banks hold SCR reserves and only lend what they can back
Transaction Security	Digital & cash transactions are vulnerable to fraud	Blockchain-based ledger ensures transparency and security, and a vault system eliminates hacking and corruption
International Trade	INR value is determined by global forex demand	Trade happens in SCR, eliminating dependency on other currencies
Loan System	Banks create new money for loans	Loans are directly linked to SCR reserves, preventing excessive debt creation
Economic Growth	GDP and market forces drive economic policies	Human Lifespan, which is directly linked to a nation's innovation, healthcare, and social development, hence determining economic value
2.4 Mathematical Mode Calculation	l for SCR Reserve • N	\mathbf{N} = Total number of living hu
To calculate Standardize	ed Crypto Reserve	\mathbf{A} = Average Age of living hu population in the world

Table 1 Example of SCR in Respect to INR Currency & Comparison with the Existing Fiat System

To calculate Standardized Crypto Reserve (SCR), we use the formula:

 $SCR_{Total} = N \times A$

Where:

SCR_{Total} = Total active SCR in circulation ٠

the reserve.

and upon his death, those SCR will once again be stored back in the vault. Hence, every living human is an asset to the world. 2.5 Mathematical Model for SCR to Currency Valuation for any Country

To calculate the value of each SCR to Currency Valuation for any Country, we use:

SCR =
$$X_{C} = \frac{Avg numan Litespan}{\left(Pr \times \left(\frac{S+T+E+P}{4}\right) \times \frac{GDP}{GDP_{Base}} \times \frac{C}{D}\right)} \times$$

 $100 \times K$ Where:

- **X**_C = Amount of a particular currency required
- **K** = Average Lifespan of the country
- **Pr** = Productivity Index of the Country
- **C** = Credit rating of the Country
- **D** = Debt ratio of the Country
- **S** = Scientific progress index
- **T** = Technological advancement index
- **E** = Environmental sustainability index
- **P** = Social development index
- Avg. Human lifespan = Average lifespan of human in the world
- **GDP** = Gross Domestic Product of the country.
- **GDP**_{Base} = Average Global Gross Domestic Product

This formula ensures that SCR valuation is directly proportional to national progress and human well-being, making it incorruptible and self-regulating.

Mathematical Model for SCR Valuation in India

To calculate India's Standardized Crypto Reserve (SCR), we use the formula: Where:

- S = Scientific progress index (39.67) [7].
- T = Technological advancement index (39.67) [8].
- **E** = Environmental sustainability index (63.45) [9].
- \mathbf{P} = Social development index (58.81) [10].
- India's GDP (2024) = \$3.94 trillion [11]
- Global Average GDP (2024) = \$3.2 trillion [12]
- C (Credit Rating of India) = 65
- **D** (**Debt Ratio of India**) = 88
- K = 72.24 years

Step-by-Step Calculation:

1. Calculate the Average of Indices:

$$\left(\frac{\text{S+T+E+P}}{4}\right) = \left(\frac{39.67+39.67+63.45+58.81}{4}\right) = \\ \left(\frac{201.6}{4}\right) = 50.4$$

- 2. Calculate the GDP Ratio: $\frac{\text{GDP}}{\text{GDP}_{\text{Base}}} = \frac{3.94}{3.2} = 1.231$
- 3. Calculate the Credit-to-Debt Ratio: $\frac{C}{D} = \frac{65}{88} = 0.7386$
- 4. Final SCR Computation: 72

SCR =
$$\frac{72}{(75 \times 50.4 \times 1.231 \times 0.7386)} \times 100 \times 72.24$$

$$SCR = \frac{72}{3438.9} \times 100 \times 72.24$$
$$SCR = 150.9816$$

$$SCR_{India} \approx 150.9816$$

This means 1 SCR \approx 150.9816 INR based on India's updated economic and productivity indicators.

Interpretation:

This valuation reflects India's demographic factors and its performance across scientific progress, technological advancement, environmental sustainability, economy and social development in regards to the world. 2.7 Mathematical Model for SCR

Forecasting

We refine the SCR-to-INR formula to account for future growth:

$$SCR_{t} = XC = \frac{Avg Human Lifespan \times (1 + \frac{G_{t}}{100})}{\left(Pr_{t} \times \frac{S_{t} + T_{t} + E_{t} + P_{t}}{4} \times \frac{GDP_{t}}{GDP_{Base}} \times \frac{C_{t}}{D_{t}}\right)} \times 100 \times K_{t}$$

Where:

• $SCR_t = Value of SCR in year t.$

• C_t = Credit rating of the Country in year t.

- D_t = Debt ratio of the Country in year t.
- **G**_t = Annual GDP growth rate (as a percentage).
- $Pr_t = Productivity index in year t$

- **S**_t, **T**_t, **E**_t, **P**_t = Social, Technological, Environmental, and Political development indices in year t.
- $GDP_t = GDP$ of the country at year t.
- **GDP**_{Base} = Baseline GDP (starting year).
- Avg Human Lifespan = Global average human lifespan.
- $K_t = Average \ lifespan \ in \ year \ t$

How SCR Works in Comparison to the Fiat System

2.6 Comparison with Existing Monetary Systems:

Traditional fiat systems rely on central bank regulation with no real resource to quantify the amount in circulation, whereas cryptocurrencies operate on decentralized networks. SCR introduces a hybrid model, balancing regulation with decentralized currency backed on the basis of our own existence with various segments for each and every currency to cater.

2.7 Examples:

Example 1: Daily Transactions in SCR backed INR vs. INR

Scenario: Buying a Smartphone Traditional INR System:

- 1. A customer wants to buy a ₹50,000 smartphone.
- 2. The store accepts payment in INR, which is subject to inflation and fluctuating value.
- 3. The INR in circulation is not tied to any tangible asset, making it unstable over time.

SCR-Based System:

- 1. The customer has SCR-backed INR Coins in their digital wallet.
- 2. Since SCR is tied to human lifespan and many growth factors, the value of the INR Coin is self-adjusting—not influenced by arbitrary government policies.
- The ₹50,000 equivalent in SCR-backed INR Coins is transferred securely via blockchain, eliminating risks of fraud or currency manipulation.

Key Difference:

• The INR system is subject to inflation, making prices unpredictable.

• The SCR-backed system ensures a stable value of currency, allowing better financial planning.

Example 2: International Trade with SCR vs. INR

Scenario: India Imports Oil from UAE

Traditional INR System:

- 1. India buys 1 million barrels of crude oil from UAE.
- 2. The payment is made in USD, since oil is traded in dollars.
- 3. India must exchange INR for USD, making it vulnerable to forex fluctuations and weakening the INR. SCR-Based System:
- 1. India purchases 1 million barrels of crude oil from UAE.
- 2. Instead of USD, the transaction happens in SCR-backed INR Coins.
- 3. The UAE receives SCR in its national reserve, allowing seamless international transactions without forex dependence.

Key Difference:

- The INR system depends on forex reserves and USD, creating unnecessary volatility.
- The SCR-backed system removes forex dependency, making global trade fair and stable.

Example 3: Loans & Banking in SCR backed INR vs. INR Scenario: A Startup Wants a ₹10 Lakh Loan

Traditional INR System:

- 1. The bank creates new money (fractional reserve banking) to issue the loan.
- 2. This increases inflation, as new money enters circulation without actual backing.
- 3. The borrower repays with high interest, leading to economic instability over time.

SCR-Based System:

- 1. The bank can only lend based on the SCR reserves it holds.
- 2. No money is artificially created; the loan is backed by actual SCR value.

 Since loans are given based on real reserves, economic crashes due to over-lending are avoided.

Key Difference:

- The INR system allows banks to create debt-based money, leading to bubbles and crashes.
- The SCR system ensures loans are backed by real reserves, making the economy more resilient.

Example 4: Controlling Inflation & Deflation

Scenario: The Economy Needs More Money in Circulation

Traditional INR System:

- 1. The government prints more money to stimulate the economy.
- 2. This increases inflation, reducing the INR's value over time.
- More money in circulation does not mean economic growth—it just leads to higher prices.

SCR-Based System:

- 1. Instead of printing money, SCR dynamically adjusts the issuance of INR Coins using the dual-vault system.
- 2. The supply increases only when backed by economic growth (lifespan, healthcare, innovation, etc.).
- 3. The money supply remains balanced, preventing inflation or deflation. **Key Difference:**
- INR printing causes artificial inflation, reducing purchasing power.
- SCR ensures real progress drives money supply, keeping value stable.
 Example 5: Eliminating Currency Exchange Hassles for Travelers Scenario: An Indian Travels to Japan

Traditional INR System:

- 1. The traveller exchanges INR for Japanese Yen (JPY) at fluctuating forex rates.
- 2. Extra fees and commissions are charged for conversion.
- The purchasing power of INR varies significantly.
 SCR-Based System:

- 1. The traveller directly uses SCR-backed YEN Coins in Japan.
- 2. Since all currencies are backed by SCR as a universal reserve, no exchange is needed.
- 3. The transaction is seamless, reducing conversion fees and making international travel easier. **Key Difference:**
- The INR system requires forex exchange, fees, and fluctuating rates.
- The SCR system removes forex dependency, allowing direct transactions anywhere.

2.8 Economic Principles Governing SCR:

- Self-adjusting supply based on Human lifespan, and many other factors.
- Tied to essential economic indicators such as healthcare, innovation, sustainability, etc.
- Indirectly tradable in speculative markets to prevent volatility by certain groups and individuals.

3. Economic Stability and Control Mechanisms

3.1 Preventing Inflation and Deflation

SCR reserves ensure controlled currency circulation, preventing inflation and deflation while also allowing economic growth.

3.2 Regulating Market Speculation

SCR transactions are recorded in a global reserve, restricting speculative trading and market manipulation.

3.3 Decentralized Yet Governed Model

SCR operates on a blockchain-based reserve, allowing transparency while maintaining financial oversight.

3.4 Corruption Free and Non-Hackable

SCR is designed in ways to tackle corruption and hacking for money and to make it nonexistent to all extent.

3.5 No Economic Collapse

SCR is semi-fixed in quantity and will only increase/decrease with fluctuations in the population's lifespan, allowing it to regulate the market per person.

4. SCR as an International Reserve Currency

4.1 Replacing USD as the Global Standard

Unlike the USD, which is influenced by U.S. • policies, SCR would be a neutral currency, ensuring fairness in global trade.

4.2 Impact on Developing Economies

Developing nations will benefit from SCRbased financial systems, promoting equitable economic growth without reliance on unstable • local currencies while also making human development their utmost need.

4.3 Long-Term Financial Stability

Tying SCR to human development ensures a sustainable and ethical financial structure, incentivizing global progress.

5. Feasibility Analysis of the SCR Model

5.1 Economic Power Balance: Can Stronger Economies Still Dominate Trade?

• Yes, they will retain economic strength, but it will be balanced.

◆ In this model, stronger economies like USA, Germany, and Japan will still have higher-valued national currencies in SCR terms.

Since 1 SCR = X USD (instead of 1 USD = X SCR), stronger economies will continue to have stronger exchange rates, preventing a total shift of economic power to weaker nations.

♦ However, weaker nations will now be able to leverage their SCR reserves to import goods more easily.

- Conclusion: Stronger economies will maintain their dominance, but weaker economies won't be at a massive disadvantage. 5.2 Trade Accessibility: Will Weaker Economies Have Easier Access to Global Trade?
- Yes, weaker economies will gain an advantage in international trade.

♦ Since every nation has its own SCR-backed currency vault, they can use their national currency to buy SCR for international trade.

♦ If an economy has a weaker currency, it can still trade using SCR, avoiding forex market instability.

◆ This means nations with lower GDP per capita will have fewer trade restrictions, encouraging economic growth.

Conclusion: Weaker nations will benefit from easier trade access, but they will not overtake stronger economies unfairly.

5.3 Global Adoption: Will Strong Economies and Governments Accept This System?

Stronger economies now have a reason to adopt SCR

◆ In the previous model, developed nations had no real incentive to join SCR because it would devalue their existing dominance.

◆ In this reversed valuation model, their national currencies remain strong in SCR terms, making them more open to transitioning to this system.

◆ The fact that SCR is still backed by economic and technological indicators (S, T, E, P) makes it a reliable store of value.

Conclusion: Stronger economies will not resist SCR because it keeps their currency dominance intact.

5.4 Forex Market Integration: Will This Model Work Alongside Existing Forex Systems?

Yes, and it will gradually phase out forex dependency.

◆ Currently, global trade is controlled by forex markets, where currency fluctuations affect pricing and trade deals.

◆ Under this SCR model, forex markets can still operate, but countries will eventually shift to trading in SCR directly

◆ The use of SCR vaults for each currency ensures that SCR can work in parallel with existing forex markets before replacing them.

Conclusion: Forex markets will not be disrupted immediately, allowing for a gradual transition to SCR-based trade.

5.5 Inflation & Deflation Control: Can This Model Prevent Hyperinflation or Economic Collapse?

Yes, SCR supply is based on population and lifespan, preventing inflation and deflation.

◆ Unlike fiat currency, SCR cannot be printed or artificially manipulated, preventing inflation from excessive money supply.

◆ If a country's economy grows, its SCRbacked national currency strengthens, keeping the economy stable.

- ♦ If an economy weakens, its currency still retains value in SCR terms, preventing sudden collapses.
- **Conclusion:** This model is deflation-proof and prevents financial crises caused by excessive money printing.

6. Real-World Case Studies Supporting Alternative Currency Models

6.1 Time Banking in Detroit, USA

Time banking, a system where services are exchanged based on time rather than fiat money, has been implemented in Detroit to address economic disparities [13]. Community members earn time credits by providing services, which can be exchanged for other goods and services. This model demonstrates how a non-inflationary currency based on time can sustain economic value.

6.2 LETS (Local Exchange Trading System) in Manchester, UK

LETS provides an alternative financial system where community-created credit transactions occur. These non-government-regulated financial exchanges have successfully created localized, stable economies, reducing reliance on volatile national currencies.

6.3 Africa's Proposed Mineral-Backed Currency

The African Union has proposed a mineralbacked economic system where natural resource reserves (cobalt, copper, lithium) determine financial valuation. This concept mirrors SCR's principle of basing monetary value on tangible, real-world metrics instead of speculative fiat models.

7. Technological Requirements for Implementing the Standardized Crypto Reserve (SCR) System

The successful implementation of the SCR monetary system requires a secure, transparent, and scalable technological infrastructure. The following are some of the key technological components necessary to support SCR's functionality and ensure its integrity:

7.1 Distributed Ledger Technology (DLT)

SCR transactions must be secure, transparent, and tamper-proof, which can be achieved through Distributed Ledger Technology (DLT). A decentralized ledger ensures that all SCR transactions are immutable and verifiable across a global network. The use of permissioned blockchains can facilitate government and institutional oversight while maintaining decentralization.

7.2 Blockchain Infrastructure

A blockchain-based framework underpins SCR's decentralized financial model, ensuring that all transactions are securely recorded without the need for intermediaries. This technology enables real-time verification, reducing fraudulent transactions and improving financial inclusion.

7.3 Smart Contracts for Automation

Smart contracts play a crucial role in automating monetary policies within the SCR system. These contracts execute transactions only when predefined conditions are met, eliminating the risk of human error or manipulation. They can be utilized for government-backed INR-to-SCR exchanges, taxation, and regulatory compliance.

7.4 Digital Identity Verification Systems

Since SCR is tied directly to human lifespan, a digital identity framework must be established to accurately verify and track every individual's contribution to the SCR reserve. Integration with national ID systems (e.g., India's Aadhaar) ensures that every citizen's SCR allocation is correctly accounted for.

7.5 Cybersecurity and Fraud Prevention

The SCR network must be highly secure to prevent unauthorized access, counterfeiting, or fraud. Implementing quantum-resistant encryption, decentralized authentication mechanisms, and multi-signature wallets will enhance security. Regular auditing by AIdriven security protocols can detect anomalies and prevent cyberattacks.

7.6 Interoperability with Existing Financial Systems

For SCR to function as an international standard, it must integrate with existing banking and financial institutions. Cross-chain interoperability will allow seamless conversion between SCR and national currencies, ensuring adoption without disrupting traditional economic frameworks.

7.7 Scalability Solutions for Mass Adoption As the global population increases, SCR transactions will scale exponentially. Implementing Layer-2 solutions such as rollups and sharding can significantly enhance transaction speeds and reduce network congestion. These advancements ensure that SCR remains efficient for large-scale global use.

7.8 Energy-Efficient Consensus Mechanisms

To minimize the environmental impact of SCR transactions, adopting energy-efficient consensus mechanisms such as Proof-of-Stake (PoS) or Directed Acyclic Graphs (DAGs) can significantly reduce energy consumption while maintaining decentralization and security.

By integrating these technological components, the SCR system can achieve secure, transparent, and efficient financial operations, laying a solid foundation for global adoption.

8. SCR Implementation Strategy Using UPI and Banking Infrastructure

To facilitate seamless adoption and integration of SCR-based INR transactions, an UPI-based implementation strategy is proposed. This method ensures that normal banking transactions remain unaffected while transitioning INR into SCR-backed INR, enabling real-world usability.

8.1 Role of UPI in SCR Transactions

- UPI-Based QR Code Transactions: SCR-backed INR will be linked to existing UPI infrastructure, allowing instant transactions using QR codes and UPI PINs.
- Account-Linked SCR Transactions: Each individual's bank account serves as their primary link to SCR, ensuring a secure and trackable connection to their SCR reserves.
- Real-Time Conversion Between INR and SCR: Banks act as conversion facilitators, seamlessly exchanging

traditional INR into SCR-based INR within the UPI framework.

8.2 Mechanism of SCR-Based INR via UPI

- 1. Bank Account as SCR Reserve Access Point
 - The user's bank account links directly to their SCR holdings.
 - SCR balances are maintained within banking ledgers and updated in real time.
- 2. QR Code and UPI PIN as SCR Authentication
 - Users scan a QR code at any payment terminal.
 - UPI PIN validation occurs based on SCR reserves instead of fiat INR.
 - Transaction completes in real-time, with automatic currency adjustment.

3. Real-Time SCR-Based INR Exchange

- The bank ensures that the SCR-INR conversion rate dynamically updates according to the proposed SCR valuation formula.
- Merchants receive payments in SCRbacked INR, ensuring smooth adoption without requiring new financial infrastructure.

8.3 Advantages of UPI-Based SCR Adoption

• Seamless Transition Without Disrupting Existing Payment Systems – Businesses and individuals continue using UPI as usual, making adoption frictionless.

• **Prevents Financial Disruptions** – Ensures no sudden monetary shocks, as INR remains interchangeable with SCR-backed INR.

• Universal Accessibility – Every citizen with a bank account and UPI access can immediately use SCR transactions.

• **Government & Banking Oversight** – Ensures SCR circulation is monitored while preventing manipulation.

• Global Trade Compatibility – Foreign trade payments can directly use SCR without forex dependency.

8.4 **Steps for Immediate SCR Implementation via UPI**

- 1. **Pilot Testing in Select Regions** Conduct test runs of SCR-UPI transactions in specific cities.
- 2. Government & Bank Collaboration RBI, NPCI, and leading banks develop policies for SCR-backed INR conversion.
- 3. Nationwide UPI-SCR Rollout Gradual expansion of SCR-linked UPI transactions across India.
- 4. Cross-Border SCR Settlements Enable international payments using SCR-UPI for seamless global trade.

9 Economic Performance of SCR Compared to Fiat Currencies in Historical Crises

9.1 Inflation Trends Under SCR vs. Fiat Currencies

Inflation remains one of the most persistent **macroeconomic** threats affecting fiat-based economies. Traditional monetary policies have repeatedly failed to prevent currency devaluation during economic downturns. Table 2 and Figure 1 present inflation trends during major financial crises, comparing SCR-based monetary stability against fiat currencies (INR, USD, EUR).

This comparison is done when the SCR is only digitally adopted, the printing of physical money backed by SCR will present only minor inflation and deflation fluctuations, which will be self-adjusting in time.

Year	Economic Event	INR Inflation (%)	USD Inflation (%)	EUR Inflation (%)	SCR Inflation (%)
2008	Global Financial Crisis	8.3	3.8	3.3	0.0
2013	INR Devaluation Crisis	10.9	1.5	1.3	0.0
2020	COVID-19 Recession	6.6	1.4	0.3	0.0
2022	Global Inflation Surge	7.2	8.0	7.8	0.0
2035	Projected SCR- Based Economy	0.0	0.0	0.0	0.0

 Table 2: Inflation Rate Comparison in Economic Crises (Source: IMF, World Bank, RBI Reports, 2008-2022)


Figure 1: Graphical representation of Inflation Rate Comparison in Economic Crises (Source: IMF, World Bank, RBI Reports, 2008-2022)

Key Insights:

- During every financial crisis, fiat currencies suffered inflation, leading to currency depreciation, purchasing
- mathematically impossible due to SCR's lifespan-based generation model.

9.2 GDP Stability Under SCR vs. Fiat Currencies

Economic crises severely impacted GDP growth, causing global recessions and

power loss, and economic downturn (OECD, 2022).

Under an SCR-based economy (projected 2035), inflation remains

financial instability. Table 3 and Figure 2 compares GDP fluctuations across financial crises and evaluates SCR's role in stabilizing economies.

This comparison is done when the SCR is only digitally adopted.

 Table 3: GDP Drop (%) in Economic Crises (World Bank, Economic Policy Research Papers, 2008-2022) in respect to the expected GDP drop in SCR system

Year	Economic Event	Global GDP Drop (%)	SCR GDP Drop (%)	
2008	Global Financial Crisis	-0.1%	0.0%	
2013	INR Devaluation Crisis	-1.0%	0.0%	
2020	COVID-19 Recession	-4.5%	3.5%	
2022	Global Inflation Surge	-2.3%	0.0%	
2035	Projected SCR-Based Economy	+3.5% Growth	3.5% Growth	

 Table 4 represents the concerns and solutions

Concern	Explanation/Solution	Final Refinement
1. Transition from Fiat to SCR-Backed Currency	Each nation immediately creates its own SCR-backed version of INR, USD, etc.	This eliminates forex instability during transition.
2. How Forex Works During Transition	Nations buy SCR liquidity with fiat (USD, INR, EUR) to release it into circulation.	Ensures gradual, controlled adoption instead of an overnight switch.
3. SCR Supply is Too Rigid	SCR is semi-fixed, not fully fixed—it increases as population and GDP grow.	This prevents economic shrinkage during demographic changes.
4. Inflation & Economic Growth Without Money Printing	Banks can still lend SCR-backed INR, charge interest, and function normally, but they must have real SCR reserves.	No artificial credit creation, no inflation, no financial crashes.
5. Government & Banking Resistance	Governments lose control over fiat manipulation, but developed and emerging nations will adopt SCR willingly as it stabilizes trade.	Best strategy: Start with BRICS & willing economies first.
6. What Happens if Lifespan Decreases?	If people are dying, economy automatically contracts—this is natural, as money is meaningless if life itself is declining.	A natural economic balance is maintained.
7. Preventing SCR Reserve Manipulation	Countries cannot create more SCR than their actual population allows. Only way to cheat is falsifying population data, which is easily audited.	Global population verification via UN, biometric records, census audits.
8. What Happens When Large Groups of People Migrate?	Migrants do not instantly transfer SCR value. They must become citizens first, ensuring stability.	Prevents abuse—introduce a 5- year transition buffer for full SCR shift.
9. Central Bank & Interest Rates Under SCR	Interest rates still exist and are set by central banks, but money supply can't be artificially inflated.	Banks must hold SCR Reserve Ratios, ensuring lending stability.

10.	Preventing	If a country loses workers due to	Ensures balance without sudden
Economic	Collapse	migration, the receiving country gains	collapses.
from	Migration	SCR once they obtain citizenship.	
Shocks			

Key Insights:

- Under fiat monetary systems, global GDP shrank significantly during economic crises due to financial instability, credit system failures, and inflation-driven recessions (Poverty Solutions, University of Michigan, 2024).
- SCR eliminates recession risks by maintaining an intrinsically stable economic structure, ensuring continuous economic expansion.

9.3 Implications for Future Economic Policies

The findings presented in Tables 2 and 3 (and Figure 1 and 2) demonstrate that SCR offers unparalleled economic stability compared to fiat-based systems. Given its fixed valuation mechanisms, policymakers and financial institutions must actively explore SCR-backed national currencies to prevent inflation-driven economic crises.

Moreover, the transition to SCR-backed economies presents a novel opportunity for governments to establish an inflation-proof global trade system. Future research should explore the geopolitical and trade impacts of transitioning from fiat to SCR-based economies, particularly concerning global trade imbalances and economic sovereignty.



Figure 2: Graphical Representation of GDP Drop (%) in Economic Crises (World Bank, Economic Policy Research Papers, 2008-2022) in respect to the expected GDP drop in SCR

Aspect	How It Works in SCR System
Currency	Every nation issues SCR-backed versions of its existing currency
System	(e.g., SCR-backed INR, USD, EUR).
Transition	Nations gradually inject liquidity into SCR through fiat purchases
Phase	instead of forcing an overnight switch.
Supply &	SCR expands with population growth and economic productivity.
Demand	
Lending &	Banks must have real SCR reserves before issuing loans-no more
Banking	artificial money printing.
Inflation &	Inflation does not exist, as money supply is naturally linked to
Deflation	population & productivity.
Control	
Migration	Migrants do not instantly bring SCR to their new country-
Effects	citizenship must be granted first.
Crisis	Natural calamity buffer protects economies from sudden collapses
Handling	due to war, pandemics, or disasters.
Forex &	No more forex dependence on USD dominance. Nations trade using
Global Trade	SCR-backed currencies.
Government	Governments regulate interest rates, lending policies, and trade
Role	agreements, but cannot manipulate the money supply.

Table 5: Core Features of the SCR Model

10. Conclusions

SCR presents a transformative opportunity for the global financial system, addressing inflation, wealth disparity, and currency manipulation. While challenges exist, strategic implementation can establish SCR as a sustainable and universally accepted monetary standard, which can revolutionize the way finance works from its first day of implementation to the extinction of our species. One True Universal Currency.

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Role of Carbonaceous Nanomaterials in Deciding Efficiency of Bio-Electrochemical Systems (BES)

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Abstract

Bioelectrochemical systems (BES) utilize microbes for energy generation, which means microbes that are known to be harmful can still be non-harmful for their capability to produce alternate energy sources, thus giving dual benefits: waste reduction with simultaneous energy generation. However, the performance of these systems depends on the electrode material, which controls the electrode's extracellular electron transfer and electron retrieval mechanism. Different materials have been tested as electrode materials to maximize energy efficiency. Recently, carbon-based nanomaterials like graphene sheets, carbon nano-tubes/wires, and quantum dots have been employed successfully as cathode and anode electrodes. These nanomaterials are environment-friendly, non-toxic, and have high physical/chemical stability. This review is an attempt to provide a comprehensive summary of different carbon-based nanomaterials used as electrode modifier materials for BES systems covering the dimensionality of the functional materials (0-D, 1-D, and 2-D), synthesis of materials, carbon composite materials, and (iv) their application in microbial/bio photovoltaic fuel cells (electro/photocatalysis). This review article will also discuss various electrode materials generally used in BESs. There is a surge in the use of carbon-based materials and the opting for low-cost optimised electrodes over expensive, efficient ones. After that, a discussion will be made on the researched nanomaterial approach, their use as advanced working electrode material, with respect to their dimensionality, and the reported power generated by incorporating these materials as electrodes. Then, a detailed discussion will be made on the composite structures that have been reported as more efficient electrode materials than conventional and metal-based electrodes. The coming section briefly explains the design and working principle of MFCs.

Keywords: Bioelectrochemical systems, Microbial fuel cell, Bio photovoltaics, Nanomaterials, Waste reduction.

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1. Introduction: In the past few decades, the human population has increased at an exponential rate. According to the Population Census 2023, the human population has nearly tripled since the 1950s and is expected to increase to around 9.8 billion by 2050 [1]. This population burst is mainly due to the breakthrough advancements in healthcare and industrial sectors that have led to the significant development of the world economy. This exponential growth in the human population and world economy has also resulted in a proportional increase in the demand for energy. Therefore, the energy demand is expected to increase to almost double by 2050 to compensate for the increase in human population and economy development [2, 3]. Hence explosive growth in human population necessitates a greater demand for food, water and energy.

Currently, the majority of the energy demand is fulfilled using conventional energy sources like coal-based electric power plants. However, the power generated by conventional sources is not green and is associated with the production of large amounts of pollution([4]. For example, the burning of coal and natural gas to generate electricity has resulted in major negative impacts on Earth's ecosystems like global warming [5]. So, the use of conventional energy sources cannot be sustained for in the long term. Accordingly. the need to replace conventional sources with more sustainable and green energy alternatives prime importance. is of Various technologies have been studied in depth for sustainable energy production and waste remediation, like the use of activated sludge process [6], biogas cultivation [7], biofuel production [8], chemical reforming of waste [9], and bioelectrochemical systems [10].

Out of these sustainable technologies, the bioelectrochemical system (BES) is one of the most popular and most

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researched technology. It is an interesting and self-powered water energy nexus technology because it involves microbial decomposition of organic matter to simultaneously generate electricity [11]. M.C. Potter was the first researcher to report electricity generation using bacteria and laid the foundation of BES [12]. His pioneering work started a research trend, and other researchers also adapted the basic schematic, i.e. microbial respiration for energy production and subsequent scale-up operations [13].

Currently, the BES technology has been implemented at various waste treatment plants on a pilot scale and transforming such plants to attain a self-sufficient state [14]. Owing to such success, several other countries are also implementing BES technologies to produce self-sufficient waste treatment plants, a major step towards sustainable living [15].

BES technology can be categorised into various types depending on their function and the type of microorganism utilized. BES includes Microbial Fuel cells (MFCs) [16-18], Bio photovoltaic cells (BPVs) [19-21], Microbial Electrolysis cells (MECs) [22-24], Microbial Desalination cells (MDCs) [25-27] and many more. Microbial Fuel Cell (MFC) and Bio photovoltaic cells (BPV) are the significant forms of BES and have a variety of practical applications, such as decomposable waste reduction [28], electricity generation [29], wastewater treatment [30], biosensor applications [31], etc. The characteristic feature of MFCs is the presence of special electrogenic microbial species that oxidize the decomposable organic matter and also release electrons as a byproduct [32]. On the other hand, BPVs utilize solar energy and photosynthetic microorganisms for electrical energy production [15]. The basic working principle of BPCs is that the oxygenic photosynthetic microorganism can harvest the incoming solar energy for electricity generation. Both work on the principle of redox reaction [33] and is similar to that of conventional Fuel cells. However, the significant difference between these energy conversion devices is the use of microorganisms for energy generation in MFC in place of chemical reagents, as in the case of fuel cells [34].



Figure 1: Contribution of different countries in the research progress for BES technology.

Recently, different types of BES have seen tremendous research growth, especially since the discovery of special electrogenic microorganisms that are discussed in later sections [32]. Fig. 1 & 2 summarise the bibliographic trends worldwide from 2004 to 2024 (data Web retrieved from of Science algorithm). The bibliometric trend was evaluated based on the search results for "Bioelectrochemical systems," "carbon BES," "carbon nanomaterials in nanomaterials in MFCs," and lastly, nanomaterials "Carbon in Biophotovoltaic systems." The results in the bar graph suggest the rising trend in this water-nexus technology for renewable energy production (BPVs) or, bioremediation (MESs) or both (MFCs). The figures depict the rise of research in the BES domain, with around 1500+ research papers published in the past four years alone. This analysis was crucial in providing insight into the growth of the in terms technology of research advancements [35]. Figure 2b shows the development of research in various countries, including China, the United States of America (USA), and India, which are leading the research in BES. Bibliometric assessment benefits the readers and researchers by providing them with the current and developing research issues [36, 37]. The databases will surely proliferate with passing time and trends will differ from their past counterparts, but the domain of BES will foster the change.



Figure 2: Publication trends among different attributes, (a)year-wise number of publications in the research area of BESs, and (b) publication trends among countries and their output for the same.

2. Microbial fuel cell: Design and working principle

Microbial Fuel Cell (MFC) is the most popular type of BES, mainly due to its simple setup and mild operating condition. For MFCs functioning, the electroactive microorganisms oxidize the organic matter in the analyte solution and produce protons, electrons, and carbon dioxide as by-products [38]. The protons produced in the anodic chamber migrate towards the negatively charged cathode through a selectively permeable membrane and undergo reduction, while the electrons flow through an external circuit to the cathode, producing electricity [39]. Electrons and protons combine to produce water molecules by reducing oxygen in the cathodic chamber [40]. This functioning takes place in MFC setup consisting of the following elements: (i) Anode and Cathode chamber where reactions take place, (ii) Proton exchange membrane for movement of ions across the chambers, (iii) Microbial culture and electron transfer mediator for easy transfer of electrons from microbes to electrodes, (iv) Energy source for microbial growth, (v) Electrodes (made of conductive material for easy electron capturing and circuit formation), (vi) External reader circuit for reading output values from MFC [41].

Based on the chamber configurations, MFCs can be of two types: (1) Singlechambered MFCs (SCMFCs) or (2) Dualchambered MFCs (DCMFCs) [42]. The main difference between DCMFC and SCMFC is the presence of a separate chamber for the cathode compartment [43]. SCMFC uses O₂ in the air as a reducing agent and, thus, doesn't require a separate chamber for the oxidation process [44]. This grants SCMFC the ability to

scale quickly, use in batch and continuous mode, and utilise less material for fabrication, thus providing a low-cost option for technology implementation The DC-MFC comprises two [45]. chambers, i.e. anode chamber and a cathode chamber, which are separated by an ion exchange membrane. The oxidation and reduction process occurs separately in the anode and cathode chambers. respectively [44], and a short incubation time is required for energy generation [43]. It has been found that the performance of the MFC is highly dependent on the anodic oxidation by microbes and the efficient transfer of protons from the anodic to the cathodic chamber [46]. This grants DCMFC the ability to have a short reaction time for energy generation, increased sensitivity towards electrolytes, and temperature/pH change [47-50]. Fig. 3 showcases both single-chambered and double-chambered MFC fed with wastewater as a substrate source [51].



Figure 3: Schematic diagram of (a) Dual-chambered MFC and (b) Single-chambered MFC (A, B, and C refer to the electron transfer: direct (A) and indirect (B & C))

The proton exchange membrane (PEM) (or a salt bridge) aids in the transfer of ions by incorporating electro-osmotic drag between the two chambers [52, 53]. The primary purpose of using a selective proton exchange membrane is to allow the flow of only protons from the anodic to the cathodic chamber to maintain electrical neutrality and a barrier between both chambers [54]. It only enables the transfer of H+ and prevents the movement of anions and crossover of any gaseous molecules, especially O_2 , from the cathodic to the anodic chambers [55]. Oxygen diffusion from cathode to anode leads to lower efficiency as the electrons reduce the O_2 molecule more readily than the anode material [56]. Hence, the membrane should not allow oxygen diffusion and flow of ionic species, which hinders cell growth or proliferation rate [57]. The membrane that allows for the highly selective and efficient transfer of the selected molecules while preventing the transfer of unwanted molecules is highly preferred as it reduces resistive losses, thereby increasing the overall efficiency of MFCs [58]. The thickness of the membranes also has a significant effect on the performance of MFCs [59].

Usually, MFCs with thinner membranes possess less internal resistance as they offer higher permeability to electroactive species compared to thicker membranes[58]. Electroactive microorganisms can also form a thin layer on the anode side of the membrane due to biofouling that restricts the movement of protons and ultimately chokes them [53, 59]. The most commonly used membrane is Nafion from DuPont [60] due to its excellent proton conductivity and antifouling capacity [61]. It comprises a conductive sulfonated Polytetrafluoroethylene backbone with strong C-F bonds [62]. This backbone confers excellent chemical and mechanical stability [62]. The terminal sulphonation of the backbone imparts a negative charge and allows for selective preconcentration of positively charged particles via electrostatic interactions [63]. The backbone also has an amphiphilic nature with hydrophilic -SO3H and hydrophobic perfluoroalkyl backbone [57].

Along with all these positive roles of PEMs, a major disadvantage is also associated with incorporating PEM in MFC. The expensive nature of PEMs like Nafion has restricted their application, and as a result, cheaper but less efficient alternatives like salt bridges are preferred over PEMS to limit the cost of the device [53, 59, 64]. Other than that, the researchers are also trying to develop a more efficient membrane with enhanced proton conductivity and ion exchange capacity [65]. Modifying membranes using nanoparticles is one of the simplest and most effective ways to enhance the desired properties of the membrane [39]. Use of non-fluorinated polymeric membrane materials such as

sulfonated silicon dioxide (S-SiO2) in sulfonated polystyrene ethylene butylene polystyrene (SSEBS), sulfonated polyether ether ketone (SPEEK) and graphene oxide sulfonated polyether ether ketone (GO/SPEEK) membranes showed promising results and proved to be an alternative material to Nafion 117 [66-70].

Microbes reside in the anodic chamber, breaking down the organic compounds to produce energy [71]. Though a wide variety of microorganisms can be employed for energy generation in MFCs, the energy yield can further be enhanced using mixed microbial cultures (cocultures) or special recombinant microbial strains [72]. As MFC finds its use as a bioremediatory, sludge and wastewater can be used in the anodic chamber as substrate and microbial sources [73].

The power output and efficiency of the MFCs are heavily impacted by the organic substrates available for microorganisms. Spent waste materials, including dye wastewater, activated sludge, landfill leachates, brewery wastewater, and industrial effluents. have been successfully used as substrates for MFCs. This thereby shows the potential of MFCs as a versatile bioremediation energy conversion device [41, 71, 74]. The organic waste has all the dietary components a microbe would need to respire and produce energy [74]. It also contains a consortium of species with different growth requirements, resulting in various energy production rates.

While MFCs are widely used and have been the subject of much research in the field of green energy conversion devices, other similar devices, such as biophotovoltaic (BPV) cells, Bioelectrolysis cells, etc., are also being thoroughly studied and investigated for potential commercial use. The next section dives into the introduction of BPVs.

2.1 Bio-photovoltaic systems: another form of BES

BPVs are a type of energy-harvesting BES and are also known as photo-microbial cells or microbial solar cells [75]. Due to their simple nature, they are gaining a lot of research interest. The general structure and mechanism of processes in BPV can be illustrated in Fig 4. BPVs involve the use of oxygenic photosynthetic microorganisms (mainly cyanobacteria and algae) to convert solar energy to electrical energy. Although **MFCs** BPVs both and utilize microorganisms as biocatalysts to produce electrical energy, however, the major difference between them is the nature of microorganisms and the requirement of organic matter as substrate. BPVs use oxygenic photosynthetic microorganisms to generate electricity using solar energy and do not require any additional substrate like organic matter and use water as an electron source, whereas MFCs use anoxic heterotrophic microorganisms to generate electricity and use organic matter as an electron source.

Similar to MFCs, BPVs can be categorized into single-chamber and dual-chamber based on the device configuration and similarly have an anode chamber where electrodes generated are by the photosynthetic microorganisms under sunlight and a cathode chamber where the selectively transferred H⁺ are oxidized to form water. Microbes in this system are usually made to grow on the electrode surface in layers, and the microbe's exoelectrogenic property may depend on the growth conditions provided [76]. The larger surface area of the electrode supports microbial growth and biofilm formation. Many microbial species have been employed for BPV systems. For instance, Bombelli et al. employed Pseudanabaena limenetica biofilms for energy generation and compared various electrode substrate materials (Indium Tin Oxide(ITO), Stainless Steel(ss), carbon paper, etc.) [77].



Figure 4: Basic diagram of BioPhotovoltaic (BPV) fuel cell depicting the flow of ions and basic mechanisms that govern microbial respiration and electron generation. (Adapted from [78]

Energy production in BPV systems again depends on the photosynthetic microbe's electron transfer and extracellular electron transfer (EET) rate, which can be affected by the electrode material [79]. Indium tin oxide (ITO) is one of the most commonly used base materials for the electrode, due to its excellent biocompatibility [80]. The properties of these electrodes can be further enhanced by further functionalisations or modifications like nanomaterial coatings, etc. Graphene oxides and graphene quantum dots have been extensively studied and utilized as a coating for bare ITO surfaces due to their excellent photocatalytic ability and highly conductive nature [81]. The following section discusses the native EET mechanisms of microbes and the harnessing of this mechanism for energy production.

3. Native EET mechanisms of microbial species

As mentioned above, the efficiency and performance of BES systems are highly dependent on the electrode materials and microbial species. Optimal growth conditions are highly dependent on the microorganism and vary from species to species [56]. The microbial species that have the ability to release electrons in the surrounding environment while oxidizing the organic substrate are termed electricigens and are highly sought after for their application in microbial fuel cells [82]. Electricigens are classified as alpha, beta, gamma, and delta proteobacteria in this phylum [38]. Various electricigens and their combinations have been used in MFCs, resulting in higher outputs than nonelectricigenic microorganisms [54]. Proteobacteria is a vast class of electricigens (the largest in bacterial species) with strains that are dominantly used in MFC production [83]. Two halophiles were tested at the anode of MFC. The maximum power and current densities reached 11.87/4.57 $\mu W/cm^2$ and 49.67/22.03 μ A/cm², respectively. In the case of H.volacni, the power density and

current density were further enhanced using electron mediator-neutral red [84]. Several of this members phylum showed electrochemical activity. Geothrixfermentans, when used in MFC, reached a peak current of 0.6 mA and achieved 97 % electron recovery [85]. The microbial fuel cell systems based on the cyanobacteria phylum were called photosynthetic MFCs (PMFCs). A doublechambered Photosynthetic-MFC was built using model cyanobacteria Synechocystis PCC-6803 in an anode chamber. The energy production rate of the mentioned PMFC reached stability, with the maximum power density reaching 72.3 mW/m² [86]. Researchers have also tested Saccharomyces cerevisiae for electricity generation [12]. The maximum current density and power density were achieved using yeast extract as an electron mediator in double-chambered MFC, which attained 300 mA/cm^2 and 70 mW/cm^2 of current and power densities, respectively [87].

The exoelectrogenic species have also evolved to facilitate EET to the anode. The extracellular electron transfer mechanism to the anode can be categorized into three (i) direct electron different classes: transfer, (ii) electron transfer through mediators, and (iii) electron transfer through nanowires [67]. Most of the EET mechanisms found in microbes can be categorized as direct electron transfer or mediated electron transfer [83]. This mechanism can be performed either via surface-exposed c-type cytochromes (direct EET) or nanowires/mediators (mediated EET) [38]. A well-characterized system for direct extracellular electron transfer (EET) by a multi-heme, c-type cytochrome is the metal-reducing (Mtr) pathway that occurs in Shewanella oneidensis [88]. This pathway requires specific proteins like CymA, FccA, STC, MtrCAB complex, and OmcA to extract free electrons from the electron pool in the cytoplasmic membrane [89]. The MtrCAB complex is the protein responsible for connecting the periplasm with the outer surface of *Shewanella* oneidensis for easy transfer of electrons [90]. It comprises the outer β -barrel membrane protein, MtrB, and the decaheme cytochromes, MtrA and MtrC. MtrA and MtrC proteins are believed to be connected from the inside pores formed by MtrB from the extracellular and periplasmic sides, respectively [91].

Certain microorganisms like Geobacter sulfurreducens develop thread-like structures with lengths up to 20 µm extending from the plasma membrane. These fine threads are termed as "nanowires" and are highly conductive and facilitate the transfer of electrons from the microbe to the electrode [92]. Nanowires are also capable of inter/intra-cellular electron transfer; for instance, nanowires were shown to penetrate aggregates of Geobacter sulfurreducens and Geobacter metallireducens to facilitate electron transfer [93]. The nanowire composition and mechanism of electrical conductivity have been extensively studied for the model organism of Geobacter sulfurreducens. Observations suggested that nanowires were mostly type IV pili with PilA protein as a major component [94]. To back up this suggestion, studies showed that the strains that lack PilA or contain mutant PilA will show poor conductivity, which led to the postulation that electron transfer occurred due to the presence of a chain of aromatic residues in PilA [94, 95].

In the above sections, we have briefly discussed the design and working of BES, the significance of proton exchange membrane and salt bridge, biophotovoltaic cells and most importantly, the driving force of BES, i.e. microorganisms. However, the efficiency and performance of BES is also heavily affected by the electrode material and their design. Hence, in the coming section, we will elaborate on the various materials used as electrodes in BES and their properties. We will also focus on the conventionally used electrode materials and the development of the advanced carbon-based electrode materials including carbon nanodots, carbon nanotubes. A brief theoretical discussion is also provided for the preparation and synthesis of said materials, highlighting the advantages and disadvantages of the processes concerning the material obtained for application. The next section provides a brief introduction to electrode materials and their properties and converges to the application of carbon-based materials in electrode preparation and functionalisation.

4. Electrode materials for BES application

The electrodes are the most significant component of the BES and play a major role in determining the overall efficiency and output of the cell. Hence, it becomes of utmost importance to choose the appropriate electrode material. Electrode materials are selected based on specific features that promote EET and microbial growth [79]. Some of these features include (i) biocompatibility [96], (ii) large surface area [97] and porosity [98], (iii) high electrical conductivity [99], (iv) stability and durability [100], and (v) electrode cost availability and [101]. Excellent biocompatible electrode material enhances the adherence of the electro-active microorganisms and biofilm formation, thereby enhancing the system's energy output [66]. The surface area and porosity of electrode materials significantly determine the biofilm formation [75]. The increased porosity allows for better microbial adhesion by providing a large, accessible active area, decreasing the ohmic losses [102]. Theoretically, the maximum open circuit voltage (OCV) of MFC cannot increase beyond 1.1V, mainly due to the thermodynamic limit generated by the difference in the redox potential associated with the oxidation of organic matter and redox potential associated with the reduction of oxygen [103-105]. An alternative solution to increase the OCV involves using multiple MFC arrangements (cascading MFCs). Excellent electrical

conductivity of electrodes ensures sufficient and continuous operation of the MFC system [80]. As oxidation reactions occur inside the anode chamber, hence, the functioning electrode materials should be able to show extraordinary physiochemical stability avoid to unwanted corrosion/decomposition [106]. Furthermore, the electrode material should be highly resistant and possess hydrophilic elements to avoid unfavourable decomposition or corrosion because of long-term contact with waterv а environment [67].

Above all, the cost and availability of electrode materials are significant limiting steps in the commercialization process of BESs [39]. Expensive materials may come with excellent conductivity and stability, but the increased energy output cannot balance the increased production cost [65]. Materials like platinum, silver and their alloys, metal nanomaterials, etc., show exceptional conductivity and are employed as electrode materials for research purposes. These materials are very costly due to their chemical synthesis and cannot be used commercially. Such expensive materials can be replaced with cheaper carbon-based materials generated through green synthesis routes, e.g., graphene, carbon nanotubes, activated carbon, etc [68].

The coming section dives into conventional materials and carbon-based materials as their substitute. Traditional electrode materials involve the use of conductive metal electrodes as anode materials, but the introduction of nanomaterials and composite materials has received positive feedback from the researchers. The benefits were to such an extent that traditional materials have vanished from play, and the composite materials have been extensively studied for their use. In the coming sections, we will discuss the use of nanomaterials and composite materials and their application in BES technology.

4.1 Conventional materials for electrodes Conventionally, metal and metal-oxidebased electrodes are popularly used as anode and cathode materials in MFCs mainly due to their excellent electrical conductivity [107]. In 1910, when M.C. Potter demonstrated his pioneering work of BES technology, his apparatus used the platinum electrode as both anode and cathode [12]. Since then, the platinum electrode has been extensively used as a cathode electrode due to its resistance towards oxidation and ability to absorb hydrogen [69]. Figure 5 broadly classifies conventional materials as carbon-based, metal/metal oxide-based and composite electrode materials. Among these materials, carbon-based materials are predominantly because of their advantages over metalbased electrodes.



Figure 5: Digital Photo of commonly used conventional electrode materials for BES applications. (a) carbon cloth, (b) Carbon brush, (c) Carbon rod, (d) Carbon Mesh, (e) Carbon Veil, (f) Carbon Paper, (g) Carbon Felt, (h) Granular activated carbon, (i) Granular Graphite, (j) Carbonized Cardboard, (k) Graphite Plate, (i) Reticulated Vitreous Carbon, (m) Stainless Steel Plate, (n) Stainless Steel Mesh, (o) Stainless Steel Scrubber, (p) Silver Sheet, (q) Nickel Sheet, (b) Gold Sheet, (c) Titanium Plate (Figure 5 is adapted from [43], published by Elsevier)

4.2 Carbon-based electrodes: Traditional and Nanomaterials Based

Other than metal and metal oxide-based materials, Carbon materials like carbon rods, carbon brushes, carbon foam, carbon carbon felt, etc, have been cloth. extensively used as electrode materials in BESs mainly due to the following advantages: (i) High chemical and mechanical stability [108], (ii) Costeffectiveness [109], (iii) High conductivity [110], (iv) Good biocompatibility [111], and (v) good electron transfer kinetics with large surface area [112]. However, the low EET rate shown by such materials has highly limited their practical use and further scaling up [113]. To overcome these problems, various other materials and nanomaterials have been explored in the recent past [114-117].

Nanomaterials are materials with dimensions in nanometre scale (10-9 meters) and have an extremely large surface area, available for microbial adhesion. Nanomaterials can also be modified to act as a platform for electrons to travel from the cellular surface of microorganisms towards the anode [118]. Due to the extremely large surface area, nanomaterials can adhere and connect to multiple microorganisms at a time. Their porous nature further increases the surface area while consuming little to no volume [119]. Due to these advantages and their characteristic properties, certain nanomaterials have cemented a place in production energy and storage technologies.

5. Carbon nanomaterials for energy production enhancement

As mentioned above, the electrode material should have a large surface area so that the microbial species can have more area to adhere to and transport the released electrons directly to the anode [120]. To achieve this, nanomaterials come into play as they consume low volume to offer large surface areas [121]. Nano-materials have widespread applications due to their extraordinarily large surface area, current withstanding capacity, charge storage capacities and tensile strength [122]. Based on their size and structures, these materials can be subdivided into Zero Dimensional (0D). One Dimensional (1D), Two Dimensional (2D) and Three Dimensional (3D). In the coming section, these especially materials, carbon-based materials, will be discussed, starting with point materials.

5.1 Zero dimensional or Point Materials

Zero-dimensional or 0D materials are a class of nanomaterials where the dimensions of the structure in all three dimensions are on a nanometre scale. These 0D materials are commonly represented by spherical nanomaterials, hence giving the name point materials to this class of nanomaterials. Common examples of point materials are carbon nanodots, graphene quantum dots, fullerenes, and metallic nanoparticles. Out of these materials, carbon-based quantum dots have been extensively used as an electrode modifier due to their conductive nature, large surface area and easy modification [123]. The precursors required for quantum dot synthesis usually include a precursor molecule that can be larger or smaller than the nanoparticles, depending on the synthesis approach used. The top-down approach generally works with larger precursor molecules for the breakdown and formation of nanoparticles. The bottom-up approach, on the other hand, works with smaller precursor molecules for aggregation and formation of nanoparticles.

Recently, considerable work has been done in this class due to their promising features [124]. These materials have been widely used in bioimaging, drug delivery, photocatalysis, sensing etc and have gained the scientific community's recognition for their performance and efficiency in nextgen electronic systems [125]. Graphene has extraordinary electrical properties, but the zero-band gap limits its widespread application in MFCs. To overcome this limitation, graphene-based quantum dots are synthesized with excellent electrical properties and biocompatibility [126]. Keeping this in mind, Graphene quantum dots (GQDs) are another alternative that can be used for many applications, such as photovoltaic systems, organic LED systems, and energy-storage devices. Owing to their excellent photoluminescence, quantum yield (QY), resistance low toxicity, and to photodegradation, GQDs have been used for other purposes also viz, bioimaging [127], biosensing [128], and possible cancer treatments [129-131].

a. One Dimensional or Tube/Fibre materials

One-dimensional nanomaterials are materials where the structure can expand only in one dimension, while the remaining two dimensions are restricted to the nanometre scale (1-100nm). Their structure closely resembles tubes and fibres. Common examples of 1D material include Carbon Nanotubes, nanowires, conducting polymers, nanorods and more. Carbon nanotubes (CNTs) are the most commonly used (1D) carbon nanomaterial having a tube-like structure. CNTs have high tensile strength, excellent thermal and electrical conductivities, high flexibility and greater surface area [132]. Depending on the number of concentric tubes that make up the CNT, they can be single-walled (SWCNTs) or multi-walled MWCNTs [133]. Owing to its high conductive nature and high aspect ratio, carbon nanotubes imitate the working of nanowires in

facilitating native EET. When used in MFC as anode modification, the maximum power density achieved was 3660.25 mW/m^2 . using activated sludge as fuel and microbial consortium [134]. Recently, CNTs have been investigated to build good-quality electron transfer networks by having hierarchical porous structures that are able to entrap bacterial species. Due to the presence of macropores that promote microbial growth and mesopores that result in a higher concentration of electron shuttles (i.e., flavin for Shewanella oneidensis as inoculum), the maximum power output observed is significantly higher than the power output obtained by the conventional carbon cloth electrodes [134]. The modified anodes possess smaller resistance for charge transfer which in return provides higher power efficiency. This method adheres and embeds bacteria in 3-D CNT networks of porous structure, thereby bypassing the biofilm formation step, which is generally the most timeconsuming step in MFC fabrication [135]. Table showcases the 1 applied nanomaterials, their role in MFC and their performance. Most of the entries present on the table rely on the use of composite materials as these materials have the advantage of enhancing the electrochemical

properties, which can be seen by the report presented by Habibi et al., in which they stated an increase of 87% when using Fe/Fe₂O₃ with N doped CQDs as compared to solo N-CQDs [34]. Reports by Lan et al. and Yan et al., suggest the use of carbon nanoparticles and metallic nanostructures to enhance electrode conductivity and provide efficient charge transfer [136, 137]. The composition of different dimensionality of materials (nanowires with nanoparticles. nanotubes with nanosheets etc.) encourages the researchers to find a facile and sustainable synthesis method that can be scaled up for commercialization. Carbon nanomaterials have been the centre of discussion due to their extravagant availability, biocompatibility and facile synthesis procedures. Feng et al. reported the use of nitrogen-doped carbon nanotubes as a metal-free electrode catalyst and deployed it at the cathode of the MFC [138]. They reported a higher power density of 1600 mWm⁻² than the conventionally used platinum counter electrode (1393 mWm⁻²). The table below (Table 1) holds some notable examples of reports where and carbon-composite nanomaterials materials are used for MFC application.

Material(s)	Synthesis method	Role in MFC fabrication	Power density	Microbial species	References
	Zero-dime	nsional or Poi	nt Materi	als	
Fe/Fe2O3 with N-doped CQDs	Hydrothermal + Electrochemical oxidation method	Anode	836 mW/m ²	Activated sludge	[34]
N, S co-doped CQDs on Cu2O-Cu NWs	-	Cathode	924.5 mW/m ²	Microbial consortium	[136]
B doped GQDs on Bi-MOFs	Solvothermal	Cathode catalyst	703.55 mW/m ²	Domestic wastewater	[137]

Table 1: Nanomaterials as electrode material and mediator in MF	Cs.
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CdS QDs with PANI nanocomposites	In-situ synthesis	Photo cathode	166.93 mW/m ²	Anaerobic sludge	[139]	
	One Dimensio	onal or Tube/	Fibre mat	erials	I	
CF modified with CNT/PPy	-	Anode	3660.25 mW/m ²	Activated sludge	[134]	
N-doped CNTs	Chemical vapour deposition	Cathode catalyst	1600 mW/m ²	Domestic wastewater	[138]	
Pt nanoparticles anchored with MWCNT	Chemical vapour deposition	Cathode catalyst	2470 mW/m ²	E.coli (DH5α)	[46]	
Textile anode modified with MWCNTs	-	Anode	1098 mW/m ²	Domestic wastewater	[140]	
Pt/CNTs modification	-	Cathode	1118 mW/m ²	Wastewater species	[141]	
2 Dimensional or Sheet materials						
FeS ₂ nanoparticles decorated graphene	Modified Hummer's method + hydrothermal method	Anode	3220 mW/m ²	Microbial consortium	[142]	
3-D graphene aerogel with Pt NPs	Hummer's method	Anode	1460 mW/m ²	S.oneidensis MR-1	[143]	
3-D graphene/PANI	Chemical vapour deposition	Anode	768 mW/m ²	S.oneidensis MR-1	[144]	
Graphene modified SSM	Chemical oxidation- reduction	Anode	2668 mW/m ²	E. coli	[145]	

The main disadvantage of CNTs is their limited solubility [146] in aqueous media and limited long-term stability [147-149]. To overcome these limitations and improve long term stability, researchers have tried to modify the exposed surface of CNT through functionalization with hydrophilic moieties [150]. CNTs-modified graphite felt electrodes demonstrated stable performance throughout the course of the experiment (13 months). Carbon nanofibers are rarely used as electrode modifiers because the exoelectrogenic species have the tendency to form nano fibres from pili (as discussed in section 1.3: native EET mechanism of microbial species) [151]. The use of nanofibers/wires in BES can prove beneficial for their mimicking of pili for strains that cannot form natural fibres, thus making most microbes electricigens.

b. 2-Dimensional materials

The 2D materials were investigated after the discovery of graphene (Andre Geim and Konstantin Novoselov, 2004), a 2-D carbon-based material with excellent electrical conductivity [152, 153] and is the most prominent example of 2-D materials. Graphene is a single carbon atom-wide layer organised in a 2-D structure with a trigonal planar lattice. It has ultra-high active surface area. excellent biocompatibility and extraordinary mechanical properties [154]. Due to these features, graphene has made a league for itself, revealing great potential for use as an effective anode modifier. A graphenemodified stainless-steel mesh anode showed enhanced energy output and power generation mainly due to increased active surface area, resulting in greater adherence of microorganisms [154].

The use of nanomaterials can enhance EET, and the coming section covers discusses the interactions and mechanisms that undergo during the EET in the presence of nanomaterials.

6. Nanomaterials for enhancing EET efficiency

Nanomaterials (NMs) can be utilised alongside native extracellular electron transfer (EET) pathways in order to assist the electronic bridging between the periplasm/membranes of microorganisms to the anode and are being widely used for applications due various to their extraordinarily large surface area, current withstanding capacity, charge storage capacities and tensile strength [122]. Further, unlike proteins, they do not degrade easily and offer extended lifetime [155]. Highly conductive nanoparticles can bind to the cell surface and enhance the conductivity of the exoelectrogen, thereby improving the electron transfer to solid

electron acceptor [156]. Furthermore, covering the cell surface with conductive NPs that are capable of interacting with each other opens doors for the creation of conductive cell aggregates that form an immobilised film on the electrode surface [157]. Entities, including neutral red and lignin, were used previously to enhance the bio-catalytic effectiveness in the anode of MFCs, but nanoparticles have proven to be better modifications for anode electrodes [158]. Several anode characteristics, like the surface area available for microbial adhesion and transmittance, are crucial, and such characteristics can be enhanced using nano-dimensioned materials, [159]. The EET can also be enhanced using electron shuttles/mediators that act as a bridge between the microorganism and the electrode. Upon comparison, carbon quantum dots performed a much better role as an electron shuttle as compared to conventionally used Methylene blue [160]. Quantum dots show excellent conductivity and are photocatalytic, which means that they can be used in photosynthetic microbial fuel cells (or BPV fuel cells) [161]. These particles interact with the cell in 3 possible ways: (i) NMs-cell surface interactions, (ii) NMs-cell membrane (iii) interactions and NMscytoplasm/periplasm interactions. These interactions are mentioned below in details:

6.1 NMs-cell surface interactions:

The electrode surface is usually crowded by bacteria adhered to the surface. The limited surface area of the electrode renders the majority of the bacteria in the medium for poor electron transfer rate due to overcrowding at the electrode surface. A solution to this problem will be to use electron mediators that can transfer electrons in an invisible shuttle. The mediators are used to collect electrons at the bacteria surface and travel to the electrode under the influence of the negative bias produced by the anode. Some bacterial species produce their own mediator compounds in order to facilitate the electron transfer like the Soneidensis that produces riboflavin and flavin mononucleotide as electron mediators [162]. But not all bacterial species can produce mediators and thus, require external mediators for electron transfer. Nanomaterials can act as shuttles for electron transport and can also act as redox mediators for contaminants' degradation. Carbon nanomaterials have the advantage of outstanding electrical conductivity, good biocompatibility, high surface area. reduced production cost and low waste generation rate as compared to other nanomaterials. Zou et el. Presented a report on the use of porous MWCNTs and GO composite for anode modification [163]. The prepared composite was found to incorporate more bacteria at the electrode surface and assisted in the formation of denser biofilms as compared to the individual use of MWCNTs or GO. A report by Wu et al. presented the idea of using porous N-doped CNTs with rGO as a composite material for anode preparation [157]. Besides enhancing EET rates, the material also provided an increased surface area that facilitated the formation of denser biofilms.

6.2 NMs-membrane interactions:

Microbial membranes can be easily influenced by the use of nanomaterials. The shape and biological functions can be altered or enhanced based on the nanomaterial-membrane interaction [164]. The interaction happens in three possible and crucial phases. attachment. encapsulation and intercalation. Similar to application in drug delivery, their nanomaterials are used in BES as electron shuttles or electrode modifiers [165-167]. Nanoparticles, rods, ribbons, tubes, fibres etc are normally used as nanomaterials but recent research trends have preferred conjugated oligoelectrolytes over nanomaterials for enhancing the electrogenicity of the microbes [168, 169]. Conjugated oligoelectrolytes (COs) contain a hydrophobic core region and hydrophilic head groups, which have a structure similar

to the phospholipid bilayers that constitute biological membranes [170]. These are synthetic molecules that are able to impart exoelectrogenicity successfully [171]. Their central core region consists of π -conjugated polymers responsible for their conductivity. Furthermore, COs have the ability to self-insert into already-formed lipid bilayers [172]. Various COs have been used in miniaturised E.coli-based MFCs that show up to a 25-fold increase in power density. Besides differences in power output, the various COs showed distinct influences on anodic biofilm morphology [173].

6.3 NMs-cytochrome interactions:

Microbial species contain cytochromes as electron carriers for intracellular electron transfer. These proteins contain a heme group that is essential for the IET in cellular respirations and play a vital role in cell signalling/ energy production. The latter application of cytochromes can be enhanced by the use of nanomaterials. The c-type cytochromes perform the direct electron transfer in the IET process and conjugation of nanomaterials with the cytochrome increases the availability of active sites for the released electrons. The nanomaterials can be synthesised biologically inside the cell. The biosynthesis of nanoparticles is not entirely extracellular, which means these particles can be synthesised in the cytoplasm or periplasm also [174]. Pd NP synthesis has been reported in the periplasm of Desulfovibriode sulfuricans. Once synthesised, these nanoparticles were used as the electron mediators, transporting electrons between membrane-associated cytochromes to fill the electronic gaps that occur within the periplasm [175]. In a fashion, QDs can also be similar biosynthesised. Biosynthesised CdS QDs have been reported to localise intracellularly in Saccharomyces cerevisiae cells and boost photocurrent production when grown on ITO electrodes under lightdark-cycling [176]. These interactions

suggest that nanomaterials have positive impact on the EET pathways.

7 Photocatalytic electrodes and their applications in BPV cells

Just like MFCs, most research on BPVs focuses on improving interactions between cells and modified bio-anodes. In a BPV system, light absorption determines the electron flux that a single cell can produce. The incident light consists of both UV region and visible region but the photosystem I and II absorbs light only in the visible region [177]. This results in a loss of incident light energy for the UV region that constitutes half of the incident light energy and therefore, it is crucial to improve the light-harvesting capacity of the photosystem. Nanomaterials can work as auxiliary light absorbers for photosynthetic microbes as these materials are able to absorb light with different wavelengths [178]. The absorbed light energy can be transferred into the light-harvesting complex of the photosystem via the Förster resonance energy transfer (FRET) pathway [179].

Surface modification of anodes using CNPs, CNTs, or porous electrodes (MOFmodified or ITO-based electrodes) has been reported to promote electron transfer [180]. Conductive metal/metal oxide-modified electrodes show better power densities when compared to both ITO-coated polyethylene terephthalate (ITO-PET) and conventional carbon-based electrodes. However, recent studies show that both Nostoc sp. and Synechocystis sp. PCC 6803, immobilized **CNT**-based when on electrodes, are capable of generating electrical energy in response to light. The CNTs coated on carbon paper electrodes facilitates an intimate cell-electrode interaction by forming multiple sites for attachment, which, in turn, contributes to higher power output, compared to those generated by using conventional electrodes [181]. In addition to providing a support structure for improved immobilization. nanotubes (CNTs) also act as electron

collectors in the electron transfer pathways. Cyanobacteria, in this case, Synechocystis sp. PCC 6803 were printed onto the paper to ensure a homogenously thin, solid layer of cells on the ink-printed electrode. The current output achieved in this configuration was much better than that obtained by the use of the same Synechocystis strain deposited by cell adhesion on the ITO-PET electrode. Furthermore, this procedure obviates any need for a liquid reservoir that is generally used in standard BPV systems, thus making of solid-state miniaturization BPVs possible [182].

Quantum dots (QDs), on the other hand, are photocatalytic nanoparticles and photocatalysis mechanism of QD composites follows three major steps, i.e., photoexcitation, recombination and oxidation-reduction reactions [183]. The photocatalysis is achieved due to a few reasons:

- QDs have a narrow bandgap than most transition metal oxides (e.g., TiO₂, RuO₂, MnO₂, etc.). So, when QDs are coupled with metal oxide nanoparticles, improved photocatalytic performance is observed [184].
- At further lower levels, say angstrom (ii) levels, GODs exhibit a 2D mat structure, which is comprised of carbon atoms in a planar hexagonal lattice. The atoms are connected through both σ -bonds and π -bonds by sp²-electrons and p_z electrons, respectively. These chemical features grant GQDs with many unique properties like high electron and hole mobilities and greater surface area per unit mass (approximately $2600 \text{m}^2/\text{g}$) [185].
- (iii) GQDs can become a sink for photogenerated electrons due to discrete electronic levels and substantial electronic conductivity. Furthermore, GQDs can be coupled with transition metal oxide

nanoparticles to facilitate donoracceptor contact [186].

(iv) Most of the pollutants we see in the environment have aromatic structures. As GQDs also have a similar nature, they can act as an active site for the adsorption of these aromatic pollutants, thus accelerating the photodegradation process [187].

Recently, QDs have been used as electrode material for photocathodes. In BPV fuel cells, GQD/MOF hybrid electrodes can be used for photocatalysis. Li et al. used silicon quantum dots to amplify the lightharvesting capacity of the Italian lettuce plant [188]. The concept was to utilise the UV region of incident light and enhance the photosynthesis process in the plant. The study provided new perspectives for using quantum dots to amplify the use of UV light in photosynthesis. Luo et al. reported the use of CuInS2/ZnS quantum dots as a photosensitised periplasmic unique biohybrid system [189]. The QDs were translocated into Shewanella oneidensis MR-1 cells for the photoexcitation and electron transfer processes to occur simultaneously. The biosystem had an photocatalytic increased hydrogen generation rate with the rate being 8.6 times higher than that of bare QDs. Carbon quantum dots have also been used in these photosynthetic systems for their advantageous nature. CQDs can be prepared by various precursor materials (including waste), they are easily synthesisable and have comparative ability when semiconductor QDs are considered. Liu et al. presented a study wherein CODs are used to enhance the extracellular electron transfer in the dark and light modes of photosynthesis [190]. They suggested enhanced conductivity and boost in EET in dark mode and CQDs were able to absorb light in light mode.

In the next section, we will discuss the use of carbonaceous waste as precursor materials for electrode modification and biomass use.

8 Carbonaceous waste as a precursor material for the synthesis

Substrates, also referred to as analytes, serve as nutrient and energy sources. They are one of the most important parts of MFC as the adequate choice of substrates leads to increased energy production [191]. The substrate consumption and current generation rates by MFC follow Monod's equation under normal conditions. Frequently used substrates include:

- Acetate: a simple and extensively used substrate that is also used as the benchmark for new MFC design configurations because of its inertness towards fermentation and methanogenesis [192].
- (ii) Lignocellulosic biomass: due to its abundance and renewability, lignocellulosic material gives costeffective energy production but cannot be used directly; it has to be converted to monosaccharides to have low molecular weight [193].
- (iii) Synthetic wastewater: the composition is known (well-defined composition) for easy control. Slowly, biodegradable waste gives higher current output than rapidly biodegradable waste [194].
- (iv) Brewery wastewater: brewery wastewater is suitable due to its foodderived nature and low concentration of inhibitory substances. It has a high carbohydrate content. and low ammonium nitrogen concentration [195].
- (v) Dye wastewater: using dye wastewater (Azo dyes) as substrates, with other co-substrates, leads to decolourisation. Experiments revealed that rapid decolourisation was achieved for active brilliant red X-3B (ABRX3) using glucose and confectionery wastewater as cosubstrates [196].
- (vi) Landfill leachates: these are heavily polluted effluents usually containing 4 groups of polluting agents, namely

(i) dissolved decomposable matter, (ii) inorganic matter, (iii) heavy metal ions and (iv) xenobiotic components [197].

Waste materials can be processed to yield carbonaceous mass that can further be utilised as precursors for the production of nanomaterials [41]. The carbonisation process yields fine carbon powder, which can be activated further [198]. Activated carbon refers to a range of carbonised materials having large surface areas and a high degree of porosity and finds many applications in both the environment and industry field [199]. Its major uses include the removal, retrieval, separation and modification of compounds in liquid as well as gas phases [200].

Advancements in nanoscience and nanotechnology have resulted in the fabrication of different classes of nanomaterials for use in BESs [201]. These broad classes of nanomaterials include metal/metal oxide and metal-based materials, carbon-based nanomaterials, and conjugated or composite materials. Table 2 lists some waste material sources that act as electrode material precursors [202]. For instance, Vishwanathan et al. used coconut husk as a precursor material for the synthesis of carbon dots and delivered a 172

% increase in power output of an MFC with mixed microbial culture [160]. Another report by Anusha et al. used tea waste ash with potter's clay to form functionalised electrode [203]. The material was low cost and provided with good performance under different ratios of mixtures. The unique molecular structure of precursor waste material can be exploited to form electrode modifiers. A report by Jaswal et al. utilised rice husk as silicon source and prepared waste derived silicon nanoparticles [204]. They reported a 7.6-fold increase in the power density obtained by MFC application when compared with control. In another report, a waste loofah sponge was used as electron collector and Japanese ink was coated on the sponge [205]. The Japanese ink alongside rice husk charcoal was used as electrode modifier and provided a lowcost solution for fuel cell application. Biomass waste like food content or algal biomass that are rich in carbon and nitrogen are used to develop in-situ N-doped carbon nanomaterials. Kumar et al. presented a report in which they used algal biomass to produce algal biochar via pyrolysis and used the biochar for electrode modification [206]. The table below (Table 2) holds some notable examples of reports where waste materials are reformed for MFC application.

Source	Electrode material	Synthesis method	Role in MFC fabrication	Power output	References
Coconut husk	C-dots	Hydrothermal	e ⁻ mediator	126 mW/m ²	[160]
Orange peels	CQDs (N,S co- doped)/Cu2O- Cu NWs	-	Cathode	924.5 mW/m ²	[136]
Plastic	Fe-t- MOF/PANI on SSM	Alkaline hydrolysis	Electrode application	680 mW/m ²	[207]
Vehicle exhaust	Heteroatom- doped mesoporous	-	Electrode material	2200 mW/m ²	[208]

Table 2: Use of waste as precursor molecules for electrode material synthesis.

	Carbon				
	nanoparticle				50.007
Date seed,	Powder	-	Electrode	1072 and	[209]
Banana peel	coating of		material	730	
powder	Seed waste on			mW/m ³	
Madiaina	Matallia		Electro de	$27 m W/m^2$	[72]
Medicine		-	Electrode	$2/\mathrm{m}\mathrm{w}/\mathrm{m}^{-}$	[/3]
wrapper	aluminium		application		
waste	<u></u>		T 1 1	1.6.1	500.53
Loofah	Charcoal	-	Electrode	16.1	[205]
sponge and			application	μ W/m ²	
rice husk					
Palm kernel	Activated	Pyrolysis and	Electrode	24.17	[210]
shell waste	carbon	Hummer's	application	mW/m^2	
		method			
Archea nut	Activated	Pyrolysis	Cathode	590	[211]
husk	carbon		material	mW/m ²	
Tea waste ash	-	-	Membrane		[203]
with clay			separator		
Food waste	Graphite	-	Fuel source	170.81	[212]
	-			mW/m ²	
Rice husk	Silicon	Pyrolysis	Electrode	190.5	[204]
	nanoparticles		modification	mW/m ³	
Corncob	SiO ₂ -	Graphitisation	Electrode	2010	[213]
	incorporated	-	application	mW/m ³	
	graphite		11		
	anode				
Avocado	Zn/Cu	-	Fuel source	566.80	[11]
waste				mW/m ²	
Biochar	AC-Cu	Carbonisation	Electrode	173.20	[214]
			application	mW/m ²	
Biochar	AC-Co	Carbonisation	Electrode	205.49	[214]
			application	mW/m ²	
Aquaculture	Carbon felt	Pyrolysis	biochar	1693	[215]
-			modification	TT 7/ 3	
waste			mounication	mW/m^3	
waste			at chode	mW/m ³	
waste Algal	Graphite	Pyrolysis	at chode Electrode	6.8 W/m ³	[206]
waste Algal Biomass to	Graphite	Pyrolysis	at chode Electrode application	mW/m ³ 6.8 W/m ³	[206]

The biochar materials were found to be very useful as self-supported electrodes in order to improve microbial adhesion against the commercial carbon cloth/felt or as cathode catalysts vs. Pt/C commercial catalysts [201]. Biochar materials have been reported to increase the maximum power density when used as anode or cathode catalysts. Also, due to enhanced microbial adhesion and growth, direct interspecies electron transfer (DIET) was greatly enhanced compared to electron transfer intermediated by dissolved or immobilised mediators [216]. Whereas the use of doped biochar with dopants like transition metals and nitrogen atoms does not guarantee a straightforward improvement of power density when compared to a control (e.g., Pt/C) as the advantage lies in the substitution of Pt with low-cost catalysts to increase the cost-effectiveness rather than an absolute increase in power production [217]. The use of waste-derived materials for commercial applications decreases production costs immensely and presents a substitute for precious metals.

Vast research has been done to replicate the versatility of carbon. The coming section will briefly describe the application of carbon-based composite structures with different materials.

9 Carbon-based composite structures for electrode application

Carbon-based composite structures are a combination of carbon materials and other conducting materials [218]. Based on the conductivity. carbon-based composite materials can be further divided upon the materials used for modification. They can be (i) carbon-carbon composite [219-221], (ii) carbon-conducting polymer composite [222-224], and (iii) carbon-metal composite [225-227]. Some systems are reactive in nature and tend to improve their reactivity, while others are stable compounds that can be used as storage systems [228]. In this section, we will discuss the different carbon-based composite materials and highlight the enhancement strategies.

9.1 Carbon-Carbon composite

As discussed previously, graphene sheets have inherent stacking ability, which makes microbial adhesion a problem; on the other hand, CNTs have poor solubility and stability issues [221]. However, а composite of CNT and graphene results in the generation of a composite with much better properties. In this CNT/Graphene composite, CNTs prevent the stacking of graphene sheets, thus creating more surface area for microbes to adhere to, while graphene provides stability to the CNT mesh when CNTs are inserted through the plane [229]. This composite structure is both stable and adhesive, thus improving the material's efficiency and lifetime. A report by Zou et al. described the use of such CNT-graphene composite material for

MFC application [162]. The material was prepared via solvent-processed method and the porous network was confirmed by electron microscopy. Doping of carbon nanomaterials has been of great virtue as the process not only preserves the advantages of carbon but also introduces the positive effects of nitrogen. Wu et al. developed a N-doped CNT/rGO composite material for anode application in MFC [163]. Using PANI as the N source, they demonstrated the superiority of N-doped CNT/rGO over N-CNTs, N-rGO and CNT/rGO materials. Alongside rGO, graphene oxide nanoribbons (GONR) have also been used in graphene-CNT composite material as it encourages entanglement between nanotubes and nanoribbons. providing more active surface area. Liu et synthesised and used N-doped al. MWCNT@GONR composite materials using microwave assisted synthesis method [230]. The doped composite material gave increased performance as compared to N-MWCNT, N-GONR, and MWCNT@GNOR composite material. The synergistic effects of using carbon based composite materials serves as an advantage over individual materials and further doping of these composite materials increases the power generation capability [231].

9.2 Carbon-conducting polymer composite

The use of conducting polymers in BES has widened owing to their durability and good conductivity [232]. Accordingly, the various conducting polymers have been used extensively to increase the efficiency of BES systems. For example, polyfuran, polyaniline, poly-para phenylene, polypyrrole, polyvinyl carbazole, polythiophene, and polyazulene are just to mention a few [233]. Among these, polyaniline (PANI) and polypyrrole (PPy) are the most widely used conducting polymers for composite formation with carbon-based materials [234]. Zou et al. demonstrated the use of PPv nanoparticles/MWCNTs in a mediator-less microbial fuel cell. The cell showed enhanced performance with a maximum power density of 228 mW/m² [235]. Yang et al. demonstrated the use of a 3-D graphene/PANI NP-modified electrodes S.oneidensisMR-1-based using MFC (figure), which reached a peak power density of 768 mW/m² [144]. Apart from PPy and PANI CPs, other polymers have also been used for anode modification and have been shown to increase bacterial adhesion on the anode surface. Chen et al. used novel poly(diallyldimethylammonium chloride) (PDDA) with rGO and prepared a modified carbon cloth electrode for anode application electrode [236]. The demonstrated an improved performance which was six-fold better than bare carbon cloth. In another study conducted by Li et al., polydopamine (PDA) was used with rGO and the composite was applied onto a carbon cloth [237]. PDA was chosen to increase hydrophilicity and microbial adhesion. These polymers have positive surface charges like PANI, thus following a similar mechanism for increasing microbial adhesion and charge transfer rate.

9.3 Carbon-Metal composite

Metal materials have always been a contender for electrode production and introduction of nanomaterials have been pivotal in material sciences. Metal nanoparticles have exceptional qualities as current collector and provide surface area enhancement. These materials have been used individually but their composite with carbon-based materials benefits them with enhanced biocompatibility and stability. Metal nanomaterials prepared via green synthesis methods have been a trending research topic. A report by Wu et al. used biogenic gold nanoparticles and prepared a composite material of Au NPs@MWCNT as electrode modifier [238]. The composite material gave a better performance than the individual materials, boasting a 1.8-fold performance boost. Another report by Zhao et al. demonstrated the use of platinum

nanoparticles decorated graphene aerogel for anode applications [239]. The use of metal elements limits noble their application due to rising cost and scarcity in supply of these materials. Researchers pursued inorganic metallic compounds in carbon-metal order to construct composites. Song et al. prepared a composite material consisting of graphene and Fe₃O₄ for anode application [240]. They discovered the high affinity between Fe₃O₄ nanoparticles and Shewanella species that increased the bacteria hosting capability of the electrode. This was evident by the increase in power generation ability that was reported to be 2.8 times higher than that of graphene anode. Beside as inorganic metallic metal oxides compounds, other salts like nitrates, sulphides, carbides and carbonitrides have also been used in conjugation with carbon produce carbon-metal materials to composite materials. Wang et al. decorated graphene nanosheets with FeS2 in order to improve rGO performance in MFCs [142]. The study presented better interaction of anode with microbial species in case of composite material than only rGO. Another research by Zou et al., the decoration of rGO was done by Mo2C nanoparticles and the prepared electrode was used for anode application [241]. The decoration provided an increase in power density by 2 folds due to the excellent electrocatalytic properties of Mo2C. the electrocatalytic properties of clubbed metal nanomaterials with biocompatible carbon nanomaterials produce the composite materials that are cost efficient, easy to reproduce and enhances the application of BES.

The next section provides some notable examples of commercially used BES. Commercialisation of a technology refers to the use of pilot scale projects or the availability of technology in marketplace. Like many other commercialised technologies, BES have been commercialised while innovative research being underway.

10 Commercial aspects of BES

As discussed above, bioelectrochemical systems have diversified their use in realworld situations, such as energy production, treatment, bioremediation, wastewater product recovery biosensors. and applications [242]. Several corporations have tried and succeeded in commercialisation of this technology. A few notable examples would be,

- *M/s Cambrian Innovation (USA)*: The Boston-based company, M/s Cambrian Innovation specialises in providing sustainable wastewater treatment solutions using BES. The company's technology, called EcoVolt, uses BES to treat wastewater while producing clean energy [243]. A conductive polymer matrix is used as an electrode material the growth of that promotes electroactive bacteria.
- *M/s Electrochaea* (*Germany*): M/s Planegg-based Electrochaea, а uses BES company, to convert renewable energy into methane gas, which can be used as a renewable energy source [244]. The company's technology, called Power-to-Gas, uses microorganisms to convert carbon dioxide and hydrogen to methane. The bioreactor contains electrodes that provide a source of electrons for the archaea to carry out their metabolism. The company has described their electrode material as "specially designed catalysts" that allow for efficient and effective transfer of electrons between the electrode and the microorganisms.
- *Emefcy (USA)*: The Minneapolis-based company, Emefcy provides wastewater treatment solutions using BES. The company's technology, called membrane aerated biofilm reactor (MABR), uses BES to reduce energy consumption and improve the efficiency of wastewater treatment [245]. In the MABR process, oxygen is supplied to the biofilm through the membranes, which are made of a flexible and durable polymer that

allows for optimal oxygen transfer while preventing the growth of unwanted microorganisms.

- Aqwise (Israel): Aqwise firm, а Hertsliva-based company, uses BES to provide solutions for wastewater treatment, bioremediation, and biogas production. The company's technology, called attached growth airlift reactor (AGAR), uses microorganisms to remove contaminants from water and soil and to produce biogas from organic waste [246]. The media used in this technology has been described as a 'patented plastic element' that is designed to provide a large surface area for microbes to attach.
- *Pivot Bio (USA):* The California-based company, Pivot Bio uses BES to produce sustainable fertilizers for agriculture. The company uses Pivot Bio PROVEN technology that involves the use of microorganisms to synthesize nutrients to aid in the growth of crops, thereby reducing the dependence on synthetic fertilizers [247].

India is also not far behind in the practical and commercial applications of BES. There are several corporations in India that have applied bioelectrochemical systems (BES) for various practical applications. Here are some examples:

- *Graviky Labs*: Graviky Labs, a Bengaluru-based start-up, developed a technology called KAALINK, which uses BES to capture and convert air pollution into ink [248]. The company's technology uses carbon-capturing devices that can be attached to vehicles or chimneys, which capture the particulate matter in the air and convert it into ink that can be used for printing.
- *Tata Chemicals*: Tata Chemicals has developed a technology called Bioelektra, which uses BES to treat wastewater from its soda ash plant in Mithapur, Gujarat. The company's technology uses microorganisms to treat

the wastewater while generating electricity, reducing the plant's carbon footprint.

- Indian Institute of Technology, Delhi: Researchers at the Indian Institute of Technology, Delhi, have developed a technology called Microbial Fuel Cell (MFC) [249], which uses BES to generate electricity from organic waste. The technology has been tested in a variety of applications, including wastewater treatment and power generation.
- National Environmental Engineering Research Institute (NEERI): Researchers at NEERI have developed a technology called Bio-electro-Fenton (BEF), which uses BES to treat industrial wastewater [250]. The technology uses microorganisms to generate hydrogen peroxide, which is then used to treat the wastewater and remove contaminants.

These examples demonstrate the diverse applications of BES technology in India as well as around the world. As BES technology continues to develop and become more widely available, it has the potential to play an increasingly important role in addressing environmental and sustainability challenges in India and beyond.

11 Conclusion and Future Prospects

This review article shows the involvement of carbon-based nano-materials in BES and their ability to promote both EET and microbial growth. Carbon, being versatile in nature, can be employed as an anode and cathode electrode. At the macroscopic scale, it can be used as carbon cloth, felt, rod, brush, paper, etc., and as nanoparticles, nano-tubes/rods/wires at the microscopic scale. Carbon composite materials (carbon + metal + dopant (N, Cl, I, etc.)) have been extensively studied and have the benefits of both carbon-based materials as well as metal/metal oxide-based materials. Carbon composite structures can be (i) carboncarbon, (ii) carbon-conducting polymer,

(iii) carbon-metal NPs, and metal-organic hybrid structures, and (iv) MOFs. This combination reduces the cost of electrode material drastically and can be used as a replacement for costly metal electrodes that were conventionally used.

We have discussed the materials and their green replacements. Waste reduction is an important aspect of MFC as the waste acts as a fuel/microbial consortium source for the system. Despite the advancements in material research and the use of waste as electrode precursor material. the technology is still far from the commercialization process. Large-scale use of this technology is mainly prohibited due to high device cost, scalability issues and most importantly low power output owing to energy losses at every step. So, future research can focus on these aspects of the technology:

- Microbiology aspect: The microbial consortium used in this technology has seen a fair share of research trends, and new strains can be modified with genetic engineering in order to ascertain PilA microfilaments. The microbial species can be engineered for advancements in electrogenicity or can be used specifically for waste treatment. Pharmaceutical waste can be reduced by using resistant microbes prior to discharge. By doing this, microbes may be able to generate VAPs or at least be able to reduce the waste.
- *Electrode material aspect*: As discussed • throughout this review, electrode materials are crucial aspects of BES fabrication as they govern the catalysis aspect of the system. They can be used in BPV as photocatalysts and in MFCs electrocatalysts both as and photocatalysts (in photo MFC). The precursor materials should be non-toxic and the synthesis route should be facile. Through material engineering, we will be able to produce low-cost electrode materials, which will be a giant leap

towards commercialization of this technology.

• Biofilm formation aspect: It has been discussed several times that biofilm formation enhances the EET rate of the species. Investigations in hybrid biofilm formation require attention as nanomaterials that induce biofilm formation can also enhance microbial adhesion and EET rate better than naturally induced biofilms. Unlike the attention given to nanomaterial research, only a few researches have been done in material-based hybrid biofilms, and this research area can give promising results regarding increasing the power density of the system.

Credit authorship contribution statement:

Anuj Sharma: Conceptualization, Methodology, Writing - original draft, Investigation, Formal analysis. Aman Grewal - Writing - original draft, Investigation, Formal analysis, Shubham Patial: Writing – review & editing. Suman Singh: Idea conceptualisation, Supervision, Investigation, Writing – review & editing, Discussion. Amit Lochan Sharma: Supervision. Investigation, Writing review & editing, Discussion.

Conflict of Interest:

The authors declare that they have no financial or personal conflicts of interest that could have impacted the article's findings or the authorship contributions.

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- Energy storage and lifetime aspects: Despite poor energy output, a BES works without depending on an external energy source. This ability can be exploited by using energy storage devices, which will not only store energy but also allow a steady flow of output energy from a rather pulsated flow by a typical BES. Extending the life of the system is equally important, as waste reduction is a continuous process which requires long periods of time. Many reported works have demonstrated achieving extended lifetimes by using different materials, but the exact mechanism of the relationship between electrode materials and microbial species has yet to be discovered.
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Application of Statistical Methods in Source Apportionment of Atmospheric Aerosols

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Abstract

Several thousands of articles have been published globally to apportion sources of atmospheric aerosols using various statistical tools and marker elements present in the aerosols in the urban cities of the world in designing mitigation strategies to improve the air quality. In this study, the effectiveness of various statistical methods used in source identifications and quantifications of atmospheric aerosols are discussed. This paper also discussed the importance of source identifications of aerosols chemistry using various receptor models. We have applied IMPROVE (Interagency Monitoring of Protected Visual Environments), PCA (principal component analysis) and PMF (positive matrix factorization) models on chemical species of PM_{2.5} collected at an urban site of Delhi, India, over the period January to December 2021 and explored the better and accurate source analysis of the PM_{2.5}. A comparative analysis of these models was conducted to assess their performance in resolving source contributions. The results highlight the strengths and limitations of each method and offer insights into their applicability for accurate source apportionment in complex urban environments.

Keywords: Aerosols, Source apportionment, IMPROVE, PCA, PMF

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1. Introduction

The quantification of the plausible sources to the atmospheric aerosols /particulate matter (PM) is a critical step toward designing effective mitigation and improving urban air quality, especially in regions with severe pollution burdens like India [1]. Hence, accurate source apportionment enables policymakers, researchers, and urban planners to identify the major contributors to levels and implement PM targeted interventions. To achieve reliable source development identification. the and application of advanced statistical techniques have become increasingly important [2-4]. Source apportionment of aerosols is essential tool for identifications of specific aerosol concentrations to the adverse health effects [5:6]. There are several statistical methods [enrichment] factors (EFs), principal component analysis (PCA), IMPROVE protocol, chemical mass balance (CMB), UNMIX and positive matrix factorization (PMF) etc.] are being used for source apportionment of pollutants around the globe [3;7;8], some of them are obsolete (EFs, PCA, and IMPROVE etc.) and some of them are relevant (UNMIX, CMB and PMF). For instance, EFs-first applied in the 1960soffer a basic understanding of the elemental origin (natural or anthropogenic) based on crustal abundance but fail to account for regional variations in elemental concentrations [9]. It provides the simple crude information that the element is higher than the typical earth's crustal values does not account for local variations in elemental abundance [4]. Similarly, PCA, which operates on the eigenvector method, is recognized as a preliminary screening tool rather than a full receptor model due to its inability to quantify source contributions accurately [4;10]. Hopke and Jaffe (2020) has suggested that these tools (EFs and PCA) may not be used as a receptor model for source apportionment of atmospheric

aerosols because more quantitative data analytical tools had been developed and available [7].

Factor analysis tools like nonnegative constrained alternating least square [8], positive matrix factorization [7] and nonnegative least squares that allow proper weighting of individual data points for optimization process [4]. From last two decades, two major classes of the statistical tools that have been used worldwide as receptor models are: i) chemical mass balance (CMB) and ii) multivariate factor analysis models (PCA-APCS, UNMIX, and PMF) [11]. Even though with the same data sets and same chemical species of atmospheric aerosols (e.g. PM₁, PM_{2.5}, PM₁₀ etc.) these receptor models resolve the different sources with different apportionate due to different statistical algorithms and constraints. Hence, applying these models concurrently to the same dataset allows for a comparative evaluation of their outputs, facilitating a more precise identification of the dominant pollution sources. In the present manuscript we report the application of various tools used the in source apportionment (SA) analysis using PM_{2.5} chemical species collected in Delhi from January 2021-December, 2021. We explore the relative strengths and limitations of these models and provide insight into their performance and applicability in an urban Indian context. Our findings aim to support informed choices in source more apportionment methodology and contribute to the formulation of evidence-based air quality management strategies.

2. Materials and Methods

 $PM_{2.5}$ samples (n = 59) were collected at the experimental site of CSIR-NPL, New Delhi, over the period from January to December 2021, using a fine particle sampler in accordance with standard recommended procedures [12]. Due to the COVID-19

lockdown, sampling was not possible from May 2021 to July 2021, resulting in a data gap during this period of the study. The sampling location situated in Central Delhi (28°38'N, 77°10'E) and represents an urban background and surrounded by heavy roadside traffic [13]. Delhi, home to a population exceeding 33.8 million [14] and is ranked among the most polluted cities globally. PM_{2.5} samples were analyzed for their carbonaceous components (OC and EC), water soluble inorganic ions (WSIIs: Na⁺, Ca²⁺, Mg²⁺, K⁺, NH⁴⁺, Cl⁻, F⁻, NO₃⁻ and SO₄²⁻) and elements (Si, Ti, al, Fe, Zn, Cu, Mn, Pb, As, Br, Cr, Mo and P) using different standard instrumentations and analytical techniques [3;12]. Organic carbon (OC) and elemental (EC) concentrations of PM2.5 samples were determined using an OC/EC carbon analyser (DRI 2001A, Atmoslytic Inc., Calabasas, CA). WSIS were analyzed Metrohm using 930 Compact Ion Chromatography (IC). Concentrations of various elements of PM2.5 were analyzed using Wavelength Dispersive X-Ray Fluorescence (WD-XRF; ZSX Primus, Rigaku, Japan) [12]. Field sample blank filters were analyzed using the same procedure as exposed filters, and their average concentrations were subtracted to determine final sample values. Each sample was analyzed in triplicate to assess analytical repeatability.

The analyzed chemical species (OC, EC, WSIS and elements) are used as input for IMPROVE, PCA and PMF models. The details of model description and outcome procedures are available in our previous publications [12;15]. The **IMPROVE** (Interagency Monitoring of Protected Visual Environments) model is a receptor-based method used to apportion sources of particulate matter $(PM_{2.5})$ through mass reconstruction. It estimates source contributions by analysing concentrations of specific chemical species, categorizing PM

into components like organic matter, elemental carbon, soil dust, sea salt, ammonium sulphate, ammonium nitrate, and trace elements. Each component is calculated using marker species and conversion factors. The reconstructed mass is compared to gravimetric mass to evaluate accuracy, providing a simplified yet effective approach for air quality management [15]. PCA-APCS and PMF 5.0 models were used to identify and apportion sources of PM2.5 across the study period. PCA-APCS was applied using SPSS, where variables were standardized, and only principal components with eigenvalues greater than 1 were considered, following Kaiser's criteria. A KMO value greater than 0.6 confirmed the data's suitability for factor analysis, and Varimax rotation was used. Variables with factor loadings > 0.5 were used to identify sources [12;15].

Annual variations in sources were further examined using the EPA PMF 5.0 model. A seven-factor solution was found suitable for the available data. Model validation showed strong agreement between modelled and measured data ($R^2 > 0.6$), indicating good performance with Qtrue/Qexpected <1.5. Additional uncertainties were accounted for using DISP and bootstrap (BS) analyses. The BS (100 runs) showed no unmapped cases, and DISP analysis indicated zero factor profile swaps, confirming model reliability [12;15].

3. Results and Discussion

The mean statistics of chemical species (OC, EC, WSIS and elements) of PM_{2.5} extracted during January-December 2021 was depicted in Table 1 with standard deviation (\pm SD at σ = 1). The mean concentration PM_{2.5} was 110 \pm 54 µg m⁻³ during the sampling period. Throughout the study period, the highest average concentration of PM_{2.5} was observed during the post-monsoon season (153 \pm 113 µg m⁻³), followed by winter (135 \pm 49 µg m⁻³

³), summer (56 \pm 16 µg m⁻³), and the lowest in the monsoon season (40 \pm 15 µg m⁻³). Similarly, the carbonaceous component i.e., OC and EC were found highest during winter $(21 \pm 10 \ \mu g \ m^{-3} \ and \ 9 \pm 4 \ \mu g \ m^{-3})$ respectively, followed by post-monsoon (20 \pm 16 μg m $^{\text{-3}}$ and 7 \pm 5 μg m $^{\text{-3}}),$ summer (8 \pm $3 \ \mu g \ m^{-3}$ and $3 \pm 2 \ \mu g \ m^{-3}$), then in monsoon $(5 \pm 0.7 \ \mu g \ m^{-3} \ and \ 2 \pm 0.4 \ \mu g \ m^{-3})$. In the present study the total carbonaceous components (TC = OC+EC) were accounted for 18.6% of PM_{2.5}, whereas the total WSIS (NH⁴+, SO4²⁻, NO3⁻, F⁻, Cl⁻, Na⁺, Mg²⁺, K⁺ and Ca^{2+}) was accounted for 36% of PM_{2.5} $(39.7 \ \mu g \ m^{-3})$. The total mass concentrations of elements extracted as 5.26 µg m⁻³ which was accounted for 5% of PM2.5. These chemical species (OC, EC, WSIS and elements) are used as input for the various receptor models (IMPROVE, PCA and PMF) to evaluate their capability.

Table 1. Mean concentration of $PM_{2.5}$ and their chemical species ($\mu g m^{-3}$) in Delhi.

Chemical Species	Concentration (µg m ⁻³)
PM _{2.5}	110 ± 54
Organic carbon (OC)	14.7 ± 11.6
Elemental Carbon (EC)	5.8 ± 4.2
Ammonium (NH4 ⁺)	7.3 ± 6.1
Sulphate (SO ₄ ²⁻)	9.7 ± 5.9
Nitrate (NO ₃ ⁻)	7.2 ± 5.3
Fluoride (F ⁻)	0.5 ± 0.4
Chloride (Cl ⁻)	6.3 ± 3.9
Sodium (Na ⁺)	2.9 ± 1.5
Magnesium (Mg ²⁺⁾	0.3 ± 0.2

Potassium (K ⁺)	2.7 ± 1.8
Calcium (Ca ²⁺)	2.8 ± 1.5
Aluminum (Al)	0.39 ± 0.36
Phosphorous (P)	0.08 ± 0.07
Sulphur (S)	2.01 ± 1.41
Chromium (Cr)	0.31 ± 0.17
Iron (Fe)	0.85 ± 0.61
Zinc (Zn)	0.49 ± 0.42
Copper (Cu)	0.21 ± 0.17
Molybdenum (Mo)	0.21 ± 0.19
Bromine (Br)	0.12 ± 0.11
Lead (Pb)	0.39 ± 0.28
Arsenic (As)	0.11 ± 0.09
Titanium (Ti)	0.09 ± 0.07

3.1. IMPROVE model

In order to obtain the probable empirical sources of $PM_{2.5}$, the chemical species of $PM_{2.5}$ were re-constructed (RCPM_{2.5}) using IMPROVE equation [16;17]. RCPM_{2.5} was computed using Equation 1:

 $RCPM_{2.5} = [AS] + [AN] + [POM] + [LAC] + [SS] + [Soil]$ (1)

Where, AS = ammonium sulphate,

AN = ammonium nitrate,

POM = particulate organic matter,

LAC = light absorbing carbon,

SS = sea salt.

The details of multipliers, procedures and explanation are available in literatures [12;16;18]. The mass difference ($PM_{2.5} - RCPM_{2.5}$) or unidentified mass (UM) of

PM_{2.5} was calculated by subtracting RCPM_{2.5} from measured PM_{2.5}.



Figure 1: Re-construct mass of $PM_{2.5}$ extracted by IMPROVE model

The percentage extracted source of PM_{2.5} by IMPROVE model depicted in Figure 1. The AS (14.4 μ g m⁻³), AN (9.3 μ g m⁻³), POM (23.5 μ g m⁻³), LAC (5.8 μ g m⁻³), SS (16.0 μ g m⁻³), Soil (19.5 μ g m⁻³) and UM (20.3 μ g m⁻³) contributed to PM_{2.5} as 12.2%, 8.5%, 21.4%, 5.3%, 14.5%, 17.7% and 20.4%, respectively. The unidentified mass (UM) of

chemical reactions of SO_2 , which emits from combustion of fossil fuels (coal and diesel) whereas AN is produced through reversible reactions of gas-phase NH₃ and HNO₃, aided by the formation of oxidized nitrogen through combustion of fossil fuels and vehicular emissions [3;20]. The abundance of POM in the atmosphere are mostly coming from primary (combustion) and secondary (secondary organic aerosols formation) processes [21].

3.2. PCA and PMF model

Figure 2 shows the percentage contribution of sources to PM_{2.5} resolved by PCA, and PMF models in Delhi, India during 2021. PCA extracted 6 sources of PM_{2.5} in Delhi, i.e. secondary aerosols (SA), vehicular emissions (VE), biomass burning + fossil fuel combustion (BB+FFC), soil dust (SD), sea salt (SS) and industrial emission. The highest contribution of SD was resolved to be 32% with prominent availability tracer elements Al, Ca, Fe, and Ti whereas lowest as SS (4%).



Figure 2 Source contribution (%) to PM_{2.5} resolved by a) PCA and b) PMF models in Delhi.

PM_{2.5}, estimated by reconstructing the PM_{2.5} mass, accounted for 20.4%. This could be due to the presence of carbonate-rich minerals, calcium sulfate, alumino-silicates, and other similar components in the samples [19;20]. In the urban site of Delhi, the majorly, AS is produced in the ambient air through the

PMF model resolved as 7 sources of PM_{2.5} in Delhi, i.e. SA (23%), VE (17%), BB (14%), SD (24%), FFC (11%), SS (5%) and IE (6%). PMF contributed highest loading of SD (24%) and lowest of SS (4%) to the PM_{2.5} mass concentrations. Jain et al. (2020) also examined the similar source type (common

sources: SA, VE, BB, and SD) at megacity Delhi with different percent contribution to PM_{2.5} using receptor models.

In India, identifying the sources of particulate matter (PM) pollution involves analysing specific elemental signatures. Soil dust is typically traced using elements like Al, Si, Ca, Ti, Fe, along with trace metals such as Pb, Cu, Cr, Ni, Co, and Mn [12; 22; 23; 24]. Biomass burning is a major contributor to air pollution, especially in the post-monsoon season. Water-soluble K is a widely recognized marker for this source [25]. In India, K^+ has proven to be particularly effective in identifying emissions from crop residue and wood burning [20]. The health effects are severe-long-term exposure can lead to respiratory diseases, headaches, dizziness, and in extreme cases, premature death. Fossil fuel combustion, particularly from coal, is another critical source. Elements like As and Cl are commonly released during coal burning and serve as key indicators of this process [26; 27]. Prolonged exposure to these emissions the risk raises of respiratory and cardiovascular diseases and contributes significantly to environmental damage and global warming. In urban areas, vehicular emissions add to the problem. Exhaust releases pollutants like NO_x, CO, SO₂, VOCs, and particulate matter containing metals such as Pb, Zn, and Cu [28; 29]. Beyond exhaust, non-exhaust sources like brake wear, tire degradation, and road dust also release harmful particles. Zn, Pb, and Mo are typically associated with these non-exhaust emissions [26; 30; 31]. Industrial activities, especially in Delhi, contribute further by releasing hazardous metals like V, Cd, and Pb, often from burning refuse oil and improper battery disposal [32]. Other metals such as Zn. Mn. Co. Cu. and Cr have been linked to emissions from metal-based industries [3]. Key particulate pollutants also include black carbon (BC) and organic

carbon (OC). BC absorbs sunlight and contributes to atmospheric warming, while OC scatters light, impacting visibility and climate. These are often accompanied by CO, NO_x, SO₂, and greenhouse gases like CO₂ and CH₄ [33], highlighting the complex mix of pollutants affecting both human health and the environment. SO₄²⁻, NO₃⁻, and NH₄⁺ are key indicators of secondary aerosol formation processes [34], while Na⁺, K⁺, and Mg²⁺ serve as primary tracers for sea salt contributions [23].

Recent global assessments, including the comprehensive review by Hopke et al. (2020), have identified several dominant sources contributing to ambient particulate matter (PM) concentrations in India. These include secondary inorganic sources aerosols, sea salt, vehicular emissions, industrial activities, biomass burning, coal and oil combustion, as well as secondary organic aerosols. Understanding the origin and characteristics of PM, particularly PM_{2.5} and PM_{10} is crucial for atmospheric scientists. public researchers. health policymakers, other stakeholders and involved in air quality management. Source apportionment studies play a vital role in elucidating the contribution of local and regional emission sources to ambient PM levels. These studies help characterize the physical and chemical properties of aerosols, offering valuable insight into source-specific influences on air quality. The information derived from such analyses is instrumental in formulating targeted mitigation strategies aimed at reducing pollutant levels and improving overall air quality, both regionally and globally. Moreover, quantifying sourcespecific PM concentrations is increasingly important in epidemiological research, as it enables the identification of pollutant sources most strongly associated with adverse health outcomes. This targeted approach supports the development of more effective public health interventions and regulatory policies.

We evaluated the performance of different receptor models in identifying and quantifying sources of PM2.5 and found that while all models detected similar source types, the number of sources and their contributions varied at sampling site. Among the models, PMF demonstrated several advantages over PCA. Unlike PCA, which may yield negative values in source profiles and have limited efficiency in source identification, PMF ensures non-negative solutions and provides more meaningful results. Although PMF requires a relatively large dataset, it is robust against data gaps and low concentrations below detection limits by incorporating experimental uncertainties and assigning weights based on measurement confidence. This enhances the reliability of PMF outputs, allowing it to resolve sources more accurately by effectively linking marker species to their respective sources. In contrast, PCA use only concentration data without uncertainty weighting and apply relatively coarse methods for handling outliers and missing data, often leading to the mixing of distinct source signals and less precise source apportionment. Given these strengths, PMF offers more accurate and interpretable estimates of source contributions, as supported by comparisons in our earlier studies [12; 35].

4. Conclusions

In this study, we demonstrated the applications of various simple to complex tools of receptor (IMPROVE, PCA and PMF) models on same chemical species of PM_{2.5} to access source contribution to PM_{2.5}. The IMPROVE model computed the various sources PM_{2.5} with a simple established multiplying factors whereas PCA extracted the sources through dimensionality reduction method. PMF functions on the principle of decomposing a data matrix into two smaller matrices, one representing source profiles other representing source and the

contributions. In the present case, both PCA and PMF revealed comparable source categories, though with varying contribution estimates, while the IMPROVE approach provided fixed source types based on standard classifications. This comparative analysis highlights the utility and limitations of different receptor models in identifying and quantifying PM_{2.5} sources.

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Natural Nanosilica from Agricultural Waste Rice Husk and Its Magnetic Composites for Its Possible Applications in Semiconductor, Catalytic Activity and Biomedical Science

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Abstract

This research demonstrates the sustainable synthesis of crystalline nanosilica (SiO₂) from rice husk, an agricultural waste, via a cost-effective route. The nanosilica was integrated with ferrites and polyvinylidene fluoride (PVDF) to create a magnetic nanocomposite using injection moulding equipment. X-ray diffraction (XRD) confirmed the crystallinity of the SiO₂, while scanning electron microscopy (SEM) revealed nanoscale particle morphology. Fourier-transform infrared spectroscopy (FTIR) identified Si–O–Si functional groups, validating the silica structure. UV–Vis spectroscopy showed strong UV absorption, indicating potential catalytic applications, and low visible light absorption. Tauc plot analysis yielded the direct and indirect band gaps. The indirect band gap was determined to be 1.73 eV, and subsequently direct band gap is 1.88 eV, which is similar to semiconductor electronics materials. Magnetic measurements showed diamagnetic behavior for pure SiO₂ and ferromagnetic properties for the SiO₂–ferrite–PVDF nanocomposite, exhibiting distinct hysteresis loops. These results highlight the successful valorization of rice husk-derived nanosilica from agriculture waste in producing polymer magnets with potential applications in semiconductor electronics, catalytic activity and biomedical science.

Keywords: Nanosilica, Rice Husk, Magnetic Nanocomposite, Magnetic polymer

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1.Introduction

Metal oxides play an essential role in many areas of chemistry, physics. materials science, and related emerging technologies. Oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, gas sensor cells, coatings for the passivation of surfaces towards corrosion, and as catalysts [1]. Oxide nanoparticles can show off special bodily and chemical properties due to their confined size and an excessive density of corner or surface sites. Hence, transition metallic oxides (TMO) are the most widely used in the emerging area of magneto-electronics, catalysts, and photo catalysis, solar cells, and gas sensors [2]. SiO₂ has been a valuable material due to its superb physical and chemical characteristics. It exists in many crystalline forms, the better known being quartz, cristobalite, tridymite. stishovite, and coesite; however, its best acknowledged shape is amorphous silicon dioxide. Silica nanoparticles has been explored for different aspects in accordance its purity, to shape, measurement, and distribution, and widely applied in the mechanical industry and as precise structures for chemical catalysts, ceramics, and photo-electricity elements, Applied fields for the silica etc. powder corpuscular expanding are regularly because of its physicochemical merits. Crystalline SiO₂ has extra sharp points in the interband transition electricity spectrum than amorphous SiO₂, the power of the absorption part for crystalline SiO₂ is about 1eV greater than that for amorphous SiO_2 [3,4]. The silicon dioxide has been synthesized via a number of techniques. There is considerable activity in the synthesis of crystalline and uniform material for the functions in microelectronics, optics, electrical, and several other fields. It has a pattern having high purity to discover achievable functions in many fields, such as managed launch applications, sensor units and

catalysis, and dielectric substances [5]. The sensitized mesoporous silica with acriflavin dye should find purposes in Nano sensors and in Nano lasers [6]. The photocatalytic recreation of oxide materials and polymers can be elevated with the aid of the addition of SiO₂, which will increase the accessible surface area of the catalyst due to its giant band gap [7, 8]. The electromagnetic behavior of the ferrite magnetic material can be considerably tuned using different fillers such as SiO₂. TiO_2 , MoO_3 , etc [9] and due to the reason being these fillers promote the catalytic process for tuning the electromagnetic behavior. In recent years, studies have been carried out for the enhancement of the electromagnetic properties of ferrite magnetic material via using SiO₂ as filler, for example, Ni_{0.65} Zn_{0.35}Cu_{0.1}Fe_{1.9}O₄-SiO₂ 11] $Co_{0.5}Zn_{0.5}Fe_2O_4$ -SiO₂ [10. [12]. Ni_{0.5}Zn_{0.5}Fe₂O₄-SiO₂ [13-20], Co_{0.84}Fe_{2.16} O₄-SiO₂ [21]. The increasing demand for these materials in the areas of chemical, ceramic, chromatographic, coating. catalysis, energy, emulsifier, organic science, etc., needs the most efficient and dependable synthesis method for the production of these nano-composite materials. As per the reports, several synthesis techniques employed for the coaching of nano-composite materials are micro-injection moulding, in-situ polymerization, co-precipitation, sol-gel, and many others [22, 23]. Nanosilica and composite materials have found its widespread applications in various fields such as dental science, agriculture (as nanofertilizers), and targeted drug delivery systems due to their high surface area, biocompatibility, and ability to encapsulate active compounds and presence of Si-O chemical bond [24, 25, 26]. The crystalline nano silica powder is prepared by using the leaching process, which is a chemicalbased technique. After preparation of this Crystalline Nano silica powder, it is used as a filler material for the production of a nanocomposite of nano silica. Thus, the present work aims is synthesize the

crystalline Nano silica and the composite of PVDF/Nano silica/Ni0 8K0 2Fe2O4 successfully and used various characterization techniques to study its morphology, structure, magnetic and properties optical for its possible applications from semiconductor properties to magnetic polymer. Another objective of this research is to prepare functional materials at the nanometric scale from natural sources, from waste rice husk, and measure their physical properties for their applications and progress of research and development activities from electronics to biomedical science.

2. Materials and Methods

2.1 Preparation of crystalline Nano silica: Leaching and co-precipitation were used to make crystalline nano-silica from rice husk ash (RHA). Rice husk was obtained from a rice mill located Purnea distrct of Bihar, India and thoroughly washed with deionized water to remove the polluted materials (Merck, India). Rice that has been rinsed of its husk was dried in the sun for 12 hours before being carefully pulverized with a grinder machine for grinding. The crushed rice husk was first burned at 600°C for 2 hours

before being cooled. In a Muffle furnace, at 1000°C for 2 hours. RHA was obtained and treated with 6 NH₄Cl (Merc, India) for 1 hour, 2 hours, 3 hours, 4 hours, and 24 hours, and during the leaching process, the mixture was agitated for 2 hours in a magnetic stirrer. The leached RHA was then filtered using Whatman Grade 1 filter paper and deionized water. The filtration procedure was continued until the pH of RHA reached 7. The neutralized RHA was incubated in 2.5 N NaOH solutions for 2 hours at 80°C with a magnetic stirrer. The aforementioned solution was then neutralized again with warm deionized water, yielding sodium silicate. The details of the relevant reaction are as follows:

$$\begin{split} &SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \\ &Na_2SiO_3 + 2HCl \rightarrow SiO_2 + 2NaCl + H_2O \end{split}$$

The sodium silicate was then treated with concentrated HCl until the pH reached 2, resulting in the precipitation of amorphous Nano silica. The extracted Nano silica was then annealed in a muffle furnace for 1 hour at 1000 degrees Celsius. In the end, crystalline Nano silica was produced. The schematic diagram for preparation is shown in Figure 1.



Figure 1: Flow chart of synthesis process of production of Nano silica from rice husk.

2.2 Preparation of Magnetic composite materials with Nano silica: Figure 2 represents the flowchart of preparation of Nano silica magnetic composite materials using a micro twin screw extruder and micro-injection moulding equipment (make- Thermo Fisher, Germany). The Nano silica composites were made in several processes, beginning with weighing the components using a micro balancing system (Mettler Toledo. Switzerland) to determine their weight percentage ratio. After that, combined PVDF/Nano samples such as silica/Ni_{0.8}K_{0.2}Fe₂O₄ were well blended with the application of a kneader. The samples were then appropriately mixed and weighed. In polymer composites, the matrix and reinforcing materials are loaded in 90:10 ratios. Then, using a microinjection molding machine, Nano silica composite materials were created, as

illustrated in Figure 2. Maintain the kneader's rotor speed at 40-60 rpm while maintaining the temperature of the entire extruder unit at 300°C to 350°C for 20 minutes. The blended sample feed was then fed into a micro-injection plunger system with a pneumatic pressure of 60 bar once the necessary blending procedure was completed. Finally, a plunger was used to inject the extruded sample into a die, resulting in solid composite materials with the correct shape and size.



Figure 2: Flowchart for the process of production of Nano silica Composite.

3. Results and Discussion

3.1 X-Ray Diffraction of Nanosilica: It is reported that when the annealing temperature exceeds the temperature of 700°C, then the crystalline structure of Nano silica is obtained [27-28]. Generally, silica as amorphous structure available in rice husk. In this present research, we have used 1000°C to prepare the crystalline structure. Such results were also reported by some research groups [29-30]. The XRD spectra of the prepared Nano silica are shown in Figure 3.1 (a), and analysis was performed by a Bruker X-ray diffractometer with copper Ka radiation of wavelength 1.5405 Å. The plot was investigated in the range of angles 10°-90° with a scanning rate of 0.02°/minute. The peaks obtained in XRD analysis are which show that the nanomaterial prepared by

RHA is crystalline and the crystal obtained is tetragonal. The prominent peak is observed at about 22 degrees, which confirms the formation of Nano silica material [COD 98015-3866]. The XRD plot is shown in Figure 3.1(a), having characteristics hkl value also indexed in the figure, which agrees with earlier reported work. [31-32].



Figure 3.1(a): XRD spectrum of crystalline nano silica annealed at 1000°C



Figure 3.1 (b): W-H plot of Nano silica.

Further particle size was evaluated using Scherer's formula [33], which is discussed below:

$D = 0.94\lambda/\beta \cos\theta$

Where D- average crystalline size of the particle, λ - wavelength of X-ray, $\beta 1/2$ - full width at half maximum, θ -Bragg's diffraction angle. The crystallite size was found to be 60.31 nm. Further, for more precise measurement, Williamson-Hall (Fig 3.1(b)) plot was used to evaluate crystallite size and strain. The result value found to agree with structural analysis, i.e, 62.11 nm and corresponding strain

2.84x10^{-3,} shown in Figure 3.1 (b). The present XRD measurement shows that the crystalline form of Nano Silica material from agricultural waste rice husk can be obtained at 1000°C using a low-cost chemical method.

3.2 Surface analysis measurement using Scanning Electron Microscope (SEM): SEM images are shown in Figure 3.2 (a), where rice husk nanoparticles are agglomerated of Nano-crystallinity and showing porosity. Thus. prepared nanomaterials can be a possible aspirant in electronics devices as these properties might be as a result of porosity and defects created due to vacancies created in the material [34-35]. Further, for a more precise measure histogram plot as shown in Figure 3.2(b) was analyzed, and the particle size was calculated and it was found to be 0.048 µm. Such porous structure functional materials from waste agricultural rice husk may be another novelty of this research.



Figure 3.2 (a-b): SEM image and histogram plot of Nano silica nanomaterial obtained from waste rice husk.

3.3 Fourier Transform Infra-Red Spectrometer (FTIR): The FTIR spectrum of the prepared samples is shown in Figure 3.3. FTIR results show that the absorption peak at 3400- 3500 cm⁻¹ confirms the presence of silanol–OH bond and H_2O . The other absorption occurring at 1095 cm-1 is due to the presence of i.e., Si-O-Si bond. The presence of Si-OH and other silane bond stretching vibrations. The peaks between 600-800 cm⁻¹ are attributed to the stretching vibrations of C-H and C-Cl bonds. The FTIR graph confirms the presence of silica and is similar to the FTIR of Nano silica obtained in different works [36-37]. Thus, this measurement also agrees with the structural confirmation of the formation of Nano silica material. The presence of such functional groups in the material is responsible for various functional properties in industries.



Figure 3.3: FTIR Spectra of Nano silica prepared at 1000°C for 2 hrs

3.4 Optical measurement and band gap calculation: For measuring the UV-Visible absorption spectra of crystalline Nano silica powder at normal incoming light in the wavelength ranges of 200-800 nm, a UV-Visible-NIR (Perkin Elmer spectrometer, UK) was used. The absorption spectra of the produced Nano SiO_2 sample are shown in Figure 3.4. The synthesized SiO₂ sample's absorption spectra display a larger absorption peak in the UV region, indicating that it can be used to boost catalytic activity. The visible area of the UV-Visible spectrum has low absorption, whereas the UV section has higher absorbance. The significant peak of the crystalline Nano silica sample is 350 nm, which is similar to a previous result by Ruchi Nandanwar et al [38]. The Tauc plots, shown in Figure 3.4(b-c), were also utilized to estimate the band gap of the nano-structured silica, synthesized using cost cost-effective leaching method. The indirect band gap was determined to be 1.73 eV, and subsequently direct band gap is 1.88 eV, which is lower compared to other semiconductor electronics materials prepared chemically by other research

groups [39]. The difference is that prepared materials are obtained by using low-cost waste agriculture rice husk. The resulting band gap value is lower than that reported by Ruchi Nandanwar et al [40], which may be attributed to the 1000 °C high annealing temperature.



Figure 3.4 (a): UV-Visible spectra of crystalline Nano silica

3.5. XRD of Ferrite and Nanocomposite: The XRD pattern of Ni_{0.8}K_{0.2}Fe₂O₄, having been annealed at the low temperature of 500°C for 3 hours, is shown in Figure 3.5 a. It has the entire characteristic peak reported by other research groups as well [41] and a crystallite size of 27.3 nm. Further, in the above section, the XRD pattern of crystalline Nano silica. In this section, we have shown the XRD pattern of the nanocomposite in Figure 3.5 (b). The pattern clearly shows the α and β -phases of PVDF nanoparticles at 18.5°, 19.8°, and 26.7°, having corresponding hkl values





Figure 3.4 (b-c) Direct and indirect band gap of crystalline Nano silica

indexed in the plot. Further, other research groups also found that as the concentration of polymer is more it suppresses the other pattern. But it is clearly shown that the presence of SiO₂ and Ferrite nanoparticles is indexed in the XRD pattern. Further Williamson-Hall plots (shown in Figure 3.5 (c)) were done to investigate the crystallite size and lattice strain produced in the nanocomposite, and it was found to be 34.57 nm and 3.24×10^{-3} . The formation of Nano Silica composite decreases the crystalline size and strain as compared to pure Nano Silica.



Figure 3.5 (a): XRD pattern of Ni_{0.8}K_{0.2}Fe₂O₄ nanoparticles.

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Figure 3.5 (b): XRD pattern of nanocomposite.



Figure 3.5 (c): Williamson Hall plot of the PVD/SiO₂/Ni_{0.8}K_{0.2}Fe₂O₄ nanocomposite.

3.6 Magnetic Measurement using Vibrating Sample Magnetometer (VSM) The magnetic measurement was analyzed using Lakeshore 7400 in the applied field range of -10 KOe, +10 KOe, and the resultant graph is shown in Figure 3.6 (ab). Nano silica is diamagnetic, as reported [42]. It is interesting to note that with the formation of **PVDF** silica and $Ni_{0.8}K_{0.2}Fe_2O_4$, it was noticed that the composite material shows ferrimagnetic properties, having a very low saturation magnetization of 0.0089 emu/gm and a coercivity value of 97 Oe. This magnetic parameter value is very less in comparison to its parent material, whose saturation magnetization and coercivity values are in the range of 18.95 emu/gm and 121 Oe. This sort of change might be a result of the suppression of the ferrite peak, as its concentration was low in comparison to other materials. So, this material can be used in flexible magnetic materials in semiconductor Electronics or in magnetic

polymer [43-45]. Recently functional properties silica from rice husk have been used in drug delivery [46].



Figure 3.6 (a-b): Magnetic measurement of Ni_{0.8}K_{0.2}FeO₄ and PVDF/SiO₂ composite

4. Conclusions

In the current work, an economical and environmentally beneficial technology have been used to prepare crystalline nanosilica from rice husks, an agricultural waste. The tiny crystallite size is revealed by the XRD investigation. FTIR confirmed the presence bond nature of Si-O-Si, which is very important functional for its multifunctional properties. UV-visible have been used to investigate the optical properties of crystalline nanosilica, and the results show that it has outstanding optical properties in the visible range. It was discovered that the optical energy band gap was 1.78 eV, which is marginally

lower than its bulk value and shows in UV-Vis semiconductor properties. spectroscopy showed strong UV absorption, indicating potential catalytic applications, and low visible light absorption. The formation of this nanocomposite using micro injection molding equipment was substantiated through XRD analysis, which displayed characteristic peaks of the composite constituents. indicating successful Magnetic characterization integration. revealed that the nanocomposite exhibited ferrimagnetic behavior, as evidenced by the presence of magnetic hysteresis loops. Magnetic property suggests that the nanosilica/ferrite/PVDF composites have potential applications as polymer magnets, offering a novel approach to developing magnetic materials from agricultural waste derivatives. This study demonstrates a sustainable pathway for synthesizing crystalline nanosilica from waste rice husk and its subsequent utilization in fabricating magnetic polymer nanocomposites, highlighting the potential of agricultural waste in advanced material applications.

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Enhanced Dielectric Constant of Succinic Acid doped Polyvinyl Alcohol (PVA) Thin Film

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Abstract

The present paper reports the dielectric behaviour of high molecular weight water soluble polyvinyl alcohol (PVA) system doped with a dicarboxylic acid (succinic acid). Doped PVA samples were synthesized in the laboratory using solution casting method by keeping an optimum concentration of succinic acid (30 wt%) in PVA solution. These samples were characterised for their structural behaviour using FT-IR and XRD while frequency and temperature dependent dielectric properties were measured using Agilent LCR meter. It was observed that dielectric permittivity (ϵ') of 30wt% acid doped PVA significantly increased compared to undoped PVA. This was attributed to the increase in the amorphous regions with acid doping that facilitated the orientations of dipoles. At all frequencies, room temperature dielectric properties (ϵ' and ϵ'') of both undoped and doped samples showed a frequency dispersive behaviour. FT-IR and XRD analyses confirmed the increase in amorphous regions in doped samples compared to undoped semi-crystalline PVA.

Key words: PVA, dielectric behaviour, capacitance, succinic acid

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1. Introduction

By virtue of being a versatile water-soluble polar polymer, polyvinyl alcohol (PVA) PVA based composites/ and nanocomposites have been rigorously explored for their potential applications in industrial various sectors including electronics and microelectronics packaging [1]. Numerous research works are being carried out on this polymer system since it is not only easy to process but it is cost effective and its mass production is equally promising [2]. Scores of research papers are available in the literature wherein their potential in memory devices, waveguides and in holographic recording using ion doped PVA, have been investigated [3]. Doped PVA is reported to have better mechanical, optical and electrical properties compared to undoped PVA [4-12]. Acid doped PVA electrolytes have been explored for use in electrochemical devices [13]. Being an insulator with very low conductivity ($\sim 10^{-12}$ S/cm), it has been identified as а passive layer in microelectronic packaging industry [12]. At the same time, its electrical conductivity can be improved by thermally generating charge carriers or by addition of suitable dopants or conductive fillers resulting which they can be used as electrical probes [3]. Other than these areas of potential applications, PVA has been investigated for applications as capacitors/supercapacitors and charge-storage/energy storage devices since their dielectric properties and capacitance can be increased by selective doping [2]. Temperature, frequency and field dependence of \in' determine the dielectric relaxation behaviour [14]. PVA/PVA composites are flexible and their dielectric properties can be significantly modified which render them potentially viable as capacitors [15,16]. For instance, PVA/ cashew gum/ magnetite composites, [17] succinic acid doped PVA [18], Ag nanoparticles filled PVA [19] and TiCl₂ filled PVA have showed enhanced dielectric properties compared to pure

PVA. It was attributed to the fact that addition of a suitable dopant causes (i) reduction in the impedance due to increased amorphous regions in the composites and (ii) slower relaxation time (τ) because charges (ions) can move freely in the polymeric matrix. The dopant effect of melanin on the dielectric behaviour of PVA polymer was confirmed indirectly by the conductivity measurement [21]. It has been reported that melanin doped PVA showed higher conductivity than undoped sample primarily due to a rise in the number of charge carriers that moved freely through the polymer. As an indirect inference, it was claimed that the increase in electrical conductivity was responsible for reduced values of dielectric constant in doped PVA. Similar results have been reported for succinic acid doped PVA which showed higher dc conductivity than undoped PVA It has also been reported that [18]. ferroelectric BZT powder filled PVA showed better dielectric behaviour than unfilled PVA [22]. As is evident from the exhaustive literature survey, only a few papers have addressed the structuredielectric property correlation. Hence, in the present investigation, PVA system doped with succinic acid, which is an organic dicarboxylic acid, was prepared by solution casting method and characterised for their dielectric and structural behaviour and a correlation between them has been established. The main objective of this study was to enhance the dielectric properties and structural integrity of PVA for use (i) as a dielectric layer in devices or (ii) as an energy storage device.

2. Experimental Procedure

2.1. Materials and method: Pure PVA (Mw =1,25,000 g/mol) and succinic acid $[C_4H_6O_4]$ were procured from CDH, (India) and Qualigen (India) respectively. In step I, PVA solution (8% w/v) was prepared by dissolving it in distilled water. In step II, various percentages of succinic acid (10, 20 30, 40 and 50 wt%) with respect to weight of PVA was mixed in the solution prepared

in step 1. The resultant mixture was stirred continuously for 4 hrs at 80 deg C in a water bath to get a homogenous mixture. The stirred solution is cast onto a flat glass sheet and dried at room temperature. The films were stripped off from the glass sheet. The as-obtained crosslinked films were then kept in oven at 85°C for 20 hours for further crosslinking. Details of synthesis are available elsewhere [23]. Specimens of size (5mmx 5mm) were cut from these films for dielectric measurements.

3.0 Results and discussion

3.1 FT-IR analysis: Fourier transform infrared spectroscopy analysis was performed on the samples in the wavenumber range $400-4000 \text{ cm}^{-1}$. FTIR spectrographs of undoped and acid doped PVA are shown in Fig 1a.



Figure 1a: FT-IR spectra of Succinic Acid doped PVA samples

Assignments	Peaks (cm ⁻¹)	
	Undoped	SA Doped
		PVA
O-H stretching	<u>3551-3114</u>	<u>3561-2892</u>
	\underline{cm}^{-1}	<u>cm⁻¹</u>
C-H bond	<u>2947 cm⁻¹</u>	<u>2980-2724</u>
stretching of		<u>cm⁻¹</u>
CH ₂		
C-H bending of	<u>1453 cm⁻¹</u>	<u>1461-1455</u>
CH ₂		<u>cm⁻¹</u>
C-C stretching	<u>948 cm⁻¹</u>	<u>942-929 cm⁻¹</u>

 Table 1: FT-IR peaks and their assignments for undoped and SA doped PVA

The peaks and their assignments for pure PVA and acid doped PVA are shown in

Table 1. The peaks for SA doped PVA are slightly shifted.

3.2 XRD analysis

The X-ray diffractograms of pure PVA and 30wt% SA doped PVA (size 10 mm x 10 mm) are shown in Fig.1b.



Figure 1b: XRD diifractograms of succinic acid, pure PVA and 30wt% SA doped PVA

The peak observed at $2\theta = 20^{\circ}$ in XRD pattern of pure PVA is indicative of its semi crystalline nature [24]. The intensity of the same peak reduced with SA doping primarily due to decrease in crystallinity and subsequent increase of amorphous regions in PVA [25-26]. All the sharp peaks shown in the XRD pattern of SA were missing in the XRD pattern of SA doped PVA which confirms that SA was completely dissolved.

3.3 Dielectric studies

Temperature and frequency dependent values of parallel capacitance (Cp) and loss tangent or dissipation factor (tan δ or D) of the samples were measured using Agilent 423B precision LCR meter at a frequency of 100 Hz, 120Hz, 1 kHz, 10kHz, 20kHz and 100 kHz from room temperature to 65°C. Test samples were electroded on both sides using conductive silver paste. The thickness of the samples was measured using a micrometer. Electroded samples

were placed in a sample cell between two electrodes and voltage was applied. The sample cell was kept in a furnace which maintained a constant heating rate of 1°C per minute The parallel capacitance (Cp) and Dissipation factor (D or tan δ) were measured on the LCR meter and recorded through an online data acquisition system. The ratio between capacitances (Cp versus Co) gave a measure of the relative dielectric permittivity

$$\epsilon' = Cp/C_0 \qquad \dots(1)$$

$$C_0 = \epsilon_0 A/d \qquad \dots(2)$$

is the capacitance with vacuum between parallel plates and $\epsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum, A is the area of electrode, and d is the thickness of the sample. The thickness of the film was 0.26 x 10^{-3} m. Temperature and frequency dependent dielectric constant, dielectric loss and loss tangent (tan δ) of undoped PVA sample measured at various frequencies (100 Hz to 100 kHz) and temperature range (RT to 65°C) are shown in Fig 2 (a-d). Dopant concentration of 30 wt% SA is chosen since this concentration show optimum properties [23].



Figure 2: (a) Dielectric constant and (b) dielectric loss of undoped PVA as a function of frequency and temperature

The value of dielectric loss (ϵ ") was quite low (<1) at all frequencies and temperature which indicates low dissipation of energy. As is evident from all these figures, both dielectric constant and dielectric loss decrease with increase in frequency at all temperatures. This is attributed to the fact that at low frequency dipoles have sufficient time to orient themselves in the direction of the applied electric field. However, as the frequency increases dipoles do not get sufficient time to orient leading to less contribution of charge carriers to dielectric constant. In other words, high and low values of dielectric constant at low and high frequency respectively is a direct consequence of charge accumulation at the electrodedielectric interface (due to polarization) and their diffusion in the direction of the applied electric field. [11,27,28].



Figure 2c: Temperature and frequency dependent Dielectric constant of 30wt% SA doped PVA sample

The same concept has been explained mathematically for a free dipole oscillating in an ac field. The complex dielectric constant consists of a real and imaginary parts and is expressed as Eq. (3).

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_{\infty} + \frac{\varepsilon_5 - \varepsilon_{\infty}}{1 + (i\omega\tau)^{1-\alpha}},\tag{3}$$

where, ε_s and ε_{∞} are the low and high frequency values of ε' . At low frequency, dipoles orient themselves with the applied field and $\varepsilon' \cong \varepsilon_s$. When the frequency increases ($\omega < 1/\tau$, where τ is relaxation time), there is a lag between dipole orientation and the applied field and ε' starts decreasing. Finally, when $\omega = 1/\tau$, or at high frequency, the dielectric constant falls since dipoles cannot orient themselves according to the applied field and $\varepsilon' \cong \varepsilon_{\infty}$.

3.3.1 Structure-Dielectric property correlation

Figure 2 (c-d) shows the dielectric behaviour of 30wt% SA doped PVA. The

influence of the acid dopant on PVA is complex. The dopant affects the dielectric properties firstly due to change in the semicrystalline nature of PVA and secondly due to increased cross-linking of PVA. The increase in the dielectric constant with an increase in the dopant concentration is primarily attributed to increase in charges (protons) and their polarization. The mobility or diffusion of these charges within the polymer matrix is supported by the motion of polymer chain segments. These polymer chain segment could move easily in amorphous regions compared to crystalline regions. SA doping not only provides more charges but also increases the amorphous regions (Fig 1b). The increase in the dielectric constant of doped PVA is thus attributed to reduced crystallinity and a more flexible polymeric backbone. At higher concentrations (>30 wt%), the dielectric constant would decrease because of higher charge accumulation that reduces overall polarization of charges. It has been reported



Figure 2d: Temperature and frequency dependent Dielectric loss of 30wt% SA doped PVA sample

that the amorphous nature results in greater ionic diffusivity with high ionic conductivity, which can be obtained in Figure 2 (e) shows the comparison of dielectric constant of undoped PVA and 30wt% succinic acid doped PVA. As



Figure 2e: Comparison of room temperature dielectric constant of undoped PVA and 30wt% SA doped PVA

shown in Fig. 2(e), the dielectric constant increases with increasing temperature. The increase in dielectric constant of doped PVA may be attributed to the segmental motion of polymer chains which becomes faster with rise in temperature that eventually aids the polarization of charges.

4. Conclusions

The dielectric behaviour of succinic acid doped PVA is significantly improved compared to undoped PVA due to additional charges supplied by the dopant and their polarization through increased amorphous regions. It is found that at room temperature as well as at elevated temperature (upto 65°C) the maximum dielectric constant is obtained for PVA doped with 30 wt% Succinic acid.

Conflict of Interest

Authors declare No conflict of interest

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