



RECENT PROGRESS IN NITROGEN FIXATION

R Rajalakshmi*, S Nadaradjan, K Manoj kumar, D Deerajkumar, D Prethikaa, S Priyanga and R Savitha

*Pandit Jawaharlal Nehru college of Agriculture and Research Institute, Karaikal,
UT of Puducherry.*

*Corresponding Author Mail ID: rajilakshmiramesh2810@gmail.com

INTRODUCTION

Recent advances in nitrogen fixation technologies are transforming the face of sustainable ammonia synthesis, beyond the traditional energy-intensive Haber-Bosch process. Among these technologies, electrocatalytic nitrogen reduction has drawn much attention due to its potential to reduce atmospheric nitrogen to ammonia at ambient conditions using renewable electricity. Efforts are focused on designing new catalysts—from boron- and graphene-based materials to transition metal complexes—to efficiently activate the strong $\text{N}\equiv\text{N}$ bond without the undesired hydrogen evolution. At the same time, photocatalytic nitrogen fixation harnesses sunlight to fuel the nitrogen reduction reaction with semiconductor catalysts, aiming for a green, solar-based pathway that mimics nature's photosynthesis. Biologically, gene-edited microbes are also great hope, where gene editing tools enhance or introduce nitrogen-fixing activity in bacteria, expanding their functionality and host range to facilitate biological nitrogen fixation in important crops. A fascinating biological discovery is the nitroplast, an ancient nitrogen-fixing organelle of cyanobacterial endosymbiont origin found in some algae, which demonstrates a novel nitrogen fixation integration in eukaryotic cells. In addition, the innovative bubble burst ammonia synthesis method employs dynamic microenvironments generated by bursting gas bubbles to facilitate

nitrogen activation and optimize catalytic efficiency. Finally, transition metal dinitrogen complexes continue to be a valuable source of information regarding nitrogen activation at the molecular level and a model system for the design of new catalytic systems. Together, these technologies are a multidisciplinary approach to effective, sustainable nitrogen fixation, required to satisfy global agricultural demands with minimal environmental footprint.

DEVELOPMENTS IN NITROGEN FIXATION:

Recent research on nitrogen fixation has added a number of new procedures to the process, which increase efficiency and sustainability. These are:

1. Electrocatalytic nitro reduction, with emphasis on:
 - I. Graphene-based electrocatalysts
 - II. Boron nitride electrocatalysts
2. Genetically modified microbes to enhance biological nitrogen fixation
3. Catalyst-based photocatalytic nitrogen fixation excited by light for atmospheric nitrogen conversion
4. Transition metal dinitrogen complexes as models and catalysts for the activation of nitrogen
5. The nitroplast, an organelle specialized in nitrogen fixation occurring in some algae
6. Catalyst-free "bubble-burst" ammonia synthesis that takes advantage of the physical

dynamics of bursting gas bubbles to enhance ammonia formation

Together, they form a multidisciplinary thrust towards more efficient and more sustainable nitrogen fixation technology.

1. ELECTROCATALYTIC NITROGEN REDUCTION

Electrocatalytic nitrogen reduction (NRR) is gradually coming into prominence as a green substitute for the Haber–Bosch process, which facilitates ammonia synthesis under mild conditions through the usage of electrical energy. NRR, however, is promising but confronted with highly daunting challenges such as high energy needed to break the stable $\text{N}\equiv\text{N}$ triple bond and the interference of the hydrogen evolution reaction (HER), which is likely to reduce ammonia yield and selectivity in electrochemical reactions. Furthermore, the poor aqueous solubility of nitrogen gas limits its availability on the catalyst sites, further hindering efficient conversion. To overcome such drawbacks, various innovative catalysts have been synthesized. Non-metal catalysts like boron-based nanomaterials, i.e., boron carbide-modified carbon nanotubes (B_4C -CNT), have exhibited excellent Faradaic efficiencies up to 78%. Boron nanosheets and carbon-doped boron nitride have also exhibited improved nitrogen activation. Metal-based catalysts like bismuth molybdate (Bi_2MoO_6) and palladium supported on manganese dioxide ($\text{Pd}/\gamma\text{-MnO}_2$) exhibit medium efficiencies owing to synergistic surface interactions.

New materials like MXene derivatives and heterostructures like Mo_2C - Mo_2N and cobalt-molybdenum in carbon nanofibers are studied for their dense surfaces of defects and electronic properties that can be adjusted to facilitate adsorption of nitrogen. Physical electrode structure also influences activity; amorphous catalysts like gold-cerium oxide composite offer

multiple active sites, and hierarchical nanofibers offer higher surface area and stability.

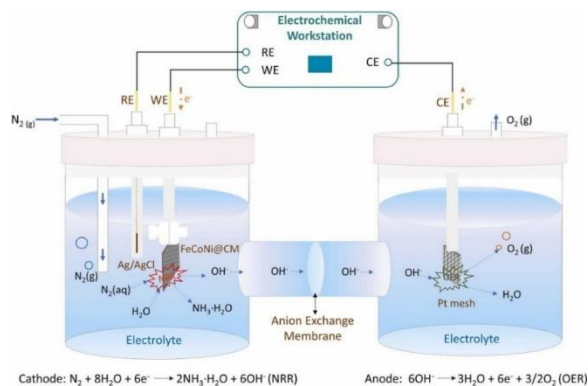


Fig.1. Electrocatalytic nitrogen reduction process

Cu_2O - CeO_2 -carbon and Ag-Cu nanosheets hybrid composites have achieved impressive Faradaic efficiencies, even up to 77%, with notable ammonia yields under neutral pH. System-level advancements include electrolyte engineering using water-in-salt solutions, ionic liquids, and non-aqueous solvents to suppress HER and increase nitrogen availability. Lithium-mediated approaches have been at top levels, offering nearly full Faradaic efficiencies and excellent ammonia yields, particularly upon optimization with oxygen or additives, to the order of tens to hundreds of grams of ammonia per square meter per hour.

1.1. GRAPHENE BASED ELECTROCATALYSTS

Graphene materials have generated significant attention to nitrogen reduction reactions due to their superior electrical conductivity, high surface area, mechanical strength, and ability to be surface-functionalized. Although pristine graphene is chemically inert, its catalytic activity is greatly enhanced by functionalization techniques such as doping with heteroatoms of boron, nitrogen, or transition metals.

Nitrogen doping introduces defect sites and lone-pair electrons that present active sites

for nitrogen molecule adsorption and activation. Nitrogen-doped graphene, especially when combined with suitable substrates or composite materials, has been demonstrated experimentally to deliver moderate ammonia production rates and Faradaic efficiencies. Furthermore, graphene hosting transition metal nanoparticles such as iron, molybdenum, or cobalt has a synergistic benefit: metal sites enable to break the stable $\text{N}\equiv\text{N}$ bonds, and the graphene network enables efficient electron transport as well as suppresses catalyst agglomeration.

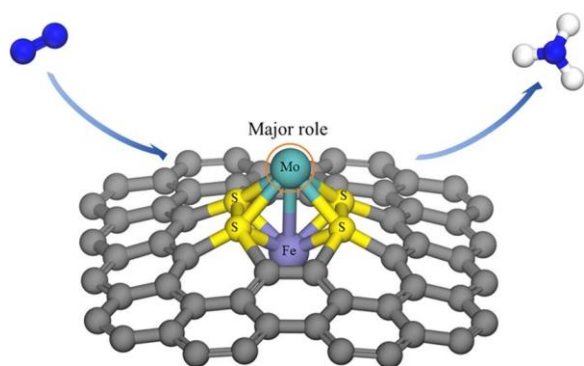


Fig.2. Fe, Mo-co- doped graphene

In addition, vacancy-rich graphene with vacancy-engineered positions and edges provides high-density nitrogen adsorption sites that help in lowering the activation energy barrier. Notably, single-atom catalysts supported on graphene matrices, for example, $\text{Fe-N}_4\text{-C}$ complexes, provide promising results by replicating the active site environment in native nitrogenase enzymes.

1.2. BORON NITRIDE-BASED ELECTROCATALYSTS

Boron nitride (BN)-derived electrocatalysts have also been found to be suitable candidates for nitrogen fixation on account of their improved structural stability, wide bandgap, and tunable electronic properties. Hexagonal boron nitride (h-BN), which has a layer-structured morphology analogous to that of graphene and consists of alternating boron

and nitrogen atoms, offers polar sites that are highly conducive to the adsorption and activation of nitrogen molecules.

While pure BN is typically chemically inert, researchers have attempted to enhance its catalytic activity in a number of ways, such as doping, defect creation, and heterostructure formation. Doping of BN with carbon, for instance, improves electrical conductivity and induces desirable charge redistribution, resulting in increased nitrogen adsorption and relatively moderate ammonia synthesis—around $36.7 \mu\text{g NH}_3$ per mg of catalyst per hour at -0.55 V vs. RHE.

Besides, vacancy formation through extrusion of boron or nitrogen atoms results in localized unpaired electrons as efficient binding sites for nitrogen, reducing the activation energy for cleavage of $\text{N}\equiv\text{N}$ bonds and improving ammonia selectivity by inhibiting the side reaction of hydrogen evolution. Besides, incorporation of single metal atoms into the BN matrix has been tried to mimic enzyme-like activity for nitrogen reduction, paving the way for highly selective and efficient electrocatalyst design.

2. GENE EDITED MICROBES

Gene-manipulated microbes provide a potential solution in biological nitrogen fixation, with the goal of reducing the application of synthetic fertilizers through genetic modification of microorganisms to more efficiently convert atmospheric nitrogen (N_2) into usable forms such as ammonia (NH_3). This is done by directing the genetic modification of nitrogen-fixing bacteria—e.g., *Azotobacter*, *Rhizobium*, and *Klebsiella*—to boost their nitrogenase enzyme activity, improve their compatibility with a number of plant hosts, or make them work efficiently in non-leguminous crops.

The recent development of CRISPR-Cas9 genome editing has made it possible to edit the microbial DNA with high precision, and it is now possible for scientists to introduce or engineer the key nitrogen fixation genes, especially the *nif* gene cluster encoding the nitrogenase complex. For example, synthetic biology has made it possible to transfer and express the *nif* genes successfully in organisms like *Escherichia coli*, creating tailored free-living nitrogen-fixing strains. Furthermore, gene editing tools are used to silence the regulatory networks that suppress nitrogenase activity under oxygen-rich or nitrogen-rich conditions in order to achieve maximum fixation efficiency.

Some engineered microorganisms are designed to reside inside the plant roots as endophytes, establishing symbiotic associations with the principal cereal crops such as maize, wheat, and rice, with associative nitrogen fixation without the development of root nodules. This new approach has the potential to make a significant contribution towards the reduction of chemical nitrogen fertilizer dependence in global agriculture.

3. PHOTOCATALYTIC NITROGEN FIXATION

Photocatalytic nitrogen fixation is a green technology that promises to use light energy—preferably sunlight—to fix atmospheric nitrogen (N_2) to ammonia (NH_3) at ambient pressure and temperature. It mimics natural photosynthesis and is a greener alternative to the conventionally energy-intensive Haber–Bosch process. The efficiency of this process hinges upon the synthesis of effective photocatalysts that can absorb light, generate electron-hole pairs, and transfer the excited electrons to the adsorbed nitrogen molecules on their surfaces so that the stable $N\equiv N$ bond can be cleaved and reduced to ammonia.

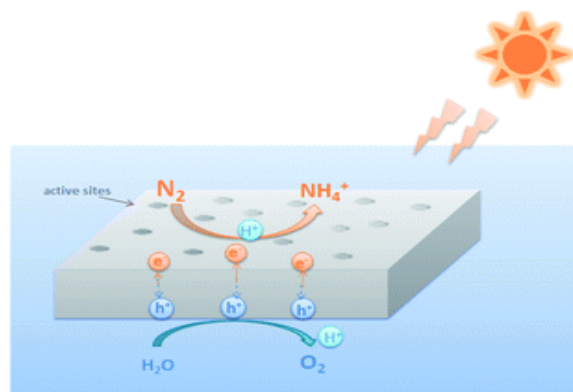


Fig.3. Photocatalytic nitrogen fixation

Various photocatalytic compounds have been explored, such as metal oxides TiO_2 and $BiVO_4$, sulfides CdS and MoS_2 , carbonaceous semiconductors such as graphitic carbon nitride ($g-C_3N_4$), and complex heterostructures and single-atom catalysts. The photocatalytic activity is typically enhanced by means such as bandgap engineering, doping with transition metal or non-metal atoms, introduction of defects, and Z-scheme or type-II heterojunction construction to increase charge separation and extend the charge carrier lifetime.

For instance, oxygen vacancy and metal dopants create active sites for N adsorption and activation. Under usual conditions, the reaction occurs in mild conditions in aqueous solutions to yield ammonia with oxygen as a byproduct. Experimental photocatalytic systems have been reported to produce ammonia at rates of the order of micromoles per gram per hour, but Faradaic and quantum efficiencies are low, precluding practical applications hitherto.

4. TRANSITION METAL DINITROGEN COMPLEXES

Transition metal dinitrogen complexes are at the heart of the nitrogen fixation concept, since they resemble how atmospheric nitrogen (N_2) is trapped and activated in nature catalysts and industrial catalysts. Transition metal complexes are, in general, assemblies of nitrogen

molecules coordinated around transition metal centers, typically early transition metals such as molybdenum (Mo), iron (Fe), tungsten (W), or vanadium (V).

The metal transfers electron density into the nitrogen molecule π^* antibonding orbitals, destabilizing the strong $N\equiv N$ triple bond and making it reducible. The nitrogen ligand may coordinate in a wide range of modes, e.g., end-on (η^1-N_2), side-on (η^2-N_2), or as a bridging ligand between two metal centers. One of the most significant biological model systems is the FeMo-cofactor in nitrogenase enzymes, where nitrogen is sequentially reduced to ammonia. In synthetic chemistry, pioneering complexes such as Schrock's molybdenum dinitrogen complex and Chatt's iron complex have demonstrated the capability to reduce N_2 to ammonia under relatively mild conditions, often with the assistance of strong reductants and proton donors.

Efforts have focused on constructing ligands for low oxidation state metal stabilization and proton-coupled electron transfer, a key step in the cleavage of the $N\equiv N$ bond to yield NH_3 . While some of these systems are catalytically active, turnovers and efficiencies are low relative to biological nitrogenase or industrial catalytic processes.

5. NITROPLAST

The nitroplast is a newly discovered, organelle-like structure in certain marine algae, recognized as an exceptional example of a genuine nitrogen-fixing organelle within a eukaryotic cell. It derived from the unicellular cyanobacterium UCYN-A, a nitrogen-fixing cyanobacterium, and became fixed within algal hosts such as *Braarudosphaera bigelowii*.

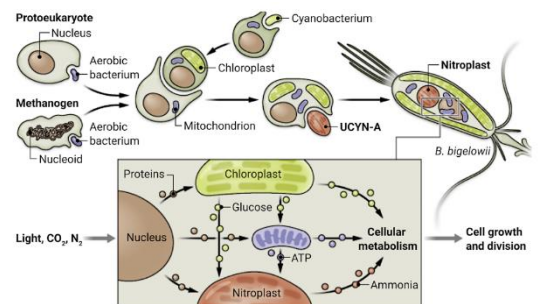


Fig. 4. Analysis and function of the nitroplast

In contrast to normal symbioses where the microbial symbiont is an independent cell, the nitroplast is stably accommodated in the algal cell and is passed on during cell division, like chloroplasts and mitochondria. It has the enzymic and genetic equipment needed to fix atmospheric nitrogen (N_2) to ammonia (NH_3) via nitrogenase activity, and is capable of existing and functioning in oxygenated conditions by maintaining a specialized internal environment. Research with high-resolution molecular and imaging technology has shown that the algal host supplies the nitroplast with necessary metabolites and proteins, with an extremely integrated metabolic relationship and dependence.

This finding is a significant departure from what we earlier understood regarding nitrogen fixation in eukaryotes, providing a possible template for engineering such nitrogen-fixing systems into crop plant species. This would have a revolutionary impact on reducing the agricultural industry's reliance on chemical nitrogen fertilizers, enabling more sustainable agriculture and feeding more of the world's population.

6. BUBBLE BURST AMMONIA SYNTHESIS

Bubble burst ammonia synthesis is a new process of nitrogen fixation that takes advantage of the dynamic physical and chemical events produced when gas bubbles burst at the air-liquid interface. Nitrogen gas (N_2) is supplied in the process into a liquid phase where it is bubbled

and rises to burst at the surface of the liquid to form short-lived microenvironments of high localized energy, reactive intermediates, and mass transfer intensification.

The destructive bursting of such bubbles generates microjets and shock waves strong enough to transfer the required energy to excite and split the stable triple bond of nitrogen molecules ($N\equiv N$). The process also facilitates more mixing in the system and more exposure of catalytic surfaces and therefore facilitates more contact between nitrogen, protons, electrons, and catalytic active sites. In combination with electrocatalytic or photocatalytic systems, catalyst positioning at or near the bubble interface can dramatically enhance nitrogen accessibility and reaction rates.

These transient interfaces have been found in studies to also repress the competing hydrogen evolution reaction (HER) by modifying local concentrations and pH conditions, resulting in higher selectivity for ammonia synthesis. Though still under research, this process shows strong promise for energy-efficient, scalable ammonia synthesis. To realize this process to its best potential, current research is aimed at optimizing parameters such as bubble size, gas flow dynamics, and catalyst architecture to achieve its best efficiency in sustainable nitrogen fixation.

CONCLUSION:

Recent breakthroughs in nitrogen fixation have revealed new paths to sustainable and energy-efficient pathways to ammonia synthesis, addressing the growing demands of agriculture and reducing environmental impact. While the Haber–Bosch remains the industrial workhorse, newer alternatives can be run under gentler, more sustainable conditions. Among them, electrocatalytic and photocatalytic reductions of nitrogen have been of interest,

using new catalysts—such as graphene, boron nitride, and single-atom materials—and sunlight to drive nitrogen conversion to ammonia. Gene-edited microbes, enabled by technologies like CRISPR, are another promising route through enhanced nitrogen fixation in symbiosis with crops, particularly non-legume crops. Transition metal dinitrogen complexes provide mechanistic insight into nitrogen activation at the molecular level and guide effective catalyst design. The discovery of the nitroplast, a nitrogen-fixing organelle of marine algae, provides a unique example of intracellular nitrogen fixation in eukaryotes, with potential implications for crop biotechnology. Bubble burst ammonia synthesis also provides a new physical route that leverages the dynamics at gas-liquid interfaces to enhance nitrogen activation. Collectively, these breakthroughs suggest a future in which nitrogen fixation can be decentralized, environmentally benign, and integrated into sustainable agriculture.

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