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Research Article

Research Progress in Electrocatalytic Reduction of Nitric Acid to Ammonia by Nonmetallic Element Doped Catalysts

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Abstract

The investigation of novel strategies for nitrate pollution reduction should be considered by its substantial environmental danger. The paper summarizes the research advances in electrocatalytic reduction of nitric acid to ammonia, emphasizing the utilization of nonmetallic element-doped catalysts. The concepts of catalyst construction are a key component explaining a variety of approaches including defect engineering, lattice replacement, substrate doping (nitrogen-doped carbon nanotubes, for example), and other creative approaches taken from recent research. The precise regulation of the nitrate electrocatalytic reduction process by these catalysts is examined in this work. The study delves into the regulation of particular phases, including adsorption, electron transport, and other significant elements, and includes specific evaluations for catalysts doped with phosphorus (P), sulphur (S), nitrogen (N), and boron (B). The information provided highlights the part that every component plays in attaining higher removal rates and selectivity when nitric acid is electrochemically converted to ammonia. These catalysts have the benefits of being inexpensive, safe for the environment, and having the potential to be used widely in the electrocatalytic reduction of nitric acid to create ammonia. To fully realize the potential of nonmetallic element-doped catalysts in this application, however, issues including low catalytic efficiency, competition with the hydrogen evolution reaction, and the need for a deeper comprehension of the reaction mechanisms must be resolved.

Keywords: *Nitrate Pollution Reduction; Electrocatalytic Reduction; Nonmetallic Element-Doped Catalysts; Catalyst Engineering; Ammonia Synthesis*

1. Introduction

Nitrogen (N), known as the life element, is indispensable to our lives. It can exist in a variety of forms, including dinitrogen (N_2) gas, nitrogen oxides (NO, NO_2, etc.), nitrogen oxyanions (NO_3 and NO_2), hydrazine (N_2H_4), ammonia (NH_3), and ammonium compounds. Its valence states range from +3 to 5 (Thakur and Medhi, 2019). The nitrogen cycle (N-cycle) of biogeochemistry is facilitated by the majority of those nitrogen compounds' ability to convert to one another through related nitrogen transformation reactions, which are conventionally split into three processes: N_2 fixation, nitrification, and denitrification. The nitrogen cycle is essential to the continuation of life in the natural world. Most biological components needed for life, including amino acids, proteins and nucleic acids, include nitrogen (Zhang et al., 2020). The nitrogenase enzyme converts nitrogen gas (N_2) into ammonia (NH_3), which is an essential component for the creation of these and other nitrogen-containing compounds. Ammonia is a fundamental component of industrial chemical synthesis, particularly of high-volume compounds like fertilizers, just like it is in nature. It is also a high energy density fuel for transportation because of its ease of condensation into a liquid state. Presently, the industrial production of ammonia amounts to over 200 million tonnes annually, with the Haber-Bosch process accounting for nearly all of this production (Einsle and Rees, 2020).

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However, human activity has severely disturbed the global N-cycle and inevitably resulted in a number of environmental issues that have a negative impact on public health. Nitrogen oxides (NOx) are harmful atmospheric pollutants that are mainly produced by human combustion in factories (such as power plants and industrial kilns) and traffic (Medhi, 2021). The rapid build-up of NOx in the atmosphere has resulted in severe environmental problems like acid rain, smog, depletion of the ozone layer, and global warming. Significant environmental problems such aerosol nitrates, acid rain, photochemical smog, haze, and ozone layer depletion, as well as detrimental impacts on neurological and respiratory health, are caused by the nitric oxides (NO_x) generated by the combustion of fossil fuels (Moloantoa et al., 2022).

The discovery and design of renewable energy sources and related equipment to replace traditional fossil fuels have become the focus of scientific research nowadays due to the growing environmental harm and energy problems. Hydrogen is a clean energy source that has the potential to reduce excessive reliance on fossil fuels and provide a foundation for alternative energy sources in the future. Many nations are currently working to create hydrogen energy as a solution to the global energy dilemma (Ebhota and Jen, 2020). Low efficiency and a large overpotential are the outcomes of the multi-step electron transfer mechanisms used in the HER and OER phases of the water electrolysis reaction. With a low working current of 0.2–0.4 A/cm2 and a high potential of 1.8–2.0 V, which is significantly higher than the theoretical potential of 1.23 V, alkaline KOH electrolyte is currently mostly utilized in industry for water electrolysis. This leads to high energy consumption and low efficiency. Enhancing the effectiveness and decreasing the cost of electrolytic water hydrogen generation can be achieved through the utilization of high-performance electrocatalysts (Khan et al., 2018).

The best catalysts for HER and OER right now are Pt/C, IrO2, and RuO2, but their high cost, poor reserves, and unsatisfactory stability prevent them from being used on a broad scale. Transition metal-based catalysts are unique in that they are less expensive, have plentiful deposits, and exhibit strong stability (Tahir et al., 2017). Currently, there has been more advancement in OER and HER with transition metal-based catalysts, including transition metals, transition metal oxides, hydroxides, hydroxyl oxides, carbides, nitrides, phosphides, sulphides, and single-atom catalysts. However, because of their poor conductivity and low number of active sites, they still require improvement in order to function well in electrolytic water. Additionally, the properties of adsorption and desorption during the reaction process are inappropriate (Chen et al., 2019).

Catalysts doped with nonmetallic elements are essential to this process. These catalysts are modified with nitrogen, phosphorus, or sulphur. They are frequently based on materials like carbon. Doping modifies the electronic structure and surface characteristics of the catalyst, improving its capacity to support the electrochemical reduction of nitrate to ammonia (Jyothi et al., 2019). When compared to conventional metal-based catalysts, this method has benefits like higher catalytic activity, better selectivity, and maybe reduced cost. There are many routes and uses for non-metal doping regulation. In transition metal-based catalysts, the cation functions as the real active site most of the time (Zhang et al., 2021). However, the presence of neighboring anions can modify the cation's electronic state—including its surroundings and structure—and boost its intrinsic catalytic activity. Non-metal elements can directly dope or substitute into transition metals to change their electronic structure. This can strengthen or weaken the interactions between the active centre and products both before and after the catalytic process, which can effectively control the intrinsic catalytic activity (Yadav et al., 2020). Nitrate electrocatalytic reduction is important because it can reduce nitrate pollution and provide a more ecologically friendly and sustainable method of producing ammonia. This strategy is further improved by the use of catalysts doped with nonmetallic elements, which increase selectivity, efficiency, and may lessen the need for expensive or environmentally harmful ingredients. All things considered, this technique has the potential to alleviate environmental issues pertaining to nitrate pollution as well as the requirement for more environmentally friendly ways to produce ammonia (Xu et al., 2022).

2. Construction principle of non-metallic element doped catalyst

The construction of non-metallic element-doped catalysts follows a variety of concepts, all of which are intended to improve the catalyst's electrocatalytic activity by altering its structure and characteristics.

2.1 Defect engineering

Defect engineering is the foundation upon which non-metallic element doped catalysts for ammonia synthesis are built. In order to modify the catalyst's structure and surface characteristics, as well as to introduce flaws and alter its electrical structure, non-metal materials must be added. It has been demonstrated that non-metal doping works in concert with loading and other modification strategies to enhance the catalytic characteristics of the catalyst and increase its overall performance (Qiu et al., 2023). The concept of defect engineering pertains to the deliberate introduction of imperfections or aberrations into the structure of the catalyst. These flaws may have edges, voids, or dislocations that could operate as catalytic reaction sites (Yu et al., 2023). The reactivity and surface area of the catalyst can be increased by adding these flaws, which may improve the catalyst's effectiveness in electrocatalytic reactions such the reduction of nitrate to ammonia. The non-metallic elements boron (B), nitrogen (N), phosphorus (P), sulphur (S), silicon (Si), antimony (Sb), selenium (Se), chlorine (Cl), fluorine (F), bromine (Br), and iodine (I) are the most often employed elements for doping catalysts in ammonia production (Liang et al., 2023). These non-metallic components are preferred because they can adjust the catalyst's surface characteristics and electronic structure, increasing its catalytic activity in the ammonia production process.

Defect engineering is an adaptive method for altering surface characteristics and electrical structures of electrocatalysts (Wang et al., 2018). To create defect-rich Cu nanoplates (dr-Cu NPs), for instance, Ren et al. (2022), synthesised CuO nanoplates using in-situ electroreduction, enabling effective and selective electrocatalytic NO_3^- reduction to yield NH_3. Nanoplates with flaws can promote the adsorption of NO_3^- and its associated intermediates on the surface of the electrocatalyst while preventing unintended reactions. Thus, in comparison to the defect-free Cu nanoplates, the as-prepared dr-Cu NPs demonstrated a notable NH_3 production of 781.25 $\mu g\,h^{-1}\,mg^{-1}$, an exceptional NO_3^- conversion rate of 93.26%, exceptional ammonia selectivity of 81.99%, and a high FE of 85.47%. By utilizing defect engineering, our study provides fresh insights into the design of effective NO_3 $^-$RR electrocatalysts (Liang et al., 2023) as shown in (Figure 1). Furthermore, using a simple one-step hydrothermal process, Wang et al. created the Cu/oxygen vacancy-rich Cu–Mn3O4 heterostructured ultrathin nanosheet arrays on Cu foam to make Cu/Cu–Mn_3O_4 NSAs/CF. Specifically, the structure features an abundant Ov and a rich Cu/Cu–Mn_3O_4 interface (Gu et al., 2024). Therefore, Cu/Cu–Mn_3O_4 NSAs/CF demonstrated outstanding NO_3^-RR performance, with exceptional nitrate conversion rate (95.8%), strong NH_3 selectivity (87.6%), perfect NH_3 production (0.21 $mmol\,h^{-1}\,cm^{-2}$), and high faraday efficiency (92.4%) at −1.3 V (vs SCE). This study shows that nitrate can be effectively converted to ammonia using an electrocatalyst built using a combination interface and defect engineering approach (Ullah et al., 2023).

Another example is the Cu(100)-rich rough Cu-nanobelt (Cu-NBs-100) that Hu et al. presented. During this process, the NO_3 $^-$RR intermediate exhibited a strong contact with the Cu(100) facets, which might greatly aid in the Cu(100) surface's exposure (Niu, 2023). They discovered that several flaws on the Cu(100) plane were caused by the rough surface of Cu NBs. Cu(100) facets and surface defects can jointly increase the adsorption strength of H* and NO_3 *, as demonstrated by DFT calculations and adsorption studies. This lowers the reaction barrier of NO_3 $^-$RR and inhibits HER, respectively (Hu et al., 2021). Consequently, the as-prepared Cu-NBs-100 shows outstanding NO3 −RR performance, with a maximum NH_3 production of 650 $mmol\,h^{-1}$ gcat $^{-1}$ at −0.15 V against RHE and a high FE of 95.3%. This discovery offers a novel approach to harnessing the combined benefits of Cu(100) and faults to enhance the conversion of NO_3 $^-$RR to NH_3 (Lu et al., 2023).

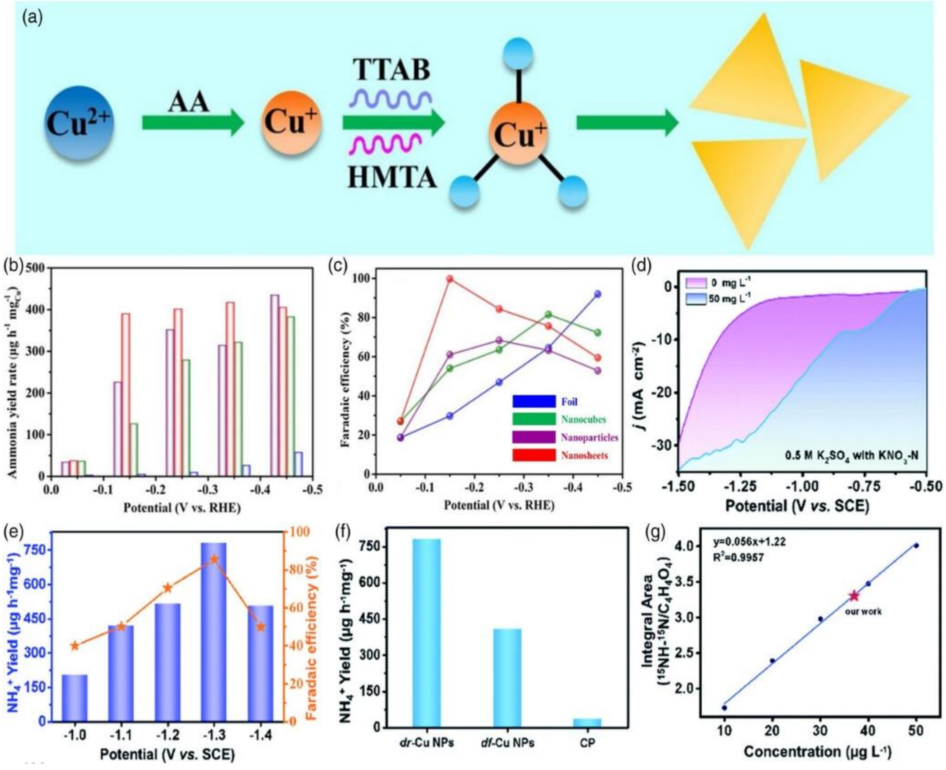

Fig 1: a) Synthesis plan of Cu nanosheets; b) NH_3 yield rates and c) FE of various Cu catalysts. reproduced with consent. Elsevier (C) 2021 Copyright. d) Dron-Cu nanoparticle linear sweep voltammetry (LSV) curves; e) FE and NH_3 yield at various potentials; f) NH_3 yield over a range of catalysts. g) The integral area standard curve. reproduced with consent. The Royal Society of Chemistry. (Li et al., 2021)

2.2 Lattice substitution

The construction principle of non-metallic element-doped catalysts by lattice replacement involves the following steps. Select an appropriate catalyst material first that can accept the addition of non-metallic components and has a well-defined structure. This substance ought to be chemically stable and have a large surface area (Chen et al., 2021). By using lattice substitution, incorporate non-metallic elements into the catalyst material, such as boron (B), nitrogen (N), phosphorus (P), sulphur (S), silicon (Si), antimony (Sb), selenium (Se), chlorine (Cl), fluorine (F), bromine (Br), and iodine (I). During this procedure, part of the catalyst material's lattice elements is swapped out for non-metallic ones, causing flaws and altering the catalyst's electronic structure (Gao et al., 2023).

2.3 Substrate doping (e.g., nitrogen-doped carbon nanotubes)

The integration of non-metallic elements, such as boron (B) and nitrogen (N), to provide active sites for the ammonia generation process is the fundamental building block of catalysts doped with non-metallic elements, such as nitrogen-doped carbon nanotubes, for the synthesis of ammonia. For example, doping B-N prevents competitive hydrogen evolution reactions while providing enough active sites for carbon nanosheets. The synthesis of electrocatalysts has made extensive use of non-metallic materials, especially two-dimensional nano non-metallic materials with doping heteroatoms. This has created new avenues for the environmentally friendly and sustainable synthesis of ammonia (Arulprakasam and Unni, 2023).

N-doped carbons have emerged as one of the most promising materials for energy-related applications over the past few decades, including fuel cells, batteries, and electrochemical capacitors. Recently, researchers studying catalytic uses have also become interested in carbons containing nitrogen (Wood et al., 2014). The process of doping carbons with nitrogen has evolved throughout time, and today's synthetic methods and varieties of nitrogen functions are widely recognised. The most prevalent nitrogen groups present in N-doped carbon compounds are pyrrolic, pyridinic and graphitic or quaternary. As shown in figure 2, near the graphene layer boundaries, additional oxidized nitrogen and amine groups can form (Kato et al., 2021)). As a component of a pentagon, pyrrolic nitrogen groups are bound to two carbon atoms in the graphene layer. Due to their sp2 hybridization, pyridinic nitrogen groups exhibit strong binding strengths with a variety of metals and compounds. These bonds consist of two carbon atoms forming a hexagon, each of which contributes one p electron to the π-system. Nitrogen groups that are pyrrolic or pyridinic can be found in vacancies inside graphitic layers or at their boundaries. Graphitic nitrogen groups exhibit sp2 hybridization, three-carbon bonding, and carbon atom substitution. For such functionalities, there are two alternative configurations: "valley" (next to the layer end) and "centre" (within the layer) (Talukder et al., 2021).

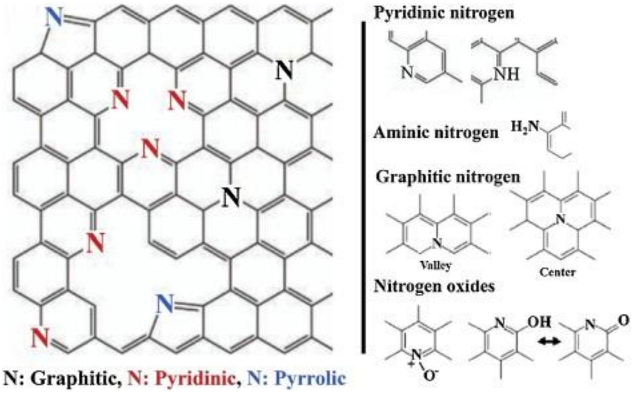

Fig. 2. Common nitrogen groups in a graphene layer of nanostructured carbons. Adapted with permission from (Lee et al., 2014).

There are several different ways to manufacture N-doped carbons synthetically, making it challenging to categorize them clearly. They can be categorised into two main groups, though, based on whether the nitrogen precursor is heat-treated in conjunction with a pre-synthesized carbon material or if the carbon precursor and nitrogen-containing source are thermally treated simultaneously to produce the N-doped carbon material (He et al.,2022) (summarized in Fig 3).

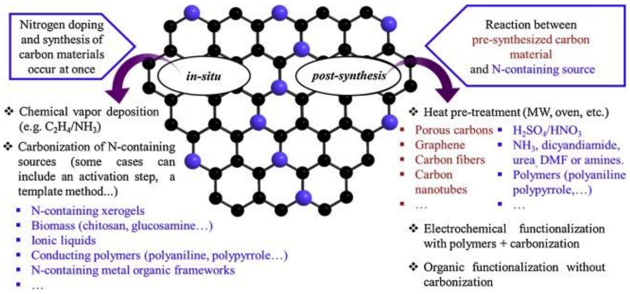

Fig 3: Summary of methods to synthesize nitrogen-containing carbon materials

2.3.1 Post-synthesis doping methods

The direct reaction between a pre-synthesized carbon material and N-containing sources, such as urea, ammonia, dicyandiamide, dimethylformamide (DMF), melamine, and so forth, is the post-synthesis doping strategy. In order to help nitrogen, integrate into the carbon network, these techniques typically entail high temperatures, extended reaction times, the addition of transition metals, or preparation of the carbon surface (Salinas-Torres et al., 2019). Notwithstanding these disadvantages, post-synthesis doping techniques remain popular due to their ease of application in producing N-doped carbons. According to this method, the temperature and duration of the thermal treatment determine the nitrogen content and configuration (Sandoval and Tobias, 2020).

The nitrogen content generally decreases with increasing temperature. Determining the ideal temperature to achieve the highest nitrogen content is challenging, though, as the starting non-modified carbon material and the source of nitrogen also significantly influence the final nitrogen configuration and overall content (Al-Naggar et al., 2023). Some research suggests that, when utilising NH_3 as a nitrogen precursor, an ideal temperature range of 500–600 °C might be chosen to provide the maximum nitrogen content for N-doped carbon material. But other scientists have also written on the synthesis of N-doped carbon materials, and they discovered that at temperatures higher than 900 °C, the nitrogen content was at its greatest. Concerning the use of NH_3 as a precursor in the nitrogen configuration (Zhao et al., 2019).

According to Hu et al. (2020), the resultant N-doped graphene primarily displayed pyridinic groups below 600 °C and pyridinic/graphitic groups beyond 800 °C. Another popular source of N-containing precursor is urea, which has several benefits for the environment, low pyrolysis temperature, and low cost. Microwave-assisted (MW) carbonizations is another intriguing method for obtaining N-functionalized carbon materials. It's an eco-friendly, quick-reaction method that works well (Li et al., 2016). Yang et al. described the synthesis of N-doped reduced graphene oxide (N-RGO) from urea by heat-treatment utilizing MW, leading to N-RGO containing pyridinic, pyrrolic and graphitic nitrogen groups. It was found that the latter ones' concentration was influenced by the reaction time (Mandal et al., 2022).

N-doped GO was also created from graphite using the MW technique, resulting in GO with a high surface area and high nitrogen content (8–11 at%). The functionalization of carbon materials by N-containing precursors that were first deposited onto the carbon surface and then carbonized is another method of post-synthesis doping (Megawati et al., 2017). Using hydrazine and ammonia at temperatures below 200 °C, Long et al. hydrothermally reduced graphene oxide (GO) to produce N-doped graphene sheets (NG) with a nitrogen content of 5%. Nitrogen has also been added to the carbon network by the use of monomers containing N. Aniline was chemically polymerized, followed by carbonization, to create N-doped carbon fibres (Zhang et al., 2014). For example, the Tour technique has made it possible to tune the kind and quantity of N-functionalities in carbon nanotubes (CNTs) or graphene. It involves utilizing aryldiazonium salts (such as 4-aminopyridine, 9-aminoacridine, or 3-aminocarbazole) under mild circumstances (Guo et al., 2013). According to González-Gaitán et al. (2015), functionalizing carbon nanotubes (CNTs) with aminobenzene acids electrochemically produces a polymer thin layer on the surface of the CNTs. Due to the carbonizations of these N-modified CNTs in the presence of low O_2 concentration, high concentrations of nitrogen and oxygen groups, such as pyridinic, pyrrole, and pyridone, were produced. Moreover, it is worth mentioning that the addition of nitrogen functionalization to carbon-based materials through nitric acid treatment has been successfully studied for the creation of various N-containing materials with a wide range of uses (Wong et al., 2013).

Actually, nitric acid is primarily employed as a pretreatment to make it easier to later functionalize various carbon materials by employing N-containing compounds like amines, amides, and so forth. It does not directly introduce the nitrogen groups in this type of functionalization. By preoxidizing petroleum coke with nitric acid at a moderate temperature. (Mohan et al., 2023). Yang et al. produced N-doped carbon compounds with a nitrogen content of around 4 weight percent. Subsequently, the urea-modified pretreatment material showed a nitrogen content of 11.08 weight percent, which improved the carbon materials' ability to collect CO2 (Chen et al., 2016). Other carbon materials, such single-walled carbon nanotubes (CNTs), have also been effectively functionalized by the use of nitric acid and amine functionalization, resulting in the production of soluble CNTs. This process was also utilized to functionalize carbon materials under mild circumstances and then they were hydrolyzed at high temperatures to achieve the necessary N-doped carbon material (Mallakpour and Soltanian, 2016). For example, N-doped ordered mesoporous carbons were synthesized by Lu et al. (2013), to be used in the oxygen reduction reaction (ORR). Nitric acid was used to treat a commercial mesoporous carbon at 70°C, and room temperature melamine was added as a source of nitrogen. The final product was then hydrolyzed to produce N-doped carbon, which was used as an electrocatalyst. Consequently, the approach that involves pretreating nitric acid and then reacting chemically with molecules containing nitrogen provides a good foundation for the preparation of N-doped carbon compounds for a variety of uses (Ba et al., 2020).

2.3.2 In-situ doping methods

In in-situ doping synthesis, carbon material synthesis and nitrogen doping take place simultaneously. Chemical vapor deposition (CVD) is one of the most popular techniques because it can be utilized to achieve evenly dispersed nitrogen groups throughout the carbon network. N-doped carbon compounds, such as graphene, CNTs, CNFs, or microporous carbon, have been prepared with success using it (Song et al., 2016). Castro-Muñiz and colleagues have presented a new technique for creating co-doped microporous carbons with a large surface area. The approach involves infiltrating a Y zeolite with 1-ethyl-3-methylimidazolium tetracyanoborate, an ionic liquid containing nitrogen, and then applying CVD. By using this method, co-doped microporous carbon was produced, which primarily displayed pyridinic nitrogen but also showed pyrrolic and graphitic nitrogen (Han et al., 2021).

By employing C_2H_4/NH_3 combinations, CVD has also been used to create N-CNFs, which exhibit an increased pyridinic group content as the N-containing precursor increases. To create N-doped porous carbons, carbonization of N-containing precursors has been widely employed, sometimes followed by chemical activation (Suboch et al., 2021). There are numerous N-containing sources in this regard, such as conducting polymers, ionic liquids (ILs), biomass, and so forth. The fact that N-doped carbons with a variety of architectures and nitrogen contents can be produced has drawn a lot of attention to the well-established syntheses of conducting polymers (Matsagar et al., 2021). According to Gavrilov et al., (2012), N-doped carbon materials were prepared from polyaniline (PANI) by carbonization at 800 °C using various salt precursors. This resulted in nitrogen contents of about 9%, and the most abundant groups were pyridinic and graphitic, as revealed by the deconvolution of N1s spectra. However, depending on the initial precursors, the graphitic/pyridinic ratio varies. Therefore, a major factor in the final nitrogen groups is the choice of experimental parameters, such as carbonization temperature, monomer type, or polymerization duration. N-doped carbon compounds, which were created from PANI under various experimental settings and carbonized at 800 °C, provide evidence of this by clearly demonstrating the involvement of pyrrolic/pyridone groups in addition to graphitic and pyridinic ones (Saha and Kienbaum, 2019).

N-doped carbon compounds have also been prepared using imidazolium/pyridinium ILs because of their nitrogen concentration and physicochemical characteristics. By carbonising N-butyl-3-methylpyridinium with a hard template, mesoporous N-doped carbon was produced. This resulted in conductive carbon materials with a high nitrogen content (>15 wt%), which was explained by the presence of pyrrolic, pyridinic, and graphitic groups (Wang et al., 2020). A variety of applications have recently looked at Metal Organic Frameworks (MOFs) with N-organic ligands as a precursor for N-doped carbon materials due to their intriguing properties, which include huge pore volumes, high surface areas, and a wide spectrum of nanostructures (Payattikul et al., 2023).

Lu et al. (2020), reported using electrospun polyacrylonitrile (PAN) and ZIF-8 to create hollow particle-based N-doped carbon nanofibers. The hierarchical porous nanofibers exhibited graphitic domains and a high nitrogen content (about 8 weight percent) that was achieved following carbonization at 900°C. In terms of N-containing groups for the final N-CNFs, pyridinic and pyrrolic groups were the most prevalent, and the latter became graphitic as the temperature of carbonization rose (Liu et al., 2022). N-doped carbon compounds generated from biomass must be discussed in order to wrap up the in-situ techniques. Because of its abundance, affordability, and environmental friendliness, biomass is a good option for increasing the production of N-doped carbon compounds. The most popular method for obtaining carbon materials from biomass is hydrothermal carbonization, or HTC (Zhou et al., 2018).

Carbonization of N-containing biomass or a combination of biomass and N-containing precursors can be used to create biomass-derived N-doped carbon compounds. Unfortunately, the resulting hydrochars often have closed porosity and low surface area, necessitating a heat-treatment or chemical activation step that depletes a significant portion of their nitrogen content (Matsagar et al., 2021). Carbon compounds with a high surface area have been produced using conventional pyrolysis of biomass, which includes a carbonization process that can assist retain more nitrogen groups. Liu et al. described the production of N-doped carbon nanosheets from chitosan without chemical activation, producing high surface area and moderate nitrogen content corresponding to pyridinic and graphitic groups (Tong et al., 2019). In order to increase the porosity in biomass and melamine mixtures, Ma et al. recently reported a carbonization technique that uses KCl/ZnCl2. This technique produced mesoporous N-doped carbons with an impressive nitrogen content (11.9%) in the case of N-doped carbon materials formed from biomass, the creation of N-doped carbon materials with adjustable nitrogen speciation and content remains difficult, nevertheless the previously described advancements and objectives reached in the synthesis of N-doped carbon materials using various techniques (Zhang et al., 2017).

2.3.3. Synthesis of metal catalysts supported on N-doped carbon materials

N-doped carbon has been proposed as a viable substitute for carbon to support NPs in order to produce small and well-dispersed NPs. Generally speaking, this leads to higher catalytic performances because there are more surface atoms (Nichols et al.,2022). Historically, the most effective method for regulating NP growth and achieving tiny NPs on the support surface has been the application of capping agents. However, due to their negative impact on catalytic activity caused by partial occlusion of the NPs' active sites, the usage of such compounds is still up for debate. A promising substitute for achieving small and evenly distributed NPs that avoid the drawbacks of those capping agent-protected NPs is N-doped carbon supports (Rafeeq et al., 2022).

Not without justification, the nitrogen functionalities are said to behave as a "tether," increasing the catalytic performance by facilitating the NPs' dispersion and giving them resistance to agglomeration and coarsening (Sun et al., 2021). However, as has been shown by both theoretical and experimental research, the nitrogen functional groups added to the carbon supports alter not only the growth kinetics during NPs deposition and metal-support interaction but also the electronic characteristics of the NPs and the acid-base characteristics of the final materials. The literature and previous recapitulations on the role of N-containing carbons in regulating the nucleation, growth, and stabilization of NPs and their characteristics while taking into account different synthetic techniques are available (Fiorio et al., 2023). Similar to non-doped carbon catalysts, the literature offers a wide range of substitutes for the production of NPs supported by N-doped carbon materials; only a few of the most popular methods will be touched on in this brief article. They fall into one of three categories: (i) loading of NPs on an N-doped carbon material that has already been synthesized; (ii) simultaneously incorporating nitrogen and metal phase on a carbon material that has already been synthesized; and (iii) in-situ synthesis of NPs on an N-doped carbon support (Feng et al., 2021). Conventional techniques, such as impregnation (either wet or incipient wetness impregnation), deposition-precipitation, and sol-immobilization and subsequent reduction of the metal precursors, are required for loading of NPs onto pre-synthesized N-doped carbon materials (Rossi et al., 2018). Then, because of the several steps required, these methods—while allowing control over the support properties—are not the best choice. The in-situ synthesis of NPs on N-doped carbon supports is also typically prepared by following a pyrolysis step in which the carbon precursor is added to the mixture instead of the pre-synthesized carbon support. This allows for the simultaneous incorporation of metal and nitrogen functionalization, which is commonly achieved by pyrolysis of mixtures containing metal and nitrogen precursors and carbon supports under certain conditions. It was said that the synthetic approach has a significant influence on the characteristics of the resultant NPs (Zhang et al., 2015).

In keeping with this, Yang et al. carried out a thorough investigation in which Pt NPs were supported on N-doped carbon nanotubes (Pt/N-CNTs) through the use of a variety of synthetic techniques (e.g., ethylene glycol reduction, sodium borohydride reduction, etc.). Because of the various mechanisms involved in their production, it was discovered that the approach employed had an impact on the electrical characteristics of the NPs (Zhou et al., 2018). Moreover, the metal-support interaction between Pt and N adjusted the electrical characteristics, which in turn impacted the catalysts' ultimate performance. In addition to these traditional synthetic pathways, a novel and appealing approach for obtaining metal/N-carbons is the use of MOF as a sacrificial template. MOFs are made of metal joints and organic linkers, which, with precise pyrolysis, can turn the linkers into carbon metal-carbon composites with nitrogen when the linkers are chosen correctly (Cheng et al., 2021). Catalysts with intriguing compositions and architectures have been created using this approach, such as gold nanoparticles embedded in N-doped nanoporous carbon NPs, cobalt nanoparticles embedded in N-doped porous carbons, one-dimensional N-doped carbon nanotube encapsulated Co NPs (Co/N-BCNTs), two-dimensional N-doped carbon nanosheet (N-CNS) and three-dimensional N-doped carbon nanotube framework encapsulated Co NPs, and FeCo alloy core@nitrogen-doped carbon shell NPs anchored on carbon nanotubes (Shen et al., 2016).

3. Regulation of reaction by nonmetallic doped catalysts

3.1 B doped

Boron-doped catalysts have demonstrated potential as active sites for the electrocatalytic and photocatalytic reduction of nitrogen to ammonia. This is especially true of B-N-doped materials. It has been discovered that these materials provide enough active sites to generate ammonia while inhibiting competitive hydrogen evolution processes, which makes them advantageous for effective and focused electrocatalytic nitrogen reduction (Zhang et al., 2021). The mechanism of ammonia synthesis utilizing boron-doped catalysts involves the electrocatalytic reduction of nitrate to ammonia. The boron-doped catalyst converts nitrate (NO_3) to nitrite (NO_2) by a series of redox reactions. By moving electrons from the catalyst to the nitrate, this process lowers the nitrate's oxidation state and produces nitrite. Adsorbed nitrogen species are created when the nitrite species adsorbs on the boron-doped catalyst's surface. These species are easily reduced to ammonia due to their strong reactivity (Gou et al., 2023).

Ammonia is produced by further reduction of the adsorbed nitrogen species on the boron-doped catalyst. This process involves the loss of electrons from the nitrogen species, which interacts with hydroxyl groups (OH^-) on the catalyst surface to create ammonia. In order to facilitate these redox processes, decrease the energy barrier for nitrogen reduction, and increase the overall reaction rate, the boron-doped catalyst is essential. The synthesis process is finished when the generated ammonia desorbs from the catalyst surface. Due to the special structure and electrical characteristics of the boron-doped catalyst, ammonia can be desorbed effectively, producing large yields of ammonia (Kuang et al., 2020) as shown in figure 4.

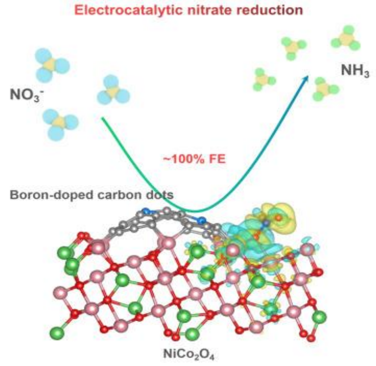

Fig 4: Electrocatalytic nitrate reduction to ammonia by boron doped carbon catalyst

Research is still being done to determine how boron concentration affects the efficiency of boron-doped catalysts for ammonia synthesis. Research has indicated that the reduction of nitrogen to ammonia through electrocatalysis and photocatalysis can be greatly impacted by the amount of boron present in the catalyst structure (Liang et al., 2022). For instance, it has been discovered that adding a single boron atom to the structure of N-doped graphene increases the catalytic activity for the synthesis of green ammonia. In a similar vein, it has been demonstrated that doping g-C3N4 with boron increases its photocatalytic activity for ammonia generation. Furthermore, research has demonstrated that the efficiency and selectivity of electrocatalytic nitrogen reduction to ammonia can be influenced by the boron content in boron-doped carbon nanosheets (Ren et al., 2019). In one study, at a boron doping concentration of 6.2%, boron-doped graphene demonstrated one of the best faradic efficiencies for NH_3 generation together with a good NH_3 yield (Majumder et al., 2021). An additional investigation revealed that the electrocatalytic nitrogen reduction reaction was influenced by the dispersion of distinct boron structures in boron-doped graphene.

Greater catalytic activity is indicated by a larger ratio of boron-doped materials. However, the type of catalyst material and the boron concentration can affect the specific catalytic activity (Ouyang et al., 2021). One study found that low boron concentration boron-doped Ni/SBA-15 catalysts had decreased catalytic activity. The distribution of different boron structures in boron-doped catalysts can impact the electrocatalytic nitrogen reduction reaction (Singh et al., 2020). For instance, compared to other boron types, the highest percentage of boron clusters (BC3) in a boron-doped graphene sample indicates that BC3 functions as a substantial electrocatalytic NRR site. The reactivity of graphene towards atomic hydrogen and oxygen-containing molecules is enhanced when boron is present. The amount of boron present can affect the catalyst's surface oxidation, which can affect the catalytic activity (Wang et al., 2021).

3.2 N doped

The electrocatalytic reduction of nitrate (NO_3) to ammonia (NH_3) is the process by which nitrogen-doped catalysts have been employed for electrocatalytic ammonia synthesis. The nitrogen atoms in inert N_2 molecules are firmly connected to one another because of the N≡N bond's extraordinarily high binding energy (948 kJ/mol−1). Catalysts doped with nitrogen, like boron-doped catalysts, produce active sites that have the ability to degrade the N-N bond, facilitating the adsorption of N_2 molecules onto the catalyst surface (Wang et al., 2021). The inert N2 molecules are activated by the active sites on the nitrogen-doped catalysts, increasing the susceptibility of the nitrogen atoms to reduction. Adsorbed nitrogen species are created during this activation phase; these species are extremely reactive and easily reduce further to ammonia. On the nitrogen-doped catalyst, the adsorbed nitrogen species are further decreased (Yan et al., 2019).

This process involves the loss of electrons from the nitrogen species, which interacts with hydroxyl groups (OH^-) on the catalyst surface to create ammonia. These redox reactions are made possible by the nitrogen-doped catalyst, which also lowers the energy barrier for nitrogen reduction and increases the pace of the reaction overall. The synthesis process is finished when the generated ammonia desorbs from the catalyst surface. Due to the nitrogen-doped catalyst's special structure and electrical characteristics, ammonia can be desorbed effectively, producing large yields of ammonia. In the manufacture of ammonia, nitrogen-doped catalysts—such as nitrogen-doped phosphorene—have demonstrated exceptional electrocatalytic performance (Peng et al., 2021).

3.2.1 Synthesis and characterization of N-doped phosphorene

N-methyl-2-pyrrolidone (NMP) solvent was mixed with ball milling and microwave-assisted exfoliation in a series of processes that produced N-phosphorene. In order to increase surface reactivity, bulk BP crystals were first ground (Xu et al., 2020). They were then ball milled in NMP with or without NH4OH to produce N-doped or O-phosphorene, respectively. Ball milling aided in exfoliation by weakening van der Waals contacts and producing a large number of reactive species at the nanosheet boundaries (Yang et al., 2019). Ultrathin phosphorene nanosheets were also produced by liquid-phase exfoliation assisted by microwaves. Differential thickness measurements (AFM) revealed non-doped (about 4.9 nm), O-phosphorene (approximately 5.5 nm), and N-phosphorene (approximately 8.6 nm) with plausible doping and functional group effects. Ball milling significantly decreased flake sizes, which affected the difference in lateral diameters between doped and non-doped nanosheets (Batmunkh et al., 2017). No structural changes were seen after treatments, according to Raman spectra. Characteristic peaks were seen in the UV-vis spectra, and doped samples showed blueshifts because of the smaller flakes. P–P and P–O bonds were found in all samples by XPS analysis, and significant variations in PxOy peak intensity suggested successful N–doping and reduced oxygen groups in N–phosphorene, which were further supported by the HR N 1s spectrum and XPS survey scan (Xu et al., 2020).

3.2.2 Electroreduction of N_2 to NH_3

In a N_2-saturated 0.1 M KOH solution, the electrocatalytic N_2 reduction reaction (NRR) of several catalysts was evaluated. In N_2-saturated circumstances, N-phosphorene showed a higher current density, indicating successful NRR catalysis. N-phosphorene's NRR onset potential was in proximity to the thermodynamic equilibrium potential. N-phosphorene, O-phosphorene, and phosphorene were used in the electrolysis process under N_2 gas bubbling, and the generation of NH_3 was detected and measured using an ammonia selective electrode and indophenol blue techniques. Comparing N-phosphorene to O-phosphorene and phosphorene, the former showed a substantially higher FE (19.08% at 0 V) and NH_3

production rate (16.67 μg h^{-1} $mgCAT^{-1}$) (Chen et al., 2020).

N-doping's improved active sites and electronic structure most likely played a role in N-phosphorene's higher catalytic activity. Consistent trends in NH_3 yield rates were observed using both approaches. With no by-product N_2H_4 found using the Watt and Chrisp technique, N-phosphorene exhibits exceptional selectivity for the NRR, matching or even exceeding the performance of some reported metal catalysts (Xu et al., 2019). A number of control studies were carried out to verify the source and mode of NH_3 generation. In Ar-saturated electrolytes employing N-phosphorene on a copper foam (CF), NH_3 detection was lacking, suggesting that NH_3 originated from injected N_2 gas (Xu et al., 2020). Similarly, pure CF electrodes in N_2-saturated electrolytes did not exhibit any NH_3, suggesting that electrocatalysts using the N_2 gas present in the electrolyte were the only ones capable of catalyzing the synthesis of NH_3 (Ni et al., 2023).

When N^-, O^-, and phosphorene were compared at various potentials, the NH_3 yield rates were found to be approximately 15 μg h^{-1} $mgCAT^{-1}$ at all potentials, although FEs declined as potentials got more negative because of the hydrogen evolution reaction's dominance (HER). N-phosphorene consistently demonstrated better NH_3 yield rates and FEs across all potentials, indicating superior NRR activity and HER suppression, particularly at low overpotentials. N-phosphorene had a lower charge transfer resistance (Rct) (24.2 Ω) than phosphorene (56.3 Ω) and O-phosphorene (34.1 Ω), according to electrochemical impedance spectroscopy (EIS), showing that the heteroatom presence in N-doped phosphorene contributes to favourable charge transfer mechanisms (Luo et al., 2023).

Durability assessment includes six consecutive electrolysis cycles at 0 V, revealing minimal declines in NH3 yield rate and FE, indicating high stability during continuous NRR electrocatalysis. N-phosphorene's constant current density was confirmed by long-term testing conducted over a period of 15 hours, indicating its durability for NRR electrocatalysis. After six cycles, structural and compositional analysis demonstrated the remarkable stability of N-phosphorene, with P, O, and N components present and negligible surface composition changes caused by N_2 adsorption during catalysis (Kong et al., 2023).

Table 1: Summary of electrocatalysts for the reduction of NO_3^- to NH_3.

Catalyst Category	Catalyst	Reactant	Electrolyte	Potential (V vs. RHE)	Ammonia Yield	FE
Noble metal catalyst	Pd-NDs/Zr-MOF	NO_3^-	_	−1.3	287.5 $mmolNH_3\ h^{-1}\ g_{cat}^{-1}$	60%
Noble metal catalyst	Ag-NDs/Zr-MOF	NO_3^-	_	−13	275 $mmolNH_3\ h^{-1}\ g_{cat}^{-1}$	55%
Monometallic Catalyst	Cu	NO_3^-	_	−0.15	390.1 $\mu g\ mg_{Cu}^{-1}\ h^{-1}$	99.7%
Monometallic Catalyst	Fe	NO_3^-	_	−0.85	~20,000 $\mu g\ h^{-1}\ mg_{cat}^{-1}$	~66%
metal oxide catalyst	Fe_2O_3-CNT	NO_3^-	0.5 M KOH	−0.5	41.4 $\mu g\ h^{-1}\ mg_{cat}^{-1}$	17%

3.3 P doped

The electrocatalytic reduction of nitrogen to ammonia is the process by which phosphorus-doped catalysts have been employed for electrocatalytic ammonia synthesis. A study reports that the N_2-to-NH_3 conversion can be effectively improved by a phosphorus-doped potassium peroxyniobate (P-KNO) electrocatalyst with enriched oxygen vacancies. The NH^3 production rate at −0.45 V vs. reversible hydrogen electrode (RHE) is 23.01 μg h^{-1} $mgcat^{-1}$, and the faradaic efficiency (FE) in a 0.1 M solution is 39.77% at −0.4 VRHE. Furthermore, it has been shown that N-doped porous carbon (NPC) is an inexpensive electrocatalyst for ammonia production from electrocatalytic N_2 reduction in ambient circumstances (Fan et al., 2022).

It has also been reported that phosphorus-doped carbon nitride with abundant nitrogen vacancy exhibits outstanding NRR catalytic performance in 0.1 M Na_2SO_4 electrolyte, with a faradaic efficiency of 22.5% and an NH3 production of 28.67 μg h^{-1}mgcat. $^{-1}$ (Zhang et al., 2023). In phosphorus-doped catalysts for electrocatalytic ammonia synthesis, phosphorus has the role of increasing the activity of the N_2 reduction reaction (NRR) and raising the faradaic efficiency (FE) of NH_3 generation. Phosphorus-doped catalysts, such as phosphorus-doped potassium peroxyniobate (P-KNO), have been found to effectively increase N_2-to-NH_3 conversion, attaining a high NH_3 yield rate and FE (Yuan et al., 2022).

The addition of phosphorus in the catalyst structure boosts the N_2 fixation activity and accelerates N_2 adsorption and activation during the NRR process, resulting to higher NH_3 generation and improved selectivity. Furthermore, it has been demonstrated that phosphorus-doped catalysts with enriched oxygen vacancies increase the electrocatalytic NRR, leading to higher NH_3 generation rates and FE. The electrocatalytic reduction of nitrogen to ammonia depends on the N_2 fixation activity, which is improved by the presence of phosphorus in the catalyst structure. It has been demonstrated that phosphorus-doped catalysts with enriched oxygen vacancies increase the electrocatalytic NRR, leading to higher NH_3 generation rates and FE (Shi et al., 2020).

The modification of surface hydrophobicity is responsible for the increased N_2 fixation activity and faradaic efficiency. This, in turn, speeds up N_2 adsorption and activation throughout the NRR process. The combination of phosphorus and potassium in phosphorus-doped catalysts, such as phosphorus-doped potassium peroxyniobate (P-KNO), has been found to efficiently increase N_2-to-NH_3 conversion (Mushtaq et al., 2023). Although it is regarded as a dangerous process, the fast surface oxidation of phosphorene in ambient settings is employed in this case to accomplish effective heteroatom doping. The preparation of highly crystalline nitrogen-doped phosphorene (N-phosphorene) involves the use of both ball milling and microwave methods. The prepared N-doped phosphorene nanosheets showed outstanding electrocatalytic performance, with an NH_3 yield rate and faradaic efficiency (FE) of up to 18.79 µg h^{-1} mgCAT^{-1} and 21.51%, respectively, at a low overpotential (0 V) versus the reversible hydrogen electrode (RHE) (Rehman et al., 2021).

3.4 S doped

The electrocatalytic production of ammonia via nitrogen reduction has demonstrated potential with the use of sulfur-doped catalysts. The addition of sulphur into various carbon-based materials, such as graphene and porous carbon, has been shown to boost the electrocatalytic performance for ammonia synthesis from electrocatalytic N_2 reduction (Xia et al., 2019). For promoting the nitrogen reduction to ammonia, sulfur-doped graphene (S-G) and sulfur-doped porous carbon (S-NPC) have been suggested as effective and stable electrocatalysts. Sulfur-doped graphene (S-G) has been presented as an efficient and stable electrocatalyst for driving the nitrogen reduction reaction (NRR) under ambient circumstances, resulting to efficient electrocatalytic N_2-to-NH_3 fixation (Qin et al., 2022).

The development of catalytic active sites, improved nitrogen species adsorption, electron transfer facilitation, high NH_3 yield, and Faradaic efficiency are all part of the suggested mechanism for sulfur-doped graphene (S-G) in electrocatalytic N_2-to-NH_3 fixation. Density functional theory simulations suggest that carbon atoms adjacent to substituted sulphur atoms are the underlying catalytic active sites for the NRR on S-G. Sulphur increases nitrogen species adsorption in the graphene structure, which is important for the electrocatalytic NRR. By facilitating electron transmission between the reactants and the electrolyte, sulfur-doped graphene lowers the energy barrier for the NRR and increases the pace of the reaction as a whole. Significantly greater than that of undoped graphene, S-G produces a relatively large NH_3 production of 27.3 µg h^{-1} mgcat.$^{-1}$ and a high Faradaic efficiency of 11.5% at −0.6 and −0.5 V vs. a reversible hydrogen electrode, respectively, in 0.1 M HCl (Ruan et al., 2023). Therefore, the inclusion of sulphur into graphene boosts the electrocatalytic performance for ammonia synthesis from electrocatalytic N_2 reduction, making sulfur-doped graphene a viable electrocatalyst for effective electrocatalytic N_2-to-NH_3 fixation. In 0.1 M HCl, sulfur-doped graphene (S-G) has shown an exceptionally high Faradaic efficiency of 11.5% at -0.6 and -0.5 V vs. a reversible hydrogen electrode, respectively, and a surprisingly large NH_3 production of 27.3 µg h^{-1} mgcat.$^{-1}$. The difference between these values and those of undoped graphene (6.25 µg h^{-1} mgcat.$^{-1}$; 0.52%) is substantial. Sulfur-doped graphene has an effective electrocatalytic N_2-to-NH_3 fixation performance, as demonstrated by its high NH_3 yield and Faradaic efficiency. This makes it a viable option for environmentally benign and sustainable ammonia synthesis (Braun et al., 2022).

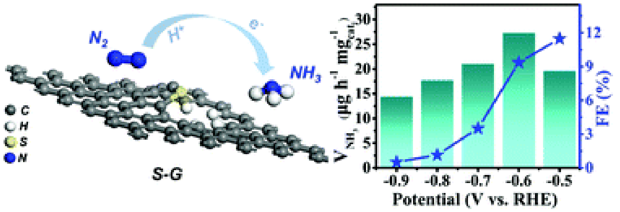

Fig:5 Sulfur-doped graphene for efficient electrocatalytic N2-to-NH3 fixation

4. Electrocatalyzed N_2 Synthesis of Ammonia

The competition between hydrogen evolution (HER) and nitrogen reduction (NRR) reactions poses difficulties for ammonia production via electrocatalytic nitrogen reduction. Inhibiting HER competition with electrocatalysts is essential to improving NRR efficiency (Zhao et al., 20210. In order to efficiently synthesise ammonia, two main types of catalysts are investigated: metallic and non-metallic. Because of the sensitivity of their catalytic structure, precious metal catalysts such as Ru and Rh exhibit increased activity. Ru electroplated on titanium felt, for example, increases the production of NH_3. Additionally, by managing the active site size and local chemical environment, a model based on Ru on a porous graphite carbon nitride matrix improves NRR performance (Zhang et al., 2019).

It is imperative to remove airborne contaminants' interference and confirm nitrogen's source when producing NH_3. Experiments using $15N_2$ isotope labelling verify that NH_3 comes from N_2, not from contaminants. Accurate electrocatalytic NRR results require rigorous testing techniques, such as cross-checked product yield measurements, comparing studies, and gas purification (Insausti et al., 2020). Monatomic catalysts have a strong chemical interaction with nitrogen atoms, which results in great metal dispersion and outstanding activity. Large-scale application is, however, limited by their cost and scarcity, which has led to research into less expensive alternatives like Mo, which exhibits potential electrocatalytic performance (Sanetuntikul et al., 2018).

The Faraday efficiency (FE) of catalysts made of non-precious metals is low despite their low cost. Their superiority over d-orbital metallic catalysts for N_2 activation is due to their activation mechanism via sp hybrid orbitals, indicating their potential utility in ammonia synthesis studies (Singh et al., 2017). Metal-free catalysts have drawn interest lately, especially those made of carbon-based compounds doped with N and P. In nitrogen reduction processes (NRR), certain materials, like polymer carbon nitride with abundant N vacancies (PCN-NVs), have demonstrated potential in increasing ammonia yield and Faraday efficiency. PCN-NVs' networked structure facilitates excellent N_2 adsorption and activation; precision is ensured by isotope labelling. Focusing on exposed surfaces, researchers investigated Ni-based catalysts, such as nickel telluride (NiTe) nanocrystals (Zhang et al., 2017).

Dissociation and association are the two pathways that the NRR normally uses. On the catalyst surface, the dissociation pathway splits the N-N bond into isolated N atoms, which are then hydrogenated to create NH_3. Meanwhile, the association process includes distal, alternating, and enzymatic pathways, each involving various adsorption configurations of N_2 and sequential reduction to produce NH_3. In electrochemical systems, one of the main challenges is to activate the strong N-N bond (Chen et al., 2019). In order to address this, research has focused on creating catalysts that can cleave the N-N link, enabling a more effective synthesis of ammonia. NRR is generally represented using the following reaction formula:

$$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$$

Perovskite, a material well-known for its effectiveness in oxidation processes, and non-thermal plasma (NTP) were found to be viable agents for mildly oxidizing N_2. Using $LaFeO_3$ as a catalyst, N_2 and O_2 in NTP oxidize to form NOx, which then reacts with H_2O to generate NO_3^- and NO_2^-. Combining these findings led to a revolutionary method. Ultimately, NH_3 is reduced electrochemically from NO_x^- using a Cu/CuO catalyst. The plasma area's current density greatly enhanced in the presence of $LaFeO_3$, which improved N_2 and O_2 activation (Palma et al., 2020). Using theoretical estimates of the Gibbs free energy spectrum (ΔG) at 50°C and 1 atm, the involvement of $LaFeO_3$ in the atomic and molecular-level reaction process was further investigated. When $LaFeO_3$ was present on catalyst surfaces with oxygen, both oxygen-rich and oxygen-poor, the energy needed to activate N_2 was significantly lower than that of gaseous free radicals. With less energy used, this catalytic approach efficiently activates N_2, increasing NRR Faraday efficiency (Kembo et al., 2023).

In the quest for better options in electrocatalytic ammonia production, scientists are exploring nitrogen sources like NO_3^-, which offers excellent water solubility and lower bond energy than N≡N. While potentially lowering energy usage, NO_3^- electrocatalysis shows promise in addressing water contamination brought on by nitrogenous fertilisers and industrial wastewater discharge. There are several steps involved in the NO_3^- reduction process: first, NO3− adsorption on the catalyst surface, then reduction to intermediate NO_2 (Mou et al., 2021). This intermediate breaks down even more to produce NH_4^+ and NH_3, as well as OH^- in water:

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$$

However, NO_2's relatively large N–O bond energy poses challenges, limiting the overall reaction rate. Additionally, intermediate products like NO and N_2O may form by-products, reducing the reaction selectivity and leading to competing hydrogen evolution reactions. Researchers have focused on catalyst selection, structural alterations, and new catalyst development to enhance NO_3^- reduction selectivity and activity. Nonetheless, the comparatively high N–O bond energy of NO_2 presents difficulties, restricting the total reaction rate (Liang et al., 2023). Furthermore, byproducts such as NO and N_2O, which are intermediate products, might reduce the selectivity of the reaction and result in competing hydrogen evolution events. To improve NO_3^- reduction selectivity and activity, researchers have concentrated on catalyst selection, structural modifications, and the invention of novel catalysts (Zhang et al., 2016).

Table 2: Summary of recently reported catalysts for electrochemical NRR in aqueous electrolytes

Catalyst	Cell type, electrolyte	NH_3 yield	FE (%)	Potential (V *vs.* RHE)
Pd-TA	H-cell, 0.1 mol L^{-1} Na_2SO_4	24.12 μg h^{-1} $mg_{cat.}^{-1}$	9.49	−0.45
Ag/CPE	H-cell, 0.1 mol L^{-1} HCl	4.62×10^{-11} mol s^{-1} cm^{-2}	4.8	−0.6
Nb_2O_5/CC	H-cell, 0.1 mol L^{-1} Na_2SO_4	1.58×10^{-10} mol s^{-1} cm^{-2}	2.26	−0.6
$TiO_2/Ti_3C_2T_x$ MXene	H-cell, 0.1 mol L^{-1} Na_2SO_4	44.17 μg h^{-1} $mg_{cat.}^{-1}$	44.68	−0.95, −0.75
Mn_3O_4@rGO/CP	H-cell, 0.1 mol L^{-1} Na_2SO_4	17.4 μg h^{-1} $mg_{cat.}^{-1}$	3.52	−0.85
Cr_2O_3/CP	H-cell, 0.1 mol L^{-1} Na_2SO_4	25.3 μg h^{-1} $mg_{cat.}^{-1}$	6.78	−0.9
Fe-TiO_2/CP	H-cell, 0.5 mol L^{-1} $LiClO_4$	25.47 μg h^{-1} $mg_{cat.}^{-1}$	25.6	−0.4
Mn-TiO_2/CP	H-cell, 0.1 mol L^{-1} Na_2SO_4	20.05 μg h^{-1} $mg_{cat.}^{-1}$	11.93	−0.5
Cu-TiO_2/CP	H-cell, 0.5 mol L^{-1} $LiClO_4$	21.31 μg h^{-1} $mg_{cat.}^{-1}$	21.99	−0.55
B-TiO_2/CPE	H-cell, 0.1 mol L^{-1} Na_2SO_4	14.4 μg h^{-1} $mg_{cat.}^{-1}$	3.4	−0.8
C-TiO_2/CP	H-cell, 0.1 mol L^{-1} Na_2SO_4	16.22 μg h^{-1} $mg_{cat.}^{-1}$	1.84	−0.7
Fe_2O_3-rGO/CP	H-cell, 0.5 mol L^{-1} $LiClO_4$	22.13 μg h^{-1} $mg_{cat.}^{-1}$	5.89	−0.5
MoS_2/CC	H-cell, 0.1 mol L^{-1} Na_2SO_4	8.08×10^{-11} mol s^{-1} cm^{-2}	1.17	−0.5
MoS_2/C_3N_4	H-cell, 0.1 mol L^{-1} $LiClO_4$	18.5 μg h^{-1} mg^{-1}	17.8	−0.3
CuS-CPSs/CP	H-cell, 0.1 mol L^{-1} HCl	18.18 μg h^{-1} $mg_{cat.}^{-1}$	5.63	−0.15
MV-MoN@NC	H-cell, 0.1 mol L^{-1} HCl	76.9 μg h^{-1} $mg_{cat.}^{-1}$	6.9	−0.2

Mo_2N/GCE	H-cell, 0.1 mol L^{-1} HCl	78.4 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	4.5	−0.3
Mo_2C/C	H-cell, 0.5 mol L^{-1} Li_2SO_4	11.3 $\mu g\ h^{-1}\ mg_{Mo2C}^{-1}$	7.8	−0.3
Mo_3Fe_3C	H-cell, 0.1 mol L^{-1} Li_2SO_4	72.5 $\mu mol\ h^{-1}\ mg_{cat.}^{-1}$	27.0	−0.5
V_8C_7/C-CP	H-cell, 0.1 mol L^{-1} HCl	34.62 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	12.2	−0.4
VP/VF	H-cell, 0.1 mol L^{-1} HCl	8.35×10^{-11} mol s^{-1} cm^{-2}	22	0.0
CoP_3/CC	H-cell, 0.1 mol L^{-1} Na_2SO_4	3.61×10^{-11} mol s^{-1} cm^{-2}	11.94	−0.2
Cu_3P NRs	H-cell, 0.1 mol L^{-1} HCl	18.9 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	37.8	−0.2
Cu_3P-rGO/CP	H-cell, 0.1 mol L^{-1} HCl	26.38 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	10.11	−0.45
FeP_2-rGO/CP	H-cell, 0.5 mol L^{-1} $LiClO_4$	35.26 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	21.99	−0.4
Bi ND/CP	H-cell, 0.1 mol L^{-1} HCl	25.86 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	10.8	−0.6, −0.55
S-G/CP	H-cell, 0.1 mol L^{-1} HCl	27.3 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	11.5	−0.6, −0.5
d-FG/CP	H-cell, 0.1 mol L^{-1} Na_2SO_4	9.3 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	4.2	−0.7
BP/CP	H-cell, 0.1 mol L^{-1} HCl	26.42 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	12.7	−0.6
BNS/CP	H-cell, 0.1 mol L^{-1} Na_2SO_4	13.22 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	4.04	−0.8
B_4C/CPE	H-cell, 0.1 mol L^{-1} HCl	26.57 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	15.95	−0.75
h-BNNS/CP	H-cell, 0.1 mol L^{-1} HCl	22.4 $\mu g\ h^{-1}\ mg_{cat.}^{-1}$	4.7	−0.75

5. Prospects for the development of nonmetallic doped catalysts and key challenges of nitrate electrocatalytic reduction

The major worldwide issue of nitrate pollution, which endangers both human health and the ecosystem, has focused a lot of emphasis on the electrochemical reduction of nitrate to restore the nitrogen cycle. For nitrate reduction, a variety of electrocatalyst materials have been investigated, including non-metallic catalysts, noble metal catalysts, and non-noble metal catalysts (such as transition metal, transition metal compound, transition metal composite, and single-atom catalysts). Research has focused on the mechanisms and pathways of electrochemical nitrate reduction as well as the unwanted products (such nitrite and ammonium) that can be produced from them (Wang et al., 2023). Factors impacting the conversion and selectivity of electrochemical nitrate reduction, such as electrolyte design and electrode material structure, have also been explored.

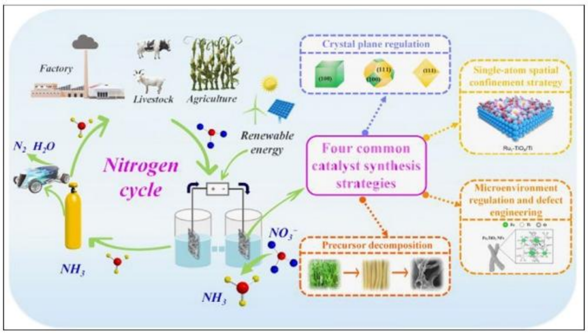

Fig 6: Nitrogen cycle and role of ammonia in different mechanisms

The commercialization process is hindered by several obstacles despite the progress made, such as low catalytic efficiency, competition from the hydrogen evolution reaction, and issues in breaking the N-N triple bond. The production of non-toxic nitrogen compounds can be achieved efficiently and under control thanks to recent advancements in non-noble metal electrocatalysts for nitrate reduction. One such catalyst is phosphorus-doped carbon nitride, which has a rich nitrogen vacancy and exhibits outstanding NRR catalytic activity. The investigation and creation of metal-free catalysts, such as carbon nitride doped with phosphorus, have enormous potential because of their cheaper prices, improved environmental friendliness, and decreased toxicity (Flores et al., 2022).

Ammonia and nitrogen gas, two non-toxic nitrogen compounds that can aid in the restoration of the nitrogen cycle, can be produced effectively and under control using electrochemical nitrate reduction. Full-scale water treatment systems may benefit from the use of nonmetallic doped catalysts in electrochemical nitrate reduction processes (Xu et al., 2022). In order to reduce nitrate pollution, nonmetallic doped catalysts can be utilized to efficiently and precisely synthesize non-toxic nitrogen compounds like nitrogen gas and ammonia. Nonmetallic doped catalysts are a good option for removing nitrate since they are affordable, safe for the environment, and devoid of harmful heavy metals. The nitrogen cycle, which is vital to the ecology and human health, can be restored through electrochemical nitrate reduction utilizing nonmetallic doped catalysts (Suriyaraj and Selvakumar, 2016).

The difficulties in increasing the use of nonmetallic doped catalysts in electrocatalytic nitrate reduction stem from the possibility that these catalysts' catalytic effectiveness is lower than that of noble metal catalysts, which may restrict their usefulness in large-scale nitrate reduction. In terms of kinetics, the hydrogen evolution reaction (HER) is preferable to the nitrate reduction reaction (NRR), which can have an adverse effect on the NRR's efficiency and lessen the generation of ammonia. Because nitrogen's N-N triple bond is tough to break, the NRR's effectiveness may be limited and ammonia output may be decreased. The optimization of catalyst design and performance may be limited by our incomplete understanding of the reaction processes and pathways involved in electrochemical nitrate reduction employing nonmetallic doped catalysts. For large-scale nitrate reduction to be a feasible application, nonmetallic doped catalysts must be stable and reasonably priced (Garcia-Segura et al., 2018).

Further research and development was necessary to optimize the design of nonmetallic doped catalysts, such as phosphorus-doped carbon nitride and sulfur-doped graphene, to improve their catalytic efficiency and selectivity for nitrate reduction. This was one way to address potential challenges in scaling up the use of nonmetallic doped catalysts in electrocatalytic reduction of nitrate. The creation of novel electrolytes can assist increase the efficiency and selectivity of nonmetallic doped catalysts for nitrate reduction. Integration of electrocatalytic nitrate reduction with other technologies, such as membrane separation and adsorption, can assist increase the efficiency and selectivity of the process. One difficulty that needs to be addressed is the scaling-up of nonmetallic doped catalysts for large-scale applications such as sewage treatment. In order to optimize catalyst design and performance, more study is required to better understand the reaction processes and pathways of electrochemical nitrate reduction employing nonmetallic doped catalysts.

Conclusion

A major advancement in sustainable catalysis has been made by the growing body of research on the electrocatalytic reduction of nitric acid to ammonia utilizing catalysts doped with nonmetallic elements. The development of these catalysts, which were informed by concepts including substrate doping, defect engineering, and lattice replacement, highlights the variety of approaches used to improve their efficiency. These catalysts, loaded with nonmetallic elements like boron (B), nitrogen (N), phosphorus (P), and sulphur (S), demonstrate a remarkable capacity for precise control over the nitrate electrocatalytic reduction process. The key to their effectiveness is the methodical control of different phases, with special attention to electron transport and adsorption. There's a lot of space for optimization with a focus on stability and scalability because to the flexibility of construction concepts. It will be essential to overcome obstacles in these areas if nonmetallic element-doped catalysts are to fulfil their promise of reducing nitrate pollution and revolutionizing the traditional ammonia production process. Essentially, the novel advances in this research have profound implications for solving environmental problems as well as for the scientific knowledge of catalysis. Catalysts doped with nonmetallic elements stand out as a symbol of sustainability, providing an effective and environmentally benign means of addressing nitrate contamination and changing the ammonia synthesis landscape.

Reference

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