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# Single-Atom Catalysts for C-N Coupling and Sustainable Catalysis: A Survey

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## Abstract

Single-atom catalysts (SACs) have emerged as a transformative force in heterogeneous catalysis due to their unparalleled atomic efficiency and enhanced catalytic performance. This survey paper explores the multifaceted role of SACs in advancing C-N coupling reactions, electrocatalytic urea synthesis, nitrogen reduction reactions (NRR), and carbon dioxide reduction, with a focus on sustainable catalysis. SACs maximize atom utilization, reduce reliance on precious metals, and offer unique coordination environments that enhance reaction efficiency and selectivity. Recent advancements highlight their potential in pharmaceuticals and advanced materials synthesis, leveraging dual photoredox/nickel-catalyzed C-N cross-couplings and renewable carbon catalysts. The paper delves into the mechanisms of electrocatalytic processes, emphasizing the integration of theoretical and experimental approaches to unravel SACs' complex mechanisms. The exploration of SACs in electrocatalytic urea synthesis underscores their contribution to improved reaction dynamics and stability. The challenges in NRR, primarily due to competitive hydrogen evolution reactions, are addressed through innovative SAC designs that enhance selectivity and efficiency. In CO<sub>2</sub> reduction, SACs offer promising solutions to mechanistic challenges, facilitated by advanced techniques like dynamic metastable dimer catalysis and 2D-conjugated metal-organic frameworks. The environmental and practical implications of SACs are profound, offering reduced environmental impact and enhanced catalyst stability. However, challenges in scaling and economic viability remain, necessitating further research into synthesis processes and theoretical models. This survey concludes that SACs hold significant potential to revolutionize sustainable catalysis, promoting efficient and environmentally friendly chemical production.

## 1 Introduction

### 1.1 Significance of Single-Atom Catalysts (SACs)

Single-atom catalysts (SACs) have emerged as a transformative force in heterogeneous catalysis, primarily due to their exceptional atomic efficiency and enhanced catalytic activity. By minimizing the use of precious metals, SACs offer a cost-effective alternative while maintaining high performance [1]. Their unique characteristics, such as atomic dispersion and specific coordination environments, significantly improve reaction efficiency and selectivity, addressing the limitations of traditional catalysts that often suffer from low atom utilization and high material costs [2, 3].

The stabilization of single metal atoms, exemplified by Rh on  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> surfaces, underscores the importance of SACs in sustaining catalytic activity, with OH ligands playing a crucial role in this stabilization [4]. SACs integrated into two-dimensional materials, like zirconium porphyrins (ZrPP), have shown improved activity and selectivity, particularly in nitrogen reduction reactions [5]. Furthermore, the adoption of advanced computational methods, such as the AutoRXN workflow, enhances research capabilities by facilitating extensive calculations without requiring deep computational expertise [6].

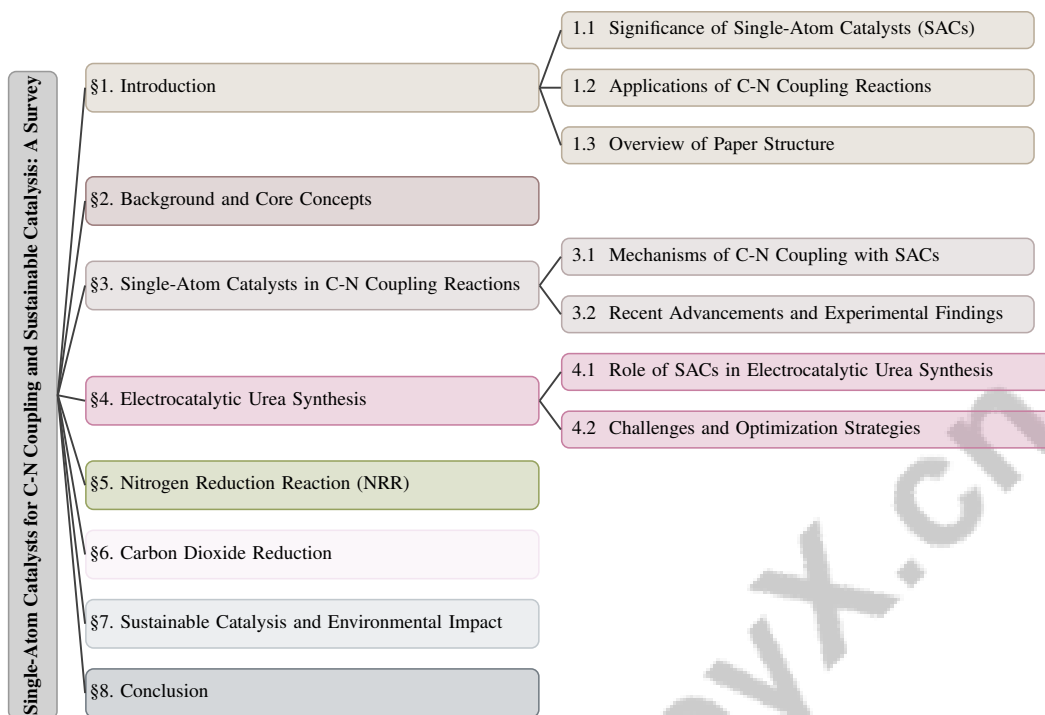


Figure 1: chapter structure

In electrochemical contexts, SACs like cobalt-nitrogen-carbon (Co–N–C) materials are pivotal in improving reaction efficiency and selectivity [7]. The interplay between spin states and catalytic activity in hydrogen evolution reactions (HER) reveals deeper insights into the mechanisms driving SAC performance [8]. Despite their potential, SACs are predominantly limited to small-molecule transformations, highlighting the need for advancements in catalyst technology to tackle more complex reactions [9]. This limitation emphasizes the urgency for innovative strategies to enhance catalyst efficiency, as illustrated in the context of lithium-sulphur (Li-S) batteries [10]. The ongoing development of SACs is crucial for advancing sustainable catalysis, providing innovative solutions to complex chemical processes and paving the way for more efficient catalytic systems [11].

## 1.2 Applications of C-N Coupling Reactions

C-N coupling reactions are integral to sustainable chemistry, serving as foundational processes for synthesizing various industrial and environmental compounds. Notably, Buchwald-Hartwig couplings, catalyzed by palladium complexes, facilitate the formation of critical C-N bonds essential for pharmaceuticals and advanced materials, thereby advancing medicinal chemistry and materials science. The integration of machine learning tools to predict optimal conditions and yields enhances the efficiency of these reactions, streamlining the discovery of novel compounds tailored for diverse applications [12, 13]. However, traditional methods face limitations due to the need for specific ligands and complex bond-forming steps, prompting the development of more efficient and recyclable catalytic systems.

Recent advancements have introduced dual photoredox/nickel-catalyzed C-N cross-couplings as effective alternatives to palladium-catalyzed reactions, yielding enhanced efficiency and selectivity [14]. These innovations are essential for overcoming the limitations of existing methodologies, which often rely on established literature and practices that may not accommodate novel reactant combinations [9].

In sustainable catalysis, carbon catalysts derived from renewable resources, such as Himalayan pine leaves, have been proposed for C-N coupling reactions in synthesizing pyrrole derivatives, illustrating the potential for incorporating renewable materials into catalytic processes [15]. Additionally, the use of transition-metal-based layered double hydroxides (TM-LDHs) nanosheets in electrocatalytic

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reactions underscores the significance of C-N coupling in sustainable chemistry, particularly for nitrogen reduction and urea oxidation [5].

A comprehensive understanding of the mechanisms underlying C-N coupling is vital for enhancing the efficiency of urea electrosynthesis, a process promising for sustainable chemical production [16]. Ongoing research into SACs highlights their potential across various catalytic reactions, especially in electrochemistry and photocatalysis, paving the way for more sustainable industrial processes.

### 1.3 Overview of Paper Structure

This paper is structured to provide an in-depth analysis of the pivotal role of single-atom catalysts (SACs) in facilitating C-N coupling reactions, emphasizing their unique properties such as high catalytic activity, selectivity, and stability, which have the potential to revolutionize sustainable catalysis through innovative synthesis techniques and enhanced reaction mechanisms [17, 9, 18]. The discussion commences with an introduction to the significance of SACs, detailing their advantages in catalysis, particularly in improving reaction efficiency and selectivity.

Subsequently, the applications of C-N coupling reactions are explored, underscoring their importance in industrial and environmental contexts. The background section elaborates on core concepts related to SACs, C-N coupling, and sustainable catalysis, providing definitions and discussing the role of SACs in C-N bond formation. A detailed examination of the mechanisms involved in electrocatalytic processes is presented, focusing on the influence of SACs on these reactions. Additionally, the relationship between SAC structure and catalytic activity is analyzed, highlighting key performance factors.

The paper further investigates the application of SACs in C-N coupling reactions, delving into specific mechanisms, efficiency, selectivity, and recent advancements. The following section addresses the critical role of SACs in the electrocatalytic synthesis of urea, emphasizing the mechanisms of C-N bond formation, challenges in improving electrosynthesis efficiency, and a review of recent studies utilizing advanced computational and experimental methodologies to tackle these challenges. This comprehensive examination reveals the importance of understanding the narrow potential window for C-N coupling and the dynamic interactions of reactants and solvents, which are crucial for optimizing electrochemical systems aimed at effective urea production [19, 20, 21, 22].

Subsequently, the application of SACs in nitrogen reduction reactions (NRR) is discussed, analyzing reaction pathways and summarizing recent research efforts. The section on carbon dioxide reduction explores the role of SACs in this process, detailing mechanisms, performance factors, and recent advancements. The environmental benefits of employing SACs in catalytic processes are evaluated, alongside challenges and future research directions.

The survey concludes by reflecting on the potential of SACs to transform C-N coupling and sustainable catalysis. A framework categorizing SACs based on their synthesis methods and applications is introduced, emphasizing the significance of single-atom dispersion for enhanced catalytic performance [17]. The following sections are organized as shown in Figure 1.

## 2 Background and Core Concepts

### 2.1 Mechanisms of Electrocatalytic Processes

Electrocatalytic processes are pivotal in sustainable catalysis, with single-atom catalysts (SACs) enhancing catalytic activity through their unique electronic properties and coordination environments [2]. The atomic dispersion of SACs forms distinct catalytic sites, boosting reaction efficiency and selectivity. The dynamic behavior of adatoms, particularly in nitrogen-rich environments, exemplifies the enhanced pathways facilitated by SACs [9].

Theoretical frameworks integrating surface science experiments, ab-initio calculations, and kinetic Monte Carlo simulations have been developed to elucidate interactions like those of Pt on ceria, providing insights into SAC stability and reactivity [11]. Advanced computational techniques, notably density functional theory (DFT) and machine learning (ML), are crucial for predicting and optimizing catalytic behaviors. ML approaches that leverage DFT calculations have been used to optimize lithium polysulphide (LiPS) binding energies on SACs, impacting electrocatalytic processes [10].

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Experimental methods such as mid-infrared and terahertz spectroscopy are essential for examining the effects of charged and neutral nanoparticles on hydration water properties, offering molecular-level insights into SAC interactions [23]. These findings are vital for validating theoretical predictions and enhancing our understanding of SAC mechanisms.

## 2.2 Structure-Activity Relationships in SACs

Understanding the relationship between SAC structure and catalytic activity is critical for optimizing performance in electrocatalytic applications. The spatial arrangement and interactions of metal atoms within SACs significantly influence their catalytic properties. For instance, the distance between Fe and Co SACs impacts their catalytic activities, offering insights for optimizing interatomic distances [24].

Advanced characterization techniques are crucial for elucidating these structure-activity relationships. An integrated nanophotonic-electrochemical SEIRAS platform enhances molecular signal detection during electrochemical experiments, facilitating SAC structure optimization [25].

The complexity of correlating downsized M-N<sub>x</sub> architectures with macrostructures of entire catalysts underscores the challenges in optimizing SAC performance [26]. Comprehensive understanding of these structural nuances is necessary for improving catalytic activity.

Innovative computational strategies, combining first-principles modeling and symbolic regression, have been employed to design SACs on Mo<sub>2</sub>CO<sub>2</sub> MXenes, enhancing their electrocatalytic performance for the oxygen evolution reaction (OER) [27]. These methodologies enable precise tuning of SAC structures to achieve desired catalytic outcomes.

The significance of rate-determining steps (RDS) in M-N-C catalyst reaction mechanisms is crucial for understanding structure-activity relationships [28]. Identifying and optimizing these RDS can lead to substantial improvements in catalytic efficiency.

Moreover, the stability and activity of SACs are influenced by their support structures. Graphene with a single vacancy serves as an effective support for SACs, preventing aggregation and enhancing catalytic activity under harsh conditions [29]. Selecting appropriate support materials is crucial for maintaining SAC stability and performance.

Variability in binding energy predictions due to different initial structures and optimization methods illustrates the complexity of accurately predicting SAC performance [10]. Incorporating uncertainty in adsorption energies can enhance the accuracy of predicted reaction mechanisms, refining our understanding of SAC structure-activity relationships [30].

A nuanced understanding of the interplay between SAC structures and their catalytic performance is essential for advancing the design of more efficient, selective, and stable catalysts, enhancing their applicability in renewable energy and environmental sustainability [17, 18, 20, 31, 16]. By leveraging advanced characterization techniques, computational models, and strategic support materials, researchers can optimize SAC designs to meet the demands of sustainable catalysis.

In recent years, the development of single-atom catalysts (SACs) has garnered significant attention due to their potential to enhance catalytic efficiency in various chemical reactions. A comprehensive understanding of the mechanisms involved is crucial for optimizing their performance, particularly in carbon-nitrogen (C-N) coupling reactions. As illustrated in Figure 2, the hierarchical structure of SACs in C-N coupling reactions is depicted, highlighting key mechanisms and recent advancements in the field. At the top level, the figure categorizes the mechanisms of C-N coupling with SACs, focusing on critical aspects such as catalytic performance, active sites, stability, and computational techniques. The second category emphasizes recent advancements and experimental findings, detailing innovative methodologies, structural dynamics, and the current challenges and breakthroughs faced by researchers. This structured overview underscores the interplay of experimental and theoretical approaches that are integral to advancing SACs for efficient and sustainable chemical syntheses.

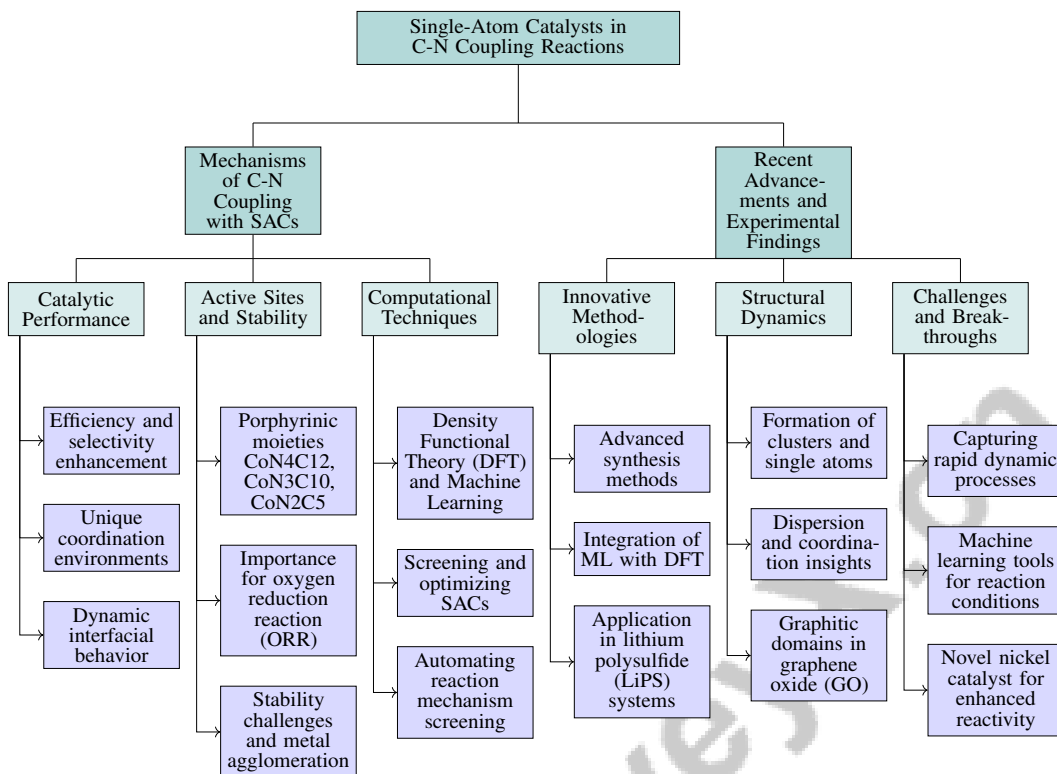


Figure 2: This figure illustrates the hierarchical structure of single-atom catalysts (SACs) in C-N coupling reactions, highlighting key mechanisms and recent advancements. The top level categorizes the mechanisms of C-N coupling with SACs, focusing on catalytic performance, active sites, stability, and computational techniques. The second category emphasizes recent advancements and experimental findings, detailing innovative methodologies, structural dynamics, and current challenges and breakthroughs. This structured overview underscores the interplay of experimental and theoretical approaches in advancing SACs for efficient and sustainable chemical syntheses.

### 3 Single-Atom Catalysts in C-N Coupling Reactions

#### 3.1 Mechanisms of C-N Coupling with SACs

Single-atom catalysts (SACs) enhance the efficiency and selectivity of carbon-nitrogen (C-N) coupling reactions, crucial for synthesizing pharmaceuticals and advanced materials. Their unique coordination environments enable mechanistic pathways unavailable to traditional catalysts. The dynamic interfacial behavior of SACs, such as nickel, is pivotal in improving catalytic performance in C-C and C-N bond formations [9]. The co-adsorption of water with rhodium adatoms forms stable  $\text{Rh}(\text{OH})_x$  complexes, mitigating sintering and sustaining catalytic activity [4].

Active sites like porphyritic moieties  $\text{CoN}_4\text{C}_{12}$ ,  $\text{CoN}_3\text{C}_{10}$ , and  $\text{CoN}_2\text{C}_5$  within Co-N-C materials illuminate SACs' mechanisms in promoting C-N coupling reactions [7]. These sites are critical for the oxygen reduction reaction (ORR), sharing mechanistic similarities with C-N coupling processes. Theoretical calculations of binding energies and adsorption configurations further clarify SACs' facilitation of Cr(VI) reduction, highlighting the importance of their electronic and structural properties [2].

Maximizing SAC performance involves addressing challenges such as stability during reactions and preventing metal agglomeration [16]. The innovative use of main-group metals as active centers for SACs, alongside nonmetal and transition-metal atoms, offers promising prospects for enhancing C-N coupling reactions [3]. Modified graphene surfaces as SAC supports improve stability and reactivity compared to conventional supports [29].

Advanced computational techniques, integrating density functional theory (DFT) and machine learning, are crucial for screening and optimizing SACs in nitrogen reduction reactions, which share mechanistic pathways with C-N coupling [32]. Automating reaction mechanism screening via cloud-based platforms enables extensive quantum chemical calculations, providing a comprehensive understanding of SAC-catalyzed processes [6].

The intricate mechanisms by which SACs facilitate C-N coupling involve advanced computational techniques, innovative catalytic strategies, and strategic material design. These include employing machine learning to optimize reaction conditions and identifying key precursors in electrocatalytic processes, enhancing the efficiency of critical transformations such as urea production and Buchwald-Hartwig couplings [12, 19, 32]. Collectively, these approaches deepen the understanding of C-N coupling processes, paving the way for more sustainable and efficient chemical syntheses.

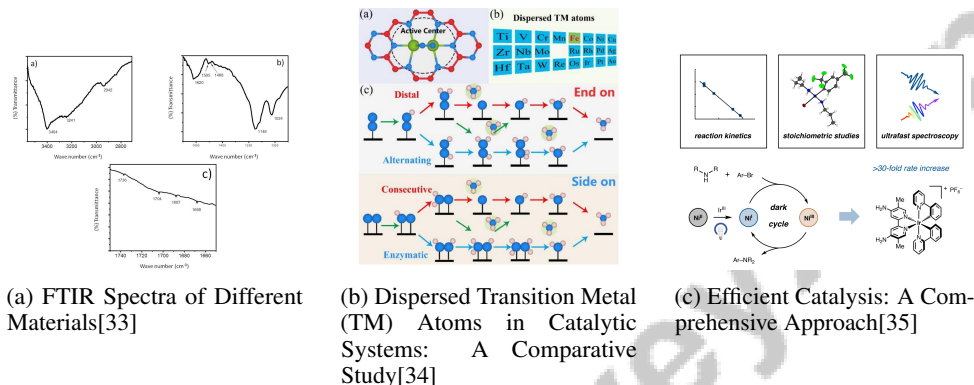


Figure 3: Examples of Mechanisms of C-N Coupling with SACs

As illustrated in Figure 3, the study of SACs in C-N coupling reactions offers insights into atomic-level catalysis mechanisms. FTIR spectra of various materials reveal vibrational characteristics crucial for understanding SAC-substrate interactions, providing foundational data on the molecular environments of these reactions. Examining dispersed transition metal (TM) atoms in catalytic systems offers a comparative perspective on how different dispersion methods—such as distal and end-on—impact SAC catalytic activity and stability, emphasizing atomic dispersion's role in optimizing performance. Lastly, the comprehensive approach to efficient catalysis highlights Ni(II)-catalyzed Ar-NR<sub>2</sub> reactions, showcasing methodologies that enhance catalytic efficiency through detailed reaction kinetics and mechanistic studies. Together, these examples underscore the interplay of spectroscopy, atomic dispersion, and kinetic analysis in advancing our understanding of SACs in C-N coupling reactions [33, 34, 35].

### 3.2 Recent Advancements and Experimental Findings

Recent advancements in SACs for C-N coupling reactions have led to significant improvements in catalytic efficiency and selectivity, driven by innovative experimental methodologies and theoretical insights. As illustrated in Figure 4, these advancements can be categorized into experimental methodologies, theoretical insights, and challenges with future directions. Advanced synthesis methods have been crucial for achieving high-performance SACs, optimizing their catalytic mechanisms across various processes [17]. Integrating machine learning (ML) techniques with DFT has enhanced the predictive accuracy of binding energies, exemplified by their application in lithium polysulfide (LiPS) systems [10]. This synergy underscores the potential of computational tools to enhance SAC performance in C-N coupling reactions.

The combination of DFT and ML frameworks has been vital in the rational design of nitrogen reduction reaction (NRR) SACs, emphasizing the significance of unpaired d electrons and charge transfer from transition metals (TMs) in enhancing NRR activity [32]. These findings suggest that similar strategies could optimize SACs for C-N coupling, improving their catalytic efficacy.

Experimental investigations have revealed the structural dynamics of SACs, including the formation of clusters and single atoms in systems involving Pt, Ni, Rh, and Ir [36]. Insights into the dispersion and coordination of single atoms are essential for designing catalysts with enhanced performance

characteristics. Additionally, exploring graphitic domains in graphene oxide (GO) has shown that thermal treatment can enhance GO properties without significant functionality loss, which is crucial for supporting SACs in C-N coupling applications [37].

Despite these advancements, challenges persist in capturing rapid dynamic processes and achieving high temporal resolution in electrochemical reactions [38]. Addressing these limitations is vital for a deeper understanding of SAC dynamics during C-N coupling processes.

Recent advancements in SACs for C-N coupling reactions highlight the intricate relationship between empirical research and theoretical modeling. Breakthroughs include developing machine learning tools to predict optimal reaction conditions for Buchwald-Hartwig couplings and first-principles simulations elucidating SAC reaction dynamics, particularly a novel nickel catalyst demonstrating enhanced reactivity and selectivity. These innovations not only enhance our understanding of C-N bond formation under various conditions, including electrocatalytic processes, but also pave the way for more efficient synthetic methodologies in organic chemistry [12, 19, 9]. Continued exploration and development in this field promise to revolutionize sustainable catalysis and expand the potential for innovative chemical syntheses.

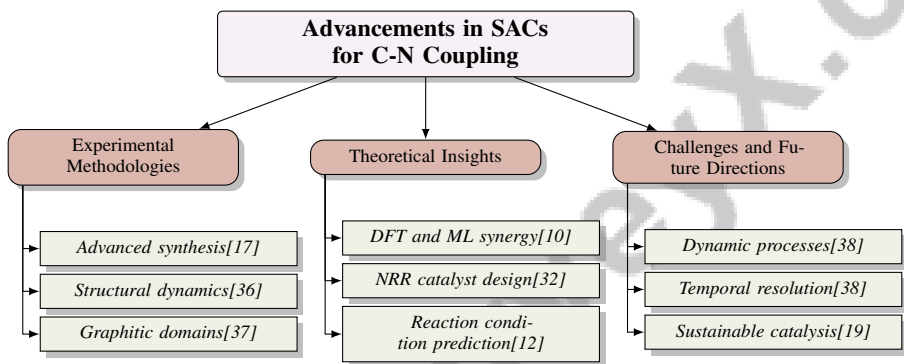


Figure 4: This figure illustrates the recent advancements in single-atom catalysts (SACs) for C-N coupling reactions, categorizing them into experimental methodologies, theoretical insights, and challenges with future directions. It highlights key experimental methods such as advanced synthesis, structural dynamics, and graphitic domain exploration. Theoretical insights include the synergy between DFT and ML, NRR catalyst design, and prediction of reaction conditions. The challenges and future directions focus on understanding dynamic processes, improving temporal resolution, and pursuing sustainable catalysis.

## 4 Electrocatalytic Urea Synthesis

### 4.1 Role of SACs in Electrocatalytic Urea Synthesis

Single-atom catalysts (SACs) are instrumental in enhancing the efficiency and sustainability of electrocatalytic urea synthesis due to their unique structural and electronic attributes that optimize catalytic interactions. The precise exposure of active sites in SACs, particularly within transition metal-nitrogen-carbon (TM-N-C) frameworks, facilitates effective electron transfer [16]. This is exemplified by manganese SACs, which utilize dual-coordination methods to enhance electronic properties for CO<sub>2</sub> reduction [39]. Advanced support structures, such as graphene with single vacancies, further bolster SAC stability and activity, crucial for hydrogen evolution reactions [29], supported by covalent metal-support interactions [16]. Dynamic synthesis of nickel-nitrogen catalysts with axial oxygen ligands showcases SAC adaptability in optimizing CO<sub>2</sub> reduction reaction dynamics [40].

Cobalt-based SACs demonstrate weaker binding to oxygen intermediates than iron-based counterparts, facilitating favorable reaction pathways for urea synthesis [7]. Additionally, modulation of spin states in transition metal-doped PtN<sub>2</sub> monolayers underscores the importance of electronic structure in optimizing hydrogen adsorption characteristics [8]. Strategic control of redox conditions, such as those applied to Pt nanoparticles on ceria substrates, enhances size and stability management,



optimizing catalytic performance [11]. The Ni SAC approach extends catalytic applications, enabling reactions previously challenging for traditional catalysts [9].

SACs also significantly contribute to nitrogen reduction reactions (NRR), as demonstrated by Ru-dimer decorated GeSe, which enhances nitrogen activation [41]. Furthermore, the hydration properties of nanoparticles provide insights into charge effects on water dynamics, essential for optimizing catalytic performance [23].

To visualize the interconnections among these concepts, Figure 5 illustrates the hierarchical categorization of key concepts related to electrocatalytic urea synthesis, highlighting the roles of single-atom catalysts, cobalt and nickel catalysts, and nitrogen reduction reactions. Each category is supported by specific research studies that contribute to the understanding and advancement of catalytic efficiency and sustainability. The strategic design and application of SACs, supported by advanced characterization techniques and computational models, significantly enhance the efficiency and sustainability of electrocatalytic urea synthesis. Innovations in metal single-atom-site technology and high-throughput computational methods promise to transform industrial chemical processes, improving catalytic efficiency and selectivity to foster greener chemical production, crucial for reducing reliance on fossil fuels and minimizing environmental impact [42, 13, 43, 44, 16].

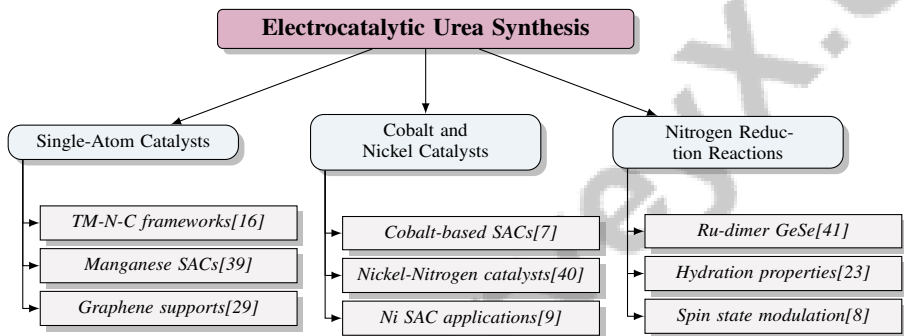


Figure 5: This figure illustrates the hierarchical categorization of key concepts related to electrocatalytic urea synthesis, highlighting the roles of single-atom catalysts, cobalt and nickel catalysts, and nitrogen reduction reactions. Each category is supported by specific research studies that contribute to the understanding and advancement of catalytic efficiency and sustainability.

## 4.2 Challenges and Optimization Strategies

The electrocatalytic synthesis of urea using SACs faces challenges that must be addressed to optimize performance and scalability. A primary issue is the complexity in optimizing multiple steps within the reaction pathway, complicating the tuning of overpotential for specific catalysts [27]. This complexity is compounded by the lack of systematic guidance for catalyst design, as current theoretical models often fail to capture the intricate pH-dependent catalytic behaviors observed in practical applications [28].

The synthesis and scalability of SACs also present significant hurdles. For instance, while Fe<sub>2</sub>/g-CN exhibits superior catalytic performance with high Faradaic efficiency and low energy costs for nitrogen reduction, scaling this synthesis method for industrial applications remains challenging. The potential detachment of axial oxygen atoms during prolonged use, observed in certain dynamic synthesis methods, can affect the stability and performance of SACs, highlighting the need for improved material durability [40]. Computational limitations further complicate accurate modeling of the solvent's role in reaction mechanisms, critical in proton-transfer processes where the solvent acts as a catalytic participant [45]. Moreover, the demand for lower energy requirements and higher selectivity in NRR compared to traditional methods necessitates exploration of novel approaches, such as the TM-TCNQ method, which offers significant advantages [46].

Future research should prioritize optimizing synthesis processes and exploring other transition metals or combinations to enhance SAC performance [47]. Investigating the experimental synthesis of novel materials, such as tile germanene, and developing methods to enhance their stability and performance in practical applications are crucial areas for further exploration [48]. Addressing the challenges in electrocatalytic urea synthesis requires a multifaceted approach integrating advanced computational



models, innovative synthesis techniques, and strategic material design. Overcoming existing challenges in catalytic efficiency, selectivity, and stability of SACs is essential to unlocking their full potential for transforming sustainable chemical production processes, such as the electrochemical reduction of nitrogen to ammonia and the conversion of carbon dioxide into valuable chemicals and fuels, crucial for advancing the chemical industry towards greener practices and achieving carbon neutrality [42, 49, 16].

## 5 Nitrogen Reduction Reaction (NRR)

### 5.1 Challenges in NRR and Role of SACs

The nitrogen reduction reaction (NRR) in electrocatalytic ammonia synthesis faces formidable challenges, primarily due to the complex charge injection required to activate the N-N bond. This difficulty results in low Faraday efficiency and a predisposition for catalysts to favor the hydrogen evolution reaction (HER) over NRR, thus limiting ammonia production [32]. The inherent inertness of nitrogen and its low solubility in aqueous solvents further complicate the catalytic process, necessitating innovative strategies for effective N-N bond cleavage [41]. The competitive nature of HER with NRR underscores the need for catalysts that can preferentially enhance ammonia yields.

Single-atom catalysts (SACs) present a promising solution by offering unique, tunable active sites that enhance NRR performance. Their atomic dispersion allows for effective management of adsorption behaviors, facilitating better nitrogen activation and reduction processes [21]. By promoting a selective pathway for NRR over HER, SACs can significantly improve reaction efficiency and selectivity [5]. Moreover, SACs advance the understanding of active-site structures, particularly in Co-N-C materials, optimizing their catalytic performance [7]. The integration of advanced computational models with experimental techniques enables the design of SACs with enhanced activity and stability, addressing the limitations of traditional catalysts [50].

### 5.2 Innovative Catalyst Designs

Method Name	Catalyst Composition	Performance Enhancement	Methodological Approaches
Fe2/g-CN[34]	Fefe Dual-atom	Defect Engineering	High-throughput Screening
Ru2@GeSe[41]	RU Dimer	State Hybridization	Electrochemical Conditions

Table 1: Overview of catalyst compositions, performance enhancements, and methodological approaches used in recent innovative catalyst designs for nitrogen reduction reactions. The table highlights dual-atom catalyst configurations and the role of defect engineering and state hybridization in enhancing catalytic efficiency.

Recent advancements in catalyst design have significantly enhanced the performance of single-atom catalysts (SACs) in nitrogen reduction reactions (NRR), driven by strategies that optimize active sites and boost catalytic efficiency. The use of ionic liquids (ILs) has been shown to stabilize intermediates and facilitate electron transfer, creating a favorable environment for nitrogen adsorption and activation [51]. Table 1 provides a detailed overview of the innovative catalyst designs, focusing on catalyst compositions, performance enhancements, and methodological approaches that have been recently developed to improve nitrogen reduction reactions.

The construction of dual-atom catalysts, such as Fe2/g-CN, leverages the synergistic properties of transition metal pairs on heterogeneous substrates to effectively capture and convert nitrogen [34]. This configuration enhances electron sharing and cooperative interactions, improving nitrogen activation and reduction capabilities.

Defect engineering and doping in nanocarbon materials offer further opportunities for enhancing NRR performance. Interactions between nanocarbon and metal-oxide nanoparticles generate active sites with tailored electronic properties, facilitating efficient catalytic processes [52]. Additionally, employing transition metal atoms like Sc and Ti on tetracyanoquinodimethane (TCNQ) monolayers capitalizes on the strong interactions between metal atoms and the TCNQ support to enhance catalytic site stability and activity [46].

Combining Ru dimers with GeSe has demonstrated superior catalytic activity by facilitating efficient state hybridization and N2 bond activation compared to traditional methods [41]. These innovative

designs highlight the importance of strategic material engineering and the exploration of new catalytic frameworks to advance sustainable nitrogen reduction. Employing methodologies such as high-throughput screening and tailored atomic structures, researchers are making substantial progress in developing catalysts that enhance selectivity and efficiency in NRR while improving stability. For example, the innovative design of Fe-Fe dual atom sites on graphite carbon nitride has achieved a Faradic efficiency of 100

## 6 Carbon Dioxide Reduction

The imperative to curtail carbon emissions has intensified research into carbon dioxide (CO<sub>2</sub>) reduction technologies, with single-atom catalysts (SACs) at the forefront. This section delves into the challenges and mechanistic insights of CO<sub>2</sub> reduction, underscoring the necessity for a profound understanding of the underlying mechanisms to enhance catalytic performance and surmount barriers to efficient CO<sub>2</sub> conversion. The discussion addresses the complexities of the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) and spotlights innovative strategies devised to tackle these challenges.

### 6.1 Mechanistic Insights and Challenges

Single-atom catalysts (SACs) for CO<sub>2</sub> reduction face several mechanistic obstacles that hinder the development of efficient catalytic systems. A major challenge is the sluggish kinetics of CO<sub>2</sub>RR, complicating the conversion and selectivity of desired products [40]. The slow activation of stable CO<sub>2</sub> into the CO<sub>2</sub> radical ion significantly hampers reaction efficiency, often leading to low Faraday efficiency and undesirable by-products [40]. Understanding SACs' electronic structure is crucial for optimizing CO<sub>2</sub> reduction. Nitrogen oxides like NO and NO<sub>2</sub> exacerbate CO<sub>2</sub> electroreduction, requiring more electrons for reduction than CO<sub>2</sub> and affecting efficiency [53]. Modeling excitonic effects using methods such as the Bethe-Salpeter formalism presents computational challenges, complicating their integration into materials discovery [54].

Recent advancements like the Dynamic Metastable Dimer Catalysis method, employing (PtCO)<sub>2</sub> dimers in non-equilibrium configurations, have shown promise in overcoming these challenges by reducing the energy barrier for oxygen extraction and enhancing catalytic activity and selectivity [55]. The Re-Bpy-sp<sup>2</sup> c-COF method demonstrates improved light absorption and stability due to its crystalline structure, facilitating efficient charge separation and transfer during photocatalysis [56]. Innovative reactor designs, such as vapor-fed electrochemical reactors, increase CO<sub>2</sub> concentration at the electrode-catalyst surface, improving the electrochemical reduction process [57]. This design optimizes CO<sub>2</sub> and SAC interactions, promoting efficient catalytic processes. Furthermore, CO<sub>2</sub>'s role as a Lewis acid in bicarbonate mechanisms enhances selectivity for CO production [58].

To effectively address CO<sub>2</sub> reduction's mechanistic challenges using SACs, a thorough understanding of electronic structures and reaction pathways is essential, as this knowledge is vital for optimizing catalyst performance and selectivity in electrocatalytic processes [59, 60, 20, 22, 49]. By leveraging advanced catalytic methods and innovative reactor designs, researchers can develop more efficient and sustainable catalytic systems for CO<sub>2</sub> reduction.

### 6.2 Advanced Techniques and Innovations

Recent advancements in single-atom catalysts (SACs) design and application for CO<sub>2</sub> reduction have been significantly influenced by innovative techniques and frameworks that enhance catalytic efficiency and selectivity. The dynamic interaction of SACs with CO<sub>2</sub> and resulting intermediates is pivotal in advancing CO<sub>2</sub> reduction technologies. Copper-complex materials undergoing reversible structural changes have demonstrated enhanced catalytic activity for CO<sub>2</sub> reduction, underscoring the potential of adaptive catalyst structures [61]. This adaptability is crucial for optimizing reaction pathways and improving catalytic performance.

Exploring 2D -conjugated metal-organic frameworks (MOFs) as electrocatalysts for CO<sub>2</sub>RR represents a promising strategy, leveraging their tunable pore sizes and compositional structures to enhance product selectivity [62]. These frameworks provide a versatile platform for tailoring catalytic properties to specific reaction conditions, thus improving CO<sub>2</sub> reduction processes' efficiency and selectivity. In situ techniques, such as surface-enhanced infrared absorption spectroscopy (SEIRAS), have emerged as powerful tools for elucidating reaction pathways and determining metal catalysts'

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affinities for various intermediates [53]. By offering detailed insights into catalyst-intermediate interactions, SEIRAS plays a crucial role in SAC design, enabling precise tuning of catalyst properties to enhance selectivity and efficiency.

Manganese-based catalysts, such as the (Cl, N)-Mn/G catalyst, have achieved remarkable performance metrics, including a maximum CO faradaic efficiency of 97

These advanced techniques and innovative approaches underscore SACs' potential to revolutionize CO<sub>2</sub> reduction technologies, paving the way for more efficient and sustainable catalytic systems. By employing methodologies such as electro-redeposition and operando characterization techniques, researchers can enhance catalyst design for CO<sub>2</sub> reduction, leading to significant improvements in selectivity for desired products, overall efficiency, and long-term stability. These innovations facilitate precise control over catalyst morphology and oxidation states, while providing valuable insights into the reaction mechanisms and surface interactions dictating performance under real-world conditions [59, 44, 49].

## 7 Sustainable Catalysis and Environmental Impact

### 7.1 Environmental and Practical Implications

Single-atom catalysts (SACs) mark a significant advancement in sustainable catalysis, offering environmental and practical benefits by enhancing catalytic activity and selectivity while reducing reliance on precious metals [63]. This reduction in resource consumption mitigates environmental impacts, as demonstrated by their effective application in Cr(VI) reduction to diminish toxic pollutants [2]. SACs also tackle traditional catalyst challenges like sintering and stability through advanced designs that improve resilience in practical applications [11]. The integration of excitonic effects in material discovery has led to the identification of photocatalysts for visible light CO<sub>2</sub> reduction, underscoring their role in efficient CO<sub>2</sub> conversion and sustainability.

SACs improve catalyst utilization and stability, fostering the development of efficient catalytic systems without conventional drawbacks [29]. Machine learning has further enhanced SAC design, as seen in advancements in Li-S battery designs, which have implications for sustainable energy storage [10]. Despite these advantages, challenges remain in large-scale SAC synthesis and understanding the complex mechanisms of CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR) [62]. Innovative approaches and strategic material design are crucial for maximizing SACs' environmental and practical benefits.

SACs have the potential to revolutionize sustainable catalysis by minimizing the environmental footprint of chemical processes and enhancing scalability and efficiency in catalytic applications. Their unique properties and advanced design methodologies can significantly improve sustainable chemical production and energy conversion technologies, particularly in electrocatalytic CO<sub>2</sub> reduction and high-performance lithium-sulfur batteries, where optimized reaction mechanisms and material design can lead to enhanced efficiency [10, 49, 16, 13].

### 7.2 Challenges in Scaling and Economic Viability

The scaling and economic viability of SACs present significant challenges for widespread industrial adoption. Capturing dynamic changes in catalyst states and intricate pathways in processes like CO<sub>2</sub> reduction is essential for optimizing SAC performance, yet current methodologies often struggle with reproducibility and consistency, critical for commercial-scale synthesis [41]. Economic feasibility is further challenged by the extensive optimization required for experimental conditions, including exploring additional metal catalysts and refining theoretical models to enhance predictability and performance [10].

Large-scale SAC synthesis faces limitations in substrate scope and economic constraints due to high production costs. Specific environmental conditions, such as visible light activation for photocatalysts, may restrict their practical use in various industrial settings. This limitation is critical, as photocatalytic processes like CO<sub>2</sub> conversion to fuels depend heavily on precise light conditions, as demonstrated by advancements in covalent organic frameworks that enhance photocatalytic efficiency under visible light [64, 53, 56, 13]. Catalyst activation efficiency in these scenarios is crucial for broader SAC applications, necessitating innovative solutions to overcome these limitations.

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Future research should focus on optimizing synthesis processes for various transition metals and exploring doping elements to enhance catalytic performance. Comprehensive investigations into the role of ionic liquids (ILs) in nitrogen reduction reactions (NRR) and the influence of solvent environments on CO<sub>2</sub> capture are essential, as these factors can substantially improve the sustainability of ammonia production and CO<sub>2</sub> mitigation processes [21, 51]. Enhancing catalyst design and electron transfer rates, particularly in CO<sub>2</sub> reduction reactions, is vital for improving the economic viability of SACs.

Further exploration of the electro-redeposition process, long-term catalyst stability, and scalability for industrial applications is essential. Some methods' reliance on specific temperature conditions to access metastable states may not be universally applicable across different catalytic systems. Enhancing energy storage technologies, especially Li-S batteries, requires prioritizing the optimization of symbolic regression models for predicting catalyst performance, investigating a broader range of transition metals for suitable SACs, and assessing the scalability of these catalysts for practical industrial applications [10, 12, 16]. Extending methodologies to other multi-electron reactions and refining uncertainty quantification processes are also critical areas for future research.

The practical implementation of SACs encounters significant challenges, particularly regarding their effectiveness in real-world applications. Further experimental validation is crucial to confirm theoretical predictions associated with their performance in catalyzing reactions such as Li-polysulphide adsorption, which is vital for enhancing lithium-sulfur battery efficiency [10, 12, 13, 65]. The accuracy of electronic structure models impacts the reliability of explored reaction pathways, with current studies often lacking rigorous controls and reproducibility, leading to uncertainty in reported yields. Additionally, the limitations of Tafel analysis in uniquely identifying mechanisms and the influence of mass transport limitations on observed Tafel slopes must be addressed.

## 8 Conclusion

The exploration of single-atom catalysts (SACs) underscores their pivotal role in advancing C-N coupling and sustainable catalysis. Innovations in SAC design have notably enhanced nitrogen reduction reactions, leading to improved ammonia production and Faradaic efficiencies. The development of automated systems like AutoEIS has expedited research in electrochemical materials, crucial for the evolution of sustainable catalytic processes. Future research should prioritize optimizing reaction conditions and broadening substrate scopes to maximize SAC applicability. The design of durable active sites, especially for materials on the strong binding side of the activity volcano, is essential to enhance both catalytic activity and selectivity in ammonia synthesis. Investigating kinetic isotope effects using ultrapure deuterated electrolytes in alkaline environments is vital for obtaining precise electrocatalytic measurements. Advanced operando spectroscopic and computational techniques are key to unraveling electrocatalytic processes, particularly in CO<sub>2</sub> reduction. The bridge-adsorbed oxygen mechanism has improved oxygen reduction reaction performance in weak-binding M-N-C SACs, suggesting promising future directions for catalyst development. Additionally, the need for rapid measurement techniques in single-entity electrochemistry is paramount to support advanced catalytic systems. Enhancing high-throughput workflows and integrating property calculations could extend the reach of SACs across various chemical systems, reinforcing their importance in sustainable catalysis. Future initiatives should also focus on modifying the carbon matrix around cobalt moieties to optimize oxygen binding energy and enhance performance in diverse electrochemical reactions. These advancements position SACs to significantly advance the field of catalysis, offering innovative solutions for more efficient and sustainable chemical processes.

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