

Single-Atom Catalysts for Clean Energy

Ashok Kulkarni¹, Pooja Joshi²

Associate Professor¹, Students²

Department of Chemical Sciences

Eastern Plateau University, India

Email ID : Ashokkulkarni242@yahoo.com¹, pooja15.joshi@gmail.com¹

Abstract

Single-atom catalysts (SACs) have emerged as a new frontier in heterogeneous catalysis and are attracting strong attention for clean energy applications. In SACs, isolated metal atoms are anchored on suitable supports, combining the advantages of homogeneous and heterogeneous catalysis. The unique electronic structure, maximum atom utilization, and tunable coordination environment make SACs promising for energy-related reactions such as hydrogen evolution, oxygen reduction, oxygen evolution, CO₂ reduction, and nitrogen fixation. This review discusses the fundamental concepts of single-atom catalysis, synthesis strategies, characterization techniques, and structure–performance relationships. Recent advances in SACs for clean energy conversion and storage are critically analyzed, highlighting both achievements and limitations. Challenges related to stability, scalability, and realistic operating conditions are also discussed. Finally, future perspectives on the rational design of SACs for sustainable energy technologies are provided. Overall, single-atom catalysis offers a viable pathway toward high-efficiency and low-cost catalysts for next-generation clean energy systems.

Keywords: *Single-atom catalysts, clean energy, electrocatalysis, hydrogen evolution, CO₂ reduction, sustainable catalysis*

INTRODUCTION

The increasing global demand for energy, combined with growing concerns over climate change and environmental pollution, has accelerated the search for clean and sustainable energy technologies. Renewable energy sources such as solar, wind, and biomass are central to this transition, but efficient energy conversion and storage systems are equally critical. Catalysis plays a key role in enabling many clean energy processes, including fuel cells, electrolyzers, and artificial photosynthesis systems.

Traditional heterogeneous catalysts often rely on metal nanoparticles, where only surface atoms actively participate in catalytic reactions. A large fraction of metal atoms remain buried inside the particles and do not contribute to catalysis, leading to low atom utilization and high material costs, especially for noble metals. Homogeneous catalysts, on the other hand, offer high activity and selectivity but suffer from poor stability and difficult separation. Single-atom catalysts (SACs) bridge this gap by dispersing individual metal atoms on solid supports, providing isolated active sites with uniform coordination environments.

The concept of single-atom catalysis was proposed several decades ago, but practical realization became possible only with advances in synthesis and characterization techniques. The development of aberration-corrected transmission electron microscopy (AC-TEM), X-ray absorption spectroscopy (XAS), and scanning tunneling microscopy (STM) has enabled direct observation of isolated atoms on supports. As a result, SACs have rapidly evolved from a scientific curiosity to a practical catalyst platform.

In the context of clean energy, SACs are particularly attractive because they allow precise tuning of active sites to favor desired reaction pathways while minimizing side reactions. This review focuses on the role of SACs in clean energy applications, emphasizing design principles, synthesis routes, and catalytic performance. The discussion aims to provide a balanced overview, acknowledging both progress and remaining challenges.

Fundamentals of Single-Atom Catalysts

Single-atom catalysts (SACs) are defined as catalytic systems in which metal atoms are atomically dispersed on a solid support, without forming metal clusters or nanoparticles. In contrast to conventional heterogeneous catalysts, where active metal species are typically present as nanoparticles with a wide size distribution, SACs consist of isolated metal atoms stabilized by strong interactions with the support surface. This atomic dispersion maximizes the utilization efficiency of metal atoms and generates well-defined active sites with uniform chemical environments.

The isolated nature of single atoms gives rise to catalytic properties that are fundamentally different from those observed in bulk metals or nanostructured catalysts. In bulk or nanoparticle catalysts, metal–metal interactions dominate the electronic structure, whereas in SACs, the metal atom interacts primarily with the support atoms. As a result, SACs often exhibit unique electronic configurations, modified adsorption behavior, and distinct reaction pathways. These characteristics make SACs particularly attractive for clean energy applications, where high efficiency, selectivity, and reduced noble metal usage are essential.

Another defining feature of SACs is their resemblance to homogeneous catalysts in terms of site uniformity, while retaining the robustness and recyclability of heterogeneous systems. This hybrid nature allows SACs to bridge the gap between homogeneous and heterogeneous catalysis, offering new opportunities for mechanistic understanding and catalyst optimization.

Electronic Structure and Coordination Environment

The electronic structure of a single metal atom in SACs is strongly governed by its coordination environment and the nature of the support. Unlike metal atoms in nanoparticles, which are surrounded by other metal atoms, single atoms are typically coordinated to heteroatoms such as nitrogen, oxygen, sulfur, or carbon atoms present in the support matrix. Common coordination motifs reported in the literature include $M-N_4$ structures in nitrogen-doped carbon materials, $M-O_4$ units on oxide supports, and mixed coordination environments such as $M-N_2O_2$ or $M-N_3C$.

These coordination structures play a critical role in determining the electronic properties of the active site. The interaction between the metal atom and the coordinating atoms leads to charge transfer, which can result in partial oxidation or reduction of the metal center. This charge redistribution directly influences the position of the d-band center, a key parameter controlling the adsorption strength of reaction intermediates. For clean energy reactions such as hydrogen evolution, oxygen reduction, or CO₂ reduction, optimal adsorption energies are essential to achieve high catalytic activity and efficiency.

Compared to metal nanoparticles, SACs often exhibit unsaturated or low-coordination environments, which can increase the density of active orbitals available for reactant binding. This unsaturation frequently enhances catalytic activity, particularly for reactions involving bond activation. However, excessively strong adsorption of intermediates can also be detrimental, as it may slow down reaction kinetics by hindering product desorption or blocking active sites. Therefore, a delicate balance between adsorption strength and desorption capability must be achieved.

Fine control over the coordination number, ligand type, and local geometry is thus crucial for optimizing SAC performance. Recent studies have demonstrated that even subtle changes in coordination, such as replacing one nitrogen atom with oxygen, can significantly alter catalytic behavior. This sensitivity highlights the importance of atomic-level precision in SAC design.

Advantages of Single-Atom Catalysts

One of the most significant advantages of single-atom catalysts is their nearly 100% atom utilization efficiency. In SACs, every metal atom is potentially accessible as an active site, whereas in nanoparticle-based catalysts, a large fraction of atoms remains buried within the particle core and does not participate in catalysis. This feature is particularly beneficial for noble metals such as platinum, palladium, and iridium, which are scarce and expensive. By reducing the required metal loading without compromising activity, SACs offer a cost-effective solution for clean energy technologies.

Another important advantage is the high selectivity often observed in SACs. The uniform and well-defined nature of single-atom active sites minimizes the presence of multiple reaction pathways that commonly occur on heterogeneous nanoparticle surfaces. As a result, SACs can favor specific reaction routes, leading to improved product selectivity. This is especially valuable in reactions such as CO₂ reduction, where controlling product distribution is a major challenge.

The tunability of SACs is also a key strength. By selecting appropriate metal centers, supports, and coordination environments, the electronic and catalytic properties of SACs can be systematically tailored. This level of control enables rational catalyst design guided by theoretical calculations and structure–activity relationships. Furthermore, the uniformity of active sites simplifies mechanistic studies, allowing clearer correlations between atomic structure and catalytic performance.

Despite these advantages, SACs are not universally superior to conventional nanoparticle catalysts. Stability remains a critical issue, as isolated metal atoms may migrate and aggregate under harsh thermal or electrochemical conditions. Additionally, achieving high metal loadings while maintaining atomic dispersion is technically challenging. These limitations underline the importance of understanding the fundamental behavior of single atoms under realistic reaction environments, which is essential for translating SACs from laboratory studies to practical clean energy applications.

Synthesis Strategies for Single-Atom Catalysts

The successful preparation of single-atom catalysts requires precise control over both metal dispersion and metal–support interactions. Unlike nanoparticle catalysts, SACs are thermodynamically less stable because isolated metal atoms tend to migrate and aggregate into clusters. Therefore, synthesis strategies must be designed to kinetically or thermodynamically stabilize single atoms by anchoring them to suitable sites on the support surface. Over the past decade, a variety of chemical and physical approaches have been developed to achieve stable atomic dispersion while maintaining catalytic accessibility.

An effective synthesis strategy typically relies on three key factors: (i) strong interactions between metal atoms and the support, (ii) uniform distribution of metal precursors prior to activation, and (iii) controlled thermal or chemical treatment to prevent sintering. The most widely used synthesis methods include wet-chemical techniques, pyrolysis of metal–organic precursors, and atomic-level deposition approaches.

Wet-Chemical Methods

Wet-chemical methods remain among the most commonly employed strategies for synthesizing single-atom catalysts due to their operational simplicity, low cost, and potential scalability. Techniques such as incipient wetness impregnation, deposition–precipitation, and co-precipitation involve introducing a metal precursor solution onto a solid support that contains abundant anchoring sites. These anchoring sites may include surface defects, oxygen vacancies, heteroatoms, or functional groups that can bind metal ions strongly.

Following impregnation, thermal treatment under controlled atmospheres is typically used to decompose the metal precursor and immobilize the metal atoms onto the support. If the metal–support interaction is sufficiently strong, isolated metal atoms can be stabilized without forming clusters. Oxide supports such as TiO_2 , CeO_2 , and Fe_2O_3 are particularly effective because their surface vacancies and lattice oxygen atoms can trap metal atoms.

Despite their advantages, wet-chemical methods face notable challenges. Controlling metal loading while maintaining atomic dispersion is difficult, especially at higher precursor concentrations. Excessive metal loading often leads to aggregation during thermal treatment, resulting in the formation of nanoparticles. Additionally, achieving uniform distribution of single atoms across the support surface can be challenging, leading to heterogeneity in active sites. As a result, careful optimization of precursor concentration, pH, temperature, and calcination conditions is required to obtain high-quality SACs.

Pyrolysis of Metal–Organic Precursors

Pyrolysis of metal–organic frameworks (MOFs), coordination polymers, or metal–ligand complexes has emerged as one of the most effective and versatile routes for synthesizing single-atom catalysts. In this approach, metal ions are pre-distributed within an organic matrix, ensuring atomic-level dispersion before thermal treatment. Upon high-temperature pyrolysis, the organic components decompose to form a carbonaceous support, while the metal atoms become anchored to heteroatoms such as nitrogen or sulfur.

This strategy is particularly well-suited for the preparation of M–N–C type SACs, where transition metal atoms (e.g., Fe, Co, Ni) are coordinated to nitrogen atoms embedded in a carbon matrix. Such catalysts have shown exceptional performance in electrocatalytic reactions including oxygen reduction, hydrogen evolution, and CO₂ reduction. The uniform distribution of metal centers in the precursor significantly reduces the likelihood of aggregation during pyrolysis.

The pyrolysis temperature and atmosphere play a crucial role in determining the final coordination environment and electronic structure of the metal atoms. Higher temperatures can improve electrical conductivity and structural stability but may also promote metal migration if anchoring sites are insufficient. Although this method offers excellent control over atomic dispersion, scalability and reproducibility remain concerns, particularly when using complex MOF precursors.

Atomic Layer Deposition and Physical Methods

Atomic layer deposition (ALD) represents one of the most precise techniques for synthesizing single-atom catalysts. ALD is based on sequential, self-limiting surface reactions that allow atomic-level control over metal deposition. By carefully controlling the number of deposition cycles, isolated metal atoms can be anchored onto the support surface with high uniformity.

ALD is especially valuable for fundamental studies because it enables systematic variation of metal loading and direct correlation between structure and catalytic performance. It has been successfully used to deposit single atoms of noble metals such as Pt, Pd, and Ir on oxide and carbon

supports. However, the strong dependence on specialized equipment, high operational costs, and low throughput significantly limit its application for large-scale catalyst production.

Other physical methods, including sputtering, thermal evaporation, and mass-selected soft landing techniques, have also been explored for SAC synthesis. While these approaches offer high precision, they are primarily limited to laboratory-scale studies and are not yet practical for industrial deployment.

Concluding Remarks on Synthesis

Overall, no single synthesis strategy is universally optimal for all single-atom catalysts. Wet-chemical methods offer simplicity and scalability, pyrolysis approaches provide excellent atomic dispersion, and ALD delivers unmatched precision. The choice of synthesis route depends strongly on the target reaction, metal species, support material, and intended application. Continued development of cost-effective, scalable, and controllable synthesis techniques will be critical for advancing SACs toward real-world clean energy technologies.

Characterization Techniques

Accurate and reliable characterization is essential for the development of single-atom catalysts, as confirming the presence of isolated metal atoms is significantly more challenging than characterizing conventional nanoparticle catalysts. Since single atoms are present at very low concentrations and lack long-range order, no single technique is sufficient to fully describe their structure. Instead, a combination of advanced microscopic, spectroscopic, and operando techniques is typically required to obtain convincing evidence of atomic dispersion and to understand the coordination environment, electronic structure, and stability of the active sites.

A major challenge in SAC characterization lies in distinguishing truly isolated atoms from ultra-small clusters or transient species. Therefore, careful interpretation of results and cross-validation using multiple complementary techniques are necessary to avoid misleading conclusions.

Electron Microscopy

Electron microscopy plays a central role in the direct visualization of single-atom catalysts. Aberration-corrected transmission electron microscopy (AC-TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) are particularly powerful due to their atomic-scale spatial resolution. In HAADF-STEM images, isolated metal atoms appear as bright spots against a darker background, owing to strong atomic number (Z) contrast. This allows heavier metal atoms to be distinguished from lighter support elements such as carbon or oxygen. These techniques have provided some of the most compelling visual evidence for the existence of single atoms on catalyst supports. They also enable the identification of metal dispersion, surface defects, and support morphology. However, electron microscopy has inherent limitations. The high-energy electron beam can induce migration or aggregation of single atoms during imaging, potentially altering the original structure. In addition, electron microscopy probes only a very small area of the sample, which may not be representative of the bulk catalyst.

As a result, while electron microscopy is invaluable for confirming atomic dispersion, it must be complemented by ensemble-averaged techniques to obtain a complete and reliable structural picture.

Spectroscopic Methods

Spectroscopic techniques provide critical information on the electronic structure and coordination environment of single atoms, often without the risk of beam-induced artifacts. Among these, X-ray absorption spectroscopy (XAS) is one of the most widely used and informative tools for SAC characterization. XAS includes two main components: X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS).

XANES is sensitive to the oxidation state and electronic configuration of the metal atom, allowing researchers to determine whether the metal exists in a metallic, oxidized, or partially charged state. EXAFS, on the other hand, provides quantitative information on the number and type of neighboring atoms surrounding the metal center. The absence of metal–metal coordination peaks in EXAFS spectra is often considered strong evidence for atomic dispersion.

Other spectroscopic techniques, such as X-ray photoelectron spectroscopy (XPS), Mössbauer spectroscopy (for Fe-based SACs), and infrared spectroscopy with probe molecules, are also commonly employed. These methods offer complementary insights into surface chemistry, metal–support interactions, and adsorption behavior of reactants. However, spectroscopic data must be interpreted carefully, as signal averaging may obscure local heterogeneities.

Operando and In Situ Techniques

Operando and in situ characterization techniques have become increasingly important for understanding the true behavior of single-atom catalysts under realistic reaction conditions. Unlike ex situ measurements, which are performed before or after catalysis, operando techniques allow real-time monitoring of structural and electronic changes while the reaction is occurring.

Operando XAS, for example, can track changes in oxidation state and coordination environment as a function of applied potential, temperature, or reactant atmosphere. Such studies have revealed that single atoms can undergo dynamic restructuring during catalysis, including changes in coordination number or temporary aggregation. These transformations often play a crucial role in determining activity, selectivity, and long-term stability.

In situ infrared and Raman spectroscopy provide valuable information on reaction intermediates adsorbed on single-atom sites, helping to elucidate reaction mechanisms. Combined with electrochemical measurements, these techniques offer direct correlations between structure and performance. Despite their complexity and experimental challenges, operando approaches are essential for developing a realistic understanding of SAC behavior and for identifying deactivation pathways.

Concluding Remarks on Characterization

Overall, the characterization of single-atom catalysts requires a multi-technique approach that integrates microscopy, spectroscopy, and operando studies. Each method provides unique insights but also has limitations when used in isolation. By combining these techniques, researchers can obtain a more complete understanding of the atomic structure, electronic properties, and dynamic

behavior of SACs. Such comprehensive characterization is fundamental for the rational design of stable and efficient single-atom catalysts for clean energy applications.

Single-Atom Catalysts in Clean Energy Applications

Hydrogen Evolution Reaction (HER)

The hydrogen evolution reaction is a key process for green hydrogen production via water electrolysis. Platinum-based catalysts are highly active but expensive. SACs based on Pt, Ni, Co, and Mo have shown promising HER activity with reduced metal loading. For example, Pt single atoms anchored on nitrogen-doped carbon exhibit near-optimal hydrogen adsorption energy and high mass activity.

Oxygen Reduction Reaction (ORR)

ORR is a critical reaction in fuel cells and metal–air batteries. Fe–N–C and Co–N–C SACs have demonstrated high ORR activity, approaching or even surpassing that of Pt-based catalysts in alkaline media. The well-defined M–N₄ sites facilitate efficient O₂ adsorption and reduction.

Oxygen Evolution Reaction (OER)

OER is kinetically sluggish and requires efficient catalysts for water splitting. Single-atom Ir and Ru catalysts supported on oxides have shown enhanced activity and stability. The strong metal–support interaction helps stabilize high oxidation states required for OER.

CO₂ Reduction Reaction (CO₂RR)

Electrochemical reduction of CO₂ offers a route to convert greenhouse gases into valuable fuels and chemicals. SACs based on Cu, Ni, and Fe have shown high selectivity toward products such as CO, formate, and hydrocarbons. The isolated nature of active sites suppresses C–C coupling, allowing better control over product distribution.

Nitrogen Reduction Reaction (NRR)

Ambient nitrogen fixation is an attractive alternative to the energy-intensive Haber–Bosch process. SACs with Fe or Mo centers have been explored for electrochemical N₂ reduction. While reported

activities are still low, SACs provide a platform for studying N₂ activation mechanisms at the atomic level.

Structure–Performance Relationships

Understanding the relationship between atomic structure and catalytic performance is central to SAC design. Factors such as metal identity, coordination environment, support type, and electronic properties all influence activity and selectivity.

Density functional theory (DFT) calculations are widely used to predict adsorption energies and reaction pathways. Combined with experimental studies, these calculations help identify optimal active site configurations. However, discrepancies between theoretical models and real catalysts remain, especially under operating conditions.

Stability and Scalability Challenges

Despite impressive laboratory-scale results, several challenges hinder the practical application of SACs. Single atoms may migrate and aggregate under high temperature or electrochemical potentials, leading to performance degradation. Designing supports with strong anchoring sites is therefore essential.

Scalability is another concern. Many synthesis methods are complex or expensive, limiting industrial adoption. Developing simple, low-cost, and scalable synthesis routes remains an important research direction.

Tables and Figures

Table 1. Representative single-atom catalysts for clean energy applications

Reaction	Metal Center	Support	Key Advantage
HER	Pt, Ni	N-doped carbon	High mass activity
ORR	Fe, Co	Carbon	Low cost, high selectivity
OER	Ir, Ru	Metal oxides	High stability
CO ₂ RR	Cu, Ni	Carbon	Tunable selectivity

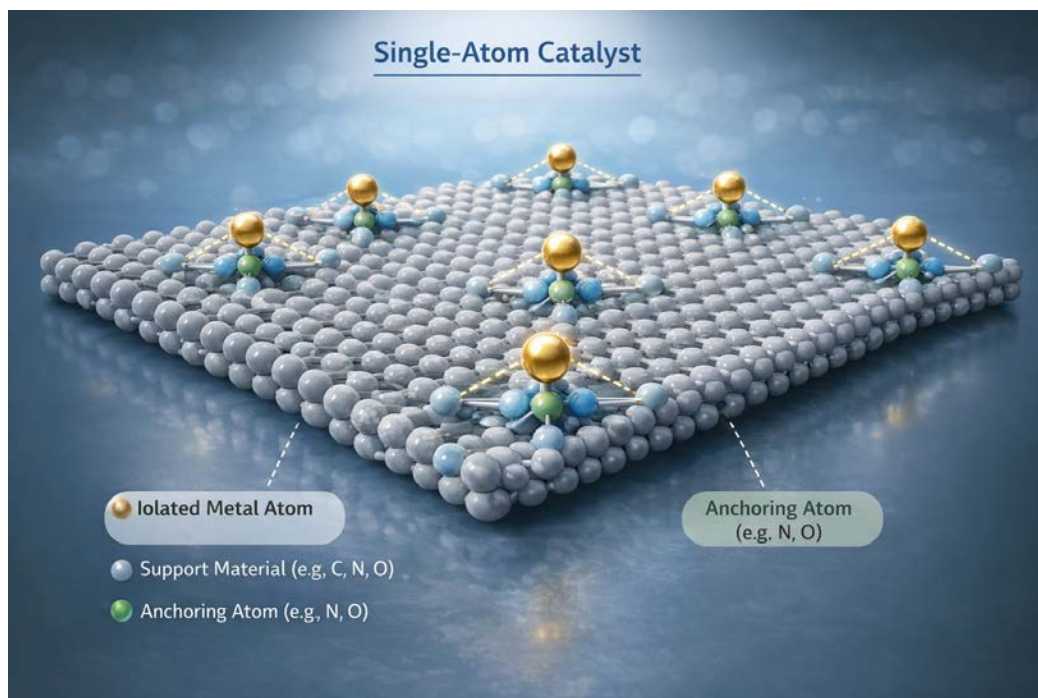


Figure 1. Schematic illustration of a single-atom catalyst showing isolated metal atoms anchored on a solid support with defined coordination environment.

Future Perspectives

The future of single-atom catalysis lies in the rational design of active sites with precise control over atomic structure. Combining machine learning with high-throughput experiments may accelerate catalyst discovery. Additionally, integrating SACs into real devices such as electrolyzers and fuel cells will be crucial for assessing their practical viability.

Interdisciplinary collaboration between chemists, physicists, and engineers is expected to drive further progress. Although challenges remain, the potential impact of SACs on clean energy technologies is significant.

CONCLUSION

Single-atom catalysts represent a transformative approach in the field of clean energy catalysis. By maximizing atom utilization and enabling precise control over active sites, SACs offer new

opportunities to design efficient and sustainable catalysts. Significant advances have been achieved in reactions such as HER, ORR, OER, CO₂RR, and NRR. However, issues related to stability, scalability, and real-world performance must be addressed before widespread application. Continued research into synthesis methods, characterization techniques, and theoretical modeling will be essential for overcoming these challenges. Overall, single-atom catalysis holds strong promise for enabling next-generation clean energy systems and contributing to a more sustainable energy future.

REFERENCES

1. Qiao, B. et al., Single-atom catalysis of CO oxidation, *Nat. Chem.* 2011.
2. Zhang, H. et al., Single-atom catalysts: emerging multifunctional materials, *Chem. Rev.* 2020.
3. Wang, A. et al., Single-atom catalysis: a new frontier, *Acc. Chem. Res.* 2013.
4. Liu, J., Catalysis by supported single metal atoms, *ACS Catal.* 2017.
5. Yang, X. F. et al., Single-atom catalysts: a new class of heterogeneous catalysts, *Chem. Rev.* 2015.
6. Li, X. et al., Design of single-atom catalysts for electrochemical reactions, *Energy Environ. Sci.* 2021.
7. Chen, Y. et al., Single-atom catalysts for hydrogen evolution, *Adv. Mater.* 2018.
8. He, T. et al., Single-atom catalysts for CO₂ reduction, *J. Am. Chem. Soc.* 2020.
9. Guo, X. et al., Supported single-atom catalysts for energy applications, *Nat. Catal.* 2018.
10. Zhao, S. et al., Metal single-atom catalysts for nitrogen reduction, *Chem. Soc. Rev.* 2021.