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JOURNAL OF CARBON CATALYSIS

Research Article

Graphene-Supported Single-Atom Catalysts for Sustainable Organic Conversions: Coordination Engineering, Selectivity, and Atom-Efficient Catalysis

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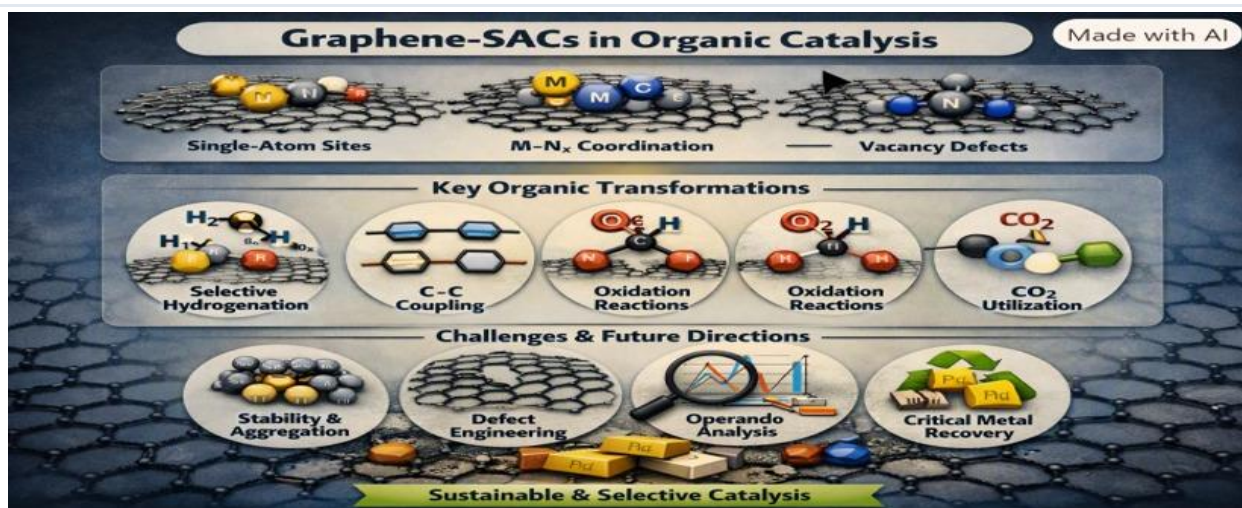
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Received: 05.07.2026

Accepted: 17.09.2026

Published online: 30.09.2026



Graphical Abstract

ABSTRACT

Graphene-supported single-atom catalysts (G-SACs) combine the maximized metal utilization of isolated atoms with the recoverability, conductivity and structural tunability of a heterogeneous carbon support. They are therefore attractive for sustainable organic synthesis, where precious-metal economy, chemoselectivity and product purification are major concerns. This review examines the design, synthesis, characterization and catalytic application of isolated transition-metal atoms stabilized on graphene, graphene oxide and heteroatom-doped graphene. Particular attention is given to M-N_x-C coordination environments, vacancy defects, support-induced electronic effects and the distinction between stable single atoms and dynamically generated clusters.

Organic transformations discussed include selective hydrogenation, oxidation, C-C and C-heteroatom bond formation, carbon dioxide incorporation and emerging bimetallic single-atom catalysis. Graphene-supported Pd single atoms illustrate how isolated sites can suppress ensemble-dependent over-hydrogenation, while Cu, Ni and Au single atoms demonstrate the ability of vacancy and nitrogen coordination to tune redox chemistry. A 2026 Pd₁Au₁/graphene bimetallic single-atom system has further shown that neighboring unlike single atoms can unlock C-C coupling pathways that are inactive on the corresponding monometallic SACs, highlighting the next stage of atomic-site engineering. Challenges include low or uncertain site density, agglomeration under reaction conditions, energy-intensive support preparation, limited substrate-scope data and inconsistent reporting of metal-normalized productivity. Future progress requires operando spectroscopy, scalable defect engineering, structured graphene supports, explicit leaching tests, critical-metal recovery and process-level green metrics. G-SACs offer a powerful bridge between homogeneous and heterogeneous catalysis when the atomic structure of the active site is demonstrably preserved during organic conversion.

Keywords: *Single-atom catalysts; graphene; N-doped graphene; organic synthesis; atom economy; hydrogenation; coupling; sustainable catalysis*

INTRODUCTION

Single-atom catalysis has transformed the concept of heterogeneous active sites by reducing the metal phase to isolated atoms stabilized by a support. The theoretical atom-utilization advantage is obvious: nearly every supported atom can be exposed to reactants, whereas a substantial fraction of atoms in nanoparticles remain buried. For expensive metals such as Pd, Pt, Rh and Au, this can lower metal inventory dramatically. More importantly, an isolated atom lacks the extended ensembles found on a metal surface, producing distinct adsorption geometries and often unusual selectivity.

Graphene is an appealing support because it provides a two-dimensional platform with high conductivity, accessible surface area and controllable defects. Pristine graphene binds many metals too weakly to prevent migration, but vacancies, oxygen groups and heteroatom dopants create high-affinity anchoring sites. Nitrogen-doped graphene is particularly important because pyridinic N atoms can form coordination environments analogous to molecular ligands, creating M-N_x-C sites with tunable electron density.

Review the most relevant literature critically, avoiding an Organic synthesis is a demanding test for SACs. Catalysts must tolerate functional groups, maintain activity in liquid media, avoid metal leaching and provide predictable chemoselectivity across a substrate scope. These requirements distinguish synthetic catalysis from many gas-phase model reactions. This review therefore asks not only whether graphene SACs are active, but whether they deliver reproducible, recoverable and process-relevant organic transformations.

2. Scope and review methodology

The review covers experimental and mechanistic studies of isolated metals on graphene, graphene oxide and N-doped graphene, with emphasis on organic or molecule-building conversions. Electrocatalytic and small-molecule studies are included selectively when they provide transferable insight into coordination, support effects or atomic stability. Primary studies with HAADF-STEM, X-ray absorption spectroscopy, Mössbauer spectroscopy where appropriate, or rigorous indirect evidence are prioritized.

A key methodological principle is that a catalyst should be called a single-atom catalyst only when atomic dispersion is demonstrated before reaction and preferably after or during catalysis. Because isolated atoms can migrate and cluster, post-reaction characterization is central to mechanistic claims.

3. Graphene support engineering and single-atom stabilization

Vacancy engineering creates under-coordinated carbon atoms that bind transition metals strongly. Single vacancies, divacancies and larger defect motifs provide different coordination numbers and electronic structures. Oxygen-containing groups in graphene oxide can also anchor metals, although reduction or reaction conditions may alter them. Nitrogen doping provides stronger, more chemically interpretable coordination and is widely used to form M-N₄, M-N₃C and related motifs.

Universal synthesis strategies based on defect-rich hollow N-doped graphene frameworks have demonstrated gram-scale stabilization of Fe, Co, Ni and Cu atoms. Such approaches are important because many early SAC syntheses produced only milligram quantities. Other strategies include atomic layer deposition, wet impregnation followed by

high-temperature trapping, metal-organic precursor pyrolysis and defect capture of mobile atoms.

Single-atom loading presents a thermodynamic challenge. Increasing metal concentration promotes aggregation unless the support provides a matching density of strong anchoring sites. High-load SAC synthesis therefore requires simultaneous control of defect density, heteroatom coordination and metal chemical potential.

4. Characterization: proving the single-atom state

Aberration-corrected HAADF-STEM can visualize individual high-Z atoms as bright spots on a carbon background, but only a tiny fraction of the sample is imaged. X-ray absorption spectroscopy provides ensemble-averaged information about metal coordination and can distinguish metal-metal from metal-N/C scattering. XPS helps establish oxidation state, while inductively coupled plasma analysis quantifies total loading.

Operando characterization is increasingly important. An isolated atom that becomes a cluster under hydrogenation conditions may still be a useful catalyst, but its performance should not be attributed to a static single-atom site. Conversely, reactant-induced reversible atom pairing may be intrinsic to the catalytic cycle. Dynamic restructuring should therefore be treated as chemistry rather than as an inconvenience.

For organic synthesis, leaching tests, hot filtration and analysis of the liquid phase are essential because a small amount of dissolved metal can catalyze coupling reactions homogeneously. Product metal contamination should be reported for pharmaceutical relevance.

5. Selective hydrogenation over graphene SACs

Selective hydrogenation is a prototypical application because many undesired pathways require multi-atom ensembles. Isolated Pd atoms on graphene have shown strong selectivity to butenes during 1,3-butadiene hydrogenation, with substantially less propene hydrogenation than Pd nanoparticles. The absence of contiguous Pd sites changes adsorption geometry and suppresses over-hydrogenation.

The concept extends to alkynes, nitro compounds and carbonyls. By tuning the electron density of an isolated metal through N coordination, adsorption of C=C, C≡C, C=O or NO₂ groups can be differentiated. In principle, this can reduce the need for poisoning agents traditionally used to moderate highly active metal surfaces.

A central practical question is hydrogen activation. Some isolated atoms dissociate H₂ readily, while others require support participation or neighboring heteroatoms. Hydrogen spillover from an atom to graphene may be important, but direct experimental quantification remains limited.

Table 1. Representative graphene single-atom coordination environments.

Support motif	Typical metal coordination	Catalytic consequence	Characterization priority
Single vacancy graphene	M-C _x	Strong anchoring ; unusual electron density	HAADF-STEM + XAS
N-doped graphene	M-N ₄ / M-N ₃ C	Ligand-like electronic control	N 1s/metal XPS + EXAFS
Graphene oxide	M-O _x /C	Wet-chemical anchoring ; redox-sensitive	XPS before/after reaction
Bimetallic atomic pair	M1-M2 / separated dual sites	Cooperative bond activation	Atomic-resolution STEM + operando XAS

Oxidation and C-H functionalization

Graphene-supported single atoms can activate oxygen, peroxides and C-H bonds with coordination environments that resemble molecular complexes. Cu and Fe single atoms coordinated by nitrogen are particularly relevant because multiple oxidation states can be accessed without forming large oxide particles. The support can act as an electron reservoir that stabilizes redox intermediates.

For direct methane-to-methanol chemistry, theoretical studies of Ni single atoms on vacancy graphene illustrate how single-site geometry can suppress methanol overoxidation. Although methane conversion is not yet a general synthetic method, the design principle is relevant to selective C-H activation of organic substrates: an isolated site can stabilize a desired transition state while preventing multi-site pathways to deeper oxidation. Future organic oxidation studies should report oxygen source, radical involvement, site-normalized kinetics and substrate scope. SAC performance is most compelling when selectivity arises from a mechanistically demonstrated atomic environment rather than from very low conversion.

7. C-C and C-heteroatom bond formation

Cross-coupling chemistry is highly attractive for SACs because homogeneous Pd and Cu catalysts create separation and metal-residue challenges. Graphene-supported single atoms offer potential heterogeneous alternatives, but oxidative addition, transmetalation and reductive elimination may require flexible coordination or transient atom pairing.

Recent work has demonstrated that bimetallic atomic sites can overcome limitations of isolated monometallic centers. In 2026, a Pd₁Au₁/graphene catalyst was reported for arylboronic-acid homocoupling, reaching a turnover number up to 19,192 and retaining more than 90% yield after seven cycles. The corresponding monometallic Pd or Au SACs were inactive for the same C-B activation/coupling pathway, indicating a genuine cooperative effect between unlike atomic centers.

C-N and C-O bond formation is another promising direction because ligand-free or low-ligand

heterogeneous catalysis could simplify purification. However, the substrate scope and long-term metal balance of many reported systems remain narrower than established homogeneous protocols.

Table 2. Organic-conversion opportunities for graphene-supported SACs.

Reaction	Representative SAC concept	Potential advantage	Key uncertainty
Diene hydrogenation	Pd ₁ /graphene	Suppresses over-hydrogenation	Hydrogen activation pathway
C-C coupling	Pd ₁ Au ₁ /graphene	Cooperative atomic sites; very high TON reported	Generality across coupling classes
C-H oxidation	Ni ₁ /Cu ₁ on defect graphene	Controlled adsorption/redox	Operando atomic stability
CO ₂ conversion	Sn ₁ /Ni ₁ -Nx-graphene	High atom utilization and tunable intermediate binding	Translation to preparative organic synthesis

8. CO₂ incorporation and sustainable feedstocks

Single atoms on N-doped graphene are widely

studied for CO₂ activation in electrocatalysis and hydrogenation. The fundamental chemistry—binding of CO₂, stabilization of formate or CO intermediates and control of hydrogenation depth—is relevant to organic synthesis using CO₂ as a C1 building block. Graphene-supported Sn, Ni and other isolated metals have been modeled or tested for formate-related pathways.

From a sustainability perspective, SACs can reduce critical-metal use but do not make an intrinsically unsustainable reaction green. The complete route should be evaluated for pressure, solvent, hydrogen source and product separation. CO₂ utilization is most meaningful when the carbon is incorporated into durable products or replaces a more hazardous carbonylation reagent.

9. Sustainability, recyclability and process considerations

Metal atom economy is the most direct sustainability advantage of SACs. A catalyst with 0.1-1 wt% precious metal may deliver similar active-site density to a nanoparticle catalyst containing substantially more metal. Heterogeneous recovery can also lower metal contamination. Yet graphene production, oxidation, exfoliation, nitrogen doping and high-temperature pyrolysis can carry significant environmental burdens.

The relevant metric is therefore catalyst productivity per unit of critical metal and per unit of catalyst-manufacturing impact. Turnover number, space-time yield, grams of product per gram of precious metal, catalyst lifetime, leaching and end-of-life metal recovery should be reported. Structured graphene foams, coated monoliths and membranes can reduce handling losses compared with powders. For liquid-phase organic synthesis, solvent wetting

and pore-free external surface are advantageous, but graphene sheets can restack. Three-dimensional porous graphene frameworks increase accessible area and reduce filtration difficulties. Continuous-flow packed or coated reactors could provide the most realistic path to manufacturing.

10. Challenges and future research

The first major challenge is atomic-site heterogeneity. A nominal M-N₄ catalyst may contain several coordination motifs. Advanced XAS fitting, vibrational probes and theory should be integrated to identify the catalytically dominant population. Second, SAC stability must be examined under realistic concentrations, temperatures and reducing/oxidizing atmospheres.

Third, synthetic routes must become more scalable and lower energy. Universal defect-trapping strategies, pressure-controlled metal deposition and low-temperature coordination chemistry are promising. Fourth, more studies should compare SACs with the best homogeneous and nanoparticle catalysts using identical conditions.

Fifth, dual-atom and bimetallic single-atom catalysts are likely to expand because many organic reactions require cooperative activation of two substrates. The goal should be atomically precise multifunctionality rather than simply maximizing metal loading.

11. Conclusions

Graphene-supported single-atom catalysts provide a powerful strategy for atom-efficient organic synthesis. Their unique selectivity derives from isolated coordination environments, support-mediated electron transfer and suppression of extended metal ensembles. The field is now moving toward higher loading, operando structural

verification, cooperative dual-atom sites and process intensification. Their sustainable value will be realized when precious-metal savings, catalyst recovery and selectivity improvements outweigh the footprint of graphene-support preparation.

12. Comparison with homogeneous molecular catalysts and nanoparticles

Graphene SACs occupy an intermediate conceptual space between homogeneous complexes and conventional supported nanoparticles. Like molecular catalysts, a SAC can possess a defined first coordination sphere and isolated metal center. Like a heterogeneous catalyst, it can be recovered as a solid. This hybrid character is responsible for much of the interest in SACs but also creates demanding characterization requirements. In homogeneous catalysis, ligand identity is known precisely; in a graphene SAC, a nominal M-N₄ environment may coexist with M-N₃C, M-N₂C₂ and defect-bound species.

Relative to nanoparticles, SACs maximize atom utilization and suppress ensemble chemistry. However, nanoparticles can offer cooperative multi-atom activation that isolated centers cannot. The emergence of dual-atom and bimetallic atomic-pair catalysts reflects this limitation. The most rational catalyst choice therefore depends on the elementary steps required by the reaction rather than on a presumption that atomic dispersion is universally superior.

13. Substrate scope and synthetic relevance

For G-SACs to become established in organic synthesis, reports must move beyond single model substrates. A meaningful substrate-scope study should test electron-rich and electron-poor aromatics, sterically hindered substrates,

heterocycles and sensitive functional groups. Isolated yields and product purity are more informative than GC conversion alone. Pharmaceutical-relevant chemistry also requires quantification of residual metal in the isolated product.

Chemoselective hydrogenation is particularly well suited to SACs because functional groups compete for adsorption at a single site. In coupling reactions, however, catalyst poisoning by sulfur- or nitrogen-containing heterocycles may be significant. Understanding reversible versus irreversible coordination will help define the synthetic window of each SAC family.

14. Reactor integration and structured graphene supports

Powdered graphene can be difficult to filter because thin sheets form stable dispersions. Three-dimensional graphene foams, aerogels, coated monoliths and carbon-cloth-supported graphene provide more practical forms. A structured support can retain atomic dispersion while reducing pressure drop and catalyst loss in flow.

Flow reactors can also limit the residence time of reactive intermediates and allow rapid screening of temperature and gas composition. For hydrogenation and oxidation, immobilized G-SACs could combine high site accessibility with safe gas handling. The field needs demonstrations lasting hundreds of hours to establish structural stability under manufacturing conditions.

15. Data science and atomic-level catalyst discovery

The discrete nature of single-atom coordination sites is attractive for computational screening. Density-functional theory can compare adsorption and

transition-state energies across M-N_x-C motifs, while machine learning can search large combinations of metal, coordination and defect structure. The bottleneck is experimental correspondence: synthesized materials often contain multiple motifs not represented by a single theoretical model.

A productive workflow would integrate high-throughput synthesis, operando XAS, atom-resolved microscopy and theory. Experimental descriptors such as coordination number, edge position and support curvature should be incorporated into databases. Predictive models should target selectivity and stability, not merely adsorption energy or reaction energy.

16. Organic synthesis opportunities with atomically dispersed metals

The most compelling synthetic opportunities for graphene SACs are transformations in which chemoselectivity is controlled by the absence of extended metal ensembles. Semihydrogenation of alkynes and dienes is an obvious example, but selective reduction of nitro groups in the presence of halides, hydrogenation of carbonyls without aromatic-ring reduction and controlled hydrogenolysis of protecting groups are also promising. For coupling chemistry, isolated Cu, Pd or Ni centers may reduce metal loading and residual metal in products, provided the catalytic cycle does not require large clusters.

Heteroatom-rich pharmaceutical substrates are an important stress test because amines, thioethers and heteroaromatics bind strongly to isolated metal atoms. These groups may either poison the site or act as directing ligands that improve selectivity. Systematic poisoning and competitive adsorption

experiments would help establish practical functional-group compatibility.

Chiral catalysis is an ambitious future direction. If a graphene defect can be decorated with a chiral organic environment around a single atom, heterogeneous asymmetric catalysis may become possible. Achieving a uniform chiral coordination sphere on a carbon surface is difficult, but molecular grafting or covalent organic interlayers could provide a route.

17. Practical criteria for calling a graphene SAC 'sustainable'

A sustainable graphene SAC should satisfy more than high turnover number. The preparation route should minimize strong oxidants, fluorinated reagents and repeated washing; metal loading should be justified by productivity; the support should remain stable over long reuse; and the metal should be recoverable at end of life. If graphene is produced through energy-intensive exfoliation and the catalyst is used only a few times, precious-metal savings may not compensate for the support footprint.

For publication and technology assessment, authors should report grams of product per gram of metal over total catalyst lifetime, not only turnover frequency measured during a short initial period. Product-metal contamination, catalyst loss during filtration and regeneration energy should also be included. Comparison with a conventional homogeneous catalyst under identical reaction conditions can reveal whether the SAC actually simplifies purification.

These criteria connect atomic-scale catalyst design with process-scale sustainability. A G-SAC that performs slightly worse kinetically but dramatically reduces precious-metal inventory and product

contamination may still be the preferred manufacturing catalyst.

Declarations

Funding: [Insert funding source and grant number, or state that no specific funding was received.]

Conflicts of interest: The authors declare [insert appropriate statement after author verification].

Data availability: No new experimental dataset was generated for this review. The information synthesized in this article is derived from the cited literature.

Author contributions: [Insert CRediT contribution statement according to the target journal.]

Generative AI and AI-assisted technologies: Before submission, the authors should insert the disclosure required by the selected publisher based on their actual use of AI-assisted tools. All references, numerical values, interpretations and scientific statements must be independently verified and approved by the authors.

DATA AVAILABILITY STATEMENT

Datasets are deposited under repository registry identifier [DOI/URL].

CONFLICTS OF INTEREST

The authors declare no competing interests.

ACKNOWLEDGEMENTS

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