

Electron microscopy of carbon-supported metal catalysts: From atomic-scale structural characterization to operando mechanistic insights

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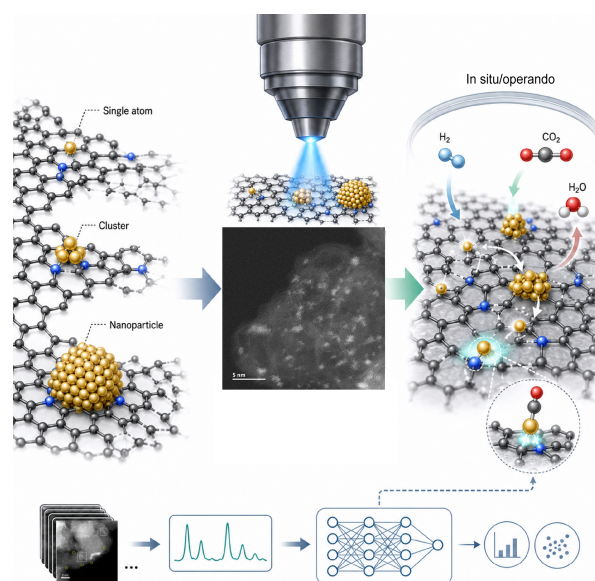


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ABSTRACT: Carbon-supported metal catalysts, ranging from isolated single atoms and subnanometer clusters to nanoparticles, are widely used in heterogeneous catalysis because carbon supports offer large surface area, conductivity, tunability, and abundant defects. However, their catalytically relevant structures are often local, heterogeneous, and dynamically evolving, making ensemble-averaged characterization insufficient for establishing reliable structure–activity relationships. In this context, electron microscopy has emerged as an essential tool for directly visualizing metal dispersion, coordination environments, and metal–carbon interfaces across multiple length scales. The combination of aberration-corrected scanning transmission electron microscopy, electron energy loss spectroscopy, energy-dispersive X-ray spectroscopy, and complementary spectroscopies enables the identification of atomically dispersed sites, clusters, and confined nanoparticles. In addition, in situ and operando microscopy reveals catalyst formation, restructuring, and deactivation under working conditions. Future advances will rely on realistic operando cells, statistically robust analysis, and artificial intelligence–assisted workflows, transforming electron microscopy from a descriptive imaging tool into a quantitative platform for understanding and designing carbon-supported metal catalysts.



KEYWORDS: Electron microscopy, carbon-supported metal catalysts, operando characterization, AI-assisted analysis

1 Introduction

Carbon-supported metal catalysts occupy a technologically important space across thermal catalysis^{1–10}, electrocatalysis^{11–15}, and related energy-conversion processes^{16–20}. In these systems, catalytically relevant metal species often coexist as isolated atoms, subnanometer clusters, and nanoparticles, whereas the carbon host contributes not only large surface area but also electrical conductivity, heteroatom anchoring sites, confinement effects, and transport pathways^{21–23}. In fact, representative studies of N-doped graphene-supported catalysts, carbon black-supported catalysts,

graphene nanoplatelet–carbon nitride core–shell architectures, and metal (M)–N–C single-atom systems collectively underscore that the carbon support is an active structural variable rather than a passive carrier^{24–26}.

This structural complexity renders electron microscopy (EM) essential for the characterization of carbon-supported metal catalysts. Although ensemble-averaging techniques provide information on coordination environments, oxidation states, and average compositions^{27–29}, they cannot directly resolve the spatial organization of isolated sites, clusters, nanoparticles, pore architectures, and metal–carbon interfaces within heterogeneous carbon matrices. EM uniquely bridges morphology, atomic structure, and chemical mapping. In addition, in favorable cases, it captures time-resolved structural evolution under external stimuli^{30–32}. In practical terms, it provides a rare capability to connect the size continuum from single atoms to nanoparticles with the topological continuum from external surfaces to internal meso- and microporous networks^{33–35}.

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The scope of this Review can therefore be framed around two linked questions. First, how can electron microscopy identify catalytically relevant static structures across the size continuum from isolated atoms to nanoparticles on carbon supports? Second, how can in situ and operando electron microscopy reveal the pathways by which these structures form, restructure, deactivate and, in some cases, regenerate? An important caveat should be stated at the outset. In the current literature, the most mature operando mechanistic demonstrations still arise disproportionately from oxide-supported benchmark catalysts rather than carbon-supported systems. This imbalance suggests that operando EM of carbon-supported catalysts is advancing but remains limited, mainly because of beam effects, low support contrast, and the difficulty of achieving realistic gas, liquid, or electrochemical environments while preserving delicate carbon-supported nanostructures^{31, 36, 37}. Artificial intelligence (AI) is probably the most transformative tool, not by replacing microscopy but by making it more quantitative, scalable, and reliable. Existing studies have demonstrated data-realistic augmentation of scanning transmission electron microscopy (STEM) images, automated identification of single-atom defects, atom- and feature-level segmentation, four-dimensional (4D) STEM analysis pipelines, and human-in-the-loop experimental feedback^{38–42}. For carbon-supported catalysts, the clearest near-term value of AI lies in denoising, segmentation, uncertainty-aware single-atom detection, dynamic-event tracking, and multimodal fusion across imaging, spectroscopy, tomography, and catalytic performance datasets.

2 Electron microscopy toolbox

Conventional transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) remain workhorse techniques for

determining particle-size distributions, morphology, faceting and lattice-fringe structures, particularly for nanoparticle catalysts^{32, 43–46}. Aberration-corrected STEM, especially high-angle annular dark-field STEM (HAADF-STEM), extends this capability to atomic columns and, in favorable cases, single-atom regime, because heavy metal atoms can be resolved with strong Z-contrast against lighter carbon supports^{18, 33, 47–50}. Meanwhile, STEM–energy-dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) provide elemental and electronic state information, while electron tomography, 4D-STEM, ptychography, low-dose imaging, and cryogenic strategies expand the accessible parameter space for porous and beam-sensitive catalysts^{33, 51–56}. The practical lesson is that the modern microscopy toolbox (Table 1) should not be viewed as a linear hierarchy of increasingly advanced techniques, but rather as a complementary set of approaches that balance spatial resolution, chemical sensitivity, statistical representativeness, dose efficiency, and environmental realism.

The critical point is that no single imaging mode can simultaneously resolve geometry, chemistry, three-dimensional (3D) architecture, and dynamic evolution. A high-quality microscopy section should therefore emphasize methodological complementarity rather than present a simple catalogue of techniques. Tomography, for example, can determine whether metal species reside inside internal pores or on external carbon surfaces, HAADF-STEM evaluates atomic dispersion and cluster formation, and 4D-STEM or ptychography improves contrast and extracts local structural fields when conventional imaging is limited.

Nevertheless, important challenges remain, especially for carbon materials. The field still lacks broadly accepted protocols for quantifying uncertainty in atom counting on amorphous carbon, robust 3D chemical mapping of highly dilute metal sites in porous

Table 1 Electron microscopy toolbox

Technique	Typical practical resolution regime	Dominant information type	Typical use in carbon-supported catalysts	Main limitations
TEM/HRTEM	nm to lattice-resolved	Morphology, particle size, crystallinity, lattice fringes	Nanoparticle dispersion, faceting, average size distributions	Weak sensitivity to isolated atoms on low-Z-contrast carbons; projection overlap
Aberration-corrected HAADF-STEM	Atomic columns to single atoms	Z-contrast imaging of heavy atoms on light supports	Single atoms, subnanometer clusters, ultrafine nanoparticles, interface motifs	Contrast depends on thickness, depth, defocus, dose, and support heterogeneity
STEM–EDS/STEM–EELS	Typically lower than pure imaging modes; local to nanoscale/atomic column depending on sample and dose	Elemental maps, valence/coordination fingerprints, support chemistry	Alloying, dopant distribution, metal–C/N/O environments, support graphitization	Signal weak for dilute samples; dose and delocalization penalties
Electron tomography	3D nanoscale	3D morphology and pore/network connectivity	Internal/external particle populations, carbon pore accessibility, catalyst-layer architecture	Missing wedge, dose accumulation, demanding reconstruction
4D-STEM/ptychography	Low-dose high resolution; sub Å lateral resolution	Diffraction at every probe position, phase, strain, orientation, ptychographic reconstruction	Strain/phase mapping, dose-efficient imaging, weak-phase or beam-sensitive materials	Heavy computational load, calibration and detector artifacts
ETEM/closed-cell gas TEM	Lower than vacuum atomic-imaging optimum but environmentally enabled	Dynamic morphology and reaction-induced restructuring	Formation, sintering, redispersion, coking/oxidation tendencies	Limited pressure realism, beam-gas chemistry, cell transport effects
Liquid-cell/electrochemical TEM	Environment enabled more than ultimate spatial resolution	Dissolution, redeposition, growth, corrosion, electrochemical restructuring	Electrocatalyst degradation and redispersion pathways	Thick liquid pathlengths, radiolysis, window effects, electrochemical artifacts
Cryo/low-dose strategies	Dose-limited but structure-preserving	Beam-sensitive structure retention, frozen intermediate states	Preserving fragile carbon–electrolyte interfaces or transient states	Lower throughput; demanding transfer/preparation

carbon matrices, and low-dose workflows that preserve catalytic states while remaining statistically representative. Because these limitations are major methodological bottlenecks, not incremental technical refinements, addressing them is essential to transform EM from a structural imaging tool into a quantitative platform for catalyst discovery.

3 Atomic-scale structural identification

Structural identification of carbon-supported metal catalysts has advanced well beyond conventional particle size analysis. In particular, the development of aberration-corrected EM and spatially resolved spectroscopy has enabled the evaluation of both the carbon support and the supported metal species with near-atomic precision. This capability is essential because the catalytic behavior of carbon-supported metals is governed not only by the size and dispersion of metal species but also by the hybridization state, defect architecture, heteroatom distribution, and local coordination environment of the carbon matrix^{57–61}.

As shown in Figs. 1a and 1b, high-resolution EM can distinguish different carbon configurations. Thus, Fig. 1a shows the coexistence of sp^3 -rich regions and distinct graphitic fringes, indicating the presence of local sp^2 – sp^3 interfacial structures rather than merely sp^3 carbon. Meanwhile, Fig. 1b shows a control state dominated by graphitized sp^2 carbon. In 3D N-doped nanocarbons containing sp^3 – sp^2 carbon interfaces, high-resolution imaging visualizes the coexistence of graphitic and disordered carbon regions, and carbon K-edge EELS provides complementary evidence for the electronic differences between sp^2 and sp^3 carbon¹. This is particularly important for carbon-supported metal catalysts because sp^2 domains, sp^3 -rich defect sites, and their interfaces provide distinct anchoring environments and electronic interactions for metal atoms or clusters. Beyond carbon hybridization, recent advances have enabled direct discrimination of light elements within carbon frameworks. In N-doped amorphous monolayer carbon, atomically resolved annular dark-field (ADF) STEM combined with EELS mapping can directly differentiate C and N atoms, as shown in Figs. 1c and 1d⁶². This represents an important methodological advance for carbon-supported catalysts, especially M–N–C and heteroatom-doped carbon systems, in which the location and coordination type of nitrogen species strongly influence metal anchoring, charge redistribution and catalytic activity.

On this basis, aberration-corrected HAADF-STEM provides a direct tool for identifying the size continuum of supported metal species, ranging from isolated atoms and subnanometer clusters to nanoparticles⁹. In fully exposed Pd cluster catalysts for H_2 production from nitrogen heterocycles, isolated Pd atoms, Pd clusters, and larger Pd particles can be distinguished by their characteristic Z-contrast features and spatial distributions (Figs. 1e–1g). In addition, combining HAADF-STEM with density functional theory (DFT) calculations allows correlating the experimentally observed Pd clusters with their electronic structure and catalytic behavior, revealing how metal nuclearity and coordination environment govern reactant adsorption and activation (Fig. 1h)⁹. This integration of microscopy and theory elevates EM from a descriptive imaging technique to a structure–function analysis platform. Beyond identifying isolated metal atoms, advanced EM can reveal their local coordination environments. For metal single-atom catalysts, HAADF-STEM confirms atomic dispersion, and EELS and complementary spectroscopic techniques reveal neighboring light elements around

the metal centers⁴. As shown in Figs. 1i and 1j, the coordination number and local composition of Pt single atoms on N-doped carbon can be regulated and characterized, providing direct insight into the effect of metal–support coordination on electronic structure, catalytic activity, and stability.

The ability to distinguish isolated single atoms from dual-atom sites provides further structural precision. For homonuclear dual-atom catalysts, paired bright features in aberration-corrected HAADF-STEM images can be assigned to adjacent metal atoms rather than isolated single atoms, as exemplified by Pt dual-atom catalysts for selective hydrogenation and epoxidation (Fig. 1k)⁷. This distinction is critical because dual-atom sites exhibit cooperative adsorption and activation properties that are inaccessible to isolated single-atom catalysts. However, for heteronuclear clusters and dual-atom pairs, imaging contrast alone is often insufficient, making element-specific spectroscopy indispensable. In fully exposed Pt–Fe cluster catalysts for preferential CO oxidation, HAADF-STEM combined with EELS, EDS mapping identifies the coexistence and spatial association of Pt and Fe species at the atomic or subnanometer scale (Figs. 1l–1n)⁸. Similarly, in Ir_1 –Cu₁ dual-atom catalysts for low-temperature alkane dehydrogenation, the combination of atomic-resolution imaging and elemental mapping allows heteronuclear atomic pairs to be distinguished from isolated Ir or Cu atoms (Figs. 1o and 1p)⁶³.

Overall, modern EM can resolve multiple structural levels in carbon-supported metal catalysts, including the hybridization state and heteroatom distribution of the carbon support, the nuclearity of supported metal species, the local coordination environment of single atoms, and the elemental identity of homo- or heteronuclear atomic pairs and clusters. These capabilities provide structural insights into the stabilization of carbon supports on metal species and the effect of local metal–carbon interactions on catalytic performance.

4 In situ and operando electron microscopy

In situ and operando EM offers the most direct route from structure to mechanism because it can monitor catalysts during activation, restructuring, and deactivation under external stimuli. For carbon-supported metal catalysts, in situ and operando EM should not be limited to visualizing general dynamic processes. Instead, it should focus on three catalytically relevant questions: the formation and anchoring of metal species on carbon supports, the restructuring of the true working-state structure under reaction conditions, and the dynamic pathways of deactivation, including migration, coalescence, shell formation, and site loss. Following this logic, the following sections prioritize studies directly involving carbon-supported systems, while briefly referring to methodological benchmark systems only when the corresponding carbon-supported examples are lacking.

For carbon-supported metal catalysts, different in situ and operando TEM modes offer distinct advantages and limitations⁶⁴. Gas-phase or closed-cell in situ TEM is currently most directly relevant to thermal catalysis because it allows introducing temperature and reactive atmospheres simultaneously, thereby capturing realistic working-state processes such as particle migration, coalescence, surface-shell formation, and interfacial re-exposure⁶⁴. In situ heating TEM is better suited for studying catalyst activation, thermal stability, and sintering tendencies; however, in

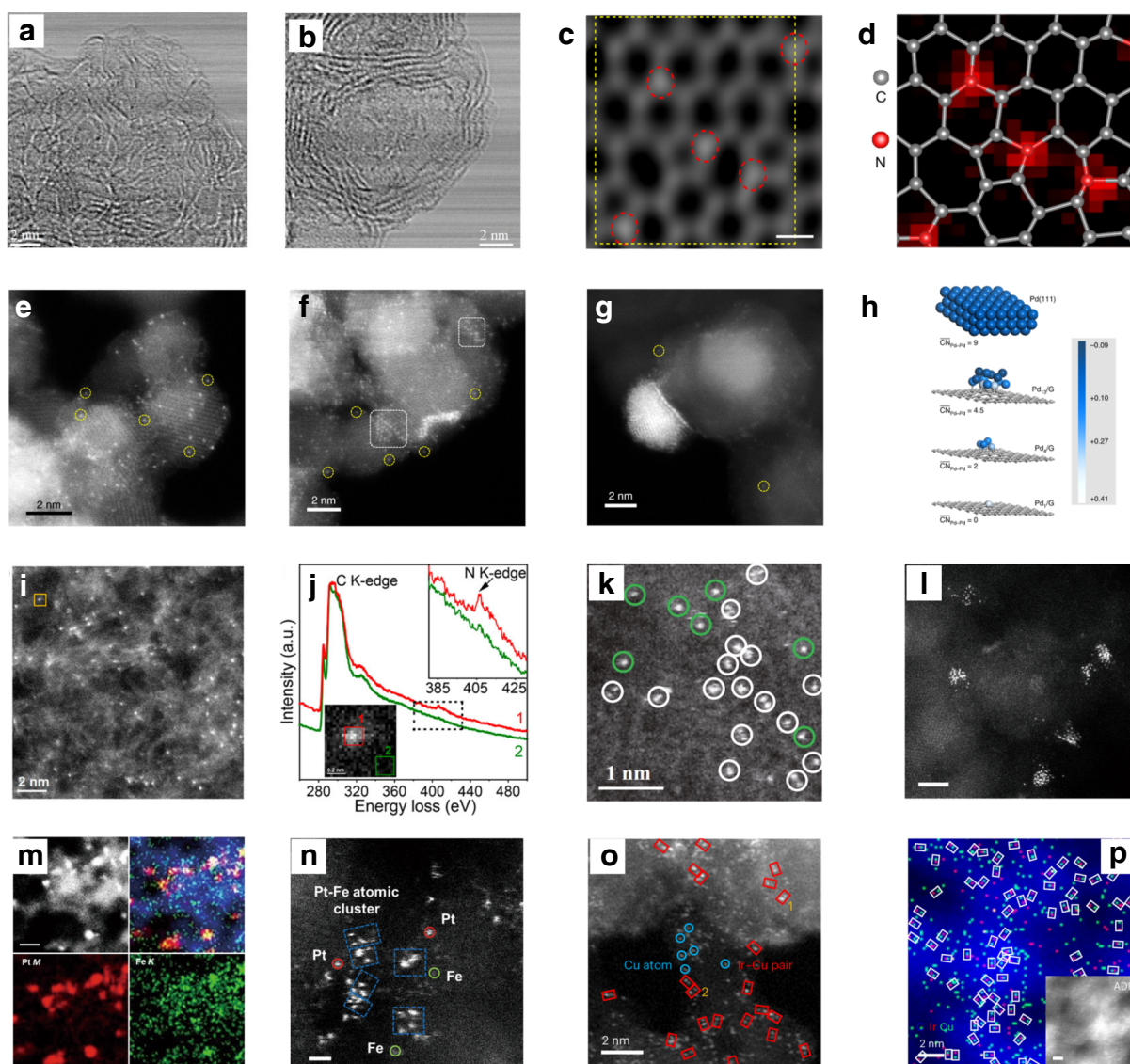


Fig. 1. **a**, Bright-field STEM image of a carbon sample showing predominantly sp^3 -rich domains together with graphitic fringes, indicating local coexistence of sp^2 and sp^3 carbon. **b**, Bright-field STEM image of an sp^2 carbon sample. Reproduced with permission from Ref.¹, © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2019. **c**, Representative high-magnification STEM-ADF image of N-doped amorphous monolayer carbon. The N atoms, which have a slightly higher image contrast, are highlighted by the red dashed circles. Scale bar: 0.2 nm. **d**, EELS map of N obtained from the area in (c) highlighted by the yellow box and overlaid with the corresponding atomic structural model. C and N atoms are represented by gray and red balls, respectively. Reproduced with permission from Ref.⁶², © Bai, X. H. et al. under exclusive licence to Springer Nature Limited. **e–g**, Atomic-resolved HAADF-STEM images of Pd1/ND (e), Pd₄/ND (f), and PdNP/ND (g). The yellow circles and white rectangles highlight Pd1 and Pd₄, respectively. **h**, Bader charge states for model configurations of Pd1/G, Pd₄/G, Pd13/G, and Pd(111). The color gradient in (h) indicates the Bader charge states, with the lighter color suggesting a decrease in the electron density of Pd. Reproduced with permission from Ref.⁹, © Dong, C. Y. et al., under exclusive licence to Springer Nature Limited. **i**, Representative HAADF-STEM image of Pt1/NC-1000-3h. **j**, Atomic-resolution EELS spectra recorded at positions 1 and 2 in the STEM image inset. The STEM inset image in (i) is an enlargement of the orange rectangle area in (i). The dotted rectangular area of the EELS spectra is also enlarged in (j). Reproduced with permission from Ref.⁴, © American Chemical Society 2021. **k**, AC HAADF-STEM images of Pt₂/mpg-C₃N₄. Reproduced with permission from Ref.⁷, © Tian, S. B. et al. 2021. **l**, HAADF-STEM images of 0.75Pt0.2Fe/ND@G at high magnification. Scale bar: 2 nm. **m**, Energy-dispersive X-ray (EDX) mapping images of 0.75Pt0.2Fe/ND@G catalyst. Scale bar: 2 nm. **n**, High-resolution HAADF-STEM image of 0.75Pt0.2Fe/ND@G, where representative isolated Pt and Fe atoms and atomic Pt–Fe clusters are highlighted by red and green circles and dashed blue rectangles, respectively. Scale bar: 0.5 nm. Reproduced with permission from Ref.⁸, © Jia, Z. M. et al. 2022. **o**, HAADF-STEM image of refreshed Ir₁Cu₁/ND@G at high magnification. The Ir₁Cu₁ atomic pairs are highlighted by red rectangles, and abundant Cu single atoms are highlighted by blue circles. **p**, EDX mapping showing the existence of abundant Ir₁–Cu₁ neighbors on Ir₁Cu₁/ND@G. The Ir₁Cu₁ atomic pairs are highlighted by white rectangles. Reproduced with permission from Ref.⁶³, © Chen, X. W. et al., under exclusive licence to Springer Nature Limited 2025.

the absence of reactive molecules, the observed changes more closely reflect structural evolution under thermal perturbation⁶⁵. Liquid-cell and electrochemical TEM are equally important for electrocatalytic systems such as Pt on carbon (Pt/C), particularly for probing dissolution/redeposition, corrosion, and electrochemical restructuring³⁷. Nevertheless, their broader applicability is

constrained by liquid-layer thickness, radiolysis effects, and window-related artifacts; therefore, they should not be regarded as more widely applicable than gas-phase in situ approaches. For carbon-supported thermal and electrocatalytic systems, gas-phase and in situ heating TEM are more suitable for evaluating thermal treatment, sintering, and working-state interfaces, whereas liquid-

cell and in situ electrochemical TEM are better suited for examining catalyst-layer restructuring and degradation in electrolytes^{64,66,67}.

Fig. 2 shows three representative examples of in situ TEM of carbon-supported materials under reaction conditions. Hu *et al.* compared Pt supported on carbon nanotubes (Pt/CNTs) and Pt on Vulcan (Pt/Vulcan) in a liquid electrochemical cell (**Figs. 2a–2f**)⁶⁷. Liquid-cell TEM showed that Pt/Vulcan catalysts suffered severe particle migration and coalescence, whereas Pt/CNTs underwent corrosion of the CNT support. This highlights the effect of the carbon nanostructure and metal–carbon binding on catalyst stability. As shown in **Figs. 2g–2j**, Liu *et al.* used sequential HRTEM to study the effect of heating on Ir on carbon (Ir/C)⁶⁵. Heating to 800 °C under vacuum induced graphitization of the carbon support and a carbon shell that partially encapsulates Ir nanoparticles, a

stability-enhancing strong metal–support interaction (SMSI)-like effect. This thermal in situ case illustrates how heating TEM can reveal dynamic restructuring at the metal–carbon interface. Finally, Luo *et al.* performed an environmental TEM (ETEM) study of Pt/C under controlled O₂ and H₂O pressures (**Figs. 2k–2m**)³⁷. In this classic example, exposure to O₂ drives Pt nanoparticle migration and coalescence on the carbon support, while H₂O vapor causes particles to rotate and merge. This complements the liquid-cell example by showing gas-phase dynamics. Together, these examples focused on liquid, heating, and gas-phase TEM on carbon-supported metal systems under realistic in situ conditions.

In situ TEM has revolutionized our understanding of catalyst structure and dynamics by capturing growth and reaction processes at the atomic scale. For example, Yuk *et al.* used graphene liquid-

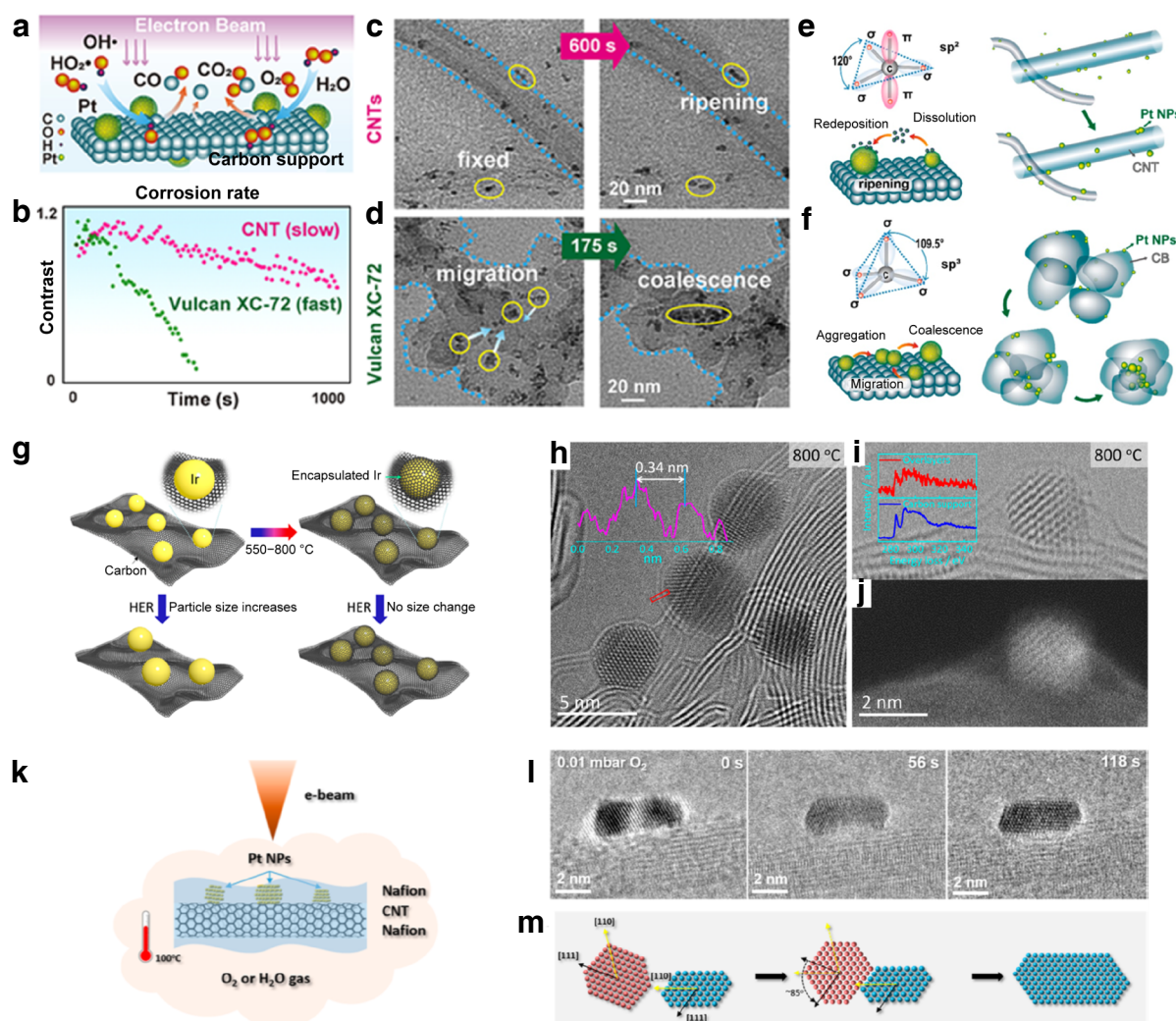


Fig. 2. **a**, Schematic of carbon corrosion pathways in liquid-cell TEM. **b**, Measured corrosion rates of two carbon supports as a function of time. **c**, Sequential images showing the main evolution behaviors of Pt nanoparticles loaded on CNTs. **d**, Sequential images showing the main evolution behaviors of Pt nanoparticles loaded on Vulcan. **e**, Illustration of carbon hybridization models demonstrating the degradation behaviors of Pt nanoparticles loaded on CNTs. **f**, Illustration of carbon hybridization models demonstrating the degradation behaviors of Pt nanoparticles loaded on Vulcan. Reproduced with permission from Ref.⁶⁷, © American Chemical Society 2024. **g**, Schematic of carbon encapsulation of supported metallic Ir nanoparticles. **h–j**, In situ HRTEM (**h**), BF-STEM (**i**), and SE-STEM (**j**) images of Ir/C recorded at 800 °C showing the formation of a carbon overlayer on Ir nanoparticles (green arrows). Inset in (**h**) shows the lattice d-spacing (0.34 nm) of the overlayer. Inset in (**i**) shows EELS spectra recorded from the overlayer and from the carbon support (red and blue traces, respectively), indicating that the encapsulated layer is carbon. Reproduced with permission from Ref.⁶⁵, © American Chemical Society 2023. **k**, Schematic of in situ ETM experimental setup showing the working conditions of Nafion/Pt/CNTs in O₂ or H₂O gases at 100 °C. **l**, Time-lapsed HRTEM images showing the coalescence process of two Pt nanoparticles after switching the gas from H₂O to O₂. **m**, Schematic of the coalescence of two Pt nanoparticles, which involves rotation of one nanoparticle and growth via orientation match. Reproduced with permission from Ref.³⁷, © American Chemical Society 2017.

cell TEM to film Pt nanocrystal formation in solution, revealing site-selective nucleation, particle coalescence, reshaping, and facet development in real time⁶⁸. Beyond classical studies of liquid-phase nucleation, recent advances in ETEM have enabled the tracking of nucleation processes under conditions closer to realistic growth environments^{69, 70}. For example, Ye *et al.* visualized the chemical vapor deposition growth of MoS₂, revealing its evolution from 2D amorphous embryos to ordered nuclei beyond a critical size, followed by oriented coalescence⁷¹. This work represents a recent methodological advance in the in situ study of nucleation. In gas environments, ETEM or operando TEM has monitored the evolution of metal-support interactions under reaction conditions. Using in situ spectroscopy, Qin *et al.* demonstrated that photogenerated electrons flow from TiO₂ to Ni in a TiO_{2-x}-Ni catalyst, promoting C-C coupling⁷². Similarly, advanced STEM imaging with EELS can trace chemical changes during catalyst activation, revealing that Mo precursors on carbon form highly dispersed MoO_x clusters upon H₂ treatment, with EELS confirming their carbide nature after carburization².

Operando ETEM studies further reveal catalyst restructuring under realistic conditions. Fig. 3 displays an example of working-state reconstruction in a carbon-supported catalyst. This operando electrochemical liquid-cell STEM (EC-STEM) study tracked a Cu single-atom catalyst on carbon during electrochemical CO₂ reduction (Figs. 3a–3f)⁷³. The initial frame shows atomically dispersed Cu on porous carbon. Over time, the Cu atoms aggregate into several-nanometer Cu nanoparticles that contain multiple grains. Finally, 4D-STEM diffraction images of the formed Cu particles reveal different crystallographic orientations and internal strain. Thus, the active catalyst is not the original single-atom catalyst but polycrystalline Cu nanoparticles. This directly shows that true catalytic states may differ from initial ex situ states under reaction conditions; here, isolated Cu atoms are transformed into nanograined particles, consistent with SMSI-like restructuring. Monai *et al.* showed that TiO_x encapsulates Ni nanoparticles on TiO₂ during reduction (a classic SMSI), followed by partial de-encapsulation under CO₂ hydrogenation⁷⁴. Specifically, TiO_x overlayers grown at 400 °C were fully removed under hydrogenation, whereas thicker overlayers remained on some Ni facets upon heating above 600 °C, creating Ni-TiO_x interfaces that act as carbon reservoirs. These interfaces favored C-C bond formation in hydrocarbon synthesis. Thus, ETEM, in concert with operando infrared (IR) spectroscopy and DFT analysis, directly linked dynamic overlayer formation to catalytic behavior. Remarkably, single-molecule reactions can also be visualized. Yuan *et al.* performed ETEM on a (1 × 4)-(001) TiO₂ surface exposed to H₂O vapor and CO (Figs. 3g–3i). They imaged a H₂O-adsorbed twin-protrusion structure on Ti_{4c} rows, corresponding to neighboring OH groups from a dissociated H₂O molecule (Figs. 3j–3p)⁷⁵. Time-resolved imaging showed the appearance and disappearance of these protrusions as H₂O was consumed by CO, directly identifying H₂O dissociation-active ridge sites. This direct adsorbate imaging, combined with complementary Fourier transform IR spectroscopy and DFT, provided an unprecedented view of a catalytic reaction at the atomic level.

These examples illustrate the reach of in situ/operando EM: from nanoparticle nucleation and growth to dispersion and activation of metal species and from support overlayer dynamics to single-molecule surface chemistry. In each case, the main observations, including growth steps, electron transfer, SMSI layers, and adsorbates, were correlated with complementary analyses, such as

in situ X-ray absorption spectroscopy (XAS)-EELS, IR-diffuse reflectance infrared Fourier transform spectroscopy, and DFT^{76, 77}. These integrated approaches have uncovered fundamental mechanisms that control catalytic activity and selectivity, including SMSI overlayer cycling and interfacial charge transfer.

These examples highlight the evolution of modern in situ EM into a quantitative tool for catalysis: aberration-corrected STEM yields single-atom contrast, fast cameras capture transient states, and combined spectroscopy-DFT elucidate electronic effects. When carefully calibrated to mitigate beam damage and pressure gaps, these techniques link dynamic structure to function, revealing, for instance, the governing effect of metal sintering and redispersion, support SMSI cycles, and adsorbate binding on catalyst performance. Continued integration of operando EM with spectroscopy, electron energy-loss mapping, and AI-driven image analysis will deepen the mechanistic understanding of carbon-supported metal catalysts under real reaction conditions.

5 Summary and outlook

EM has evolved from a largely static, morphology-centered characterization tool into a dynamic and increasingly quantitative platform for evaluating carbon-supported metal catalysts across the full hierarchy of catalytically relevant length scales, i.e., from isolated atoms and subnanometer clusters to nanoparticles and porous catalyst layers. Conventional TEM and HRTEM remain indispensable for analyzing particle size, morphology, lattice fringes, and support texture. However, aberration-corrected STEM and HAADF imaging, EELS/EDS spectrum imaging, 3D electron tomography (Figs. 4a and 4b)⁷⁸, pixelated-detector-based 4D-STEM⁷⁹, and in situ or operando gas- and liquid-cell microscopy have enabled the most decisive conceptual advances. Electron tomography is particularly critical for porous carbon supports, because 2D projection images cannot reliably distinguish whether metal nanoparticles or atomic clusters are located on external surfaces, within internal pores, in interlayer spaces, or inside locally enclosed cavities⁸⁰. For fuel-cell and porous carbon catalyst layers, recent cryoelectron tomography has enabled quantitative identification of the external carbon skeleton, the spatial distribution of ionomer networks, and the accessibility of Pt sites to both ionomers and mass transport channels⁸¹. These advances have allowed shifting the research focus from the location of the particles to their real accessibility and transport-relevant and catalytic usefulness. Thus, for carbon-supported metal catalysts, the value of tomography lies not only in 3D localization but also in establishing structure-function relationships among particle position, pore openness, and reactant/ion accessibility. By exploiting these techniques, researchers can not only determine the location of catalytically relevant metal species on the carbon support but also monitor their migration, coarsening, restructuring, or stabilization under thermal, electrochemical, and reactive environments.

Fig. 4 depicts schematics of studies focusing on 3D imaging and accessibility of carbon-supported catalysts as well as metal location (interior vs exterior) and site accessibility. Girod *et al.* used cryogenic STEM tomography to image an entire Pt/C catalyst layer (Figs. 4c–4e)⁸⁰. In the tomographic 3D reconstruction, Pt nanoparticles are segmented according to their location on the carbon pores (inside or outside, pink vs green). The analysis shows that about 46% of Pt particles reside inside the carbon pores (with mean diameters of ~ 2.7 nm vs 3.0 nm outside), clearly demonstrating that tomography can be used to measure pore

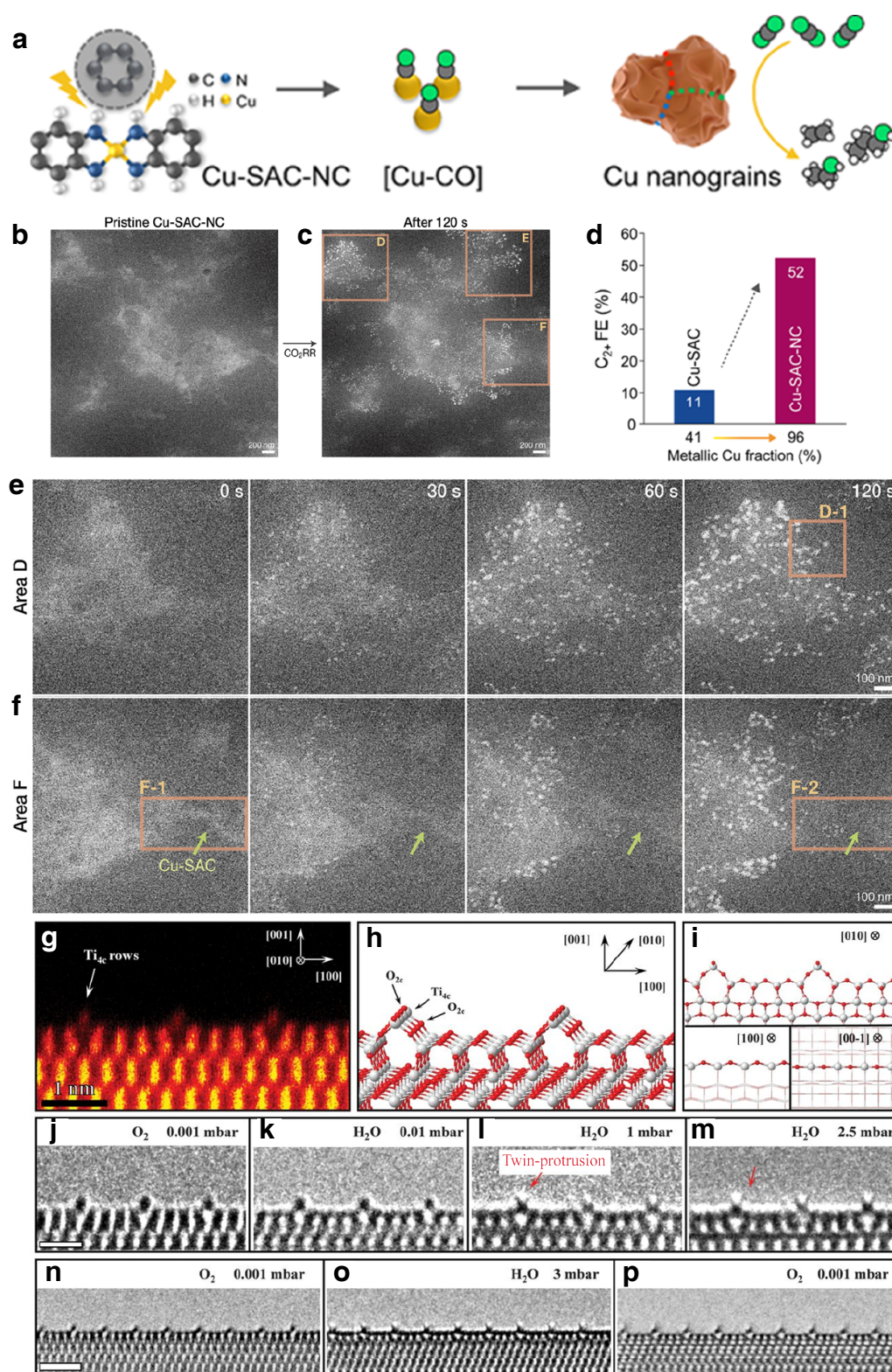


Fig. 3. **a**, Schematic of dynamic evolution from single-atom catalysts (SACs) to active nanograins. **b**, **c**, Low-magnification EC-STEM images of (b) pristine single-atom catalysts (SACs) and (c) Cu nanograins after CO_2 reduction reaction (CO_2RR) for 120 s in liquids. **d**, Structure–activity correlations of major C_{2+} products. **e**, **f**, Selected magnified EC-STEM images during CO_2RR of (e) ‘Area D’, and (f) ‘Area F’ indicated by orange boxes in (c). Reproduced with permission from Ref.⁷³, © American Chemical Society 2025. **g**, HAADF-STEM image of the $(1 \times 4)-(001)$ surface, viewed from the $[010]$ direction, acquired at 700 °C under vacuum (TEM column pressure: $\sim 10^{-7}$ mbar). **h**, ADM reconstruction models of the $(1 \times 4)-(001)$ surface (Ti , gray; O , red). **i**, Atomic models of a Ti_{4c} row. **j–m**, Aberration-corrected in situ ETEM images of the same area of a $TiO_2(001)$ surface at 700 °C under O_2 (j), 0.001 mbar and H_2O vapor (k, 0.01 mbar; l, 1 mbar; m, 2.5 mbar) conditions. Scale bar, 1 nm. **n–p**, Reversible structural transition induced by changing the gas environment at 700 °C from O_2 (n), 0.001 mbar to H_2O vapor (o, 3 mbar) and then back to O_2 (p), 0.001 mbar. Scale bar, 2 nm. Reproduced with permission from Ref.⁷⁵, © Yuan, W. T. et al., some rights reserved; exclusive licensee American Association for the Advancement of Science 2020.

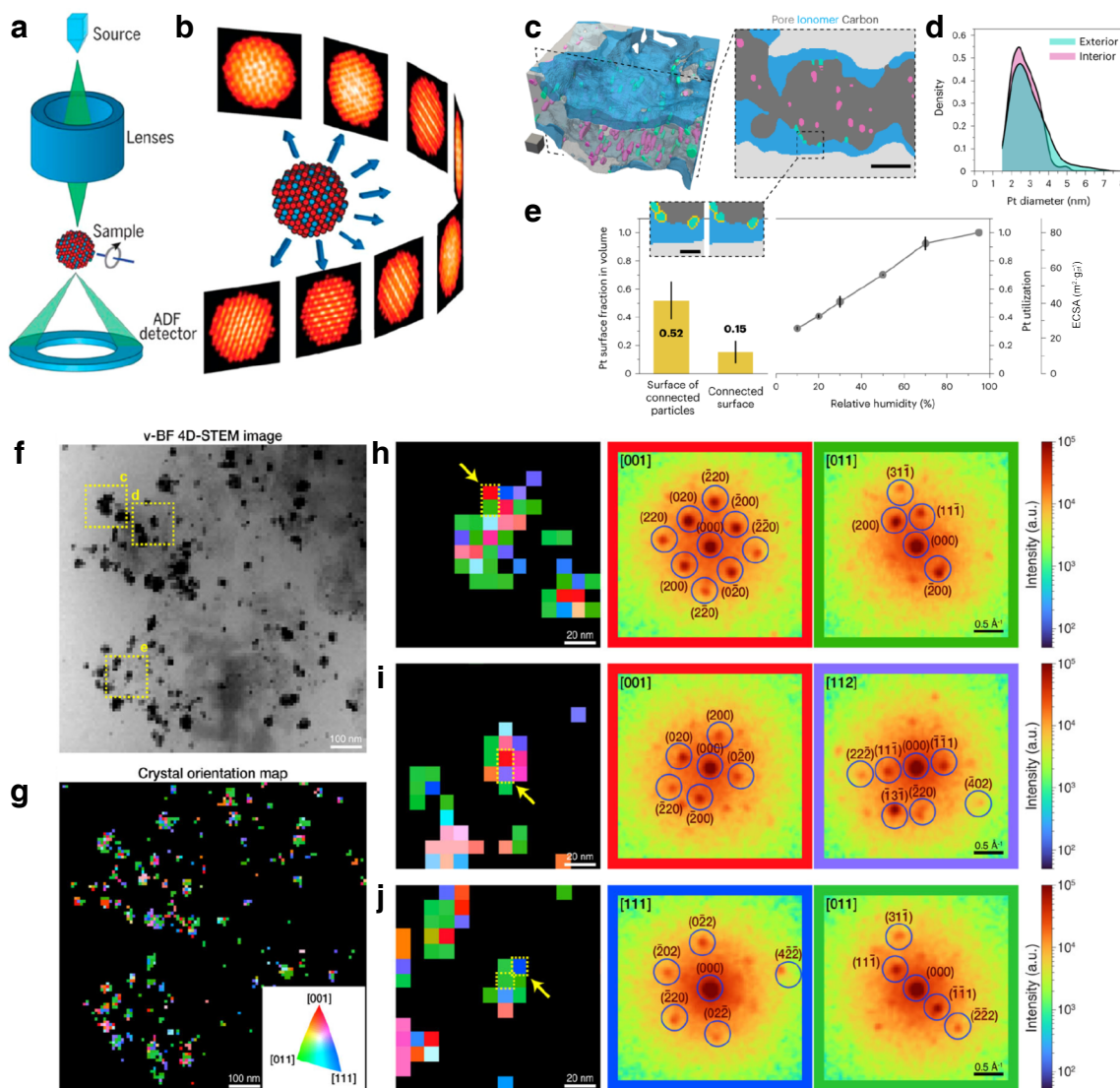


Fig. 4. **a, b,** Schematic of an atomic electron tomography experiment. An electron beam is focused on a small spot and scanned over the sample to form a 2D image, which is recorded by an ADF detector (**a**). By rotating the sample around a tilt axis, 2D images are recorded at different tilt angles, enabling 3D reconstruction by advanced computational algorithms (**b**). Reproduced with permission from Ref.⁷⁸, © American Association for the Advancement of Science 2016. **c,** Subvolume and magnified 2D maps demonstrating the localization of Pt nanoparticles, i.e., inside (pink) or outside (green) the porous carbon supports. Scale cube, 10^3 nm^3 ; scale bar, 20 nm. **d,** Distribution of Pt diameters as a function of their location. The cutoff at 1.5 nm accounts for the resolution limit. **e,** Comparison of Pt surface measurements from tomography and electrochemistry. As illustrated in the magnified slices (scale bar, 5 nm), the measurements from the tomographic reconstruction represent the fraction of Pt surface in direct contact with the ionomer (connected surface), and the fraction of Pt surface of all particles in contact with the ionomer (surface of connected particles). Reproduced with permission from Ref.⁸⁰, Girod, R. et al. 2023. **f, g,** v-BF 4D-STEM image (**f**) and the corresponding 4D-STEM analysis (**g**) of a crystal orientation map. Inset in (**g**): inverse pole figure of Cu metal. **h–j,** Enlarged crystal orientation maps of selected examples of Cu nanograins from the areas indicated by yellow dashed boxes in (**f**). Color-coded diffraction patterns of colored pixels, indicated by yellow arrows and dashed boxes, are presented next to the enlarged maps. Each crystal orientation is indexed at the top-left of the diffraction patterns. Simulated diffraction patterns from the matched orientations are denoted and marked with blue circles. Reproduced with permission from Ref.⁷³, © American Chemical Society 2025.

accessibility and Pt distribution. The included connected-surface analysis quantifies contacts between the Pt surface and the ionomer, matching electrochemical surface area. Figs. 4f–4j illustrate that operando 4D-STEM can complement tomography by providing in situ crystallographic information⁷³. For the Cu particle in Fig. 3, 4D-STEM orientation maps show multiple diffraction spots corresponding to different grain orientations, showing that 4D-STEM provides atomic-scale detail (grain orientation/strain) during reactions. As shown in Fig. 4, combining 3D pore imaging with operando diffraction imaging fully addresses 3D site distribution and accessibility in carbon supports.

For carbon-supported metal catalysts, the most robust mechanistic advances fall into four areas. First, EM has clarified the structural continuum of metal species on carbon, showing that isolated atoms, subnanometer clusters, and nanoparticles can coexist and interconvert, particularly on defect-rich or heteroatom-doped carbon materials^{82, 83}. Second, it has revealed the functions of the carbon support: support topology, pore accessibility, graphitic order, and nitrogen-containing anchoring motifs are no longer passive descriptors but variables that govern dispersion, corrosion resistance, and mass transport^{17, 84}. Third, it has provided direct evidence that catalyst aging on carbon often proceeds via particle

migration and coalescence^{72, 74}. Fourth, in situ and operando microscopy, albeit more mature for model oxide systems than for carbon powders, has established a methodological framework for linking dynamic restructuring to turnover, selectivity, and deactivation^{85–88}.

The next stage of the field will probably focus more on reliability under working conditions than on further gains in spatial resolution. This will require better-calibrated reaction cells, larger and more representative datasets, rigorous beam-effect control, correlative multimodal workflows, and AI-assisted analysis that can convert high-volume microscopy data into validated structure–activity relationships. Therefore, the central question is: Can we demonstrate that what we image is catalytically relevant, statistically representative, and quantitatively reproducible?

The outlook for the field can be summarized as follows:

(1) Operando EM for carbon-supported catalysts will benefit from more realistic gas and electrochemical cells, including higher-pressure and higher-temperature compatibility, better local environmental calibration, and closer coupling to online kinetic readouts. Open-cell environmental approaches for transient hydration, improved holders for biasing and heating, and correlative workflows that bridge EM with X-ray spectroscopy, mass spectrometry, and electrochemical analytics are especially promising because they can reduce the interpretation gap between nanoscale observation and measured performance.

(2) Detector technology and multidimensional acquisition will become as relevant as microscope optics. Pixelated detectors and mature 4D-STEM analysis have enabled the extraction of virtual detector images, orientation maps, local deformation information, and related descriptors from the same raw dataset (Figs. 4f–4j)⁷⁹. For carbon-supported catalysts, such approaches could become particularly valuable for mapping strain in alloy nanoparticles, detecting subtle restructuring in confined pores, and separating structural heterogeneity from mere projection effects. Similarly, atomic electron tomography will become more influential wherever atomic-scale 3D site structure, not only average composition, controls activity and stability⁸⁹.

(3) AI and machine learning will probably have a pronounced impact not by replacing expert interpretation but by making advanced EM quantitatively scalable^{39, 41, 90}. Several directions are already concrete. Simulation-trained deep denoisers have shown that high-noise TEM data can be enhanced without paired clean ground truth; in this context, a study released an 18,000-image TEM benchmark dataset, which is precisely the kind of infrastructure the catalysis community has lacked. Weakly supervised deep learning has also identified atomic positions and defects in STEM images and tracked local transformations over time, while Bayesian AI-STEM frameworks have classified crystal structures and interfaces and return uncertainty estimates rather than only hard labels. The next step is to adapt these capabilities to catalyst-specific tasks. For carbon-supported metal catalysts, the most immediately useful AI applications are the following. First, denoising and drift correction can make low-dose imaging of beam-sensitive carbon structures more reliable. Second, semantic segmentation and object detection can convert thousands of frames into statistically meaningful distributions of particle size, shape, interparticle distance, and motion trajectories. Third, single-atom and cluster recognition, especially when paired with simulated training data, can help distinguish true isolated sites from close projections, contamination, or weak-contrast artifacts. Fourth, multimodal fusion can integrate HAADF-STEM, EELS, XAS,

electrochemistry, and DFT-derived descriptors into structure–activity models that are more chemically meaningful than image-only classifiers. Finally, active-learning microscopy could allow the instrument to allocate dose and acquisition time preferentially to rare restructuring events rather than uniformly scanning the whole field. These recommendations are natural extensions of existing open and AI-enabled EM systems, not speculative applications.

The next generation of miniaturized catalyst science will depend less on proving that EM can image a single atom and more on making such observations quantitative, conditional, and predictive. To this end, carbon-supported metal catalysts will need more realistic gas and liquid microreactors, tighter coupling of EM with online catalytic readouts, broader adoption of correlative spectroscopy, higher-throughput image analysis, and benchmarked AI pipelines that report uncertainty rather than only classification confidence. If those pieces come together, electron microscopy will move from being primarily a structural witness to becoming a genuine mechanistic engine for catalyst design.

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Data availability

Not applicable.

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Conceptualization and supervision: X. Q.; Investigation, resources, and visualization: X. C.; Writing of original draft: X. C.; Review and editing: X. Q..

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

Use of AI statement

None.



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