



CVD graphene on iron, iron alloys and nanoparticles: a review of its growth, characterization, applications and challenges

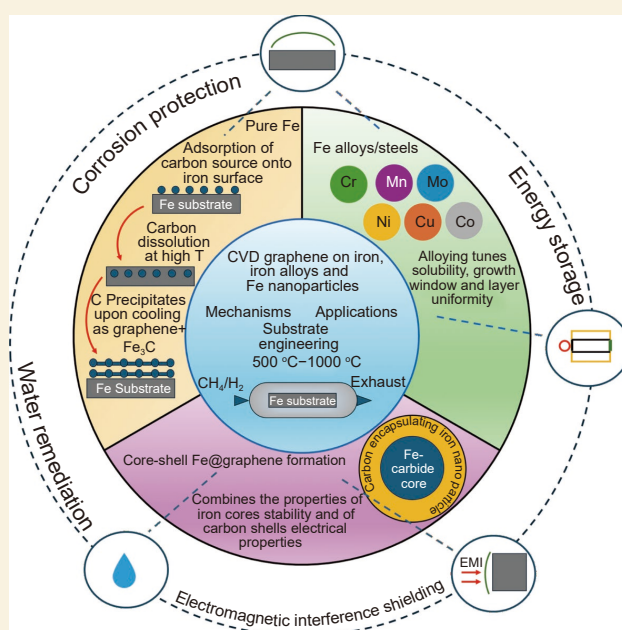
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Abstract: Graphene's outstanding electrical, thermal, mechanical, and chemical properties make it a promising material for electronics, energy storage, protective coatings, catalysis, and environmental remediation. Nevertheless, its large-scale use is hindered by high synthesis costs, process complexities, and integration issues. Among the available methods for its production, chemical vapor deposition (CVD) on metals is the most scalable, in which copper is widely used because of its low carbon solubility and excellent monolayer control. However, Cu substrates are costly (\$8–10/kg), subsequent transfer steps introduce defects, and the obtained graphene is poorly matched to structural components. Iron-based substrates provide an attractive alternative, offering much lower material cost, direct compatibility with steel infrastructure, reduced growth temperatures, and intrinsic functionalities such as magnetism and catalytic activity that enable new applications. The growth of graphene on pure iron, iron alloys, and iron-based nanoparticles is analyzed, focusing on growth mechanisms, substrate engineering, and characterization approaches tailored to specific challenges like carbide formation.

Applications including corrosion-resistant coatings, electronics, energy storage, catalysis, water treatment, and electromagnetic shielding are considered. Despite the limitation of high carbon solubility, iron can be exploited for controlled multilayer formation which is useful for barrier and energy applications, while alloying and process control enable the production of tunable mono layer or few-layer films, making iron-based CVD graphene a versatile, cost-effective platform.

Key words: CVD graphene; Iron-based substrates; Growth mechanism; Substrate engineering; Steel integration



1 Introduction

Graphene was isolated in 2004 by Geim and Novoselov through micromechanical exfoliation of graphite, earning them the 2010 Nobel Prize in Physics^[1]. This monolayer of sp^2 -hybridized carbon atoms arranged in a honeycomb lattice features a C—C bond length of 0.142 nm, Van der Waals radius of 0.11 nm and thickness of 0.334 nm^[2]. Graphene remains chemically inert under ambient conditions up to 400 °C while exhibiting exceptional properties: specific surface area of 2600 m²/g^[1], tensile strength of 130 GPa, Young's modulus of 1 TPa^[3], thermal conductivity of 3000–5000 W·m⁻¹·K⁻¹^[4] and electron mobility of

200 000 cm²/V·s^[5], enabling applications in coatings, electronics, and energy storage.

Graphene synthesis approaches divide into top-down (mechanical/liquid exfoliation, chemical reduction of graphene oxide) and bottom-up (epitaxial growth on SiC, chemical vapor deposition on metal catalysts) methods^[6]. Top-down exfoliation yields high-quality graphene but lacks scalability and con-

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trol. Bottom-up approaches synthesize graphene from carbonaceous precursors on substrates such as copper, nickel, silicon, or silicon carbide^[7–9].

Chemical vapor deposition (CVD) is the state-of-the-art technique for synthesizing high-quality graphene on metal substrates, where substrate choice critically affects the quality of graphene, layer number, and properties^[10–11]. Transition metals exhibit varying carbon solubility due to *d*-orbital configuration. Metals with unfilled *d*-orbitals (Ni, Co, Fe, Pd) have high carbon affinity, allowing carbon dissolution into the substrate^[12–13], leading to multilayer graphene formation with variable uniformity. In contrast, metals with filled *d*-orbitals (Cu, Zn) exhibit low carbon solubility, favoring uniform monolayer graphene growth.

Numerous studies demonstrate graphene growth on transition metals (Ni, Pd, Cu, Co) using CVD^[14–17], with carbon solubility decreasing as Fe > Co > Ni > Pd > Cu^[18]. Copper is the most widely used substrate due to its low carbon solubility, which promotes high-quality monolayer graphene formation and simplifies the transfer process to other substrates^[19]. However, copper's high material cost (\$8–10/kg vs. \$1–2/kg for iron^[20]) limits widespread commercialization for large-area applications such as protective coatings or structural composites.

As the most abundant structural metal globally, with annual production exceeding 1.9 billion tons, iron provides unmatched availability and cost advantages^[21]. Iron's high carbon solubility makes it a promising candidate for graphene synthesis, enabling unique capabilities: direct integration with steel components (eliminating transfer processes), lower synthesis temperatures due to its high catalytic activity, and multilayer graphene production suitable for applications where few-layer structures provide adequate or superior performance (corrosion protection, tribological coatings, EMI shielding, energy storage).

Iron-graphene research has evolved substantially since early demonstrations in 2010. Initial studies established feasibility and revealed complex interplay

between surface-mediated segregation and bulk precipitation-dissolution processes^[22–23]. Recent advances in in-situ characterization provide unprecedented insight into growth dynamics, while computational methods have elucidated atomic-scale interfacial phenomena^[24–25].

Despite iron's advantages, comprehensive analysis of graphene synthesis on iron-based substrates remains absent from review literature. Existing reviews on CVD graphene synthesis focus predominantly on copper and nickel substrates, with iron receiving minimal attention^[18,26–28]. Reviews addressing iron-graphene systems focus on composite materials (iron oxide nanoparticles with graphene derivatives for sensing or catalysis^[29]) rather than synthesis mechanisms on metallic iron. This gap persists despite pioneering demonstrations over a decade ago^[22,30]. To the best of our knowledge, this review offers the first comprehensive and systematic analysis of graphene synthesis on iron-based substrates, covering growth mechanisms, substrate engineering (pure iron, alloys, steels), characterization methodologies, and applications in protective coatings, electronics, energy storage, catalysis, water remediation, and electromagnetic shielding.

2 Fundamentals of graphene growth on transition metals

2.1 General mechanism of graphene synthesis on transition metals

Graphene synthesis on transition metal foils occurs primarily through CVD, where gaseous hydrocarbons mixed with hydrogen are exposed to high temperatures^[31]. During CVD, the growth mechanism of graphene depends critically on substrate carbon solubility. Graphene growth on these transition metal substrates proceeds through 2 overarching mechanisms: surface adsorption and carbon dissolution-precipitation. The dissolution-precipitation mechanism manifests in 2 distinct variants: precipitation-driven (supersaturation-controlled) and segregation-driven (surface-mediated)^[32].

2.1.1 Surface adsorption mechanism (low carbon solubility metals)

Surface adsorption occurs on substrates with low carbon solubility, such as copper ($\text{Cu} \sim 0.008\%$ at 1084°C), gold (Au), and silver (Ag)^[18]. Hydrocarbons adsorb and catalytically dehydrogenate on these metal surfaces, forming sp^2 -bonded carbon without significant bulk diffusion^[28,33] (Fig. 1). At high temperatures ($\sim 900^\circ\text{C}$), molecular hydrogen (H_2) dissociates into atomic hydrogen (H), which dehydrogenates adsorbed hydrocarbons (C_xH_y) into carbon atoms that form sp^2 -hybridized graphene on the surface^[27]. This self-limiting process yields uniform monolayer graphene, making copper the standard for single-layer synthesis^[10,12].

2.1.2 Precipitation-driven mechanism (high carbon solubility metals)

On transition metals with high carbon solubility, iron ($\text{Fe} \sim 2.09\%$, mass fraction, at 1147°C), cobalt ($\text{Co} \sim 0.9\%$, mass fraction, at 1320°C), and nickel ($\text{Ni} \sim 0.6\%$, mass fraction, at 1326°C) graphene growth proceeds by carbon segregation and precipitation^[18,34]. During high-temperature CVD, carbon atoms adsorb onto the surface and diffuse into the bulk lattice, potentially forming metastable carbides^[35]. Upon cooling below the eutectoid temperature, these carbides decompose, releasing carbon that migrates to the surface and reorganizes into hexagonal graphene^[18,35] (Fig. 2). This dissolution-precipitation process typically produces multilayer graphene^[36–37]. While the high carbon solubility is beneficial for the catalytic breakdown of hydrocarbon precursors, it complicates the control of graphene layer thickness and uniformity due to carbon precipita-

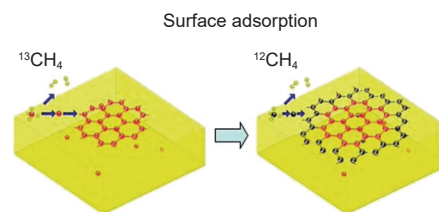


Fig. 1 CVD graphene synthesis by surface adsorption mechanism on low carbon solubility metals (reprinted with permission, copyright 2009, ACS^[34])

tion during the cooling stage^[28,38].

2.1.3 Segregation-driven mechanism (moderate carbon solubility metals)

Metals with moderate carbon solubility, such as ruthenium ($\text{Ru} \sim 0.34\%$, atom fraction, at 1000°C) and iridium ($\text{Ir} \sim 0.041\%$, atom fraction, at 1256°C), exhibit segregation-driven growth^[39–41]. Carbon atoms remain subsurface and segregate to the surface upon cooling to form graphene. This mechanism offers enhanced control over layer thickness and uniformity compared to precipitation-driven growth, with high-quality graphene films demonstrated on both Ru ^[42] and Ir ^[42–43].

2.2 Iron as a catalyst: unique challenges

Despite its abundance, low cost, and high catalytic activity, iron presents several challenges for CVD graphene synthesis^[44]. Like other high-carbon-solubility metals (Co , Ni), iron facilitates precipitation-driven growth but exhibits more complex behavior due to phase transitions and stable carbide formation governed by Fe-C phase diagram thermodynamics.

2.2.1 Fe-C phase diagram and carbon solubility

The iron-carbon phase diagram (Fig. 3) reveals complex temperature-dependent behavior critical to graphene formation. Above 912°C , iron exists as FCC austenite ($\gamma\text{-Fe}$) with maximum carbon solubil-

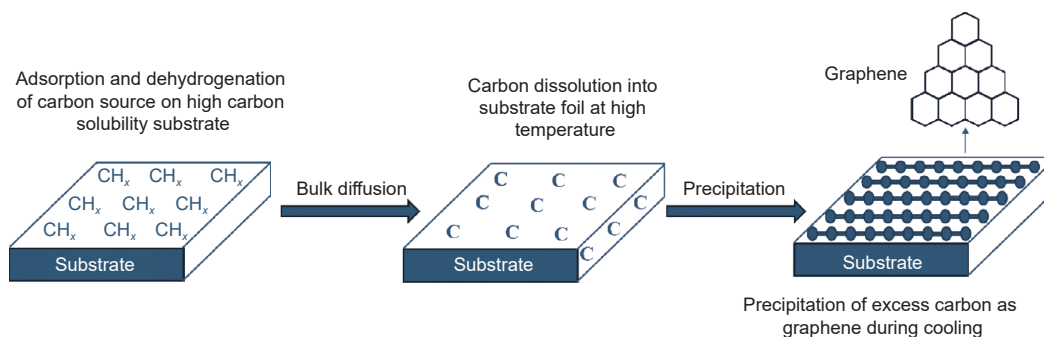


Fig. 2 Schematic illustration of general precipitation mechanism for graphene growth on high carbon solubility metal substrates

ity of 2.09% (mass fraction) at 1147 °C, 250 times greater than copper's 0.008% (mass fraction)^[40]. This high solubility enables substantial bulk carbon dissolution, fundamentally altering the growth mechanism compared to low-solubility metals.

During cooling, carbon precipitates as graphene and form γ -iron (austenite). Further cooling to the eutectoid temperature of ~ 727 °C transforms FCC austenite to BCC ferrite (α -Fe, carbon solubility of 0.022%, mass fraction) and excess or residual carbon that remain supersaturated within the iron matrix react to form iron carbide (Fe_3C , C $\sim 2.14\% - 6.67\%$) under suitable thermodynamic and kinetic conditions^[30,45]. Unlike meta-stable carbides in Ni and Co (Ni_3C , Co_3C) that decompose to release carbon for graphene formation^[18,39], Fe_3C is thermodynamically stable at room temperature. This stability means that the carbide competes with graphene formation and can trap carbon atoms within the bulk.

This carbide competition, coupled with strong carbon-iron interactions and uncontrolled multilayer precipitation during cooling, produces graphene with significant defects and poor layer uniformity, limiting precise thickness control despite iron's abundance and low cost.

While the Fe-C phase diagram (Fig. 3) provides a useful thermodynamic framework for understanding carbon solubility and phase stability, however, graphene growth by CVD on iron occurs under strongly non-equilibrium conditions. During typical processing, rapid heating and cooling (5-100 °C/min), continuous carbon supply, and finite diffusion rates prevent the system from reaching equilibrium, resulting in kinetic supersaturation ($\Delta c_{\text{kinetic}} > \Delta c_{\text{equilibrium}}$) and meta-stable phase formation^[46]. These non-equilibrium effects strongly influence phase selection. Although graphene is thermodynamically favored at the surface under appropriate conditions, Fe_3C (cementite) often forms as the kinetically preferred phase due to its lower nucleation barrier and faster formation rate. Consequently, graphene and Fe_3C often coexist, particularly in regions where local supersaturation and diffusion flux vary spatially across the sub-

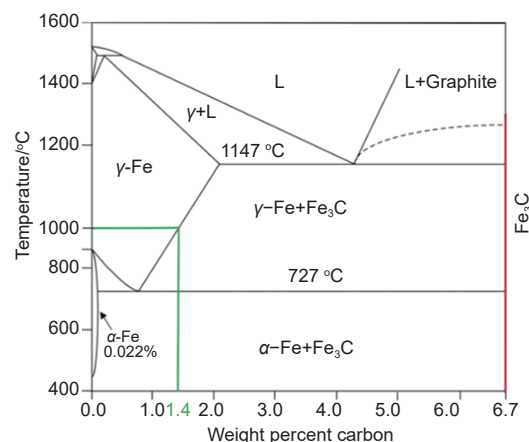


Fig. 3 Fe-C phase diagram. Adapted from^[18]

strate. In-situ and ex-situ studies on Fe-based and Ni-based catalysts show carbide peaks appearing at higher temperatures and with larger volume fractions than predicted by equilibrium diagrams when cooling is rapid, while slower cooling suppresses carbide formation by allowing closer approach to equilibrium^[47]. Similar precursor carbide effects have been observed on Ni-based catalysts^[48], confirming the general importance of kinetic pathway selection in high-solubility metal systems. Nucleation behavior is also governed by kinetic supersaturation. According to classical nucleation theory ($J \propto \exp(-\Delta G/kT)$), increase in supersaturation exponentially enhances nucleation rates, leading to higher graphene nucleation density and reduced domain size. This results in multilayer overlap, increased grain boundary density, and non-uniform thickness distributions^[46]. Conversely, lower efficiency supersaturation favors fewer nucleation sites and promotes the lateral graphene growth.

These kinetic effects manifest in several experimentally observed morphological features on iron substrates, including: (1) heterogeneous graphene thickness arising from spatially and temporally varying Δc , (2) coexistence of graphene and Fe_3C phases due to arrested phase separation, (3) wrinkle formation driven by thermal mismatch between graphene ($\alpha \approx -8 \times 10^{-6} \text{ K}^{-1}$) and Fe ($\alpha \approx +12 \times 10^{-6} \text{ K}^{-1}$)^[25], and (4) increased grain boundary (defect) density associated with elevated nucleation rates. Importantly, these features cannot be explained solely by equilibrium thermodynamics, instead they reflect the dominant

role of kinetic constraints.

Collectively, these observations demonstrate that graphene growth on iron is governed by a kinetically controlled supersaturation–precipitation process, in which thermal history and diffusion kinetics determine phase evolution and morphology. The Fe–C phase diagram remains an essential thermodynamic reference, but quantitative process design for CVD must incorporate kinetic corrections for heating/cooling rates and diffusion limitations, which suggests that the actual growth pathway is dictated by non-equilibrium dynamics.

2.2.2 Mechanism competition and dominant regimes

As detailed in the Sections 2.1.1 and 2.1.3, the relative importance of surface-mediated vs. precipitation-dissolution mechanisms on Fe remains incompletely understood. Literature reports show apparent contradictions, with studies at similar temperatures (700–800 °C) attributing graphene formation to different mechanisms^[24,49]. Growth mechanism reflects complex interplay of multiple factors rather than temperature alone:

Temperature influences both thermodynamics (carbon solubility^[50]) and kinetics (diffusion rates), with low temperatures (<700 °C) favoring surface segregation due to limited bulk diffusion^[24] while high temperatures (>900 °C) enable significant precipitation^[49]. Carbon chemical potential, determined by precursor flow rates and reactivity, controls whether carbon preferentially adsorbs on surfaces or dissolves into bulk^[51]. Cooling rate critically affects graphene growth, rapid cooling (>100 °C/min) kinetically traps dissolved carbon forcing precipitation, while slow cooling allows surface equilibration^[49]. Substrate orientation introduces variations in adsorption energies and diffusion barriers, causing Fe(110) single crystals to behave differently than polycrystalline iron foils^[25,52]. Substrate purity including pre-existing carbides, surface oxides, and vacuum quality significantly alters nucleation and carbon partitioning^[51,53]. This complexity provides synthesis flexibility: surface-dominated growth for layer control, precipitation-dominated growth for rapid multilayer formation.

Controlling graphene coverage and thickness requires simultaneous optimization of multiple parameters rather than temperature control alone.

These fundamental principles manifest differently across iron-based substrate systems: pure iron, iron alloys, and iron nanoparticles with substrate composition and morphology determining synthesis outcomes.

3 Iron-based substrates for graphene growth

Graphene synthesis on iron-based substrates varies significantly across pure iron, iron alloys, and iron nanoparticles. This section reviews the synthesis mechanisms, results, and performance outcomes for each substrate class.

3.1 Pure iron substrates

Pure iron substrates present unique challenges for graphene synthesis due to high carbon solubility, iron carbide formation, and lattice mismatch with graphene. However, iron's abundance, low cost, and high catalytic activity make it attractive for large-scale applications where multilayer graphene is acceptable or even preferred. Understanding iron optimization for graphene synthesis requires investigating the fundamental mechanisms governing graphene growth on transition metals and the unique thermodynamic context of iron.

3.1.1 Growth mechanisms and challenges

Achieving uniform single-layer graphene on iron is inherently more difficult than on copper or nickel due to fundamental differences in carbon solubility and phase behavior. Following the precipitation-driven mechanism described in Section 2.1.2, iron's high carbon solubility promotes bulk dissolution and carbide formation, complicating surface-controlled graphene growth.

Although iron's nearest-neighbor Fe–Fe spacing (0.248 nm) closely matches graphene's lattice constant (0.246 nm), similar to Ni and Co, iron crystal faces lack the hexagonal symmetry required for epitaxial matching with graphene's honeycomb lattice. Consequently, graphene on iron experiences significant

ant registry mismatch and anisotropic strain, producing morphologies that differ substantially from the relatively flat, epitaxial films on close-packed surfaces of other 3D transition metals such as Ni(111), Co(0001) or Ru(0001)^[54]. This structural incompatibility makes uniform single-layer growth particularly challenging^[25]. Challenges and strategies developed for producing high quality graphene are further explained in Section 6.

3.1.2 Thermal CVD on Fe film and foil

Thermal CVD remains the most widely used method for growing graphene on iron foil and film. The mechanism follows the classic dissolution–precipitation pathway for high-carbon-solubility metals: (1) adsorption and catalytic breakdown of carbon precursors on the Fe surface, (2) dissolution and diffusion of carbon into bulk Fe (especially the high-solubility γ -Fe phase), and (3) precipitation of carbon onto the surface during cooling, where decreased carbon solubility drives graphene formation^[55].

Edwards et al.^[56] demonstrated multilayer graphene growth on Fe by low-pressure CVD at 600–800 °C using acetylene. The authors observed that the precursor exposure critically affects graphene growth: shorter exposure yields lower surface coverage and thinner films. Fe film thickness also influences growth, with thicker Fe layers producing thinner graphene due to modified carbon solubility and diffusion. Within temperature range of 600–800 °C, higher temperatures favor thicker, more graphitic films with fewer defects. Obtaining thin, high-quality graphene requires jointly optimizing growth temperature, Fe film thickness, and precursor exposure.

Xue et al.^[22] pioneered large-area graphene synthesis on iron foil by CVD at 920 °C with CH_4/H_2 precursors, achieving few-layer graphene with room temperature field carrier mobility of 300–1150 $\text{cm}^2/(\text{V}\cdot\text{s})$. Graphene thickness strongly depends on methane flow rate and cooling protocols. Decreasing methane flow rate systematically reduced layer number, consistent with iron's precipitation-controlled growth mechanism. Controlled cooling at 24 °C/min from 920 °C to the eutectoid temperature (727 °C), followed by rapid

quenching to room temperature, produced few-layer graphene. Methane flow rates of 300, 270, 200 and 180 mL/min (10 min growth) yielded approximately 6-, 4-, 3- and 2-layer graphene, respectively, highlighting the sensitivity of layer number to carbon chemical potential.

An et al.^[30] extended graphene synthesis on iron to lower temperatures (600–800 °C) using acetylene (C_2H_2). At 5 mL/min C_2H_2 for 5 min, discontinuous single- to few-layer graphene formed, whereas 25–50 sccm for 15–30 min produced continuous multilayer films. Transmission electron microscopy (TEM) revealed film thicknesses of ~ 15 nm at 700 °C and ~ 29 nm at 750 °C. Raman spectroscopy showed reduced defect density with increasing temperature, while scanning electron microscopy (SEM) observations at 800 °C revealed thick graphite flakes attributed to excessive carbon dissolution and uncontrolled precipitation during cooling.

While dissolution–precipitation on iron substrates has historically resulted in uncontrolled multilayer graphene growth, targeted process trajectories can, in principle, enable layer–number control through regulation of carbon supersaturation ($\Delta c = c_{\text{actual}} - c_{\text{equilibrium}}$) and precipitation kinetics^[46]. Temperature-trajectory engineering replaces continuous cooling with stepwise profiles incorporating isothermal holds (eg, 800–850 °C during cooling from 1000 °C). These holds allow partial equilibration of dissolved carbon, establishing controlled supersaturation prior to precipitation, yielding narrower thickness distributions. In contrast, rapid continuous cooling maintains high and spatially variable Δc across the 700–900 °C precipitation window, promoting non-uniform multilayer growth^[47]. Phase-boundary exploitation leverages the $\alpha\text{Fe}/\gamma\text{Fe}$ - transition (~ 912 °C), where carbon solubility decreases sharply. Controlled thermal cycling across this boundary can generate pulsed supersaturation, analogous to carbide-mediated, phase-boundary-limited single-layer growth on Ni(111)^[57]. Such strategies suggest a pathway toward controlled graphene precipitation on iron, although direct experimental validation remains limited. Dynamic precurs-

or/pressure modulation provides an additional degree of control by coupling CH_4 flow and total pressure in concert with the temperature-dependent carbon solubility. This approach enables maintenance of near-constant Δc , thereby favoring 2D graphene precipitation over 3D carbide formation, consistent with established CVD kinetics^[46]. Collectively, these strategies define a supersaturation-governed growth framework: low supersaturation (Δc) favors monolayer-dominated films, intermediate supersaturation yields few-layer graphene, and high supersaturation produces thick multilayers with enhanced carbide co-formation. While these principles are well-established for high-carbon-solubility metals, systematic validation for iron remains limited, representing a key direction for future work.

3.1.3 Plasma-enhanced CVD methods

Plasma-enhanced CVD (PECVD) has been explored for graphene growth on metal substrates. Unlike thermal CVD requiring temperatures near or above 1000 °C, PECVD enables synthesis at significantly lower temperatures (600–800 °C). Plasma generates highly reactive ions, radicals, and excited hydrocarbon fragments that accelerate precursor dissociation and facilitate faster nucleation and growth compared to thermal processes^[58].

Despite these advantages, graphene growth on pure iron by PECVD remains highly elusive and experimentally challenging. However, several studies report plasma-based graphene growth on other transition metals including Cu and Ni. Nang et al.^[59] investigated growth kinetics on Cu and Fe_2O_3 using inductively-coupled plasma CVD at 700 °C. Growth kinetics were governed by competition between graphene formation through C atoms and carbon etching by atomic hydrogen, strongly amplified by plasma. Rapid graphene formation occurred on Fe_2O_3 , with few-layer graphene developing within seconds on Cu and within about a minute on Fe_2O_3 . Increased plasma power improved crystalline quality while decreasing film thickness on both substrates due to enhanced hydrogen-induced etching, ultimately enabling self-limiting single-layer formation.

On pure iron substrates, PECVD faces distinct challenges. Energetic ion bombardment induces surface roughening and defect sites promoting heterogeneous nucleation, while iron's high carbon solubility combined with plasma-enhanced reactivity creates competing processes (graphene formation, carbide nucleation, hydrogen etching) that are difficult to balance. These factors limit PECVD success on pure Fe despite effectiveness on Cu, Ni and iron oxides^[28,60].

Li et al.^[61] highlighted plasma activation's role in transition-metal-assisted graphene growth. PECVD leverages energetic electrons to enhance ionization, excitation, and dissociation of hydrocarbon precursors. In high-carbon-solubility metals, PECVD growth follows dissolution-precipitation mechanisms similar to thermal processes, whereas in low-solubility metals like copper, growth is driven by surface-catalyzed dissociation aided by plasma-generated reactive carbon radicals.

Although graphene formation on iron is thermodynamically feasible, PECVD growth occurs under strongly non-equilibrium conditions that impose significant kinetic constraints^[28]. Indeed, molecular dynamics simulations confirm graphene-Fe interfaces are energetically favorable ($\sim 1\text{--}2$ eV/atom adhesion, comparable to graphene-Cu/Ni)^[62], and thermal CVD routinely produces graphene on Fe^[22,63], proving no fundamental thermodynamic barrier exists. PECVD growth is governed by non-equilibrium plasma-driven kinetics. In PECVD, plasma-generated species such as ions and reactive radicals introduce high carbon flux and energetic bombardment, which disrupt the balance between carbon incorporation and lattice ordering^[64]. On iron substrates, these effects are amplified by the metal's high carbon solubility and tendency toward carbide formation. Ion bombardment generates surface defects faster than they can be annealed, while the rapid arrival of carbon species exceeds the rate of sp^2 reorganization, favoring amorphous carbon deposition. Simultaneously, Fe_3C can form a kinetically preferred phase due to its lower nucleation barrier relative to graphene under non-equilibrium conditions. As a result, PECVD on iron is dominated by kinetically controlled pathways, leading to

carbide-rich or disordered carbon structures rather than well-ordered graphene. This behavior reflects limitations in surface diffusion and phase selection under plasma conditions, rather than thermodynamic constraints on graphene formation.

3.1.4 Graphene growth by molecular beam epitaxy (MBE)

MBE has been explored for graphene synthesis on iron substrates. MBE offers exceptional control over film composition and thickness at the atomic level, with high reproducibility, ultrahigh vacuum environment, and well-defined atomic or molecular fluxes making it attractive for growing graphene films with minimized defects^[65].

Zheng et al.^[66] investigated temperature-dependent graphene growth on iron using gas-source MBE, revealing a unique carbide-mediated mechanism. Unlike low-carbon-solubility metals like Cu where graphene forms directly on the surface without carbide intermediates, or Ni where precipitation dominates without significant carbide formation, graphene growth on Fe proceeds through formation and decomposition of metastable iron carbides (Fe_xC_y). This carbide-mediated pathway enables more precise regulation of carbon supply to the growing graphene layer. Temperature plays a critical role in controlling growth dynamics and film morphology. Initial graphene nucleation begins at 400 °C, with continuous coverage achieved at temperature range of 500–550 °C. Above 600 °C, graphitic islands dominate, indicating enhanced carbon surface mobility and faster Fe_xC_y decomposition. This approach enables graphene growth on Fe at significantly lower temperatures compared to other transition metals, underscoring a key advantage of MBE for Fe-based systems.

Table 1 summarizes the experimental conditions and key observations for graphene growth on various Fe substrates using different CVD techniques and molecular beam epitaxy.

3.1.5 Structure and quality of graphene grown on iron substrate

The structure and quality of graphene grown on iron are strongly influenced by graphene–iron interfacial interactions, which govern surface conformity,

film strain, and ultimately electronic, mechanical, and catalytic properties. Final graphene morphology is dictated by competition between adhesion energy promoting conformal contact and strain energy from bending to accommodate substrate corrugation^[68–69].

Wang et al.^[62] investigated the adhesion behavior of monolayer and multilayer graphene nanosheets (GNs) on different iron substrates using molecular dynamics (MD) simulations. Using the embedded-atom method (EAM) potential, the Fe{110} surface exhibited the highest adhesion strength for monolayer GN (26.83 J/m²), followed by Fe{111}, Fe{112} and Fe{100}. This high adhesion produces very small graphene-Fe separation (~ 1.4 Å), causing highly corrugated morphology and a distinct moiré superstructure reflecting registry mismatch between graphene's hexagonal lattice and the BCC Fe surface. Vinogradov et al.^[25] demonstrated this registry mismatch on Fe(110) produces a unique periodically corrugated wave structure with ~ 4 nm periodicity, representing an energy-minimizing accommodation mechanism (Section 6.1).

As the number of GN layers increased, the overall adhesion energy increased proportionally, while the average graphene-iron separation remained nearly unchanged, consistent with stronger van der Waals interactions at greater thickness. On the other hand, lower adhesion energies for monolayer GN were observed when using the Lennard-Jones (LJ) potential, corresponding to weaker Fe-C interactions. Under these conditions, simulations produced disordered moiré patterns and randomly distributed ripples, thereby hindering the formation of an ordered GN structure^[62].

MD studies reveal defects arise primarily from strong graphene-iron adhesion causing rapid normal displacement of carbon atoms toward the substrate followed by lateral shrinkage. This strong adhesion creates local strain, increasing defect formation compared to smoother surfaces. Strain and deformation energies scaled linearly with root mean square height (Sq) of the Fe substrate in the 2–7 Å range. The graphene-substrate roughness difference decreased gradually with reduced Sq while adhesion energy in-

Table 1 Experimental conditions for the growth of graphene on Fe substrate

Fe substrate type	Growth method and conditions	Observations/results	Ref.
Fe film {Fe (110)}	Method: CVD Carbon source: propylene gas (C ₃ H ₆) Temp: 520-600 °C Pressure: 2-4×10 ⁻⁶ mbar	• High-quality graphene monolayer • Low defect density Complex corrugated moiré-type superstructure	[25]
	Method: CVD UHV* Carbon source: ethylene (C ₂ H ₄) Temp: ~ 650 °C Pressure: ≤10 ⁻⁹ mbar (*UHV: ultra-high vacuum)	• Single-layer graphene formation, negligible multilayer regions • Graphene strain due to lattice mismatch with Fe (110) • No rotational domains in iron and graphene layers, indicating high crystallinity	[53]
	Method: atmospheric-pressure CVD (APCVD) Carbon source: methane gas (CH ₄) Other gases: H ₂ Temp: 920 °C Pressure: 1.0×10 ⁵ Pa	• Formation of few-layer graphene (FLG) on Fe surface, controlled by methane flow rate • Presence of well-crystallized graphene • No D-band, indicating low-defect density and high-quality graphene • Wrinkles from thermal expansion mismatch and overlapping flakes	[22]
Polycrystalline Fe foil	Method: APCVD Carbon source: methane gas (CH ₄) Other gases: H ₂ Temp: 900-1050 °C Pressure: 1.0×10 ⁵ Pa	• Predominant monolayer graphene at 1025 °C and 0.25 (v/v) of CH ₄ /H ₂ flow rate ratio. Raman reveals high quality of graphene film, characterized by a high I _{2D} /I _G ratio (~2.9) and a low I _D /I _G ratio (~0.026), which suggest minimal defects	[67]
Fe metal foil (gallium assisted CVD)	Method: APCVD Carbon source: acetylene gas (C ₂ H ₂) Other Gases: H ₂ Temp: 600-1000 °C Pressure: 1.0×10 ⁵ Pa	• Formation of a chemically stable antiperovskite layer suppressing undesired carbon precipitation • Uniform monolayer graphene • Low defect graphene density • High crystallinity and atomically flat graphene	[63]
Fe metal foil	Method: hot filament CVD Carbon source: acetylene gas (C ₂ H ₂) Other gases: Ar Temp: 600 °C Pressure: 0.67 - 1.33 kPa	• Increasing the cooling rate provoked a structure transition from carbon nanotubes (CNTs) to graphene sheets • Raman indicated fewer defects on the graphene sheets, with optimum crystal quality achieved at the cooling rate of 20 °C/min • The stacked graphene sheets were approximately 8-11 monolayers with thickness of 2.9-3.8 nm.	[47]
	Method: MBE Carbon source: methane gas (CH ₄) Carrier gas: H ₂ Temp: 250 - 800 °C Pressure: ~ 1 × 10 ⁻² to 1 × 10 ⁻³ Pa	• No visible graphene growth below 350°C • At 500-550 °C, continuous FLG film with some defects • At 600 °C, graphitic islands dominate the surface	[66]

creased. However, when Fe Sq exceeded 6 Å, linear dependence no longer held because increasingly large graphene portions lost consistent substrate contact, reducing effective adhesion and altering deformation behavior^[70].

Graphene growth on pure iron is typically inhomogeneous and challenging due to iron's high carbon solubility and strong temperature dependence. During cooling, substantial dissolved carbon precipitates to the surface, causing non-equilibrium, uncontrolled precipitation leading to non-uniform film thickness and multilayer patches. These issues stem from the Fe-C phase diagram where carbon solubility drops sharply during γ to α transformation. Strategies to overcome these challenges, including controlled cooling rates, alloying approaches, and non-equilibrium growth conditions, are discussed in Section 6.1.

3.2 Iron alloy substrates

Alloying iron with elements such as Ni, Co, Cr, Mo, Mn and Cu provides additional degrees of freedom for controlling graphene growth. These alloying

elements modify carbon solubility, diffusion kinetics, and surface chemistry, enabling improved control over graphene layer number, morphology, and quality.

3.2.1 Carbon solubility engineering principles

Graphene growth on iron-based alloys presents additional complexities beyond pure Fe substrates. Graphene formation on Fe is governed by complex thermodynamic and kinetic factors notably: carbon solubility, diffusion behavior, and iron carbide formation during cooling. These challenges intensify in Fe alloys where variations in alloying composition and microstructural phases modify the Fe-C phase diagram and influence carbon uptake and precipitation pathways^[71]. Iron alloys often exhibit multi-phase microstructures (e.g., ferrite-austenite mixtures, Fe-Ni or Fe-Cr phases), each with distinct carbon solubilities and diffusion mobilities^[72]. Consequently, carbon does not dissolve and segregate uniformly, complicating the controlled precipitation required for high-quality graphene growth and making continuous monolayer synthesis more challenging than single-phase Fe

films or high-purity Fe foils.

Most studies of graphene on Fe alloys employ CVD-based methods, although non-traditional approaches like high-pressure high-temperature (HPHT) have been explored. Parvizi et al.^[73] reported graphene growth from natural graphite using molten Fe-Ni catalysts under extreme HPHT conditions (5–6 GPa, 1300–1700 °C). The Fe–Ni alloy melt enables complete carbon precursor dissolution. Upon cooling, purified carbon recrystallizes on the surface forming graphene with exceptional crystallinity. Micro-Raman analysis confirmed high quality, including absence of the *D* band and progressive *G*-peak intensity decrease from bulk graphite to large-area single-layer graphene, consistent with reduced interlayer interactions.

A detailed comparison of alloy compositions, growth parameters, and graphene characteristics for Fe-alloy systems is summarized in Table 2.

3.2.2 Low-alloy and mild steels

Hood et al.^[71] investigated the influence of growth time, temperature, and surface microstructure on graphene formation in 8620 low-alloy and 1018 mild steel surfaces. It was found that the alloying elements (Mn, Cr, Ni, Cu and C) present in 8620 steel significantly enhance the coverage of graphene, achieving up to 95% coverage. These elements play a crucial role in regulating carbon solubility and diffusion during CVD growth by stabilizing surface phases like cementite and pearlite, which act as localized carbon reservoirs and determine the formation of few-layer graphene (FLG) or multi-layer graphene (MLG). The authors manipulated surface carbon activity without excessively increasing bulk carbon solubility, which hinders the growth of crystalline graphene at elevated temperatures by using lower synthesis temperatures of 660 and 680 °C. At 660 °C, the surface was dominated by cementite, promoting FLG formation, whereas at a temperature of 680 °C, pearlite became more stable, favoring MLG growth. The alloying elements effectively localize carbon near the surface, reducing the carbon diffusion depth and enabling the formation of microstructures that support high

graphene coverage. By manipulating the surface transformation and localized behavior of carbon, these elements contribute to the creation of high-coverage graphene coatings that protect against oxidation and corrosion, highlighting the practical relevance of alloy-assisted growth.

3.2.3 Engineered alloy systems (Fe-Mo, Fe-Cu)

3.2.3.1 Iron-molybdenum (Fe-Mo) alloy system

Iron's high carbon solubility and strong carbon interaction make uniform graphene growth challenging without alloying modifications that reduce carbon solubility. Carbon dissolves extensively into bulk iron and precipitates during cooling, often producing non-uniform multilayer graphene on pure iron substrates. Binary alloying provides a promising strategy to suppress this segregation.

Zhang et al.^[81] developed a complementary binary alloy catalytic method using Fe-Mo alloys. Iron serves as the primary catalytic site while molybdenum binds carbon as stable Mo₂C, effectively trapping dissolved carbon and preventing bulk precipitation during cooling. This suppresses segregation and enables self-limiting single-layer graphene growth with 100% surface coverage, marking significant progress toward scalable monolayer graphene synthesis.

3.2.3.2 Iron-copper (Fe-Cu) alloy system

A theoretical study^[82] explored CH₄ dissociation and carbon formation mechanisms on Fe-Cu(100) alloy surfaces. The Fe-doped Cu surface exhibits a synergistic catalytic effect crucial for promoting graphene growth. The doped Fe atom serves as both the dissociation activity center and carbon polymerization hub for graphene nucleation, ensuring atomic carbon migrates to stable positions or graphene island edges, ultimately forming perfect graphene structures.

From thermodynamic and kinetic perspectives, Fe introduction accelerates CH₄ dissociation by lowering the total energy barrier from 3.83 eV on pure Cu (100) to 2.85 eV on Fe-doped Cu. This enhanced activity stems from electronic structure shifts, where the charge transfers from Fe to Cu atoms, indicating Fe–Cu bond polarization. Additionally, Fe's average *d*-band center (−1.87 eV) moves closer to the Fermi

Table 2 Experimental conditions for the growth of graphene on steel substrates

Fe/Fe alloy	Growth method and condition	Observations/result	Ref.
8620 steel	Method: CVD Carbon source: Acetylene gas (C_2H_2) Other Gases: H_2 Temp: 660–680 °C Pressure: $\sim 5.3 \times 10^4$ Pa	<ul style="list-style-type: none"> Alloying elements (Mn, Cr and C) stabilize cementite/pearlite MLG (multi-layer graphene) forms on pearlite at 680 °C FLG forms on cementite at 660 °C Surface coverage (FLG: >95%, MLG: 90%–95%) 	[71]
1018 mild steel	Method: CVD Carbon source: acetylene gas (C_2H_2) Other gases: H_2 Temp: 680 °C Pressure: $\sim 5.3 \times 10^4$ Pa	<ul style="list-style-type: none"> Carbon precipitates at grain boundaries and pearlite MLG forms on pearlite at 680 °C Surface coverage (MLG: $\sim 80\%$) 	[71]
Stainless steel meshes (304/316 SS; 400 meshes, diameter of 14 mm)	Method: CVD Carbon source: methane gas (CH_4) Other gases: H_2 Temp: 1020 °C Pressure: constant pressure (not reported)	<ul style="list-style-type: none"> Formation of single-layer to few-layer graphene on the SS meshes The surface SS meshes changes from smooth to rough, improving adhesion of active materials and facilitating electron transfer, which is beneficial for use in supercapacitors 	[74]
Stainless steel foils (supported on an alumina base plate)	Method: thermal CVD Carbon source: ethanol (CH_3CH_2OH) Other gases: H_2 Temp: 850 °C Pressure: 1.01×10^5 Pa	<ul style="list-style-type: none"> The presence of Cr_2O_3 and $MnCr_2O_4$ spinel hinders the growth of graphene, FeO promotes the formation of graphene Formation of single-, bi- and tri-layers of graphene over a large area Due to the surface chemical variations of the substrate, the formation of graphene is non-uniform with inherent defects 	[75]
Stainless steel foils (electroplated with a nickel layer)	Method: CVD Carbon source: methane gas (CH_4) Other gases: Ar and H_2 Temp: 850 °C Pressure: not reported	<ul style="list-style-type: none"> Scanning electron microscopy and transmission electron microscopy images confirmed complete surface coverage with multilayer graphene Graphene grew along the boundaries of the grains, creating ripples because of mismatched thermal expansion Graphene-covered stainless-steel exhibits excellent low interfacial contact resistance (ICR) of $36 \text{ m}\Omega \text{ cm}^2$ and outstanding drainage characteristics 	[76]
Stainless steel (SS) cylinder	Method: Microwave plasma CVD Carbon source: 10% methane gas (CH_4) Carrier gas: 90% H_2 Temp: ~ 500 °C Pressure: 4.0×10^4 Pa Microwave power: 1200 W	<ul style="list-style-type: none"> Formation of 1 to 3-layered graphene with defects The Graphene Sheets (GSs) are flexible, easily corrugated and evenly transparent, indicating uniform thickness throughout the film The selected-area electron diffraction (SAED) pattern of the sheets displayed sharp diffraction spots with a typical sixfold asymmetry characteristic of graphene/graphite, indicating the graphene sheets have better crystallinity 	[77]
Stainless steel (SS 316L) surgical cylinder wires	Method: APCVD Carbon source: methane gas (CH_4) Other gases: Ar and H_2 Temp: 850–1000 °C Pressure: 1.01×10^5 Pa	<ul style="list-style-type: none"> Formation of 2 - 7 few-layered graphene, covering the entire surface of the SSS 316 L cylinders Raman revealed variation in band intensities across the steel surface which could be attributed to the non-homogeneity of the sample at the micro-scale High temperature and SSS composition led to the growth of metal oxides ($MnCr_2O_4$). However, after optimizing the process, a reduction of the metal oxides and a decrease in band intensities were observed In-vitro test revealed that the graphene-covered implants do not enhance bacterial growth 	[78]
Stainless steel (piston ring)	Method: CVD Carbon source: oil palm fiber and polystyrene Other gases: hydrogen gas (H_2) Temp: 1000 °C Pressure: 1.01×10^5 Pa	<ul style="list-style-type: none"> The quality of graphene is significantly affected by hydrogen flow rates Graphene-coated piston rings developed at 600 mL/min and 800 mL/min show improved tribological properties using oil palm fiber and polystyrene, respectively 	[79]
Stainless steel (SS) foils	Method: liquid-phase CVD Carbon source: hexane Other gases: Ar/ H_2 Temp: 800 °C Pressure: 70.9 Pa	<ul style="list-style-type: none"> Modified carburization process, carbon diffusion during CVD simultaneously produces surface graphene and hardens substrate Slow cooling results in few-layer graphene formation and rapid quenching results in carbon trapping in disordered domains Graphene serves as both current collector and mechanical support, avoiding transfer steps 	[80]

level compared to surface Cu (−2.41 eV), making Fe more active and favorable for CH_x radical adsorption^[82]. A *d*-band center closer to the Fermi level indicates stronger metal-adsorbate interactions.

3.2.4 Stainless steel (Fe-Cr-Ni) substrates

Iron alloying significantly impacts graphene CVD growth by complicating nucleation and stability through interactions in the iron-carbon system and increased side reactions. Elements like chromium and manganese form stable surface oxides that hinder

catalytic activity, which is essential for ordered graphene production. Maintaining careful kinetic balance around the Fe-C eutectoid temperature (727 °C) is crucial for managing high carbon solubility and preventing unwanted carbon precipitation.

In complex steels, surface oxide reduction is necessary for homogeneous nucleation, while high-carbon steels may require pre-oxidation to remove surface carbon. Carbon diffusion into the Fe substrate during CVD mirrors industrial carburizing processes,

simultaneously enhancing graphene growth and substrate hardness, creating an advantageous route for scaling graphene production on Fe-based substrates^[83].

Gullapalli et al.^[80] investigated a modified carburization process for growing high-quality, few-layer graphene directly on stainless steel (SS) foils by liquid-phase CVD. Nucleation is largely influenced by cooling rate: carbon diffusion and precipitation into few-layer graphene predominantly occur during slow or optimal cooling rate due to limited carbon solubility at elevated temperatures, whereas rapid cooling or quenching tends to trap carbon, producing disordered domains.

Stainless steel offers enhanced chemical and thermal stability compared to pure metals like copper and nickel, enabling functional graphene modifications without compromising the substrate. The stable SS base ensures excellent electrochemical properties and maintains stability when employed directly as a current collector in lithium-ion battery. This method is highly scalable, utilizing established steel industry techniques and eliminating complex transfer processes by enabling direct growth onto SS current collectors.

3.3 Iron nanoparticles for core-shell structures

Iron nanoparticles offer a unique platform for graphene synthesis, producing carbon-encapsulated iron nanoparticles (CEINP) with core-shell structures^[84]. These materials combine the magnetic and catalytic properties of iron cores with the chemical stability and electrical conductivity of graphene shells, enabling applications in catalysis, water remediation, and electromagnetic shielding.

3.3.1 Biomass-derived synthesis and growth mechanisms

Over the past decade, high-quality graphene has been synthesized primarily using thermal CVD and PECVD with gaseous hydrocarbon precursors and transition metals, which lower activation energy for graphene growth at elevated temperatures^[85]. Although these techniques enable rapid synthesis and excellent crystallinity, they are expensive, hazardous, require high temperature and vacuum, and involve

complex processes hindering large-scale manufacturing. To overcome these limitations, researchers have adopted biomass and biomass-derived sources as sustainable, low-cost alternatives for graphene growth^[86–87].

Graphene formation in biomass-derived systems follows the dissolution-precipitation mechanism described in Section 2.1.2. During high-temperature pyrolysis, carbonaceous vapors and solid carbon from biochar interact with Fe nanoparticles, enabling carbon dissolution and subsequent precipitation according to the Fe-C phase diagram. Unlike planar Fe foils in conventional CVD, nanoparticle geometry promotes three-dimensional shell formation, producing carbon-encapsulated iron nanoparticles (CEINP)^[84], leveraging the same fundamental mechanism in a dispersed rather than bulk catalyst system.

3.3.2 Structure, quality and temperature effects

Neeli et al.^[84] synthesized carbon-encapsulated iron nanoparticles (CEINP) to understand iron catalyst formation using biochar from biomass model compounds (lignin, cellulose, hemicellulose) as carbon supports. CEINP exhibited a core-shell structure with iron/iron-carbide core surrounded by graphitic carbon shell (Fig. 4). Their findings supported a dissolution-precipitation growth mechanism consistent with the Fe-C phase diagram, demonstrating that rapid cooling ($\sim 200\text{ }^{\circ}\text{C min}^{-1}$) favored metastable iron carbide retention along with α -Fe and Fe_3C phases.

Structural characterization revealed highly ordered graphitic layers in cellulose- and hemicellulose-derived CEINP, while lignin-derived CEINP showed more disordered graphitic carbon. Cellulose and hemicellulose-derived CEINP had similar phase compositions, whereas cementite was absent in lignin-derived nanoparticles due to limited free carbon dissolution in the iron core. Higher annealing temperature and longer reaction time disrupt lignin biochar's amorphous carbon matrix, enabling greater Fe-C interaction and promoting more graphitic carbon formation^[84].

Ghogia et al.^[88] investigated graphene growth through iron-catalyzed graphitization of cellulose-de-

rived biochar at 1000–1800 °C. Increasing pyrolysis temperature led to larger iron particle sizes from thermal sintering, greater iron oxide reduction to metallic Fe, and increased carbon crystallite sizes (L_a , L_c) in the resulting graphene. Graphene formation proceeded through initial iron oxide reduction to metallic iron by carbon monoxide (CO) at lower temperatures, followed by carbon dissolution into liquid Fe and eventual precipitation as graphitic layers. At 1800 °C, Fe particles were predominantly metallic, with larger particles providing advantageous surfaces for ordered graphene shell growth.

Ishii et al.^[89] proposed new method of synthesizing graphene-based material directly from lignin using iron catalysts through catalytic carbonization, leveraging lignin's water solubility and ion exchange capacity for homogeneous Fe dispersion. The authors indicated that the solidification of the lignin molecules in a sparse state (low-density, well-dispersed) and appropriate Fe support for the lignin molecules were key factors in influencing the growth of high-quality graphene. Optimal Fe loading (0.56 mmol g⁻¹) with freeze-dried lignin produced high-quality graphene, whereas excessive Fe loading (2.8 mmol g⁻¹) or oven drying led to amorphous carbon and poor Fe dispersion. Analysis confirmed thin graphene-like

films only in well-prepared samples where lignin microstructure and Fe distribution were properly controlled, with metallic Fe and Fe₃O₄ particles as active catalytic species. The synthesized graphene exhibited excellent oxidation resistance due to fewer edge defects and larger sheet sizes. These findings highlight the critical role of iron catalyst structural attributes (nanoparticle size, phase state, reduction behavior) in biochar graphitization and graphene quality.

3.3.3 Comparison with planar substrates and application

Unlike CVD-grown graphene on planar Fe substrates (Section 3.1), biomass-derived graphene typically exhibits higher defect densities and smaller crystalline domains due to heterogeneous biochar and heteroatoms (O, N, S). However, biomass-derived approaches offer significant advantages: sustainability, cost-effectiveness, waste biomass feedstock utilization, and simpler equipment without high-vacuum systems. The resulting carbon-encapsulated Fe nanoparticle materials possess multifunctional properties for energy storage, electromagnetic shielding, and catalysis where perfect crystallinity is not essential. Fe-catalyzed biomass graphitization represents a promising route for sustainable, large-scale graphene production, particularly for applications benefiting

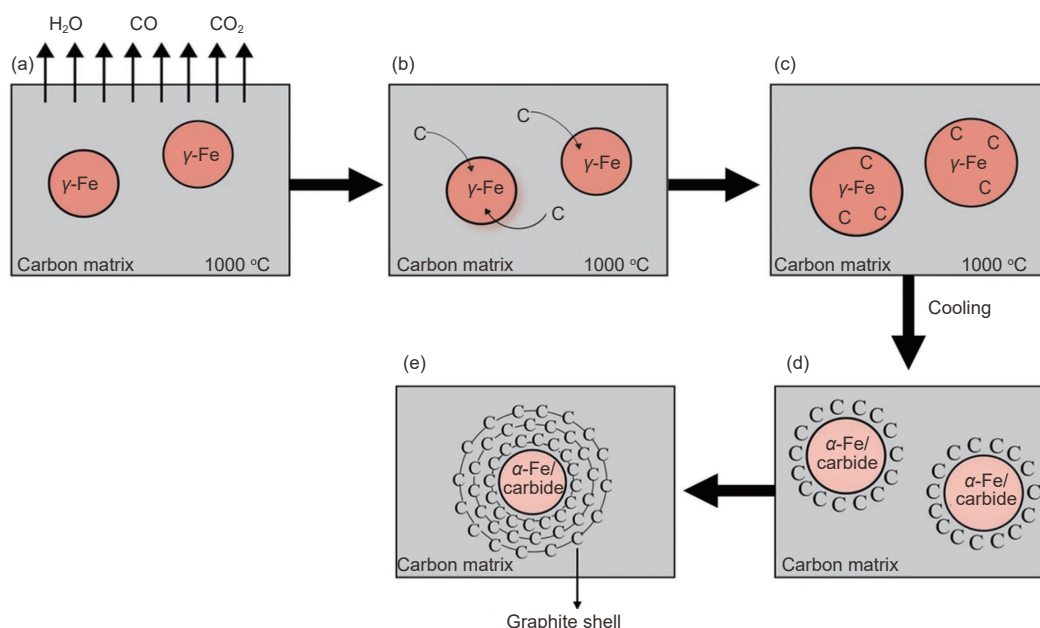


Fig. 4 Carbon-encapsulated iron nanoparticle (CEINP) formation mechanism. (a–c) Carbon dissolution into γ-Fe at 1000 °C, (d) cooling-induced phase transformation precipitates carbon forming carbide cores, (e) continued precipitation forms graphitic shells (reprinted with permission, copyright 2018, Elsevier^[84])

from unique core-shell nanostructures while tolerating higher defect densities.

3.4 Comparative performance of graphene growth on Fe alloys vs. pure Fe

Pure iron's high carbon solubility promotes bulk dissolution and segregation-driven precipitation during cooling, often producing non-uniform multilayer graphene with limited layer control. Growth is highly sensitive to temperature, cooling rate, and carbon content, resulting in a narrow process window and poor reproducibility. Fe alloys provide additional control by modifying carbon solubility, diffusion kinetics, and surface chemistry through elements like Ni, Mo, Mn, Cr and Cu. This enables improved layer uniformity, broader growth windows, and more uniform films at reduced temperatures. However, alloying may introduce oxides or phases that diminish catalytic activity without proper surface pretreatment. Table 3 summarizes key differences between pure Fe and Fe alloy graphene growth.

While Fe alloys often improve carbon solubility control, diffusion kinetics, and graphene layer uniformity compared to pure Fe, benefits depend strongly on alloy composition and processing conditions. Certain alloying elements may introduce stable oxides or phases suppressing catalysis activity. Optimized surface treatment, alloy selection, and thermal protocols are essential to realize Fe alloy advantages for controlled graphene growth.

3.4.1 Electronic and kinetic origins of alloying effects

Alloying iron with transition metals (Ni, Cr, Mo) provides a powerful route to modulate graphene growth by altering both electronic structure of the catalyst surface and the kinetics of carbon dissolution

and diffusion. These effects can be rationalized using concepts from *d*-band theory and carbon transport in (transition) metal systems^[90]. To rationalize these trends, Table 4 summarizes the mechanistic differences in carbon diffusion, partitioning, and surface interactions between pure Fe and Fe-based alloys, providing a framework to interpret the observed variations in graphene thickness, uniformity, and corrosion behavior.

From an electronic perspective, the interaction strength between carbon species and the metal surface is governed by the position of the metal *d*-band center (ϵ_d) relative to the Fermi level^[90]. Pure iron's *d*-band provides moderate carbon binding, consistent with its intermediate oxygen adsorption strength observed in DFT calculations^[91]. Alloying elements such as Ni, Co and Cr modify the electronic density of states of iron, thereby altering carbon adsorption energies and surface diffusion barriers. In general, a *d*-band center closer to the Fermi level increases metal-carbon hybridization, strengthening adsorption and favoring surface-mediated growth, whereas a lower *d*-band center weakens adsorption and promotes bulk dissolution or carbide formation^[90,92].

In Fe-Ni binary systems, Ni addition is expected to shift the *d*-band center (ϵ_d) upward. Ni's *d*-band lies higher than Fe because of its electronic configuration^[93], enhancing C-metal interaction strength and reducing carbon surface diffusion length. This stronger binding kinetically suppresses excessive bulk carbon dissolution, confining carbon to near-surface regions where two-dimensional graphene nucleation is favored over bulk carbide precipitation. The observed experimental tendency toward thinner, more uniform graphene films on Fe-Ni substrates (Table 4) and re-

Table 3 Comparative analysis of graphene growth on Fe vs Fe alloy

Key parameter	Pure iron (Fe)	Fe alloys
Carbon solubility	High (2.09% at 1147 °C); promotes bulk dissolution and multilayer precipitation on cooling	Carbon solubility reduces by Ni, Co, or Mo alloying; limits supersaturation and promotes few-layer uniformity
Process window and reproducibility	Narrow; highly sensitive to temperature, cooling rate, and precursor flow; results in poor reproducibility	Broader window; alloy composition buffers temperature fluctuations; improves batch reproducibility
Layer uniformity and thickness control	Spatially non-uniform; multilayer patches dominate; monolayer and few-layer graphene requires optimized protocols ^[67]	More uniform distribution; 95% coverage demonstrated on low-alloy steels ^[71] and monolayer on Fe-Mo ^[81]
Adhesion and protective performance	Strong Fe-C bonding (26.83 J m ⁻² from MD simulations ^[62]) enables mechanical interlocking; continuous coverage provides durable protection; interfacial oxides can accelerate corrosion	Cr-containing Fe/SS alloys provide oxidation resistance; lower initial adhesion but provides superior long-term durability ^[75,80]

Table 4 Mechanistic comparison of graphene growth on Fe and Fe-based alloys

Mechanism/effect	Pure Fe	Fe-Ni alloys	Fe-Cr/stainless steels
d-band position (relative to Fe)	Intermediate	Shifted towards Fermi Level (composition-dependent) ^[90–91]	Lower effective d-band/strong carbide forming tendency ^[90]
C diffusion barrier	High carbon mobility (bulk-dominated diffusion) ^[93]	Modified diffusion kinetics; reduced effective bulk transport due to solute interaction ^[94–95]	Restricted diffusion due to carbide formation and oxide barriers ^[75,94]
Carbon partitioning	Bulk dissolution-precipitation dominant ^[22]	Increased surface-confinement of C; reduced bulk supersaturation ^[22,96]	Competition with carbide formation (Cr_3C_2 , Cr_7C_3) ^[73]
Typical graphene thickness	Multilayer (few to tens of layers) ^[22,97]	Few layer (1–3 layers) to thin multilayer ^[96]	Variable: Thin layers or suppressed growth depending on carbide/oxide state ^[75]
Thickness uniformity	Non-uniform (supersaturation-driven precipitation) ^[22]	Improved uniformity due to moderated carbon flux ^[96]	Highly variable due to carbide/oxide heterogeneity ^[75]
Process controllability	Narrow window; highly sensitive to temperature and cooling rate ^[22]	Improved controllability via reduced carbon solubility and diffusion ^[96]	Limited; requires strict control of oxidation and carbide formation ^[73,98]

duced multilayer formation is consistent with this surface-confinement mechanism. In contrast, alloying with strong carbide-forming elements such as Cr or Mo promotes the formation of stable carbides (eg, Cr_3C_2 , Mo_2C), which compete with graphene precipitation by sequestering carbon within the bulk. Indeed, Cr and Mo possess lower *d*-band centers than Fe (ϵ_d is about -2.2 eV; Mo is simulating due to 4d/5d orbital energy), weakening graphene-metal binding.

Alloying also significantly affects bulk carbon transport kinetics. The diffusion of carbon in iron is sensitive to lattice structure and alloy composition, with substitutional elements introducing local strain fields and modifying diffusion barriers^[94]. While systematic E_a measurements across all Fe-alloy compositions remain limited, available carburization studies and computational estimates suggest Ni is known to increase the activation energy for carbon diffusion, thereby limiting bulk carbon transport and promoting surface precipitation. This reduced bulk diffusivity complements the enhanced surface binding, collectively shifting the growth regime from dissolution-precipitation (bulk-mediated) toward surface-adsorption-dominated mechanisms analogous to those observed on Cu and low-solubility metals. Conversely, elements such as Cr can form surface oxides (e.g., Cr_2O_3), which act as diffusion barriers that inhibit both carbon dissolution and graphene nucleation unless reduced under reactive conditions^[92].

These combined electronic and kinetic effects determine the dominant growth pathway. Pure iron favors a bulk-mediated dissolution–precipitation mechanism with significant multilayer formation, whereas

Fe–Ni alloys tend toward surface-limited growth with improved thickness control. Fe–Cr systems, depending on oxidation state, may suppress graphene formation entirely or promote carbide-dominated pathways.

While these trends are supported by experimental observations and established catalytic principles, quantitative first-principles studies directly linking *d*-band (ϵ_d) shifts, carbon adsorption energies, and diffusion barriers (graphene growth behavior) specifically for Fe-based alloy systems remain sparse in current literature. As such, the framework provided here draws on electronic structure trends in the transition metal series, available pure-metal data, and analogies to related catalytic systems. Comprehensive DFT studies across the compositional space would enable predictive alloy design for targeted graphene properties and represent an important future research direction.

4 Characterization techniques for graphene on iron substrates

Comprehensive characterization of graphene synthesized on iron-based substrates requires integrated, multi-technique approaches addressing challenges unique to iron systems. Unlike inert substrates like copper, iron’s metallic nature, high carbon solubility, and carbide formation during high-temperature growth introduce significant analytical complexity. Strong Fe signals can obscure graphene features, iron carbide phases must be distinguished from graphene/graphitic carbon, and interfacial Fe-graphene coupling can modify electronic signatures, complicating interpretation. No single technique suffi-

ciently describes graphene–iron systems.

Effective characterization relies on correlative analysis combining spectroscopic, structural, surface-sensitive, and computational methods to disentangle overlapping signals and capture bulk and interfacial phenomena. Raman spectroscopy provides rapid, spatially resolved assessment of graphene quality and thickness but requires careful interpretation given fluorescence and iron-induced strain effects. X-ray diffraction (XRD) distinguishes carbide from graphitic phases, while electron microscopy enables direct visualization of layer morphology and interface structure. Surface-sensitive techniques such as X-Ray photoelectron spectroscopy (XPS) and Kelvin probe force microscopy (KPFM) offer insight into chemical bonding, oxidation state, and electronic uniformity at the graphene–iron interface. Computational approaches support experimental interpretation by linking observed signatures to underlying thermodynamic and kinetic processes.

Table 5 summarizes technique capabilities, limitations, and synergistic use for iron-graphene systems.

4.1 Spectroscopic techniques

4.1.1 Raman Spectroscopy

Raman spectroscopy is a rapid, non-destructive technique widely used to assess quality of graphene, layer number, and defect density through characteristic vibrational modes: the *G* band ($\sim 1580\text{ cm}^{-1}$) from in-plane C—C stretching, the *2D* band ($\sim 2700\text{ cm}^{-1}$) sensitive to layer number, stacking order, and electronic coupling, and the defect-activated *D* band ($\sim 1350\text{ cm}^{-1}$). The I_{2D}/I_G intensity ratio decreases

with increasing layers, while I_D/I_G measures defect density and disorder.

Xue et al.^[22] demonstrated bilayer graphene identification on iron foil by Raman spectroscopy, reporting $I_{2D}/I_G \approx 2$ with a symmetric *2D* peak at 2700 cm^{-1} and negligible *D*-band intensity, indicating high quality. Decreasing methane flow rate during CVD systematically reduced graphene thickness, yielding films ranging from 2 to 5 layers. However, An et al.^[30] highlighted a critical limitation: physically thick films (15–29 nm by TEM) exhibited I_{2D}/I_G values characteristic of few-layer graphene (Fig. 5a), attributed to poor interlayer registry and weak electronic coupling between stacked layers. This decoupling renders Raman-based layer counting unreliable for disordered multilayer graphene.

Hood et al.^[71] compared multilayer graphene (MLG, 4–5 layers) and few-layer graphene (FLG, 3–4 layers) on steel substrates (Fig. 5b), observing superior MLG crystallinity ($I_D/I_G = 0.08$; $I_{2D}/I_G = 0.330$) relative to FLG ($I_D/I_G = 0.21$; $I_{2D}/I_G = 0.446$), with Raman mapping confirming >90% areal coverage. For optimized monolayer graphene, Lavin-Lopez et al.^[67] established benchmark metrics: $I_D/I_G \approx 0.026$ (minimal defects), *2D*-peak FWHM $\approx 22\text{ cm}^{-1}$, and $I_{2D}/I_G \approx 2.9$, with single-Lorentzian *2D*-peak deconvolution confirming monolayer character.

Raman characterization on iron substrates faces additional challenges. Strong Fe-induced fluorescence can obscure graphene signals, particularly for monolayer films. Charge-transfer doping at the Fe-graphene interface shifts *G* and *2D* peak positions rel-

Table 5 Characterization techniques for graphene on iron substrates

Technique	Key information	Resolution	Main limitation for iron	Complementary tool
Raman spectroscopy	Layer number (I_{2D}/I_G), defects (I_D/I_G), strain/doping, spatial uniformity	$\sim 0.5\text{--}1\text{ }\mu\text{m}$ (lateral)	Strong Fe fluorescence: I_{2D}/I_G becomes ambiguous for >5 layers; peak shifts influenced by Fe–graphene coupling	TEM, XPS, SEM
XRD	Crystallinity, d-spacing, Fe_3C and oxide phase identification	Bulk (mm^3 sampling volume)	Fe_3C and graphite (002) peak overlap; low sensitivity to few-layer graphene	XPS, Raman
TEM/SEM	Exact layer count (TEM), morphology, stacking order, grain boundaries	<0.1 nm (TEM), 1–10 nm (SEM)	TEM requires Fe removal or cross-section prep; SEM cannot directly resolve layer number	Raman, AFM
XPS	Chemical bonds (sp^2/sp^3), Fe/C interaction, oxidation states	2–10 nm (surface sensitive)	Limited depth sensitivity; buried interfaces inaccessible without sputtering	XRD, Raman
Optical Microscopy	Areal coverage, thickness contrast (interference color)	$\sim 0.5\text{ }\mu\text{m}$	Requires Raman calibration; insensitive to defects	Raman
AFM	Thickness steps, wrinkles, surface topology	<1 nm (vertical)	Wrinkles and folds complicate thickness interpretation; limited chemical info	TEM, Raman
DFT/MD	Binding energy, adhesion strength, diffusion barriers, interface stability	Atomic scale (simulation)	Computationally intensive; relies on model assumptions	AFM, STM, tribology

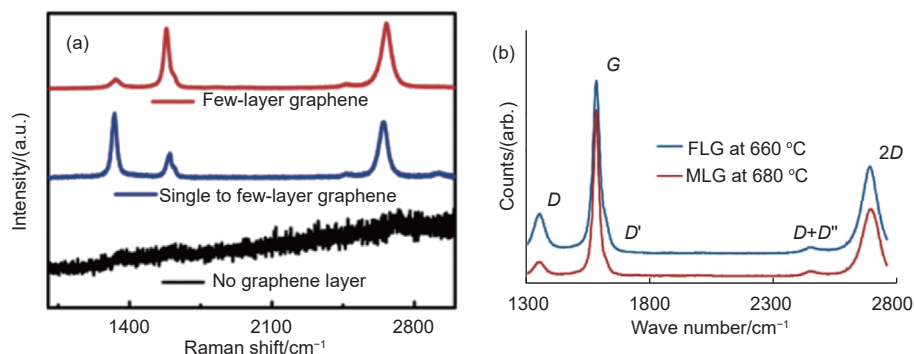


Fig. 5 (a) Single-layer graphene ($I_{2D}/I_G > 2$) to few-layer (2-3) graphene ($I_{2D}/I_G < 1$) growth on iron foil (Reprinted with permission, copyright 2011, Elsevier^[30]). (b) Raman spectra of FLG (660 °C) and MLG (680 °C) on 8620 steel, with $I_{2D}/I_G \approx 0.446$ indicating 3–4 layers for FLG and $I_{2D}/I_G \approx 0.330$ indicating 4–5 layers for MLG (Reprinted with permission, copyright 2025, Elsevier^[71])

ative to freestanding graphene. Critically, Raman metrics become unreliable for thick multilayer films (>5 layers), necessitating TEM verification or complementary structural techniques. Despite these limitations, Raman spectroscopy remains the primary technique for rapid quality screening, spatial mapping, and reliable layer counting for monolayer to few-layer graphene on iron.

4.1.2 X-ray photoelectron spectroscopy (XPS)

XPS provides chemically specific, surface-sensitive analysis of graphene–iron systems by probing elemental composition and bonding states through photoelectron binding energies. For graphene grown on iron-based substrates, XPS serves 2 primary roles: (1) confirming sp^2 -bonded carbon characteristic of graphene, and (2) elucidating interfacial chemistry, including iron encapsulation, oxidation state, and carbide formation.

Xue et al. and Zheng et al.^[22,66] identified characteristic sp^2 peaks in C 1s XPS near 284.8 eV in graphene-coated iron samples (Fig. 6), consistent with graphitic carbon, alongside higher-binding-energy components attributed to C—O species (288.3 eV). Simultaneous Fe 2p XPS peaks indicated chemical reactions between carbon and iron during growth, reflecting iron's reactive nature compared to inert substrates like copper, underscoring XPS's sensitivity to both graphene bonding and metal–carbon interfacial chemistry.

Ghogia et al.^[88] demonstrated XPS utility for monitoring iron particle encapsulation by graphitic carbon during high-temperature biochar pyrolysis.

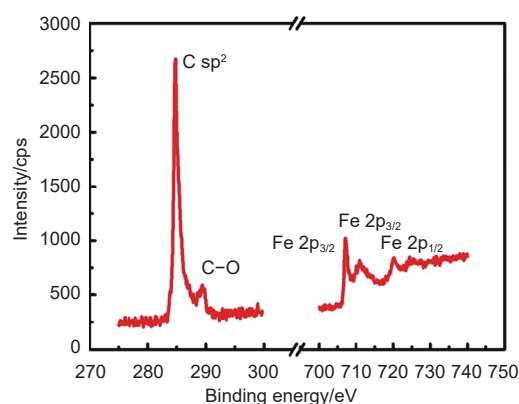


Fig. 6 XPS showing C sp^2 spectrum peak at ~ 284.8 eV representing predominantly sp^2 -bonded graphene on the iron substrate, C—O peak (288.3 eV), Fe $2p_{3/2}$ and $2p_{1/2}$ (reprinted with permission, copyright 2017, Elsevier^[66])

Tracking Fe/C atomic ratio evolution revealed systematic decrease with increasing temperature (1000–1800 °C), corresponding to enhanced sp^2 carbon content. This provided direct evidence of progressive graphitic shell formation around iron particles, with graphene layers shielding the iron core from XPS probe depth (2–10 nm). Complete encapsulation suppressed Fe oxidation signals, confirming the graphene shell's protective nature.

Beyond carbon bonding analysis, XPS uniquely quantifies the Fe-graphene interface through Fe/C ratio evolution and distinguishes metallic iron, oxides, and carbides by Fe 2p binding energy shifts, complementing XRD phase identification. This surface-sensitivity makes XPS particularly valuable for assessing interfacial bonding, completeness, and oxidation resistance in graphene-coated iron nanoparticles and thin films where surface chemistry governs functional per-

formance.

4.1.3 X-ray diffraction (XRD)

XRD identifies crystalline phases, determines interlayer spacing, and detects iron carbide formation in graphene–iron systems. XRD primarily provides bulk structural information, complementing surface-sensitive techniques like Raman spectroscopy and XPS.

Xue et al.^[22] confirmed graphene crystallinity on iron foil through a sharp graphitic (002) reflection at 26.5° , corresponding to interlayer spacing of 0.336 nm, consistent with bulk graphite (0.335 nm). Vinogradov et al.^[53] used grazing incidence XRD (GIXRD) to investigate temperature-dependent graphene stability on iron, revealing degradation onset at $\sim 630^\circ\text{C}$ evidenced by decreased graphene G(100) reflection. This degradation accompanied iron carbide formation (increased Fe_xC_y (211) reflection), indicating carbon dissolution into the iron lattice. At higher annealing temperatures ($>720^\circ\text{C}$), Debye-Scherrer rings indicated substantial carburization with cementite (Fe_3C) and Eckström-Adcock carbide (Fe_7C_3) formation. Zheng et al.^[66] reported that the graphitic carbon (002) peak at $2\theta \approx 27.5^\circ$ appears only above 600°C and intensifies with temperature (Fig. 7). XRD patterns consistently show polycrystalline Fe peaks for Fe(110), Fe(200) and Fe(211), while iron carbide (Fe_xC_y) peaks at $2\theta \approx 38.2^\circ$ and 43° appear between 350 – 650°C , indicating a temperature-dependent carbide intermediate that must be carefully controlled to favor graphene formation over bulk graphite.

A central XRD challenge in Fe–C systems is iron carbide background interference in the graphene (002) peak region, complicating quantitative phase identification and requiring complementary techniques^[99]. During synthesis, iron carbide formation competes with graphene precipitation, producing diffraction features potentially misinterpreted as graphitic carbon. Consequently, XRD alone cannot distinguish surface graphene from subsurface carburization, and corroborative analysis using XPS (Fe 2p and C 1s) and Raman spectroscopy is essential. Despite these limitations, XRD remains indispensable for bulk phase identification, tracking carbide phase evolution with temperat-

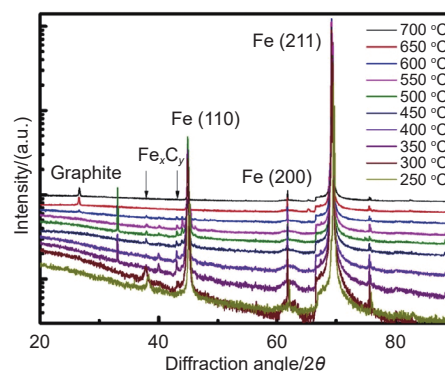


Fig. 7 X-ray diffraction patterns of graphene/Fe samples grown by MBE at different temperatures (250–700 °C), showing persistent Fe (110), (200), and (211) reflections, temperature-dependent Fe_xC_y carbide peaks at $2\theta \approx 38.2^\circ$ and 43° (350 – 650°C), and emergence of the graphitic (002) peak at $2\theta \approx 27.5^\circ$ above 600°C , demonstrating carbide-mediated graphene formation on Fe substrates (Reprinted with permission, copyright 2017, Elsevier^[66])

ure and processing conditions, and assessing the balance between graphene formation and iron carburization during synthesis.

4.1.4 Electron microscopy (TEM/SEM)

Electron microscopy provides direct structural and morphological characterizations of graphene grown on iron substrates. Transmission electron microscopy (TEM) offers atomic-scale structural information, while scanning electron microscopy (SEM) enables large-area surface assessment. SEM complements TEM by providing non-destructive, large-area morphological information without sample transfer. Xue et al.^[22] reported vein-like surface wrinkles attributed to thermal expansion mismatch between graphene and the iron substrate during quenching with the electron diffraction pattern confirming AB-stacked graphene. An et al.^[30] used SEM to track the transition from continuous graphene films at 600°C to surfaces decorated with large graphite flakes at 800°C on Fe foils (Fig. 8b), directly visualizing how increasing temperature promotes excessive carbon precipitation and thick graphitic growth. Lavin-Lopez et al.^[67] demonstrated that SEM contrast variations correlate with graphene thickness: darker areas correspond to thicker multilayer graphene, lighter regions indicate fewer layers, enabling rapid optimization toward monolayer growth. Abdolahi et al.^[47] showed that cooling rate strongly influences morphology with

slow cooling ($\sim 7^\circ\text{C}/\text{min}$) producing carbon nanotube networks while faster cooling yielded stacked graphene sheets.

TEM provides definitive layer counting, stacking order determination, and grain boundary visualization through direct measurement of graphitic interlayer spacing ($\sim 0.34\text{ nm}$). Xue et al.^[22] demonstrated precise growth control on Fe foils by correlating methane flow rate with graphene thickness, observing reduction from 6 to 2 layers as methane flow decreased from 300 to 180 mL/min. An et al.^[30] quantified graphene thickness on iron using TEM, reporting film thicknesses of 15 nm (700°C) and 29 nm (750°C) when synthesized using 25–50 mL/min acetylene for 15–30 min, highlighting iron's high carbon solubility and precipitation-dominated growth. Zheng et al.^[66] employed cross-sectional TEM (Fig. 8a) showing conformal but non-uniform graphene coverage, with SAED yielding in-plane lattice spacings (0.211 nm) matching theoretical graphene values.

TEM analysis requires iron substrate etching or cross-section preparation, potentially introducing artifacts or residual Fe nanoparticles. Despite being destructive, TEM remains essential for definitive layer counting and stacking analysis when Raman spectroscopy becomes unreliable for thick or disordered multilayers. SEM, although unable to directly determine layer number, offers non-destructive morphological assessment and, when combined with Raman mapping, enables comprehensive characterization of graphene–iron systems.

4.1.5 Atomic force microscopy (AFM)

AFM generates high-resolution topographic maps for graphene–iron systems, enabling quantitative analysis of surface morphology, wrinkle formation, and step heights with sub-nanometer vertical resolution. AFM is particularly valuable for assessing mechanical features like wrinkles and folds arising from thermal expansion mismatch and cooling-induced strain.

Xue et al.^[22] employed AFM to characterize graphene directly on iron substrates, revealing wrinkle height distributions ranging from several nanometers

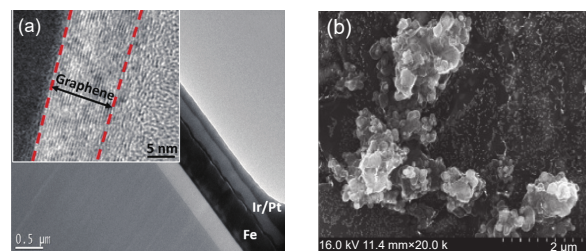


Fig. 8 (a) Cross sectional TEM image of graphene sample grown on iron substrate at 550°C , where the graphene layer is sandwiched between the substrate and the Ir/Pt protection layers (reprinted with permission, copyright 2017, Elsevier^[66]). (b) SEM image of graphene grown on Fe foil showing surface decorated with large, flake-like graphite aggregates at 800°C illustrating the transition from uniform graphene coverage to excessive graphitic precipitation at higher growth temperature (reprinted with permission, copyright 2011, Elsevier^[30])

to tens of nanometers. Wrinkle height increased with growth time while wrinkle density decreased, correlating with increasing graphene layer number. These topographical features were interpreted as strain-relief mechanisms stabilizing multilayer films and enhancing mechanical compliance during deformation. Abdolahi et al.^[47] analyzed transferred graphene on silicon substrates, reporting typical thickness of ~ 2.9 – 3.8 nm corresponding to approximately 8–11 monolayers (assuming 0.36 nm per layer), consistent with turbostratic stacking. Chen et al.^[63] further demonstrated that AFM of graphene grown on Ga-modified Fe and transferred onto SiO_2/Si reveals a continuous monolayer film over an area of $\sim 100\text{ }\mu\text{m}^2$ with nanometer-scale wrinkles and uniform thickness (Fig. 9), confirming that the antiperovskite layer enables wafer-scale, wrinkle-suppressed monolayer graphene growth on iron-group metals.

AFM's primary limitation for graphene grown on iron is the metallic substrate nature, which complicates reliable thickness determination due to tip-sample force sensitivity and electrical interference. Consequently, thickness measurements typically require transfer to insulating substrates, potentially introducing artifacts such as contamination, folding, or strain relaxation. Surface roughness and wrinkles can obscure true step heights, necessitating careful selection of flat regions for analysis. Despite these constraints, AFM complements TEM by enabling statistical analysis of surface features over large areas ($\sim 10^2\text{ }\mu\text{m}^2$),

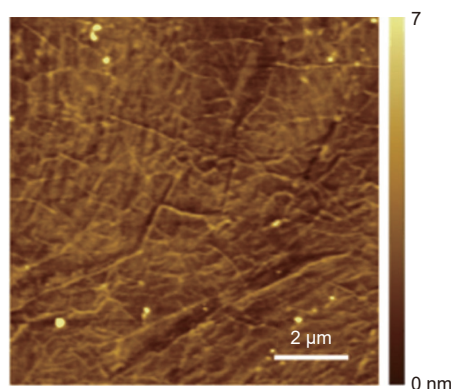


Fig. 9 AFM image of uniform monolayer graphene grown on Ga-assisted Fe substrate and transferred onto SiO₂/Si, showing a continuous film with nanometer-scale wrinkles and a thickness consistent with single-layer graphene (reprinted with permission, copyright 2015, ACS^[63])

whereas TEM provides atomic-scale detail over small fields of view. Together, AFM and TEM offer multiscale insight into graphene morphology and mechanical accommodation on iron substrates.

4.1.6 Optical microscopy

Optical microscopy enables rapid, non-destructive assessment of large-area graphene coverage and thickness variations on Fe substrates through color-based optical contrast from thin-film interference effects. This technique is particularly effective for high-throughput synthesis optimization and spatial heterogeneity assessment.

Zheng et al.^[66] used optical microscopy to monitor temperature-dependent graphene growth on iron, observing no film formation at temperature ≤ 350 °C, initial flake nucleation at a temperature of 400 °C, continuous film coverage at temperature range of 500–550 °C, and graphite grain emergence at temperature ≥ 600 °C. An et al.^[30] similarly exploited optical contrast on Fe foils (Fig. 10a), showing that partially covered films at 750 °C display bare (black), defective single/few-layer (blue), and higher-quality few-layer (red) regions (Fig. 10b), while higher C₂H₂ flow and longer growth time yield uniformly dark foils whose progressively darker tone from 600 to 800 °C tracks increasing graphene thickness.

Optical microscopy serves as an essential first-line diagnostic tool, allowing millimeter-scale inspection of coverage uniformity, defect-rich regions, and thickness gradients. Its wide field of view enables rap-

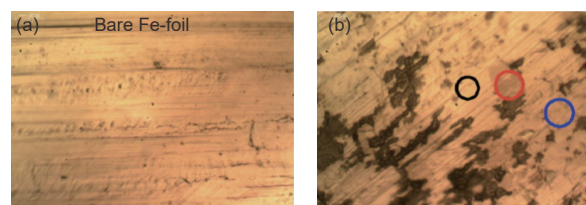


Fig. 10 Optical microscope images of (a) bare Fe foil before synthesis and (b) Fe foil after CVD growth at 750 °C (5 mL/min C₂H₂, 5 min), showing bare (black), defective single/few-layer (blue), and higher-quality few-layer (red) graphene regions (Reprinted with permission, copyright 2011, Elsevier^[30])

id identification of representative areas for subsequent Raman mapping, AFM, or TEM analysis. While lacking chemical specificity and crystallographic resolution, optical microscopy's speed, scalability, and accessibility make it essential for high-throughput growth optimization and process control in graphene–iron systems.

While spectroscopic and microscopy techniques provide direct experimental characterization of graphene grown on iron substrates, computational methods complement these approaches by elucidating atomic-scale mechanisms, interfacial energetics, and diffusion processes inaccessible experimentally.

4.2 Computational methods: density functional theory (DFT) and molecular dynamics (MD)

Computational methods complement experimental characterization by enabling interpretation of atomic-scale phenomena and prediction of properties beyond experimental measurement capabilities. In graphene–iron systems, DFT and MD simulations elucidate interfacial bonding, lattice mismatch effects, adhesion energetics, and mechanical response, bridging synthesis conditions with observed structural and functional behavior.

Vinogradov et al.^[25] employed DFT calculations for graphene on Fe(110) using local density approximation, successfully reproducing experimentally observed scanning tunneling microscopy (STM) topography. The simulations predicted graphene corrugation amplitude of ~ 0.9 Å, closely matching experimental measurement (0.6 ± 0.2 Å), while revealing substrate reconstruction as topmost Fe layer buckling (0.18 Å). DFT-simulated STM images closely matched experimental patterns, attributing wave-like

corrugation to lattice mismatch and strong Fe-graphene interaction. Importantly, DFT enabled quantification of binding energies and charge redistribution at the interface parameters not directly accessible experimentally but central to understanding adhesion and electronic coupling.

Molecular dynamics (MD) simulations further extend insight into interfacial mechanics and adhesion. Wang et al.^[62] utilized MD to assess graphene adhesion on iron surfaces, comparing Lennard-Jones (LJ) and embedded-atom method (EAM) potentials. LJ-based simulations predicted weak adhesion (0.47 J/m² on Fe{110}) and larger equilibrium separations (2.0-2.2 Å), producing disordered graphene structures inconsistent with experiment. In contrast, EAM potentials indicated strong Fe—C bonding (26.83 J/m² on Fe{110}) with shorter interfacial distances (1.3-1.4 Å), yielding well-ordered graphene with moiré patterns consistent with STM observations, highlighting the necessity of many-body potentials for accurately modeling Fe—C interactions.

He et al.^[100] employed large-scale MD simulations to investigate tribological behavior, revealing that graphene layers convert shear forces into rolling-like motion, prevent subsurface atom extrusion, promote dislocation annihilation, and reduce vacancy accumulation. These atomistic mechanisms explain experimentally observed reductions in friction and wear on graphene-coated iron surfaces.

Collectively, DFT-validated STM simulations and MD-predicted adhesion and mechanical response enable computational exploration of synthesis parameters and performance limits beyond practical experimental throughput. This synergy between computational predictions and experimental measurements underscores the value of integrated experimental-computational frameworks for understanding and engineering graphene growth and functionality on iron-based substrates.

5 Applications of graphene grown on iron substrates and alloys

Applications of graphene synthesized on iron-based substrates demand fundamentally different

structural requirements, ranging from pristine, low-defect graphene for barrier and mechanical applications to defect-engineered graphene for catalysis and energy storage. To clarify these requirements, Table 6 was divided into three categories based on target graphene structure: (1) pristine graphene applications where continuous sp² C-C networks and minimal defects are critical (corrosion protection, tribology, FET devices); (2) defect-engineered applications requiring active sites, porosity, and functional groups (energy storage, catalysis); and (3) synergistic architectures leveraging both graphene's conductivity and Fe's magnetic properties (water remediation, EMI shielding). The subsections discuss each application domain with explicit reference to these structure-property applications.

Table 6 highlights that graphene grown directly on iron substrates consistently outperforms conventional coatings and transferred graphene in applications where adhesion, scalability, and defect tolerance dominate performance.

5.1 Protective coatings against corrosion and wear

Protective coatings and tribological applications exploit the intrinsic properties of pristine graphene impermeability from dense atomic packing and mechanical strength from the sp² C-C network making them ideal matches for as-grown graphene on Fe substrates. Direct CVD growth of graphene on iron and steel substrates has emerged as a highly effective strategy for corrosion and wear protection. Hood et al.^[71] synthesized multilayer graphene (MLG) and few-layer graphene (FLG) directly on 8620 steel, achieving significant improvements in corrosion resistance. Electrochemical test revealed that FLG coatings reduced corrosion rates to 0.128 mm/yr compared to 0.665 mm/yr for uncoated steel (an 81% reduction) while MLG coatings exhibited 0.214 mm/yr, corresponding to a 68% reduction. Both coatings also shifted the corrosion potential (E_{corr}) positively, with MLG and FLG exhibiting increases of +101 mV and +94 mV, respectively, relative to bare steel (Fig. 11a). Superior performance of MLG was attributed to high-

Table 6 Application-specific performance metrics and iron substrate advantages

Application	Target structure (S) & governing property (P)	Performance outcome (Iron-graphene vs. control)	Testing conditions	Iron-specific advantage	Ref.
Applications requiring pristine graphene					
Corrosion protection	S: Multilayer, high coverage (>90%), low defect density P: Impermeability, electrical continuity	Corrosion rate: 0.128 mm/yr (few-layer), 0.214 mm/yr (multilayer) vs. 0.665 mm/yr (bare steel), reduced by 67%–81%	3.5% NaCl, 60 min OCV stabilization, ± 100 mV sweep	Strong Fe–C bonding prevents delamination and suppresses under-film corrosion	[71]
Tribology (wear/friction)	S: Few- to multilayer, continuous coverage P: Low shear strength, lubricity	COF: 0.11 (30 min), 0.12 (60 min) vs. 0.36 (bare steel), reduced by 67% ~ 70%	22 °C (295 K), 0.3 N load, 10 mm/s, 398 MPa contact stress	Direct growth on A36 steel ensures coating adhesion and integrity	[101]
Field-effect transistors (FET)	S: Monolayer or few-layer, low defect density P: Carrier mobility, minimal substrate coupling	Mobility: 300–1150 $\text{cm}^2/\text{V}\cdot\text{s}$ vs. 100–2000 (CVD on other metals); >10 000 (exfoliated graphene)	300 nm SiO_2/Si substrate, back-gated, V_G : ± 40 V, V_{DS} : -0.5 V, room temp, air	Direct growth without transfer step and field mobility comparable to other CVD metals	[22–23]
Applications requiring defect engineered graphene synthesis					
Li-ion battery electrodes	S: Few layers, conductive, adherent P: Electrical conductivity, interfacial contact, defects for Li^+ intercalation	Capacity retention: 75% after 50 cycles	Li half-cell, 1 mol/L LiPF_6 in EC/DMC (1 : 1), 10 $\mu\text{A}/\text{cm}^2$, 0.02–3.2 V vs. Li/Li^+ , room temp	Fe serves dual role as growth catalyst and industry-standard current collector	[80]
Fischer-tropsch catalysis	S: Defective or porous graphene shells P: Mass transport, active site accessibility	CO conversion: ~ 75% (Fe@G) vs. ~ 20% (bare Fe NPs), increased by 3.75 times	553 K, 40 h, 50 mg, H_2/CO : 2, fixed bed	graphene shell stabilizes Fe particle integrity while maintaining catalytic activity	[102]
Application requiring dual mechanism of graphene conductivity and iron magnetic property					
Water remediation	S: Few layers + defective graphene P: Adsorption sites, electron transfer	Adsorption capacity (mg/g): Pb(II): 17.3, Cr(VI): 18.55, As(V): 38.5, Cu(II): 42.24	2.5 g/L adsorbent, 20 mL heavy metal solution, 24 h contact, pH 4–5.5	Magnetic Fe core enables separation and redox; graphene provides adsorption sites	[103]
EMI shielding	S: Multilayer graphene + magnetic core P: Dielectric + magnetic loss (dual mechanism)	Reflection loss: -72.2 dB (FeCo@C), -58 dB (Fe@G)	Paraffin matrix, 1–5 mm thickness	Dual mechanism: magnetic Fe loss + graphene dielectric loss	[104–105]

er graphene coverage (>90 %), proved larger grain sizes, and reduced defect density, underscoring the importance of continuous multilayer films for barrier protection.

Graphene grown on iron substrates has also shown significant promise in tribological applications. Borba Cardoso et al.^[101] employed low-pressure CVD to grow single-layer graphene directly on ASTM A36 steel, demonstrating a reduction in the coefficient of friction (COF) from 0.36 (uncoated bare steel) to 0.11–0.12 (graphene coated steel at varying deposition times (30–60 min)), representing a 67% decrease (Fig. 11b). Notably, no complete debonding occurred during tribological testing, demonstrating robust adhesion of CVD-grown graphene to the steel surface. Acunaş Karagöz et al.^[106] compared three graphene coating approaches on nodular cast iron piston rings from a Honda GX270 engine (a) monolayer graphene transferred from copper, (b) direct monolayer grown on chromium-coated cast iron, and (c) direct multilayer grown on uncoated cast iron. All graphene-coated samples significantly reduced friction relative to un-

coated rings (COF = 0.15), and direct monolayer graphene on chromium-coated iron exhibited the best performance with the lowest COF (0.0924), followed closely by direct multilayer on cast iron (0.0942). The transferred monolayer exhibited slightly higher friction (0.0968). The direct synthesis approach eliminates transfer-related defects while maintaining strong interfacial bonding, critical for industrial wear-resistant applications. Collectively, these studies demonstrate that direct graphene growth on iron and steel substrates provides superior corrosion and wear resistance by combining high coverage, strong interfacial bonding, and elimination of transfer-related limitations. These attributes position iron-grown graphene coatings as particularly attractive for industrial, automotive, and infrastructure applications, where durability, scalability, and cost are paramount.

5.2 Field-effect transistor (FET) devices

As-grown graphene-on-Fe achieves mobilities of 300–1150 $\text{cm}^2/\text{V}\cdot\text{s}$ ^[22], comparable to CVD graphene on other metals. However, π - d hybridization between Fe d -orbitals and graphene π -states limits perform-

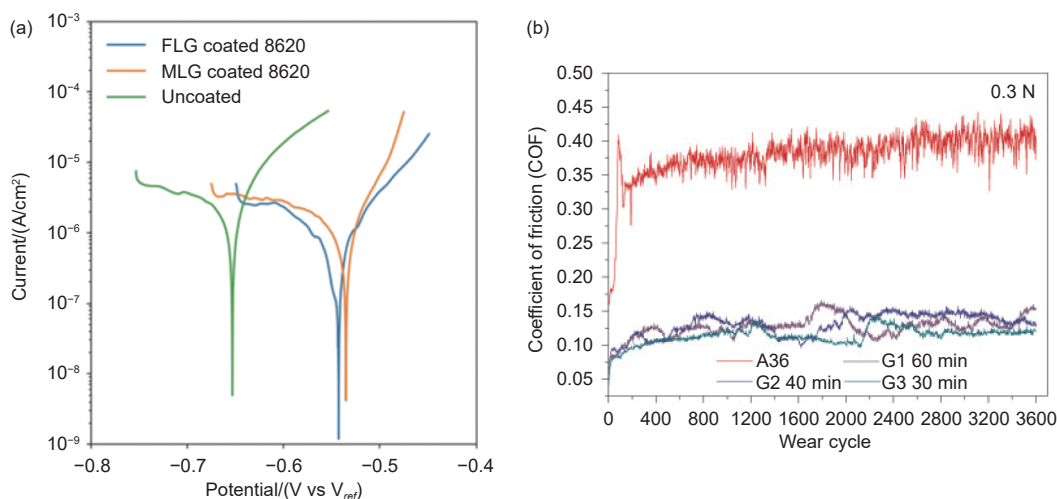


Fig. 11 (a) Tafel plots showing enhanced corrosion protection of graphene-coated 8620 steel: FLG and MLG coatings shift E_{corr} positively by +94 mV and +101 mV, respectively, compared to uncoated steel, indicating increased corrosion protection (Reprinted with permission, copyright 2025, Elsevier^[71]); (b): Coefficient of friction for ASTM A36 steel substrates: uncoated (0.36, red) versus single-layer graphene coated samples synthesized using liquid precursor CVD at 400 mTorr for 60 min (G1, COF = 0.12), 40 min (G2, COF = 0.12), and 30 min (G3, COF = 0.11). (Adapted from Cardoso et al.^[101])

ance while transfer to h-BN substrates recovers mobilities of $40\,000\text{ cm}^2/(\text{V}\cdot\text{s})$ ^[107] by eliminating substrate coupling. For high-performance FET applications, substrate transfer is necessary; for modest-performance applications (transparent conductors, flexible electronics), direct growth on Fe is acceptable. Iron substrates have enabled both transfer-free and transfer-based FET fabrication, offering alternative device integration routes compared to conventional Cu-grown graphene. Kondo et al.^[23] pioneered transfer-free device fabrication by growing few-layer and multilayer graphene at $650\text{ }^\circ\text{C}$ on patterned Fe films deposited on SiO_2/Si substrates. After defining source/drain electrodes (Au/Ti) to mechanically anchor the graphene edges, the underlying Fe was selectively etched, leaving suspended graphene channels. The resulting top-gated FETs exhibited ambipolar behavior, with maximum transconductance of 22 mS/mm and field-effect mobility up to $230\text{ cm}^2/(\text{V}\cdot\text{s})$. Additionally, multilayer graphene channels demonstrated sustained current-carrying capacity of 10^7 A/cm^2 for over 100 h, highlighting their robustness for high-current applications such as large-scale integrated LSI interconnects.

In a transfer-based approach, Xue et al.^[22] synthesized few-layer graphene on $100\text{ }\mu\text{m}$ iron foil by ambient-pressure CVD, optimizing growth conditions

based on the Fe-C phase diagram. Following wet-etching transfer to $\text{SiO}_2/\text{p}^+\text{Si}$ substrates, the fabricated back-gate FETs achieved mobilities ranging from 300 to $1150\text{ cm}^2/(\text{V}\cdot\text{s})$, placing them within the upper range reported for CVD-grown graphene devices (typically 100 – $2000\text{ cm}^2/(\text{V}\cdot\text{s})$) and substantially exceeding values typical of reduced graphene oxide-based FETs. While these mobilities remain below those of state-of-the-art Cu-grown monolayer graphene, iron-grown graphene FETs offer lower synthesis temperature, reduced substrate cost, and potential transfer-free integration, making them attractive for cost-sensitive and high-current electronic applications rather than ultra-high-mobility logic.

A key limitation of graphene grown on iron substrates arises from the strong Fe-graphene interfacial interaction that provides mechanical robustness but can also introduce significant electronic drawbacks. Hybridization between Fe d-states and graphene π orbitals induces charge transfer and Fermi level pinning, which reduces gate tunability and carrier mobility and limits modulation depth in FET devices. Charge transfer from Fe (typically n-doping of 0.2 – 0.5 eV) and interface scattering degrade carrier mobility to 500 – $2000\text{ cm}^2/(\text{V}\cdot\text{s})$ for as-grown graphene-on-Fe^[22,30,63] which is substantially lower than the $10\,000$ – $40\,000\text{ cm}^2/(\text{V}\cdot\text{s})$ routinely achieved on

weakly-interacting substrates like h-BN^[107–108]. Consequently, for high-performance FET applications, transfer to insulating or weakly-interacting substrates is often required to restore intrinsic electronic properties. This highlights a trade-off between direct growth and electronic performance in Fe-based systems.

5.3 Energy storage electrodes

In energy storage applications, Fe serves dual roles: as both the growth catalyst and industry-standard current collector, eliminating transfer steps while enabling direct integration of graphene electrodes. Iron-based substrates have enabled direct integration of graphene electrodes for energy storage, eliminating transfer and binder-related limitations common in conventional graphene electrodes. Gullapalli et al.^[80] demonstrated direct CVD growth of graphene on SS substrates for lithium-ion battery electrodes. In this architecture, graphene serves as electrochemically active material while SS functions as the current collector, providing excellent electrical contact and mechanical stability without the need for polymer binders or conductive additives. The graphene-on-stainless steel electrodes exhibited reversible lithium intercalation and stable electrochemical performance over repeated charge-discharge cycles. The three-layer graphene electrode retained approximately 75 % of its nominal capacity (0.05 mAh/cm) under high current densities, with full capacity recovery upon returning to lower current operation, indicating robust rate capability and structural integrity (Fig. 12). The strong adhesion afforded by direct-growth prevented delamination during cycling, a common failure mode in electrodes fabricated from transferred or slurry-cast graphene flakes. This transfer-free approach leverages the chemical stability, mechanical robustness, and electrical conductivity of stainless-steel substrates, while exploiting graphene's high surface area and fast charge transport, making iron-based substrates particularly attractive for scalable, integrated energy storage architectures.

5.4 Catalysis: Fischer-Tropsch syngas conversion

Catalytic applications leverage Fe@G core-shell architectures where defective graphene shells enable reactant access while stabilizing Fe nanoparticle integ-

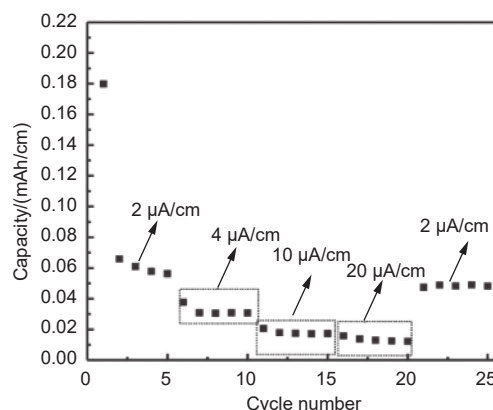


Fig. 12 Rate capability of graphene on 304 stainless steel. Discharge capacity versus cycle number at current densities of 2, 4, 10 and 20 $\mu\text{A}/\text{cm}$. The electrode retains $\sim 75\%$ capacity at high rates and recovers to $\sim 0.05 \text{ mAh}/\text{cm}$ upon returning to 2 $\mu\text{A}/\text{cm}$ (Reprinted with permission, copyright 2011, John Wiley and Sons^[80])

ity. Unlike pristine-graphene applications, the defect-engineered approach (Table 6) transforms structural imperfections into functional advantages. Graphene-iron hybrid catalysts have demonstrated substantial performance enhancements in syngas conversion by stabilizing active iron phases under harsh reaction conditions. Wang et al.^[102] synthesized graphene-encapsulated iron nanoparticles (Fe@G) for Fischer-Tropsch synthesis (FTS), where a few-layer graphene shell conformally coated the iron core. The graphene encapsulation acted as a selective diffusion barrier, protecting iron nanoparticles from oxidation and sintering while preserving access of reactants to catalytic sites. Under FTS condition (280 °C, 553 K), Fe@G catalysts achieved CO conversion of $\sim 75\%$ (Fig. 13) with space-time yields of 746 $\text{mg}/(\text{g}\cdot\text{cat}\cdot\text{h})$ for $\text{C}_2\text{-C}_4$ olefins and 706 $\text{mg}/(\text{g}\cdot\text{cat}\cdot\text{h})$ for C_{5+} hydrocarbons. These values represent more than three-fold improvement over uncoated iron nanoparticles. This enhanced performance was attributed to the graphene's ability to suppress particle agglomeration, stabilize carburized iron phases critical for FTS activity, and maintain high dispersion of active sites during prolonged operation. This work highlights graphene encapsulation as a powerful strategy for engineering durable, high-performance iron catalysts, combining the catalytic activity and earth abundance of iron with graphene's chemical stability and confinement effects, an approach directly relevant to scalable, low-cost

catalytic systems.

While graphene encapsulation enhances catalyst stability by preventing oxidation and sintering of iron nanoparticles, strong graphene–Fe interactions can limit catalytic accessibility. The same complete graphene coverage that provides corrosion resistance also blocks access to surface Fe atoms that could serve as catalytic sites. The strong Fe–C bonding stabilizes the graphene lattice, reducing defect density (edge sites, vacancies, heteroatom dopants) that typically drive catalytic activity in graphene-based materials^[109]. This creates a fundamental trade-off: enhancing catalytic activity through defect engineering (controlled oxidation, plasma treatment, nitrogen doping) inherently reduces corrosion protection by introducing pathways for electrolyte penetration. For catalytic applications, graphene-on-Fe is most effective when Fe serves as a corrosion-resistant current collector rather than the active catalyst. Hybrid approaches such as depositing catalytic nanoparticles atop graphene or creating intentionally defective graphene with balanced activity and protection represent promising directions. The direct synthesis approach reviewed here is therefore complementary to, rather than competitive with, traditional graphene catalysis strategies that prioritize defect-rich structures.

5.5 Water remediation

Water remediation exploits defects and functional groups for adsorption while leveraging Fe's magnetic properties for separation, combining defect-engineered adsorption with iron's magnetic and redox properties. Graphene–iron hybrid materials have shown strong potential for water remediation, combining iron's redox activity with graphene's adsorption capacity, chemical stability, and electron transport properties. Zhang et al.^[110] developed lignin-derived few-layer graphene-encapsulated zero-valent iron nanoparticles (LC-FLG@Fe⁰) for removal of inorganic water contaminants. These nanoparticles with sizes of 5–15 nm consist of nZVI cores protected by graphene shells, which effectively suppress surface passivation and particle agglomeration, which are two major lim-

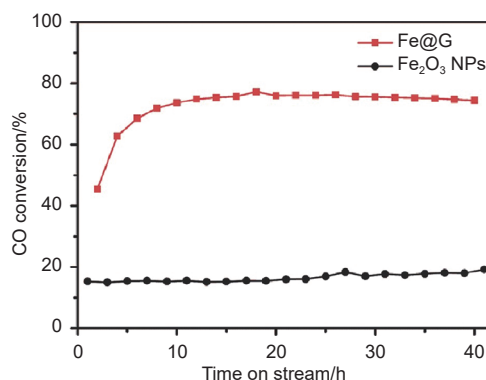


Fig. 13 CO conversion versus time on stream for Fe@G and Fe₂O₃ NPs at 553 K (280 °C), showing Fe@G achieves ~75% stable conversion compared to ~18% for bare Fe₂O₃ nanoparticles (Reprinted with permission, copyright 2015, John Wiley and Sons^[102])

itations of conventional nZVI systems. The LC-FLG@Fe⁰ material demonstrated high adsorption capacities: 127.5 mg/g for Pb (II), 214.7 mg/g for phosphate, and 356.8 mg/g for nitrate. Remediation were governed by a combination of redox reactions, precipitation, and chemisorption mechanisms, with the graphene facilitates shell electron transfer from the iron core to target species, thereby enhancing reactivity. This approach utilizes low-cost industrial byproducts (kraft lignin) as the carbon precursor and avoids hazardous chemical synthesis, offering economic and environmental advantages.

Neeli et al.^[103] synthesized carbon-encapsulated iron nanoparticles (CEINPs) for heavy metal remediation. CEINPs containing 10% Fe demonstrated dual functionality, reducing toxic Cr (VI) to less toxic Cr (III) while simultaneously adsorbing multiple contaminants (Fig. 14). Reported adsorption capacities were 18.55, 38.5, 42.24 and 17.30 mg/g for Cr (VI), As (V), Cu (II) and Pb (II), respectively. The carbon shell enhanced particle stability and controlled electron transfer, enabling sustained remediation performance. Collectively, these studies demonstrate that graphene-encapsulated iron nanoparticles offer a versatile, low-cost, and sustainable platform for water treatment, combining high adsorption capacity, redox activity, and resistance to deactivation. The use of bio-derived carbon sources further strengthens the case for scalable environmental remediation technologies based on iron–graphene systems.

5.6 Electromagnetic interference (EMI) shielding and microwave absorption

EMI shielding requires multilayer graphene for dielectric loss combined with a magnetic Fe core for magnetic loss, a dual-mechanism absorption unattainable with non-magnetic substrates. This application demonstrates that Fe-based synthesis provides value beyond catalytic graphene growth: the Fe substrate itself becomes a functional component. Graphene-encapsulated iron-based nanoparticles have emerged as effective highly materials for electromagnetic interference (EMI) shielding and microwave absorption, exploiting the synergistic combination of magnetic loss from iron-based cores and dielectric loss from graphene shells. This dual-loss mechanism enables strong attenuation of incident electromagnetic waves through impedance matching, interfacial polarization, and multiple internal reflections. Kuang and Wang et al.^[104] synthesized FeCo-C core-shell nanoparticles by metal-organic CVD and demonstrated that carbon shell thickness critically influences performance. Reducing shell thickness to approximately 0.8 nm achieved optimal impedance matching, yielding minimum reflection loss of -72.2 dB and a broad effective absorption bandwidth of 7.6 GHz. In this architec-

ture, the iron-cobalt core provides strong magnetic loss, while the thin graphitized carbon shell facilitates dielectric loss and enhanced interface polarization, maximizing electromagnetic dissipation.

Similarly, Zhang et al.^[105] developed graphene-encapsulated iron nanoparticles (Fe@G) achieving a minimum reflection loss of -58 and -22 dB at 11 GHz (Fig. 15) when the nanoparticles were dispersed in paraffin (for 1–3 mm thickness) and epoxy composites (for 2 mm thickness), respectively. The composites demonstrated effective absorption across a wide frequency range (2–18 GHz), spanning the C-, X- and Ku- bands relevant to telecommunications and radar systems. The graphene shell served multiple functions: protecting the iron core from oxidation, suppressing particle agglomeration, reducing eddy current losses, and improving impedance matching between the absorber and free space. Together, these studies highlight graphene-encapsulated iron-based nanostructures as high-performance, lightweight, and broadband EMI shielding materials, where tunable graphene shell thickness and magnetic core composition enable precise control over absorption mechanisms. The use of earth-abundant iron further supports scalability and cost-effectiveness for next-generation electromagnetic protection technologies.

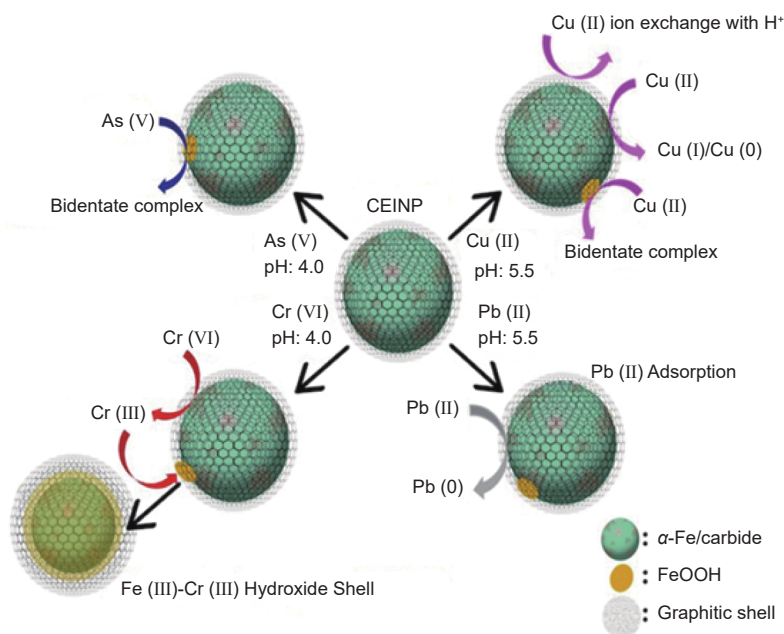


Fig. 14 Illustration of heavy metal adsorption mechanisms on carbon-encapsulated iron nanoparticles, showing reduction Cr (VI), Cu (II), Pb (II) and surface complexation As (V) pathways mediated by the metallic iron core and FeO(OH) corrosion products (Reprinted with permission, copyright 2020, Elsevier^[103]).

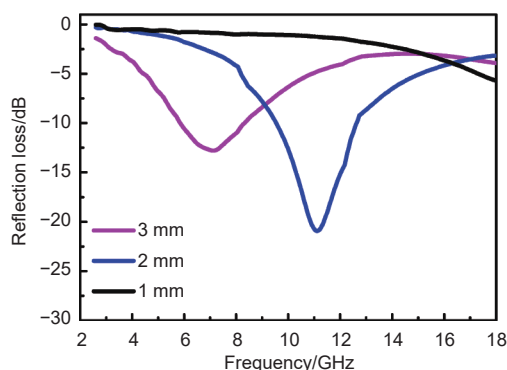


Fig. 15 Measured reflection loss of Fe(G)/epoxy coatings (60%, mass fraction loading) at 1-, 2-, and 3-mm thicknesses, showing minimum R of -22 dB at 11 GHz for 2 mm coating and effective bandwidth ($R < -10$ dB) of ~ 9 –13 GHz. (Adapted from Zhang et al.^[105])

6 Challenges and strategies for improvement

The intrinsic thermodynamic properties of iron and its strong interaction with carbon present fundamental challenges for the synthesis of high-quality graphene. High carbon solubility, stable carbide formation, surface oxidation, substrate roughness, and strong graphene–Fe adhesion collectively complicate control over layer control, uniformity, and integration. Major obstacles in graphene growth on Fe and Fe-alloy substrates include high carbon solubility, carbide formation, surface oxidation, and substrate roughness. Experimental strategies to mitigate these challenges are reviewed below.

6.1 Controlling layer number and uniformity

Iron exhibits exceptionally high carbon solubility, reaching 2.09% at 1147 °C, leading to substantial carbon dissolution during CVD growth^[18,36]. Upon cooling, carbon solubility decreases sharply, most notably during the γ -Fe (FCC) to α -Fe (BCC) phase transition at ~ 912 °C, leading to uncontrolled carbon precipitation from the bulk to the surface until the eutectoid temperature (727 °C). This precipitation-dominated mechanism typically produces non-uniform, multilayer graphene with substantial thickness variations across the substrate^[22,30].

Several strategies have been developed to address this challenge. As discussed in Section 3.2, alloying strategies are among the most effective methods for controlling layer number by systematically re-

ducing carbon solubility and modifying precipitation kinetics^[71,81–82]. Chen et al.^[63] introduced gallium pellets in combination with iron-group metals to form a chemically stable antiperovskite interlayer (Fe_3GaN), which blocks carbon diffusion pathway and enables the growth of monolayer graphene at temperatures as low as 600 °C on iron substrates.

Temperature-based strategies provide an additional lever. Operating CVD processes below 912 °C, thus avoiding the formation of the austenite phase, restricts carbon dissolution into Fe and favors surface-limited growth rather than precipitation-dominated mechanisms^[25,56,66,71].

Vinogradov et al.^[25] demonstrated synthesis of high-quality single-layer graphene on Fe (110) substrate by optimizing the conventional CVD process and deliberately operating under non-equilibrium growth conditions, suppressing bulk carbon dissolution while enabling surface-confined graphene formation. Notably, this non-equilibrium strategy produced a unique periodically corrugated wave structure on Fe (110) rather than flat epitaxial films. LEEM and STM revealed one-dimensional waves with ~ 4 nm periodicity along [001], accommodating the lattice mismatch between graphene hexagonal lattice and the rectangular Fe (110) surface. Density functional theory (DFT) confirmed this corrugated morphology as the energetically favored configuration, balancing lattice-mismatch strain against strong Fe–C interfacial bonding. This work demonstrates that high-quality graphene on iron is achieved not by enforcing perfect epitaxy but by allowing natural energy-minimizing morphologies under carefully controlled growth conditions.

6.2 Carbide formation and its suppression

A key distinction between iron and other transition-metal catalysts lies in iron's tendency to form thermodynamically stable Fe_3C (cementite) below the eutectoid temperature. Unlike the decomposable carbides in Ni and Co systems (Section 2.2.1), Fe_3C remains stable at room temperature^[30,59,111].

Mitigation strategies primarily focus on precise thermal control. Growth conducted near (slightly

above) the eutectoid point, combined with carefully controlled cooling schedules^[30,59], can shift the balance towards graphene precipitation over carbide formation^[71]. Hydrogen partial pressure is another critical parameter: low H_2 concentrations favor high-quality graphene formation, whereas high H_2 partial pressures enhance etching, reducing surface coverage and increasing defects^[27,28,33].

Beyond thermal control, alloying approaches (Section 3.2) suppress carbide formation through multiple mechanisms. Hood et al.^[71] demonstrated austenite stabilization by Mn and Ni, which prevents the eutectoid transformation that favors Fe_3C formation, thereby promoting graphene precipitation at lower temperatures. Alternatively, carbide formation can also be indirectly suppressed through selective carbide trapping. Alloying Fe with elements such as Mo leads to the formation of highly stable carbides (e.g., Mo_2C) that sequester dissolved carbon, preventing Fe_3C formation and enabling controlled graphene growth from surface-segregated carbon^[112].

6.3 Surface oxidization

Iron's high reactivity and oxidation susceptibility present significant challenges for graphene growth^[30,44]. At elevated temperatures, residual oxygen in iron substrates can readily form oxide phases such as FeO , Fe_2O_3 (hematite), and Fe_3O_4 (magnetite)^[75,113], which block the catalytic sites and inhibit carbon dissolution and surface diffusion^[75]. Effective oxide management is therefore essential.

Multiple studies have demonstrated that exposure to high-purity H_2 during CVD growth effectively reduces native oxides and restores catalytic activity, enabling efficient hydrocarbon decomposition and improving graphene quality^[28,31,75]. Complementary strategies include maintaining inert atmospheres (eg, Ar or N_2) during both growth and cooling stages to suppress re-oxidation, as reported by Xue et al.^[22] and Chen et al.^[63].

In multicomponent substrates, oxide chemistry plays a more nuanced role. John et al.^[75] showed that thin oxide layers such as Cr_2O_3 , formed by controlled alloying with Cr and Mn, can stabilize the surface

without hindering catalytic activity, whereas thicker oxide layers act as passive barriers that disrupt graphene growth.

6.4 Substrate roughness and defects

Polycrystalline iron substrates, particularly commercial Fe foils, generally exhibit significantly higher surface roughness than high-quality Cu foils^[70–71]. Surface roughness introduces localized strain and promotes heterogeneous nucleation, leading to non-uniform graphene growth with spatial variations in thickness and crystallinity^[62,70]. Surface defects further exacerbate thickness variations by acting as preferential nucleation sites^[22,71].

Surface engineering strategies have proven effective in mitigating these effects. Mechanical polishing followed by electropolishing effectively reduces surface roughness and improves nucleation uniformity^[71]. High-temperature annealing in H_2 atmospheres promotes grain growth and surface smoothing through atomic diffusion, resulting in improved graphene continuity^[22,25]. An alternative approach involves depositing thin Fe films on atomically smooth substrates such as Si or Si/ SiO_2 by molecular beam epitaxy or sputtering, effectively decoupling roughness from bulk Fe behavior^[25,66]. Edwards et al.^[56] and Zheng et al.^[66] further reported that optimizing surface roughness by limiting the effective iron thickness reduces total carbon uptake, enabling improved layer control and uniformity.

6.5 Transfer vs. direct integration

Many applications require graphene on dielectric or flexible substrates, necessitating transfer from metal catalysts. However, the strong adhesion between graphene and Fe complicates transfer relative to Cu-grown graphene^[62,114]. Traditional wet-etch transfer methods (using $FeCl_3$ or similar etchants to dissolve the Fe substrate) often introduce contamination, wrinkles, tears, and residues, while generating significant chemical waste^[32,114].

For applications such as corrosion protection, catalysis, and energy storage, direct integration of graphene on Fe or stainless steel eliminates the need for transfer and offers clear advantages, including su-

perior adhesion, electrical contact, and mechanical robustness^[40,77,80]. Accordingly, many iron-based graphene applications favor direct-use architectures^[62,69,71].

For applications where transfer is unavoidable, alternative methods have been developed. Kang et al.^[114] demonstrated electrochemical delamination, in which a gas generation at graphene-metal interface enables controlled separation with reduced damage compared to chemical etching. Sacrificial metal interlayers (e.g., Ni or Cu) deposited on Fe substrates have also been used to mediate growth and enable subsequent etching-based removal^[76,113].

Polymer-assisted transfer methods (e.g., PMMA or PDMS) remain widely used but often introduce residues and metal-ion contamination, limiting device performance^[32,114].

7 Conclusions

This review demonstrates that graphene synthesis on iron-based substrates has evolved from early proof-of-concept studies into a technologically credible and application-relevant platform distinguished by its low cost, direct integration with steel infrastructure, and unique functional synergies. Over the past fifteen years, this field has progressed from demonstrating feasibility to delivering measurable performance in protective coatings, catalysis, energy storage, and functional composites, while simultaneously revealing persistent mechanistic and materials challenges that must be addressed for broad commercialization. The iron-graphene landscape presents a complex picture: compelling advantages in scalability, direct integration, and multifunctionality coexist limitations in layer control, uniformity, and electronic quality. By integrating insights across growth mechanisms, substrate engineering, characterization methodologies, and application outcomes, this review provides actionable guidance for researchers and technologists navigating this rapidly maturing field.

7.1 Synthesis of key findings

Growth Mechanisms: Graphene formation on iron substrates occurs through competing and comple-

mentary pathway-surface-mediated segregation and bulk dissolution-precipitation-whose relative contributions are governed by the complex interplay of temperature, carbon chemical potential, cooling rate, substrate orientation, and iron purity rather than any single controlling parameter. Although this mechanistic complexity complicates predictive control, it also enables synthesis flexibility. Surface-dominated growth at moderate temperatures (700-800 °C) with rapid cooling favors few-layer graphene, whereas precipitation-dominated growth at higher temperatures (850-1000 °C) with slower cooling produces multilayer films suitable for protective coatings and energy applications. Iron carbide formation, long regarded as detrimental, emerges as a potentially useful intermediate for interface engineering and controlled carbon delivery. However, definitive mechanistic understanding will require expanded use of in-situ and operando techniques capable of tracking real-time carbon partitioning between surface and bulk during growth: capabilities that are only now becoming experimentally accessible.

Substrate Engineering: Comparative studies across pure iron, iron-nickel alloys, iron-cobalt alloys, iron carbides, and stainless steels establish clear substrate-property relationships. Nickel alloying reduces carbon solubility, improving layer control and quality; cobalt addition enhances magnetic properties while maintaining catalytic activity; carbide substrates suppress excessive carbon dissolution enabling better layer control at lower temperatures; and SS allow direct integration into electrochemical and structural devices. No single “best” substrate exists. Instead, optimal substrate selection is application-specific: pure iron for cost-sensitive protective coatings, FeNi alloys for moderate quality electronic and tribological applications, Fe₃C for maximum layer control, and FeCo alloys for magnetically enabled applications such as EMI shielding and spin-dependent devices.

Characterization Methodologies: Iron-based substrates introduce unique characterization challenges, including Raman fluorescence interference, XRD peak overlap with carbides, TEM transfer require-

ments, and XPS surface sensitivity. These constraints necessitate correlative, multi-technique characterization strategies. Raman spectroscopy provides rapid quality screening for few-layer films; TEM offers definitive layer counting for ambiguous cases; XRD identifies carbide phases; XPS tracks encapsulation in core-shell nanoparticles; and computational methods validate experimental observations and predict inaccessible properties. The growing availability of in-situ techniques (ambient-pressure XPS, environmental TEM, synchrotron-based GIXRD) coupled with advanced computational approaches (DFT, MD, machine learning potentials) is transforming the field, enabling mechanistic insights that were inaccessible through ex-situ analysis alone.

Application Demonstrations: Graphene grown on iron substrates has been validated across a wide spectrum of applications, with technology readiness levels varying substantially. Protective coatings represent the most use case, with pilot-scale deployment showing 81% corrosion reduction and 67% friction reduction compared to uncoated steel, positioning them for near-term commercialization in non-critical environments. Iron-graphene core-shell nanoparticles demonstrate exceptional catalytic performance, superior pollutant adsorption, outstanding EMI shielding but remain constrained to laboratory scale, requiring synthesis scaling before industrial deployment. Electronics applications, while demonstrated, face a fundamental quality gap (mobility 300-1150 cm²/V·s versus 2000-5000 cm²/V·s for copper-grown graphene) limiting them to cost-sensitive, quality-tolerant niches unless significant advances in defect control and mobility are achieved.

7.2 Outlook and future directions

Despite significant progress, the primary limitation in iron-based graphene synthesis is not feasibility, but predictability and transferability across substrates, geometries, and scales. Future advances will rely on closing this gap through targeted use of operando diagnostics and mechanistic models to translate process parameters into predictable growth outcomes, partially under industrially relevant, non-equilibrium conditions. Near-term impact is expected in direct-integ-

ration applications, where multilayer graphene, strong Fe-C coupling, and carbide tolerance are advantageous rather than detrimental. These include protective coatings, tribological surfaces, catalysis, energy storage electrodes, and EMI shielding, which represent the most immediate deployment pathways, especially where hydrogen-free or solid-carbon growth routes can reduce the cost and environmental burden. Longer-term opportunities lie in extending mechanism understanding from model Fe substrates to commercial carbon steels and stainless steels, enabling graphene functionality to be embedded directly into structural materials.

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