



Polymer-derived carbon electrocatalysts for water splitting: from bottom-up design to mechanistic insights

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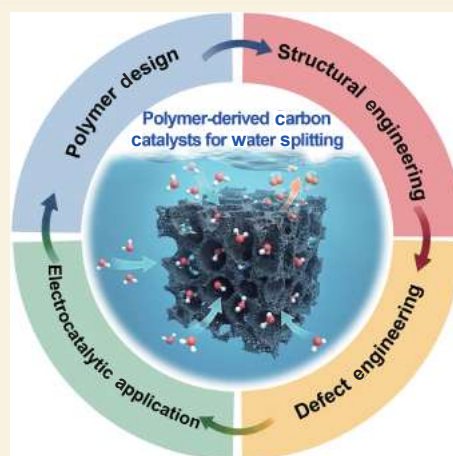
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Abstract: Electrochemical water splitting is a pivotal technology for sustainable green hydrogen production. While carbon-based and metal-free electrocatalysts have emerged as highly promising alternatives to scarce precious metals, conventional “top-down” carbon post-treatments suffer from uncontrollable active-site distribution and compromised structural integrity. Recent paradigm-shifting advances in the “bottom-up” synthesis of highly efficient carbon electrocatalysts derived from rationally designed polymer precursors are detailed, as is the structural engineering of the polymers, ranging from block copolymer templating to the dimensional transformation of two-dimensional networks. These strategies effectively optimize the porosity and prevent the restacking of active sites. In-depth mechanistic insights are provided into how precision heteroatom pre-organization and pyrolytic topological defects break the charge symmetry of the carbon lattice, thereby accelerating the kinetics for both the hydrogen and oxygen evolution reactions. By critically examining state-of-the-art applications in overall water splitting, we outline design strategies for tailoring polymer-derived carbons. Finally, we discuss current challenges and propose future research, aimed at inspiring the rational design of next-generation sustainable energy materials.

Key words: Polymer-derived carbon; Electrocatalysis; Water splitting; Heteroatom doping; Defect engineering



1 Introduction

Global energy crises and environmental concerns have fueled intensive research on sustainable energy conversion technologies. Among these, electrochemical water splitting—comprising the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER)—is paramount for green hydrogen production^[1–3]. While noble metals (e.g., Pt, Ir and Ru oxides) serve as benchmark electrocatalysts, their scarcity and high cost severely hinder large-scale commercialization^[4]. Consequently, carbon-based metal-free electrocatalysts (CMFECs) have emerged as highly promising alternatives due to their cost-effectiveness, robust acid/alkaline corrosion resistance, and highly tunable physicochemical properties^[5–7].

Historically, CMFECs are synthesized by post-treating traditional carbon matrices, such as carbon

nanotubes or graphene, with heteroatom-containing precursors under harsh conditions^[5–8]. However, these “top-down” or post-functionalization strategies suffer from inherent limitations. The aggressive treatments often lead to a random distribution of dopants, unpredictable pore structures, and the destruction of the intrinsic conductive carbon framework. Consequently, it remains a grand challenge to precisely tailor the specific active sites (e.g., targeted nitrogen configurations) and mass-transfer channels, which restricts the further optimization of their electrocatalytic performance.

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To overcome these hurdles, the “bottom-up” synthesis utilizing polymer precursors has garnered immense attention^[9–12]. Unlike conventional carbon sources, macromolecules offer an unprecedented platform for the rational design of carbon architectures at the molecular level. By meticulously selecting functional monomers (e.g., N–, S–, or boron-rich moieties) and employing controlled polymerization techniques, researchers can realize the pre-organization of heteroatoms and precise structural templating. During the subsequent carbonization and activation processes, these tailor-made polymers transform into highly porous, heteroatom-doped carbon frameworks. More importantly, the thermal decomposition of specific polymer segments naturally induces abundant intrinsic carbon defects (e.g., non-hexagonal topological rings and edge sites). These topological defects have been proven to fundamentally alter the local electron density, redistribute charge, and significantly boost electrocatalytic kinetics^[13–15].

In this mini-review, we highlight recent advances in the polymer-based architecture of doped carbons for sustainable electrocatalysis. We systematically discuss the structure-activity relationships, tracing the pathway from the rational design of polymer precursors to the engineering of multi-scale pore structures, precise heteroatom doping, and topological defect creation (Fig. 1). Furthermore, we provide mechanistic insights into how these polymer-derived features dictate the HER and OER performances. Fi-

nally, we outline current challenges and future perspectives, aiming to provide a roadmap for developing next-generation metal-free carbon electrocatalysts.

2 Structural engineering: from polymers to porous carbons

The rational design of the initial polymer precursor is the most critical step in determining the final physicochemical properties of the derived carbon electrocatalysts. Unlike the aggressive post-treatment of bulk carbon, the controlled pyrolysis of polymers allows for the “bottom-up” regulation of pore architectures, graphitization degree and microscopic morphology. This structural engineering is fundamentally dictated by the choice of polymerization methods, templating strategies, and the intrinsic chemical structure of the monomers.

More specifically, the polymer-to-carbon conversion is not a single-step stoichiometric reaction but a dynamically coupled and multi-pathway thermal transformation involving bond cleavage, volatilization, aromatization, and lattice reconstruction^[9–12]. At relatively low temperatures (<300 °C), physically adsorbed species are removed, while labile oxygen- or nitrogen-containing groups may undergo dehydration, condensation, cyclization, or pre-crosslinking, thereby stabilizing the initial char framework. In the primary pyrolysis region (ca. 300–600 °C), weak aliphatic and heteroatom-containing bonds, such as C–O, C–N,

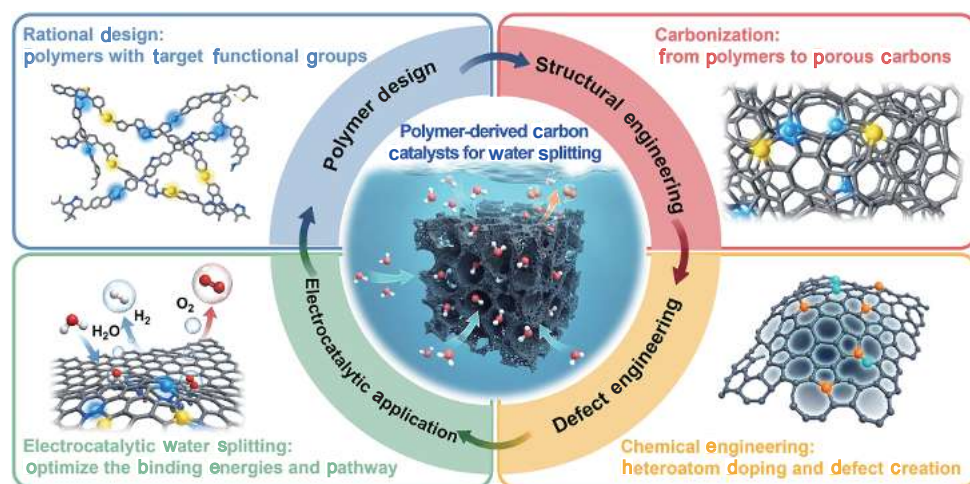


Fig. 1 Schematic illustration of the structural and defect engineering strategies for polymer-derived carbon electrocatalysts

C—S and C—H bonds, are progressively cleaved, generating radical fragments and volatile species including H_2O , CO/CO_2 , NH_3 , HCN , H_2S and light hydrocarbons. Meanwhile, dehydrogenation and ring condensation promote the formation of conjugated/aromatic domains. At higher temperatures (ca. 600–900 °C), these polyaromatic fragments further fuse into sp^2 -hybridized carbon nuclei; simultaneous outgassing and atomic rearrangement create micropores, vacancy/edge defects, and heteroatom-doped carbon configurations^[13–15]. Further thermal treatment above 900 °C generally enhances graphitic ordering and electrical conductivity, but may also decrease heteroatom retention and partially annihilate defect sites. Therefore, rather than being described by a single balanced chemical equation, polymer pyrolysis is more appropriately understood as a set of competing and overlapping reactions governed by precursor chemistry, crosslinking density, heating rate, residence time, atmosphere and activation conditions. This dynamic reaction pathway explains why rationally designed polymer precursors can simultaneously regulate pore architecture, graphitization degree, heteroatom retention, and topological defects in the resulting carbon electrocatalysts.

As schematically illustrated in Fig. 2, the structural engineering of polymer-derived carbons can be systematically categorized into 3 main strategies: templating architectures via block copolymers, carbonization chemistry of targeted precursors, and topological morphology evolution.

2.1 Block copolymers and templating strategies

In electrocatalytic water splitting, the sluggish mass transfer of reactants (water molecules) and the timely detachment of generated gas bubbles (H_2 or O_2) heavily limit the current density. Therefore, constructing a hierarchical porous network—comprising micropores for exposing active sites, mesopores for ion transport, and macropores for bubble release—is indispensable^[16].

Block copolymers (BCPs) are extraordinarily powerful tools in this regard^[17–20]. In a typical soft-templating approach, amphiphilic BCPs co-assemble

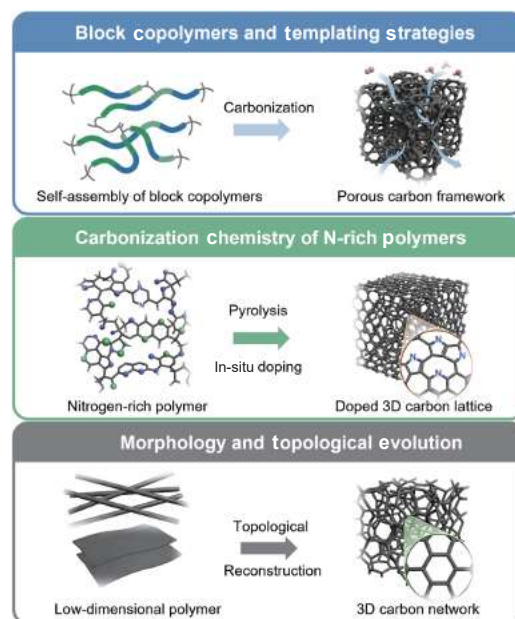


Fig. 2 Structural engineering of polymer-derived carbons

with carbon-yielding precursors driven by hydrogen bonding or electrostatic interactions. During the solvent evaporation and thermocuring stages, these BCPs direct the formation of highly ordered meso-structured organic composites. Upon subsequent high-temperature carbonization under an inert atmosphere, the BCP templates decompose and volatilize, leaving behind well-defined mesopores^[21]. Beyond conventional isotropic pores, recent breakthroughs highlight the precise capability of BCPs in driving nanoconfined self-assembly to construct highly ordered 2D layered architectures^[22]. For instance, stable endmerged lamellar micelles can be synthesized by employing block copolymers, which are further transformed into 2D ordered mesoporous nanosheets with a finely controlled interlayer space (e.g., ~ 20 nm) (Fig. 3a). This tailored lamellar space substantially decreases diffusion tortuosity and increases active site accessibility, thereby significantly boosting the acidic OER.

Furthermore, BCP micellar films exhibit exceptional dynamic tunability for advanced structural engineering^[23]. Solvent treatment can trigger an in-situ sphere-to-cylinder phase transition within metal ion-accumulated micellar films directly on targeted substrates. The direct one-step pyrolysis of these dynamically regulated precursors yields mesoporous metal-

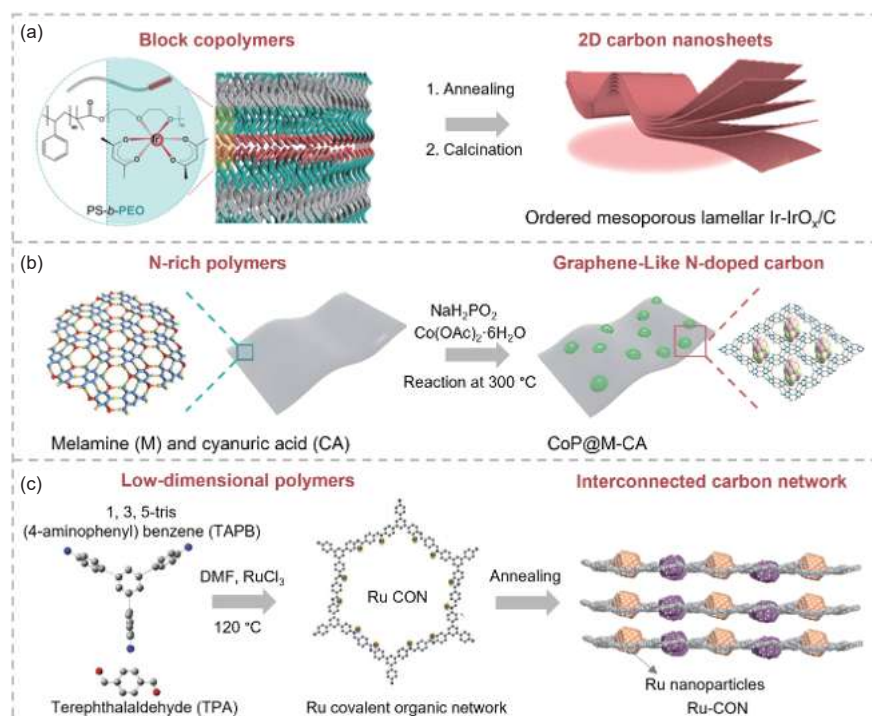


Fig. 3 Structural engineering of polymer-derived carbons. (a) Block copolymer-derived 2D carbon nanosheets. Reproduced with permission, Copyright 2022, American Chemical Society^[22]. (b) Melamine and cyanuric acid precursor-derived graphene-like N-doped carbon. Reproduced with permission, Copyright 2021, Wiley^[27]. (c) Covalent organic frameworks-derived interconnected carbon network. Reproduced with permission, Copyright 2022, Wiley^[32]

lic composites featuring open cylindrical channels. Compared to isolated spherical cavities, these continuous cylindrical channels provide an open buffer space that significantly accelerates mass transfer, facilitates rapid gas bubble escape, and exposes more reactive sites for enhanced overall water splitting kinetics.

2.2 Carbonization chemistry of N-rich polymers

Beyond structural templates, the intrinsic molecular backbone of the polymer dictates the localized chemical environment of the resulting carbon. Conducting polymers, such as polyaniline (PANI) and polypyrrole (PPy), along with nitrogen-rich networks like melamine-formaldehyde resins, are the most prominent precursors for fabricating heteroatom-doped carbons^[24–30]. The carbonization chemistry of these polymers involves a complex sequence of dehydrogenation, ring-opening, and polycondensation reactions.

For rigid conjugated polymers like PANI and PPy, thermal treatment (typically 600–1000 °C) induces the cleavage of C–H and C–N bonds, accompanied by the emission of volatile gases^[24–26]. The carbonization temperature plays a decisive role in balan-

cing electrical conductivity and active-site retention. Increasing the temperature generally improves graphitization and electron transport, whereas excessive thermal treatment can remove nitrogen species and heal structural defects^[6,24]. Conversely, lower temperatures favor the retention of pyridinic/pyrrolic nitrogen and defect sites but may lead to insufficient conductivity. Therefore, an optimized carbonization window is required to maximize the synergy between conductivity, heteroatom configuration, and defect density. Due to their pre-existing aromatic rings, these polymers readily undergo graphitization, transforming into sp²-hybridized carbon networks^[25]. Crucially, a significant portion of the nitrogen atoms is retained, evolving into highly active pyridinic-N and graphitic-N configurations. Recent advancements demonstrate that the controlled pyrolysis of customized polypyrrole architectures can further induce specific topological defects alongside nitrogen doping, thereby fine-tuning the electronic structure and significantly boosting intrinsic electrocatalytic activity^[24].

In the case of melamine-based or urea-derived networks, the thermal pathway involves the formation

of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) intermediates^[27–30]. As the temperature exceeds 800 °C, the $\text{g-C}_3\text{N}_4$ scaffold decomposes, releasing nitrogen-rich gases that act as in-situ blowing agents. This process simultaneously generates abundant micropores and leaves behind highly N-doped, topological defect-rich carbon nanosheets, significantly modulating the local electronic structure for catalytic water splitting. To achieve even greater morphological control, Wu and co-workers have utilized hydrogen-bonded supramolecular networks, such as melamine-cyanuric acid (MCA) assemblies, as advanced precursors (Fig. 3b)^[27]. These graphene-like supramolecular nanosheets serve as excellent pseudo-porous templates; upon carbonization, they structurally evolve into highly stable, ultra-thin 2D N-doped carbon supports that maximize the exposure of catalytic sites. Furthermore, systematically engineering the carbonization conditions of these melamine-derived networks allows for the precise regulation of the nitrogen configuration and defect density, directly translating to superior energy conversion performances in sustainable electrocatalysis.

In essence, manipulating the chemical composition and thermal degradation pathways of N-rich polymers enables the atomic-level customization of heteroatom dopants and topological defects. This chemical engineering strategy provides a robust foundation for transforming inert carbon frameworks into highly active, noble-metal-free electrocatalysts.

2.3 Morphology and topological evolution

The macroscopic and microscopic morphology of the carbon catalyst directly originates from the dimensional constraints of its polymer precursor. However, in gas-evolving electrocatalysis such as the HER and OER, preserving a strict two-dimensional (2D) planar morphology is often detrimental. Pristine 2D carbon nanosheets suffer from severe van der Waals-driven restacking during pyrolysis and catalytic operations, which buries intrinsic active sites and hinders electrolyte penetration^[9,31]. Furthermore, flat planar surfaces typically exhibit high gas-bubble adhesion, blocking continuous mass transfer.

To overcome these physical limitations, the current paradigm in structural engineering emphasizes “dimensional transformation”—specifically, the topological reconstruction from 1D or 2D polymers into robust 3D carbon architectures^[32–36]. Rather than maintaining a flat topology, Shao and co-workers intentionally designed polymer precursors with disrupted planarity^[32]. A compelling strategy involves the utilization of 2D “twisted” polymers; this intentional structural distortion at the molecular level naturally prevents inter-layer restacking and facilitates the stabilization of highly active, amorphous catalytic species during the pyrolysis process (Fig. 3c). Similarly, 2D polymer precursors, such as covalent triazine frameworks (CTFs) or covalent organic frameworks (COFs), can be structurally directed to assemble into 3D hierarchical networks or hollow carbon spheres^[9,33–35]. These topologies not only maximize the exposure of active sites by utilizing both the interior and exterior surfaces but also create highly efficient pathways for mass transport.

Driven by the thermal elimination of non-carbon elements and the generation of topological defects, these low-dimensional precursors experience further structural shrinkage and curling upon carbonization. The initially isolated planes intertwine and cross-link, evolving into 3D interconnected carbon aerogels or crumpled nanosheet networks^[36–37]. This topological evolution from low-dimensional precision polymers to 3D hierarchical carbon architectures provides a dual advantage: it effectively prevents the restacking of active nanosheets to preserve a high electrochemically active surface area, and it constructs an aerophobic, open-pore framework that ensures rapid bubble detachment and robust mechanical stability against the intense gas evolution dynamics. The aerophobic behavior of polymer-derived 3D carbon networks is generally associated with the post-carbonization morphological evolution, including interconnected macro/mesopores, rough surface textures, and open channels that reduce gas-bubble adhesion and facilitate bubble release^[16]. Residual oxygen- or nitrogen-containing functional groups derived from poly-

mer precursors may further improve electrolyte wettability and interfacial affinity, thereby synergistically promoting gas-evolving electrocatalysis.

Beyond these 2D-to-3D topological transformations, 0D carbon quantum dots (CQDs) and 1D carbon fibers or fiber-like carbonaceous nanostructures are also important complementary morphology platforms for carbon electrocatalysts. CQDs, such as halogen-doped carbon dots, possess abundant edge/defect sites, tunable surface functional groups, and short charge-transfer pathways, which are beneficial for exposing accessible catalytic centers and regulating local electronic structures for water-splitting-related reactions^[15]. However, their aggregation and relatively limited conductivity usually require coupling with conductive carbon frameworks or active phases. In contrast, one-dimensional carbon fibers or fiber-like carbonaceous structures provide continuous transport pathways, mechanically robust architectures, and open channels for electrolyte penetration and gas-bubble release^[30]. Therefore, 0D CQDs and 1D fibrous carbonaceous structures complement 2D nanosheets and 3D porous carbons by offering morphology-dependent advantages in active-site exposure, charge transport, and mass transfer.

In summary, morphology engineering across 0D, 1D, 2D and 3D carbon architectures is a deliberate and crucial strategy for optimizing polymer-derived carbon electrocatalysts. By synergistically overcoming the physical bottlenecks of active-site masking, sluggish charge/mass transfer, and gas-bubble release, rational morphology and topological evolution pave the way for scalable, high-current-density water splitting.

3 Defect engineering: heteroatom doping and defect creation

While the rational design of polymer architectures dictates the mass-transfer properties of the derived carbons, the intrinsic electrocatalytic activity is fundamentally governed by their localized chemical environments. Pristine sp^2 -hybridized carbon is generally catalytically inert for water splitting due to its

electroneutrality and uniformly distributed π -electron system^[38–40]. Activating this inert carbon framework relies heavily on targeted chemical engineering, primarily executed through precision heteroatom doping and the intentional creation of topological defects.

3.1 Precision heteroatom doping via polymer precursors

The primary advantage of the “bottom-up” polymer carbonization strategy lies in the ability to “pre-program” heteroatom configurations at the molecular level before thermal transformation. By strategically choosing monomers or assembling supramolecular structures, researchers can achieve atomic-level precision in dopant distribution and coordination environments, which is unattainable through stochastic post-treatment methods^[41–43].

A prominent example of this precision is the utilization of covalent triazine polymers (CTPs). Huo et al. demonstrated that CTPs, characterized by inherent nitrogen-rich triazine units, served as ideal self-doped precursors^[9]. During pyrolysis, the rigid triazine rings act as structural “anchors” that retain nitrogen atoms with high efficiency. This molecular-level pre-organization ensures that the nitrogen is predominantly converted into high-activity pyridinic-N and graphitic-N configurations. The resulting multi-heteroatom-doped (N, S, P) carbon spheres exhibit exceptional bifunctional electrocatalytic performance for ORR/OER, largely because the “pre-designed” nitrogen sites effectively stabilize the active amorphous MnO_2 lamellae and modulate the local electron cloud (Fig. 4a). The versatility of amphiphilic block copolymers (BCPs) provides another sophisticated platform for precision doping through coordination-driven self-assembly. Wang et al. developed a system utilizing PS-*b*-P2VP micellar films, where the pyridine moieties in the P2VP segments serve as dynamic coordination sites to capture various metal ions (e.g., Ru^{3+} , Pt^{2+} , Ir^{3+})^[23]. Upon direct pyrolysis, the metal ions and the nitrogen-rich polymer matrix transform synergistically. This approach not only ensures the uniform in-situ nitrogen doping of the carbon matrix but also constructs specific metal-nitrogen ($M-N_x$) motifs^[11].

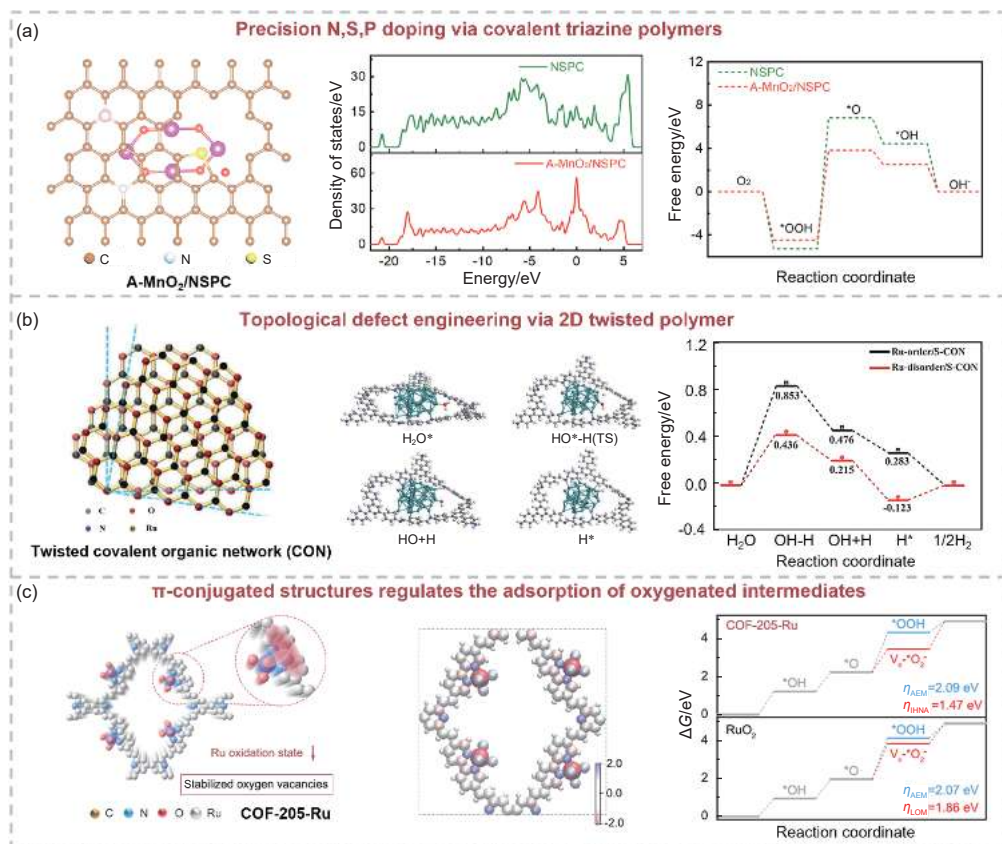


Fig. 4 Chemical engineering of polymer-derived carbons. (a) Precision N, S, P doping via covalent triazine polymer. Reproduced with permission, Copyright 2024, Wiley^[9]. (b) Topological engineering of Ru-covalent organic network (CON) catalyst via 2D twisted polymer. Reproduced with permission, Copyright 2022, Wiley^[32]. (c) Regulation of oxygenated-intermediate adsorption by a π -conjugated, sp^2 -carbon-linked covalent organic framework. Reproduced with permission, Copyright 2024, Nature Publishing Group^[33]

These motifs, coupled with the open cylindrical channels of the mesoporous film, significantly accelerate the kinetics of water splitting at high current densities by optimizing the adsorption energies of intermediates.

Beyond covalent and block polymers, hydrogen-bonded supramolecular assemblies offer a unique “pseudo-porous” doping strategy. Utilizing melamine-cyanuric acid (MCA) supramolecular nanosheets as precursors allows for the formation of graphene-like N-doped carbon supports^[27]. The intrinsic 2D hydrogen-bonded network of MCA directs the evolution of nitrogen configurations and the creation of adaptive defects during carbonization. This “molecular-template” effect leads to ultra-thin carbon structures with optimized spin density and charge distribution, which significantly modulates the electronic properties of embedded nanoparticles for superior hydrogen evolution activity.

In summary, these examples underscore that the choice of polymer precursor is the decisive factor in achieving precise heteroatom configurations. This “molecularly programmed” doping provides the necessary electronic refinement to transform inert carbon into a highly efficient electrocatalyst. The long-term stability of multi-heteroatom dopants should also be considered, especially under harsh acidic OER conditions. Weakly bonded or surface-enriched S— and P—containing species may undergo oxidation, reconstruction, or partial leaching during prolonged anodic operation^[9,33,41]. In this regard, bottom-up polymer-derived doping is advantageous because heteroatoms can be more homogeneously and covalently embedded into the carbon framework, although operando and post-reaction characterizations are still necessary to clarify their dynamic evolution.

3.2 Topological defect engineering

Beyond heteroatom doping, the pyrolytic trans-

formation of polymers inherently incorporates structural imperfections. As the polymer backbone undergoes severe dehydration, dehydrogenation, and the vigorous emission of volatile gases (e.g., CO_2 , NH_3), the reconstructing carbon lattice often fails to achieve perfect graphitization^[11,44]. This rapid thermal cleavage and outgassing organically generate abundant edge sites and intrinsic topological defects within the basal plane^[45–47]. Crucially, the density and nature of these structural imperfections can be rationally controlled by the initial polymerization and condensation conditions. For instance, in nitrogen-rich polymeric frameworks, modulating the polycondensation environment (e.g., by molten salt synthesis) allows for the precise tuning of the balance between extended π -conjugation and the concentration of structural defects, thereby profoundly optimizing the electronic band structure for enhanced water splitting^[47].

Instead of perfectly symmetrical six-membered rings, the carbon matrix reconstructs to include non-hexagonal topological rings, predominantly pentagons and heptagons, alongside abundant vacancy defects. Unlike simple heteroatom substitution, these topological defects provoke a severe structural distortion, reshaping the local geometry and strain of the carbon network. For example, recent advancements in the controlled pyrolysis of customized polypyrrole (PPy) architectures demonstrate that these self-generated topological defects effectively redistribute the local electron cloud^[24]. This electronic redistribution not only activates the carbon network as a powerful, independent active center but also provides robust “trapping” sites to stabilize highly dispersed atomic species for durable hydrogen evolution.

Furthermore, the integration of topological defects within highly ordered polymer precursors can fundamentally alter the catalytic reaction pathways. In sophisticated systems such as crossed π -conjugated COFs, the engineered defective structures interact synergistically with the robust carbon lattice^[33]. This unique topological and electronic regulation is powerful enough to activate coordinated oxygen species and stabilize critical active intermediates (such as oxygen

vacancies) even under the harsh oxidative conditions of the acidic OER. This effectively suppresses structural dissolution and significantly triggers more favorable adsorbate evolution mechanisms. Consequently, topological defect engineering presents a programmable approach to tailoring highly active and stable polymer-derived carbon electrocatalysts.

3.3 Mechanistic insights into activity enhancement

At the atomic level, both heteroatom doping and topological defects serve an identical fundamental purpose: they break the charge symmetry of the pristine carbon lattice. Heteroatoms with differing electronegativities (e.g., N is more electronegative than C, while B is less) induce intense charge polarization, creating adjacent electron-deficient (Lewis acid) or electron-rich (Lewis base) carbon sites^[48–50]. Similarly, topological defects rearrange the local electron cloud due to the geometric frustration of the sp^2 bonds, shifting the density of states closer to the Fermi level^[33,51–52]. Furthermore, controlling the degree of polycondensation and the spatial arrangement of the precursor can finely tune the extended π -conjugation network. This structural refinement fundamentally optimizes the overall electronic band structure, which is crucial for accelerating interfacial charge transfer during electrocatalytic processes.

To provide a clearer comparison between nitrogen doping and other heteroatom-doping strategies, the typical structural configurations, physicochemical effects, and electrocatalytic roles of representative non-metal dopants are summarized in Table 1.

These electronic modulations directly dictate the adsorption thermodynamics and reaction kinetics of key intermediates. According to density functional theory (DFT) investigations, the localized electron redistribution at these engineered sites optimally tunes the binding free energy of hydrogen (ΔG_{H^*}) towards thermoneutrality (≈ 0 eV) for the HER^[53]. Beyond simple adsorption thermodynamics, the asymmetric electron distribution—such as that induced by 2D twisted polymer architectures—has been proven to significantly lower the kinetic energy barrier for ini-

Table 1 Comparison of nitrogen doping with other heteroatom-doping strategies in polymer-derived carbon electrocatalysts.

Doping mode	Typical structures	Key physicochemical effects	Electrocatalytic roles and comparison with N doping	Ref.
N doping	Pyridinic-N, pyrrolic-N, graphitic-N, oxidized-N	Charge/spin redistribution; improved conductivity	Most widely studied; effectively tunes H* and oxygenated-intermediate adsorption in HER/OER	[24,27,38,41]
B doping	B-C, BC ₃ -like, B-O sites	Electron-deficient Lewis-acidic sites; charge polarization	Complements N doping; facilitates OH ⁻ /oxygenated-intermediate adsorption, especially in co-doped carbons	[38,41,43,50]
S doping	Thiophenic-S, oxidized-S, edge-S sites	Lattice distortion; defect generation; spin-density modulation	Causes stronger structural distortion than N; helps regulate H* and OER-intermediate adsorption	[9,38,41]
P doping	P-C, P-O, P-N species	Strong local polarization; defect-rich sites; improved wettability	Promotes water dissociation and intermediate binding; usually more effective in co-doped systems	[9,15,38,41]
Halogen doping, especially F	C-F, edge halogen sites	Strong dipoles; surface polarity regulation	Less universal than N doping; tunes adsorption behavior when coupled with B/N doping	[15,38,41,43]
Multi-heteroatom co-doping	N/S/P, B/N/F, N/P, N/S sites	Synergistic polarization, defects, and wettability regulation	Broader tunability than single N doping; often improves bifunctional HER/OER activity	[9,41,43,50]

tial water dissociation (the Volmer step) (Fig. 4b)^[32]. This dual optimization of water cleavage and hydrogen desorption is a hallmark of advanced polymer-derived catalysts.

Simultaneously, the optimized charge distribution regulates the scaling relations between oxygenated intermediates (ΔG_{OOH^*} , ΔG_{O^*} and ΔG_{OH^*}), thereby significantly lowering the theoretical overpotential for the OER^[54–55]. More profoundly, recent advanced theoretical models reveal that precise electronic modulation within polymer-derived frameworks can dictate the fundamental OER pathway^[9,33]. For instance, creating specific crossed π -conjugated structures can elevate the O 2p band center and stabilize oxygen vacancies (Fig. 4c)^[33,47]. This electronic reconfiguration strategically suppresses the kinetically favorable but structurally destructive lattice oxygen oxidation mechanism (LOM), while triggering the highly durable adsorbate evolution mechanism (AEM) even under harsh acidic oxidative conditions^[33].

Compared with conventional top-down post-treatment strategies, bottom-up polymer-derived routes offer distinct advantages in controllability but still face practical challenges in scalability. Top-down approaches, such as thermal or chemical post-doping of preformed carbon matrices, are generally simple and potentially scalable, yet they often lead to random dopant distribution, poorly defined defect structures, and partial damage to the conductive carbon framework^[5–8]. In contrast, bottom-up polymer routes enable the molecular-level pre-organization of heteroatoms, programmable carbonization pathways, and more controllable generation of pores and topological defects, thereby providing a clearer structure–activity

relationship for mechanistic optimization^[9–12]. However, the scalability of bottom-up strategies strongly depends on precursor availability, synthetic complexity, and carbonization reproducibility. Therefore, future development should combine the atomic-level controllability of designed polymer precursors with low-cost, scalable polymer sources and simplified processing routes.

Thus, the synergistic combination of heteroatom dopants, topological defects, and modulated π -conjugation transforms inert polymer-derived carbons into highly active, noble-metal-free bifunctional electrocatalysts, achieving exceptional performance driven by profound atomic-level electronic regulations.

4 Electrocatalytic applications in water splitting

The ultimate goal of structural and chemical engineering of polymer-derived carbons is to achieve exceptional performance in electrocatalytic water splitting. The transition from fundamental design to practical application involves optimizing the specific activity for the HER, ensuring stability and promoting synergistic effects for the OER, and ultimately realizing efficient overall water splitting using bifunctional catalysts. A comprehensive blueprint for such electrocatalyst, integrating both targeted HER and OER within a carbon network, is conceptually illustrated in Fig. 5.

4.1 Hydrogen evolution reaction (HER)

In the HER, the catalytic performance of polymer-derived carbons is primarily dictated by the identity, density, and local electronic environment of the

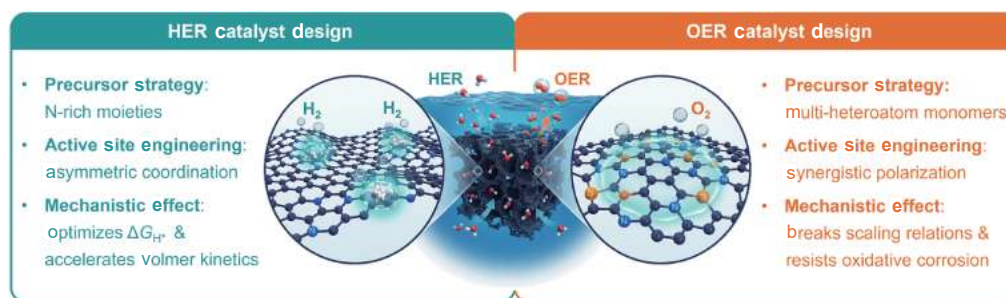


Fig. 5 Schematic illustration of the polymer-derived carbon electrocatalyst for water splitting. The left panel highlights the cathodic hydrogen evolution reaction (HER) catalyst design, targeting optimized Gibbs energy of $^*\text{H}$ (ΔG_{H^*}) and accelerated Volmer kinetics. The right panel displays the anodic oxygen evolution reaction (OER) catalyst design, emphasizing multi-heteroatom doping and breaking of scaling relations

active centers. Beyond the traditional substitution of heteroatoms, recent advancements emphasize that the synergistic interplay between the polymer-derived support and the active species is the key to achieving platinum-like kinetics^[53,56]. Polymer-derived frameworks offer a unique platform to enrich specific active motifs, such as pyridinic-N and graphitic-N, while simultaneously engineering the physical landscape to facilitate gas-bubble detachment and electrolyte access.

A pioneering strategy involves the use of structural distortion to stabilize high-activity species. Shao et al. demonstrated that utilizing a twisted covalent organic network (CON) as a precursor can provide “twisted” carbon layers that act as a sophisticated structural template^[32]. This twisted morphology induces an asymmetric distribution of nitrogen sites, which effectively triggers the amorphization of stabilized Ru nanoclusters. Compared to their crystalline counterparts, these amorphous clusters (ca. 1.5 nm) anchored on the twisted polymer-derived framework exhibit a much higher density of unsaturated active sites. This dual optimization of morphology and crystallinity allows the Ru-CON catalyst to achieve an extremely low overpotential of 12.8 mV at 10 mA cm⁻² in 1.0 mol L⁻¹ KOH, along with exceptional mass activity and long-term durability. Furthermore, supramolecular assembly strategies offer a route to construct ultrathin, “pseudo-porous” supports that maximize active site exposure. Wu et al. reported the exfoliation of hydrogen-bonded melamine-cyanuric acid (MCA) supramolecular co-crystals into graphene-like nanosheets with a thickness of only ~ 1.6 nm^[27].

These dynamic nanosheets function as structural protectors and electronic modulators during the growth of cobalt phosphide (CoP) nanoparticles. By creating adaptive defects and pores, this polymer-based support significantly enhances the electron modulation effects, resulting in a composite catalyst with high hydrogen evolution activity, requiring an overpotential of only 66 mV to reach 10 mA cm⁻².

The most sophisticated paradigm for HER involves the rational design of the polymeric coordination environment to anchor single atoms. As shown in Fig. 6a, Zhang et al. proposed a landmark strategy using polypyrrole (PPy)-based polymeric electrocatalysts to stabilize atomically dispersed platinum (Pt)^[24]. The core of this strategy lies in leveraging cation- π interactions between the polymeric backbone and the Pt precursors. This interaction fundamentally addresses the critical challenges in acidic HER, such as the low concentration of hydrogen intermediates ($^*\text{H}$) and the inherently weak adsorption on isolated metal sites. By meticulously designing the support material to facilitate these specific electronic interactions, the authors transformed the polymer matrix into a proactive modulator that optimizes the adsorption strength of $^*\text{H}$. The resulting Pt single-atom polymeric catalyst exhibits exceptional efficiency and durability in harsh acidic environments. Specifically, the Pt-polymeric system achieves a mass activity several orders of magnitude higher than commercial Pt/C, maintaining its structural integrity and catalytic performance over long-term cycling. This strategy of using polymer-derived “trapping” sites to redistribute the local electron cloud provides a powerful roadmap for maximizing

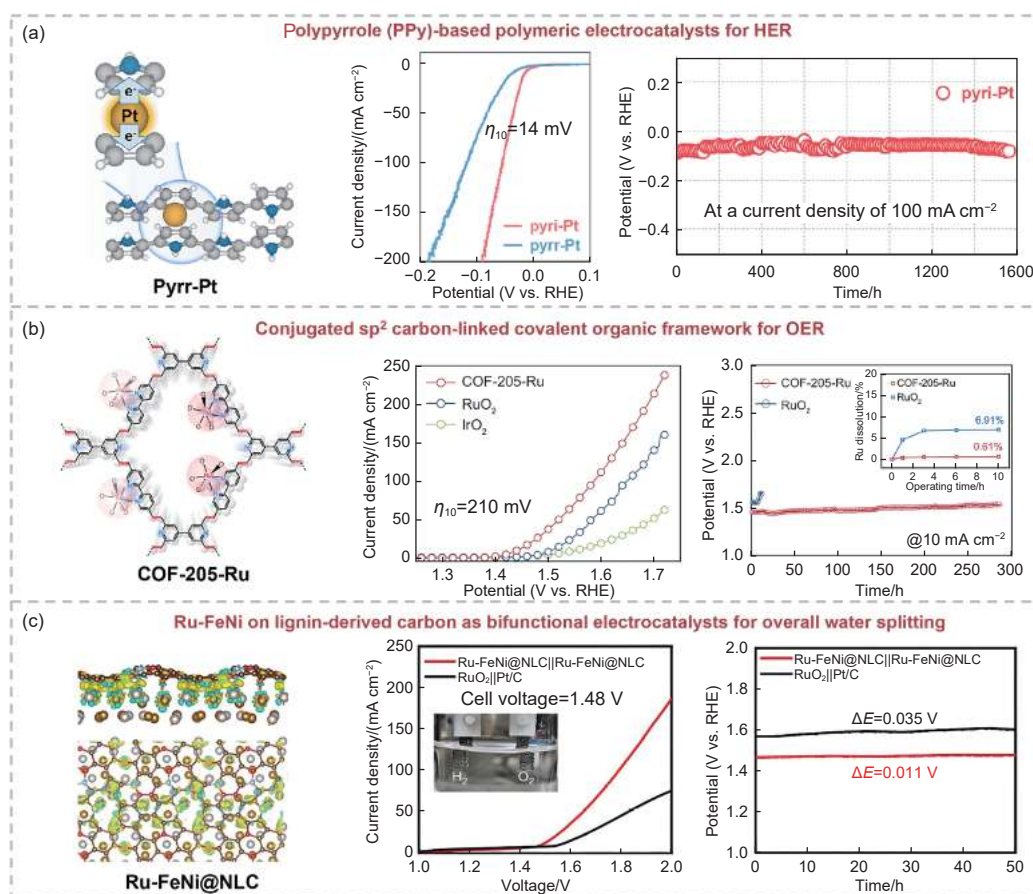


Fig. 6 Polymer-derived carbon electrocatalyst for electrocatalytic water splitting. (a) Polypyrrole-based polymeric electrocatalysts for hydrogen evolution reaction (HER). Reproduced with permission, Copyright 2026, Wiley^[24]. (b) Conjugated sp^2 carbon-linked covalent organic framework for oxygen evolution reaction (OER). Reproduced with permission, Copyright 2024, Nature Publishing Group^[33]. (c) Lignin-derived carbon as bifunctional electrocatalysts for overall water splitting^[57]. Reproduced with permission, Copyright 2023, Wiley^[57]

the utilization of noble metals while achieving superior intrinsic HER activity, bridging the gap between theoretical molecular design and practical large-scale water splitting.

4.2 Oxygen evolution reaction (OER)

The oxygen evolution reaction (OER) is a complex four-electron transfer process characterized by sluggish kinetics and high overpotentials^[54–55]. For polymer-derived carbon materials, structural instability under harsh oxidative conditions (typically >1.23 V vs. RHE)—such as carbon corrosion and the leaching of active species—remains a critical bottleneck for practical applications. Recent progress indicates that molecular-level design of polymer precursors to precisely tune electronic structures and geometric morphologies is the most effective strategy to enhance both OER activity and long-term durability. As shown in Fig. 6b, Jia et al. recently reported a landmark study

addressing the stability of carbon-based catalysts in acidic OER^[33]. The authors designed covalent organic frameworks (COFs) with crossed π -conjugation architectures to overcome the common issue of structural dissolution. This crossed π -conjugation system significantly enhances electron delocalization, which effectively elevates the O 2p band center and stabilizes critical oxygen vacancies. Such electronic modulation not only provides a high density of active sites but also strategically suppresses the kinetically favorable yet structurally destructive LOM, instead triggering the more robust AEM. Consequently, the resulting polymer-derived catalyst maintains exceptional electrochemical stability in acidic electrolytes, showing negligible structural degradation over extended cycling—a breakthrough for metal-free or low-metal carbon catalysts operating under oxidative stress. In addition to electronic refinement, precise structural engi-

engineering using block copolymers has yielded significant improvements in mass transport. Zu et al. demonstrated a sophisticated method to regulate the interlayer spacing of 2D nanosheets using lamellar micelles^[22]. Through molecular-level nanoconfined assembly, the researchers achieved precise control over the interlayer space (ca. 20 nm) of the derived carbon nanosheets. This ordered, open architecture drastically reduces the diffusion resistance of the electrolyte and maximizes the accessibility of internal active sites. This leads to a marked decrease in OER overpotential and enhanced reaction kinetics, particularly in acidic media where mass transfer is often a limiting factor.

Addressing the challenges of high-current-density operation in industrial water splitting, Wang et al. proposed a dynamic phase-transition strategy^[23]. By utilizing solvent-induced transitions from spherical to cylindrical BCP micelles, the authors constructed 3D mesoporous carbon films featuring vertically aligned open channels. These cylindrical channels act as “high-speed pathways” for the rapid detachment of oxygen bubbles produced during the OER, preventing bubble accumulation that would otherwise mask active sites and increase local resistance. Under practical testing conditions, the catalyst maintains a stable voltage even at high current densities, underscoring the immense potential of morphological evolution in polymer precursors to solve mass-transfer bottlenecks.

In summary, the synergistic integration of molecular conjugation design and multi-scale pore engineering within polymer precursors allows researchers to not only boost intrinsic OER activity but also tackle the stability challenges inherent in extreme electrochemical environments. These advancements provide a solid foundation for the next generation of sustainable and durable water-splitting technologies.

4.3 Overall water splitting

Realizing efficient overall water splitting requires catalysts that are “bifunctional”—exhibiting high performance for both HER and OER in the same electrolyte. Polymer-derived 3D hierarchical carbon nanostructures have emerged as the premier candid-

ates for this purpose^[57–60]. Their balanced active-site exposure, highly tunable electronic environments, and rapid mass-transport channels allow them to simultaneously lower the activation barriers for both cathodic and anodic reactions. A highly innovative and sustainable approach to achieving such bifunctionality involves the utilization of abundant, oxygen-rich natural polymers. As shown in Fig. 6c, Lin et al. capitalized on the abundant oxygen-containing functional groups (such as hydroxyl and methoxyl groups) inherent in the lignin macromolecular backbone to strongly coordinate with multiple metal ions (Ru, Fe and Ni)^[57]. Upon controlled pyrolysis, this lignin-metal supramolecular precursor transforms into a highly conductive carbon matrix that perfectly anchors precisely constructed Ru/FeNi alloy heterojunctions. The lignin-derived carbon support acts as a physical barrier that effectively prevents the severe agglomeration of these metal nanoparticles during high-temperature carbonization. More importantly, from a mechanistic perspective, the constructed heterojunction interface induces a directional interfacial electron transfer from the FeNi alloy to the Ru sites. This unique electronic reconfiguration optimizes the local *d*-band center, synergistically balancing the adsorption free energies for both hydrogen (*H) and oxygenated intermediates (*OOH, *O, *OH). Consequently, this lignin-derived bifunctional catalyst delivers exceptional overall water-splitting performance, requiring an ultra-low cell voltage of only 1.48 V to reach a current density of 10 mA cm⁻², alongside outstanding long-term stability. Building upon this robust polymer-coordination concept, the same group further addressed the critical issue of oxidative degradation during continuous overall water splitting^[59]. By pyrolyzing a specifically designed lignin-Co-Ru supramolecular framework, they fabricated carbon-coated CoRu alloys. The ultrathin carbon shell, which is seamlessly derived from the lignin backbone in situ, acts as an impenetrable armor. It protects the encapsulated metallic active sites from severe oxidative corrosion and structural dissolution, conferring the catalyst with remarkable “self-healing” properties and ultra-long durability in practical al-

kaline water splitting.

Beyond natural macromolecules, synthetic polymer architectures also provide powerful platforms for overall water splitting. For instance, customized bi-metallic-ion-coordinated porous organic polymers (POPs) or Schiff-base networks can be thermally transformed into 3D porous carbons co-doped with robust transition metal sites (e.g., Fe/Ni or Fe/Co)^[60–61]. These 3D architectures prevent the restacking of active nanosheets and construct an “aerophobic” surface that facilitates the rapid detachment of H₂ and O₂ bubbles, a feature critical for maintaining steady catalysis at high current densities. Furthermore, the direct pyrolysis of metal-ion-accumulated block copolymer micellar films allows for the precise fabrication of mesoporous metallic composites featuring open cyl-

indrical channels^[22]. These tailored, continuous channels expose an ultra-high density of reactive sites and provide an expansive buffer space for deep electrolyte penetration, enabling stable and efficient overall water splitting across a wide range of industrial current densities.

To complement the representative examples illustrated in Fig. 6 and provide a more quantitative comparison, the catalytic efficiencies of selected polymer-derived carbon electrocatalysts for HER, OER, and overall water splitting are summarized in Table 2. In this table, the overpotential required to reach 10 mA cm⁻² (η_{10}) and the Tafel slope are listed as the primary activity-related parameters for HER and OER, while the cell voltage at a specified current density is included for overall water-splitting systems.

Table 2 Representative catalytic efficiencies of polymer-derived carbon electrocatalysts for HER, OER, and overall water splitting

Catalyst	Polymer-derived strategy	Reaction	Electrolyte	η_{10} / mV	Tafel slope / mV dec ⁻¹	Cell voltage	Ref.
Pyri-Pt	PPy-based polymeric framework with atomically dispersed Pt	HER	0.5 M H ₂ SO ₄	14	38.5	—	[24]
CoP@M-CA	Melamine-cyanuric acid supramolecular nanosheet-derived support	HER	0.5 M H ₂ SO ₄	107	61.9	—	[27]
Ru-CON	2D twisted covalent organic network-derived Ru/carbon catalyst	HER	1.0 M KOH	12.9	25.0	—	[32]
Ni/CNFs/ECNFs	Cellulose acetate-derived 3D hierarchical carbon nanofiber network	HER	1.0 M KOH	88	170.0	—	[36]
Ir-IrO _x /C nanosheets	Block-copolymer-confined assembly of ordered mesoporous nanosheets	OER	0.5 M H ₂ SO ₄	198	106.3	—	[22]
COF-205-Ru	Conjugated sp ² carbon-linked COF stabilizing atomic Ru sites	OER	0.5 M H ₂ SO ₄	210	70.0	—	[33]
Salen-based POPs	Salen-based porous organic polymer framework	OER	1.0 M KOH	270	81.0	—	[60]
		HER		8	31.6	—	
N-Ru/RuO ₂ /NiO film	PS-b-P2VP micellar film-derived mesoporous metallic composite	OER	1.0 M KOH	—	27.4	—	[23]
		Overall		—	—	1.53 V @ 200 mA cm ⁻²	
		HER		36	38.0	—	
Ru-FeNi@NLC	Lignin-derived carbon-supported Ru-FeNi alloy heterojunction	OER	1.0 M KOH	198	72.0	—	[57]
		Overall		—	—	1.48 V at 10 mA cm ⁻²	
		HER		13	69.4	—	
CoRu@NCHNSs	MOF/polymer-derived hollow N-doped carbon loaded with CoRu alloy	OER	1.0 M KOH	238	240.7	—	[58]
		Overall		—	—	1.56 V at 10 mA cm ⁻²	
		HER		90	81.0	—	
CoRu@OALC	Lignin-metal supramolecular framework-derived carbon-coated CoRu alloy	OER	1.0 M KOH	200	284.0	—	[59]
		Overall		—	—	1.50 V at 10 mA cm ⁻²	

Note: η_{10} denotes the overpotential required to reach a current density of 10 mA cm⁻². The catalytic metrics are summarized as reported in the original literature, with η_{10} , Tafel slope, and overall water-splitting cell voltage used as the main comparable efficiency indicators. “—” indicates that the corresponding parameter was not reported or not emphasized in the cited work. M: mol L⁻¹

5 Conclusion and prospects

The rational design and controlled carbonization of polymer precursors have revolutionized the development of high-performance carbon-based electrocatalysts. By transitioning from stochastic “top-down” post-treatment to molecularly programmed “bottom-up” synthesis, researchers can achieve unprecedented control over both the macroscopic mass-transfer architectures and the microscopic electronic environments. As highlighted in this review, the strategic utilization of block copolymers, synthetic covalent networks, and supramolecular assemblies enables precise heteroatom doping, the targeted generation of topological defects, and the construction of aerophobic 3D frameworks. These rationally engineered features synergistically optimize intermediate adsorption thermodynamics, stabilize critical active species (e.g., single atoms or amorphous clusters), and ensure robust structural durability, ultimately driving exceptional performance in HER, OER and overall water splitting.

Despite these remarkable advancements, the field of polymer-derived carbon electrocatalysts is still evolving, and several challenges and exciting opportunities remain for future exploration. As summarized in Fig. 7, future efforts should focus on 4 interrelated directions: operando tracking of polymer-to-carbon pyrolysis, scalable precursor design, device-level integration under practical electrolyzer conditions, and direct polymer electrocatalysis that avoids energy-in-

tensive carbonization:

Operando Pyrolysis Tracking: Currently, the dynamic evolution from a polymer backbone to a defective carbon lattice remains somewhat of a “black box.” Future research must leverage advanced operando techniques (such as in-situ transmission electron microscopy and synchrotron radiation-based X-ray absorption spectroscopy) coupled with high-throughput density functional theory to continuously monitor the bond-cleavage and defect-reconstruction processes during pyrolysis. This will provide the precise mapping needed to establish quantitative structure-activity relationships.

Scalable Precursor Design: From a practical perspective, the cost and scalability of polymer precursors remain critical considerations. Biomass-derived polymers such as lignin, cellulose, and chitosan are particularly attractive because of their abundance, renewability, low cost, and rich functional groups, which facilitate coordination, heteroatom incorporation, and carbon-framework formation. In contrast, synthetic block copolymers such as PS-*b*-P2VP offer more precise control over mesostructure, pore size, and spatial organization, but their multi-step synthesis, purification, and relatively high cost may limit large-scale implementation. In addition, large-scale production of polymer-derived carbons must address several practical issues, including precursor batch-to-batch variability, carbon yield, energy consumption during pyrolysis, reproducibility of pore/defect structures, and preservation of designed morphologies after

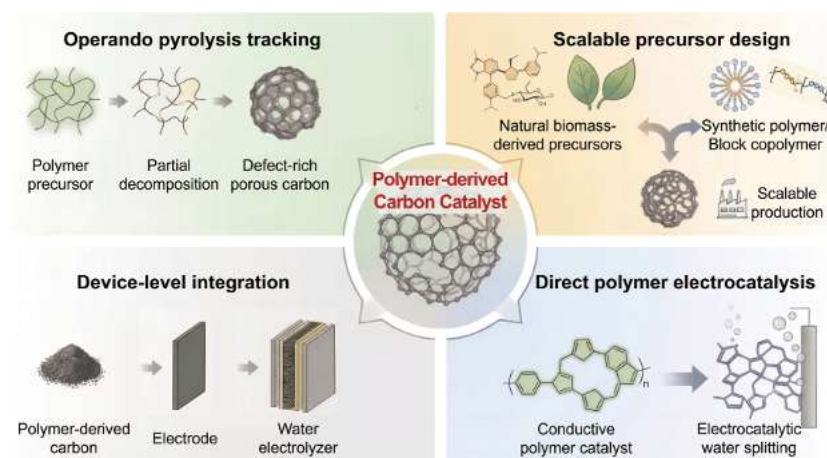


Fig. 7 Roadmap for the future development of polymer-derived carbon electrocatalysts

scale-up. Therefore, future efforts should balance the structural precision of synthetic polymers with the economic and sustainability advantages of natural polymer precursors, while developing simplified, reproducible, and energy-efficient processing routes.

Device-Level Integration: Although polymer-derived carbons exhibit promising performance in idealized half-cell tests, their translation to industrial-scale electrolyzers, such as proton exchange membrane and anion exchange membrane water electrolyzers, remains challenging. Future studies should go beyond powder-catalyst evaluation and focus on electrode architecture, catalyst-layer thickness, ionomer distribution, gas-bubble management, and membrane electrode assembly engineering. In particular, the hierarchical porosity and aerophobic architectures of polymer-derived carbons should be rationally integrated with practical electrodes to manage complex tri-phase interfaces and maintain efficient mass transport at industrial current densities. Establishing standardized testing protocols under practically relevant conditions will also be essential for evaluating their real technological potential.

Direct Polymer Electrocatalysis: While the thermal carbonization of polymers successfully generates robust active sites, the extreme pyrolysis process inevitably consumes massive amounts of energy and releases greenhouse gases, partially undermining the goal of green energy conversion. A highly promising and disruptive future paradigm lies in bypassing the pyrolysis step entirely. Exploring the direct utilization of intrinsically conductive and functionally conjugated polymers as electrocatalysts could perfectly preserve the atomic precision of the pre-designed molecular active sites. Advancing this frontier of direct polymer electrocatalysis will not only deepen our fundamental understanding of non-metallic catalytic mechanisms but also pave a more energy-efficient and potentially lower-carbon pathway toward sustainable hydrogen production.

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