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International Journal of Materials Science and Technology Studies
ISSN: 3006-7693 (Print), ISSN: 3006-3744 (Online) | Volume 5, Number 1, Year 2026
DOI: https://doi.org/10.62051/ijmsts.v5n1.04
Journal homepage: https://wepub.org/index.php/IJMSTS/index

Synthesis of Three-Dimensional Covalent Organic Frameworks and Applications in Electrocatalysis

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ABSTRACT

Covalent organic frameworks (COFs) are a novel class of materials held together by covalent bonds, sparking a research boom in recent decades. However, due to the challenges involved in research, studies on COFs have often focused on two-dimensional covalent organic frameworks (2D COFs), while research on three-dimensional covalent organic frameworks (3D COFs) which are more difficult to prepare remains in its initial stages. 3D COFs offer a novel material platform for photocatalysis due to their tunable frameworks, adjustable pore channels, and abundant organic functionalization sites. This paper first focuses on the synthesis methods of 3D COFs. Subsequently, characterization techniques for 3D COFs are introduced. Then, the applications of 3D COFs in electrocatalysis are highlighted. Finally, the challenges and prospects for the future development of 3D COFs are discussed.

KEYWORDS

3D COFs; Synthesis methods; Electrocatalysis

1. INTRODUCTION

In the current stage of social development, environmental governance faces numerous challenges. Accelerated industrialization and urbanization, coupled with increased consumption of traditional fossil fuels and emissions of organic pollutants, have intensified damage to atmospheric, aquatic, and soil environments. Traditional remediation methods such as physical adsorption, chemical precipitation, or biological treatment exhibit limitations in energy consumption and secondary pollution. Consequently, developing highly efficient, energy-saving, clean, and environmentally friendly treatment technologies has become an urgent priority. Against this backdrop, catalytic technology plays a vital role in both industrial and environmental sectors due to its ability to accelerate reactions, alter reaction selectivity, and enhance reaction efficiency. Its objective is to achieve maximum desired products with minimal energy consumption and cost, making research on catalytic materials particularly crucial [1]. COFs represent a class of materials widely applied in the field of catalysis [2-4].

COFs represent a novel class of porous crystalline materials characterized by tunable porosity, stability, and chemical functionality [5-8]. They can be categorized into two-dimensional layered and three-dimensional network structures. 2D COFs find extensive applications in fields like electrocatalysis [9-12], but their stacked structures may shield active sites, limiting catalytic efficiency. In contrast, three-dimensional COFs possess higher specific surface areas, hierarchical pore networks, and permanently exposed active sites, offering greater catalytic potential but posing greater synthetic challenges. In 2007, the Yaghi group first reported four 3D COFs [13], advancing network chemistry and laying the foundation for subsequent research. Despite widespread interest in 3D COFs due to their unique properties, relevant reviews remain relatively scarce. This paper systematically reviews the synthesis methods, characterization techniques, and applications of three-dimensional COFs in electrocatalysis, concluding with an exploration of future challenges and development prospects.

2. SYNTHESIS METHOD OF 3D COFS

Since the Yaghi group first reported 3D COFs in 2007, related research has grown rapidly. Their synthesis methods are primarily categorized into traditional approaches and novel strategies. Traditional methods mainly rely on solvothermal synthesis, but they suffer from limitations such as lengthy reaction times, harsh conditions, and the need for repeated optimization. Currently, novel approaches such as ionothermal synthesis, mechanochemical synthesis, and microwave-assisted synthesis have been applied, yet sufficient reference examples remain scarce. Therefore, further development of more efficient and practical synthetic methods is essential, alongside continuous advancement in structural design and topological diversity studies of 3D COFs to propel progress in this field.

2.1. Solvent-thermal Synthesis

Solvothermal synthesis is the most commonly used method for preparing COF materials, yielding products with high crystallinity and excellent porosity. This method is typically conducted in pressure-resistant sealed vessels and primarily involves three steps: First, suitable reactant monomers are dissolved in a solvent, a catalyst is added, and the mixture is homogenized by ultrasonication. Second, oxygen and moisture are removed from the mixture through a “freeze-evacuate-freeze” process, after which the vessel is sealed. Finally, the sealed reaction vessel is placed in an oven at a constant temperature for a specified duration. Upon reaction completion, the solid product is obtained through cooling and filtration, followed by vacuum drying to yield the target COF material.

The synthesis of 3D COFs predominantly employs solvothermal methods. For instance, Zhu et al. [14] synthesized highly crystalline 3D COFs with pto and mhq-z topologies by dissolving specific ratios of amino and aldehyde monomers in organic solvents, adding acetic acid as a catalyst, and reacting at 120°C for 3–7 days. These materials exhibited excellent thermal stability and CO_2 adsorption capacity (Figure 1a). Meanwhile, Yin et al. [11] designed novel hexa-connected trigonal prism nodes and successfully constructed highly crystalline 3D-TMTAPB-COF with macroporous structures after a 3-day reaction at 120°C (Figure 1b), demonstrating the feasibility of synthesizing macroporous 3D COFs under solvothermal conditions. Concurrently, Gui et al. [15] discovered that by controlling reaction temperature (80°C vs. 120°C), identical monomers could yield 2D-PATB-COF and 3D-PATB-COF respectively, achieving structural transformation from two-dimensional to three-dimensional (Fig. 1c). Chang et al. [16] synthesized two highly crystalline 3D COFs by reacting monomers such as HAPTM and HFPTP at 120°C for 7 days, which exhibited excellent selectivity in benzene/cyclohexane separation (Figure 1d). Li et al. [17] synthesized three nitrogen-containing bicyclic 3D COFs under similar conditions by controlling the nitrogen-containing heterocyclic type. These structures exhibited high activity and stability in the photocatalytic synthesis of urea from NH_3 and CO_2 (Figure 1e).

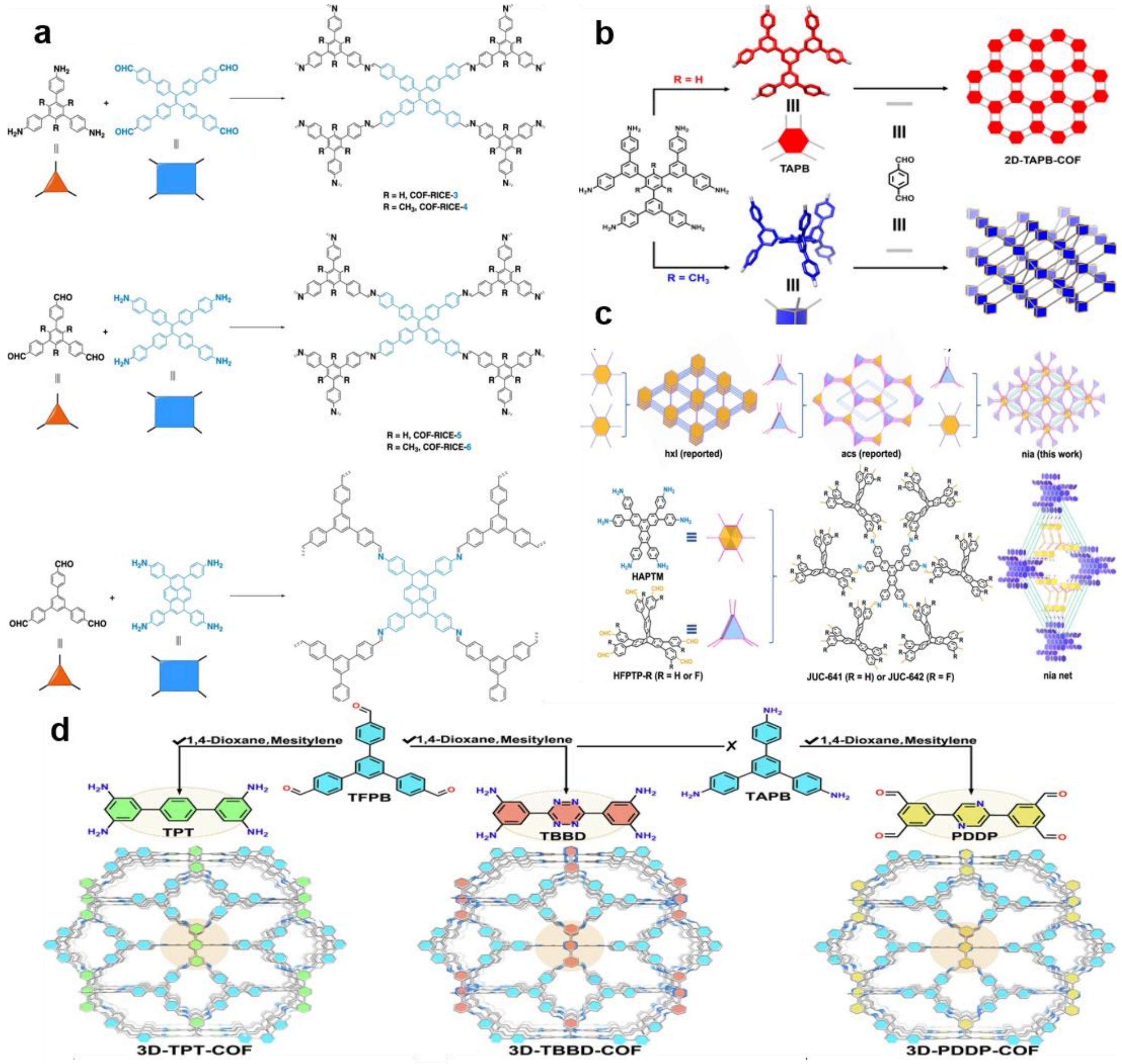

Figure 1. (a) Synthesis scheme for the preparation of 3D imine-linked COFs. All COFs prepared under solvothermal reaction conditions. (b) Schematic Representation of the Synthesis of 2D-TAPB-COF and 3D-TMTAPB-COF by Introducing Steric Hindrance to Precisely Control the Precursor Conformation. (c) Configuration Change of PATB and the Construction of 2D-PATB-COF and 3D-PATB-COF Isomers from the Same Building Blocks. (d) Molecular structures of HFPTP-R (R = H or F, and HAPTM. Two 3D COFs, JUC-641 and JUC-642, constructed from the condensation reaction of HFPTP-R and HAPTM. (e) Schematic synthesis of 3D-TPT-COF, 3D-PDDP-COF, and 3D-TBBD-COF.

2.2. Ionic Thermal Synthesis

The synthesis methods for 3D COFs remain under active exploration, with ionic liquid-assisted synthesis emerging as a novel approach. Ionic liquids are entirely ionic liquids composed of ions, exhibiting a liquid state at low temperatures (<100°C). Also known as low-temperature molten salts, they typically consist of organic cations and inorganic anions.

The following are examples of the application of ionothermal synthesis in 3D COFs: Guan et al. [18] first reported the synthesis of COFs using ILs as reaction solvents. The experiment employed ionothermal synthesis to apply pressure to ions at ambient temperature in an open system. The synthetic strategy involved reacting monomers with a catalyst in the reaction solvent at room temperature. Within the IL solvent, linear linkages formed between monomers, yielding the products 3D-IL-COF-1, 3D-IL-COF-2, and 3D-IL-COF-3 (figure 2a). The synthesis process involves adding proportional amounts of TFPM and PDA, DABP, or DATP to a fixed quantity of [BMIm][NTf$_2$] under ambient temperature and pressure conditions, yielding a crystalline solid. The synthesis duration does not exceed 12 hours, significantly faster than the 3-7 days required for the solvent-thermal method. Moreover, the synthesis of 3D-IL-COF within the experimental process took only 3 minutes, with minimal material loss. Experiments demonstrate that 3D-IL-COFs exhibit excellent crystallinity, along with favorable BET surface area and adsorption selectivity for CO_2/N_2 and CO_2/CH_4. Furthermore, the IL can be reused throughout the experimental process, offering a novel strategy for synthesizing 3D COFs and advancing the development of carbon nanotubes for green applications.

2.3. Microfluidic Synthesis

Microfluidic synthesis is a synthetic technique that precisely manipulates minute volumes of fluid within micrometer-scale channels. Its core principle involves rapidly and uniformly mixing multiple reaction fluids in flow through specific structures (such as Y-shaped or T-shaped channels), enabling reactions to proceed under controlled temperature and residence time conditions. This method, with its exceptionally high mass and heat transfer efficiency, enables precise control over reaction conditions. It is suitable for synthesizing nanoparticles with uniform particle size and metal-organic framework materials, offering advantages such as excellent reproducibility and low reagent consumption.

Mattera et al. [19] proposed a method for synthesizing and processing 3D COFs using a three-dimensional continuous fluidic device. COF-300 and COF-320 were synthesized via microfluidic technology. The device features three inlets and a main microfluidic channel, enabling experimental results to be obtained by controlling parameters such as flow rate (figure 2b). The successful synthesis of COF-300 and COF-320 demonstrates the pathway selectivity of microfluidic synthesis. Simultaneously, within the main microfluidic channel, it can alter the dimensions of 3D COF crystals at the microscopic scale and modify the size of fibers at the macroscopic scale. This novel synthesis technique has opened new avenues for the synthesis and practical application of 3D COFs, advancing their synthetic applications and expanding the possibilities for future 3D COF synthesis.

2.4. Microwave-assisted Synthesis

Compared to the solvothermal synthesis method, microwave-assisted synthesis offers distinct advantages. While the solvothermal approach exhibits slower temperature regulation, microwave-assisted synthesis rapidly achieves the required reaction temperature with uniform heating. Furthermore, this method delivers higher product yields, cleaner products, and lower energy consumption. The typical process for microwave-assisted synthesis involves adding a mixture of reactive monomers to a suitable solvent, placing it in a microwave-safe vessel, sealing it, and heating it. Stirring is then performed at a specified temperature.

In 2009, the Cooper team and others synthesized 2D COF, COF-5, and 3D COF, COF-102, using microwave-assisted synthesis, demonstrating that this method is applicable for synthesizing both 2D and 3D COFs [20] . The synthesis of COF-102 proceeds as follows: Tetraphenyl boronic methane undergoes autocatalytic condensation in a 1:1 mixture of mesitylene and 1,4-dioxane solvent system. The resulting mixture is placed in a 35 ml glass microwave-safe tube, sealed with nitrogen, and subjected to microwave irradiation at 100°C under stirring for 20 minutes at 200 W power. The resulting product is washed with THF. The washed product is then subjected to microwave heating and separation in the microwave reactor. The final product obtained is COF-102. The reaction process can be observed to involve color changes (figure 2c). Cooper et al. concluded from this experiment that microwave-assisted synthesis accelerates the reaction process while yielding products with comparable physical properties .

Microwave-assisted synthesis methods have also been continuously refined. In 2017, Zhang and colleagues employed this technique to design a novel ionic 3D COF, CD-COF-Li [21]. Under microwave-assisted synthesis conditions, LiOH, γ-CD, and $B(OMe)_3$ were mixed together. During the reaction, γ-CD and $B(OMe)_3$ copolymerized, yielding a highly crystalline CD-COF-Li (figure 1d). During the experiment, the ligand in the reaction was simultaneously changed to dimethylamine (DMA) or piperazine (PPZ), yielding the corresponding products CD-COF-DMA and CD-COF-PPZ. The products obtained through microwave-assisted synthesis exhibit characteristics such as high productivity, high yield, and high purity. Experimental measurements reveal that CD-COFs are flexible components and charge-carrying frameworks with high porosity, demonstrating significant potential in the fields of ion conduction and gas separation. The successful preparation of 3D CD-COFs offers a novel design approach. During the experimental process, the introduction of a pillar facilitates the synthetic procedure and advances the development of charged porous materials .

2.5. Mechanochemical Synthesis

Mechanochemical synthesis is a green synthetic strategy that utilizes mechanical energy (such as grinding or ball milling) to drive chemical reactions. This method enables the synthesis of materials like covalent organic frameworks under solvent-free or minimal-solvent conditions through techniques like ball milling or resonant sonication. Compared to the traditional solvothermal method, the mechanochemical approach reduces solvent usage and reaction time, and eliminates the need for complex post-treatment. The product can be obtained simply through vacuum drying.

Ehsan et al. [22] synthesized the first 3D COF via ball milling. The reaction process involved using a 10 ml zirconia ball milling jar, with 1,4-benzenediboronic acid as the monomer, with trimethylborane as the dehydrating agent and structure regulator. A 1:1 mixture of mesitylene and tetrahydrofuran (or dioxane) served as the liquid additive. The mixture was ball-milled for 30 minutes using zirconia balls, followed by vacuum drying to yield the product without requiring subsequent purification steps (figure 2e). This method provides a novel approach for the green synthesis and preparation of 3D COFs materials.

2.6. Water-based Nanoreactor Technology

Solvothermal synthesis is the most commonly used method for synthesizing 3D COFs. However, the solvent systems employed in this process are generally toxic and pose health hazards to humans. Additionally, solvothermal synthesis requires high-temperature conditions. Therefore, Veciana et al. [23] proposed a water-based nanoreactor technology, using the representative COF-300 to demonstrate the feasibility of this approach. The synthesis process involves loading two reaction precursors, TAM and BDA, into a mixed micelle composed of cationic hexadecyltrimethylammonium bromide (CTAB) and anionic sodium dodecyl sulfate (SDS) mixed in a specific ratio. The two micelles are then combined, and acetic acid catalyst is added. The mixture turns yellow, and the resulting product is characterized. It is confirmed that COF-300 is obtained at low catalyst concentrations, successfully demonstrating the formation of a stable colloidal solution of COF-300 via the micellar method. Experiments demonstrate that COF-300 can be successfully synthesized using water-based nanoreactor technology. Compared to traditional solvothermal synthesis methods, this approach offers distinct advantages for synthesizing 3D COFs. During the process, reaction precursors dissolve in an aqueous medium, eliminating contact with toxic or hazardous solvents. Reactions can proceed under mild conditions, and this method enables precise control over nanoparticle synthesis and growth. Through the exploration and validation of water-based nanoreactor technology, new insights have been provided for the synthesis and application of

3D COFs. This approach has demonstrated breakthroughs in practical applications, expanding the scope of 3D COFs application.

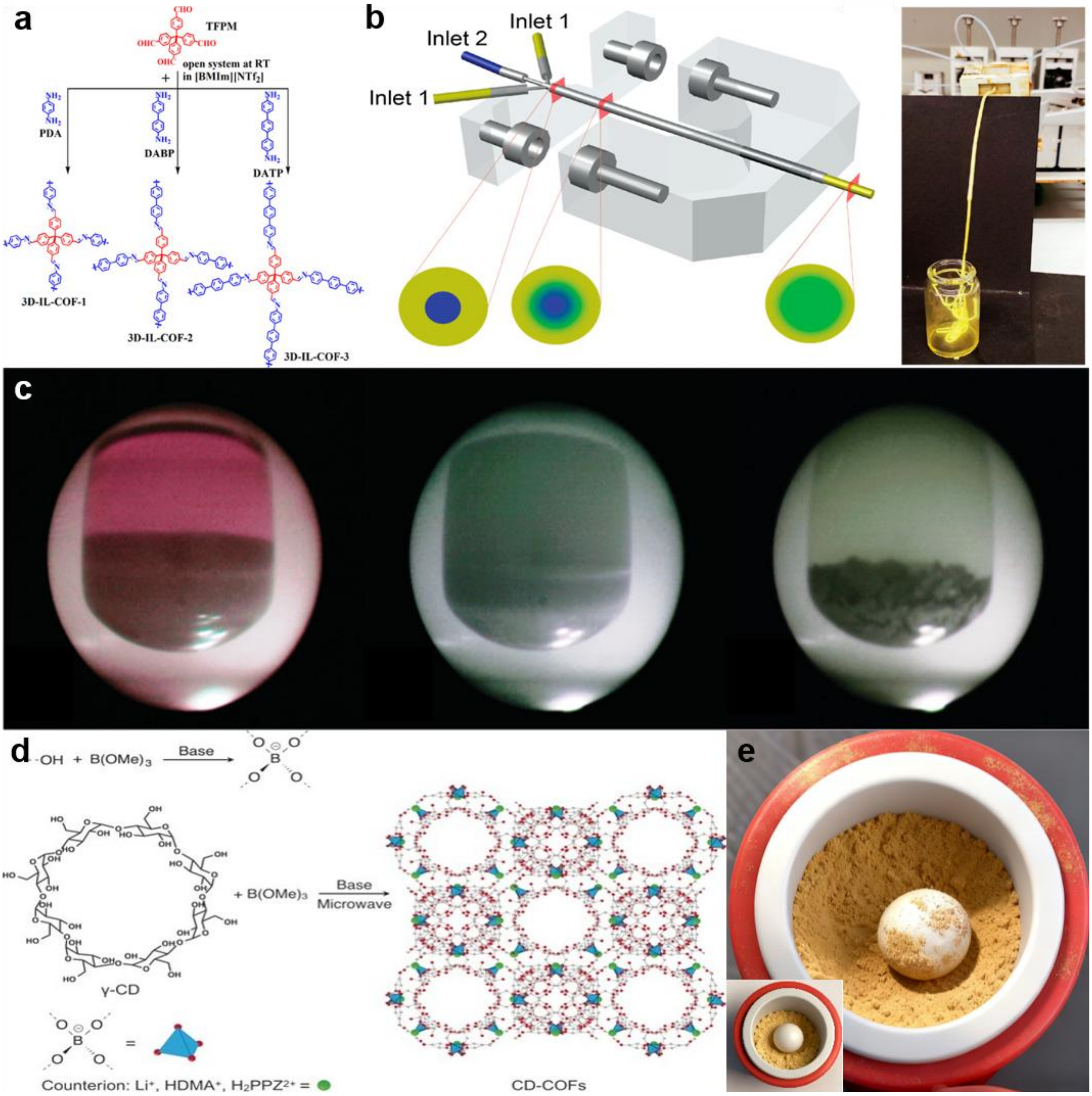

Figure 2. (a) Strategy for Preparing 3D Ionic Liquid-Containing COFs (3D-IL-COFs). (b) Illustration of the microfluidic device used to synthesize COF-300 and COF-320; Photograph of the device while producing a self-standing COF-300 fiber. (c) Digital camera images recorded from the observation port of the microwave reactor showing COF-5 reaction and purification: gray-purple COF-5 powder formed after initial synthesis; removal of trapped HHTP-oxidation impurities by microwave extraction process (acetone); second microwave extraction results in purified gray COF-5 powder (SBET = 2019 m^2 $g^{-1)}$. (d) Condensation of g-CD and $B(OMe)_3$ with LiOH, DMA,or PPZ under microwave conditions to afford CD-COFs with different counterions. (e) Take photos in accordance with the reference materials. Photographs of the COF-1BM reaction mixture before and after ball-milling.

3. CHARACTERIZATION OF 3D COFS

The complex structure of 3D COFs necessitates characterization encompassing composition, morphology, crystal structure, pore properties, and stability. Compositional analysis typically employs Fourier transform infrared spectroscopy, Raman spectroscopy, solid-state nuclear magnetic resonance, and X-ray photoelectron spectroscopy to confirm bonding configurations. Morphology characterization predominantly employs scanning electron microscopy (SEM) combined with transmission electron microscopy (TEM). Crystal structure analysis relies primarily on powder X-ray diffraction (XRD), continuous rotation electron diffraction (CRED), and three-dimensional electron diffraction (3D ED) techniques.

As porous materials, their specific surface area and pore size distribution are typically determined via nitrogen adsorption isotherms and calculated based on the BET theory. Thermal stability is assessed via thermogravimetric analysis. For electrochemical applications, cyclic voltammetry, dynamic polarization curves, and electrochemical impedance spectroscopy are also performed to investigate interfacial reaction kinetics and charge transport behavior.

These systematic characterization methods facilitate a deeper understanding of material properties, reveal material-related relationships, and provide a basis for subsequent experimental design and application.

4. APPLICATIONS IN ELECTROCATALYSIS

4.1. H_2O_2 Production

H_2O_2 has extensive applications, with global annual demand exceeding 5 million tons. It is used for cleaning, bleaching, and in the pulp and paper industry. Additionally, it serves as an oxidizing agent in the chemical industry, a disinfectant in food processing and healthcare, and a treatment for hazardous pollutants in environmental remediation. Therefore, exploring efficient production methods for H_2O_2 is of particular importance.

In electrocatalytic applications, to enhance the yield of H_2O_2, Wu et al. [10] proposed a two-dimensional/three-dimensional interlocked topological regulation strategy to construct a covalent organic framework (TAE-COF) featuring alternating unsaturated two-dimensional units and saturated three-dimensional backbones. This structure simultaneously exhibits the high electron conductivity of a two-dimensional planar conjugated system and the structural stability of 3D COFs, enabling the formation of highly efficient charge transport pathways. Experimental and theoretical results demonstrate that TAE-COF achieves a Faradaic efficiency of up to 98.2% and H_2O_2 production rate of 8.50 mol g^{-1}, significantly outperforming pure 2D or 3D COFs (figure 3a). This study achieves a breakthrough in metal-free COF electrocatalytic performance through structural dimensional synergy, providing new insights for enhancing electrocatalytic efficiency through multidimensional structural design.

4.2. CO_2 Conversion to CO

CO has a wide range of applications. It can be used in chemistry to prepare certain organic compounds, serve as a reducing agent in metallurgical processes for smelting metals, be employed in the production of new materials, and function as a fuel.

In the field of electrocatalysis, for the efficient recycling of CO_2 and improve the carbon dioxide reduction reaction (CDRR) and oxygen evolution reaction (OER), Li et al. [24] synthesized a bifunctional catalyst, Co/Ni-TPNB-COF, obtained via a solvothermal condensation reaction. Experimental results demonstrate that this bifunctional catalyst exhibits the highest CO_2-to-CO selectivity, a turnover frequency (TOF) of 4.10 s^{-1}, and a Faradaic efficiency (FE) reaching 95%.

Subsequent validation demonstrated that the Co/Ni-tpnb-cof bifunctional electrocatalyst exhibits high activity in both the CDRR and OER processes catalyzed by the Co(II)-porphyrin and Ni(II)-porphyrin centers, respectively. The conversion frequency achieved by the Co/Ni-TPNB-COF bifunctional catalyst developed in this study far exceeds that of previously reported 2D CoPc-Cu-O MOFs, offering novel approaches and insights for developing more effective electrocatalysts. Zhang et al. [25] achieved 3D-NiPc-COF through dimensional regulation, enhancing the accessibility of active sites and demonstrating superior activity in CO_2 electro-reduction. The CO Faradaic efficiency was observed over a broader potential range (figure 3b), facilitating electron transfer and intermediate adsorption while providing additional CO_2 adsorption sites. This study provides a significant example of optimizing COF electrocatalytic performance through structural dimensional regulation.

4.3. H_2 Production

H_2 offers numerous advantages and applications as a new energy source. Its benefits include extremely clean combustion products, producing only water along with a high calorific value and the ability to serve as a storable energy carrier. H_2 can serve as a fuel for applications in aerospace, military, and other fields. Additionally, due to its reducing properties, hydrogen can be utilized in the smelting of certain metallic materials. Therefore, research should continue to expand the pathways for H_2 production and continuously improve hydrogen yield.

To investigate the electrocatalytic performance of 3D COFs in hydrogen evolution reactions, Chen et al. [26] constructed a 3D COF (3D-Por-SP-COF). They then introduced Co^{2+} ions through the coordination of porphyrin rings, yielding the metal-functionalized framework material Co@3D-Por-SP-COF. Within this structure, Co^{2+} ions uniformly distribute within the channels via Co-N_4 coordination, enabling full exposure of electrocatalytic active sites and providing a reaction platform for hydrogen evolution. To evaluate its performance, linear sweep voltammetry (LSV) was employed in a 1.0 M KOH alkaline electrolyte. The results indicate that Co@3D-Por-SP-COF exhibits an onset potential of 72 mV (at 1.0 $mA \cdot cm^{-2}$) and an overpotential of 175 mV at a current density of 10 $mA \cdot cm^{-2}$, significantly outperforming the metal-free 3D-Por-SP-COF (524 mV) and the carbon cloth reference electrode (670 mV) (figure 3c). Simultaneously, Tafel curves and electrochemical impedance spectroscopy demonstrated that this material exhibits outstanding electrocatalytic hydrogen evolution performance and long-term stability, outperforming numerous previously reported electrocatalysts. This research provides a novel material design approach for achieving highly efficient hydrogen evolution electrocatalysis through 3D COFs.

4.4. NH_3 Production

NH_3 does not produce CO_2 during combustion, offering numerous applications and promising prospects. It serves as a pH regulator in the electronics industry, an alkalizing agent in food processing, and a standard gas in chemical manufacturing and scientific research. Additionally, it can be used to produce ammonia water and liquid ammonia, both of which have extensive applications. With growing emphasis on utilizing ammonia energy, efficient NH_3 production has become particularly crucial.

Simultaneously, in the field of electrocatalysis, continuous exploration is being conducted regarding the generation of NH_3. Shan et al. [27] developed high-performance electrocatalysts for ammonia regeneration under ambient conditions, designing and synthesizing two types of 3D COFs. The characteristic feature is the presence of metal ions (Fe, Cu) at the center, which enhances the activity and selectivity of electrocatalysis. Notably, COFs with Fe-N_4 catalytic sites exhibit higher NH_3 yield and Faradaic efficiency (figure 3d), reaching maximum values of 94.26 ± 4.9 μg^{-1} mg^{-1} and $18.37 \pm 0.96\%$, respectively, making them ideal materials for electrocatalysis. This study provides a novel approach for the electrocatalytic nitrogen reduction on 3D COFs, enriching the topological structures of 3D COFs.

Given that 3D COFs are still in the early stages of exploration for electrocatalytic applications, numerous studies have been conducted on their electrocatalytic properties. The following are some examples in this area:

To investigate the effect of size on electrocatalytic performance, Cheng et al. [28] expanded the 2D COF (3D-Tr-COF) into a 3D COF (3D-Tr-COF) at the molecular level. The increased size led to a larger lattice spacing and reduced degree of electrocoupling, resulting in the generation of more electroactive species. This facilitates the enrichment of active sites for electrocatalytic reactions. During the experiment, 2D-Tr-COF, 3D-Tr-COF, and Pt/C electrocatalysts were prepared and tested for comparison. It was found that the maximum power density in the 3D-Tr-COF aqueous solution could reach 170.5 MW cm^{-2}, nearly matching that of commercial Pt/C (175.9 MW cm^{-2}), and significantly exceeding that of 2D-Tr-COF (figure 3e). The relationship between voltage and current density was simultaneously compared. The figure reveals that the voltage drop rate of 3D-Tr-COF is significantly slower than that of 2D-Tr-COF, demonstrating superior charge transfer efficiency in 3D-Tr-COF.

Feng et al. [29] employed an in situ synthesis strategy to incorporate Pd precursors during the 3D COF synthesis process, forming uniformly dispersed Pd nanoparticles. Following carbonization treatment, the resulting Pd@NC catalyst demonstrated superior performance to commercial Pt/C in both ORR and zinc-air batteries (figure 3f). This study provides a novel approach for constructing efficient and stable non-platinum ORR electrocatalysts using 3D COFs as metal nanoparticle carriers.

Regarding research on the electrocatalytic properties of 3D COFs, Liao et al. [29] constructed a three-dimensional interconnected COF and incorporated high-density nitrogen atom Co-N4 sites, significantly enhancing its point-catalytic performance. This material exhibits a high half-wave potential (0.78 V) in the oxygen reduction reaction (ORR) (figure 3g). Simultaneously, it demonstrates a low overpotential of only 240 mV in the oxygen evolution reaction (OER), showcasing excellent kinetics and long-term stability. Overall, this material has achieved a synergistic optimization in terms of structural design, active site construction, and electronic property regulation, thereby demonstrating outstanding dual-function catalytic performance for ORR/OER. This study represents a significant advancement in the field of 3D COFs for electrocatalysis.

Qiao et al. [30] designed and synthesized three-dimensional porphyrin and phthalocyanine-based COFs featuring cyt topology. By comparing 3D TAPP-OFPc[Ni]-COF with amorphous organic porous polymers (TAPP[Fe]-OFPc[Ni]-POP) and 2D polymers, they demonstrated that 3D TAPP-OFPc [Ni]-COF demonstrates superior performance in seamlessly integrating charge transport, electron transfer, and oxidation reactions within an electrocatalytic framework. Density Functional Theory (DFT) calculations indicate that Ni sites exhibit slightly higher activity during the initial stage of UOR, while Fe sites demonstrate stronger activity in subsequent stages (figure 3h). The synergistic interaction between the two metal sites highlights their complementary roles in promoting the efficient reduction of urea to nitrogen within the TAPP[Fe]-OFPc[Ni]-COF structure. This enhanced performance demonstrates that fully exposed metal catalytic sites and bimetallic synergistic effects can significantly boost catalytic activity, thereby validating the effectiveness of the COF structure. This provides new design insights for the structural design of 3D COFs in the future.

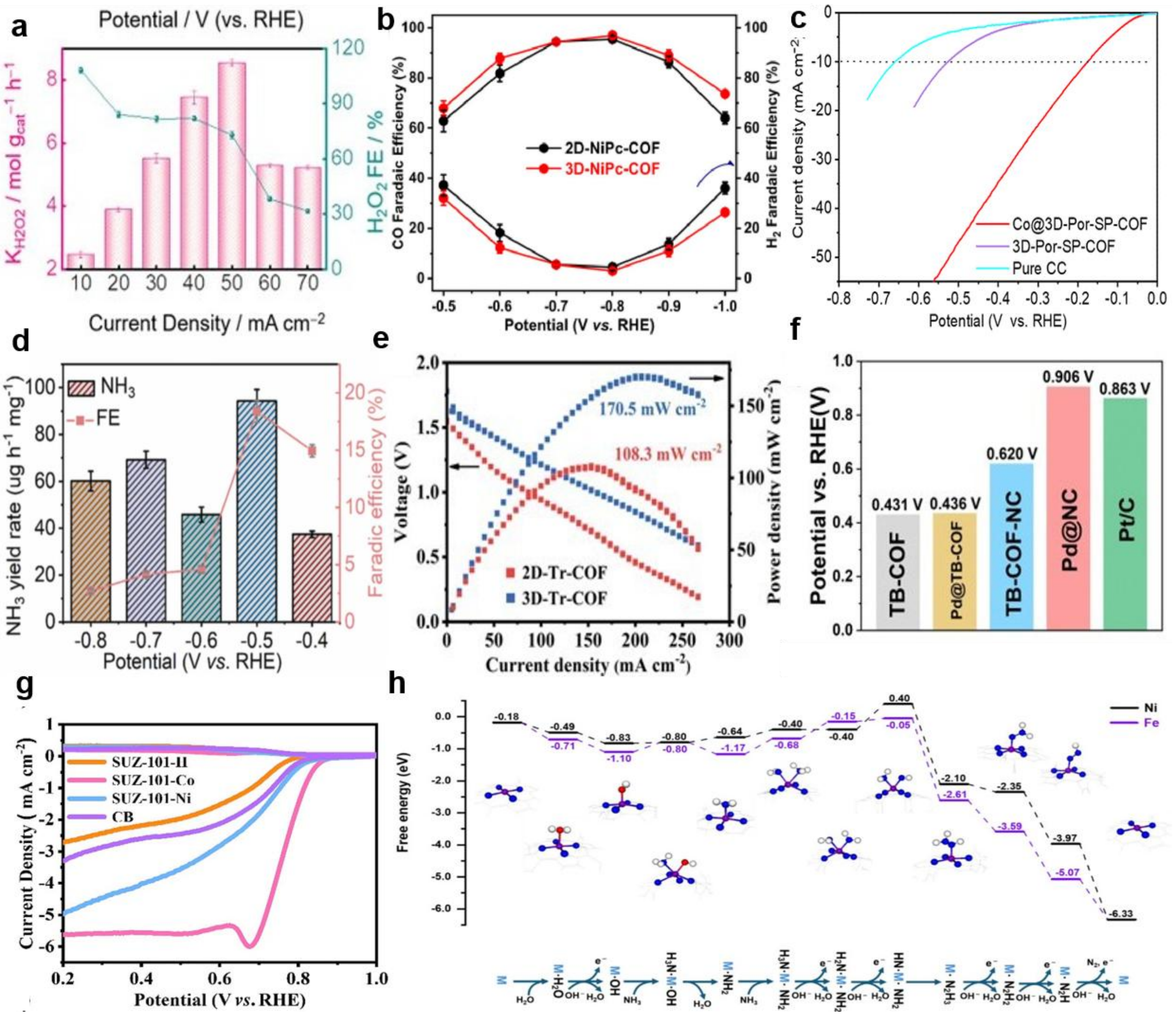

Figure 3. (a) H_2O_2 production rate and Faraday efficiency under different current densities. (each experiment was independently tested three times; sample size n=3; mean ± standard deviation (mean±SD) was analyzed using Origin software; SD reflects the degree of dispersion among individual samples; a small SD means that the value of the test is close to the average; the P-value indicates significant differences: ET-COF to ETT-COF: $P<0.0001$; ETT-COF to TAE-COF : $P<0.0001$; TAE-COF to TA-COF : $P<0.0001$; the statistical test was two-sided testing, the α-value was 0.05 and related P-values were analyzed by a Student's two-side t-test of GraphPad Prism software; P-values less than 0.0001 indicate that the differences between ET-COF to ETT-COF, ETT-COF to TAE-COF, and TAE-COF to TA-COF is particularly significant). (b) Faradaic efficiency test of 2D-NiPc-COF and 3D-NiPc-COF. (c) The electrocatalytic performances. HER LSV curves. (d) NH_3 yield rates and Faradaic efficiencies (FEs) at different applied potentials. (e) Discharge polarization curves with power density curves of aqueous AABs with 2D-Tr-COF and 3D-Tr-COF. (f) ORR comparison of $E_{1/2}$ for the as prepared catalysts at rotation rate of 1600 rpm in 0.1 M KOH. (g) LSV curves of SUZ-101-H, SUZ-101-Co, SUZ-101-Ni and CB in an O2-saturated 0.1 M KOH electrolyte for the ORR. (h) DFT calculations of electrocatalytic UOR over TAPP[Fe]-OFPc[Ni]-COF. Gibbs free energy profile for the first stage from urea to NH_3. Calculated Gibbs free activation barrier for $M·CO_2$ NH_2 to $M·NH_2 + CO_2$ at the Ni and Fe sites. Gibbs free energy profile for the second stagefrom NH_3 to N_2.

5. SUMMARY OF MECHANISMS

Based on the above review of applications for 3D COFs, we can analyze and summarize the mechanisms underlying their use in electrocatalysis.

In electrocatalytic processes, the electrocatalytic mechanism of 3D COFs primarily involves electron conduction-reaction adsorption-intermediate conversion-product desorption. Their catalytic performance mainly depends on the frameworks conductivity, active site types, and pore structure. Conductivity is often optimized by expanding π-conjugated systems to form continuous electron pathways, introducing metal–ligand centers (e.g., $M–N_x$ or M–O–C structures) into the framework to enhance charge transfer rates, and compositing with conductive materials (such as carbon nanotubes or graphene) to construct efficient electron conduction networks. Taking the hydrogen evolution reaction (HER) as an example, its mechanism involves the Volmer step ($H^+ + e^- \rightarrow H^*$), the Tafel step ($2H^* \rightarrow H_2$), or the Heyrovsky step ($H^* + H^+ + e^- \rightarrow H_2$). The multi-level pore structure of 3D COFs simultaneously provides proton transport pathways and abundant adsorption sites, enabling more efficient generation and desorption of the H* intermediate. Additionally, COFs exhibit outstanding activity in systems such as CO_2 reduction reactions (CO_2RR), nitrogen reduction reactions (NRR), and the electrochemical reduction of heavy metal/radioactive ions. Within these systems, C=N, $M–N_x$, or O–C bond structures often serve as electrochemical active sites, facilitating the adsorption of reactants and electron transfer.

6. CONCLUSION AND PROSPECT

Due to their ultra-high surface area, abundant active sites, and excellent chemical stability, 3D COFs have stimulated significant research interest and are considered highly promising application platforms. So far, a great deal of research has been conducted on 3D COFs, and various methods have been developed for their preparation, including ion thermal method, mechanical chemical method, microwave-assisted method, microfluidic synthesis method and water-based nano-reactor technology. However, most of the currently reported 3D COFs have been obtained via solvothermal synthesis, making the development of new synthetic techniques essential—particularly for those 3D COFs that are difficult to obtain using conventional methods. At the same time, since 3D COFs are a novel material, crystallization is relatively challenging, and characterization methods are still insufficient. Additional characterization techniques are required to demonstrate the material's excellent crystallinity and other properties. Additionally, 3D COFs have already found extensive applications across numerous fields and hold tremendous development potential. Currently, it has been established that 3D COFs possess significant application potential in the fields of photocatalysis and electrocatalysis. However, further expansion of their applications in these areas is required, along with more in-depth research into their use in electrocatalysis. By employing tunable strategies, the performance of 3D COFs in these fields can be further enhanced. Overall, research on 3D COFs is still in its infancy and faces numerous challenges.

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