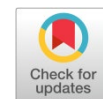


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Review article

Crystallinity control in covalent triazine frameworks: Synthetic approaches and mechanistic insights

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ABSTRACT

An important class of emerging porous organic materials is covalent triazine frameworks (CTFs), which have attracted much attention in wastewater treatment, energy conversion, and gas absorption due to their chemical and thermal properties and high nitrogen content. The synthesis of CTFs faces several challenges, including the reversibility of the reactions, which leads to structural defects and poor crystallinity. As a result, achieving high crystallinity is a major goal in the research and development of CTFs. This brief review focuses on the latest advances in the synthesis and control of crystallinity of these nitrogen-rich materials. The paper proceeds in order to review the principles governing crystal formation, the synthesis methods and factors affecting the reactions, and the final operations to prepare the product to enhance crystallinity. In addition, common crystallinity assessment techniques, including powder X-ray diffraction, Fourier transform infrared spectroscopy and advanced analysis, are reviewed. The effect of framework crystal structure on performance optimization is also discussed. Finally, challenges and future prospects in the development of synthesis techniques for the technological advancement of CTFs are presented.

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KEYWORDS

Covalent triazine frameworks
Crystallinity
Synthesis
Defect density
Structure–property correlations



1. Introduction

Polymeric organic compounds have found widespread applications due to their unique properties, such as low density-high porosity, excellent specific surface area, controllable structure, and favorable mechanical stability. Covalent triazine frameworks (CTFs) are a class of porous organic polymers and have tempted scientific interest due to their excellent stability. CTFs are two- or three-dimensional porous organic solids with extensive crystalline structures. They belong to the family of aromatic ring-based materials that have been used in catalysis, gas adsorption, drug delivery, water splitting, hydrogen (H₂) production, energy storage, pollutant degradation, and membrane separations. The well-defined periodic molecular network and deep pores are the

inherent characteristics of CTFs, which form the special relationships between their structure and properties. CTFs incorporate aromatic triazine, which is rich in N– bonds, has stable carbon–nitrogen bonds, and demonstrates good porosity, high surface area, and tolerance of humidity [1–4].

Semi-crystalline networks of CTFs were first obtained from the ionothermal trimerization reaction of simple aromatic nitriles over molten zinc chloride at high temperature [5]. Later, several techniques were used in the synthesis of crystalline CTFs with top-down and bottom-up strategies to achieve novel molecular networks [6]. Unlike many conventional porous materials, the aromatic triazine-rich

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framework of CTFs provides abundant active sites and facilitates charge transport, making these materials particularly attractive for catalytic and electrochemical processes [7]. By changing the preparation method, reaction conditions, and monomer structure, different two-dimensional and three-dimensional morphologies can be achieved [8].

Despite significant advances in the development of CTF synthesis methods, achieving frameworks with high crystallinity and long-range order remains one of the most important challenges in this field. Although the majority of early CTFs prepared by ionothermal synthesis showed very good performance in terms of thermal stability, chemical resistance, and specific surface area, they often had structures with limited crystallinity. This is mainly due to the harsh reaction conditions, especially high temperatures and prolonged exposure to molten salt, which can cause partial carbonization of the network, the creation of structural defects, the formation of unwanted side bonds, and the reduction of the periodic order of the framework. As a result, many CTFs synthesized by this method are semicrystalline or even mostly amorphous in nature, instead of forming fully crystalline networks [9, 10].

In addition to the reaction conditions, the irreversible nature of the trimerization reaction of nitrile groups is another factor limiting the formation of highly ordered structures. Unlike many covalent organic frameworks (COFs), which utilize dynamic covalent chemistry and allow for the correction of structural errors during crystal growth, the formation of triazine bonds under ionothermal conditions has limited self-correction capability. Therefore, defects introduced during the early stages of nucleation and crystal growth tend to remain in the final structure, leading to reduced crystallinity and increased structural heterogeneity [3].

The structural and functional characteristics of porous framework materials are largely determined by their crystallinity; higher crystallinity typically promotes the formation of ordered pore channels, increases charge carrier mobility, enhances mass transfer, and allows for more precise structure–property correlations. For instance, a more regular and uniform crystal structure has a higher adsorption capacity in gas separation and adsorption processes. Similarly, in photocatalysts, efficiency is highly dependent on framework order because it enhances charge carrier separation and transport. It is worth noting that there is no simple relationship between crystallinity and the performance of CTFs, as the final properties depend on other parameters, including flexibility, pore accessibility, network vacancies, and defect density [11–14].

To overcome defects and improve the performance of CTFs, various synthetic approaches, including interfacial polymerization and monomer tuning, superacid-catalyzed, template-directed assembly, microwave-assisted synthesis, solvothermal, mechanochemical technique, and low-temperature polymerization, have been designed and implemented. These methods differ significantly in terms of reaction temperature, degree of crystallinity, porosity, specific surface area, and retention of functional groups [15, 16]. Understanding the basic mechanisms controlling nucleation, crystal growth, defect generation, and reversibility in CTF formation has also received considerable attention. Establishing logical design rules for the upcoming generation of highly organized frameworks requires such mechanistic insights [11].

Strategies for controlling the crystallinity of CTFs are currently one of the most attractive and relatively under-researched topics in

this field. If the relationship between synthesis conditions, crystallinity, and final performance can be systematically demonstrated, the need for researchers to achieve a structure with desirable properties will be met. In this short review, the latest achievements in the synthesis of CTFs with the approach of increasing structural order and controlling crystallinity are summarized. Then, the analytical methods used to dissect CTFs are listed, and their application in the final crystal assay is described. In addition, a brief overview of the formation chemistry of these materials and the limitations of the synthesis methods is given. Furthermore, the effects of crystallinity on pore order and uniformity, charge transport, the possibility of precise structure determination, and photocatalytic and electrocatalytic properties are critically analyzed. Finally, the challenges ahead and the future horizon in the development of porous network polymers are highlighted.

2. Principles of CTFs crystallization

The formation of CTFs can be studied from both thermodynamic and kinetic perspectives. The difference between these two factors is the main reason why most CTFs are amorphous and only a few have high crystallinity.

Thermodynamically, the system tends to reach the lowest Gibbs free energy (ΔG). In the formation of CTFs, $\Delta G = \Delta H - T \cdot \Delta S$, where ΔH is the energy of new bond formation, and ΔS is the entropy change. The three nitrile groups ($-\text{CN}$) during cyclotrimerization form a triazine ring, where the aromatic bonds of the triazine are very stable, and the formation of the ring is energetically favorable. When forming a three-dimensional network, the free molecules become a connected network, and the freedom of movement is reduced. Therefore, ΔS are negative, and of course, at high temperatures, the $T \cdot \Delta S$ term becomes more important. Ultimately, if the bond formation energy is greater than the entropy decrease, the network will be stable. For this reason, CTFs are very stable thermodynamically and do not degrade until high temperatures [17, 18].

The main problem with CTFs is their formation kinetics, because in typical synthesis with molten zinc chloride, the temperature is around 400–600 °C, and the reaction rate is very high. As a result, nucleation occurs rapidly, and there is not enough time for crystal growth; in fact, the reaction is faster than the lattice can organize itself. In CTFs, once the triazine ring is formed, it rarely opens again, and the reversibility is very low. As a result, defects remain, and the network becomes amorphous. Whereas if an error occurred during bond formation, the bond could break and re-form, leading to the growth of ordered crystals [15, 19].

Crystallinity is a function of the ratio of the two processes of nucleation versus crystal growth, such that if nucleation occurs, it results in small particles, amorphous shape, and many defects [20, 21]. In contrast, with the growth process, a small number of nuclei are formed, so there is enough time for regular arrangement and larger crystals are formed. As previously mentioned, in the formation of CTFs, the reactions are irreversible, which is why it is difficult to control their crystallinity [22]. Fig. 1 schematically shows the CTF formation pathway from monomer design to crystal growth.

An energy barrier must be overcome to form the triazine ring. This is why high temperatures or acid catalysts are required [2]. However, high temperatures lead to rapid nucleation, carbonization, and defect formation. Therefore, although high temperatures increase the reaction rate, they do not necessarily improve crystallinity [23].

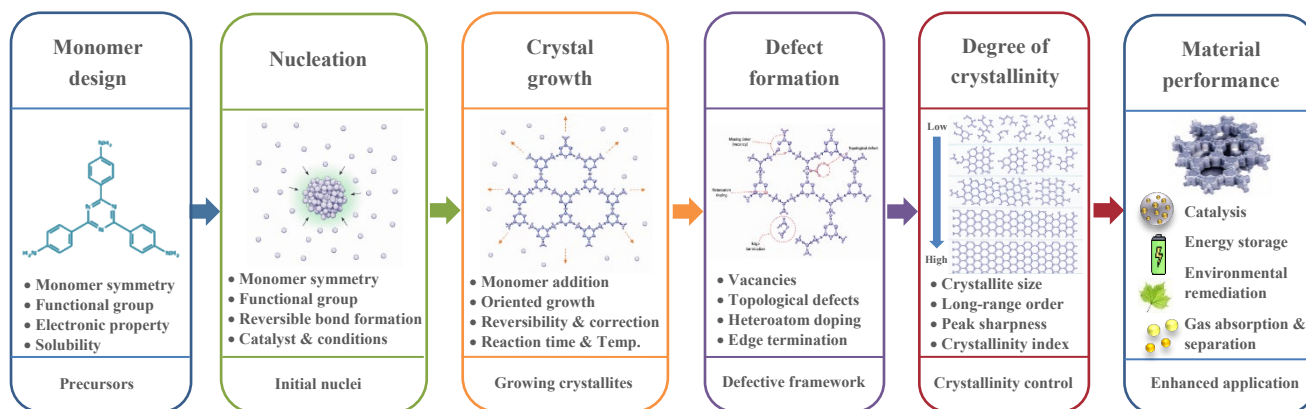


Fig. 1. Schematic drawing of the synthesis pathway of CTFs. The CTF formation process occurs hierarchically, and its prerequisite is the selection of an appropriate monomer. Monomer properties such as symmetry, electronic properties, and functional groups play an effective role in the formation of the initial framework. The production of stable nuclei is controlled by the catalyst, the reversibility of the bonds, and the reaction conditions. Crystal growth continues with the addition of monomer, and a set of factors influence the development of long-range ordered structures. During network formation, topological irregularities, vacancies, and end-edge irregularities as structural defects lower the crystallinity of the product. The structural integrity and physicochemical properties of CTF ultimately depend on crystal size, the long-range lattice order, and the crystallinity index. Inspired by [3, 5, 14, 17].

From a thermodynamic and kinetic perspective, there are several strategies:

- Reducing the reaction rate so that crystal growth dominates nucleation.
- Using mild catalysts (such as strong acids at lower temperatures) to lower the activation energy without excessively increasing the reaction rate.
- Designing rigid and symmetrical monomers so that a regular arrangement is energetically more favorable.
- Creating conditions with relative reversibility to allow for error correction.
- Adjusting the concentration, temperature, and reaction time so that nucleation is controlled and crystal growth is enhanced.

In general, from a thermodynamic point of view, the formation of triazine rings and the CTFs network is favorable because the aromatic triazine bonds are very stable and reduce the free energy of the system. However, from a kinetic point of view, the formation of these bonds is usually rapid and largely irreversible. This irreversibility prevents defects formed during network growth from being corrected, and as a result, most synthesized CTFs have an amorphous or semi-crystalline structure. For this reason, recent research has focused on controlling the reaction kinetics and possibility of error correction to produce CTFs with higher crystallinity and predictable properties.

3. Strategies for synthesis of CTFs

In recent years, the synthesis of CTFs has moved from the classical ionothermal towards milder and more controllable methods [24]. The main goals of these methods have been to reduce the synthesis temperature, increase crystallinity, preserve the functional groups, and better control the structure [25].

In general, CTF synthesis methods can be classified into three groups: Group 1) ionothermal synthesis with molten zinc chloride. Group 2) mild synthesis (solvothermal, strong acids, and microwave). Group 3) controlled methods (low-temperature polymerization, template-assisted method, microwave-assisted synthesis, mechanochemical production,

interfacial polymerization, and superacid-mediated approach). Fig. 2 shows an overview of these synthetic pathways and their sub-branches. Among these groups, controlled methods have attracted the most attention in recent years, as they allow for more precise structure tuning, reduction of lattice defects, and improvement of crystal order [2].

This classification also reflects the gradual evolution of CTF synthesis strategies, as the focus has shifted from simply achieving porous polymer networks to engineering the structure at the molecular scale and controlling the crystallization process. As a result, today the choice of synthesis method has a decisive impact not only on the reaction yield, but also on properties such as crystallinity, crystal size and morphology, porosity, specific surface area, defect density, and ultimately the performance of CTFs in applications such as photocatalysis, electrocatalysis, CO₂ absorption, and energy storage.

Table 1 lists the most important methods used in the synthesis of CTFs along with their advantages and disadvantages.

Accordingly, recent research is no longer focused solely on developing new synthesis methods, but rather on designing strategies that can simultaneously improve structural quality, scalability, and process stability. The most important goals of current research are:

- Reducing the synthesis temperature.
- Controlling crystallinity and crystal size.
- Increasing the relative reversibility of reactions (dynamic covalent chemistry).
- Creating two-dimensional CTFs with greater order.
- Synthesis of single-crystal CTFs (which is still one of the great challenges in this field).
- Using green, solvent-free, or energy-saving methods.

Furthermore, the integration of novel synthetic methods with computational modeling, machine learning, and data-driven optimization as an emerging approach has enabled the prediction of optimal synthesis conditions and the design of CTFs with targeted structure and function. These intelligent approaches are expected to play an important role in the development of the next generation of highly crystalline and functional CTFs.

Table 1. New methods for synthesizing CTFs, conditions, advantages, and disadvantages.

Synthesis approach	Conditions	Advantages	Disadvantages	Ref.
Ionothermal	400–600 °C, molten zinc chloride	High specific surface area, easy synthesis	Low crystallinity, carbonization	[26–29]
Solvothermal	120–250 °C	Better control of network growth	Usually less specific surface	[24, 30]
Superacid-catalyzed polymerization	Room temperature to 150 °C, usually with trifluoromethanesulfonic acid	Greater crystallinity, possibility of achieving more regular CTFs, preservation of functional groups	Sensitivity to moisture, higher cost, strong acid causes skin burn, inflammation, and edema	[31, 32]
Microwave-assisted method	A few minutes to an hour	Short time, less energy consumption, growing application in photocatalysts	Difficulty in controlling crystallinity	[33]
Polycondensation	< 200 °C	Reducing structural defects	Limited monomers can be used.	[20, 34–36]
Salt-template/molten salt synthesis	Various molten salts	Better control of morphology	Difficult optimization	[12, 37]
Template-assisted synthesis	Using hard or soft molds	Excellent pore size and morphology control, widely used in electrocatalysts and batteries	Need to remove the template	[38, 39]
Interfacial polymerization	At the boundary of two phases	Production of CTF thin films, suitable for separation and sensor applications	Can be used on a small scale.	[40, 41]
Mechanochemical production	Ball milling under solvent-free (neat grinding) or liquid-assisted grinding	Solvent-free or low-solvent, green method	Not yet developed	[42, 43]
Catalyst-assisted trimerization	Lewis or Brønsted acids	Decrease in activation energy	Still in development	[44]
Low-temperature polymerization	Room temperature–150 °C, mild catalytic conditions	Prevent carbonization and maintain crystallinity	Still in development	[20, 45]

Currently, research is being developed based on increasing framework order and hierarchical porosity while minimizing defect formation [46]. Methods for the synthesis of CTFs have developed significantly in the last two decades, and each method has its own advantages and limitations [47]. The most common method for synthesizing CTFs is

the ionothermal method, which is suitable for obtaining CTFs with very high thermal and chemical stability, large crystallinity domains, high porosity, and consequently high specific surface area [11]. The ionothermal method offers the possibility of synthesizing a wide range of CTFs with different structures, pore sizes, and properties. However,

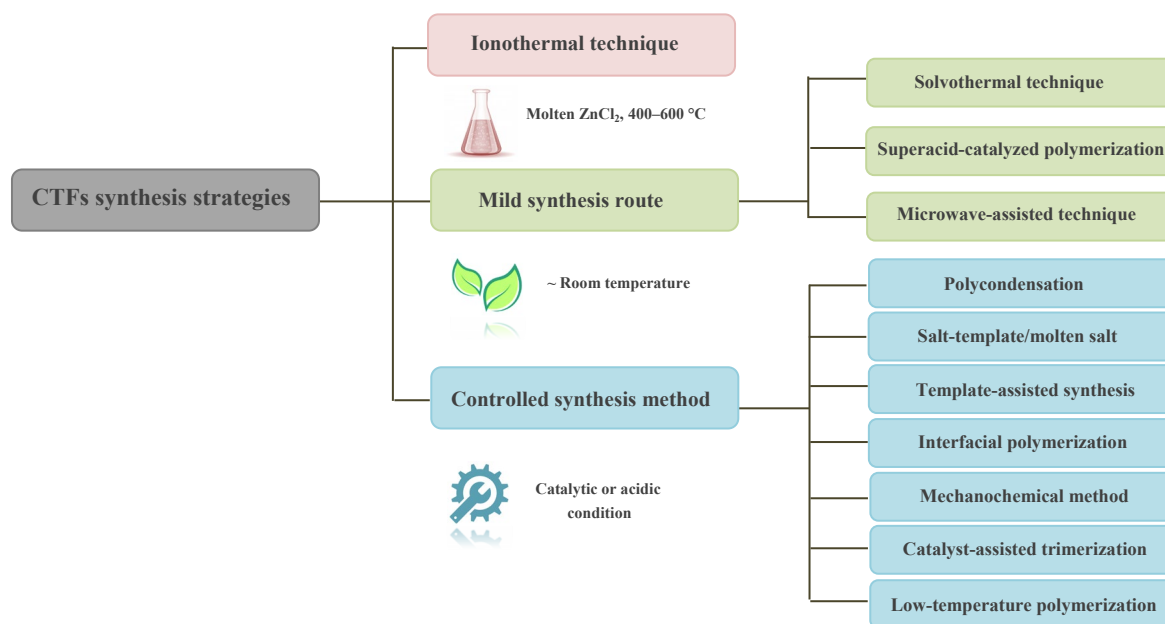


Fig. 2. CTF synthesis methods from major techniques. There are three main routes for the synthesis of CTFs: 1- ionothermal synthesis, 2- synthesis under mild conditions, and 3- synthesis under controlled conditions.

very high temperatures cause partial carbonization of the network, reduce structural order, generate abundant defects, and make it difficult to control the chemical composition. Therefore, although the resulting CTFs are generally suitable for applications such as gas adsorption, energy storage, and electrocatalysis, this method has limitations for studies that require precise control of the molecular structure [2].

To overcome these limitations, a solution polycondensation method was developed using solvents such as dimethyl sulfoxide at relatively low temperatures. This method allows for more precise introduction of electron donor and acceptor units and avoids thermal degradation of the monomers. However, the resulting CTFs are usually amorphous and have lower crystallinity and surface area than those obtained by the ionothermal method [48].

Another method is superacid-catalyzed synthesis, in which dinitrile monomers are converted to triazine rings in the presence of very strong acids such as triflic acid at room temperature or relatively low temperatures. This method is much milder than ionothermal synthesis and provides better control over the chemical structure, the amount of defects, and the remaining functional groups. As a result, it is a suitable method for investigating the relationship between local structure and electronic properties [49]. However, the porosity and specific surface area of the resulting CTFs are usually lower than those of ionothermal samples, and complete removal of acidic residues after synthesis can also be challenging.

Mechanochemical production of CTFs can be performed by grinding alone or with the assistance of a solvent as a green chemistry principle. In the solvent-assisted method, the solvent used not only acts as a bulking agent but also acts as a factor to increase molecular diffusion, improves mixing, and reduces the activation barrier for bond reorganization. As a result, the solvent-assisted technique effectively promotes the formation of triazine bonds and improves the network order compared to the solvent-free strategy (dry milling), although the crystallinity remains system-dependent [43, 50].

Overall, the choice of synthesis method depends on the end-use of the CTF. If the goal is to obtain highly porous materials with high thermal stability, the ionothermal method is often preferred the best option; however, if precise control of the molecular structure, preservation of functional groups, or the design of engineered photocatalysts is desired, solution polycondensation and superacid synthesis methods are preferable, which enrich the toolbox of building blocks and extend the structural design and diversity [21]. For this reason, recent research trends have shifted towards the use of low-temperature and controllable methods, as these methods allow for the targeted design of CTFs with tunable optical, electronic, and photocatalytic properties. This result suggests that the development of mild synthesis methods will play an important role in expanding the applications of CTFs in areas such as photocatalysis, solar energy conversion, sensors, and energy storage. Despite promising results, the scalability of these synthesis methods from laboratory milligram scale to industrial ton scale production has not yet been fully demonstrated [51].

4. Key factors affecting crystallinity

Crystallinity in CTFs is one of the most important challenges in the synthesis of these materials. Unlike many covalent organic frameworks (COFs), most CTFs have a semi-crystalline or even amorphous structure due to harsh synthesis conditions. Several factors affect their crystallinity, which is explained below.

4.1. Synthesis method

The most important factor is the synthesis method. In the ionothermal approach, it is usually carried out using a molten salt such as ZnCl_2 at high temperatures $> 400^\circ\text{C}$ and the crystallinity of the product is moderate. At very high temperatures, there is a possibility of carbonization of the network, which reduces crystallinity [5, 52].

Solvothermal synthesis has the possibility of correcting structural errors more because it is carried out at lower temperatures $< 200^\circ\text{C}$. Usually, more ordered and more crystalline CTFs are produced, and the polymerization of the metal mediator provides better control over crystal growth [7].

4.2. Reaction temperature

The reaction temperature plays a dual role. Incomplete reaction, incomplete network formation, and low crystallinity are the drawbacks of low-temperature synthesis. At very high temperatures, decomposition of ligands, carbonization, defect formation, and reduction of crystallinity lead to the production of undesirable products [53]. Therefore, for ionothermal synthesis, temperatures around $400\text{--}500^\circ\text{C}$ are usually more suitable than 600°C to increase network order and form more complete triazine bonds [26]. Additionally, increasing the temperature to more than 400°C causes hemolytic cleavage of nitrile-carbon bonds, which is accompanied by a decrease in the amount of nitrogen in the network [52, 54].

4.3. Reaction time

Temperature is one of the most important factors affecting the degree of crystallinity of the framework, because it increases the crystal order by controlling the reaction rate, mobility, and diffusion of molecules, the rate of formation of crystal nuclei, and the possibility of structural rearrangement [55].

The reaction time affects both nucleation and crystal growth. If the time is too short, the network does not have enough time to organize, and if the time is too long, the possibility of network destruction increases. In many reports, times of 20 to 40 hours have given good results [2, 24].

4.4. Catalyst selection

The type of catalyst can also have a significant effect on the crystallinity of CTFs, but this effect is usually indirect. The catalyst affects the degree of crystal order by changing the reaction pathway and the kinetics of network formation [2, 9].

Strong acid catalysts, such as ZnCl_2 , accelerate the formation of triazine rings by more effectively activating the nitril groups [5]. However, excessive catalyst activity causes the bond formation reaction to proceed too quickly, leaving insufficient time for structural rearrangement and repair of defects. As a result, the likelihood of irregular frameworks forming increases and the final crystallinity of the materials decreases [18].

Various catalysts play a significant role in crystal growth by differing the kinetics of skeleton formation. When structure forms at a controlled and gradual rate, the constituent units have sufficient time to rearrange and remove structural defects. This results in the formation of more ordered frameworks, with a higher crystallinity and fewer defects [18, 56].

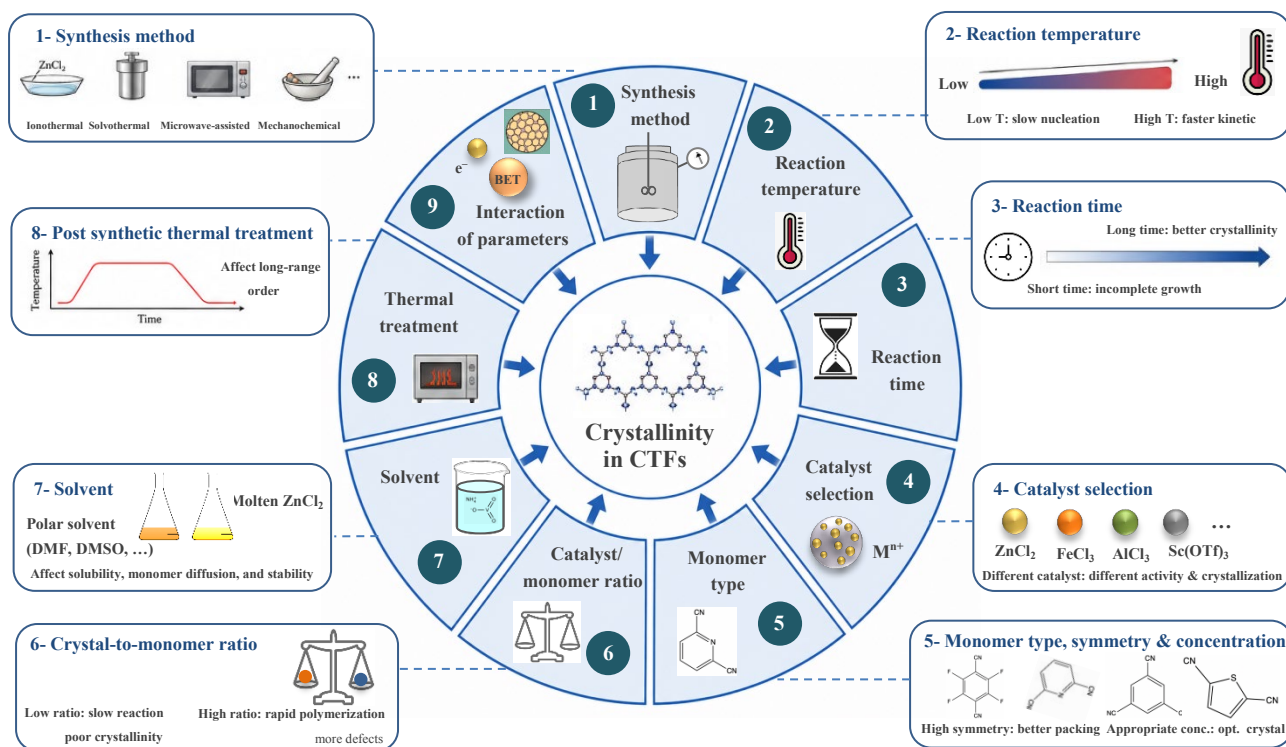


Fig. 3. Parameters affecting the crystallinity of CTFs. Inspired by [2, 5, 11, 52, 55].

The type of catalyst plays an important role in the amount and type of structural defects by affecting the reaction kinetics and the path of covalent bond formation. Some catalysts, by better controlling the network formation, provide the condition for the generation of more ordered networks with a lower density of structural defects; in contrast, others can lead to an increase in defects and a decrease in framework order due to excessive acceleration of bond formation or an increase in the likelihood of side reactions [56].

In ionothermal synthesis, compounds such as ZnCl_2 , in addition to playing a catalytic role, also act as a solvent for molten salt. Therefore, the choice of catalyst type not only affects the rate and path of the reaction, but also affects processes such as mass transfer, monomer dissolution, and crystal growth by affecting the properties of the reaction medium [2].

In the synthesis of CTFs by the ionothermal procedure, the reaction temperature and the ZnCl_2 -to-monomer ratio usually have a greater impact on the properties of the final products than the type of catalyst alone. This is because in most studies, ZnCl_2 was used as a fixed catalyst and molten salt solvent, and the observed variations were mainly due to differences in the amount of ZnCl_2 and the reaction conditions [2]. In contrast, in newer synthetic methods, such as the solvothermal approach, the choice of catalyst has become one of the key factors in controlling the reaction kinetics, improving the structural order, and increasing the crystallinity of CTFs.

4.5. Monomer type, symmetry, and concentration

Monomer design is one of the most important factors affecting the crystallinity of CTFs. Properties such as molecular geometry, symmetry, rigidity, and electronic properties of monomers directly

affect the arrangement of constituent units and the formation of long-range order in the network [57]. Therefore, the structure of the monomer plays a decisive role in the degree of order and crystallinity of the final framework. In general, planar, rigid, and highly symmetrical monomers provide more suitable conditions for the generation of ordered networks, and as a result produce CTFs with higher crystallinity. For example, monomers derived from benzene, pyridine, and pyrazine usually form frameworks with higher structural order and crystallinity compared to flexible monomers [53]. Furthermore, the targeted design of the building blocks attached to the electron-withdrawing triazine unit allows for the tuning of the electronic structure and energy band engineering of CTFs, thus optimizing the functional properties of these compounds to suit the desired applications [58].

Monomers with high symmetry facilitate more uniform crystal growth by providing favorable conditions for the regular arrangement of the constituent units and reducing the possibility of structural defects by reducing the lattice free energy. Therefore, monomers with threefold (C_3) and sixfold (C_6) symmetry usually form frameworks with higher structural order and crystallinity. In addition, planar aromatic monomers, due to their strong π - π interactions, facilitate more regular stacking of layers, thereby increasing structural order, improving crystallinity, and promoting lattice stability [9, 59].

Monomer concentration is a determining factor in the crystallization of CTFs because it affects the quality of the final structure by controlling the supersaturation, the nucleation rate, and the kinetics of network growth [21]. Enhancing the concentration of monomer usually accelerates the nucleation and formation of a large number of crystal nuclei, which ultimately leads to the creation of smaller crystal

domains and an increased probability of structural defects. Although rapid nucleation can increase the rate of framework formation and the synthesis yield, due to the limited opportunity for rearrangement of the constituent units, it prevents the formation of long-range order and reduces the final crystallinity of the product. In contrast, the use of lower monomer concentrations, by reducing the nucleation rate and providing sufficient time for the gradual growth of crystals, enables the formation of larger, more orderly, and higher-crystallinity domain networks.

4.6. Catalyst-to-monomer ratio

Precise control of the stoichiometric ratio of the reactants is an important factor in achieving CTFs with high structure order and crystallinity. Appropriate selection of the molar ratio and concentration of precursors ensures uniform network generation and reproducibility of the synthesis process. On the other hand, deviation from the optimal stoichiometric conditions can disrupt the formation of the ordered network, reduce the crystal order and the crystallinity of the final product by leaving the efficiency of triazine ring formation, and increasing the density of structural defects [60].

The importance of controlling the ZnCl_2 -to-monomer ratio in the ionothermal technique is greater than other factors, because this ratio directly affects the activation of nitrile groups and the path of framework generation. A low ZnCl_2 ratio usually leads to insufficient activation of nitrile groups, incomplete conversion of monomers, reduced crystallinity, and a drop in specific surface area. On the contrary, an excessive increase in the ratio can be accompanied by the intensification of side reactions, destruction of the network, and the formation of mesoporous and amorphous carbon phases. Therefore, choosing the optimal ratio of ZnCl_2 to monomer, which has been reported in many studies in the range of 5 to 20, is essential to achieve complete formation of triazine rings and to generate a balance between polymerization, porosity, and crystallinity [61].

4.7. Solvent

The environment of the reaction is a main parameter in determining the crystallinity of CTFs, because it plays an important role in the formation by affecting the solvent of monomers, mass transfer, intermolecular interactions, nucleation, and crystal growth. The combination of these factors determines the arrangement of the constituent units, the assembly of the framework, and ultimately the structural order and the crystallinity of the final product [57].

The selection of an appropriate solvent could help in achieving high crystalline CTFs by maintaining a uniform distribution of monomers in the reaction medium, providing the necessary conditions for nucleation and controlled crystal growth. Solvents with appropriate polarity enhance the solubility of precursors and prevent their premature precipitation; as a result, network formation is more uniform, the possibility of structural defects is reduced, and frameworks with greater structural order and crystallinity are obtained. In addition, the solvent can affect the bond formation pathway, self-assembly, and network growth by stabilizing the reaction intermediate species [62].

The use of mixed solvent systems is considered an effective strategy for controlling the crystallization of CTFs. Adjusting the ratio of solvent compounds allows for simultaneous control of the solubility of monomers and their diffusion rate, thereby establishing a proper balance between the rate of nucleation and crystal growth. Establishing this balance prevents excessive formation of primary nuclei, facilitates

the gradual growth of crystal domains, and ultimately leads to an increase in the size of crystal domains, improved long-range order, and enhanced crystallinity of the frameworks [21].

Additionally, the boiling point of the solvent affects the crystallinity of the final network. Solvents with high boiling points allow the reaction to be carried out at higher temperatures without disturbing the homogeneity of the reaction medium, thus creating more favorable conditions for nucleation and orderly growth of crystals. On the other hand, solvents with low boiling points can disrupt crystal growth due to rapid evaporation or the possibility of phase separation, and ultimately reduce the crystallinity of the product [63]. After ZnCl_2 , the most common solvent in the synthesis of covalent frameworks is DMF (N,N-dimethylformamide) with the formula $\text{C}_3\text{H}_7\text{NO}$. With its high polarity and suitable boiling point, it can dissolve nitrile-containing aromatic monomers and is especially used in ionic/microwave polymerization techniques [18]. Of course, NMP (N-methyl-2-pyrrolidone) is also used as a substitute for DMF because it has a higher boiling point and is more suitable for synthesis under high temperatures. Dimethyl sulfoxide (DMSO) is most widely used solvent, with its strong polarity, weak oxidizing properties, good thermal stability, and high boiling point [51].

4.8. Post-synthetic thermal treatment and annealing

Post-synthesis treatments of CTFs can be used to enhance the crystallinity and boost the structural order after initial formation of frameworks. This operation promotes crystal order and improves the quality of the final CTFs structure by providing the necessary conditions for local structural rearrangement, removing residual impurities, and defects, and strengthening interlayer interactions [11]. Heat treatment at optimal temperature promotes long-range order in the networks by enhancing the mobility of compounds, partially repairing defects, and providing suitable conditions for the rearrangements of disordered parts. As a result, crystallinity is increased, which is usually visible as the appearance of narrower and more intense diffraction peaks in X-ray diffraction patterns [42, 64].

However, applying excessively high temperatures can have the opposite effect, causing framework degradation, structural carbonization, or pore collapse. Therefore, choosing the right temperature and carefully controlling the heat treatment conditions are essential to achieve the highest degree of crystallinity without compromising structural integrity [6, 56].

In addition to conventional thermal treatments, various post-synthetic strategies, including rearrangement in the presence of solvent or steam, have been considered in porous organic frameworks and in some CTF systems as methods to reduce structural defects, enhance the growth of crystalline domains, and improve the framework order [9, 64].

In addition to synthesis temperature and heat treatment, controlling post-synthesis heating and cooling conditions can also be effective in maintaining structural integrity and preventing thermal stresses in CTFs, although the role of cooling rate in these materials has been investigated to a limited extent so far.

4.9. Interaction of synthesis parameters and crystallization process

Although each synthesis parameter alone can affect the degree of structural order of CTFs, the final crystallinity of these materials is the result of the interaction of a set of factors, including monomer design,

reaction conditions, catalyst type and performance, and post-synthesis processes [18]. These factors determine the quality and degree of framework order by influencing the balance between nucleation, crystal growth, and the creation of structural defects [21].

Generally, increasing the crystallinity of CTFs requires striking a balance between the rate of network formation and the possibility of its structural rearrangement, in a way that prevents rapid and uncontrolled framework generation and the system from becoming trapped in kinetic states, while the constituent units still have sufficient time [3, 9].

5. Methods for characterization of CTFs' crystallinity

Characterization techniques play a fundamental role in identifying and evaluating the properties and quality of materials and help to better understand the factors affecting their performance limitations. These methods provide detailed information about the structure, morphology, chemical composition, and behavior of materials, allowing for the understanding of the mechanisms governing performance. As a result, the use of characterization techniques reduces the time and costs associated with trial and error in experimental studies and accelerates the development and optimization of electrode materials. Common methods for measuring the crystallinity of CTFs are described below.

The most common method is powder X-ray diffraction (PXRD or XRD), which helps evaluate the degree of order and crystallinity of the sample by examining the presence and intensity of diffraction peaks and comparing the experimental pattern with the simulated pattern [64].

Transmission electron microscopy (TEM) is one of the most important characterization methods for studying the microstructure, morphology, size, and distribution of particles at the nanometer scale. In addition to high-resolution imaging, this technique also allows the study of the crystal structure of materials by utilizing selected area electron diffraction (SAED). The patterns obtained from SAED provide valuable information about the crystallinity or amorphousness of the sample, the identification of crystalline phases, the determination of crystal orientation, the assessment of the degree of crystal order, and the detection of structural defects [2]. Therefore, the simultaneous use of TEM and SAED plays an important role in identifying microstructural features and examining the quality of crystallinity of materials.

High-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM) are the most advanced structural characterization techniques that allow direct observation of atomic arrangement and lattice fringes at angstrom-scale resolution. This technique provides valuable information about the degree of crystallinity, d-spacing, crystal orientation, grain boundaries, and structural defects. In porous materials such as CTFs, HRTEM plays an important role in confirming the presence of crystalline regions, examining the degree of structural order, and evaluating the quality of the crystal structure. Also, comparing HRTEM images with PXRD and SAED results allows for more accurate analysis of the crystal structure and validation of the crystallographic properties of these materials [65]. Despite the extensive capabilities of HRTEM and SEM in investigating structural and morphological features, the use of these techniques is also associated with some limitations. Among the most important of these limitations is the possible damage caused by irradiation of high-energy electron beams to sensitive CTF samples, especially semi-

crystalline or amorphous samples, which can change their structure or destroy them. In addition, sample preparation for HRTEM and SEM analyses requires high precision because the amount of sample that can be loaded on the holders is limited and obtaining a sample with the appropriate thickness and dispersion can be challenging, especially for CTFs as porous material [3].

Rietveld refinement is an advanced method for quantitative analysis of powder X-ray diffraction (PXRD) patterns that is widely used in studying the crystal structure of CTFs. In this method, by simultaneously fitting the entire experimental diffraction pattern with a calculated structural model, crystal parameters such as lattice constants, space group, atomic positions, occupancy factor, crystallite size, and lattice strain are determined with high accuracy [66]. In crystalline or semi-crystalline CTFs, Rietveld Refinement allows for evaluating the agreement of the synthesized structure with theoretical models, determining the layer stacking pattern (such as AA and AB arrangements), and examining the quality of crystallinity. Since many CTFs have relatively low crystallinity and broad diffraction peaks, using Rietveld Refinement along with HRTEM and SAED data can help provide a more accurate description of the crystallographic structure and validate the structural model of these materials.

The Scherrer equation is one of the most common methods for estimating crystallite size from powder X-ray diffraction (PXRD) data [67]. It is based on measuring the full width at half maximum (FWHM) of the diffraction peaks and calculates the average size of coherent crystalline regions. In materials such as CTFs, which typically have limited crystallinity and relatively broad diffraction peaks, the Scherrer equation is a convenient tool for estimating crystallite size and indirectly assessing the quality of crystallinity. In general, a decrease in the width of the diffraction peaks indicates an increase in crystallite size and improved structural order, while an increase in the width of the peaks can be due to small crystallites, the presence of lattice strain, or structural defects. However, since the Scherrer relation only considers the effect of crystal size and does not fully separate the contribution of lattice strain, device errors, and other factors affecting peak broadening, its results are usually interpreted in conjunction with other characterization methods such as Rietveld analysis, HRTEM, and SAED to obtain a more accurate assessment of the crystal structure of CTFs. When applying the Scherrer equation, instrumental line broadening (B_{inst}) should be corrected by subtracting it from the observed peak width before crystallite size calculation. Neglecting this correction may overestimate peak broadening and consequently underestimate the crystallite size [68].

Synchrotron X-ray diffraction (Synchrotron XRD) is one of the most advanced structural characterization methods that uses high-intensity, coherent, and monochromatic X-rays generated in synchrotron accelerators to provide a detailed investigation of the crystal structure of materials [69]. Compared to conventional PXRD devices, this technique has much higher resolution, signal-to-noise ratio, and sensitivity, and can reveal weak or overlapping diffraction peaks with greater accuracy. Therefore, Synchrotron XRD is very valuable for studying CTFs with low crystallinity or small crystallite size, and provides precise information about lattice parameters, long-range order, layer arrangement, and structural changes. Also, this method, along with Rietveld analysis, can help refine structural models and increase the accuracy of determining the crystal structure of CTFs [70].

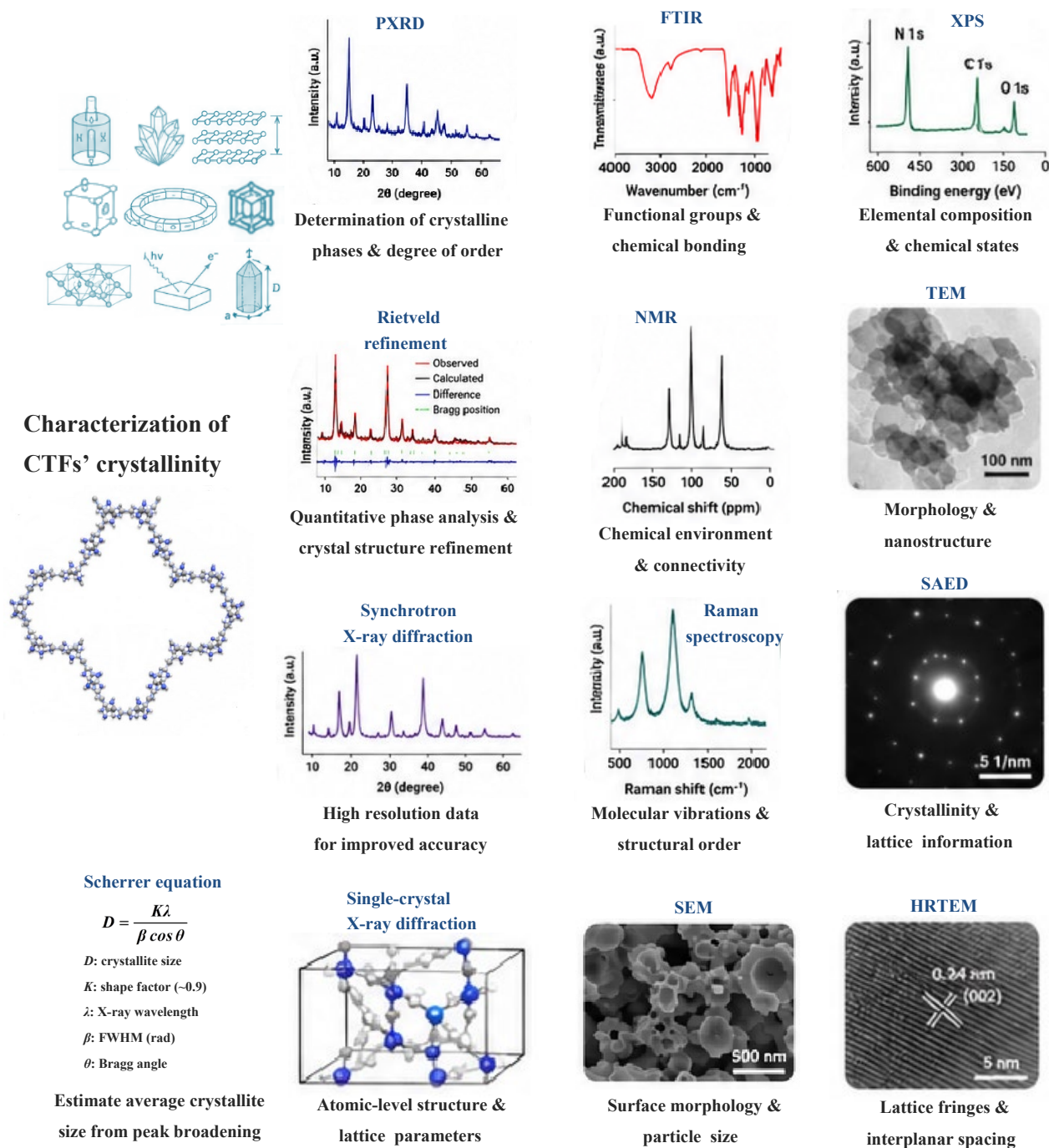


Fig. 4. Some methods for providing complementary information about the crystallinity of CTFs, from atomic-scale structure and bonding to long-range order and overall crystallinity, enabling a comprehensive understanding of the structure-property relationship. Inspired by [2, 3, 5, 14].

Single-crystal X-ray diffraction (SCXRD) is the most accurate method for determining the three-dimensional structure of crystalline materials at the atomic scale. By analyzing the diffraction pattern obtained from a high-quality single crystal, this technique provides complete information about the position of atoms, bond lengths and angles, lattice parameters, space group, and three-dimensional arrangement of the structure [71]. In research on

CTFs, the use of SCXRD is very limited due to the difficulty of synthesizing large, high-quality single crystals, and most CTFs are synthesized as powders or semi-crystalline materials. However, in cases where single crystals are available, SCXRD is the most accurate and reliable method for determining the crystal structure, validating structural models, and investigating the connection of constituent units in CTFs.

Fourier transform infrared spectroscopy (FTIR) is one of the most widely used characterization methods to identify functional groups and investigate the formation of chemical bonds in CTFs. This technique is based on the absorption of infrared radiation by chemical bonds and provides valuable information about molecular vibrations [72]. In the synthesis of CTFs, FTIR is commonly used to confirm the formation of triazine rings and to check the completion of the polymerization reaction. Typically, the reduction or elimination of the stretching band of the nitrile group ($C \equiv N$) and the appearance of characteristic bands related to the triazine ring indicate the successful formation of the triazine framework. In addition, FTIR can also reveal the presence of residual functional groups, impurities, and chemical changes caused by surface modification or functionalization of CTFs. Although this method does not provide direct information about the degree of crystallinity or crystal structure, it plays an important role, along with techniques such as PXRD, XPS, and NMR, in confirming the chemical structure and evaluating the quality of CTF synthesis [73].

Raman spectroscopy is a complementary method to FTIR for investigating the chemical structure and vibrational properties of materials, which is based on the inelastic scattering of laser light by molecules [74]. This technique provides valuable information about the type of chemical bonds, structural order, the degree of aromaticity, and the defects present in CTFs. In CTFs, Raman spectra are commonly used to confirm the formation of triazine rings, investigate the structure of the conjugated network, and evaluate the degree of order of the framework. In addition, the presence or intensity of characteristic bands can reveal structural changes caused by synthesis, chemical modification, or thermal treatment. Since Raman is highly sensitive to vibrations related to covalent bonds and carbon structures, this method, along with FTIR, XPS, and PXRD, provides comprehensive information about the chemical structure and degree of order of CTFs and plays an important role in confirming the success of the synthesis and evaluating the structural quality of these materials [59]. In many studies on CTFs, Raman spectroscopy is used to confirm the formation of the framework, as well as to investigate the degree of graphitization and the amount of structural defects, especially when CTFs are pyrolyzed to form carbon-derived materials. In this case, the analysis of the intensity ratio of the D and G bands (I_D/I_G ratio) is an important indicator for evaluating the degree of disorder and carbon structure.

X-ray photoelectron spectroscopy (XPS) is one of the most important surface analysis methods for investigating the elemental composition and chemical state of elements in CTFs. By measuring the binding energy of photoelectrons emitted from the sample surface, this technique allows the identification of elements, determination of their atomic percentages, and investigation of the type of chemical bonds [75]. In CTFs, XPS is widely used to confirm the presence of carbon and nitrogen atoms, identify different nitrogen species in triazine rings, and investigate chemical changes caused by functionalization or doping. Therefore, XPS, along with FTIR and PXRD, plays an important role in confirming the chemical structure and evaluating the quality of CTF synthesis [14].

6. Relationship between crystallinity and functional properties

Crystallinity is one of the most important factors affecting the functional properties of CTFs and can significantly affect the performance of these materials in various applications. Increasing the

degree of crystallinity leads to greater structural order, a decrease in the number of defects, improved charge transport pathways, and increased framework stability, which ultimately leads to improved properties such as electrical conductivity, electrocatalytic activity, gas adsorption and storage, molecular separation, and performance in energy storage systems [76]. In contrast, the presence of amorphous or semi-crystalline structures, although they may create a greater number of active sites and structural defects, usually leads to a decrease in lattice order, limited electron transport, and reduced long-term stability of the material. Therefore, balancing the degree of crystallinity, porosity, and defect density is one of the most important strategies in the design and development of CTFs with optimal performance for various applications [77].

6.1. Crystallinity and porosity

Porosity represents one of the defining characteristics of CTF materials and is strongly influenced by the degree of structural ordering. In CTFs with high crystallinity, the regular and periodic arrangement of the constituent units leads to the formation of uniform porous channels and a narrow pore size distribution. Such an orderly structure increases the accessibility of guest molecules to the pores and facilitates the mass transfer process throughout the framework [2].

In contrast, amorphous or low-crystalline CTFs typically have a disorganized network of pores, which is caused by random growth of the framework and the presence of structural defects. In these materials, some pores may be blocked, some channels may remain dead ends, or parts of the network may be collapsed. These factors ultimately reduce the available surface area and limit the efficiency of the porosity [52].

However, the relationship between crystallinity and Brunauer–Emmett–Teller (BET) is not always direct and linear. Although increasing crystallinity usually improves the order of the porous network, some amorphous CTFs can also have very high specific surface areas due to their abundant microporosity. Therefore, crystallinity cannot be considered the only criterion for evaluating porosity; rather, this characteristic affects the quality, uniformity, and accessibility of the pore network. In addition, the presence of a regular porous structure makes the adsorption behavior more repeatable and allows for more accurate prediction and modeling of the interactions between the host framework and guest molecules [78].

6.2. Defect engineering and crystallinity

Although achieving high crystallinity in CTFs is usually considered an important goal in the design of these materials, recent studies have shown that the highest crystallinity does not necessarily lead to the best performance. In many cases, the presence of a certain amount of structural defects can have positive effects on the performance of the material. These defects can act as catalytically active centers, modulate the electronic structure of the framework, increase the adsorption capacity of molecules, and even provide new pathways for charge transport [79].

Accordingly, new approaches to the design of CTFs emphasize the concept of “controlled disorder”. In this strategy, structural defects are intentionally engineered into the framework while maintaining a high degree of order and crystallinity [9]. Such a design allows for the simultaneous exploitation of the advantages of crystalline structures, such as efficient charge carrier transport, pore network uniformity, and structural stability, as well as the advantages of the presence of defects,

such as an increase in the number of active sites and improved reactivity [80].

Therefore, the current perspective in CTF research has moved away from focusing solely on increasing crystallinity. Today, the main goal is to achieve an optimal balance between structural order and defect density, since the final performance of these materials is the result of the interaction of these two factors. Therefore, future studies should focus on simultaneously identifying and controlling crystallinity and structural defects to design frameworks with the highest efficiency in applications such as catalysis, absorption, energy storage, and energy conversion.

6.3. Crystallinity and electronic properties

One of the most prominent advantages of highly crystalline CTFs is their significant improvement in electronic properties. In these materials, charge transport depends on the degree of overlap of electron orbitals and the continuity of conduction paths throughout the framework. Therefore, the greater the structural order, the easier the movement of charge carriers [81].

In contrast, amorphous or poorly crystalline CTFs have discontinuous charge transport pathways due to structural defects and irregular arrangement of the constituent units. This disorder increases the probability of charge carrier trapping and accelerates the electron-hole recombination process. Such a phenomenon has a significant negative impact, especially in photocatalytic and electrochemical applications, where effective charge carrier separation plays a decisive role in the performance of the material [82].

Increased crystallinity leads to the formation of more ordered π -paired networks and the strengthening of π - π interactions between adjacent layers. This orderly arrangement reduces energy disorder and provides more favorable conditions for faster electron transport and increased charge carrier mobility. In addition, crystal frameworks usually exhibit more efficient exciton diffusion and longer charge carrier lifetimes, which ultimately leads to increased efficiency of electronic and optical processes [83].

Therefore, increasing crystallinity is recognized as one of the key strategies in the design and development of CTF-based semiconductor materials, because this feature plays an important role in enhancing charge transport, reducing carrier recombination, and consequently improving performance in photocatalytic, photoelectrochemical, and electronic applications.

6.4. Structural stability, durability and crystallinity

Crystallinity plays an important role in maintaining the long-term stability of CTF materials under operational conditions. Frameworks with greater crystal order typically exhibit higher thermal, chemical, and mechanical stability due to a more uniform distribution of internal stresses and reduced defect-prone regions [2].

Furthermore, highly crystalline structures are more resistant to structural changes such as pore collapse, network degradation, and framework rearrangement during successive adsorption-desorption cycles or catalytic processes. Conversely, an increase in the amount of structural defects can create stress concentration points and accelerate the material degradation pathway [9, 11].

From an industrial application perspective, structural durability is a key factor in maintaining the long-term performance of materials, as performance degradation is often due to the gradual degradation of the

framework. Therefore, improving crystallinity not only improves the initial performance of the material but also improves its reliability and operational lifetime by increasing structural stability.

6.5. Photocatalytic activity and crystallinity

Photocatalysis is one of the most important and widely used areas of application of CTFs and has been widely used in processes such as hydrogen production, photocatalytic reduction of CO_2 , and decomposition of organic pollutants. The efficiency of these materials in such reactions is largely dependent on the degree of crystallinity of their structure [4].

In general, CTFs with high crystallinity have more favorable photocatalytic performance than less crystalline or amorphous ones. The higher structural order enables more efficient charge carrier transport and separation and prevents electron-hole recombination. Also, the increased π -conjugation and regular arrangement of the constituent units facilitate charge transfer to the catalytically active sites, thereby improving the quantum efficiency of the reaction [84].

On the other hand, crystal frameworks usually have more uniform active sites and a network of pores with well-defined dimensions. These features allow easier penetration and transport of reactants into the structure, increasing their accessibility to the active sites, and ultimately improving reaction kinetics and increasing the number of catalytic cycles [12].

The results of various studies show that increasing the degree of crystallinity can significantly improve the hydrogen production rate and increase the efficiency of photocatalytic CO_2 reduction [85]. However, crystallinity is not the only factor determining the photocatalytic performance. Parameters such as the energy band structure, the type and concentration of structural defects, the use of cocatalysts, and the chemical modification of the surface also have a significant impact on the activity of these materials. In some cases, structural defects can act as catalytically active centers or effective sites for charge carrier separation. Therefore, the highest photocatalytic efficiency is usually observed in CTFs that, in addition to appropriate crystallinity, also have a controlled and optimal amount of structural defects.

6.6. Crystallinity and electrocatalytic performance

The influence of the crystallinity degree of CTFs is not limited to photocatalytic systems but also plays a decisive role in their performance in electrocatalytic processes. These materials have been considered as promising catalysts in reactions such as the hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and electrochemical reduction of carbon dioxide (CO_2RR), and their structural features have a direct impact on the efficiency of these reactions [86].

In electrocatalytic systems, rapid and efficient electron transfer between the electrode surface and the catalytically active sites is of great importance. Increasing crystallinity improves the electrical conductivity of the framework by creating continuous and regular pathways for charge transfer and reducing the resistance due to structural disorder. In addition, the presence of a regular network of pores facilitates the movement of ions and the transport of reactive species, thereby improving the kinetics of electrochemical reactions [87].

In nitrogen-rich CTFs, increased crystal order can lead to a more uniform distribution and better access to catalytically active sites. Also, crystal frameworks provide a stable and controllable environment for the stabilization of metal species, single-atom catalysts, and impurity atoms, which can enhance the activity, selectivity, and stability of the catalyst in electrochemical reactions [88].

Despite the numerous advantages of high crystallinity in improving charge transport and electrical conductivity, the presence of controlled structural defects remains a key factor in electrocatalytic performance. Many of the active sites involved in electrochemical reactions originate from these defects and can facilitate the adsorption and activation of reactants. Therefore, modern approaches to the design of CTF-based electrocatalysts focus on striking a balance between crystal order and optimal density of structural defects to maintain the desired charge transport while maximizing the number of active sites.

6.7. Gas adsorption and separation performance

Gas adsorption and separation are among the applications whose performance is significantly dependent on the crystallinity of CTF skeletons, because the transport of molecules in porous materials depends on the continuity of the pore network and the uniformity of the internal structure. Increasing the crystal order creates more regular transport pathways and reduces diffusion barriers, thereby facilitating mass transfer [2].

CTFs with high crystallinity typically have a more uniform distribution of adsorption sites and a narrower pore size distribution than amorphous samples. These features create homogeneous adsorption environments, reduce adsorption energy heterogeneity, and improve selective interactions between the framework and gas molecules. In addition, the presence of regular channels in the crystalline structure allows for faster and more efficient diffusion of gases throughout the framework [18].

In CO₂ adsorption, increased crystallinity is usually associated with improved selectivity, as the more regular arrangement of nitrogen-rich triazine units enhances specific interactions with CO₂ molecules. Similarly, in CTF-based membranes, greater structural order can enhance the molecular screening effect and, consequently, improve the efficiency and selectivity of the gas separation process [76].

However, maximum crystallinity does not always mean the best adsorption performance. In some cases, the presence of a controlled amount of structural defects can enhance the adsorption capacity by creating new active sites or increasing the accessibility of the internal surface [89]. Therefore, the optimal performance of CTFs in gas adsorption and separation processes usually results from striking a balance between crystal order and the appropriate density of structural defects, rather than simply achieving the highest degree of crystallinity [90–92].

7. Current challenges and future perspectives

Despite significant advances in the development of synthesis methods and characterization of structural features of CTFs, precise control of the crystallinity of these materials remains one of the most important challenges facing researchers. Although various synthetic strategies have been proposed to increase crystal order and improve the framework structure, many reported CTFs still have limited crystallinity and relatively poor long-range order. On the other hand, there is no complete understanding of the fundamental processes

affecting nucleation, crystal growth, and the creation of structural defects, which limits the targeted design of CTFs with fully controlled structures. Therefore, a deeper understanding of these processes and the development of more effective synthetic methods will be a fundamental step towards achieving CTFs with high crystallinity, greater stability, and optimal performance in applications such as catalysis, gas absorption and separation, energy storage and conversion, and other advanced technologies.

- One of the most important research challenges in the field of CTFs is to achieve long-range crystallinity and high structural order. Unlike many covalent organic frameworks (COFs) that utilize reversible dynamic covalent chemistry, the conventional synthesis of CTFs is mainly based on irreversible triazine ring formation reactions. As a result, defects introduced during the early stages of framework growth cannot be repaired and remain permanently in the structure, which often leads to the formation of small crystalline domains next to amorphous regions. Therefore, the development of synthetic methods based on increasing the reversibility of reactions, the use of dynamic intermediates, or self-repairing routes can be an effective strategy to achieve CTFs with higher structural order and crystallinity.
- Despite significant progress in improving the crystallinity of CTFs, a complete understanding of the fundamental mechanisms governing the crystallization process of these materials has not yet been achieved. Many key aspects, including nucleation pathways, crystal growth kinetics, the role of intermediate species, and the formation of structural defects, are still not fully understood. Since most of the existing knowledge is based on post-synthesis analysis of the materials, the information obtained only provides an indirect picture of the framework formation process, and as a result, the relationship between synthesis conditions and the degree of crystallinity is often explained based on experimental observations, not mechanistic understanding. Therefore, performing mechanistic and online (in situ/operando) studies to identify the growth steps and intermediate species will play an important role in explaining the crystallization process and can pave the way for the rational and targeted design of synthetic methods, rather than relying on a trial-and-error approach.
- Structural defects in CTFs play a dual role; on the one hand, they reduce crystallinity by disrupting the framework order, and on the other hand, they can improve catalytic activity, adsorption capacity, and some electronic properties by creating new active sites. Therefore, achieving optimal performance is not only dependent on increasing crystallinity, but also on controlling the type, amount, and distribution of structural defects. In this regard, defect engineering, as a novel approach, provides the possibility of creating a balance between structural order and performance and can lead to the design of CTFs with superior properties compared to fully crystalline or fully disordered structures.
- Despite the achievement of highly crystalline CTFs on a laboratory scale, the translation of this success to industrial production still presents significant challenges. Many existing synthetic methods rely on optimized reaction conditions, long times, and relatively low yields, and on a large scale, changes in heat transfer, mass transfer, and mixing can negatively affect crystal growth and structural order. Therefore, the development of scalable, cost-effective, low-consumption, and environmentally friendly synthetic methods, including continuous processes, low-temperature

synthesis, and process intensification strategies, is essential for the mass production of highly crystalline CTFs and to facilitate the commercialization of these materials.

- One of the major limitations in CTF research is the inability to directly observe the crystallization process during synthesis; therefore, most of the available information is obtained from post-synthesis analyses, making it difficult to identify intermediate species, nucleation steps, and framework growth mechanisms. Advances in *in situ/operando* techniques, including PXRD and synchrotron-based spectroscopic methods, have made it possible to study framework formation, crystal growth, and the evolution of structural defects in real time. The application of these methods can provide a deeper understanding of the crystallization mechanism of CTFs and accelerate the targeted development of frameworks with higher crystallinity and performance.
- Computational approaches have increasingly become a key tool in the development of CTFs. Methods such as molecular simulations, density functional theory (DFT) calculations, crystal growth modeling, and data-driven and machine learning approaches allow the prediction of framework stability, defect formation, crystallization behavior, and the influence of synthesis conditions. By establishing a link between molecular structure and the crystallization process, these tools reduce the reliance on trial-and-error methods and facilitate the targeted design of CTFs with optimal crystallinity and performance; hence, their role in the engineering and optimization of the next generation of these materials is expected to increase significantly.
- Although many past studies have focused on improving the performance of CTFs in various applications, increasing evidence suggests that crystallinity, as the link between synthesis conditions and final performance, plays a decisive role in the properties of these materials. Therefore, future research should focus on elucidating quantitative structure–property relationships through systematic comparison of CTFs with different degrees of crystallinity and development of predictive models to clarify the relationship between crystallinity and properties such as porosity, charge transport, catalytic activity, and stability. Such an approach will pave the way for rational material design and accelerate the development and commercialization of CTF-based technologies.

Achieving highly crystalline CTFs is one of the most important challenges and opportunities. Despite significant advances in synthesis and characterization methods, precise control of crystallinity, structural analysis, and reproducibility is increasingly needed. It is expected that the integration of strategies such as dynamic covalent chemistry, advanced *in situ/operando* methods, engineering, computational modeling, and data- and machine-driven structures will pave the way for the development of CTFs with structural order and higher performance. In this, crystallinity should be considered not only as a structural feature, but also as a controllable design that determines the relationship between synthesis and structure performance. Achieving this level of control will play a key role in the development of the next generation of advanced CTFs for energy, catalysis, adsorption, and separation applications.

8. Conclusions

Covalent triazine frameworks (CTFs) are recognized as one of the most promising porous organic materials for applications such as gas

adsorption and separation, catalysis, energy storage and conversion, and environmental remediation due to their excellent thermal and chemical stability, engineerable porosity, high nitrogen content, and favorable electronic properties. Despite significant advances in the synthesis and development of these materials, achieving precise control over the crystallinity and long-range order of the framework remains a fundamental challenge that plays a decisive role in the ultimate properties and performance of CTFs.

As discussed in this review, crystallinity is not only a structural feature but also a determining parameter in the performance of CTFs. The degree of crystal order has a direct impact on the effective porosity, mass transfer, charge transfer, framework stability, and catalytic activity, and thus plays a mediating role between the synthesis conditions, the final structure, and the material performance. Therefore, targeted control of crystallinity will be one of the most effective strategies for designing CTFs with optimal performance in advanced applications.

The crystallization behavior of CTFs is a result of a complex interplay of thermodynamic and kinetic factors, the reversibility of bond formation reactions, nucleation, crystal growth, and the molecular design of the precursors. In recent years, several synthetic strategies, including ionothermal, solvothermal, microwave, interfacial, template-assisted, and low-temperature synthesis, have been developed to improve the crystal order of these materials. Despite the relative success of these methods, achieving a general synthetic protocol that can stably and reproducibly produce CTFs with high crystallinity remains one of the fundamental challenges in this field.

This review shows that the control of crystallinity of CTFs depends on a set of synthetic parameters, including monomer symmetry, reaction temperature, catalyst type, solvent environment, precursor concentration, and post-synthesis operations, and optimization of these factors plays a decisive role in achieving frameworks with higher structural order. Also, advances in advanced characterization methods, including PXRD, electron microscopy, solid-state NMR spectroscopy, and synchrotron radiation-based techniques, have enabled more accurate evaluation of crystallinity and deeper understanding of the framework formation process, and have significantly improved our understanding of the relationship between synthesis conditions and the final structure of CTFs.

Existing evidence suggests that crystallinity and CTF performance have a complex and multidimensional relationship, and maximum crystallinity does not necessarily lead to the best performance. While highly ordered frameworks often exhibit superior porosity, charge transport, stability, and catalytic activity, controlled structural defects can also improve material performance by creating active sites and tuning physicochemical properties. Therefore, future approaches should go beyond a focus on increasing crystallinity and focus on the targeted design of CTFs with an optimal balance between crystal order and defect engineering, an approach that could pave the way for the development of materials with performance beyond that of purely crystalline or completely disordered structures.

Despite significant progress in the development of CTFs, several challenges still hinder the achievement of frameworks with high crystallinity and optimal performance. The most important of these challenges include designing synthetic methods to create long-range order, better understanding of crystallization mechanisms, employing advanced *in situ/operando* techniques to monitor the framework formation process, and developing scalable methods to produce

crystalline CTFs. In addition, the use of computational modeling, molecular simulations, data-driven approaches, and machine learning is expected to play an increasing role in advancing the research and development of the next generation of CTFs by facilitating rational material design and predicting optimal synthesis conditions.

In general, crystallinity has now become more than a structural property but a key principle in the design of CTFs. Advances in synthesis methods, characterization techniques, and understanding of crystallization mechanisms will allow for more precise control of the structural order of these materials. Ultimately, the future success of CTF research depends on the ability to design and control crystallinity in a targeted manner, along with the synthesis of ordered frameworks; an approach that will accelerate the development of a new generation of high-performance CTFs for energy, catalysis, and environmental technology applications.

CRediT authorship contribution statement

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