

Recent trends in synthetic Top-down approach for Mesoporous Carbon: A seminal review

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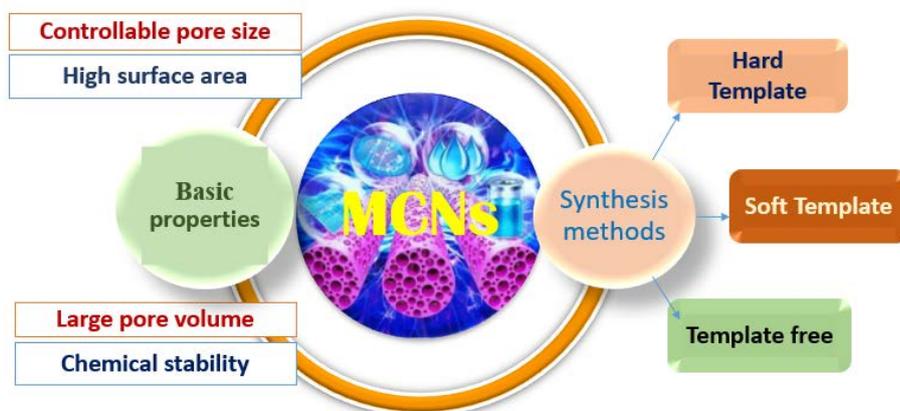
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Review

ABSTRACT This review is focused on the different synthetic methods of mesoporous carbon for exotic applications. In the 21st century, doped carbon nanostructures and composites have cutting-edge applications in materials sciences due to their superior physicochemical properties. Porous carbon has enticed material scientists because of its excellent properties like ordered porous structure, tunable pore size, and high specific surface area. As a result, the extensive studies on the synthesis and

modification of mesoporous carbon are being performed. The most enticing approaches for synthesis of ordered mesoporous carbon are hard template and soft template methods. On the other hand, non-templating pathways are equally important to synthesize mesoporous carbon as that are templating pathways. This report includes details of different synthetic methods for synthesis of mesoporous carbon materials by templating as well as non-templating methods.

Keywords: Synthetic methods; Carbon Nanomaterials; Mesoporous, template methods, non-template method,



INTRODUCTION

In recent times, the significance of nanomaterials has risen significantly due to their remarkable characteristics; as a result, researchers are concentrating on new approaches in the field of materials science to modify the physicochemical properties of nanomaterials by incorporating carbon nanomaterials. The carbon and synthesis of mesoporous carbon nanomaterials are of trending topics in the scientific community.^{1,2} The designing of mesoporous carbon nanomaterials with unique properties and controllable porous structure,^{3,4} high specific surface area, large pore volume,⁵ and

excessive stability has gained enormous curiosity from scientists around the globe. Porous carbon nanomaterials can be synthesized using a variety of techniques, including hard template synthesis, template-free method, hydrothermal carbonization, mechanochemical assembly, nano casting, and soft template.⁶⁻¹⁶ These techniques provide several benefits. Carbonaceous solids can be produced from biomass without the need for an energy-intensive drying process attributable to an ordered mesoporous structure, a simple and adaptable approach, the ability to retain small particle sizes during carbonization, easy synthesis, and control, etc. Mesoporous carbon materials with their distinctive physicochemical characteristics, tunable pore size, and uniform structure frame it a perfect skeleton for various applications such as electrochemical energy storage, adsorption, catalysis, sensing, and biomedical applications.¹⁷⁻²⁴

The term “mesoporous material” refer to a material containing a pore diameter between 2 to 50 nm. The method for the production of mesoporous ordered carbon was initially established by scientist Ryoo *et al.* Mesoporous material can be ordered or disordered in a mesostructure. And the ordered

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structure favors the addition of new functionalities and emerging new approaches, enhancing their applications in various fields.^{25,26} However, MCNs could be produced from carbon sources by employing the hard template approach, soft template method, or template-free methods (Table. 1).^{27,28} The ultimate significance of template-based synthesis of MCNs is the control over pore size and morphology of mesostructure.²⁹ The prevailing technique for template-based synthesis comprises the following steps, preparation of template material, infiltration of necessary precursors in the template, tempering of template shell, and removal of the template.

For the past few decades, researchers have been working on producing MCNs with ordered mesostructure by employing templating approaches (Table. 1).³⁰ Typically, there are two types of templates: “hard” templates and “soft” templates. Hard templates employ solid, rigid materials to define the size and shape of the sample, whereas soft templates typically have no fixed structure and are in a fluid state. The synthesis of nanomaterials using templates has progressed to a breakthrough stage since the 1990s. Introductory in 1999, Ryoo *et al.* synthesized mesoporous carbon by using MCM-48 silica as template material, which is merely a hard template approach.³¹ Lee *et al.* asserted a co-assembly approach i.e., a soft templating way to transform nonporous substance into an extremely ordered mesoporous framework.³² This review provides an overview of the templating and non-templating methods used to produce mesoporous carbon nanomaterials.

SYNTHESIS OF MESOPOROUS CARBON

The crown jewel of mesoporous stuff is mesoporous carbon, which is thus extensively applied in energy storage,³³ drug delivery (Table. 1),^{34,35} catalysis,³⁶ and other fields. Predominantly, there are two methods to form well-ordered mesoporous carbon nanomaterials that can be used: the hard template method, also known as the nano-casting approach, and the soft template method, also known as the co-assembly or supramolecular self-building approach. Presently, new template-free techniques are also used to produce mesoporous carbon nanomaterials, such as hydrothermal³⁷ or mechanochemical (Table 1)³⁸ techniques. Templating techniques are typically used to dope heteroatom in the structure of carbon mesopores. Mesoporous carbon nanomaterials (MCNs), their genesis, synthesis process, functionalization, etc., have been the subject of numerous research studies. In this article, we will discuss the most recent developments in MCN synthesis techniques. The various synthetic techniques for mesoporous carbon are depicted in Figure 1.

1. Hard Template Method

In this approach, we obtain a carbon copy of a well-ordered mesoporous solid template material that serves as a mold. A mold is something that has an appropriate size, shape, and hollow inside of which liquid material is poured and then allowed to set, leaving a molded picture. The hard template is a method where template material is in solid form. Synthesis of the hard templating method entails the following steps: (a) the creation of a rigid template made of well-ordered mesophase silica

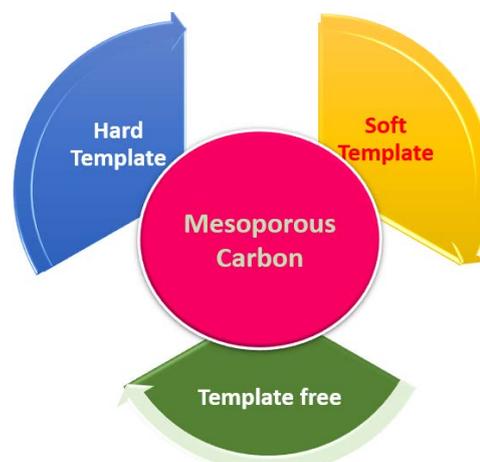


Figure 1: Different ways of synthesis of mesoporous carbon.

(b) infiltration of required carbon precursors into template material, involving the solidification of precursor (c) the template is eliminated. The hard template method is also known as the exotemplate method. The first and foremost stage in the hard template manufacturing process is a regular addition of silica precursors in liquid form to a homogeneous solution containing surfactant. Interlinkage between the silicate precursor and the surfactant causes the production of rod-like micelles, and the hexagonal phase is produced by encapsulating rod-like micelles that have been covered in silica. The subsequent hydrolysis and polymerization of the silicate precursor produced silica walls. Followed by precipitation and filtration resulting in a solid product. After the mesophase silica hard template synthesis is complete, the surfactant is removed by the calcination procedure, yielding the desired hard template material. Secondly, infiltration of carbon precursor into the pores of the mesoporous hard template could be done by the impregnation method or chemical vapor deposition method. The impregnation procedure provides a comparably simplistic task to exactly reproduce the image of the hard template. Consequently, the hard templating synthesis method or exotemplate method requires acid treatment for the withdrawal of hard template silica material.^{39,40} The general methods for producing mesoporous carbon are shown in Figure 2.

The class of silica-based hard template namely MCM-41 is a mesoporous framework comprised of the typical composition of cylindrical mesopores, that mold a unidimensional pore system. It has a high surface area, variable pore volume, and adaptive pore size. MCM-41 has mesopores in the range of 2 to 6.5 nm.^{41,42} The pore size can be potentially tailored by differing reaction precursors and conditions such as hydrothermal reaction conditions, pH value, and removal of the template. One more mesoporous silica sieve is SBA-15 with homogeneous hexagonal pores and small pore size distribution. SBA-15 has a tunable pore diameter between 5 to 15 nm. It has a high surface area of 400-900 m²g⁻¹ and strong mechanical and thermal stability (Table. 1).⁴³ The following are certain benefits of hard templates. The size, form, and configuration of nanomaterials formed by

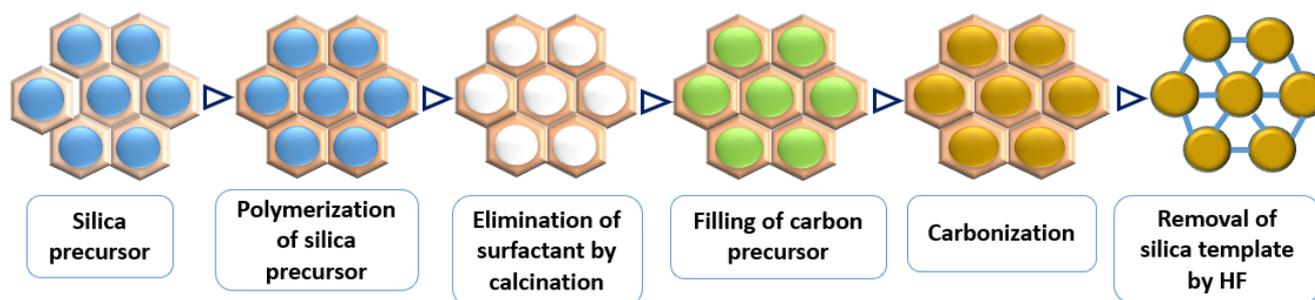


Figure 2: Schematic diagram of a hard templating pathway to synthesize mesoporous carbon.

template procedures are typically well-defined, which is generally advantageous. The meso-channels are filled using the hard template technique. Due to the hard template's resistance to high temperatures, hard templating can therefore produce a variety of materials, especially ultimate crystals in addition to even single-crystal substances. The hard templates are capable of sustaining and supporting nanomaterial grain development. X. Deng and K. Chen *et al.* reviewed the entire procedure that conceals the synthesis of broadly used ordered mesoporous hard templates such as MCM-41, SBA-15, and KIT-6. They discussed the use of hard templates in the synthesis of templated transition metal oxides and factors influencing the synthesis of hard mesoporous templates, such as mold growth, which play a significant role in the synthesis of hard templates. Additionally, the series of techniques colloidal crystal template creation, soft template creation, and bioinspired template creation modifies the template to introduce changes to the functionality and morphology of the replica.⁴⁴

The development of the hard template-based approach for the synthesis of ordered mesoporous carbon nanomaterials (MCNs) was evaluated by Vinu *et al.* In recent times, Vinu *et al.* reported the synthesis of mesoporous carbon nitrides with a 3D porous arrangement from the unimolecular precursor, 5-amino-1H-tetrazole with diverse stoichiometries like g-C₃N₄, C₃N₅, C₃N₆, C₃N₈ by utilizing KIT-6 as a hard template. With the controllable variation in the calcination temperature, the nitrogen contents in mesoporous carbon nitrides and their chemical composition were finely graduated (Table. 1).⁴⁵ B. Karimi *et al.* reported a well-projected exotemplate approach for the synthesis of magnetically detachable ordered mesoporous carbon codoped with a set of nitrogen and sulfur by using SBA-15 as a hard template and imidazolium-based ionic liquid and guanine as a carbon and nitrogen source respectively (Table. 1).⁴⁶

2. Soft Template Method

The soft template method is also named an endo-template method. In addition to the hard templating approach, the soft templating process has currently received widespread approval for the synthesis of a variety of mesoporous carbon nanomaterials. Endotemplated mesoporous carbon is molded by

coaction within i.e., micelle formation between amphiphilic surfactants and phenolic carbon precursors. The same micelle formation strategy ensued in the leading steps of the hard templating approach which assimilates rod-like micelle formation and ultimately reforms into the hexagonal arrangement. Advancing amphiphilic surfactant subsists hydrophilic and hydrophobic end that enforces to form micelle in the relevant solvent system. The surfactant micelles and phenolic carbon precursors are linked over weak coordination like hydrogen bonding or electrostatic interactions. Moreover, the hydrophilic end of the micelle structure is positioned toward the verge, whereas the hydrophobic end is aligned with the center. Meanwhile, a suitable phenolic carbon precursor is added to the reaction medium; it then undergoes polymerization by hydrogen bonding with the hydrophilic end of the micelle or the outer section of the structure. Mesoporosity is generated from the hydrophobic part of the micelle which has not interacted with carbon precursors. An ordered mesoporous structure results from the supramolecular assembly of a micelle formed. At the end soft template material, nothing but surfactant is removed by pyrolysis or carbonization and the remaining carbon precursor yields an ordered mesoporous carbon framework with a prescribed shape, size, and morphology.^{47,48} While employing a soft templating method, the interaction between the structure-directing compounds as well as the nitrogen source as a fundamental parameter is the most crucial factor to keep in mind. With advantages like its high reproducibility, accessibility, and potential for self-assembly of precursor materials like copolymers as well as carbonaceous materials, the soft template possesses enormous potential for advancement in the synthesis of nanomaterials. Surfactants and other amphiphilic compounds

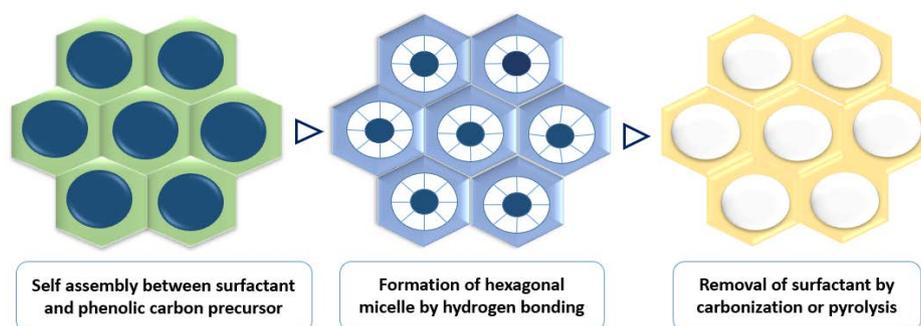


Figure 3: Schematic diagram of a soft templating pathway to synthesize mesoporous carbon.

were frequently employed as soft templates in the construction of structured mesoporous materials.⁴⁹ Herein, no supplementary step is needed for the removal of template material. A cluster of surfactants such as Brij surfactants, Pluronic surfactants like P127 and P123, CTAB (Cetyl trimethylammonium bromide), Triton X-100 are used as cast (mold) for the synthesis of mesoporous carbon nanomaterials by soft templating pathway. The experimental process used to manufacture mesoporous carbon using a soft template is illustrated in Figure 3.

Chen *et al.* expand the effective synthetic application of the soft templating method for the synthesis of the metal counter electrode. Their group creatively evolved a synthetic scheme by interpolymerization between resorcinol and melamine with formaldehyde under distinct conditions. The melamine-formaldehyde-resorcinol resin is a carbon-nitrogen source and F127 is a soft template to synthesize nitrogen-doped mesoporous carbon (Table. 1).⁵⁰ X. Wang proclaimed the synthesis of nitrogen-doped mesoporous carbon nanoparticles (NMCs) by direct carbonization method using F127 (triblock amphiphilic copolymer) as an endo-template and chitosan as a carbon-nitrogen source. Additionally, NMCs have a specific surface area of 804 m²/g and 0.87 cm³/g pore volume and they expedite oxidative modification where surface area decreased to 322 m²/g and pore volume of 0.63 cm³/g contrived for the adsorption and release study of hydroxycamptothecin drug (Table. 1).⁵¹

3. Template-free methods

Indeed, there are innumerable reports on the synthesis of ordered mesoporous carbon nanomaterials (MCNs) by hard template and soft template approaches to generate mesoporosity in the carbon framework.⁵² The template-based approach endures a few pitfalls such as a lengthy synthesis course of action with template material and monotonous template removal tasks. In addition, uneconomical is the prime obstacle to large-scale production and application of mesoporous carbon material by templating methods. Consequently, many endeavors have been made to synthesize MCNs by a template-free approach. The template-free method as the name itself admires that there is no inclusion of any template material in the synthetic procedure of MCNs. In this template-free approach, the synthesis strategy depends on the laboratory probing settings that encompass thermal, mechanochemical, and sonochemical conditions. However, this approach has been procuring colossal significance due to time saving and cost-effective synthesis procedure of MCNs. Nevertheless, it has been still effortful to synthesize MCNs by a template-free method due to weak structural properties and it is under continuous evolution. The following are some benefits of template-free techniques. The template-free approach is distinct from the prior templating synthesis in that numerous surface-step defects have been seen on the surface of the nanostructure. It has been demonstrated that these defect-rich nanostructures have enhanced catalase as well as peroxidase-like activity, 130 times more potent than the commercial version and 10 times more active than mesoporous nanostructures constructed from hard templating. Without any templates, the removal of tiny molecules like CO₂ and H₂O causes mesoscopic porosity in size from 3 to 8 nm.⁵³ Henceforth, it is essential to

study and appraise the template-free methods that are environmentally benign and can be employed for the huge production and commercialization of mesoporous materials. In this stratagem, we will compile some template-free methods for the synthesis of mesoporous carbon nanomaterials. The different template-free methods for the synthesis of mesoporous carbon as displayed in Figure 4.

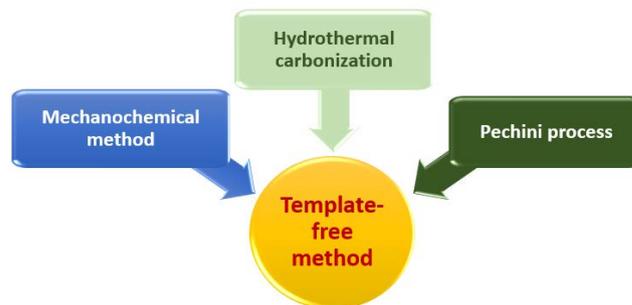


Figure 4: Template-free methods for the synthesis of mesoporous carbon.

3.1 Mechanochemical method

The ideal templating synthesis methods of mesoporous materials are time-consuming and toxic chemicals like HF have been used for the elimination of hard template material. Hence, eco-friendly methods such as the mechanochemical method could be replaced by classic template-based methods. In this method, shearing, grinding, milling, and compression would generate mechanical power.⁵⁴ Due to solvent-free reaction conditions or the use of limited solvents, low-cost and ecologically friendly synthesis stages, and quick reaction times, this technology permits quick and significant solid-form synthesis. (Table. 1).⁵⁵⁻⁵⁸

Hereunder, the synthesis processes are simple and easy to follow. The carbon precursor and the rest of the ingredients such as linkers or metal salts are added to the milling machine and supplemented with milling balls for a certain period. After completion of the reaction, the milled stuff from the milling machine was subjected to carbonization deprived of any secondary steps. The carbonization could be carried in the inert tubular furnace which outcomes hierarchical porous carbon materials.^{59,60} In particular, the subsequent methodical concern should be taken into consideration while performing ball milling techniques such as (1) quantity of milling substratum (2) size, density, number, and material of milling balls (3) momentum of balls and period of milling. In this synthesis strategy, the ball milling duration has been the key determining factor.^{61,62} D. Leistenschneider *et al.* evinced synthesis of ordered porous carbon in the solvent-free environment by ball milling procedure. It was their first testimony that explicit definite porous structure of carbon by solid-phase ball milling set up. Their group carried out a mechanochemical reaction between ethylene glycol, citric acid, and titanium isopropoxide in the ratio of 3:1:1. They claimed that the colour change in the reaction mixture proved the mechanochemical reaction was complete. And retrieved titanium citrate polymer treated with chlorine treatment to remove titanium as TiCl₄ to achieve ordered porous carbon with a high

surface area. The procured carbon with a high specific surface area and high capacitance has been applied as electrode material in supercapacitor application (Table. 1).⁶³

Currently, a wide range of equipment, including shakers, balls, extruders, cryo-mills, and drums, are used to perform mechanochemical reactions. A mortar and pestle are among the above simple and easy-to-use tools, but it is not recommended due to the possibility of contamination and the weakened reproducible sustaining state of the grinding material. The electromechanical synthesis strategy promotes the contamination-free synthesis environment and homogenous disintegration of the reaction mixture.⁶⁴

Nowadays, templating techniques of porous carbon have been relocated by a solid-state ball milling mechanism. W. Xiao *et al.* overwhelmed the limitation of the wet template-based synthesis method by the mechanochemical exotemplate method and developed a solid-phase synthesis strategy for porous metal oxide by the ball milling process. They demonstrated a simple method and perfect integration of template-assisted mechanochemical synthesis techniques.⁶⁵ C. Schneidermann and the group reported the one-pot quick and extensible solvent-free synthesis of nitrogen-doped porous carbon by intense milling of industrial waste material lignin as a carbon precursor, urea, and potassium carbonate as nitrogen source and activation agent respectively.⁶⁶ Thus, the mechanochemical synthesis route stands up for ascendable, economical, time-saving, and eco-friendly synthesis processes. Figure 5 depicts the graphical diagram of materials that were synthesized using a mechanochemical process.

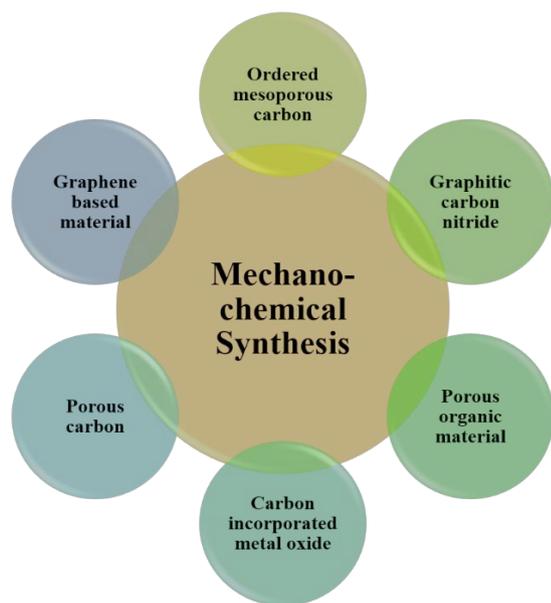


Figure 5: Pictorial diagram of mechanochemically synthesized materials.

3.2 Hydrothermal carbonization

In modernistic synthesis strategies, hydrothermal carbonization (HTC) has been gaining remarkable importance due to the production of inexpensive, environmentally friendly porous material from reused biomass.⁶⁷ Currently, mass

production of sustainable products and renewable energy are both essential. Additionally, hydrothermal carbonization supports the development of effective methods and tools for the synthesis of porous materials that are environmentally friendly. The name hydrothermal carbonization (HTC) itself reveals the thermal treatment of reaction mixture in liquid media under desired pressure.^{68–71} The general HTC synthesis procedure entails, the aqueous solution of dissolved biomass has been sealed in stainless steel Teflon autoclave and subjected to heat around 160–220 °C in a muffle furnace for a specified period. After the reaction was completed, the carbon precipitate was recovered by centrifugation and repeatedly rinsed with water and the appropriate solvents. And the perceived carbon is dried in an oven and carbonized in the tubular furnace under a nitrogen environment which results in a porous structure. Further activated carbon could be doped with any element and applied in diverse fields.⁷² In the interim of hydrothermal carbonization, water serves as a solvent and promotes the hydrolysis and breakage of biomass. The high temperature and pressure of a Teflon-lined autoclave enforce hydrolysis of organic biomass. The following specifications would be taken into consideration while performing HTC the concentration of cellulose or biomass used, temperature, duration of reaction, and catalyst used (Table. 1).⁷³ The pore size, shape, and morphology of porous carbon can all be modified by changing the aforementioned characteristics.^{74–76} S. Nicolae *et al.* examined recent progress and accomplishment in hydrothermal carbonization from renewable green biomass and its conversion into environmentally friendly energy.⁷⁷ W. Zhao *et al.* described the synthesis of new adsorbent mesoporous carbon with high surface area by HTC using sodium lignosulfonate as a carbon precursor and Cetyl trimethylammonium bromide (CTAB) as templating material. The synthesized carbon had been applied in the adsorption study of uranium from radioactive wastewater (Table. 1).⁷⁸ Therefore, hydrothermal carbonization (HTC) provides an economical, potent, and eco-friendly synthesis pathway of mesoporous carbon from environmental waste biomass material. Figure 6 illustrates the hydrothermal synthesis of mesoporous carbon.



Figure 6: Schematic diagram of hydrothermal synthesis of mesoporous carbon.

3.3 Pechini process

The pechini process is an alternative and a modified form of sol-gel chemistry. Pechini method is also named a liquid-mix process. This technique gets over the drawbacks and imperfections of the sol-gel mechanism.

Table 1: Different techniques of synthetic methods of mesoporous carbon, experimental conditions, and its special features.

Sr. No.	Type of carbon nanomaterial synthesized	Method of synthesis	Reaction precursor	Experimental Conditions	Properties of MCNs (Surface area, size, etc.)	Applications	Ref.
1	Two dimensional (2D) mesoporous carbon material	Simple carbonization process	p-conjugated C ₆₀ -micro sheets (C ₆₀ -MSs)	Carbonization at 1000°C under nitrogen atmosphere	Specific surface area of FMS1000 = 1507.6 m ² g ⁻¹ , pore size of FMS1000 = 1.7nm (microporous) and 4nm (mesoporous)	Energy storage and electrochemical catalysis	6
2	Ordered mesoporous carbon (MCS)	Hard template method (SBA-15)	Carbonated soft drink Coca-Cola	Carbonization at 900°C for 5 h under nitrogen atmosphere	High surface area = 1635 m ² g ⁻¹	CO ₂ adsorption	8
3	Mesoporous carbon hollow sphere (MCHS)	SiO ₂ as template	Silica precursor [tetra propyl orthosilicate (TPOS) or tetraethyl orthosilicate (TEOS)], resorcinol, formaldehyde	Heated at 700°C for 5 h under nitrogen atmosphere	High surface area of MCHS-TPOS = 1362.4m ² g ⁻¹ , pore size of MCHS-9:1=5.48 nm	Electrocatalysts for oxygen reduction to hydrogen peroxide in neutral electrolytes	12
4	Graphitic mesoporous carbon nitride C ₃ N ₅ (MCN-8)	Nano hard templating method	3-amino-1,2,4-triazole (3-AT)	Self-condensation of 3-AT inside the mesoporous of KIT-6 silica at high temperature	Specific surface area = 286.7 m ² g ⁻¹ , pore size = 3.42 nm	Photocatalytic activity for hydrogen generation and sensing of acid molecules	13
5	Ordered mesoporous carbon (OMCs)	Mechanochemical assembly	Polyphenols, metal complexes, and triblock copolymers	Thermal treatment under nitrogen atmosphere at 450-800°C	Surface area = ~1000 m ² g ⁻¹ , Pore size = ~4-10nm	Catalytic hydrogenation	27
6	Nitrogen- and sulfur- codoped 3D cubic ordered mesoporous carbon (KNOMC)	Nanocasting strategy	KIT-6 as the template and pyrrole as the precursor	Complete carbonization at 650-950°C for 2 h under argon atmosphere	Surface area of KNOMC-650 = 1064 m ² g ⁻¹ , KNOMC-800 = 693 m ² g ⁻¹ , KNOMC-950 = 880 m ² g ⁻¹ , pore size of KNOMC-650 = 6.20 nm, KNOMC-800 = 3.27 nm, KNOMC-950 = 4.29nm	Supercapacitors	30
7	Nitrogen-doped mesoporous carbons (N-OMCs)	Nanocasting method	SBA-15 as silica template, polyamide precursors: m-aminobenzoic acid (MABA) and p-aminobenzoic acid (PABA)	Carbonized using a two-step program under nitrogen flow. First step: 1°C/min at 160°C for 1 h, Second step: 2°C/min up to target temperature (700°C) for 30 min	Pore size maxima at 3.37 nm confirm mesoporous	Drug delivery	34

8	Mesoporous carbon nanoparticles	(Soft template) Hydrothermal process	Phenol as carbon precursor and polystyrene-block-poly (ethylene oxide) (PS-b-PEO) as block copolymer soft template	The reaction was conducted at 160°C for 5 h in an oven set, pyrolyzed at 400°C for 1 h at a rate of 5°C min ⁻¹ and 800°C for 4 h under nitrogen atmosphere	Surface area = 832 m ² g ⁻¹ and pore size = 3 nm	Energy storage	37
9	Alkaline-metal oxide-doped mesoporous carbons (MCs)	Mechanochemical process	Tannin as polyphenol and alkaline metal acetates [Mg(OAc) ₂ or Ca(OAc) ₂]	Mixing and grinding for 0.5 h by using vibrating ball miller and carbonization under nitrogen atmosphere at a heating rate of 5°C min ⁻¹	Surface area = ~571 m ² g ⁻¹ and pore size = ~5-9 nm	CO ₂ adsorption	38
10	Three dimensional hierarchically porous N/O doped carbon foam (3DHPNCF)	Hard template	SBA-15 as hard template and ethylenediaminetetraacetic acid tripotassium (EDTA-3K)	Heated at 700, 800, and 900°C with a rate of 3.0°C min ⁻¹ under nitrogen flow for 1 h	Surface area = ~1481-2578 m ² g ⁻¹ and pore size mainly between 2.0-8.0 nm	Supercapacitors	43
11	Ordered mesoporous carbon nitrides (MCN)	Hard template	KIT-6 as hard template and 5-amino-1H-tetrazole	Carbonization temperature altered from 350-550°C	Surface area = ~101.8-148.5 m ² g ⁻¹ and pore diameter = ~3.25-5.8 nm	Basic catalytic activities on Knoevenagel condensation	45
12	Nitrogen and sulfur-doped ordered mesoporous carbon	Hard template	Imidazolium based ionic liquid as carbon source, guanine as nitrogen source, FeCl ₃ as the iron source, and SBA-15 as hard template	Heated in argon atmosphere upto 800°C (5mL min ⁻¹)	Surface area = ~401 m ² g ⁻¹ and pore size = 3.3 nm	Aerobic oxidation of alcohols	46
13	Cobalt phosphide highly nitrogen-doped mesoporous carbon (CoP-NMC)	Soft template	Melamine-formaldehyde-resorcinol as carbon-nitrogen cosources and F127 as soft template	Pyrolyzed at 900°C under argon atmosphere for 1 h	Surface area = 529 m ² g ⁻¹ and mesopore size 4.2 nm	Electrocatalyst for highly efficient dye-sensitized solar cells	50
14	Chitosan-based nitrogen-doped mesoporous carbon (NMCs)	Soft template	Chitosan as carbon-nitrogen source and F127 as a soft template	Heated at temperature 410°C under nitrogen atmosphere at a rate of 2°C/min, thermal insulation for 2 h and then temperature increased to 900°C at a rate of 5°C /min for 2 h	Surface area = 804 m ² g ⁻¹ and pore size = 2-4nm	Adsorption and release of drug hydroxycamptototecin	51

15	Nitrogen-doped mesoporous carbon materials	Mechanochemical coordination assembly	Tannin as carbon source, natural nitrogen precursors and F127	Carbonized at 450°C at a heating rate of 5°C min ⁻¹ for 2 h under nitrogen atmosphere and continued heating up to 800°C for another 2 h	Specific surface area = ~203-707 m ² g ⁻¹ and pore size = 7-10nm	Gas sorption	57
16	Hierarchical porous carbon	Mechanochemical method	Ethylene glycol (EG), citric acid (CA), and titanium isopropoxide (TIPP)	Carbochlorination at 900°C	Specific surface area = ~1814 m ² g ⁻¹ and mesopore diameter = 8nm	Supercapacitors	73
17	Nitrogen-doped mesoporous carbon	Template free approach	Citrate salts (calcium or zinc) and melamine	Heated up to 800°C under nitrogen atmosphere at a heating rate of 3°C min ⁻¹ for 1 h	Specific surface area = ~1190-1350 m ² g ⁻¹ and mesopores size = ~11 nm	Oxygen reduction reaction (ORR) catalysts	73
18	Mesoporous carbon	Hydrothermal and template method	Sodium lignosulfate (LSs) and cetyltrimethylammonium bromide (CTAB) as templating agent	Calcined at 800°C at a heating rate of 5°C min ⁻¹ for 2 h under nitrogen atmosphere	Specific surface area of Carbon-LSs+CTAB = 633.14 m ² g ⁻¹ and Carbon-LSs = 66.734 m ² g ⁻¹ , pore size of Carbon-LSs+CTAB = 4.589 nm and Carbon-LSs = 5.171 nm	Adsorption of uranium (VI)	78
19	Mesoporous carbon foam (MCF)	Template free method (Pechini method)	Citric acid (CA) and ethylene diamine tetraacetic acid (EDTA) as carbon source and magnesium nitrate as chelating mediators and cation precursors	Calcined at 900°C for 60 min under argon atmosphere	Specific surface area = 1435.65 m ² g ⁻¹ and pore size = ~5-10 nm	Electroanalytical determination of epinephrine in the presence of uric acid	81

For the last few years, the pechini method had been employed for the synthesis of mesoporous carbon materials (Table. 1).⁷⁹⁻⁸¹ The process is governed by chelate formation between dissolved salts i.e., metal cations and hydroxycarboxylic acid ideally citric acid is used. Esterification of chelated acid and polyalcohols results in gel formation. In the actual synthesis procedure, a uniform solution of metal precursor and carboxylic acid is prepared by sonication. The prepared sol is heated in an oven, and the gel that forms is then calcined under inert gas. To remove any decomposed metal precursor material, the obtained carbon must be neutralized. The pechini method produces porous carbon at a low cost and has potential applications in a variety of sectors including adsorption, catalysis, and battery technology.⁸²⁻⁸⁴ M. Jahanbakhshi *et al.* reported the synthesis of mesoporous carbon foam (MCF) by the pechini method and fabricated a biosensor to determine H₂O₂ concentration from the samples of fetal bovine serum.⁸⁵ This research could be expanded in the future by altering the reactants, such as chelating agents and metal precursors, under more favorable conditions.^{86,87} Figure 7 depicts a summary

of the pechini method-based mesoporous carbon preparation procedure.

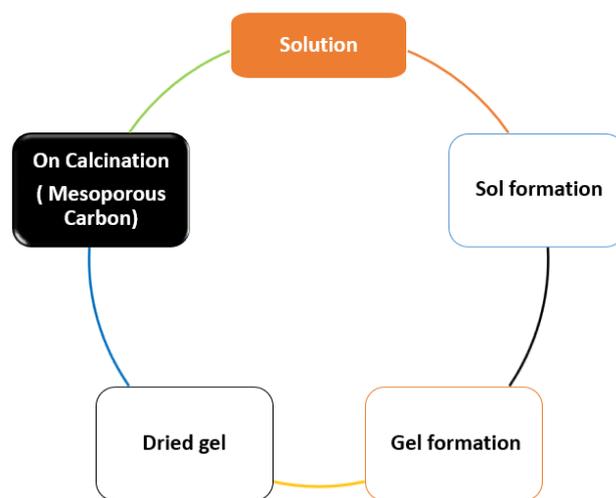


Figure 7: The preparation process of mesoporous carbon based on the pechini method.

3. Comparability between hard template, soft template, and template-free methods

In hard templating strategy, hitherto framed materials like zeolites, and mesoporous silica are used as a template for the introduction of mesoporosity in solid carbon materials. In this process, the casting mold is filled with suitable carbon precursor and after a certain period, the time mold is eliminated resulting negative image of the mold. A hard templating method can be used to effectively produce ordered mesoporous carbon. The hard template-based synthesis's key benefit is its ability to manipulate the morphology and structural characteristics of carbon-based materials. However, the elimination of the hard template used in the synthesis procedure is not eco-friendly i.e., hazardous chemical like HF is used to etch away exotemplate material, and detachment of mold can lead to harm to the mesoporous structure formed.

The organic-organic self-assembly of polymers by electrostatic or hydrogen bonding is the basis for the soft templating method. Compare to other synthesis strategies, ordered mesoporous carbon can be directly synthesized by co-assembly among polymerizable reactant and copolymer template material. In this soft templating synthesis, mold is formed internally i.e., hexagonally micelle formation between the surfactant and phenolic precursor while in a hard template, externally presynthesized mold is used. Mesoporosity is produced in this case as a result of the carbonization of the micelle's hydrophobic region. In contrast to hard templates, which involve complex synthesis conditions, soft templates are simple to manage. Template removal is also easier in soft templates simply by pyrolysis or carbonization, unlike the hectic and hazardous process in a hard template. Therefore, for producing porous structured materials, a soft template may be favored over a hard template. However, upcoming template-free methods are also capable of producing mesoporosity in carbon-based materials. Yet, compared to non-templating approaches, the templating mechanism is time-consuming, expensive, and lengthy. In template-free methods, there is no involvement of any template material, it totally depends on experimental settings that are environmentally benign and low-cost. Non-templating methods have been earning immense importance to synthesize mesoporous carbon as no complexity of expensive templates and hazardous chemicals. The majority of the time, hydrothermal carbonization or a mechanochemical process has been used to produce porous carbon from environmental waste biomass (HTC). Since template-free approaches follow the green synthesis pathway, they are currently more important to develop and comprehend than template-based methods.

CONCLUSION, CURRENT CHALLENGES, AND FUTURE PROSPECTS

In this article, we have reviewed synthetic methods of mesoporous carbon nanomaterials. Speedy development in the template-based synthesis methods of MCNs with well-structured pore size, shape, and morphology subjugate the classical synthesis method. In addition to their remarkable structural qualities, which we have already discussed in this paper, such

as their high surface area, and tunable pore size, they can also expand their viability and attainability in a variety of fields. Templating methods are advantageous in synthesizing uniform and ordered structure, even though it has some drawbacks of extortionate chemical prices, complications in the removal of the template, and the possibility of the destruction of the ordered porous structure of carbon after the elimination of the template. Here, we have also focused on substituted methods to template-based synthesis that are non-templating ways that are economical and most important environment benign from natural biomass. It is still necessary to develop template-free techniques for creating hierarchical porous structures.

In this phase of the development of material science, template-based techniques are essential. The search for low-cost and environmentally benign template materials is the impulsion of people working in this field. Nowadays, non-templating pathways are also gaining equal importance and accomplishment as templating ways. Undeniably mesoporous carbon is acquiring the interest of material chemists as they are burrowing advanced development in their structure and applications. So, there is a requisite for new studies and exploration of templating and non-templating methods in the field of porous materials synthesis.

In the review report, we summarize the different synthetic methods for mesoporous carbon by different strategies across the world. The subject of carbon and its derivatives has been the subject of more than a thousand research articles, and various organizations are currently engaged in research in this area. However, the purpose of the current paper is to investigate the most recent advancements in mesoporous carbon employing a variety of templates and template-free techniques. Therefore, we reviewed study on the synthesis of mesoporous carbon around the globe.

Abbreviations

- MCNs: Mesoporous carbon nanomaterials
- NMC: Nitrogen-doped mesoporous carbon
- HTC: Hydrothermal carbonization
- MCF: Mesoporous carbon foam
- MCHS: Mesoporous carbon hollow sphere
- OMC: Ordered mesoporous carbon
- MCN: Ordered mesoporous carbon nitride

AUTHORS CONTRIBUTIONS

Sneha R. Bhosale constructed the idea and collected the data for review, and writing, and Rakhee R. Bhosale and Kishor S. Jagadhane participated in the alignment and drafting of the manuscript. Also, Sanjay S. Kolekar and Govind B. Kolekar resources for this review article. Prashant V Anbhule supervised the work as well as finalized the drafting, and Anil H Gore critically reviewed and suggestions in the manuscript. All the other authors contributed to and read the manuscript meticulously.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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