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Polymer-templated films of ordered mesoporous carbon: preparation, characterization and applications

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Ordered mesoporous carbons (OMCs), typically prepared as fine powders, provide a striking combination of beneficial properties, which can be considered as crucial for many current and future technological applications. These properties, which include light weight, high surface areas, tunable pore sizes and pore arrangements, variable surface chemistry and electric conductivity, can be further boosted if more complex OMC morphologies are realized. Perhaps most rewarding in this regard are film-like structures, either as defined layers on specific surfaces or even as self-supporting, free-standing films/membranes. Such materials are of high relevance, yet their synthesis and characterization is also significantly more demanding than powder formation. As a consequence, this research field is only just emerging and the number of publications describing self-supporting and well-defined OMC film structures is still rather limited. The presented mini-review thus aims to highlight this exciting type of material in a compact manner, focusing on aspects of synthesis, characterization and applications, with the overall aim of encouraging further research efforts. Such efforts are particularly dependent on the polymer community, as the realization of well-defined OMC properties very much depends on polymers (e.g., as templates) and polymerization processes (e.g., cross-linking of carbon precursors). The translation of well-defined template block copolymers into well-defined OMC properties (especially pore size and pore geometry/connectivity) is an ongoing research focus, which is highly important for film morphologies.

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Introduction

The preparation and application of nanostructured, porous carbon materials, including in particular ordered mesoporous carbons (OMCs), has attracted considerable interest in recent years.^{1–3} This is down to a straightforward synthesis, an array of beneficial properties and numerous applications, which together make these materials attractive. Applications include, among others, the employment of mesoporous carbons as sensors,^{4,5} drug delivering matrices,^{6,7} electrodes,⁸ catalyst supports^{9,10} or adsorbents for purification processes.^{11,12}

Such broad usage is only possible since many of the OMC key properties are also well tuneable. This is true for surface areas,^{13,14} pore sizes (2–50 nm, by definition mesopores),^{15–17} pore arrangements (e.g., hexagonal, gyroidal, etc.),^{16–19} pore volumes,²⁰ surface chemistry and surface polarity,^{21,22} electric conductivity (heavily dependent on heteroatom content and carbonization temperature)^{23–25} and density.^{26,27} While adaptation of these properties is not always trivial – precise control

can be defeated by distributions (such as pore size distributions) or gradients (of, e.g., surface functional groups) – these tuning sites nonetheless allow for highly specialized and optimized OMC products.

On top of these advantageous aspects, the preparation of OMCs can also be relatively simple, at least from the chemical point of view. For example, the popular soft-templating^{28,29} approach requires only a carbon precursor (most frequently based on very well-established phenolic resin chemistry or readily available carbohydrates), a template (typically an amphiphilic block copolymer, which may be commercial) and a suitable solvent (e.g., ethanol). Further preparation is then largely covered by thermal treatment, which can also be done on a somewhat larger scale. Interest in OMC materials is therefore well founded and will certainly continue to grow.

One particularly promising area of OMC research is that the corresponding materials can be realized as powders,^{30,31} discrete particles,^{32,33} monoliths^{19,34} or films.^{25,35} Especially the latter type seems rewarding for a number of reasons.

Firstly, successful OMC film preparation can render the use of so-called binders obsolete.^{25,35,36} Binders are typically polymers, which are used to glue OMC powders together in film-like layers or coatings (e.g., for making electrodes^{37–39}).

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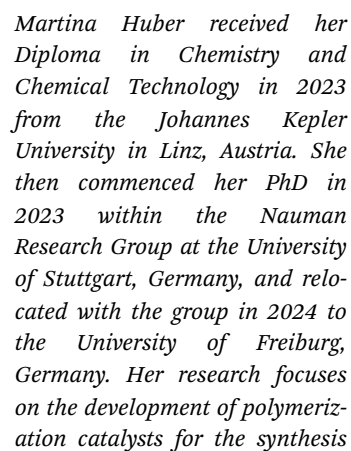


Expectedly, the level of detail with which different publications have examined film properties and/or applications varies considerably, and a full set of properties is rarely given. Nonetheless, wherever possible, film properties (pore sizes, surface areas *etc.*) are provided. Both substrate-supported and self-supported films are included in this work. In some cases, OMC powders are considered for comparison purposes.

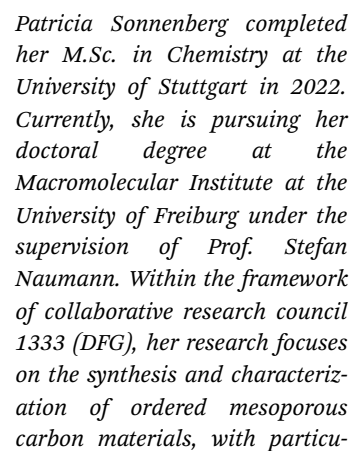
Preparation of OMC films

In principle, OMC film morphologies can be accessed *via* soft-templating,^{15,45,46} hard-templating^{47,48} or even *via* template-free⁴⁹ approaches.

Hard templating strategies involve the use of solid, porous materials (*e.g.* silica) coated and filled with a carbon precursor. The template is then etched to yield the desired porous carbon material as an inverse image of the template structure.^{47,48} However, adjusting the pore size and structure is more complicated because the hard template first has to be adapted, which is often time-consuming. Etching the template also leads to defects and instabilities in the porous structure, which impacts film formation.^{47,48} The etching process is chemically rather harsh and difficult to conduct on a larger scale.



of polymeric SDAs, as well as the optimization of OMC materials.



lar emphasis on OMC film preparation and the development of highly defined support materials with selectively immobilized metal catalysts.

In contrast, template-free methods employ the direct carbonization of citrate salt to yield mesoporous carbon^{50,51} or use methods like molten coassembly⁵² (see also below). This is intriguing, yet more detailed investigations are needed for confident OMC film production this way.

Hence, for well-defined and especially for self-supporting carbonaceous membranes, soft-templating is the superior and preferred methodology. Accordingly, the following focuses on this synthesis route, discussing the major aspects of (a) chemical setup and self-assembly, (b) (film) casting and (c) carbonization. Soft-templating for generating OMCs, developed and pioneered by Dai⁴⁵ and Zhao⁵³ about 20 years ago, is usually employed to prepare powders, so particular attention is paid to modifications of the traditional approach for the formation of film-like layers or self-supporting, crack-free OMC membranes.

Chemical setup and self-assembly

The typical composition of a soft-templating mixture for the preparation of OMCs includes (a) the template, also referred to as a structure-directing agent (SDA), (b) the carbon precursor and (c) a suitable solvent. Additional additives,^{35,54,55} catalysts^{56,57} or dopants^{58,59} may also be added.

As templates, amphiphilic block copolymers are usually employed. Thus, these polymers display hydrophilic and lipophilic blocks of varying lengths; apart from diblocks, triblock architectures are also popular choices for this application. Fig. 1 displays some of the more frequently employed SDAs. It should be noted that the examples given are a selection of a much wider field of templates. The polar blocks are commonly based on poly(ethylene oxide) (PEO)/poly(ethylene glycol) (PEG),^{15,23,60–62} poly(acrylonitrile) (PAN)^{63–70} or polymers with ionic functionalities (e.g., sulfonic groups).^{71,72} PAN, unlike

the others, can fulfill the dual function of being a carbon precursor and the polar block of the SDA.⁶⁶

For the lipophilic blocks, the constitutional variety is significantly larger, ranging from substituted epoxides (propylene oxide (PO),^{15,23,60–62} 1-butylene oxide (BO))⁷³ to various acrylic monomers and poly(styrene) (PS)^{71,72} or even poly(isoprene).¹⁹

Some of the above examples are commercially available, in particular the popular *Pluronic*[®] triblock copolyethers (Fig. 1). These are available in a number of grades (e.g., F127 or P123, among many others) with different HLB (hydrophilic-to-lipophilic balance) values and varying molar masses.^{74,75} Also reversed *Pluronic*[®] architectures (Fig. 1), which display more complex self-assembly behavior, can be used to template OMCs.^{76–79} Another approach for a simple and robust option to create hierarchically mesoporous carbon materials can be achieved by using thermoplastic elastomer blends. By incorporating a triblock copolymer into the matrix of another polymer, followed by crosslinking, mesopores are generated through the controlled removal of the polystyrene component.⁸⁰

The choice of the SDA is a crucial step for successful soft-templating. One of the more obvious requirements is that the template and carbon precursor fit together, regarding polarity and interactions (see below). Moreover, it is essential that the template polymer is well-defined, meaning it should display a narrow molar mass distribution (D_M), as well as highly controlled architectures and end groups. Indeed, the impact of dispersity effects, which have been discussed by O'Reilly and co-workers in detail, can be rather severe for polymeric self-assembly.⁸¹ In terms of OMC formation, such dispersity effects could negatively impact the clean formation of pore arrangements or broaden pore size distributions. Consequently, well-behaved polymerization techniques, such as anionic polymerization or controlled radical polymerization, have proved to be best suited for the synthesis of tailored polymeric SDAs.^{79,82–85}

Apart from molar mass distribution, the architectural purity is also crucial: homopolymer impurities (such as PPO in commercial *Pluronics*[®] or diblock impurities in triblock copolymers⁸⁶) can act as swelling agents for the micellar structures formed during self-assembly or modify the ordered gel phases.

When designing an SDA, the HLB and the packing parameter can provide the first orientation of the desired polymer constitution. The HLB value is defined as the ratio of the hydrophilic mass proportion of the polymer to the total polymer mass.^{87,88} It can thus serve as a quick tool for comparing different SDAs or to undergo systematic variations of the template, for example in order to adjust pore sizes.¹⁵ The well-known packing parameter,⁸⁹ which connects the molecular structure of a surfactant (= SDA in this context) and the geometry of the self-assembled structures, can be useful in a general sense to categorize template polymers. However, it must be considered that the actual structure formation (see discussion below and Fig. 2) occurs in conjunction with the carbon precursor, so looking at the SDA alone is not enough to predict the phase separations and resulting pore structure in the OMC. Also, standard application of the packing parameter may underestimate the impact of some structural features of the template.⁹⁰



Stefan Naumann

Stefan Naumann received his PhD in 2014 as a member of the Buchmeiser Group (University of Stuttgart, Germany). He was granted a DFG research stipend to join Prof. Andrew P. Dove at the University of Warwick (UK) as a postdoc. After returning to Stuttgart in 2015, he worked as an independent Research Group Leader and successfully concluded his habilitation in polymer chemistry in 2021. Since 2018 he has been PI in colla-

borative research council (CRC) 1333 ("Molecular Heterogeneous Catalysis in Confined Geometries"). Since 2024, he has been a full professor of macromolecular chemistry at the University of Freiburg, Germany. His current research interests encompass the development of polymerization catalysts as well as the preparation of ordered mesoporous carbon materials and their application in catalysis.



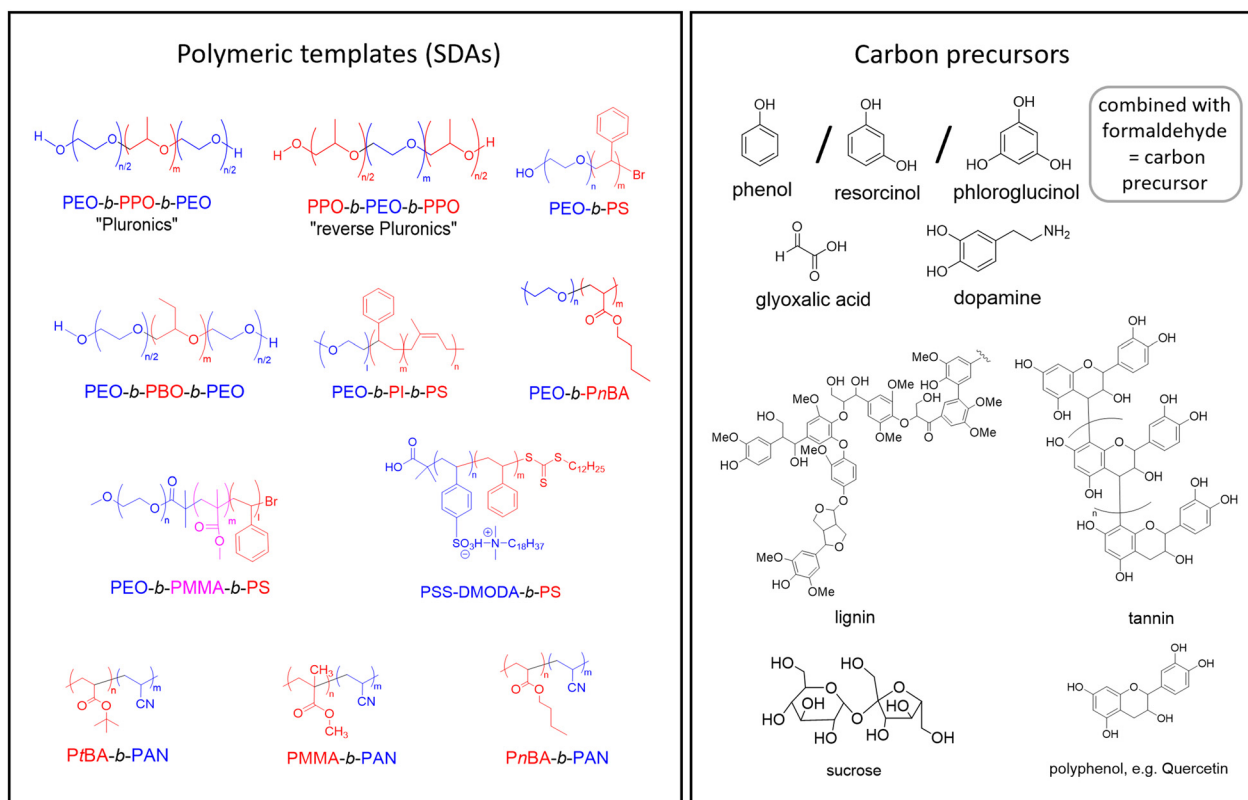


Fig. 1 Left: SDAs that have been employed for OMC preparation *via* soft-templating. Red = lipophilic, blue = hydrophilic moieties. PEO: poly(ethylene oxide), PPO: poly(propylene oxide), PS: polystyrene, PEA: poly(ethylene adipate), PSS-DMODA: poly(*N,N*-dimethyl-*n*-octadecylammonium *p*-styrenesulfonate), PBA: poly(*n*-butyl acrylate), PtBA: poly(*tert*-butyl acrylate), PAN: polyacrylonitrile, PMMA: poly(methyl methacrylate), PI: polyisoprene. Right: Frequently applied carbon precursors.

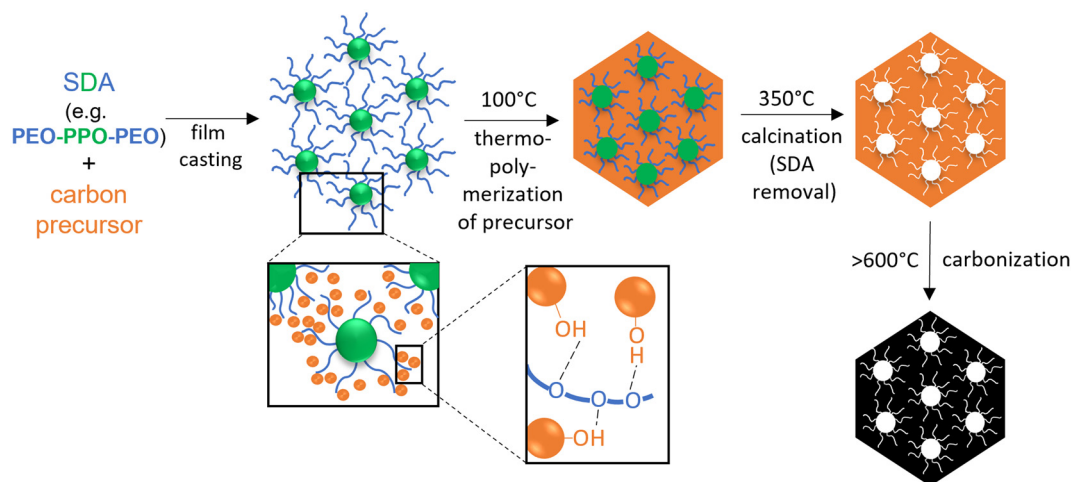


Fig. 2 Scheme of SDA/carbon precursor self-assembly through the soft-templating process, according to Dai.⁴⁵

The carbon precursor is the second crucial addition to the soft-templating process. While carbon precursors are usually chemically simple and well-available components (Fig. 1), their role is actually quite complex, because they have several requirements to fulfill. Firstly, the carbon precursor must

interact with the SDA in a selective manner, in order to enable well-defined self-assembly. Selective in this regard typically refers to an exclusive interaction with the polar part of the template polymer (e.g. PEO), for example *via* H-bonds⁴⁵ (Fig. 2). Thus, the carbon precursor will not migrate into the lipophilic,



The third critical component of soft-templating OMCs is the applied solvent. The most straightforward way to create a film-like structure that can later be carbonized is soft-templating *via* evaporation-induced self-assembly (EISA).¹⁰⁶ This requires the mixing of the SDA and carbon precursor in a solvent that readily evaporates and competently dissolves the other components. Very frequently, ethanol^{35,102} is used for this purpose. After casting the mixture *via* a suitable method on a fitting substrate (next section), the solvent evaporates, entailing a growing concentration of SDA and carbon precursor, upon which self-assembly (Fig. 2) takes place. The residue is typically a soft film that later needs to be thermally stabilized and subsequently carbonized. While polymer self-assembly and soft-templating have been discussed in excellent reviews^{28,31,107,108} and more detailed aspects shall not be reiterated here, it must be noted that the specifics of this process very much depend on the polymer employed. For example, with regard to well-established F127 *Pluronic*®, it has been demonstrated that actual self-assembly is thermally induced¹⁰⁹ (not occurring at the evaporation stage). Rather subtle changes, such as a higher molar mass of the SDA or blocks with a more pronounced bias in hydrophilicity and lipophilicity, can be expected to favor self-assembly at room temperature. *In situ* investigations, for example *via* (GI) SAXS, of the self-assembly processes and their kinetics will certainly prove highly valuable for further development of the field.

After a suitable soft-templating mixture has been created according to the considerations briefly touched above, film casting is the next step. Thereby, a number of techniques can be employed (Fig. 3), depending on the type of desired substrate, viscosity of the casting solution and intended application of the OMC afterwards.

Perhaps the most versatile of these casting techniques is the dip coating process (Fig. 3 (1)). This technique involves the immersion of a device in the soft-templating suspension or solution, thereby enabling the coating of a diverse range of

In a landmark publication, Zhao and co-workers⁹⁷ demonstrated that, using commercial *Pluronic*® templates and resol-type carbon precursor, the resulting pore symmetry (hexagonal, gyroidal and others) could be neatly addressed by adapting the template/precursor ratio. The overall phase separation can be rationalized by considering that the carbon precursor belongs to the polar phase, as do the PEG blocks of the SDA, while the lipophilic phase is constituted by the PPO blocks. This strategy has since been employed numerous times to tailor pore arrangements,^{18,102} including for OMC films (see below), but also to modulate pore sizes.¹⁰³

It should be noted that in some cases the addition of an external carbon precursor (such as resol) can be avoided. This also circumvents complications in the prediction of the pore morphologies formed, as discussed above. One strategy that can be employed utilizes block copolymers for templating in the bulk state, whereby one block of the compound can undergo decomposition under certain conditions.¹⁰⁴ To illustrate this point, consider the previously mentioned PAN-containing copolymers. Following the thermal stabilization of the



devices. Such devices may include wires,¹¹⁰ plates,^{30,111} or foils of varying length.²⁴ The formation of free-standing films represents a challenging issue using this technique, as the entire device is coated during the process, which can complicate delamination of the OMC film formed later in the process. Thus, dip-coating is often used for forming OMC film layers rather than self-supporting structures and is especially interesting for soft/flexible substrates. An instructive example in this regard was published by Vogt and co-workers,²⁴ who coated a sheet of *Kapton* (polyimide) in this way. Subsequent thermal treatment and carbonization delivered a defined OMC layer on the carbonized substrate, as revealed by SAXS and nitrogen sorption. The whole structure was mechanically robust, allowing for gentle bending or cutting. Nevertheless, the most frequently referenced technique in the scientific literature for the fabrication of OMC films is spin coating^{23,25,71,112–114} (Fig. 3 (2)). The process uses centrifugal forces to disperse the soft-templating mixture across the surface of the device through the application of a specific rotational velocity, very often moderate ones such as 500 rpm.¹¹⁵ In general, spin coating can deliver films with higher uniformity than dip-coating, and by adjusting the spin speed it is possible to accommodate very different coating liquid viscosities and to realize different coating thicknesses. Obviously, the substrate scope is limited to flat, rigid structures such as silicon wafers.²⁵

An alternative method for the production of OMC films is the tape casting process³⁵ (Fig. 3 (3)). This technique has also been employed in the context of ceramics,¹¹⁶ within the field of battery research^{117,118} and innumerable other applications. The templating mixture is placed on a flat substrate and distributed through a doctor blading process. The uniform spreading of the suspension across the device is achieved through the application of the blade under constant speed and pressure. This can be used for relatively large surfaces, and defined coating thicknesses can be addressed by regulating the blade–substrate distance.¹¹⁹ For the specific case of OMC films, *Mylar*®-foil has been described as a beneficial substrate choice,³⁵ as it is easily available, flexible (important for OMC film delamination, see below) and, as a polyester (based on poly(ethylene-terephthalate), PET), provides balanced polarity. Moreover, it is thermally stable enough to endure during the cross-linking process, which facilitates easy application, allowing for the film to be effortlessly transferred afterwards. The foil can also be reused.¹²⁰

Techniques that are analogous to the aforementioned process but exhibit a less uniform distribution of material include drop casting^{94,96} (Fig. 3 (4)) and zone casting²⁴ (Fig. 3 (5)). Both of these techniques are based on the pouring of a suspension/solution into or onto a device, and both have been employed to obtain OMC films, for example by Tang *et al.*⁶⁵ The differentiating factor between zone casting and drop casting is the movement of the device on which the suspension/solution is poured. In zone casting, the device is in motion in a single direction, whereas in drop casting, the device remains stationary.

The above methods require casting mixtures containing considerable amounts of solvent. It must be acknowledged that some drawbacks are associated with that, including sustainability and safety aspects of the organic solvents employed, and higher costs in comparison with solvent-free approaches.¹²¹ Established ways to circumvent the use of solvents *via* chemical ball-milling strategies^{121,122} cannot be used if film structures are targeted. Thus, novel approaches are needed. In this regard, obtaining porous polymer films *via* melt shear organization of core-shell particles is promising. An example of this approach for OMC film preparation was published by Gallei and coworkers.¹²⁷

Finally, it must be considered that the thickness of the film that is created by one of the above methods can also impact the self-assembly process (*e.g.*, “thin film confinement”). In a very thin film (*ca.* 100 nm and below), these templating polymer chains are constrained in their ability to arrange freely due to surface and substrate interactions.¹²⁸ The properties and structures of thin films vary with the type of substrate support and interfaces/surfaces. As a consequence, the process is rather complex.^{129,130}

Thermal treatment and carbonization

After casting, the solvent is evaporated, typically for 2–72 h,^{24,25,35} depending on the specific setup and whether information about the self-assembly kinetics is known. If the carbon precursor is of the resol type, which is true for the majority of cases known in the literature, the resulting soft film and the nanophase separated structure is then stabilized by mild thermal treatment. This is usually conducted at 80–120 °C for 24 h^{24,25,35} and results in the cross-linking and more complete polymerization of the oligomeric carbon precursor. Chemically, this corresponds to the hardening of phenolic resins.

This cross-linking step is a delicate matter, in particular if self-assembly and phase separation processes are occurring in parallel. As cross-linking proceeds, the molecular mobility of all components involved is increasingly restricted. The conflicting kinetics of phase separation and cross-linking can therefore negatively impact clear structure formation.¹⁰⁹

Such cross-linking delivers a fixed and stable nanostructure, very often in the shape of off-white or orange-colored layers. These can be removed from the substrate and further processed. This is also where the OMC powder synthesis and OMC film formation fully diverge. For OMC powders, the polymeric, cross-linked film is subsequently shredded or ball-milled and then carbonized.³⁰

For films, on the other hand, it is important that the polymeric layer is uniform and crack-free. This stage is also a good opportunity to delaminate the film from its substrate prior to carbonization.²⁵ Delamination at this point is not a strict requirement for OMC film preparation (including those examples where free-standing films are targeted³⁵). However, carbonizing a structure that is not fixed to a surface has the fundamental advantage of facilitating a crack-free shrinking process (see below).



The polymeric and, in the case of resol carbon precursors, cross-linked film structure is then subjected to further thermal treatment at higher temperatures under protective conditions (e.g., nitrogen or argon atmosphere). Samples treated to 300–400 °C are often referred to as calcined.^{61,71} This process ensures that the template polymers are thermally degraded (forming the mesopores) and a significant mass-loss alongside shrinkage is observed.¹¹² Importantly, the bulk of the material is not carbonized, but still rather polymeric in nature. Treatment to at least 600 °C,^{61,71} but frequently considerably higher, then results in carbonization, forming the black, often shiny OMC films.

During carbonization, the sp^2 -configured carbon bulk is formed,^{131,132} whereby the mass loss from the cross-linked film to the carbonized structure can easily amount to 75%. The subsequent (anisotropic) volume shrinkage puts the film structure under stress, which can result in cracks or even complete fragmentation. This issue is exacerbated when the film strongly adheres to the substrate surface or very fast carbonization is conducted. For carbonization directly on a substrate, the latter must be either able to withstand high temperatures (for example, Si wafers) or degrade in a desired way (e.g., carbonize). Carbonization of a film that has previously been delaminated, on the other hand, often requires protection and “flattening” during the process, which can be ensured by placing the film between carbon papers and ceramic plates.²⁵ This way, rolling-up of the film during carbonization can be avoided.

The specific carbonization temperature has a major impact on the resulting OMC. A higher carbonization temperature generally entails fewer heteroatoms and more sp^2 -configured carbon,¹⁰³ smaller pores,^{103,133} fewer functionalities on the surface (such as hydroxyls) and thus a less hydrophilic surface,²²

higher electrical conductivity¹⁰³ and higher danger of structural collapse.¹⁰⁹ The surface can also be strongly influenced by altering the ratio of reactive to protective gases. For example, introducing varying amounts of oxygen can change the surface functionalities or increase the surface area during pyrolysis.¹⁰³ The majority of papers cited in this review have applied carbonization temperatures in the range of 600–1200 °C.^{24,25,31,35} Importantly, this also means that amorphous carbon is formed (and 5–15% of heteroatoms, usually oxygen, may still be present in the material), in contrast to true graphitization.

Calcination and carbonization are often conducted together in one programmed heating cycle. Very often, these contain plateaus for several hours at 300–400 °C.^{25,35} In particular for film preparation, the dimensions of the gas-tight oven apparatus are important. Especially tube furnaces with a small tubular diameter may be unsuitable to prepare the larger OMC films (typical areas for the self-supporting structures as discussed in this review are 4 cm²).²⁵

After carbonization, the resulting films can be very brittle, which is a major stumbling block for their preparation and application. Zhao and colleagues demonstrated that film thickness is a critical factor determining flexibility and, consequently, mechanical strength. Their experiments involved synthesizing films with thicknesses ranging from 90 to 3000 nm. Their observations indicated that films with high thickness were often rather brittle, while very thin films were obviously fragile.²⁵ In this context, Hou's group demonstrated an alternative method for producing flexible, elastic carbon material through the direct carbonization of polymer foam.¹³⁴

Selected practical examples for OMC film preparation

To illustrate the more general aspects discussed above, Table 1 lists successful published examples of OMC film preparation

Table 1 Examples of syntheses and preparative details for successful OMC film preparation

	SDA	Carbon precursor	Solvent ^a	Casting method	Carbonization <i>T</i>	Pore structure and size	Ref.
1	F127	Phenol + formaldehyde	EtOH	Spin	600 °C	<i>Fmmm</i> ; 4.3 nm	25
2	F127	Phloroglucinol + formaldehyde	EtOH	Tape	850 °C	Worm-like; 5.7–6.4 nm	35
3	F127	Phenol + formaldehyde	EtOH	Dip, tape	800 °C, 1000 °C, 1200 °C	Hexagonal packed cylinders; 5.8 nm	24
4	F127	Phenol + formaldehyde	EtOH	Drop	800 °C	—	123
5	PBA- <i>b</i> -PAN	^b	DMF	Zone	800 °C	Lamellar; —	65
6	F127	Resorcinol + phloroglucinol + formaldehyde	H ₂ O + EtOH	Dip	200–800 °C	<i>Fmmm</i> ; —	30
7	PEO- <i>b</i> -PEA- <i>b</i> -PS	Phenol + formaldehyde	MEK	Spin	800 °C	<i>Ia1d</i> ; 12 ± 2 nm	113
8	PS- <i>b</i> -PSS-DMODA	Phenol + formaldehyde	Not given	Spin	800 °C	Hexagonal packed cylinders; 6–9.2 nm	71
9	F127	TMB ^c	H ₂ O + EtOH	Dip	600 °C	Hexagonal honeycomb; 10 nm	124
10	F127	Resorcinol	EtOH	Dip	800 °C	Different structures (cubic, tetragonal, etc.); 8 nm	125
11	PAN- <i>b</i> -PMMA	^b	DMF	Spin	800 °C	40–50 nm	63
12	F127	Resorcinol + phloroglucinol	H ₂ O + EtOH	Spin	800 °C	<i>Fmmm</i> ; 3.7–4.7 nm	126

^a EtOH = ethanol, DMF = dimethylformamide, THF = tetrahydrofuran, MEK = methyl ethyl ketone. ^b PAN also acted as a carbon precursor. ^c TMB = trimethylbenzene



Another illustrative example (Table 1, entry 3) for OMC film preparation was published by Vogt and colleagues²⁴ in 2013. Here, rather than aiming for a self-supporting film, enhanced flexibility of the OMC structure was targeted. In contrast to the approach taken by Zhao and co-workers²⁵ mentioned previously, who used a PMMA layer to enhance flexibility and avoid fragmentation of the film, in this case a layer of *Kapton* (polyimide, 7.5 μm thickness) was employed as a substrate for

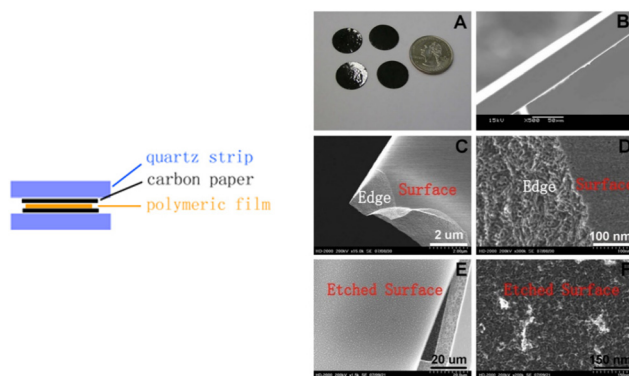


Fig. 5 Left: Sandwich-type-carbonization. Right: Photograph (A) and cross-sectional SEM image (B) of the OMC film. STEM images of as-made (C and D) and surface-etched (E and F) OMC. Reproduced from ref. 35 with permission from Elsevier, copyright 2025.

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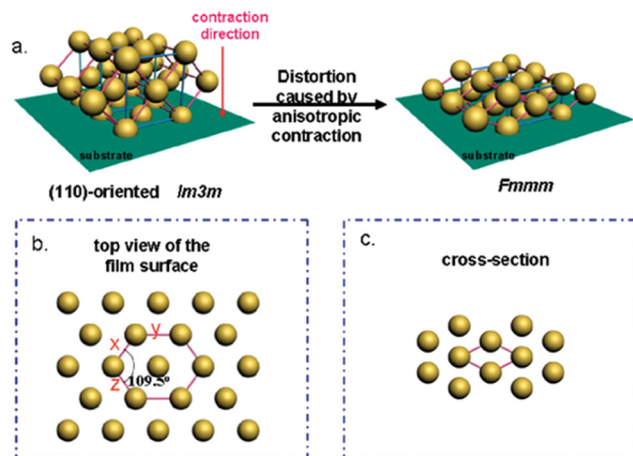


Fig. 8 Illustration of (a) structural transformation of the OMC from $Im3m$ to $Fmmm$ symmetry during carbonization; distorted lattice from (b) the top and (c) cross-section. Reproduced from ref. 25 with permission from ACS, copyright 2025.

the generation of different mesophases (pore arrangements) in the same film layer.¹³⁶

Additionally, it must be considered that mesoporous films are not “monocrystalline” in a way that pore orientation stays truly aligned over large length scales. Rather, different domains and corresponding grain boundaries can be observed (Fig. 9); this is well-described for mesoporous silica materials¹³⁷ and can be assumed to be true for most OMC films, too.

In addition to shrinkage, the formation of a skin layer during the heating process alters the exposed surface both visually and in terms of surface functionality and porosity.^{35,138} This skin layer, which is frequently microporous or nonporous, can have a strong impact on characterization results and film applicability (e.g. permeability, sieving effects, catalyst loading), so it is advisable to check for its existence *via* suitable techniques, for example TEM. Importantly, it has been shown that oxygen plasma etching, a straightforward and relatively simple method, can be employed to remove the skin layer and reveal the underlying pore system.^{97,139}

In summary, the above means that, when reporting OMC film properties, care must be taken to properly portray such deviations from ideal behavior and structure. If possible,

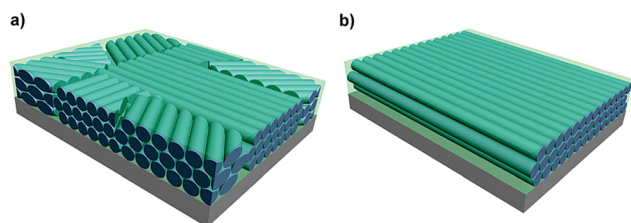


Fig. 9 2D hexagonal ordered porous material with (a) alignment defects and (b) uniform parallel orientation to the substrate. Reproduced from ref. 137 with permission from ACS, copyright 2025.

average grain/domain sizes should be determined and the actual occurrence of the dominant pore symmetry (as determined by SAXS) should be established in different parts of the film (e.g., middle part *versus* surface) by a complementary technique (usually TEM).

(GI)SAXS

Various types of 2D- and 3D-ordered mesostructures have been successfully realized for carbon thin films, including hexagonal ($p6mm$),^{61,113,140} gyroidal ($Ia3d$)^{82,113} or cubic ($Im3m$)^{102,113} pore arrangements, among others. The type of pore connectivity and symmetry has a major impact on the applicability of the corresponding OMC film and is thus a key interest for material characterization and optimization.

In contrast to powder samples, which can be directly analyzed in capillaries, films require special holders and specific techniques for SAXS analysis.¹⁴¹ In this regard, grazing incidence small-angle X-ray scattering (GI-SAXS) is especially beneficial, as it allows for direct measurement of the film, either applied to a support material (e.g., silicon wafer) or without (Fig. 10).

The measured film is thus neither cut nor milled and film-specific information (such as pore alignment or grain sizes) is best preserved. GI-SAXS allows for a detailed structural understanding of the mesoporous structure.¹⁰⁹ For optimal results, it is recommended to use a film thickness between 60 nm and 250 nm, with a sample size up to 1 cm². The incident angle should be set relatively high (around 0.3°),¹⁰⁹ to ensure penetration of the full film thickness. Typically, the sample is placed on a flat, smooth silicon wafer or a grooved copper plate¹⁰⁹ for measurement. Using rough substrates will lead to significant diffuse scattering.



Fig. 10 General GI-SAXS setup: (a) medium 1 = vacuum; medium 2 = mesostructured thin film with thickness d ; medium 3 = substrate with infinite thickness. (b) α_i = incident angle; α_f and $2\theta_f$ = exit angles of the X-ray beam. k_i and k_f = wave vector of the incident and scattered X-ray beams. q_x , q_y , and q_z = components of the scattering vector q . Reproduced from ref. 142 with permission from ACS, copyright 2025.



Due to the small angle of incidence, the analysis typically focuses on a specific region of the sample, which is defined by the elongated profile of the X-ray beams on the sample surface.^{142,143} The arrangement of a sample can be quickly recognized by the GI-SAXS signature. Parallel channels to the substrate will be measured as diffuse sheets, perpendicular channels will be received as scattering rods and a random arrangement (with ordered channels) or thick films will lead to a powder ring. There may also be a superposition of two arrangements where *e.g.* a powder ring and a scattering rod are visible.¹⁴³ Fig. 11 displays typical patterns obtained *via* GI-SAXS.

Very importantly, the sample holder can also be equipped with heating coils for *in situ* GI-SAXS measurements, allowing for observation of the self-assembly/structure formation (and the corresponding kinetics) at different temperatures. Additionally, rotational GI-SAXS can be performed by rotating the sample stage through a range of 180°, allowing a complete scan of the in-plane mesostructured orientation.²⁴

Surface area, pore volume and pore sizes

Physisorption analysis of OMC materials is crucial for obvious reasons; applicability and structure–property correlations can only be meaningful if the key parameters of specific surface area, pore size (diameters) and pore volumes are known, ideally also differentiating between micro- and mesoporous regimes. Doing so correctly can be a challenging task, in particular for film morphologies. Apart from choosing the right measurement conditions (and correct algorithm for data interpretation) for determining the parameters mentioned above, which can also be a difficulty, using actual film samples rather than powdered samples is only possible with specific adaptations.¹⁴⁴ Certain techniques require specially manufactured tubes or measurements under cryogenic conditions to keep the uniform film intact and reduce the limit of detection, respectively.¹⁴⁵

Also, interpreting isotherms can be complex, due to the quadrupole moment of N₂ and its specific interactions with surface groups or metal ions. Kr at 77 K provides exceptional

sensitivity for detecting low surface areas as small as <0.05 m². Since the low vapor pressure reduces the number of molecules in the measurement cell by a factor of 300 compared to N₂ (or Ar), sensitivity for samples with small surface areas is thereby greatly enhanced.¹⁴⁶ However, adsorption is limited to the filling of pores smaller than 10 nm in thin films.¹⁴⁷

In spite of these challenges, it is very informative to keep the film structure intact in order to gain highly relevant insights, especially regarding deviations from the perceived, ideal structural order. This can encompass pore blockages or smaller than expected pore volumes, multimodal pore size distributions (indicative of, among other things, different pore arrangements), specific hysteresis curves (*e.g.* regarding bottle-necks or cage-window structures) or excessive microporosity resulting from high carbonization temperatures.

SEM/TEM

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are valuable tools for the characterization of mesoporous materials; again, for film morphologies their contribution is especially valuable.

Thus, SEM is a straightforward method to determine film thicknesses (which can go down to few nanometers)^{124,148} and their respective uniformity. Also, smoothness and integrity of the film (occurrence of cracks, larger defects) is quickly established through this approach.

TEM is a useful tool for structural analysis, as it reveals a more detailed pore structure and pore orientation (Fig. 12).¹¹¹

Such analysis can substantiate results from (GI)-SAXS and physisorption investigations (pore symmetry, pore sizes) and together provide an informative picture of the respective OMC material.¹⁴⁹ For films, it is highly recommendable to have a look *via* TEM at different sections of the film (middle, upper/lower surfaces) to identify structural defects such as the transition from one type of pore arrangement to another, which might be difficult to spot *via* other techniques. As pointed out above, it is also vital to check for the existence of skin layers, otherwise a lack of the desired applicability might be wrongly interpreted. Energy-dispersive X-ray spectroscopy (EDX)-type measurements can be helpful for investigating the uniformity of doping or catalyst loadings of the OMC film.¹⁵⁰

For OMC film measurement, a TEM specimen can be prepared using the focused ion beam (FIB) method.¹²⁵ A small

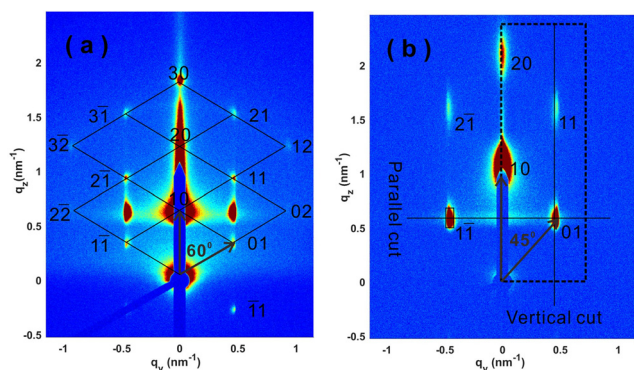


Fig. 11 GI-SAXS pattern of the mesoporous film before (a) and after (b) template removal. Reproduced from ref. 112 with permission from Elsevier, copyright 2025.

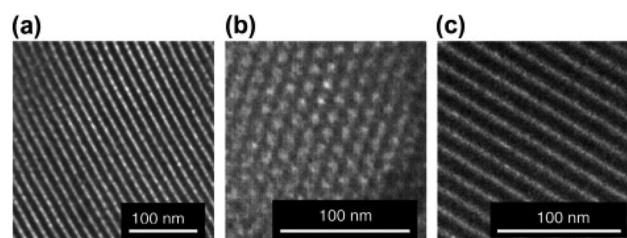


Fig. 12 TEM images of carbon films with well-ordered hexagonal structure (a–c). Reproduced from ref. 114 with permission from Elsevier, copyright 2025.



the template and carbonization, which is observed as a common phenomenon in soft templated films.^{28,126,158} The pore diameter was determined to be 6 nm parallel and 4 nm normal to the surface of the film. The resulting current densities were observed to reach levels that were twice as high as those achieved by commercially available Pt/C catalysts.³⁶

A similar process was also employed by the same group for the incorporation of RuPt^{56,159} and Pd⁵⁷ nanoparticles into OMC films. The RuPt-NP film comprises 0.85 wt% of Pt and 4.3 wt% of Ru, embedded in a 200 nm thick film. The mesopores of this film were of an ellipsoidal shape with a diameter of 9 nm. The Pd-NP film had a thickness of approximately 430 nm and exhibited elliptical pores with sizes of 8 nm parallel and 6 nm perpendicular to the surface, structured in a 50% contracted bcc organization. The Pd loading was 1.15 $\mu\text{g cm}^{-2}$. This film exhibited activity not only in the HER but also in the hydrogenation of butadiene. It demonstrated a threefold increase in yield for the HER and a markedly higher space-time yield for the hydrogenation of butadiene compared to a Pd/C system.⁵⁷ Kraehnert and co-workers employed the aforementioned process to incorporate rhenium and ruthenium nanoparticles into OMC films for utilization in the HER, also demonstrating high platinum mass-based activities.^{56,159} The 174 nm-thick film exhibited contracted bcc-ordered mesopores as a consequence of the 75% perpendicular shrinkage that resulted from template removal and carbonization, as previously indicated.

An alternative approach for the HER was adopted by the group of Li.^{160,161} Both studies employed the deposition of soft templated OMC films on carbon cloth as a 3D self-supported electrode as a support for the catalytic species (Fig. 15). Huang *et al.*¹⁶¹ employed cobalt-doped iron disulfide as the catalytic species, resulting in exceptional HER activity and rapid kinetics. This was attributed to the utilization of the OMC film mesopores, which served as nanoreactors to restrict the growth of sulfide particles and prevent agglomeration during the electrochemical reaction, thereby maximizing the exposure of active sites. The deposited OMC film exhibited an ordered hexagonal arrangement of one-dimensional mesopores with a diameter of 7 nm. These mesopores were oriented parallel to the surface of the carbon cloth. Liu *et al.*,¹⁶⁰ on the other hand, synthesized FeP nanocrystals as catalytic species directly on the substrate.



Fig. 15 Metal catalysts intended for HER incorporated into OMC-coated carbon cloth. Reproduced from ref. 161 with permission from ACS, copyright 2025.

Their device exhibited a notable HER activity and favorable kinetics, in addition to excellent stability under acidic conditions. The OMC film deposited in this study has an approximate thickness of 200 nm and exhibits pores with a uniform diameter of approximately 6 nm in an interconnected three-dimensional arrangement.

A hard-templated film as a catalytic material, created as a replica of a mesoporous silica film, was developed by Kwon and colleagues.¹⁶² They conducted research on nitrogen-doped films for use in electrocatalytic iodine/iodide redox reactions. To achieve nitrogen doping, they employed polypyrrole as a carbon precursor through electrodeposition in the silica pores, resulting in the formation of predominantly active pyridine groups on the OMC film. The porosity of the OMC film could not be determined due to strong adhesion to the substrate, which is a general issue for hard-templated OMC film structures. Another illustrative example of the catalytic application of an OMC film is the electrocatalytic oxidation of estrogens.¹⁶³ In a study conducted by Luo, a hard-templated OMC was created using SBA-15 as the template and sucrose as the carbon source. The utilization of the aforementioned material as a catalytic film on a glassy carbon electrode (GCE) was achieved through a two-step process.

Initially, L-proline and the OMC were suspended in phosphate buffered saline (PBS). Thereafter, the GCE was immersed in this suspension, and OMC/L-proline was deposited on the GCE through an electrochemical technique (10 segments at a scan rate of 100 mV s^{-1} , with a potential range of -0.8 – 2.4 V). The device demonstrated effective electrocatalytic activity towards natural estrogens and high sensitivity for the analysis of E2 (estradiol, $\text{estra-1,3,5-(10)-triene-3}\beta,17\beta\text{-diol}$) in real samples.

Energy storage/conversion

One of the most common applications of carbon materials is their use as electrodes in electrochemical devices, including batteries and capacitors.^{16,164,165} To provide a representative overview, in Table 2 three studies^{23–25} that report on the use of soft-templated OMC films and three studies^{162,166,167} that report on the use of hard-templated OMC films are summarized. Direct comparison of different films is challenging, not only because of the various preparation routes, but also because pore sizes, pore arrangements and electrolytes vary considerably. Also, some of the entries represent fully self-supporting OMC films (entry 6) while others refer to coatings that are not removed from their substrate (entry 3). However, all these examples serve as successful proof-of-concept studies. Indeed, the capacities achieved seem very comparable to OMC powder-type examples²⁵ – with the added benefit of being able to avoid binders and thus provide much better access to structure–activity correlations for future systematic investigations.

It is instructive to notice the different strategies the authors employ to overcome the challenges connected with the preparation of crack-free and well-defined OMC films for supercapacitors and similar applications. Thus, Cheng and colleagues²⁶ employed a methodology that integrated two distinct SDAs to generate a double layer film with varying mesopores. Another approach for overcoming the difficulties presented by



	Templating	Doping	Morphology	Geometric C (mF cm ⁻¹)	Gravimetric C (F g ⁻¹)	Electrolyte	Ref.
1	Hard	N	12 nm pores		252	H ₂ SO ₄	166
2	Hard		Loss of structural order compared to silica, 2–3 nm pores	7		H ₂ SO ₄	167
3	Hard	N	TEM: 7 nm pores	3.92	140–250 ^b	HClO ₄ , HCl	162
4	Soft		Bcc, 6.3–8.2 nm ^a	3.5		H ₂ SO ₄	23
5	Soft		Hexagonal, 5.8 nm pores		85	Na ₂ SO ₄	24
6	Soft		Hexagonal, 20 nm and 8 nm pores		136	KOH	25

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lized for measuring diffusion, with and without applied external electrical fields.

The findings illustrate the molecular sieving effect on molecules transported through the pores of OMC film membranes, with a particular focus on the relationship between pore size and molecular dimensions. Thus, a high selectivity of $\alpha = 56.9$ for anilinium over the larger rhodamine B molecule was found. The utilization of an external applied electric field enables the adjustment of ion selectivity, thereby facilitating the selective separation of ions of varying sizes.¹⁷⁶

In the context of the separation of aqueous solutions of proteins, another example was reported in 2011 by Zhao,²⁵ whereby free-standing OMC films (distorted body-centered cubic pore arrangement, uniform mesopores with 4.3 nm diameter) were also employed. The film served as a membrane for the filtration of a solution comprising cytochrome *c* and bovine serum albumin (BSA), whereby the OMC film was sandwiched between commercial, macroporous membranes for mechanical support. This resulted in an almost quantitative permeation of cytochrome *c*, while only 53% of BSA managed to diffuse through the film. This difference can be explained by the sizes of the respective proteins ($2.5 \times 2.5 \times 3.7$ nm for the former and $4.0 \times 4.0 \times 14.0$ nm for the larger BSA). The fact that BSA could still partially overcome the OMC film barrier, in spite of it having at least one dimension that was larger than the mesopore window, was explained by defects. The direct usage of OMC films is also shown in solid phase microextraction (SPME), which is employed as a sample preparation method for the analysis of organic compounds at trace levels,¹⁷⁷ whereby a variety of polymer coatings^{178–181} are utilized on silica fibers.^{180,182}

Inherently, this leads to certain limitations: the polymer-silica composite can only be applied in a low-temperature environment ($240\text{--}280$ °C)¹⁸³ and is unstable in organic solvents,¹⁸⁴ which can result in removal of the coating.¹⁸⁵ Consequently, carbon materials have been investigated as potential alternatives.^{186–189} Among these, OMC coatings warrant particular attention. In their 2015 study, the groups of Li and Wang¹¹⁰ investigated a simplified method for producing OMC-coated graphite fibers through soft-templating and dip coating. This approach was in contrast with the previous method, which involved hard templating and coating with OMC powder and chemical glue or polymeric adhesive.¹⁸³ The OMC film was characterized by various techniques, whereby a crack-free layer of 8.5 μm thickness was found (hexagonal pore arrangement, 4.5 nm pore size, 630 $\text{m}^2 \text{g}^{-1}$ BET surface). The utilization of this coated fiber was demonstrated through the examination of five benzene series in aqueous samples, revealing wide linear ranges of detection and low detection limits. Interestingly, the extraction efficiency of the OMC coated fiber was found to be improved by a factor of two compared to commercial setups.

Biomedical applications

OMC materials have been employed in a variety of biomedical applications^{37,190–192} due to their relative inertness, high surface area and electrical conductivity. Crucially, the biocompatibility of OMCs is comparable to or higher than that

observed for other biomaterials.¹⁹³ Vogt, Zhao and co-workers investigated the effects of the pore morphology of OMC films on cell adhesion for tissue engineering.¹⁴⁰ Interestingly, the calcined samples (treated at 350 °C, which ensures pore formation but not carbonization) displayed a significantly higher cell adhesion than that observed for a dense film analogue without mesopores. Conversely, the same samples, but now carbonized at 800 °C, showed a lower adhesion of osteoblasts – in particular, if a cubic mesostructure was applied. This effect was attributed to the ability of the carbonized samples to adsorb adhesion promoters or nutrients vital for cell growth. Overall, these findings suggest carbonization temperature and pore morphology as being potentially valuable for tuning cell adhesion.

In 2012, Vogt and colleagues¹⁹⁴ highlighted an application of OMC films as a possible drug delivery system as an alternative to mesoporous silicates.^{195–199} They showed that loading with mitoxantrone as a model drug was possible, although they concluded from their results that smaller drug molecules would be better suited for achieving high loading. They inferred this from the fact that loading did not increase with thicker OMC films, which they attributed to the hydrophobic nature of the carbons, resulting in only the pores near the surface being filled with the mitoxantrone molecules. The drug delivery system is comprised of two distinct steps: an initial burst release, followed by a slow release over a period of 5–8 days. However, only a fraction of the loaded drug was released. This phenomenon was attributed to the strong interactions between the carbon surface within the pores and the mitoxantrone molecule. These interactions can be tuned slightly through the carbonization temperature, with lower temperatures leading to a more hydrophilic surface and, consequently, a higher release rate.¹⁹⁴

Optimization of the carbon properties for similar drug delivery applications thus seems readily possible, since adjustment of the pore size, pore connectivity and surface chemistry are well established concepts for OMCs.^{15,103}

Another application field that has emerged in recent years is electrochemical sensing. One key employment is in the sensing of amino acids, which is of obvious interest in the context of medical diagnostics. The electrochemical sensing of dopamine with an OMC film electrode was published by Zhao and co-workers¹²⁴ in 2021, detailing the use of swelling agents to achieve precisely controlled vertical alignment in the OMC film. The latter was utilized as a sensor to attain enhanced efficacy and, consequently, an ultralow limit (50 nmol L^{-1}) and high sensitivity for dopamine detection.¹²⁴ Wang employed a combination of soft and hard templates to generate stable, ultrasonic-regenerable sensors.²⁰⁰ Similarly, an L-tryptophan sensor was developed using a hard-templated, nitrogen-doped OMC film.

Conclusion and outlook

OMC films provide access to a unique combination of beneficial properties. As outlined above, this has led to a number



of exciting applications, ranging from electrochemistry to the biomedical field, and encompassing both highly specialized and (prospective) high-volume end uses.

Since this is coupled to a straightforward chemical setup and typically cheap starting compounds, it is very realistic that at some point OMC films will break out from lab use and enter commercial production; interest to do so is certainly there.

In order to further this desired development, interdisciplinary efforts are required, in particular involving the polymer field (for precisely tailored, yet well-accessible templates), process technology (for the development of semi- or even fully continuous OMC film production) and materials science (for optimizing OMC properties and, maybe most importantly, well-understood structure–property correlations).

More specifically, research areas that seem very relevant for further advances in the field include a better understanding of the self-assembly kinetics, a more successful suppression of ubiquitous structural defects, better mechanical properties in particular for the self-supporting structures and a more whole-some insight into the confinement-related (catalytic) effects, which are inherently present in OMC films, yet to date only addressable to a very limited degree.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Conflicts of interest

There are no conflicts to declare.

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