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Processing of Covalent Organic Frameworks: An ingredient for a material to succeed

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Covalent Organic Frameworks (COFs) are an emerging class of new organic polymers showing tuneable permanent porosity and crystallinity. They are formed, using modular chemistry concepts, by condensation reactions between their molecular precursors based on the formation of dynamic bonds. Despite much effort having been devoted towards the design of the physical and/or chemical properties of these materials by selecting their initial building blocks, towards applications, processability has only recently emerged. This tutorial review article rationalizes the strategies used so far on COF processability leading to the formation of thin-films, membranes, or individual particles with controlled shape and size as well as composite fabrication. We aim to provide a rational perspective of the importance of COF processability towards potential applications of COFs in many different fields which are at the forefront of research in materials science.

Key Learning Points

- (1) Covalent Organic Frameworks are porous designable and versatile materials.
- (2) COFs can be processed in the form of thin-films, membranes and individual particles with controlled shape and size.
- (3) Composite materials can be prepared combining COFs with many other (nano)materials.
- (4) Advantages and drawbacks of each COF processing method.
- (5) Processing COFs is critical to implement them in applications.

1. Introduction

Modular chemistry aims to connect molecular building blocks to build up a programmed extended structure. This approach offers the advantages of molecular tuning in the creation of new materials. Thus, the building blocks can be designed to achieve the formation of target structures with specific physical and/or chemical properties. Using this approach, we can build robust frameworks with permanent porosity. The first examples of these new materials were metal-organic frameworks (MOFs) which are formed by connecting organic ligands with metal complexes.¹ A key factor determining both crystallinity and

coordination bond used to link the building blocks, which allows self-healing and error correction of the structure during synthesis and crystallization, this is the concept of “chemically induced reversibility”.²

More recently, this topological design principle has been enlarged with the so-called Covalent Organic Frameworks (COFs).³ COFs are a family of designed and ordered mesoporous materials based on the assembly of organic molecular precursors by means of reversible covalent bonds using condensation reactions (Figure 1a).⁴ As such, reaction temperature plays a central role in COF quality and crystallinity, but its range is limited by the thermal stability of the organic building blocks. On the other hand, water, being a side-product of the condensation reaction, is the other determining factor of the final COF crystallinity.

The first successful examples of COFs³ were based on self-condensation reactions of boronic acids or their condensation with catechols leading to boronate esters (Figure 1b). Boron-based COFs have been largely explored despite their limited chemical stability; they easily undergo hydrolysis in water, which is a significant hindrance for many potential applications. More recently, Schiff-base chemistry (Figure 1b) has been demonstrated as a versatile alternative for the construction of

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permanent porosity in MOFs is the dynamic nature of the

COFs with enhanced chemical robustness, in polar and non-polar organic solvents or in inorganic acid and base solutions, while retaining crystallinity and porosity.⁵

Based on their porous nature, most of the initial applications suggested for COFs were pointed towards gas adsorption, storage and separation.^{6–8} However, more recently, they have been explored as catalysts,^{9,10} sensors,¹¹ in the fabrication of electronic devices¹² or for renewable energy applications.¹³

completely insoluble powders formed by randomly aggregated crystallites. This results in the impossibility of using most of the currently available technologies, which were designed to process materials with different features.

However, even if considerable research has been carried out since the beginning towards the exquisite molecular design of the initial building blocks to enhance COF performances for many potential applications, only during the last four years has COF processability emerged as a fundamental issue towards their applications. In this Tutorial Review, we aim to introduce and rationally discuss the most relevant and promising processing methodologies for COFs, highlighting their respective advantages and disadvantages for producing specific morphologies. Additionally, some examples in which these processing methods have been successfully used to integrate COFs into functional devices will also be discussed.

2. Processing

2.1 Shaping of powdered materials

The simplest and most straightforward option to process COFs is to accept what is offered by most solvothermal syntheses and try to make the most out of it. Overall, the situation would not be so different to that of other materials such as zeolites if not for the lower mechanical resistance of COFs. However, this small difference turns into a significant handicap, since powdered insoluble materials are commonly pressed into pellets. In the case of COFs, this process is guaranteed to damage the structure to certain extent. As a consequence, it is necessary to carefully control the applied pressure, which affords acceptable and interesting results, as shown by a detailed study of this method published in 2016.¹⁴ In this work, it was found that, as expected, high pressures amorphized COFs. But remarkably, delicately finding the balance between the fragility of the porous framework and the compression needed to shape it, provides crystalline pellets with a much desired alignment of the COF layers parallel to the flat surface of the pellet, as depicted in Figure 2. This process appears to be general for most 2D COFs and compared to other layered materials such as graphite or MoS₂ that can be oriented in the same way, it requires much lower pressures.

Figure 1. a) Scheme of a 2D hexagonal COF formation from two building blocks with appropriate geometry and functional groups. b) Reaction scheme of boronate ester and imine formation, the two most common reversible reactions used for COF synthesis. c) Sketch indicating some important aspects for the applicability of materials and highlighting the important role of processability towards material applications.

In order to successfully perform in any of these applications, COFs need not only to be stable and feature exceptional properties but also to be integrated in devices, which is done by processing them (Figure 1c). Therefore, it is necessary to use processing methodologies that afford a certain degree of cohesion and allow shaping, placing and orienting COFs as needed, while interfacing them with the other components of the device. In fact, a suitable processing determines the usefulness of a material and is of the utmost importance in allowing it to perform at its best, being an example the huge success of plastics, which main asset is their extremely simple and powerful processing. In contrast, despite their outstanding properties and potential, integrating COFs in devices is a challenging task since most synthetic methods take place inside sealed glass tubes in solvothermal conditions and yield

Figure 2. a) Scheme of a crystallite showing the orientation and stacking of COF-5 layers in it and the directions of the unit cell axis and orthogonality between d_{hko} and d_{001} plane normal vectors. b) Scheme of the random orientation of COF-5 crystallites in powder and their alignment in a pellet formed by pressing the COF-5 powder with uniaxial pressure. c,d) COF pellet oriented c) parallel and d) perpendicular to the optical axis allows diffraction from $00l$ planes and $hk0$ planes, respectively. e,f) PXRD of a COF-5 pellet in e) parallel and f) perpendicular mode at varying uniaxial pressure. Adapted with permission from ref. 14 (copyright 2016, American Chemical Society).

Other more elaborated strategies have been developed that allow the creation of macroscopic COF objects with enough mechanical resistance to be used without the need of a matrix for additional support. For example, it has been demonstrated that keto-enamine COFs can be processed in a manner akin to that of terracotta.¹⁵ For this, the amine is mixed with *p*-toluenesulfonic acid and the resulting mixture is ground with the aldehyde and a small amount of water to form a dough that after baking yields a highly porous and crystalline material (Figure 3). The multiple possibilities of this methodology range from the use of molds to shape centimetre-sized pieces of COF (Figure 3b), to large-scale continuous production by extrusion. Despite the breakthrough represented by this approach, it seems to be restricted to COFs based on keto-enamine linkages

since the basis of this fast procedure lies in the templating effect of the *p*-toluenesulfonic acid, which forms a supramolecular aggregate with the amine and is later replaced by trimethylphloroglucinol owing to their similar size.

Figure 3 a) Scheme of keto-enamine COF preparation by a terracotta process. b) Sculpting of keto-enamine COFs using molds. Adapted with permission from ref. 15 (copyright 2017, American Chemical Society).

2.2. Thin films

Growth on surfaces

For electronic applications, tight contacts and sharp and clean interfaces are generally preferred, which none of the methods described above is likely to provide. Therefore, methodologies that allow the integration of COFs on surfaces have been developed as well. A variety of strategies have been reported that serve this purpose.

The strictest is the synthesis of single and few-layer COFs in ultra-high vacuum (UHV) by evaporating the building blocks onto a substrate on which they polymerise. Under these conditions, the evaporation rate is critical to obtain an ordered network, as in UHV there is no water to promote reversibility. As shown in Figure 4a, the product can be analysed by scanning tunnelling microscopy (STM) to confirm the correct formation of the framework and the number of layers created.¹⁶ A variation of this procedure afforded large defect-free coverage of the substrate with an imine-linked COF, in order to favour bond formation reversibility, it is carried out in a humid atmosphere instead of under UHV conditions (Figure 4b).¹⁷

Figure 4 a) STM image of single-layer boronic ester-based COF prepared in UHV. The inset shows the COF-5 network with the overlaid chemical structure obtained by DFT calculations. Adapted with permission from ref. 16 (copyright 2008, American Chemical Society). b) STM Image of a large defect-free area of an imine-linked COF. The inset depicts the corresponding FFT of the STM image. Adapted with permission from ref. 17 (copyright 2013, American Chemical Society).

Additionally, a less strict approach to this problem has been employed with certain success even for the preparation of functional devices, it consists in simply introducing the substrate in the reaction vessel. As rudimentary as this

methodology may seem, it yields continuous and crystalline films with a homogeneous tuneable thickness of not more than a few hundred nanometres like the one shown in Figure 5a and has been used in many times in a wide variety of COFs and linkages. More importantly, the COF crystallites forming the film show a highly preferential tendency to being oriented with the stacking direction perpendicular to the substrate, as illustrated in the drawing in Figure 5b. Another strength of this method is the wide range of materials that can be used as supports, being graphene¹⁸ and indium-doped tin oxide (ITO)¹⁹ just two examples. Adding even more flexibility, it has been proven that COF films are able to endure the evaporation of metal films on top of them, making it possible to obtain alternating COF and platinum multilayers.¹⁹

In a further development of this technique, it was demonstrated that reaction conditions can be adjusted in order to restrict COF growth to graphene coated areas of a silicon oxide wafer. The importance of this discovery is that by patterning the graphene layer with lithographic methods prior to COF growth, the pattern of the graphene can be transferred to the COF film, as shown in Figure 5c-d.²⁰

However, this selective growth is not attainable with all substrates, thus limiting its applicability to certain devices. In order to cover this gap, a bottom-up approach for patterning surfaces with imine-COF nanolayers by confining the reaction in specific areas of the substrate was developed. This approach takes advantage of one of the first procedures for the synthesis of COFs at room temperature to adapt the conditions to the requirements of ink-jet printing or lithographically controlled wetting (LCW). With these two already established and widely developed techniques it is possible to quickly pattern large areas of both rigid and flexible substrates with resolutions of hundreds of nanometers (Figure 5e-f)²¹.

Figure 5 a) Cross-sectional SEM image of a boronate ester COF film grown on single layer graphene on silicon oxide. b) Schematic illustration of the orientation of the boronate ester COF grown on graphene. Adapted with permission from ref. 18 (copyright 2011, American Association for the Advancement of Sciences). c) and d) Optical micrographs of patterned single layer graphene on silicon oxide c) before and d) after COF growth. The change of colour of the squares indicates an increase in their thickness. Adapted with permission from ref. 20 (copyright 2015, Wiley-VCH). e) Scheme of the LCW procedure for imine COF patterning, in which a droplet of the monomers is cast onto a substrate, then a PDMS stamp is approached to the substrate, confining the liquid by capillary forces, finally, addition of acetic acid starts COF growth and the pattern in the stamp is reproduced by the newly formed COF. f) Representative FESEM image of 500 nm wide COF stripes fabricated by LCW. g) Representative FESEM image of 40 μm -in-diameter dot array of COF on flexible acetate paper generated by ink-jet printing. Adapted with permission from ref. 21 (copyright 2015, Wiley-VCH).

Interfacial synthesis

Films do not necessarily have to be attached to a substrate, free-standing materials that can form membranes can also find many applications, for example in filtration and separation processes.

A method for obtaining large area, free-standing, COF thin films is interfacial synthesis, whether it is done at the air-liquid interface or at a liquid-liquid interface, the results can be fairly satisfactory. Actually, synthesis at the air-water interface has proven successful for the preparation of monolayers of 2D polymers. The strategy relied on the use of amphiphilic monomers that, when organized in a Langmuir film, would arrange in such a way that the anthraceno moieties from different molecules would face each other. Thus, upon irradiation, the covalent network would polymerize by a cycloaddition reaction. However, demonstrating an ordered structure in such thin materials turned out to be extremely difficult and only STM images provided proof of it.²² This approach has also been tested for the formation of networks with imine linkages, unfortunately, although spectroscopic analysis showed the formation of imine bonds, it was not possible to demonstrate crystallinity and prove an ordered structure.²³ This issue has not been solved yet, so in the examples that will be presented next, diffraction patterns matching the expected ones were only observed in thicker films. One of these cases was reported in 2015.²⁴ A thin film of an imine-linked COF was obtained at the air-liquid interface, although not using a Langmuir film approach. A DMF solution of the aldehydes and amines at a low concentration that would not trigger precipitation was left undisturbed in a water-saturated atmosphere. This resulted in the formation of crystalline 50 nm thick films on the DMF-air interface. Remarkably, changing the incubation time allowed tuning of film thickness down to 1.8 nm, although an ordered structure could not be demonstrated in these thinner films.

Syntheses at the liquid-liquid interface have also been performed. An example is the formation of keto-enamine linked COFs at the interface between a dichloromethane solution containing the aldehyde and a water solution of the protonated amine with *p*-toluenesulfonic acid (Figure 6a). As the aldehyde is not soluble in water and the cationic protonated amine will stay on the aqueous phase, the reaction is thus confined at the interface. The result are crystalline, porous and transparent films with thickness that depends on the concentration of the monomers and can be as thin as 50 nm.²⁵

Instead of separating the monomers in different phases, it is also possible to confine the reaction at the interface by segregating the catalyst from the monomers. In order to carry out this strategy successfully it is necessary to adjust the concentration of the organic monomers so that they will not polymerise in the absence of a catalyst, and to choose a catalyst with different solubility than the building blocks. An example is the use of water soluble scandium(III) triflate as a Lewis acid catalyst for imine COF formation in an immiscible water-dioxane mixture. In such a system, the reaction can only take place at the liquid-liquid interface, where the metal salt catalyst comes in contact with the organic building blocks. Similarly to the previous cases, thicker films show good powder X-ray

diffraction (PXRD) patterns and the thickness can be reduced to a few tens of nanometres by changing monomer concentration.²⁶

One of the most remarkable facts about all these examples is that the films showed enough mechanical stability to be handled and transferred to different supports as the glass disc in Figure 6b or the TEM grid in Figure 6c. The only common downside of this methodology is that, even if the generation of the films at the interface is largely reproducible and controlled, once the film is formed, the transfer to the substrate commonly results in cracks or ripples in the films, thus generating an uneven coating.

Figure 6 a) Scheme of the preparation of keto-enamine COF films at the liquid-liquid interface. The bottom colourless layer corresponds to aldehyde in dichloromethane solution, the blue layer contains only water as a spacer solution, and the top yellow layer is the amine/*p*-toluenesulfonic acid aqueous solution. b) Photograph showing a transparent keto-enamine COF film prepared following the method in a) on a glass disc. c) SEM image of a free-standing keto-enamine COF thin-film on a TEM grid. Adapted with permission from ref. 25 (copyright 2017, American Chemical Society).

2.3 Exfoliation of 2D-COFs

Exfoliation of layered materials in a solvent is an alternative top-down approach to the bottom-up methodologies described above for generating 2D structures. The most widespread procedure is liquid-phase exfoliation (LPE), which is widely used in other materials,²⁷ graphene being the best known. The basis of this process lies in the fact that in 2D COFs the forces that maintain the structure within the layers (covalent bonds) are much stronger than the interlayer interactions (π - π stacking), therefore, when energy is applied in the form of ultrasounds, layers separate without breaking apart. This approach was used to isolate the first COFs nanolayers exfoliating bulk crystals of an archetypal boronate ester COF, COF-8, with ultrasound. Flakes with a thickness corresponding to *ca.* 8-10 molecular layers were obtained.²⁸ However, apart from the possibility of residual solvent being trapped between the flakes and the substrate, the main drawback is the large amount of defects created by ultrasonication, as these materials are not as robust as graphene.

An alternative related procedure is based on the grinding of COF powder in the presence of a few drops of solvent. A suspension of nanosheets is thus generated. These nanosheets are found to retain some crystallinity and their thickness ranges between 3 and 10 nm while their length and width span for several micrometres.²⁹

Figure 7 a) Synthesis of DaTp-COF and its chemical delamination through formation of a Diels-Alder adduct. b) DaTp-COF nanolayers in dichloromethane. c) Layer-by-layer assembly upon dichloromethane evaporation. d) A thin layer of DaTp-COF inside a copper loop. e) Schematic representation of the procedure for thin film formation at an air-water interface. Adapted with permission from ref. 30 (copyright 2016, Wiley-VCH).

Finally, the mildest method for the isolation of few layers of 2D COFs is based on the distortion of the stacking by post-synthetic modifications.³⁰ In the example shown in Figure 7a, the synthesised COF contains anthraceno moieties on which a post-synthetic Diels-Alder reaction is performed. The corrugation induced by the formation of the Diels-Alder adduct disrupts the interlayer interactions making exfoliation as easy that a dispersion is obtained directly from the reaction, without applying additional external energy. Moreover, casting a few drops of the nanosheet dispersion in dichloromethane onto a water surface generates a continuous thin film upon solvent evaporation, in an interfacial self-assembly of the nanosheets (Figure 7b-e). Notwithstanding the clear advantages of this last procedure, it is limited to COFs with specific functionalities and the significant modification of the chemical structure may modify other properties of the framework.

2.4 Shaping and sizing micrometre-sized particles

Extended thin films are not the only interesting morphology; it can be very useful for some applications such as catalysis to have access to nanosized materials that can be dispersed in liquid media. The requirements are usually not as simple as preparing small particles, they are also expected to be monodisperse and tuneable in size and shape.

As spheres are one of the simplest shapes, there are many reports that describe their formation, although most of them are empirical findings that do not use a rational approach and are unable to control the diameter. One of the first examples is noteworthy because of the simplicity of the procedure, which consists in mixing ethanolic solutions of the building blocks at room temperature to yield the spheres shown in Figure 8a,

which have a diameter of 500 nm, decent crystallinity and good porosity.³¹

An attractive modification of the spherical morphology is the generation of hollow capsules, a general procedure for imine-based COFs involves the use of spray-drying. In a first stage, the fast spray-drying process generates spherical and microscale hollow superstructures of amorphous polyimine nanocrystals (Figure 8b-c). In a second step this polymer can be transformed into a crystalline COF without modifying the morphology of the superstructure (Figure 8d-e) by refluxing it under acidic conditions in a mixture of dioxane-mesitylene for several days.³² Besides being key for controlling the morphology, a further advantage of the spray-drying step is that it enables the encapsulation of other functional materials such as nanoparticles or even organic molecules into these hollow superstructures.

Figure 8 a) TEM image of spheres of an imine COF prepared at room temperature. Adapted with permission from ref. 31 (copyright 2015, The Royal Society of Chemistry). b) Schematic representation of the spray drying synthesis of COF-TAPB-BTCA. c) Representative FESEM images of amorphous COF-TAPB-BTCA spheres obtained by spray-drying. d) Representative FESEM images of microspherical COF-TAPB-BTCA superstructures obtained by postsynthetic treatment of the spheres in c). e) FESEM and HRTEM (inset) images of a mechanically broken COF-TAPB-BTCA hollow superstructure, revealing the cavity and that they are formed by COF nanocrystals. Adapted with permission from ref. 32 (copyright 2017, The Royal Society of Chemistry).

More anisotropic morphologies can also be prepared, as shown by the remarkable case of the construction of hollow tubular COFs.³³ This interesting feat was achieved by using zinc nanorods as templates in the reaction mixture for COF formation. Once the composite material was obtained, aqueous acid was used to etch the zinc template, yielding the hollow COF nanostructures (Figure 9a-b). Of course, this process can only be extended to acid stable COFs.

Interestingly, also aiming towards the preparation of elongated structures, we have demonstrated that the formation of an imine COF in acetic acid at room temperature under continuous flow microfluidic conditions yields highly crystalline and porous fibres. This morphology is formed by COF nanolayers that, due to the controlled diffusion in the microfluidic device, can only aggregate forming a fibrillar micro-structure (Figure 9c-d). Additionally, the material generated in the microfluidic chip has a high mechanical stability that allows direct drawing of COF objects on different surfaces (Figure 9e-g).³⁴ A further

advantage of the use of microfluidic techniques for the processing of COFs is the high reproducibility of these systems, as under laminar flow conditions, the mixing rates and reaction times are completely controlled.

Figure 9 a) Scheme of the preparation of hollow tubular COFs via a templating strategy. b) TEM image of a hollow COF rod after template removal. The SAED in the inset shows the absence of diffraction from the template. Adapted with permission from ref. 33 (copyright 2015, The Royal Society of Chemistry). c) Scheme of the preparation of fibres of an imine-based COF in a microfluidic chip. d) High magnification SEM image of the COF fibres prepared in a microfluidic system. e-g) Photographs of the word 'COF' written with COF fibres on e) polystyrene, f) aluminium foil and g) tissue paper. Adapted with permission from ref. 34 (copyright 2016, The Royal Society of Chemistry).

Finally, some works have appeared that try to push the limit of COF miniaturisation as far as possible. In one of them, Dichtel *et al.* have proved that the addition of acetonitrile to the classical dioxane:mesitylene mixtures used for boronate-ester COF synthesis inhibits precipitation. This gives rise to stable colloidal suspensions of COF particles with diameters between 45 and 60 nm that retain their structure and crystallinity. The colloid size can be modulated upon adjustment of reaction conditions, e.g. solvent and temperature. Moreover, casting the colloid on a substrate produces a free-standing and transparent COF thin film upon evaporation³⁵.

2.5 Hybrid materials

Besides controlling size and shape, a good processability also endows a material with the possibility of becoming part of hybrid materials that combine the functionalities of the different components and, if carefully designed, may result in synergistic effects.

Many materials are susceptible of being combined with COFs, may serve as a first example carbon nanotubes, which are expected to interact rather strongly and favourably with the extended π system of 2D COFs. Thus, when the synthesis of boronate ester based COFs is conducted in the presence of carbon nanotubes, the COF grows around them, creating a material that combines the redox properties of the framework with the electrical conductivity of the nanotubes and shows great promise for electrical energy storage.³⁶

Similarly, PVP functionalised gold, palladium and magnetic nanoparticles can be encapsulated inside COF spheres.³⁷ Of course, achieving this requires an additional control over the

morphology of the COF and solvents compatible with the nanoparticle suspensions, making it difficult to combine these requirements with conditions that also afford crystalline frameworks. Therefore, this process can be simplified by using a two-step approach analogous to the described previously for spray-drying. In the first step, the nanoparticles are mixed with the COF building blocks under conditions that lead to the formation of amorphous polyimine spheres. Thus, the growing spheres trap the metal or magnetic nanoparticles in their inside, creating the composite, e.g. **a-1** (Figure 10 a and c). In the second step, harsher conditions are used to increase bond reversibility and crystallize the amorphous organic polymer into an imine-linked COF, while the nanoparticles stay protected inside the organic matrix e.g. **c-1** (Figure 10 b and d). The integrity of the nanoparticles was later confirmed by testing the catalytic activity and magnetic properties of the composite.

Figure 10 HAADF-STEM images of a) gold nanoparticles encapsulated inside amorphous imine COF spheres, b) gold nanoparticles in crystalline imine COF spheres, c) palladium nanoparticles in amorphous imine COF spheres, and d) palladium nanoparticles in crystalline imine COF spheres. The crystalline COF spheres are obtained by postsynthetic crystallization treatment of the amorphous spheres. Adapted with permission from ref. 37 (copyright 2017, Wiley-VCH).

If there is no such dominion over the growth of the COF, the other material can be used as a template. For instance, this was the approach used for coating 200 nm in diameter Fe_3O_4 spheres with a 100 nm thick COF layer.³⁸ The same two-step procedure described above of polymerization of an amorphous network and subsequent crystallisation of the COF shell without change of the morphology was followed.

The preparation of all these hybrids is driven by non-covalent interactions, however, some applications may require a stronger anchoring of the COF to the other material. A common strategy to achieve this in imine COFs has consisted on the functionalisation of the surface of the other material with amino groups (Figure 11a). Then, a layer of the aldehyde building block is grafted by formation of imine bonds with these amino groups. Finally, both the aldehyde and the amine are added and COF nucleation begins at the anchored aldehydes. For instance, using this method it has been possible to coat 200 nm iron oxide spheres with an imine linked COF, obtaining a nearly identical result to the one achieved using the two step polymerization-crystallization process in the previous paragraph, as shown by TEM images (Figure 11b-c).³⁹

Figure 11 a) Scheme of the synthesis of grafted core-shell Fe_3O_4 @COF spheres from amine functionalized Fe_3O_4 nanoparticles (black sphere) prepared by first anchoring the aldehyde (red) and then adding both amine (blue) and aldehyde in order to grow the COF (orange shell). b,c) TEM images of Fe_3O_4 @COF spheres prepared by b) polymerising in the presence of the Fe_3O_4 spheres and c) previously anchoring a monomer to the metal oxide sphere. Adapted with permission from refs. 38 (copyright 2016, Wiley-VCH) and 39 (copyright 2017, The Royal Society of Chemistry).

2.6. Membranes

An extremely versatile and useful form of processing is the creation of membranes, which can be used for separations in both gas and liquid phase.

The preparation can be as simple as dispersing the COF powder in the polybenzimidazole solution typically used for casting polymer membranes.⁴⁰ However, this methodology may not yield optimal results, as it has been reported that MOF containing membranes perform better if a homogeneous and oriented distribution of the filler particles is obtained.⁴¹ Preparing membranes with these characteristics usually involves an elaborate process and can benefit from the methodologies discussed above. For example, an uncomplicated improvement on the modification of polymeric membranes can be done by previously delaminating COFs by mechanical grinding. The resulting suspension of nanosheets can then be homogeneously distributed in the polymer matrix. Moreover, if poly(ether sulfone) (PES) is used as a matrix, COF gradients can be generated taking advantage of the densification step necessary to cast this type of membrane (Figure 12). During this process, the good diffusion of the nanosheets allows them to migrate to the denser region of the matrix, in which they become trapped.⁴²

Figure 12 a) Cross-sectional SEM image of a poly(ether sulfone) membrane with a gradient of an imine-based COF as filler. b) EDX N-mapping of the membrane in a) showing the gradient in the amount of COF across the membrane. Adapted with permission from ref. 42 (copyright 2018, The Royal Society of Chemistry).

An alternative to embedding COF particles in a matrix is covering porous supports by directly growing the framework on the support. As a good mechanical stability of the final product is needed because under operation conditions the COF coating has to withstand the drag forces of the liquid flow, strategies that bond the COF crystallites to the support have generally been preferred. As explained before, surface functionalisation with amines is quite common, and it has been done on alumina supports to first graft a dialdehyde and then proceed to the growth of the framework. This process afforded a continuous, homogenous and compact coverage (Figure 12a-b).⁴³ In an example of the degree of complexity that is possible to reach with this strategy, a porous silica support was coated with polyaniline; then, an imine based COF was grown on it, with the polyaniline acting as a bridge between the support and the aldehyde groups of the COF. Finally, a MOF was synthesised on this multilayer membrane, with the interaction between the metal ions or the carboxylic acids used to build the MOF and the unreacted amino groups of the COF connecting the two phases (Figure 12c-d). Thus, a composite of four different materials (silica, polyaniline, COF and MOF) was created.⁴⁴

Finally, if enough mechanical resistance is imparted on the COF by a suitable processing method, it is not necessary to blend them with other materials and pure COF membranes can be prepared. The terracotta-like processing described above (see Section 2.1) has been employed to prepare COF membranes by spreading the dough in a very thin sheet using knife-casting before baking. The resulting membranes are a few hundreds of micrometres thick, self-standing and flexible.⁴⁵ This is a very interesting result, as in principle it should be applicable to many keto-enamine linked COFs and it enables the production of flexible membranes of pure crystalline porous materials, something not yet reported in the case of MOFs. Moreover, owing to the presence of just the porous material in the membrane, they display extremely high surface areas, rivaling with ceramic and polymeric membranes.

Figure 13 a) Cross-sectional SEM image of an α - Al_2O_3 porous support with a 4 μm thick COF layer grown on top. b) SEM image of the surface of the α - Al_2O_3 support covered with COF. The inset is an amplified image. Both show a homogeneous coverage. Adapted with permission from ref. 43 (copyright 2015, The Royal Society of Chemistry). c) and d) Cross-sectional elemental mapping images of zinc and silicon, respectively, of a [COF-300]-[ZIF-8] composite membrane. e) Cross-sectional SEM image of the [COF-300]-[ZIF-8] composite membrane shown in c) and d). f) Scheme of the fabrication of COF-MOF composite membranes, including the reactions or interactions that bridge the new layer to the existing ones in each step. Adapted with permission from ref. 44 (copyright 2016, American Chemical Society).

3. Applications enabled by processing of COFs

As indicated in the introduction, COFs can display excellent and diverse properties. However, examples of applications are still scarce and those reported generally do not show competitive performances and durability. The reason behind this is that, beside surface supported films, all the processing strategies discussed above are very recent, in fact, the earliest works described in the previous section date from 2015. This implies that there has not been enough time to fully combine into devices the existing knowledge of how to design functional COFs and how to process them. The examples chosen in this section aim to highlight to what extent processing affects some properties and applications.

As it was one of the first processing methods to be developed, many of the earliest applications were those using COF thin-films. For example, a field in which COFs can offer unique advantages over other materials is photovoltaics, as their structure allows to order in close proximity arrays of electron-donor and -acceptor groups, thus generating an interpenetrated three-dimensional heterojunction. For this reason, a COF with a structure inspired in this concept was prepared in the form of 50 nm thick oriented films on an ITO electrode with a 10 nm molybdenum oxide layer that acts as a hole extractor. Over the COF film, an aluminium electrode with a 20 nm hole-blocking layer of zinc oxide was deposited. This device contains all the components of a solar cell, being the COF the active layer. Therefore, upon irradiation, the device shows efficient charge separation, although the performance is hindered by the high rate of recombination.¹³

Another example of COF thin-films adapted to an application is found in the field of electrical energy storage. An anthraquinone containing COF thin-film was prepared on gold with the goal of using its redox properties for charge storage. However, the poor conductivity of the network precluded most of the redox active moieties from participating. In order to overcome this problem, the conductive polymer PEDOT was polymerised inside the channels of the COF (Figure 14a). The conductive effect of PEDOT in transporting the charge throughout the whole COF and allowing all the anthraquinones to be reduced and oxidized was clearly seen by the 40-fold current increase in cyclic voltammetries (Figure 14b). The full electrochemical studies showed good performance over a range of charge-discharge rates and decent cyclability. As a visual proof-of-concept, two coin cells with COF electrodes were fabricated and succeeded in lighting a LED (Figure 14c).⁴⁶

Figure 14 a) Depiction of the incorporation of PEDOT in the pores of a DAAQ-TFP COF film by electropolymerisation. b) Cyclic voltammetry response in 0.5 M H₂SO₄ of a DAAQ-TFP COF film before (red) and after (blue) PEDOT modification. The inset presents the cyclic voltammetric response for the unmodified film using an expanded current scale. c) Photographs of a PEDOT-modified DAAQ-TFP COF working device powering a green LED. Adapted with permission from ref. 46 (copyright 2016, American Chemical Society).

Regarding the use of sensors, exfoliation of COFs has proven a useful tool. It is remarkable the example of the stable aqueous suspensions of pyrene containing COFs prepared by ultrasonication in water (Figure 15a).¹¹ These colloidal nanosheets show strong fluorescence that gets quenched in the presence of certain aromatic molecules (Figure 15b). This has allowed the use of the colloid to detect the presence of several organic dyes and polynitro-aromatic derivatives, suggesting the great potential of COF colloids for sensing of water contaminants, an area in which MOFs suffer from poor stability in water and amorphous porous organic polymers (POPs) offer poor pollutant-host interactions.

Figure 15. a) Representation of the structures and preparation of the water colloids of IMDEA-COF-1 and IMDEA-COF-2. The Tyndall effect of the colloids is shown. b) Fluorescence quenching data of the IMDEA-COF-1 aqueous colloid upon addition of Janus Green, photographs of the colloid irradiated with UV light before (left) and after (right) Janus Green addition are also shown. Adapted with permission from ref. 11 (copyright 2019, The Royal Society of Chemistry).

Other example of application made possible by the availability of a suitable processing technique is the use of COFs for nanofiltration. This is a field in which COFs also present some characteristics that distinguish them from many other candidate materials. Mainly the fact that, being composed of stacked atomically thin layers, their thickness can be reduced without significantly affecting their separation capability, but increasing their permeability. Additionally, their modular design allows for an easy control of their highly precise pore size. Several works have explored the potential of COFs in this regard. On the one hand, COF films were formed at the dichloromethane-water interface (see Section 2.2) with a thickness of a few micrometres to ensure its mechanical stability. The films were placed between two macroporous supports in order to study their performance when a solution is passed through them in a dead-end cell. The solvent permeance values were better than those of other materials used for nanofiltration and the rejection of solutes was high showing good size selectivity.²⁵

On the other hand, cross-flow nanofiltration (Figure 16a) has also been achieved with COFs. To reach this goal, an alumina tube commonly used for this type of filtration was functionalised with amino groups to graft an imine-based COF to its surface. The coverage with a 400 nm thick COF layer was complete and uniform (Figure 16b-c). As in the previous example, good rejection of dyes dissolved in water was found (Figure 16d-f), hinting towards its potential for water purification, as it outperforms many other materials such as polymer membranes and MOF composites.⁴⁷

Figure 17 a) Scheme of cross-flow filtration. The mixture is fed from the left and flows around the tubular membrane. Only part of the solvent and small molecules can cross the membrane and are collected at the bottom, while larger molecules and the rest of the solvent exit the system through the right. b) Photographs of an untreated (left) and COF functionalised (right) alumina tubes for cross-flow filtration. c) EDX mapping of the cross-section of a COF functionalised tube. C is the tracer for the COF layer and Al for the alumina support. d) Water permeance and rejection rates of different dyes with tubular COF membranes. e) Stability test of the tubular COF membranes. f) Comparison of the performance of COFs in

An example that clearly highlights the influence of processing in the performance in an application can be found in the use of COFs as proton conducting membranes in proton exchange membrane fuel cells (PEMFC). A common way of shaping COFs for this task is pressing the powdered solid into discs. Interestingly, if a small amount of acetic acid is added to the material before pressing it, quasi-transparent and flexible films showing crystallinity are generated. Remarkably, even though these films show lower proton conductivities than COFs designed to excel at it, the films outperform conventional pellets of more conductive COFs when tested in a fuel cell setup.⁴⁸ The explanation of this unexpected result arises from the fact that when operating a fuel cell, other factors than conductivity, for instance hydrogen permeability, come in play and affect the final performance. In this case, the more homogeneous packing of COF crystallites in the film makes it more gastight, compensating for the lower conductivity. In fact, the power densities obtained by these COF films were only recently surpassed by a COF containing groups to enhance proton conductivity and at the same time properly processed as flexible continuous thin films.⁴⁹

Figure 18 a) Scheme of the synthesis of imine COFs loaded with water (RT-COF-1), acetic acid (RT-COF-1Ac and RT-COF-1AcB) and lithium ions (LiCl@RT-COF-1). b) Photographs showing the films obtained by pressing RT-COF-1AcB and their flexibility. c) Polarization (filled) and power density (open symbols) curves of RT-COF-1Ac, RT-COF-1AcB and LiCl@RT-COF-1 films measured at 323 K for a single H₂/O₂ PEMFC. d) Comparison between conductivity versus power density values

4. Conclusions and Perspectives

COFs have recently emerged as a new family of organic polymers with outstanding structural features. They can be designed using concepts of molecular chemistry, allowing the selection of their molecular precursors. The only limitation in their design are the covalent bonds that can be used to connected them as only some reversible condensation reactions have proven to be useful to generate crystalline COFs. Thus, these new materials show promise for application in many fields. However, there are serious limitations in their commercial use arising from different aspects: i) Large scale availability: production methods; ii) Chemical and thermal stability and iii) Processability.

Production methods for COFs have experienced some development but are mostly limited to solvothermal processes. Therefore, this is a very important aspect still to be tackled. Just a few research works, some of them highlighted here have shown alternative procedures for upscaling COF production such as continuous microfluidic and spray-drying synthesis or solvent-free preparations.

Importantly, the two major COF families developed so far, boron-based COFs and nitrogen-based COF, both show similar thermal stability (typically limited to *ca.* 400 °C), with the latter being the most chemically stable type of COFs in a large variety of organic solvents and water under acidic or basic conditions. The better performance of nitrogen-based COFs regarding chemical stability has motivated a change towards nitrogen-based COFs being currently more developed than their boron-analogues. Despite most of the work being focused on these two types of frameworks, we believe that in the near future the number of possibilities will increase by incorporation of other alternative reactions to produce new COFs.

Finally, the third aspect (COF processability) has been described in detail in this tutorial review. We consider that material processability is a fundamental aspect for commercializing COFs as useful materials for different applications. As such, in this review we have analysed different procedures already explored to generate COFs in a variety of morphologies. In our view, a general analysis shows that the most promising methods used so far mostly come from the adaptation of those already reported for similar materials, e.g. spray-drying, microfluidics, ink-jet printing, and pellet formation.

As a summary of the procedures already reported, we can divide them in two general groups: i) material processability from the initial COF powder obtained during the solvothermal reaction, this includes exfoliation to produce colloids; and ii) processability obtained directly from the COF formation reaction, such as the terracotta process.

But probably, the most important conclusion is that once it is accepted by the research community that processability is a requirement for COF to be useful as alternative commercial

materials, new procedures will be rapidly developed to provide better material performances in a wide range of applications.

Conflicts of interest

There are no conflicts to declare

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