

Covalent Organic Framework Composites

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Covalent organic frameworks (COFs) are crystalline, porous materials formed by the self-assembly of organic building blocks. Composite materials containing COFs have raised increasing interest. To date, various synthesis techniques have emerged that allow for the preparation of crystalline and porous COF composites with different materials offering highly efficient tools for analytical applications.

Keywords: covalent organic frameworks ; composite ; analytical applications ; separation ; sensing ; environmental remediation

1. Introduction

Covalent organic frameworks (COFs) are crystalline, porous materials formed by the self-assembly of organic building blocks [1][2][3]. They have attracted a lot of interest due to their unique properties, such as large surface area, ordered channels, high porosity, tunable structure through pre-selection of the building blocks, easy functionalization, and good thermal and chemical stability. To tackle challenges in sample treatment, separation, and sensing processes, COF materials have attracted much attention in the last few years, offering highly efficient tools for analytical applications.

In order to impart additional functionality to these materials, COFs can be combined with other functional materials, such as metal and SiO₂ nanoparticles or graphene, or grown on substrates, such as alumina or stainless steel. Such COF composite materials open various further possibilities of exploitation for a wide variety of applications. In the last few years, development of synthetic approaches to obtain bulk COFs and COF-based composites with favorable characteristics, such as large surface area, high crystallinity, high chemical and thermal stability, durability, etc., has received increasing attention. This fact, together with the rapid development of analytical applications of COF materials, has resulted in different reviews since 2017 focusing on COF synthesis [3][4], design [5], and applications as sensing platforms [6][7][8][9][10], adsorbents in sample pretreatment [11][12][13][14][15][16][17], stationary phases in chromatographic separation [18][19][20], and novel tools in water treatment [21][22]. However, since research on COF composites in the analytical chemistry field is relatively recent as compared to bulk COFs, to the best of our knowledge, no reviews have focused on COF composites developed for analytical applications.

2. Synthesis of COF Composites

2.1. Iron Oxide—COF Composites

Magnetic composites are the most reported COF composite materials. Magnetic nanoparticles (NPs) are attractive for a wide range of applications due to their remarkable magnetic properties, stability, biocompatibility, and fast separation using an external magnetic field [23]. The majority of magnetic COF composites contain iron oxide, Fe₃O₄, as the magnetic NP, although a few other examples with NiFe₂O₄ [24] and CuFe₂O₄ [25] NPs have been reported. Superparamagnetic iron oxide NPs are Fe₃O₄ particles with cores below 100 nm in diameter [26]. These particles become magnetized up to their saturation magnetization upon application of an external magnetic field, and on removal of the magnetic field, they no longer exhibit magnetic interactions. Therefore, gaining access to nanocomposites that combine the functionality of COFs with magnetic separability is of great interest.

In a typical procedure, magnetite is prepared first, followed by surface functionalization with anchoring groups, such as amino functionalities. Thereafter, one of the COF building blocks can be attached to the anchoring groups prior to COF growth, a step that can be crucial to obtaining a crystalline COF composite. Finally, the COF is typically grown under solvothermal conditions.

A bouquet-shaped Fe₃O₄-TpPa-1 nanocomposite [27] was developed by a synthetic procedure starting with amino-functionalized Fe₃O₄ NPs (NH₂-Fe₃O₄ NPs) with a size of ≈25 nm (Figure 1a). NH₂-Fe₃O₄ NPs were prepared using FeCl₃·6H₂O, sodium acetate, and 1,6-hexamethylenediamine by first stirring at 50 °C and then heating in an autoclave at

198 °C for 6 h [28], after which their surface was modified with 1,3,5-triformylphloroglucinol (Tp) [27]. The COF composite was prepared by room-temperature solution-phase method from Tp and *p*-phenylenediamine (Pa-1) in ethanol, and the resulting composite featured crystallinity, a specific surface area of 248 m²·g⁻¹ (lower than that observed for bulk COF), and superparamagnetic nature. The transmission electron microscopy (TEM) image (Figure 1b) showed that interconnected nanofibers of TpPa-1 sprouted from clustered NH₂-Fe₃O₄ nanoparticles. In another study, Espiña, Salonen, and co-workers [29] developed a synthesis protocol to prepare magnetic COF composites by installing the anchoring groups on the magnetic nanoparticles already during the NP synthesis. The mTpBD-Me₂ composites were synthesized via a facile three-step procedure, starting with dopamine (DOPA) being introduced as capping ligand during co-precipitation to produce spherical Fe₃O₄@DOPA NPs with free amino groups and an average diameter of 5 nm. Fe₃O₄@DOPA NPs were then pre-functionalized with Tp to provide the NP surfaces with nucleation points for directed growth of COF around the nanoparticles. TpBD-Me₂ was grown onto the NPs under solvothermal conditions using Tp and *o*-tolidine as building blocks. The crystalline composite exhibited, with 538 m²·g⁻¹, no loss in Brunauer-Emmett-Teller (BET) surface area as compared to the bulk COF material and was easily collected using an external magnetic field. In TEM images small Fe₃O₄ aggregates were observed encapsulated within a shell of COF. In a later study [30] the composite was prepared on 0.5 g scale, maintaining both crystallinity and porosity.

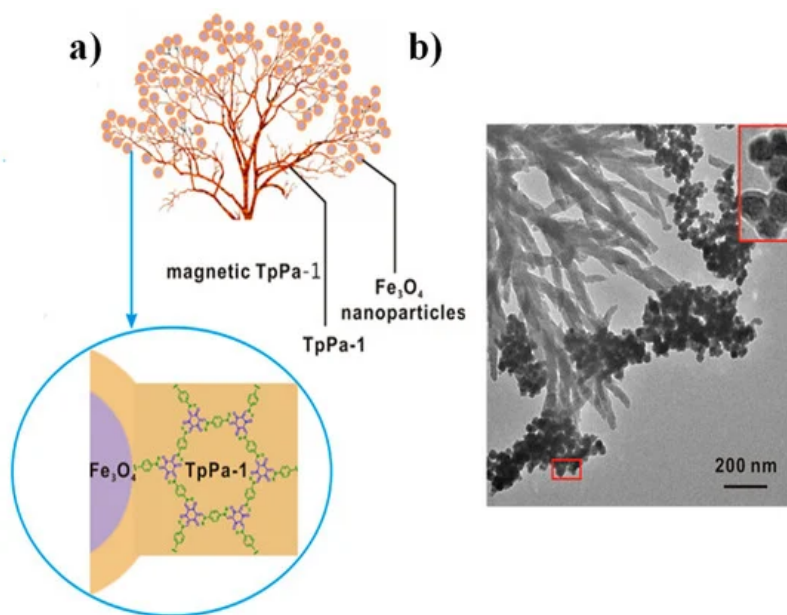


Figure 1. (a) The structure of the bouquet-like magnetic TpPa-1 sorbent, and (b) TEM image of magnetic TpPa-1. Reprinted with permission from [27]. Copyright (2017) American Chemical Society.

An alternative to the most common solvothermal synthesis was offered by Liao, Thomas, and co-workers [31], who combined mechanochemical and crystallization approaches to obtain COF-LZU1 composites. First, mechanical grinding of 1,3,5-triformylbenzene (TFB), Pa-1, and commercially available Fe₃O₄ followed by Soxhlet extraction led to Fe₃O₄/amorphous polymer network. The following mild crystallization reaction in the presence of a small amount of 1,4-dioxane/mesitylene/acetic acid at 70 °C for 5 days yielded a crystalline COF composite with a surface area of 872 m²·g⁻¹, which is more than double that reported for the bulk COF-LZU1 material. The composites consisted of aggregated microparticles covered by a 15–35 nm thick COF shell with continuous and smooth appearance. This method was also applied to the synthesis of COF composites with Co₃O₄ and NiO.

Another example of a mechanochemical method for magnetic COF (MCOF) composite synthesis was presented by Shuai, Huang, and co-workers [32], where first, amino-functionalized silica-coated Fe₃O₄@SiO₂ nanoparticles (MNP-NH₂) were prepared following a solvothermal method [33]. For amino functionality incorporation [32], the Fe₃O₄ NPs were modified sequentially with tetraethyl orthosilicate (TEOS) and 3-aminopropyl trimethoxysilane (APTMS) to give MNP-NH₂. For introduction of the COF, MNP-NH₂ (50, 100, 150, and 200 mg for MCOF-1, MCOF-2, MCOF-3, and MCOF-4, respectively) were ground in a mortar for 5 min with *p*-toluenesulfonic acid monohydrate (PTSA), Tp, and Pa-1, and heated to 170 °C during 1 min. X-ray diffraction (XRD) confirmed the crystallinity of the MCOFs and the materials featured surface areas ranging from 122 to 352 m²·g⁻¹. TEM imaging of MCOF-2 showed MNP-NH₂ to be encapsulated within the COF.

In a recent study, a simple and rapid coprecipitation method was used to prepare COF-(TpBD)/Fe₃O₄ for solid-phase extraction [34]. First, TpBD was synthesized by solvothermal method, delaminated by mechanical grinding to nanosheets, and then added to a dispersion of FeCl₃·H₂O and FeSO₄·7H₂O in water. The suspension was stirred at 80 °C, followed by

addition of 30% aqueous ammonia. The TEM images of COF-(TpBD)/Fe₃O₄ showed that Fe₃O₄ NPs were spherical in shape, had a size of <50 nm, and were embedded in TpBD nanosheets. In addition, powder XRD studies demonstrated that TpBD retained its crystallinity during the coprecipitation process.

A two-step strategy enabling the encapsulation of several types of NPs, including Fe₃O₄, into crystalline imine COF spheres, was reported by Maspoch, Zamora, and co-workers [35]. First, COF building blocks TFB and 1,3,5-tris(4-aminophenyl)benzene (TAPB) were separately dissolved in a suspension of Fe₃O₄ NPs (9.8 ± 3.9 nm) in acetone/acetic acid. To encapsulate the NPs in a polymer, the resulting solutions were combined and ultrasonicated for 1 h, and the precipitate was collected to yield amorphous imine-based Fe₃O₄@a-1 spheres. These spheres were then subjected to solvothermal COF growth conditions for 7 days. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and powder XRD studies of the samples revealed the successful formation of crystalline spherical Fe₃O₄@c-1 NPs with Fe₃O₄ located mostly in the center, with BET surface area of 880 m²·g⁻¹ (Figure 2).

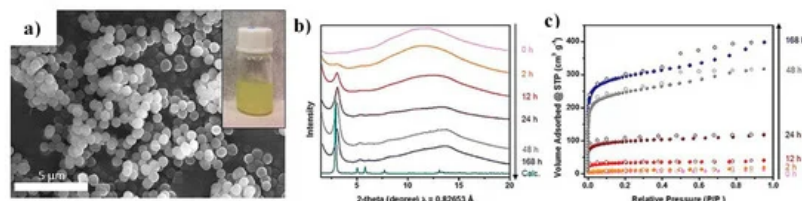


Figure 2. (a) Field emission scanning electron microscopy (FESEM) image of c-1 spheres, and evolution of the crystallinity (b) and porosity (c) of the composite during the amorphous-to-crystalline transformation. Reprinted with permission from [35]. Copyright (2017) Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim.

In a similar amorphous-to-crystalline approach, core-shell microspheres were prepared by template-mediated precipitation polymerization of an Fe₃O₄ nanocluster core with an amorphous polyimine shell, followed by crystallization to COF under solvothermal conditions (Figure 3) [36]. The employed citrate-stabilized Fe₃O₄ nanoclusters [37] had ample carboxylate groups on the surface to offer high dispersibility. In addition, these moieties also serve as anchoring groups to initiate the polyimine network formation through H-bonding interactions with the benzidine (BD) monomer. Thereafter, the amorphous polyimine network shell was formed via the template-controlled precipitation polymerization of BD and Tp. Subsequent treatment of the NPs under solvothermal conditions using pyrrolidine as catalyst resulted in highly crystalline Fe₃O₄@COF(TpBD) microspheres with a well-defined core-shell structure, narrow particle-size distribution, and uniform spherical shape with a high BET surface area of 1346 m²·g⁻¹.

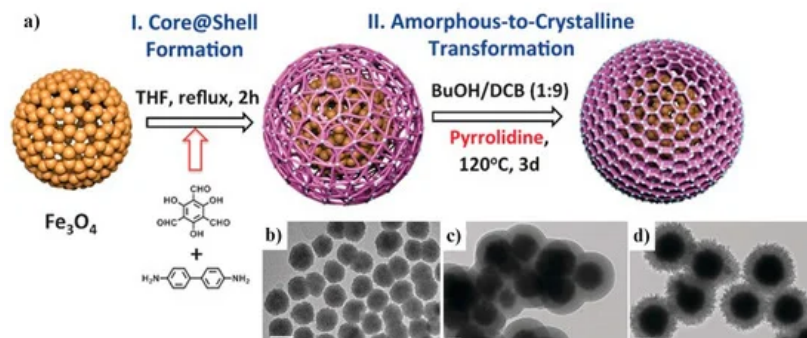


Figure 3. (a) The preparation of imine-linked COF composite microspheres via the amorphous-to-crystalline conversion process. High-resolution TEM images of (b) Fe₃O₄ nanoparticles, (c) amorphous Fe₃O₄@polyimine, and (d) Fe₃O₄@COF(TpBD) microspheres. Reprinted with permission from [36]. Copyright (2016) Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim, Germany.

Core-shell nanostructures can have the advantages of hindering the aggregation of the magnetic cores and reducing losses of magnetism that stem from high organic content, while allowing surface modification. Using a layer-by-layer (LBL) assembly protocol, a COF shell was assembled on the surface of 1,6-hexamethylenediamine-functionalized Fe₃O₄-NH₂ NPs [38] of 100 nm. First, 2,5-dimethoxyterephthalaldehyde (DMTP) was added to a suspension of Fe₃O₄-NH₂ NPs in 1,4-dioxane with aqueous acetic acid and heated at 70 °C for 2 h. After washing, TAPB was added with aqueous acetic acid and the reaction mixture was again heated at 70 °C for 2 h followed by washing and drying to form Fe₃O₄-NH₂@TAPB-DMTP-COFs. The resulting TAPB-DMTP-COF layer had a thickness of about 12 nm, the spherical NP structure was preserved, and no interconnectivity between the particles was observed. The composite showed high crystallinity and excellent performance as electrochemical sensor material with good sensitivity and recovery, high stability, low detection limit, and wide linear range due to the catalytic activity of Fe₃O₄ NPs and the high electroactive surface area of TAPB-DMTP-COF layer.

Controllable preparation of core-shell $\text{Fe}_3\text{O}_4@\text{TpBD}$ nanospheres [23] was achieved by growing the COF on magnetic NPs functionalized by TEOS and (3-aminopropyl)triethoxysilane (APTES) (Figure 4a). The obtained $\text{Fe}_3\text{O}_4\text{-NH}_2$ was pre-functionalized with Tp for subsequent in situ growth of a TpBD shell. Pre-functionalization of the nanosphere surface with Tp was crucial to obtain uniform crystalline COF shells, whereas the COF shell crystallinity and thickness were controlled by the solvents, concentration of building blocks, and reaction time. The thickness of the COF shell around the nanosphere was tuned from 15 to 65 nm by varying the concentration of COF monomers from 2.5 to 20 $\text{mmol}\cdot\text{L}^{-1}$ (Figure 4b,c).

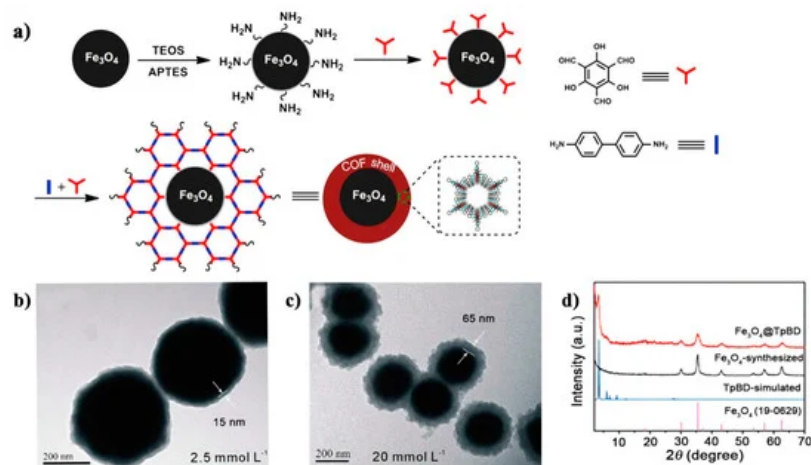


Figure 4. (a) Illustration of the monomer-mediated in situ growth of core-shell $\text{Fe}_3\text{O}_4@\text{TpBD}$. (b,c) TEM images of the monomer concentration effect on $\text{Fe}_3\text{O}_4@\text{TpBD}$. (d) The XRD patterns of $\text{Fe}_3\text{O}_4@\text{TpBD}$, Fe_3O_4 , and simulated TpBD. Reproduced from [23] with permission from The Royal Society of Chemistry.

2.2. Silicon Dioxide–COF Composites

COFs have been successfully used as stationary phases in gas chromatography and capillary electro-chromatography [39]. In high-performance liquid chromatography (HPLC), irregular shape, sub-micrometer size, or broad size distribution of pristine COFs may cause low column efficiency and column backpressure of the COF-packed columns. Growing a uniform COF shell on SiO_2 microspheres is a promising approach to resolve the above-mentioned problems. There are three methods to prepare COF- SiO_2 composites: (i) in situ growth strategy, (ii) layer-by-layer (LBL) method, and (iii) bottom-up strategy.

In situ growth strategy was employed to gain access to uniform core-shell COF@ SiO_2 microspheres with controllable thickness [39]. For the fabrication, spherical 5 μm $\text{SiO}_2\text{-NH}_2$ served as both the core and the amino group source for reaction with Tp to induce controllable TpBD shell growth. The resulting $\text{SiO}_2\text{-Tp}$ was further reacted with BD to form the TpBD shell on the silica core. The thickness of the TpBD shell can be easily controlled by adjusting the monomer concentrations. Only a few TpBD crystals were formed on TpBD@ SiO_2 when 0.10 mmol of Tp and 0.15 mmol of BD were used. Raising the amount of Tp to 0.30 mmol and the amount of BD to 0.45 mmol increased the shell thickness from 50 to 150 nm. Further increases in Tp and BD monomer amounts, to 0.50 and 0.75 mmol, respectively, did not lead to clear improvement in the shell thickness, indicating the full occupation of the amino groups on $\text{SiO}_2\text{-NH}_2$ by Tp. In the powder XRD, the peak intensities of TpBD@ $\text{SiO}_2\text{-0.10}$, TpBD@ $\text{SiO}_2\text{-0.30}$, and TpBD@ $\text{SiO}_2\text{-0.50}$ increased, revealing the controllable synthesis of TpBD@ SiO_2 microspheres.

The LBL method was first reported for the preparation of a 3D COF on SiO_2 [40]. Aminosilica ($\text{SiO}_2\text{-NH}_2$) nanoparticles with 5 μm size were consecutively refluxed with terephthalaldehyde (TPDA) and tetra(4-anilyl)methane (TAM) for several cycles to obtain polymer@ SiO_2 , which was converted into ordered COF-300@ SiO_2 under solvothermal conditions (Figure 5a). The powder XRD patterns did not show any main characteristic reflections for COF-300 until three reaction runs, after which they gradually increased with each run (Figure 5b). The increase in the amount of COF-300 attached to SiO_2 was also evident from the scanning electron microscopy (SEM) images (Figure 5c–f). The BET surface area of COF-300@ SiO_2 was 431 $\text{m}^2\cdot\text{g}^{-1}$, while the surface area of the pristine COF-300 was 1033 $\text{m}^2\cdot\text{g}^{-1}$.

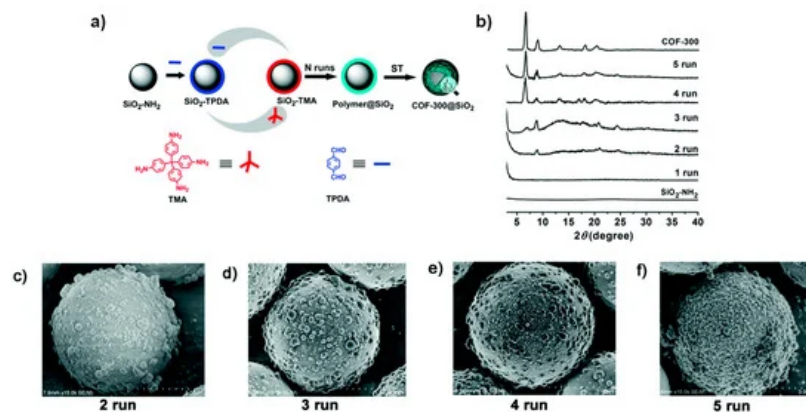
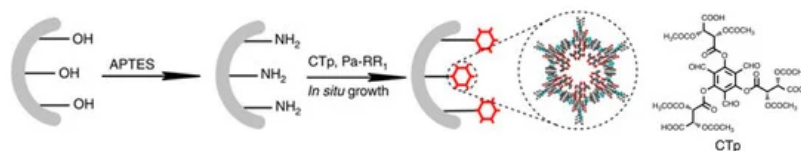


Figure 5. (a) Schematic illustration of the synthesis of COF-300@SiO₂ via LBL method; (b) powder XRD patterns of COF-300@SiO₂ after different reaction runs; (c–f) SEM images of COF-300@SiO₂ after (c) 2, (d) 3, (e) 4, and (f) 5 runs. Reproduced from [40] with permission from The Royal Society of Chemistry.

An in situ growth approach for the fabrication of chiral COF-containing capillary columns was reported by Yan and co-workers [41]. Tp functionalized with chiral (+)-diacetyl-I-tartaric anhydride, CTp, was pre-polymerized with Pa-1. The fused silica capillary column was modified with APTES, and a solution of pre-polymerized CTpPa-1 was injected into the modified column, which was incubated at 80 °C to in situ synthesize the CTpPa-1-bound capillary column (Scheme 1).



Scheme 1. In situ synthesis of chiral COF-bound capillary columns. Reprinted from [41].

2.3. Aluminum Oxide–COF Composites

Aluminum oxide, Al₂O₃, is one of the most studied ceramic materials, and it has been used as porous ceramic support in practical applications, such as purification, separation, and catalysis, due to its high mechanical strength, high porosity, low cost, and good chemical and thermal stability [42]. The first report of a COF membrane grown on a commonly used porous α-Al₂O₃ ceramic substrate was based on boronic-ester-based COF-5 [42]. Surface functionalization of the porous α-Al₂O₃ ceramic support by APTES and subsequent treatment with 4-formylphenylboronic acid rendered a surface modified with boronic acid groups. Then, supported COF-5 membrane was prepared via the co-condensation reaction of 1,4-benzenediboronic acid and 2,3,6,7,10,11-hexahydroxytriphenylene under microwave irradiation. The SEM images indicated that the functionalized α-Al₂O₃ support was completely covered with COF-5 with ≈1 μm membrane thickness, without visible defects or cracks. However, the B–O bonds exhibit poor chemical stability, which leads to rapid decomposition upon exposure to moisture, thereby limiting the practical applications of boronic ester COFs [43]. Following a similar procedure, a structurally stable imine-based 3D COF-320 was grown on the α-Al₂O₃ support under solvothermal conditions. The COF-320 membrane was homogeneous and compact without defects, with a thickness of ≈4 μm.

Caro, Meng, and co-workers reported the development of continuous and high-quality imine-linked COF-LZU1 membranes supported on alumina tubes [44]. Commercial ceramic tubes were chosen as substrates to allow for facile scale up and cleaning, and good chemical and thermal stability. The COF-LZU1 membrane was fabricated on the surface of the tube by a typical in situ solvothermal method involving APTES-functionalization of the alumina tubes, decoration with TFB, and COF-LZU1 growth (Figure 6a). The dark-yellow tubes (Figure 6b) were analyzed by SEM, revealing a continuous COF layer with well-intergrown grains with sizes of 100–300 nm without any visible cracks or pinholes. Cross-sectional SEM images (Figure 6c) showed that the thickness of the COF-LZU1 layer was about 400 nm. Recently, the 2D COF layers were grown in a vertically aligned manner within a skeleton of vertically aligned CoAl-layered double hydroxide (LDH) layers, which served as a template for COF-LZU1 growth (Figure 6d) [45]. The aminated platelets of the ordered CoAl-LDH layer, perpendicular to the α-Al₂O₃ surface, served as a skeleton for the in situ growth of COF-LZU1. In this manner a continuous and defect-free membrane was formed, with ca. 2 μm membrane thickness, having straight vertical channels between the 2D COF layers (Figure 6e,f).

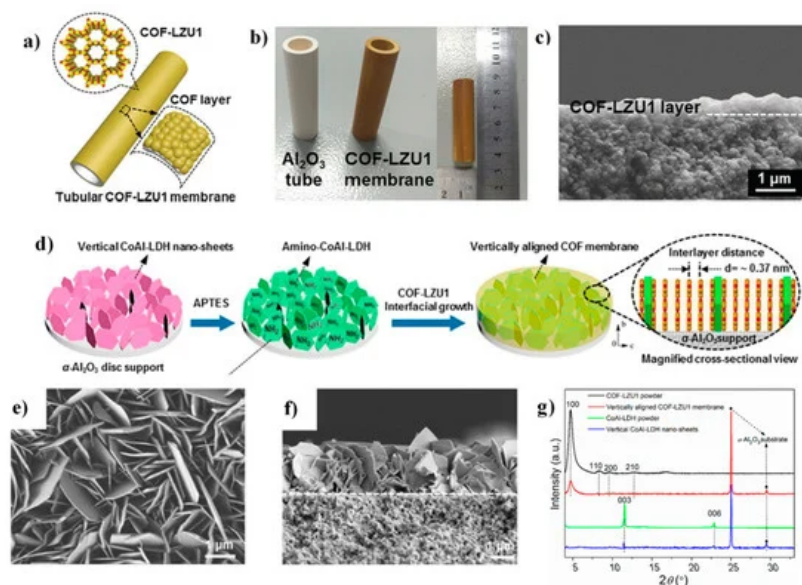
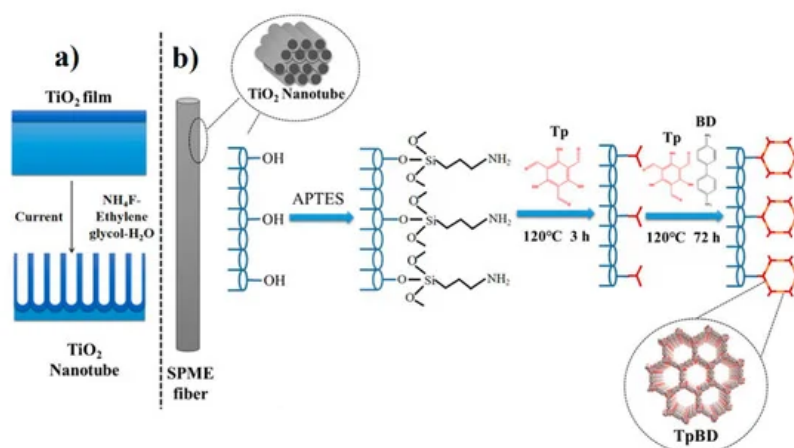


Figure 6. (a) Tubular COF-LZU1 membrane; (b) photographs of an untreated Al_2O_3 tube and a tubular COF-LZU1 membrane; (c) cross-sectional SEM image of a tubular COF-LZU1 membrane; (d) schematic illustration of the vertically aligned COF membrane; top-view (e) and cross-sectional (f) SEM images of the CoAl-LDH layer consisting of vertically oriented nanosheets; (g) PXRD patterns of the powders and membranes. (a–c) Reprinted with permission from [44]. Copyright (2018) Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim. (d–g): Reprinted with permission from [45]. Copyright (2020) American Chemical Society.

2.4. Titanium Dioxide–COF Composites

Titanium is a metal with high corrosion resistance and high stability, and easy surface modification and high chemical activity [46]. The surface of titanium can be modified via anodization to titanium dioxide, TiO_2 , nanotubes, which have provoked widespread interest due to their long-term chemical stability, low cost, facile synthesis, and relative non-toxicity [47]. TpBD COF was covalently bonded on titanium wire via titanium dioxide nanotube arrays and used for solid-phase microextraction of phthalates in vegetables [46]. TiO_2 nanotubes on the surface of the titanium wire, prepared via electrochemical anodization (Scheme 2a), provided Ti-OH moieties for direct modification with APTES, followed by Tp functionalization, and COF growth under solvothermal conditions (Scheme 2b). Spherical TpBD particles were observed by SEM on the surface of the fiber, the estimated thickness of the coating being 15–20 μm .



Scheme 2. Schematic illustration of (a) electrochemical anodization on the surface of titanium wire; (b) preparation of TpBD- TiO_2 solid-phase microextraction fiber. Reprinted with permission from [46]. Copyright (2020) Elsevier Ltd, Amsterdam, The Netherlands.

2.5. Graphene-Based COF Composites

Graphene is a hexagonal honeycomb 2D material formed by sp^2 hybridization of carbon atoms, forming the thinnest possible atomically flat layers that are stacked via weak van der Waals interlayer forces [48][49]. Due to the thinness of the graphene layer, it can be flexible with bending, twisting, and other deformation modes [49]. The in-plane electrical and thermal conductivities are the highest among known materials, but the through-thickness properties are very poor for

stacked graphene. In addition, it exhibits good physicochemical stability and excellent electrical, optical, and mechanical properties, and it has been applied in many fields related to analytical chemistry, such as nanofiltration, separation, and absorption [48].

To gain access to an adsorbent material with both radiation- and acid-resistant properties, a graphene-synergized (GS) TpDAAQ COF composite was fabricated from graphene, Tp, and 2,6-diaminoanthraquinone (DAAQ) via solvothermal method [48]. The obtained GS-COF was then post-synthetically modified to oxime-containing o-GS-COF by treatment with hydroxylamine hydrochloride. The SEM images showed that GS-COF exhibited a lamellar structure, evidencing that the composite retained the laminated structure, but attachment and intercalation effects between graphene and the COF led to changes in the surface and local morphology.

Graphene oxide (GO) is a graphene derivative, which features a limited amount of oxygen-containing functional groups on its lamellar edges and defective parts [50]. It has attracted increasing interest for desalination, purification, and molecular separation due to its hydrophilicity, nearly frictionless surface, and fast water-transporting channels. Additionally, GO has been widely considered as a candidate for nanofiltration membranes because of its ultrathin 2D structure and excellent tolerance towards harsh chemical environments and organic solvents [51]. The nanochannels between the GO flakes provide pathways for organic solvents and water while blocking larger molecules and ions. However, GO membranes suffer from poor flux of water and organic solvents as well as instability under practical application conditions. To improve the permeate flux, nanostructured GO/COF hybrid membranes with different GO/COF ratios, using COF prepared from TFB and Pa-1 under solvothermal conditions, were prepared by vacuum filtration method. For example, GO/COF 4:1.71 hybrid membrane was fabricated by dispersing 4 mg of GO and 1.71 mg of COF in *N,N*-dimethylformamide (DMF), followed by vacuum filtration on a nylon membrane with a pore size of 0.22 μm . The membrane thickness was adjusted by filtrating different amounts of GO and COF while keeping the COF content at 30 wt%, and the flexible hybrid membranes were easily peeled from the nylon substrate. As visualized by SEM, compared with stacked layered structure of GO (Figure 7a), the COF nanoparticles are stacked between the GO layers across the GO/COF membranes (Figure 7b,c).

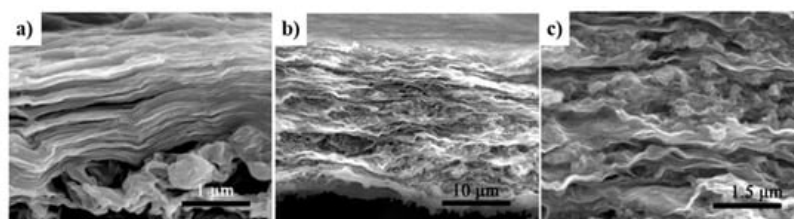
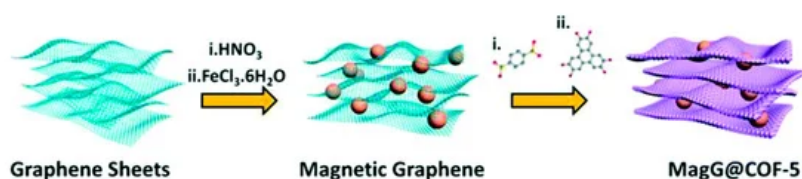


Figure 7. SEM images of GO/COF hybrid membranes: the cross-section of (a) a pure GO membrane and (b,c) a GO/COF 4:1.71 hybrid membrane. Reprinted with permission from [51]. Copyright (2020) Elsevier Ltd.

Hybrid materials based on the combination of graphene with magnetic nanoparticles have drawn intensive interest due to their high surface area, good stability, biocompatibility, unique electrical properties, and strong magnetic response [52][53]. A COF-decorated graphene/magnetite composite, MagG@COF-5, was synthesized by assembling COF-5 layers on the surface of magnetite-decorated graphene (MagG) for recognition of N-linked glycopeptides [53]. The synthetic procedure for the synthesis of MagG@COF-5 is presented in Scheme 3, where MagG is first obtained by graphene functionalization with Fe_3O_4 nanoparticles in a hydrothermal reaction, followed by COF-5 growth. The TEM images revealed that after COF coating the graphene nanosheets became thicker and magnetic NPs were fully covered, demonstrating that MagG sheets were successfully coated with COF-5. The BET surface area of MagG@COF-5 was $201 \text{ m}^2\cdot\text{g}^{-1}$, higher than that of MagG ($65 \text{ m}^2\cdot\text{g}^{-1}$). In another study, magnetite-decorated graphene was coated with a polydopamine (PDA) layer to enhance hydrophilicity [54].



Scheme 3. Synthesis of the MagG@COF-5 composite. Reproduced from [53] with permission from The Royal Society of Chemistry.

Carbon nanotubes (CNTs) are rolled-up graphene sheets, in which the in-plane properties are translated to axial properties, making them among the stiffest axial fibers ever created. CNTs can be either single-walled (SWNTs) or multi-walled nanotubes (MWNTs), which notably affects their mechanical properties [49]. An electroactive COF assembled from 1,3,5-tris(*p*-formylphenyl)benzene (TFPB) and thionine (Thi) was capped with amino-functionalized carbon nanotubes

(CNTs) to form COF_{Thi-TEPB}-CNT composites for sensing [55]. The composite was prepared by simply subjecting the CNTs to the solvothermal COF growth conditions. In electrochemical sensing, the composite structure led to a more uniform and stable electrode surface without losing the catalytic activity of the CNTs.

2.6. Metal Nanoparticle-COF Composites

The synthetic approaches to metal nanoparticle-COF composites comprise three main pathways: (i) growth of NPs on pre-synthesized COFs [56][57], allowing for NP growth controlled by the framework, yielding NPs with relatively small sizes, as low as 1.7 nm, as a result of COF pore dimensions. (ii) Growth of COF on pre-synthesized NPs [35][58], where composites containing metal NPs as large as 50 nm have been employed without compromising NP activity and COF crystallinity. These metal NPs have to either be resistant to the COF formation conditions in terms of solvents, acidity, and temperature, or a polymer shell can be first grown under mild conditions, to form a shell around the NPs, protecting them from subsequent COF recrystallization under acidic conditions. (iii) NP precursors are incorporated onto COF building blocks prior to COF synthesis [59], allowing for simultaneous growth of both the COF structure and the NPs. Following this procedure, NPs with size distribution of 12 ± 4 nm have been grown attached to the COF.

First reported strategy for the growth of metal NPs on COFs was carried out by solvent-free gas-phase infiltration of volatile organometallic precursors [60]. In this procedure, volatile precursor $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)]$ was diffused into the pores of COF-102, and subsequent treatment by UV-light irradiation gave access to Pd NPs. Average NP size was measured to be 2.4 ± 0.5 nm, comparably larger than the pore diameter of COF-102 of 0.9 nm. However, crystallinity of the network was retained, and therefore, the alignment of the pores was proposed to allow these NPs to grow without compromising the structure.

To date, one of the most reported strategies for the synthesis of metal NP-COF composites is simple solution infiltration of NP precursors onto a previously synthesized COF [56][57]. Pioneers were Banerjee and co-workers, who grew gold [56] and palladium [57] NPs on pre-synthesized TpPa-1 by addition of metal NP precursors followed by reduction using NaBH_4 . Metal precursor, HAuCl_4 or $\text{Pd}(\text{OAc})_2$, was uniformly dispersed throughout the TpPa-1 framework through interactions mainly with nitrogen and oxygen atoms. Subsequent reduction by NaBH_4 resulted in a loading of approximately 1.2 wt% Au NPs on TpPa-1, with complete reduction of HAuCl_4 while preserving the chemical composition of the network [56]. However, a slight loss in crystallinity was observed after treatment with the reducing agent, and it was shown that treatment with NaBH_4 alone leads to reduction in COF pore size and surface area, highlighting that it is important not to use an excess of the reducing agent [61]. The TEM images showed Au NPs of 5 ± 3 nm uniformly distributed throughout the framework (Figure 8a). Using $\text{Pd}(\text{OAc})_2$ as precursor, Pd NP loading of 6.4 wt% on TpPa-1 was observed with a size distribution of 7 ± 3 nm (Figure 8b) [57]. However, XRD indicated a slight decrease in the peak attributed to π - π stacking, which, along with the larger NP size, could suggest that Pd NPs were incorporated in the interlayer space and inside the COF pores. The resulting composite materials were applied for the reduction of environmental pollutants and other transformations [56][57]. In another study using a similar approach, ruthenium NPs were loaded on a heteroatom-rich acylhydrazone-linked COF-ASB, prepared from condensation of benzene-1,3,5-tricarbohydrazide and benzene-1,4-dicarboxaldehyde, through RuCl_3 infiltration and NaBH_4 reduction [62]. A total amount of 4.1 wt% of Ru was loaded onto the framework, and the NPs in the size range of 2-5 nm were homogeneously distributed in the composite without compromising the crystallinity and chemical composition of the COF.

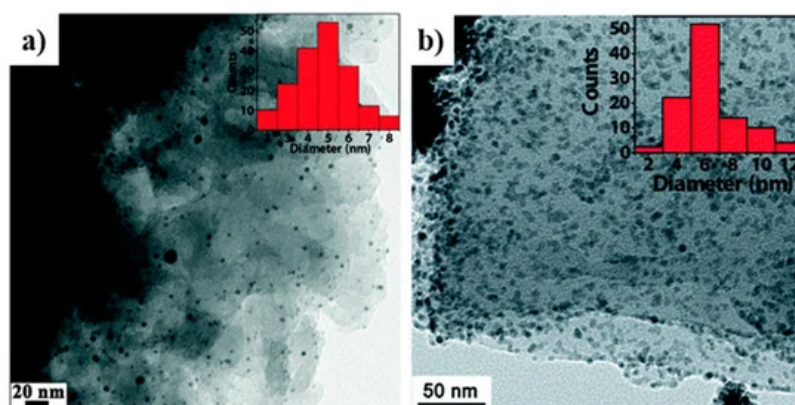


Figure 8. TEM images of (a) Au NP-TpPa-1 [56] and (b) Pd NP-TpPa-1 [57] composites. Inset image: NP size distribution histogram. (a) Reproduced from [56] with permission from The Royal Society of Chemistry. (b) Reproduced from [57] with permission from The Royal Society of Chemistry.

Pt and Pd NPs with narrow size distributions of 1.7 ± 0.2 nm were synthesized on a thioether-containing COF material also using NaBH_4 as reducing agent [63]. The formation of NPs with such narrow size distribution was attributed to the presence of the thioether chains inside the pores of the COF, onto which the metal NP precursors could bind, resulting in greater control of NP growth inside the pores and preventing agglomeration beyond the dimensions of the pores. A total Pt content of 34 wt% and a total Pd content of 26 wt%, respectively, were observed for the composite materials. Furthermore, it was demonstrated that the order of the framework is crucial for the synthesis of such small and uniformly dispersed NPs, whereas using an amorphous thioether-containing polymer formed from the same building blocks as those utilized for the COF resulted in a random size distribution of Pt NPs.

Silver NPs have been grown on pre-synthesized COF-LZU1 in a single step by addition of Ag in the form of AgNO_3 in deionized water at room temperature [64]. The success of this straightforward strategy was attributed to the high affinity of the Ag ions to nitrogen, as has been observed for other ions, such as copper [65]. Reduced BET surface area indicated that the NPs were successfully dispersed either inside or on the surface of the COF, corresponding to 2.8 wt% of the composite [64].

Strategies consisting of COF growth on pre-synthesized NPs result in the confinement of the metal NPs within a COF shell. In this method, pre-synthesized NPs are subjected to COF growth conditions [35][58]. However, harsh conditions used for COF formation, such as elevated temperature and highly acidic medium, may hinder the use of this methodology for some NP classes.

Gold and platinum NPs were successfully encapsulated in TAPB-DMTP-COF [58] by pre-functionalization of the NP surface with polyvinylpyrrolidone (PVP), used as a stabilizer in the NP synthesis [59][66], followed by COF growth [58]. Following this strategy, on one hand, a single Au NP of 50 nm was incorporated within a COF shell (Figure 9a), whereas on the other, a cluster of Pt NPs of 3.8 nm was encapsulated by the COF (Figure 9b). The structure and composition of TAPB-DMTP-COF were not compromised. Furthermore, both the COF material and the metal NP-COF composite featured identical surface areas. Therefore, adsorption capacity of the framework was retained. It was proposed that this procedure can be used for the incorporation of other metal NPs resistant to the acidic COF formation conditions. In contrast, using the same amorphous-to-crystalline approach as for Fe_3O_4 composites (for the synthesis), MasPOCH, Zamora, and co-workers grew COF around Au and Pd NPs by a two-step approach of polymer growth under mild conditions and recrystallization of the polymer into COF [35].

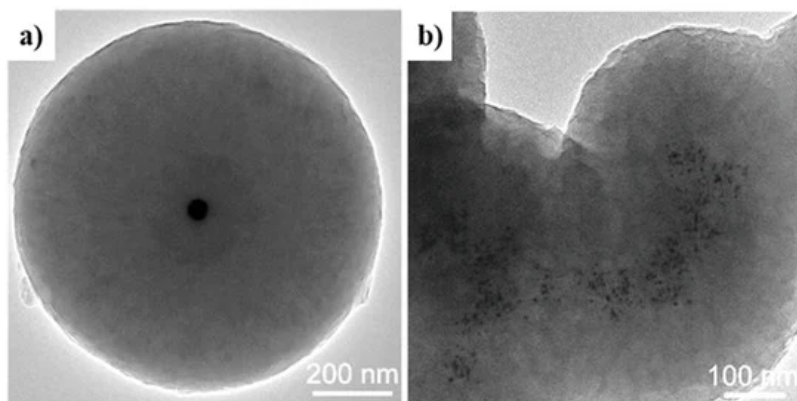


Figure 9. TEM image of (a) 0.38 wt% 50 nm Au NP (dark middle circle) and (b) 3.8 nm Pt NPs within the COF. Reprinted with permission from [58]. Copyright (2017) American Chemical Society.

Wang, Hu, and co-workers reported a procedure for the in situ growth of Au NPs on the surface of TAPB-DMTP COF [67]. The synthesized Au NPs were successfully immobilized by electrostatic interactions with the unsaturated amino groups present on the TAPB-DMTP surface. The obtained composite retained the COF crystallinity with a high surface area of $1915 \text{ m}^2\cdot\text{g}^{-1}$. However, the surface area of the composite was lower than that obtained for the bulk COF ($2385 \text{ m}^2\cdot\text{g}^{-1}$), which was attributed to the growth of Au NPs also inside the COFs pores, evidencing the difficulty of controlling the nanoparticle growth.

By pre-functionalizing the building blocks for COF formation with NP precursors, it is possible to simultaneously grow NPs during COF formation, as shown by Balaraman, Banerjee, and co-workers [59]. A bipyridine (Bpy) building block pre-functionalized with PdCl_2 was employed for the formation of TpBpy (Figure 10), where Pd NPs grew during COF synthesis due to the rupture of the linkage between the NP precursor and the building block. Importantly, the composite was crystalline in nature, showing pore dimensions in the range of 1.4 to 2.3 nm, the latter corresponding to the pore size of TpBpy, which could suggest partial blocking of the pores by the NPs. Total Pd content of 15.2 wt% was found, with Pd NP

size being 12 ± 4 nm. Thus, the size of the Pd NPs well exceeded the pore size of the COFs, and it was proposed that the NPs grew into the space between the COF layers and on the surface. Overall, a uniformly dispersed Pd NP-TpBpy composite was formed.

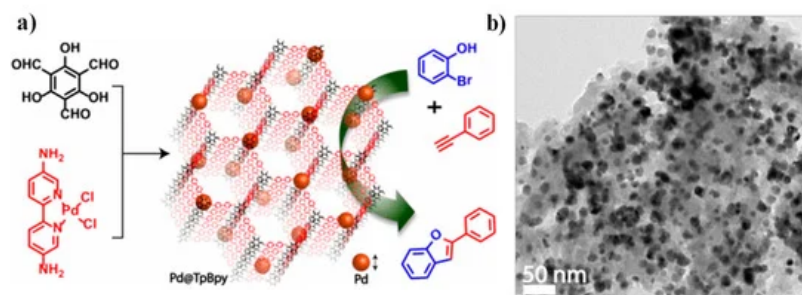


Figure 10. (a) Schematic illustration of the composite synthesis and (b) a TEM image of Pd NP-TpBpy composite. Reprinted with permission from [59]. Copyright (2017) American Chemical Society.

2.7. Stainless-Steel COF Composites

For solid-phase microextraction (SPME) composite fibers, stainless-steel wire is usually used as support to load the chosen COF [68]. The most used strategy to fabricate such COF-coated fibers consists of four main steps: (i) pre-cleaning of the stainless-steel wire with aqua regia or hydrofluoric acid to obtain a rough surface; (ii) dip-coating of the raw wire with a thin layer of silicone glue; (iii) careful rotation into COF powder; and (iv) drying/curing. Once cured, the COF-coated fiber can be further coated to protect the COF layer. This strategy provides a chemically and thermally stable coating. In addition to this strategy, in situ COF growth or layer-by-layer synthesis have also been reported. Recently, in situ room-temperature fabrication of TFPB-BD-bonded fiber was reported [69], where an APTES-functionalized stainless-steel wire was treated with one of the COF building blocks, TFPB, and subsequently immersed in a solution containing the other COF building block, BD, and the catalyst acetic acid, leaving the reaction to continue for 3 days at room temperature. In addition, in a layer-by-layer approach [70], the APTES-functionalized stainless-steel wire was immersed alternately in building block solutions containing the organic solvent and the corresponding catalyst. After repeating the process until a desirable thickness (≈ 5 μm) was reached, the coating was cured by thermal treatment.

2.8. Others: COF Composites with Polymeric Substrates and MOFs

In recent years, the fabrication of polymer-based COF composites has gathered increased attention in solid-phase extraction and separation. To rapidly extract anti-inflammatory drugs from wastewater, a COF-functionalized poly(styrene-divinyl benzene-glycidylmethacrylate) composite, COF@PS-GMA, was prepared by growing COF on the surface of the PS-GMA particles via solvothermal reaction [71]. SEM images (Figure 11) showed that the PS-GMA particles are porous spheres with a size of ≈ 6 μm , whereas the COF-coated particles exhibit a smooth surface. Additionally, the BET surface area increased from 201 to 404 $\text{m}^2\cdot\text{g}^{-1}$ after COF growth.

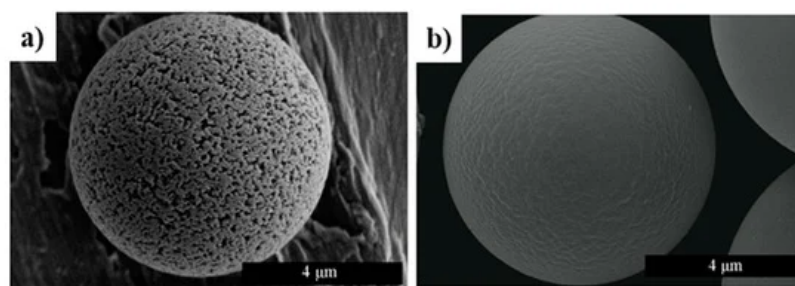


Figure 11. The scanning electron micrographs of (a) bare PS-GMA and (b) COF@ PS-GMA. Reprinted with permission from [71]. Copyright (2018) Elsevier B.V.

Polymeric membrane materials are widely used in various separation applications because of their mechanical stability and easy processability [72]. However, physical aging, thermal stability, plasticization, and permeability–selectivity trade-off are limiting the applications of polymeric membranes. To enhance the performance of polymeric membranes, COFs can be used as fillers in the polymer matrix. For the preparation of COF-based composite membranes, unidirectional diffusion synthesis (UDS) of TpPa-1 [73] on commercial polyvinylidene fluoride (PVDF) microfiltration substrates was carried out at room temperature. In the synthesis, an aqueous solution of Pa-1 and a solution of Tp in *n*-hexane were simultaneously charged into the two sides of a diffusion cell (Figure 12). During the reaction, Pa-1 molecules could pass through the macropores of PVDF to react with Tp molecules at the phase interface formed by the solution pair, leading to the in situ

synthesis of TpPa-1 crystallites on the top side of the PVDF substrate. A continuous and dense TpPa-1 layer was observed by SEM that was distinctly different compared to the pristine PVDF substrate having a macroporous morphology.

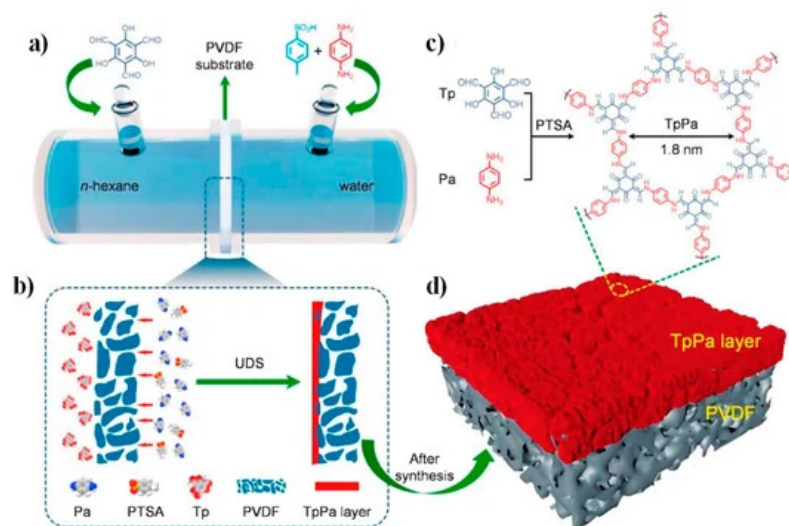


Figure 12. Schematic illustration of the preparation process of the COF-based membranes via the UDS method. (a) Schematic illustration of a diffusion cell for the COF growth by UDS. (b) Schematic illustration of the formation of the COF layer on the top side of PVDF support via unidirectional diffusion of Pa-1 and PTSA molecules through the pores of the PVDF support to react with the Tp molecules. (c) Synthesis of the COF through the condensation of Tp and Pa-1. (d) The schematic illustration of intergrowth appearance of COF/PVDF membranes after synthesis. Reprinted with permission from [73]. Copyright (2019) Elsevier B.V.

Stable TpPa-1 and TpBD COFs were also used as active phase and incorporated within substituted polybenzimidazole polymer (PBI-Bul) matrix to fabricate self-supported TpPa-1@PBI-Bul and TpBD@PBI-Bul hybrid membranes [72]. Six hybrid membranes were prepared with a sequential increase of COF content in the PBI-Bul polymer (Figure 13). To prepare highly flexible COF(*n*)@PBI-Bul hybrid membranes, where *n* = 20, 40, or 50 wt% of TpPa-1 and TpBD, a solution-casting method using dimethylacetamide (DMAc) as solvent was employed. PBI-Bul solution in DMAc was mixed with the stock suspension of COF. Then, the reaction mixture was poured onto a flat glass surface and heated to 85 °C for 16 h to remove the solvent, after which the membrane was peeled off from the glass surface and dried. In the hybrid membranes, the COF loading could be successfully achieved up to 50%, beyond which defects in the membrane were observed. The average thicknesses of the hybrid membranes were from 47 to 80 μm. The crystallinity of TpPa-1(*n*)@PBI-Bul and TpBD(*n*)@PBI-Bul hybrid membranes was confirmed by wide-angle X-ray diffraction (WAXD). The SEM cross-section of TpBD(*n*)@PBI-Bul hybrid membranes confirmed the distribution of COF particles throughout the membrane matrix. No visible cracks or tears at the COF-polymer interface were seen in the membrane cross-section or the surface. Furthermore, the COF particles were firmly bound within the PBI-Bul backbone, not allowing the COF to leach out from the polymer matrix.

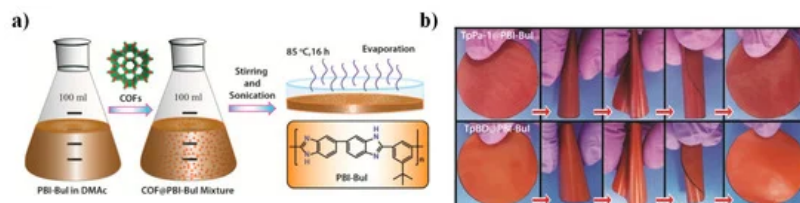


Figure 13. (a) Schematic illustration of the preparation of COF@PBI-Bul hybrid membranes. (b) Digital photos showing the flexibility of TpPa-1 and TpBD(50)@PBI-Bul hybrid membranes. Reprinted with permission from [72]. Copyright (2016) Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim.

Electrospinning has been used to gain access to COF-based films [74]. Dual-pore COF was first synthesized using 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetraaniline (ETTA) and [1,1'-biphenyl]-4,4'-dicarbaldehyde (BPDA) as monomers, and dispersed homogeneously in DMF with polyacrylonitrile (PAN) to obtain the spinning solution. Then, the PAN@COF nanofiber films with different COF-loading ratios were prepared using a co-electrospinning method. Randomly distributed spindle-shaped COF particles could be clearly observed in the SEM images of the PAN@COF film (Figure 14). XRD

characterization indicated that the COF crystals remained intact in the films. Furthermore, the films maintained the dual-pore structure of the COF and showed good stability and excellent reusability in removing phytochromes from vegetable extracts by filtration or immersion.

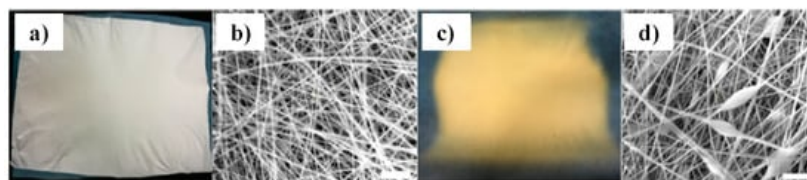


Figure 14. (a) Digital photo and (b) SEM image of the pure PAN film. (c) Digital photo and (d) SEM image of the PAN@COF film. Reprinted with permission from [74]. Copyright (2020) American Chemical Society.

Mixed matrix membranes (MMMs) using TpPa-2 COF as nanofiller were prepared for water treatment by Xu and co-workers [75]. To prepare the MMMs, TpPa-2 prepared from Tp and 2,5-dimethyl-1,4-phenylenediamine (Pa-2) by microwave (MW) synthesis or mechanochemical (MC) method was blended with polysulfone (PSf) via non-solvent induced phase inversion. The resulting solution was casted onto a glass plate with a thickness of 150 μm , and the casting film was immersed in deionized water for 12 h. The TpPa-2(MW)/PSf membrane had a much smoother surface and less fouling accumulated on the surface compared to the TpPa-2(MC)/PSf membrane. The cross-sectional SEM images showed that nanoparticles with a diameter of about 200 nm were uniformly embedded in both TpPa-2(MW)/PSf and TpPa-2(MC)/PSf membranes, while the pristine PSf membrane was neat, although an asymmetry structure consisting of a dense layer and a macro-void middle region with finger-like pores was observed in all three membranes.

COFs and MOFs are porous materials that have both been used in membrane-based gas separation [76]. However, the fabrication of membranes with both high permeability and high selectivity is a great challenge. To enhance the performance of the membranes, a MOF was grown on a COF membrane to produce COF-MOF membranes. At first, polyaniline (PANI) modified SiO_2 disks were coated by COF-300 by subjecting them onto COF growth conditions in a Teflon-lined autoclave. Subsequently, the MOF was anchored on top in a similar manner. The SEM images of [COF-300]-[$\text{Zn}_2(\text{bdc})_2(\text{dabco})$] composite showed that the thicknesses of the COF and MOF layers were 42 and 55 μm , and in the case of [COF-300]-[ZIF-8], 40 and 60 μm , respectively. In the XRD, only the diffraction peaks of the MOF material were observed, which indicated that the top of the composite membranes was built of pure MOF phase and COF layer was covered completely by it. The COF-MOF membranes showed better selectivity of H_2/CO_2 gas mixtures compared to the respective MOF and COF membranes alone.

Highly water-selective membranes based on hollow COF nanospheres were synthesized using a template-directed method starting from magnetic COF composite $\text{Fe}_3\text{O}_4@\text{TpBD}$ (Figure 15a) [77]. The Fe_3O_4 core of $\text{Fe}_3\text{O}_4@\text{TpBD}$ was etched in HCl solution to yield hollow TpBD (H-TpBD) nanospheres. The H-TpBD nanospheres had a hollow structure with a diameter of around 400 nm and COF shell thickness of around 50 nm (Figure 15b). The H-TpBD nanospheres with well-defined morphology were then incorporated into sodium alginate (SA) polymer to fabricate hybrid membranes for ethanol dehydration. The homogeneous membrane casting solution was spin-cast on PAN substrates to obtain SA-H-TpBD (X)/PAN, where X (=2, 4, 6, 8, 10) is the mass percentage of H-TpBD to the total of SA and H-TpBD. The field-emission scanning electron microscope (FESEM) images of the membranes showed that the pure SA/PAN membrane had a smooth and dense surface. With the incorporation of H-TpBD, the exposed nanospheres on the membrane surface could be observed. When the H-TpBD content ranged from 2 to 6 wt%, no visible voids at the interface between SA and H-TpBD could be observed. However, when the content was larger than 8 wt%, obvious aggregation of H-TpBD nanospheres was observed. The cross-section images of the membranes showed that for all membranes, the active layers adhered tightly to the porous PAN substrate with a uniform thickness of about 1 μm .



Figure 15. (a) Schematic illustration of the synthesis protocols and chemical structures of the H-TpBD. (b) TEM image of the synthesized H-TpBD. Reprinted with permission from [77]. Copyright (2018) Elsevier B.V.

3. Analytical Applications

The number of reported analytical applications for COF composites has dramatically increased in the last two years (Figure 16A), showing the growing impact that these novel materials have in the field of analytical chemistry. Reported works for COF composites can be classified in two main groups: (i) separation applications, e.g., chromatographic separation, environmental remediation, and extraction techniques, and (ii) chemical sensing, including electrochemical, colorimetric, luminescence, fluorescence, and surface-enhanced Raman scattering (SERS) approaches (Figure 16B).

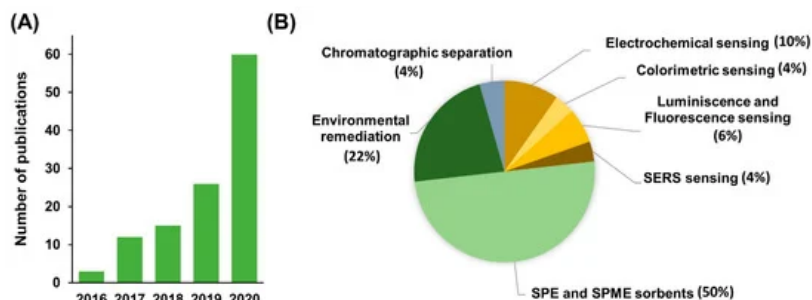


Figure 16. (A) Number of publications related to COF composites for analytical applications from 2016-2020 (data obtained from Scifinder® database—August 2020), (B) number of publications related to COF composites divided by the analytical application.

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