Application of microporous organic networks in separation science

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ABSTRACT

Microporous organic networks (MONs) are a new class of advanced porous materials built from versatile aromatic alkynes and halides via Sonogashira coupling. The extremely large surface areas, excellent solvent and thermal stabilities, tunable pore sizes and functions, as well as convenient post-modification and easy engineering on other matrices make MONs highly convincing in analytical chemistry from sample pretreatment to chromatographic separation. This review briefly introduces recent application and progress of MONs and MONs-based composites in separation science including solid phase extraction, solid phase microextraction, gas chromatography and high-performance liquid chromatography. In the end, the challenge and outlook about the application of MONs in separation science are also presented.

1. Introduction

Exploration of novel and advanced porous materials in separation science has received great concerns for the revolution of sample pretreatment and chromatography [1–3]. Microporous organic networks (MONs), a subclass of conjugated microporous polymers (CMPs), are an emerging type of porous materials constructed with aromatic alkynes and halides via Sonogashira-Hagihara coupling [4–8]. As a novel class of microporous materials, MONs possessed diverse structures, large surface areas, good solvent and thermal stabilities, tunable porosity and functions [9–13]. Since Jia et al. reported the first example of MONs in sample pretreatment in 2016 [14], researchers have drawn a lot of attention on the application of this new type of advanced materials in separation science. Recently, pure MONs particles, MONs coatings, magnetic Fe₃O₄@MONs composites and spherical SiO₂@MONs microspheres were designed and prepared to address the bottleneck issues of MONs in practical use and to meet the growing demand of analytical technologies from sample pretreatment to chromatography. These explorations make MONs highly potential in separation science.

This review summarizes recent advances and applications of MONs in separation science. MONs with different structures and functions have been designed and engineered as advanced adsorbents in sample pretreatment including column solid phase extraction (SPE) [15], magnetic SPE [16–19], on-line SPE [20] and solid phase microextraction (SPME) [14,21], and as novel stationary phases in chromatographic separation such as gas chromatography (GC) [22–24] and high-performance liquid chromatography (HPLC) [25,26]. The prospects of MONs in separation science are also discussed.

2. Microporous organic networks

Since Cooper' group firstly reported the concept of CMPs in 2007 [4], researches have made great efforts to the progress of this new type of advanced materials. CMPs were constructed by a variety of regular microporous poly (aryleneethynylene) networks. The methods used to synthesize CMPs covered Sonogashira-Hagihara coupling, Suzuki-Miyaura coupling, Yamamoto coupling, Heck coupling, Cyclotrimerization reactions, Alkyne metathesis, Schiff-base condensations, Phenazine ring fusion, Heterocycle linkages, Buchwald-Hartwig amination, Oxidative coupling, Hypercross linking method, Electropolymerization and some unconventional synthesis methods [4,27–39]. Because of the irreversibility in kinetic coupling process, CMPs were amorphous and without long-range molecular order [4].

Microporous organic networks (MONs), a sub-class of CMPs synthesized via Sonogashira-Hagihara coupling, was firstly defined by Son' group in 2012 [6]. MONs were constructed with the

"skeleton" of alkyne-containing monomer and the "linker" of aryl halide under alkaline conditions utilizing palladium and copper as the catalysts. The common used synthetic methods for MONs included refluxed synthesis, copper-free solvothermal synthesis, and room-temperature stirring synthesis [4,40,41]. The organic building blocks of alkyne monomers mainly included C2 linear, C3 triangular, C4 quadrangular and Td tetrahedral types (Fig. 1). The aryl halide monomers displayed much more forms, facilitating the construction of different MONs with various topologies (Fig. 2). Similar to the metal-organic frameworks and covalent-organic frameworks, the MONs' topologies also showed different polygon skeletons, which can be obtained by assembling rigid basic building blocks as vertices and edges. The common topologies of MONs covered hexagonal, tetragonal and rhombic structures (Fig. 3). Moreover, based on the asymmetry of building blocks, some noncyclic structures can also be generated (Fig. 3). Fig. 4 shows the common used MONs' skeletons. Given their extended conjugation network structures, large specific surface area, tunable properties, high porosity, and excellent thermal and chemical stabilities, MONs have been widely investigated in catalysis [42,43], sensing [44,45], lithium-ion batteries [46,47], drug delivery [48,49], nanofiltration [50], and adsorption [51–54]. Recently, the application of MONs in analytical separation science has owned increasing concerns (Table 1). MONs and their composites have presented bright application prospects in sample pretreatment and chromatography.

Table 1 summarizes the basic properties and applications of the reported MONs or their composites in separation science. All MONs used in separation science possess good solvent and thermal stabilities (>300 °C), and large Brunauer-Emmett-Teller (BET) surface area (>500 mg g^{-1}). The pore sizes of these MONs are less than 2 nm, agreeing with the microporous nature of MONs. The water contact angles of MONs range from 55° to 143°, depending on the functional groups introduced on MONs' networks. Because of small and uneven particle size, only very few MONs can be directly used as efficient sorbents for SPE. MONs-based magnetic solid phase extraction (MSPE) and on-line SPE have been developed on MONs' composites prepared by engineering MONs shell onto proper matrices such as magnetic Fe_3O_4 microspheres and spherical SiO_2 particles [16–20]. MONs' coatings have also been prepared via dynamic coating, physical adherent, *in situ* growth and chemical coupling methods for SPME and GC [14,21–24]. In addition, spherical SiO_2@MONs composites have been also rationally designed and engineered as novel packing materials for HPLC separation of diverse analytes [25,26].

3. MONs for sample pretreatment

3.1. MONs for SPE

The large surface area, excellent chemical stability, versatile properties, aromatic pore wall and networks make MONs good candidates as novel and efficient adsorbents in SPE of aromatic contaminants. However, tedious and time-consuming centrifugation or filtration procedures are usually needed to collect and recycle the MONs from sample matrices because of their quite low densities and small particle sizes, which may hinder the potential application of MONs in SPE.

To solve the above mentioned obstacles and to show the applicable prospects of MONs, our group [15] represented the preparation of a carboxyl groups introduced MON (MON-COOH) SPE column for enriching four hazardous phenols from river and lake water samples before HPLC analysis. The MON-COOH was facilely obtained by a simple refluxing method and then packed into an empty SPE carriage to avoid the above mentioned obstacles for recycling the adsorbents. Depending on the π-π, hydrophobic and hydrogen bonding interaction between phenols and MON-COOH, the proposed MON−COOH−SPE-HPLC-UV method showed good analytical performance for chlorophenols and nitrophenols with wide linear range, low limits of detection (LODs) and limits of quantification (LOQs), large enhancement factors (EFs), and good
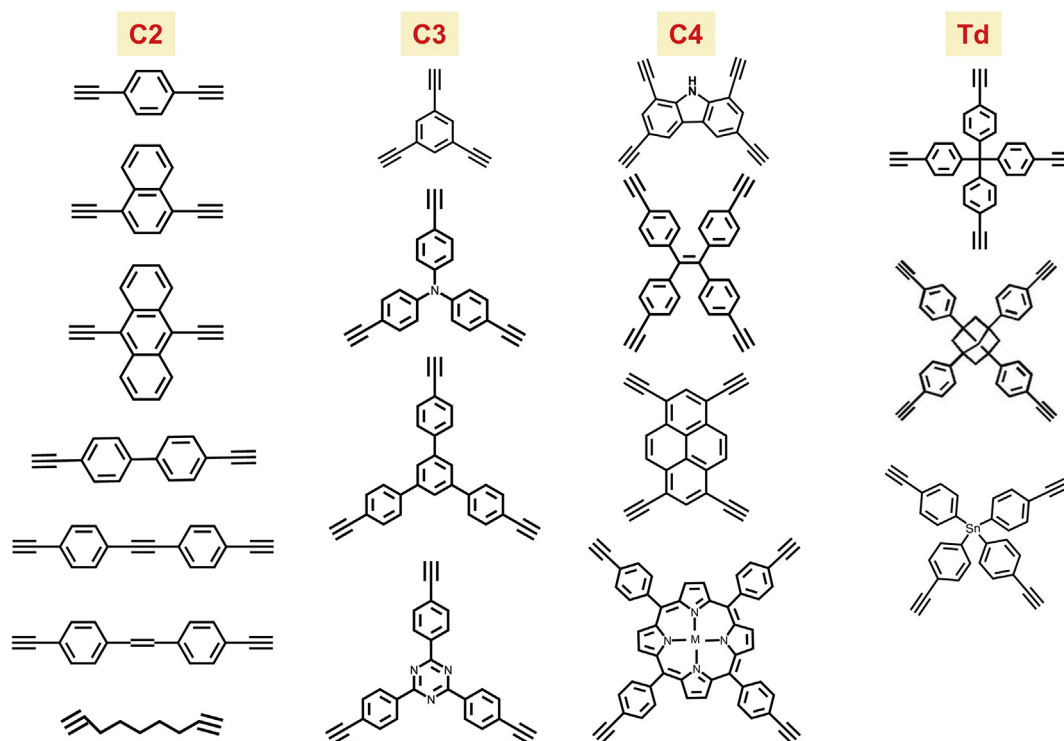

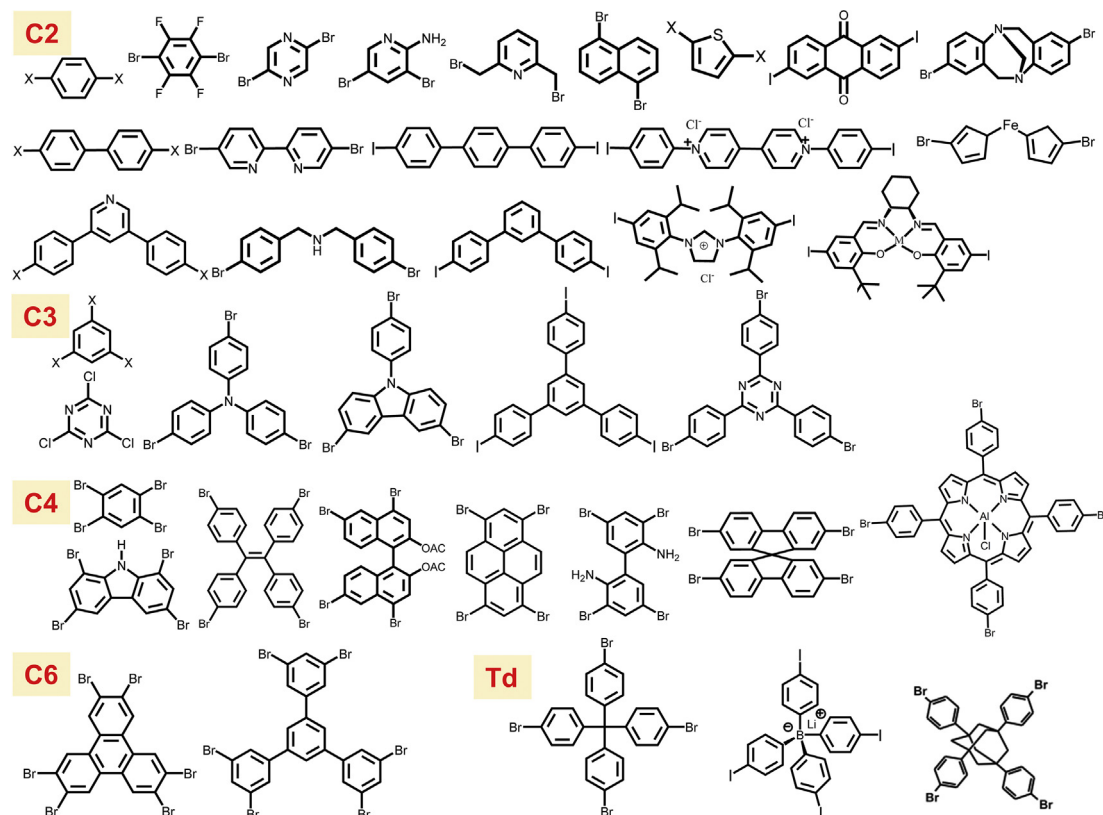**Fig. 1.** Alkynyl building units for MONs.

Fig. 2. Aryl halide building units for MONs.

intra-day, inter-day and column-to-column precisions (relative standard deviations, RSDs). The prepared MON-COOH SPE column could be reused at least 80 times without any decrease of the extraction efficiency for the selected phenols, which was superior to many reported porous adsorbents-based methods. MON-COOH also gave better extraction efficiency for the studied phenols than D113 acrylic resin (a commercially carboxyl-ion-exchanger). These results revealed the feasibility and potential of MONs in SPE of trace contaminants from aqueous solution.

Magnetic solid phase extraction (MSPE) had been regarded as a high-efficiency and convenience sample pretreatment technique in diverse areas due to the inherent advantages of easy separation and recycling from complex matrices, environmentally friendly and costless. Therefore, the synergistic combination of the good extraction performance of MONs and the convenience of magnetic separation to synthesize magnetic MONs or their composites should be a feasible way to avoid the above mentioned obstacles and to promote the application of MONs in SPE.

In 2018, Lei et al. [16] reported the fabrication of spherical magnetic poly (phenylene ethynylene) MON composites with covalently built-in Fe_3O_4 nanoparticles and conjugated three-dimensional networks for MSPE of six bactericides from vegetables and fruits prior to the ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) determination (Fig. 5). The novel magnetic MON networks with the dense poly (phenylene ethynylene) conjugation system largely improved the extraction efficiency for phenyl containing bactericides via the hydrophobic and π-π interaction. Such design and hypothesis were further confirmed by the subsequent experimental and Gaussian simulation data. Benefit from the embedded Fe_3O_4 nanoparticles, the adsorbent could be conveniently separated and recycled from sample matrix with the aid of an external magnet. The developed method displayed wide linear range (0.0010−20 μg L^{-1}) and low LODs (0.27−3.1 ng L^{-1}) for bactericides. Six bactericides at the concentrations between 0.038 and 0.62 μg kg^{-1} were detected in vegetable or fruit samples with the recoveries of 80.2−119%, revealing the good practicability of magnetic MONs for sensitive and accurate determination of trace bactericides in complex samples.

Recently, Du et al. [17] represented the design and synthesis of a well-defined core-shell structured magnetic Fe_3O_4@MON-NH$_2$ composite for efficient MSPE of endocrine disrupting chemicals (EDCs) from water, beverage bottle and juice samples (Fig. 6). The uniform MON-NH$_2$ shell was well decorated on magnetic Fe_3O_4 core via a facile *in-situ* growth method to provide numerous π-π, hydrophobic and hydrogen bonding interaction sites for EDCs containing hydrophilic −OH groups, aromatic benzene rings and hydrophobic alkyl chains. The Fe_3O_4 acted as the magnetic separation module to avoid the cumbersome and time-consuming centrifugation or filtration steps during the conventional SPE procedures. A Fe_3O_4@MON−NH$_2$−based MSPE-HPLC-UV method with large EFs (172−197), wide linear range (0.05−1000 μg L^{-1}), low LODs (0.015−0.030 μg L^{-1}) and good reusability was proposed for four typical EDCs. The developed method also gave less adsorbent consumption and lower LODs than many other reported methods. This work has well integrated the advantages of Fe_3O_4 core for convenient magnetic separation and of MON-NH$_2$ shell for efficient extraction, providing a new way to promote the progress of MONs in SPE.

Subsequently, Wang' group [18] reported a step-by-step assembly method to fabricate Fe_3O_4@UiO-66-NH$_2$@MON as a novel hybrid composite for the enrichment of trace aflatoxins in food and agricultural crops (Fig. 7). The magnetic Fe_3O_4 core was firstly decorated with UiO-66-NH$_2$ to form Fe_3O_4@UiO-66-NH$_2$
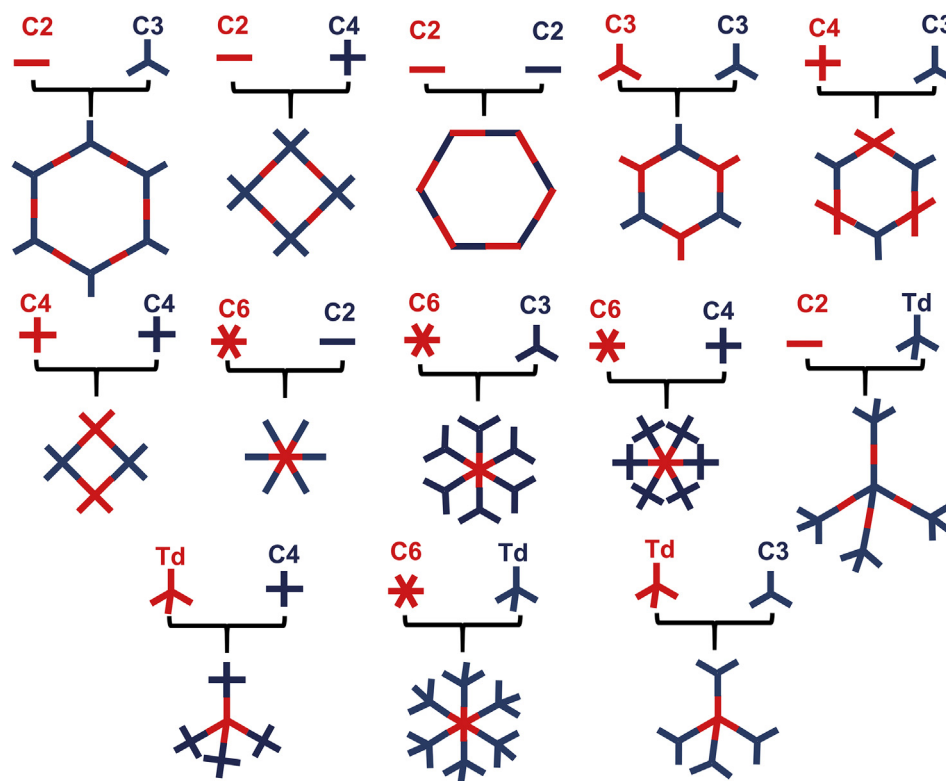
Fig. 3. Typical topologies of MONs.

composite. The hydrophobic MON shell was then introduced via Sonogashira coupling reaction to yield Fe$_3$O$_4$@UiO-66-NH$_2$@MON microsphere. The proposed MSPE-HPLC-FLD method possessed good selectivity, sensitivity and reusability, and low LODs (0.15–0.87 μg L^{-1}) for aflatoxins. The hydrophobic MON shell largely strengthened the adsorbents' hydro-stability, thus favoring their practical applications in diverse matrices. This work revealed the feasibility of magnetic MONs for selective enrichment and determination of trace aflatoxins from complex agricultural samples.

Magnetic adsorbents for MSPE are conventionally comprised with two components, the magnetic response component for separation and the functional component either straightly decorated or the composites subsequently introduced for extraction. Reasonable design and combination of functional extraction component and magnetic response component to synthesize novel magnetic adsorbents are essential to improve the selectivity and efficiency in MSPE.

As the above magnetic MONs composites were all on the basis of Fe$_3$O$_4$ nanoparticles, He et al. [19] reported a new method to engineer uniform MON-2NH$_2$ shell on a nitrogen-doped carbon derived from zeolitic imidazolate framework-67 (ZIF-67) to fabricate Co@NC-MON-2NH$_2$ microsphere for efficient MSPE of trace plant growth regulators (PGRs) (Fig. 8). As carboxyl groups, and aromatic benzene or naphthalene rings are usually involved in PGRs' structures, the positively charged MON-2NH$_2$ shell with multiple π-π and hydrogen bonding sites to PGRs was designed and decorated. The magnetic Co and N co-doped porous carbon (Co@NC) was firstly obtained by calcinating the Co, N and C enriched ZIF-67. The Co@NC was then served as the magnetic response component for quickly separation under magnetic field and as the support for the facile decoration of MON-2NH$_2$ coatings, as well as the porous graphite carbon to promote the enrichment

efficiency for PGRs. The synthesized Co@NC-MON-2NH$_2$ gave low LODs (0.009–0.150 μg L^{-1}), wide linear range (0.03–500 μg L^{-1}), large EFs (151–196) and good precisions for PGRs via the predesigned hydrogen bonding sites (-NH$_2$) and π-π and hydrophobic interaction sites (aromatic conjugated networks and alkynyl groups). The synergistic effect of MON-2NH$_2$ shell and Co@NC core was also observed during the extraction, showing the better performance of Co@NC than Fe$_3$O$_4$ for the fabrication of MONs-based magnetic adsorbents for PGRs. The PGRs with the concentrations of 0.3–9.6 μg L^{-1} in diverse vegetable samples were determined by the developed Co@NC-MON-2NH$_2$-MSPE-HPLC-UV method. This study offered a promising way to the efficient construction of MON-based magnetic adsorbents and disclosed the promise of MONs for the extraction of PGRs from complex natural water and vegetable matrices. Fe$_3$O$_4$ and Co@NC all can be used as the magnetic core to construct MONs-based magnetic adsorbents, but the C–O, C–N and C=C bonds within the porous carbon of Co@NC definitely improved the extraction efficiency for PGRs to a certain extent during MSPE [19]. However, the preparation process of Co@NC is more complex and time-consuming than that of Fe$_3$O$_4$.

The above works have completely exhibited and proved the convenient and great prospects of magnetic MONs or their composites in MSPE and the feasibility to promote the application of MONs in SPE. MONs such as MON, MON-NH$_2$, MON-2NH$_2$, and MON-OH with different functional groups are all capable to decorate on magnetic Fe$_3$O$_4$ and Co@NC cores to fabricate magnetic MONs. However, fabrication of mono-dispersed magnetic MONs with controllable shell thickness and multiple interaction sites is still challenging. In addition, all these works were carried out under the off-line SPE mode. The intrinsic disadvantages of off-line SPE such as tedious and multi-step operations, easy contamination, low repeatability and reproducibility might affect the accuracy to a certain degree and would impede the progress of
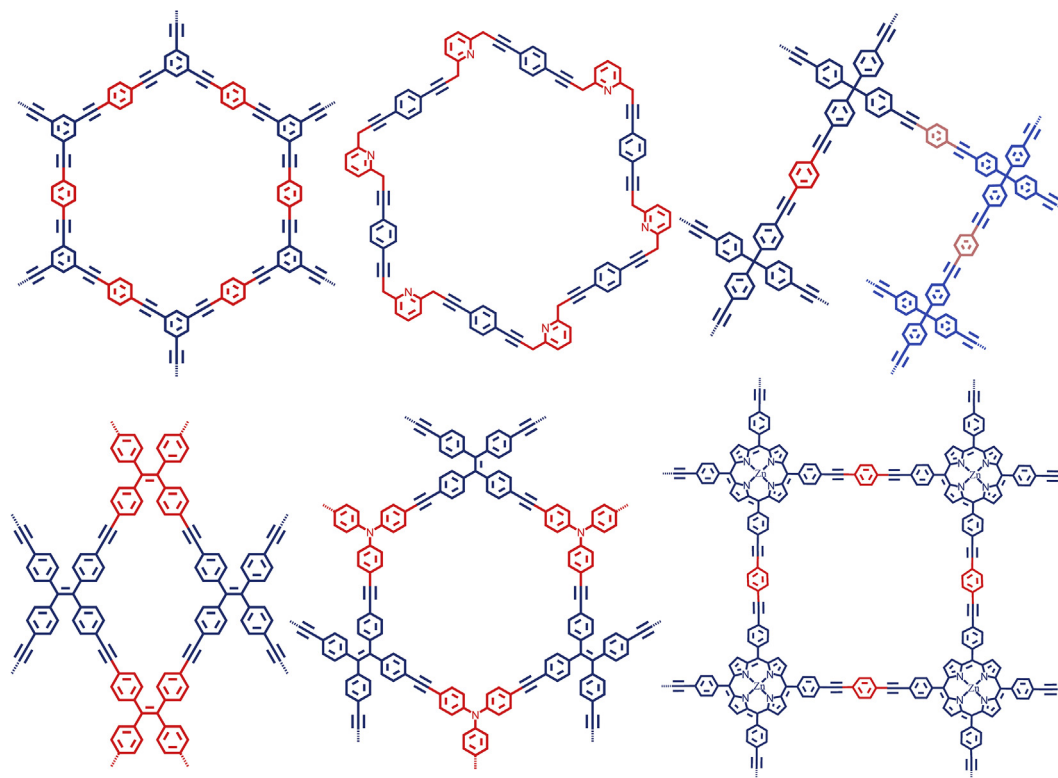
Fig. 4. Schematic representation of common used MONs.

Table 1
Properties and applications of typical MONs or their composites in separation science.

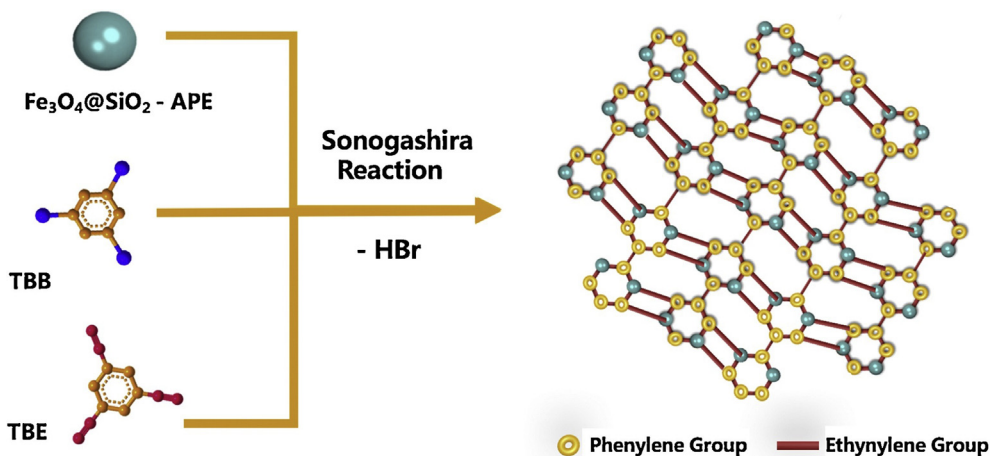| Adsorbents	Properties					Application	Refs
	Surface area (m^2 g^{-1})	Pore size (Å)	Thermal stability (°C)	Chemical stability	Water contact angle (°)		
MON-COOH	584	—	300	Good	129	SPE	[15]
MON-NH$_2$	1039	13	350	Good	143	SPE/GC/HPLC	[17,20,24,25]
MON	635−1032	13	320−360	Good	142	SPE/SPME/GC/HPLC	[14,16,18,21−23,26]
MON-2NH$_2$	1209	18	—	Good	130	SPE	[19]
MON-OH	1080	14	350	Good	55	GC	[24]

Fig. 5. Schematic illustration for the fabrication of magnetic MON with conjugated three-dimensional network structure. Reprinted with permission from Ref. [16]. Copyright 2018 Elsevier.
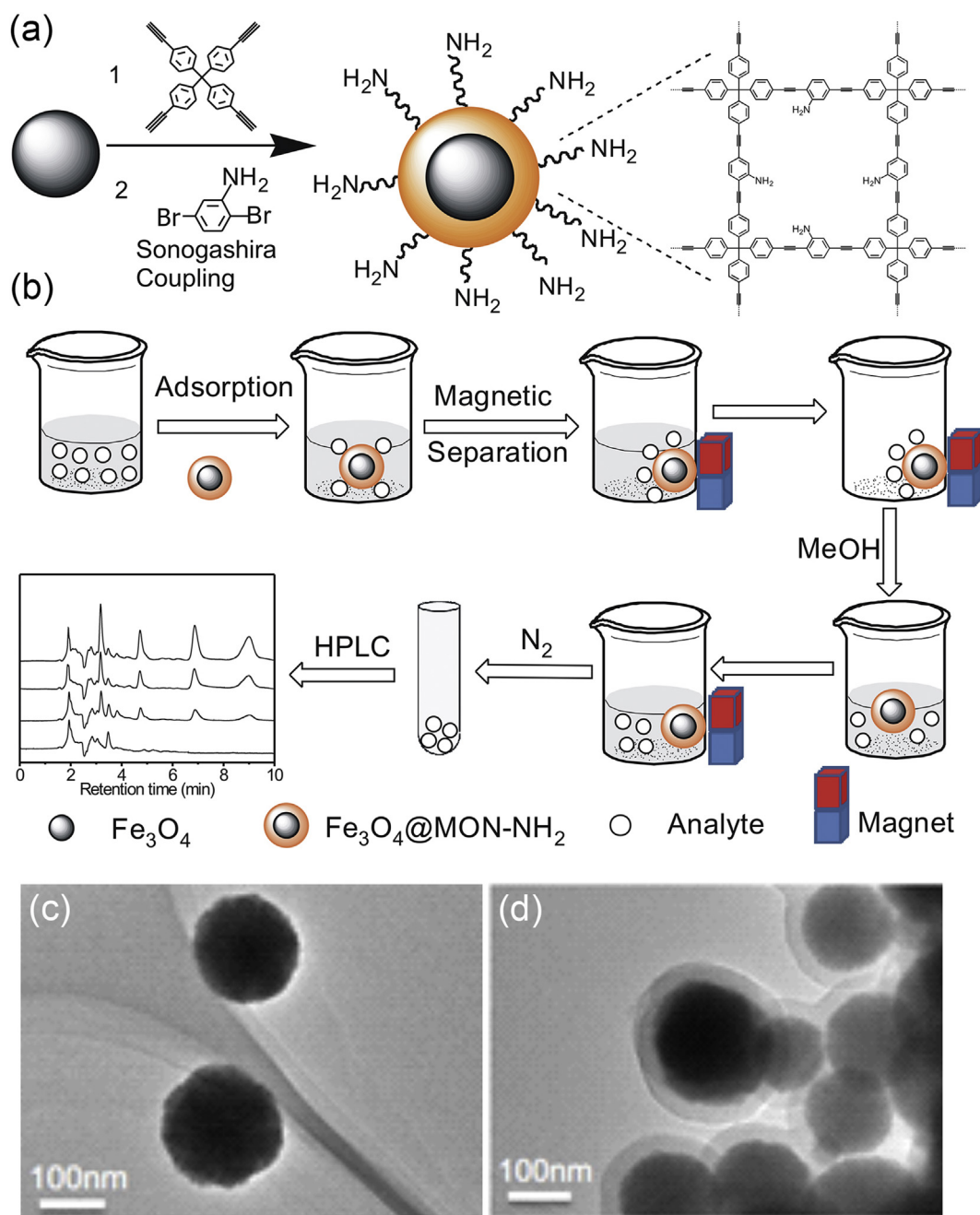
Fig. 6. (a) Fabrication of Fe$_3$O$_4$@MON-NH$_2$ for (b) MSPE of EDCs. TEM images of (c) Fe$_3$O$_4$ and (d) Fe$_3$O$_4$@MON-NH$_2$. Reproduced with permission from Ref. [17]. Copyright 2020 Elsevier.

MONs in SPE. Development of the MONs-based on-line SPE methods was highly essential to accelerate the application of MONs in sample pretreatment. Nevertheless, direct employ of the traditional synthesized submicron-sized MONs to fabricate SPE columns for on-line SPE was very hard and impossible because of the subsequent column leakage and the high back pressure. Synthesis of MONs with large particle size, good stability and fast adsorption/desorption dynamics should be an alternative for on-line SPE adsorbents, but which is still challenging at present. Decoration of MON on proper matrix to fabricate MON's composites should be an efficient way. Recently, Du et al. [20] demonstrated the first example of MONs in on-line SPE of phenols from water samples. The uniform SiO$_2$@MON-NH$_2$ microsphere

was facilely fabricated as a novel adsorbent to prepare SPE column for on-line SPE before the HPLC analysis (Fig. 9). The shell thickness and morphology of SiO$_2$@MON-NH$_2$ were facilely controlled by regulating the initial concentration of MONs monomers. The SiO$_2$@MON-NH$_2$ microsphere integrated the good packing property of spherical SiO$_2$ and the outstanding extraction ability of MON-NH$_2$, allowing its efficient on-line SPE of five phenols with large EFs, low LODs, wide linear range and good reproducibility. The hydrophobic, π-π and hydrogen bonding interaction between phenols and the SiO$_2$@MON-NH$_2$ played key roles during the extraction. The good reproducibility and easy automation made SiO$_2$@MON-NH$_2$ highly promising in on-line SPE. This work opened the way of MONs in on-line SPE and also largely promoted
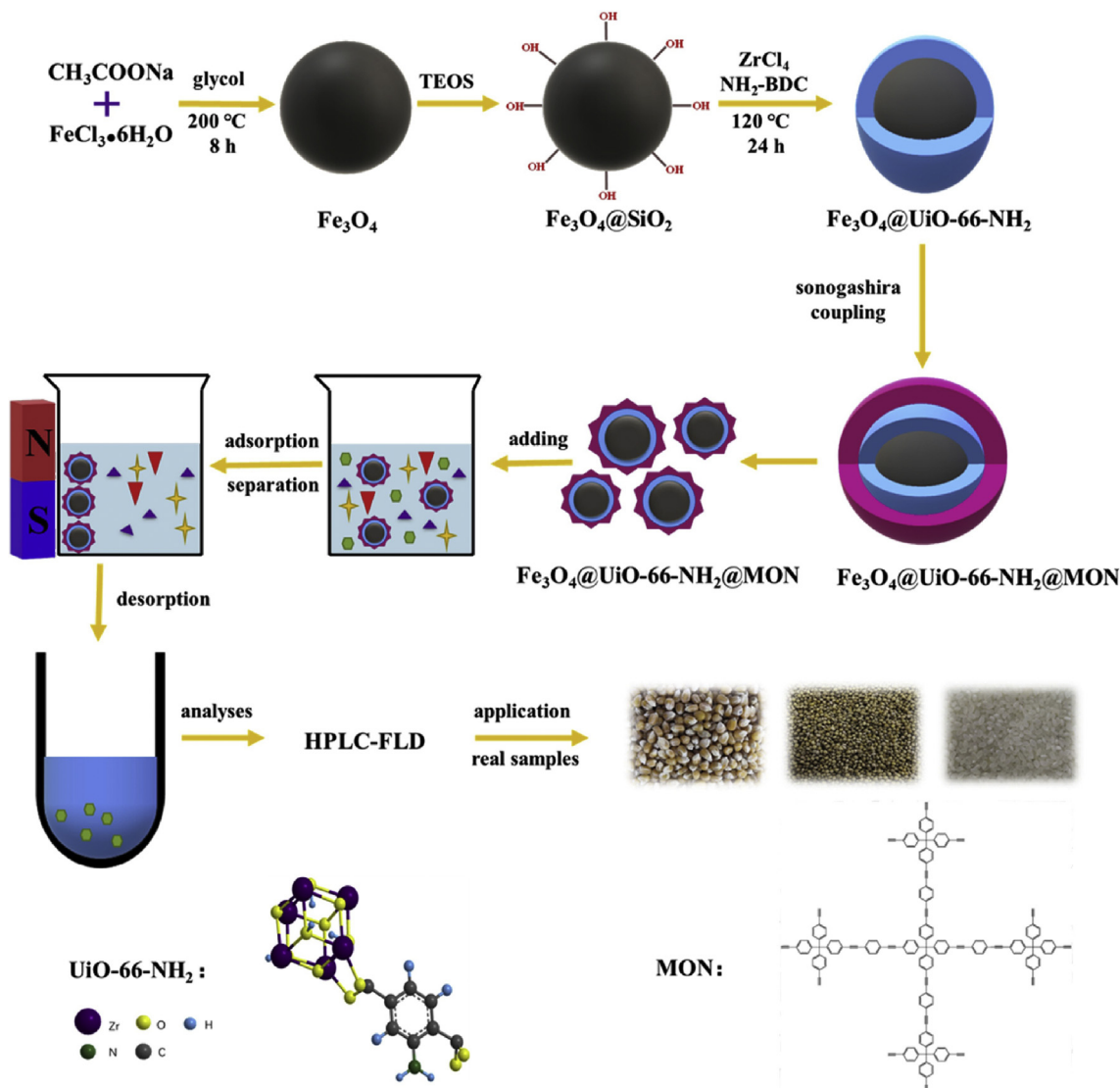
Fig. 7. Synthesis of Fe₃O₄@UiO-66-NH₂@MON composites for MSPE of aflatoxins. Reprinted with permission from Ref. [18]. Copyright 2020 Elsevier.

the application of functionalized MONs or MONs' composites in sample pretreatment.

The above works proved the good prospects of MONs in SPE. MONs with conjugated and hydrophobic frameworks are favorable to extract the aromatic and hydrophobic analytes such as polycyclic aromatic hydrocarbons (PAHs), aflatoxins, polychlorinated biphenyls, brominated flame retardants, etc. In addition, after incorporating hydrogen bonding sites (NH₂, COOH, OH, etc.) within structures, the functionalized MONs are possible to extract the polar aromatic analytes such as OH-PAHs, phenols, PGRs, EDCs, etc.

3.2. MONs for SPME

Since Pawliszyn and co-workers firstly introduced solid phase microextraction (SPME) in 1990, SPME has been regarded as a promising approach in sample enrichment. SPME with less solvent consumption can integrate multiple steps including sampling, enrichment, and sample injection into one step, and has been widely utilized in food, biological, environmental and many other areas. The adsorbents coated on the fibers play key factors during the extraction and the novel coating exploitation remains the

interesting topic in SPME. The MONs with excellent thermal and chemical stability, large surface area, tunable pore size and selectivity, conjugated and hydrophobic frameworks are good candidates in SPME coating preparation for PAHs. In 2016, Jia et al. [14] firstly explored the preparation of MOF@MON composites as novel fiber coatings in SPME of 16 PAHs from environmental particulate matter (PM₂.₅), food and water samples (Fig. 10). The MON shell not only served as a hydrophobic "shield" to enhance the hydrostability of the fiber but also acted as an efficient coating to enhance the affinity between MOF@MON and the PAHs via the hydrophobic and π-π interaction. The MOF@MON based SPME method showed wide linear range (0.1–500 ng L⁻¹), low LODs (0.03–0.30 ng L⁻¹) and LOQs (0.10–1.25 ng L⁻¹) for PAHs under GC-MS/MS determination. The MOF@MON based fiber also exhibits low LODs, short extraction time, and high EFs compared with many reported and commercial coatings such as PDMS, PDMS/DVB, PA, graphene, MIL-101(Cr), etc. The modified MONs obviously improved the extraction performance of pure MOF either for the selectivity or the sensitivity. Furthermore, the MOF@MON coated fiber could be reused at least 60 cycles without any decline of the extraction efficiency. These results revealed the great promise of MONs in SPME.
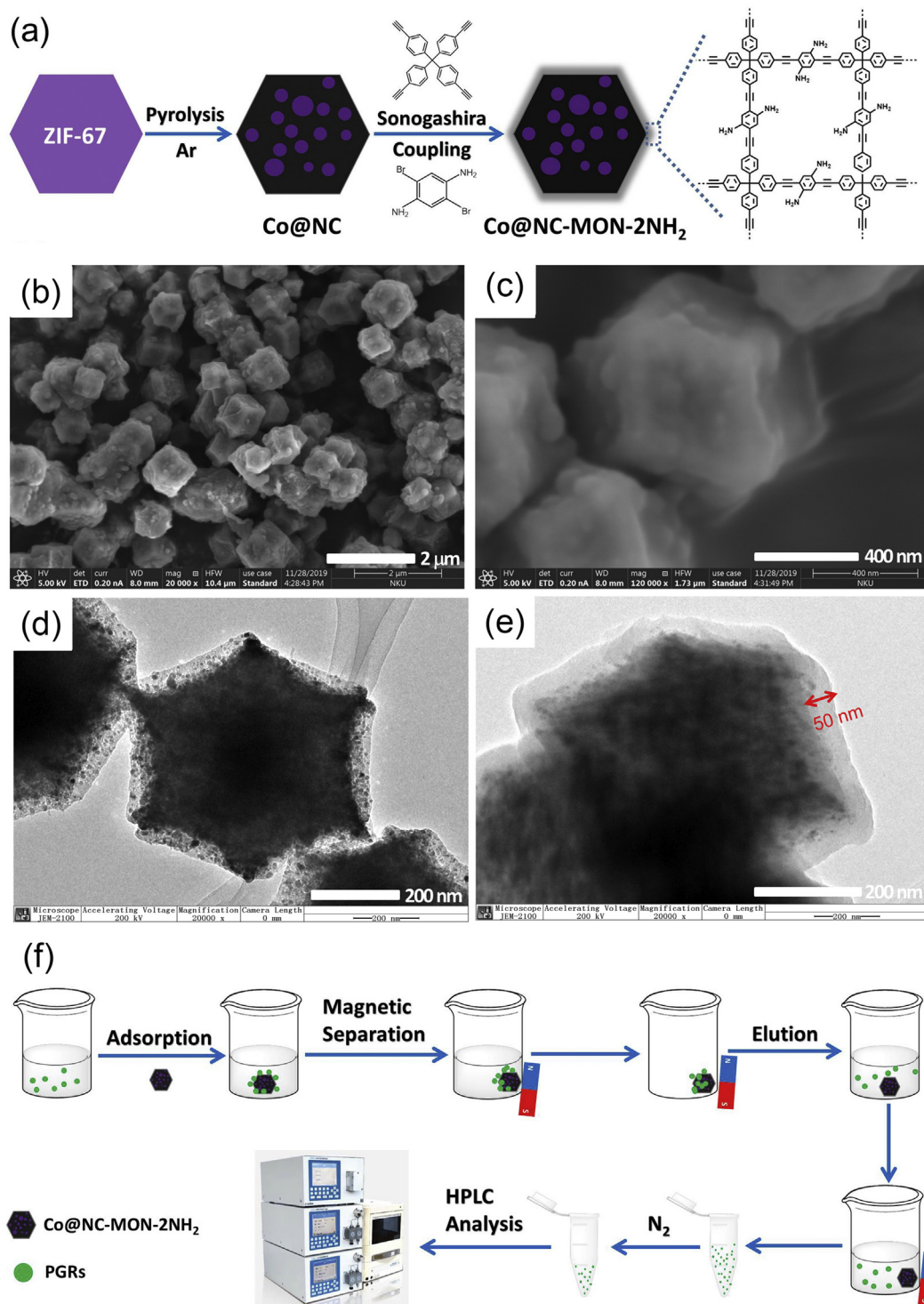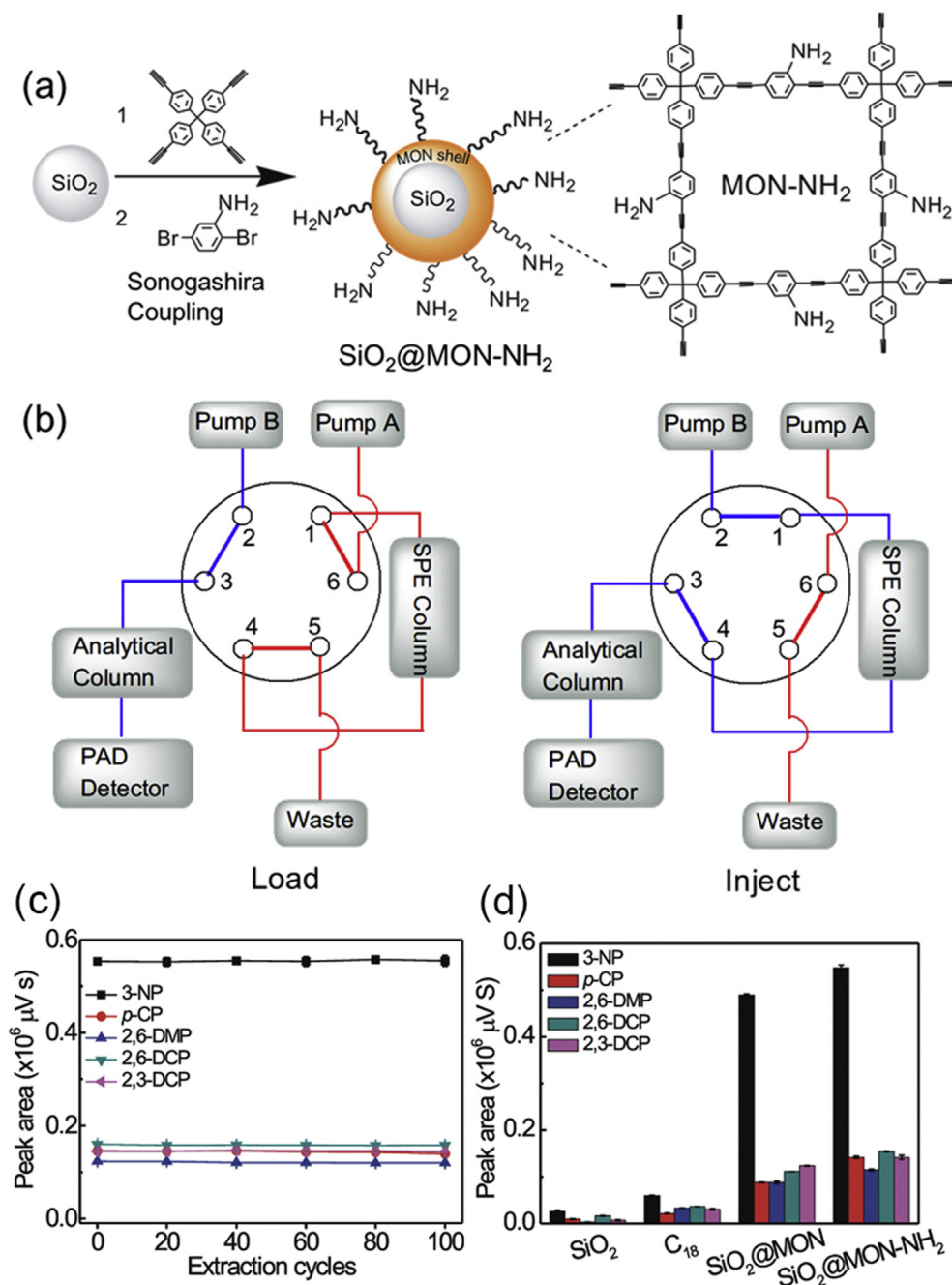
Fig. 8. (a) Schematic illustration for the synthesis of Co@NC-MON-2NH$_2$; (b,c) SEM and (d,e) TEM images of Co@NC-MON-2NH$_2$; (f) procedures of Co@NC-MON-2NH$_2$ for MSPE of PGRs. Reproduced with permission from Ref. [19]. Copyright 2020 Elsevier.

Zhao' group [21] reported the fabrication of a hollow MON (H-MON) immobilized fiber for enrichment of short-chain chlorinated paraffins (SCCPs) (Fig. 11). The developed H-MON-based head-space SPME method gave a higher enrichment factor value (1773) than direct immersion manner (983) for SCCPs. The proposed method also exhibited the low LOD (0.03 ng mL^{-1}), wide linear range (0.05–10 ng mL^{-1}), good repeatability and excellent lifetime ($\geq$100 times). Importantly, the homemade H-MON fiber showed higher extraction efficiency than those on commercial fibers such as PA, PDMS, and PDMS/DVB. Quantitative analysis of SCCPs in water, sediments, organisms, and atmospheric particulate matter samples was also achieved. This work uncovered the good prospect of H-MON-based adsorbents in SPME.

The above works proved the potential of MONs in SPME. How-ever, all these fibers were prepared via the physical adhesive method. The lack of strong force between the MONs and the stainless

Fig. 9. Schematic illustrations of (a) synthesis of SiO$_2$@MON-NH$_2$ microsphere; (b) sample loading (Load), and elution and analysis (Inject) steps in on-line SPE coupled with HPLC system using SiO$_2$@MON-NH$_2$ microsphere as the adsorbent; (c) reuse cycles of SiO$_2$@MON-NH$_2$ based on-line SPE-HPLC method for phenols; (d) on-line SPE of these five phenols on SiO$_2$, C18, SiO$_2$@MON and SiO$_2$@MON-NH$_2$. Reproduced with permission from Ref. [20]. Copyright 2020 Elsevier.

steel fibers may make them difficult to introduce onto SPME fibers and prone to being lost during thermal and solvent desorption. Therefore, the fabrication of robust MONs coatings with good stability, durability, and reproducibility is challenging at present.

4. MONs for chromatography

4.1. MON for GC

The excellent thermal stability, large surface area and permeable pores also made MONs good stationary phases in gas chromatography (GC). In 2019, Cui et al. [22] firstly reported the fabrication of

MON coated capillary column via an *in situ* growth method for high resolution GC separation (Fig. 12). An uniform MONs coating was successfully grew on the capillary inner wall via Sonogashira *in situ* coupling the monomers of tetra(4-ethynylphenyl)methane and 1,4-diiodobenzene. The fabricated MON capillary column was determined to be non-polar under the McReynolds constant evaluation and showed good GC separation for hexane and heptane isomers, and many other important hydrocarbons via the van der Waals, π-π and hydrophobic interaction. Separation of the five structure isomers of hexane is still a great challenge and has achieved only on very few porous materials-based GC columns such as CC3R, Fe$_2$(BDP)$_3$, and MIL-53(Fe)-(CF$_3$)$_2$. The prepared MONs capillary
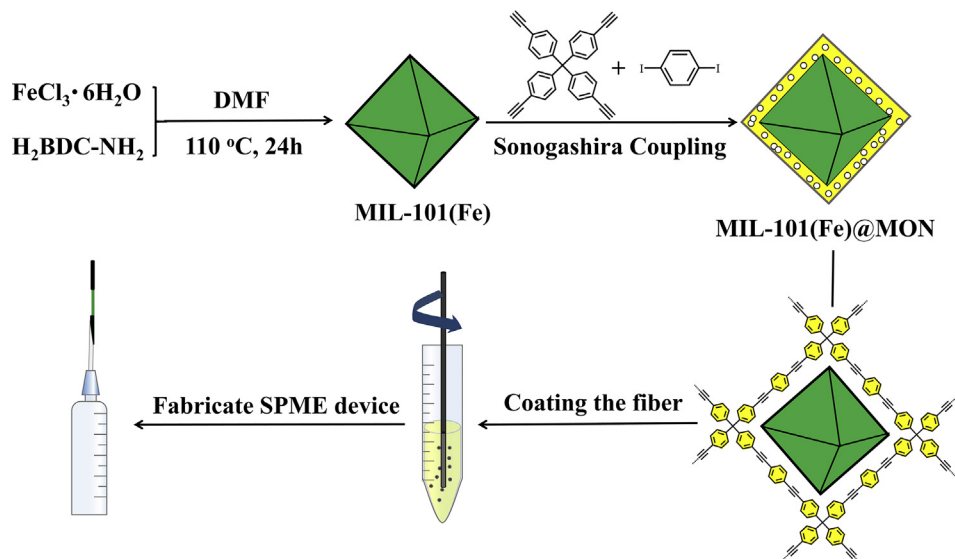
Fig. 10. Schematic illustration for the fabrication of MOF@MON fiber for SPME. Reproduced with permission from Ref. [14]. Copyright 2016 American Chemical Society.

column exhibited higher resolution for the separation of hexane and heptane isomers than commercially non-polar and weak-polar InertCap series capillary columns, highlighting the great prospects of novel MONs-based stationary phases in GC.

Chiral separation is still being the challenging but significant topic in analytical chemistry and material science [55,56]. However, the usage of chiral MONs in chiral separation or chromatography remains an unexplored domain because of their challenging synthesis. Cui et al. [23] reported the first example of post-synthesis of chiral MONs via a thiol-yne click strategy for chiral GC (Fig. 13). Three chiral MONs with different chiral recognition sites were reasonably devised and prepared using the thiol-yne click reaction between alkyne enriched MONs and thiol-based small chiral molecules. Their individual capillary columns were engineered through a simple dynamic coating method for efficient GC resolution of various chiral racemates through the chiral matching, π-π, and hydrogen bonding interaction. The chiral selectivity of these chiral MONs capillary columns was quite different on the difference of chiral recognition site and steric matching between enantiomers and chiral MONs. The prepared three chiral MON capillary columns all provided good resolution for 3-substitute alcohols (3-heptanol and 3-octanol), which were quite difficult to separate and could

not be separated either on chiral MOF, COF, and porous organic cage coated columns or on three typical commercial columns. This work established a facile and convenient method to construct and synthesize chiral MONs and also substantially promoted the devise, prepare, and utilization of chiral MONs in chiral separation.

The above MONs-based GC capillary columns were all prepared under the *in situ* physical growth or the dynamic coating method. These coatings were easily to being lost in GC performance because of the absent of a strong force between the capillary columns and MONs. To address this issue and to further enlarge the broad potential applications of MONs in chromatographic separation, Li et al. [24] reported a novel and universal covalent coupling approach to prepare robust and uniform MONs-based capillary columns for high resolution GC separation of alkyl and halogen substituted position isomers and diverse hydrocarbons (Fig. 14). MON-OH and MON-NH$_2$ with different functional groups were bonded onto the Br-modified capillary columns through the coupling reaction of alkynyl monomers. The well distributed MON-OH and MON-NH$_2$ capillary columns were acquired and displayed favorable separation of many position isomers such as chlorotoluene, dichlorobenzene, propylbenzene, and bromotoluene. In addition, these MON-based capillary columns showed excellent
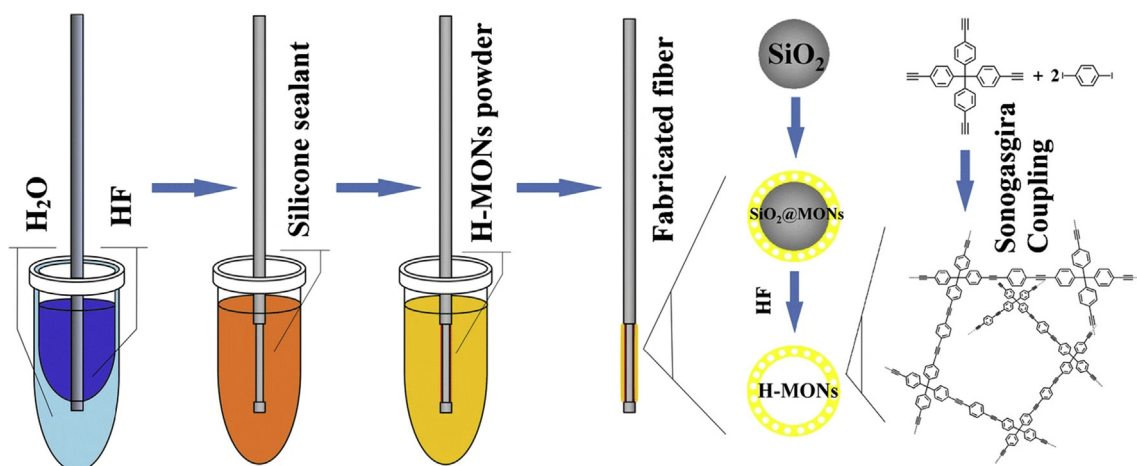
Fig. 11. Schematic illustration for the fabrication of H-MON-based SPME fiber. Reprinted with permission from Ref. [21]. Copyright 2018 Springer Nature.
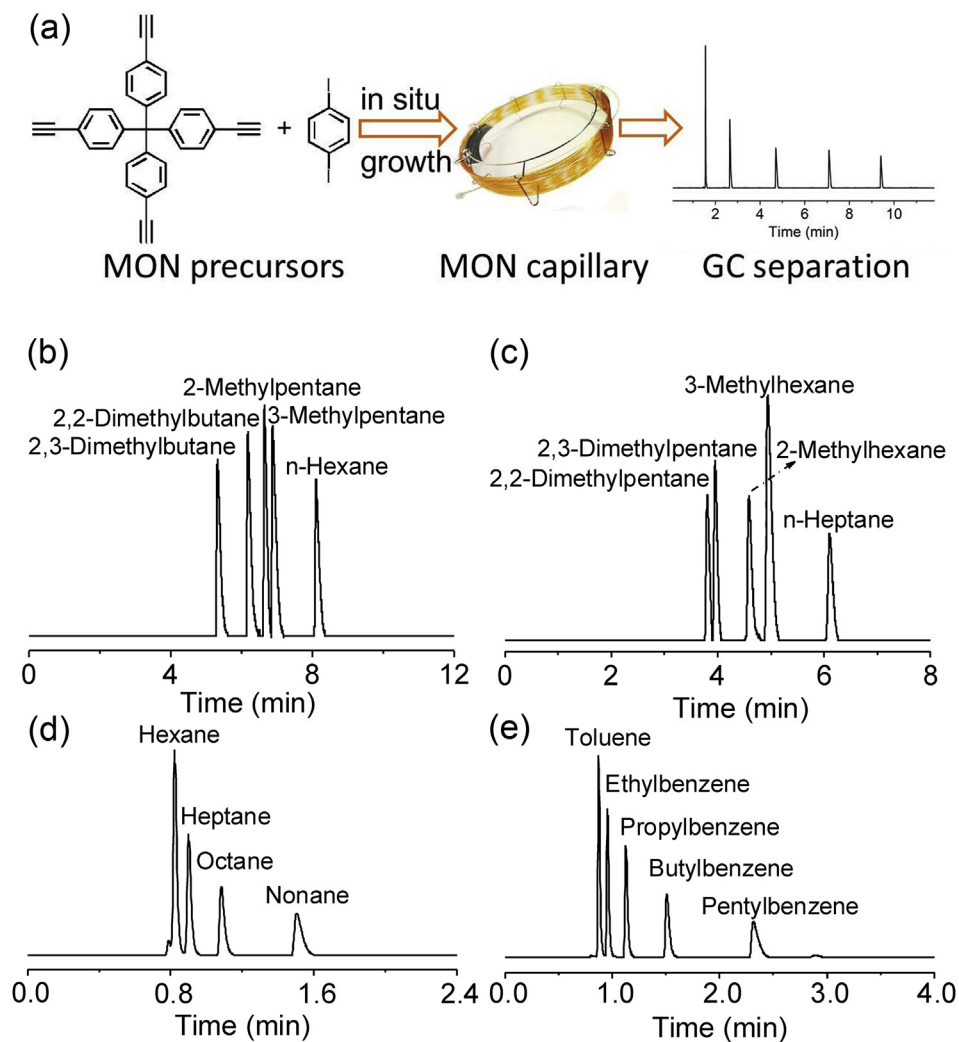
Fig. 12. (a) Schematic illustration for *in situ* fabrication of MON capillary for GC; chromatograms of MONs coated column for GC separation of: (b) hexane isomers; (c) heptane isomers; (d) linear alkanes and (e) alkylbenzenes. Reproduced with permission from Ref. [22]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
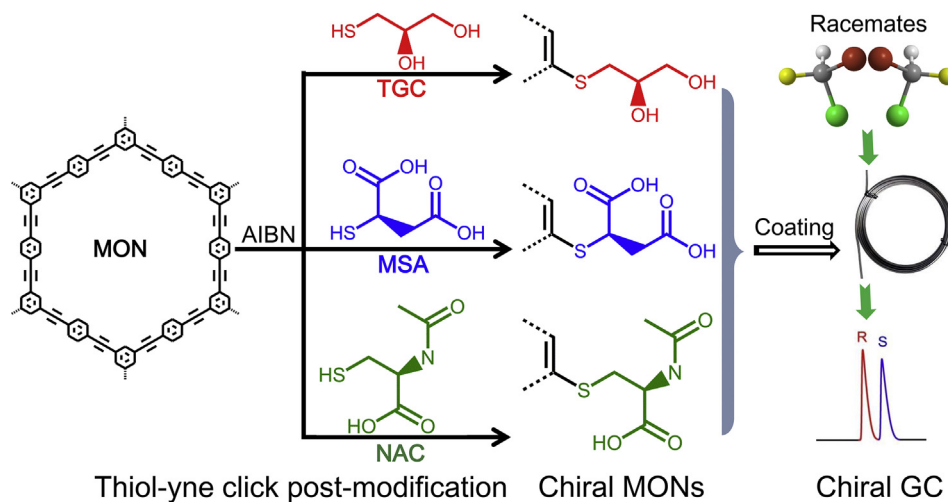
Fig. 13. Illustration for the thiol-yne click strategy to post-synthesize chiral MONs for chiral GC. Reprinted with permission from Ref. [23]. Copyright 2020 American Chemical Society.
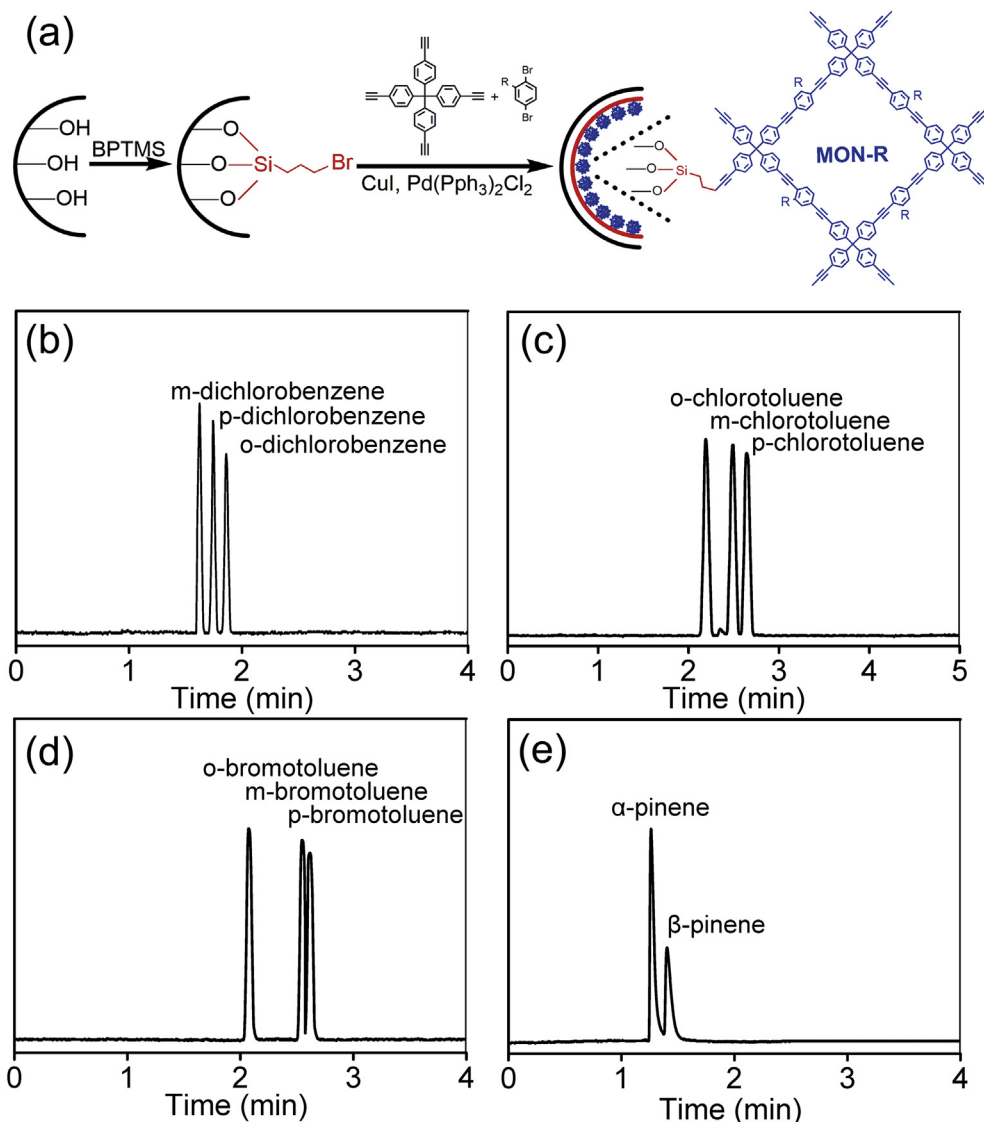
Fig. 14. (a) Illustration for the fabrication of MONs bonded capillary columns via the covalent coupling strategy; GC chromatograms for the separation of (b) dichlorobenzene isomers; (c) chlorotoluene isomers, (d) bromotoluene isomers and (e) pinene isomers on MON-NH$_2$ bonded capillary column. Reproduced with permission from Ref. [24]. Copyright 2020 Elsevier.

lifetime and repeatability for the separation of dichlorobenzene isomers. Furthermore, the prepared MONs capillary columns gave higher resolution for the separation of chlorotoluene and bromo-toluene position isomers than four commercial InertCap series capillary columns. This work demonstrated the possibility of co-valent coupling method to prepare uniform and robust MONs-based capillary columns for GC, underlining the promise of MONs in separation science.

The above works uncovered the promise of MONs in GC, but its exploration is still in infancy. The separation resolution of MONs-based GC needs to be improved by controlling coating thickness to regulate the partition of the analytes or synthesizing efficient MONs to provide multiple/synergistic separation mechanisms to the targets.

4.2. MON for HPLC

As great efforts have been made in sample pretreatment and GC, the application of MONs in HPLC has largely lagged. Synthesis of mono-dispersed and micron sized spherical MONs with large sur-face area and good solvent stability is desired for their application in HPLC, but is quite difficult at present. The bottleneck problem for MONs in HPLC is that the high column pressure and low column efficiency resulting from the directly packing of sub-micron sized and irregular MONs into columns. Thanks to the excellent combi-nation property of MONs, decorating MONs onto proper matrix should be an efficient way to promote the usage of MONs for HPLC.

To solve these issues and to prove the feasibility of MONs in HPLC, Du et al. [25] firstly reported the fabrication of uniform core-shelled and mono-dispersed spherical SiO$_2$@MON-NH$_2$ composite as a novel stationary phase for HPLC separation of diverse analytes including neutral, acidic and alkaline probes, benzenediol, dichlorophenol, chlorophenol and phenylenediamine position isomers, deoxynucleosides and nucleosides (Fig. 15). The 5 μm SiO$_2$−NH$_2$ microsphere was chosen as the spherical core to reduce the column pressure and to support the *in situ* growth of MON-NH$_2$ shell with hydrogen bonding and hydrophobic inter-action sites. The column efficiency for *n*-propylbenzene was 21,246
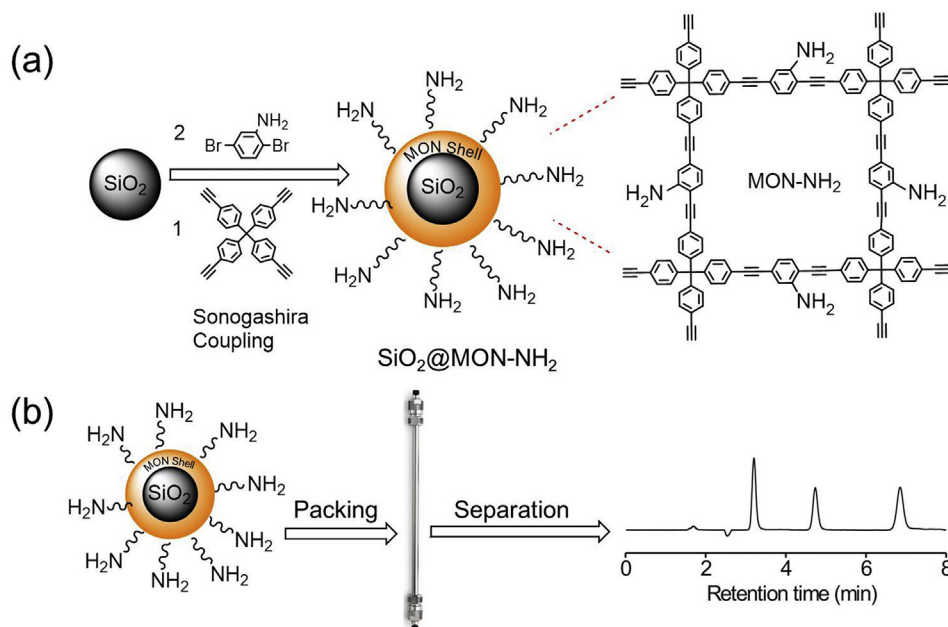
Fig. 15. The preparation of spherical SiO$_2$@MON-NH$_2$ composite (a) and its packed column for HPLC (b). Reprinted with permission from Ref. [25]. Copyright 2020 Elsevier.

plates m^{-1}. The hydrophobic interaction was the main mechanism during the HPLC separation. The SiO$_2$@MON-NH$_2$ packed column also offered better resolution for dichlorophenol isomers, deoxynucleosides and nucleosides than SiO$_2$−NH$_2$ and commercial C18 columns. The spherical SiO$_2$@MON-NH$_2$ composite had combined the good separation ability of MON-NH$_2$ and the excellent packing property of spherical SiO$_2$, providing a new way for the use of submicron sized or irregular MONs in HPLC. The above results indicated the good prospects of MONs as novel HPLC stationary phases.

Recently, Yu et al. [26] showed the fabrication and application of SiO$_2$@MON composite as the HPLC stationary phase. The SiO$_2$@MON material was also fabricated via *in situ* Sonogashira coupling of monomers on spherical silica. Due to the super hydrophobic nature of MON, the packed SiO$_2$@MON column displayed good resolution of both hydrophilic and hydrophobic analytes with good resolution. The prepared HPLC column was successfully applied to monitor the silane coupling agents' hydrolysis and to analyze the cooking oils' quality relying on its good separation abilities.

The above MONs-based HPLC separations mainly relied on the hydrophobic mechanism, fabrication of functionalized MONs composites should be a feasible way to provide multiple separation mechanisms to the targets and to promote the application of MONs in HPLC. In addition, the targets evaluated are limited in small substituted benzenes, investigation of mesoporous and macroporous MONs in HPLC may be a possible method to inspire their further application for biomacromolecule.

5. Conclusions and perspectives

In conclusion, the above works have uncovered the great potential and bright prospects of MONs in analytical separation science from sample pretreatment to chromatographic separation. MONs' composites and functionalized MONs have been designed and synthesized to meet the increasing requirements and challenges in separation science. However, the usages of MONs in analytical chemistry and separation science are still in an initial stage, development of novel MONs or MONs' composites in their

subsequent applications for analytical separation science is quite desirable and challenging. The following issues should be considered in the near future. (1) As the number and type of MONs are still quite limited, design and synthesis of more MONs with different topological structures and functions should be a promise way to accelerate the progress of MONs in separation science. (2) Engineering of MONs on proper matrices is still being a powerful strategy to promote the usage of MONs in separation science. (3) Rational construction and preparation of chiral MONs are very essential to expedite the performance of MONs in chiral separation.

However, the cost of MON is high and achieving large-scale synthesis remains a challenge at present. Moreover, it is still a difficult problem to regulate the morphologies of MONs to meet their demands in analytical applications. Compared with crystalline materials, the amorphous property of MONs still limits their separation performances to some extent. Of course, these disadvantages encourage us to further study the synthesis and application of MONs in depth.

Declaration of competing interest

The authors declare no known competing financial interests or personal relationships related to the work reported in this paper.

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