Chapter 2
Development of Novel Solid-Phase Microextraction Fibers

Jianqiao Xu and Gangfeng Ouyang

Abstract The basic principles for the preparation of SPME fibers with satisfying selectivity, sensitivity, loading capacities and stabilities are summarized here in terms of the physicochemical properties of the coating materials and the supporting substrates of SPME fibers. While the main part of this chapter focuses on the advances in developing the most widely used coating materials, including ionic liquids, polymeric ionic liquids, carbonaceous materials, molecularly imprinted polymers, metal-organic frameworks, metals and metal oxides, conductive polymers, modified silica, as well as their composites, into SPME fibers. Meanwhile, the applications of novel SPME fibers in analyzing diverse analytes in different sample matrices are briefly reviewed, including the emerging applications of SPME in the extraction of bioactive compounds in living animals and plants.

Keywords SPME fiber coating · Ionic liquid · Polymeric ionic liquid · Graphene · Carbon nanotube · Molecularly imprinted polymer · Metal-organic framework · Metal and metal oxide · Conductive polymer · Modified silica

2.1 Introduction

The outstanding features of solid-phase microextraction (SPME), including rapid and simple operating procedures, slight disturbance to investigated systems, reduced consumption of solvents, and feasibility of automation, continuously inspire new explorations of SPME in various frontiers, such as metabolome detection [1], central nervous systems studies [2], pharmacokinetic studies [3], environmental analysis [4], and food analysis [5]. On the other hand, the diversity of the physicochemical properties of the target analytes and the complicity of the sample matrices require the development of new SPME devices to nourish the new

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explorations. Since the conception of SPME, multiple configurations (Table 2.1) [6], extensive extraction materials [7], and numerous preparation methods for SPME devices [8] have been introduced for the implementation of novel SPME.

Different configurations are designed mainly with three benefits: (1) to be conveniently coupled to analytical instruments (Table 2.1) [4, 9–16], (2) to deal with different samples (e.g., the in-tube SPME and stir bar microextraction are mostly used in aqueous samples, and SPME fibers can be used in liquid, gaseous, and semisolid samples), and (3) to improve analytical sensitivity by increasing surface areas or surface area-to-volume ratios of extraction phases (such as thin-film and coated blade SPME) [12]. Nowadays, fiber is the most widely used SPME configuration, mainly for its wide applicability in gaseous, liquid, and semisolid samples. For this reason, the preparation of SPME fibers has been more extensively studied than the SPME devices in other configurations. In fact, the strategies of preparing SPME fibers can also be readily extrapolated to the preparation of SPME devices in other configurations [9, 10].

The development of novel SPME fibers aimed at promoting the sensitivity, selectivity, loading capacities, and mechanical/thermal/chemical stabilities of SPME fibers, and lowering the costs of preparing SPME fibers as well [7]. Figure 2.1 presents the principles for the preparation of SPME fibers with the desirable features. In general, the extraction performances of SPME fibers, i.e., sensitivity, selectivity, and loading capacities, are determined by the chemistry and physics of the extraction materials. On the other hand, the preparation method (Table 2.2) plays an important role in improving the stabilities and inter-fiber reproducibility, which, however, should be developed according to the coating materials and supporting substrates selected.

The development of new SPME fibers is recently one of the most active research field of this technique, a large quantity of works on this topic have been published in recent years. This chapter is to sketch the progresses in developing the most

Table 2.1 Direct coupling of SPME in different configurations to analytical instruments and automatic sample preparation platforms

Configuration	Instrument coupled to	References
Coated stainless steel mesh	Direct analysis in real time (DART)–MS/MS	[9]
Coated blade	Electrospray ionization (ESI)–MS/MS	[10]
	96-well automatic sample preparation platform	[11]
Thin-film SPME	GC	[12]
In-tube SPME	Direct analysis in real time (DART)–MS/MS	[13]
	Online LC	[14]
SPME fibers	GC	[4]
	Online LC	[15]
	Multiple MS	[16]

Many configurations of SPME samplers, such as thin-film SPME and SPME fibers, can be coupled to off-line LC, i.e., solvent desorption prior to LC analysis, which are not included in the direct coupling strategies

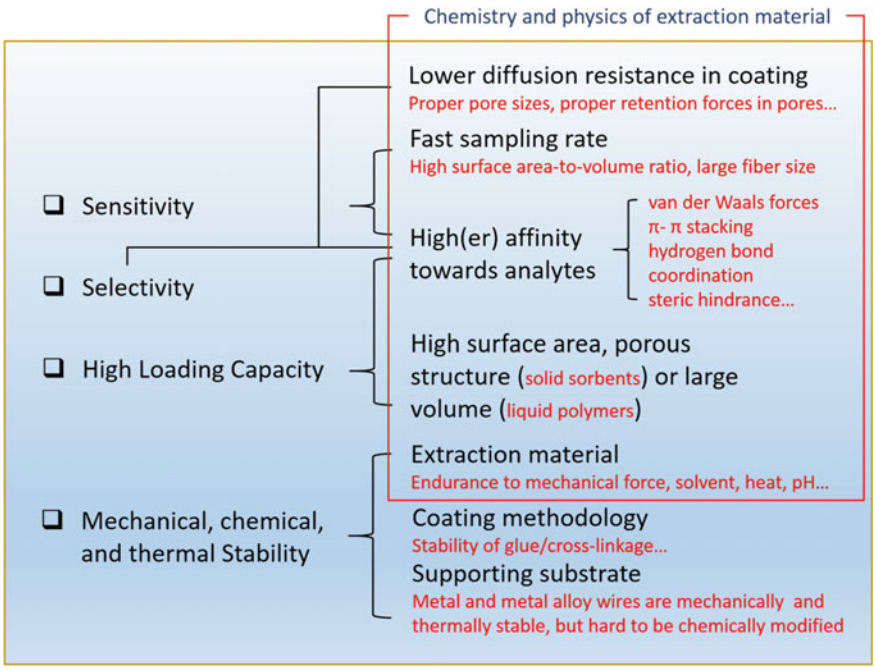


Fig. 2.1 Principles in chemical and physical perspectives for preparing SPME fibers with desirable features

widely used extraction materials into SPME fibers with selected works, and to provide examples to show the utilization of these fibers in practical uses with satisfactory extraction performances. Extraction materials, including ionic liquids (ILs) and polymeric ionic liquids (PILs), carbonaceous materials, molecularly imprinted polymers (MIPs), metal-organic frameworks (MOFs), metals and metal oxides, conductive polymers, and modified silica, are reviewed. In addition, a separate section for reviewing the latest progress of preparing fibers for direct immersion (DI) SPME in complex biological matrices is presented.

2.2 An Overview of Preparation of Fibers with Desirable Features

Figure 2.1 presents the principles from the perspectives of chemistry and physics for the preparation of fibers that fulfill the proposed requirements. Here, an overview of preparation of desirable fibers is provided with several special notes.

To achieve high sensitivity to target analytes, various interactions can be introduced for trapping the target analytes in fiber coatings, including not only the

Table 2.2 Comparison of different preparation methods of SPME fibers

	Technical difficulty	Reproducibility	Stability
Physical deposition	Slight	Poor	Mechanically unstable, the thermal and chemical stability depends on the coating materials used
Electrodeposition/electrophoretic deposition	Slight	Fair	Mechanically unstable, the thermal and chemical stability depends on the coating materials used
Gluing	Slight	Fair	Mechanically stable, the thermal and chemical stability depends on the coating materials and glue used
Sol–gel	Fair	Poor	Mechanically stable, unstable under high temperature and extreme pH
Chemical bonding	High	Fair	Mechanically stable, the thermal and chemical stability depends on the coating materials and cross-linkages used
Electrospinning	Fair	Good	Mechanically stable, the thermal and chemical stability depends on the coating materials used
Anodizing	Fair	Fair	Mechanically and thermally stable, the chemical stability depends on the coating materials used
In situ polymerization/hydrothermal growth	High	Poor	Fair mechanical stability, the thermal and chemical stability depends on the coating materials used

non-covalent interactions such as π–π stacking effect and dipole–dipole interaction, but also the covalent bonds. For example, when using boronate sorbent to extract glycoproteins, covalent bonds formed between the boronate groups of the sorbent and the glycosyl groups of the proteins [17]. It is also notable that thorough

desorption of the analytes from fiber coatings is also important for improving sensitivity, which should be realizable under the conditions which the coating materials can endure. For example, the boronate ester bond can be broken under relative mild acidic pH [17]. In addition, increasing surface area-to-volume ratios of the coatings can accelerate the extraction kinetics; thus, a porous morphology can be expected to improve the sensitivity of SPME. In particular, improving the accessibility of the inner surfaces of nanomaterial-based fibers can further accelerate the sampling kinetics, as the inner surfaces in the nanomaterial-based coatings might be blocked due to the highly stacking structures [18]. Fibers with larger dimensions can extract more analytes than smaller fibers in the same time duration; thus, fibers with larger dimensions can potentially possess higher sensitivity [12].

High selectivity toward target analytes mainly depends on higher affinities to target analytes than other compounds coexisted in the sample matrices (thermodynamic factors). In addition, high selectivity might also originate from the differences in adsorption kinetics. For example, diffusion resistances in pores of MOF might differ for analytes due to the different interactions between the analytes and the ligands of MOF, which could result in different adsorption kinetics [19]. High selectivity is ideal for lowering backgrounds and interferences, and thus, it guarantees a satisfactory sensitivity of SPME. However, in contrast to the conventional applications, the applications of SPME in metabolomic studies require the fibers with wide metabolome coverage [1].

Larger extraction-phase volumes or more available binding sites in the extraction phases can lead to higher loading capacities. Simultaneously, the partition coefficient between the extraction phases and the sample matrices should be large for guaranteeing high loading capacities, which also requires that the extraction phases should possess high affinities toward the target analytes.

Immobilizing extraction materials on substrates is an essential step for preparing substrate-supported coating fibers. Table 2.2 presents a brief comparison among the most widely used preparation methods in terms of technical difficulty, reproducibility, and stability. Silica fibers and stainless steel wires (SSWs) are usually used as the supporting substrate. Silica fibers are fragile; however, their surfaces are easy to be modified with reactive functional groups to chemically bond the coatings (Fig. 2.2a). SSWs are popular substrates mainly for the outstanding flexibilities under mechanical forces. Except for the difficulty in chemically bonding the coatings on SSWs, other preparation methods can be readily realized with SSWs as the substrates, especially the wires can be used as electrodes or electrospinning receptors in the preparation of conductive polymer coatings and electrospun nanofibrous coatings [18, 20]. Actually, fiber coatings can be chemically bonded on SSWs by precoating noble metals [21–23], silicon [24] and polydopamine (PDA) [25], which can be further functionalized with reactive functional groups. Figure 2.2b summarizes the strategies of chemically bonding coatings on SSWs. The reactive functional groups can chemically bond coatings through specific covalent bonds. For example, amino groups can react with carboxyl groups [21, 26], vinyl groups can participate in polymerization [25], sulfhydryl groups can act as chain transfer agent in polymerization reactions [22] and can chemically bonding noble metal nanoparticles [23],

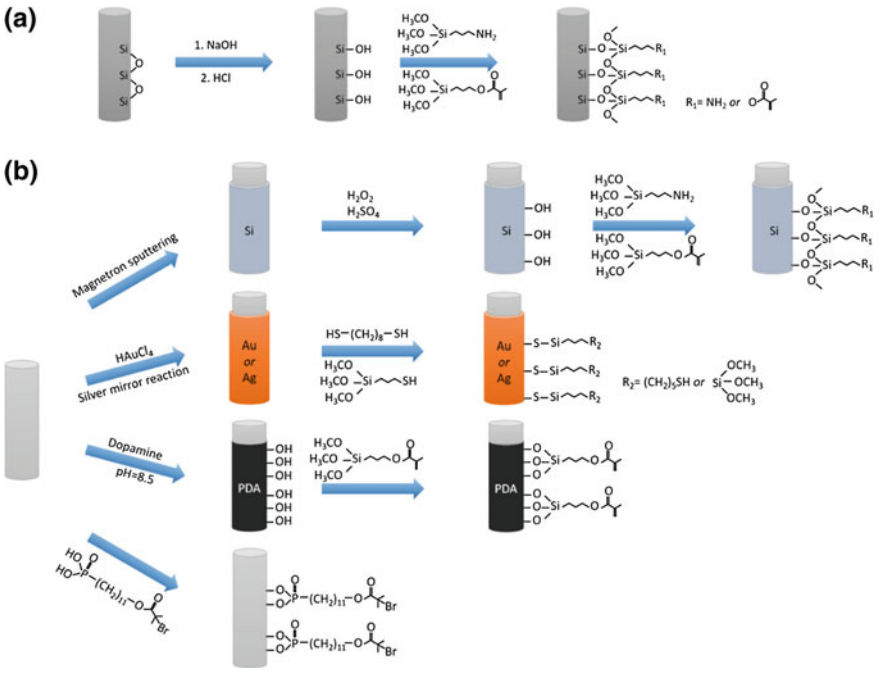


Fig. 2.2 **a** Modification of fused-silica fibers and **b** modification of SSWs for chemical bonding of coatings

methoxysilyl can react with other alkoxysilyls [21], and bromine atoms can also act as chain transfer agent in polymerization reactions [27]. Other metal and metal alloy wires, such as gold wires [28] and NiTi alloy wires [29], have also been used as supporting substrates. Substrateless fibers, i.e., monolithic fibers, were also reported in the literature [30, 31]. Polymeric monoliths are also flexible under mechanical forces. However, monolithic SPME fibers are not as much reported as substrate-supported ones, probably because not all the extraction materials can be facilely prepared into monoliths.

When the fibers are used for DI SPME in complex sample matrices, such as in biological samples and in sediments, besides the requirements aforementioned in Fig. 2.1, the fibers should be resistant to binding of proteins and humic substances on the coatings, which could hinder the surfaces of fibers, and shorten the lifespans of fibers [32]. In addition, SPME fibers used for in vivo sampling in biological tissues are also required to be biocompatible to avoid triggering rejection reactions [18].

2.3 ILs and PILs

ILs are now extensively studied for the applications in organic chemistry, electrochemistry, and analytical chemistry [33–35], due to the versatile and intriguing physicochemical properties including low volatility, thermal stability, electrical conductivity, tunable miscibility with solvents, tunable viscosity, and designable and anticipatable solvation properties [33]. For the perspective of providing high affinities to target analytes by introducing proper functional groups on the cations and by using anions with different Lewis basicity, ILs are recently explored for preparing task-specific SPME fiber coatings. Polymeric ionic liquids (PILs) are prepared by polymerization of alkenyl-functionalized ILs and have also been used as SPME fiber coatings.

IL was first used as a disposable SPME fiber coating by Liu et al. [36] by dipping a fused-silica fiber in the mixture of dichloromethane and 1-octyl-3-methylimidazolium hexafluorophosphate. Later, to load more ILs on fused-silica fibers, fused-silica fibers were etched or coated with a Nafion membrane prior to dipping in ILs [37, 38]. Cui et al. [39] also found etched SSWs could load more IL than non-etched SSWs. Even though Ho et al. [40] demonstrated their IL coating prepared on untreated fused-silica fiber with the dipping method could stand no less than eight extraction–desorption circles, these IL coatings were not stable enough, recoating was required during uses [36–40]. The first relatively long-term reusable IL-based SPME fiber was prepared by fixing IL-impregnated silicone elastomer on a bare fused-silica fiber [41], followed by Carda-Broch et al. [42] and Wanigasekara et al. [43] who glued IL-functionalized silica particles on fused-silica fibers, which loaded more IL on the fiber as well. IL was also chemically bonded on a fuse silica fiber by using 3-chloropropyltrimethoxysilane as a cross-linker [44]. In other works, reusable IL-based SPME fibers were also prepared by chemically bonding allyl-ILs to sol–gel substrates [45–49], or using 3-triethoxysilylpropyl-ILs as sol–gel precursors [49, 50]. Electrodeposition of aniline at the presence of ILs in aniline solution could prepare fibrous nanostructured polyaniline-IL composites, which were also stable for repeated uses [51, 52]. Abolghasemi et al. [53] prepared IL-based periodic mesoporous organosilica (PMO-IL) and glued PMO-IL on a SSW to prepare a SPME fiber. Other two studies used ILs as porogens in sol–gel processes, where ILs were actually not used as coating materials [54, 55]. However, Pena-Pereira et al. [56] used sol–gel technique to entrap IL in the gel, this SPME fiber coating was demonstrated to contain the high content of IL and, therefore, exhibited excellent EEs.

At the same time, PILs were also introduced as SPME fiber coatings through polymerization of allyl-, vinyl- or vinylbenzyl-ILs. Anderson and colleagues for the first time used PILs in SPME coatings [57]. In the pioneer works, PILs were firstly prepared in solutions, and then, the dipping method was used for coating sealed fused-silica capillaries with the PILs [57–63]. Later, on-fiber polymerization initiated by ultraviolet was also utilized for the preparation of a PIL coating [64]. To improve the stability of PIL fibers, silver- and gold-coated SSWs were used as the supporting

substrates and subsequently functionalized with 3-mercaptopropyltriethoxysilane, and then with vinyltrimethoxysilane or 1-vinyl-3-(3-triethoxysilylpropyl)-4,5-dihydroimidazolium chloride, to functionalize the surface with reactive site for polymerization [21, 65, 66]. In another work of Feng et al. [67], 1,8-octanedithiol was also used to chemically bond the PIL coating on the silver-coated SSW. Anodized titanium wire [68, 69] and hydrogen peroxide-oxidized nitinol wire [70, 71] were also used as supporting substrates. In some cases, cross-linker with two vinylbenzylimidazolium ends or vinylimidazolium was used to improve the stabilities of PIL coatings [68–71]. Even though cation moieties of PILs were polymerized, many PIL coatings were still inapplicable for DI SPME, since the anion moieties might be exchanged with anions in sample matrices. Feng et al. [67] introduced a double-confined PIL, of which the cation and anion moieties were both polymerized, to be used for DI SPME (Fig. 2.3).

Of particular interest is that by tuning the structures of ILs and PILs, the affinities toward the target analytes could be possibly tuned. Amini et al. [72] prepared fibers based on four different ILs (1-butyl-3-methylimidazolium tetrafluoroborate, 1-octyl-3-methylimidazolium tetrafluoroborate, 1-octyl-3-methylimidazolium hexafluorophosphate, and 1-ethyl-3-methylimidazolium ethylsulfate) to extract methyl tertbutyl ether in gasoline samples. Both the cations and the anions affected the EEs. Cations with longer carbon chains exhibited higher EEs. And ethylsulfate exhibited a higher EE than tetrafluoroborate and hexafluorophosphate.

In another work [46], the SPME fiber coating based on a crown ether-functionalized IL, 1-allyl-3-(6′-oxo-benzo-15-crown-5-hexyl)imidazolium hexafluorophosphate, exhibited higher EEs over the 1-allyl-3-methylimidazolium hexafluorophosphate coating for extracting polar compounds (e.g., alcohols, phthalate esters, environmental phenolic estrogens, fatty acids, and aromatic amines).

Three different ILs with the same anion but different cations were used to analyze PAHs in aqueous samples with the headspace (HS) mode [37]. 1-methyl-3-octylimidazolium trifluoromethanesulfonate-coated fibers exhibited the highest EEs, followed by 1-benzyl-3-methylimidazolium trifluoromethanesulfonate-coated

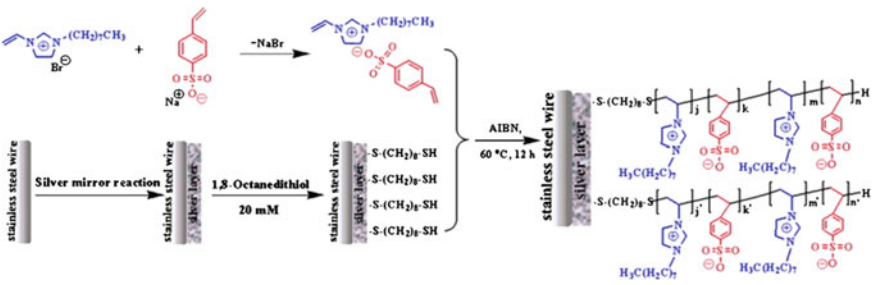


Fig. 2.3 Preparation of the double-confined PIL coating. Reprinted with the permission from Ref. [67]. Copyright 2012 Elsevier

fibers and 1-methyl-3-phenyl-propylimidazolium trifluoromethanesulfonate-coated fibers. The diffusion rates of analytes in fiber coatings other than the affinities toward analytes were thought to be the predominant factor that affected the EEs, which suggested a better understanding of the thermodynamics and kinetics of SPME was needed when ILs were used as fiber coatings.

Three PILs with the same anion, poly(1-vinyl-3-hexylimidazolium bis[(trifluoromethyl)sulfonyl]imide), poly(1-vinyl-3-dodecylimidazolium bis[(trifluoromethyl)sulfonyl]imide), and poly(1-vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide), were coated on fused-silica capillaries for comparison studies [57]. The PIL-based fibers could be satisfactorily used to extract fatty acid methyl esters from complex and hydrophilic matrices, while few differences in EEs among the fibers were observed.

In another work [63], the extraction performances of poly(1-vinyl-3-hexylimidazolium chloride) and poly(1-vinyl-3-hexylimidazolium bis[(trifluoromethyl)sulfonyl]imide) toward volatile fatty acids and alcohols were compared to evaluate the counter-anion-tuned selectivity. Poly(1-vinyl-3-hexylimidazolium chloride) exhibited better extraction performance because of the higher hydrogen-bond basicity of Cl^-, which also demonstrated the importance of anions in determining the extraction properties.

Two PILs with different cations and anions were used as SPME coatings in the study by López-Darias et al. [61] to analyze complex coffee aromas. Despite of their small film thicknesses, the coating of poly(1-(4-vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide) exhibited superior selectivity to aldehydes, while the poly(1-vinyl-3-hexylimidazolium chloride) coating showed good EEs to aromatic alcohols and organic acids possessing alkyl chains lower than pentadecyl.

Meng et al. [62] and López-Darias et al. [73] also reported remarkable selectivity toward aromatic compounds resulted from the aromatic groups in PILs in their works.

2.4 Carbonaceous Materials

Many carbonaceous materials have been developed into SPME fiber coatings; here, we will focus on the most studied ones in recent years, i.e., graphene and carbon nanotubes (CNTs). These two allotropes are much closed to each other on many aspects. Their basic constructing units are both hexatomic rings with sp^2 hybridized carbon atoms. They both possess excellent mechanical strength, thermal stabilities, and high specific surface areas. And both of them can form hydrogen bonds, π–π stacking, dispersion forces, and hydrophobic interactions with organic compounds to exhibit good affinities toward organic compounds. And they both can be functionalized after being oxidized.

Recent studies were also searching other carbon sources those could be facilely obtained for the preparation of SPME fibers, which provided intriguing protocols for preparing inexpensive SPME fibers. The relevant studies are also discussed below.

2.4.1 Graphene

Graphene has been used as an SPME fiber coating, mainly due to its high specific surface area, remarkable thermal and chemical stabilities, high mechanical strength, and high affinities to organic compounds. In addition, graphene can be readily prepared from the low-cost graphite by oxidation exfoliation, and followed by reduction with hydrazine, *p*-phenylene diamine, or ascorbic acid, or by using electrochemical method, which also facilitates its application as an extraction material in SPME fibers.

The first graphene-based SPME fiber was prepared by physical deposition of graphene on SSWs [74]. After that, graphene was also immobilized on substrates by gluing [75, 76], using sol–gel method [77–79], or codepositing in polypyrrole [80, 81]. The aggregation of graphene sheets during the preparation of graphene-based SPME fibers hindered the adoption of the aforementioned methods. Thus, in the following studies, graphene oxide (GO), which is less likely to aggregate in its suspension than graphene, was firstly chemically bonded to substrates, then reduced to graphene on the substrates [26, 82, 83]. Banitaba et al. [84] prepared a SPME fiber by electrochemically reducing GO on the surface of copper wire. Liu et al. [31] directly oxidized the surface of pencil lead and then reduced it for the preparation of a graphene fiber (Fig. 2.4). And Luo et al. [85] prepared another substrateless graphene fiber by hydrothermal reduction of graphene oxide in a capillary mold. In addition, GO, functionalized graphene, and the composites of graphene were also developed into SPME fiber coatings by using the similar methods aforementioned [86–90].

Up to now, almost all the custom-made graphene-based fibers were used to extract analytes with aromatic rings (Table 2.3). Still, in some works, the

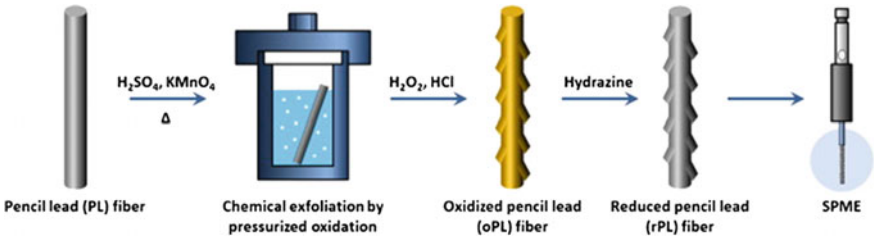


Fig. 2.4 Preparation of the graphenized pencil lead fibers. Reprinted with the permission from Ref. [31]. Copyright 2014 Elsevier

Table 2.3 The applications of graphene in the preparation of SPME fibers

References	Preparation method	Graphene format	Graphene source	Supporting substrate	Analyte	Sample matrix	SPME mode
[74]	Physical deposition	Graphene	Graphite	SSW	Pyrethroids	Pond water	DI
[75]	Silicone glue	MA-reduced GO	Graphite	SSW	Organochlorine pesticides	River water	MA-HS
[76]	Ultrafast gluing	Graphene	Graphite	SSW	Polycyclic aromatic hydrocarbons	Tea productions	HS
[77]	Sol–gel	GO	Graphite	Stainless steel plunger	Polybrominated diphenyl ethers	Canal water	DI
[78]	Sol–gel	Graphene	Commercial graphene	SSW	Organochlorine pesticides	Rainwater	DI
[79]	Sol–gel	Graphene	Not described	SSW	Halogenated aromatic hydrocarbons	Mineral water, lake water, and tap water	HS
[80]	Electrochemically polymerization of pyrrole and graphene	Graphene	Graphite	SSW	Phenols	Pond water	DI
[81]	Electrochemical polymerization	Graphene	Commercial graphene	Platinum wire	Tricyclic antidepressant	Plasma, milk, urine, hair	HS
[26]	Chemical bonding	On-fiber-reduced GO	Graphite	Silica fiber	Polycyclic aromatic hydrocarbons	River water and pond water	HS
[82]	Chemical bonding	On-fiber-reduced GO	Graphite	Titanium fiber	Phthalates	Bottled water and intravenous drip samples in plastic-packaging	DI

(continued)

Table 2.3 (continued)

References	Preparation method	Graphene format	Graphene source	Supporting substrate	Analyte	Sample matrix	SPME mode
[83]	Chemical bonding	On-fiber-reduced GO	Graphite	Silver-coated SSW	*n*-Alkanes	Rainwater and water solution of ethanol extract from a soil sample	DI
[84]	Electrochemical reduction	Electrochemically reduced GO	Graphite	Copper wire	Tricyclic antidepressants	plasma	HS-CF
[31]	In situ chemical exfoliation	Graphene	Pencil lead	None (monolith)	Bisphenols	Tap water and effluent of WWTP	DI
[85]	Hydrothermal method	GO	Graphite	None (monolith)	Organochlorine pesticides	Lake and pond water	HS
[86]	Sol–gel	Composite of dehydrated Zn $(OH)_2$ and reduced GO	Graphite	Fused-silica fiber	Sulfur volatiles	Chinese chive and garlic sprout	HS
[87]	Sol–gel	Poly(ethylene glycol) grafted graphene	Graphite	SSW	Volatile aromatic compounds	Tap, river, and mineral water	HS
[88]	Electrochemically polymerization of 3,4-ethylenedioxythiophene and GO	GO	Graphite	Gold wire	Polycyclic aromatic hydrocarbons	Seawater	DI, HS and HS-CF
[89]	Electrochemical polymerization	Sulfonated graphene	Graphite	SSW	Terpenes	Star anise and fennel	HS
[90]	Electrochemical polymerization of pyrrole and GO	GO	Commercial GO	Platinum wire	Phthalate esters	Boiling water from disposable drinking cups	DI

MA Microwave assisted, *CF* cold fiber

graphene-based fibers were also reported with high EEs to compounds without aromatic rings, such as some organochlorine pesticides [78] and *n*-alkanes [83], which might be owing to the hydrophobic interactions [83]. It is also notable that the composites of graphene with other materials could exhibit high EEs to some specific analytes due to the combination effects of each component of the composites. For example, the composite coating of graphene and ZnO exhibited high EEs to sulfur volatiles, where ZnO provided the coordination sites for binding the sulfur volatiles, and graphene helped to form a large specific surface area in the coating [86].

Due to the superior thermal conductivity of graphene and GO, the fibers of graphene and GO coated on the metal wires were also used for headspace-cold fiber-SPME [84, 88]. Cooling the fibers could increase the partition coefficients between the fibers and sample matrices, since adsorption of analytes on graphene coatings were exothermic processes, which could potentially promote the sensitivity of SPME.

2.4.2 CNTs

The methods for preparing CNT-based SPME fibers were very similar to those for preparing graphene-based ones. Up to now, physical deposition [91], gluing [92–99], sol–gel method [100–103], electrophoretic deposition [104, 105], depositions in conductive polymers [106–109], and chemical bonding [24, 27, 28, 110, 111] have also been adopted to immobilize CNTs on supporting substrates. Besides, CNTs and β-cyclodextrin-functionalized CNTs were also entrapped in pores of polypropylene hollow fibers for the preparation of novel SPME fibers (Fig. 2.5) [112, 113].

The CNT-based SPME fibers were used to analyze various analytes in a wide range of sample matrices via DI extraction mode or HS extraction mode, such as:

- Polybrominated diphenyl ethers in water (DI [91] and HS [100]) and milk (DI [91]),
- Phenols in water (DI [24, 27, 92, 96, 98, 104, 110, 111] and HS [101, 106]),
- Pesticides in water (HS [28, 93] and DI [108]), and tea samples (DI [95]),
- Butyltin compounds in seawater (HS) [94],
- *p*-Nitroaniline, aniline, *o*-dinitrobenzene in water (DI) [96],
- Aniline, 4-methylaniline, 4-methoxybenzoic acid, benzyl alcohol, benzoic acid, and 3-chlorobenzoic acid in water (DI) [97],
- Hydrocarbons in water (DI) and soil samples (HS) [99],
- Benzene series in water (HS) [27, 101, 103],
- Furan in food samples (HS) [102],
- F^-, Cl^-, Br^-, NO_3^-, and SO_4^{2-} in water (DI) [105],
- Phthalate esters in water (DI) [107],
- Polycyclic aromatic hydrocarbons in water (HS) [109],

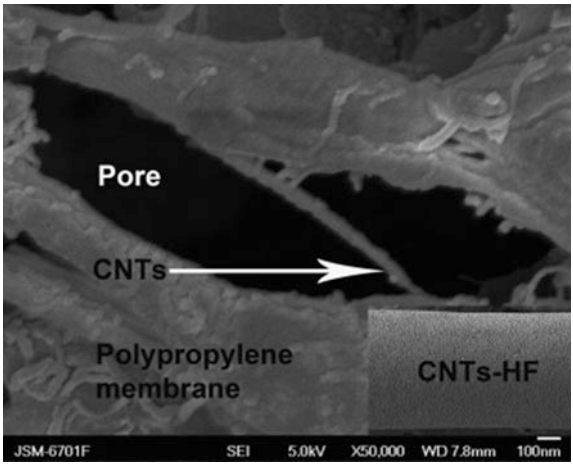


Fig. 2.5 Scanning electron microscopic image of carbon nanotube-reinforced hollow fiber. Reprinted with the permission from Ref. [112]. Copyright 2013 Elsevier

- Benzaldehyde, acetophenone, and 2-octanone in water (HS) [27],
- Strychnine and brucine in urine (DI) [112],
- Hormones of tomatoes (DI) [113].

Most analytes aforementioned contain aromatic rings. Due to the electrical conductivity of CNTs, CNT-based fiber, which were prepared by Nafion gluing [97] and electrophoretic deposition [105], were also used to extract organic ions [97] and inorganic anions in water [105]. When the CNT-based fibers were used to extract target analytes in complex sample matrices, the analytes were firstly extracted by solvents, and then, the solvents were vaporized and the residues were dissolved in water for DI SPME [91, 95].

2.4.3 Other Carbonaceous Materials

Gluing bamboo charcoal on SSWs for the preparation of SPME fiber was reported by Zhao et al. [114]. Bamboo charcoal is facilely available and environmentally friendly. And bamboo charcoal possesses porous structure and large specific surface area up to 300 $m^2\ g^{-1}$. The SPME fiber prepared with bamboo charcoal exhibited good sensitivities for the extraction of phthalate esters from environmental water samples, with the detection limits reached 4–23 ng L^{-1}.

Sun et al. [115] prepared a carbon nanoparticle-based fiber coating by simply deploying the SSWs in the flame of a common alcohol burner. After a very short time duration (60 s), carbon derived from incomplete combustion of alcohol deposited on the wire and presented a nanoscale brushy structure. The fiber exhibited high sensitivities to phthalate esters and polycyclic aromatic hydrocarbons, the detection limits were at parts-per-trillion levels. Similarly, Lin et al. [116] prepared mesoporous carbon coatings on metal wires by carbonizing ethanol with

room-temperature atmospheric-pressure dielectric barrier discharge plasma. The detection limits of polycyclic aromatic hydrocarbons were also at parts-per-trillion levels.

Huang et al. [117] reported another SPME fiber by carbonizing polydopamine spontaneous polymerized on SSWs at a very mild alkaline pH. The fiber exhibited high sensitivities to organochlorine pesticides with the detection limits at parts-per-trillion levels.

2.5 MIPs

MIPs are widely used as artificial recognition systems for macromolecules, small organic molecules, metal ions, and even virtues and cells. Compared with biological recognition systems, MIPs also possess many other intriguing characteristics, such as mechanical/chemical/thermal stabilities, low cost, and ease of preparation. These features have also facilitated the application of MIPs in the preparation of SPME fibers (Table 2.4).

MIPs are usually synthesized through polymerization of functional monomers in the presence of templates. After removing the templates, the cavities formed in MIPs can trap the analytes of interest. Cross-linkers are also needed to form rigid polymer networks to keep the cavities for target molecules stable, and make the polymer robust both mechanically and thermally. Porogens are sometimes used to realize porous morphologies, which could facilitate the removal of the templates and make the cavities for the target analytes more accessible. The functional groups on the monomeric units of MIPs trap the target analytes via non-covalent interactions or covalent bonds. Non-covalent interactions, such as hydrogen bonds, are more common for trapping the target analytes. The covalent interactions are rare, because it is not easy to find functional monomer that can readily form covalent bonds with the template and target analyte, and avoid suffering from the difficulty of removing the template [118].

The works applied MIPs in SPME in recent years are selectively listed in Table 2.4. Hydrogen bonds were the most common interactions in these works. For examples, when the target compounds contained Lewis basic or Lewis acidic groups, methacrylic acid or acrylamide was often used as the functional monomer. The reason for the wide adoption of hydrogen bonds is that, compared with van der Waals forces, hydrogen bonds are much stronger and have specific directions, which would result in stronger affinities and better recognition abilities toward the target analytes. Still, π–π stacking effect was also adopted for recognizing target analytes [119, 120]. In addition, metal ion coordination, which plays an important role in biological recognition systems, was used in MIP coating for the recognition of target analyte as well [121].

Generally, MIP coatings were immobilized on silica fibers [119–132]. Prior to coating, silica fibers needed to be activated and silylated in ahead [121–130]. However, it was no easy to prepare uniform MIP coatings with the thickness well

Table 2.4 The applications of molecularly imprinted polymers in the preparation of SPME fibers

References	Functional monomer	Template	Cross-linker	Substrate	Target compounds	Sample matrix	SPME mode
[119]	Phenyltrimethoxysilane	BDE-209	Tetraethoxysilane	Activated silica fiber	Polybrominated diphenyl ethers	Municipal wastewaters	DI in samples with salinity adjusted
[120]	Calix[4]arene	Parathion methyl		Activated silica fiber	Organophosphorus pesticides	Apple and pineapple	HS
[121]	4-vinylpyridine	2,2′-dipyridine		Silylated silica fiber	2,2′-dipyridine	Tap water, laboratorywastewater, human urine samples	DI in pH adjusted samples
[122]	MAA	Sudan I	TRIM	Silylated silica fiber	Sudan dyes	Chilli tomato sauce and chilli pepper	DI in hexane solutions
[123]	MAA	Testosterone	TRIM	Silylated silica fiber	Anabolic steroids	Human urine	DI in samples
[124]	MAA	17β-estradiol	TRIM	Silylated silica fiber	Estrogens	Fishery samples	DI in hexane and acetonitrile solutions
[125]	MAA	Terbutylazine	TRIM	Silylated silica fiber (HF protected)	Triazine herbicides	Sludge water, watermelon, milk, and urine samples	DI in samples, milk was filtered
[126]	Acrylamide	Biphenol A	TRIM	Silylated silica fiber	Biphenol A	Tap water, human urine, milk	DI in tap water and diluted urine, and diluted ACN extract of milk
[127]	MAA	Propranolol	TRIM	Silylated silica fiber	β-blockers	Urine and plasma samples	DI in toluene solutions
[128]	Acrylamide	Tetracycline	TRIM	Silylated silica fiber	Tetracyclines	Chicken feed, chicken muscle, and milk	DI in toluene solutions
[129]	MAA	Prometryn	TRIM	Silylated silica fibers	Triazines	Soybean, corn, lettuce, and soil samples	DI in benzene solutions
[130]	MAA	Ofloxacin and sulfamethazine	TRIM	Silylated silica fiber	Antibiotic drugs	Pork liver and chicken	DI in dichloromethane solutions

(continued)

Table 2.4 (continued)

References	Functional monomer	Template	Cross-linker	Substrate	Target compounds	Sample matrix	SPME mode
[131]	Melamine and chloranil	Ascorbic acid		Polymethyl methacrylate-coated silica fiber	Ascorbic acid	Diluted aqueous, blood serum and pharmaceutical samples	DI in samples with pH adjusted
[132]	Polyethylene glycol	Diazinon		Activated silica fiber	Organophosphorus pesticides	Vegetables	HS of homogenized samples
[133]	MAA	Propazine	EDMA	Monolith	Triazines	Soil, potato, pea	DI in toluene solutions
[134]	MAA	Biphenol A	EDMA	Monolith	Biphenol A and analogues	Tap water, sewage, human urine	DI in aqueous matrices
[135]	MAA	Epinephrine	EDMA	Monolith	Catecholamines	Human urine and serum	DI in acetonitrile solutions
[136]	MAA	Epinephrine	EDMA	Monolith	Ephedrine and pseudoephedrine	Human urine and serum	DI in toluene solutions
[137]	MAA	Dibutyl phthalate	EDMA	Monolith	Phthalates	Reservoir and bottled water	DI in samples
[138]	MAA	Atrazine	EDMA	Monolith	Triazine herbicides	Tap water, rice, onion	DI in aqueous or methanol solutions
[139]	MAA	Ametryn	EDMA	Monolith	Triazine herbicides	Tap water, rice, maize, onion	DI in aqueous solutions
[140]	MAA	Thiabendazole	TRIM	Monolith (HF protected)	Thiabendazole	Orange juices	DI in samples
[25]	MAA	Ofloxacin	EDMA	Polydopamine-coated SSW	Ofloxacin	Milk	DI in diluted samples
[141]	MAA	Sudan I	TRIM	Silylated SSW	Sudan dyes	Hot chili powder and poultry feed samples	DI in hexane solutions
[142]	Pyrrole, thiophene, 3-methylthiophene	Linezolid		SSW	Linezolid	Synthetic body fluid and human plasma	DI in aqueous matrices

(continued)

Table 2.4 (continued)

References	Functional monomer	Template	Cross-linker	Substrate	Target compounds	Sample matrix	SPME mode
[143]	MAA	Estradiol	EDMA	Fe_3O_4@SiO_2 microspheres	Estrogens	Milk powder	DI in acetone solutions
[144]	ABBA	Estradiol		Fe_3O_4@ZIF-8 particles	Estrogens	Fish and pork	DI in hexane solutions
[145]	MAA	Dopamine	EDMA	Polypropylene hollow fiber supported	Dopamine	Human serum and dopamine hydrochloride injection	DI in aqueous solutions
[146]	MAA	Chlorogenic acid	Vinyltriethoxysilane	Polypropylene hollow fiber supported	Chlorogenic acid	Herbal product	DI in hydro-alcoholic extract of samples

MAA Methacrylic acid, *ABBA* 3-aminobenzeneboronicacid, *TRIM* trimethylopropane trimethacrylate, *EDMA* ethylene dimethacrylate

controlled. To ensure the uniformity and control the thicknesses of the MIP coatings, the polymerization conditions, such as the temperature, the polymerization time, and the doses of functional monomer and cross-linker, all needed to be investigated [128]. It is notable that using a capillary as a mold has been an intriguing approach for controlling the diameter of the fiber [116].

Monolithic MIP fiber was first prepared by Turiel et al. [133] by in-mold polymerization (Fig. 2.6). Compared with the supported coatings on fused-silica fibers or SSWs, the extraction would need longer time to reach equilibrium for monolithic fibers, and it might be more difficult for removing the templates and eluting the adsorbed analytes from the fibers. However, monolithic fibers were much flexible and would not be easily broken during uses. In addition, monolith fibers could be readily prepared in batch with the diameters well controlled through in-mold polymerization, and there is no worry about the exfoliation of the coatings [133–140].

MIP coatings were also immobilized on polydopamine-coated SSWs [25], silylated SSWs [141], or electropolymerized on SSWs [142]; these fibers would be much more flexible than those with the silica fibers as the supporting substrates. Lan et al. [143, 144] immobilized MIPs coated magnetic particles on electromagnets, which were readily used for automatic SPME practices. MIPs were also supported by polypropylene hollow fibers to be used as SPME fibers [145, 146].

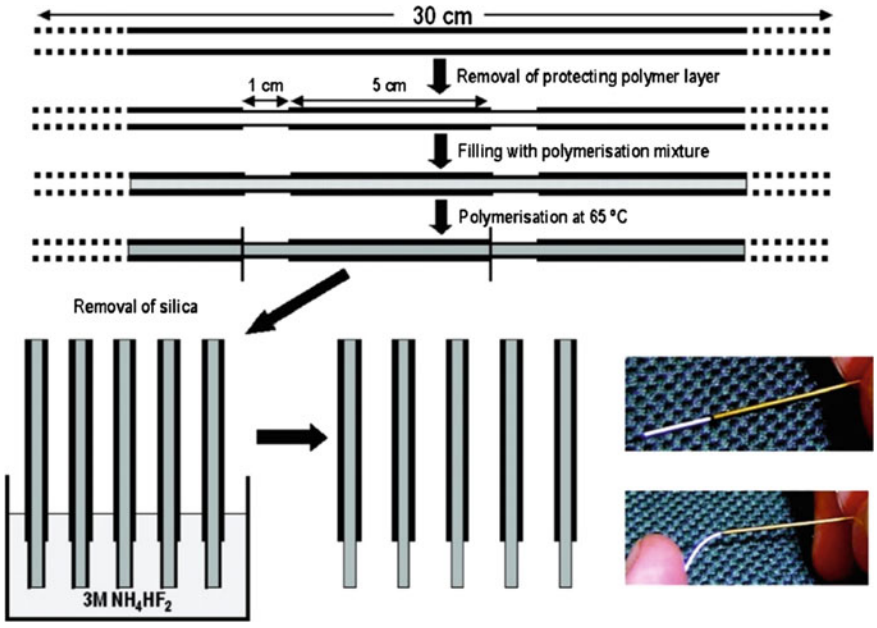


Fig. 2.6 Preparation of monolithic molecularly imprinted fibers. Reprinted with the permission from Ref. [133]. Copyright 2007 American Chemical Society

As shown in Table 2.4, in most cases, MIP fibers were not directly used in aqueous sample matrices. That is because in aqueous sample matrices, MIPs would act as reverse-phase sorbents that retain both the target analytes and other matrix components through non-specific interactions [125, 139]. In other words, the selectivity of MIPs would be ruined in aqueous sample matrices. Therefore, the analytes in the sample matrices were first extracted with organic solvents, and then, the MIP fibers were immersed in the organic solvents for the extraction of the analytes. In other studies [125, 139], to enable direct sampling in aqueous sample matrices, and to simplify the sample preparation procedures using MIP fibers, liquid–liquid extraction was coupled with SPME by inserting MIP fibers in polypropylene hollow fibers filled with organic solvents. This technique was named as liquid–liquid–solid microextraction by Hu et al. (Fig. 2.7) [125].

For biomolecule templates which slightly solubilize in organic solvents, an aqueous imprinting process might be preferred. To achieve this goal, Golsefidi et al. [146] developed an organic–inorganic hybrid MIP. In the preparation procedure, functional monomer and cross-linker were dissolved in organic phase, while the template was dissolved in the mixture of ethanol and water, and then, the two phases were mixed and solidified to form the MIP.

Metal complex imprinted polymer was also used as SPME fiber coatings, which could trap the analytes through coordination bonds [121]. Coordination bonds exhibit higher strength, specificity, directionality than hydrogen bond and van der Waals forces; therefore, the metal complex imprinted polymer could achieve higher selectivity in aqueous sample matrices. In addition, sol–gel method was also used for preparing MIP coatings, by incorporating calix[4] arene [120] and polyethylene glycol [132] for trapping the target analytes.

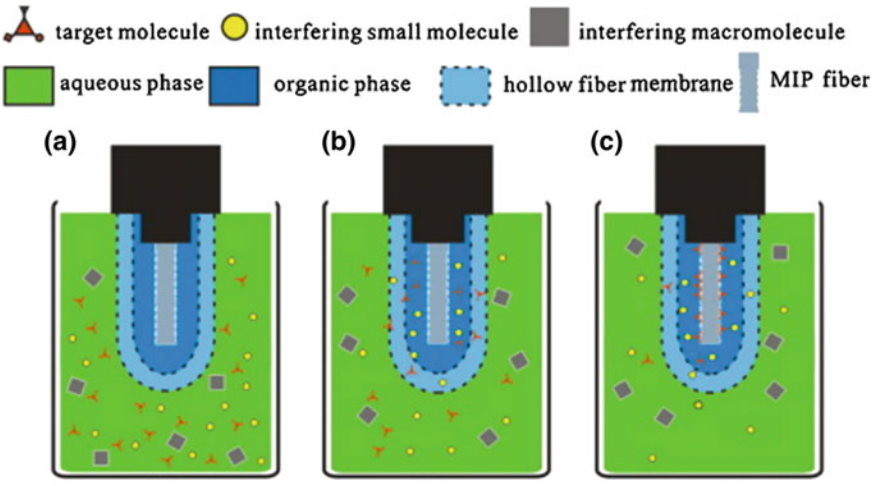


Fig. 2.7 Extraction process of the liquid–liquid–solid microextraction technique. **a** Before extraction, **b** during extraction and **c** after extraction. Reprinted with the permission from Ref. [125]. Copyright 2009 Elsevier

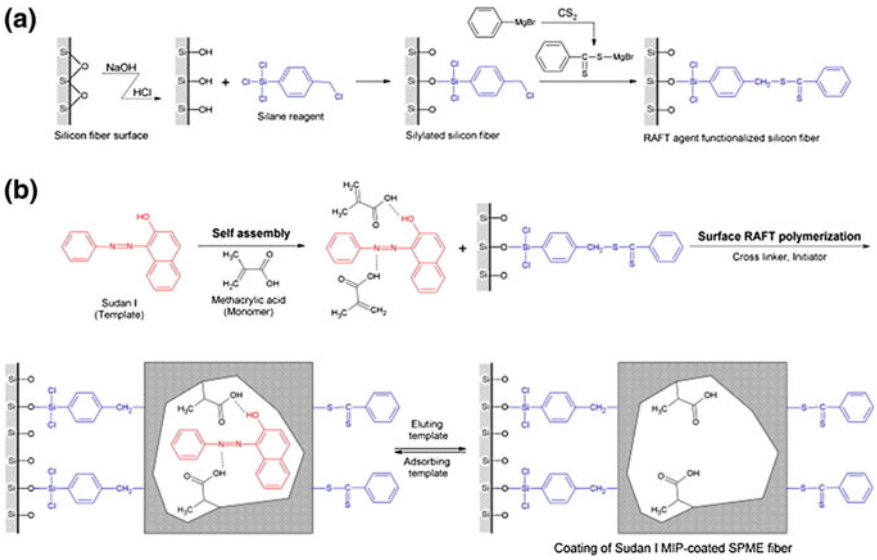


Fig. 2.8 Preparation of MIP coating through surface reversible addition-fragmentation chain transfer polymerization. Reprinted with the permission from Ref. [122]. Copyright 2012 Elsevier

The main drawbacks those limit the applications of MIPs are the incomplete removal of templates and incompletely accessible cavities. These limitations are mainly attributed to the high cross-linking nature of MIPs [122]. Preparing thin MIP coatings provides a solution for these problems. Recently, surface reversible addition-fragmentation chain transfer polymerization was applied to coat MIP on the surface of fused-silica fibers (Fig. 2.8) [122]. The coating prepared by this method was reported to be about only 0.55 μm thick, which resulted in effective removal of template and fast adsorption/desorption kinetics. Similarly, MIP coatings on microparticles with small thicknesses also exhibited fast adsorption/desorption kinetics [143, 144].

2.6 MOFs

MOFs are inorganic–organic hybrid microporous crystalline materials, in which metal ions and organic bridging ligands assemble autonomously to form orderly packed three-dimensional networks. With diverse metal ions and organic ligands available for preparing MOFs, MOFs exhibit extensive structures, topologies, and porosities. Recently, due to the unique properties of MOFs, such as high specific surface areas, uniform structured cavities, and good thermal stabilities, they are also extensively studied for the potential in sample preparation and chromatographic separation, including the use as SPME fiber coatings [147]. Generally, MOFs used

as SPME fiber coatings for selectively extracting target analytes via: (a) van der Waals interactions between organic ligands and analytes, such as π–π stacking effect and hydrophobic interaction; (b) Lewis acid–base interactions between metal ions and analytes, when open metal sites are available in MOFs and the analytes contain electron-rich structures; and (c) size selectivity of the nanoscale pores in MOFs.

Table 2.5 lists the recent studies in using MOFs as SPME fiber coatings. MOF-199 was the first reported MOF utilized as an SPME fiber coating material. It was immobilized on etched stainless wire via an in situ hydrothermal method [148]. This homemade fiber exhibited wide linear ranges, low detection limits, high enrichment factors, and higher extraction efficiencies than the commercial SPME/DVB fiber with benzene homologues as the target analytes. The large surface area (1458 cm^2/g) and unique porous structure (two large pores of 12 Å in diameter and pore windows about 8 Å in diameter), the π–π interactions between the analyte molecules and the ligand molecules, and the π-complexation of the electron-rich analytes to the open metal sites in the network of MOF-199 were thought the determining factors that contributed to the high EEs. Chang et al. [149] demonstrated the importance of pore sizes in determining the selectivity of MOF-based coatings with a comparison study between ZIF-7-, ZIF-8-, and MOF-199-coated SPME fibers. In their study, ZIF-7-coated SPME fiber could not extract linear and branched alkanes since the pores of ZIF-7 were too small, whereas the ZIF-8 with the median-sized pores exhibited great selectivity to *n*-alkanes over branched alkanes, and MOF-199 exhibited no selectivity since its pores were too large. In other works, hydrophobic interactions [150–153], π–π stacking effects [150–152, 154], Lewis acid–base interactions [151, 154], size selectivity [150, 153], as well as dipole–dipole interactions [150], were also reported to play key roles in selectively and effectively extracting the analytes of interest.

He et al. [19] observed a profound selectivity to benzene homologues over phenols by using MAF-X8 as the coating material. Experimental and simulation results revealed that the selectivity originated from the differences in adsorption kinetics between benzene homologues and phenols. As shown in Fig. 2.9a, the adsorption of toluene can rapidly reach saturation within 8 min; however, the adsorption of 2-chlorophenol was almost neglected in the first 15 min. And as shown in Fig. 2.9b, the simulated diffusion resistance of 2-chlorophenol in MAF-X8 was much larger than that of toluene.

Owing to the long-range ordered structures of MOFs, the molecular mechanics simulation could be a good approach to explain the selectivity of other MOFs. Liu et al. [155] also observed good compatibility between the simulated results and experimental results.

The endurances of MOFs to humidity are very important for their applications as fiber coating materials. Cui et al. [148] observed that humidity decreased the extraction efficiencies, since the coordination structure would be unstable under certain humidity. Some MOFs are stable to humidity and water, such as MIL-53 [156] and $[Cd(L)_2(ClO_4)_2]\cdot H_2O$ (L = 4-amino-3,5-bis(4-pyridyl-3-phenyl)-

Table 2.5 The applications of metal-organic frameworks in the preparation of fiber coatings

References	MOF	Supporting substrate	Preparation method	Analytes	Sample matrix	SPME mode
[148]	MOF-199	SSW	In situ hydrothermal growth	Benzene homologues	Indoor air samples	HS
[149]	MOF-199, ZIF-7, ZIF-8	SSW	Layer by layer deposition	*n*-Alkanes	Diluted petroleum-based fuel and human serum	HS
[150]	MIL-88B	SSW	In situ hydrothermal growth	Polychlorinated biphenyls	Lake water, river water samples and soil	HS
[151]	UiO-66	SSW	Gluing	Phenols	River water and lake water	HS
[152]	$[Yb_4(AIP)_6(2,2'\text{-bipy})]_n^b$	SSW	In situ hydrothermal growth	Polycyclic aromatic hydrocarbons	Spring water, wastewater and soil	HS
[153]	$[Cu_3(\mu_3\text{-O})(\mu\text{-OH})(\text{triazolate})2]^+$	SSW	Gluing	Polychlorinated biphenyls	Tap water, river water, underground water and pond water	DI
[154]	MIL-101(Cr)	SSW	Gluing	Benzene homologues and polycyclic aromatic hydrocarbons	River water	HS
[19]	MAF-X8	SSW	In situ hydrothermal growth	Benzene homologues	Water	HS
[155]	bio-MOF-100, bio-MOF-101, bio-MOF-102	SSW	Gluing	Organochlorine pesticides and polycyclic aromatic hydrocarbons	Pond water and river water	DI
[156]	MIL-53	SSW	Gluing	Polycyclic aromatic hydrocarbons	Wastewater	DI
[157]	$[Cd(L)_2(ClO_4)_2]\cdot H_2O^a$	Fused-silica fiber	In situ growth under room temperature in aqueous solution	Benzene homologues	Seawater	DI

(continued)

Table 2.5 (continued)

References	MOF	Supporting substrate	Preparation method	Analytes	Sample matrix	SPME mode
[158]	IRMOF-3	SSW	In situ hydrothermal growth	Polycyclic aromatic hydrocarbons	Rainwater	HS
[159]	MOF-199/GO composite	Fused-silica fiber	Chemical bonding	Organochlorine pesticides	River water, soil, water convolvulus and longan	HS
[160]	MOF-199/CNT composite	Fused-silica fiber	Chemical bonding	Ethylene, methanol and ethanol	Durian husk, wampee, blueberry, and grape	HS
[161]	MOF-5	Porous copper foam	In situ solvothermal growth	Plant volatile sulfides	Chinese chive and garlic sprout	HS
[162]	MOF-177	SSW	Gluing	Polychlorinated biphenyls and polycyclic aromatic hydrocarbons	River water, lake water and wastewater	HS
[163]	MIL-101, MOF-199	SSW	Sol–gel	Polycyclic aromatic hydrocarbons	River water and lake water	HS
[164]	MIL-101(Cr)	SSW	Sol–gel	Volatile aromatic compounds	Tap water and lake water	HS

[a]L = 4-amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole; [b]AIP = 5-aminoisophthalic acid radical, 2,2′-bipy = 2,2′-bipyridine

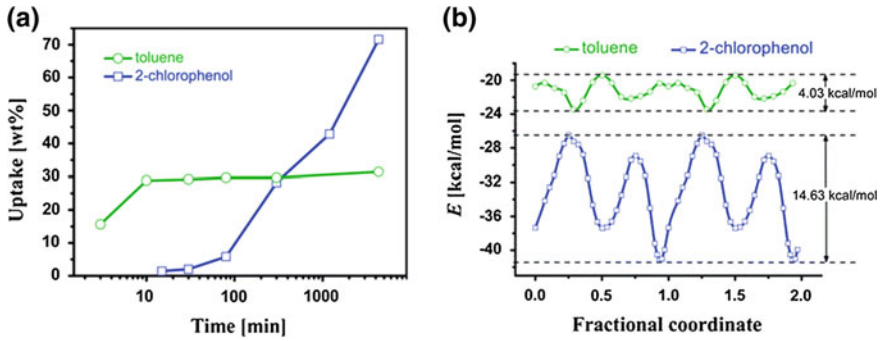


Fig. 2.9 **a** Adsorption kinetics of saturated toluene and 2-chlorophenol vapors on microcrystalline MAF-X8; **b** potential profiles and diffusion barriers of guest molecules passing through the 1D channels of MAF-X8. Reprinted with the permission from Ref. [19]. Copyright 2012 Royal Society of Chemistry

1,2,4-triazole) [157], which were used for DI SPME in aqueous solutions. On the other hand, MOFs, which are sensitive to humidity, can be protected by other humidity-resistant materials for guaranteeing their applications. For example, after covering bio-MOFs with silicone glue, the fibers were used for DI SPME in aqueous samples [155]. In another study [158], IRMOF-3, which is very sensitive to humidity, was used in the headspace of aqueous samples after being protected with ionic liquid and polydimethylsiloxane (PDMS).

The composites of MOFs and other materials have also been used as SPME fiber coating materials, which showed some intriguing properties. The MOF-199/graphene oxide (GO) composite exhibited higher extraction efficiencies than MOF-199 and graphene oxide, since new small pore spaces were created at the interface between graphite layers and MOF units after incorporating MOF-199 in GO [162]. In the MOF-199/carbon nanotubes (CNTs) composite coating [160], CNTs acted as hydrophobic shield to protect MOF-199, and the joint effects of the open metal sites of MOF-199, the oxide atoms surrounding the copper ions and the pores in MOF-199, and the conjugated aromatic rings of CNTs, together contributed to the high extraction efficiencies toward ethylene.

It is notable that due to the highly ordered structures of MOFs, the mass transfer of the target analytes in the MOF coatings might be very fast. He et al. [19] observed that the time needed to reach the SPME equilibrium was less than 10 min. And Li et al. [157] observed the equilibrium time was about 15 min, and 15 s was enough for effective thermal desorption with their MOF-based fiber.

In situ growth is popular for preparing MOF-based SPME fibers [19, 148, 150, 152, 157, 158, 161]. Generally, the substrates needed to be etched to provide rough surfaces to enhance the adhesive strength of the coatings. The idea of using porous copper foam to entrap the as-grown nanosized MOF particles in its pores would promote the mechanical stability of the fiber [161]. Other immobilization methods, such as physical deposition [149], gluing [153–156, 162], sol–gel [163, 164],

chemical bonding [159, 160], were also used in the preparation of MOF-based SPME fibers.

Another class of inorganic–organic hybrid material, i.e., metal-organic aerogels (MOAs), which possess hierarchically porous structures, were also used as SPME fiber coatings for the extraction of phenols, benzene homologues, organochlorine pesticides, and polycyclic aromatic hydrocarbons [165, 166]. However, the applications of MOAs in SPME are contemporarily far less studied than those of MOFs.

2.7 Metals and Metal Oxides

Metals and metal oxides are also popular extraction materials utilized in SPME fibers (Table 2.6). The relatively facile strategies for preparation of diverse nanostructures and morphologies, and the excellent thermal, mechanical, and chemical stabilities facilitate the applications of metals and metal oxides in SPME fiber coatings. In addition, the unique selectivity toward analytes could be easily understood and possibly be anticipated due to the well-understood electronic structures of metals and metal oxides [167].

Noble metals could be reduced from their oxidation states to prepare SPME fiber coatings. For example, a porous silver coating was prepared on a SSW through the silver mirror reaction for the extraction of phthalate esters and polycyclic aromatic hydrocarbons [167]. And Au nanoparticles were prepared from $HAuCl_4$ and subsequently immobilized on SSWs via chemical bonding [23] or in situ deposition [168] for the preparation of SPME fibers. Black Pd coating was prepared on SSWs by reducing the Pd(II) cations in the aqueous solution with the SSW substrate [169]. The satisfactory EEs of the noble metal coatings to phthalate esters and polycyclic aromatic hydrocarbons might be owing to the hydrophobic interactions and the electron-transfer effect between the π–donor system and the empty valency shells of the noble metals [23, 167–169].

Due to the outstanding malleability of metals, metal wires at extremely small dimensions could be prepared. Gong et al. [170] used tungsten wires with the tip diameters of about 1 μm to sample metabolites in single *Allium cepa* cells. Subcellular analysis was realized in nucleus and cytoplasm.

SSW, which is widely used as supporting substrates of SPME fibers nowadays, was simply etched with hydrofluoric acid to be used as a SPME fiber [171]. The fiber possessed a porous and flower-like structure with Fe_2O_3, FeF_3, Cr_2O_3, and CrF_2 on the surface (Fig. 2.10), which exhibited high EEs to polycyclic aromatic hydrocarbons due to cation–π interaction.

Au and Ag can form valent bonds with sulfhydryl groups; this property was used to modify Au and Ag nanoparticles with organic functional groups to promote their EEs to the target analytes [172–174]. Tungsten wire was also functionalized with *n*-octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride after being oxidized, the modified wire exhibited excellent EEs to perfluorinated compounds [175].

Table 2.6 The applications of metals and metal oxides in the preparation of SPME fibers

References	Coating	Substrate	Preparation procedure	Analyte	Sample matrix	SPME mode
[167]	Ag	SSW	Silver mirror reaction	Phthalate esters and polycyclic aromatic hydrocarbons	Aqueous extracts of disposable paper cup and instant noodle barrel	DI
[23]	Au nanoparticles	Au coated SSW	Chemical bonding	Polycyclic aromatic hydrocarbons	Rainwater and soil extract	DI
[168]	Au nanoparticles	SSW	Chemical deposition	Polycyclic aromatic hydrocarbons	River water and wastewater	DI
[169]	Black Pd	SSW	In situ oxidation–reduction	Polycyclic aromatic hydrocarbons and phthalate esters	Tap water, snow water, bottled water, and hot water in disposable paper cup	DI
[170]	Tungsten	Tungsten		Metabolites	Single *Allium cepa* cells	DI
[171]	Etched SSW	SSW	Hydrofluoric acid etching	Polycyclic aromatic hydrocarbons	River water	HS and DI
[172]	Mercaptoundecanol-functionalized Au nanoparticles	SSW	Chemical deposition followed by mercaptoundecanol-functionalization	Polycyclic aromatic hydrocarbons	River water, snow water, and influent wastewater	DI
[173]	Octanedithiol-functionalized Au nanoparticles	SSW	Electrochemical deposition followed by octanedithiol-functionalization	UV filters	River water, influent and effluent wastewater, and rainwater	DI

(continued)

Table 2.6 (continued)

References	Coating	Substrate	Preparation procedure	Analyte	Sample matrix	SPME mode
[174]	Propanethiol-functionalized Ag nanoparticles	Ag–Cu fiber	Galvanic displacement reaction followed by propanethiol-functionalization	Polycyclic aromatic hydrocarbons	Spring water	DI
[175]	*n*-Octadecyldimethyl[3-(trimethoxysilyl)propyl]ammonium chloride	Tungsten microdissecting needles	Chemical oxidation followed by silanization	Perfluorinated compounds	*Daphnia magna*	DI
[176]	Anodized aluminum	Aluminum wire	Anodization	Alcohols, benzene homologues and alkanes	Gaseous samples	HS
[177]	Ordered nanoporous anodic alumina	Aluminum wire	Anodization	Volatile organic compounds	Human exhaled breath	HS
[178]	Anodized aluminum	Aluminum wire	Anodization	Volatile compounds	Medicinal plant	HS
[179]	Alumina nanowires	Aluminum wire	Anodic oxidation followed by chemical etching	Volatile esters and alcohols	Banana	HS
[180]	Anodized zinc	Zinc wire	Anodization	Organic compounds	Gaseous samples and aqueous solutions	HS
[181]	TiO_2 nanosheets	Titanium wire	Anodization	Ultraviolet filters	River water and wastewater	DI
[182]	Phenyl-functionalized TiO_2 nanosheets	Ti wire	Anodization followed by phenyl-functionalization	Polycyclic aromatic hydrocarbons	River water and wastewater	DI
[183]	Nanostructured titania	Titanium wire	In situ oxidation with H_2O_2	Dichlorodiphenyltrichloroethane and its degradation products	Aqueous solutions	HS
[184]	Zn–ZnO	SSW	Electrochemical deposition followed by spontaneous oxidation	UV filters	River water, influent and effluent wastewater	DI

(continued)

Table 2.6 (continued)

References	Coating	Substrate	Preparation procedure	Analyte	Sample matrix	SPME mode
[29]	ZrO_2	NiTi alloy wire	Electrochemical deposition	Halophenols	Wastewater	HS
[185]	PbO_2 nanoparticles	Pt wire	Electrochemical deposition	Volatile organoselenium	Milk, apple juice, grape juice, urine, and plasma	HS
[186]	Nanostructured Co_3O_4	Platinum wire	Chemical bath deposition	Benzene homologues	River water, sewage water, and orange juice	HS
[187]	ZnO nanorod	Fused-silica fiber	Chemical deposition	Chlorobenzenes	Seawater, wastewater, soil	HS
[188]	TiO_2	SSW	Coating with titania sol, then heated in the resistance furnace at 400 °C for 10 min	Phosphopeptides	Protein digestion samples	DI
[189]	TiO_2 nanoparticles	SSW	Electrophoretic deposition	Phthalate esters	Bottled mineral water	DI
[190]	Mesoporous TiO_2 nanoparticles	SSW	Gluing	Organochlorine pesticides	Rainwater and lake water	DI

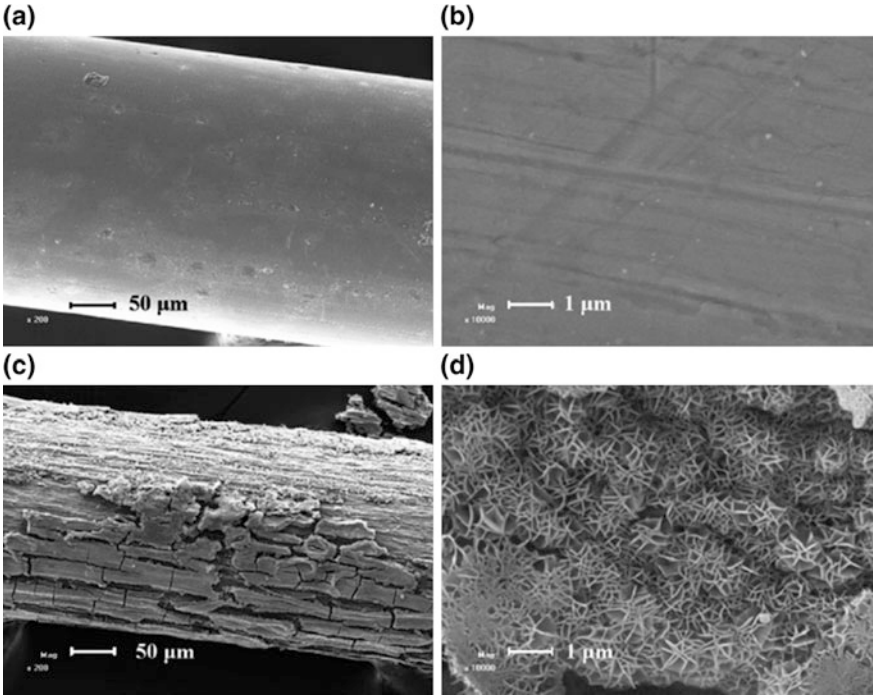


Fig. 2.10 Scanning electron micrographs of the surface of the SSW before (**a**, **b**) and after (**c**, **d**) etching. The images **a** and **c** are at a magnification of 200; images **b** and **d** are at a magnification of 10,000. Reprinted with the permission from Ref. [171]. Copyright 2009 American Chemical Society

Nanostructured metal oxide coatings could be readily prepared by anodizing metal wires. Aluminum oxide was one of the most studied coating materials; under different anodizing conditions, different morphologies were obtained [176–179]. Zhang et al. [179] even coupled chemical etching to anodization to prepare a nanowire coating. Similarly, zinc wire and titanium wire were also anodized to prepare ZnO and TiO_2 coatings [180, 181]. After TiO_2 coating formed by anodizing, phenyl groups could be subsequently functionalized on TiO_2 for extracting PAHs through π–π stacking effect [182]. In another work, TiO_2 coating was also prepared by oxidizing the surface of titanium wire with H_2O_2 [187]. Electrochemical deposition and chemical deposition were also widely used for preparing metal oxide coatings in situ [29, 184–187]. Heating titania sol coated on a SSW for the preparation of TiO_2 coating was also reported in the literature [188]. In other works, TiO_2 nanoparticles were firstly prepared and then immobilized on substrates by electrophoretic deposition [189] or gluing [190]. The metal oxide coatings could be used to extract analytes with hydroxyl groups and halogen atoms probably due to the Lewis acidic sites offered by the metal cations [184].

2.8 Conductive Polymers and Modified Silica

Among various conducting polymers, polypyrrole (PPY), polythiophene (PTH), polyaniline (PANI), and their derivatives have been utilized as SPME fiber coatings [191–197]. The introduction of these conducting polymers to SPME may be attributed to the ease and the controllability of their preparation. Typically, metal wires were used as working electrodes to perform electropolymerization. Based on the preparation protocol, the fibers were reported with thicknesses ranging from dozens to hundreds micrometers and often possessed rather rough and granulated morphologies. To date, various analytes including organochlorine pesticides [191], phenols [192], phthalate esters [193], antibiotic drugs [194–196], and adrenolytic drugs [197], have been analyzed in different sample matrices, even in human plasma [195–197] and whole blood [194]. It is notable that Olszowy et al. [196] have used several different poly(3-alkylthiophene)-coated SPME fibers to extract linezolid, which showed that the functional groups on the monomeric units could affect the EEs. In addition, PANI and PPY were often used as binder to immobilize other extractive materials on metal wires for the preparation of SPME fibers, as discussed in the sections above [51, 52, 80, 81].

Even though the application of silica fibers as the supporting substrates of SPME fibers is declined due to the fragility, the facile functionalization property of silica, however, makes it a versatile and promising material for preparing SPME fiber coatings. For example, nanoporous silica (SBA-15) was functionalized with 3-[bis (2-hydroxyethyl)amino] propyl-triethoxysilane and subsequently glued to copper wire for the preparation of a novel SPME fiber. This fiber exhibited much higher EEs to phenols than the commercial PDMS fiber [198]. In other works, phenyl-functionalized SBA-15 was used for the extraction of PAHs [199], and mercaptopropyl-functionalized nanoporous silica was used for the extraction of phenols [200] Query ID=``Q3'' Text=``Please check and confirm the inserted citation of Table 2.6 is correct. If not, please suggest an alternative citation. Please note that Tables should be cited in sequential order in the text.''.

2.9 Fibers for DI SPME in Biological Matrices

Solid-phase microextraction of endogenous and exogenous bioactive compounds from various complex biological sample matrices, such as semisolid tissues of animals and plants, whole blood, and so on, has been a very popular method in recent years, which showed great potential in pharmacokinetic studies [3], metabolome detection [1], field sampling of pollutants in animals and plants [8, 201], food quality assessment [5], and so on. For the implementation of DI SPME in biological matrices, it is critical to select proper SPME fibers which, besides possessing high EEs to target analytes, are also required to be biofouling resistant, i.e., the fibers should avoid binding of biomacromolecules, such as proteins and lipids

on their surfaces. In addition, for in vivo SPME in tissues of animals or plants, the fibers are also required to be biocompatible to avoid causing rejection reactions when the fibers are deployed in living tissues.

PDMS is one of the most widely used fiber coatings for DI SPME in biological matrices. A study showed that by overcoating the commercial PDMS/DVB fiber with a PDMS layer, the lifetime of the commercial fiber was greatly prolonged for DI SPME in grape pulp. This study demonstrated that PDMS was a material that was resistant to biofouling [202]. In addition, even though PDMS is thought to be low biocompatible due to its possible surface instability, PDMS was still widely used as a coating for in vivo SPME in fish bodies [4, 201], probably because PDMS was stable enough during the relatively short extraction processes. And since PDMS is low cost, disposable PDMS fibers were also prepared in multiple dimensions (dimeter of 640 or 300 μm) [4, 201].

Another class of fiber coatings, those are prepared by incorporating sorbents of high extraction capacities in biocompatible polymers such as polyacrylonitrile (PAN) and poly(ethylene glycol) (PEG), have also been widely used in SPME in complex biological sample matrices. Up to now, sorbents such as C18, HLB (hydrophilic–lipophilic balanced sorbent), and a mixed-mode sorbent (C18/benzenesulfonic acid) have been incorporated into biocompatible polymers. These fibers have been widely used in detecting pharmaceuticals and their metabolites in blood in vivo and in vitro, as well as metabolomes in human plasma and living rat brains [1–3].

Restricted access materials (RAMs) are silica particles with pore radius of about 3 nm, and the outer surfaces of RAMs are functionalized with hydrophilic diol groups, and the pore are modified with hydrophobic alkyl chains and/or ion exchange groups. RAMs were also used as SPME fiber coatings for extracting pharmaceuticals in whole blood [203]. In addition, as described in the last section, PPY- and PTH-coated fibers were also used to detect drugs in human plasma and whole blood [194–197].

To promote the EEs of in vivo SPME in animal tissues, a polystyrene@polydopamine (PS@PDA) core–sheath nanofibrous coating was reported [18]. PDA sheath was spontaneously covered on electrospun PS nanofibers under mild alkaline pH. PDA is of good biocompatibility. And the PDA sheath also made the coating hydrophilic that the body fluids could enter the inner pores of the fibrous structure under capillary effect, which made the inner surface of the coating accessible to analytes. In addition, the water layers surrounding the nanofibers could avoid the binding of biomacromolecules on the coating. In another work [204], polyelectrolyte was dispersed in silicone rubber to prepare a new fiber coating for the extraction of pharmaceuticals in living fish brains and muscle. Due to the incorporation of polyelectrolyte in silicone rubber, the novel coating could simultaneously extract neutral and protonated analytes, which also promoted the extraction efficiencies of analytes partially protonated under physiological pH.

Compared with analysis of several specific analytes or specific groups of analytes, metabolomics studies require extraction of metabolomes at wide polarity ranges. Vuckovic et al. [205] revealed the mixed-mode sorbents could be good

candidates for extracting metabolomes. Subsequent studies successfully used the coating for extracting metabolomes from rat blood and rat brains. And the coating showed a great potential to extract metabolites missed by microdialysis [2].

2.10 Conclusions

Development of new fibers is one of the hottest research fields of SPME. A lot of extraction materials have been developed into fiber coatings and monolithic fibers. Among these materials, the aforementioned ones are the most studied in recent years. This chapter presents a brief review of the applications of aforementioned extraction materials in developing SPME fibers with an emphasis on: (1) the strategies for preparation of fibers with the aforementioned extraction materials, (2) the target analytes that each extraction material could effectively and selectively extract and the corresponding thermodynamic or kinetic mechanisms, and (3) the potential of promoting or modifying the affinities of the extraction materials to analytes by functionalizing different functional groups or compositing with other materials. With these key points reviewed in this chapter, we hope this chapter could be a guide to the future explorations of developing other extraction materials into SPME fibers.

In addition, recent studies of DI SPME in complex biological matrices put forth more restrictive requirements for the development of new fibers. As the fibers for DI SPME in complex biological matrices were not as diverse as those for conventional uses, further studies are needed.

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