Recent advances in nanomaterials utilized in fiber coatings for solid-phase microextraction

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Since the introduction of solid-phase microextraction (SPME) in the 1990s, different types of coating have shown their crucial role in extraction efficiency. In the past decade, unique properties of nanostructured materials (e.g., large surface area, and remarkable thermal, mechanical and chemical stability) led to their application as desirable coatings in SPME.

The current review classifies nanomaterial–based SPME coatings as based on carbon, polymer, silica or metal nanoparticles. It also briefly discusses new developments and methods in preparing nanomaterial-based SPME coatings.

Keywords: Carbon nanomaterial; Extraction; Extraction efficiency; Fiber coating; Metal nanoparticle; Nanomaterial; Nanomaterial-based coating; Polymer nanomaterial; Silica nanomaterial; Solid-phase microextraction (SPME)

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1. Introduction

Since proposed by Pawliszyn and co-worker [1] in the early 1990s, solid-phase microextraction (SPME) has been widely accepted and applied as a sample-preparation technique due to its solvent-less nature and simplicity. SPME is based on the partitioning of target analyte(s) between the sample or the headspace (HS) above the sample and a stationary phase (coating), which is typically immobilized on a fiber or wire. Subsequently, analytes are thermally desorbed directly onto the injection port of a gas chromatograph or eluted with a suitable solvent for further analysis by liquid chromatography (LC). The coating type of SPME plays a crucial role in the efficiency of the extraction, as it is the main factor affecting the distribution constant between the sample matrix and the immobilized phase. The chemical and physical properties of the sorbent material have a great impact on the overall extraction performance, including method sensitivity, selectivity and reproducibility.

In recent years, nanomaterials have been attractive for extraction techniques because of their high porosity, which improves the extraction rate [2] and the extraction efficiency [3]. The remarkable thermal, mechanical and chemical stability of nanomaterials has resulted in their usage as SPME coatings [4]. Review articles about SPME coatings [4,5] and application of nanomaterials in analytical sample-preparation methods [6–9] suggest the need to pay particular attention to nanomaterial-based SPME coatings. The aims of this review are to compile and to evaluate nanomaterials used as SPME coating.

2. Carbon nanomaterial-based SPME coatings

Carbon-based nanomaterials have emerged in the past decade as a robust alternative to commercial coatings because of their remarkable electronic properties and their excellent mechanical, electrical and chemical properties. Although procedures for modifying side walls of carbon nanotubes (CNTs) enlarge their potential as SPME coatings, recently other forms of carbon [e.g., fullerenes, graphene and ordered mesoporous carbons (OMCs)] were considered more (see Table 1).

2.1. Carbon nanotube-based coatings

CNT-SPME fibers were first introduced by Wang et al. [3]. Since then, various CNTs

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Table 1. Applications of carbon-based nanomaterials in coatings for solid-phase microextraction

Coating type	Substrate	Analyte	Matrix	Recovery	LOD (ng/L)	Life span	Thermal stability (°C)	Ref.
TSO-SWCNTs	FS fiber	PBDEs	Wastewater	74–109	0.08–0.8	200	340	[10]
TSO-SWCNTs	FS fiber	OCPs and chlorophenols	Lake water and wastewater	90–101	0.07–4.36	–	–	[11]
PEG/SWCNTs	FS fiber	Chlorinated organic carriers	Polyester textile	82–105	0.02–7.5	200	340	[12]
SWCNTs	SS wire	VOCs	Human urine	90–95	10	150	350	[13]
SWCNTs	SS wire	Butyltin compounds	Seawater	73–85	4–10	150	350	[14]
SWCNTs	SS wire	Bisphenol derivatives	Food samples	79–86	100 ng/g	150	350	[15]
SWCNTs	SS wire	OCPs	Lake water and wastewater	88–111	0.19	150	350	[16]
SWCNTs	FS fiber	13 multi-class pesticides	Tea samples	75–118	27–230	70	–	[17]
SWCNTs	Pt wire	Phenols	Seawater and tap water	88–102	900–3800	80	–	[18]
SWCNTs	Pt wire	BTEX	Sea water, tap water and wastewater	75–105	5–26	120	350	[19]
SWCNTs	Pt plate	Inorganic ions	Deionized water	65–121	60–260	50	–	[20]
SWCNTs	Pt wire	Endocrine-disrupting compounds	Seawater and tap water	82–97	320–520	120	–	[21]
PEG/MWCNTs	FS fiber	VOCs	River, well and tap water	103–124	300	150	320	[22]
PEG/MWCNTs	FS fiber	VOCs	Environmental water samples	94–112	1–500	–	–	[23]
PEG/MWCNTs	FS fiber	BTEX	Tap, mineral and well water, and wastewater	90–102	0.6–3	200	320	[24]
PEG/MWCNTs	FS fiber	Non-steroidal anti-inflammatory drugs	Tap, river and well water, and wastewater	84–107	7–30	150	320	[25]
PEG/MWCNTs	FS fiber	Furan	Babyfood and fruit juice	92–103	0.1–2.5	–	–	[26]
MWCNTs	FS fiber	PBDEs	River water and skimmed milk	90–119	3.6–8.6	–	–	[3]
COOH-MWCNTsOH-MWCNTs	SS wire	VOCs, phenols, PAHs and pyridine	Deionized water	–	–	–	350	[27]
Nafion/MWCNTs	SS wire	Polar aromatic compounds	Pond water	83–106	30–570	–	–	[28]
Nafion/MWCNTs	SS wire	Basic drug	Pure aqueous matrix and urine samples	–	120–260	100	–	[29]