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Letters to the Editor

A simple thermal CVD method for carbon nanotube synthesis on stainless steel 304 without the addition of an external catalyst

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ABSTRACT

A method is described to synthesize carbon nanotubes (CNTs) by thermal chemical vapour deposition (th-CVD) directly on stainless steel substrates of various geometries. This method allows the bulk metal surface to act as both the catalyst and support for the CNT growth, thus enhancing the contact and adherence of the tubes to the substrate and eliminating the requirement of adding an additional catalyst in the process. The procedure was optimized to obtain a uniform layer of CNTs on the substrate.

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Carbon nanotubes (CNTs) are widely studied and are starting to be used for electrode and sensor applications [1,2]. In such cases, a conducting substrate is most often required. Particularly, stainless steel (SS) seems an attractive candidate for CNT growth due to its high iron content (~66%) and the possibility to tailor active sites for the growth process. A direct growth of the CNT on the bulk metal substrate should enhance the adherence of the tubes to the electrodes and favour a better electron/thermal transfer. Various procedures have been used thus far to synthesize CNTs on this material. These include plasma-enhanced chemical vapour deposition (PE-CVD) [3–5], thermal CVD [6–10], partial oxidation of methane [11], pyrolysis of iron phthalocyanine (FePc) [12], a flame method [13] and a liquid phase method [14]. The majority of these methods require the SS substrate to be treated prior to CNT growth. Typical substrate preparation methods include treatment in a hydrogen atmosphere [4,5], etching in HF or sulphuric acids [4,6] and a combination of oxidation and reduction [7]. It is important to note that in addition to the substrate treatment, these techniques require an additional catalyst to

be added in order to grow CNTs on the SS surface [6,10,12]. For example, Masarapu and Wei [6] indicate in their direct growth method that ferrocene was required as a catalyst, and that no nanotubes were observed on the SS substrate without a catalyst precursor. In such cases the SS substrate essentially acts as a support for the catalyst nanoparticles, and may not provide an optimal efficiency for electron transport to the bulk of the electrode. We report here a simple procedure to synthesize multi-walled nanotubes (MWNTs) directly on SS 304 by thermal CVD without any external addition of a catalyst precursor. In the present case, the SS itself provides the active sites for CNT growth, enhancing in this way the CNT-substrate surface interaction efficiency. The process is optimized to achieve the growth of CNTs as a uniform layer on various substrate geometries.

The CVD furnace used is a Lindberg/Blue HTF 55000 series. A quartz tube is located inside the furnace such that approximately half the tube is covered. The substrates are placed directly in the quartz tube at the center of the furnace, parallel to the gas flow. The carbon source and carrier gases are

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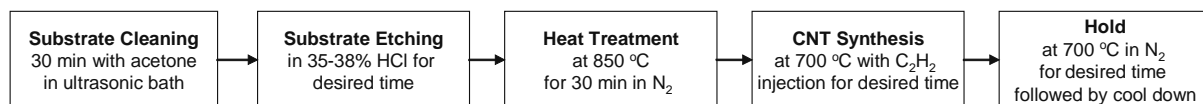


Fig. 1 – Simple procedure for CNT growth on SS 304.

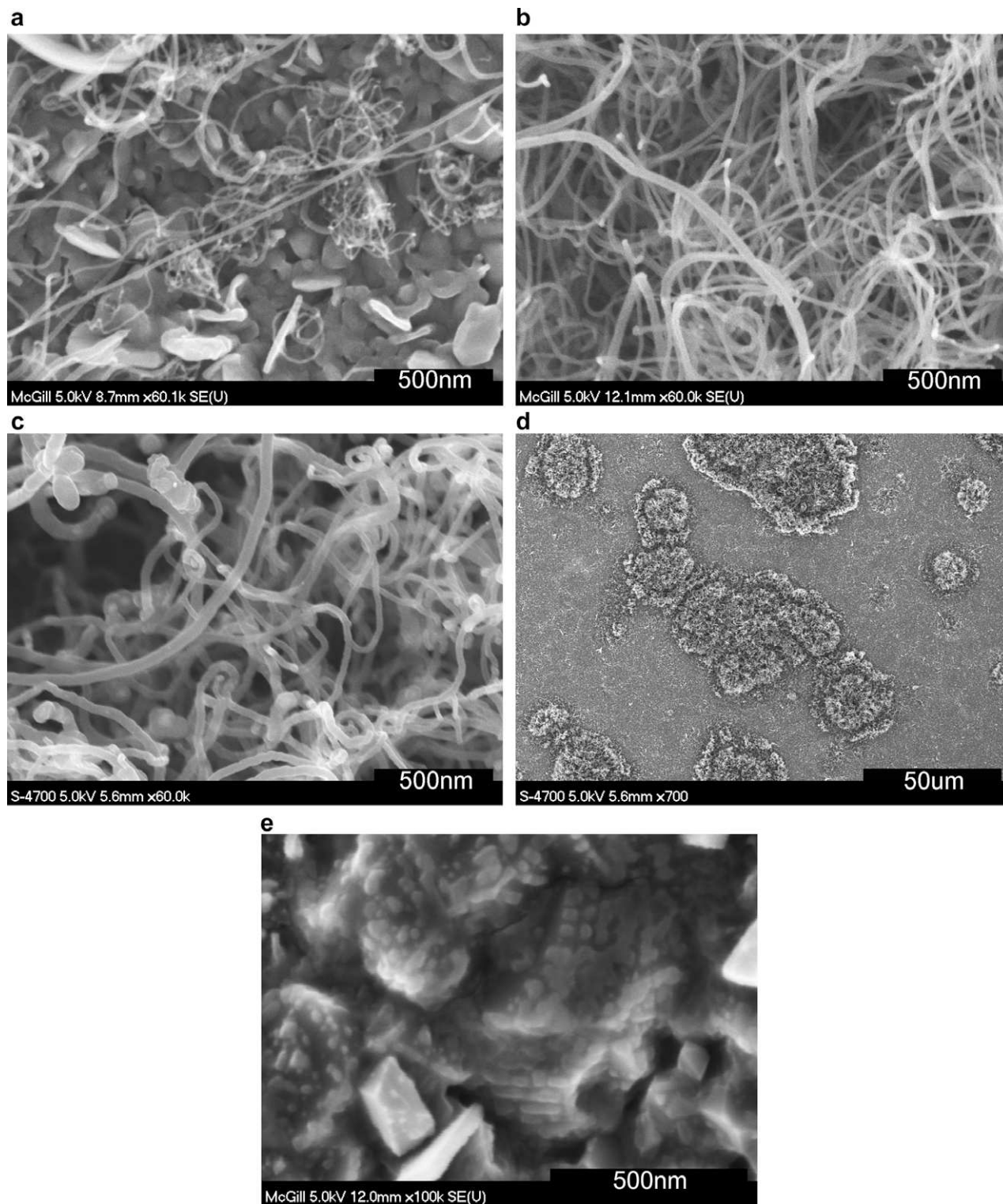


Fig. 2 – SEM images of CNTs synthesized at (a) 650 °C, (b) 700 °C, (c) 800 °C (close-up of CNT island), (d) 800 °C (distant view of CNT islands) and (e) surface defect morphology observed on SS plate. All substrates were etched for 5 min in HCl and preheated at 850 °C for 30 min.

Table 1 – Effect of HCl etching time on % CNT coverage.

HCl etching time (min)	1	3	5	10
% CNT coverage	7	38	92	97

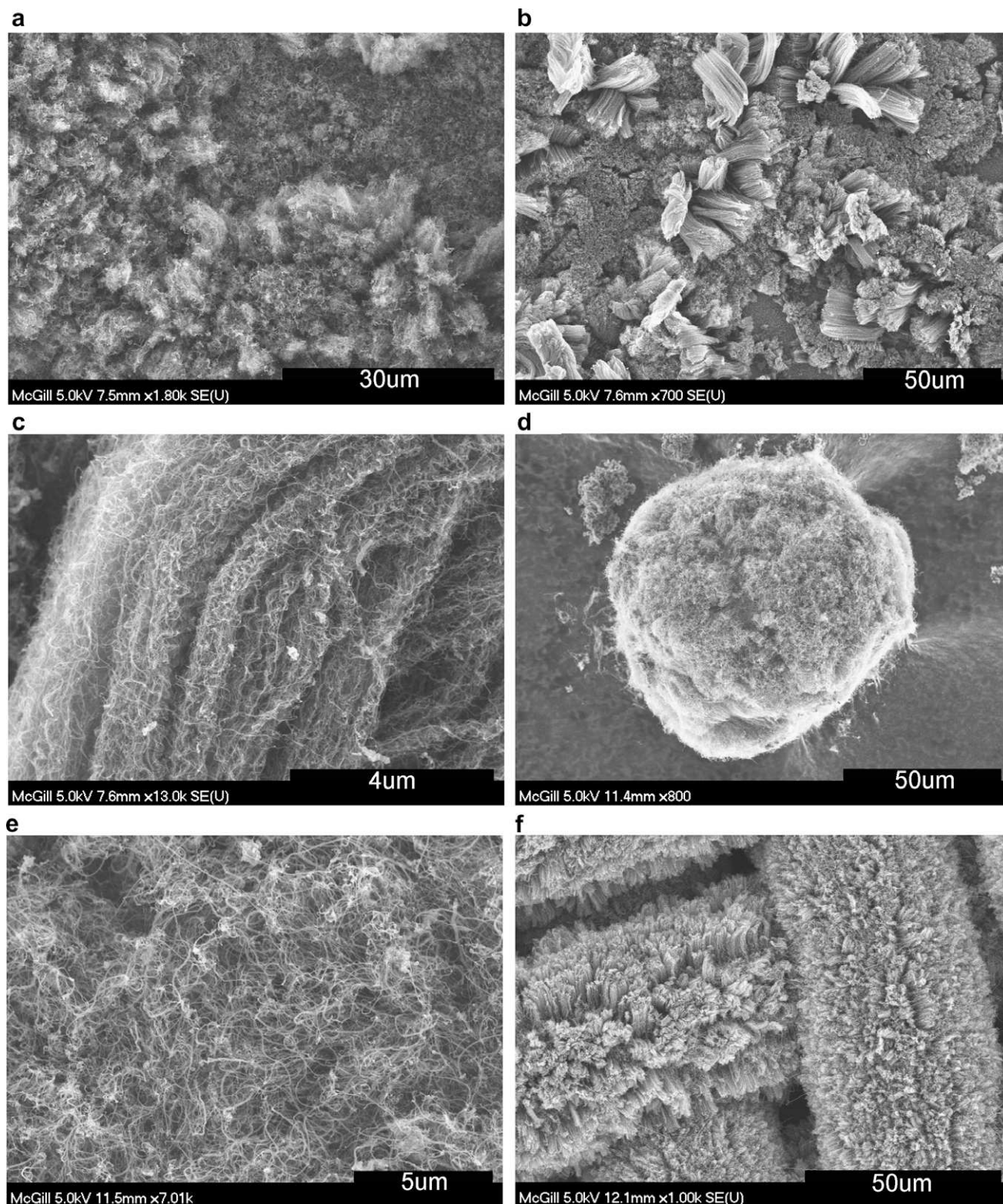


Fig. 3 – (a)–(c): CNT synthesized at 700 °C with growth times of (a) 10 min, (b) 20 min and (c) close-up of the bundles observed in (b). Substrates were preheated at 850 °C for 30 min and etched in HCl for 5 min. **(d)–(f):** CNT synthesized on SS 304 powders and grids, (d) distant view of CNTs on SS particle (e) close-up of (d) and (f) distant view of CNTs on SS grid.

acetylene (C_2H_2) and nitrogen (N_2), respectively. The gas inlet tube ($\Phi = 6.35$ mm) is long enough to carry the gases to the center of the furnace, while the gas outlet tube carries the exhaust to a ventilation system. Commercial grade multi-purpose type 304 SS strips (0.762 mm thickness) with mirror-like finish are used as both the catalyst and the support mate-

rial. Fig. 1 summarizes the procedure. The N_2 and C_2H_2 flow rates are set at 592 ± 5 sccm and 45 ± 5 sccm, respectively.

CNTs were synthesized at 650, 700 and 800 °C with substrate preheating at 850 °C for 30 min, and at 650, 700, 800 and 850 °C without preheating. Fig. 2 illustrates the typical results obtained with substrate preheating. In both cases

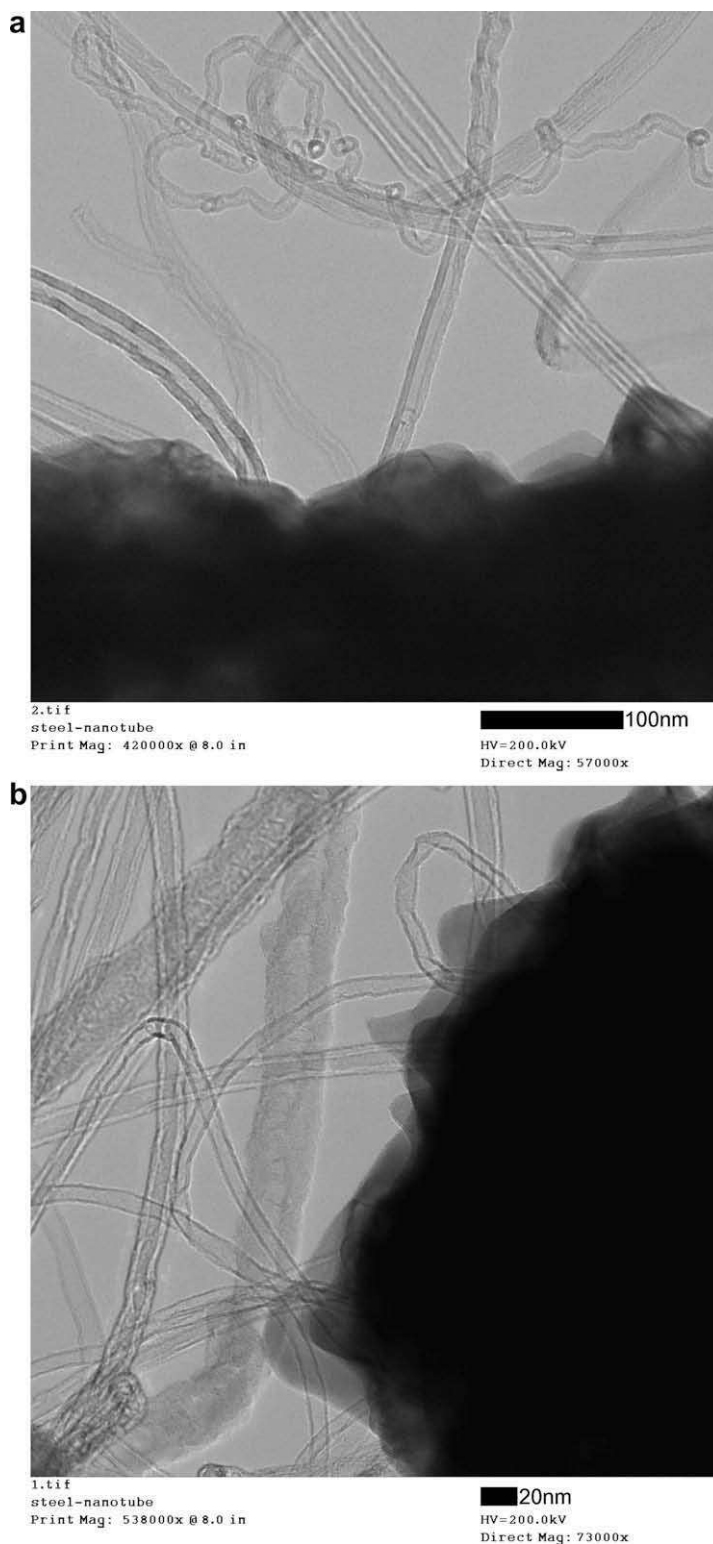


Fig. 4 – TEM images of MWNTs grown on SS TEM grids.

with/without preheating, the least amount of amorphous carbon occurred at a synthesis temperature of 700 °C. At this temperature, there was less amorphous carbon in the sample which was preheated at 850 °C (Fig. 2b) compared to the sample which was not preheated. The percent CNT coverage by area was 92% for the former and 87% for the latter. The nanotubes observed are multiwalled with diameters ranging from 20 to 70 nm and mainly grew with random orientation. It is known that particle-like active catalytic sites are required for the growth of CNTs [7]. The objective of the substrate pre-treatment method is to generate these favourable growth sites. We believe the heat treatment at 850 °C favours the recrystallization process, and generates nanometer scale grain structures providing particle-like active catalytic sites such as surface defects (Fig. 2e).

The substrates were initially etched in HCl for, respectively, 1, 3, 5 or 10 min in order to determine the effect of etching time on CNT growth. The amount of CNTs produced increased with substrate etching time in HCl. Table 1 summarizes the results. It should be noted the highest etching time of 10 min produced a double layer of CNT growth. A base layer of CNTs with small diameters (5–20 nm) was observed, while the upper layer contained larger (40–70 nm) and much longer CNTs, which grew in islands. The distance between the individual islands was typically around 65 µm.

During the synthesis process, C₂H₂ at a flow rate of 45 ± 5 sccm was injected for respectively 1.5, 3 or 5 min. Small amounts of CNTs were produced with C₂H₂ injections times of 1.5 and 3 min, whereas the most enhanced CNT growth was observed with a C₂H₂ injection time of 5 min. With respect to CNT density, a C₂H₂ injection time of 10 min did not further improve CNT growth [15].

CNT growth times of 0, 10, 20 and 30 min were tested. We defined the growth time as the time the sample remained in the furnace at the synthesis temperature in a N₂ atmosphere after the C₂H₂ flow was stopped. The residence time of C₂H₂ gas in the furnace is in the order of 3–5 min. Very few CNTs were observed when no growth period was imposed. In contrast, an irregular CNT layer was observed with a growth time of 10 min. A low magnification image (Fig. 3a) shows CNT bundles reaching 5–10 µm in length. As seen in Fig. 3b, larger and longer bundles with lengths up to 30–40 µm are observed at a growth time of 20 min. These dense bundles contain 0.6 mm-diameter coils of intertwined CNTs with diameters of 5–30 nm (Fig. 3c). As previously shown in Fig. 2b, a growth time reaching 30 min resulted in a uniform layer of CNTs on the substrate surface.

The procedure described here was also applied to SS 304 powders (70 µm mean diameter) and grids (400 mesh size). A uniform layer of CNTs was obtained on both the powders and grids, as shown in Fig. 3d–f. For the powders, the conditions were: 7 min HCl etching, 30 min heat treatment at 850 °C, 675 °C synthesis temperature, 12 min C₂H₂ injection and 30 min growth time. The grids were etched in HCl for 2.5 min and the synthesis temperature was 700 °C. No heat treatment was necessary in this case. SS transmission electron microscopy (TEM) grids for high resolution imaging were tested under the following growth conditions: 30 min heat treatment at 850 °C, 700 °C synthesis temperature, 5 min C₂H₂ injection and 30 min growth time. As shown in Fig. 4,

the MWNTs produced on SS TEM grids include nanotubes with a small number of walls possibly reaching down to single, double and triple-walled tubes.

To conclude, we present a simple method to grow a dense layer of CNTs directly on SS 304 substrates such as plates, grids and powders without the need of adding an additional catalyst. The substrate preparation method is based on a simple acid etching technique followed by a heat treatment. TEM imaging confirmed the presence of MWNTs including CNT structures with a small number of walls. In contrast to other treatment methods, the present method has no scale up limitations and could easily be applied to large SS surfaces and geometries. In addition, a catalyst precursor is not required to grow the CNTs; the iron-based material surface of a commercial-grade SS 304 itself acting as the catalyst. The technique is inexpensive and capable of producing a uniform layer of CNTs on SS with minimal substrate treatment.

Acknowledgements

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Formation of nanocarbons during activation of mesocarbon microbeads with potassium hydroxide

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ABSTRACT

Carbon nanotubes (CNTs) together with carbon nanofibers (CNFs) have been produced on the surface of and inside mesocarbon microbeads containing Co nanoparticles during their activation with potassium hydroxide (KOH). The resulting CNFs consist of a number of platelet-shaped sub-units with width of about 500 nm and thickness of 50 nm. The CNTs, with diameter of about 200 nm, grow from the inside to the surface of the activated carbon beads. The results indicate that, in addition to the Co nanoparticles, the existence of KOH also plays an important role in the nanocarbon growth.

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To improve the performance of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) in some potential applications, activated carbon/CNT or CNF hybrids have been extensively studied [1–8]. They combine the exciting characteristics of CNTs or CNFs with the extensive porous structure and rapid adsorption capability of activated carbon, and offer great potential in applications such as energy storage [1,2], water desalination [3], pollution control [4] and gas phase catalysis [7]. Activated carbon/CNT hybrids have been prepared by mixing the activated carbon and CNTs with adhesive [1–3] or by ball milling [4]. Moreover, the immobilized CNFs or CNTs on the surface of and inside activated carbon have been prepared by chemical vapor decomposition of organic molecules in or on the activated carbon embedded with catalyst [5–8]. This paper reports that CNTs and CNFs can be produced on the surface of and inside activated mesocarbon microbeads during activation of mesocarbon microbeads containing Co nanoparticles (MCMB/Co) with KOH. CNTs have been prepared by the co-carbonization of an aromatic heavy oil and ferrocene [9,10]. However, different from the growth mecha-

nism of nanocarbon in their report, the activation process plays an important role in the nanocarbon growth in present work.

MCMB/Co containing 4.45 wt% Co nanoparticles was prepared by pyrolyzing the mixture of coal tar pitch and cobalt acetate (12.5 wt%) at 410 °C for 0.5 h under nitrogen atmosphere. The experimental process has been described elsewhere [11]. MCMB/Co was mixed with KOH and the weight ratio of KOH:MCMB/Co was 5. The mixture was heated at 2.3 °C/min up to 900 °C and held at this temperature for 1 h in N₂ flow. After cooling down, the sample was washed with diluted HCl and distilled water and then dried in vacuum. The activation product was named as AMCMB/Co. For comparison, MCMB/Co was carbonized at 1000 °C for 1 h under nitrogen.

Activated carbon with a specific surface area of 2336 m²/g was produced by activation of MCMB/Co and its adsorption isotherm and pore size distribution was shown in Figs. 1 and 2, respectively. As seen from Fig. 1, the isotherm has a steep initial portion and oblique line upward, which refer to

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Different configurations of carbon nanotubes reinforced solid-phase microextraction techniques and their applications in the environmental analysis

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ABSTRACT

Since its introduction in 1990s, solid-phase microextraction (SPME) has grown increasingly popular due to its simplicity, environmental benignity and adaptability to a wide variety of sample types and analytes. The application of carbon nanotubes (CNTs) in SPME is receiving great attention since their introduction would bring an enhancement of partition coefficient, an increase of diffusion coefficients and better selectivity to the target analytes. CNTs have been feasibly applied in almost all of the developed configurations of SPME technique such as fiber SPME, thin-film SPME, in-tube SPME, stir-bar microextraction, in-needle SPME and in-tip SPME. The objective of this literature review is to elucidate the advances of the configurations of CNTs based SPME techniques and their applications in the environmental analysis.

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1. Introduction

Carbon nanotubes (CNTs) were first prepared with an arc-discharge evaporation method by Iijima in 1991 [1]. CNTs resemble one (single-walled carbon nanotubes, SWCNT) or more graphite sheets (multi-walled carbon nanotubes, MWCNTs) rolled up into a cylinder, consisting entirely of covalently bonded sp^2 carbon atoms [2–4]. The structure of CNTs and an enlargement of their hexagonal becomb sp^2 carbon structure are shown in Fig. 1. Despite CNTs have the simplest chemical composition and atomic-bond configuration; they exhibit the most extreme diversity in structure and structure-dependent properties [5,6]. CNTs have nm-sized diameters and μm -sized lengths, so they have around 1000 of the length-to-diameter ratio, resulting in large surface area and

high absorption capacity. Their absorbability, especially to organic compounds, is mainly due to non-covalent forces including hydrogen bonding, electrostatic forces, π – π stacking, hydrophobic interactions and van der Waals forces and mainly occur on their highly hydrophobic surface [7], internal tube cavity and interstitial spaces between nanotubes [8]. So organic compounds with functional groups (e.g., $-OH$, $-NH_2$, $-COOH$) or large π electron conjugated system could have strong interactions with CNTs. Besides being effective absorbents, CNTs are also excellent transporters due to their smooth and frictionless surfaces [9,10]. In addition, there are several widely-used solutions to modify the side walls of CNTs via non-covalent method (surfactant-assisted dispersion) [11] or covalent method (functionalization and sol-gel technology) [12,13] to improve their dispersion or solubility in solvents [14]. The modification could also bring CNTs some important enhancement of their properties like the polarity, hydrophilicity and selectivity [15,16].

The effective absorbability, high mass transfer, and ease of modification endow CNTs with the potential of wide applications in the separation science. In recent years, CNTs, as novel sorbent materials, were investigated in different types of sample preparation techniques. Among them, solid-phase microextraction (SPME) is a novel solvent-free technique which integrates sampling, extraction

Abbreviations: CNTs, carbon nanotubes; SPME, solid-phase microextraction; CNTs-TF-SPME, CNTs reinforced thin film SPME; CNTs-FF-SPME, CNTs reinforced flat film protected SPME; CNTs-HF-SPME, CNTs reinforced hollow fiber SPME; CNTs-SBSE, CNTs reinforced stir bar sorptive extraction; MEPS, microextraction by packed sorbent; NSPME, needle SPME; SPDE, solid-phase dynamic extraction; PNME, packed needle microextraction.

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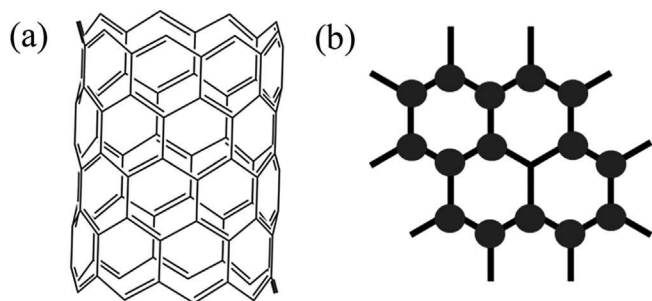


Fig. 1. The structures of CNTs. The right figure is an enlargement of the hexagonal beecomb sp^2 carbon structure. The delocalized π -electrons are not shown.

and sample introduction into one step [17]. Compared to conventional solid-phase extraction technique, SPME owns many outstanding merits, including high sensitivity, ease of operation, simplicity, and environmental benignity. So after its introduction, it has been successfully applied to preconcentrate and extract various compounds from environmental, biological and food samples [18]. For SPME, its efficiency depends on the distribution constant between the analytes and the stationary coating phase, so the type of coatings plays a crucial role in the extraction efficiency and the selectivity [19]. Besides their outstanding absorption and mass-transfer properties, CNTs also meet other requirements of SPME coatings including resistance to the organic solvents, thermal and chemical stability [19], so they have shown wide applications and commercial prospects. Till now, analytical researchers have developed various methods to prepare CNTs coatings for SPME such as physical deposition, sol-gel technology, chemical bonding, electrochemical and electrophoretic depositions. The main preparation process, their advantages and disadvantages have been discussed in detail [19]. Recently, the introduction of CNTs in SPME technique has gained growing interest in analytical chemistry. Their combination could open new avenues to achieve efficient, green and economical separation and preconcentration procedures, thus expanding the application of SPME techniques in many analytical areas. The properties and advantages of CNTs combined with SPME are shown in Fig. 2. In addition, environment problem has become a great issue. The efforts to sensitively detect and analyze trace compounds in environmental samples drive the development of microextraction techniques. The objective of this work is to present an overview of the advances of different configurations of CNTs-SPME techniques and their applications in the environmental analysis.

2. CNTs-SPME technique

Recently, much effort has been paid on developing novel configurations of SPME to obtain sensitive, feasible and low-cost techniques to preconcentrate and determine trace analytes in complex matrices. Till now, there are several relatively mature configurations of SPME, and their theory models and applications are being developed continuously. Roughly, SPME techniques can be classified into static batch equilibrium microextraction and dynamic flow through equilibrium microextraction methods. The classifications and configurations of SPME techniques are shown in Fig. 3 [20]. Fibers and capillary tubes coated with an appropriate stationary phase are usually used for SPME. Currently, stir bars (stir bar sorptive extraction, SBSE), thin films (thin film microextraction, TFME), microsyringe (syringe SPME) and pipette tips (in-tip SPME) have been used as the new supporting matrices and developed novel SPME techniques. This review focuses on the introduction of CNTs into these SPME modes, and their recent applications in environmental analysis.

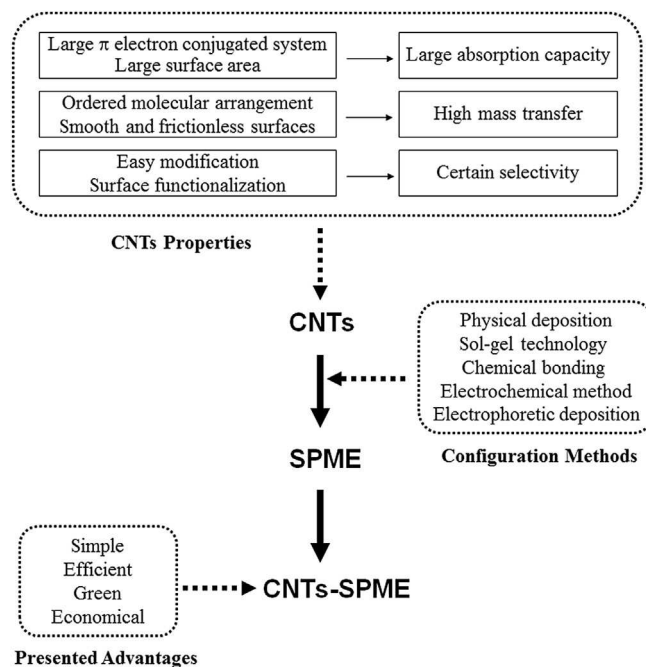


Fig. 2. The properties and advantages of CNTs combined with SPME.

2.1. CNTs reinforced fiber SPME

The fiber SPME is the conventional configuration, utilizing supporters made of the fused silica or the metal wire inside an assembly holder [20]. During the extraction, analytes could be effectively adsorbed onto the fiber coating in direct-immersion SPME (DI-SPME) or headspace SPME (HS-SPME) mode [21]. After on-site extraction, the fiber can be inserted into the inlet of a portable gas chromatography (GC) instrument or use organic solvent to desorb the analytes for the following qualitative and quantitative analysis with suitable analytical apparatuses. CNTs could be easily modified onto the surface of the fused silica by the dipping method [22,23], the sol-gel method [24–26], the physical adsorption [27], chemical bonding method [28–31], and the electrophoretic deposition [32–34]. However, the most outstanding disadvantage of the silica support is its inherent fragility. To overcome this, metal or other alloy wires act as supports to improve the durability and the thermal stability of SPME fiber. However, because of the chemically inert property, modification of the metal wire is difficult and complicated, so usually other accessory materials would be involved in the coating process. The coating types and the main preparation methods of CNTs reinforced fiber SPME are shown in Fig. 4.

2.1.1. CNTs coating on silica substrate

When silica is treated with basic solution, the surface hydroxyl group will be exposed, and could react with CNTs to form the homogenous coating via sol-gel method. The formed coating is high mechanically, thermally and solvent stable due to the strong chemical bonding between CNTs and the fused silica fiber [35].

Even though CNTs could be coated onto the surface of silica substrate by the sol-gel technology [24,36], CNTs have strong intermolecular van der Waals interactions which lead to their poor dispersion into the polymeric networks and weak interfacial interactions [37]. Thus, polymer-functionalized CNTs and ionic liquid-assisted sol-gel method were introduced to overcome the above problems.

Poly(ethylene glycol) (PEG), a hydrophilic polymer, is widely used to modify CNTs and assist to prepare organic-inorganic hybrid

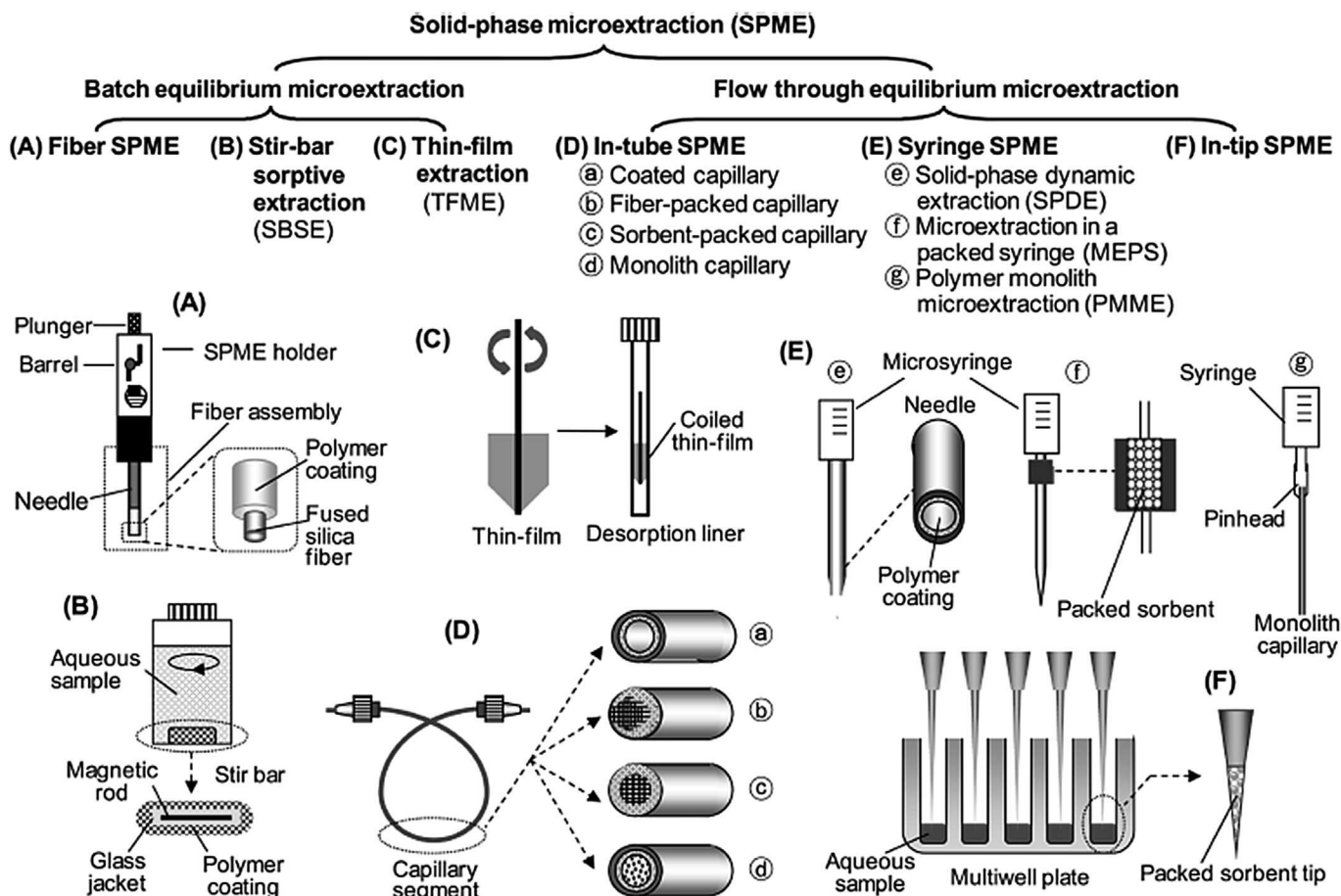


Fig. 3. The classifications and configurations of SPME methods [20].

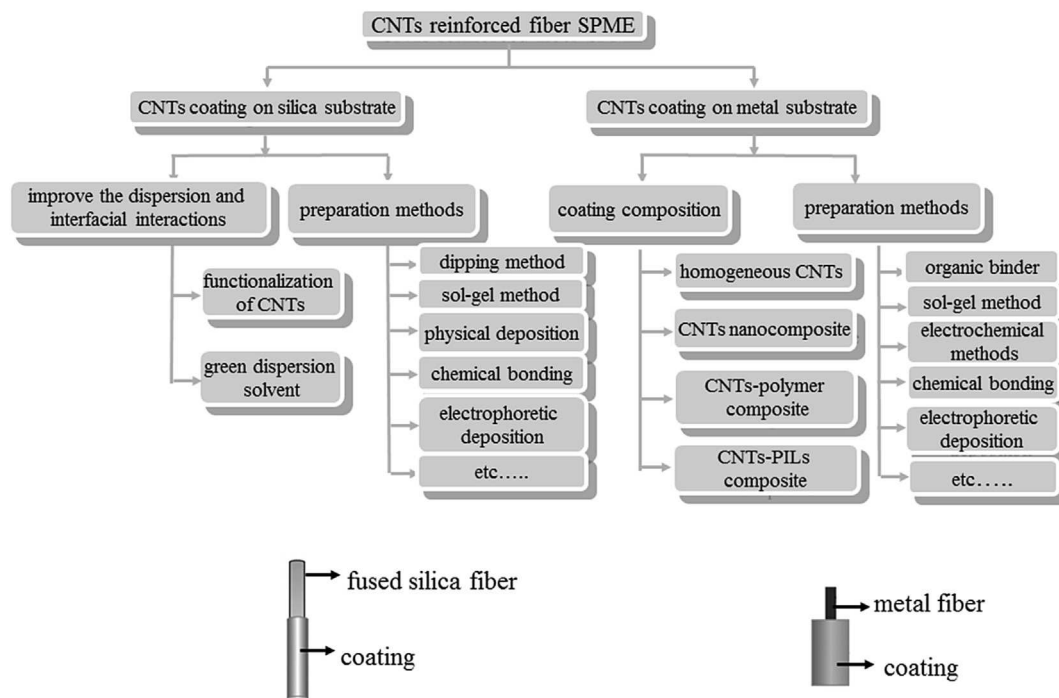


Fig. 4. The coating types and the main preparation methods of CNTs reinforced fiber SPME.

sol solution. The obtained PEG-g-CNTs sol solution could get CNTs-bonded stationary-phase coating with effective chemical immobilization, good thermal stability and higher extraction efficiency [38]. The new prepared fiber is demonstrated to be robust and reproducible and could obtain high recoveries and low LODs when it was used to determine BTEX, methyltert-butyl ether (MTBE) and non-steroidal anti-inflammatory drugs in environmental water samples [38–41].

The functionalization of CNTs with PEG could improve their solubility and viscosity in organic solvents as well as their selectivity to the target analytes [42]. However, the functionalization needs chemical reactions like acid-treatment and chloroformylation reaction which would destroy the properties of CNTs and increase the preparation difficulty. So green solvents that could increase the dispersion of CNTs by themselves are much more attractive. Ionic liquids (ILs) consisting of large organic cations and organic or inorganic anions attract great interest in the separation and analysis due to their negligible vapor pressure, non-flammability, high melting points and environmental benignity [43]. Researches illustrated that ILs had significant effects on the porous structure of sol-gel materials and the formed ILs-mediated organic-inorganic hybrid sorbents possessed favorable material characteristics like porous morphology, enhanced surface area, improved stability, and thus good extraction efficiency. CNTs could be directly dispersed in ILs and in some other case, a stable aqueous or organic solution of an IL due to the van der Waals' interaction between them [44]. Moreover, the cationic ILs would increase the amounts of dispersed CNTs via cation- π interaction increase the homogeneity of the gel. It should be noted that the "critical gel concentration" and the type of ILs play great roles in the properties of the final sol solution [45–48].

2.1.2. CNTs coating on metal substrate

To overcome the inherent fragility problem of fused silica fiber, the metal wire like the stainless steel, gold, platinum or alloy as supports could enhance the mechanical stability. The sol solution is not easily coated onto the most metal wires. Compared with the simple mechanical deposition of the coatings onto the fused silica fiber, the metal supports could be painted with a sticky paste layer of polymers like nafion [22] to assist CNTs to be coated. CNTs could also be integrated with others materials to enhance their adhesion on the metal wire.

2.1.2.1. Homogeneous CNTs coating on metal substrate. CNTs could be attached onto a stainless steel wire through organic binder made up of terpeneol, ethylcellulose, and dibutyl phthalate. Compared with the commercial PDMS fiber, the new fiber demonstrated to have better thermal stability and longer life span (over 150 times). When it was used to determine trace organochlorine pesticides in lake water and wastewater samples, satisfactory recoveries were obtained. In addition, the newly developed coating showed outstanding advantages including the ease of preparation, low cost and high sensitivity [49].

The main problem of the organic binder is the potential interferences with the analytes during the thermal desorption [50]. Compared with the organic binder, the electrophoretic deposition method could prepare the CNTs coating without the use of adhesive and the obtained coating would not swell in organic solvents nor strip off from substrate. This method could prepare unbreakable microextraction fiber by coating CNTs on the Pt wire [51,52].

Functionalized CNTs such as CNTs-OH, CNTs-COOH and CNTs-NH₂ [53] would have enhanced dispersibility in organic solvent and increased interaction with the metal fiber. In 2011, J.J. Feng *et al.* proposed a novel protocol that the polydopamine was used as the binding agent to immobilize amide-functionalized CNTs onto the

surface of the stainless steel fiber via Michael addition or Schiff base reaction [54]. To investigate the extraction performance of the developed fiber, six phenols were used as model compounds and the developed SPME coating could get low LODs, good fiber-to-fiber reproducibility, high temperature stability and good durability to acid, alkali and organic solvent [54].

2.1.2.2. CNTs involved nanocomposite coating on the metal substrate. CNTs not only can be applied as novel and efficient SPME coatings, but also act as a reinforcement agent in nanocomposites to enhance the porosity and thermal stability of SPME coatings. CNTs involved nanocomposites like carbon nanotubes-silicon dioxide (CNTs-SiO₂) [55], carbon nanotubes-titanium oxide (CNTs-TiO₂) [56] and carbon nanotube/hydroxide nanocomposite (Al(OH)₃ and Mn(OH)₂) [57] are used to prepare coatings of SPME fibers. During the preparation process, biocompatible compounds like glucose could act as a bridge to attach intact CNTs to the silica network [55].

In 2013, M. Sun *et al.* applied electrolytic plating and sol-gel technique to bind CNTs-TiO₂ nanocomposite onto the stainless steel wire. The stainless wire was first activated with silver layer via electroless plating, and then functionalized by the silane reagent to derive silanol groups. Finally, the CNTs-TiO₂ nanocomposite was bonded to the above reactive stainless steel wire through the sol-gel method. When applied to determine polycyclic aromatic hydrocarbons (PAHs), the prepared SPME fiber exhibited strong mechanical strength, excellent durability in strong acid or alkali solution and good extraction performance [56].

2.1.2.3. CNTs-polymer composite coating on the metal substrate. Polymers like polypyrrole [33,58,59], nafion [22,60], poly(o-toluidine) [61,62], polyacrylonitrile [63], polyaniline [64,65] and polyortho-aminophenol [66,67] could also assist CNTs to make composite coatings of SPME fibers.

Polypyrrole, a widely-used conducting polymer, is quite commercially available and good environmental stability. It could be coated onto the surface of metal supports by electrochemical methods and acts as an extraction phase for both small molecules and peptides. The combination of CNTs and the polypyrrole could obtain better thermal stability and higher charge delocalization properties. In addition, the electrochemical growth of CNTs-conducting polymer composites has the potential to produce 3-dimensional nano-structured films that combine the redox pseudo-capacitive charge storage mechanism of conducting polymers with the high surface area and the conductivity of CNTs [68].

Recently, many effects have focused on the introduction of CNTs into the polypyrrole matrix, which could obtain the novel SPME coating with considerable porosity and higher specific surface areas. The study found that the prepared CNTs/polypyrrole exhibited porous surface structure, reproducible preparation, high sensitivity, long lifetime, high thermal stability and strong adhesion of the coating to the steel wire [69].

Nafion is a sulfonated tetrafluoroethylene based fluoropolymer-copolymer with the merits of high conductivity, high operating temperature and high chemical stability. Nafion not only plays the role of a binder but also acts as a sorbent with the good affinity for polar compounds [22].

2.1.2.4. CNTs-PILs coating on the metal substrate. Recently, PILs (polymeric ionic liquid) have got much attentions in SPME due to the improved thermal stability and viscosity [70]. In 2015, J.J. Feng *et al.* developed an available method to increase the thickness of PILs-CNTs coating by cross-linking copolymerization [70]. And then, this group investigated excellent tunability of PILs for different analytes by on-fiber anion exchange. When the anion of PILs changed to NTf₂, the hydrophobicity of the fiber increased,

leading to better extraction efficiencies for hydrophobic *n*-alkanes. In comparison, NapSO_3^- anions would endow the SPME with better extraction ability for aromatic analytes. Therefore, the extraction properties of PILs-CNTs could be optimized by the feasible on-fiber anion exchange process.

Usually, the inert stainless steel wire needs suitable pretreatment to enhance its affinity to CNTs. In 2015, M. Wu *et al.* coated the PIL functionalized CNTs on an electrodeposited polyaniline fiber to fabricate a novel SPME coating. Due to the synergetic effect of the porous polyaniline and the rich π electron stacking of the CNTs-PIL, the obtained coating achieved high enrichment efficiency for the benzene derivatives [71].

To enhance the durability and stability of the coating, this group developed another method. Poly(3,4-ethylenedioxythiophene)-polymeric ionic liquid (PEDOT-PIL) functionalized CNTs composite was coated onto the surface of a stainless steel wire by the electrodeposition method. And then, the wire was dipped in nafion solution to obtain nafion-modified coating. Finally, the obtained SPME coating exhibited much higher sensitivity than commercial coatings for the direct extraction of carbamate pesticides due to its strong hydrophobic effect and π - π interaction with the analytes [72].

2.2. CNTs reinforced thin film SPME (CNTs-TF-SPME)

Besides the fused silica and the metal wire could support CNTs, commercial polymer membranes could also play the similar role. Commercially available carbon nanotube film (CNTF) which not only maintains the adsorbing properties of CNTs but also possesses a stable cross-linked carbon structure, could be an excellent alternative for CNTs in a feasible and operational platform [73]. Besides CNTF, flat films and hollow fibers are the two main configurations of membranes that use to support CNTs. In the thin film SPME (TF-SPME), thin films are used to protect absorbents [74]. In addition, the membrane also acts as the filter and the protector to exclude interfering compounds and avoid the runout of CNTs. The PDMS flat film and the Accurel Q3/2 polypropylene hollow fiber (HF) have become novel and feasible substrates of SPME by virtue of their specific porous structures. The main configurations and preparation methods of CNTs-TF-SPME are shown in Fig. 5.

2.2.1. CNTs reinforced flat film protected SPME (CNTs-FF-SPME)

The flat film could load CNTs by a feasible and simple way. Usually, a certain area of the flat film is trimmed off and then cut into individual rectangular pieces. After one end is heat-sealed, CNTs are introduced into the above membrane envelope via a

glass pipet and funnel from the remaining open end, followed by heat-sealed to protect CNTs and avoid their runout. The π - π electrostatic interaction between the analytes and the large surface area of CNTs facilitated the adsorption of analytes with good selectivity and reproducibility. Under the optimized extraction conditions, the method showed good linearity, good repeatability, low LODs and the device could be used for up to 30 extractions [75].

However, due to the small pore size and low wettability to the aqueous sample, the polypropylene membrane involved SPME always suffer from long extraction time and low extraction rate. Thus, researchers examined the possibility of replacing the polypropylene membrane with other supports with a high porosity and permeability. In 2014, T. Pelden *et al.* tried the application of the tea bag filter which is very cheap, nontoxic, permeable, hydrophilic and has high mass transfer. The preparation steps were followed as reported previously for the polypropylene membrane protected SPME [76].

Another green polymer, agarose, could also act as the CNTs holder for CNTs-SPME technique [77]. The agarose is a polysaccharide extracted from seaweed [78]. Due to its biodegradable nature, hydrophilic and inert properties, it has been extensively studied and applied as a feasible and green support in SPME. Usually, the CNTs impregnated agarose film is freshly prepared in a simple way. The obtained high enrichment factors and high sensitivity demonstrated that the developed agarose protected CNTs-SPME technique is suitable for trace analysis of environmental pollutants [79].

2.2.2. CNTs reinforced hollow fiber SPME (CNTs-HF-SPME)

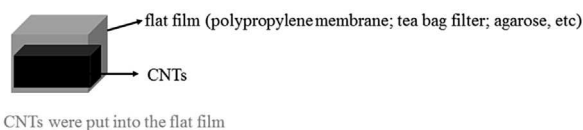
The HF is another configuration of membrane that widely used in SPME. Due to its self-supporting and large surface area properties, the HF is currently a preferred choice for applications in catalysis, energy storage and electronics. It could avoid tedious procedures such as centrifugation or isolation, or adhesion onto the support materials, so it is affordable and has favorable characteristic for template synthesis [13]. In addition, the HF could be used as an individual device, so its handling is much more convenient than the other traditional SPME fibers [80]. The introduction of HF into SPME could improve the stability and reliability of the extraction process through the protection of microdroplets of organic solvents or solid sorbents [81]. Owing to its low cost, the HF could be discarded after each extraction cycle, thus eliminating possible carry-over effects. In addition, the HF could provide excellent clean-up function by excluding macromolecules and other interfering compounds [80]. Recently, the CNTs-HF-SPME has attracted wide attention and application. Both the lumen and the wall pores of the HF could hold CNTs, so the CNTs-HF-SPME has many feasible formats.

First, researchers investigated the application of CNTs in the lumen of the HF. To achieve it, CNTs sol solution is injected into the lumen of HF for in situ gelation. The obtained extraction fiber could be operated in direct immersion sample mode or head-space sampling mode. The prepared fiber is commercially available, fiber-to-fiber reproducible and sensitive. In addition, the experimental setup is simple and highly affordable [82].

However, the physical load would lead to the run-out of CNTs, especially in the vigorous stirred sample solution. Fortunately, the HF has special wall pore size (usually 0.2 μm) which offers the potential for the stable immobilization of CNTs.

Our group has done much work about the properties and applications of CNTs-HF-SPME. In terms of the preparation method, we have developed three methods to disperse CNTs, that is sol-gel method [83], organic solvent dispersion [81] and surfactant assisted dispersion [84,85]. CNTs could be immobilized into the HF from the homogeneous solution driven by the ultrasonication force and capillary force.

(a) CNTs-FF-SPME



(b) CNTs-HF-SPME

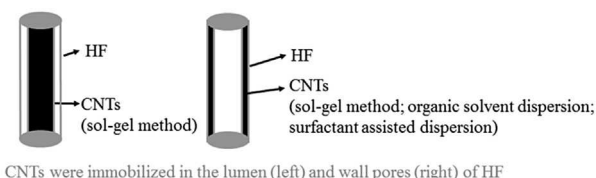


Fig. 5. The main configurations and preparation methods of CNTs-TF-SPME.

Sol-gel technology could efficiently incorporate CNTs into the silane agents under mild conditions. In this technique, precursors and CNTs are mixed at molecular level, so the obtained CNTs-silica coatings have good thermal stability, fine porous structure and high degree of flexibility. Moreover, CNTs could also be modified by suitable inorganic and organic compounds as well as amino acids such as Keggin polyoxometalates [86], ethylenediamine [87], and glycine [88] to enhance the extraction selectivity and extraction efficiency. However, this method displays some limitations. First, CNTs should be functionalized to increase their dispersibility in the sol solution, leading to a certain destruction of their effective properties. Besides that, various factors like pH, the molar ratios of precursor, organic solvent and water, the type and amount of catalytic agent are involved in the preparation process and affect the performance of the coating as well as the batch-to-batch reproducibility of the extraction fiber. Compared to the conventional sol-gel technology, the developed surfactant-assisted method is particularly attractive since it preserves the delocalized π -electron network of the CNTs sidewall through various interactions such as the hydrophobic interaction, π - π interaction and Lewis acid-base interaction [89].

Suitable organic solvents could effectively disperse functionalized CNTs to prepare homogeneous dispersion solution. For example, C.X. Wu developed a feasible method to prepare CNTs immobilized HF [90]. The HF segment was impregnated with 1-octanol solution dispersed with CNTs and then sonicated until the CNTs were spread within the fiber pores. This method was demonstrated to be simple, sensitive, feasible and cost-effective. When applied to determine triazine herbicides residues in water, the method showed a good linearity within a range of 0.5–200 ng mL⁻¹, LODs between 0.08 and 0.15 ng mL⁻¹ and recoveries of 86.6%–106.8%.

In 2014, A.A. Matin *et al.* used polyvinyl chloride to obtain CNTs dispersion solution and then prepared the corresponding CNTs-HF [91]. The result further demonstrated that the prepared CNTs-HF had uniform porous structure and CNTs displayed their outstanding adsorptive characteristics.

2.3. CNTs reinforced in-tube SPME

Different from fiber SPME, in-tube SPME typically uses a short fused-silica capillary to load CNTs [92]. Moreover, the in-tube SPME shows outstanding merits of miniaturization, automation, high-throughput performance, on-line coupling with analytical instruments and reduction of solvent consumption [93,94]. In the in-tube SPME operating system, solutions are either passed continuously in one direction through an extracting capillary column or repeatedly aspirated into and dispensed from the extracting segment. After extracted, the analytes could be desorbed by introducing a stream of mobile phase or a static desorption solvent and then analyzed with off-line mode or on-line system. In-tube SPME technique requires lower sample volumes as well as is easy to automate and versatile [21]. In recent years, the development of new materials for in-tube SPME has been a significant trend.

Researchers also examined the application of CNTs in the in-tube SPME. In 2015, Y. Moliner-Martinez *et al.* immobilized CNTs onto the activated surface of the capillary column via glutaraldehyde [95]. And then, the prepared capillary column was connected to a conventional six-port injection valve and used as the injection loop. Samples were manually loaded into the system for extraction. After that, the valve was manually rotated, making analytes desorbed from the extraction phase, and transferred into the analytical column for the following separation and detection. The proposed method showed quite low LODs in the range of 0.02–0.1 $\mu\text{g L}^{-1}$ and good recoveries. In conclusion, the proposed method can be

considered as an environmentally friendly and cost-effective alternative for routine monitoring of triazines and their degradation products in water.

The narrow lumen of the capillary column increases the loading difficulty [96]. In 2007, X.Y. Liu *et al.* developed another CNTs involved in-tube SPME [31]. Firstly, CNTs were coated onto the outer surface of the fused-silica tube and then inserted into the polyether ether ketone (PEEK) tubing, which was fixed directly on the six-port injection valve instead of the sample loop. During the extraction process, the six-port valve was set to the load position and the analytes were adsorbed by CNTs. After that, the valve switched to the injection position, so the extracted analytes were desorbed by mobile phase in the dynamic mode. The developed fiber demonstrated to be more sensitive and effective. However, the selectivity should be increased further. The configuration of the CNTs reinforced in-tube SPME coupling with HPLC was shown in Fig. 6 [30].

There is another way to increase the extraction efficiency. The use of monolithic capillaries would increase the amount of extraction phase and enhance the convective mass transfer [21]. The monolith, a continuous piece of a highly porous materials, allows solvents to flow through their large pores. It has the merits of easy synthesis, mechanical stability and direct linkage of the solid with the inner walls of the support. In addition, its tolerance to high flows would obtain fast separations of target analytes and efficient mass transfer [97]. During the preparation process, reagents, reaction time and temperature are crucial factors and largely affect the extraction performance. In 2014, X. Wang *et al.* prepared poly(MAA-EDMA-SWCNT) monolith by the one-step thermally initiated polymerization method to analyze triazine herbicides in environmental samples [98]. The prepared monolith capillary was online connected to MS detector. The results showed that this proposed method greatly improved the detection sensitivity, decreased LODs (0.02–0.14 ng mL⁻¹) and had negative matrix effects. In 2016, B. Fresco-Cala *et al.* synthesized monolithic poly(butyl acrylate-co-ethyleneglycoldimethacrylate) [poly(BA-co-EGDMA)] inside a fused silica capillary via free-radical polymerization and then an ethanoic dispersion of CNTs was passed through the above capillary to obtain hybrid monoliths. The introduction of CNTs resulted in improved extraction efficiency to the target triazines in tap and river water samples [97].

2.4. CNTs reinforced stir bar sorptive extraction (CNTs-SBSE)

In 1999, E. Baltussen *et al.* developed a new solventless SPME technique, stir bar sorptive extraction (SBSE) [96]. For SBME, the extraction coating is placed on a magnetic bar and such configuration would increase the volume of the extraction phase and improve the sensitivity and the accuracy [21]. Till now, polydimethylsiloxane (PDMS) [96], polyethyleneglycol (EG) modified silicone [99], and polyacrylate (PA) coatings [100] become commercial while various homemade coatings like organic polymers and modified polymers [101–105] are developing. Recently, homemade coated stir bars have mainly focused on the detection of moderately polar compounds. Therefore, the development of new coatings is highly expected. CNTs could serve as effective adsorbents for hydrophobic compounds and their adsorption ability and selectivity could be changed via functionalization. So CNTs have a great potential in the application of SBME to determinate various analytes. The main configurations of CNTs-SBSE are shown in Fig. 7.

In 2015, C. Hu *et al.* developed a polyaniline/hydroxyl CNTs composite-coated SBME for simultaneous determination of polar and apolar compounds [104]. As shown in Fig. 7a, the activated stir bar was first coated with a thin film of the PDMS sol solution, and then rolled in the homogeneous mixture of polyaniline and CNTs-OH to allow the composite deposit on the surface of the stir bar.

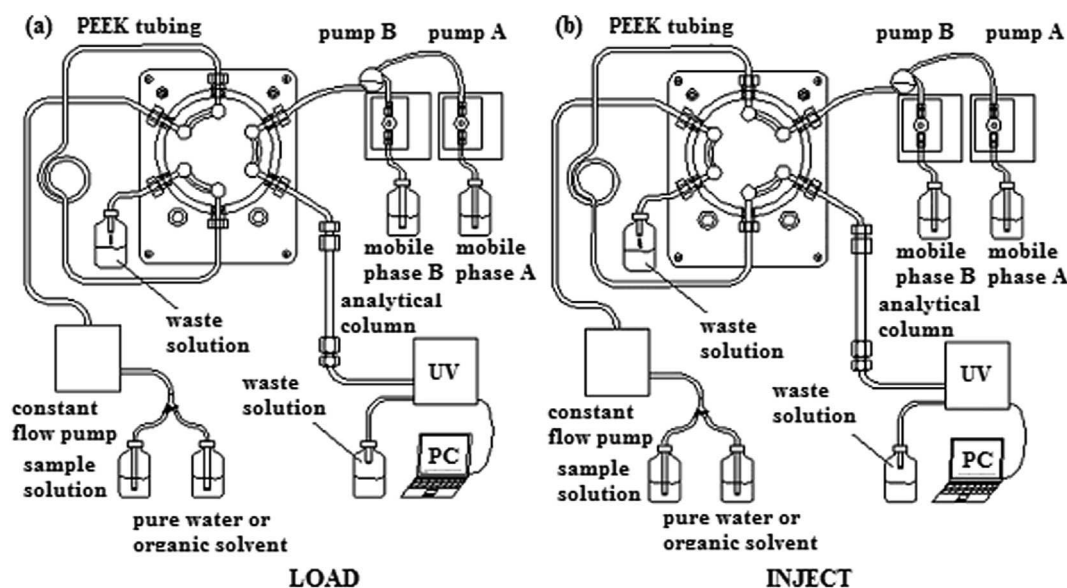


Fig. 6. The configuration of the CNTs reinforced in-tube SPME coupling with HPLC [30].

In this experiment, the direct-immersion stirring extraction and the ultrasonic liquid desorption were employed. Compared with the commercial PDMS-coated stir bar, the newly developed stir bar showed better extraction efficiencies for the polar and apolar compounds due to the hydrophobic interaction, hydrogen bonding and π - π interaction between the adsorbents and the analytes. In addition, the developed method was successfully applied to analyze these pollutants in environmental samples and exhibited many advantages such as low LODs, high extraction efficiency and wide linear range.

One of the better ways to prepare the stir bar coating is electrochemical deposition which is flexible and easily controlled by adjusting the electropolymerization conditions. During the preparation, CNTs-conductive polymer composites would offer a three-dimensional nano-structured film and the prepared stir bar showed good porosity, stability and solvent-resistance without coating damage [106].

In 2013, C. Hu *et al.* developed another method to change the extraction selectivity of the commercial PDMS stir bar coating [105]. Aromatic diamine was used to modify CNTs and mixed with PDMS to prepare the composite sol solution. The activated bare bar was immersed into the above sol solution and then thermally aged. The developed amino modified CNTs/PDMS coating exhibited excellent extraction efficiency for medium polar phenols with conjugation, hydrophobic interaction and intermolecular hydrogen bond, so this method showed a potential applicability for the analysis of phenols in various complex environmental samples.

In 2011, Z. Es'haghi *et al.* developed another feasible and affordable pseudo-stir bar microextraction (Fig. 7b) [107]. In this mode, the author packed the CNTs solution into the pores and lumen of the HF, and then used magnetic stoppers to seal the two ends of the HF segment, making the extraction fiber rotating freely in the sample solution. Besides magnetic stoppers, cleaned stainless steel magnetic bar could be inserted into the lumen of the HF

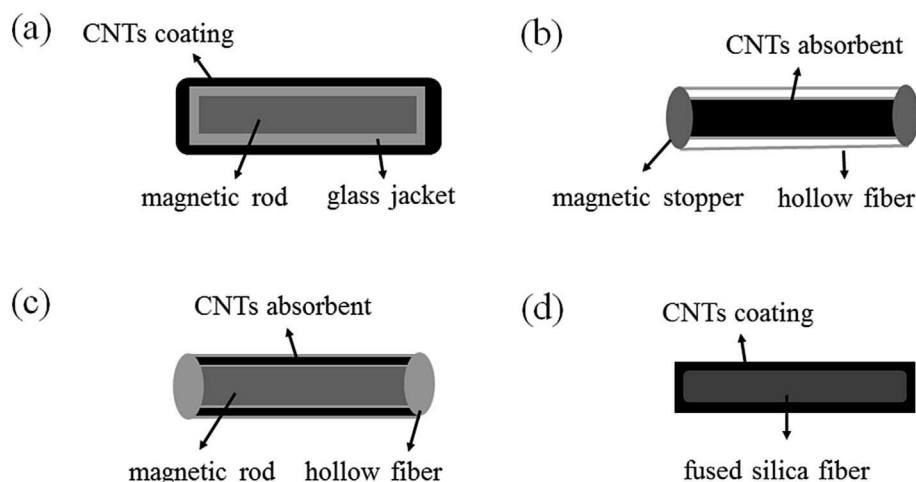


Fig. 7. The main configurations of CNTs-SBSE (a) CNTs-SBSE: CNTs coating was put on the surface of the magnetic rod. (b) CNTs-HF-SBSE: CNTs absorbent was packed into the lumen of the HF and the magnetic stopper was put in the two ends of the HF. (c) CNTs-HF-SBSE: the magnetic rod was inserted into the lumen of the HF and CNTs were immobilized into the pores of HF. (d) CNTs-SBSE: CNTs coating was put on the surface of the fused silica fiber.

and then immersed into the synthesized CNTs sol solution for in-situ aging to form the pseudo-stir bar (Fig. 7c) [108].

Besides magnetic bar and HF, the fused-silica fiber could also be used to support CNTs coating in the stirring and sorptive mode (Fig. 7d). Since the fused-silica fiber could not automatically rotate in the sample solution under the magnetic stirrer, a necessary stir bar should be added. In 2016, N. Zou *et al.* applied sol-gel technique to coat CNTs/PDMS onto the surface of the activated fused-silica fiber. The obtained stir bars had excellent thermal stability, good reproducibility and reusability (more than 30 times). The extraction performance of the developed method was investigated for the determination of triazine herbicides in five surface and ground water samples. As expected, the developed CNTs/PDMS coated fused fiber stir bar obtained low LODs ($0.006\text{--}0.015\text{ ng mL}^{-1}$), wide linearity range ($0.05\text{--}10\text{ ng mL}^{-1}$), good recovery ($89.6\text{--}104.3\%$) and negligible matrix effects [109].

2.5. CNTs reinforced in-needle SPME

Needle solid-phase microextraction (NSPME) combines the concept of miniaturized exhaustive active sampling and passive diffusive sampling with new microextraction concepts [110]. For NSPME, the stationary phase was placed inside a stainless steel needle. In addition, sample introduction and determination can be performed in a single step, making it as a good technique for workplace surveys of occupational exposure to hazardous compounds [111].

Since it was introduced, it has got much attention. As shown in Fig. 8, it has been evolved into several types like solid-phase dynamic extraction (SPDE), packed needle microextraction (PNME) and microextraction by packed sorbent (MEPS) [74]. Their applications in various areas have been summarized in previous reviews [20,74,92]. For the SPDE, a syringe with an inner coated is used as the extraction device. The volume of the coating on the inner wall of the needle is several μL , leading to high enrichment factor. In addition, the needle is hard to damage mechanically, so NSPME is more robust than the fragile SPME fiber. In 2009, O. Sae-Khow *et al.* used the chemical vapor deposition to make CNTs self-assemble onto the surface of the needle to form a quite thin film [112]. The developed method showed excellent linearity, reproducibility, relatively high extraction efficiency and low method detection limits. To apply CNTs to the PNME mode, CNTs could be dispersed into the sol solution and the obtained CNTs/silica composite is followed packed into the lumen of the needle. The scheme of NSPME with side hole, glass wool and CNTs/silica composite as sorbent is shown in Fig. 9 [111].

In the MEPS mode, CNTs could be inserted directly into the syringe as a plug or between the needle and the barrel as a cartridge

but not in the needle. This technique could be seen as the miniature of SPE. After pulling and pushing the sample solution through the syringe several times, the analytes would be extracted by the sorbents [113].

In 2007, to further improve the extraction selectivity, Y. Wei *et al.* adopted electrochemical deposition method to prepare MIPs-CNTs composite and then packed it inside a 22-gauge syringe needle [114]. The results demonstrated that the developed extraction fiber displayed a significantly selective enrichment of the target analyte and got a low LOD (0.04 ng mL^{-1}) as well as be reusable.

2.6. CNTs reinforced in-tip SPME

The stainless steel needle could effectively load the CNTs and the set-up is rather robust. Based on the NSPME, researchers developed another novel mode, in-tip solid-phase microextraction. It is a feasible operation mode and uses the tip of pipette to hold and protect adsorbents. The detailed preparation is as follows.

CNTs were packed into a polypropylene membrane folded in a scalene triangle shape. The sharp end of a $1000.0\text{ }\mu\text{L}$ pipette tip was cut-off and slightly compressed. Then, the membrane was inserted into the above treated tip and fully fitted the tip-end prior to extraction. Finally, the developed device was carried out in the semi-automated dynamic mode [115].

In 2012, W.H. Gao *et al.* applied the same technique to detect organochlorine and pyrethroid pesticides [116]. The results obtained around three orders of magnitude and low LOD of pg mL^{-1} level, demonstrating this method is a simple, feasible, and low-cost microextraction technique. For ionized analytes, zinc sulfide (ZnS) could be used to modify CNTs to enhance the surface complexation reactions including protonation, deprotonating and ion exchange between the adsorbent (ZnS-CNTs) and the analytes [117]. The operational process of ZnS-CNTs reinforced in-tip SPME is shown in Fig. 10 [117].

3. The applications of CNTs-SPME in the environmental analysis

Recently, the efforts to sensitively detect and analyze trace or hence compounds in environmental samples have been considered as the main force driving analytical chemists to develop feasible, green, commercial available and environmental friendly microextraction techniques [118]. SPME techniques are widely used in the environmental analysis by virtue of its positive features, *i.e.*, simplicity of operation, versatility, relatively short time of exaction and ease of coupling to chromatographic systems. However, environmental samples are usually complex and often have various matrix compositions, most of the existing conventional coatings of

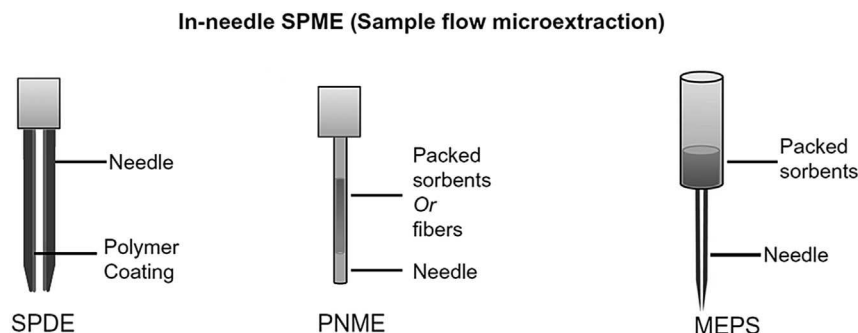


Fig. 8. Different types of in-needle SPME. Solid-phase dynamic extraction (SPDE), packed needle microextraction (PNME), microextraction by packed sorbent (MEPS) [74].



Fig. 9. Schematic of NSPME with side hole, glass wool and CNTs/silica composite as sorbent [111].

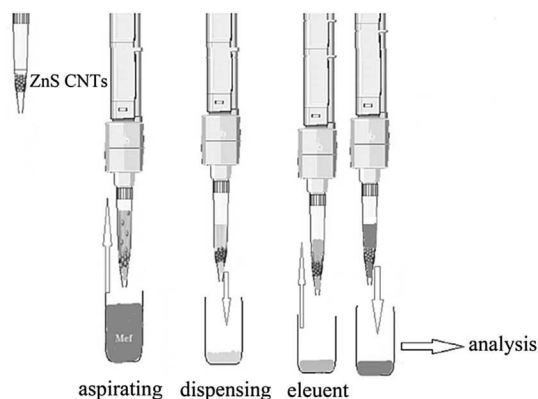


Fig. 10. The operational process of ZnS-CNTs reinforced in-tip SPME [117].

SPME are not sensitive enough to directly determine trace analytes in these samples.

Most environmental pollutants and toxicants such as PAEs, PAHs, phenols, VOCs as well as hydrophobic drugs and pesticides have phenyl ring structure and relatively high hydrophobic partition coefficients. Fortunately, CNTs have large π electron conjugated system and hydrophobicity, ensuring them have strong interaction with the analytes. Thus, as shown in the literature, the introduction of CNTs into conventional SPME methods would display better extraction efficiency and higher sensitivity, which is quite critical for the determination of trace analytes in the environmental samples. As compared, the newly developed CNTs-HF could be used as an individual device and its handling is more convenient than the other traditional SPME fibers. In addition, the disposable nature of the device would effectively eliminate the possibility of cross-contamination and carry-over effects, which could avoid the complex and time-consuming sample pretreatment procedure and increase the measurement accuracy.

The main application areas of CNTs-SPME in environmental analysis are shown in Table 1. As seen in Table 1, CNTs fiber SPME is the most widely used configuration to determine various analytes in environment. Meanwhile, different configurations have been continuously developed to obtain more effective, environmental-friendly and selective analytical methods. In 2011, Z. Es'haghi *et al.* applied CNTs-HF-SPME technique to determine BTEX [82]. To achieve it, CNTs-HF was prepared by injecting CNTs nanocomposite into the lumen of HF segment and followed in-situ aging. It was validated that high active adsorbent sites and strong chemical bonds between analytes and extractors were produced, resulting in higher extraction efficiency than the conventional CNTs fiber SPME. For the determination of phenols, the newly developed CNTs SBME configuration would increase the volume of the extraction phase and enhance the contact area between the extraction phase and the

sample solution, resulting in higher enrichment factors and lower LODs [104,105].

4. Conclusion

The use of CNTs in SPME technique is a topic of growing interest in analytical chemistry since CNTs have exceptional mechanical, absorptive, electrical, optical and magnetic properties. The applications of CNTs have been extensively exploited in different configurations of SPME. As shown in the literature, most CNTs involved SPME coatings show higher sensitivity and extraction efficiency, better selectivity as well as improved thermal and physical resistance than the conventional ones. The employment of porous polymeric membranes to support CNTs has displayed outstanding advantages, especially the disposable nature of HF could effectively avoid carry-over effects which is an obvious problem of the conventional SPME techniques.

In addition, carbon nanotubes could be functionalized with various functional groups, ionic liquids, molecularly imprinted polymers and organic polymers to further enhance the porous structure, selectivity, mechanical and thermal stability of the formed coatings, thus improving the extraction performance of the developed microextraction methods.

In comparison with commercial coatings of SPME, the improved thermal and chemical resistance of CNTs involved coatings enlarge their application. However, till now the commercialized CNTs-SPME is rare, and the bottleneck of the commercialization is mainly due to the cost, safety and reproducibility. In some cases, CNTs involved coatings are a little more expensive than the conventional ones. However, the published literature showed that only small quantities of CNTs would be used to prepare the coatings. In addition, several works have also reported that high economic CNTs are also available, acting as a good economic alternative. The manufacturer is also aiming to develop effective purification and characterization procedures to obtain the commercial, pure and well-characterized carbon nanomaterials, which would largely promote the transmission of their use to the laboratory. In terms of the safety, although CNTs are demonstrated to be not very toxic, their long-term impact on the people's health and environment should be further studied to ensure a safe manipulation and application. By virtue of the well-developed preparation method like physical deposition, sol-gel technology, chemical bonding, electrochemical and electrophoretic depositions, the reproducibility of the prepared CNTs coatings could meet the requirement (most RSDs of the same batch repeatability and the batch-to-batch reproducibility are less than 10%). The involvement of carbon nanotubes in microextraction techniques will not doubt increase in the future, since the combination of unique properties of carbon nanotubes and solid-phase microextraction promises good applications in various fields of separation science. In addition, new coatings and formats of SPME are important for expanding its application, so their development may still be the main topics in the future.

Table 1
The application of CNTs-SPME in environmental analysis.

Analytes	Microextraction mode	Sample matrix	Detection method	Linear range/ng mL ⁻¹	LOD/pg mL ⁻¹	Recovery/%	Ref.
NSAIDs	CNTs fiber SPME	River, tap, well, waste water	GC-FID	0.07–200	7.0–30	84–107	[39]
	CNTs SBSE	River water	HPLC-UV	2–1000	350–430	78.1–106	[104]
Phenobarbital	CNTs-HF-SPME	Sediment	HPLC-UV	0.50–5000	320	81.8–119.5	[13]
		Waste water				102	
Cadmium; Cobalt	CNTs SBSE	Sewage, waste water	FAAS	0.05–5	18.6–24	76.7–102.4	[108]
Mercury	CNTs fiber SPME	River, sea water	GC-FID	0.005–500	1.0	93.7–98.3	[119]
		Mineral, tap water				90–113	
PAEs	CNTs fiber SPME	Mineral, tap water	GC-FID	0.1–300	30–80	91–115	[67]
		Mineral, river, tap water				79.6–109.3	
PAHs	CNTs fiber SPME	Tap, well, waste water,	GC-MS	0.05–20	2–10	89–108	[66]
		Hubble-bubble, river water				—	
CNTs-HF-SPME	CNTs fiber SPME	Tap, well, waste water,	GC-FID	0.04–1000	9–13	88.9–102.5	[91]
		Tap, well, waste water,				81–112	
CNTs fiber SPME	CNTs fiber SPME	Tap water	GC-FID	0.5–50	30–70	88–105	[122]
		River, waste water				75.7–104.5	
BIFs	CNTs fiber SPME	River water	HPLC-UV	5–500	300–1500	75.7–104.5	[123]
OCPs	CNTs fiber SPME	Lake, waste water	GC-ECD	0.5–5.0	0.43–2.13	72.4–134.7	[124]
		Pool, river water				44.7–116	
OCPs; Pyrethroid	CNTs in-tube SPME	Pond, sea, tap water	GC-ECD	1–500	18–1064	90–106	[116]
Pyrethroids	CNTs fiber SPME	Bottled, river, tap water	GC-ECD	5–10,000	120–430	83.6–112.0	[33]
		Drainage, lake, tap water				70–108	
Triazine herbicides	CNTs-HF-SPME	Lake water	HPLC-DAD	0.1–250	80–150	86.6–106.8	[90]
		Sea, transition water				85–106	
CNTs in-tube SPME	CNTs in-tube SPME	Ground, surface water	DART-MS	0.5–50	20–140	98–120	[98]
		Soil				89.6–104.3	
Various pesticides	CNTs-SBSE	River water	PGD-IMS	0.05–10	6–15	85.9–89.2	[109]
		Sea, tap water				—	
Phenols	CNTs fiber SPME	River water	GC-MS	0.5–100	20–100	87.5–102	[126]
		River water				81.5–110	
CNTs fiber SPME	CNTs fiber SPME	River water	GC-FID	0.5–200	20–100	—	[54]
		River water, wastewater				70.8–145.6	
CNTs fiber SPME	CNTs fiber SPME	River water, wastewater	GC-MS	1–100	5–80	86.1–111.6	[31]
		River water, wastewater				23.5–118.6	
CNTs fiber SPME	CNTs fiber SPME	Seawater	GC-FID	1–100	1.5–10	87.1–102.9	[127]
		River, well, waste water				85.3–99.5	
CNTs SBSE	CNTs SBSE	River water	HPLC-UV	0.5–100	1–100	73.9–97.4	[104]
		Sediment				84.6–118.4	
CNTs SBSE	CNTs SBSE	Lake water	HPLC-UV	5–1000	140–1760	79.2–123.2	[105]
		Soil				71.0–119.2	
BTEX	CNTs fiber SPME	Mineral, tap, well, wastewater	GC-FID	2.0–8.0	0.6–3	90.2–101.9	[38]
		Tap, well, waste water				91.0–106.7	
CNTs fiber SPME	CNTs fiber SPME	Mineral, river, tap, well, wastewater	GC-FID	0.06–100	5–20	93.7–106.2	[58]
		River, well water				89–101	
CNTs fiber SPME	CNTs fiber SPME	River, waste water	GC-FID	0.09–300	10–40	—	[59]
		Soil				—	
CNTs fiber SPME	CNTs fiber SPME	Mineral, river, tap, well, waste water	GC-FID	0.25–100	30–60	93–112	[26]
		Wastewater				—	
CNTs-HF-SPME	CNTs-HF-SPME	Filtrate, tap, waste water	GC-FID	0.0035–3.0	0.28–1.1	85–108	[130]
		Air				—	
CNTs in-tube SPME	CNTs in-tube SPME	Air	GC-MS	1–90	110–200	—	[36]
		Air				—	
CNTs fiber SPME	CNTs fiber SPME	Air	GC-MS	0.01–60	14	—	[131]
		Air				—	
TBE	CNTs fiber SPME	River, tap, well, waste water	GC-FID	1–70	90–200	91–112	[40]
		River, tap, well, waste water				94–104	

AMP: amphetamine; BIFs: Benzimidazole fungicides; BTEX: Benzene, toluene, ethylbenzene, *o*-xylene; DART-MS: direct analysis in real time-mass spectrometry; EPE: ephedrine; FAAS: flame atomic absorption spectroscopy; HOVs: Halogenated volatile organic compounds; MET: methamphetamine; NSAIDs: non-steroidal anti-inflammatory drugs; OCPs: organochlorine pesticides; PAEs: Phthalate esters; PAHs: polycyclic aromatic hydrocarbons; PGD-IMS: pulse glow discharge-ion mobility spectrometry; TBE: *tert*-butyl ether; VOCs: volatile organic compounds.

^a ng g⁻¹.

^b pg g⁻¹.

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