



Progress in stationary phases modified with carbonaceous nanomaterials for high-performance liquid chromatography



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ABSTRACT

Carbonaceous nanomaterials (CNMs) are prevalent in many disciplines. In separation science, CNMs have made great contributions to the innovation of stationary phases for various chromatographic technologies. In this review article, we present an up-to-date overview of the development of stationary phases based on CNMs for high-performance liquid chromatography (HPLC). We devote a large part of this review to the accomplishments in the past five years with regard to retention and selectivity offered by new HPLC stationary phases modified with different types of CNMs, mainly including carbon nanotubes, fullerenes, nanographene and nanodiamonds. We pay specific attention to the approaches to chemical immobilization involving different types of CNM in synthesizing stationary phases.

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1. Introduction

High-performance liquid chromatography (HPLC), as an efficient analytical separation method and an important preparative separation technique, has rapidly evolved into an innovative, fast and highly selective analytical tool with widely-distributed application in biology, chemical engineering, pharmaceuticals, food, environment protection and the oil and petrochemical industries [1–5]. HPLC was built on innovations, which require continuous development of sub-units, including pumps, injectors, detection units, data recorders and processors, mobile phases and stationary phases (SPs). The diversity of the SPs is the foundation of the establishment and the development of the various modes of HPLC separation,

such as reversed-phase (RP), normal-phase (NP), ion-exchange (IE) and hydrophilic interaction liquid chromatography (HILIC). Thus, as the core components of the HPLC system, LC packings enable effective separation and are powerful propellants for HPLC. SP innovations include better supports, bonded phases, (polar) end-capping, and immobilization procedures.

Packings in HPLC can be sub-categorized into three types (i.e., inorganic, organic and inorganic-organic hybrid) [6,7]. The inorganic materials cover metal oxides, graphite and silica. Among these candidates, porous spherical silica is the most popular substrate for HPLC SPs so far [8], due to its monodispersity, modifiable surface, controllable porosity, surface area and pore diameter, high mechanical strength and chromatographic efficiency, despite its well-known limitations, such as instability in extreme pH conditions and gradual loss of bonded phase at elevated temperature. In contrast, the organic materials resist harsh pH, but they often suffer excessive swelling, lower mechanical stability and unsatisfactory

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chromatographic performance [9]. The inorganic-organic hybrid materials were claimed to inherit the merits of both inorganic and organic compositions. To a certain extent, they demonstrated improved thermal stability and chemical stability, but they were by no means completely immune to hydrolysis and disintegration of the silyl-ether bond in an alkaline mobile phase [10–13].

Silica and silica-based HPLC SPs have been extensively employed in different LC modes. The most useful, readily available column packings use SPs based on siloxanes, or organosilane-bonded phase, prepared by reaction between organosilane and the silanol groups on the silica surface. The organosilane reagents can have pure alkyl chains of different lengths (C8 or C18), or alkyl chains with reactive groups, such as amino, chloro, epoxy, mercapto and isocyanate groups. SPs of this type can be hydrolytically stable and feature high chromatographic efficiency because of their fast mass-transfer effects [8,14,15].

Among the bonded silica materials, alkylated silica, especially that functionalized by octadecyl chain (C18), is the most widely used SP for RP separation. There are two types of C18 chromatographic sorbents based on the bonding chemistry, one is monomeric, the other polymeric. The monomeric type is usually prepared by monofunctional silane, whereas the polymeric materials are prepared via polycondensation of multifunctional silanes [16]. The monomeric phases are preferred due to their better mass-transfer capability. But, polymeric sorbents offer enhanced selectivity towards molecularly rigid solutes, so they are more favored for separation of constitutional isomers, such as polycyclic aromatic hydrocarbons (PAHs) [17,18].

However, the organosilanes with reactive groups have substantially enriched the family of HPLC SPs via further derivatization with ligands of suitable size; meanwhile, chromatographers' efforts to explore new SPs have never abated. The new SPs were specifically designed for separation of a diversity of solutes. Usually, ligands with multifunctional groups, such as cyclodextrin (CD) [19,20], calixarene [21–23], crown ethers [24–26] and ionic liquid (IL) [27–29] and some embedded polar groups [30–33], were tethered to the silica. With these new SPs, separation of desired solutes from complex matrix can be achieved due to the involvement of multiple interactions. It is noteworthy that towards certain kinds of analytes poorly held on conventional C18 phase, these new materials exhibit superior chromatographic retention and selectivity, due to the diversified moieties of the ligands, such as aromatic ring, polar groups and hetero atoms, which enable a reciprocal combination of π - π , hydrogen-bonding, dipole-induced dipole and electrostatic interactions and at the same time special mechanisms involving the structure and the rigidity of the ligands, such as shape and planarity selectivity.

Over the past decade, the separation-science community has witnessed an ever-accelerating expansion of HPLC SPs induced by interdisciplinary studies of new materials. The research highlights of the novel SPs are promising and useful ligands and/or substrates, amongst which carbonaceous nanomaterials (CNMs) [34–38], ILs [27–29,39], and metal-organic frameworks (MOFs) [40–42] have attracted great interest due to their unique nature, and their far-reaching influence within separation science has been reviewed in detail.

This review article focuses exclusively on the development of CNM-based SPs in the past five years, with a number of previous reports of significance. We attempt to evaluate comprehensively the contribution of CNMs to LC-SP innovations, with particular emphasis on the value of their applications in HPLC. The citations herein may not be exhaustive but are intended to represent work and progress.

NMs, a class of materials with sizes or features of 1–100 nm in one or more dimensions, play an exceptionally important role in the coming technology revolution [43–45]. The commendable properties are large surface-area/volume ratio, easy derivatization

procedures and decent thermal, mechanical, electronic and biological qualities. These intrinsic advantages, plus their amazing recognition capability, have greatly facilitated systems with enhanced performance and new applications across modern science and technology [43,44,46–52]. The surface and structural characteristics of NMs combined with their ability to undergo hydrogen and dative bonds formation, π - π stacking, and dispersion force and hydrophobic interactions have sparked ever-growing interest in analytical chemistry.

CNMs have found interesting analytical applications since their discovery. In recent years, CNMs were intensively investigated as sorbents in sample preparation, including carbon nanotubes (CNTs), fullerenes (FLNs), nanographene (NG), nanodiamonds (NDs), carbon nanofibers (CNFs) and carbon nanohorns (CNHs) (Fig. 1), and their derivatives [35,53–57]. Within separation science, CNMs have also played an important role. Through exploitation of their unique physical and chemical properties, a remarkable range of new HPLC SPs has been developed. We should mention that they also considerably benefitted the development of SPs in gas chromatography (GC) and pseudo-SPs in capillary electrophoresis (CE) and capillary electrochromatography (CEC), as reviewed by several authors [34,38,58–60].

Nevertheless, from an analytical viewpoint, most applications of HPLC SPs have by far employed CNTs, FLNs, NG and NDs. And there has been a continuous growth of interest in SPs modified by these four types of CNMs, generally due to their specific selectivity. The following section specifically addresses the preparation and the application of HPLC SPs involving CNTs, FLNs, NG and NDs. Table 1 summarizes preparation of CNM-based SPs and their applications in HPLC analysis.

2. Application of carbon nanotubes

CNTs can be viewed as graphene (G) sheet (sp^2 hybridized carbon) curled into a cylinder and are classified into two types: single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) [94,95]. Due to their unique mechanical, electronic, thermal and magnetic properties, CNTs have attracted the attention of many researchers to develop new SPs with improved separation performance (Fig. 2).

The first involvement of CNTs in preparing LC SPs was by incorporating SWCNTs into an organic polymer monolith to form an SP for micro-HPLC [96]. The chromatographic behavior of the monolithic column indicated that SWCNTs could enhance the retention of small molecules and the selectivity towards polar molecules, due to the hydrophobic interaction between SWCNTs and analytes and the influence of structure, size and charge characteristics of CNTs on adsorption and partition of analytes.

Later, a silica-based CNT-modified SP was prepared by covalent immobilization [97], where the oxidized SWCNTs were pretreated with thionyl chloride and then covalently grafted via amide bonds on an aminopropylated silica sphere, while MWCNTs with protonated amino groups along their side walls were attached to the same substrate via hydrogen bonds. In resolving nitroaromatics, isomeric terphenyls and peptides, the packed column with carboxyl-functionalized SWCNTs showed reduced hydrophobicity compared to that with MWCNTs functionalized by 1,3-dipolar cycloaddition, which exhibited behavior similar to a C18 column, highlighting the advantage of further functionalization. These CNT-modified SPs were suitable for separating apolar and polar compounds with water-rich eluent, although the resolution had hardly been improved, probably due to the relatively lower carbon content (~5 w.t.%) compared to the C18 counterpart.

Interestingly, CNTs were likely to increase the SP affinity and selectivity towards peptides having proline residues, which could foreshadow CNT's potential for more applications outside analytical techniques, such as a simple screening method for biomolecules

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