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Graphene-Based Materials Used in as Stationary Phase for Chromatography: A Mini Review

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Abstract

Graphene has fascinated the scientific community since its discovery. Graphene is a one atom thick planer sheet. Graphene exhibited great potential to be application in analytical chemistry due to its exceptional properties. Chromatography is a versatile, powerful separation and analysis technique. In this article, an overview of graphene and graphene-based materials used in stationary phase for gas chromatography, liquid chromatography and ion chromatography is presented. Detail separation fabrication methods and separation mechanisms, characteristic of graphene-based materials column was discussed in this article.

Keywords: Graphene-based materials; Stationary phase; Gas chromatography; Liquid chromatography

Introduction

Graphene has fascinated the scientific community since its discovery. It is a two-dimensional sheet of sp^2-hybridized carbon. It has received the attention of many researchers due to its extraordinary properties (e.g., large surface area, π-electron-rich structure, and good thermal and chemical stability) [1]. These remarkable properties make graphene an optimal candidate material for analytical chemistry applications. Graphene and graphene-based materials has widely used in analytical chemistry, such as sample preparation, electrochemical analysis [2], photochemical analysis, extraction, chemical sensing [3] and so on. All kinds of chromatography such as Gas Chromatography (GC), Liquid Chromatography (LC) are versatile, powerful separations and analysis technique in analytical chemistry. Columns/stationary phases are considered the "heart" of the chromatograph and are responsible for the separation process [4]. In this article, the recent research progress of graphene and graphene-based materials in stationary phase for gas chromatography, liquid chromatography and ion chromatography were reviewed. Detail separation characteristic of graphene-based materials applied in column were reported and discussed in this paper.

Stationary Phase for GC

Gas Chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analyzing compounds. There are novel Materials were used as GC stationary phases in gas chromatography [5]. Novel material includes polysiloxane polymers, polyethylene glycols, metal-organic frameworks (MOFs) and ion liquids [6] etc. Graphene-based materials used for GC stationary phase were reported in recent years. Feng et al. [7] investigation of Graphene Oxide (GO) nanosheets as a stationary phase for capillary Gas Chromatographic (GC) separations in 2015. The GO column was fabricated by a one-step column coating approach for GC separations. Column efficiency were 1350 plates/m of the GO column by detection with naphthalene at 120°C. Separation performance of the GO capillary column was tested by 11 analytes, including n-alkanes, aromatic hydrocarbons, alcohols, amines and a mixture of 11 analytes. The result [7] indicating the good reproducibility of GO column for the GC separations.

Zhang et al. [8] fabricated Capillary Column Coated with Graphene Quantum Dots (GQDs) for alkanes and aromatic isomers separation in 2015. Schematic representation of column was shown Figure 1. the GQDs coated capillary column with 3-aminopropyl diethoxy methyl silane (3-AMDS) as coupling reagent. GQDs coated column exhibits high separation efficiency of ethylbenzene, styrene, xylene, propyl benzene, alkanes, and dichlorobenzene isomers at low temperature. The result shown [8] GQDs coated column allowed fast and efficient separation of the analytes at low temperature without temperature-programming.

Yang et al. [9] developed a method to graphene-based porous carbon material as a stationary phase for gas chromatography separations. 3D Graphene-based N-doped Porous Carbon Material (GPCM) was synthesized and applied in fabrication GPCM capillary column. Isomers of alkanes, alcohols and phenols and complex mixture of analytes were detected by GPCM capillary column. The GPCM column exhibited good column repeatability and reproducibility with RSD values on retention times in the range of 0.01-0.03% for intra-day. The result was shown in Table 1.

The separation mechanism of GPCM phase can be mainly ascribed to the comprehensive result of dipole-dipole, π-π and halogen-bonding interactions. Yuan et al. [10] proposed the method for Micro Electromechanical System (MEMS)-based column coated with reduced graphene oxide as stationary phase. MEMS-based column was designed as Multi-Capillary Column (MCC). The columns were fabricated by reduced graphene oxide immobilized onto the column wall through sol-gel-derived ZnO particles as a supporting layer between the Reduced Graphene Oxide (RGO) film and the MEMS channel wall. The maximum column efficiency [10] were 11363 theoretical plates per meter by n-dodecane detection.

Yang et al. [11] successfully used Graphene-ZIF8 (G-Z) composite material as stationary phase for capillary gas chromatography. G-Z

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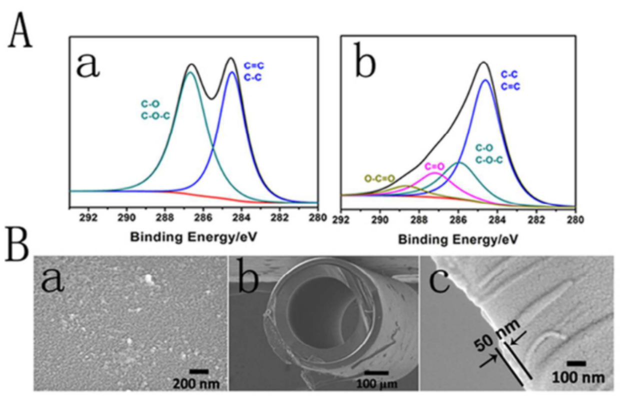

Figure 1: (A) XPS spectra of C1s of the original graphene oxide film (a) and XPS spectra of C1s of the as-produced GQDs (b); (B) (a). SEM image of the GQDs deposited on the inner wall of the capillary column; (b) the SEM image of the GQDs coated capillary column, (c) SEM image of the cross-section view of the inlet of GQDs coated capillary column [8].

capillary column were fabricated by statically coated methods. Three types of analytes include structural and geometric hydrocarbon isomers, aromatic positional isomers, complex mixture were separated by G-Z capillary column. The repeatability datum of the G-Z capillary column was shown in Table 2. The high resolving capability of the G-Z composite material may derive from its specific structure and diverse types of molecular interactions covering-stacking and π-π Electron-Donor/Acceptor (EDA), H-bonding, halogen-bonding and van der Waals interactions. The result endows the G-Z composite stationary phase with distinctly different retention behaviors from the conventional stationary phase.

Stationary Phase for HPLC and Ion Chromatography

High-Performance Liquid Chromatography (HPLC; formerly referred to as high-pressure liquid chromatography), is a technique in analytical chemistry used to separate, identify, and quantify each component in a mixture [12]. The typically column of HPLC were made by granular material made of solid particles such as silica, hybrid Silica [13], hydride Silica [14] and polymers [15], etc. Graphene-based materials used for HPLC stationary phase were also reported in recent years. Qu et al. [16] developed a method to graphene and graphene Oxide as Stationary Phase for Capillary Electrochromatography and Capillary Liquid Chromatography. The Schematic of the fabrication processes of GO and G-coated capillary columns were shown in Figure 2. Graphene Oxide (GO) coated Capillary Column were made by GO nanosheets immobilized onto the capillary wall using 3-aminopropyl diethoxy methyl silane as coupling agent. Graphene coated Capillary Column were fabricated by hydrazine reduction of GO coated column. GO and graphene coated column were used for open-tubular capillary electrochromatography and open-tubular capillary liquid chromatography experiment. GO coated column were suitable for open-tubular capillary chromatography separation. Graphene coated column is helpful achieve unique adsorption behavior with relative weak interaction benefit for separated normal compounds as well as proteins.

Li et al. proposed a method for Capillary Electrophoresis (CE) method by using Graphene Oxide (GO) as a stationary phase [17]. The separation performance, reproducibility and stability of GO-coated capillary were tested by separation of brucine and strychnine. The result shown that GO-coated capillary electrophoresis method was successfully applied for the determination of these two alkaloids in a pharmaceutical formulation of traditional Chinese medicine [15]. Liang et al. [18] developed a method to octadecylsilane functionalized

Analytes	Intra-day	
	t_R(min)	RSD (%)
2,2,4-Trimethylpentane	1.176	0.02
2,2-Dimethylhexane	1.287	0.03
3-Methylheptane	1.592	0.04
n-Octane	1.838	0.04
2,2,3-Trimethylbutane	2.033	0.01
2,3-Dimethylpentane	2.174	0.01
n-Heptane	2.352	0.01
2,6-Dimethylnaphthalene	2.897	0.1
1,3-Dimethylnaphthalene	3.163	0.06
2,3-Dimethylnaphthalene	3.417	0.05
1,2-Dimethylnaphthalene	3.658	0.03
2-Methylnaphthalene	5.008	0.15
1-Methylnaphthalene	5.557	0.19

Table 1: Column repeatability and reproducibility of G-Z capillary column on retention times for separations of the isomer mixtures of octanes, heptanes, dimethylnaphthalenes and methylnaphthalenes [9].

	Experiment number (*n*=5)					
Analyte	t_{R1} (min)	t_{R2} (min)	t_{R3} (min)	t_{R4} (min)	t_{R4} (min)	RSD (%)
(a) Alkanes						
Pentane	0.068	0.066	0.066	0.067	0.067	1.25
Hexane	0.111	0.108	0.106	0.108	0.109	1.68
Heptane	0.222	0.212	0.213	0.209	0.208	2.6
Octane	0.47	0.462	0.444	0.436	0.446	3.09
Nonane	0.831	0.876	0.826	0.787	0.817	3.88
Decane	1.228	1.311	1.225	1.244	1.234	4.4
Undecane	1.63	1.726	1.652	1.707	1.697	2.38
Dodecane	2.022	2.119	1.97	2.204	2.124	4.41
(b) Esters						
Butyl acetate	0.23	0.234	0.225	0.24	0.243	3.11
Ethyl lactate	0.761	0.756	0.705	0.792	0.782	4.44
Ethyl heptanoate	1.162	1.139	1.155	1.182	1.179	1.52
(c) Alcohols						
Butyl alcohol	0.054	0.054	0.048	0.055	0.052	5.31
Hexanol	0.516	0.472	0.533	0.572	0.566	7.61
Octanol	1.287	1.232	1.412	1.435	1.465	7.39
Lauryl alcohol	2.932	2.899	3.087	3.133	3.226	4.5

Table 2: The repeatability datum of the RGO/ZnO column, reprint from [11].

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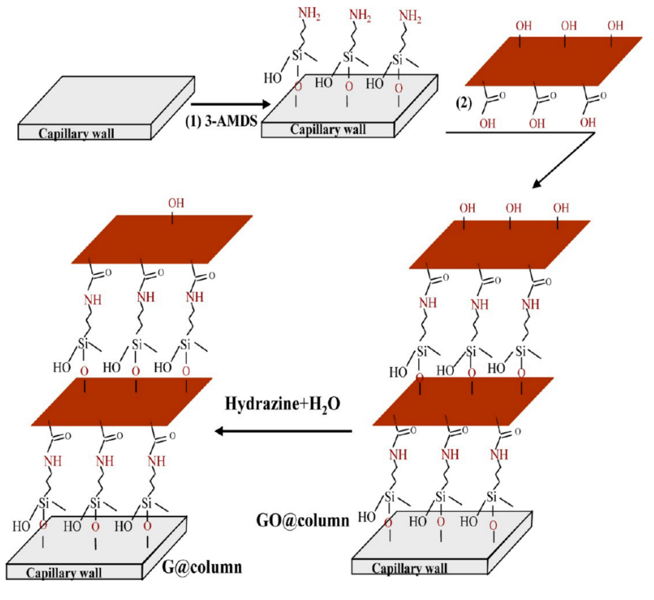

Figure 2: Schematic representation of the fabrication processes of GO and G-coated capillary columns [14].

graphene oxide/silica stationary phase as HPLC column. The column was made by graphene oxide assembling onto the silica particles through an amide bond and subsequent immobilization of octadecylsilane. Four kinds of analyses include alkylbenzenes, polycyclic aromatic hydrocarbons, phenolic, amines were separated by the column. The column performance conclusion indicted that the column exhibited both large π-electron system and hydrophobicity characteristic.

Wu et al. [19] successfully used Graphene Quantum Dots (GQDs) bonded silica as stationary phase for HPLC. GQDs were synthesis from GO aqueous dispersion using a hydrothermal synthesis method with H_2O_2 as an etching agent and ammonia as an assistant. The column was fabricated by GQDs bonded silica spheres packed into stainless steel tubes by a slurry packing method. Aromatic compounds including anilines, phenols and Polycyclic Aromatic Hydrocarbons (PAHs) were tested by GQDs column and commercial C_{18} column [19]. The separation mechanism of column includes hydrophobic interaction, π-π stacking, π-π-electron-donor/acceptor EDA and hydrogen bond interaction with analytes. Synthetic process of GQDs bonded silica stationary phase were shown in Figure 3.

Zhang et al. [20] investigation of graphene and graphene oxide bonded silica microspheres as stationary phases for high performance liquid chromatography. GO and SiO_2 composites were made of GO sheets assembly onto amino silica particles by coupling the carboxyl groups of GO and the amino groups of amino silica with 1-(3-dimethylaminopropyl)-3- Ethyl carbodiimide hydrochloride (EDC)and N-hydroxysuccinimide (NHS) as coupling agent. Graphene and SiO_2 composites were reduction by GO /SiO_2 composites. Effective separations of the tested neutral and polar compounds on both graphene oxide bonded silica and graphene bonded silica columns were achieved. The different chromatographic performances of GO and graphene bonded columns were ascribed to their unique mixed-mode retention mechanisms.

Zhang et al. [21] developed a method to Graphene-coated polymeric anion exchange column for analysis by ion chromatograph. Graphene-coated particles were fabricated by a facile evaporation reduction method. The Graphene-coated polymeric anion exchanger column was packed by graphene-coated particles into stainless-steel column. Schematic diagram of fabrication course of graphene-coated polymeric reverse phase column was shown in Figure 4. The result shown that the column has the good efficiencies and symmetries. Sun et al. Proposed a method for capillary electrophoresis separation by using graphene quantum dots as additives [22]. Graphene Quantum Dots (GQDs) were synthesized by chemical oxidization, and further purified. cinnamic acid and its derivatives were separated by capillary electrophoresis methods. The separation mechanism may be due to aromatic characteristics interacted with GQDs through π-π electrostatic stacking interaction or hydrogen bonding interaction, the increased mass to charge ratio of the analytes resulted in the migration slow down.

Conclusion

In this article, an overview of graphene-based materials used for chromatographic stationary phases is presented. The graphene-based materials include graphene, graphene oxide, graphene hybrid material and graphene quantum dot. The mechanism of separation maybe abundance with the graphene-based materials involve in chromatography. More research work maybe appeared about graphene-based materials used in chromatographic stationary phases.

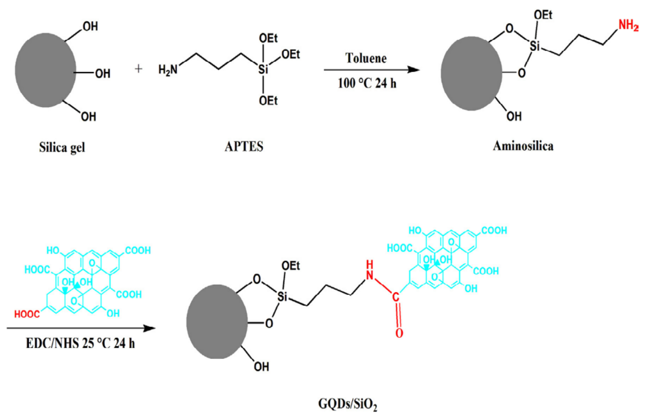

Figure 3: Synthetic process of GQDs bonded silica stationary phase [19].

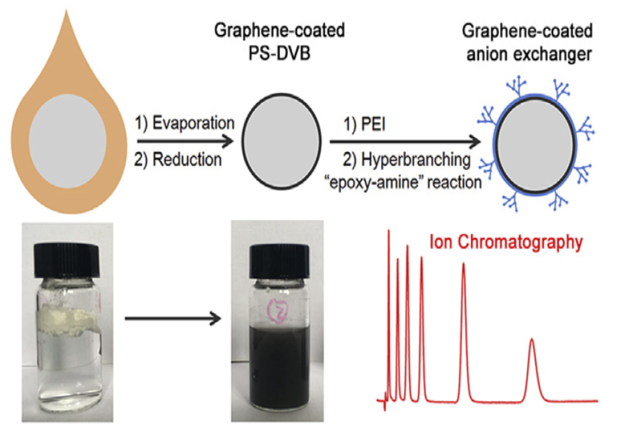

Figure 4: Schematic diagram of fabrication course of graphene-coated polymeric column and used for ion chromatography analysis [20].

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