Application of graphene in analytical sample preparation

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As a new member of the carbon family, graphene has fascinated the scientific community since its discovery. Recently, graphene also exhibited great potential to be an adsorbent in analytical sample preparation due to its exceptional properties (e.g., large surface area, π-electron-rich structure, and good thermal and chemical stability).

In this article, we review the recent applications of graphene and graphene-based materials in solid-phase extraction and solid-phase microextraction, and other sample-preparation techniques. We also cover the use of graphene as extractor and matrix in matrix-assisted laser desorption/ionization mass spectrometry.

Finally, we discuss possible challenges and future perspectives in this rapidly developing field.

Keywords: Adsorbent; Extractor; Graphene; Graphene-based material; Graphene oxide (GO); Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS); Matrix solid-phase dispersion (MSPD); Sample preparation; Solid-phase extraction (SPE); Solid-phase microextraction (SPME)

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1. Introduction

New discoveries in materials science may provide new tools for analytical sample preparation. A great example is the wide use of carbon nanomaterials in solid-phase extraction (SPE) and solid-phase microextraction (SPME). Carbon nanomaterials comprise a wide range of allotropic forms of carbon, including graphite nanofibers, nanodiamond, fullerenes, and carbon nanotubes (CNTs). They can be used as new sorbent materials for sample clean-up and preconcentration.

Taking fullerenes as an example, they were discovered in 1985, and have been applied as sorbents for on-line SPE of various compounds since 1994 [1]. Due to the large surface area, these nano-sized materials could yield high preconcentration factor and good selectivity [1–3]. CNTs were discovered in 1991, and soon attracted more research interest than fullerenes. Since the first report that used multi-walled CNTs (MWCNTs) in SPE in 2003 [4], the applications of CNTs in sample preparation have greatly increase in recent years [5–8]. The primary advantages of CNTs as sorbent materials are their large surface area, ability to establish π-π interactions, and excellent chemical, mechanical and thermal stability. Furthermore, the selectivity of extraction can be tuned by covalently or non-covalently functionalizing the surface of CNTs. CNTs can also be immobilized onto a solid support (e.g., silica and steel) to fabricate SPME devices. These features give CNTs excellent extraction performance for a large range of analytes.

Graphene is a new allotropic member of carbon. Since the direct observation and characterization of a mechanically exfoliated monolayer graphene by Novoselov et al. in 2004 [9], it has sparked exponential growth of research in scientific and engineering communities. This two-dimensional single-atom-thick carbon sheet with a hexagonal, packed-lattice structure has shown many exceptional properties (e.g., large surface area, fast carrier mobility, excellent optical transparency, high values of Young's modulus, fracture strength, and thermal conductivity), and fascinating transport phenomena (e.g., quantum Hall effect and ambipolar electric field effect). By virtue of these attractive properties, graphene has inspired many applications in a variety of fields, including clean energy devices, electronics, catalysis, sensors, reinforced composites and biomedicine [10–12].

Although scientists have realized that graphene is a promising sorbent material

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in theory [13,14], the attention paid to the sorbent application of graphene has been much less than other applications. Only in the past two years has the situation begun to change and a series of works reported the use of pristine or modified graphenes as highly efficient sorbent materials in analytical extraction and removal of pollutants from aqueous solutions [15–17]. It is common to treat graphene as the parent form of graphite, fullerenes and CNTs, due to the similarity in chemical structure [18]. For example, single-walled CNTs (SWCNTs) can be considered as a graphene sheet in the shape of a cylinder, so the advantages of CNTs as adsorbents should come from graphene. In analytical sample preparation, graphene is even more exciting than CNTs and other carbon allotropes for the following reasons.

- Graphene has a very large specific surface area {theoretical value 2630 m^2/g [19]}, suggesting a high adsorption capacity. Such a large surface area is thanks to the unique nanosheet morphology of graphene, for both surfaces of the planar sheet are accessible for molecule adsorption. For CNTs and fullerenes, the inner walls are usually not responsible for the adsorption due to steric hindrance. Furthermore, the nanosheet structure of graphene is also conducive to fast adsorption equilibrium and analyte elution.
- A significant advantage of graphene over CNTs and fullerenes is that graphene can be synthesized by simple chemical methods without special devices from a very common and cheap raw material – graphite [20]. In other words, graphene can be readily obtained in most chemical laboratories. This greatly promotes its wide application and also makes possible large-scale production of graphene at low cost.
- It has been well-documented that CNTs inevitably contain a large amount of residual metallic impurities from the metal catalysts used in synthesis. These metallic impurities are practically impossible to remove and may negatively influence applications [21]. However, graphene can be synthesized from graphite without using metal catalysts, so it is easier to obtain cleaner material {Note: in this case, the purity of graphene greatly depends on the quality of the graphite used [22]}.
- The large delocalized π-electron system of graphene can provide a strong affinity for carbon-based ring structures, which are ubiquitous in drugs, pollutants and biomolecules. For other types of analytes, graphene can provide plenty of sites for functional modification to manipulate the selectivity due to its large surface area. Furthermore, graphene is very easy to be chemically functionalized through graphene oxide (GO), which is the precursor of graphene in chemical synthesis and possesses many reactive groups [23].
- Graphene sheets are relatively soft and flexible so they can be attached onto a support more easily than CNTs and fullerenes. This feature is very useful in preparing composite adsorbents and fabricating SPME devices.

From the above points, it is apparent that graphene could replace CNTs as a superior adsorbent or provide better composite adsorbents. In this review, we focus on recent applications of graphene and graphene-based materials in SPE, SPME and other sample-preparation techniques. We discuss future perspectives and possible challenges in this rapidly developing field.

2. Synthesis and characterization of graphene

Prior to realizing the applications of graphene, it is necessary to discuss its synthesis because the methods of synthesis can seriously influence the nature of graphene.

The first successful method to produce single-layer or few-layer graphene was mechanical exfoliation of graphite by Scotch tape [9]. This method can produce graphene of high quality, but its yield is extremely low and the process is difficult to control.

Scientists then made great efforts to develop methods for synthesizing graphene by following the methods for CNTs {e.g., chemical-vapor deposition (CVD), epitaxial growth, arc discharge, and substrate-free gas-phase synthesis [10,24]}. However, these methods have several problems:

(1) first, they usually require high temperature, high-quality substrates and precise temperature control, which are unfavorable for large-scale production;
(2) second, as stated above, the large amounts of metal catalysts that must be used and left in the products may affect the subsequent applications; and,
(3) third, the very strong hydrophobic property of as-prepared graphene makes it prone to agglomerate or re-stack into graphite in solutions that may decrease the specific surface area and hinder the effective elution of analytes, so it is very important to prevent graphene aggregation in solution because many unique properties of graphene are associated only with individual sheets.

Among current methods of producing graphene, chemical synthesis from graphite has been shown to be one of the most efficient methods for low-cost, large-scale production [20]. It usually involves oxidation of natural graphite, subsequent exfoliation into individual GO sheets by sonication, and final reduction to form so-called chemically-converted graphene (CCG). Fig. 1A shows the typical procedures.

The most frequently used reductant for GO is hydrazine. However, some other low-toxicity and environmentally-friendly reductants have also been proposed (e.g., NaBH, ascorbic acid, and iron powder) [25]. This