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Applications of nanoparticle-modified stationary phases in capillary electrochromatography

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ABSTRACT

Nanoparticles, novel materials with considerable potential in various applications, have made a significant contribution to the development of stationary phases in chromatography. In capillary electrochromatography (CEC), the process for creating stationary phases has a substantial effect on separation performance. Due to their extraordinary properties, nanoparticles (NPs) can generally improve the separation selectivity, the column efficiency and the chemical stability of CEC.

This review focuses on the latest applications and achievements of immobilizing NPs in stationary phases for CEC. For each type of NP, we describe different immobilization strategies, including physical adsorption on surfaces, covalent bonding and other methods. Also, we present more practical applications based on functional post-modifications of the stationary phase containing NPs. Further, we discuss potential directions and issues worth exploring for novel stationary phases containing NPs.

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1. Introduction

Nanoparticles (NPs) have sizes in the range 1–100 nm in at least one dimension. It is known that very subtle variations in size and shape have profound effects on the physicochemical properties and behaviors of molecules. When approaching the nm-size range, the intrinsic properties of NPs can dramatically change, sometimes in

an unexpected manner [1]. The performance of NPs is quite different from that of bulk materials with the same composition (e.g., NPs exhibit the small size effect, the special surface effect, the quantum size effect and the quantum tunnel effect, which place NPs and nanostructured materials at the frontier of science, with uses in catalysts, semiconductors, cosmetics, microextraction and drug carriers, among others) [2–6].

The utility of nanoscale materials in analytical chemistry due to their unique size-related features was first suggested almost 30 years ago [7]. As demonstrated by Zhang et al. [8], the addition of NPs provided unique opportunities for substantially enhancing

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selectivity, efficiency and stability of separations. The large surface area of NPs provides a platform for attaching a large number of functionalities, which are required for separations depending on interactive separation modes.

To date, accompanying the trends of instrument miniaturization and integration, increasing numbers of studies have been devoted to the applications of NPs in micro-column separation [8]. Capillary electrochromatography (CEC) has become a very active and rapidly developing technique in analysis and separation science since Jorgenson [9] first reported the separation of polycyclic aromatic hydrocarbons (PAHs) on CEC. As a hybrid technique that combines high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE), CEC possesses high separation efficiency with an electroosmotic flow (EOF) generated by an applied electric field [10]. In addition, CEC is capable of analyzing both neutral and charged solutes. Furthermore, CEC has the advantages of requiring small amounts of samples and chemical reagents, potentially higher peak capacities, shorter analysis times [11] and inherent compatibility with mass spectrometric (MS) detection [12].

NPs have been introduced to all types of stationary phases in CEC, including pseudostationary phase (PSP)-CEC, packed CEC, open-tubular CEC and monolithic column CEC. The NPs used for PSPs were developed first and rapidly in the CEC system. Nilsson and Nilsson [13] reported that various NPs as PSPs could be continuously replaced and eliminated stationary phase carry-over effects, which simplified the analysis of complex samples. This approach provides a new type of additive in CEC. However, one of the difficulties in NP-based PSP-CEC is the requirement to form a stable, uniform suspension of NPs in the electrolyte. Another limitation is the negative effect of NPs on detection. To overcome the drawbacks and to enhance the stability of the stationary phase, NPs can be immobilized on the capillaries to obtain a stable stationary phase, which improves column selectivity, efficiency, mechanical strength and even chemical stability.

In the past decade, some reviews [14–17] have presented the developments in applying NPs to the stationary phase for CEC from different perspectives. In these recent reviews, the applications of NP-modified stationary phases in CEC were just mentioned partly, and were scattered around the whole articles. To date, there is no specific summary on NP-modified stationary phases in CEC.

Last year, Nesterenko et al. [18] reviewed the latest developments and applications of nanomaterials in stationary phases for various modes of high-performance liquid chromatography (HPLC). The strategies for synthesis and immobilization of the new composite phases in LC were summarized according to the nature of each kind of nanomaterial. Due to the distinction of the stationary phases for LC and CEC, the NP-modification process makes a great difference to the type of the stationary phases. This review is therefore aimed at developments and recent progress in stationary phases containing NPs in CEC. In an attempt to interpret the advantages imparted by the NPs on the stationary phases, the immobilization strategies are demonstrated in three sections (i.e., physical adsorption, covalent bonding and other methods). Also, based on the particle size, the charge and the surface characteristics of NPs, the NP-modified stationary phases can be post-modified by functional groups to enhance the separation performance of specific analytes in CEC. We discuss the related functional groups and specific approaches to modification. Tables 1 and 2 show all the uses of NP-modified stationary phases in CEC.

2. Types of nanoparticle

A variety of NPs, such as carbon nanomaterials, silica nanomaterials, metallic and metal-oxide nanomaterials, and polymer NPs, have been increasingly applied in analytical science. Clearly, NPs with different structures require different treatments.

Consequently, the strategies for immobilizing NPs in modified stationary phases in CEC should be based on the physical or chemical properties of the specific NPs.

In recent years, a large number of allotropic carbon-based NPs were described in the literature, including nanodiamonds, fullerene C60, carbon nanotubes (CNTs), carbon nanohorns, graphene, peapods (fullerenes encased in single-walled CNTs), carbon nanofibers and nanotube rings. However, from the micro-analytical viewpoint, the various immobilization methods have been primarily limited to CNTs and graphene. The configuration of a layer of sp²-bonded carbon atoms shows high mechanical strength, high elasticity and high thermal conductivity [19], whereas, in practical applications, strong van der Waals forces significantly hamper the dispersion and the solubility of carbon-based NPs. Moreover, the parent structure of graphene sheets is hydrophobic and inherently has weak reactivity, which is unfavorable for carbon-based NPs reacted with the stationary phase. To overcome the insolubility and to improve the reactivity, different pretreatments have been proposed. The most commonly applied treatment is modifying the carbon nanomaterials through oxidation. Graphene oxide (GO) is a chemically-modified graphene sheet with a large aromatic macromolecule, which contains reactive oxygen functional groups, such as epoxide, hydroxyl, and carboxylic acid, on its basal planes and edges [20]. The reactive oxygen imparts GO with the potential to be stabilized as a stationary phase in CEC via covalent and non-covalent bonding. Analogously, oxidation of CNTs with, e.g., a mixture of sulfuric and nitric acid can lead to surface functionalization with oxygen-containing groups, such as carboxyl and hydroxyl moieties, paving the way for covalent sidewall connection of other molecules. [21]

Gold NPs (GNPs) are another type of NP widely used in CEC, and are among the promising NPs because of their availability, stability, and compatibility with biomolecules [22]. The surfaces of GNPs can be easily modified by taking advantage of the high affinity between gold and thiol ligands [23,24], providing a broad prospect of covalently bonding GNPs on the inner wall of capillaries or monoliths.

Silica is the most commonly used and original matrix of chromatographic stationary phases due to its great adsorptivity and easy of modification with functional groups. In CEC, silica particles can be packed into the capillaries to prepare micro packed columns [25,26]. However, the capillary packed column was not developed rapidly due to the high pressure caused by small size. To avoid this problem, another form of the silica particle, silica-based NPs, can be incorporated into some suitable stationary phases for CEC. The main characteristic of this type of NP is that the skeletons are based on silicane and siloxane, which can be flexibly modified and can be used to develop a hybrid matrix along with organic monomers.

Furthermore, the relationship between the properties and the immobilization methods of other NPs, which are specific to only them and cannot be described as a certain category, is not given in the general discussion in this review but is introduced when the first appearing.

3. Immobilization strategies

3.1. Physical adsorption

Some NPs are immobilized on the inner face of the capillary through electrostatic interactions with a medium with electric charges opposite to the charges of the NPs. Kitagawa et al. [27] immobilized home-made cinchonidine nanocrystals onto the inner surface of a fused-silica capillary for enantioseparation based on the electrostatic attraction between cationic poly(diallyldimethylammonium chloride) (PDDAC) and the negatively-charged organic nanocrystals. As a result, DNB-DL-Leu and DL-Phe were baseline separated by the column-adsorbed cinchona alkaloids, one category of chiral selectors. Similarly, PDDAC was

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