



The polystyrene-divinylbenzene stationary phase hybridized with oxidized nanodiamonds for liquid chromatography



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ABSTRACT

A novel polystyrene-divinylbenzene microspheres hybridized with oxidized nanodiamonds (PS-DVB-OND) was synthesized by the method of seed swelling and polymerization. The oxidized nanodiamonds (OND) were characterized by Fourier transform infrared (FTIR) spectra, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), X-ray diffraction (XRD). PS-DVB-OND particles were characterized by scanning electron microscopy (SEM) and transmission electron microscope (TEM). The result suggested that OND were successfully embedded into the polymer microspheres with the diameter of $6 \pm 2 \mu\text{m}$. Compared to polystyrene-divinylbenzene (PS-DVB) microspheres, PS-DVB-OND microspheres could tolerate higher pressure. The PS-DVB-OND microspheres were used as stationary phase of reversed-phase liquid chromatography directly and anion-exchangers after further quaternized with methylamine and 1,4-butanediol diglycidyl ether. Reversed-phase liquid chromatographic performance of PS-DVB-OND beads was investigated through separating six benzenes such as toluene, benzaldehyde, phenol, benzoic acid, 1,4-hydroquinone and methyl p-hydroxybenzoate. Inorganic anions such as F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} and SO_4^{2-} , were baseline separated on the anion exchangers of PS-DVB-OND microspheres. The result suggested that the prepared PS-DVB-OND microspheres have the potential as liquid chromatographic stationary phase under high pressure and extremely pH conditions.

1. Introduction

In recent years, considerable advances have been made in designing novel stationary phase for liquid chromatography, in order to improve the rapidity of analysis, sensitivity and resolution of separations. As is known to everyone, silica usually was given preference to utilize in liquid chromatography as stationary phase due to the high mechanical stability, flexibility of chemical modification on its surface and good chromatographic characteristics. However, the drawback of silica-based stationary phase is still obvious, especially easy to hydrolyze at condition with extremely pH. In order to overcome the weakness, many different methods were introduced, for example, prolonging organosilane chain with alkyl groups or coating polymer on the surface of silica [1,2]. Although these approaches could improve the chemical stability of stationary phase at a certain extent, there are still some limits in their application. Therefore, novel materials with good chromatographic characteristics were still drawn the attention of researchers.

Traditionally, organic polymers were the alternative substrates as stationary phase of liquid chromatography for they can tolerate a wide pH range. The most prevalent organic polymers applied to liquid

chromatography are polystyrene-divinylbenzene (PS-DVB), poly(methacrylates) and poly(vinylalcohol) [3]. However, the mechanical strength of pure organic polymers is not satisfied when it comes to the ultra high pressure condition. Therefore, organic-inorganic hybridization was considered to be a practical method to prepare materials with high chemical stability and good mechanical strength. In this study, nanodiamonds as the three-dimensional nanomaterials were selected as the hybridized substance, referring to the “concrete model” with organic polymers as “binding material” and nanomaterials as “support material”.

Nanodiamonds have many beneficial properties which have been used in different areas of nanotechnology. The key factors of diamond-related materials which used as a special separation material in liquid chromatography attracting researchers are their chemical inertness and stability and high hardness [4]. These superior properties make diamond-related materials become a prospective stationary phase for rapid separation of analysis. However, bare diamond does not satisfy the requirements of separation, because there are less functional sites on the surface of diamond although it has a complex chemistry surface. Especially, the anomalous shape of diamond would decrease the column efficiency.

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Therefore, there were many literatures exploiting the methods of modifying diamond and investigating the chromatographic performance of diamond-related materials. The early literature about diamond which used as stationary phase for liquid chromatography was reported by Telepchak [5] in 1973. Natural diamond was used as packing material to separate benzene and anthracene, in order to reveal the mechanism of reverse phase liquid-solid chromatography. Unfortunately, the column efficiency was very poor. Nesterenko et al. [6] made a lot of efforts in the application of diamond for stationary phase of liquid chromatography. Microdispersed sintered nanodiamonds (MSDNs) were used as stationary phase for HPLC to separate aromatic hydrocarbons. Although the results demonstrated MSDNs were capable of separating some derivatives of benzene, there was still great space to be improved. By the utilization of the similar materials in ref [7], cation separation ability of MSDNs was investigated through the mixtures of Mg^{2+} , Mn^{2+} , Co^{2+} , Cd^{2+} and other cations. However, tailing peaks were observed distinctly. With the deepening of research, many new methods used to modify diamond were exploited, which made the chromatographic performance of diamond-based stationary phase improved greatly. Pellicular particles with spherical carbon cores and porous nanodiamond/polymer shells were prepared by Wiest et al. [8] for reversed-phase high performance liquid chromatography. The mechanical stability of the particle was enhanced by cross-linking with a mixture of 1,2-epoxyoctadecane and 1,2,7,8-diepoxyctane, simultaneously, the C_{18}/C_8 bonded stationary phase was obtained. The chromatographic performance and stability of this stationary phase was investigated by separating the mixture of phenol and some drugs at extremely conditions. The results showed the cross-linked phase exhibited good stability at condition with pH = 11.3. Diamond as stationary phase of solid-phase extraction (SPE) was proposed by Wiest et al. [9]. There are also other applications of nanodiamonds in electrophoresis [10], gas chromatography [11] and mass spectrometry [12]. To the best of our knowledge, there are no literatures about the applications of polystyrene-divinylbenzene microspheres hybridized with oxidized nanodiamonds for stationary phase of liquid chromatography.

In this work, a novel method was proposed to synthesize stationary phase of liquid chromatography, which comprised of oxidized nanodiamonds and organic polymers. Nanodiamonds were oxidized with the mixture of concentrated sulfuric and nitric acid in order to increase the hydrophilicity. Sequentially, the oxidized nanodiamond was embedded into polystyrene-divinylbenzene through the method of seed swelling and polymerization. Schematic diagram of seed swelling and polymerization was shown in Fig. 1. The mechanical strength of the obtained polystyrene-divinylbenzene microspheres hybridized with oxidized nanodiamonds (PS-DVB-OND) was improved. Finally, PS-DVB-OND microspheres were applied to reversed-phase liquid chromatography directly and anion-exchanger ion chromatography after further quaternized with methylamine and 1,4-butanediol diglycidyl ether.

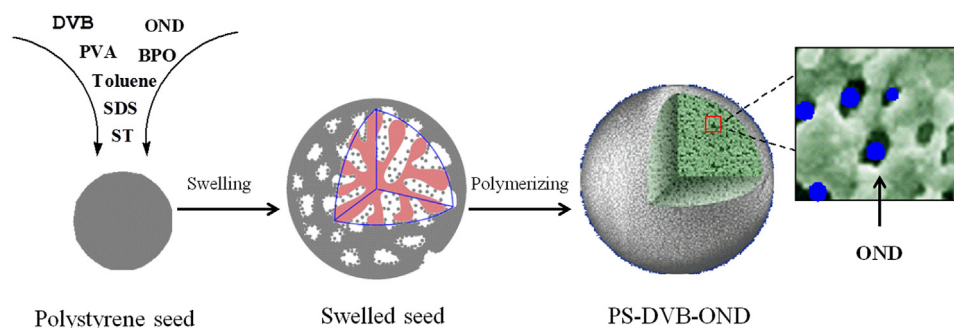


Fig. 1. Schematic diagram of seed swelling and polymerization.

2. Experimental

2.1. Equipment

A HPLC system (Waters Corp., Massachusetts, USA) equipped with a Waters 1525 binary HPLC pump and a Waters 2998 photodiode array detector was employed for reversed-phase liquid chromatography with methyl alcohol and deionized water as eluent. An ICS-1100 Ion Chromatography system (Thermo Fisher Scientific, Agawam, USA) comprised of a dual-piston serial pump, a DS6 heated conductivity detector with an ion suppressor was used for ion chromatography with carbonate/bicarbonate as eluent. The eluent flow rate was generally 1.0 mL/min. Fourier transform infrared (FTIR) spectra were obtained by a Spectrum 100 spectrometer (PerkinElmer, Massachusetts, USA). X-ray photoelectron spectroscopy (XPS) was recorded on an X-ray photoelectron spectrometer (AXIS ultra DLD, Kratos, Japan). Thermogravimetric analysis (TGA) was performed by TG 209F3 (Netzsch, Bavarian, Germany). X-ray diffraction (XRD) was obtained using X'pert Pro diffractometer (PANalytical, Netherlands). The scanning electron microscopy (SEM) images were obtained using a HITACHI S-4700 field emission scanning electron microscope (Hitachi, Tokyo, Japan). Cross-section pictures of the particles were characterized with a JEOL JEM-1200EX transmission electron microscope TEM (Jeol, Japan). The specific surface area and porosity of all the samples were calculated from the nitrogen adsorption-desorption isotherms at $-196^{\circ}C$ with a Micromeritics 3Flex Surface Characterization Analyzer (Georgia, USA). A JY92-ultrasonic disrupter (Scientz Biotechnology Co. Ltd., Ningbo, China) was employed to emulsify organic compounds. A packing pump (RPL-ZD10) utilized in column packing was purchased from DaLian Replete Science and Technology Co., Ltd.

2.2. Reagents

These reagents including methylamine (MA, 40% in H_2O , v/v), 1,4-butanediol diglycidyl ether (BDDE, 60% in H_2O , v/v), styrene (St) (99%), divinylbenzene (DVB)(55%), azobisisobutyronitrile (AIBN), dibutyl phthalate (DBP), sodium dodecylsulfonate (SDS), polyvinylpyrrolidone (PVP, K-30), polyvinyl alcohol (PVA, 1750 ± 50), benzyl peroxide (BPO) were purchased from Aladdin Chemical Co., Ltd. (Shanghai, China). Nitric acid, sulfuric acid, glacial acetic acid and dichloromethane were purchased from LingFeng Chemical Reagent Co., Ltd. (Shanghai, China). Pristine nanodiamonds (PND) (the average diameter about 100 nm) were purchased from Beijing Grish Hitech., Ltd. (Beijing, china). A water purification system (Millipore, Milford, MA, USA) was used to further deionize distilled water for all eluents and sample mixtures. The standard stock solutions of 1000 mg/L of target ions were prepared by dissolving appropriate amount of salts that contained ions of interest into 100 mL deionized water. The methanol solutions of benzenes with the concentration of 1000 mg/L were used to investigate the reversed-phase liquid chromatographic performance.

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