Journal of Chromatography A, 1496 (2017) 133–140

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Graphitic carbon nitride nanofibers in seaweed-like architecture for gas chromatographic separations

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ARTICLE INFO

Article history:
Received 30 October 2016
Received in revised form 1 March 2017
Accepted 19 March 2017
Available online 23 March 2017

Keywords:
Seaweed-like graphitic carbon nitride
Stationary phase
Capillary gas chromatography
Separation performance
Isomers

ABSTRACT

Seaweed-like graphitic carbon nitride (g-C_3N_4) has a unique porous architecture composed of interlocking g-C_3N_4 nanofibers (NF-C_3N_4) with much higher surface area than bulk g-C_3N_4 and shows good potential in separation science. This work investigated the separation performance of NF-C_3N_4 as stationary phase for capillary gas chromatographic (GC) separations. The NF-C_3N_4 column exhibits weak polarity and high column efficiency of 4728 plates/m for *n*-dodecane. Importantly, it displays good separation performance for a wide range of analytes and shows different retention behaviors from the bulk g-C_3N_4 column and commercial HP-5MS column with 5% phenylpolysiloxane. Particularly, it shows high resolving capability for both aliphatic and aromatic isomers. In addition, NF-C_3N_4 column has high thermal stability up to 280 °C and good separation repeatability with relative standard deviation (RSD) values in the range of 0.29–0.61% for intra-day, 0.56–1.1% for inter-day and 2.0–4.9% for between-column, respectively. Moreover, it was applied for the determination of isomer impurities in real samples, showing good potential in GC applications.

1. Introduction

Graphitic carbon nitride (g-C_3N_4), which possesses a unique 2D structure with high in-plane nitrogen content and specific delocalized electronic structure, shows specific photochemical features and high chemical/thermal stability [1,2] and has drawn great attention as a metal-free organocatalyst, mainly focusing on its photo/electrocatalytic performance [1–4]. Recently, beyond catalysis, other applications emerge in sensing, bioimaging and separations [5,6]. In separation science, only limited reports are available and mainly concern employing g-C_3N_4 as the adsorption sorbent for sample pretreament *via* solid-phase microextraction [6], solid-phase extraction [7–9] and others [10]. It shows high extraction ability for deltamethrin, nerolidol, amphetamine, dodecane and ametryn [6], and aromatic organic compounds of diverse variety [7–10]. However, its potential as chromatographic stationary phase is rarely investigated. Up to now, only one report from our research group is available, which utilized g-C_3N_4 for gas chromatographic (GC) separations [11], showing preferential retention for aromatic analytes and high-resolution capability for mixtures of diverse types of analytes, especially some structural and positional isomers such as methylnaphthalenes, dimethylnaphthalenes and alkanes.

Currently, almost all the reports in separation science employ the bulk form of g-C_3N_4, which is usually prepared by direct polycondensation of N-rich precursors and has limited surface area that may restrict its adsorption capability to some extent. To overcome the limitations, g-C_3N_4 nanomaterials with different morphology are reported with significantly enhanced specific surface area [12–15]. Among them, seaweed-like g-C_3N_4 that is composed of interlocking g-C_3N_4 nanofibers (NF-C_3N_4) with porous structures shows greatly improved photochemical performance for hydrogen-evolution [15]. Compared to the bulk g-C_3N_4 with the BET surface area of ca.12 m^2/g, NF-C_3N_4 has over 10-times higher surface area (ca.130 m^2/g) and good dispersibility in water and other solvents. Used as GC stationary phase, NF-C_3N_4 could be expected to exhibit enhanced adsorption capability and improved selectivity over the bulk g-C_3N_4.

Herein, we report the investigation of NF-C_3N_4 as stationary phase for capillary GC separations. NF-C_3N_4 capillary column was statically fabricated and evaluated for its column efficiency, general and average polarity and separation performance in comparison to the bulk g-C_3N_4 column as well as commercial HP-5MS column. Also, the retention mechanism of NF-C_3N_4 stationary phase was elucidated by thermodynamic parameters. After column repeata-

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http://dx.doi.org/10.1016/j.chroma.2017.03.060
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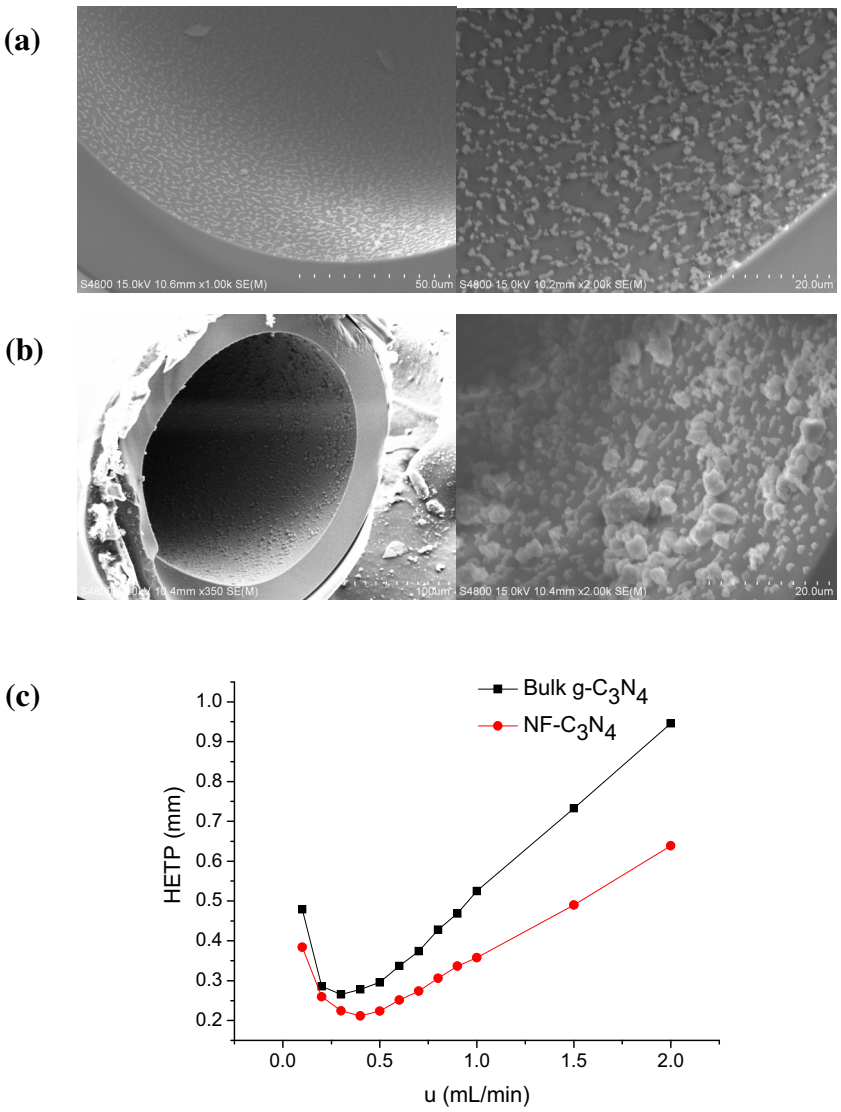

Fig. 1. (a and b) SEM microphotographs showing the cross-section and the coated stationary phase on the inner wall of (a) NF-C_3N_4 capillary column and (b) bulk g-C_3N_4 capillary column; (c) Golay curves of NF-C_3N_4 and bulk g-C_3N_4 capillary columns determined by *n*-dodecane at 120 °C.

bility and thermal stability were examined, NF-C_3N_4 column was applied for the determination of isomer impurities in real reagent samples.

2. Experimental

2.1. Materials and equipment

NF-C_3N_4 was synthesized from the monomer dicyandiamide and characterized according to the method in our previous report [15]. All the analytes used in this work were of analytical grade. *n*-nonane, *n*-undecane, *n*-dodecane, *n*-tridecane, *n*-tetradecane, *n*-pentadecane, benzene, 1-butanol, 1-nitropropane, pyridine, methyl nonanoate, 1-nonanol, methyl decanoate, 1-decanol, methyl undecanoate, 1-undecanol, methyl dodecanoate and 1-dodecanol were purchased from J&K. Scientific. Ltd. (Beijing, China). Cyclohexanone, acetophenone, 1,6-dibromohexane, biphenyl, acenaphthene, phenanthrene, anthracene, diethyl phthalate, dipropyl phthalate and diisobutyl phthalate were purchased from Aladdin Industrial Corp. (Shanghai, China). The rest of the chemicals were purchased from Beijing Chemical Reagent Company (Beijing, China).

Untreated fused-silica capillary tubing (0.25 mm, i.d.) was purchased from Yongnian Optic Fiber Plant (Hebei, China). A HP-5MS capillary column (10 m × 0.25 mm, i.d., 0.25 μm film thickness, 5% phenylmethylpolysiloxane) was purchased from Agilent Technologies (Palo Alto, CA, USA). An Agilent 7890A gas chromatograph equipped with a split/splitless injector, a flame ionization detector (FID) and an autosampler was used for the GC separations. All the separations unless otherwise specified were performed under the following GC conditions: nitrogen (99.999%) were used as the carrier gas at a flow rate of 1 mL/min, injection port temperature at 250 °C, split injection mode at a split ratio of 50:1 and the detector temperature at 300 °C. Scanning electron microscopic (SEM) microphotographs of the fabricated capillary columns were recorded on a Hitachi S4800 microscope (Tokyo, Japan).

2.2. Capillary column fabrication

Prior to coating, a fused-silica capillary column (10 m × 0.25 mm, i.d.) was rinsed with dichloromethane and purged with nitrogen at 200 °C for 2 h and was pretreated with a saturated solution of sodium chloride in methanol for capillary inner surface roughing [16]. Then, the pretreated column was