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In-situ carbonizing of coal pitch on the surface of silica sphere as *quasi*-graphitized carbon stationary phase for liquid chromatography

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ABSTRACT

A novel chromatography stationary phase with a *quasi*-graphitized carbon modified shell has been developed. Coal pitch was directly carbonized on the surface of porous silica with *in-situ* carbonization. The carbonized coal pitch coating exhibits some degree of graphitization with a 78 nm-thick layer on the surface of silica and a 0.5 nm-thick layer on the inner surface of the mesopores. Based on the special structure of the graphitized carbon coating, the novel stationary phase can provide multiple interactions such as hydrophobic interaction, π-π interaction and dipole-dipole interaction. The novel composite material exhibited unique separation selectivity and excellent separation efficiency for polar compounds, including imidazoles, nucleosides and pesticides. Besides, the packed column also exhibited great repeatability with the RSDs of the retention time of nucleosides between 0.07%-0.50% ($n = 5$). Finally, satisfied result was achieved in the separation of fullerenes on the new column, suggesting the great potential in the industrial-scale purification of fullerenes.

Owing to the excellent chemical stability, wide pH tolerance range and high adsorption capacity [1], carbon materials have been widely used in the fields of gas storage [2], chemical sensing [3] and catalysis [4]. Since HalÁSz [5] first used graphited carbon black (GCB) as a stationary phase for gas chromatography in 1963, carbon materials have received increasing attention due to their unique separation selectivity. Recently, a variety of novel carbon materials have been developed as the chromatography stationary phase, such as graphene [6–8], graphene oxide [9–11], carbon nanotubes [12–14] and carbon dots [15–17]. However, the poor mechanical strength and complicated preparation process of carbon-based materials have limited their applications [18]. Carbon material-silica composites not only retains the high mechanical strength of porous silica, but also inherits its pore structure and large specific surface area, becoming an important strategy for preparing carbon material stationary phase [19]. The combination of carbon materials with silicon can prepare the novel stationary phase with high mechanical strength and unique separation selectivity, which is of great significance in the separation of complex samples. Yu *et al.* [20] prepared a novel π-conjugated polymer modified porous silica as adsorbent. Due to the existing of large conjugate structure and rich polar groups on the amorphous carbon, the composites can provide efficient interactions with quaternary ammonium alkaloids. Hu *et al.* [21] synthesized a novel mixed-mode polymer-grafted column by the copolymerization of 1,5-dihydroxynaphthalene and 1,3,5-trioxane in a simple solvent on NH_2-modified silica. The new column can be used in HILIC as well as RPLC to separate various polar and non-polar compounds. Qiu's group [22–26] has prepared a series of carbon dots/silica composite stationary phases with different properties by a chemical bonding strategy, the newly stationary phases show special selectivity and excellent separation performance for polar analytes. However, this strategy of bonding pre-prepared carbon materials to silicas is complicated and difficult due to the steric hindrance.

Herein, we developed a novel silica composite chromatography stationary with a *quasi*-graphitized carbon modified shell by *in-situ* carbonizing of coal pitch (SiO_2@CTP) (the scheme for the synthesis of the SiO_2@CTP was shown in Fig. S1 in Supporting information). Coal pitch was used as the carbon source. Since the strongly hydrophobic of coal pitch has an extremely poor moistening effect on the silica particles, the surface of the silica must be hydrophobically modified to ensure the uniformity of the coal pitch coating. Then the SiO_2@CTP was prepared by *in situ* carbonization of coal pitch coated on porous silica (more details were described in Supporting information). The scanning electron microscope (SEM)

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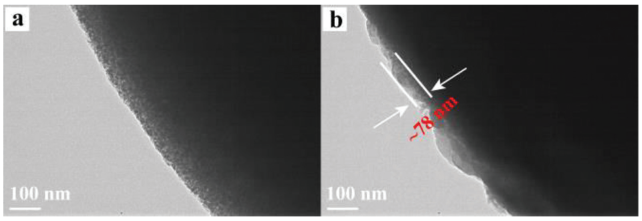

Fig. 1. The TEM images of (a) bare silica, (b) SiO_2@CTP.

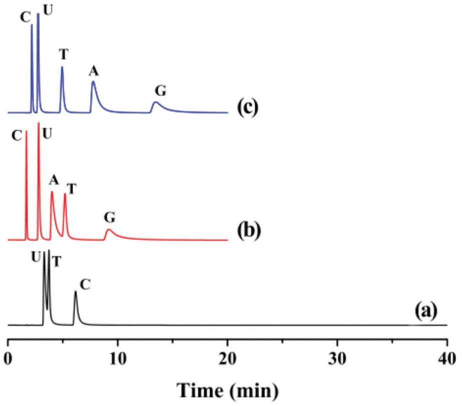

Fig. 2. Separation of nucleobases on SiO_2@CTP packed column. Chromatographic conditions: column size: 4.6 mm*150 mm; flow rate: 1 mL/min; column temperature: 25 °C; detection wavelength: UV 254 nm; mobile phase: (a) acetonitrile/water, (b) acetonitrile/0.1% TFA, (c) acetonitrile/0.5% TFA; isocratic elution: 15% acetonitrile. Analytes: C: cytosine, U: uracil, T: thymine, A: adenine, G: guanine.

images showed that the surface of the silica particles became obviously rough after carbonization (Fig. S2 in Supporting information). The transmission electron microscopy (TEM) images showed that the coating thickness is about 78 nm (Fig. 1). Nitrogen adsorption and desorption isotherms and pore distribution measurement (Fig. S3 in Supporting information) further recognized that the average pore size of the silica particles decreased from 11.6 nm to 10.6 nm after carbonization, indicating that the coal pitch was also coated to the pore surface of the silica microspheres with a thickness of about 0.5 nm. Besides, the specific surface area was 243.6 m^2/g, which meets the requirements of chromatographic stationary phases. The elemental composition and chemical status on the surface of SiO_2@CTP was characterized by XPS. The characteristic peaks of O 1s, C 1s, Si 2p were observed (Fig. S4 in Supporting information), which might be ascribed to the successful modification of *quasi*-graphitized carbon. In the Raman spectrogram, the D peak represents the defects in the lattice of C atoms, while the G peak represents the in-plane stretching vibration of the sp2 hybridized C atoms. As seen from Fig. S5 (Supporting information), when the coating time increased from 2 h to 12 h, the intensity of G peak in SiO_2@CTP significantly increased and the ratio of the intensity of D peak to G peak (I_D/I_G) decreased from 0.968 to 0.883, which indicated that the material has a certain degree of graphitization. Additionally, there was a broad peak between 20° and 40° in XRD pattern (Fig. S6 in Supporting information), which indicated that the material was amorphous with no fine structure. After smoothing the XRD diffraction peaks, the degree of graphitization was calculated to be about 37%. The above characterization results demonstrated that SiO_2@CTP was successfully synthesized.

To evaluate the chromatographic separation performance of the SiO_2@CTP column, various compounds were selected as probe molecules. As shown in Fig. S7A (Supporting information), three strongly polar imidazoles achieved baseline separation on SiO_2@CTP column, and the elution order was imidazole-2-carboxaldehyde (log *p*, −0.329), imidazole (log *p*, −0.038) and 2-methylimidazole (log *p*, 0.198), which was consistent with their hydrophobicity. However, due to the high hydrophilicity, they could not be separated by conventional RPLC (Fig. S7B in Supporting information). Graphitized carbon has a special planar two-dimensional structure, and sp2-hybridized carbon atoms can form a large-scale delocalized π electron cloud of conjugated structure, which can provide strong π-π interactions for solute molecules. Meanwhile, the large delocalized π electron cloud endows its surface with high polarizability, which can act as both electron donor and electron acceptor [18]. The surface of stationary phase is easily polarized and can provide dipole-dipole interaction with polar solute molecules due to charge-induced effects, thus showing excellent separation of polar compounds. However, the strong π-π interaction can result in the peak tailing of some aromatic compounds such as alkylbenzenes and halogenated benzenes (Fig. S8 in Supporting information). So the SiO_2@CTP column is more suitable for the analysis of compounds without benzene ring structure. As can be seen in Fig. 2, the selectivity of the SiO_2@CTP column can be conveniently adjusted by adding TFA into the mobile phase. Because TFA is a kind of strong acid and positively charged after dissociation. On one hand, it can interact with polarized *quasi*-graphitized carbon stationary phases to weaken the dipole-dipole interaction between the stationary phase and the polar compounds. On the other hand, the excess TFA will form ion pair with the basic compounds such as G and A, thus resulting in enhancing their retention on the SiO_2@CTP column. The *k*' (capacity factor) values of five nucleosides showed 'U' shape relationship with the content of acetonitrile in the mobile phase, which indicated existence of HILIC/RP mixed retention mechanism (Fig. S9 in Supporting information). Fast baseline separation of five nucleosides can be achieved both in RPLC and HILIC modes (Fig. S10 in Supporting information). Additionally, the RSDs of the retention time for all the nucleosides were in the range of 0.07%−0.50% ($n = 5$, Table S1 in Supporting information), indicating a good repeatability of the column (Fig. S11 in Supporting information). After used for 2000 column bed volumes, no significant change in the surface morphology of packing material was observed (Fig. S12 in Supporting information). Furthermore, the separation performance of three batches of SiO_2@CTP packed columns was comparable (Fig. S13 in Supporting information). Therefore, the above results demonstrated the excellent structural stability of the stationary phase and the reproducibility of the synthesis process.

Furthermore, the chromatographic selectivity of SiO_2@CTP column was evaluated with eight pesticides (chemical structures of 8 pesticides were shown in Fig. S14 in Supporting information) and compared with C18 column. As the results shown in Fig. 3, all the peaks showed different degrees of tailing on the SiO_2@CTP column, and the elution order was different from that on C18. It is well known that the separation of analytes on C18 column merely depends on the hydrophobic interaction with the stationary phase. While the SiO_2@CTP column can provide π-π interaction, dipole-dipole interaction in addition to hydrophobic interaction, the multiple retention mechanism endows SiO_2@CTP column with unique selectivity. The addition of the electron modifier TFA significantly weakened the retention of some weakly conjugated solutes, while had minor effects on the trailing solutes, which further confirmed that the TFA weakened the charge-induced polar interactions but had little effect on the π-π interaction.

Fullerenes are a class of spherical or ellipsoidal molecules with large delocalized π bonds [27]. Due to their special structures and unique properties, fullerenes have been widely applied in many fields, in which C_{60} and C_{70} are the two most studied components [28–30]. However, the current commercial packing materials for fullerene separation are scarce and expensive, which limits the development of fullerenes. Therefore, developing effective

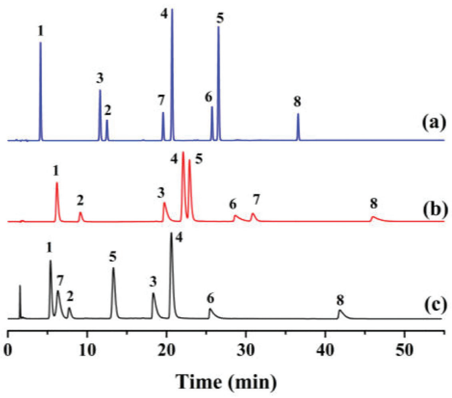

Fig. 3. Separation of 8 pesticides on (a) C18 and (b, c) SiO_2@CTP packed columns. Chromatographic conditions: detection wavelength: 214 nm; mobile phase: (a, b) A: water, B: acetonitrile, (c) A: 0.1% TFA, B: acetonitrile; gradient elution: 0–5–40–55 min (20%−20%−100%−100% B). Other conditions are same as in Fig. 2.

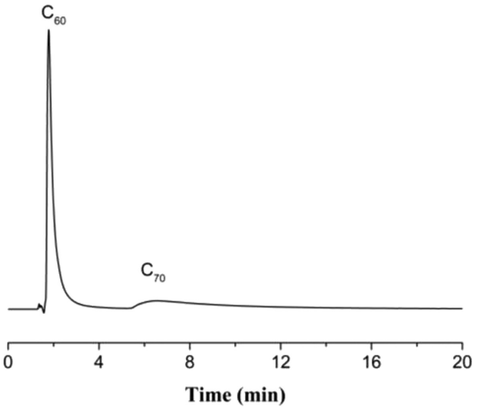

Fig. 4. Separation of C_{60} and C_{70} on SiO_2@CTP packed column. Chromatographic conditions: detection wavelength: 310 nm, mobile phase: *o*-dichlorobenzene/acetonitrile = 90/10. Other conditions are same as in Fig. 2.

methods for analysis and purification of fullerenes has always been a significant and challenging work. Considering the strong π-π interactions of the SiO_2@CTP, it is a good candidate for the separation of fullerenes. As shown in Fig. 4, the baseline separation of C_{60} and C_{70} was achieved within 5 min under isocratic elution. The separation of fullerenes on the SiO_2@CTP were attributed to multiple interactions, such as hydrophobic interactions, π-π interactions and dipole-dipole interactions. In our previous work [31,32], poly(pentabromostyrene) silica composite and COF-rLZU1 silica composite also successfully applied to separation of fullerenes. Compared to the previous works, the SiO_2@CTP can provide stronger π-π interaction to achieve a comparable separation by using high concentration of *o*-dichlorobenzene as the mobile phase, which has a good solubility for C_{60} up to 24 mg/mL. Consequently, the SiO_2@CTP column has great potential for industrial-scale preparation of fullerenes.

In summary, a *quasi*-graphitized carbon silica composite stationary phase was prepared by *in-situ* carbonization strategy with coal pitch as carbon source. The preparation process was simple and fast. The prepared SiO_2@CTP can provide multiple interactions with solute molecules, including π-π, hydrophobic and dipole-dipole interaction. Besides, the newly SiO_2@CTP column has HILIC/RPLC retention mechanism, its separation selectivity can be conveniently adjusted by the addition of TFA to the mobile phase. The newly prepared stationary phase has great potential in the industrial-scale purification of fullerenes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.108024.

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