Open-tubular Capillary Electrochromatography with Janus Structured Au-Fe₃O₄ Nanoparticles Coating as Stationary Phase

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A novel Au-Fe₃O₄ nanoparticles-based capillary column was fabricated by magnetic approach for open-tubular capillary electrochromatography (OT-CEC). The bifunctional dumbbell-like Janus Au-Fe₃O₄ nanoparticles (Au-Fe₃O₄ NPs) were prepared through a hydrothermal synthesis strategy, and the morphology was characterized by transmission electron microscopy (TEM). Multilayers Au-Fe₃O₄ NPs were easily coated onto the inner surface of silica capillary by an external magnetic field to generate an Au-Fe₃O₄ NPs-based column. Compared with a bare capillary, the modified surface exhibited more stable and suppressed electroosmotic mobility. The column showed good separation efficiency for neutral analytes in the OT-CEC separation mode, with theoretical plate numbers of up to 79705 per meter for naphthalene. The successful separation of dihydroxy benzene isomers and proteins demonstrated that the column exhibits a reasonable separation performance. The reproducibility of the Au-Fe₃O₄ NPs capillary was studied, with relative standard deviations (RSD) for day-to-day and column-to-column less than 1 and 1.75%, respectively.

Keywords Au-Fe₃O₄ NPs, stationary phase, OT-CEC

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Introduction

Capillary electrochromatography (CEC), combining the high efficiency of CE and the high selectivity of HPLC, has emerged as a powerful technique in the separation field during the past decade.1,2 An open-tubular (OT) column, one type of columns in CEC, is a comparatively simple one because of easy preparation, the absence of bubble formation, and simple instrumental handling.3 Moreover, it does not require the fabrication of frits and particles packing.4 However, the low phase ratio and sample capacity, due to the limited amount of stationary-phase coating, restrict its wide application in chromatographic separations.5

To date, several modification methods, such as polymer coatings,6 chemical bonding7 porous silica layers,8 etching,9 sol-gel techniques,10,11 and nanoparticle phases12 have been developed to overcome the above-mentioned problems. Among them, nanoparticles (NPs), such as polymer NPs,13 silica NPs,14 carbon NPs,15,16 and metallic NPs,17,18 which create sufficient surface area for separation after their non-covalent or covalent bonding onto the column, encourage a widespread interest of researchers. Compared with other nanoparticles, gold nanoparticles (Au NPs),19 which possess the merits of a high surface area to volume ratio, long-term stability, and easy chemical modification,20,21 were the major coating matrix in recent studies. Rezanka et al.22,23 demonstrated for the first time the utilization of bare Au NPs immobilized on the sol-gel pretreated fused-silica capillary as a stationary phase for the OT-CEC separation of polycyclic aromatic hydrocarbons and peptides. Glennon et al.24 immobilized dodecanethiol gold nanoparticles onto the inner surface of fused-silica capillaries pre-derivatized with (3-aminopropyl)trimethoxysilane. Efficient separation of selected pyrethroid pesticides was obtained, which confirmed the use of dodecanethiol gold nanoparticles as a novel phase for OT-CEC. Qu et al.25 investigated the use of an octadecylamine-capped Au NPs capillary column for bioanalysis. A column efficiency of up to 189000 plates per meter for testosterone was obtained. The stationary phase was stable and the separation performance was unchanged after 60 runs of tested aromatic mixtures. Moreover, Au NPs were employed as pseudo-stationary phase in an Au NPs coated capillary for CEC separation of acidic and basic proteins at low pH, achieving plate numbers as high as 1000000 per meter for lysozyme with good run-to-run reproducibility.26 All of these experimental results confirmed that Au NPs can be used as a promising stationary phase for OT-CEC separation. However, the procedure to prepare an Au NPs modified capillary column is time consuming. In addition, a short column lifetime is still another problem.

In order to overcome these shortcomings, an efficient method of incorporating Au NPs with a magnetic core was proposed. Liang et al.27 presented the first application BSA-conjugated Fe₃O₄@Au NPs as a novel stationary phase of MCE for the efficient separation of chiral amino acids and ofloxacin enantiomers. Bao et al.28 prepared flower-like bifunctional Au-Fe₃O₄ NPs which combined the merits of both Au and
Fe₃O₄ NPs by chemical bond linkage, and used them in protein separation. The size of bifunctional Au-Fe₃O₄ NPs was about 100 nm, though they were too large to enhance the phase ratio and sample capacity due to the limited amount of Au NPs (less than 12% by weight). Janus-structured Au-Fe₃O₄ NPs, other bifunctional NPs, have been synthesized and studied for catalysis, probes, magnetic gene transfection and drug-delivery applications, because of their unique physical and chemical properties induced by the synergetic effect between Au and Fe₃O₄. To the best of our knowledge, there are no reports of using Janus-structured Au-Fe₃O₄ NPs as a stationary phase for electrochromatographic separation in OT-CEC. In this investigation, the Au NPs (~5 nm) were chemically bonded to Fe₃O₄ NP (~11 nm), resulting in Janus-structured Au-Fe₃O₄ NPs; the Au NPs served majorly as a reversed phase stationary phase for OT-CEC, and the Fe₃O₄ NP were responsible for adsorption to the column as a magnetic media. The separation performance of the Au-Fe₃O₄ NPs column for neutral compounds, isomers, and proteins was evaluated. The results demonstrated that the Au-Fe₃O₄ NPs modified column had a good performance in terms of the phase ratio, repeatability and efficiency for the OT-CEC analysis of various analytes, which would greatly broaden the application scope of this novel Janus bifunctional nanomaterial.

### Experimental

#### Reagents and chemicals

Chloroauric acid (HAuCl₄·4H₂O), sodium oleate, 1,2-dihydroxybenzene, 1,3-dihydroxybenzene, 1,4-dihydroxybenzene, avidin, ovotransferin, ovalbumin, ovomucoid, ovoflavoprotein, lysozyme, and oleic acid (OA), oleylamine (OAm) and 1-octadecene (ODE) were obtained from Sigma-Aldrich (St. Louis, MO, USA). FeCl₃ and tert-butylamine borane (TBAB) complex solutions were purchased from Sinopharm Chemical Reagent (Shanghai, China). Analytical-grade thiourea, naphthalene, biphenyl, cyclohexane and HPLC-grade methanol (MeOH) were all purchased from Shanghai Chemical Reagent of Chinese Medicine Group (Shanghai, China). Chicken eggs were obtained from the local market. The egg white was separated from egg yolk, and then diluted with a buffer solution (10 mM sodium phosphate buffer, pH 8.6) in 1:6 ratios and filtered through a 0.22-μm membrane prior to use. All chemicals were used without any further purification. Water used in all experiments was doubly distilled and purified by a MilliQ system (Millipore, Milford, MA, USA). The samples were injected by applying a pressure of 0.5 psi for 5 s.

#### Apparatus

A CE-1000 system (Unimicro (Shanghai) Technologies, Shanghai, China) with a UV detector was used for all experiments. Bare-fused silica capillaries (50 μm i.d., 365 μm o.d.) were obtained from Yongnian Optic Fiber (Hebei, China). The total length of the capillary was 55 cm (20 cm effective length). The temperature of the capillary was maintained at 25°C. A JEM-2100F transmission electron microscope (TEM) (JEOL, Tokyo, Japan) was employed to characterize the nanoparticles.

#### Synthesis of Au NPs

Gold seeds with a diameter of 4 nm were prepared using previously reported procedure with slight modifications. Briefly, 0.1 mmol of HAuCl₄, 4 mL of OAm, and 4 mL of cyclohexane were mixed and magnetically stirred at the desired temperature of 10°C under a gentle stream of nitrogen gas to form a precursor solution. After 0.2 mmol of the TBAB complex was dissolved in 0.4 mL of OAm and 0.4 mL of cyclohexane, the resulting solution was injected into the precursor solution. The color of the solution changed to deep red immediately after injection of the TBAB complex solution. The mixture was aged for 40 min, followed by the addition of 30 mL of ethanol to precipitate Au seeds. The resultant Au seeds were harvested by centrifugation at 10000 rpm for 5 min and then re-dispersed in n-hexane for use. The synthesis achieved nearly a quantitative yield as the solution after NP centrifugation was colorless.

#### Synthesis of Janus Au-Fe₃O₄ NPs

Janus Au-Fe₃O₄ NPs were synthesized using a previously reported procedure with slight modifications. An iron-oleate complex, Fe(OL)₃, was obtained by dissolving ferric chloride and sodium oleate in a mixture containing ethanol, water, and hexane, and then 1 mmol of Fe(OL)₃, 0.1 mmol of Au seeds, 0.5 mmol of OA and 0.5 mmol of OAm were mixed into 5 mL of ODE. The solution was heated to 120°C for 20 min to remove hexane and then refluxed for 30 min at 320°C. After cooling down to room temperature, the hetero-structures were separated by adding ethanol, centrifuged, and re-dispersed into n-hexane.

#### Synthesis of Fe₃O₄ NPs

The Fe₃O₄ NPs were prepared by using the same procedure as described above, except for no addition of Au seeds.

#### Column preparation

The columns were prepared according to references, with only a few practical deviations. Thirty pairs of concentric cylindrical permanent magnets (the flux density of magnets was 1500 GS) were oppositely nipped to the capillary of a 20-cm long column. The first pair of magnets was placed at a distance of 5.5 cm from the inlet of the capillary, and the last pair of magnets was placed at a distance of 4.5 cm from the detection window. Then, 2.0 mg mL⁻¹ of a Janus Au-Fe₃O₄ NPs solution (dispersed in n-hexane) was injected into the capillary from the inlet of capillary at a flow rate of 15 μL min⁻¹ for a variable flushing time. When approaching the magnet zone, the nanoparticles were immobilized onto the inner wall of the capillary to form a layer. After that, uncaptured nanoparticles were moved out of the column by washing with 10 mmol L⁻¹ of a sodium phosphate buffer (pH 7.0) with 45% CH₃OH. The effective length of the nanoparticle coating was 20 cm, and the operation length of capillary (from the inlet to the detection window) was 30 cm with a total length of 55 cm (Scheme 1).

#### Characterization of the Janus structured Au-Fe₃O₄ NPs

The TEM technique was employed to confirm a successful synthesis of the nanoparticles. The photograph in Fig. 1a shows that the well-dispersed Au NPs were spherical with a mean size about 5 nm; and in Fig. 1b the size of Fe₃O₄ NPs was 14 nm. A typical TEM image of Janus nanoparticles in Fig. 1c shows that the size of Au-Fe₃O₄ was about 11 nm and Au NPs was about 4 - 5 nm. The specimens were then analyzed by an energy dispersive spectroscopy (EDS) to reveal their elemental composition (Fig. 1d). The content of the Au NPs was as high as 36.19% in weight, and was abundant to enhance the phase ratio and sample capacity.

#### Optimization of coating time

In the previous experiment, the effect of the concentration of
Au-Fe₃O₄ NPs (1 – 5 mg mL⁻¹), flushing speed (1 – 50 μL min⁻¹) and time on the separation performance were investigated, the flushing speed was fixed at 15 μL min⁻¹ and the concentration of Au-Fe₃O₄ NPs was kept at 2 mg mL⁻¹. The effect of the flushing time on the separation performance was investigated (Fig. 2). Thiourea was chosen as an electroosmotic flow marker. Table 1 shows the data obtained from Fig. 2. The $\mu_{eo}$ values were decreased from $2.94 \times 10^{-4}$ to $1.87 \times 10^{-4}$ cm² V⁻¹ s⁻¹, with the coating time increased from 0 to 15 min. In addition, it can be seen that both the $k$ value and resolution increased significantly with increasing coating time, which indicated that the stationary-phase capacity was enhanced greatly by using this simple coating method. Considering the better resolution and shorter analysis time, we chose 15 min as the best coating time.

**Comparison of columns**

In order to demonstrate the reversed-phase chromatographic retention mechanisms of the Au-Fe₃O₄ NPs as a stationary phase, a test mixture of naphthalene and biphenyl were used, as reported in the literature. Fig. 3 compares the separation performance of three capillaries, denoted as (A) bare capillary, (B) Fe₃O₄ coated column, and (C) Au-Fe₃O₄ coated column. It is obvious that both Fe₃O₄ NPs and Au-Fe₃O₄ NPs coated columns displayed lower electroosmotic flow than the bare silica column, and the Fe₃O₄ NPs-coated column had no separation power for the test mixture. However, naphthalene was separated from biphenyl and thiourea in C, owing to the reversed-phase retention mechanism between the surface of Au-Fe₃O₄ NPs and the aromatic rings.²³

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**Scheme 1** Schematic diagram for the synthesis of Au-Fe₃O₄ NPs and the preparation of Au-Fe₃O₄ NPs based magnetic column.

**Fig. 1** TEM images of the Au NPs (a), Fe₃O₄ NPs (b), Janus structured Au-Fe₃O₄ NPs (c) and (d) EDS image of Au-Fe₃O₄ NPs.

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Repeatability and reproducibility

The run-to-run, day-to-day and column-to-column repeatability of the Au-Fe₃O₄ NPs capillary column was evaluated in terms of the relative standard deviation (RSD) of EOF obtained from replicated runs. The results are listed in Table 2. All RSDs of EOF ranged from 0.34 to 1.75%, indicating good reproducibility.

Separation of dihydroxybenzene isomers

A mixture of three dihydroxybenzene positional isomers (1,2-dihydroxybenzene, pKₐ (9.25, 13); 1,3-dihydroxybenzene, pKₐ (9.2, 10.9); 1,4-dihydroxybenzene, pKₐ (9.9, 11.6) with same molecular weight was chosen as a test sample to investigate the chromatographic performance of the Au-Fe₃O₄-coated column according to references. The separation conditions, such as the voltage, buffer and its concentration, were also optimized. However, we found that the running buffer pH was an important factor affecting the resolution. It is known that Fe₃O₄ NPs are not stable under acidic conditions, so we choose a basic condition for our experiments. As shown in Fig. 4, when the pH was <9.0, 1,3-dihydroxybenzene could be separated from 1,2-dihydroxybenzene gradually, while at pH >9.0, the column efficiency of 1,3-dihydroxybenzene and 1,4-dihydroxybenzene began to decrease from 224842 to 171164 plates/m, and 269422 to 171128 plates/m, respectively. In consideration of the best column efficiency and separation resolution, a buffer solution of pH 9.0 was selected to separate three isomers. Although the exact dihydroxybenzene isomers separation mechanism by OT-CEC using AuNPs has not been clearly established, we mainly speculated on the different position of the –OH group in isomers that had different interactions with the Au surface, especially 1,2-dihydroxybenzene (the ortho-dihydroxy group may form the strongest bond with the empty valency shell of the GNPs). The observed interaction is thus expected to be due to dipole-dipole interactions.

Meanwhile, the coated capillary with Au-Fe₃O₄ NPs and the bare capillary were compared for the separation of three dihydroxybenzene isomers (Supporting Information). While 1,3-dihydroxybenzene and 1,2-dihydroxybenzene were not separated on the bare capillary, the three dihydroxybenzene isomers were separated with the modified column under the same experimental condition.
the egg white was directly injected into the Au-Fe₃O₄ NPs coated capillary. Experimental conditions: capillary, 50 μm i.d. × 20 cm effective length; buffer, 10 mM sodium phosphate buffer pH 8.6; separation voltage, −10 kV; detection, UV@214 nm. Injection, 0.5 psi for 10 s; temperature, 25°C. Peaks: 1, ovotransferrin; 2, ovomucoid; 3, 4, 5, are glycoisoforms of ovalbumin.

Separation of proteins
A real biological sample of egg white was selected to demonstrate the applicability of the Au-Fe₃O₄ NPs column. The component of egg white was dominated by ovalbumin (54%, pI 11.0, MW 43000 Da), and avidin (0.05%, pI 10.0, MW 51600 Da), ovotransferrin (13%, pI 5.16, MW 45000 Da), and lysozyme (3.5%, pI 11.0, MW 14300 Da), and ovalbumin (54%, pI 5.16, MW 43000 Da). After dilution with phosphate buffer and filtration, the egg white was directly injected into the Au-Fe₃O₄ NPs column in phosphate buffer (10 mM, pH 8.6). As shown in Fig. 5, all basic proteins were eluted out within 10 min, which indicates that the adsorption is greatly suppressed by the high-surface coverage of the Au-Fe₃O₄ NPs on the capillary surface. In addition, the Au NPs composite provided a reversed-phase mechanism to interact with the proteins in the analyzed samples. Though the separation efficiencies and resolution of proteins were not very good, with further improvement the Au-Fe₃O₄ NPs coated column performance could be improved, and had the potential to be used for the analysis of complex biological samples.

Conclusions
A capillary modified with Janus structured Au-Fe₃O₄ NPs by a magnetic immobilizing approach was fabricated for OT-CEC. Compared with the conventional physical coating and chemical bonding, the magnetic method greatly simplifies the preparation procedure. With the prepared column, neutral analytes and isomers were separated with satisfactory efficiency and reasonable reproducibility. A real biological sample of egg white was also tried to demonstrate the feasibility of the OT column for protein separation. With further improvement, this novel stationary phase could be used for the analysis of more complicated analytes in OT-CEC.

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Supporting Information
Figure S1: Separation of three dihydroxybenzene isomers with Au-Fe₃O₄ NPs coated column (A) and the bare capillary (B).

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