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Gold Nanoparticle-Modified Etched Capillaries for Open-Tubular Capillary Electrochromatography

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The use of gold nanoparticles in conjunction with etched capillary-based open-tubular capillary electrochromatography (OTCEC) to improve the efficiency of separation and the selectivity between selected solutes is described. The fused-silica capillaries (50-μm i.d.) were etched with ammonium hydrogen difluoride, followed by prederivatization of the new surface with (3-mercaptopropyl)-trimethoxysilane (MPTMS) for the immobilization of dodecanethiol gold nanoparticles, for OTCEC. The electrochromatography of a "reversed-phase" test mixture and of selected polycylic aromatic hydrocarbons was investigated, and efficient separations and high theoretical plate numbers per meter were obtained. The electroosmotic flow characteristics of the etched gold nanoparticle capillary, unetched gold nanoparticle capillary, bare capillary, and etched bare capillary were studied by varying the percentage of organic modifier in buffer, buffer pH, and separation voltage. Optical microscopy and scanning electron microscopy were used to examine the process of etching and modification and the surface features of the etched gold nanoparticle capillary. The results confirm that dodecanethiol gold nanoparticles bonded on the etched inner wall of the fused-silica capillary can provide sufficient solute-bonded phase interactions to obtain OTCEC separations with reproducible retention, as well as characteristic reversed-phase behavior, even with the inner diameter of the capillary of 50 μm.

In the past two decades, nanosized particles have attracted extensive attention in various fields of chemistry, physics, materials, medicine, and optics,[1−4] due to their unique physical and chemical properties, relative to the bulk material.

To date, very little research has been devoted to the application of nanoparticles in separation science, accompanying the trends toward capillary coating and monolithic stationary phases. However, the significant advances, which have been made in electrophoresis and microchip separations, show the promise to enhance separation performance by using nanoparticles. For example, our research group employed latex nanoparticles to coat a micromachined channel on-chip, and on-chip ion chromatography of inorganic anions, nitrate, nitrite, and iodide was demonstrated.[5] Kleindienst et al. used polymer-based nanoparticles to coat fused-silica capillaries and obtained high-resolution capillary electrophoresis of proteins and peptides.[6] Neiman et al. reported on the use of colloidal gold nanoparticles, which were added to the run buffer, for CE separation of toluidines.[7] Fujimoto and Muranaka also described the use of commercially available silica gel nanoparticles as a run buffer additive.[8] Viberg et al. published a novel technique that uses polymer nanoparticles as a pseudo-stationary phase in CEC, with electrospray ionization mass spectrometric detection.[9] The application of gold nanoparticles in conjunction with chip-based electrophoresis to improve selectivity and separation efficiency was also reported by Pumera and coworkers as well as Lin et al.[10,11]

Recently, our group immobilized dodecanethiol gold nanoparticles on prederivatized (3-aminopropyl)trimethoxysilane (APTMS) or (3-mercaptopropyl)trimethoxysilane (MPTMS) fused-silica capillaries, which confirmed the use of dodecanethiol gold nanoparticles as a novel phase for open-tubular capillary electrochromatography (OTCEC).[12] In that work, efficient separation of selected pyrethroid pesticides was obtained by coating a 20-μm-i.d. capillary with APTMS−Au nanoparticles. The dodecanethiol gold capillaries were easier to produce and operate than packed capillaries. However, one significant drawback of the gold nanoparticle-coated capillary is its low loading capacity and high mobile-to-stationary phase ratio since only the inner wall is available as a site for bonding dodecanethiol gold nanoparticles. The theoretical plate number per meter for solutes decreased greatly with increase of the inner diameter of the capillary to 50 μm, although

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it has been demonstrated in a theoretical study that useful electrochromatographic separation might be possible in OTCEC with an inner diameter as great as 50 μm.[13]

To date, several options, such as polymer coatings,[14−15] porous silica layers,[16−17] etching,[18−25] and sol−gel techniques[26−32] have been advanced to overcome the major problems of low sample capacity and high phase ratio associated with OTCEC. The etching method, which can increase the surface area of the inner wall of the capillary by a factor of up to 1000,[33] has proved to be a powerful approach to increase the surface area and interaction between solutes and coated phase. The etching process was first introduced by Onuska et al. for GC and then modified for OT-CEC by Pesek and co-workers.[18−24]

In this work, fused-silica capillary (50-μm i.d.) was etched with ammonium hydrogen difluoride to increase the surface area of the inner wall, before modification of the capillaries with dodecanethiol gold nanoparticles. The electrochromatographic properties of the etched gold nanoparticle capillaries, unetched gold nanoparticle capillaries, bare capillaries, and etched bare capillaries were investigated through variation of the percentage of the organic modifier, pH, and separation voltage. Efficient separations of a "reversed-phase" test mixture and of selected polycylic aromatic hydrocarbons (PAHs) were obtained on etched gold nanoparticle capillaries. The synthesis of dodecanethiol gold nanoparticles and their subsequent immobilization on prederivatized fused-silica capillaries are also detailed, as well as TEM and UV−visible spectroscopic analysis of the synthesized gold nanoparticles.

EXPERIMENTAL SECTION

Chemicals and Materials. HPLC-grade methanol, hexane, chloroform, propan-2-ol, diethyl ether, and acetone were purchased from Sigma (St. Louis, MO). Sodium dihydrogen phosphate and disodium hydrogen phosphate were obtained from Sigma-Aldrich (Poole, U.K.). Phosphoric acid was obtained from J.T. Baker (Deventer, Holland). Thiourea, gold trichloride, tetraoctylammonium bromide (TOAB), 1-dodecanethiol, and sodium borohydride were obtained from Aldrich (Steinheim, Germany). Both biphenyl and naphthalene were purchased from BDH (Poole, U.K.). Fluorene, anthracene, and triphenylene were obtained from Sigma-Aldrich (Fluka, Switzerland). MPTMS and the etching agent (ammonium hydrogen difluoride) were obtained from Aldrich. All water used was Milli-Q grade with a resistivity of 18.2 mΩ cm. Disposable plastic syringes were purchased from Becton Dickinson (Dublin, Ireland). Microtight tubing sleeves, microtight unions, adapters, and PEEK tubing, were also purchased from Sigma-Aldrich. Aqueous filter membranes (0.45 μm) were purchased from Millipore (Cork, Ireland).

Equipment. All capillary electrochromatography (CEC) separations were obtained using an Agilent capillary electrophoresis instrument (Agilent Technologies Deutschland GmbH). The capillary tubing used was 375 μm o.d. × 50 μm i.d. (Composite Metals, Worcester, U.K.). The oven used for etching and modifying the capillaries was a component of a gas chromatograph 8000 series (Fisons Instruments).

UV−visible spectra of the synthesized dodecanethiol gold nanoparticles were recorded with a Shimadzu UV-2101PC scanning spectrophotometer at 20 °C. TEM was performed using a JEM 1200 EX TEMSCAN, and scanning electron microscopy (SEM) pictures of capillaries were obtained using a Hitachi S4000 SEM microscope.

Mobile Phase and Sample Preparation. Thiourea (1 g/L), naphthalene (1 g/L), biphenyl (1 g/L), fluorene (1 g/L), anthracene (0.4 g/L), and triphenylene (0.4 g/L) were dissolved in methanol, respectively. The test mixtures were made up in methanol−water (70:30; 0.1 g/L of each component) with thiourea (3 mM) as the dead volume marker. Phosphate buffer solutions (25 mM, 10 mM) were prepared by dissolving either sodium dihydrogen phosphate or disodium hydrogen phosphate in deionized water, and the pH was adjusted to the desired value using phosphoric acid. All the eluants were filtered using an aqueous 0.45-μm Millipore filter membrane and sonicated (ULTRAsonik NEY) for 10 min to remove dissolved air prior to use.

Synthesis of Gold Nanoparticles. Dodecanethiol gold nanoparticles were synthesized according to the following procedure: $AuCl_3$ was dissolved in deionized H_2O (0.1131 g in 13 mL), and the phase-transfer catalyst TOAB was dissolved in $CHCl_3$ (0.9645 g in 24.5 mL). Both solutions were then combined to form a two-phase mixture and stirred for 1 h at room temperature. The mixture was added to a separatory funnel, and the $CHCl_3$ layer was collected. Dodecanethiol (86 μL) was then added to the stirring solution with stirring continued for 5 min. A solution of $NaBH_4$ in distilled water (0.1786 g in 11 mL) was added drop by drop with stirring to the organic solution and the mixture allowed to be stirred overnight. The mixture was added to a separatory funnel, and $CHCl_3$ was collected. A polar solvent (MeOH) was added and the solution was then centrifuged (MSE MISTRAL 1000) at 4000 rpm for 30 min. After centrifugation, the clear supernatant was removed carefully from the centrifugation tube and the nanoparticles remaining in the tubes were reconstituted in hexane.

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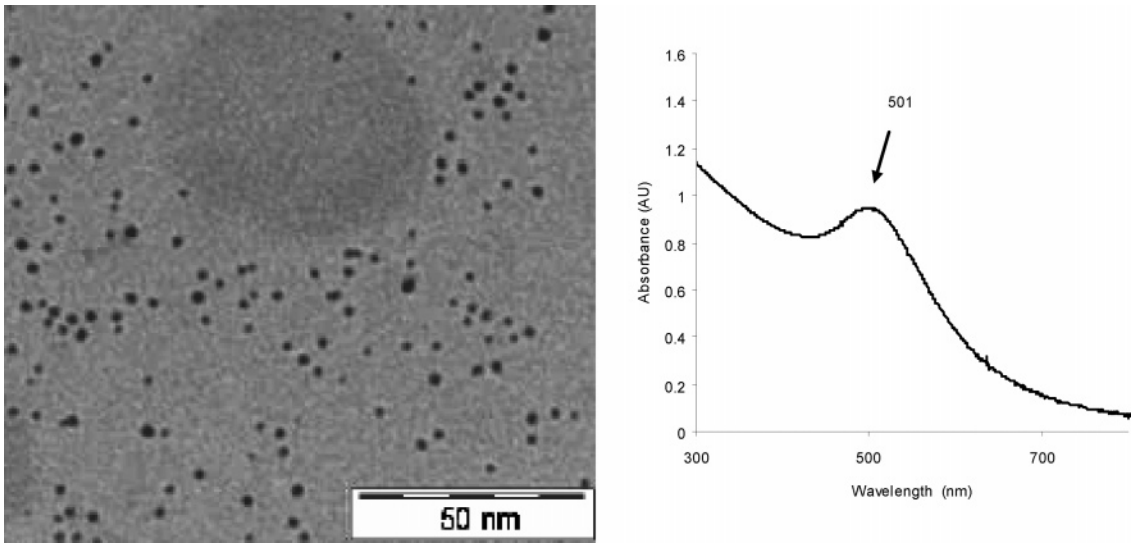

Figure 1. (a) TEM micrograph of dodecanethiol gold nanoparticles dispersed in hexane, on a carbon film 400-mesh copper grid; (b) visible absorption spectrum of dodecanethiol nanoparticles dispersed in hexane. $\lambda_{max} = 501$ nm.

Etching Procedure. The etching procedure is referred to the published method[18] and described as following: The bare capillary (1 m) filled with 12 mM HCI was sealed with PEEK tubing and a microtight union and then heated overnight at 80 °C. After washing with distilled water, acetone, and diethyl ether successively, the capillary was dried at 25 °C for 1 h under nitrogen flow in the GC instrument. Then, the capillary was filled with a saturated solution of ammonium hydrogen difluoride in methanol and allowed to stand for 1 h with both ends sealed. The methanol was removed by a uniform nitrogen flow through the capillary for 0.5 h. After removing methanol, the capillary was sealed at both ends by oxygen−ethyne flame and heated in a GC oven at 300 °C for 4 h under nitrogen.

Chemical Modification Procedure. Before modifying with the organosilane-coupling agent (MPTMS), the capillary was washed with methanol for 1 h and dried with nitrogen flow for 0.5 h. MPTMS solution prepared in propan-2-ol (1:12) was then pumped through the capillary with a plastic syringe for 1 h and allowed to stand overnight with both ends sealed. The modified capillary was then rinsed with propan-2-ol and annealed at 110 °C for 10 min in the GC oven under nitrogen. A solution of dodecanethiol gold nanoparticles in hexane was pumped through the capillary with a plastic syringe and allowed to stand for 1 h with both ends sealed. The excess gold solution was removed from the capillary with distilled water and stored in distilled water until use.

For the modification of unetched bare capillary, the capillary was preconditioned by washing with 1 M NaOH and distilled water for 1 h, respectively, and then drying by nitrogen flow in the GC oven under 100 °C for 1 h.

Electrochromatography Conditions. Both unetched and etched gold nanoparticle capillaries were conditioned first in the CEC instrument by pressure rinsing with running buffer for 30 min prior to use. If the pH of the running buffer was changed, the capillaries were rinsed with the new buffer for 30 min. Between runs, the capillary was rinsed for 2 min and stored in water when not in use. Samples were injected by pressure for 2 s at 34.5 mbar. The detection wavelength was 254 nm.

Separations were performed at 25 kV with a ramp time (time taken for voltage to rise from 0 to 25 kV) of 0.5 s. Normal polarity conditions were used for all separations.

RESULTS AND DISCUSSION

The synthesized dodecanethiol gold nanoparticles dispersed in hexane were characterized by TEM and UV−visible spectroscopy as shown in Figure 1a and b, respectively. The TEM micrograph shows that the dispersed phase of the gold nanoparticles in hexane consisted of spherical particles with the size range of 2−3 nm. The size distribution of the gold nanoparticles was determined by measuring the diameters of at least 200 individual particles located in representative regions of the micrographs. Figure 1b shows the relatively weak plasmon resonance absorption maximums in the range 490−510 nm ($\lambda_{max} = 501$ nm) for the synthesized gold nanoparticles, which confirms their nanometer-scale size further.

The progress of the etching process can be observed simply by optical microscopy at a magnification of 10 × 10. The outside polyimide coating of capillaries (~2 cm in length) was burned off using an InnovaTech capillary frit former (InnovaTech, Hertfordshire, U.K.). As expected, the inner wall surface of the bare capillary is completely smooth, while it became visibly roughened after etching. That is because, during the etching, quite an amount of the original surface is dissolved by ammonium hydrogen difluoride and then deposited onto the wall in rather large particles.

The effect of the etching and modification process on the inner surface of the capillaries can be more clearly seen in the SEM photographs shown in Figure 2. The smooth surface of the bare capillary is shown in Figure 2a (10 kV × 4.5 K magnification), while a series of small hills or mounds of less varying depth, width, and shape can be seen on the inner surface of the etched bare capillary shown in Figure 2b (3 kV × 6 K magnification) and Figure 2c (10 kV × 4 K magnification). It can be seen that after etching with ammonium hydrogen difluoride for 4 h at 300 °C, the surface area of the inner wall is increased greatly and the new surface of the etched bare capillary is quite uniform and well

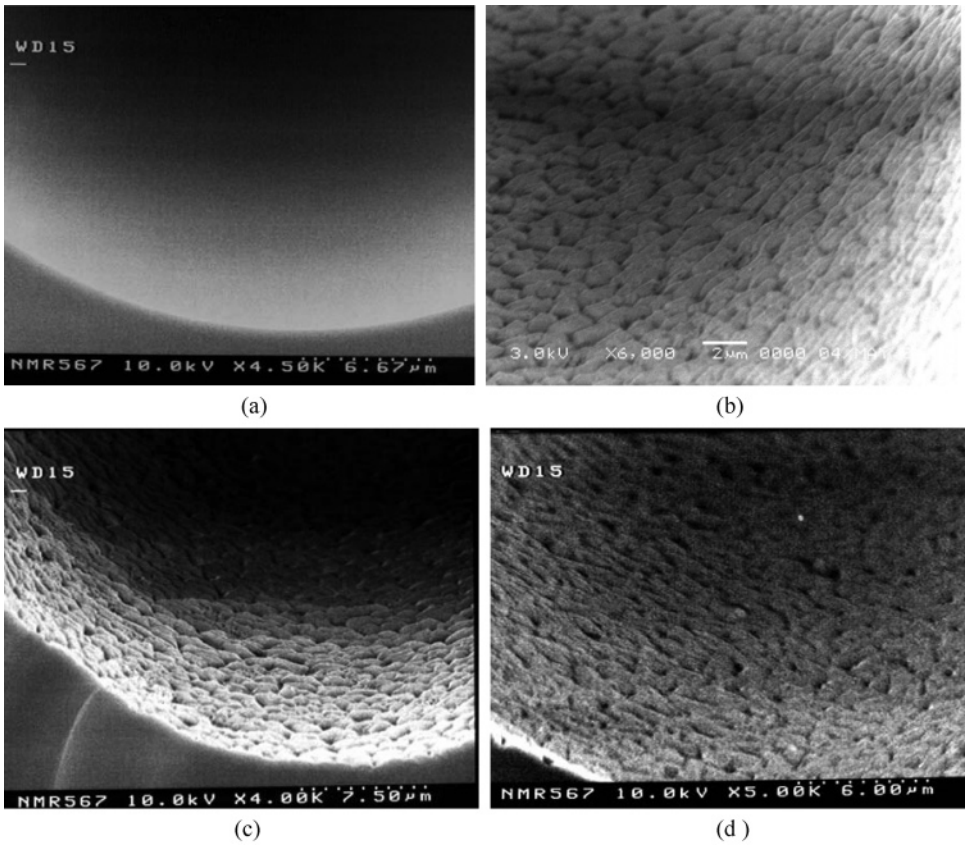

Figure 2. SEM photographs of (a) bare capillary, (b, c) etched bare capillary, and (d) etched gold nanoparticle capillary.

defined. Figure 2d shows the surface feature of the etched gold nanoparticle capillary (10 kV × 5 K magnification) with the same uniform and well-defined new surface.

To illustrate the effects of both etching and modification processes on the chromatographic properties, a mixture of thiourea, naphthalene, and biphenyl was selected as a reversed-phase test mixture. Thiourea was used as an unretained dead volume marker in our work since it is not retained on gold nanoparticle capillaries, a finding confirmed by comparing with acetone and methanol as test EOF markers.

Effect of Organic Modifier on Chromatographic Retention. The percentage of organic modifier in the buffer system influences not only the EOF mobility but also the chromatographic selectivity. Here MeOH was selected as organic modifier to test the chromatographic properties of both etched and unetched gold nanoparticle capillaries. The effect of MeOH percentage on the EOF mobility and resolution of solutes for the etched gold nanoparticle capillaries is shown in Figure 3. It can be seen that there is a steady decrease in EOF mobility as MeOH percentage increases in the range from 50 to 60%, while it increases sharply after the percentage of MeOH is further increased. In the meantime, the resolution as well as the separation factor of solutes increases with the decrease of MeOH percentage. For example, the resolution for naphthalene and biphenyl increases from 1.9 at 65% MeOH to 3.3 at 50% MeOH, while their separation factor increases from 1.05 to 1.28. As the mobile phase becomes less polar (i.e., more organic modifier), solutes partition into the mobile phase to a greater extent, so that the interaction with the stationary phase is reduced with concomitant changed migration times. As shown in Figure 3, a baseline separation of thiourea, naphthalene, and biphenyl with good peak shape can be achieved at 60 or 65% MeOH. Values of 2.4 and 2.7 for the resolution between thiourea and naphthalene and between naphthalene and biphenyl, respectively, were obtained with 60% MeOH, for example.

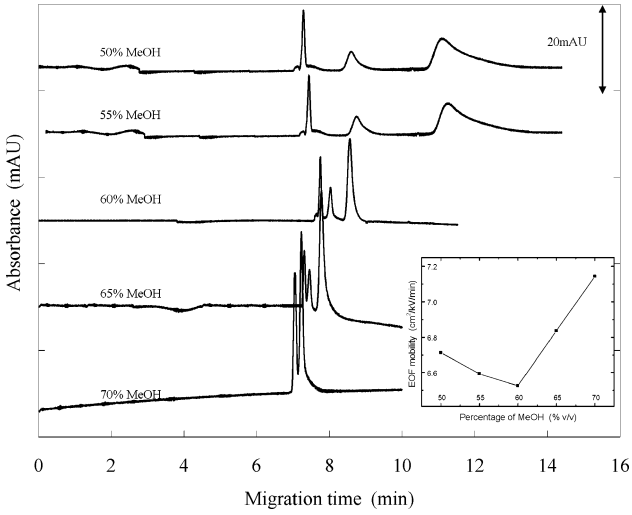

Figure 3. Effect of MeOH percentage on EOF mobility and the resolution of solutes in OTCEC on the etched gold nanoparticle capillary. Etching 300 °C for 4 h. OTCEC conditions: 40 cm (effective length of 31.5 cm) × 50 μm i.d. etched gold nanoparticle capillary, MeOH−25 mM Na_2HPO_4 buffer, pH 7.0; separation voltage, 25 kV. Analyte peaks in order of elution: thiourea, naphthalene, and biphenyl.

The effect of MeOH percentage on the EOF mobility for various capillaries is shown in Figure 4. It can be seen that EOF mobility decreases in a linear fashion with the increase of MeOH

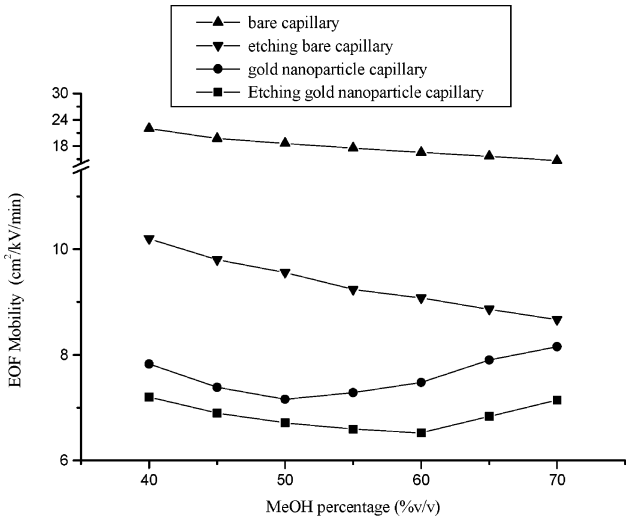

Figure 4. Effect of MeOH percentage on the EOF mobility for various capillaries. OTCEC conditions: 40 cm (effective length of 31.5 cm) × 50 μm i.d. capillaries, MeOH−25 mM Na_2HPO_4 buffer, pH 7.0; separation voltage, 25 kV.

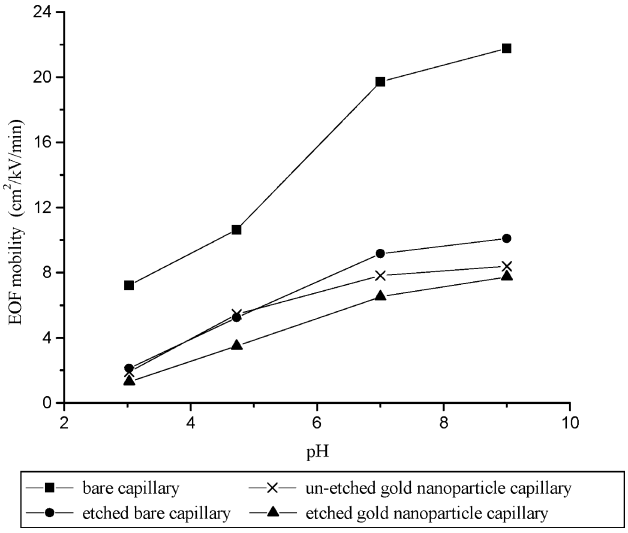

Figure 5. Effect of buffer pH on EOF mobility for various capillaries. CEC conditions: 40 cm (effective length of 31.5 cm) × 50 μm i.d., MeOH−25 mM Na_2HPO_4 buffer (60:40); separation voltage, 25 kV.

in the range from 40 to 70% for both bare capillary and etched bare capillary, with the later possessing much lower EOF mobility than the former. This can be explained by the reduction of silanols, particularly free silanols, on the surface after the etching process.[18] Unetched gold nanoparticle capillaries also show lower EOF mobility than bare capillary, as expected, due to the reduction of free silanols on the surface, following chemical bonding with MPTMS and attachment of hydrophobic dodecanethiol gold nanoparticles. Among the capillaries investigated, the lowest EOF mobility was obtained as expected on the etched gold nanoparticle capillary, since the increased surface area following etching facilitates greater coverage with gold nanoparticles.

Effect of pH on Chromatographic Retention. In the pH range from 3.0 to 9.0, the bare capillary displays a characteristic profile of pH variation, with the maximum EOF occurring at high pH as shown in Figure 5. At low pH, protonation of the silanol groups increases, with a corresponding reduction in EOF mobility. As the EOF flow on etched bare capillary is also generated by the silanol groups on the silica wall, it displays EOF behavior over the pH range similar to that of the bare capillary, but with a reduced EOF mobility due to the reduction of the free silanols by the etching process. Since the pK_a of the thiol group is ~10.6, it is not expected to influence the EOF behavior. Thus, EOF is still generated by residual silanol groups on the inner wall of a capillary, which is chemically modified with MPTMS and with gold nanoparticles. Thus, both etched and unetched gold nanoparticle capillaries display EOF profiles similar to that of bare capillary. Again, the magnitude of the EOF mobility is reduced due to the covalent functionalization of silanol groups and subsequent gold nanoparticle attachment. Meantime, it is understandable that etched gold nanoparticle capillaries possess the lowest EOF mobility because of the greater reduction of free silanols by both the etching and modification processes.

Table 1 shows the effect of buffer pH on the resolution and separation factor of selected solutes on the etched gold nanoparticle capillary. It can be seen that both separation factor and resolution of solutes were influenced by buffer pH in the range of 3.0−9.0. The decrease of pH resulted in an increase of the separation factors of solutes. Since all solutes, thiourea, naphthalene, and biphenyl, are neutral in the investigated pH range, the separation depends on the differences in the interactions between solutes and the bonded dodecanethiol gold nanoparticle phase. Low EOF mobility was obtained by using low buffer pH and resulted in more interaction between solutes and the bonded gold nanoparticle phase, as well as larger separation factors. However, excessively long migration time resulted in poorer peak symmetry. This can explain the decrease of resolution when pH changed from 4.7 to 3.0, while it increased with the decrease of pH in the range of 9.0−4.7. Good resolution and selectivity can be achieved at pH 7 with the shorter retention time compared with that at pH 4.7.

Table 1. Effect of pH on the Resolution and Separation Factor for the Etched Gold Nanoparticle Capillary (40 cm × 50 μm i.d.), MeOH−25 mM Na_2HPO_4 Buffer (60:40), Separation Voltage 25 kV

	resolution (separation factor)			
pH	9.0	7.0	4.7	3.0
thiourea and naphthalene	1.7 (1.03)	2.5 (1.05)	3.0 (1.07)	1.4 (1.08)
naphthalene and biphenyl	2.2 (1.06)	2.7 (1.09)	2.6 (1.10)	2.5 (1.12)

Effect of Electric Field Strength on Chromatographic Retention. EOF velocity was observed to increase linearly with an increase of applied electric field strength for all capillaries over the investigated range of 10−30 kV/40 cm, with thiourea as the EOF marker. Slopes were determined as follows, for etched gold nanoparticle capillary (7.6), unetched gold nanoparticle capillary (10.7), etched bare capillary (13.6), and bare capillary (25.8), using MeOH−25 mM Na_2HPO_4 buffer (60:40), pH 7.0. The different slopes obtained are related to the percentage of residual silanol groups on the inner wall of the fused-silica capillaries, which generate EOF. As expected, the etched gold nanoparticle capillary displays the smallest increase in EOF velocity with the electric field strength, while in contrast, the greatest EOF velocity with the electric field variation is achieved for the bare capillary.

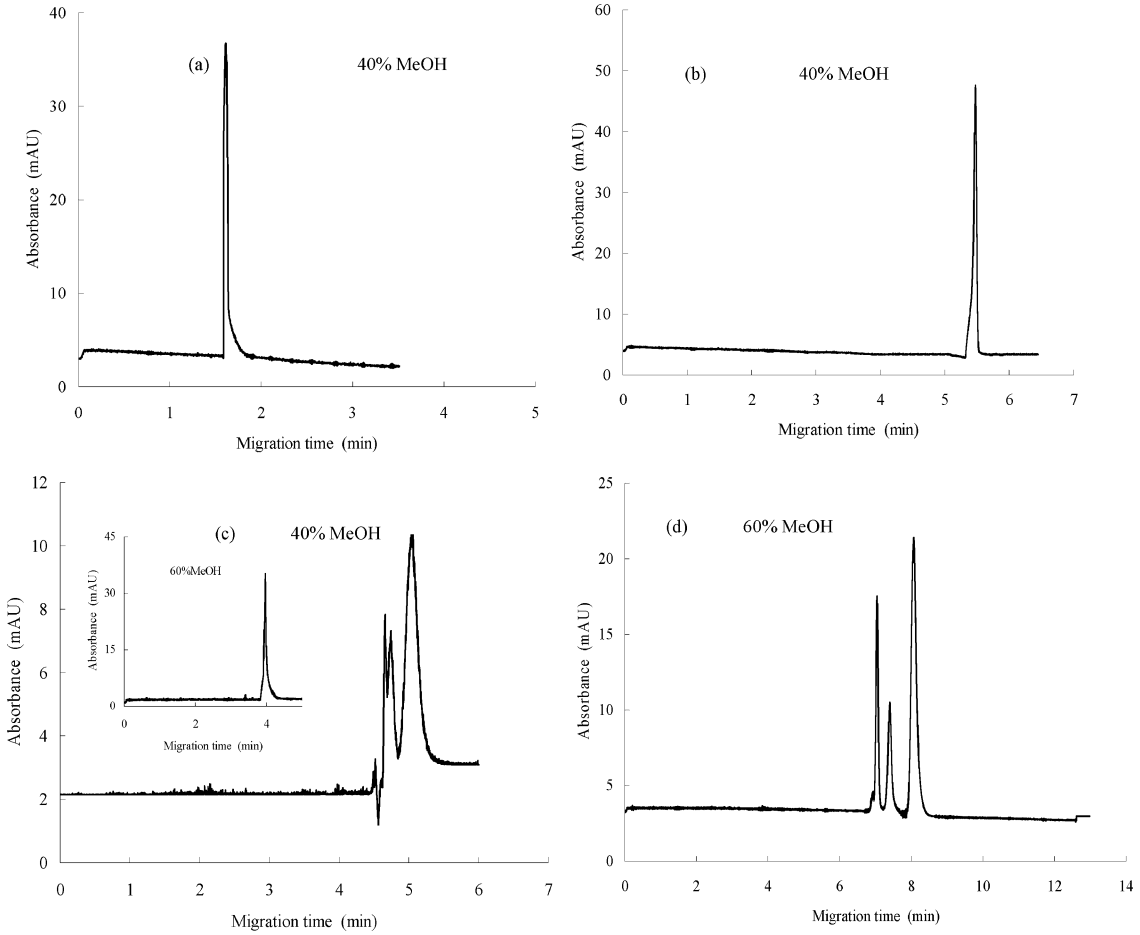

Figure 6. Electrochromatograms representing the separations of naphthalene and biphenyl with thiourea as EOF marker on various capillaries: (a) bare capillary 34 cm (25.5 cm) × 50 μm, 40% MeOH; (b) etched bare capillary 42 cm (33.5 cm) × 50 μm, 40% MeOH; (c) unetched gold nanoparticle capillary 40 cm (31.5 cm) × 50 μm, 40% MeOH; the inserted picture, 60% MeOH; (d) etched gold nanoparticle capillary 40 cm (31.5 cm) × 50 μm, 60% MeOH. Conditions: mobile phase MeOH−25 mM phosphate buffer pH 7.0; separation voltage, 25 kV. Analyte peaks in (c) and (d) (in order of elution): thiourea, naphthalene, and biphenyl.

When the effect of the applied electric field strength on the OTCEC separation of the test mixture of thiourea, naphthalene, and biphenyl was examined under these conditions, the resolution of solutes increased on decreasing the applied voltage, with corresponding longer retention times. For example, the resolution for naphthalene and biphenyl increased from 2.2 under 30 kV applied voltage to 3.1 under 10 kV applied voltage. Meanwhile the separation factors of solutes display a slight increase with decreasing the applied voltage, such as from 1.09 under 30 kV to 1.10 under 10 kV for naphthalene and biphenyl.

Chromatographic Performance of Etched and Modified Capillary. The run-to-run reproducibility of chromatographic retention was studied with both etched gold nanoparticle and unetched gold nanoparticle capillaries. For the etched gold nanoparticle capillary, the capillary was etched with ammonium hydrogen difluoride at 300 °C for 4 h and then modified with MPTMS and gold nanoparticles. For OTCEC on the unetched gold nanoparticle capillary, the ratio of MeOH to 25 mM Na_2HPO_4 in the buffer solution was reduced to 40:60, since naphthalene and thiourea cannot be separated with MeOH−25 mM Na_2HPO_4 (60:40).

Both etched and unetched gold nanoparticle capillaries yielded reproducible chromatography and retention factors. The reproducibility of 0.5−0.6% in terms of migration time was obtained on the etched gold nanoparticle capillary, with between 0.8 and 1.0% on unetched gold nanoparticle capillary, for 10 consecutive runs under the conditions used. Retention factors were increased greatly by the etching process. Mean retention factors ($\times 10^2$) were naphthalene (5.1) and biphenyl (14.7) on etched gold nanoparticle capillary, compared to naphthalene (1.6) and biphenyl (8.3) for unetched gold nanoparticle capillary. Lower retention factor RSDs for naphthalene (2.4%) and biphenyl (1.1%) obtained after the etching process compare with naphthalene (10.0%) and biphenyl (1.9%) for unetched gold nanoparticle capillary.

These capillaries appeared to be stable for up to 3 months when not in use and stored in water. Even with extensive washing when in use, there were no observable changes in the separation efficiency for at least 100 injections.

Electrochromatograms obtained for the separation of naphthalene and biphenyl, with thiourea as EOF marker, on bare capillary, etched bare capillary, unetched gold nanoparticle capillary, and etched gold nanoparticle capillary are displayed in Figure 6. The bare capillary and the etched bare capillary failed to separate the solutes as shown in Figure 6a and b. Upon coating with dodecanethiol gold nanoparticles, the resulting gold nanoparticle capillary proved capable of some separation for selected solutes at the MeOH percentage lower than 40%, limited however due to the high phase ratio (Figure 6c). However, a much better

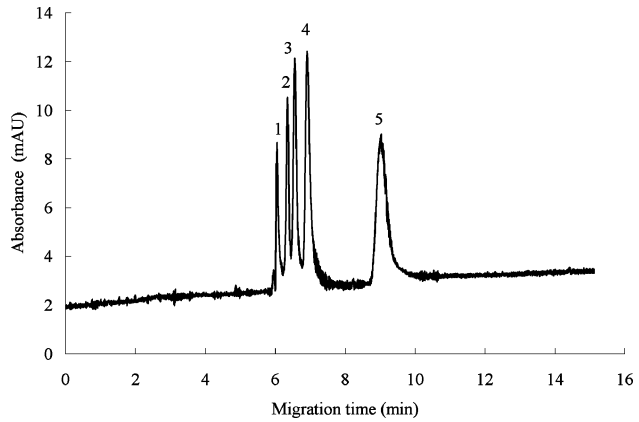

Figure 7. Electrochromatogram of the separation of PAHs, naphthalene, fluorene, anthracene, and triphenylene with thiourea as EOF marker on the etched gold nanoparticle capillaries. Conditions: mobile phase MeOH−10 mM phosphate buffer (60:40), pH 7.0; separation voltage, 25 kV. Injection 20 mbar for 2 s. The capillary (40 cm (31.5 cm) × 50 μm) was etched with ammonium hydrogen difluoride for 4 h at 300 °C. Analyte peaks (in order of elution): (1) thiourea, (2) naphthalene, (3) fluorene, (4) anthracene, and (5) triphenylene.

separation of solutes can be obtained even at higher organic modifier percentages (60%) on the etched gold nanoparticle capillary (Figure 6d). The notable improvement of chromatographic separation is not only due to the increase of the surface area of the capillary from the etching process but also to the radial extensions from the surface, which apparently facilitated the interactions between solutes and bonded gold nanoparticle phase. Theoretical plate numbers per meter of 208 000 (thiourea), 117 000 (naphthalene), and 33 000 (biphenyl) were obtained on the etched gold nanoparticle capillaries.

Application to PAH Analysis. Four PAHs, naphthalene, fluorene, anthracene, and thiphenylene, were injected in an attempt to separate them on the etched gold nanoparticle capillary (50-μm i.d.). The OTCEC separation of the selected PAHs with thiourea as EOF marker were investigated with organic modifier varied from 55−70%. Figure 7 shows an elected chromatogram of the separation of selected PAHs at 60% MeOH−10 mM phosphate buffer at pH 7.0 with the theoretical plates number per meter of 225 000 (thiourea), 153 000 (naphthalene), 125 000 (fluorene), and 38 000 (triphenylene), respectively.

CONCLUSIONS

The use of alkylthiol gold nanoparticles as a novel phase for etched capillary-based OTCEC with high separation efficiency and favorable phase ratio on 50-μm-i.d. capillaries was confirmed in this paper. The gold capillaries, which were etched with ammonium hydrogen difluoride first, followed by prederivatization with MPTMS and immobilization of dodecanethiol gold nanoparticles, are easier to produce and operate than packed capillaries. The etching process was used to increase the surface area of the inner wall of the capillaries and produce the radial extension from the wall surface. The chromatographic properties of various capillaries, etched gold nanoparticle capillaries, unetched nanoparticle capillaries, bare capillaries, and etched bare capillaries were investigated through variation of the organic modifier percentage in buffer, buffer pH and separation voltage. Effective separations of the reversed-phase test mixture of thiourea, naphthalene and biphenyl, and of selected PAHs, were obtained on the etched gold nanoparticle capillaries. The etching process and surface features of etched gold nanoparticle capillary were determined by optical microscopy and SEM. The synthesis and characterization of dodecanethiol gold nanoparticles using TEM and UV−visible spectroscopy are also detailed.

The results prove that dodecanethiol gold nanoparticles bonded on the etched inner wall of the fused-silica capillary can provide sufficient solute-bonded phase interactions with reproducible retention factors, as well as characteristic reversed-phase behavior. The eventual use of such phases in electrophoresis and chromatography as well as in microfluidic miniaturized separation devices are expected in the bioanalytical field.

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