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Electrophoretic separation of aniline derivatives using fused silica capillaries coated with acid treated single-walled carbon nanotubes

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Abstract

This paper reports on a new strategy for coating fused silica capillaries based on the ionic adsorption of acid treated single-walled carbon nanotubes (SWCNTs) on a poly(diallydimethylammonium chloride)-modified fused silica surface. The coated capillaries were used to demonstrate their performance for baseline separation of a mixture of seven nitrogen-containing aromatic compounds compared to capillary zone electrophoresis. This combined layer formed a coating material that could be useful for improvement of the selectivity of the solutes in an electrical field. We reasoned that the interaction of the solutes and the modified capillary wall occurred mainly via ionic interactions with the charged moieties of CNTs. The single-walled CNT modified capillaries were very stable and could be used for over 200 repeated analyses without compromising its analytical performance.

Keywords: Capillary electrophoresis; Single-walled carbon nanotubes; Aniline derivatives

1. Introduction

Fused silica capillaries, coated with different polymers, have been pursued in the past, motivated by the prospects of using such coated capillaries to develop novel capillary electrophoresis (CE) schemes with improved resolution power [1–5]. They have been modified with an aryl-pentafluoro group [6], epoxy-diol/maltose [7], glycero-glycidoxypropyl/polyvinylpyrrolidinone [8], glycol [9], polyacrylamide [10], polyethylene glycol [11], polyethyleneimine [12], polymethylsiloxane [13], and trimethylchlorosilane [14]. Anionic and cationic polymers are covalently attached or physically adsorbed to the inner wall of the capillary to change the properties of fused silica surfaces. Since the pioneering work of Hjerten [10] using polyacrylamide strings, some modifications of this elegant work have been reported to improve the number of double bonds grafted to the wall and the reproducibility of the separation process [15,16]. The physical adsorption or dynamic coating of polymers on capillaries has been considered as a rapid method of preparing stable coatings [17] compared to the time-consuming and complicated covalent procedure [18,19]. Of particular interest is the utilization of a cationic polymer, poly(diallyldimethylammonium chloride, PDDA) to coat the interior capillary wall for separation and analysis of basic proteins by CE [17,20]. Notice also that a considerable amount of work has been reported concerning the use of PDDA to coat capillaries in CE and modify the migration of analyte ions [21–24]. PDDA was used together with polybrene in ion-exchange electrokinetic chromatography for the separation of analyte ions having identical electrophoretic mobilities in capillary electrophoresis [25]. This polymer has also been used as a sublayer to bind an anionic polymer in a technique called successive multiple layer adsorbed coatings [26]. More detailed information and several relevant references on surface modification of silica walls can be founded elsewhere [27].

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Since the discovery of carbon nanotubes (CNTs) [28], these tube-like materials have attracted enormous attention owing to their unique structural, mechanical, and electronic properties [29–31]. However, hydrophobic CNTs are difficult to disperse and they cannot be wet by liquids with surface tensions higher than 100–200 mN/m [32]. Hence, a number of challenges must be overcome before CNTs find widespread applicability. One of these is their inherent insolubility in aqueous and even several organic solvents. CNTs tend to agglomerate as bundles in solvents and if dispersed, reagglomerate soon thereafter due to electrostatic attraction. Therefore, CNTs interact strongly with hydrophobic compounds, for example, the pyrenyl group of 1-pyrenebutanoic acid, succinimidyl ester via π-stacking and the adsorption is irreversible [33]. Therefore, little attention has been given to the application of CNTs in CE and other separation schemes although significant advances have been made in CE and CE microchip separation using nanoparticles [34]. As a prerequisite for any separation schemes, it is imperative to modify CNTs so that analytes must not irreversibly be adsorbed on inherently hydrophobic surfaces of CNTs. It is also of utmost importance to immobilize CNTs onto the inner walls of capillaries in a reliable manner. CNTs treated with strong acids and sonication become more soluble and bear negative charges due to the formation of carboxylic, carbonyl and hydroxyl groups during the course of treatment [35]. It should be noted that during the tube formation, there are some defects of the six-membered-ring carbon structure of the nanotubes. In addition to an inclusion of five-or seven membered rings in the carbon network, sp^3-hybridized defects in the sidewall introduce −CH and C−OH groups [36]. The open ends of the tubes are often closed by catalyst particles in the crude material which can be removed by oxidative cleanup with HNO_3 or H_2SO_4/HNO_3. Therefore, the tube ends are largely decorated with −COOH groups [35]. The hydrophobicity of the six-membered-ring carbon structure of CNTs and the presence of −COOH could be a promising starting point for the use of CNTs in electrophoretic separation. The acid treated CNTs are more amenable to further chemical and biochemical modification and display both hydrophobic and ionic interactions with various molecules. From such interactions together with their high surface area, CNTs can be considered as potential materials for CE or other separation schemes.

This paper describes a simple and general approach to noncovalent functionalization of the inner walls of the fused silica capillary. The functionalization involves the precoating of the capillary with a positively charged PDDA polymer, which enables and promotes the subsequent adsorption of acid treated CNTs. Seven common nitrogen-containing aromatic compounds (referred herein after as aniline derivatives) are used as a test model since such analytes cannot be resolved by capillary zone electrophoresis (CZE) or even with cyclodextrin modified CE [37]. Comprehensive information on the separation of protonated anilines by capillary electrophoresis has been reported elsewhere [38].

2. Experimental

2.1. Materials

SWCNTs (single-walled carbon nanotubes, 0.79–1.2 nm outer diameter, >95% purity) was purchased from Carbon Nanotechnologies (Houston, TX, USA). Poly (diallyldimethylammonium chloride), (PDDA, average MW ∼ 200–350 kDa, 20 wt.%), aniline, *o*-anisidine, 3-aminophenol (3-AP), 4-aminophenol (4-AP), 2-chloroaniline (2-ClA), 3-chloroaniline (3-ClA), 4-chloroaniline (4-ClA), mesityl oxide and acetonitrile (anhydrous; +99%) were obtained from Aldrich (Milwaukee, WI, USA) and used as received. All solutions were prepared using deionized water (Milli-Q, Millipore, Bedford, MA, USA). The remaining chemicals were purchased from Sigma (St. Louis, MO, USA) with the highest grade available and used as received except for concentrated sulfuric and nitric acids which were purchased from EM Science (Gibbstown, NJ, USA).

2.2. Preparation of the carbon nanotubes

SWCNTs were acid-treated according to Liu et al. [35]. In brief, 60 mg of carbon nanotubes (CNTs) were added to 60 mL of a 3:1 mixture of concentrated sulfuric and nitric acids and sonicated for 4 h. This acid mixture has been known to intercalate and exfoliate graphite and the tangled ropes of nanotubes were cut into shorter pieces. The resulting suspension was diluted in 200 mL of water and allowed to sediment overnight, decanted off and the remains diluted with 200 mL of water. Because “scission” occurs at defect sites, this acid treatment has been known to produce a broad distribution of open ended CNTs. Therefore, the CNT suspension was submitted to ultrafiltration under nitrogen pressure in an Amicon 50 mL stirred-cell device using a 0.22 μm Fluoropore-FGLP filter (Millipore, Bedford, MA, USA). The CNTs, collected from the retentate, were then extensively rinsed with water until a nearly neutral run-off was obtained. The CNTs were left to dry overnight at room temperature and finally recovered from the filter by scrapping them off.

2.3. AFM imaging

AFM micrographs were obtained using a Nanoscope IV (Digital Instruments, Veeco, Santa Barbara, CA, USA) with a silicon tip operated in tapping mode. For imaging, acid treated CNTs (1 mg/mL) were suspended in dichloromethane; after 20 min of sonication, CNTs were immobilized on a piece of oxidized silicon wafer (Virginia Semiconductor, Fredericksburg, VA, USA) by spin coating (Cee 100 spinner, Rolla, MO, USA). PDDA-SWCNT coated capillaries were prepared for imaging as follows. A piece of polyimide-coated capillary (50 μm I.D.) was heat treated to remove the coating, it was cleaned by wiping off the residues with a MeOH saturated Kimwipe. The clean fused silica surface was immersed in

0.8 wt.% PDDA solution (20 mM sodium acetate, pH 4.7) for 30 min followed by extensive rinsing with water and then immersed in a 0.05 mg/mL acid treated SWCNT suspension in 20 mM sodium acetate, pH 4.7 for 30 min. After washing with the acetate buffer and water, the sample was dried and used for AFM imaging.

2.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was carried out in a VG ESCALAB 3 Mark II, using non-monochromated Mg Kα X-rays (1253.6 eV). The base pressure in the analysis chamber was less than 10^{-9} Torr. High-resolution spectra were obtained at a perpendicular take-off angle, using a pass energy of 20 eV and 0.05 eV steps. The instrument resolution was ~0.7 eV. After Shirley background removal, the component peaks were separated by the VG Avantage software (Thermo VG Scientific). Drops of solution containing the nanotube samples for XPS analysis were placed onto substrates and dried in air. The substrates were Si wafers, onto which 10 nm Ti, followed by 100 nm Au, were evaporated by electron beam heating at a deposition rate of 0.5 A/s, under high vacuum. The Au $4f_{7/2}$ peak (84.0 eV) was used for calibration.

2.5. Capillary coating procedure

In order to make a detection window, the external polyimide coating was burned off over a length of 3 mm using a window burner (MicroSolv Technologies Corp, Brighton, NJ, USA) and rinsing with methanol, before coating the capillary. Capillaries were preconditioned by rinsing (at 20 psi) with 1N NaOH for 10 min, followed by H_2O for 10 min and finally with 20 mM sodium acetate buffer, pH 4.7 for 5 min. A voltage of +10 kV was applied to the capillary for 60 min. Fused silica capillaries were dynamically coated with PDDA by rinsing them with a 0.8 wt.% solution in 20 mM sodium acetate buffer, pH 4.7 for 30 min, followed by a 0.08 wt.% rinse for 10 min and finally with the acetate run buffer (20 mM, pH 4.7) for 5 min. After verification of the electroosmotic flow (EOF) reversal, the capillaries were rinsed with H_2O for 10 min and then with a 0.05 g/mL solution of acid treated CNTs in the run buffer for 30 min. After coating, the capillaries were washed with the run buffer for 10 min and a +30 kV potential was applied through the capillaries for 1 h before analysis.

2.6. Capillary electrophoresis

Electropherograms were obtained from a P/ACE 5000 (Beckman, Fullerton, CA, USA) instrument with a separation potential of +30 kV applied using a linear ramping time of 1 min. Instrument control and data collection were performed using an IBM computer utilizing the Beckman System Gold software. Separations were done using 50 μm I.D., 360 μm O.D. polyimide-coated fused silica capillaries (Polymicro Technologies, Phoenix, AZ, USA) with an inlet-to-detector length of 50 cm and a total length of 57 cm. Capillary temperature was regulated using a liquid coolant in a sealed cartridge. The absorbance was monitored at 214 nm with a Beckman UV detector module. Samples were injected hydrodynamically by applying 0.5 psi for 5 s and separations were carried out at 25 °C. Samples for CE analyses were prepared by appropriate dilution, in the separation buffer, from 100 mM stock solutions of each analyte prepared in acetonitrile. Peak identification was performed by spiking samples with known standards. Mesityl oxide was used as the electroosmotic flow (EOF) marker. New capillaries were conditioned with a 1 min rinse with 1N HCl, 20 min with 1N NaOH and 2 min with H_2O at high pressure (20 psi). Between the runs, the capillaries were washed with the run buffer for 2 min. Electroosmotic mobility (μ_{eo}) is used to quantify the EOF. Electropherograms were evaluated by determining separation efficiency and peak-to-peak resolution. Efficiency, defined as the number of theoretical plates (N) for each peak in the electropherograms, was calculated as $5.54(t_R/w_{1/2})^2$ [39]. Where t_R and $w_{1/2}$ represent the migration time of the analyte and the full peak width at half-maximum, respectively. The resolution (R_S) of one peak from the preceding peak was calculated as $1.18(t_2 - t_1)/(w_{1/2,1} + w_{1/2,2})$, where t and $w_{1/2}$ are as defined above for the two peaks [39]. The separation buffer consisted of 20 mM sodium acetate buffer, pH 4.7 and was prepared by titrating a 10 mM sodium acetate solution with 10 mM acetic acid to the desired pH. All solutions were prepared with Milli-Q water and filtered through 0.45 μm Millex-HV filters (Millipore, Bedford, MA, USA) before use.

3. Results and discussion

3.1. Characterization of acid treated CNTs

Pristine SWCNTs are highly entangled by van deer Waals forces to form a dense, robust, network structure. Therefore, they are virtually insoluble in organic solvents, making it difficult to chemically functionalize them and study their properties [40]. However, ultrasonicating CNTs in concentrated sulfuric and nitric acids cuts CNTs into short pieces, 100–300 nm [35]. The cut CNTs also possess oxygen-containing groups at both ends, carboxylic acids and phenolic hydroxides as a result of light etching in acids. For HNO_3 treatment, carboxylic groups have been reported as the most abundant group [41]. Therefore, acid treated CNTs become more soluble in water or organic solvents.

We conducted XPS to characterize both pristine and acid treated SWCNTs. Typical high-resolution C 1s spectra are shown in Fig. 1 for pristine and acid treated SWCNTs. Peak separations were carried out, based on our analysis of the C 1s XPS spectrum of the freshly cleaved HOPG surface [42]. As shown in the figure, component peaks are found at 284.6 eV (C_1, extensively delocalized alternant hydrocar-

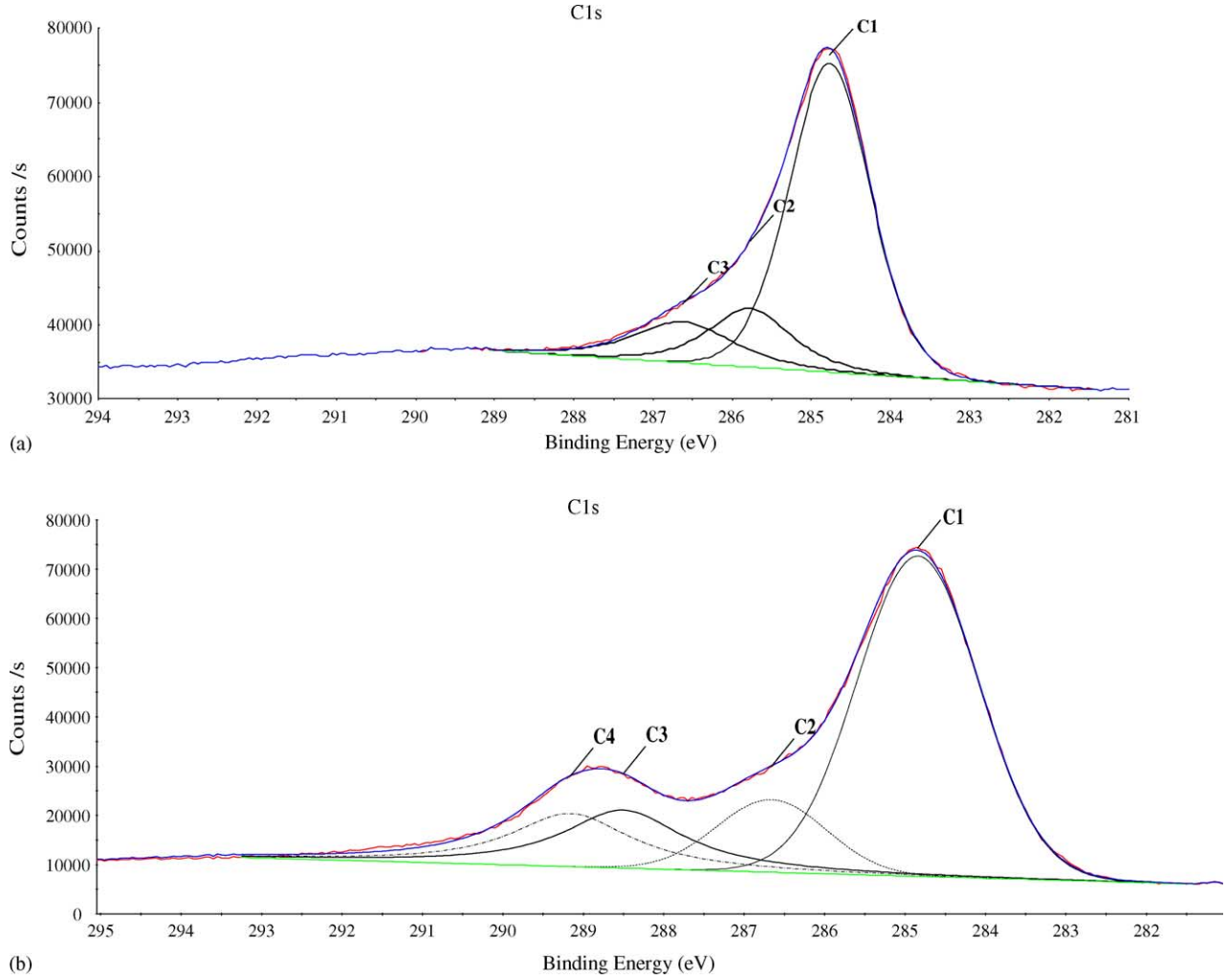

Fig. 1. C 1s XPS spectra of (a) pristine single-walled carbon nanotubes (SWCNTs) and (b) acid treated SWCNTs.

bon), 285.6 eV (C_2, defect-containing alternant hydrocarbon) and 286.5 eV (C_3, sp^3 defects). The C1 $\pi^* \leftarrow \pi$ shake-up (C_4) appears at 291.4 eV and that for C2 (C_5), at 287.8 eV. Small amounts of oxygen contaminant (~2–3%) are not normally visible in the C 1s spectrum (Fig. 1a, untreated) because they fall in the same range of energies as the C_1–C_5 peaks, and are difficult to distinguish; they are detected from the O 1s spectrum. Larger amounts (Fig. 1b) were detected in the C 1s spectrum, at ~286.5 eV for alcohols, ~288 eV for carbonyls and ~289 eV for acids. The relative oxygen content was estimated by XPS sensitivity factors and core level intensities, giving an oxygen content of ~2% for the pristine material and ~32% for the acid treated material. Therefore, XPS confirmed that these surface oxygen groups were introduced during the oxidative treatment of the SWCNTs.

Our study confirmed that cut CNTs exhibited a broad size distribution with various lengths and diameters (Fig. 2a). At low concentrations, acid treated SWCNTs dispersed relatively well in deionized water or buffers. It should be noted that before treatment, SWCNTs were shown to be highly entangled with one another and so long that their length were rarely visible (AFM micrograph not shown). It was very difficult to probe the presence of CNTs on the inner wall of the capillary. However, AFM micrographs were provided to confirm the immobilization of CNTs on its outer wall precoated with PDDA, assuming similarity between the surface chemistry of the outer and inner walls of the capillary (Fig. 2b). The CNT-PDDA-coated layer was very stable after extensive rinsing and washing with deionized water or the separation buffer. AFM was used in the characterization of acid treated CNTs since this technique inflicts no severe sample damage such as that caused by the focused electron beam in TEM measurements [43]. Recently, we have demonstrated that PDDA, even at low concentration, can disperse CNTs and the interaction between PDDA and CNTs is due to the π-orbital overlap of these two molecules. This π–π stacking interaction takes place between the π orbitals of CNTs and those of the vinyl groups present as contaminants in PDDA [44]. However, this interaction is much weaker than that of CNTs and the pyrenyl group of 1-pyrenebutanoic acid succinimidyl ester due to the hydrophobicity of the polyaromatic ring [33].

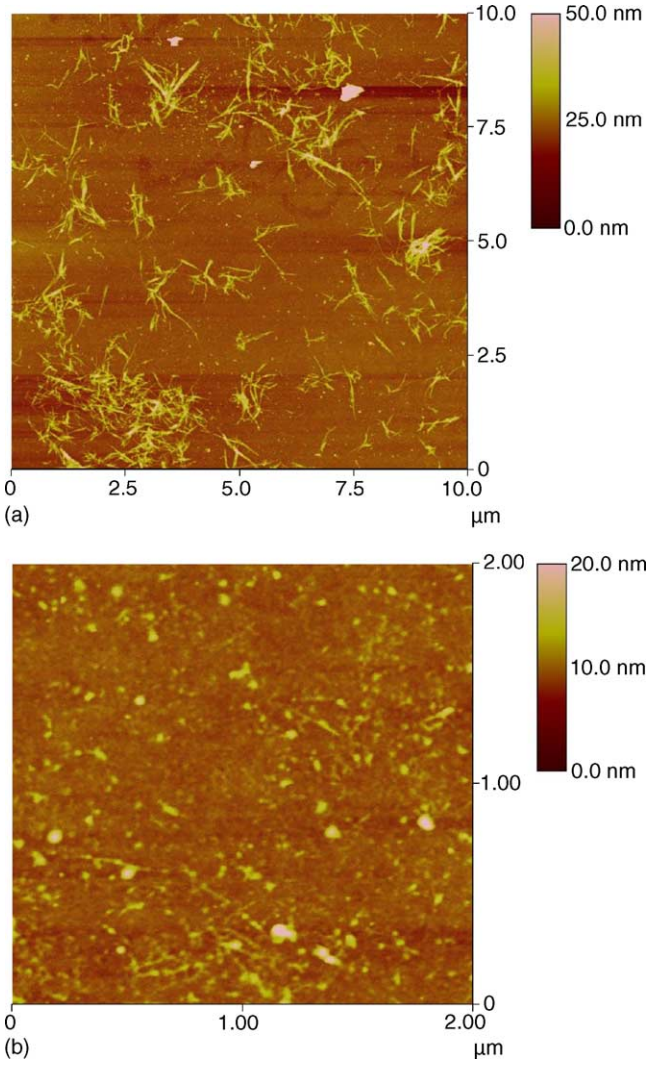

Fig. 2. AFM micrographs (height images) of the carbon nanotubes prepared by acid treatment and sonication, suspended in dichloromethane (1 mg/mL) and sonicated 20 min before immobilization onto a piece of oxidized silicon wafer via spin coating; the sample for image (b) was prepared by dipping the capillary in a PDDA solution, rinsing with buffer and water, dipping in a suspension of SWCNTs (in acetate buffer) and finally extensive rinsing with water. (a) Acid treated SWCNTs and (b) acid treated SWCNT immobilized on the outer wall of the capillary precoated with PDDA.

3.2. Electrophoretic characterization of PDDA-CNT coated capillaries

Direct coating of acid treated carbon nanotubes on the inner walls of the fused silica capillary was not satisfactory since physisorbed CNTs were easily removed by rinsing the coated capillary even with deinonized water. Such a result was not completely unexpected since both the fused silica and acid treated SWCNTs are negatively charged. The key idea of this work was to precoat the capillary with PDDA, a cationic polymer. PDDA was firmly adsorbed on the inner walls of the capillary via ionic interactions between the negatively charged SiOH of fused silica and the quaternary ammonium groups of the polymer. Indeed, it has been reported that immersion of a substrate (glass, quartz, silica wafer, gold, silver, and even Teflon) into an aqueous 1% solution of this positively charged polymer results in the strong adsorption of a monolayer (1.6 nm) of PDDA on the substrate [45]. The adsorption of a PDDA thin film on a glass substrate was also reported recently in our laboratory [46]. Acid treated CNTs became negatively charged (mainly due to the formation of –COOH and –OH groups) and were able to interact strongly with the quaternary ammonium groups of the adsorbed polymer to form a second layer. It has been reported that the positively charged PDDA layer on the capillary walls absorbs the negatively charged gold particles [20,45] to alter the electroosmotic mobility [20].

A series of experiments was conducted to characterize the electrophoretic behavior of the coated capillaries. The electroosmotic mobility of the PDDA-coated capillary (μ_{eof}), determined with mesityl oxide as the EOF marker, was estimated to be -3.95×10^{-4} cm^2 V^{-1} s^{-1} (reversal of the flow) compared to 4.63×10^{-4} cm^2 V^{-1} s^{-1} for the bare fused silica counterpart. Such a result indicated that the PDDA-coated capillary become positively charged, owing to the abundance of the quaternary ammonium groups, and effected a reversal of the EOF. It was expected that at high PDDA concentrations, not all quaternary ammonium groups of the polymer were engaged in ionic interactions with SiOH of fused silica.

The acid treated CNTs bearing negative charges were then flowed through the PDDA-coated capillary where they were adsorbed on the positively charged capillary wall via ionic interactions. At this point, the EOF returned to its original cathodic direction although its amplitude was diminished somewhat compared to the untreated capillary ($\mu_{eof} = 2.49 \times 10^{-4}$ cm^2 V^{-1} s^{-1}). The SWCNT coated layer could be stripped off by rinsing the capillary with 0.1N NaOH for 10 min whereas the PDDA layer remained intact. It was further observed that the original electroosmotic mobility of the CNT-PDDA-coated capillary could be reestablished by rinsing the capillary with a 0.05 g/L SWCNT suspension for 30 min.

3.3. Electroosmotic flow at different pHs

In order to investigate the surface behavior, the electroosmotic flow of the PDDA-CNTs coated capillaries was measured at different pHs and compared to the bare fused silica capillary (Fig. 3). As expected, the bare fused silica capillary shows an increased EOF with increased pH due to increased ionization of the silanol groups at higher pH values (pK_a of fused silica is about 2.2). A strong pH-dependence limits the use of bare fused silica to a defined pH. Although a similar trend was observed for the PDDA-SWCNT coated capillary, the coating resulted in significantly smaller EOF rates. Such a result implied that the inner wall of the bare fused silica capillary was effectively blocked by the combined PDDA-CNT layer. The EOF-pH dependence of the coated capillary was due to the presence of a fixed smaller number of ionizable –COOH groups on the carbon nanotubes, resulting from the

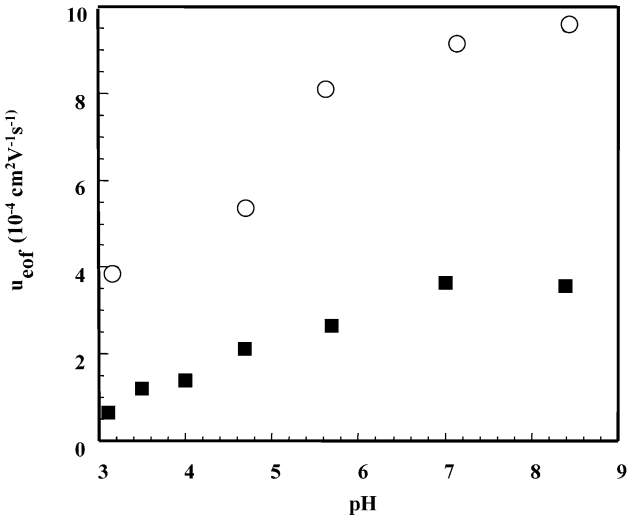

Fig. 3. Electroosmotic flow at different pHs. Capillary identification: (◯) uncoated and (■) PDDA-SWCNT coated. Conditions: capillaries of 57 cm (50 cm to detection window) × 50 μm I.D. × 360 μm O.D.; running buffers: sodium acetate (pH 3–4.7), MES (pH 5.7), sodium phosphate (pH 7), and sodium borate (pH 8.4). All buffers were of 20 mM ionic strength; UV detection at 214 nm and applied voltage of +30 kV; mesityl oxide was used as the EOF marker.

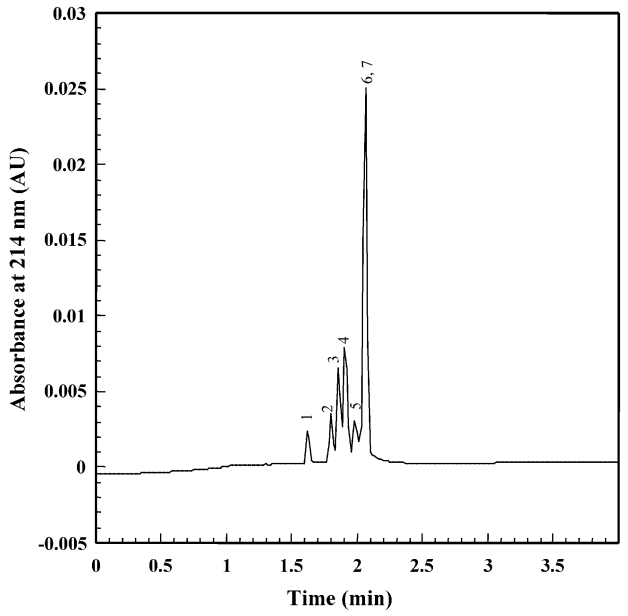

Fig. 4. Capillary electropherogram of a mixture of seven aniline derivatives (concentration: 1 mM each) obtained by a bare fused silica capillary. Peak identification: (1) 3-aminophenol (3-AP), (2) aniline, (3) *o*-anisidine, (4) 4-aminophenol (4-AP), (5) 4-chloroaniline (4-ClA), (6) 3-chloroaniline (3-ClA) and (7) 2-chloroaniline (2-ClA). Conditions: capillaries of 57 cm (50 cm to detection window) × 50 μm I.D. × 360 μm O.D.; 20 mM acetate, pH 4.7 run buffer; UV detection at 214 nm; applied voltage of +30 kV; pressure injection of 5 s at 0.5 psi.

acid treatment. Fused silica capillaries consist of a number of different acidic surface silanols which impart to the surface. There are at least three types of ionizing groups: isolated, vicinal, and germinal silanols. Therefore, EOF is strongly pH dependent at pH above 2.3 [27]. In contrast, the CNT coated capillary only possessed a fixed charge on the wall, which should minimize wall interactions and reduce the EOF rate.

3.4. Separation of aniline derivatives using SWCNT coated capillaries

Good CE resolution is normally realized when the analytes exhibit significantly different pK_as that are all different from the buffer pH. Several aniline derivatives selected for this study have similar pK_a values and could not be baseline resolved by CE with buffers prepared in various combinations of phosphate (10–50 mM) and borate (10–30 mM), for pHs ranging from 5.5 to 9. As shown in Fig. 4, the untreated capillary only partially resolved the mixture of seven anilines as the two chloroaniline isomers (2- and 3-) emerged as one single peak. Aniline was not baseline resolved from *o*-anisidine and these two compounds co-migrated with 4-aminophenol as a cluster. As reported, even a complicated buffer using a mixture of 7 mM hydroxypropyl-β-cyclodextrin and 13 mM sulfobutyl-β-cyclodextrin in 50 mM phosphate pH 8 was still unable to resolve aniline from *o*-anisidine [37]. In fact, aniline and *o*-anisidine always co-migrated even when various combinations of hydroxypropyl-β-cyclodextrin (3–35 mM) and sulfobutyl-β-cyclodextrin (2–30 mM) were used [37]. It should be noted that at this pH, the analytes were positively charged and migrated towards the cathode, i.e., the same direction as the EOF. No separation was attempted with the PDDA-coated capillary due to its reversal of EOF. Decreasing the separation potential from +30 kV to +20 kV to allow the analytes to stay longer in the capillary did not improve the separation.

With the SWCNT modified capillary, baseline resolution of all seven aniline derivatives was obtained even at +30 kV, the maximum allowable potential of the CE equipment (Fig. 5). The reduction of the separation potential from 30 kV to 25 kV only slightly improved the resolution of 3-chloroaniline and 2-chloroaniline (figure not shown, peaks 6 and 7). Although an exact mechanism for the separation is yet to be defined, such selectivity improvement, as shown in Fig. 5, could be accrued from different ionic and hydrophobic interactions between the solutes and the CNT coated capillary to effect their separation in an electrical field. In other words, the interaction of the solute and the modified capillary wall was reasoned to occur mainly via ionic interactions with the charged moieties of CNTs (–COOH groups). The migration order was not strictly dependent upon the pKa value of the analyte (Table 1) since 3-aminophenol with a pK_a value of 4.4 migrated before 4-aminophenol (pK_a = 5.3). It is, however, noted that chloroanilines are more hydrophobic than aniline and the migration order appeared to be pK_a dependent among these chloroanilines. It should also be noted that only 20 mM acetate buffer was used in the running buffer to minimize the resultant current (11–12 μA) since the separation was conducted at +30 kV to shorten the analysis time.

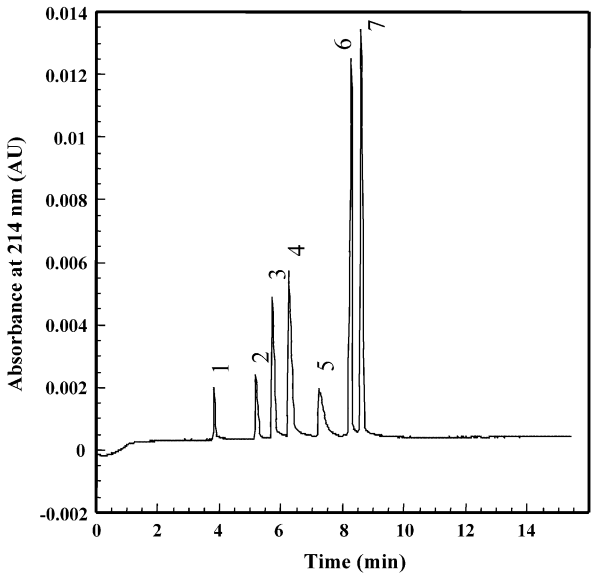

Fig. 5. Capillary electropherogram of a mixture of seven aniline derivatives (concentration: 1 mM each) in: PDDA-SWCNT coated capillary. Peak identification: (1) 3-AP, (2) aniline, (3) *o*-anisidine, (4) 4-AP, (5) 4-ClA, (6) 3-ClA and (7) 2-ClA. Conditions and abbreviations: same as Fig. 4.

Hydrophobic interaction was not completely unexpected since CNTs interact strongly with hydrophobic compounds, for example, the pyrene moiety of 1-pyrenebutanoic acid succinimidyl ester via π-stacking [33]. Hydrophobicity of CNTs is a well-known phenomenon since most metals would not adhere to CNTs [47]. Therefore, metal deposition onto CNTs has only been possible by surface modification and sensitization activation of the CNTs [48]. In particular, deposition of metal onto SWCNTs is also difficult because of the greater inertness, smaller size, and higher curvature of these materials compared to MWCNTs [49]. As mentioned earlier, we recently reported that the interaction between PDDA and CNTs is due to the π-orbital overlap of these two molecules [44]. In view of this, the π–π stacking interaction will take place between the π orbitals of CNTs and those of the benzyl groups present in anilines. However, this interaction is much weaker than that of CNTs with pyrene [33].

For both CNT modified capillaries, the separation was completed within 10 min compared to 20 min for cyclodextrin modified CE [37]. Separation efficiencies ranged from 7,000 to 51,000 plates for an effective capillary length of 50 cm (Table 1). The reproducibility was excellent with SWCNT coated capillaries, as shown by the migration time run-to-run RSD of less than 0.45% (12 runs). The SWCNT coated capillaries exceeded 70 h of use for 220 repeated analyses without compromising its performance to resolve the seven aniline compounds.

Table 1
Migration times and plate numbers resulting from the separation of the nitrogen-containing aromatic compounds using a PDDA-SWCNT coated capillary with 20 mM acetate, pH 4.7 at 30 kV (effective capillary length: 50 cm)

Analyte	Migration time (min)	Plates (*N*)	pK_a
3-Aminophenol (AP)	3.78	15000	4.4; 9.8
Aniline (A)	5.16	13000	4.6
o-Anisidine	5.70	15000	4.5
4-AP	6.21	11000	5.3; 10.5
4-Chloroaniline (ClA)	7.19	7000	4.1
3-ClA	8.25	23000	3.5
2-ClA	8.56	51000	2.7

4. Conclusion

In brief, the key idea of this paper was to combine PDDA and CNTs to modify the capillary wall to improve its interaction with the solute under an electrical field. This combined layer formed a novel material coating that could be useful for manipulation of the selectivity between solutes in CE and other separation schemes. The interaction of the solutes and the modified capillary wall could occur via a dual mechanism: ionic interactions with the charged moieties of CNTs and/or through hydrophobic interactions between the benzene ring and the surface of the CNTs. The single-walled CNT modified capillaries were used for over 200 repeated analyses without compromising its analytical performance. Important developments in the use of nanoparticles in separation science are taking place, accompanying the trends towards capillary coating and monolithic stationary phases. CNTs are promising candidates to enhance separations in CE, chromatography and chip-based systems because of their high surface area available for chemical adsorption/interaction. The CNT-coated capillary allows for achievement of the separation without the use of expensive materials that are required in cyclodextrin modified CE or micellar electrokinetic chromatography (MEKC). In particular, such coated capillaries are useful for small-molecule separation such as explosives and aromatic hydrocarbons, a subclass of high-performance capillary electrophoresis.

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