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Carbon-Nanotube–Alginate Composite Modified Electrode Fabricated by In Situ Gelation for Capillary Electrophoresis

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Abstract: This report describes the development and the application of a novel carbon-nanotube (CNT)–alginate composite modified electrode as a sensitive amperometric detector for capillary electrophoresis (CE). The composite electrode was fabricated on the basis of in situ gelation of a mixture of CNTs and sodium alginate on the surface of a carbon disc electrode in aqueous calcium chloride solution. SEM, energy-dispersive spectroscopy, XRD, and FTIR spectroscopy offered insights into the nature of the novel composite. The results indicated that the CNTs were well dispersed and embedded throughout the alginate matrix to form an interconnected carbon-nanotube network on the base electrode. The performance of this unique CNT-based detector has been demonstrated, in conjunction with CE, by separating and detecting five caffeic acid derivatives. The new CNT-based CE detector offered significantly lower operating potentials, substantially enhanced signal-to-noise characteristics, and a lower expense of operation. The simplicity and significant performance exhibited by the CNT–alginate composite modified electrode also indicate great promise for the use of this electrode in microchip CE, flowing-injection analysis, and other microfluidic analysis systems.

Keywords: alginates · composites · electrochemistry · electrophoresis · nanotubes

Introduction

Carbon nanotubes (CNTs) have attracted more and more attention since Iijima reported their existence in 1991 because of their high electrical conductivity, mechanical strength, and chemical stability.[1–3] They are ideal materials for the fabrication of electrochemical sensors and biosensors because of their unique properties.[4–6] Recently, it was demonstrated that CNTs showed strong electrocatalytic activity and minimization of surface fouling when they were employed to improve the electrochemical response of some important bioactive substances.[7–10] A variety of CNT-based electrodes have been fabricated for sensing different electroactive compounds, including a CNT-modified screen-printed carbon electrode,[11] a CNT powder microelectrode,[12] a CNT–teflon composite electrode,[13] a CNT screen-printed electrode,[14] a CNT–epoxy composite electrode,[15] a CNT–copper composite electrode,[16] and a CNT–Fe$_3$O$_4$ composite electrode.[17]

The commonly used approach to fabricating CNT electrodes is surface modification. CNTs are insoluble in most solvents so they are usually dispersed in solvents[18,19] or polymer solutions (such as nafion[20] and chitosan[21] solutions) that are cast on the surface of electrodes to load the CNTs. In addition, methods based on electrochemical deposition[22] and electrochemical polymerization[23,24] have been employed for loading CNTs onto electrodes. Recently, we developed a method based on in situ polymerization to fabricate CNT–polymer composite electrodes as end-column amperometric detectors for conventional and microchip CE. CNTs were mixed with oligomers of epoxy,[15] methyl acrylate,[25] and styrene[26] and were inserted into the inner bores of fused silica capillaries. After the mixtures had cured, CNT–polymer composite electrodes were obtained. CNT-based electrodes have been demonstrated to reduce the overpotential significantly.[4,22] The ability of CNTs to pro-

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mote electron-transfer reactions suggests great promise for the use of CNTs in amperometric sensors.[4]

Since CE in its modern form was first described by Jorgenson and Lukacs in 1981,[27,28] it has been applied to the separation and determination of a variety of samples because of its minimal sample-volume requirements, short analysis time, and high separation efficiency. CE analysis holds considerable promise for biomedical and pharmaceutical analysis, clinical diagnostics, environmental monitoring, and forensic investigations.[29–32] Amperometric detection (AD) offers great promise for CE, with features that include high sensitivity, inherent miniaturization of both the detector and the control instrumentation, low cost, low power demands, and high compatibility with micromachining technologies.[33] The performance of CE–AD is strongly influenced by the detection-electrode material. The detection electrode should provide favorable signal-to-background characteristics and a reproducible response. A range of materials, including platinum, gold, and various forms of carbon, have been found useful for CE-based electrochemical detection.[34]

Alginates are naturally occurring polysaccharides extracted from brown algae. Their block-copolymer chains are composed of (1,4)-linked β-D-mannuronate and α-L-guluronate residues.[35] They have found wide applications in the food and beverage industries, pharmaceutical manufacturing, the immobilization of enzymes and other biomaterials, water pretreatment, etc.[36] As a water-soluble monovalent cation salt of alginic acid, sodium alginate contains a large number of carboxyl and hydroxy groups that can be crosslinked by some divalent cations (such as Ca^{2+}) to form water-insoluble alginate gels.[37] However, we are not aware of any earlier reports on the preparation of conductive CNT–alginate composites for the purposes of electrochemical sensing.

In this work, a CNT–alginate composite modified electrode has been fabricated by in situ gelation and employed as the end-column amperometric detector of a CE system. The fabrication details, characterization, feasibility, and performance of the novel CNT–alginate composite modified electrode in conjunction with CE have been demonstrated by monitoring five caffeic acid derivatives, as described in the following sections.

Results and Discussion

In this work, CNTs were loaded on the surface of a carbon electrode with the aid of sodium alginate by in situ gelation (Figure 1). To prepare the modified electrode, a mixed solution of sodium alginate and CNTs was loaded on the surface of a carbon disc electrode by dip coating. The electrode was subsequently treated with an aqueous calcium chloride solution to form a layer of CNT–calcium alginate composite gel. Figure 2 A shows an SEM image of the CNT–alginate composite on the electrode. It can be seen clearly from Figure 2 A that the CNTs are well dispersed and embedded
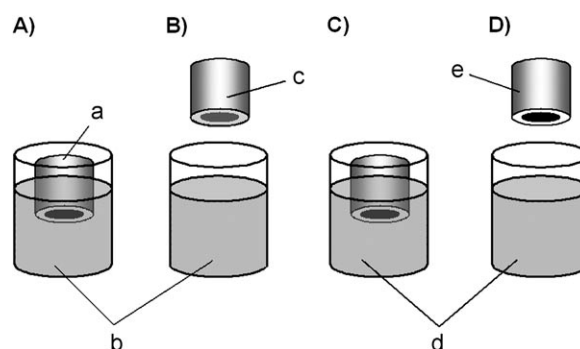

Figure 1. Schematic diagram showing the fabrication process of the CNT–alginate composite modified electrode: A) Dipping a carbon disc electrode (a) into 3% sodium alginate aqueous solution containing 3% CNTs (b) for 30 s; B) drying the sodium alginate coated electrode (c) in the air for 10 min; C) dipping the sodium alginate coated electrode (c) into 3% calcium chloride aqueous solution (d) for 2 h; D) drying the modified electrode in the air for 1 h to obtain the final CNT–alginate composite modified electrode (e).
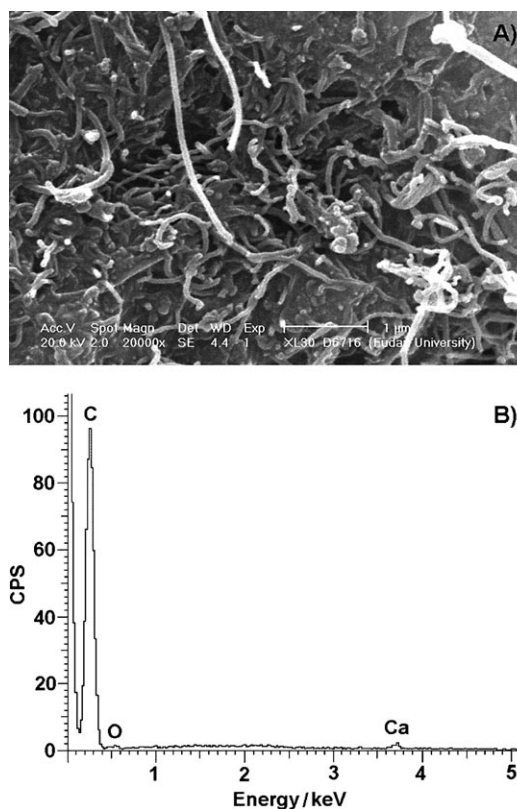

Figure 2. A) SEM image and B) energy dispersive spectroscopy (EDS) results for the CNT–alginate composite on a carbon disc electrode. Conditions for SEM: accelerating voltage: 20 kV; magnification: ×20000.

throughout the alginate matrix and that an interconnected CNT network has formed on the electrode. This conductive CNT network may establish electrical-conduction pathways throughout the whole system; these pathways would be responsible for the electrical conductivity and electrochemical sensing. As illustrated in Figure 2 B, the EDS spectrum indi-

cates that all elements in the CNT–calcium alginate composite have been identified, except hydrogen. The fact that no peak was found for sodium (1.04 keV) implies that the alginate in the composite mainly existed as the calcium salt.

Figure 3 displays the X-ray diffraction (XRD) patterns of calcium alginate, CNT, and the CNT–alginate composite. Also illustrated in the inset of Figure 3 is a photograph of a
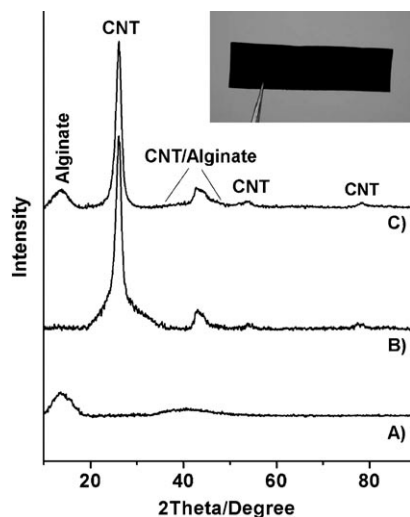

Figure 3. XRD patterns of A) calcium alginate, B) CNTs, and C) CNT–alginate composite. Inset: photograph of a piece of CNT–alginate composite 'paper'.

piece of CNT–alginate composite 'paper' for the measurement of XRD pattern. It was prepared by dipping a piece of a microscope glass slide (25.4×76.2 cm) coated with a mixture of CNTs and sodium alginate solution into aqueous calcium chloride solution. Diffraction peaks assigned to CNTs at 25.9° and 42.7° (corresponding to the graphite indices of (002) and (100))[38] were observed in the XRD curves of pure CNTs and the CNT–alginate composite; this indicates that the CNT structure was not destroyed after the in situ gelation of sodium alginate. The two broad characteristic peaks of calcium alginate were also found in the XRD curve of the CNT–alginate composite, with the second peak of the CNTs merging with the second peak of calcium alginate.

The FTIR spectra (Figure 4) of the CNTs, calcium alginate, and CNT–alginate composite were also measured. Absorption bands for CNTs pretreated with concentrated HNO_3 were observed at $\tilde{v} = 3400$, 1709, and 1565 cm^{-1} and were attributed to the stretching vibrations of O−H, C=O, and C=C bonds, respectively. The peaks at 1640, 1200, and 1090 cm^{-1} corresponded to the vibration of the carboxylic acid groups.[39] In the IR spectra of calcium alginate and the CNT–alginate composite, the peaks at about 1085, 1420, and 1610 cm^{-1} were assigned to the stretching vibration of C−O, the asymmetric stretching of COO$^-$, and the symmetric stretching of COO$^-$, respectively.[40] The weak bands between 2960 and 2840 cm^{-1} could be attributed to the stretching of C−H bonds. When the CNTs pretreated with nitric
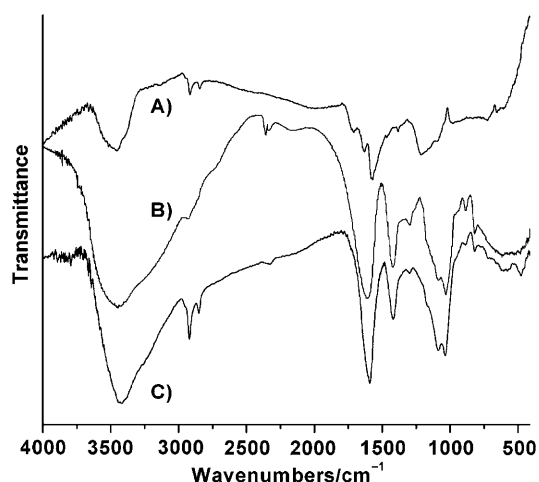

Figure 4. FTIR spectra of A) CNTs, B) calcium alginate, and C) CNT–alginate composite.

acid were mixed with calcium alginate, a marked increase was observed in the intensity ratio between the symmetric COO$^-$ stretching (at ≈ 1610 cm^{-1}) and asymmetric COO$^-$ stretching (at ≈ 1420 cm^{-1}). Absorption bands near 3430 cm^{-1} in all spectra were assigned to the O−H stretching.

Figure 5 shows the thermogravimetric analysis (TGA) and differential TGA (DTGA) curves for the CNT–alginate composite at a heating rate of 10°Cmin^{-1}. An obvious weight loss of the composite was found in the temperature ranges 120–220°C and 430–580°C, due to the decomposing of the alginate and CNTs, respectively. Based on the TGA curve, the weight fraction of CNT was estimated to be approximately 1/2, which is well in agreement with the expected value.
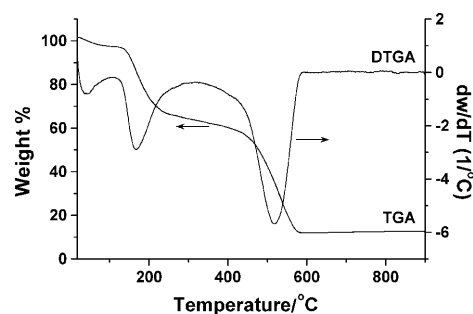

Figure 5. TGA and DTGA curves for the CNT–alginate composite.

In the present work, the CNT–alginate composite modified electrode was coupled with a CE system as an end-column amperometric detector. The attractive performance of the detector, with enhanced signal-to-noise levels and well-resolved peaks, was indicated from the detection of five caffeic acid derivatives. Figure 6 illustrates the electropherograms of a mixture containing protocathechulic aldehyde, salvianolic acid A, salvianolic acid B, caffeic acid, and proto-
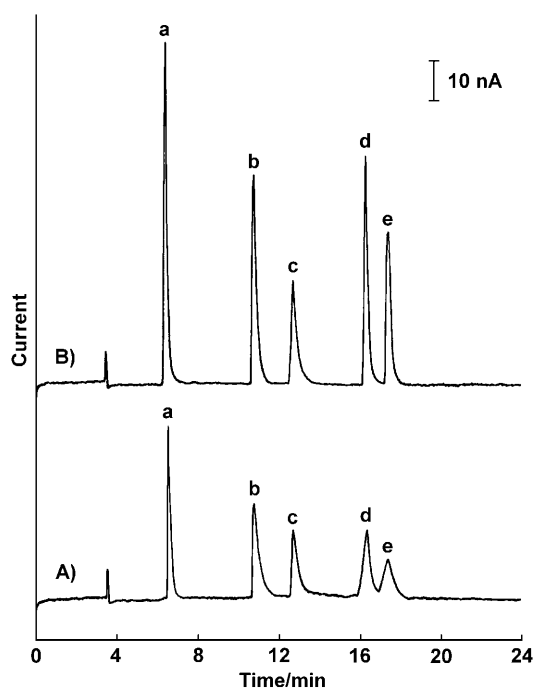
Figure 6. Electropherograms for a mixture containing 0.5 mM protocathechulic aldehyde (a), salvianolic acid A (b), salvianolic acid B (c), caffeic acid (d), and protocathechulic acid (e) at A) a bare carbon disc electrode and B) the CNT–alginate composite modified electrode. Detection potential: 0.8 V versus Ag/AgCl wire; fused-silica capillary: 25 μm ID, 40 cm length; detection electrode: 320 μm diameter disc electrode; running buffer: 50 mM borate buffer (pH 9.2); separation and injection voltage: 12 kV; injection time: 6 s; detection potential: 0.8 V versus Ag/AgCl wire.

cathechulic acid (0.5 mM each) at a bare carbon disc electrode and at a CNT–alginate composite modified electrode. The five analytes could be separated with well-defined and resolved peaks within 19 min when the CNT-based composite electrode was used. As shown in Figure 6, the peak currents of the five analytes at the CNT–alginate composite modified electrode are much higher than those at the carbon disc detector. The sensitivities of protocathechulic aldehyde, salvianolic acid A, salvianolic acid B, caffeic acid, and protocathechulic acid were 169.6, 104.3, 51.5, 113.3, and 75.6 nA mM^{-1}, respectively, at the CNT–alginate composite modified electrode and 42.8, 23.3, 16.3, 15.8, and 8.7 nA mM^{-1}, respectively, at the bare carbon electrode. The higher sensitivity of the CNT-based composite detector led to lower detection limits compared to those with the bare carbon electrode (0.18 vs. 0.70, 0.29 vs. 1.29, 0.58 vs. 1.84, 0.26 vs. 1.90, and 0.40 vs. 3.45 μM for protocathechulic aldehyde, salvianolic acid A, salvianolic acid B, caffeic acid, and protocathechulic acid, respectively (based on a signal-to-noise ratio of $S/N = 3$)).

Since the areas of the peaks in Figure 6 corresponded to the charges (Q) passed across the surface of the detection electrode for the oxidation of the five caffeic acids, the molar numbers of converted analytes (N_Q) could be calculated by using Faraday's law, $Q = zFN_Q$, in which z and F are

the number of electrons transferred per molecule and the Faraday constant, respectively. When the molar number of each analyte injected into the separation capillary (N_I) was calculated based on the injection volume (5.7 nL) and the analyte's concentration in the sample solution, the conversion efficiency ($\alpha = N_Q/N_I$) on the detection electrode could be estimated.[41] At 0.8 V versus Ag/AgCl wire, the calculated conversion efficiencies of protocathechulic aldehyde, salvianolic acid A, salvianolic acid B, caffeic acid, and protocathechulic acid were 95.4, 92.3, 76.5, 87.5, and 89.1 %, respectively, on the CNT–alginate composite modified electrode and 66.2, 64.3, 49.4, 65.0, and 45.4 %, respectively, on the bare carbon electrode. Obviously, the CNT–alginate composite on the electrode significantly enhanced the conversion efficiencies of the five analytes. Overall, the CNT–alginate composite is a promising material for electrochemical sensing. The present CNT–alginate composite electrode shows low-noise characteristics and a stable baseline. The ability of CNTs to promote electron-transfer reactions on the electrode can be attributed to their special electronic structure and high electrical conductivity.[11]

Figure 7 depicts the typical hydrodynamic voltammograms (HDVs) for the oxidation of 0.5 mM salvianolic acid A at the bare carbon and CNT–alginate composite electrodes. The curves were recorded pointwise over the +0.1 to +1.1 V versus an Ag/AgCl electrode range by changing the applied potential by 0.1 V. The current response of the CNT-based composite electrode was higher than that of the carbon electrode at the same potential. When the applied potential exceeded +0.50 V for the bare carbon electrode or +0.30 V for the CNT–alginate composite modified electrode, the peak current of the electrodes rose rapidly. However, the current responses increased much more slowly when the potential was increased above +0.90 V or +0.70 V for the bare carbon and CNT–alginate composite modified electrodes, respectively. When the detection potential was higher than 0.8 V, the current response of salvianolic acid A began to decrease. The applied potential of the CNT-based electrode was, therefore, maintained at +0.80 V, under which condition the background current was not too high and the signal-to-noise ratio was as high as possible. The half-wave potentials at the carbon and CNT–alginate composite modified electrodes were +0.65 and +0.48 V, respectively, for sal-
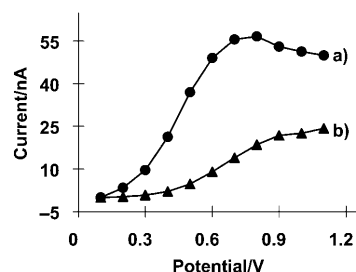

Figure 7. Hydrodynamic voltammograms for 0.5 mM salvianolic acid A at a) the CNT–alginate composite modified electrode and b) a bare carbon disc electrode. Conditions: as given in the legend for Figure 6.

vianolic acid A. The difference in electrocatalytic activity toward the investigated analyte was pronounced, because the half-wave potential on the CNT–alginate composite electrode was 170 mV lower than that on the carbon electrode; this result indicates that the CNT-based electrode allowed amperometric detection with higher sensitivity and at significantly lower detection potentials.

The suitability of the CNT–alginate composite modified electrode for measuring real samples was demonstrated by detecting the constituents in a pharmaceutical preparation after CE separation. Figure 8 illustrates the electropherogram obtained upon injection of a 1:20 diluted sample of radix Salviae miltiorrhizae in the running buffer. The concentrations of protocathechulic aldehyde, salvianolic acid A, salvianolic acid B, caffeic acid, and protocathechulic acid in the radix Salviae miltiorrhizae injection were determined to be 1.647 (relative standard deviation (RSD) 2.9%, $n=3$), 1.321 (RSD 3.2%, $n=3$), 3.184 (RSD 4.1%, $n=3$), 0.1556 (RSD 4.7%, $n=3$), and 0.6254 mg mL^{-1} (RSD 3.8%, $n=3$), values that are similar to the data in previous reports.[42,43] The results demonstrated that this method has both high accuracy and good precision for the analytes tested in the real sample.
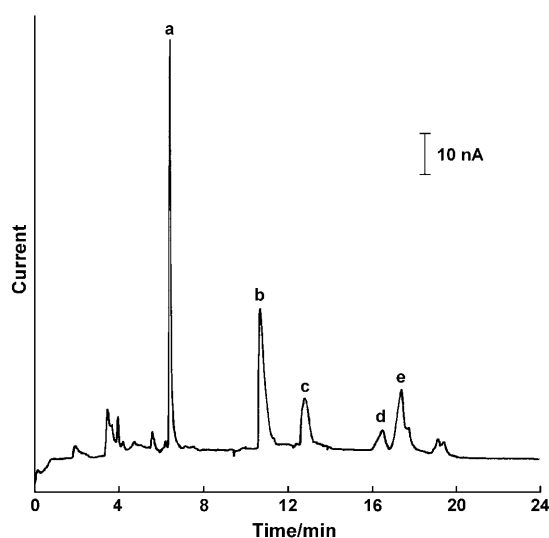

Figure 8. Typical electropherogram for a 1:20 diluted radix Salviae miltiorrhizae injection at a CNT–alginate composite modified electrode. Detection potential: 0.8 V versus Ag/AgCl wire. Peak labels and other conditions: as given in the legend for Figure 6.

Conclusion

In summary, we have developed a simple approach based on in situ gelation for the fabrication of CNT–alginate composite modified electrodes as the end-column amperometric detectors of CE. SEM, EDS, XRD, and FTIR spectra indicated that the CNT–calcium alginate composite was successfully prepared on the electrodes. The performance, utility, and advantages of the novel setup have been demonstrated by the separation and detection of five caffeic acid deriva-

tives. The modified electrode was characterized by its higher resolution and sensitivity, lower expense of operation, and smaller sample requirements. The novel CNT-based CE detector offered favorable signal-to-background characteristics, strong electrocatalytic activity, sharp peaks for the analytes, and simple design and fabrication. Hence, this technique shows great promise for a wide range of bioanalytical and other applications.

Experimental Section

Reagent and solutions: Multiwall carbon nanotubes (MWCNTs, 40–60 nm diameter, 5–15 μm long), with a purity of 95%, were provided by Shenzhen Nanoport Company (Shenzhen, China) and were pretreated by stirring in concentrated nitric acid at 60°C for 12 h prior to use. Sodium alginate, calcium chloride, and borax were all purchased from SinoPharm (Shanghai, China). Protocathechulic aldehyde, salvianolic acid A, salvianolic acid B, caffeic acid, and protocathechulic acid (the molecular structures are shown in Figure S1 in the Supporting Information,) were obtained from the National Institute for Control of Pharmaceutical and Biological Products (Beijing, China). Graphite powder was supplied by Aldrich (Wilwaukee, WI, USA). Other chemicals were all analytical grade. A sample radix Salviae miltiorrhizae injection (Batch no. 20070609, Shanghai No.1 Biochemical & Pharmaceutical Co., Ltd, Shanghai, China) was purchased from a local drug store.

Stock solutions of protocathechulic aldehyde, salvianolic acid A, salvianolic acid B, caffeic acid, and protocathechulic acid (10 mM) were all prepared in methanol. The running buffer for CE separation was 50 mM borate buffer (pH 9.2). Sample solutions were prepared by diluting the stock solutions in the running buffer.

Electrode fabrication: The fabrication process for the detection electrodes is illustrated in Figure S2 in the Supporting Information). A piece of copper wire (10 cm long, 150 μm diameter) was inserted into a 3.0 cm long fused silica capillary (320 μm inner diameter (ID), 450 μm outer diameter (OD); Hebei Yongnian Ruipu Chromatogram Equipment Co., Ltd., Hebei, China) and a 2 mm opening was left in the capillary for subsequent filling with the graphite–epoxy composite. The other end of the capillary was sealed together with copper wire and thermal adhesive. Epoxy resin and hardener (Zhejian Cixi Tiandong Adhesive Co. Ltd., Ningbo, China) were mixed thoroughly at a weight ratio of 2:1. The graphite powder and epoxy resin/hardener were hand mixed in a ratio of 1:1 (w/w). The graphite–epoxy composite was subsequently packed into the capillary by pressing the open end of the capillary (to a depth of ≈3 mm) into a sample of the composite. The graphite–epoxy composite should touch the end of the copper wire inside the capillary tightly for electric contact. The composite was then allowed to cure at room temperature for at least 3 h.

Electrode modification: Figure 1 illustrates the fabrication process of the CNT–alginate composite modified electrode. Prior to modification, the bare carbon disc electrode (320 μm diameter) needed to be successively polished with emery paper and sonicated in doubly distilled water. After the surface of the disc electrode was allowed to touch the surface of a 3% sodium alginate aqueous solution containing 3% CNTs for 30 s, the electrode was taken out and allowed to dry in air for 10 min. Subsequently, the sodium alginate coated electrode was dipped in 3% calcium chloride aqueous solution for 2 h to convert the sodium alginate into calcium alginate gel, which is water insoluble. After the in situ gelation, a layer of CNT–calcium alginate composite gel formed on the surface of the base electrode. Finally, the modified electrode was flushed with water and dried in air for 1 h to obtain a CNT–alginate composite modified electrode.

Apparatus: The CE–AD system used has been described previously.[30] A ±30 kV high-voltage DC power supply (Shanghai Institute of Nuclear Research, China) provided a separation voltage between the two ends of the capillary. The inlet of the capillary was held at a positive potential

and the outlet of the capillary was maintained at the base level. The separations were carried out in a 40 cm length of fused silica capillary (25 µm ID and 360 µm OD; Polymicro Technologies, Phoenix, AZ, USA).

As illustrated in Figure S3 in the Supporting Information, a 3-electrode electrochemical cell, consisting of a laboratory-made 320 µm diameter carbon disc electrode or a CNT–alginate modified electrode, a platinum auxiliary electrode, and an Ag/AgCl wire as the reference electrode (l, p, and q, respectively, in Figure S3 in the Supporting Information), was used in combination with a BAS LC-4C amperometric detector (Bioanalytical Systems Inc., West Lafayette, IN, USA). The filter of the detector was set at 0.1 Hz. The detection electrode was positioned carefully opposite the outlet of the capillary with the aid of a high-integrated 3D amperometric setup (Figure S3 in the Supporting Information) and arranged in a wall-jet configuration. The electropherograms were recorded by using a LKB·REC1 chart recorder (Pharmacia, Sweden). To improve the repeatability of the peak current and migration time, the whole CE system was assembled in a room that was air conditioned at 25°C to reduce temperature fluctuations.

The side view, top view, and an expanded view of the 3D adjustable device for the CE–AD are illustrated in Figure S3 in the Supporting Information (Letters in parentheses below refer to this figure). Plexiglas holders (m) were fabricated for housing the detection reservoir (i) and the separation capillary (d) sealed inside a plexiglas plate (e); this allowed convenient replacement and reproducible positioning, with silicone grease ensuring proper sealing. The three-electrode amperometric detection system was fabricated in the detection cell at the capillary outlet side. (Note that the detection cell was grounded through the grounding platinum electrode (o). The detection electrode (l) was placed opposite the capillary outlet through the stainless-steel guiding tube (j, 500 µm ID and 800 µm OD). Platinum wire (c), inserted into the buffer (a) or sample (b) vials, served as a contact to the high-voltage power supply. The end of the guiding tube (j) outside the detection reservoir (i) was sealed by a piece of small silicon-rubber holder (k, 3 mm diameter, 2.5 mm thick) with the capillary-based detection electrode (l) inserted inside. The silicon-rubber holder (k) could not only prevent solutions in the detection cell (i) from leaking, but the holder could also hold the detection electrode (l) while still allowing it to move back and forth to define a desired gap distance to the capillary outlet. It also made it possible to leave an effective gap distance (usually 30–60 µm) by pushing the detection electrode gently to the capillary outlet until soft contact was attained, due to the native elasticity of the rubber. The outlet of the separation capillary (d) was inserted into the channel of the plexiglas plate (e) until the outlet came out by 1–2 mm and it was then sealed in place with wax. The distance (20 mm) between the two screw bolts (f) on the plexiglas holder in Figure S3 in the Supporting Information is wider than the width of the plexiglas plate (e, 16 mm); this allows the sealed capillary (d) to move right and left slightly to accomplish good alignment with the detection electrode. A piece of 2.5 mm thick high-elasticity silicon-rubber sheet (n) was attached to the bottom of the plexiglas plate (e) with a capillary sealed inside and subsequently sandwiched between a plexiglas cover plate (h) and the plexiglas holder (m) with the aid of the screw bolts (f) and screw nut (g), thereby allowing the capillary (d) to be adjusted up and down within approximately 1 mm to align its outlet to the detection electrode (l). With the aid of the two-dimensionally adjustable capillary (d) and the one-dimensionally adjustable disc detection electrode (l), the present CE–AD system (as shown in Figure S3 in the Supporting Information) facilitates the three-dimensional alignment between the capillary and the detection electrode without the need for a complicated three-dimensional manipulator. The solution in the buffer and sample vials (a and b) was retained by the surface tension, although the orientation of the vial mouth is horizontal.

The surface morphology and EDS spectrum of the CNT–alginate composite were measured by using a scanning electron microscope (PHILIPS XL 30, Eindhoven, The Netherlands). Thermal gravimetric analyses and differential thermal gravimetric analyses were made with a Perkin Elemer Pyris 1 DTA-TGA instrument under nitrogen at a heating rate of 10°C min⁻¹. XRD measurements were carried out by using a Rigaku D/ max-rB diffractometer (Rigaku, Tokyo, Japan) with CuK α1 radiation (40 kV, 60 mA). The FTIR spectra of the CNTs pretreated with nitric acid, the alginate, and the CNT–alginate composite were measured by using an FTIR spectrometer (NEXUS470, NICOLET).

Procedures: Before use, the CNT–alginate composite modified disc electrode was flushed with water and the surface of the detection electrode (l in Figure S3 in the Supporting Information) was positioned carefully opposite the capillary outlet through the guiding metal tube (j in Figure S3 in the Supporting Information). The gap distance between the disc electrode and the capillary outlet was adjusted to approximately 50 µm by comparison with the inner diameter (25 µm) of the separation capillary while being viewed under a microscope.[30]

Prior to use, the capillary used for the separation was treated by flushing with 0.1 M NaOH and doubly distilled water for 10 min each. Subsequently, the capillary was filled with the running buffer and was conditioned with the running buffer for at least 10 min at a voltage of 12 kV between the two ends of the capillary. CE was performed at a separation voltage of 12 kV, unless otherwise indicated. The potential applied to the detection electrode was +0.80 V versus Ag/AgCl wire. Samples were injected electrokinetically into the capillary at 12 kV for 6 s. Before injection, both the anode end of the capillary and the platinum-wire anode were immersed in the sample solution in the sample vial (b in Figure S3 in the Supporting Information). After an injection voltage of 12 kV was applied between the two ends of the capillary for 6 s, the sample solution could be introduced into the capillary. The anode end of the capillary, together with the anode, was then quickly returned to the anode solution in the buffer vial (a in Figure S3 in the Supporting Information). A voltage of 12 kV was subsequently applied in the constant-voltage mode for the CE separation. The amperometric detector was on during the injection procedures. Note that the cathode solution in the electrochemical detection cell, the anode solution, and the sample solution were all at the same level. Moreover, sample solutions, standard solutions, and running buffer were all filtered through a polypropylene filter (0.22 µm, Shanghai Bandao Industry Co., Ltd., Shanghai, China) prior to use.

Acknowledgements

[1] S. Iijima, *Nature* **1991**, *354*, 56–58.
[2] R. H. Baughman, A. Zakhidov, W. A. de Heer, *Science* **2002**, *297*, 787–792.
[3] P. M. Ajayan, *Chem. Rev.* **1999**, *99*, 1787–1799.
[4] J. Wang, *Electroanalysis* **2005**, *17*, 7–14.
[5] R. S. Chen, W. H. Huang, H. Tong, Z. L. Wang, J. K. Cheng, *Anal. Chem.* **2003**, *75*, 6341–6345.
[6] C. E. Banks, T. J. Davies, G. G. Wildgoose, R. G. Compton, *Chem. Commun.* **2005**, 829–841.
[7] Z. H. Wang, J. Liu, Q. L. Liang, Y. M. Wang, G. Luo, *Analyst* **2002**, *127*, 653–658.
[8] G. Zhao, S. Q. Zang, K. Z. Liu, S. Lin, J. Liang, X. Y. Guo, Z. J. Zhang, *Anal. Lett.* **2002**, *35*, 2233–2244.
[9] J. Wang, M. Musameh, *Analyst* **2003**, *128*, 1382–1385.
[10] M. Musameh, J. Wang, A. Merkoci, Y. H. Lin, *Electrochem. Commun.* **2002**, *4*, 743–746.
[11] J. Wang, G. Chen, M. P. Chatrathi, M. Musameh, *Anal. Chem.* **2004**, *76*, 298–302.
[12] Y. D. Zhao, W. D. Zhang, H. Chen, Q. M. Luo, *Talanta* **2002**, *58*, 529–534.
[13] J. Wang, M. Musameh, *Anal. Chem.* **2003**, *75*, 2075–2079.
[14] J. Wang, M. Musameh, *Analyst* **2004**, *129*, 1–2.
[15] G. Chen, L. Y. Zhang, W. Wang, *Talanta* **2004**, *64*, 1018–1023.

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[16] J. Wang, G. Chen, M. Wang, M. P. Chatrathi, *Analyst* **2004**, *129*, 512–515.

[17] S. Qu, J. Wang, J. L. Kong, P. Y. Yang, G. Chen, *Talanta* **2007**, *71*, 1096–1102.

[18] H. Luo, Z. Shi, N. Li, Z. Gu, Q. Zhuang, *Anal. Chem.* **2001**, *73*, 915–920.

[19] F. H. Wu, G. C. Zhao, X. W. Wei, *Electrochem. Commun.* **2002**, *4*, 690–694.

[20] J. Wang, M. Musameh, Y. Lin, *J. Am. Chem. Soc.* **2003**, *125*, 2408–2409.

[21] M. Zhang, A. Smith, W. Gorski, *Anal. Chem.* **2004**, *76*, 5045–5050.

[22] X. L. Luo, J. J. Xu, J. L. Wang, H. Y. Chen, *Chem. Commun.* **2005**, 2169–2171.

[23] M. L. Guo, J. H. Chen, J. Li, B. Tao, S. Z. Yao, *Anal. Chim. Acta* **2005**, *532*, 71–77.

[24] M. Gao, S. Huang, L. Dai, G. Wallace, R. Gao, Z. Wang, *Angew. Chem.* **2000**, *112*, 3810–3813; *Angew. Chem. Int. Ed.* **2000**, *39*, 3664–3667.

[25] X. Yao, H. X. Wu, J. Wang, S. Qu, G. Chen, *Chem. Eur. J.* **2007**, *13*, 846–853.

[26] J. J. Xu, H. Y. Zhang, G. Chen, *Talanta* **2007**, *72*, 932–937.

[27] J. W. Jorgenson, K. D. Lukacs, *Anal. Chem.* **1981**, *53*, 1298–1302.

[28] J. W. Jorgenson, K. D. Lukacs, *J. Chromatogr.* **1981**, *218*, 209–216.

[29] G. Chen, *Talanta* **2007**, *74*, 326–332.

[30] X. Yao, X. J. Xu, P. Y. Yang, G. Chen, *Electrophoresis* **2006**, *27*, 3233–3242.

[31] C. W. Huck, G. Stecher, H. Scherz, G. Bonn, *Electrophoresis* **2005**, *26*, 1319–1333.

[32] D. Fliser, S. Wittke, H. Mischak, *Electrophoresis* **2005**, *26*, 2708–2716.

[33] G. Chen, Y. Z. Zhu, Y. F. Wang, X. J. Xu, T. Lu, *Curr. Med. Chem.* **2006**, *13*, 2467–2485.

[34] L. A. Holland, A. M. Leigh, *Electrophoresis* **2002**, *23*, 3649–3658.

[35] R. Valentin, R. Horga, B. Bonelli, E. Garrone, F. D. Renzo, F. Quignard, *Biomacromolecules* **2006**, *7*, 877–882.

[36] W. R. Gombotz, S. F. Wee, *Adv. Drug Delivery Rev.* **1998**, *31*, 267–285.

[37] C. Sartori, D. S. Finch, B. Ralph, K. Gilding, *Polymer* **1997**, *38*, 8, 43–51.

[38] M. Cochet, W. K. Maser, A. M. Benito, M. A. Callejas, M. T. Martinez, J. M. Benoit, J. Schreiber, O. Chauvet, *Chem. Commun.* **2001**, 1450–1451.

[39] D. Mawhinney, V. Naumenko, A. Kuznetsova, J. Yates, Jr., J. Liu, R. E. Smalley, *J. Am. Chem. Soc.* **2000**, *122*, 2383–2384.

[40] L. Fuks, D. Filipiuk, M. Majdan, *J. Mol. Struct.* **2006**, *792–793*, 104–109.

[41] M. Pumera, A. Merkoci, S. Alegret, *Electrophoresis* **2006**, *27*, 5068–5072.

[42] H. Y. Zhang, Z. D. Hu, G. L. Yang, Z. H. Shi, H. W. Sun, *Chromatographia* **1999**, *49*, 219–222.

[43] Y. J. You, G. Q. Cheng, M. H. Chen, *Chin. J. Pharm. Anal.* **2004**, *24*, 46–49.