A multi-walled carbon nanotube/poly(urea-formaldehyde) composite prepared by *in situ* polycondensation for enhanced electrochemical sensing†

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A novel multi-walled carbon nanotube/poly(urea-formaldehyde) (CNT/PUF) composite was prepared for enhanced electrochemical sensing. The composite electrodes were fabricated by the *in situ* polycondensation of a mixture containing CNTs, and the urea and formaldehyde prepolymer, in electrode tubes with the aid of a curing catalyst. The morphology and structure of the novel composite were investigated by scanning electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy. The results indicate that the CNTs were well dispersed and embedded throughout the PUF matrix to form an interconnected CNT network. The electrocatalytic performance of the CNT/PUF composite electrodes was demonstrated by measuring phenols using cyclic voltammetry and microchip capillary electrophoresis.

1. Introduction

Carbon nanotubes (CNTs) have attracted tremendous attention since the pioneering work of Iijima *et al.* in 1991 because of their high electrical conductivity, mechanical strength and chemical stability,[1–3] and they are ideal materials for fabricating electrochemical sensors and biosensors.[4–6] CNTs have shown strong electrocatalytic activity and minimization of surface fouling when employed to prepare electrochemical electrodes for detecting certain important bioactive substances.[7–12] Because CNTs are insoluble in most solvents, to load them, they are usually dispersed in solvents or polymer solutions cast onto the surface of electrodes.[7–12] Significant interest has been generated in recent years by mixing CNTs with various inorganic and organic substances by physical and chemical means to prepare multifunctional composites for electrochemical sensing. Polymers can be easily mixed with CNTs by various methods to manufacture conducting materials. During the past few years, a variety of polymers have been used to prepare CNT/polymer composite electrodes for sensing different electroactive compounds. These polymers include poly(methyl methacrylate),[13] epoxy,[14] polyaniline,[15] Nafion[16] Teflon,[17] chitosan,[18] alginate,[8] *etc.*

As a thermosetting polymer, poly(urea-formaldehyde) (PUF) is made from urea and formaldehyde by polycondensation. It is predominantly used as an adhesive in the manufacture of medium density fibreboard, plywood, particleboard and other non-structural wood products.[19] Recently, a variety of PUF/inorganic material composites have been prepared for various purposes. The employed inorganic materials include silica, iron oxides, tin, zinc, *etc.*[20–23] It has also been employed as a template to prepare mesoporous silica.[24] To prepare PUF, urea and formaldehyde are usually allowed to react in a basic medium under heat to produce a water-soluble prepolymer solution that can further polycondense to form a water-insoluble crosslinked polymeric network with the aid of curing catalysts such as ammonium chloride and ammonium sulfate.[25,26] As a reactive polymer mixture, urea-formaldehyde prepolymer solutions offer great promise for the preparation of CNT-based functional materials and other PUF-containing composites because they are rigid and water-insoluble. However, we are not aware of any previous reports on the preparation and application of CNT/PUF composites.

In this work, a novel method based on *in situ* polycondensation was developed for the facile preparation of CNT/PUF composites. Multi-walled carbon nanotubes (MWCNTs) were used because their electrocatalytic activity is reportedly higher than that of single-walled carbon nanotubes.[27] In addition, the CNT-containing mixture was packed into glass tubes and fused silica capillaries to prepare CNT/PUF composite electrodes for cyclic voltammetric measurements and the amperometric detection (AD) of microchip capillary electrophoresis (CE) with enhanced responses.

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† Electronic supplementary information (ESI) available: Photograph of a piece of PUF film, SEM images of PUF and CNTs, the fabrication process of composite electrodes, a photograph of the prepared electrodes, and schematic diagrams of a three-dimensionally adjustable device for the amperometric detection of microchip capillary electrophoresis. See DOI: 10.1039/b9nj00670b

2. Experimental

2.1 Reagents and solutions

MWCNTs (40–60 nM diameter, 5–15 μm long) with a purity of 95% were provided by the Shenzhen Nanoport Company (Shenzhen, China). Urea, formaldehyde, concentrated ammonia (28%), ammonium chloride, borax, 2,6-dimethylphenol, phenol,

2-naphthol, 4-chlorophenol, pentachlorophenol and 2,4-dichlorophenol were all purchased from SinoPharm (Shanghai, China). Graphite powder was supplied by Aldrich (Milwaukee, WI, USA). Other chemicals were all analytical grade. Stock solutions of 2,6-dimethylphenol, phenol, 4-chlorophenol, pentachlorophenol and 2,4-dichlorophenol (20 mM) were all prepared in 50% aqueous ethanol.

2.2 Preparation of the urea-formaldehyde prepolymer solution

About 1.5 mL of a concentrated ammonia (28% w/w) solution was added to 35 mL of a formaldehyde aqueous solution (37% w/w) to adjust the pH to 7.5–8.0. After this, 11.4 g of urea was dissolved in the solution and the mixture heated in a 60 °C water bath for 15 min. Subsequently, 0.6 g of additional urea was dissolved in the solution. The reaction was allowed to continue at 95 °C for 1 h to obtain the urea-formaldehyde prepolymer solution. The solid content in the solution was approximately 50% (w/v).

2.3 Preparation of the CNT/PUF composite

MWCNTs were treated by stirring in concentrated nitric acid at 60 °C for 12 h. When the CNTs precipitated from the solution, the nitric acid was carefully removed using a syringe. The remaining mixture of CNTs and nitric acid was diluted with doubly-distilled water. The mixture was then filtered through a sand core funnel with the aid of a vacuum. After the obtained CNTs had been washed with copious water until the filtrate was neutral, they were collected and dried in a drying oven at 105 °C for 60 min. To prepare the CNT/PUF composite, 200 mg of the treated CNTs was mixed with 400 μL of the urea-formaldehyde prepolymer solution (solid content ~200 mg) containing 4 mg ammonium chloride (a hardener) with the aid of sonication. The black mixture was then cast onto a glass plate (20 cm × 20 cm). After curing at room temperature for 10 min, coagulation of the mixture in a 95 °C oven for 30 min was allowed to further polycondense the material. Finally, it was dried completely at 105 °C for 15 min to form the CNT/PUF composite film. If no CNT was added to the mixture, pristine PUF film could be prepared in a control experiment (ESI, Fig. S2(a)†).

2.4 Fabrication of CNT/PUF composite electrodes

The fabrication process of the capillary-based composite electrodes for the amperometric detection of microchip CE is illustrated in Fig. S3(A–D).† A piece of copper wire (10 cm long, 150 μm diameter) was inserted into a 3.0 cm-long fused silica capillary (320 μm I. D. × 450 μm O. D.) and a 2 mm opening left in the capillary for subsequent filling by the mixture of the urea-formaldehyde prepolymer solution and the CNT powder mentioned above. The mixture was packed into the capillary by pressing the opened end of the capillary into it to a depth of ~3 mm. The CNT-containing mixture touched the end of the copper wire inside the capillary tightly for electrical contact. It was then allowed to cure at room temperature for 10 min, polymerize at 95 °C for 30 min and dry at 105 °C for 15 min, successively. Finally, hot melt adhesive was applied to the open end of the capillary to glue the copper wire in place. The CNT-filled end of the electrode was polished with emery paper to form a disc electrode. The graphite/PUF (graphite : PUF = 1 : 1 w/w) composite electrode used for comparison was prepared by following the same procedure. Fig. S3E shows a photograph of the prepared capillary-based composite electrodes.† In addition, CNT/PUF and graphite/PUF composites were also packed into the cavities of glass tubes (2.2 mm I. D., 5 mm O. D., 60 mm long) to prepare large-sized electrodes for cyclic voltammetric measurements. The fabrication procedures were the same as the capillary-based electrode described above.

2.5 Apparatus

The surface morphologies of the materials were measured using a scanning electron microscope (PHILIPS XL 30, Eindhoven, The Netherlands). Thermal gravimetric analyses (TGA) and differential thermal gravimetric analyses (DTGA) were undertaken using a Perkin-Elmer Pyris 1 DTA-TGA instrument under an atmosphere of air at a heating rate of 10 °C min^{-1}. X-Ray diffraction (XRD) measurements were carried out using a Rigaku D/max-rB diffractometer (Rigaku, Tokyo, Japan) with CuK-α1 radiation (40 kV, 60 mA). The Fourier transform infrared (FT-IR) spectra of nitric acid-treated CNTs, PUF and the CNT/PUF composite were measured using an FT-IR spectrometer (NEXUS470, Nicolet).

Details of the microchip CE-AD system have been previously described.[11] Briefly, a home-made ±4000 V high voltage dc power supply provided a voltage for electrophoretic separation and electrokinetic sample introduction. The simple cross, single separation channel glass microchip was obtained from Micralyne (model MC-BF4-001; Edmonton, Canada). The original detection cell was cut off, leaving the channel outlet at the end side of the chip, thus facilitating end-column AD. The 83 mm × 16 mm chip shown in Fig. S4a had a simple cross layout, with a four-way injection cross connected to three ports and the separation channel.† It consisted of a 79 mm-long main channel and a 10 mm-long injection channel. The two channels crossed each other at the middle point of the injection channel, while the distance between one end of the main channel and the injection cross was 5 mm. The 74 mm-long channel between the injection cross and the channel outlet served as the separation channel to perform microchip CE. The channels had a maximum depth of 20 μm and a width of 50 μm at the top. Short pipette tips (Fig. S4(d–f)) were inserted into each of the three ports on the glass chip for solution connection between the ends of channels in the microchip and the corresponding reservoirs (Fig. S4(h–j)). A three-dimensionally adjustable Plexiglass device (as illustrated in Fig. S4†) for microchip CE-AD[11] was fabricated for housing the glass microchip and the detection electrode, allowing their convenient replacement, and facilitating precise alignment between the outlet of the separation channel and the capillary-based microdisc electrodes for end-column AD. The fabrication and operation details of the three-dimensionally adjustable alignment device for microchip CE-AD can be found in our previous report.[13] Platinum wires, inserted into the individual reservoirs on the holder, served as contacts for the high voltage power supply.

2.6 Electrochemical measurements

Before use, the composite microdisc electrode was successively polished with emery paper and alumina powder, sonicated in doubly-distilled water, and finally the surface of the detection electrode carefully positioned opposite the outlet of the separation channel through a guiding metal tube (Fig. S4(l)).† The gap distance between the disc electrode and the channel outlet was adjusted to be approximately 50 μm by comparison with the channel width (50 μm) while being viewed under a microscope. Both cyclic voltammetry (CV) and the amperometric detection of microchip CE were performed with a CHI 830B electrochemical analyzer (Shanghai Chen-Hua Instruments Co., Shanghai, China) in combination with a three-electrode electrochemical cell consisting of a prepared composite detection electrode, an auxiliary electrode and an Ag/AgCl wire reference electrode. Electropherograms were recorded using the "amperometric *i–t* curve" mode, while a detection potential of 0.8 V (*vs.* Ag/AgCl wire) was applied to the detection electrode. Prior to electrochemical sensing, the electrodes were pre-treated by cyclic voltammetric scanning over the potential range 0 to 0.85 V at a scan rate of 100 mV s^{-1}.

2.7 Procedures

The CV measurements were carried out in the desired potential range at a scan rate of 100 mV s^{-1}; no solution agitation was necessary during the run. The channels of the glass microchip were treated before use by rinsing them with 0.1 M NaOH and de-ionized water for 10 min each. The running buffer for the separation of phenols was 50 mM borate buffer (pH 9.8). The running buffer reservoir, the unused reservoir and the detection cell were all filled with running buffer, while the sample reservoir was filled with a sample solution. The injections were performed by applying a voltage of +2500 V between the sample reservoir and the grounded detection reservoirs for 3 s while all other reservoirs were floating. Separations were performed by switching the high voltage contacts to apply +2500 V to the running buffer reservoir with the detection cell grounded while all the other reservoirs were floating. Moreover, sample solutions, standard solutions and the running buffer were all filtered through a polypropylene filter (0.22 μm, Shanghai Bandao Industry Co., Ltd., Shanghai, China) prior to use.

3. Results and discussion

Fig. 1A–D shows SEM images of the surface of the CNT/PUF composite and the cross-section of a CNT/PUF composite electrode. In comparison with the SEM images of PUF and CNTs (Figs. S2(b) and S2(c)†), it can be seen clearly in the SEM images of the composite (Fig. 1A and B) that the CNTs are well dispersed and embedded throughout the PUF matrix, and that an interconnected CNT network has formed. The SEM images of the cross-sections of a CNT/PUF composite electrode indicate that a large number of broken ends of CNTs appear on the electrode surface to form a nanoelectrode array (Fig. 1C and D). This conductive CNT network may establish electrical conduction pathways throughout the whole system that are responsible for its electrical conductivity and electrochemical sensing.

Fig. 1E displays the XRD patterns of the CNT/PUF composite, CNTs and PUF. Also illustrated in the inset of Fig. 1E is a photograph of a piece of CNT/PUF composite film prepared for the measurement of its XRD pattern. Diffraction peaks assigned to CNTs at 25.9 and 42.7° (corresponding to the graphite indices (002) and (100))[28] were observed in the XRD curves of pure CNT and the CNT/PUF composite, indicating that the CNT structure was not destroyed after the *in situ* polycondensation of the urea-formaldehyde prepolymer. The broad peak of PUF was also found in the XRD curve of the CNT/PUF composite.

FT-IR spectra (Fig. 2A) of CNTs, PUF and the CNT/PUF composite were also measured. Absorption bands of CNTs pre-treated with concentrated HNO_3 were observed at 3400, 1713 and 1578 cm^{-1}, which could be attributed to the

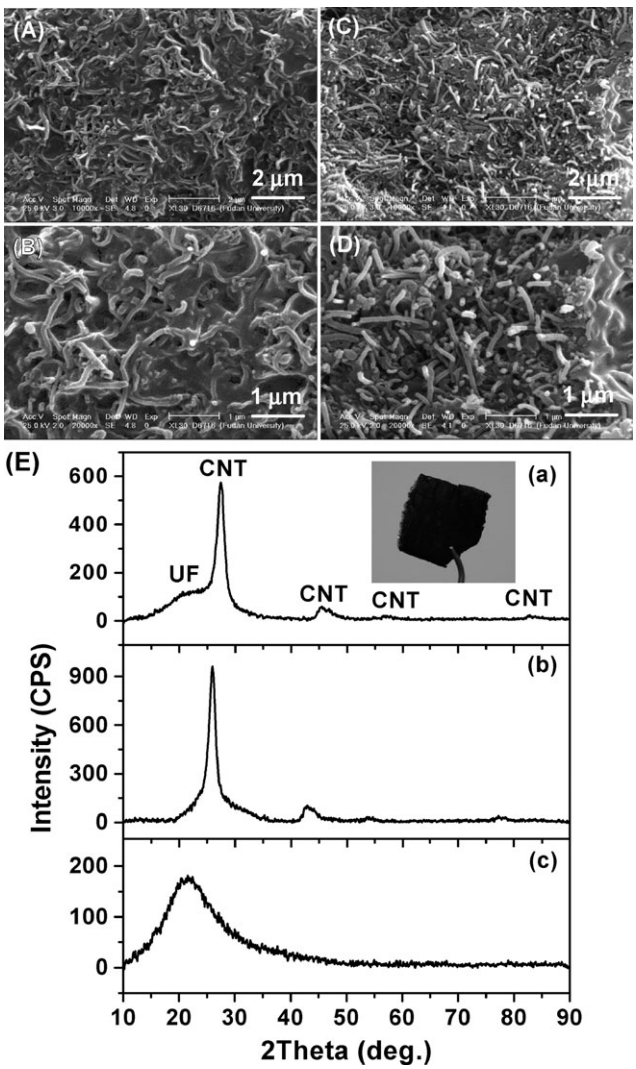

Fig. 1 SEM images of the surface of the CNT/PUF composite (magnifications: (A) ×10 000, (B) ×20 000) and the cross-section of a CNT/PUF composite electrode (magnifications: (C) ×10 000, (D) ×20 000) and XRD patterns of the (a) CNT/PUF composite, (b) CNT and (c) PUF. Also shown in the inset is a photograph of a piece of the CNT/PUF composite film.

stretching vibrations of O–H, C=O and C=C bonds, respectively. The peaks at 1634, 1214 and 1100 cm^{-1} correspond to the vibration of the carboxylic acid groups.[29] In the IR spectra of PUF and the CNT/PUF, the bands around 1640, 1520, 1380, 1290, 1180, 1020 and 940 cm^{-1} could be assigned to C=O stretching, N–H bending, CH_2 bending, C–N stretching, the asymmetric stretching of CH_2 in N–CH_2–N, the C–O stretching of –CH_2–O–CH_2– and the C–O stretching in CH_2–OH, respectively.[30,31] The weak bands between 2980–2830 cm^{-1} in the three FT-IR spectra could be attributed to the stretching vibration of C–H bonds. Strong absorption bands close to 3440 cm^{-1} in all spectra were assigned to the stretching of O–H and N–H. By comparing the FT-IR spectra of CNTs and the CNT/PUF composite, it could be seen that the absorption peak of C=O stretching at 1713 cm^{-1} in the IR spectrum of CNTs (Fig. 2(a)) disappeared in the IR spectrum of the CNT/PUF composite, indicating that the C=O groups in CNTs might react with the amino groups in the urea-formaldehyde propolymer during the *in situ* polycondensation. All of the other characteristic peaks of PUF and CNTs can be found in the FT-IR spectra of the CNT/PUF composite. Some of these peaks overlap, meaning that their relative heights and shapes change to some extent in comparison with the IR spectra of pristine CNTs and PUF.

Fig. 2B shows the TGA and DTGA curves of the CNT/PUF composite at a heating rate of 10 °C min^{-1}. In comparison with the TGA curves of PUF[20] and MWCNTs,[32] the weight loss of the composite observed in the temperature ranges 220–360 and 560–692 °C could be attributed to the decomposing of PUF and CNTs, respectively. Based on the TGA curve, the weight fraction of CNTs was estimated to be approximately 50% (w/w), which is well in agreement with the expected value.

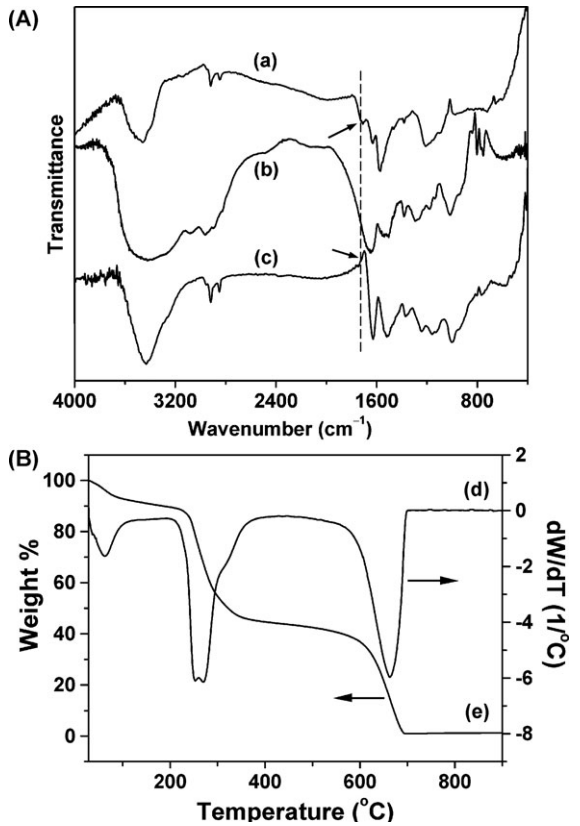

Fig. 2 (A) FT-IR spectra of (a) CNTs, (b) PUF and (c) the CNT/PUF composite. (B) (d) TGA and (e) DTGA curves of the CNT/PUF composite.

Fig. 3A illustrates the cyclic voltammograms (CVs) of 0.5 mM 4-chlorophenol. The half-wave potentials of the anode peak for the oxidation of 4-chlorophenol are approximately +0.51 and +0.43 V (*vs.* Ag/AgCl wire) at the graphite/PUF and the CNT/PUF composite electrodes, respectively. The catalytic activity of the CNT-based electrode is demonstrated by the negative shift of the half-wave potential and the significantly enhanced current response for the oxidation of 4-chlorophenol compared with the graphite/PUF electrode. Apparently, the CNT/PUF composite greatly promotes the oxidation of 4-chlorophenol, exhibiting a high electrocatalytic activity.

In the present work, the CNT/PUF composite microdisc electrode was coupled with a microchip CE system as an end-column amperometric detector. The attractive performance of the novel detector was indicated by the amperometric detection of phenols of environmental concern, offering enhanced response currents, lower noise levels and well-resolved peaks. Fig. 3B illustrates representative electropherograms for a mixture containing 25 μM 2,6-dimethylphenol, 25 μM phenol, 25 μM 4-chlorophenol, 50 μM pentachlorophenol and 50 μM 2,4-dichlorophenol, detected by a graphite/PUF electrode and a CNT/PUF composite electrode. The five phenols were well separated by microchip CE within 200 s, resulting in well-defined and resolved peaks at the CNT/PUF composite electrode. As shown in Fig. 3B, the peak currents of the five analytes at the CNT/PUF composite electrode were much higher than those at the graphite/PUF detector. The response currents of 25 μM 2,6-dimethylphenol, 25 μM phenol, 25 μM 4-chlorophenol, 50 μM pentachlorophenol and 50 μM 2,4-dichlorophenol were 2.99, 3.16, 2.85, 1.85 and 2.11 nA at the CNT/PUF composite electrode and 1.14, 1.32, 1.34, 0.97 and 1.18 nA at the graphite/PUF composite electrode, respectively. The higher S/N of the CNT-based composite detector led to lower detection limits compared to the graphite/PUF composite electrode [12.5 *vs.* 86.5, 11.9 *vs.* 74.5, 13.2 *vs.* 73.5, 40.3 *vs.* 202.8 and 35.5 *vs.* 166.7 nM for 2,6-dimethylphenol, phenol, 4-chlorophenol, pentachlorophenol and 2,4-dichlorophenol, respectively (based on $S/N = 3$)]. Overall, the results indicate that the CNT/PUF composite is a promising material for electrochemical sensing. The present CNT/PUF composite electrode shows low noise characteristics and a stable baseline. The ability of CNTs to promote electron transfer reactions can be attributed to their special electronic structure and high electrical conductivity.[27]

4. Conclusions

In summary, a CNT/PUF composite has been prepared for the first time based on the *in situ* polycondensation of a CNT-containing urea-formaldehyde prepolymer. SEM, XRD and FT-IR analyses offered insights into the morphology and structure of the novel composite. In addition, CNT/PUF

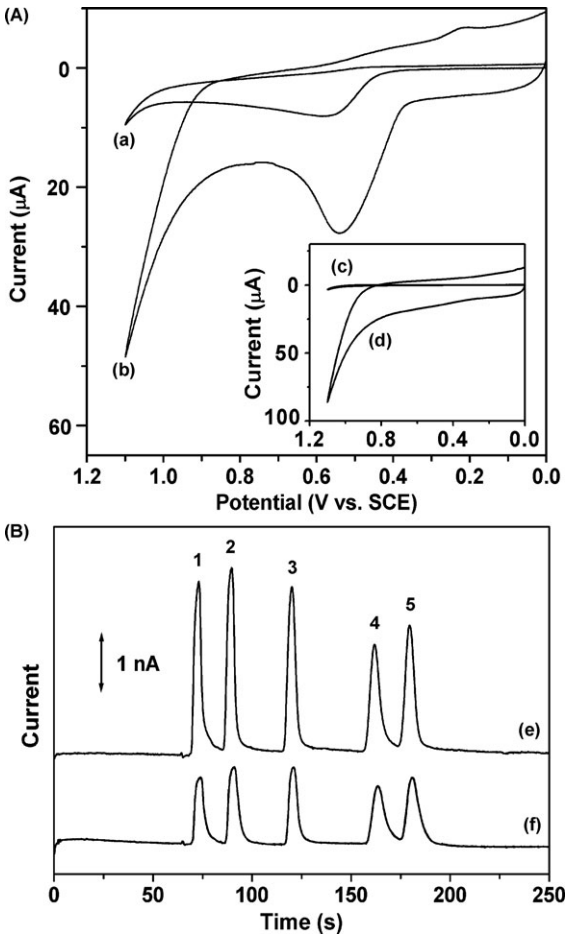

Fig. 3 (A) Typical CVs of a graphite/PUF composite electrode ((a) and (c)) and a CNT/PUF composite electrode ((b) and (d)) in 50 mM borate buffer (pH 9.8) containing 0.0 ((c) and (d)) and 0.5 mM ((a) and (b)) 4-chlorophenol (scan rate 50 mV s^{-1}). (B) Electropherograms of a mixture containing (1) 25 μM 2,6-dimethylphenol, (2) 25 μM phenol, (3) 25 μM 4-chlorophenol, (4) 50 μM pentachlorophenol and (5) 50 μM 2,4-dichlorophenol at the (e) CNT/PUF and (f) graphite/PUF composite electrodes. Separation channel in the glass CE microchip: 50 μm wide × 20 μm deep × 74 mm long. Separation and injection voltage: +2500 V. Injection time: 3 s. Running buffer: 50 mM borate buffer (pH 9.8). Detection potential: +0.8 V (*vs.* Ag/AgCl wire).

composite electrodes were fabricated by the *in situ* polycondensation of the urea-formaldehyde prepolymer. The CV results indicate that CNT/PUF composite electrodes show a higher electrocatalytic activity towards the oxidation of phenols. In combination with microchip CE, the performance, utility and advantages of these novel detection electrodes have also been demonstrated by the separation and detection of five phenolic pollutants. These novel CNT-based amperometric detectors offer significantly lower operating potentials, substantially enhanced S/N characteristics, and a lower expense of fabrication and operation, indicating their great promise for flowing injection analysis, microcolumn liquid chromatography, conventional CE and other microfluidic analysis systems.

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