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Sensitive Sulfadiazine Sensor Based on Multiwalled Carbon Nanotubes Wrapped with Polystyrene Sulfonate Polymer Chain

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A significant improvement in the solubility of multiwalled carbon nanotubes (MWCNTs) was obtained by using a sodium polystyrene sulfonate (PSS) solution as the dispersing medium. A highly sensitive amperometric sulfadiazine (SD) sensor was fabricated by immobilizing the MWCNT–PSS modifier onto a glassy carbon electrode. The modified electrode showed substantially enhanced analytical performance such as good stability, wide linear range, and lower detection limit for the determination of SD owing to the synergistic effect of MWCNTs and PSS. The significant catalytic activity exhibited by the MWCNT–PSS-based modified electrode indicates great promise for diverse analytical applications.

Keywords: carbon nanotube, sodium polystyrene sulfonate, electrochemistry, sulfadiazine.

1. INTRODUCTION

Carbon nanotubes (CNTs), an allotrope of carbon, has attracted much interest because of extraordinary inherent electrical and mechanical properties.[1] Because CNTs are very nonpolar and have a high contact energy among the tubes, they tend to assemble into large bundles and are difficult to disperse in water and organic solvents. This is a major limitation for the application of CNTs.[2] The dispersion of CNTs is unsatisfactory in water, methanol, ethanol, dimethyl formamide, and other organic solvents. In 2003, Joseph Wang and co-workers selected perfluorosulfonated polymer (Nafion) as the CNT-dispersing mediator.[3] Because the CNTs wrap into polymeric chains and the electric repulsive force of the sulfonic anion is distributed on the Nafion polymer chain, the CNTs successfully uniformly dispersed in the Nafion solution and were stable. A similar use of the polymeric materials of poly(*p*-phenylenevinylene) [4] or poly{(*m*-phenylenevinylene)-co-[2,5-dioctyloxy-(*p*-phenylene)-vinylene]} [5] has also been reported. However, the use of Nafion and other polymeric materials as the dispersing agent can be uneconomic. Thus, a similar low-cost, high-performance agent for the homogeneous dispersion of CNT is highly desirable.

Sulfonamide, a broad-spectrum antibacterial, is widely used in animal feedstuff for prophylactic and therapeutic purposes because of its low cost. The residues present in animal products such as meat, eggs, and milk are potentially damaging to human health.[6, 7] Thus, it is important to determine and control the content of sulfonamide residues in food products. Various methods such as high-performance liquid chromatography (HPLC), [8–10] mass spectroscopy, [11, 12] surface acoustic wave (SAW) technique, [13] and enzyme-linked immunosorbent assay [14] have been developed for the determination of sulfadiazine (SD). Although these methods have the advantages of good sensitivity and selectivity, some of them require expensive instrumentation, time consuming, and have a high cost of operation.[15] Electrochemical methods have several advantages including simplicity and low cost.[16] Voorhies and co-workers [17] studied electrochemical behavior using the anodic polarography method. Souza and co-workers [18] developed a diamond electrode for the determination of SD, and a detection limit of 2.19 μmol/L was obtained. Lahcen and co-workers performed a comparative study of various carbon material-based electrochemical sensors for the determination of several sulfonamides, and excellent detection limits were obtained.[19] He’s group developed a series of CNT-based modified electrodes for the determination of sulfonamides, and remarkable analytical performance was obtained.[20, 21] Recently, a disposable tyrosinase-based biosensor with satisfied function was developed by Alonso-Lomillo’s group [22] for the detection of sulfonamides. In the studies of Mazzotta’ group [23] and Quan’s group [24], a molecularly imprinted polymer was introduced to fabricate electrochemical sensors, and the selectivity of the sensors towards sulfonamides increased significantly. In our previous studies [7, 15, 25], the electrochemical determination of SD using multiwalled carbon nanotube (MWCNT)-modified electrodes was studied, and good analytical performance was achieved.

In this study, we report a new electrochemical sensor using MWCNTs combined with sodium polystyrene sulfonate (PSS) for the sensitive determination of SD in animal feedstuff.

2. EXPERIMENTAL

2.1. Materials

PSS was used as the dispersing agent and purchased from Energy Chemical (China). MWCNTs (diameter: 10–30 nm, length: 5–15 μm, purity: >95%) were supplied by JCNANO (China). The analytical probe of SD was purchased from Sigma-Aldrich. Other chemicals were of analytical grade and used as received without further purification. Double-distilled water was used throughout the entire experimental procedure.

2.2. Apparatus

Electrochemical measurements were performed using a CHI 660A electroanalysis workstation (CH Instruments, USA) equipped with a three-electrode system. A bare glassy carbon electrode (GCE)

(3.0 mm diameter) or a MWCNT–PSS-modified GCE was used as the working electrode along with an AgCl/Ag electrode (saturated potassium chloride) as the reference electrode and a platinum wire as the auxiliary electrode. Zeta potential measurements were carried out using a Zetasizer 3600 (Malvern, UK).

2.3. Fabrication of modified electrode

A homogeneous suspension of MWCNTs was prepared by dispersing them into a PSS solution by sonication, making a uniform and stable suspension. Prior to the modification, the GCE was polished thoroughly with 0.05 μm alumina slurry and rinsed with deionized water in an ultrasonic bath to obtain a mirror-like finish. After drying the electrode surface in air, 2 μL of the as-prepared MWCNT suspension was cast onto the surface of the GCE and dried under ambient conditions to fabricate the MWCNTs-PSS-GCE. Prior to the use, cyclic voltammetry scans of the fresh MWCNTs-PSS-GCE were run in 0.1 M sulfuric acid until overlapping voltammograms were obtained.

2.4. Experimental procedures

The electrochemical behavior of SD was studied by cyclic voltammetry (0.6–1.2 V, scan rate: 50 mV/s). Quantitative analysis of SD was carried out using the chronoamperometric method with a polarization potential of 0.95 V. The surface charges of MWCNT dispersion systems with different concentrations of PSS solution as the dispersing medium were determined by zeta potential measurements.

3. RESULTS AND DISCUSSION

3.1. Effect of PSS on the stability of MWCNT suspension

After 30 min of ultrasonic agitation, the MWCNTs were dispersed into 1 g/L PSS solution, forming a black uniform suspension (Figure 1-A). As shown in Figure 1, after 10 and 30 min deposition, a weak layer of MWCNTs appeared in suspension a (Figure 1-B,C), whereas a stable homogeneous form was still maintained in suspension b (Figure 1-B,C). After 20 h deposition, the MWCNT–PSS suspension (suspension b in Figure 1-D) was still stable, whereas the MWCNTs completely deposited in the deionized water media (suspension a in Figure 1-D). This phenomenon indicates that the PSS polymer chain can improve the stability of the MWCNT suspension. In MWCNT–PSS suspension system, PSS acted as the wrapping polymer. Owing to the long-train structure and the ionization of sulfonic groups anchored on PSS chain, the polymer has a high density of negative charge. [26, 27] After Wrapping MWCNT with PSS, the surface of the MWCNT fibers was also negatively charged. The electrostatic repulsion of the negatively charged sulfonic groups adsorbed on the MWCNT fibers was the major contribution to the stability of the MWCNT–PSS suspension. This statement had been confirmed by zeta potential characterization in following paragraph.

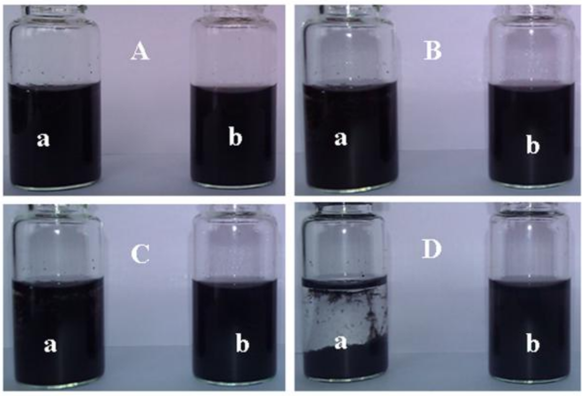

Figure 1. Stability of the MWCNT suspension prepared with (b) and without PSS polymer (a) after 0 (A), 10 (B), 30 (C), min and 20 h (D) deposition.

Zeta potential measurement was carried out to evaluate the surface charge characteristics of the MWCNTs with and without PSS wrapping. Figure 2 depicts the zeta potential change of the MWCNT fibers by the adsorption of different amounts of PSS polymer. As shown in Figure 2, the suspension first showed a weak negative zeta potential of −13.8 mV in the deionized water medium. By changing the concentration of PSS in the MWCNT suspension from 0.01 g/L to 1 g/L, the zeta potentials shifted from −15.9 mV to −103.3 mV. This phenomenon indicates that the PSS polymer chain was successively wrapped onto the MWCNT fibers, and the fibers were negatively charged, resulting in the superstability of the MWCNT–PSS suspension.

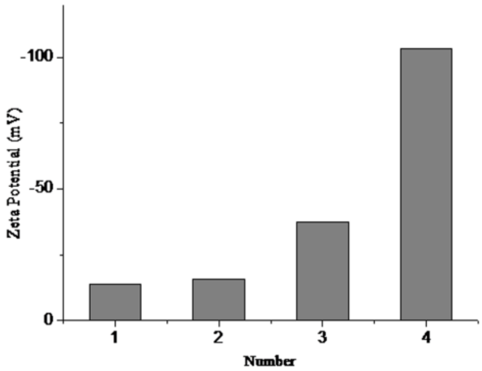

Figure 2. Zeta potentials of MWCNTs depending on the concentration of PSS solution (1. 0 g/L, 2. 0.01 g/L, 3. 0.1 g/L, and 4. 1.0 g/L).

3.2. Electrocatalytic oxidation of SD at the MWCNT–PSS-modified electrode

SD was selected as the probe to evaluate the properties of the MWCNT–PSS-modified electrode. Cyclic voltammograms of the MWCNT–PSS-modified GCE and bare GCE were obtained in

0.1 mol/L sulfuric acid solution in the presence of 1.0 mmol/L of SD. As shown in Figure 3, a weak anodic peak was observed around 1.1 V (dotted line) using the bare GCE as the working electrode. This is a typical electrochemical response of SD corresponding to the oxidation of the phenylamino group. [28] As expected, when the MWCNT–PSS-modified GCE was used, the anodic peak of SD was dramatically enhanced (solid line) and the anodic potential negatively shifted to 1 V. This exciting phenomenon of amplified anodic current and negatively shifted anodic potential can be mainly attributed to the synergistic effect of MWCNTs and PSS. It was reported that aromatic condensation polymers were excellent for dispersing CNTs to form homogeneous system due to there strong π–π interfacial between the conjugated groups of the polymers and the sidewalls of the CNTs. [29-31] The PSS molecule owns a long-train structure anchored a lot of aromatic groups, which can be adsorbed onto sidewalls of MWCNTs through π–π interaction and hydrophobic interaction. As depicted in Figure 4, the PSS chains were wrapped on the MWCNT fibers.

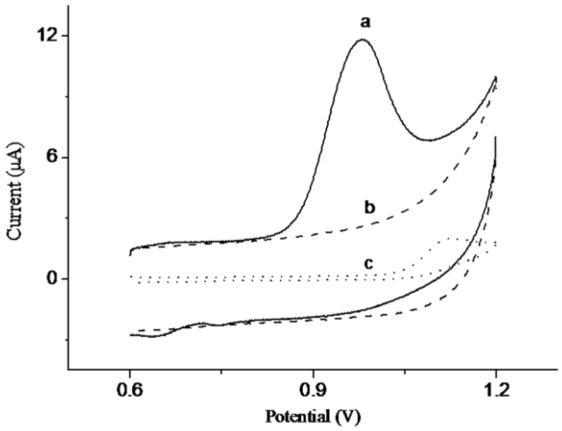

Figure 3. Cyclic voltammograms obtained on the MWCNT–PSS electrode (a, b) and GCE (c) with (a, c) and without (b) 1 mmol/L of SD as the probe.

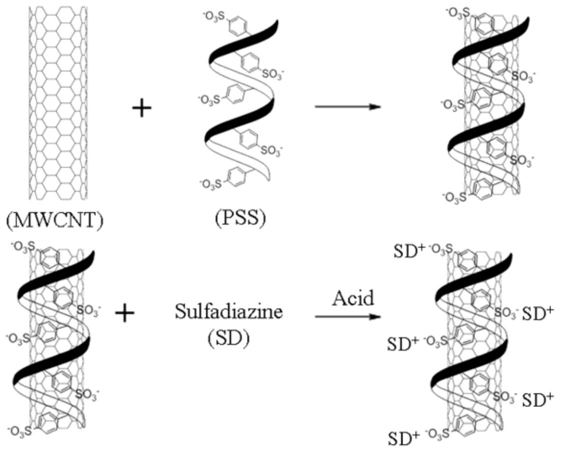

Figure 4. Schematic of the interactions between MWCNT fiber, PSS chain, and SD molecule.

And the MWCNT fibers were negatively charged and electrically repulsive, achieving a super stable performance of the MWCNT–PSS suspension. Moreover, in 0.1 M sulfuric acid electrolyte, the target SD molecule was hydrolyzed to form ammonium [17] and was positively charged. Because of the electrostatic attraction between SD molecules and the benzenesulfonic acid groups anchored on the PSS chain, a trace concentration of SD can be preconcentrated on the surface of MWCNTs, resulting in the sensitive anodic current response of the MWCNT–PSS-modified electrode.

3.3. Analytical characteristics

The chronoamperometric method was used to determine the amount of trace SD. According to the voltammetric behavior of SD shown in Figure 3 (curve a), a 0.95 V voltage (vs. AgCl/Cl, saturated KCl) was set as the working potential during the entire chronoamperometric testing. This was carried out by successively adding 1 mmol/L SD into 5 mL 0.1 mol/L sulfuric acid solution. When a drop of SD solution was added to the supporting electrolyte, the anodic current rapidly increased, reached a stable state in less than 3 s, and then leveled off. The response current of the modified electrode was recorded and plotted against the concentration of SD (Figure 5). The anodic currents were linearly proportional to the concentration of SD in the range of 1.9–160 μmol/L with a correlation coefficient of 0.998. The linear equation was $I = 0.0054\ C + 0.017$, where I (μA) is the anodic current recorded on the modified electrode and C (μmol/L) is the concentration of SD in the system. The detection limit was 0.6 μmol/L; this was calculated according to 3S/m [6], where m is the slope of the linear range of the respective calibration plot. S was estimated as the standard deviation of the signals obtained using a blank solution.

The reproducibility of the modified electrode was investigated by the repetitive determination of two different SD solutions. The relative standard deviations (RSDs) of the anodic peak currents for the repetitive determination of 30 μmol/L and 140 μmol/L SD were 7.27% and 7.42%, respectively, indicating excellent reproducibility of the modified electrode.

The long-term stability of the modified electrode was evaluated by monitoring the peak current response of a fixed concentration of SD. During the testing, the modified electrode was stored in air under ambient conditions when not in use. The anodic peak current response had only a small decrease (retaining 92.1% of its initial response) after two weeks. This satisfied phenomenon probably attribute to the use of PSS polymer in modified electrode fabrication. The PSS chain can help to fix the MWCNT fibers tightly onto the surface of the base electrode, resulting in the long-life stability of the MWCNTs-PSS-GCE.

Compared to the literature methods (Table 1), even though the HPLC method has a perfect analytical performance, electrochemical methods owns lower detection limit and wide linear response range. Goyal's group [32] even developed a differential pulse voltammetric sensor that exhibited an amazing detection limit of 0.05 nmol/L towards sulfamethoxazole (SMZ) determination. In our present report, owing to the application of PSS during the fabrication of the sensor, the inexpensive and facile polymer material helped to accelerate the enrichment of SD molecule on the surface of the sensor, resulting in an excellent detection limit and response linear range during the chronoamperometric measurement procedure. Although it is inferior to that of recent works obtained by differential pulse voltammetry (DPV) and square wave voltammetry (SWV) methods listed in Table 1, the detection limit of this work is satisfied among the works carried out by chronoamperometric method. And the linear response range is also remarkable among all electrochemical methods.

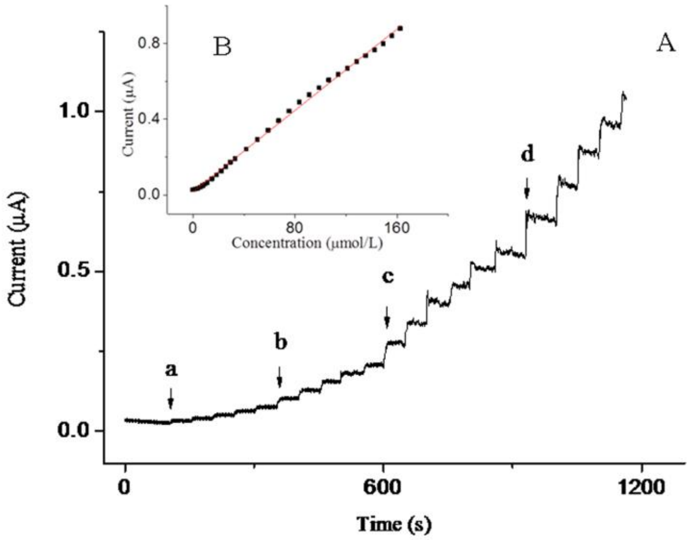

Figure 5. Current–time plot with the addition of 1 mmol/L SD at each step. Inset: calibration curve of SD.

Table 1. Comparison of different methods for the determination of sulfonamides.

Method	Analyte	Linear range (μmol/L)	Detection limit (μmol/L)	Rerefence
HPLC	SD	0.4–12	0.02	Muhammet et al. [9]
DPV (GCE)	SD	15–60	5.4	Carrazon et al. [33]
SWV (BDDE)	SD	8.01–119	2.19	Souza et al. [18]
DPV (BiFE)	SD	3.2–20	2.1	Campestrini et al. [34]
i–t (MWCNT-GCE)	SD	0.5–110	0.03	He et al. [21]
DPV (MCNT–BA-SPCE)	SSZ	1.0–14	0.3	Sadeghi et al. [35]
SWV (CNPE)	SD	1.0–75	0.4	Lahcen et al. [19]
i–t (Tyrosinase-SPCE)	SMX	20–200	––	del Torno-de Roman et al. [22]
SWV (SWCNT–DAN-GCE)	SFA	5–1500	0.11	Yadav et al. [36]
DPV (MWCNT-CPE)	SMT	0.1–180	0.05	Ghoreishi et al. [37]
DPV (FeZnO-CPE)	SMX	2.0–160	0.03	Meshki et al. [38]
SWV (DAN-GCE)	SMZ	0.5–150	0.00005	Chasta et al. [32]
i–t (MWCNT–PSS-GCE)	SD	1.9–160	0.6	This work

i-t: chronoamperometry, BDDE: boron-doped diamond electrode, BiFE: bismuth film electrode, BA: benzyl acetate, SPCE: screen-printed carbon electrode, CNPE: carbon nanopowder paste electrode, SWCNT: single-walled carbon nanotube, DAN: CPE: FeZnO: FeZnO nanorods, DAN: diaminonaphthalene, PSS: sodium polystyrene sulfonate, SSZ: sulfasalazine SMX: sulfamethoxazole SFA: sulfacetamide , SMT: sulfamethizole,

3.4. Analysis of real samples

To explore practical applications of the new modified electrode, SD in animal feedstuff was analyzed. An animal feedstuff for pet turtles obtained from the market was used for the entire testing procedure. Before the use, the feedstuff was dried in an oven and then ground thoroughly using an agate mortar. The feedstuff powder was then dispersed into 20 mL of 0.1 mol/L sulfuric acid using ultrasonic agitation. After the centrifugation, the supernatant was collected for electrochemical testing. Two additional samples of the dried feedstuff powder were prepared and spiked with different concentrations of SD using the same procedure mentioned above. The test results (listed in Table 2) indicate a good accuracy.

Table 2. Determination and recovery results in commercial feedstuff obtained using the MWCNT–PSS-modified electrode.

Samples	Added (μmol/L)	Found (μmol/L)	Recovery (%)
1	0	0	–
2	4.8	4.5	93.8
3	50.0	47.1	94.2

4. CONCLUSIONS

A MWCNT–PSS-modified electrode was fabricated for the detection of SD by dispersing MWCNTs into an aqueous solution of PSS as the dispersing agent and subsequently immobilizing the MWCNT–PSS suspension onto the surface of a GCE. The synergistic effect of MWCNTs and PSS endowed supersensitivity, good stability, and selectivity to the modified electrode for trace SD detection in solution.

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