

A Sensitive Electrochemical Sensor Using a Mesoporous Carbon and Nafion Composite for the Simultaneous Detection of Cadmium and Lead

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In this study, a mesoporous carbon (MC) and Nafion composite-modified electrode was prepared via drop-coating a dispersion of MC and Nafion, which was then dried by a lamp. This sensor was used for the sensitive detection of Cd(II) and Pb(II) by square-wave anodic stripping voltammetry (SWASV). The morphologies and electrochemical properties of the modified electrode were characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The MC layer that was formed on top of the glassy carbon electrode (GCE) could remarkably facilitate electron transfer and enlarge the specific surface area of the electrode. The Nafion film effectively increased the adhesion and stability of the MC layer. The obtained electrode exhibited effective stripping performance for the analysis of Cd(II) and Pb(II). Under optimal conditions, a linear response was observed in the range of 5 to 70 $\mu\text{g}\cdot\text{L}^{-1}$ with a detection limit of 0.05 $\mu\text{g}\cdot\text{L}^{-1}$ for Cd(II) and 0.13 $\mu\text{g}\cdot\text{L}^{-1}$ for Pb(II).

Keywords: Mesoporous carbon, Nafion, Square-wave anodic stripping voltammetry, Modified electrode, Sensor

1. INTRODUCTION

Cadmium (Cd) and lead (Pb) are highly toxic heavy metals with serious effects on human health. Heavy metals tend to accumulate in the environment because of their long-term chemical stability and nondegradable characteristics [1-3]. Heavy metals in soil can be absorbed by crops and decrease plant growth. These soil pollutants can enter livestock or human bodies through the food chain and may cause immediate or long-term health impacts. In the past few years, demand for the

detection of heavy metals has increased, which leads to the need for a rapid and decentralized analytical method [4-6].

Electrochemical stripping analysis (ESA) is an effective method for measuring trace heavy metals due to its remarkable sensitivity, fast speed, satisfactory selectivity, and low cost. Traditionally, mercury electrodes have been employed for ESA measurements. However, the high toxicity of mercury and the risks involved in its disposal make the use of mercury electrodes unfavorable. Approximately 17 years ago, a bismuth membrane-modified electrode was introduced as an alternative to mercury electrodes due to its low toxicity [7], high sensitivity, and large cathodic potential range, making the use of bismuth membrane-modified electrodes favorable. Due to their nontoxicity, strong electrical conductivity, large potential cathodic range, and reusability, glassy carbon electrodes (GCEs) are the most commonly used electrodes to be modified with bismuth membranes [8-9].

Various surface-active species have been found to adsorb on the electrode surface, which passivates the electrode. One effective method to alleviate fouling is to cast the electrode with a layer of dialysis membrane, such as Nafion [10]. However, because the modification process involves a solvent evaporation procedure, the homogeneity and reproducibility of these membranes are not completely satisfactory [11]. Composite modification is an effective method and has many advantages, such as high stability, strong adhesion, uniform structure, and controllable film thickness [12-14]. Mesoporous carbon (MC) is a type of non-silicon-based mesoporous material that is composed of carbon nanorods with a highly ordered arrangement, high porosity, positive electrical properties, chemical stability, and large specific surface area [15-17]. These properties give MC broad applications in the research of electrochemical sensors [18].

In this work, an MC/Nafion composite-modified electrode was prepared by the dispersion drop-coating of MC and Nafion, followed by lamp drying. The fabricated electrode was further applied to detect trace cadmium and lead ions by square-wave anodic stripping voltammetry (SWASV). The results show that this MC/Nafion composite-modified electrode exhibited higher sensitivity than Nafion-modified and bare GCEs because the modification of MC with Nafion provides enhanced mechanical stability, enlarged active surface areas, excellent electrical conductivity, effective ion exchange, and anti-interference properties.

2. EXPERIMENTAL

2.1 Instruments and Reagents

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai CH Instruments, China). A three-electrode system consisting of a modified glassy carbon working electrode ($\Phi = 3$ mm), an Ag/AgCl reference electrode, and a platinum wire counter electrode was used. All electrochemical measurements were carried out in a 25 mL cell.

MC was purchased from Ji Cang Nano Tech Co., Ltd. (Nanjing, China), Nafion solution was obtained from DuPont Co., Ltd., and diluted to 0.5% concentration. Alcohol, alumina powder, and potassium nitrate were obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). Potassium

hexacyanoferrate and potassium ferrocyanide were purchased from the Jin Ke Institute of Fine Chemical Engineering (Tianjin, China). Stock solutions of Cd(II) and Pb(II) ($1,000 \text{ mg}\cdot\text{L}^{-1}$) were obtained from the National Standard Reference Materials Center of China and diluted as required. Acetate buffer was used as the supporting electrolyte in the detection of Cd(II) and Pb(II). Ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$) was used for all experiments.

2.2 Preparation of MC, Nafion, and GCE

Before modification, the GCE was polished using $5 \mu\text{m}$ of alumina powder and rinsed with ultrapure water. Then, the electrode was ultrasonically cleaned in ultrapure water and pure alcohol for five minutes each. A total of 5 g of MC was weighed and added to 5 mL of 0.5% Nafion solution and dispersed via ultrasonication to form a $1 \text{ mg}\cdot\text{mL}^{-1}$ MC suspension. After 5 minutes of stirring and 15 minutes of centrifugation, $6.5 \mu\text{L}$ of the supernatant of the suspension was withdrawn and dropped onto the surface of the GCE. The modified GCE was dried with a drying lamp for 2 minutes and then dried in air to produce the MC/Nafion-modified electrode. For comparison, other electrodes were prepared using the same procedures described above.

2.3 Electrochemical Measurements

The analysis of Cd(II) and Pb(II) by SWASV was performed in a 0.1 M acetate buffer solution (pH 4.5) in the presence of $300 \mu\text{g}\cdot\text{L}^{-1}$ of Bi(III). Under stirring, a deposition potential of -1.4 V was applied to the working electrode for 400 s. After a standing time of 10 s, the SWASV potential scan was carried out from -1.4 to 0.2 V (square-wave amplitude, 25 mV ; potential step, 5 mV ; frequency, 25 Hz). Prior to the next cycle, a 120 s cleaning step at 0.3 V under stirring was performed to remove residual cadmium and lead ions.

3. RESULTS AND DISCUSSION

3.1 Basic Characteristics of the Modified Electrodes

Fig. 1 presents a comparison of the cyclic voltammetry (CV) responses of GCE, Nafion/GCE, and MC/Nafion/GCE in a $5 \text{ mM} [\text{Fe}(\text{CN})_6]^{3-/4-}$ solution. As shown, a pair of well-defined redox peaks was observed on the bare GCE, which was due to the reversible one-electron redox behavior of ferricyanide. After the GCE was modified by Nafion, the cyclic voltammograms of Nafion/GCE and MC/Nafion/GCE exhibited a pair of significantly decreased redox peaks. This suggests that Nafion, which is cation exchange membrane and impedes electron exchange, acted as a blocking layer, hindering interfacial charge transfer [19-20]. In the cyclic voltammogram of MC/Nafion/GCE, shown in Fig. 2, the redox peak currents were obviously increased compared to those of Nafion/GCE. This phenomenon can be attributed to the presence of MC due to its high porosity and a large specific surface area, which provides favorable sites to accelerate charge transfer [21-23].

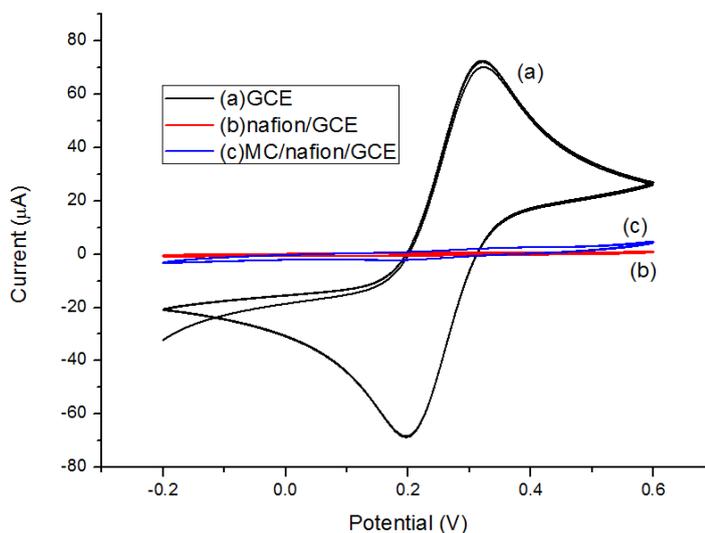


Figure 1. Cyclic voltammograms in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl for (a) GCE, (b) Nafion/GCE and (c) MC/Nafion/GCE. Scan rate: $50 \text{ mV}\cdot\text{s}^{-1}$. Initial potential: -0.2 V. Low potential: -0.2 V. High potential: 0.6 V.

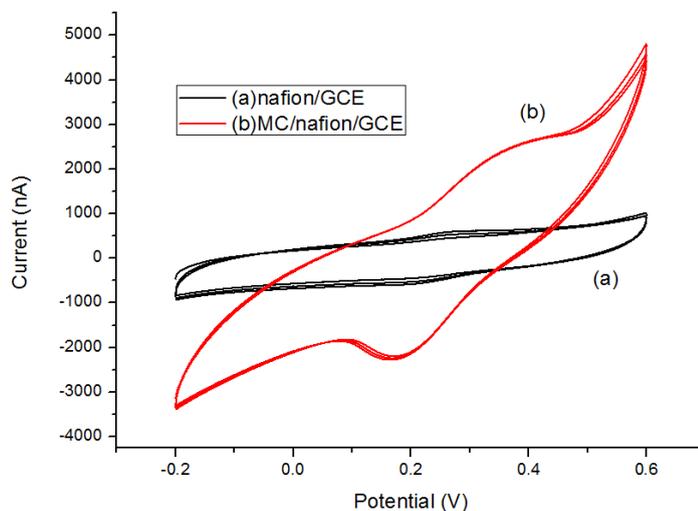


Figure 2. Cyclic voltammograms in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl for (a) Nafion/GCE and (b) MC/Nafion/GCE. Scan rate: $50 \text{ mV}\cdot\text{s}^{-1}$. Initial potential: -0.2 V. Low potential: -0.2 V. High potential: 0.6 V.

The electron transfer kinetics of the prepared electrodes were further investigated by electrochemical impedance spectroscopy (EIS). As shown in Fig. 3, the bare GCE exhibited very low impedance, while the impedance of Nafion/GCE was higher, indicating that Nafion acted as a barrier to interfacial electron transfer [24-25]. MC/Nafion/GCE exhibited a reduced impedance. Such an enhancement in the electron transfer kinetics was also found in other MC-modified electrodes, which indicates that MC acted as an electron-conducting tunnel and improved the electron transfer rate of the electrode [26].

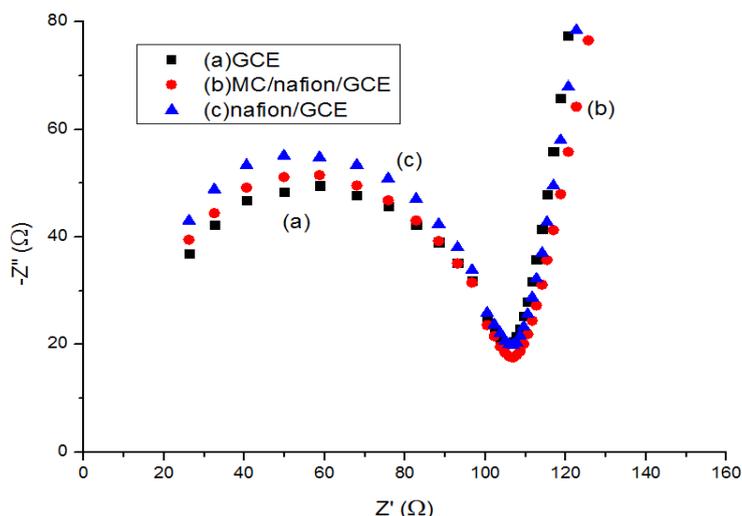


Figure 3. Nyquist plots of (a) GCE, (b) MC/Nafion/GCE and (c) Nafion/GCE in 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in 0.1 M KCl. Initial potential: 0.358 V. High frequency: 1.6×10^6 Hz. Low frequency: 1 Hz. Amplitude: 0.005 V.

3.2. Stripping Response of the Prepared Electrodes

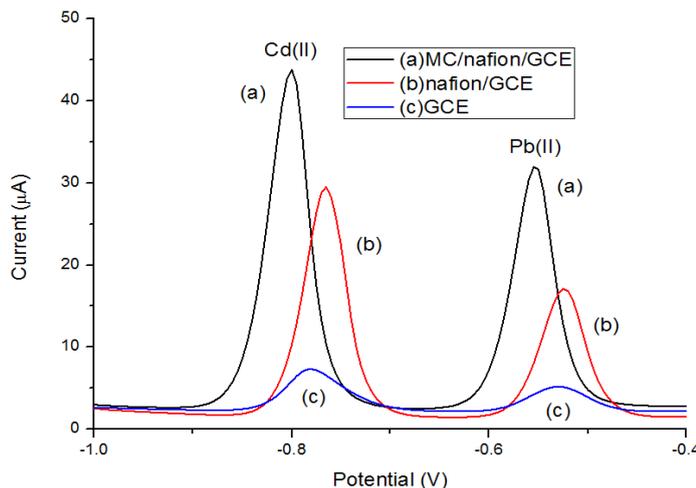


Figure 4. Square-wave anodic stripping voltammograms of $20 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) and Pb(II) in 0.1 M acetate buffer solution (pH 4.0): (a) MC/Nafion/GCE, (b) Nafion/GCE, and (c) GCE. Deposition time: 400 s. Deposition potential: -1.4 V. Concentration of Bi(III): $300 \mu\text{g}\cdot\text{L}^{-1}$.

Fig. 4 presents a comparison of the SWASV responses of $20 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) and Pb(II) on the different working electrodes. The responses of Cd(II) and Pb(II) when applied to bare GCE were very poor, showing two small peaks. After 6.5 μL of Nafion solution (0.5% concentration) was dropped onto the GCE to form Nafion/GCE, the peak current was remarkably enhanced, because the Nafion

membrane has hydrophilic sulfonic acid groups, which easily adsorb other inorganic cations, such as cadmium, lead, and zinc, therefore providing effective cation exchange [27]. A higher stripping current was observed for MC/Nafion/GCE than for Nafion/GCE. This enhancement can be attributed to two factors. First, due to the large specific surface area and special three-dimensional mesoporous structure, MC provides a large number of nucleation sites for Cd and Pb ions. Second, the high conductivity of the MC membrane efficiently expedites electron transport between the analytes and the surface of the electrode [28-29].

3.3. Optimization of the Experimental Conditions

To optimize the performance of the prepared electrode, the SWASV responses of $20 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) and Pb(II) in 0.1 M acetate buffer solution were used to investigate the different experimental parameters.

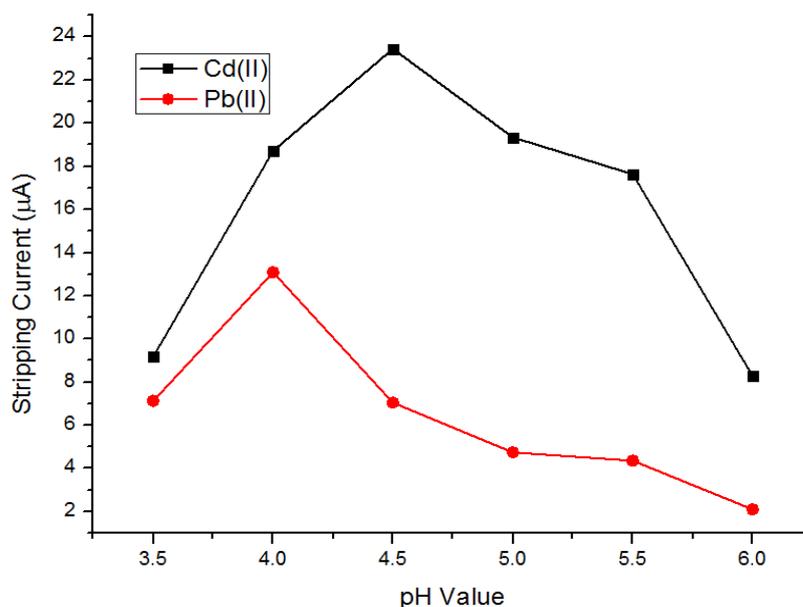


Figure 5. The relationship between the pH of the acetate buffer solution and the stripping currents of Cd(II) and Pb(II). Concentration of Cd(II) and Pb(II): $20 \mu\text{g}\cdot\text{L}^{-1}$. Deposition time: 120 s. Deposition potential: -1.4 V. Concentration of Bi(III): $500 \mu\text{g}\cdot\text{L}^{-1}$.

The stripping responses of Cd(II) and Pb(II) were closely related to the pH of the acetate buffer solution. Fig. 5 shows the relationship between the pH of the acetate buffer solution and the stripping peaks of Cd(II) and Pb(II). The maximum stripping peaks of Cd(II) and Pb(II) were observed at pH 4.5 and pH 4.0, respectively. This observation can be attributed to two factors. First, hydrogen evolution easily occurs on the prepared electrode in acidic environment. This affects the deposition of Cd(II) and Pb(II) on the electrode surface, and the cation exchange capacity of the Nafion membrane is relatively weak when the pH of the solution is low, which degrades the detection performance of the sensor [30-31]. Second, the bismuth membrane is prone to hydrolysis at high pH, which leads to the reduction of

the bismuth membrane on the electrode surface, and the electrodeposition performance becomes poor [32]. However, the decreasing amplitude of the stripping peak of Cd(II) is less than the amplitude of the stripping peak of Pb(II) at pH 4.0. Thus, an acetate buffer solution with a pH of 4.0 was chosen as the experimental medium.

Fig. 6 shows the effect of the bismuth ion concentration in the range of 0 to 900 $\mu\text{g}\cdot\text{L}^{-1}$ on the stripping response of Cd(II) and Pb(II). The maximum peak current appeared at a bismuth ion concentration of 300 $\mu\text{g}\cdot\text{L}^{-1}$, which can be attributed to the fact that bismuth forms an alloy with the cadmium and lead ions in solution, which accelerates cation exchange [33]. However, as the concentration of bismuth ions increases, the bismuth membrane becomes thicker and completely covers the electrode surface, which reduces the specific surface area of the electrode and the electron transfer rate, making cadmium and lead ions difficult to dissolve from the thick bismuth membrane [34]. Therefore, the optimal concentration of bismuth ions, as determined by the discussion above, is 300 $\mu\text{g}\cdot\text{L}^{-1}$.

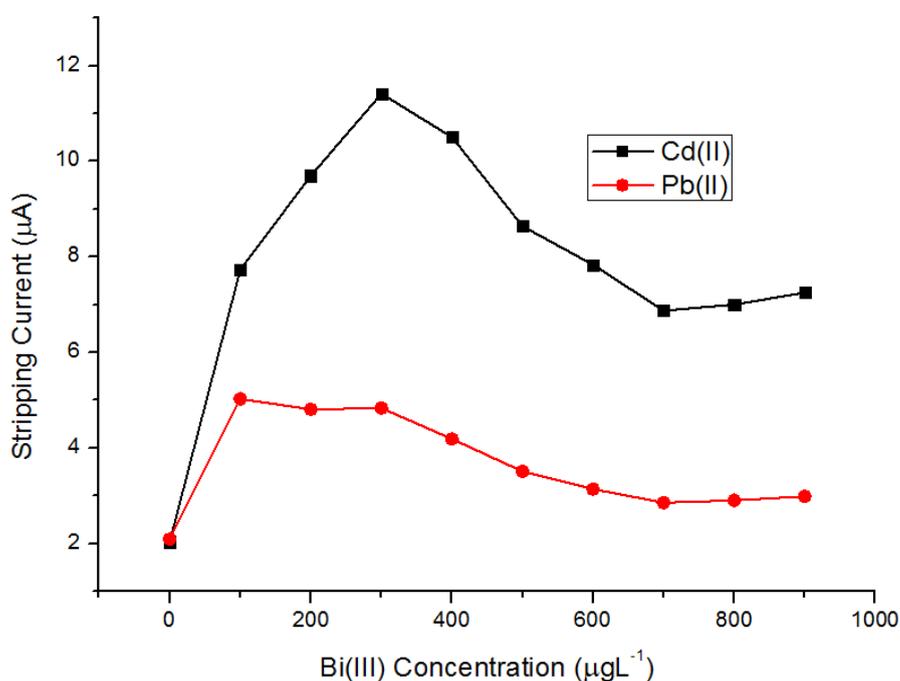


Figure 6. The relationship between the Bi(III) concentration and the stripping currents of Cd(II) and Pb(II). pH: 4.0. Concentration of Cd(II) and Pb(II): 10 $\mu\text{g}\cdot\text{L}^{-1}$. Deposition time: 120 s. Deposition potential: -1.4 V.

Fig. 7 demonstrates the effect of the deposition potential on the stripping response of Cd(II) and Pb(II). The maximum peak current of Cd(II) is achieved at -1.4 V, and the maximum peak current of Pb(II) is achieved at -1.1 V. This behavior can be attributed to the fact that an excessively low deposition potential will induce a hydrogen evolution reaction that decreases the stripping peak current; meanwhile, heavy metal ions cannot be deposited under excessively high deposition potentials [35].

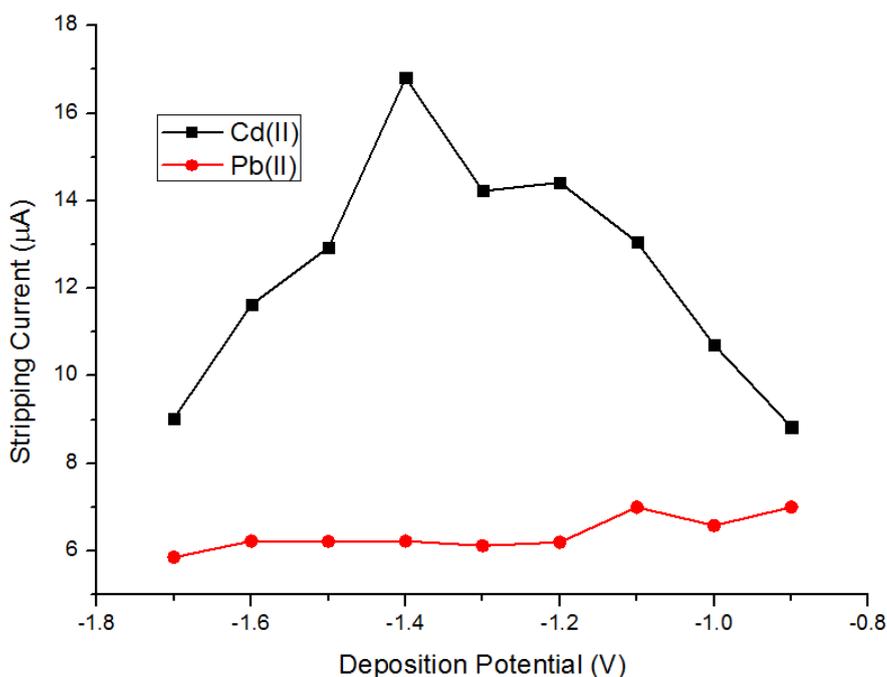


Figure 7. The relationship between the deposition potential and the stripping currents of Cd(II) and Pb(II). pH: 4.0. Concentration of Cd(II) and Pb(II): $20 \mu\text{g}\cdot\text{L}^{-1}$. Deposition time: 120 s. Concentration of Bi(III): $300 \mu\text{g}\cdot\text{L}^{-1}$.

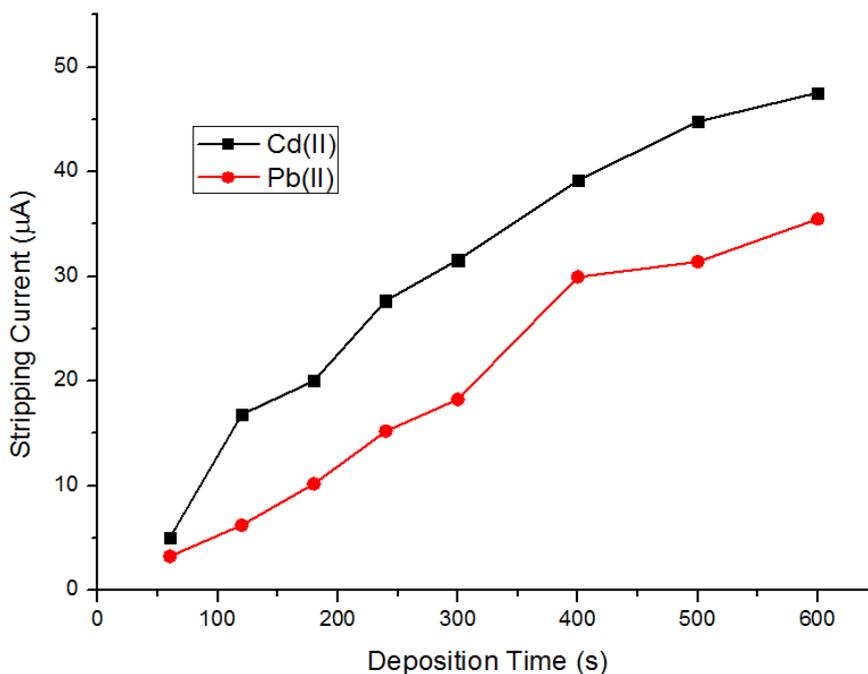


Figure 8. The relationship between the deposition time and the stripping currents of Cd(II) and Pb(II). pH: 4.0. Concentration of Cd(II) and Pb(II): $20 \mu\text{g}\cdot\text{L}^{-1}$. Deposition potential: -1.4 V. Concentration of Bi(III): $300 \mu\text{g}\cdot\text{L}^{-1}$.

Over the deposition potential range of -1.7 V to -0.9 V, the stripping peak current of Pb(II) has a small fluctuation of 1.144 μA when the deposition potential reaches -1.1 V, and the stripping peak current of Cd(II) has a small fluctuation of 7.975 μA when the deposition potential reaches -1.4 V, which is larger than the fluctuation of the stripping peak current of Pb(II). Therefore, the optimum deposition potential is -1.4 V.

Fig. 8 shows the effect of deposition time in the range from 60 to 600 s on the stripping response of Cd(II) and Pb(II). The maximum current peaks of Cd(II) and Pb(II) clearly appeared after 600 s of deposition, which results from the surface of the prepared electrode being further enriched with metal ions as the deposition time increases. However, when the deposition time is too long, the surface of the electrode becomes saturated with the metal, and the change in the stripping peak current will not be obvious. As shown in Fig. 8, the amplitude of the stripping peak current is decreased when the deposition time is over 400 s. Hence, the optimum deposition time is 400 s.

3.4. Analytical Performance of MC/Nafion/GCE

The electrode fabricated under optimized conditions was applied for the determination of the stripping peak currents of Cd(II) and Pb(II) by SWASV. The stripping responses for different concentrations of Cd(II) and Pb(II) are illustrated in Fig. 9. The peak currents exhibit a positive linear relationship with concentrations of Cd(II) and Pb(II) in the range of 5.0 to 70.0 $\mu\text{g}\cdot\text{L}^{-1}$. As shown in Fig. 10, the calibration curve of Cd(II) gave the equation $y = 1.21258x + 4.35578$ (y : μA , x : $\mu\text{g}\cdot\text{L}^{-1}$) with a correlation coefficient of 0.98767 ($S/N = 3$).

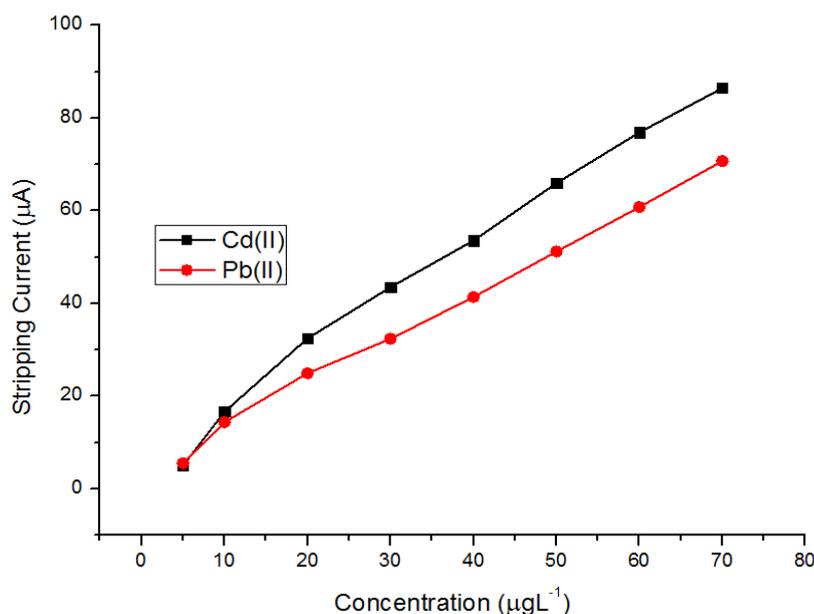


Figure 9. The relationship between the stripping currents and the concentrations of Cd(II) and Pb(II). pH: 4.0. Concentration range of Cd(II) and Pb(II): 5.0-70.0 $\mu\text{g}\cdot\text{L}^{-1}$. Deposition time: 400 s. Deposition potential: -1.4 V. Concentration of Bi(III): 300 $\mu\text{g}\cdot\text{L}^{-1}$.

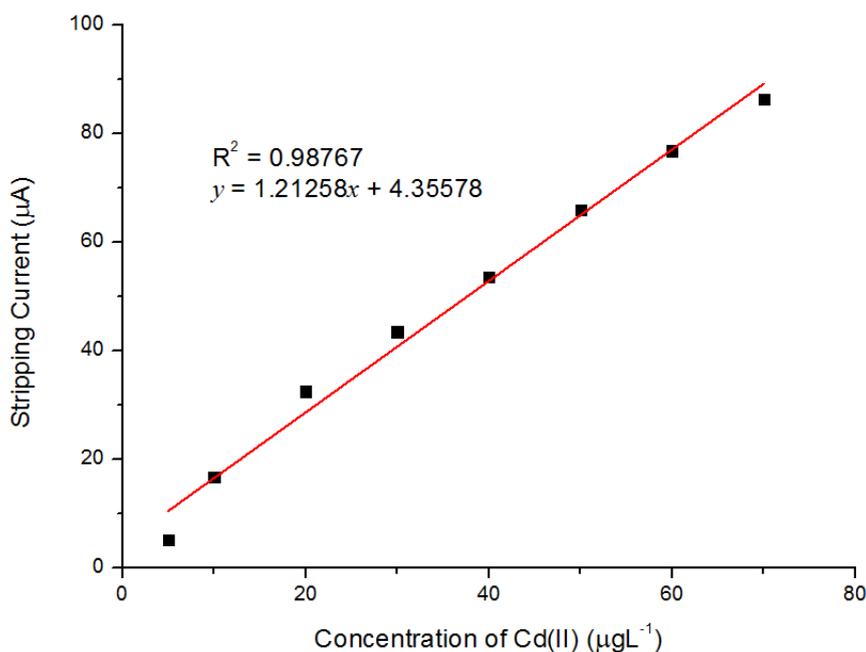


Figure 10. The corresponding calibration plots of MC/Nafion/GCE toward Cd(II) at different concentrations in 0.1 M acetate buffer solution. pH: 4.0. Concentration range of Cd(II): 5.0-70.0 $\mu\text{g}\cdot\text{L}^{-1}$. Deposition time: 400 s. Deposition potential: -1.4 V. Concentration of Bi(III): 300 $\mu\text{g}\cdot\text{L}^{-1}$.

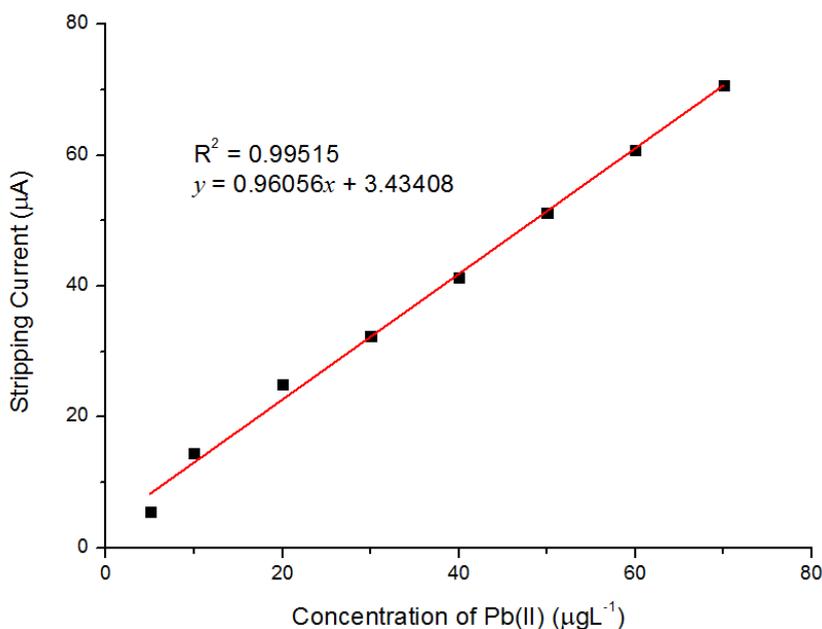


Figure 11. The corresponding calibration plots of MC/Nafion/GCE toward Pb(II) at different concentrations in 0.1 M acetate buffer solution. pH: 4.0. Concentration range of Pb(II): 5.0-70.0 $\mu\text{g}\cdot\text{L}^{-1}$. Deposition time: 400 s. Deposition potential: -1.4 V. Concentration of Bi(III): 300 $\mu\text{g}\cdot\text{L}^{-1}$.

The limit of detection (LOD) was $0.05 \mu\text{g}\cdot\text{L}^{-1}$ with a 400 s accumulation time. As shown in Fig. 11, the calibration curve of Pb(II) gave the equation $y = 0.96056x + 3.43408$ (y : μA , x : $\mu\text{g}\cdot\text{L}^{-1}$) with a correlation coefficient of 0.99515 ($S/N = 3$). The LOD was $0.13 \mu\text{g}\cdot\text{L}^{-1}$ with a 400 s accumulation time. For one electrode, the relative standard deviation (RSD) was 1.48% for five measurements, and for five electrodes prepared through identical procedures, the RSD was 3.5%. The long-term stability of the sensor was examined by intermittently detecting the SWASV response of the electrode to $20 \mu\text{g}\cdot\text{L}^{-1}$ of Cd(II) and Pb(II). The electrode lost approximately 4.7% of its original response after storage under ambient conditions for one week, which proved that the acceptable stability of the sensor can be attributed to the durability of the MC/Nafion composite. The performance of MC/Nafion/GCE compared to other reported sensors is summarized in Table 1. Table 1 shows that the proposed electrode exhibited a lower detection limit and higher sensitivity.

Table 1. Comparison of different electrodes for the determination of Cd(II) and Pb(II).

Electrode	Technique	Linear range ($\mu\text{g}\cdot\text{L}^{-1}$)		Detection limit ($\mu\text{g}\cdot\text{L}^{-1}$)		Reference
		Cd(II)	Pb(II)	Cd(II)	Pb(II)	
CB-15-crown-5/GCE	DPASV	15.7-191.1	10.9-186.5	4.7	3.3	[36]
BioCl/MWCNT/GCE	SWASV	5-50	5-50	1.2	0.57	[37]
L-cys/GR-CS/GCE	DPASV	0.56-67.2	1.04-62.1	0.45	0.12	[6]
MWCNT/poly(P CV)/GCE	DPASV	1.0-300.0	1.0-200.0	0.2	0.4	[4]
Bi-D24C8/Nafion/S PCE	SWASV	0.5-60	0.5-60	0.27	0.11	[38]
Bi/CNT/SPE	SWASV	2-100	2-100	0.8	0.2	[39]
MC/Nafion/GCE	SWASV	5.0-70.0	5.0-70.0	0.05	0.13	This work

3.5. Interference Study

An interference study was performed by adding various interfering ions into a standard solution (max: 100-fold mass ratios) containing $50 \mu\text{g}\cdot\text{L}^{-1}$ Cd(II) and Pb(II) and $300 \mu\text{g}\cdot\text{L}^{-1}$ Bi(III). The tolerated ratios for a $\pm 5\%$ change in the signals of Cd(II) and Pb(II) allowed for 100 times more NO_3^- , SO_4^{2-} , Cl^- , K^+ , Na^+ , Ca^{2+} , Ag^+ , Mg^{2+} , Mn^{2+} , Zn^{2+} , and Al^{3+} and 30 times more for Fe^{3+} ; however, upon the addition of 2 times more copper ions, the stripping responses of Cd(II) and Pb(II) decreased by 31.76% and 23.95%, respectively. This suppression effect likely resulted from the formation of

intermetallic compounds as well as competition for active sites on the surface of the electrode. However, this interference can be conveniently and efficiently eliminated through the addition of ferrocyanide ions in the test solution to form a stable and insoluble copper-ferrocyanide complex.

3.6. Soil Sample Analysis

Table 2. Recovery for the detection of Cd(II) and Pb(II) in extracted soil samples.

Ion	Added ($\mu\text{g}\cdot\text{L}^{-1}$)	Found ($\mu\text{g}\cdot\text{L}^{-1}$) ^[a]	RSD (%)	Recovery (%)
Cd(II)	—	4.75	1.8	—
	5.0	9.61	2.5	97.2
	10.0	15.08	3.8	103.3
	20.0	23.97	4.7	96.1
Pb(II)	—	12.94	2.1	—
	5.0	17.83	3.4	97.8
	10.0	22.81	4.3	98.7
	20.0	33.16	4.6	101.1

^[a]Mean of five repeat measurements

The feasibility of MC/Nafion/GCE for the detection of cadmium and lead in real samples was verified by analyzing extracted soil samples. The initial concentrations of Cd(II) and Pb(II) were $4.75\pm 0.06 \mu\text{g}\cdot\text{L}^{-1}$ and $12.94\pm 0.04 \mu\text{g}\cdot\text{L}^{-1}$ ($n = 5$), respectively. The initial results were validated through independent analysis by atomic absorption spectroscopy (AAS), which gave $4.87\pm 0.03 \mu\text{g}\cdot\text{L}^{-1}$ for Cd(II) and $13.15\pm 0.07 \mu\text{g}\cdot\text{L}^{-1}$ for Pb(II) ($n = 5$), respectively. The difference between the concentrations of Cd(II) and Pb(II) obtained by MC/Nafion/GCE and AAS was less than 5%. In addition, recovery tests were carried out to further validate the feasibility of using MC/Nafion/GCE. As shown in Table 2, the proposed method using MC/Nafion/GCE had an average recovery of 98.87% for Cd(II) and 99.2% for Pb(II). All of these results indicate that the prepared electrode can be applied to the determination of Cd(II) and Pb(II) in extracted soil samples.

4. CONCLUSION

In this study, a novel MC/Nafion composite-modified GCE for the simultaneous and sensitive detection of Cd(II) and Pb(II) is described. The MC/Nafion/GCE was further investigated by CV, EIS, and SWASV. The electrode exhibited excellent electrochemical activity and accelerated charge transfer kinetics due to the presence of conductive MC. Meanwhile, Nafion enhanced the stability and durability of the modified electrode. MC and Nafion allowed the modified electrode to be an effective sensor for the sensitive detection of Cd(II) and Pb(II) with very low limits of detection. The feasibility

of using the electrode was further confirmed by analyzing extracted soil samples, which gave satisfactory results. This work introduces a “green,” stable, and highly sensitive electrochemical sensor through the composite modification of MC and Nafion. This sensor has great potential for application in the fields of food safety and environmental monitoring.

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