

## An Ultrasensitive Method for Detecting Picomolar Levels of Cadmium(II) by Fast-Scan Anodic Stripping Voltammetry

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This work reported an approach for the determination of the heavy metal ion cadmium Cd(II) using a bismuth-film electrode (Bi-FE) with fast-scan anodic stripping voltammetry (FSASV). The experiment was divided into two steps. First, the Bi-FE was prepared by electrodepositing a metallic bismuth-film onto the electrode, and then the target metal ion Cd(II) was electrochemically preconcentrated on the Bi-FE. Second, the target metal was measured with FSASV. At a scan rate of 400 V/s, the anodic stripping peak current increased gradually with increasing Cd(II) concentration, and a linear relationship between the peak current and the logarithm of Cd(II) concentration was obtained from 0.1 μmol/L to 1.0 pmol/L, with a detection limit of 0.3 pmol/L (S/N=3). Furthermore, the method was successfully applied to detect Cd(II) in spiked tap water samples, with sufficient recoveries in the range of 94.0% to 105.2% and corresponding relative standard deviations ranging from 2.9% to 6.4%. Therefore, FSASV is a simple, rapid and ultrasensitive method for the detection of picomolar levels of Cd(II).

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**Keywords:** Fast-scan anodic stripping voltammetry; Ultrasensitive determination; Cadmium(II); Bismuth-film electrode (Bi-FE)

### 1. INTRODUCTION

Currently, the pollution of heavy metals in water and agricultural soils is becoming a problem that is being taken seriously around the world [1-3], and heavy metals have been widely found in food chains consisting of crops [4], meats and seafood [5-7]. Many toxic heavy metals, especially cadmium Cd(II), cause comprehensive damage to human health, such as renal abnormalities, liver damage and neurological diseases [8-10]. The World Health Organization regulates the amount of Cd(II) in

drinking water, with safe levels below 0.3 nmol/L [11]. Therefore, it is necessary to develop a simple and ultrasensitive method for the detection of ultratrace Cd(II).

Various analytical approaches have been devoted to the determination and quantification of trace Cd(II). Some methods, such as atomic absorption spectrometry (AAS) [12, 13], inductively coupled plasma atomic emission spectrometry (ICP-AES) [14, 15], and inductively coupled plasma mass spectrometry (ICP-MS) [16, 17], are valued as certified methods due to their outstanding specificity, accuracy and sensitivity. However, these methods often require expensive instruments and professionals for operation, in addition to being time consuming and cumbersome to operate. Colorimetric [18, 19] and other analytical methods [20-22] can also be used for the determination of Cd(II), but their practical applications are limited due to matrix interference. In contrast, electrochemical methods, especially electrochemical stripping analysis, have long been recognized as powerful techniques because of their sensitivity, relatively cheap instrumentation, ability for multielement determination and capability of determining elements accurately at trace and ultratrace levels.

Anodic stripping voltammetry (ASV) has been widely regarded as one of the simplest and most effective electrochemical techniques for the trace analysis of metal ions [23, 24]. The remarkable sensitivity of ASV is attributed to the combination of effective preconcentration and advanced measurement procedures that generate an extremely favorable signal to background ratio. Most existing studies focus on developing modified electrodes at a low scan rate for the detection of metal ions by stripping voltammetry. For example, Heineman and coworkers reported a carbon nanofiber modified electrode for the determination of Cd(II) by stripping voltammetry with a scan rate of 0.5 V/s and a detection limit of 1.5 nmol/L [25]. An electrode modified with a composite film of multiwalled carbon nanotubes and poly alizarin red S was reported for the detection of Pb(II) and Cd(II) by differential pulse anodic stripping voltammetry at a scan rate of 0.1 V/s, and the detection limits were 0.43 and 0.47  $\mu\text{g/L}$ , respectively [26]. In addition, a multiwalled carbon nanotube-emeraldine base polyaniline-nafion composite modified glassy carbon electrode was prepared to detect trace Cd(II) by the square wave anodic stripping voltammetry (SWASV) method, in which the detection limit of Cd(II) reached 0.06  $\mu\text{g/L}$  [27]. Additionally, Nagles et al. proposed a poly(3, 4-ethylenedioxythiophene)-sodium dodecyl sulfate coated antimony film electrode (PEDOTSDS-SbFE), which was prepared ex situ and employed to detect Pb(II) and Cd(II) by ASV, and the detection limits were 0.5 and 0.8  $\mu\text{g/L}$ , respectively [28]. However, the procedures for preparing these modified electrodes were cumbersome, and the sensitivity was not ideal.

Some studies showed that the sensitivity of voltammetry increases with an increase in scan rate. For example, Yao et al. proposed that detecting As(III) and As(V) at a scan rate of 10 V/s would greatly improve the detection sensitivity compared to detection at a scan rate of 0.01 V/s [29]. The detection limits of As(III) and As(V) reached 1.0 nmol/L and 5.4 nmol/L, respectively. Innuphat et al. proposed that detecting Cd(II) at a faster scan rate of 0.2 V/s would greatly improve the peak current compared to detection at a scan rate of 0.01 V/s [30]. However, when the scan rate exceeded 0.2 V/s, the peak signal widened, causing the excessive background current to affect the output of the faradaic current; as a result, the detection limit of this method only reached 0.18 nmol/L. Wipf and coworkers detected zeptomole quantities of Pb(II) on a mercury monolayer carbon fiber electrode at a fast scan

rate ( $v > 1.0$  kV/s) [31]. Although this kind of highly sensitive detection is urgently needed, the difficulty and complexity of using mercury monolayer carbon fiber electrodes has limited its use.

In this study, the development of an ultrasensitive, fast and simple method for the detection of Cd(II) on a conventional size electrode by FSASV is reported. Compared with other methods for the detection of heavy metal ions based on stripping voltammetry, our method has a much higher sensitivity for detecting Cd(II) at fast scan rates, and it exhibits a wide linear range. Furthermore, this method has been successfully applied to detect Cd(II) in real water samples.

## 2. EXPERIMENTAL

### 2.1. Reagents and chemicals

The chemicals used in the present work were of analytical reagent grade and used as received. Anthracene and tetrabutylammonium tetrafluoroborate ( $\text{NBu}_4\text{BF}_4$ ) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile, acetate and 65-68% nitric acid ( $\text{HNO}_3$ ) were purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Bismuth nitrate ( $\text{Bi}(\text{NO}_3)_3$ ) and cadmium nitrate ( $\text{Cd}(\text{NO}_3)_2$ ) were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China). All solutions were prepared with ultrapure water obtained from a Millipore Milli-Q ultrapure water system (Bedford, MA, USA).

### 2.2. Apparatus

The electrochemical tests at low scan rates were performed with a CHI 660E electrochemical workstation (Chenhua Instrument Company, Shanghai, China). A conventional three-electrode configuration was used, including a bare or modified glassy carbon electrode (GCE, 1 mm diameter, GaossUnion, Wuhan, China) as the working electrode, an Ag/AgCl (3 mol/L KCl) as the reference electrode and a platinum wire as the counter electrode. A custom-built fast-scan system was constructed mainly according to Guo's previous research [32, 33], with a printed circuit board (PCB) produced and optimized to provide positive feedback compensation of ohmic drop in the solution. Potential waveforms were generated by an AFG3021B arbitrary/function generator (Tektronix, Oregon, USA), and voltammetric data were acquired through a TBS1102 digitizing oscilloscope (Tektronix, Oregon, USA). The concentration of Cd(II) in spiked tap water samples was validated using Agilent 7500cx ICP-MS (Agilent Technologies Inc., Santa Clara, USA).

### 2.3. Ex situ preparation of Bi-FE

The GCE was hand polished using a 0.05  $\mu\text{m}$  particle size alumina slurry to obtain a mirror surface and then washed and sonicated in water for 2 minutes. Then, the GCE was immersed into an oxygen-free pH 3.0 nitric acid solution containing 10.0  $\mu\text{mol/L}$  Bi(III), which was purged with  $\text{N}_2$  for 10 min beforehand. After the electrolysis was carried out at  $-0.8$  V for 150 s under stirring at 500 rpm, the bismuth-film electrode (Bi-FE) was obtained by electrochemical ex situ deposition.

#### 2.4. Detection of Cd(II) on Bi-FE by FSASV

The detection of Cd(II) was divided into two steps: deposition and stripping. First, the electrodeposition of Cd(II) was carried out at  $-1.2$  V for 1000 s at a stirring speed of 500 rpm by immersing the three electrodes into an electrochemical cell containing 15 mL of 0.1 mol/L acetate buffer (pH 4.5) and Cd(II) at different concentrations ( $10^{-12}$ ,  $10^{-11}$ ,  $10^{-10}$ ,  $10^{-9}$ ,  $10^{-8}$  and  $10^{-7}$  mol/L). Second, a positive anodic stripping potential scan (from  $-1.2$  to  $-0.2$  V) at different scan rates (100, 200, 300, 400, 500, 600, 700 and 800 V/s) was applied after the stirring was stopped, and the resulting voltammogram was recorded.

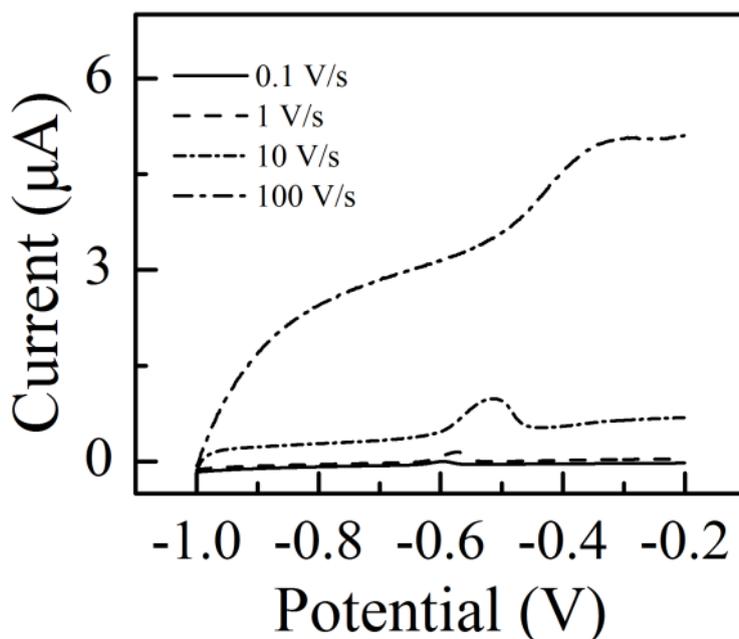
#### 2.5. Analysis of spiked tap water samples

Aliquots of spiked tap water samples were obtained by adding standard Cd(II) solution to tap water. The aliquots were simultaneously analyzed by ICP-MS to validate the method developed in this study.

### 3. RESULTS AND DISCUSSION

#### 3.1. Mechanism of detecting Cd(II) by FSASV

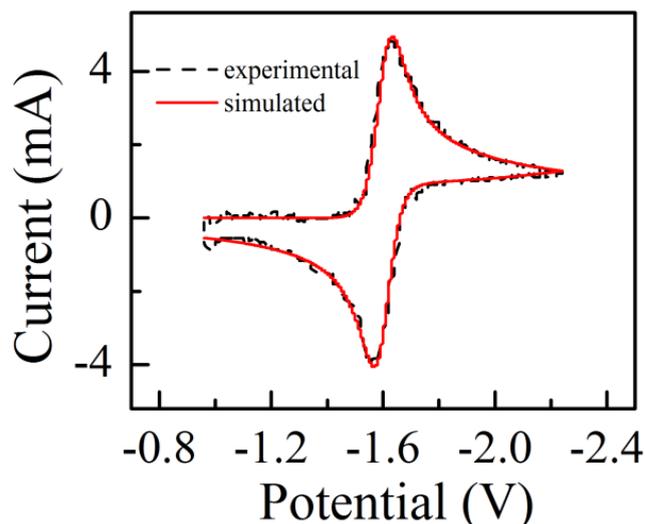
The potential ohmic drop ( $iR$  drop) is the potential drop caused by the resistance of the electrolyte solution when the current passes through the electrodes. This drop is unavoidable and has great influence on voltammetric behavior. At high scan rates, the  $iR$  drop is significant enough to cause the coupling of the faradaic current and charge current and to move the redox peaks outside the potential window. To obtain reliable and usable data, the  $iR$  drop should be compensated as much as possible. Fig. 1 shows the anodic stripping voltammograms of  $10^{-7}$  mol/L Cd(II) at different scan rates on an ordinary electrochemical workstation. Stripping faradaic currents increased with increasing scan rates from 0.1 to 10 V/s, and anodic peak potentials shifted to more positive potentials. When the scan rate was as high as 100 V/s, the faradaic current was clearly coupled to the background charge current, and the anodic stripping peak nearly moved outside the potential window due to the inefficient compensation of the  $iR$  drop. Therefore, it is difficult to improve detection sensitivity by increasing the scan rate without efficient compensation of the  $iR$  drop. To solve this problem, a circuit with nearly 100% compensation of the  $iR$  drop at a fast scan rate was developed according to our previous work [32, 33].



**Figure 1.** Anodic stripping voltammograms of  $10^{-7}$  mol/L Cd(II) at different scan rates (0.1, 1, 10 and 100 V/s).

### 3.2. Performance of the circuit with ohmic drop compensation

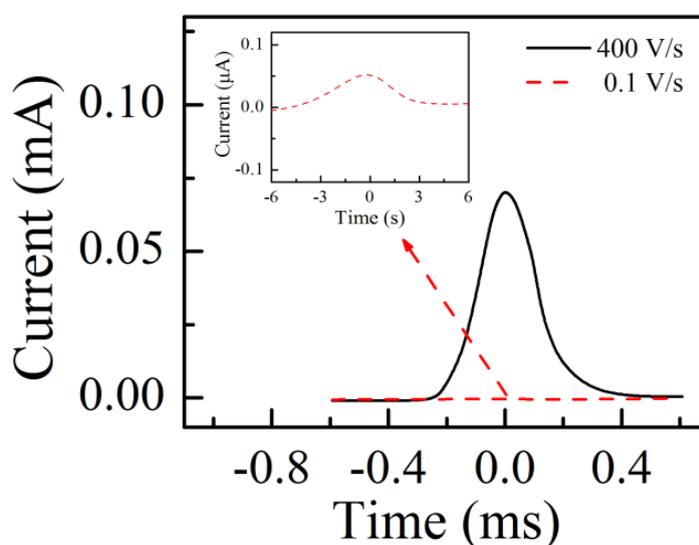
As the fastest heterogeneous electron transfer reaction in a well-established electrochemical system, the reduction of anthracene in acetonitrile on a gold electrode is a very common reaction to test the performance of fast voltammetric circuits. Thus, this approach was applied to check our circuit. Since this experiment was performed to test the validity of the circuit, only raw data are presented. A 100% compensated voltammogram for the reduction of 18.0 mmol/L anthracene in acetonitrile, containing 0.9 mol/L  $\text{NBu}_4\text{BF}_4$  as the supporting electrolyte and using a 1 mm diameter gold electrode and a scan rate of 1.2 kV/s is shown in Fig. 2. A simulated voltammogram based on a self-established simulation program [34] is also shown and compared to the experimental voltammogram. In the simulation, Butler-Volmer kinetics were observed with the following parameters: standard electrode potential  $E_0 = -1.61$  V versus the Pt reference, electron transfer coefficient  $\alpha = 0.5$ , reaction rate constant  $k_0 = 5.1 \text{ cm}\cdot\text{s}^{-1}$ , diffusion coefficient  $D_{\text{O}} = D_{\text{R}} = 1.6 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$ , electrode area  $A = 0.00785 \text{ cm}^2$ , initial potential  $V_i = -0.86$  V, reverse potential  $V_r = -2.24$  V, scan rate  $\nu = 1.2$  kV/s, temperature  $T = 20$  °C, uncompensated solution resistance  $R_u = 0$  (i.e., 100% compensation, without any ohmic drop), and double layer capacitance  $C_{\text{dl}} = 10$   $\mu\text{F}$ . As shown, the experimental and simulated voltammograms were consistent at a scan rate of 1.2 kV/s, suggesting nearly 100% compensation of the ohmic drop and demonstrating the excellent performance of the circuit.



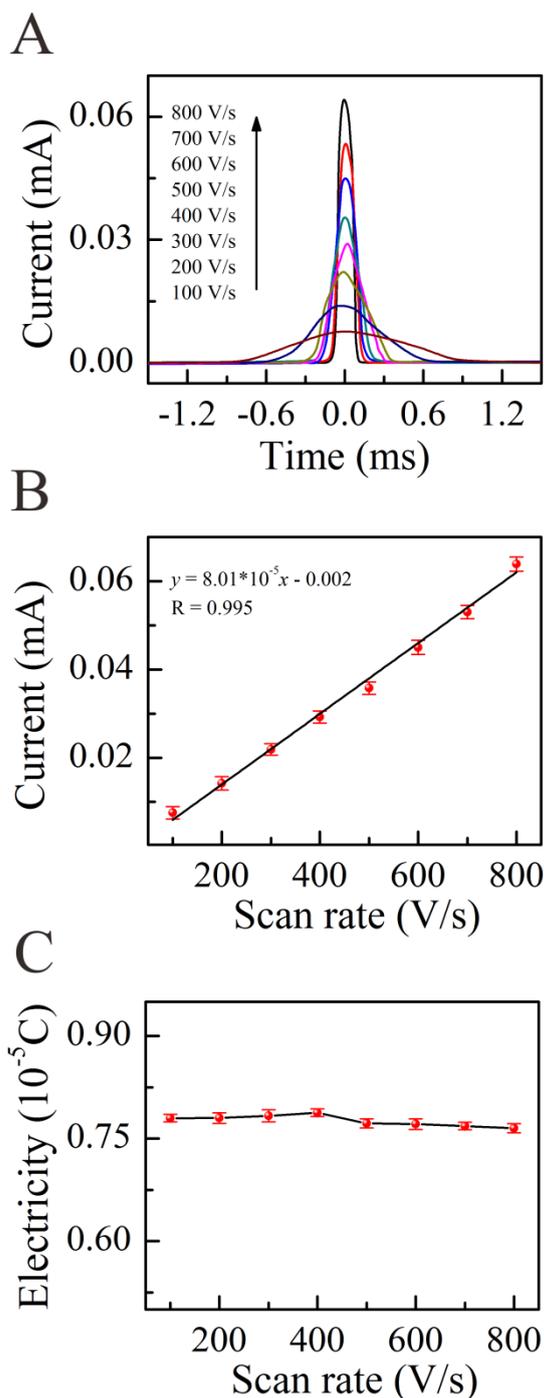
**Figure 2.** Cyclic voltammograms of 18.0 mmol/L anthracene in acetonitrile at a scan rate of 1.2 kV/s. Solid line: simulated; dashed line: experimental, with 100% compensation of ohmic drop.

### 3.3. Feasibility of detecting Cd(II) by FSASV

To clearly demonstrate the influence of scan rate, the voltammogram between the current and potential was adjusted to the present current and time. This method of plotting was used in subsequent studies. Anodic stripping voltammograms of  $10^{-7}$  mol/L Cd(II) were obtained at scan rates of 0.1 V/s and 400 V/s on the Bi-FE (Fig. 3). The peak current was approximately 0.05  $\mu$ A at a scan rate of 0.1 V/s, while it was approximately 0.07 mA at a 400 V/s scan rate, which was approximately 1400 times higher, suggesting that a much higher sensitivity could be obtained by FSASV.



**Figure 3.** Anodic stripping voltammograms of  $10^{-7}$  mol/L Cd(II) at scan rates of 0.1 V/s (dashed line) and 400 V/s (solid line).



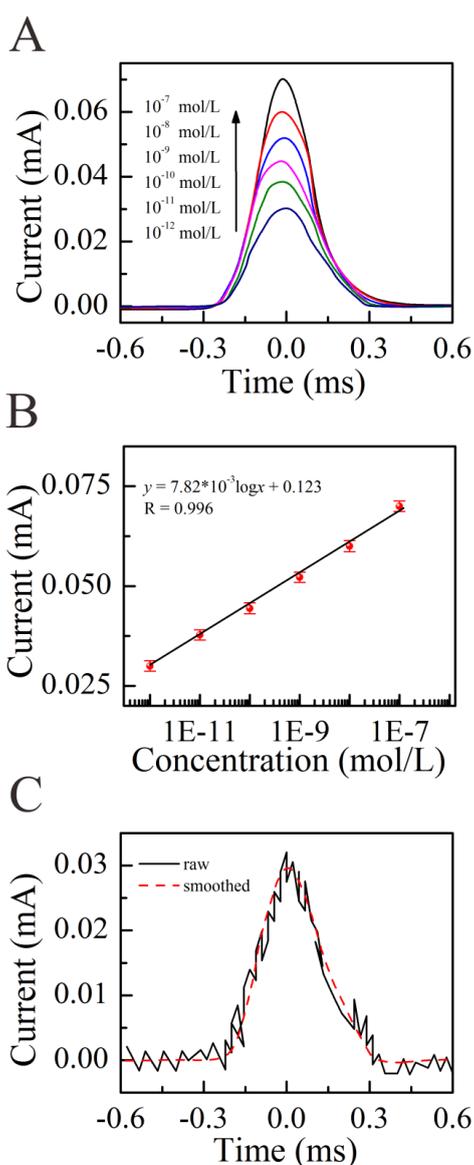
**Figure 4.** Effect of scan rate on sensitivity. (A) Fast-scan anodic stripping voltammograms of  $10^{-12}$  mol/L Cd(II) at different scan rates (100, 200, 300, 400, 500, 600, 700 and 800 V/s), (B) the linear relationship between the peak current and the scan rate, and (C) the electricity in the stripping process at different scan rates.

### 3.4. Reliability of detecting Cd(II) by FSASV

The FSASV response of  $10^{-12}$  mol/L Cd(II) at different scan rates ranging from 100 V/s to 800 V/s was explored. As shown in Fig. 4A, the peak current increased with increasing scan rate, obeying the regression equation of  $y$  (mA) =  $8.01 \times 10^{-5} x$  (V/s) - 0.002, where  $y$  is the peak current,  $x$  is the

scan rate, and the linear correlation coefficient  $R$  is equal to 0.995 (Fig. 4B). In addition, the electricity ( $Q$ ) remained nearly constant with increased scan rate (Fig. 4C). When the scan rates were greater than 400 V/s,  $Q$  decreased by approximately 1-2%, perhaps due to the accuracy limitation of the instrument at high scan rates. Therefore, 400 V/s was selected as the optimum scan rate to maintain detection accuracy. These findings could be easily explained; when all experimental conditions were fixed, the amount of Cd(II) electrodeposited on the Bi-FE was constant. Therefore,  $Q$  was constant when stripping. According to  $Q = I \times t$ , the higher the scan rate was, the shorter the time and thus the higher the stripping current. Therefore, the highly sensitive determination of Cd(II) could be reliably obtained by increasing the scan rate via FSASV.

### 3.5. Sensitivity of detecting Cd(II) by FSASV



**Figure 5.** (A) Fast-scan anodic stripping voltammograms of Cd(II) at different concentrations ( $10^{-12}$ ,  $10^{-11}$ ,  $10^{-10}$ ,  $10^{-9}$ ,  $10^{-8}$  and  $10^{-7}$  mol/L), (B) the linear relationship between the peak current and the logarithm of Cd(II) concentration, and (C) the raw (solid line) and smoothed (dashed line) anodic stripping voltammograms of  $10^{-12}$  mol/L Cd(II). Scan rate: 400 V/s.

**Table I.** Comparison of the main methods reported for the detection of Cd(II).

Technique	Detection limit		Electrodes	Linear range		References
	$\mu\text{g/L}$	$\text{mol/L}$		$\mu\text{g/L}$	$\text{mol/L}$	
ASV	0.2	$0.18 \times 10^{-8}$	GCE/MWCNT/poly(PCV)/Bi	1 - 300	$0.89 - 267 \times 10^{-8}$	[35]
ASV	0.4	$0.36 \times 10^{-8}$	nsBi-FE	20 - 100	$0.18 - 0.9 \times 10^{-6}$	[36]
SWASV	0.2	$0.18 \times 10^{-8}$	SPE/SWCNHs/BiF	1 - 60	$0.89 - 53.4 \times 10^{-8}$	[37]
SWASV	0.06	$0.53 \times 10^{-9}$	Bi/MWCNT-EBP-NA/GCE	1 - 50	$0.89 - 44.5 \times 10^{-8}$	[27]
DPASV	0.1	$0.89 \times 10^{-9}$	Bi/Graphene/MWCNT/GCE	0.5 - 30	$0.44 - 26.4 \times 10^{-6}$	[38]
DPASV	0.18	$0.16 \times 10^{-8}$	Bi/EG/GCE	1 - 100	$0.89 - 89 \times 10^{-8}$	[39]
FSASV	$0.34 \times 10^{-4}$	$0.3 \times 10^{-12}$	Bi-FE	$11.24 - 1.12 \times 10^{-4}$	$0.01 - 1000 \times 10^{-10}$	This work

The relationship between peak current and Cd(II) concentration ( $10^{-12}$  -  $10^{-7}$  mol/L) was explored by FSASV at a scan rate of 400 V/s. As shown in Fig. 5A, the peak current increased as the Cd(II) concentration increased, and a linear relationship between peak current and the logarithm of Cd(II) concentration was found. The regression equation was  $y$  (mA) =  $7.82 \times 10^{-3} \log x$  (mol/L) + 0.123 with  $R = 0.996$ , where  $y$  is the peak current, and  $x$  is the Cd(II) concentration (Fig. 5B). The raw anodic stripping voltammogram of  $1 \times 10^{-12}$  mol/L Cd(II) at a scan rate of 400 V/s and the smoothed voltammogram are both shown in Fig. 5C; there were no significant differences between them. The peak current was approximately 0.03 mA, while the noise was approximately 0.003 mA, implying that the limit of quantification (LOQ) was 1 pmol/L based on a signal-to-noise ratio (S/N) equal to 10. Based on this, the limit of detection (LOD) could be roughly estimated as 0.3 pmol/L. As shown in Table I, the proposed FSASV method performed better with regard to sensitivity compared to previously reported methods for the detection of Cd(II) at a low scan rate. This method benefitted from the significant amplification of the faradaic current, which was a result of the increase in scan rate.

### 3.6. Applications

To test the feasibility of the method developed here, detection was validated through comparison with ICP-MS analysis. Neither the FSASV method nor the ICP-MS-based system detected the presence of Cd (II) in blank tap water samples. Furthermore, the analytical results of the Cd(II) spiked samples, as presented in Table II, indicate that there is no significant difference between the two methods ( $P > 0.10$ ). Recovery studies were executed in the spiked tap water samples with varying concentrations of Cd(II). Sufficient recoveries ranging from 94.0% to 105.2% were obtained, and the corresponding relative standard deviations ranged from 2.9% to 6.4%. Therefore, the method based on FSASV is feasible and practical for the determination of Cd (II) in tap water samples.

**Table II.** Detection of Cd(II) in spiked tap water samples using ICP-MS and the method described here ( $\bar{x} \pm s$ ,  $n = 5$ ).

Samples	Spiked (pmol/L)	ICP-MS (pmol/L)	This assay (pmol/L)	This assay Recovery (%)	This assay RSD (%)
1	10	$9.7 \pm 0.5$	$9.4 \pm 0.6$	94.0	6.4
2	50	$49.7 \pm 0.6$	$52.6 \pm 1.5$	105.2	2.9
3	300	$299.6 \pm 2.6$	$295.8 \pm 12.5$	98.6	4.2

#### 4. CONCLUSIONS

In summary, an effective FSASV method was developed for the ultrasensitive detection of Cd(II). Compared with traditional ASV methods at low scan rates, this method had better detection sensitivity, with detection limits as low as 0.3 pmol/L. Moreover, this method was successfully employed for the highly sensitive detection of Cd(II) in spiked tap water samples. Thus, FSASV is an attractive candidate method for the accurate and ultrasensitive detection of Cd(II).

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