

RESEARCH ARTICLE

# Selective Recognition of Lead and Cadmium in Potable Water Using Single Polypyrrole Nanowire Decorated with Cobalt Oxide Nanoparticles Electrode

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**ABSTRACT:** The fabrication and characterization of a high-performance, robust, and highly sensitive sensor based on a single polypyrrole nanowire (sPpy NW) decorated with cobalt oxide nanoparticles (CoO<sub>x</sub>NPs) for the selective recognition of lead (Pb<sup>2+</sup>) and cadmium (Cd<sup>2+</sup>) in potable water are described in this paper. The electrodeposition technique was used to prepare the sPpyNW/CoO<sub>x</sub>NPs assembly, and square wave anodic stripping voltammetry (SW-ASV) was used to assess sensor performance. Optimizing sensor performance, such as deposition time, deposition potential, and supporting electrolyte, was used to assess for best sensor performance. The developed sensor exhibited excellent linearity and the linear range for the detection of individual Cd<sup>2+</sup> and Pb<sup>2+</sup> ions was determined to be 0.00 to 0.11 μM and 0.00 to 0.12 μM, respectively. The detection limits observed for both Pb<sup>2+</sup> and Cd<sup>2+</sup> sensors are 0.22 μM (R<sup>2</sup> = 0.9520) and 0.013 μM (R<sup>2</sup> = 0.9723), respectively. The linear range for the detection of Pb<sup>2+</sup> and Cd<sup>2+</sup> sensors present in the same sample was determined to be 0.00 to 0.09 μM, with a detection limit of 0.026 μM (R<sup>2</sup> = 0.8726) and 0.013 μM (R<sup>2</sup> = 0.9468) for Pb<sup>2+</sup> and Cd<sup>2+</sup>, respectively. The observed results revealed that the functionalization of CoO<sub>x</sub>NPs on the surface of a sPpyNW electrode seems to be a very effective way of developing a sensitive, selective, and stable electrochemical sensor for Pb<sup>2+</sup> and Cd<sup>2+</sup> ions.

**Keywords:** Polypyrrole nanowire, Cobalt oxide nanoparticle, Heavy metals ion sensors

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## 1. INTRODUCTION

Heavy metal ion contamination is one of the major issues that cause severe effects on human health and the environment. Among heavy metals, cadmium Cd<sup>2+</sup> and Lead Pb<sup>2+</sup> are notorious for being the world's most hazardous pollutants. For instance, the severity of Cd<sup>2+</sup> and Pb<sup>2+</sup> can lead to tubular dysfunction, bone degeneration, hypertension, altered normal gene expression, inhibiting DNA damage repair, inducing oxidative stress, and cancer [1-5]. Hence, it is essential to establish a highly sensitive, rapid, reliable, and cost-effective analytical technique for identifying and quantifying these heavy metal ions.

There are number of established analytical techniques for detecting heavy metals in natural water and the environment namely Hydride generation atomic fluorescence

spectrometry (HG-AFS), Hydride generation atomic absorption spectroscopy (HG-AAS) [6], Inductively coupled plasma atomic emission spectroscopy (ICP-AES), Inductively coupled plasma mass spectrometry (ICP-MS) [7], Graphite furnace atomic absorption spectroscopy (GF-AAS) [8], and Fluorescence spectrometry. As the above listed detection techniques need sophisticated equipment, experienced personnel and a well-established laboratory setup making more expensive detection of heavy metals. Additionally, these methods are time-consuming, inaccessible, and unsuitable for field investigation. A simple, low-cost, portable, and accurate method for rapidly detecting or analyzing heavy metal ions in water and the environment is required. Electrochemical methods, particularly stripping voltammetry, have been determined to be the most advantageous approach because of its cheap development costs, high integration, and high sensitivity [9, 10].

Surface modification using nanoparticles or thin films is essential to enhance the performance of the sensor for electrochemical sensing applications, and this is being widely acknowledged. It is elucidated that the nanoscale materials have the shortest path for ion transport which provide efficacious and accurate detection with higher sensitivity and selectivity. [11]. Nanostructured metal oxides such as Zirconium oxide ( $ZrO_2$ ), Vanadium oxide ( $V_2O_5$ ), Zinc oxide ( $ZnO$ ), Iron oxide ( $Fe_3O_4$ ), Tin oxide ( $SnO_2$ ), Nickel oxide ( $NiO$ ), and Cobalt oxide ( $CoOx$ ) have been used widely in the detection of heavy metals [12-14] because of their multifunctional and interesting characteristics such as non-toxicity, biocompatibility, catalytic, sensing and other properties. Metal oxide nanoparticles have a high degree of crystallinity, a high surface-to-volume ratio, and a smooth electron transport path, making them a viable choice for many sensing applications. Recently, considerable attention has been drawn to cobalt oxides ( $CoOx$ ), which show intriguing electrical, optical, electrochemical, and electrocatalytic properties. This is primarily because of its superior electrocatalytic activity toward heavy metal ions [15].

A single polypyrrole nanowire-based electrode decorated with cobalt oxide nanoparticles are used in this research to electrochemically determine heavy metal ions in potable water. The proven electrochemical sensing properties of polypyrrole modified  $CoOxNPs$ , namely efficient mass transfer, high surface area to volume ratio, and electrocatalysis heterostructures may exhibit lower detection limit and increased sensitivity for sensors.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials and Method

All reagents were analytical grade and purified further before use. Anodic aluminum oxide membrane (AAO) was purchased from Whatman International Ltd. (Maidstone, UK). The following chemicals were used in this study: Pyrrole (Sigma-Aldrich), lithium perchloric acid ( $LiClO_4$ )

(USA), Sulphuric acid ( $H_2SO_4$ ), hydrogen peroxide ( $H_2O_2$ ) (Fisher Scientific (USA)), gold colloidal solution ( $HAuCl_4$ ), cobalt chloride ( $CoCl_2$ ) Sigma-Aldrich (AR-MED, Division of Quintiles Ltd. UK), phosphoric acid, Cadmium chloride  $CdCl_2$  All reagents were prepared in Milli Q water 18M.

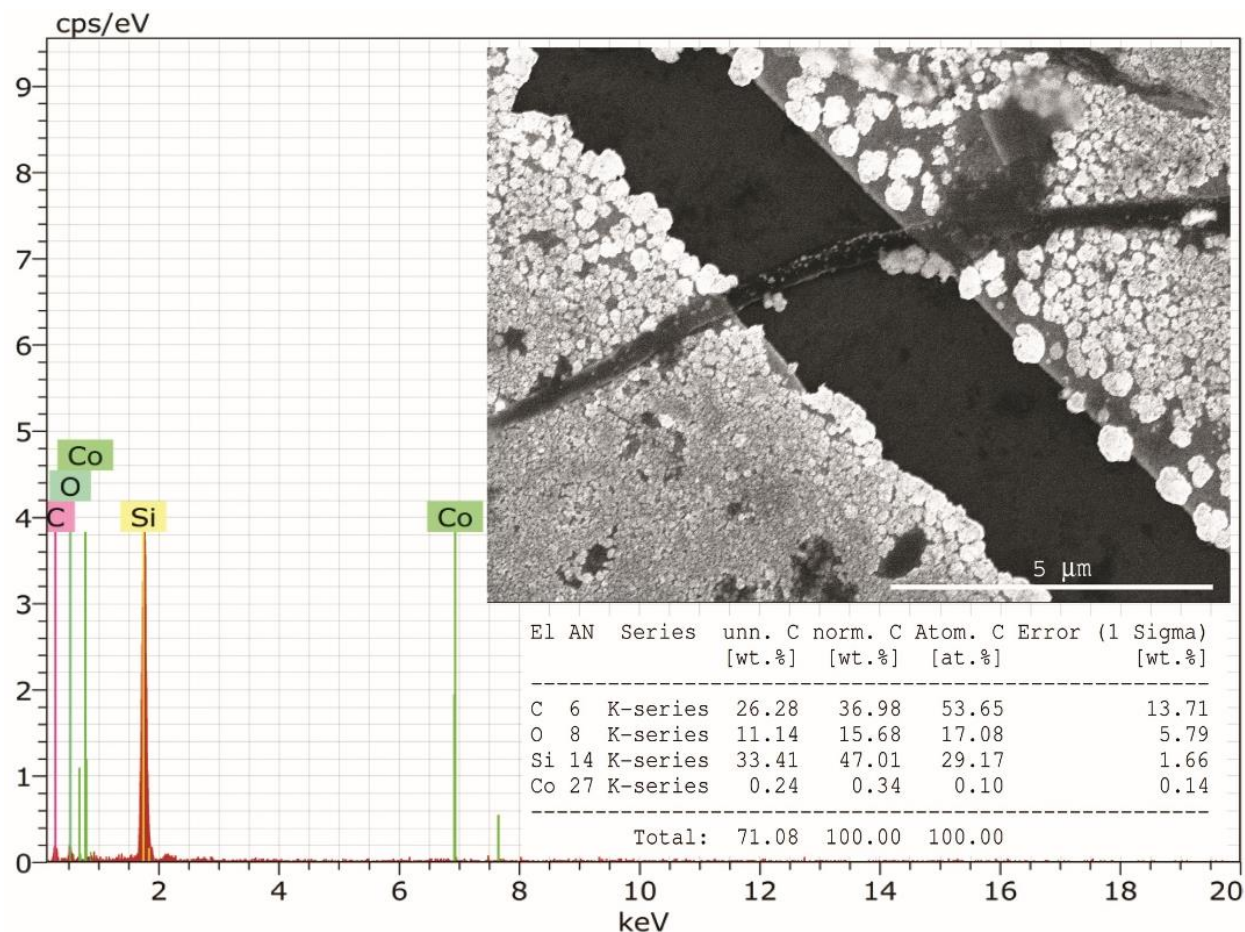
### 2.2. Preparation of cobalt oxide nanoparticles modified single polypyrrole nanowire electrode

The gold seeded AAO membrane was used to deposit polypyrrole thin film to make the polypyrrole nanowire of 6  $\mu m$  in length. (Note: The entire process of making polypyrrole nanowire is discussed in our previously published paper [16, 17]). The polypyrrole nanowire was oriented and anchored via mask-less deposition between 3  $\mu m$  gap of a gold pair of electrodes on a Si/SiO<sub>2</sub> wafer [18]. For the electrodeposition of cobalt oxide nanoparticles ( $CoOxNPs$ ), the anchored polypyrrole nanowire (sPpyNW) electrode was immersed in a solution of 1 mM  $CoCl_2$  and phosphate buffer (PBS - pH 7). The electrodeposition was carried out using cyclic voltammetry with potential between -1.2 and 1.1 V (for 10 cycles at scan rate of 100 mV/s) [19]. The deposited  $CoOxNPs/sPpyNW$  electrode was rinsed again with double distilled water and stored at room temperature (25 °C), in order to allow it dry. Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive Spectroscopy (EDS) corroborate the deposition of  $CoOxNPs$  on sPpyNW. The Cadmium (Cd) and Lead (Pb) in potable water (either separately or mixed) was traced using a  $CoOxNPs-sPpyNW$  electrode in this study.

## 3. RESULTS AND DISCUSSION

### 3.1. Structural and elemental characterization of $CoOxNPs$ modified sPpyNW

The structural and elemental characteristics of the cobalt oxide nanoparticles/single polypyrrole nanowire ( $CoOxNPs/sPpyNW$ ) electrode were evaluated using Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDS). The FESEM image, shown in the inset of Figure 1, illustrates the  $CoOx$  nanoparticles uniformly coating the sPpyNW at the nanometer scale. The EDS spectrum depicted in Figure 1 confirms the presence of cobalt oxide nanoparticles on the sPpyNW electrode. Peaks corresponding to cobalt (Co) and oxygen (O) validate the successful modification. Additionally, the silicon (Si) peak observed in the EDS spectrum is attributed to the silicon substrate used during sample preparation. The elemental percentage compositions are provided in the inset table of Figure 1. This comprehensive characterization supports the effective functionalization of the sPpyNW with  $CoOx$  nanoparticles. The modified nanowire electrode was subsequently employed to determine the concentrations of cadmium (Cd) and lead (Pb) in potable water, leveraging the enhanced sensitivity and specificity imparted by the  $CoOxNPs$ .



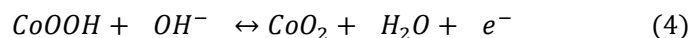
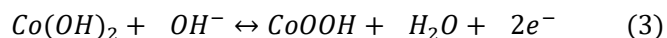
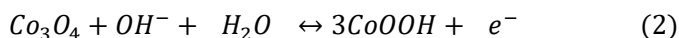
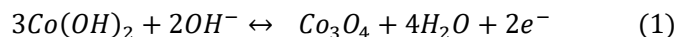
**Fig. 1.** EDS spectrum of Cobalt oxide nanoparticles decorated sPpyNW. Inset FESEM image of CoOxNPs/sPpyNW electrode and table of elemental composition.

### 3.2. Voltammetric study of CoOxNPs modified sPpyNW

A layer of cobalt oxide nanoparticles was decorated on the sPpyNW electrode by using cyclic voltammetry. Figure 2a. Depicts the cyclic voltammogram of the CoOx/sPpyNW electrode submerged in a solution containing 0.02 M of cobalt nitrate and 0.1 M acetate buffer solution (pH 7). As shown in Figures 2(a). A reduction peak developed at a negative potential of -0.8V, which corresponds to the reduction of  $\text{Co}^{2+}$  to Co [20, 21]. A tiny oxidation peak was detected on the reverse scan at a potential of -0.2 V, which may be ascribed to the removal of electrodeposited cobalt on the surface of polypyrrole nanowire.

The cyclic voltammogram of the CoOxNPs/sPpyNW electrode placed in alkaline solution confirms the deposition of cobalt oxide nanoparticles on the sPpyNW electrode surface. Figure 2(b). Shows cyclic voltammetric response of CoOxNPs/sPpyNW electrode placed in acetate buffer (pH 4.5), with applied potential in the range -1.1 to +1.3 V. In Figure 2(b) three redox peaks ascribed to various oxidation states of cobalt oxide particles. The electrochemical oxidation of aqueous Co (II) to  $\text{Co}_3\text{O}_4$  observed at Ia/Ic redox pair, as seen in Figure 2(b) and the Equation 1. According to Equations 2 and 3 [22], another redox pair (IIa/IIc) can be attributed to the formation  $\text{CoOOH}$ . The pair of redox peaks

seen at higher potentials (IIIa/IIIc) relate to the oxidation of  $\text{CoOOH}$  to  $\text{CoO}_2$  as described in the following Equation 4. These results are consistent with earlier reports on the electrochemical performance of cobalt oxide nanoparticles [23, 15]



### 3.3. Electrochemical characterization of the CoOxNPs/sPpyNW electrode

The cyclic voltammetric behavior of a cobalt oxide nanoparticles decorated polypyrrole nanowire CoOxNPs/sPpyNW electrode was investigated in the presence of 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  in 0.1 M KCl as a standard redox couple across a potential range of -0.2 to 0.7 V at a scan rate of  $100 \text{ mVs}^{-1}$  as shown in Figure 2(c), because the sensor

is reversible, it is capable of detecting target analyte in both oxidized and reduced states. There is a reversible interaction between the host and guest, thus the sensor surface is unaltered before and after the electrochemical scan is performed. The modified electrode's anodic peak current increased in comparison to the bare sPpyNW electrode, suggesting that the presence of cobalt oxide nanoparticles make ions more readily available at the electrode surface and accelerates electron transduction. The modifier creates a large number of active areas on the sensor's surface where excess analyte ions may accumulate.

Cyclic voltammetric measurements were performed to examine the scan rate influence on the redox reaction by changing the scan rate from 10 to 100 mV/s in a redox pair composed of 1 mM  $K_3Fe(CN)_6$  in 0.1 M KCl as a supporting electrolyte. Peak currents rose as scan rates increased.

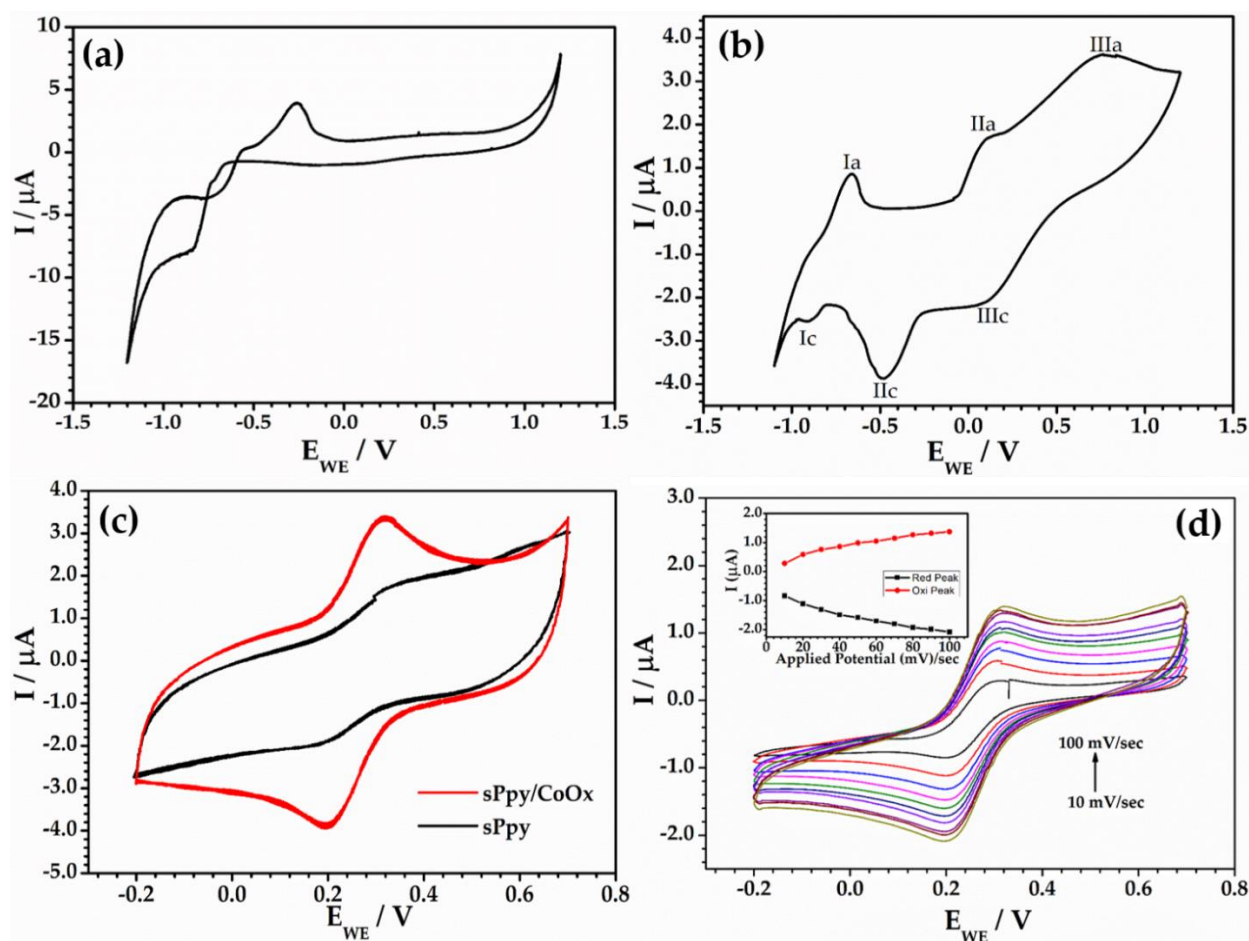
According to Figure 2(d), the redox peak current of the CoOxNPs/sPpyNW electrode was proportional to the square root of the scan rate, demonstrating that the CoOxNPs/sPpyNW electrode electrochemical reaction followed a typical diffusion-controlled mechanism [24]. It is

worth mentioning that a direct relationship between peak current and bulk concentration was found as a result of the abundant active sites on the electrode surface interacting with all incoming ion molecules, which is a critical condition for an electrochemical sensor [25]. This property enables the CoOxNPs/sPpyNW electrode to be used effectively for the determination of Lead (Pb) and Cadmium (Cd).

### 3.4. Analytical performance of the CoOxNPs modified sPpyNW electrode.

#### 3.4.1. Optimization of experimental conditions

Experimental conditions (Accumulation time, accumulation potential and supporting electrolyte) were established and optimized before constructing a calibration curve and finding a LOD of the CoOxNPs/sPpyNW electrode to produce a maximum peak current response, sharpness of the peak, and high repeatability. The test was carried out by adjusting each parameter separately while keeping others at their optimal values.

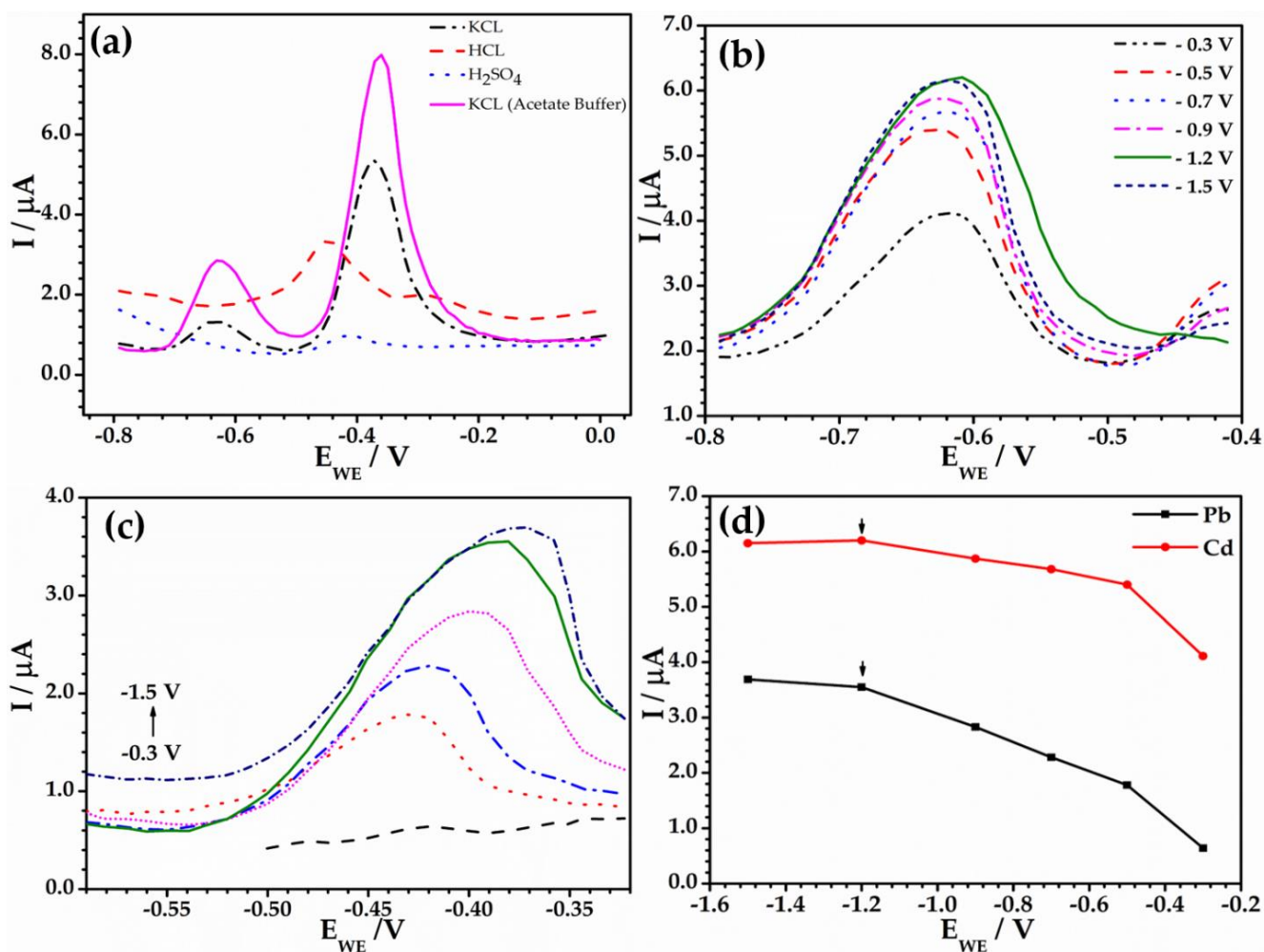


**Fig. 2.** (a) Cyclic voltammogram of deposited cobalt oxide nanoparticles on sPpyNW in 0.1 M acetate buffer solution containing 0.02 M cobalt nitrate in the potential range from -1.2 to 1.2V at 100mV/s scan rate. (b) Cyclic voltammogram (CV) response in 0.1M acetate buffer solution (without cobalt ions) in the potential range from -1.2 to 1.2V at 100mV/s scan rate, (c) CV responses of sPpyNW and CoOxNPs/sPpyNW at potential range -0.2 to 0.7V for scan rate of 100 mV/s. (d) CV response of CoOxNPs/sPpyNW electrode at different scan rates (scan rate/mV/s). Inset of (b) shows linear fitted plot of peak current vs scan rate.

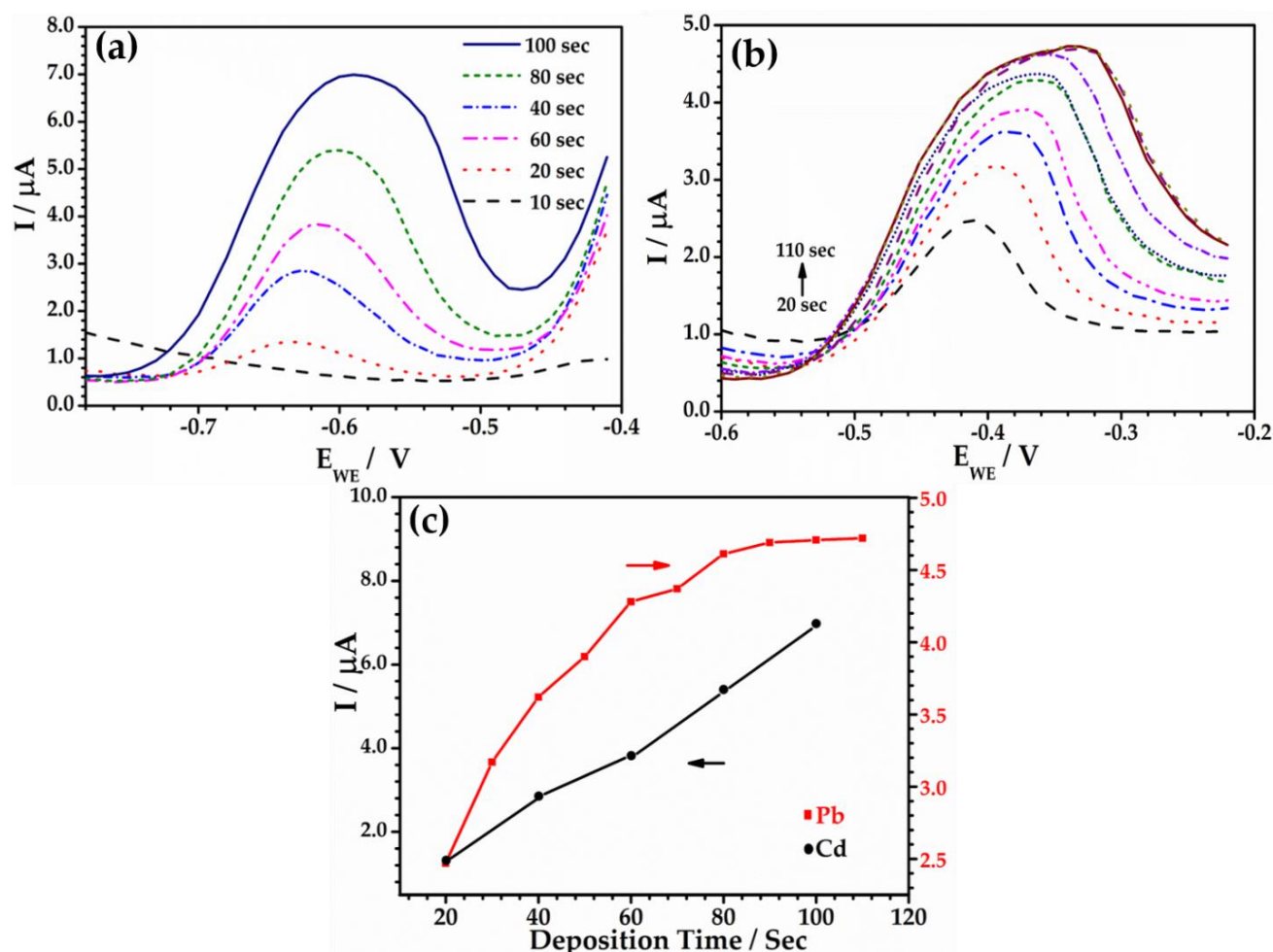
The supporting electrolyte, pH value, deposition potential, and deposition duration were adjusted to get the optimum response of the proposed sensor for trace detection of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions. The schematic representation of detection of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions using the modified electrode is shown in Scheme 1. Scheme 1(a) corresponds to the response of modified sensor in absence of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions. SW-ASV responses for  $0.05 \mu\text{M}$  of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  at pH 4.5 [26-28] were measured in four distinct supporting electrolytes: 0.1M HCL, 0.1M  $\text{H}_2\text{SO}_4$ , 0.1M KCL, and acetate buffer with 0.1M KCL (Figure 3(a)). For the  $\text{H}_2\text{SO}_4$  solution, no noticeable peaks emerged at the same potential. In the HCL solution, just one peak was seen, and the peak of  $\text{Cd}^{2+}$  was not visible. Voltammetric peaks were found in KCL. However, well-defined voltammetric peaks for both ions were detected in 0.1M acetate buffer with KCL solution. As a result, in subsequent studies, a 0.1M acetate buffer and KCL solution was used. Figure 3(b) shows the influence of deposition potential on  $\text{Cd}^{2+}$  stripping reactions. The reaction signals rose remarkably when the deposition potentials were changed from  $-0.3 \text{ V}$  to  $-1.5 \text{ V}$ . The response for  $\text{Cd}^{2+}$  increased when the deposition potential shifted towards

negative. The high response is recorded at  $-1.2 \text{ V}$ . When the deposition potential was increased to  $-1.5 \text{ V}$ , the current response was slightly dropped. This drop is most likely due to hydrogen evolution at  $-1.5 \text{ V}$  potentials, and hydrogen bubbles may obstruct metal ion deposition at the electrode surface. The deposition potential was varied from  $-0.3 \text{ V}$  to  $-1.5 \text{ V}$  for a deposition time of 100 sec. As can be seen in Figure 3(c) the current density corresponding to the  $\text{Pb}^{2+}$  signal linearly increased to  $-1.5 \text{ V}$ . The influence of the deposition potential on the peak current of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  after 100 sec accumulation was tested by keeping applied potential between  $-1.5 \text{ V}$  to  $-0.3 \text{ V}$  (Figure 3(d)). The differences in  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  trends may be ascribed to the various standard potentials. The optimum accumulation potential for the following experiment was considered as  $-1.2 \text{ V}$  in order to achieve excellent sensitivity for both  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ .

The deposition time is another important aspect that determines the sensitivity of the result in stripping analysis. As shown in Figure 4(a), stripping current for  $\text{Cd}^{2+}$  rose almost linearly as the deposition duration increased from 10 to 100 seconds. The deposition duration was evaluated between 10 and 110 sec at a deposition potential of  $-1.2 \text{ V}$ .



**Fig. 3.** Effect of a) Electrolyte b) SW-ASV response of  $0.05 \mu\text{M}$  of  $\text{Cd}^{2+}$  for varying electrode deposition potential c) SW-ASV response of  $0.05 \mu\text{M}$  of  $\text{Pb}^{2+}$  for varying electrode deposition potential d) Calibrated plot of deposition potential for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  of peak current observed in SW-ASV.



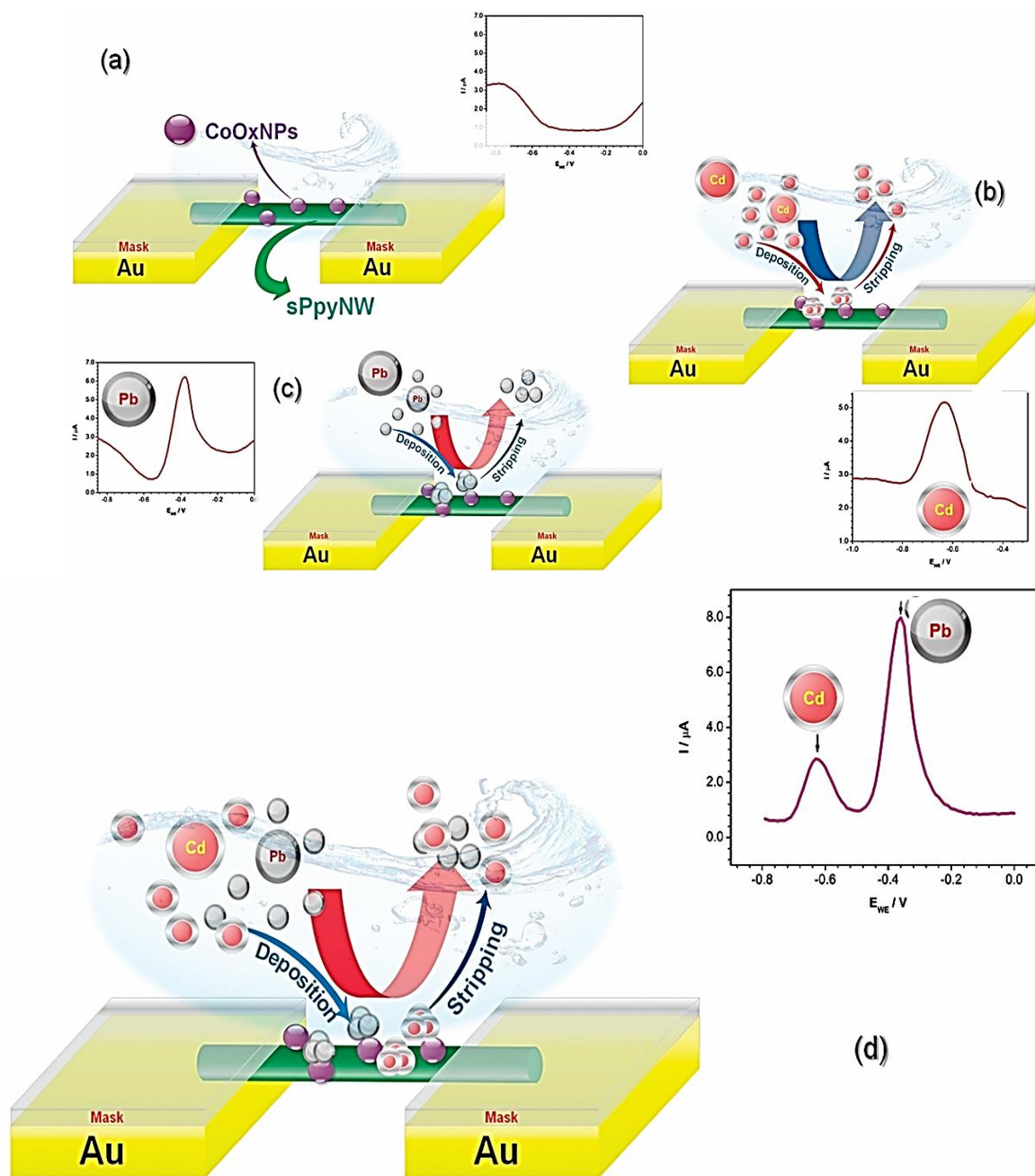
**Fig. 4.** (a) SW-ASV response of 0.05 μM of Cd<sup>2+</sup> for varying electrode deposition time (b) SW-ASV response of 0.05 μM of Pb<sup>2+</sup> for varying electrode deposition time (c) Calibrated plot of deposition time for the stripping response of 0.05 μM each of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions.

Figure 4(b) shows that the Pb<sup>2+</sup> signal increased up to 100 sec and then at 110 sec the stripping current response is almost same to the response of 100 sec. The impact of deposition duration on the peak currents of Cd<sup>2+</sup> and Pb<sup>2+</sup> was shown in Figure 4(c). Our findings show that when the deposition duration rose from 10 to 100 seconds, the response currents of Cd<sup>2+</sup> and Pb<sup>2+</sup> increased as well. The increased quantity of analyte on the modified electrode surface is responsible for this behavior. When the deposition duration was extended beyond 100 sec, no significant change in the stripping response of Cd<sup>2+</sup> and Pb<sup>2+</sup> was found, which was attributed to the electrode surface becoming saturated with large quantities of metal ions [29]. As a result, accumulation time of 100 s was chosen as the best option for achieving a larger response range while maintaining an acceptable detection limit.

### 3.4.2. Response of Cadmium (Cd) on CoOxNPs modified sPpyNW electrode in laboratory grade water

The proposed CoOxNPs/sPpyNW nanocomposites-modified electrode sensor was used to determine Cd<sup>2+</sup> using the SW-ASV technique (Scheme 1(b)) under optimum circumstances. Figure 5(a) shows the electrode sensor's SW-ASV spectra as a function of Cd<sup>2+</sup> concentration. The peak current of the electrode rises significantly as the concentration of Cd<sup>2+</sup> increases, and the peak current reaches its maximum when the concentration of Cd<sup>2+</sup> is raised to 0.1 μM. As shown in Figure 5(b), a plot of peak current intensity against Cd<sup>2+</sup> concentration in the range of 0.00 to 0.11 μM showed a linear response ( $R^2 = 0.9520$ ) with a relatively low detection limit of 0.22 μM, which is considerably lower than the drinking water standard.

The proposed technique's detection linearity range and limit were compared to other Cd<sup>2+</sup> assays (Table 1), revealing that the new approach has higher or similar detection sensitivity. The low detection limit may be due to the CoOxNPs/sPpyNW nanocomposites' capacity to enrich for Cd<sup>2+</sup>, showing that the produced CoOxNPs/sPpyNW nanocomposites-modified electrode sensor is effective at measuring low Cd<sup>2+</sup> concentrations.

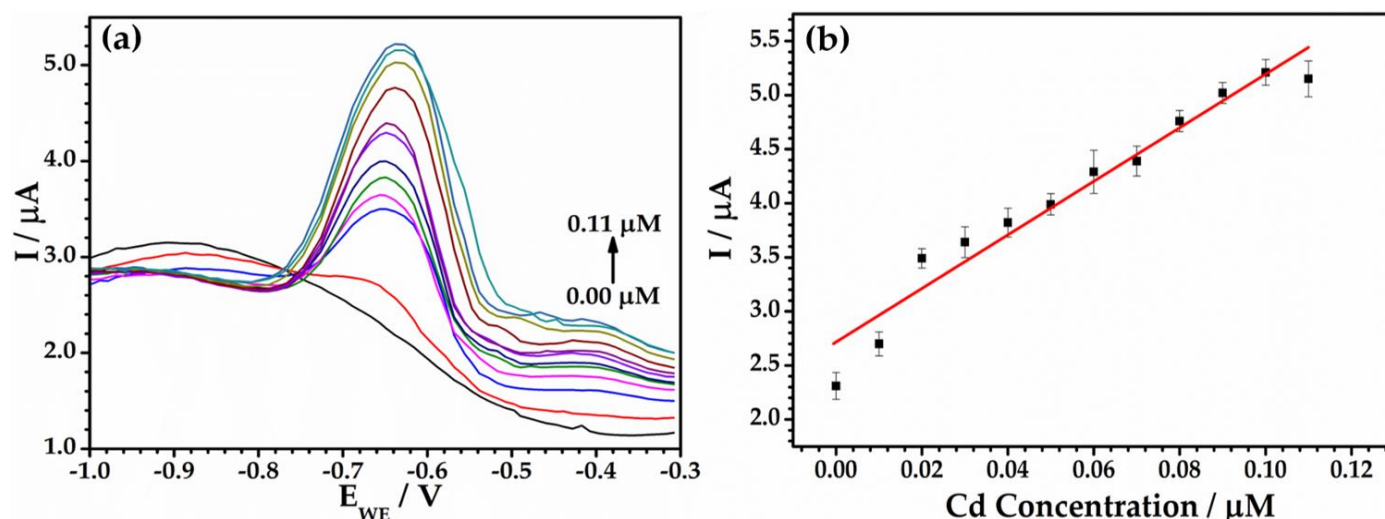


**Scheme 1.** Sensing mechanism of CoOxNPs/sPpyNW electrode (a) SW-ASV response of 0.00  $\mu\text{M}$  of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in potable water (b) SW-ASV response of  $\text{Cd}^{2+}$  ions (c) SW-ASV response of  $\text{Pb}^{2+}$  ions (d) SW-ASV response of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in potable water.

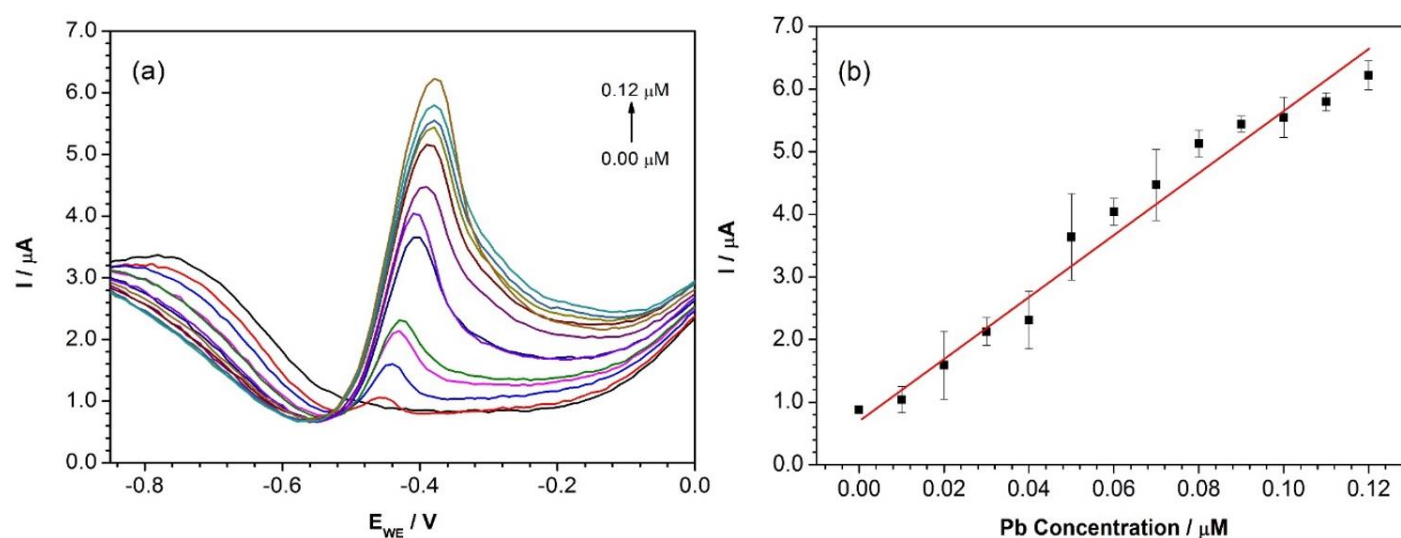
### 3.4.3. Response of Lead (Pb) on CoOxNPs modified sPpyNW electrode in potable water

SW-ASV on CoOxNPs/sPpyNW electrode was used to perform quantitative  $\text{Pb}^{2+}$  detection (Scheme 1(c)) under ideal conditions. Figure 6(a) shows the SW-ASV responses at various  $\text{Pb}^{2+}$  concentrations ranging from 0 to 0.12  $\mu\text{M}$ . The stripping peak currents increase as the  $\text{Pb}^{2+}$  concentration rises, and there is a good linear relationship between the concentrations of 0.01  $\mu\text{M}$  and 0.12  $\mu\text{M}$ . When the  $\text{Pb}^{2+}$

concentration was 0.00  $\mu\text{M}$ , the developed sensor had no response, and this concentration can be considered the sensor's quantification limit. The corresponding calibration plot, which plots the peak current vs.  $\text{Pb}^{2+}$  concentration, is shown in Figure 6(b).  $y = 48.396x + 0.807$  was the calibration plot equation, with 0.9723 as the correlation coefficient ( $R^2$ ). The limit of detection (LOD) was calculated to be 0.013  $\mu\text{M}$ , which is significantly lower (or comparable) than that of similar  $\text{Pb}^{2+}$  sensors.



**Fig. 5.** (a) SW-ASV response of the CoOxNPs/sPpyNW electrode for 0.1 M acetate buffer and 0.1 M KCL presence of  $\text{Cd}^{2+}$  from 0 to 0.11  $\mu\text{M}$ . (b) The calibration plot of peak current vs.  $\text{Cd}^{2+}$  concentrations.



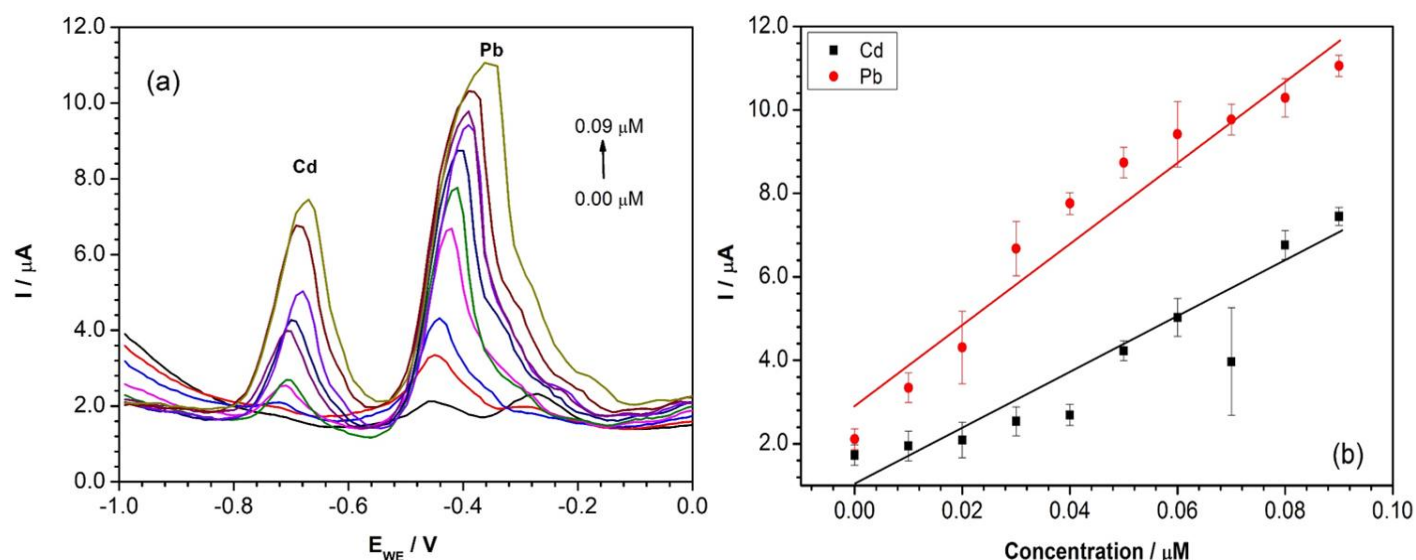
**Fig. 6.** (a) SW-ASV response of the CoOxNPs/sPpyNW electrode for 0.1 M acetate buffer and 0.1 M KCL presence of  $\text{Pb}^{2+}$  from 0 to 0.12  $\mu\text{M}$ . (b) The calibration plot of peak current vs.  $\text{Pb}^{2+}$  concentrations.

### 3.5. Response of Cadmium (Cd) and Lead (Pb) together on CoOxNPs modified sPpyNW electrode in potable water

Along with individual  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  detection, we explored simultaneous  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  detection through SW-ASV using the same modified CoOxNPs/sPpyNW electrode (Scheme 1(d)) placed in 0.1 M acetate buffer and 0.1 M KCL solution at pH 4.5. The electrochemical responses of various concentrations of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  have been studied using square wave anodic stripping voltammetry methods when both species are present in the same electrolytic solution.  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  were measured using -1.2 V and 100 sec deposition potentials, respectively. Figure 7(a) showed a series of SW-ASV responses when the concentrations of  $\text{Cd}^{2+}$

and  $\text{Pb}^{2+}$  were increased concurrently. For 0.01  $\mu\text{M}$   $\text{Pb}^{2+}$  solution, a stripping peak at -0.49 V was detected. Following the various concentration of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions to the buffer solution, two distinct oxidation peaks at -0.49 V and -0.75 V were detected, corresponding to  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , respectively. For all concentration responses, a peak separation of 260 mV between the two metal ions was found. As can be observed, both metal ions' peak current signal rises linearly with their concentration. Figure 7(b) shows the linear calibration curve for both metal ions.  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  have linear correlation coefficients of 0.8726 and 0.9468, respectively. The limit of detection can be found 0.026  $\mu\text{M}$  and 0.013  $\mu\text{M}$  for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  respectively.





**Fig. 7.** (a) Stripping voltammogram for the different concentrations of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  on an in situ plated  $\text{CoO}_x\text{NPs/sPpyNW}$  electrode in solution containing 0.1M acetate buffer + KCl. From bottom to top, 0.0  $\mu\text{M}$  to 0.09  $\mu\text{M}$ . (b) The calibration curve of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , respectively.

**Table 1:** Comparison of electrochemical performance of the electrodes for Voltammetric determination of Cadmium and Lead.

S. No.	Electrode	Method	LOD		Ref.
			$\text{Cd}^{2+}$	$\text{Pb}^{2+}$	
1	BiNP/Nafion/PGE	ASW	7.31	31.07	30
2	F-MWCNT/ $\text{Fe}_3\text{O}_4$ / 0.5% Nafion/ GCE	SWV	1.57	1.74	31
3	Bi dendritic on glassy carbon $\text{H}_2$ template	SWASV	0.4	0.1	32
4	Bi/poly(p-ABSA)/ GCE	DPASV	0.63	0.80	33
5	CB-Nafion-GCE	DPASV	0.9	1.0	34
6	Ag-RDE	SASV	0.1	0.010	35
7	polyPCA/GE	SWASV	15.4	13.6	36
8	GCE- $\text{MnCo}_2\text{O}_4$ NPs	LSASV	0.79	1.67	37
9	$\text{NH}_2 - \text{Fe}_3\text{O}_4@\text{C}/\text{GCE}$	SWASV	2.6	5.9	38
10	Sb-BDD	LSASV	38.1	25.4	39
11	BiBE	ASV	6.07	19.3	40
12	G/PANI/PS nanoporous fiber/SPCE	ASV	4.43	3.30	41
13	P(DPA-co-2ABN)/GC	DPASV	255	165	42
14	Diacetyldioxime/CPE	DPASV	4.48	2.07	43
15	PANI/ GC	SWASV	14.56	20.7	44
16	$\text{CoO}_x\text{NPs/PpyNW}$	SW-ASV	0.22 $\mu\text{M}$ and 0.026 $\mu\text{M}$	0.013 $\mu\text{M}$ and 0.013 $\mu\text{M}$	This Work

BiNP/Nafion/PGE: Bismuth nanoparticles and Nafion modified pencil graphite electrode; F-MWCNT/ $\text{Fe}_3\text{O}_4$ /0.5% Nafion/GCE: Magnetite nanoparticles and fluorinated multiwalled carbon nanotubes-modified glassy carbon electrode; CB-Nafion-GCE: Carbon black and Nafion (5 wt%)-modified glassy carbon electrode; Bi/poly (p-ABSA): Bismuth/poly(p-aminobenzenesulfonic acid) modified glassy carbon electrode; Ag-RDE: Silver rotating disk electrode; BiBE: Bismuth bulk electrode; GCE- $\text{MnCo}_2\text{O}_4$ NPs:  $\text{MnCo}_2\text{O}_4$  nanoparticles-modified glassy carbon electrode;  $\text{NH}_2 - \text{Fe}_3\text{O}_4@\text{C}/\text{GCE}$ : Amino-functionalized  $\text{Fe}_3\text{O}_4$ @carbon microspheres-modified glassy carbon electrode; Sb-BDD: Antimony nanoparticle modified boron-doped diamond electrode; BiBE: Bismuth bulk electrode; P(DPA-co-2ABN): Poly(diphenylamine-co-2-aminobenzonitrile). GC; glassy carbon electrode; CPE; carbon paste electrode.

## 4. CONCLUSIONS

Square wave anodic stripping voltammetry (SW-ASV) for the determination of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  in potable water individually and simultaneously using a sPpyNW electrode modified with CoOx nanoparticles (SW-ASV) was successfully carried out. FESEM and EDS confirms aligned sPpyNW and decorated Cobalt oxide nanoparticles, respectively. The electrochemical sensitivity in the detection of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  is greatly improved by the large surface area and electrical conductivity of Cobalt oxide nanoparticles (CoOxNPs). The linear range for the detection of individual  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions was determined to be 0.00 to 0.11  $\mu\text{M}$  for  $\text{Cd}^{2+}$  and 0.00 to 0.12  $\mu\text{M}$  for  $\text{Pb}^{2+}$ , with detection limits of 0.22  $\mu\text{M}$  ( $R^2 = 0.9520$ ) for  $\text{Cd}^{2+}$  and 0.013  $\mu\text{M}$  ( $R^2 = 0.9723$ ) for  $\text{Pb}^{2+}$ . The linear range for simultaneous detection was determined to be 0.00 to 0.09  $\mu\text{M}$ , with a detection limit of 0.026  $\mu\text{M}$  ( $R^2 = 0.8726$ ) and 0.013  $\mu\text{M}$  ( $R^2 = 0.9468$ ) for  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ , respectively.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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