

Individual and simultaneous electrochemical detection of hazardous Pb(II) and Cu(II) trace ions using Ni-doped ZIF-67 framework

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Abstract

The sensitive and reliable determination of toxic Pb(II) and Cu(II) ions is of significant importance because of their environmental persistence, bioaccumulation, and associated risks to human health and aquatic ecosystems. However, the intrinsically poor electrical conductivity and limited electrochemical performance of pristine ZIF-67 restrict its effectiveness in trace-level sensing applications. Herein, a nickel-doped zeolitic imidazolate framework-67 (Ni_ZIF-67) was rationally developed as an advanced electrochemical sensing platform for the individual and simultaneous determination of Pb(II) and Cu(II) ions. Comprehensive physicochemical characterization confirmed the successful incorporation of Ni into the ZIF-67 framework while preserving its characteristic porous structure and morphology. The Ni_ZIF-67-modified glassy carbon electrode exhibited excellent analytical performance using differential pulse voltammetry, achieving limits of detection of 0.96 nM for Pb(II) and 0.79 nM for Cu(II) during individual analysis. Furthermore, simultaneous determination yielded distinct and well-resolved stripping responses, with detection limits of 1.3 nM for Pb(II) and 1.6 nM for Cu(II). The enhanced sensing performance is attributed to the synergistic interaction between Ni species and the porous ZIF-67 matrix, which promotes efficient ion adsorption, accelerated electron transfer, and improved electrocatalytic activity. The developed sensor also demonstrated high selectivity, repeatability, reproducibility, and long-term stability, highlighting its potential as a robust and reliable platform for ultrasensitive monitoring of hazardous heavy-metal contaminants in environmental samples.

1. Introduction

The rapid expansion of industrial activities to meet the growing demands of the global population has led to significant environmental degradation. Pollution of air, water, and soil has become a serious concern, with heavy metal ions (HMIs) playing a substantial role in this crisis [1, 2]. According to recent studies, pollution contributes to approximately 9 million deaths worldwide each year, accounting for about 16% of all deaths [3]. HMIs, which include metals such as lead, copper, cadmium, mercury, and nickel, are particularly problematic due to their hazardosity and ability to accumulate in the environment, especially in aquatic ecosystems [4, 5]. Among these, copper [Cu(II)] and lead [Pb(II)] are of particular concern due to their widespread use and potential to cause severe health issues[6–9]. These ions can contaminate water sources, leading to serious consequences for human health, such as kidney damage, neurological disorders, and even cancer [10, 11].

It is essential to develop precise, sensitive, and selective determination techniques for HMIs, as their presence poses serious risks to environmental and human health [12]. Traditional methods for detecting HMIs, including Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), UV-Visible Spectroscopy, and Ion Chromatography, are well-established analytical methods known for their high sensitivity and reliability [13, 14]. However, these techniques are often expensive, require sophisticated instrumentation, and necessitate skilled personnel to operate [14]. This limits their practicality for on-site and real-time monitoring, which is crucial for effectively managing and mitigating environmental

pollution. In recent times, electrochemical sensing has gained attention as an effective and reliable approach for the determination of HMIs [12, 15, 16]. Electrochemical methods are known for their simplicity, cost-effectiveness, rapid response, and potential for miniaturization, making them suitable for on-site monitoring [17–20]. Among these methods, Differential Pulse Voltammetry (DPV) is particularly notable for its high sensitivity in detecting trace levels of metal ions [21–23]. Despite its advantages, the performance of electrochemical sensors is often limited by the properties of the electrode materials used. Glassy carbon electrodes (GCEs), which are commonly employed in these sensors, suffer from poor sensitivity and selectivity due to their weak catalytic performance and low charge transfer rate [24]. Additionally, issues related to the lower limit of determination (LOD) and instability further hinder the practical application of these sensors for HMI determination. To overcome these limitations, researchers have explored the use of various nanomaterials to enhance the performance of electrochemical sensors. Nanomaterials, including metal nanoparticles, metal oxides, carbon-based materials, and metal-organic frameworks (MOFs), have shown great potential in improving the sensitivity, selectivity, and stability of these sensors [25, 26]. Among these, MOFs are particularly attractive due to their tunable porosity, high surface area, and ability to incorporate functional groups that can interact specifically with target analytes [27–31].

In this study, we introduce a novel electrochemical sensor based on a nickel-doped ZIF-67 MOF for the sensitive and selective determination of targeted hazardous Pb(II) and Cu(II) ions. ZIF-67, a member of the zeolitic imidazolate framework (ZIF) family, is a MOF composed of cobalt ions linked by imidazolate ligands. This framework has gained attention for its thermal and chemical stability, as well as its high surface area and porosity, which make it an excellent candidate for various applications, including gas storage, catalysis, and sensing [32]. By doping ZIF-67 with nickel (Ni), we aim to enhance its electrochemical properties, specifically its ability to detect trace levels of Pb(II) and Cu(II) ions with high sensitivity and selectivity. Nickel doping is expected to improve the catalytic activity of ZIF-67, thereby increasing the charge transfer rate and overall electrochemical performance of the sensor [33, 34]. Additionally, the introduction of Ni ions into the ZIF-67 framework may create more active sites for the adsorption of Pb(II) and Cu(II) ions, further enhancing the sensor's selectivity. The combination of Ni-doped ZIF-67 with the intrinsic properties of the MOF is anticipated to result in a synergistic effect, leading to significant improvements in the determination limits and stability of the sensor.

This study marks a notable advancement in electrochemical sensing by developing a novel Ni-doped ZIF-67 (Ni_ZIF-67) framework for the selective and sensitive determination of hazardous Pb(II) and Cu(II) ions. The strategic incorporation of nickel into the ZIF-67 matrix significantly enhances its electrical conductivity, structural stability, and electrocatalytic activity, overcoming the limitations of pristine ZIF-67. The Ni-doped ZIF-67 framework-modified glassy carbon electrode (Ni_ZIF-67/GCE) demonstrated excellent analytical performance, including low determination limits, high sensitivity, and reliable repeatability in both individual and simultaneous determination modes. These results underscore the material's potential for real-time and on-site monitoring of heavy metal contamination. Overall, this work contributes to the advancement of efficient and robust electrochemical sensors for environmental monitoring, offering a promising platform for safeguarding public health and ecological systems.

2. Experimental

2.1. Chemicals and reagents

The synthesis of the Ni_ZIF-67 composite was carried out using analytical-grade reagents. Specifically, cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$ purity, Molychem, India), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$, $\geq 99.0\%$ purity, Alfa Aesar, India), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$ purity, Molychem), methanol ($\geq 99\%$ purity, Molychem), and sodium acetate ($\text{C}_2\text{H}_3\text{NaO}_2$, $\geq 99\%$ purity, Sigma-Aldrich, USA) were employed. All solutions and aqueous procedures were carried out using ultra-pure deionized (DI) water, and only analytical-grade reagents and solvents were employed throughout the investigation.

2.2 Synthesis of ZIF-67 and Ni_ZIF-67 composite

The preparation of the cobalt-based ZIF-67 MOF was carried out as reported in the literature with minor modifications [35]. The synthesis of ZIF-67 was initiated by dissolving 2.925 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 mL of methanol to prepare the first solution. Concurrently, 3.285 g of $\text{C}_4\text{H}_6\text{N}_2$ was dissolved in another 50 mL of methanol to create the second solution. These two solutions were subsequently combined and stirred vigorously for one hour at ambient temperature to ensure thorough mixing and promote the formation of the ZIF-67 framework. The resulting suspension was centrifuged at 8000 rpm for 10 min. to isolate the precipitate, which was then washed three times with methanol to eliminate any residual unreacted substances or impurities. The obtained product was dried in a vacuum oven at 60°C for 12 hours to form the ZIF-67 framework. To synthesize the Ni_ZIF-67, the same procedure was followed, except 0.727 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to the initial solution to introduce the desired amount of Ni into the framework.

2.3 Surface functionalization of GCE with ZIF-67 and Ni-doped ZIF-67

The glassy carbon electrode (GCE, Sigma-Aldrich, USA) was initially polished using alumina slurries (Sigma-Aldrich, USA) with particle sizes of 1.0, 0.3, and $0.05\ \mu\text{m}$ to eliminate any surface contaminants. After polishing, the electrode was cleaned ultrasonically in ethanol, followed by deionized water to ensure complete removal of residues, and then air-dried under ambient conditions. For electrode modification, 10 mg of Ni_ZIF-67 was dispersed in 1 mL of ethanol and sonicated briefly to achieve a uniform suspension. A $15\ \mu\text{L}$ volume of this suspension was carefully drop-cast onto the pre-cleaned GCE surface using a micropipette and allowed to dry thoroughly at room temperature over roughly 6 hours. This modified electrode was subsequently employed for various electrochemical analyses. The same protocol was applied to prepare the ZIF-67-modified GCE for comparative evaluation.

2.4 Electrochemical measurements

Electrochemical measurements for the determination of hazardous HMIs were performed using a standard three-electrode configuration at ambient temperature (approx. 20°C). The working electrode GCE was modified with the Ni_ZIF-67/GCE, while a platinum wire and an Ag/AgCl electrode served as the

counter and reference electrodes, respectively. The electrochemical performance was evaluated using Cyclic Voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS) was explored in 10 mM $K_3[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl. The determination of Pb(II) and Cu(II) ions was conducted in a 0.2 M acetate buffer solution (ABS) maintained at pH 5, employing the differential pulse voltammetry (DPV) method for precise analysis. All electrochemical studies (DPV, CV, and EIS) were performed on a CH Instruments CHI 660C (computer-controlled potentiostat) electrochemical workstation (Austin, TX, USA).

3. Results and discussion

3.1. Characterization of materials and surfaces

3.1.1. Powder X-ray Diffraction (P-XRD) Analysis

The structural properties of the synthesized ZIF-67 and Ni_ZIF-67 materials were examined using Powder X-ray Diffraction (P-XRD). The diffraction patterns were obtained using a Bruker D8 Advance diffractometer, operating over a 2θ range from 2° to 60° . As illustrated in Fig. 1(a), the P-XRD patterns of ZIF-67 exhibited sharp and intense diffraction peaks, confirming the high crystallinity and successful formation of the typical sodalite-type ZIF structure. The diffraction peaks were observed at 2θ values of 7.4° , 10.4° , 12.7° , 16.4° , 18.1° , and 22.1° corresponding to the (011), (002), (112), (022), (013), and (222) planes, in agreement with the reported literature for ZIF-67 [36]. Upon doping with Ni, the P-XRD pattern of the Ni_ZIF-67 composite exhibited slight peak shifts and broadening, suggesting the successful incorporation of Ni^{2+} ions into the ZIF-67 framework without significantly disrupting the crystallinity. The retention of characteristic peaks confirmed that the ZIF structure remained intact post-doping. However, the slight variations in intensity and peak positions are indicative of the changes in the local environment caused by Ni doping, leading to lattice distortions.

3.1.2. Fourier-Transform Infrared Spectroscopy (FTIR) analysis

FTIR spectroscopy analysis was performed using a Bruker Alpha ATR spectrometer equipped with a ZnSe crystal window. The spectral measurements were recorded in the wavenumber range of $4000\text{--}600\text{ cm}^{-1}$, as illustrated in Fig. 1(b). ZIF-67 exhibits distinct peaks at 1660 cm^{-1} , 1580 cm^{-1} , 1425 cm^{-1} , 1305 cm^{-1} , 1174 cm^{-1} , 1142 cm^{-1} , 991 cm^{-1} , 754 cm^{-1} , and 689 cm^{-1} . The peak at 1660 cm^{-1} corresponds to the C = N stretching vibration, while the band at 1580 cm^{-1} is attributed to the C = C stretching vibration of the imidazole ring. The peaks observed at 1425 cm^{-1} and 1305 cm^{-1} are associated with C–N stretching vibrations. The absorption bands at 1174 cm^{-1} and 1142 cm^{-1} are indicative of the C–N stretching of the imidazole ring, and the peaks at 991 cm^{-1} , 754 cm^{-1} , and 689 cm^{-1} are related to the out-of-plane bending vibrations of the aromatic ring and the metal-ligand interactions within the ZIF-67 framework. Ni_ZIF-67 shows similar FTIR features with peaks at 1690 cm^{-1} , 1578 cm^{-1} , 1427 cm^{-1} , 1305 cm^{-1} , 1174 cm^{-1} , 1142 cm^{-1} , 991 cm^{-1} , 754 cm^{-1} , and 689 cm^{-1} . The shift of the peak to 1690 cm^{-1} from

1660 cm^{-1} in ZIF-67 indicates a subtle change in the C = N stretching vibration due to nickel doping. The peaks at 1578 cm^{-1} and 1427 cm^{-1} are consistent with the C = C stretching and C–N stretching vibrations, respectively. The bands at 1305 cm^{-1} , 1174 cm^{-1} , and 1142 cm^{-1} also reflect similar C–N stretching vibrations as observed in ZIF-67, while the remaining peaks at 991 cm^{-1} , 754 cm^{-1} , and 689 cm^{-1} denote the characteristic out-of-plane bending vibrations. The observed shifts and the presence of similar peaks in both ZIF-67 and Ni-doped ZIF-67 suggest that the doping of nickel does not drastically alter the fundamental structure of the ZIF-67 framework but does introduce minor variations in the vibrational frequencies, reflecting the successful incorporation of nickel into the framework.

3.1.3. BET analysis

The surface area and porosity characteristics were evaluated through the Brunauer–Emmett–Teller (BET) analysis, conducted using the Autosorb iQ Station 1 instrument, as illustrated in Fig. 2. The BET surface area of the Ni_ZIF-67 composite was measured to be approximately 588 m^2/g , which is slightly lower than surface area of ZIF-67 as reported in literature because doping of Ni ions [37]. This high surface area of Ni_ZIF-67 composite indicates a significant number of accessible pores, which is crucial for applications requiring large surface-to-volume ratios, such as in catalysis and adsorption. The pore volume of 0.36 cm^3/g for Ni_ZIF-67, derived from the nitrogen adsorption-desorption isotherms, suggests a predominantly microporous structure with well-defined pores. The enhanced surface area and pore structure of the Ni-doped ZIF-67 are attributed to the incorporation of nickel ions, which likely influence the framework's stability and porosity, making it a promising material for various advanced applications.

3.1.4. FE-SEM and EDS Study

The morphological characteristics of the synthesized ZIF-67 and Ni_ZIF-67 composite were examined using Field Emission Scanning Electron Microscopy (FE-SEM) using MIRA3 LMH, TESCAN instrument (Brno, Czech Republic). The FE-SEM images, taken at a magnification of 2 μm , revealed well-defined rhombic dodecahedral structures typical of ZIF-67, confirming the successful formation of the ZIF framework. The surface of the ZIF-67 crystals appeared smooth and uniform, with an average particle size ranging from 300 nm to 500 nm, as depicted in Fig. 3(a). Upon doping with Ni, the morphology of the Ni_ZIF-67 composite remained similar, retaining the characteristic rhombic dodecahedral shape. However, slight surface roughness and irregularities were observed, which could be attributed to the incorporation of Ni^{2+} ions into the ZIF-67 structure as depicted in Fig. 3(b). This structural preservation upon doping indicates that the Ni^{2+} ions have been successfully incorporated into the ZIF-67 framework without significantly altering the overall crystal morphology. These observations are consistent with previous reports, where the doping of transition metals into ZIF-67 has been shown to affect surface properties while maintaining the integrity of the framework [37]. The Energy Dispersive X-ray Spectroscopy (EDS) analysis of ZIF-67 confirmed the presence of Co, N, and C, aligning with the expected composition of the framework as shown in Fig. 3(c). Co-originate from cobalt nitrate hexahydrate, while N and C are from the 2-methylimidazole linker. For Ni_ZIF-67, the analysis confirmed the successful incorporation of Ni, with signals corresponding to Ni, along with Co, N, and C, as shown in

Fig. 3(d). Elemental mapping showed a uniform distribution of Co, Ni, N, and C, indicating homogeneous Ni doping without phase separation, verifying the successful synthesis of both ZIF-67 and Ni_ZIF-67 framework.

3.1.5. AFM study

Surface morphology and composite structure were examined through non-contact mode atomic force microscopy (AFM) using the Park System XE-7 instrument. The AFM analysis of the synthesized ZIF-67 and Ni-doped ZIF-67 materials revealed their surface topography and morphological features as depicted in Fig. 4. For the ZIF-67 framework, the AFM images exhibited a uniform and well-defined crystalline structure with nanoscale roughness, indicative of the successful formation of the ZIF-67 framework as depicted in Fig. 4 (a). The surface appeared smooth and consisted of evenly distributed particles, demonstrating homogeneity in the synthesized material. In contrast, the AFM images of Ni_ZIF-67 showed slight alterations in surface morphology due to the incorporation of Ni ions, as depicted in Fig. 4 (b). The doped framework exhibited a more granular texture with increased surface roughness, suggesting the successful incorporation of nickel into the ZIF-67 structure, as shown in Table 1. This change in surface characteristics reflects the impact of nickel doping on the overall morphology, potentially enhancing the material’s electrochemical properties for sensing or catalytic applications. The AFM analysis confirms the nanoscale structural integrity and uniformity of both materials.

Table 1
Surface area, peak-to-valley height, and average surface roughness of synthesized nanomaterials.

Sr. No.	Material	Surface area (µm ²)	Peak-to-Valley Roughness (nm)	Average Surface Roughness (nm)
1.	ZIF-67	11.47	457.08	47.85
2.	Ni_ZIF-67	13.22	762.59	88.66

3.1.6. Electrochemical studies

For the synthesized ZIF-67 and Ni_ZIF-67 composite materials, the electrochemical performance was evaluated using Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The electrochemical behaviour of ZIF-67 and Ni_ZIF-67 composite was explored in 10 mM K₃[Fe(CN)₆]^{3-/4-} solution containing 0.1 M KCl. The CV curves showed well-defined redox peaks corresponding to the electrochemical activity of the materials, with Ni-ZIF-67 displaying enhanced peak current densities, indicating improved electrochemical performance and conductivity due to the incorporation of nickel into the ZIF-67 framework, as shown in Fig. 5(a).

EIS measurements were performed to investigate the charge transfer resistance (R_{ct}) and capacitive behaviour of the materials. The Nyquist plots, recorded over a frequency range of 100 kHz to 1 Hz,

exhibited a semicircular region at high frequencies and a linear region at low frequencies, as shown in Fig. 5(b). ZIF-67 demonstrated a significant semicircle, indicating higher charge transfer resistance. In contrast, the Ni_ZIF-67 composite showed a reduced semicircular diameter, reflecting lower R_{ct} and improved charge transfer kinetics. This enhancement in electrochemical properties can be attributed to the synergistic effects between the cobalt and nickel components in the composite, promoting better electron transport and capacitive performance.

3.2. Sensitivity and selectivity test

Figure 6 illustrates a three-dimensional selectivity curve that visualizes the selectivity patterns of the ZIF-67/GCE and Ni_ZIF-67/GCE sensors. The selectivity of the sensors was evaluated for detecting Pb(II) and Cu(II) ions among the metal ions Hg(II), Pb(II), Cu(II), Fe(II), Ni(II), and Cd(II), all at a concentration of 50 nM in 0.2 M acetate buffer solution (ABS). The ZIF-67/GCE sensor demonstrated moderate selectivity for Pb(II) and Cu(II) ions. The response of the ZIF-67/GCE sensor followed the order: Pb(II) > Cu(II) > Hg(II) > Fe(II) > Ni(II) > Cd(II). However, the stripping peak currents recorded for Pb(II) and Cu(II) ions were relatively lower compared to the Ni_ZIF-67/GCE sensor, indicating that the ZIF-67/GCE sensor has limited sensitivity towards these metal ions. In contrast, the Ni_ZIF-67/GCE sensor exhibited significantly improved selectivity and sensitivity for Pb(II) and Cu(II) ions. At a 50 nM concentration, the Ni_ZIF-67/GCE displayed a higher stripping peak current for Pb(II) (139.8 μ A) and Cu(II) (97.7 μ A) compared to other metal ions, as shown in Fig. 6. This superior performance is attributed to the synergistic interaction between the nickel ions and the ZIF-67 framework, which enhances the adsorption and determination capabilities for Pb(II) and Cu(II) ions. The Ni_ZIF-67/GCE sensor exhibited a subpar response for Hg(II), Fe(II), Ni(II), and Cd(II), with current responses significantly lower than those for Pb(II) and Cu(II). These findings confirm the higher selectivity of the Ni_ZIF-67/GCE sensor for Pb(II) and Cu(II) ions over other tested metal ions. This enhancement in selectivity and sensitivity for Pb(II) and Cu(II) ions establishes Ni_ZIF-67/GCE as a superior sensing platform compared to ZIF-67/GCE. Consequently, Ni_ZIF-67/GCE was selected for further studies due to its outstanding performance in detecting Pb(II) and Cu(II) ions.

3.3. Individual and simultaneous electrochemical determination of Pb(II) and Cu(II)

The electrochemical determination of Pb(II) and Cu(II) ions was systematically investigated using a Ni_ZIF-67/GCE sensor as the sensing platform. Differential pulse voltammetry (DPV) was employed as the analytical technique in a 0.2 M ABS solution. The study focused on both individual and simultaneous determination of these ions, revealing significant insights into their electrochemical behaviour and determination efficiency. The determination of Pb(II) and Cu(II) ions was carried out individually by varying their concentrations within the ranges of 1–9 nM for Pb(II) and 1–7 nM for Cu(II). The stripping peak responses showed a proportional increase with increasing ion concentrations, as depicted in Figs. 7(a) and (c). Calibration plots derived from four replicate experiments, illustrated in Figs. 7(b) and (d), exhibited strong linear correlations with coefficients ($R^2 = 0.97$) for Pb(II) and ($R^2 = 0.93$) for Cu(II). The linear calibration curves relating the stripping peak responses to ion concentrations demonstrated limits of determination (LODs) calculated using the 3S/N method. The LODs for Pb(II) and Cu(II) were

determined to be 0.96 nM and 0.79 nM, respectively. Additionally, the sensitivities of the sensor for individual determination were found to be 43.5 $\mu\text{A/M}$ for Pb(II) and 7.66 $\mu\text{A/M}$ for Cu(II). These findings underscore the high sensitivity and low determination limits achieved for each ion during individual analysis. Considering the frequent coexistence of HMIs in environmental systems, simultaneous determination remains a critical challenge. The simultaneous determination of Pb(II) and Cu(II) ions using the Ni_ZIF-67/GCE electrode is presented in Fig. 7(e). Two distinct stripping peaks were observed at specific potentials, -0.504 V for Pb(II) and 0.176 V for Cu(II), indicating successful differentiation of the ions. The stripping peak currents for both Pb(II) and Cu(II) exhibited a linear relationship with their respective concentrations over the range of 10–80 nM, as shown in Figs. 7(f1) and (f2). The calibration plots for individual ion detection (Fig. 7(b) and 7(d)) exhibit relatively good linearity, confirming reliable sensing performance under single-analyte conditions. However, in the case of simultaneous detection (Fig. 7(f₁) and 7(f₂)), a comparatively lower correlation coefficient (R^2) is observed. This deviation from ideal linearity can be attributed to mutual interference between co-existing ions, which may arise due to competitive adsorption at the active sites and overlapping electrochemical responses. Such behavior is commonly encountered in multi-analyte sensing systems and reflects the inherent complexity of simultaneous detection rather than a limitation in sensor stability. These results suggest that while the sensor performs efficiently for individual detection, further optimization may be required for improved linearity in simultaneous sensing applications.

The calibration curves for simultaneous determination revealed LODs of 1.3 nM for Pb(II) and 1.6 nM for Cu(II), with sensitivities of 23.2 $\mu\text{A/M}$ and 17.09 $\mu\text{A/M}$, respectively. Notably, the sensitivity for Pb(II) during simultaneous determination decreased compared to individual analysis, whereas the sensitivity for Cu(II) significantly improved. This enhancement in Cu(II) determination may be attributed to the formation of a Ni–Cu alloy on the electrode surface during the deposition process, which amplified the electrochemical response for Cu(II). The data for individual and simultaneous determination of Pb(II) and Cu(II) ions are summarized in Table 2. The achieved LODs for both individual and simultaneous determination surpass the regulatory thresholds set by organizations such as the U.S. Environmental Protection Agency (US-EPA) and the World Health Organization (WHO), emphasizing the high efficacy of the Ni_ZIF-67/GCE electrode system.

Furthermore, Table 3 provides a comparative analysis of the Ni_ZIF-67/GCE sensor with other electrochemical sensors based on MOFs. The comparison highlights the superior performance of the Ni_ZIF-67/GCE sensor in terms of LOD, determination range, and analytical technique, making it a promising candidate for the determination of HMIs in environmental monitoring.

Table 2
Comparison of individual and simultaneous analysis.

Sr. No.	Sensing material	Determination Limit (LOD)		Linear range		Determination Technique	Ref
		Pb(II)	Cu(II)	Pb(II)	Cu(II)		
01	Zn-MOF/GCE	0.22 μ M	0.17 μ M	1-300 μ M	1-300 μ M	DPV	[38]
02	MIL-47(as)/CPE	0.029 μ M	0.087 μ M	1–10 μ M	1–10 μ M	DPV	[39]
03	Ag@MOF/ITO	0.64 μ M	0.68 μ M	0–50 μ M	0–50 μ M	CV	[40]
04	EDTA_PANI/SWCNTs/SS	1.65 μ M	0.08 μ M	1.2 μ M-2 mM	2–37 μ M	DPV	[41]
05	UiO-66-NHC(S)NHMe/3D-KSC	0.0124 μ M	0.0111 μ M	-	-	SWASV	[42]
06	GCE/MIL-88B(Fe)-NH ₂	192 nM	381 nM	0.3–10.0 μ M	0.6–10.0 μ M	DPV	[43]
07	(PA/PPy)/ZIF-8@ZIF-67/GCE	2.9 nM	14.8 nM	0.02–200 μ M	0.02–200 μ M	DPV	[44]
08	Co-TMC4R-BDC/GCE	11 nM	13 nM	0.05–13 μ M	0.05–12 μ M	DPV	[45]
09	ZIF-67/EG	1.11 nM	2.23 nM	0.5-3 μ M	0.5-3 μ M	SWASV	[46]
10	Ni_ZIF-67/GCE	0.96 nM	0.79 nM	1–9 nM	1–7 nM	DPV	This work

Table 3
Comparative analysis of the Ni_ZIF-67/GCE sensor with other electrochemical sensors based on MOFs.

	HMLs	Linear range (nM)	LOD (nM)	Correlation coefficient	Sensitivity (μ A/M)
Individual analysis	Pb(II)	1–9	0.96	0.97	43.5
	Cu(II)	1–7	0.79	0.93	7.66
Simultaneous analysis	Pb(II)	10–80	1.3	0.88	23.2
	Cu(II)	10–80	1.6	0.85	17.09

3.4. Proposed Sensing mechanism

The electrochemical sensing mechanism of Pb(II) and Cu(II) ions using the Ni_ZIF-67-based electrode is governed by a combination of adsorption, electron transfer, and redox processes that take place at the electrode interface. Ni_ZIF-67 MOF, composed of cobalt-doped nickel nodes interconnected with organic linkers, possesses a highly porous structure that facilitates ion diffusion and provides abundant active sites for HMI capture. When the Ni_ZIF-67-modified GCE is immersed in an electrolyte containing Pb(II) and Cu(II) ions, these metal ions interact with the functional sites within the MOF via electrostatic attraction and coordination bonding. The nitrogen and oxygen donor atoms in the organic framework chelate Pb(II) and Cu(II), enhancing their preconcentration on the electrode surface. During the electrochemical process, a deposition step occurs where Pb(II) and Cu(II) ions are reduced to their metallic states upon applying a negative potential. This reduction is facilitated by the conductive Ni species within the MOF, which improves electron transfer efficiency. Subsequently, in the anodic stripping step, the deposited Pb and Cu undergo oxidation back to their ionic states, producing distinct stripping peaks at -0.504 V for Pb(II) and 0.176 V for Cu(II), allowing their individual and simultaneous determination. Notably, the presence of Ni species within the MOF contributes to an alloy formation with Cu during deposition, which significantly enhances the stripping current response for Cu(II), resulting in improved sensitivity. This synergistic interaction between Ni, Cu, and the MOF framework amplifies the electrochemical signal, providing a low LOD and high selectivity for Pb(II) and Cu(II) ions. The Ni_ZIF-67-based electrode thus exhibits exceptional electrochemical performance due to its high porosity, efficient ion chelation, and superior electron transfer capabilities, making it a highly promising platform for environmental monitoring of hazardous HMIs.

3.5. Repeatability, reproducibility, and stability of Ni_ZIF-67/GCE

The performance reliability of the Ni_ZIF-67/GCE sensor for detecting Pb(II) and Cu(II) ions was systematically evaluated through repeatability, reproducibility, and stability studies. Figure 9(a), (b), and (c) illustrate the evaluation of repeatability, reproducibility, and stability of the developed sensor. Repeatability was investigated by performing six successive measurements using the same Ni_ZIF-67-modified GCE in a 0.2 M acetate buffer solution (ABS) containing 10 nM concentrations of Pb(II) and Cu(II). As shown in Fig. 9(a), the electrode produced consistent stripping signals with low relative standard deviation (RSD) values of 1.36% for Pb(II) and 1.88% for Cu(II), confirming excellent repeatability. To assess reproducibility, six separately prepared Ni_ZIF-67/GCE sensors were tested under the same experimental conditions. The resulting data, displayed in Fig. 9(b), showed RSD values of 2.93% for Pb(II) and 5.07% for Cu(II), indicating reliable reproducibility. In addition, the electrode's long-term operational stability was examined over 30 days using a 10 nM solution of Pb(II) and Cu(II), with results presented in Fig. 9(c). The sensor preserved a stable electrochemical response throughout the test duration, showcasing outstanding stability. These comprehensive performance metrics underscore the Ni_ZIF-67/GCE sensor's potential for real-world applications, owing to its high sensitivity, low determination limits, excellent selectivity, and robust repeatability, reproducibility, and stability for the electrochemical sensing of HMIs.

4. Conclusions

In summary, the Ni_ZIF-67/GCE nanocomposite electrode was successfully developed and applied as an efficient electrochemical sensor for both individual and simultaneous determination of hazardous Pb(II) and Cu(II) ions. Comprehensive physicochemical analyses verified the structural stability and composition of the synthesized material. The sensor demonstrated outstanding electrochemical behaviour, achieving LOD of 0.96 nM for Pb(II) and 0.79 nM for Cu(II) in individual determination, and 1.3 nM and 1.6 nM, respectively, during simultaneous analysis. The corresponding sensitivities recorded were 43.5 $\mu\text{A/M}$ for Pb(II) and 7.66 $\mu\text{A/M}$ for Cu(II) in single-ion determination, while for dual-ion determination, sensitivities were 23.2 $\mu\text{A/M}$ for Pb(II) and 17.09 $\mu\text{A/M}$ for Cu(II). The superior sensing capability is primarily credited to the synergistic integration within the Ni_ZIF-67 matrix, offering numerous active sites, enhanced surface area, and efficient electron transport. Moreover, the electrode showed excellent repeatability, reproducibility, and long-term operational stability, highlighting its promise as a powerful tool for future electrochemical monitoring of heavy metal pollutants.

Declarations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Declaration of generative AI and AI-assisted technologies in the writing process

While preparing this work, the author used Grammarly and QuillBot tools to correct the English grammar and simple paraphrasing. After using this tool/service, the author reviewed and edited the content as needed and took full responsibility for the publication's content.

Author Statement

Kamlesh B. Deore: Conceptualization, Methodology, Visualization, Writing - Original Draft, Writing - Review & Editing. **Nilkanth B. Devkar:** Methodology. **Harshal S. Gavale:** Methodology. **Mahendra D. Shirsat:** Conceptualization, Resources, Supervision, Visualization, Writing - Review & Editing.

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Figures

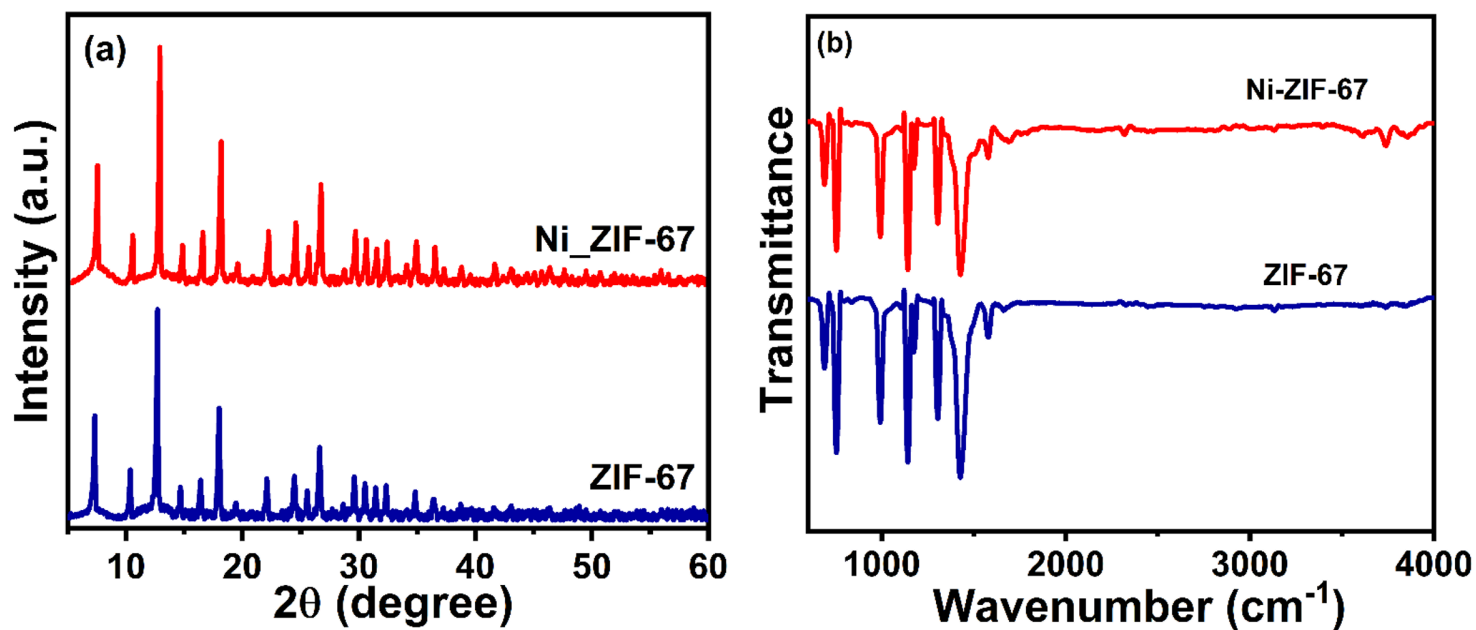


Figure 1

P-XRD pattern (a), FT-IR spectra (b) of ZIF-67 and Ni_ZIF-67 framework.

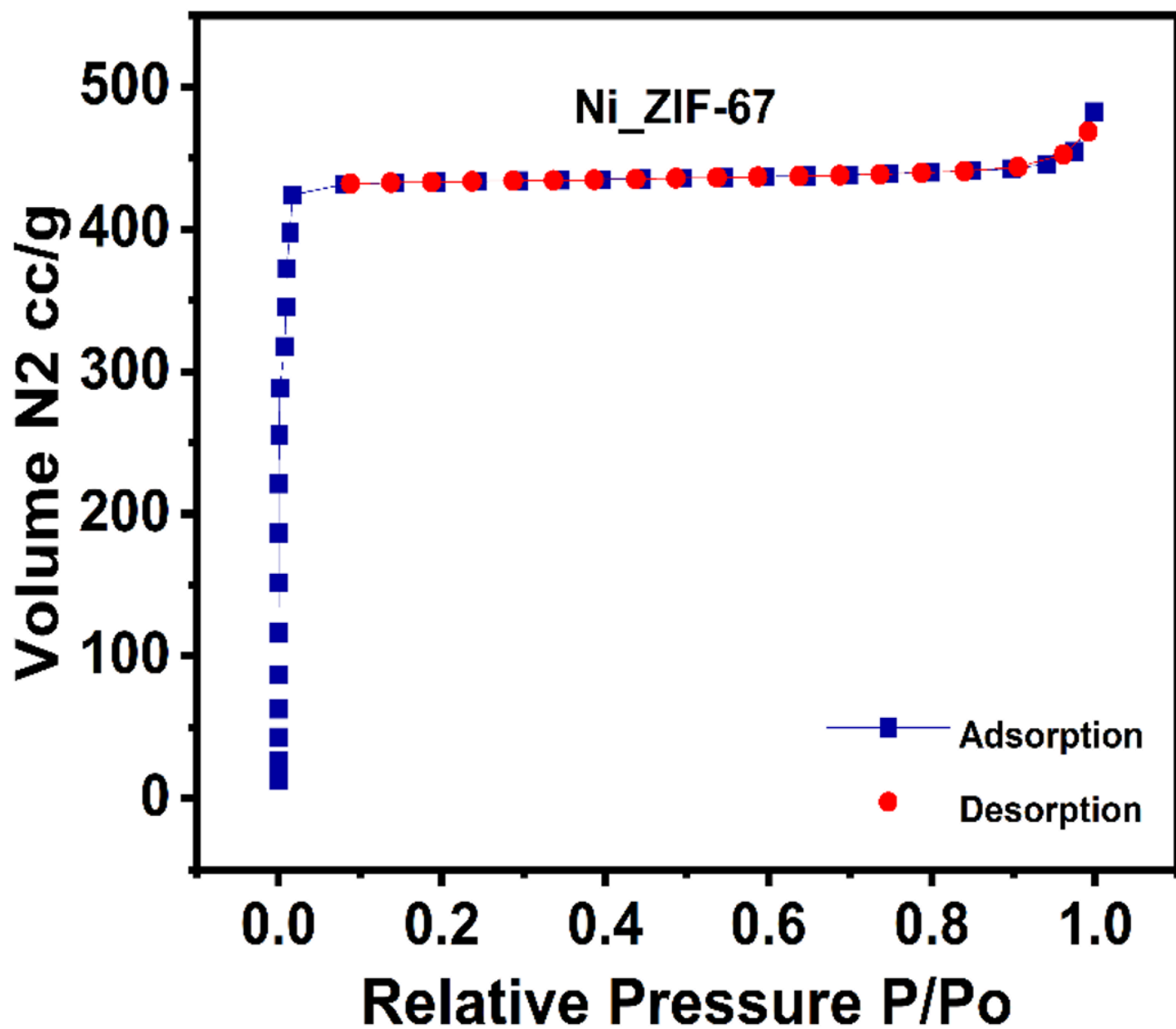


Figure 2

N₂ adsorption-desorption isotherms at 77 K of Ni_ZIF-67 framework.

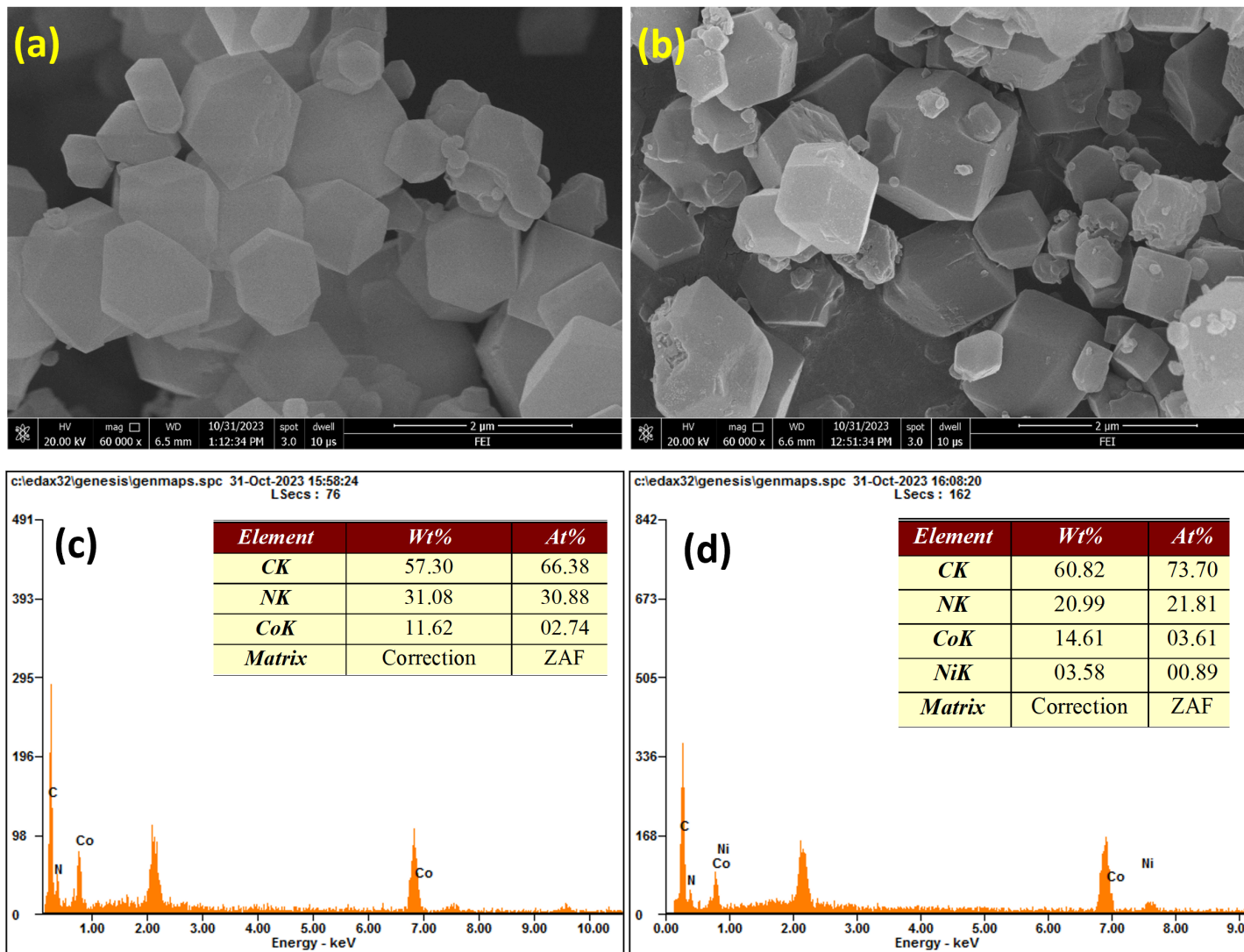


Figure 3

FE-SEM images of ZIF-67 (a), and Ni_ZIF-67 (b) & EDS of ZIF-67 (c), and Ni_ZIF-67 (d).

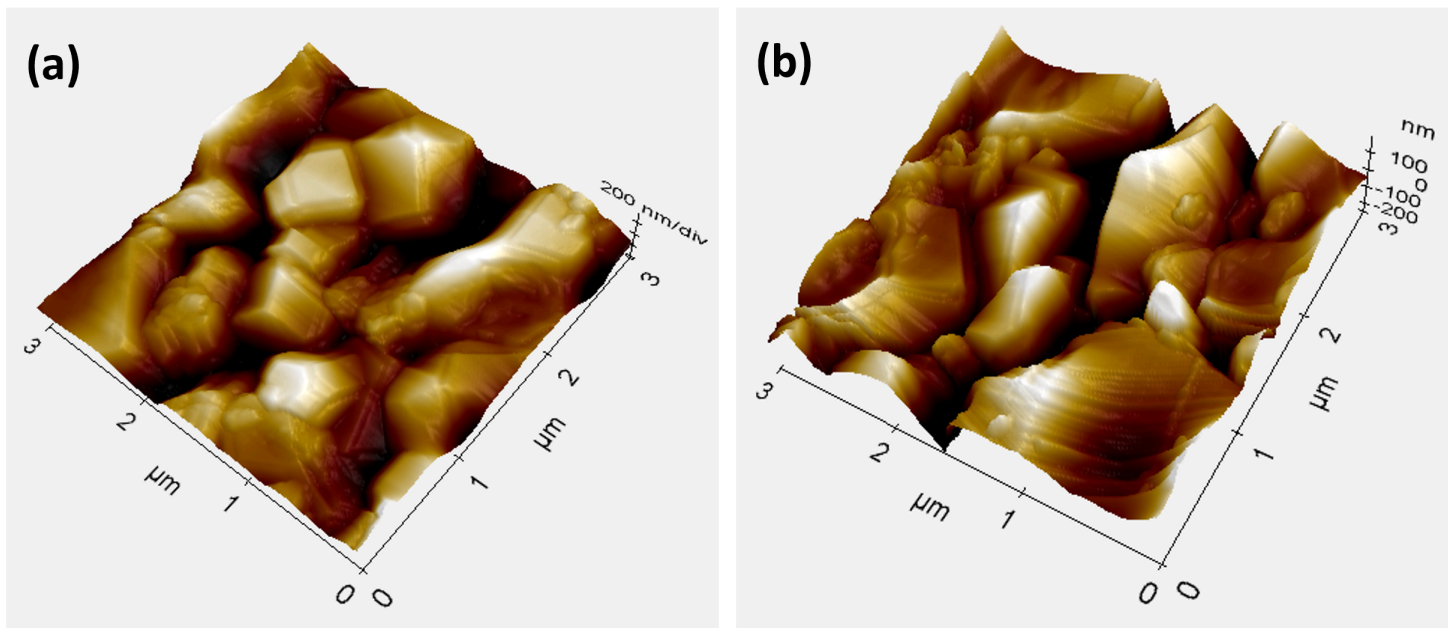


Figure 4

Atomic force microscopic images of ZIF-67 (a), and Ni_ZIF-67(b) framework.

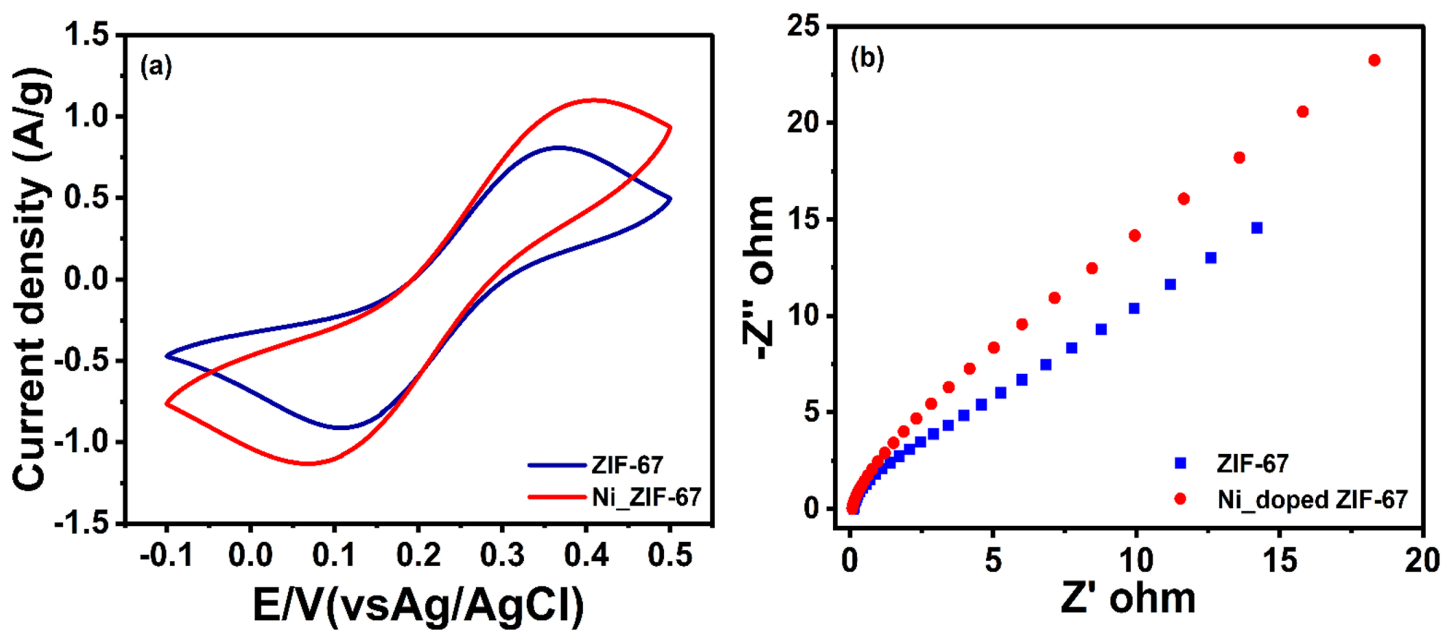


Figure 5

Cyclic voltammograms (a), Nyquist plot of electrochemical impedance spectra (b) of ZIF-67, and Ni_ZIF-67 in 10 mM $K_3[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl.

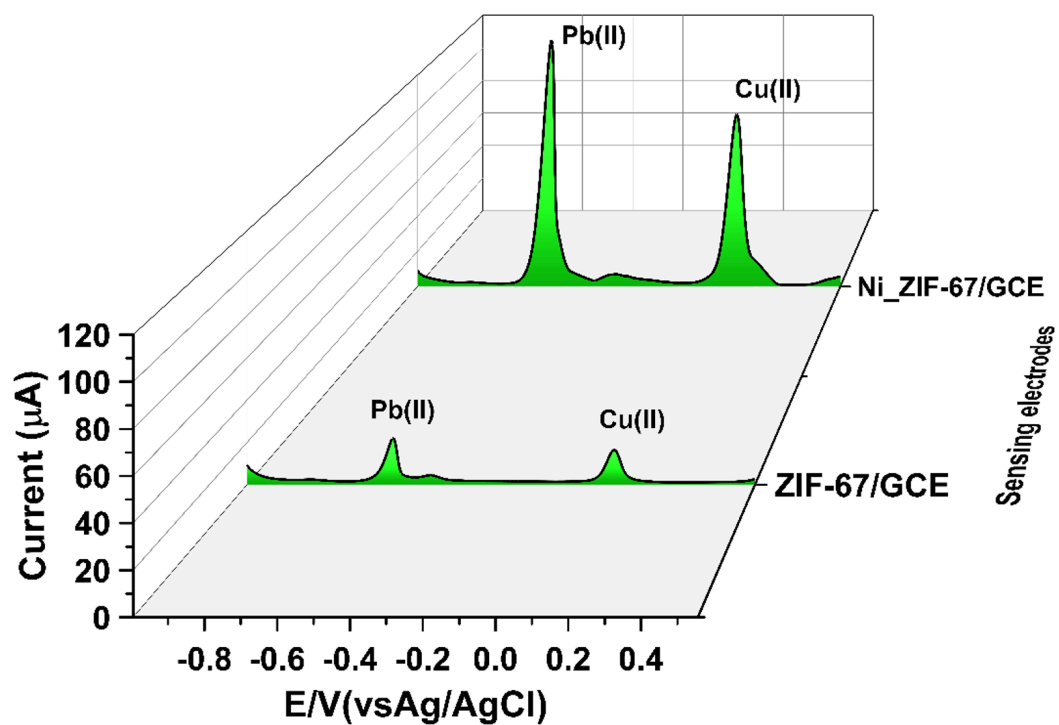


Figure 6

3D selectivity DPV curves of ZIF-67/GCE and Ni_ZIF-67/GCE electrodes in presence of Pb(II), Cu(II), Hg(II), Fe(II), Ni(II), and Cd(II) metal ions in 50 nM concentration in 0.2 M ABS.

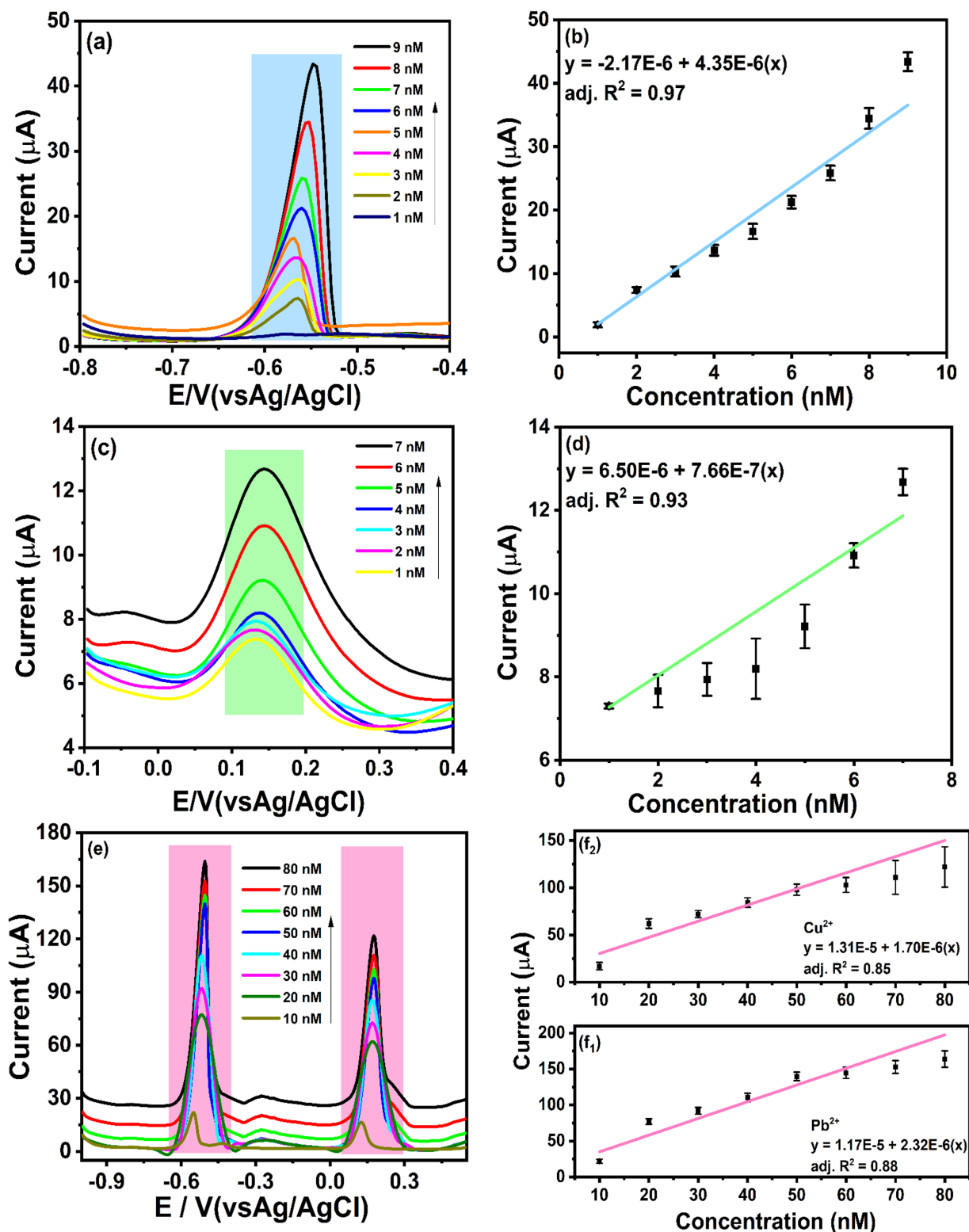


Figure 7

DPV response of the Ni_ZIF-67/GCE for individual analysis of Pb(II) (a), & Cu(II) (c) ions over the concentration range of 1 to 9 nM and 1 to 7 nM respectively. Calibration plot of individual analysis response versus Pb(II) (b) & Cu(II) (d) ions concentration. DPV response of the Ni_ZIF-67/GCE for simultaneous analysis of Pb(II), & Cu(II) (e) ions over the concentration range of 10 to 80 nM and

calibration plot of simultaneous analysis response versus Pb (f₁), & Cu (f₂) ions concentration. The results are mean±SD obtained from 4 measurements in each series.

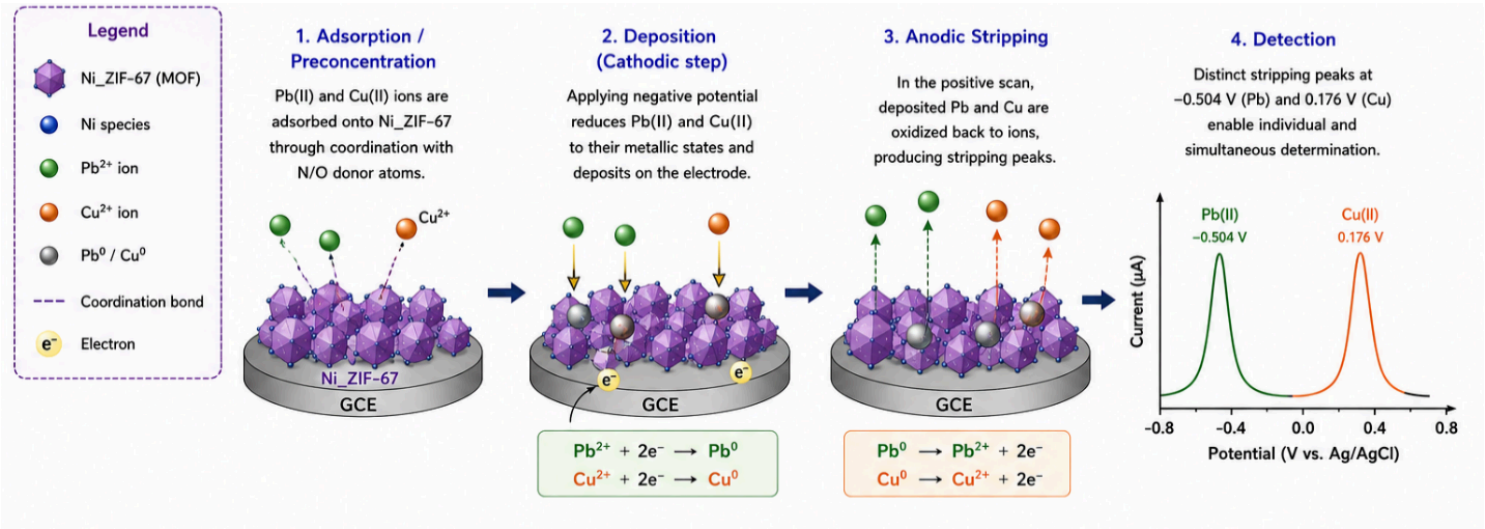


Figure 8

Schematic illustration of the proposed electrochemical sensing mechanism

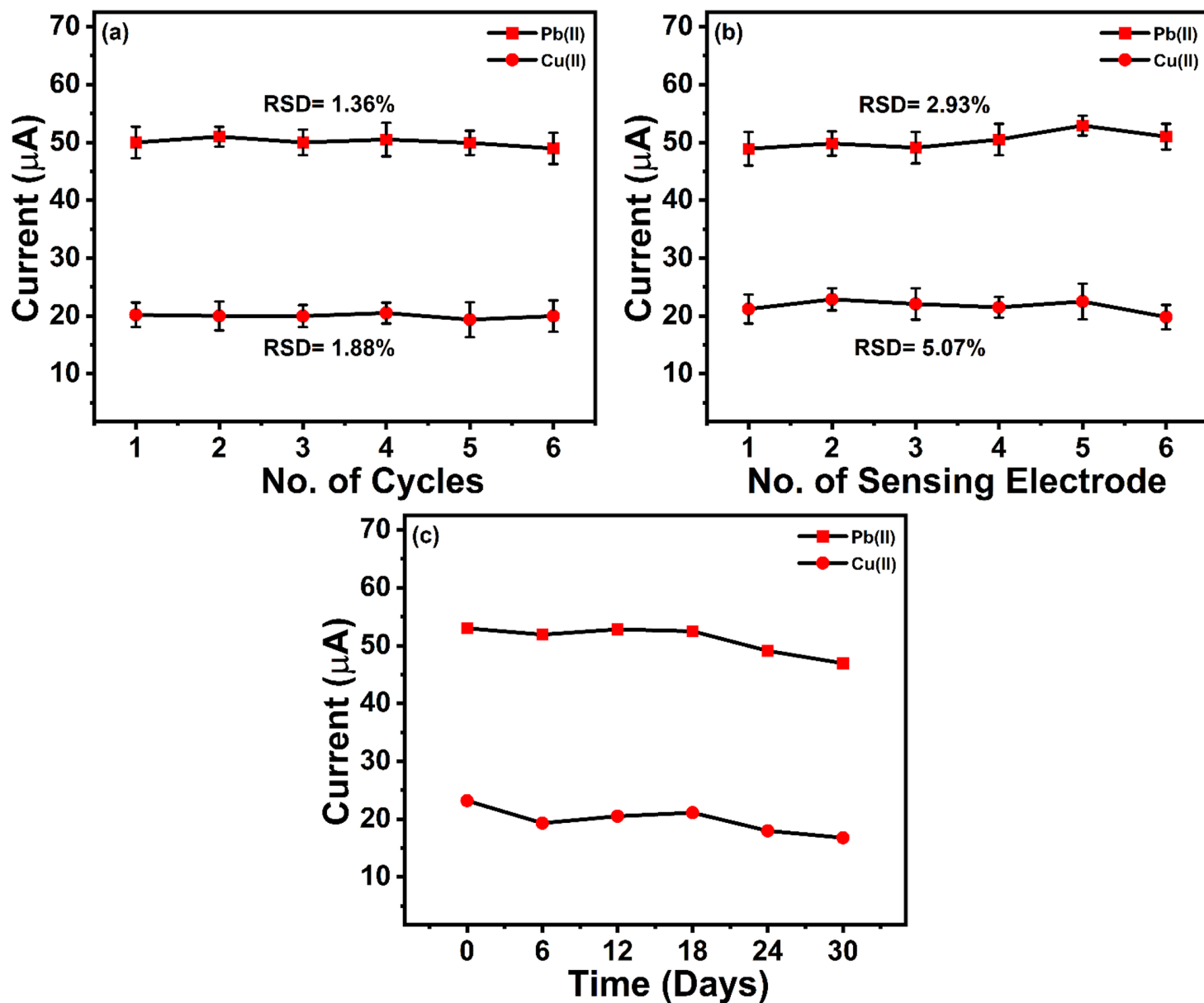


Figure 9

The repeatability (a), reproducibility (b), and stability (c) of Ni_ZIF-67/GCE sensor while determining Pb(II) and Cu(II) metal ions in 10 nM concentration in 0.2 M ABS solution. The results are mean±SD obtained from 6 measurements in each series.