Ultrasensitive electrochemical detection of metal ions using dicarboethoxycalixarene-based sensor

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A B S T R A C T

In this paper, we have reported an electrochemical detection of metal ions based on Calixarene-based sensor. In the sensing strategy, 3-aminopropylsilane (APTMS) was initially self-assembled on indium tin oxide (ITO) followed by functionalization of dicarboethoxy-calix [4]arene (EtC4). The morphology and properties of electrodes were characterized by contact angle, atomic force microscopy, cyclic voltammetry, electrochemical impedance spectroscopy and X-ray photoelectron spectroscopy. The electrochemical response characteristics of the modified electrodes (EtC4/APTMS/ITO) towards analyte ions; Zn(II), Cu(II), and Fe(II) ions were investigated by differential pulse voltammetry (DPV) under optimized conditions. It was found that the response of modified electrode towards the analytes was improved significantly as compared to the ITO electrode and resulted in limit of detections (LOD) of 9.88 pg/L, 8.33 μg/L and 1.15 μg/L, respectively. In addition, the detection limit of simultaneous detection quantification of Cu^{2+}, Zn^{2+} and Fe^{2+} ions could be achieved with the concentration 6.19 ng/L, 3.02 mg/L and 2.79 mg/L, respectively. It is worth to show that dicarboethoxy-calix [4]arene modified electrode is a promising candidate as electrochemical sensors for simultaneous and ultrasensitive heavy metal ions determination.

1. Introduction

The water contamination by heavy metals in our environment is dangerous due to their toxicity that causes to long term side effects [1]. The heavy metals such as cadmium [2], lead [3], zinc [4–6], nickel [7], copper [8], chromium [9] and their component are often used in industries for metal finishing, mining and chemical industries [10–12] that lead to natural water contamination. This phenomenon becomes a major problem all over the world, as the metals presence in excessive quantity will affect the quality in water consumption. Thus, the accumulation of heavy metal in human body will lead to kidney injury, respiratory failure, central nervous system disorder and if severe can cause death [11].

Conventional methods are available to trace heavy metal ions such as atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma atomic spectroscopy (ICP-AES) and ultraviolet-visible spectroscopy [13–15]. Despite, highly sensitive and selective metal ions detection, these techniques are inconvenient and require high cost of maintenance of instruments, and highly trained personnel [16].

As an alternative, electroanalytical methods for these metal ion detections have attracted wide attention in recent years due to selective, sensitive, inexpensive and wide linear range. Consequently, various novel materials [2,15,17–19] were fabricated for single and multiple metal ions detection to achieve sensitive, fast and facile detection which can offer on-the-spot testing of environmental samples [20–21].

Calixarenes are macromolecules that consist of linked phenolic units with methylene bridging groups. These macrocycle molecules possess hydrophobic upper rim and hydrophilic lower rim that surrounding a hollow cavity, with many dimensions dependent on the specific phenolic units incorporated [22]. The availability and easy functionalization of calixarene at either upper and/or lower rim make them very suitable platforms for assembly of various functional groups and can bind selectively specific guest molecules through non-covalent interactions such as π–π interaction, hydrogen bonding, van der Waals forces and electrostatic forces [23] [24]. Owing to their rigid and well defined frame and chemically stable intermolecular cavity with bulky organic molecules [25] and alkaline earth metal ions [26], biological molecules [27], they are frequently selected as host-guest recognition in sensor research [28–29], separation science[30] and biological analysis [26–27,31].
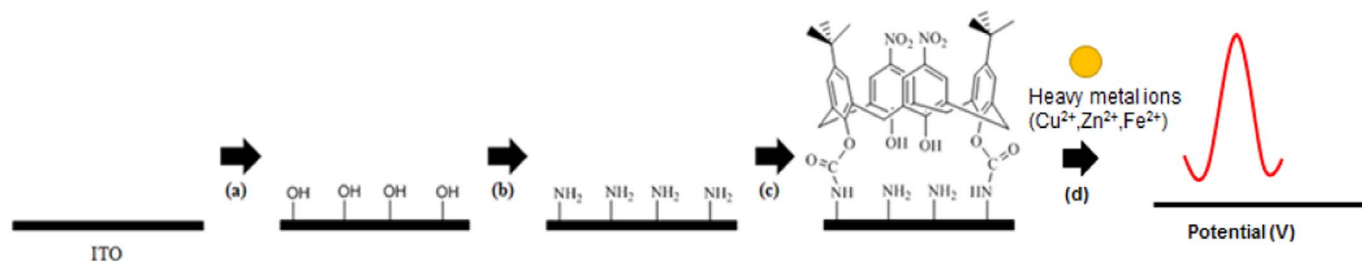
To our knowledge, little research has been conducted into the

Fig. 1. Schematic representation development of electrochemical detection of Zn^{2+}, Cu^{2+} and Fe^{2+} based on dicarboethoxy-calix [4]arene ITO electrode (EtC4/APTMS/ITO). (a) Preparation of cleaned ITO (b) Formation of self-assembled monolayer of 3-aminopropyltrimethoxysilane (APTMS) (c) Functionalization of dicarboethoxycalix [4]arene (EtC4) (d) Differential pulse voltammetry (DPV) detection of heavy metal ions.
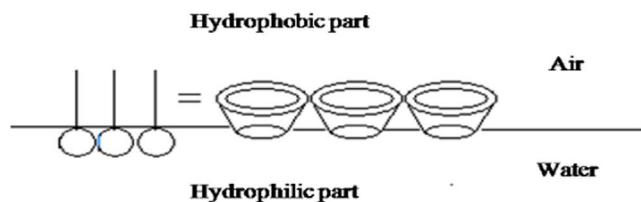

Fig. 2. Diagram of a simple amphiphilic molecules (left) and calixarenes (right). The orientation of the molecule is parallel (∥) with respect of the plane of water.

Table 1
Physical data for calixarene obtained.

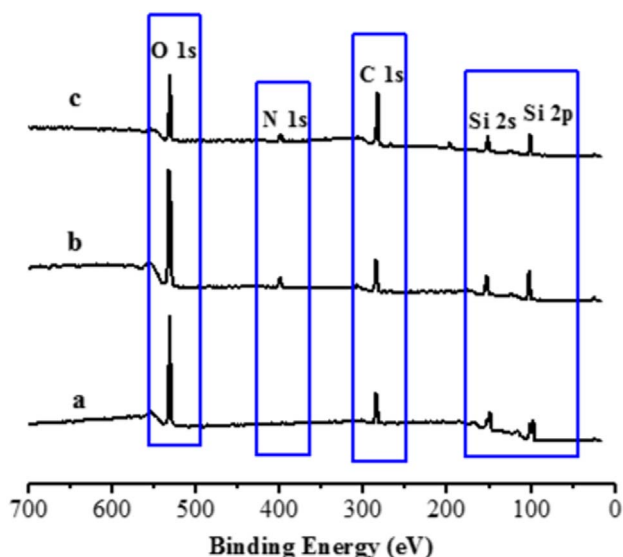| M_W (g/mol)	A_{lim} (nm^2)	Orientation	Colour
760.848	2.0	∥	Yellow

Fig. 3. Comparison wide scan X-ray photoelectron spectroscopy of (a) Bare indium tin oxide (ITO) (b) APTMS/ITO (c) EtC4/APTMS/ITO.

development of solid state metal ion electrochemical sensors based on calixarene. The hydrophobic and hydrophilic cavities enable calixarene to interact with metal ions. Herein, we report a simple method to develop electrochemical sensor based on dicarboethoxycalix [4]arene and investigate its performance for differential pulse voltammetry (DPV) measurement of selective and simultaneous Cu(II), Zn(II) and Fe(II) (See Fig. 1). On the other hand, the structural of dicarboethoxy-calix [4]arene at the water/air interface was investigated by using Langmuir-Blodgett technique.

2. Experimental

2.1. Materials

(3-aminopropyl)trimethoxysilane (APTMS) at 97% purity (Aldrich) and toluene (Merck) were used for monolayer film formation. Acetone and ethanol were purchased from Fischer Scientific, potassium ferro-cyanide [$K_4Fe(CN)_6.3H_2O$] and sodium chloride (NaCl) were purchased from HmbG Chemicals (United Kingdom). All these chemicals were used as received without any further purification. Deionized water with a resistivity of 18.2 mΩ·cm was used to prepare all the aqueous solutions. Rectangular ITO coated glass slide (75 mm × 25 mm × 1.1 mm) with a surface resistivity of 15–25 Ω/sq. were also purchased from Sigma Aldrich. The slide was cut into small pieces with a predefined-area of 25 mm × 10 mm and used as a working electrode for electro-chemical studies. The calix [4]arene used, namely 5,17,dinitro-11,23-ditert-butyl-25,27diethoxycarbonyl- methoxyleneoxy-26,28-dihydrox-ycalix [4]arene, was acquired from Dr. Mary Deasy, a chemist at the Institute of Technology, Tallaght, Dublin, Ireland. Glove bag used was obtained from Glas-Col Model X-17-17 (Indiana).

2.2. Methods

2.2.1. Determination of Π-A isotherm
Langmuir-Blodgett method was used to determine Π-*A* isotherm of calix [4]arene. A NIMA Langmuir trough with Nima 554 software was employed in this study. The Π-*A* Isotherm was recorded during a 12 mm/min compression after 150 μL of solution was dispersed drop-wise onto the cleaned deionized water subphase of the Langmuir trough.

2.2.2. Self-assembeld monolayer of APTMS on ITO (APTMS/ITO)
Prior to self-assembly of APTMS, ITO slides were cleaned in ethanol, followed by acetone and distilled water, in a sonicator for 15 min each. Then, the slides were immersed in an aqueous solution of hydrogen peroxide (H_2O_2), ammonia (NH_4) solution, and water in a ratio of 1:1:5, respectively, for approximately an hour. These slides were subsequently rinsed several times with deionized water and dried in the oven. The self-assembly of APTMS on ITO electrodes was conducted under a ni-trogen atmosphere in a glove bag, at room temperature by immersing the ITO slides in a 0.1 M solution of (3-aminopropyl)trimethoxysilane in anhydrous toluene and stopped by removal of the samples from the reaction vessel after a reaction time. The electrodes were rinsed with excess toluene for several times to remove physisorbed silane and wa-shed thoroughly with ethanol. After that, the slides were dried under a nitrogen gas stream and used immediately for surface analyses, elec-trochemical measurement and further surface modification.

2.2.3. Functionalization of dicarboethoxy-calix[4]arene (EtC4) on the electrode (EtC4/APTMS/ITO)
The surface of APTMS/ITO electrode was functionalized by im-mersing in 0.2 mg/mL EtC4 solution in chloroform ($CHCl_3$) at room
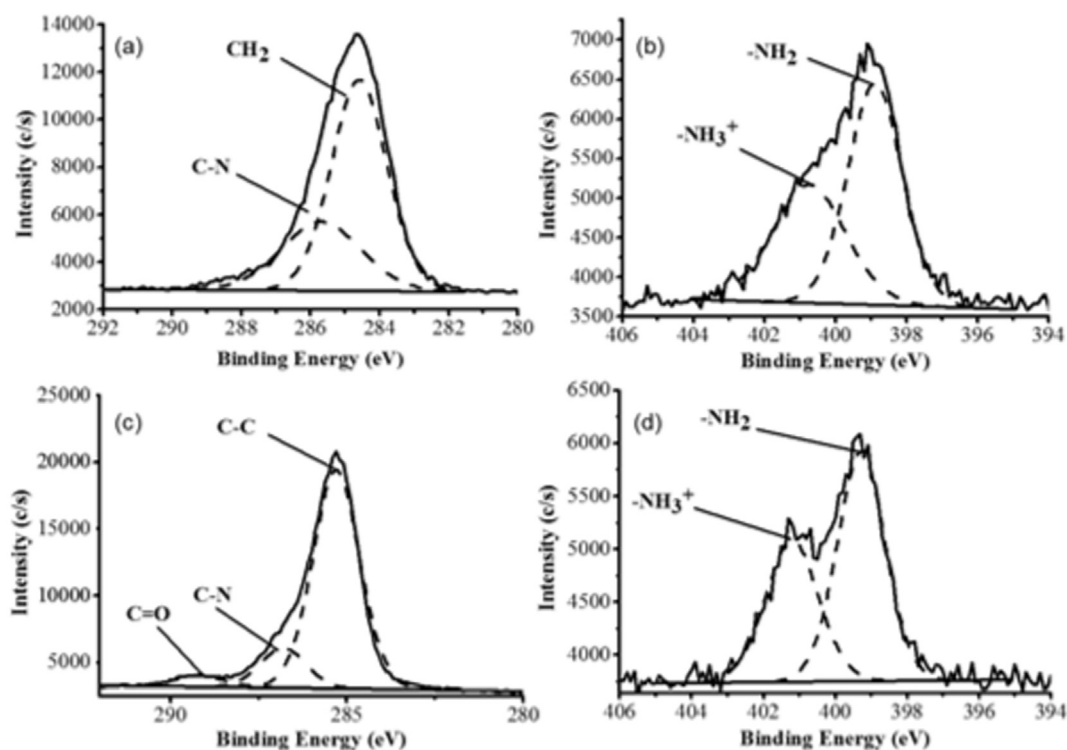
Fig. 4. C 1 s and N 1 s high resolution scans of APTMS/ITO (a) and (b) and EtC4/APTMS/ITO (c) and (d), respectively.

temperature. After completion of incubation, the EtC4/APTMS/ITO electrode was dried under a stream of nitrogen.

2.2.4. Analytical procedure

The analysis of Zn^{2+}, Cu^{2+} and Fe^{2+} ions using DPV was carried out by dipping a modified electrode in a cell containing Ag/AgCl (3.0 M KCl) reference electrode, platinum counter electrode and 10.0 mL aliquot and 0.1 M of NaCl as supporting electrolytes with solution being stirred using magnetic stirrer. The potential was scanned from -1.2 V to -0.7 V for Zn^{2+}, -0.5 V to 0.5 V for Cu^{2+} and -1.0 V to -0.1 V for Fe^{2+} at pulse time of 0.2 s, pulse amplitude of 50 mV and scan rate of 100 mV/s. The measurements were performed in the concentration range from 800 μM up to 20 μm. The peak currents were measured at -1.0 V for Zn^{2+}, -0.1 V for Cu^{2+} and -0.5 V for Fe^{2+}. All experiments were carried out at room temperature.

2.3. Apparatus

The wetting properties of the surfaces were studied using dynamic contact angle instrument with a model Thermo Cahn DCA 300 Analyzers. Wilhelmy Plate method was used to measure the value of contact angle in three different places for each samples. All the measurement were carried out at room temperature and, distilled water was used.

The surface roughness and topography were recorded using an atomic force microscope (*Quesant Instrument Corporation, Q-Scope 250*) in contact mode with a Si_3N_4 cantilever. The root-mean square (RMS) roughness was calculated from the height values in the atomic force microscopy images using the ScanAtomic software.

Cyclic voltammetry (CV) was carried out using an AUTOLAB instrument Model μAutolab *Type III potentiostat* (*Eco Chemie B. V., Netherlands*) with the modified ITO surface as the working electrode (surface area = 10 mm^2), a platinum wire and Ag/AgCl in 3 M NaCl as the counter and reference electrodes, respectively. Prior to use, the counter and reference electrodes were rinsed thoroughly with deionized water. CV measurement was performed at room temperature, in

aqueous solution of 1 mM $K_4Fe(CN)_6.3H_2O$ with 0.1 M NaCl as a supporting electrolyte a potential range between -0.3 V to 0.85 V versus Ag/AgCl. All the peaks were analyzed with *General-Purpose-Electrochemical-System*-Software (GPES). Electrochemical impendance measurements (Metrohm Autolab B.V., Netherlands) were carried out using an alternating current (AC) of 5 mV amplitude signal with wide frequency of 100 kHz to 0.1 Hz under open circuit conditions.

X-ray photoelectron spectroscopy were obtained on an *X-ray Microprobe Phi Quantera II* with a spectrometer fitted with a monochromated Al Kα scanning X-ray source (1486.6 eV). The pass energy of 280 eV and 112 eV were used for the wide and high resolution scans, respectively with the analyzing chamber operating within a pressure of 3.8 e^{-8} Pa. All the binding energies (BEs) were referenced to the C1s hydrocarbon peak at 285 eV. After background subtraction using the linear routine, the peaks were fitted with Gauss-Lorentz profiles using CasaXPS software to obtain the peak information on elements, composition, and oxidation states.

3. Results and discussion

3.1. Isotherm and size determination of calix[4]arene

By extrapolating the steepest linear solid region of isotherm to x-axis, the limiting area, A_{lim}, in the Π-A Isotherm will give the cross section value of the calix [4]arene. Assuming the area of calix [4]arene is a circle, it yields a diameter of 1.6 nm at the air/water interface. When comparing this isotherm result with Supian et al. [32], which also has the same lower rim substituents, it demonstrates that the calix [4] arene in this study possesses a parallel orientation (‖) plane with respect to the plane of the water surface (Fig. 2). The data is summarized in Table 1.

3.2. Surface characterization of bare ITO, APTMS/ITO and calix[4]arene/APTMS/ITO

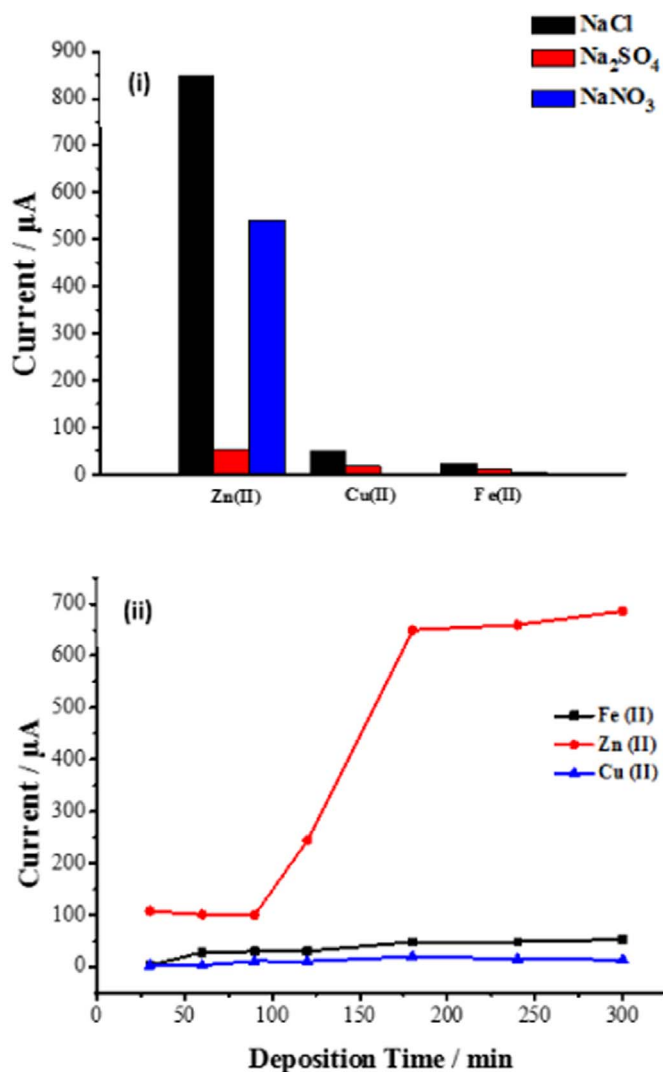Upon pretreatment, the contact angle of cleaned ITO surface was

Fig. 5. Effect of (i) supporting electrolytes and (ii) deposition time of calixarene on the stripping peak current for 80 μM of Cu(II), Zn(II) and Fe(II) solution. Condition: scan rate of 100 mV/s. Modulation time = 0.2 s, step modulation = 0.009 V and modulation amplitude = 0.04995 V.
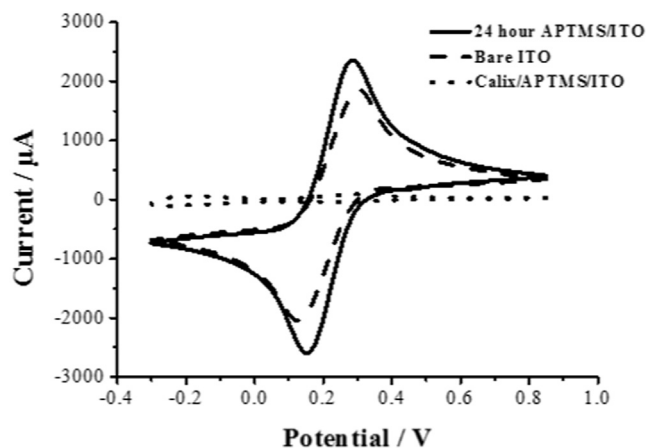

Fig. 6. Cyclic voltammograms of the bare ITO electrode (dashed line), APTMS/ITO (solid line) and EtC4/APTMS/ITO (dotted line) in 0.1 M NaCl solution containing 0.1 mM $K_4Fe(CN)_6 \cdot 3H_2O$.

below 10°, showing the hydrophilicity nature of the surface in the presence of number of hydroxyl groups for silanization reaction. The formation time of APTMS was varied to study the growth kinetic of silane molecules on ITO surface. The adsorption rate is found to be rapid after for 1 h immersion and becomes stagnant at 58 ± 2°. (Fig. S1 - see ESI). The functionalization of APTMS with calix [4]arene harbouring dicarboethoxy shows a higher value of contact angle up to 96 ± 2°, clearly indicating that the changes occurred on amine-terminated surface with the presence of bulky tert-butyl groups and benzene rings on the calix [4]arene frame. This value is supported by Zhang et al., who reported a contact angle of 87 ± 2° for monolayers formed from p-tert-butylcalix [4]crown-6 terminated SAMs [33].

While, for AFM analysis the surface morphology shows a formation of mountain due to growth of SAMs on ITO and the roughness value with increment from 0.1371 nm for bare ITO to 0.337 nm for the amino-functionalized ITO (Fig. S2-ESI). Dissimilar nanostructures were also observed for surface modified with calix [4]arene with further increase in RMS roughness, suggesting the successful performing each of surface modification. Cyclic voltammograms of the modified electrodes in redox species at different immersion time of APTMS is shown in Fig. S3-ESI.

To further confirm the each modified surface, XPS characterization was performed. Fig. 3 shows the wide scan of the (a) bare ITO (b) APTMS/ITO and (c) EtC4/APTMS/ITO. The spectra of the surfaces exhibited photoelectron lines at binding energies of ~ 104, 285, 400 and 530 eV which are attributed to Si 2p, C 1 s, N 1 s and O 1 s, respectively. The noticeable N 1 s peak started to appear after ITO surfaces were modified with APTMS and EtC4 which shows the consistent with introduction of NH_2 and NO_2 from APTMS and calixarene moieties, respectively on the electrodes. Nevertheless, the relative intensity of N 1 s peak is slightly weaker with EtC4/APTMS/ITO surface which correlates with the greater shielding of C−N bond from APTMS/ITO by the bulky calix [4]arene. In the high resolution scan of the C 1 s and N 1 s regions for APTMS/ITO and EtC4/APTMS/ITO electrodes, was shown in Fig. 4. The deconvolution of the C 1 s spectrum of APTMS/ITO (Fig. 4a) consists of two peaks (i) methylene chain carbon emissions at 285.0 eV and (ii) C−N emissions at 285.7 eV. As for N 1 s region (Fig. 4b), it was found that two different components: −NH_2 bonds found at 398.9 eV binding energy due to free aliphatic amines and –NH_3^+ bonds (H bonded amino groups) that appeared at 400.7 eV, which are also known as protonated amine, suggesting, was from two sources, either the amino groups that experience H-bonding with each other or with the hydroxyls group of the substrate [34]. Further modification of APTMS/ITO with EtC4 has resulted in the emergence of the new peak at about 289.2 eV in the C 1 s spectrum (Fig. 4c) which is assigned to C−C=O as ester and/or C−O−C bonds, confirming the covalent modification of electrode surface with dicarboethoxy group of calixarene. However, additional peak at binding energy of ~ 405.0 eV is expected to appear in N1 s scan (Fig. 4d), attributing to NO_2 group from calixarene molecules. This is due to electron-induced damage during acquisition of photoemission spectra, resulting in the reduction of nitro to amine groups and the absence of peak [35]. The results depend on the parameter that was used in the XPS system, including X-ray source intensity, exposure time, and the photon energy. All these factors will affect the nitro groups where photoreduction of nitro groups are likely to occur during XPS analysis [36].

3.3. Optimization studies of EtC4/APTMS/ITO electrode

The development of modified electrode on heavy metal ions is aimed to achieve the maximum of signal amplification. The analytical parameters like supporting electrolyte and immersion time of EtC4 on APTMS/ITO were studied which influence the analytical response of modified electrode towards analytes. Fig. 5i shows comparison of different supporting electrolytes that the highest peak currents were observed for detected metal ions when 0.1 M NaCl was used as the
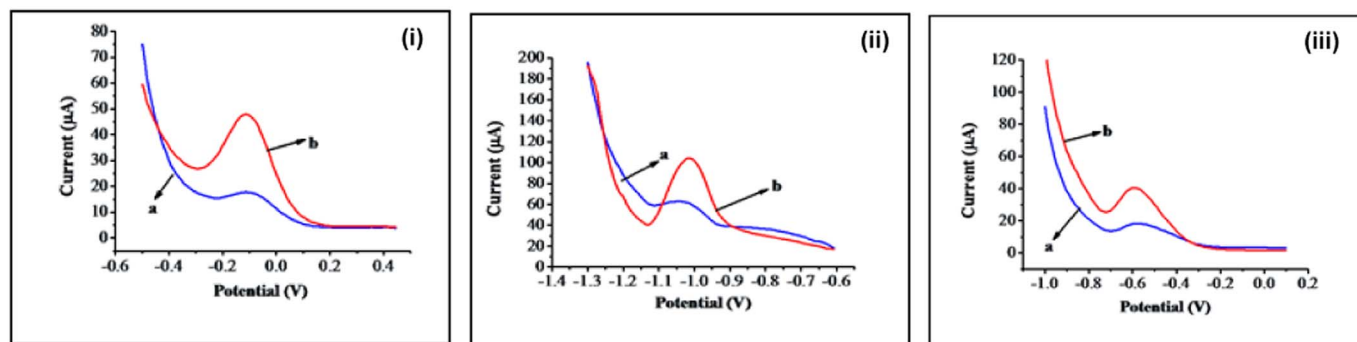
Fig. 7. Comparison of DPV voltammograms for (a) bare ITO and (b) EtC4/APTMS/ITO in 8 μM of i) Cu^{2+}, ii) Zn^{2+} and iii) Fe^{2+} in 0.1 M NaCl, potential vs Ag/AgCl at scan rate 100 mV/s.

supporting electrolyte with the lowest background current. In order to monitor the impact of number calixarene as a host-guest interaction, the effect of immersion time of calixarene was studied from 25 min to 300 min. As the amount of calixarene increase, the current response towards metal ions increases and becomes almost constant at 180 min (Fig. 5ii), likely due to either surface saturation of receptor or the attainment of equilibrium between the complexed metal ions and the ions in solution. In comparison to the metals ion responses, detection of Zn^{2+} showed more intense peak current responses under optimized conditions, indicating the modified electrode is more selective towards Zn^{2+} and form more stable complexes than with other two metals ions.

3.4. Electrochemical response of modified electrodes towards the $Fe(CN)_6^{3-/4-}$

The cyclic voltammetric response of modified electrodes (APTMS/ITO and EtC4/APTMS/ITO) towards $Fe(CN)_6^{3-/4-}$ was compared to that of bare ITO under same condition using 0.1 M NaCl as the background electrolyte (Fig. 6). For bare ITO and APTMS/ITO electrode types, the response was that of a reversible transfer with a peak separation, $\Delta E_p = E_{pa} - E_{pc}$ of 117 mV and 100 mV, respectively at a scan rate of 100 mV/s. Modification of bare ITO with APTMS causes the increasing anodic and cathodic peaks, likely due to the positively charged amino groups of the APTMS molecule which are protonated (NH_3^+) in aqueous solution and attract the negatively charged [$Fe(CN)_6^{3-/4-}$], causing an easy electron transfer reaction on the electrode's surface [37]. The observed inhibition of current at the EtC4/APTMS/ITO electrode can therefore be attributed to poor conductor of calixarene moiety.

Electrochemical impedance spectroscopy (EIS) data was used to further analyse the interface properties of the modified electrodes. Fig. S4 and S5 represent the Nyquist plot of the electrodes prepared at each step of surface modification.

The EIS data were fitted with equivalent electrical circuits (Fig. 6) to evaluate the charge transfer resistance (R_{ct}) of each modified electrode. R_{ct} for the electron transfer process between the electrolyte and the lone pair electron of amine group. However, for APTMS/ITO modified with calix [4]arene results in R_{ct} value distinctly increased to about 583 Ω, which is ascribed to the hinder of electron transfer at the electrode surface by the calix [4]arene. These results were supported by the cyclic voltammogram data.

3.5. Differential potential voltammetry behavior towards Cu(II), Zn(II) and Fe(II)

To investigate electrochemical behavior of metal ions at different electrodes, bare ITO and EtC4/APTMS/ITO electrodes were exposed to metal ions under optimized conditions. Fig. 7 shows the differential pulse stripping voltammetric responses of metal ions in 0.1 M NaCl with potential range of -1.4 V to 0.4 V (vs. Ag/AgCl). From the figure, the

bare ITO electrode produced only a slight detection of metal ions, suggesting a weak binding between negatively charged on hydroxyl groups of ITO and metal ions, while a pronounced peaks observed for EtC4/APTMS/ITO was used to detect with peak potential of Zn^{2+}, Cu^{2+}, Fe^{2+} is located at approximately -1.02 V, -0.10 V, -0.58 V, respectively. This implies the cation binding in the cavity of dicarboethoxycalix [4]arene allows the formation of the metal-guest bond.

Under the optimized conditions, the DPV responses of the EtC4/APTMS/ITO to the successive addition of Cu(II), Zn(II) and Fe(II) were quantitatively measured. As shown in Fig. 8a–c the anodic peak current apparently increases with increasing metal ions concentration and the corresponding calibration plot was derived accordingly (Fig. 8d–f). The peak currents exhibit a linear dependence on the concentration of the corresponding metal ions. The calibration curves for zinc (Fig. 8e) and iron (Fig. 8f) ions detection showed linearity with correlation coefficients 0.992 and 0.9879, respectively. The calculated LOD for zinc and iron were 9.88 pg/L and 1.15 μg/L. However, two separate linear dynamic ranges was observed for copper detection (Fig. 8d), namely 2–8 μM and 20–60 μM. In the high concentration range, a decrease sensitivity was observed, leading to a lower response. This is due to the kinetic limitation of EtC4/APTMS/ITO. Hence the LOD was calculated to be 0.145 μg/L. The limit of detection (LOD) was calculated by using formula 3 s/S in which s is defined as the standard deviation of the blank and S is the slope of the plot. The LOD estimated for each metal is still below than the World Health Organisation limit of 5 mg/L, 1.0 mg/L and 0.3 mg/L for Zn^{2+}, Cu^{2+} and Fe^{2+}, respectively in drinking water.

3.6. Simultaneous, repeatability and reproducibility studies

To investigate the sensitivity of EtC4/APTMS/ITO electrode and the intermolecular effects between Zn, Cu and Fe ions, the simultaneous detection was carried out under optimum conditions, mixing with increasing concentration of each ions ranging from 20 uM to 800 uM. Fig. 9a, DPV responses of simultaneous determination of metal ions. The current responses show the detection of three peaks with a pronounced peak observed for Zn^{2+} than Fe^{2+} and Cu^{2+}. The LOD for simultaneous detection is calculated to be 6.19 ng/L, 3.02 mg/L and 2.73 mg/L, respectively. Therefore, the results showed pronounced selectivity towards Zn^{2+} than Fe^{2+} and Cu^{2+}.

The repeatability of the electrode was evaluated by performing 5 measurements with the same standard solution of analytes. The relative standard deviation (RSD) for the response of the electrodes towards 80 μM of Zn^{2+}, Cu^{2+} and Fe^{2+} was 6.8%, 7.1% and 4.3%, respectively. The reproducibility of the developed sensor showed RSD values of Zn^{2+}, Cu^{2+} and Fe^{2+} were 2.14%, 8.62% and 3.68%, respectively. The results show that repeatability and reproducibility of the developed sensor is acceptable.

The electrochemical detection of Zn^{2+}, Cu^{2+} and Fe^{2+} was
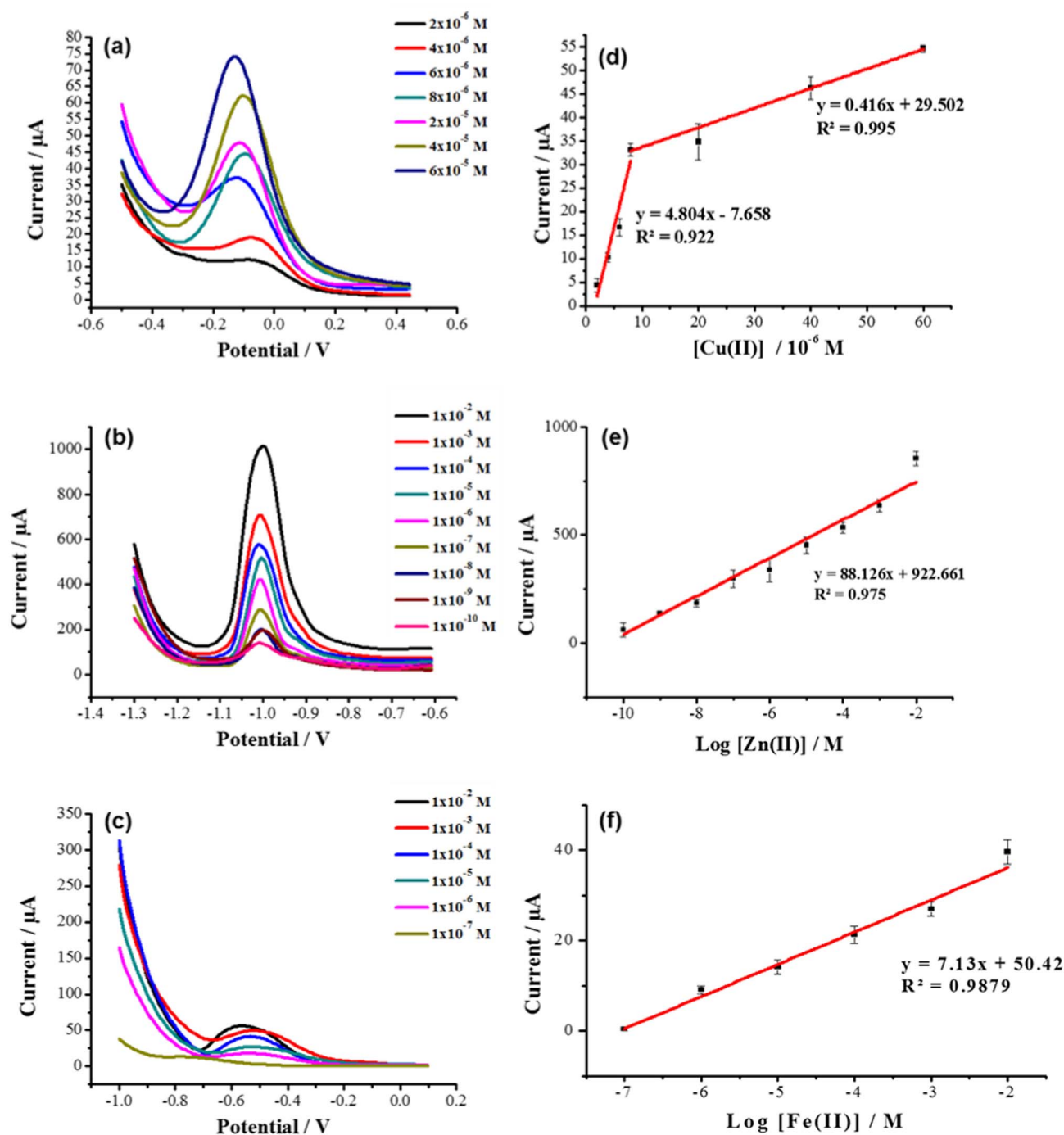
Fig. 8. DPV responses of the EtC4/APTMS/ITO electrodes for the individual analysis of (a) Cu^{2+} (b) Zn^{2+} and (c) Fe^{2+} over a concentration range of 8×10^{-4} to 2×10^{-5} M with respective linear calibration plot of peak current (d–f) against Cu^{2+}, Zn^{2+} and Fe^{2+}, respectively.

compared with previously reported from various modified electrodes, as shown in Table 2. According to the reported data, the modification ITO with dicarboethoxycalixarene showed higher sensitivity to those metal ions. This comparison confirmed that calixarene moiety is reliable for the development of electrochemical sensor for heavy metal ions detection. In addition, one of the noteworthy advantages of this study is that a simple and cheap approach for modifying electrode with calixarene, providing a new platform for designing electrochemical sensors.

4. Conclusions

A simple approach to modify electrode for Cu(II), Zn(II) and Fe(II) detection was successfully fabricated by formation of APTMS on ITO followed by further functionalization with dicarboethoxycalixarene. The development of modified electrode exhibits excellent voltametric performances which responds high selectively with Zn^{2+} and other metals (Cu^{2+} and Fe^{2+}). Furthermore, the electrode is characterize provides higher selectively with low limit of detection A simultaneous detection of multi-elements was demonstrated in which Zn^{2+} was higher selective compared to other ions. The proposed sensor possess high sensitivity, good selectivity and high stability which has potential candidate to be employed for the detection of heavy metal ions in real world samples when the fabricated electrode are miniaturized for the on-site determination.
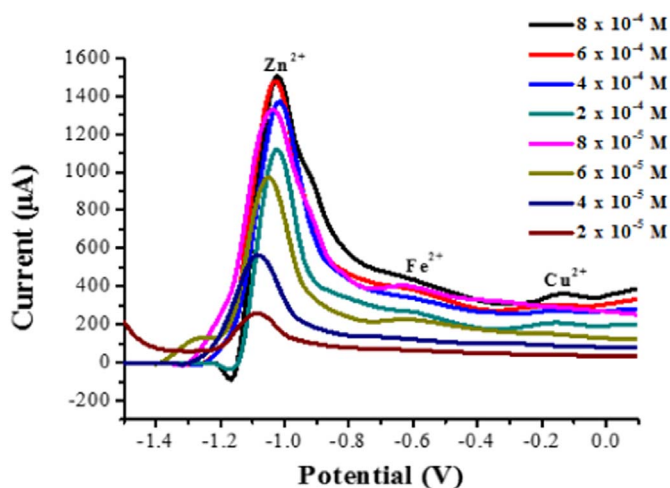
Fig. 9. DPV responses of the EtC4/APTMS/ITO electrodes for the simultaneous detection of Cu^{2+}, Zn^{2+} and Fe^{2+} over a concentration range between 8×10^{-4} to 2×10^{-5} M.

Table 2
Different studies form the literature reported for the electrochemical determination of Zn^{2+}, Cu^{2+} and Fe^{2} based on modified electrodes.

Analytes	Electrode	Analytical technique	Limit of detection	Ref.
Zn(II)	Bismuth bulk electrode	SWASV	396 ngL^{-1}	[4]
	Carbon nanotubes	SWASV	12 µg/L	[5]
	Mercury supported biochar on carbon paste electrode	DPASV	11.1 µg/L	[6]
	EtC4/APTMS/ITO	DPV	9.88 pg/L	This study
Cu(II)	Luminol on HDME	ASV	0.04 µgL^{-1}	[18]
	Thiosemicarbazide on HDME	ASV	0.007 µgL^{-1}	[38]
	Graphene oxide	SWASV	363 µgL^{-1}	[39]
	EtC4/APTMS/ITO	DPV	8.33 µg/L	This study
Fe(II)	Hanging dropping mercury electrode (HDME)	DPV	15 µgL^{-1}	[40]
	Carbon paste electrode (CPE) modified with dithiodianiline and gold nanoparticle	DPSV	19.6 ngL^{-1}	[41]
	Dimethyliminocin-namyl linked rhodamine ionophore - PVC based coated graphite electrodes (CGEs)	DPV	40.76 µgL^{-1}	[42]
	EtC4/APTMS/ITO	DPV	1.15 µg/L	This study

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jelechem.2017.06.038.

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