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Sensitive and selective Cu²⁺ sensor based on 4-(3-(thiophen-2-yl)-9*H*-carbazol-9-yl)benzaldehyde (TPCBZ) conjugated copper-complex



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ABSTRACT

4-(3-(thiophen-2-yl)-9*H*-carbazol-9-yl)benzaldehyde (TPCBZ) was synthesized under microwave irradiation with auto generated pressure (at 130.0 °C) and characterized by ¹H NMR, ¹³C NMR, Mass and FTIR spectroscopy, thin-layer chromatography (TLC), and elemental analyses. Here, a thin-layer of TPCBZ onto glassy carbon electrode (GCE) is fabricated with conducting coating agents (5% nafion) to fabricate a selective and selective Cu²⁺ sensor in short response time in phosphate buffer phase. The fabricated sensor (TPCBZ/Nafion/GCE) is exhibited higher sensitivity, large-dynamic concentration ranges, long-term stability, and improved electrochemical performances towards TPCBZ-conjugated copper complex for selective Cu²⁺ sensor. The calibration plot is linear (r^2 : 0.9979) over the large Cu²⁺ ions concentration ranges (1.0 nM–1.0 mM). The sensitivity and detection limit is ~1.12974 μ Acm⁻² μ M⁻¹ and ~0.84 ± 0.02 nM (signal-to-noise ratio, at a SNR of 3) respectively, which is calculated from the slope of the calibration plot. This novel effort is initiated a well-organize way of efficient cationic sensor improvement with carbazide for heavy metallic pollutants in environmental and health-care fields in large scales.

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1. Introduction

A long-standing goal of organic synthesis is the development of new methods that access many novel derivatives of aromatic nitrogen heterocycles for wide applications [1–4] such as carbazoles, because they are prevalent in important medicinal compounds and materials [5]. Carbazoles are among exclusive types of *N*-containing aromatic heterocycles possessing desirable electronic and chargetransport properties, as well as large pi-conjugated system [6]. The structurally rigid carbazolyl ring is also found friendly towards the introduction of various functional groups. Carbazole nucleus has always stimulated the endeavors to find new pathways for synthesis of novel derivatives because of extensive photo-physical, photochemical, and biological properties [7], especially their amazing pharmacological profile and their role as drug molecule [8]. To date, numerous researchers make efforts to develop efficient

* Corresponding author. Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia. synthetic avenues to carbazole and its well-modified derivatives, which are well documented [9,10]. Based on the documented facts which highlighted the incredible potential applications of carbazole-based derivatives in the field of chemistry, the work undertaken here relates to the synthesis of novel carbazoles and heavy cationic sensors development.

Heavy toxic metal contamination is a major concern in environmental pollution due to their serious toxic effects on plants, animals and human being [11]. Among various heavy metals, copper (Cu) are the most probable causes for the heavy metal-related diseases [12]. For example, both inorganic and organic mercury can be absorbed through the gastrointestinal tract, resulting in the damage to the nervous system, and the kidneys [13]. Cu(II) is also an essential and necessary micronutrient for many plants and animals at very low levels [14]. However, it is toxic to aquatic plants at high levels due to its association with cell membranes, preventing the transport across the wall cell [15]. Because of various applications in industrial and agricultural processes, Cu(II) can be released into the environment from many sources. Drinking water can be a potential source for an intense Cu(II) exposition because of the production and industrial use. Copper(II) is highly toxic for drinking



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water, and mercury is the only metal more toxic than copper [16]. The excessive intake of Cu(II) could be damaged in kidney and liver, increased blood pressure and respiratory rates, and damaged to central nervous system [17]. Moreover, Menkes and Wilson diseases have been found closely related to the disorder of Cu(II) metabolism [18]. Therefore, the maximum permissible limit in drinking water is not to exceed 0.05 mg/L [19]. Then the development of novel methods for simultaneous detection and removal of low levels copper from natural waters has special importance. Copper is an essential element to human bodies, but the excessive copper can seriously destroy tissue since it can interact with lipid hydroxyl-peroxides to produce some DNA damaging agents such as malondialdehyde and 4-hydroxynonenal [20]. Measurements of Cu(II) ions with atomic absorption spectrometry, inductively coupled plasma-atomic emission spectrometry, inductively coupled plasma-mass spectrometry, potentiometric techniques and X-ray fluorescence are sensitive and reliable [21,22]. However, the costly instrumentations, sampling, storage, handling, timeconsuming and complicated pretreatment make them unsuitable for on-line or field monitoring. Therefore, an effective I-V method for technological assortment is used as a noble organic compound adsorbent model for the detection and quantification of toxic heavy metal ions. Several physical and chemical methods are now developed to remove Cu(II) from water such as ion exchange, reverse osmosis, membrane technologies, chemical precipitation, and electrochemical treatment [23]. However, most of these methods required sophisticated instruments, controlled conditions, sludge problem, unable to use repeatedly and high costs. In addition, these are low efficiency, time-consuming, producing unexpected sludge, making them unattractive for the selective detection and removal of Cu(II) ions [24]. Adsorption is one of the few alternatives available to remove low level Cu(II) and widely accepted in environmental treatment applications throughout the world [25]. Cu(II)) is micronutrient constituent and carries a significant responsibility in the bone-formation collectively with definite proteins and enzymes [26,27]. Nevertheless, it is considered an unsafe pollutant when it cannot be controlled at a suitable physiological concentration. It has been commenced from different industries wastewater such as mining, metallurgy, plating, steelworks, chemical manufacturing, petroleum refining and printing circuits and affect the nature environment [28]. The excess Cu(II) consumption will cause several diseases such as gastro-intestinal symptoms and liver toxicity, Wilson, osteoporosis and Alzheimer's diseases [29]. The permissible limits given by the world health organization for Cu(II) into drinking water is 0.05 mg/L [30]. Therefore, simple, green, reliable, selective and sensitive method for Cu(II) monitoring and removal are important for environmental safety and health. Monitoring of Cu(II) ion has attracted due to the toxicity to organisms [31]. Various techniques have been developed to detect Cu(II) ions such as UV-vis spectroscopy, atomic absorption spectroscopy/emission spectroscopy, X-ray analysis method, anodic stripping voltammetry, fluorescence spectroscopy, colorimetric method and ICP-MS [32,33]. However, UV-vis spectroscopy and anodic stripping voltammetry are insensitive. The X-ray analysis and ICP-MS test procedures are time-consuming and costly, requiring sophisticated and expensive instrumentation. Therefore, simple, sensitive and selective methods are demanded for Cu(II) ions detection. Compared to these methods, optical methods allow in-situ visual detection with a naked eye is more suitable because these are cost-effective and easy-to-use without the need for sophisticated instruments [34]. Recently, several ligands impregnated materials for sensitive Cu(II) detection even in the presence of diverse competing ion [35]. The complexation mechanism and optimum condition are the key factors for selective capturing of target ions [35]. From the stand point, the specific functional group containing ligand is developed for Cu(II) detection at optimum condition [36].

Excessive Cu^{2+} ion is usually serious to health and environment, therefore it is immediately required the detection by using a reliable cationic-sensor method with TPCBZ using GCE. The Cu^{2+} ion by thin TPCBZ films on GCE is prepared and studied in details of the cationic sensors. The easy-coating method for the construction of TPCBZ thin-film within binding-agents is executed for preparation of films onto GCE. In this approach, TPCBZ fabricated films with conducting binders was utilized towards the target copper analytes using reliable Current-vs-Voltage (I-V) method. It was confirmed that the fabricated cationic sensor is unique and noble research work for ultra-sensitive recognition of Cu^{2+} ions with conjugation of TPCBZ as copper-complex onto GCE in short response-time.

2. Experimental sections

2.1. Materials and methods

Analytical grade of disodium phosphate (Na₂HPO₄), silver nitrate, auric chloride, calcium nitrate, cadmium sulphate, copper chloride, cobalt nitrate, nickel chloride, cerium nitrate, mercury chloride, magnesium chloride, lead nitrate, stannic chloride, yttrium nitrate, zinc chloride, monosodium phosphate (NaH₂PO₄) was used and purchased from Sigma-Aldrich Company, USA. They were used without further purification. All organic solvents were purchased from commercial sources and used as received unless otherwise stated. Stock solution of Cu^{2+} (0.1 M) was prepared from the purchased chemical. I-V technique was executed by using Electrometer (Keithley, 6517A, Electrometer, USA; www.keithley. nl) for measuring the current responses in two electrode systems for target Cu²⁺ sensor based on TPCBZ in buffer phase at room conditions, where flat-GCE and Pd-wire was used as working and counter electrode respectively. All organic solvents were purchased from commercial sources and used as received unless otherwise stated.

Thin-layer chromatography (TLC) was performed on pre-coated Merck 60 GF254 (www.merckmillipore.com) silica gel plates with a fluorescent indicator, and detection by means of UV light at 254 and 360 nm. The melting points were measured on a Stuart melting point apparatus and are uncorrected. IR spectra were recorded on a Smart iTR (www.thermofisher.com), which is an ultra-highperformance, versatile Attenuated Total Reflectance (ATR) sampling accessory on the Nicolet iS10 FT-IR spectrometer (www. thermofisher.com). The NMR spectra (www.bruker.com) were recorded on a Bruker Advance III 400 (9.4 T, 400.13 MHz for ¹H and 100.62 MHz for ¹³C with a 5-mm BBFO probe, at 298 K. Chemical shifts (δ in ppm) are given relative to internal solvent, DMSO- d_6 2.50 for ¹H and 39.50 for ¹³C. Mass spectra were recorded on a Thermo ISO Single Ouadrupole GC-MS. Elemental analyses (www. eurovector.it) were carried out on a EuroVector instrument C, H, N, S analyzer EA3000 Series. Microwave experiments were performed using CEM Discover & Explorer SP microwave apparatus (300 W; www.cem.com), utilizing 35.0 mL capped glass reaction vessels Automated power control based on temperature feedback. Current-vs-voltage (I-V) method (two electrodes composed onto fabricated GCE) was measured for toxic copper ions for TPCBZ/GCE by using Keithley-Electrometer from USA (www.keithley.nl).

2.2. Preparation and fabrication of GCE with TPCBZ

Phosphate buffer solution (PBS, 0.1 M) at pH 7.0 is prepared by mixing of equi-molar concentration of 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 solution in 100.0 mL de-ionize water at room conditions. GCE is fabricated with TPCBZ using 5% ethanolic nafion solution as a

conducting binder. Then it is kept in the oven at 35.0 °C for 2 h until the film is completely dried, stable, and smooth. A cell is assembled with TPCBZ/GCE and Pd-wire as a working and counter electrodes respectively. As received Cu²⁺ solution (10.0 mM) is diluted to make various concentrations (1.0 nM-10.0 mM) in DI water and used as a target analyte. A calibration plot is drawn from the data-point taken (at + 0.5 V) from each I-V curve on respective concentration of Cu²⁺ solution. The ratio of current versus concentration (slope of calibration curve) is used to calculate the Cu^{2+} sensitivity. Detection limit is evaluated from the ratio of 3 N/S (ratio of Noise \times 3 vs. Sensitivity) from the linear dynamic range of calibration curve. Electrometer is used as a constant voltage sources for I-V measurement in simple two electrode system. Amount of 0.1 M PBS was kept constant in the beaker as 5.0 mL throughout the chemical investigation. The TPCBZ is fabricated and employed for the detection of Cu²⁺ in liquid phase. I-V response is measured with TPCBZ/GCE film. The active surface area of TPCBZ/GCE is 0.0316 cm². The electrode assembly is WE (TPCBZ/Nafion/GCE) and CE (Pd-wire) for the detection of cations.

2.3. Preparation of 4-(3-(thiophen-2-yl)-9H-carbazol-9-yl) benzaldehyde (TPCBZ)

It was prepared the target TPCBZ of carbazole derivatives represented in Scheme 1. According to the Scheme 1, the derivatives of carbazole (3, 4, & 5) are explained in details of their characterization by TLC, ¹H NMR, FTIR, Elemental analysis, and ¹³C NMR.

2.3.1. 4-(9H-carbazol-9yl)benzaldehyde (3)

This compound was prepared with a modified method to the reported literature [37] in where the synthesis process was performed using microwave irradiation, the reactants flurobenaldehyde (5.0 mmol) and carbazole (5.0 mmol) were taken in DMF (15.0 ml) and K₂CO₃ (20.0 mmol) was added, The total mixture was placed in a process vial in the microwave, and was irradiated with a power of 300 W to reach a reaction temperature of 130.0 °C under auto generated pressure. The vial was exposed to microwaves irradiation for the appropriate time (2 h) until the starting materials were no longer detectable by TLC (eluent; ethyl acetate/chloroform). Upon completion of the reaction, the reaction mixture poured on ice (30.0 g) an organic fraction was extracted using ethyl acetate (3 \times 20.0 ml), the extract were washed with water dried with anhydrous sodium sulfate and the organic layers were concentrated under reduced pressure to afford yellow solid crystals. The obtained solid product was pure enough and no need for purification. The results of ¹H NMR and ¹³C NMR are presented in below.

¹H NMR (400 MHz, DMSO-*d*₆): δ 7.31–7.36 (m, 4H), 7.56 (d, 2H, *J* = 8.4 Hz), 7.92 (d, 2H, *J* = 8.4 Hz), 8.12–8.21 (m, 4H), 11.73 (s, 1H).

¹³C NMR (100 MHz, DMSO-*d*₆): 108.25, 121.06, 121.84, 123.94, 126.47, 126.98, 130.47, 135.62, 141.57, 144.28, 196.04.

2.3.2. 3,6-dibromo derivative (4)

This compound was obtained by direct bromination via bromin in acetic acid at room temperature [38].

2.3.3. 4-(3-(thiophen-2-yl)-9H-carbazol-9-yl)benzaldehyde (5) (TPCBZ)

Compound 4 (1.0 mmol) and 2-thienylboronic acid (1.5 mmol), Pd (PPh₃)₄ (0.2 mmol), aqueous Na₂CO₃ (2.0 M, 5.0 ml), THF (20.0 ml) and toluene (30.0 ml) were mixed in a flask. The mixture was refluxed for 48 h. After being cooled, a lot of water was added and the mixture was extracted with DCM. The organic phase was dried with MgSO₄. After the solvent was evaporated, the product was processed by column chromatography on silica gel with petroleum ether–acetic ether (20: 1, by volume) to give a yellow power (68% yield). The melting point was measured ($261-263 \degree C$) and characterized by ¹H NMR. The result of ¹H NMR was obtained as below.

¹H NMR (400 MHz, DMSO- d_6) δ : 6.58 (m, 2H), 7.32 (m, 1H), 7.35 (m, 1H), 7.53 (d, 2H, J = 8.2 Hz), 7.58–7.69 (m, 2H), 7.95 (m, 2H), 8.26 (d, 2H, J = 8.2 Hz), 8.68 (s, 1H), 10.20 (s,1H).

3. Results and discussion

3.1. Detection of Cu^{2+} ions with TPCBZ/GCE

The potential application of TPCBZ compound assembled onto GCE as heavy metallic sensor (especially Cu^{2+} analyte in buffer system) has been executed for measuring and detecting target Cu²⁺ ions. The TPCBZ/GCE sensors have facile advantages such as stability in air, non-toxicity, chemical inertness, electro-chemical activity, simplicity to assemble, ease in fabrication, and chemo-safe characteristics. As in the case of Cu^{2+} ions sensor, the current response in I-V method of TPCBZ/GCE considerably changes when aqueous metallic analyte is adsorbed. The TPCBZ/GCE was applied for fabrication of ionic-sensor, where heavy metallic Cu²⁺ ion was measured as target analyte. The fabricated-surface with TPCBZ/GCE sensor was prepared with conducting coating binders (5% nafion) on the GCE surface. The fabricated TPCBZ/GCE electrode was put into the oven at low temperature (45.0 °C) for 2.0 h to make it dry, stable, and uniform the surface totally. I-V signals of Cu^{2+} ion chemical sensor are anticipated having TPCBZ/GCE on thin-film as a function of current versus potential. The resultant electrical responses of target Cu²⁺ ion are investigated by simple and reliable I-V technique using TPCBZ/GCE. The holding time of electrometer was set for 1.0 s. A significant amplification in the current response with applied potential is noticeably confirmed.

The TPCBZ/GCE was employed for the detection of Cu²⁺ ion in liquid phase. I-V responses were measured with TPCBZ/GCE coated thin-film (in two electrodes system). The concentration of Cu^{2+} ion was varied from 1.0 nM to 10.0 mM by adding de-ionized water at different proportions. It is studied the control experiment about the uncoated and nanocomposites-coated electrode using I-V method and presented in Fig. 1. Here, Fig. 1(a) is represented the I-V responses for uncoated-GCE (gray-dotted) and TPCBZ/GCE (greendotted) electrodes. In PBS system, the TPCBZ/GCE electrode shows that the reaction is reduced slightly owing to the presence of TPCBZ on bare-GCE surface. A considerable enhancement of current value with applied potential is demonstrated with fabricated TPCBZ/GCE in presence of target Cu^{2+} ion analyte, which is presented in Fig. 1(b). The light-blue-dotted and deep-blue-dotted curves were indicated the response of the fabricated film after and injecting 25.0 µL Cu²⁺ ion in 5.0 mL PBS solution respectively measured by fabricated TPCBZ/GCE films. Significant increases of current are measured after injection of target component in regular interval.

I-V responses to varying Cu^{2+} concentration (1.0 nM–10.0 mM) on thin TPCBZ/GCE were investigated (time delaying, 1.0 s) and presented in the Fig. 2(a). Analytical parameters (such as sensitivity, detection limit, linearity, and linear dynamic range etc) were calculated from the calibration curve (current vs. concentration), which was presented in Fig. 2(b). A wide range of Cu^{2+} concentration was selected to study the possible detection limit (from calibration curve), which was examined in 1.0 nM–10.0 mM. The sensitivity was calculated from the calibration curve, which was close to ~1.12974 μ Acm⁻² μ M⁻¹. The linear dynamic range of the



TPCBZ

Scheme 1. Synthesis of TPCBZ. Preparation of 4-(3-(thiophen-2-yl)-9H-carbazol-9-yl)benzaldehyde (5), (TPCBZ).

TPCBZ/nafion/GCE sensor was employed from 1.0 nM to 1.0 mM (linearly, r²: 0.9979), where the detection limit was calculated about ~0.84 \pm 0.02 nM (ratio, $^{3N}/_{S}$). In presence of TPCBZ/nafion/GCE layer on electrode, the electrical resistance is decreased under with the target Cu²⁺ in PBS phase. The film-resistance was decreased gradually (increasing the resultant current) upon increasing the Cu²⁺ concentration in bulk system.

In two-electrode system, I-V characteristic of the TPCBZ/GCE is activated as a function of Cu²⁺concentration at room conditions, where improved current response is observed. As obtained, the current response of the TPCBZ-film is increased with the increasing concentration of Cu²⁺; however similar phenomena for cationic detection have also been reported earlier [39-42]. For a low concentration of Cu²⁺in liquid medium, there is a smaller surface coverage of Cu²⁺ ions on TPCBZ/GCE film and hence the surface reaction proceeds steadily. By increasing the Cu²⁺concentration, the surface reaction is increased significantly (gradually increased the response as well) owing to large surface area contacted with Cu^{2+} molecules. Further increase of Cu^{2+} concentration on TPCBZ/ GCE surface, it is exhibited a more rapid increased the current responses, due to larger surface covered by Cu²⁺ chemical. Usually, the surface coverage of Cu^{2+} molecules on TPCBZ/GCE surface is reached to saturation, based on the regular enhancement of current responses.

Selectivity was studied for Cu^{2+} sensor in presence other chemicals like Ag^+ , Au^{3+} , Ca^{2+} , Cd^{2+} , Cu^{2+} , Co^{2+} , Ce^{2+} , Hg^{2+} , Mg^{2+} , Pb^{2+} , Sn^{2+} , Y^{3+} , Ni^{2+} , and Zn^{2+} using the TPCBZ/GCE, which is

presented in Fig. 3(a). The concentrations of heavy metallic analytes are kept constant at 0.1 μ M level in PBS system. From the current response of each individual analytes, it is calculated the percentile of responses at +0.5 V of Ag⁺ (1.3%), Au³⁺ (2.2%), Ca²⁺ (1.7%), Cd²⁺ (2.1%), Cu²⁺ (83.8%), Co²⁺ (2.5%), Ce²⁺ (1.3%), Hg²⁺ (2.0%), Mg²⁺ (1.8%), Pb²⁺ (1.6%), Sn²⁺ (2.6%), Y³⁺ (1.0%), Ni²⁺(1.4%) and Zn²⁺ (0.8%) with TPCBZ/GCE sensors. Here, it is clearly demonstrated the TPCBZ/GCE electrode sensor is most selective toward Cu²⁺ (83.8%) compared with other heavy cationic components.

To check the reproducibly and storage stabilities, I-V response for TPCBZ/GCE sensor was examined and presented in Fig. 3(b). After each experiment (each runs), the fabricated TPCBZ/GCE substrate was washed thoroughly with the phosphate buffer solution and observed that the current response was not significantly decreased. Here it is observed the current loss in each reading is negligible compared to initial response of sensors using TPCBZ/GCE. A series of eight successive measurements of 0.1 μ M Cu²⁺ in 0.1 M PBS yielded a good reproducible signals at TPCBZ/nafion/GCE sensor with a relative standard deviation (RSD) of 1.6%. The sensitivity was retained almost same of initial sensitivity up to seven days, after that the response of the fabricated TPCBZ/nafion/GCE electrode gradually decreased. The Cu²⁺ sensor based on TPCBZ/ GCE is displayed good reproducibility and stability for over week and no major changes in sensor responses are found. After a week, the cationic Cu²⁺ sensor response with TPCBZ/GCE was slowly decreased, which may be due to the weak-interaction between fabricated TPCBZ/nafion/GCE active surfaces and Cu²⁺ ions.



Fig. 1. Study of control experiment. I-V responses of (a) bare-GCE and TPCBZ/GCE, (b) TPCBZ/GCE (in absence), and TPCBZ/nafion/GCE (in presence) of Cu²⁺ in the solution system.



Fig. 2. Analysis of Cu²⁺ cationic responses. I-V responses of (a) concentration variations (1.0 nM–10.0 mM) of Cu²⁺ ions and (b) calibration plot of TPCBZ fabricated GCE electrode (at +0.5 V).

Current-voltage behaviors of the TPCBZ are activated as a function of Cu²⁺ ions concentration at room conditions, where the improved current response is observed. The possible complexation bonding mechanism between Cu(II) and TPCBZ is explained here in Fig. 4. As obtained, the current response of the TPCBZ-film is increased (π - π ^{*} interaction) with the increasing concentration of Cu²⁺ ions in the bulk solution, however similar phenomena for toxic chemical detection have also been reported earlier [43-47]. For a low concentration of Cu^{2+} ions in buffer medium, there is a smaller surface coverage of Cu^{2+} ions on TPCBZ/nafion/GCE film (Fig. 4(a)) and hence the surface reaction proceeds steadily. By increasing the Cu^{2+} ions concentration, the surface reaction is increased significantly (gradually increased the response) due to surface area (assembly of TPCBZ/Nafion/GCE) contacted with bulk Cu^{2+} ions molecules (Fig. 4(b)). Further increase of Cu^{2+} ions concentration on TPCBZ/Nafion/GCE surface, it is exhibited a more rapid increased the current responses, due to larger area covered by Cu^{2+} ions and the π - π interaction of the functional groups. The π - π interaction could be approaches as inter-molecular interactions of the TPCBZ [48]. Usually, the surface coverage of Cu^{2+} ions on TPCBZ/ Nafion/GCE surface is reached to saturation, based on the regular enhancement of current responses (Fig. 4(c)).

The significant result was achieved by TPCBZ/GCE, which can be employed as proficient electron mediators for the development of efficient cationic sensors. Actually the response time was around 10.0 s for the fabricated TPCBZ/GCE to reach the saturated steadystate level. The higher sensitivity of the fabricated TPCBZ/GCE could be attributed to the excellent absorption (porous surfaces in TPCBZ/nafion/GCE), adsorption ability, and high catalyticdecomposition activity of TPCBZ. The estimated sensitivity of the fabricated sensor is relatively higher and detection limit is comparatively lower than previously reported chemical sensors based on other nano-composites or nano-materials modified electrodes measured by I-V systems [49-57]. Due to high specific surface area, TPCBZ provides a favorable nano-environment for the Cu²⁺ detection with good quantity. The modified TPCBZ/GCE sensor has also better reliability and stability. The higher sensitivity of TPCBZ/GCE provides higher electron communication features



Fig. 3. Optimization of TPCBZ/GCE sensors. (a) Selectivity study with various analytes by TPCBZ/GCE electrodes. (b) Reproducibility study with analytes using TPCBZ/GCE electrodes. I-V responses of all reproducible signals (Run-1 to Run-8) with Cu²⁺; Analyte concentration was taken at 0.1 μM; Potential range: 0 to +1.5 V; Delay time: 1.0 s.

which enhanced the direct electron transfer between the active sites of TPCBZ and nafion-coated-GCE. The TPCBZ/GCE system is demonstrated a simple and reliable approach for the detection of toxic heavy metallic cations. It is also revealed that the significant access to a large group of cations chemicals for wide-range of ecological and biomedical applications in environmental and health-care fields respectively.

binders onto GCE by electrochemical approaches, which displayed higher sensitivity and selective Cu²⁺ sensing applications. The analytical performances of the fabricated Cu²⁺ sensors are excellent in terms of sensitivity, detection limit, linear dynamic ranges, and selectivity in short response time. TPCBZ/GCE assembly is exhibited higher-sensitivity (1.12974 μ Acm⁻² μ M⁻¹) and lower-detection limit (~0.84 \pm 0.02 nM) with good linearity in short response time, which efficiently utilized as a cationic-sensor for selective Cu²⁺ onto TPCBZ/GCE via, conjugated complex formation. This novel approach is introduced a well-organized route of efficient heavy metallic cationic sensor development for environmental pollutants and health-care fields in broad scales.

4. Conclusions

TPCBZ has been prepared using simple adsorption techniques. It is fabricated a heavy metallic sensor with the conducting coating



Fig. 4. Schematic representation of Cu²⁺ interaction onto TPCBZ/Nafion/GCE electrode. Mechanism of the probable interaction of Cu²⁺ with TPCBZ with conducting nafion binders embedded onto flat-GCE. (a) Fabricated electrode, (b) Π-Π inter-molecular bonding interactions between lone-pair of nitrogen (TPCBZ) and Cu²⁺, and (c) I-V responses of fabricated TPCBZ/Nafion/GCE electrode.

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