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Efficient electro-chemical sensor for sensitive Cd^{2+}detection based on novel in-situ synthesized hydrazonoyl bromide (HB)

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ABSTRACT

In this approach, an efficient methodology for synthesis of a novel hydrazonoyl bromide (HB) containing trifluoromethyl moiety by using fluorine-containing building blocks was achieved. The synthesized HB was fully characterized with various methods such as Infra-red spectroscopy (IR), Thin layer chromatography (TLC), ^{1}H NMR, ^{19}F-NMR, ^{13}C NMR, and elemental analyses. In-situ potential examination as reliable technique, an electrochemical sensor based on prepared HB was used for the selective detection of environmental hazardous heavy metal ion, Cd^{2+}. The fabricated sensor was found to perform linearly over the concentration range (linear dynamic range) of 0.1 nM~0.01 mM of Cd^{2+} ion and the sensitivity (51.12 $\mu A \mu M^{-1} cm^{-2}$) and detection limit (53.85±2.69 pM) of the proposed sensor were estimated from the slope of calibration curve (plot of current versus concentration). Furthermore, the proposed Cd^{2+} ion sensor was exhibited good analytical performances such reproducibility, stability in phosphate buffer medium and efficiency to detect Cd^{2+} ion in real environmental samples. This progress in the field of metal ion sensor development might be a cost effective and efficient method in the detection of unsafe and hazardous ions for the safety of environmental and ecological fields in broad scales.

1. Introduction

A plethora of heterocyclic biologically active molecules has been much reported in literature synthesized via utilization of Hydrazonoyl halides [1–6]. Our previous research work has described the utility of Hydrazonoyl halides as quite reactive polyfunctional reagents in the synthesis of a variety of novel heterocyclic systems as pyrazoles and isoxazoles [7–10]. An introduction of trifluromethyl group into Hydrazonoyl bromide will help to find novel synthons of wide applications and utilization in chemistry field. Especially The highest impact of fluorine in life sciences is associated with the development of agrochemicals and pharmaceuticals [11–13]. The fact that fluorinated organic compounds and materials often show unusual physical, chemical, and/or biological properties and behavior (in comparison with their nonfluorinated counterparts) is often called "fluorine effects" or "fluorine magic" [13,14]. Therefore we intend here to synthesize novel hydrazonyl bromide containing trifluromethyl moiety identified as 2-oxo-2-phenyl-N-(4-(trifluoromethyl)phenyl)acetohydrazonoyl bromide. Meanwhile, design and development of sensor molecules for recognition and sensing of cationic analytes are of major interest since cations may be hazard and need to be detected easily [15,16]. Cadmium (Cd) is one of these elements, which element is existing in group IIB of periodic table and the toxicity of it is well known [17–19]. Due to chloric exposure of Cd^{2+} in human and animals, it is accumulated in the liver, lungs and kidney and results renal tubular dystunction, emphysema, osteoporosis and osteomala-

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cia [20,21]. It is also responsible to pathological change of central nervous system and finally the damage [22]. The various reports have been claimed that the toxicity of cadmium is destroy the soil ecosystem due to killing of microorganisms which are necessary for fertility of soil [23]. Globally, the significant amount of cadmium is accumulated in environment due to number of anthropogenic and man making activities. Industrially, Cd is widely used as anticorrosive agent, to stabilize PVC goods, pigment in cooler, in batteries and fertilizers [24–26]. There is a great possibility to affect human and animals with toxicity of Cd^{2+} ion through food chain. Thus, it is very important to check Cd^{2+} ion contamination of environment with a reliable method. The existing methods to detection of Cd^{2+} ions are atomic absorption [27], ICP-ES (inductively coupled plasma-optical emission spectrometry) [28] and ICP-MS (inductively coupled plasma-mass spectroscopy) [29]. But these methods are uncomforted with expensive, large and heavy instruments, time consuming and unfavorable for in-situ detection. Recently, a number of researches based on electrochemical approach are efficiently executed to overcome these drawbacks [30–33]. Thus, this study will be reported the synthesis of new compound based on the hydrazonyl bromide backbone scaffold bearing trifluromethyl moiety (HB). Furthermore, In this study, the desired Cd^{2+} metal ion sensor was fabricated using a GCE coated with prepare HB as thin uniform layer and applied to detect Cd^{2+} ion in phosphate buffer medium. The analytical performances of sensor prove were inspected in detail in-term of sensitivity, reproducibility, stability, efficiency, linear dynamic range and detection limit. Besides this, it was effectively to measure Cd^{2+} ion real environmental samples successively. Thus, this effectual process to development of heavy metal ion sensor might be a most reliable methodology in approaching future.

2. Experimental

2.1. Reagents and methodology

All organic solvents were purchased from commercial sources and used as received unless otherwise stated. From Sigma-Aldrich (USA), the analytical grade cobalt (II) nitrate, barium (II) nitrate, magnesium (II) chloride, silver nitrate, arsenic (III) chloride, zinc sulfate, cadmium sulfate, mercury (II) chloride, chromium (III) chloride and aluminum sulfate were procured and used without farther any treatment. The other sub-ordinary chemical such as NH_3, nafion (5% nafion suspension in ethanol), monosodium and disodium phosphate buffer were implemented to fulfill this study. All other chemicals were purchased from Merck, Aldrich or Acros and used without further purification. Thin-layer chromatography (TLC) was performed on pre-coated Merck 60 GF254 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, which is an ultra-high-performance, versatile Attenuated Total Reflectance (ATR) sampling accessory on the Nicolet iS10 FT-IR spectrometer. The NMR spectra were recorded on a Bruker Avance III 400 (9.4 T, 400.13 MHz for ^{1}H, 100.62 MHz for ^{13}C and 376.25 MHz for ^{19}F) spectrometer 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 ^{1}H and 39.50 for ^{13}C. Mass spectra were recorded on a Thermo ISQ Single Quadrupole GC–MS. Elemental analyses were carried out on a EuroVector instrument C, H, N, S analyzer EA3000 Series. dimethylphenacylsulfonium bromide **(2)** [34] and *N*-nitroso-*N*-(4-(trifluoromethyl)phenyl)acetamide **(4)** [35] were prepared according to reported literature. For electrochemical analysis, the Keithley electrometer (Model: 6517B, USA) was used to find the sensor parameters.

2.2. Synthesis of 2-oxo-2-phenyl-N-(4-(trifluoromethyl)phenyl)acetohydrazonoyl bromide (5)(HB)

Method A: To stir the solution of dimethylphenacylsulfonium bromide **(2)** (50.0 mmol) in ethanol (250.0 ml), it was added the sodium acetate trihydrate (12.0 g) into the reactor. After stirring for 10 min, the mixture was cooled to −5 °C as well as treated with 4-(trifluoromethyl)benzen diazonium salt solution [prepared by diazotizing 4-(trifluoromethyl)aniline (50 mmol) in hydrochloric acid (6.0 M, 6.0 ml) with sodium nitrite solution (3.5 g, 50.0 mmol), in H_2O (15.0 ml)]. The addition of the diazonium salt was carried out with rapid stirring over the period of 60 min. Later the reaction mixture was stirred for further 2 h at 0 °C and then left for 6 h at 4 °C into the refrigerator. The resulting solid precipitate was collected by filtration, washed thoroughly with water, then finally dried. The crude solid product was crystallized from ethanol to afforded 9.5 g (70% yield) of 2-oxo-2-phenyl-N-(4-(trifluoromethyl)phenyl)acetohydrazonoyl bromide.

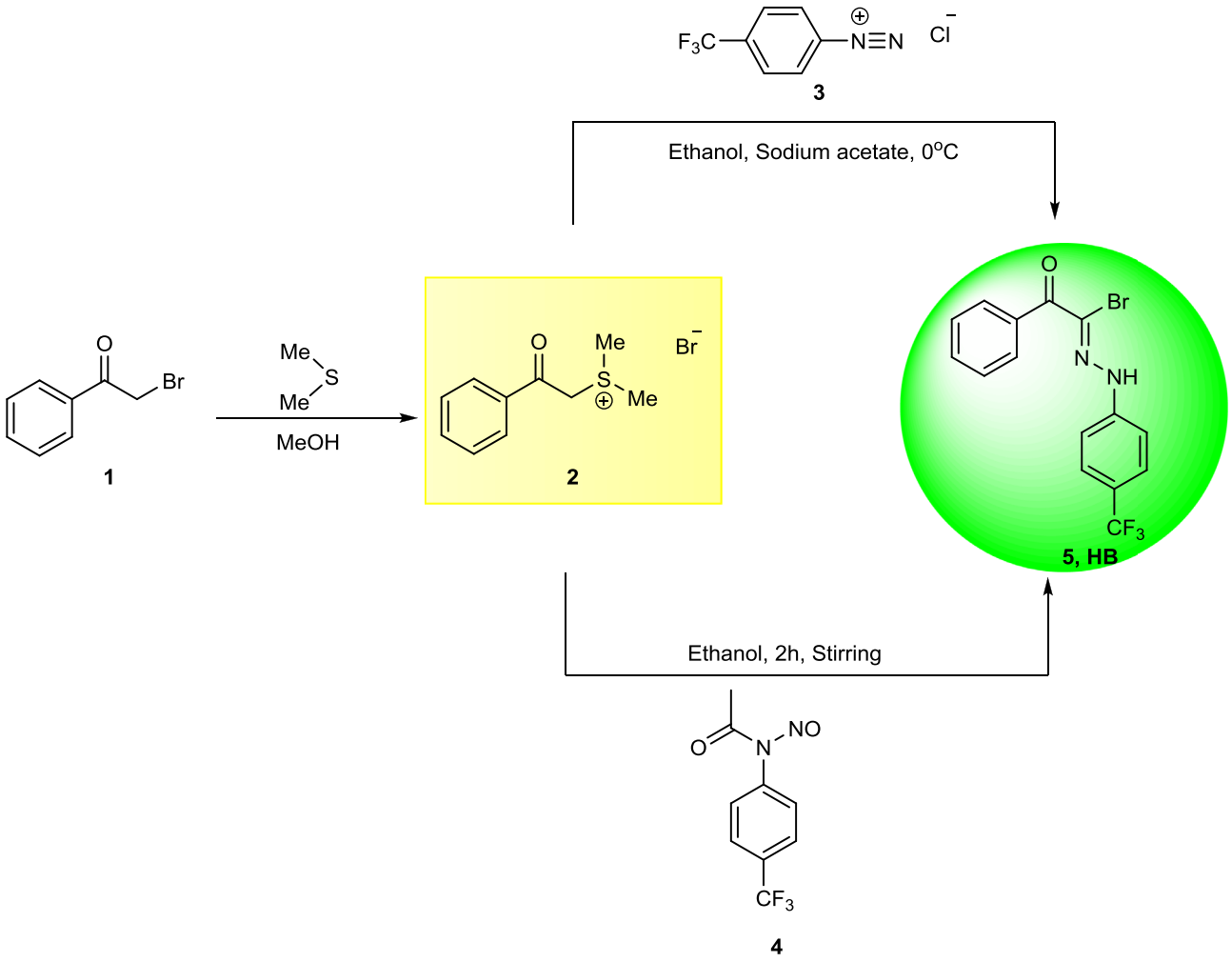
Method B: To a solution of dimethylphenacylsulfonium bromide **(2)** (10 mmol) in ethanol (50.0 ml), it was added with the *N*-nitroso-*N*-(4-(trifluoromethyl)phenyl)acetamide **(4)** (10 mmol). The reaction mixture was warmed slightly and shaken till complete dissolution of the reactants, then finally continuously stirred for 4 h. The precipitated crystalline product was collected, washed with methanol and re-crystallized from ethanol to afford compound with identical in all respects to those synthesized by method A. Finally the product is fully characterized and analyzed for melting point, mixed melting points, IR spectroscopy, and ^{1}H NMR spectrum.

The physical data of the synthesized compound are listed below:

orange solid; mp 157–159 °C; IR (KBr) ν/cm^{-1}: 3320 (NH), 1702(CO), 1601 ($C = N$);^{1}H NMR (DMSO–d_6): δ7.41–7.43 (m, 3H, ArH), 7.65–7.69 (m, 4H, ArH), 7.92–7.94 (m, 2H, ArH), 11.18 (br s, 1H, NH, D_2O exchangeable);^{13}C NMR (DMSO–d_6): δ 117.0,120.1(q, $^2J_{CF}$ = 32.93 Hz), 124.2 (q, $^1J_{CF}$= 270.10 Hz), 126.14 (q, $^3J_{CF}$ = 6.55 Hz), 128.65,129, 134.32, 137.85, 146, 164, 185;^{19}F NMR (DMSO–d_6): δ −61.21; MS (*m/z*): 369 (M^+); $C_{15}H_{10}BrF_3N_2O$: Anal. Calcd: C, 48.54; H, 2.72; N, 7.55. Found C, 48.79; H, 2.64; N, 7.39%.

2.3. Modification of glassy carbon electrode (GCE) using HB

The modification of GCE (Surface area: 0.0316 cm^2) is the most important task of this study before development of sensor HB/GCE probe. Using ethanol, the prepared HB was subjected to make thicker slurry and was to deposit onto the flat part of GCE as thin uniform layer. Then, it was kept at laboratory conditions to dry and smooth the fabricated film completely. To bringing the stability of modified GCE during the electrochemical analysis in phosphate buffer medium, a drop of 5% nafion (1.0 μL) was added on GCE and put inside a low temperature oven at 35 °C temperature to dry. After complete the modification of GCE, an electrochemical cell was arranged with Keithley electrometer, the modified GCE was used as working and a simple Pt-wire as counter electrode respectively. A series of Cd^{2+} ion solution ranging the concentration as 0.1 nM ~ 0.01 mM were prepared in deionized water and used as desired analyte. A curve known as calibration was plotted as current versus concentration of Cd^{2+} ion relation. The slope of resulted calibration curve was used to estimate the sensitivity and detection limit (DL) of desired Cd^{2+} ion electrochemical sensor. Considering the maximum linear segment in calibration curve, the linear dynamic range (LDR) was identified and related all analytical parameters were also calculated from this range.



Scheme 1. Synthesis of HB by using fluorine-containing building blocks methodology.

3. Results and discussion

The new hydrazonoyl bromide **5** were prepared by coupling of dimethylphenacylsulfonium bromide **(2)** with diazotized 4-(trifluoromethyl)aniline **3** in ethanol solution buffered with sodium acetate or with N-nitroso-N-(4-(trifluoromethyl)phenyl)acetamide **(4)** in ethanol (Scheme 1).

Noteworthy, several attempts at direct coupling of 2–bromo–1-phenylethan-1-one **(1)** with diazonium salt of 4-(trifluoromethyl)aniline **3** and *N*-nitrosoacetarylamides were failed (Scheme 1). This may be due to the extreme acidity of α-hydrogen that present in β-ketosulfonium salt **2**, which make the sulfonium susceptible for electrophilic substitution reaction.

Structure of compound **5** (HB) was confirmed on bases of elemental analysis and spectral data, in which the IR show presence of one band due to NH group at 3312 cm^{-1} in addition to two bands at 1702 and 1601 cm^{-1} due to carbonyl and $C = N$ respectively. The ^{1}H NMR of compound **5** shows a D_2O exchangeable singlet signal at δ11.18 in addition to multiple signals δ 7.41–7.95 due to nine protons of aromatics. In addition, the ^{19}F NMR spectrum is the key analysis in research that deals with fluorine chemistry. ^{19}F NMR of compound 5 shows only the signal of trifluoromethyl group was observed at δ–61.21 ppm, and always C-F coupling of compounds that contain fluorine was used to study it. The ^{13}C NMR of compound **5** shows that the ^{19}F-decoupled ^{13}C NMR spectrum of 5. A characteristic quartet signal related to the CF_3 group was found at approximately δ 124.13 ppm with $^{1}J_{CF}$ 273.70 Hz, and a quartet signal related to C-4′ was observed at approximately δ133.46 ppm with $^{2}J_{CF}$ 31.78 Hz and at δ126.38 ppm with $^{3}J_{CF}$ 3.75 Hz. Fluorinated carbons are often difficult to find in ^{13}C spectra with low signal-to-noise ratios because the signal is spread over multiple lines and can be buried in the noise. The presence of C-F coupling added sharp evidence for the proposed structure of the formed compound **5 (HB)**.

3.1. Detection of Cd^{2+} by HB

The potential application of synthesized HB onto GCE was to development of an electrochemical sensor selective to Cd^{2+} cation. As it was described, the prepared HB was deposited on the flat part of GCE with conductive nafion binder. The conductive nafion was used to improve both the binding strength and electron transfer rate of working electrode. Thus, the fabricated sensor shows long-term stability in phosphate buffer medium and enhanced activity during electrochemical analysis. Firstly, the assembled electrochemical sensor with HB/binder/GCE was implemented to measure the selectivity and to execute this performance, the heavy metal ions such as Co^{2+}, Ba^{2+}, Mg^{2+}, Ag^{+}, As^{3+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cr^{3+} and Al^{3+} were analyzed at 0.1 µM concentration of each metal ion and applied potential 0 ~ +1.5 V as illustrated in Fig. 1(a). As it is perceived in Fig. 1(a), the cadmium (Cd^{2+}) ion shows the high-

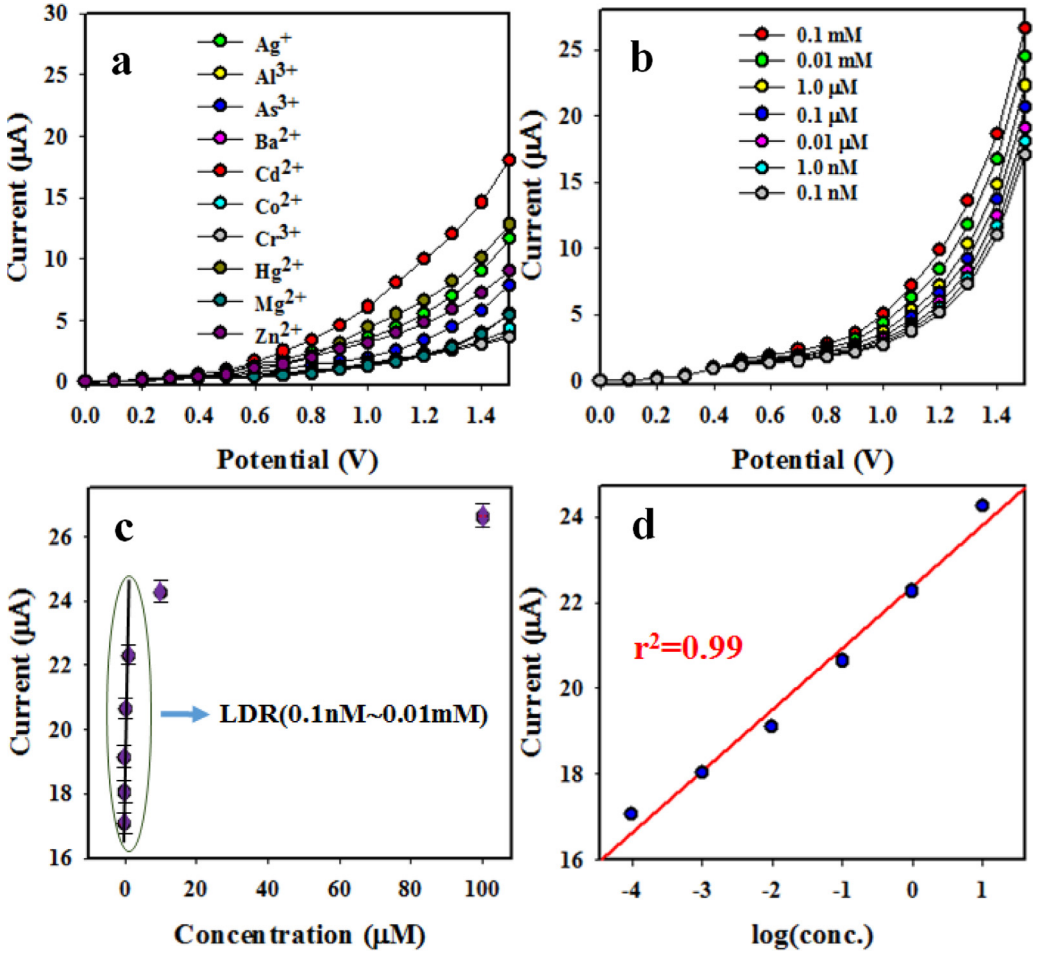


Fig. 1. The electrochemical analysis of propped sensor to fix its properties and performances. (a) Evaluation of selectivity, (b) electrochemical response based on concentration variation of Cd^{2+} ion from lower to higher, (c) calibration of Cd^{2+} ion sensor based on HB/binder/GCE, and (d) computation of the LDR.

est electrochemical response among all the metal ions. Then, the electrochemical responses of Cd^{2+} ion were investigated lower to higher concentration as represented in Fig. 1(b). From Fig. 1(b), it is clearly stated that I-V responses can be distinguished from lower to higher concentration of Cd^{2+} ion. Thus, it can be predicted that I-V responses are varied with the corresponding concentration of Cd^{2+} ion. To estimate the sensor analytical performances such as sensitivity, linear dynamic range and detection limit, it is necessary to make calibration. Thus, a relation of current vs. concentration of Cd^{2+} ion was established as demonstrated in Fig. 1(c). To establish this calibration, the current data are isolated from Fig. 1(b) at applied potential +1.5 V and plotted against the corresponding concentration of Cd^{2+} ion. As it is perceived in Fig. 1(c), the current data are contentiously distributed from 0.1 nM to 0.01 mM in linear manner and this range of concentration is identified as linear dynamic range (LDR). Obviously, the resulted LDR is a wider range of concentration. To, verify the linearity of LDR, the current vs. log (conc.) are plotted as in Fig. 1(d) and the current data are fitted with the regression co-efficient value r^2=0.99, provides the information about the linearity of LDR.

The sensitivity of projected Cd^{2+} cation sensor based on HB/binder/GCE is calculated using the slope of calibration curve and resulted sensitivity is equal to 51.12 $\mu A \mu M^{-1} cm^{-2}$, is a satisfactory sensitivity. The detection limit (53.85 ± 2.69 pM) is estimated at signal to noise ratio of 3, a result might be appreciably lower limit of detection. The response time of an electrochemical sensor is an efficiency measuring performance. This test was executed with 0.1 μM concentration of Cd^{2+} ion in phosphate buffer medium illustrated in Fig. 2(a).

As it is recorded, the Cd^{2+} cation sensor based on HB/binder/GCE shows an appreciable response time around 18.0 s. Thus, this 18.0 s. is required by proposed electrochemical sensor to complete an electrochemical response. The capability to reproduce the similar electrochemical responses in identical conditions is a reliability measuring analytical performance. As it is demonstrated in Fig. 2(b), the seven runs are completely identical and undistinguished and the intensity of electrochemical responses are not altered even the washing of electrode after each trail. This test was experimented with 0.1 μM concentration of Cd^{2+} ion and potential ranging as 0 ~ +1.5 V. The precession of current data at potential +1.5 V was measured and in-term of relative standard deviation, it is equal to 1.10%, a result provides information about high precision. From the outcome of reproducibility performance, it is clear that the projected Cd^{2+} ion sensor is capable to measure Cd^{2+} ion preciously in an identical conditions. Since, this sensor probe will perform in phosphate buffer medium, the stability is very important. Thus, the stability of this Cd^{2+} ion was inspected by reproducibility performance for elongated period of time around seven days as represent in Fig. 2(c). The similar observation as in Fig. 2(b) is found. The comparison with similar study is presented in the Table 1 [36,37] to check the validity of this newly fabricated HB/Nafion/GCE sensor probe. As it is apparent from Table 1, the comparison is executed based on the analytical performance of electrochemical sensor [36–41] such as sensitivity, LDR and DL and

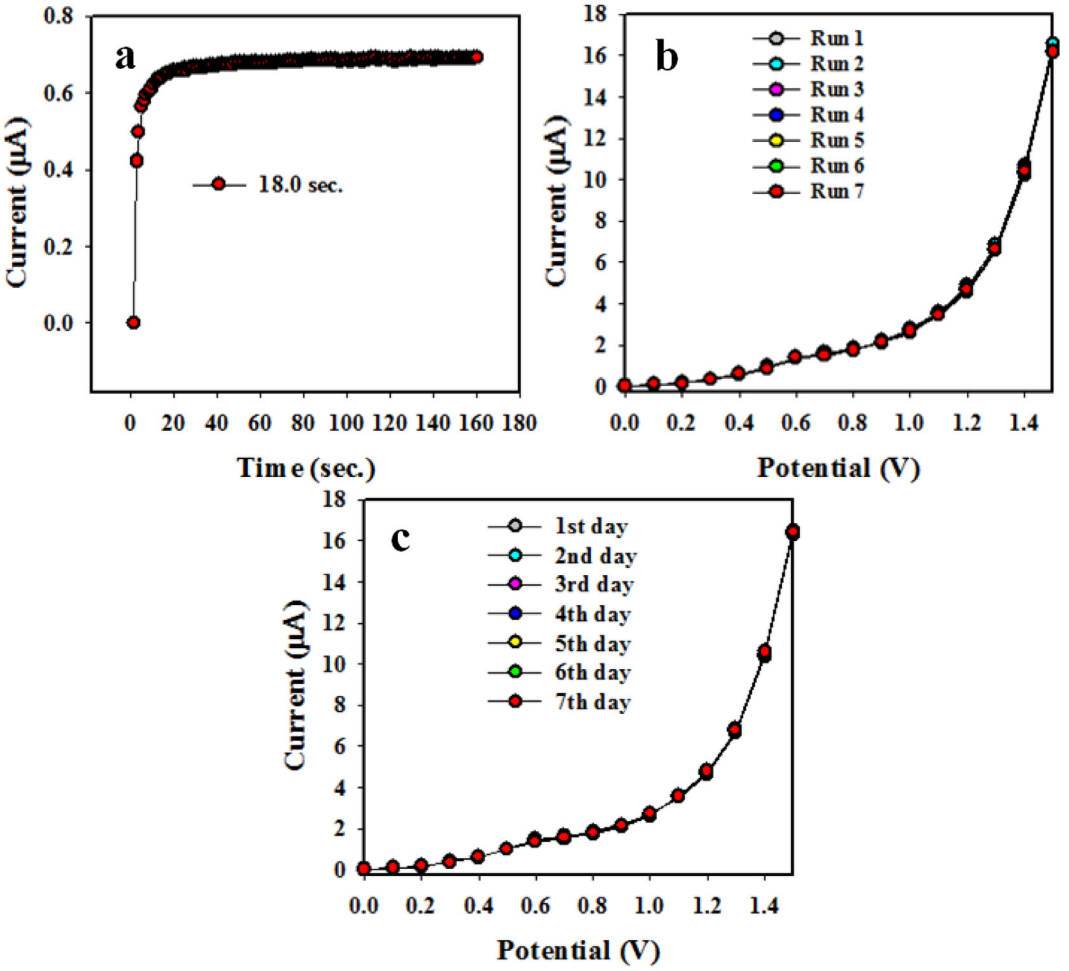


Fig. 2. Optimization of HB/Nafion/GCE sensor probe by electrochemical mehtod. (a) Response time, (b) reproducibility, and (c) stability.

Table 1
Comparison of analytical performances of Cd^{2+}cationic sensor by electrochemical method with HB/Nafion/GCE sensor probe.

Modified GCE	*DL	#LDR	Sensitivity	Ref.
MPEBSH/GCE	140.0 pM	0.35 nM – 0.35 mM	2.22 μAμM^{-1}cm^{-2}	[36]
BZNA/GCE	32.4 pM	0.1 nM – 0.1 mM	2.93 μAμM^{-1}cm^{-2}	[37]
ZnYCdO/NafionlGCE	17.39 pM	0.1 nM – 0.1 mM	5.459 μAμM^{-1}cm^{-2}	[38]
Poly(N-Methylaniline) $Ce_2(WO_4)_3$@CNT	0.11 nM	1.0 nM – 1.0 mM	5.138 μAμM^{-1}cm^{-2}	[39]
Mesoporous silica	0.33 μg/L	–	–	[40]
ZnO nanosheets	–	0 to 150.0 mg L^{-1}	–	[41]
HB/Nafion/GCE	53.85 pM	0.1 nM - 0.01 mM	51.12 μAμM^{-1}cm^{-2}	This work

*DL (detection limit)
..#LDR (linear dynamic range), pM (picomole), mM (millimole).

the Cd^{2+} cation sensor with HB/binder/GCE shows the appreciable performances. The sensitivity of this HB/Nafion/GCE sensor probe shows the highest value compared to reported sensor in similar electrochemical methods.

In this approach, current-voltage behaviors of the HB are activated as a function of Cd^{2+} ions concentration at room conditions, where improved current response is observed. The possible complexation bonding mechanism between Cd(II) and HB is explained here in Fig. 3. As obtained, the current response of the HB-film is increased (π-π^* interaction) with the increasing concentration of Cd^{2+} ions in the bulk solution, however similar phenomena for toxic chemical detection have also been reported earlier [42–47]. For a low concentration of Cd^{2+} ions in buffer medium, there is a smaller surface coverage of Cd^{2+} ions on HB/nafion/GCE film (Fig. 3a) and hence the surface reaction proceeds steadily. By increasing the Cd^{2+} ions concentration, the surface reaction is increased significantly (gradually increased the response as well) due to surface area (assembly of HB/Nafion/GCE) contacted with Cd^{2+} ions molecules (Fig. 3b). Further increase of Cd^{2+} ions concentration on HB/Nafion/GCE surface, it is exhibited a more rapid increased the current responses, due to larger area covered by Cd^{2+} ions and the π-π interaction of the functional groups in HB. The π-π interaction could be approaches as inter-molecular and intra-molecular interactions of the HB [48]. Usually, the surface coverage of Cd^{2+} ions on HB/Nafion/GCE surface is reached to saturation, based on the regular enhancement of current responses (Fig. 3c).

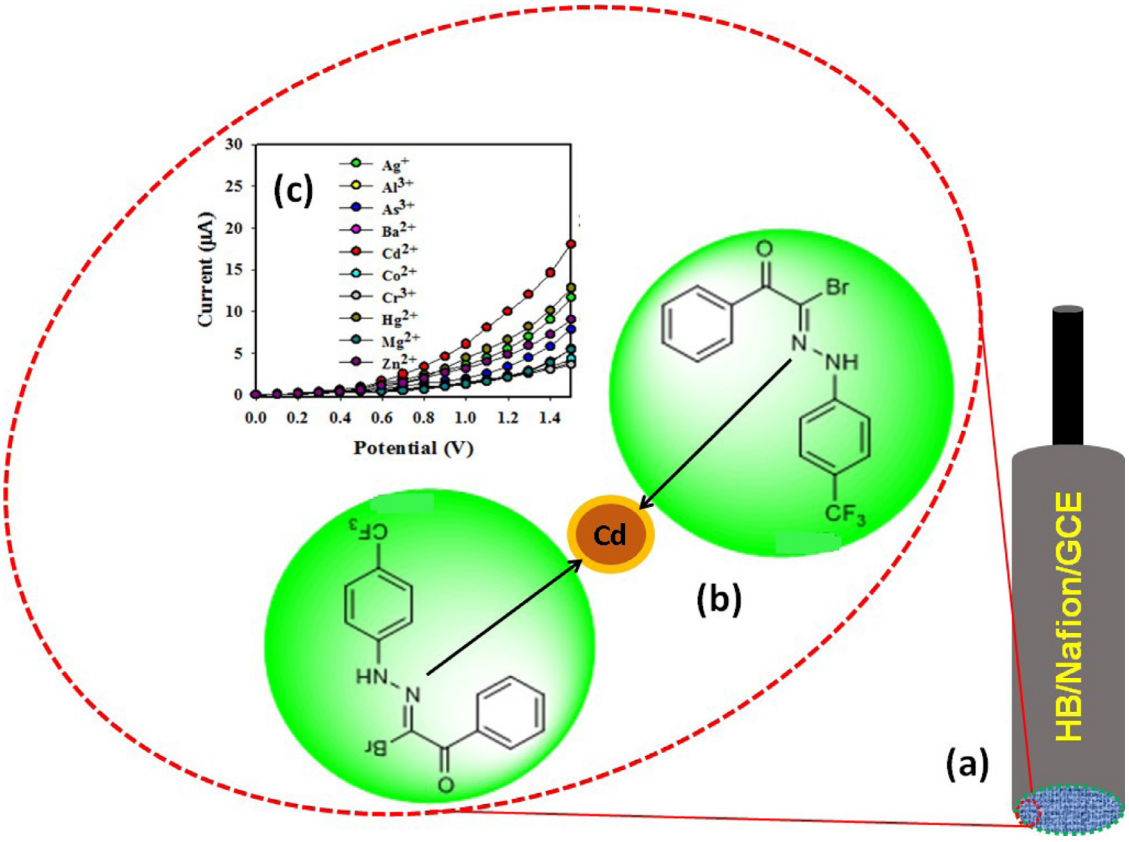


Fig. 3. Schematic representation of Cd^{2+} interaction onto HB/Nafion/GCE electrode. Sensing mechanism of the probable interaction of $Cd^{2+}$with HB with conducting 5% nafion binders embedded onto flat-GCE. (a) Fabricated GCE electrode, (b) Π-Π inter-molecular bonding interactions between lone-pair of nitrogen (HB) and Cd^{2+}, and (c) Electrochemical responses of fabricated HB/Nafion/GCE electrode.

Here, the significant result was achieved by HB/Nafion/GCE, which can be employed as efficient electron mediators for the development of efficient cationic sensors. Actually the response time was around 18.0 s for the fabricated HB/Nafion.GCE to reach the saturated steady-state level. The higher sensitivity of the fabricated HB/Nafion/GCE toward selective Cd^{2+} could be attributed to the excellent absorption (porous surfaces in HB/Nafion/GCE), adsorption ability and high electro-catalytic activity of HB compared to other cations. 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 electrochemical sensors [49–57]. Due to high specific surface area, HB provides a favorable nano-environment for the Cd^{2+} detection with good quantity. The modified HB/Nafion/GCE sensor has also better reliability and stability. The high sensitivity of HB/Nafion/GCE provides high electron communication features which enhanced the direct electron transfer between the active sites of HB and coated-GCE [58–76]. The HB/Nafion/GCE system is demonstrated a simple and reliable approach for the detection of toxic cations. It is also revealed that the significant access to a large group of cations for wide-range of ecological and biomedical applications in environmental and health-care fields respectively [77–87]. In presence and absence of target analyte (Cd^{2+}), the HB/Nafion/GCE sensor is measured and included in the Fig. 4a. The potential interference effect from the typical inorganic ions and organic compounds during this Cd^{2+} detection was studied and presented in Fig. 4b. Obtained results indicate that 10-folds of Na^{+}, Fe^{2+}, Ba^{2+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}, CO_3^{2-}, ethanol, methanoic acid, and ethanoic acid have negligible interfering effect with cadmium ion by HB/Nafion/GCE sensor probe in electrochemical process in the detection of 0.1 μM Cd^{2+}. From this observation, it is concluded that HB/Nafion/GCE sensor probe has no interfering effect during detection unsafe cadmium ion by electrochemical approach at room conditions. Finally, the analytical performances of Cd^{2+} ions using HB/Nafion/GCE sensor probe are investigated by reliable electrochemical method in terms of sensitivity and detection limit in short response time as well as reproducibility. This extensive research is performed in terms of preparation and characterization of HB and applied for the Cd^{2+} ions sensor using electrochemical method. From this novel sensor probe development, it informs the highest selectivity and fast detection for environmental carcinogenic heavy metal cadmium ion to the HB-fabricated-GCE-probe. Potentially, the same concept might be applied to the fabrication of new sensor probes with various composites or polymers for monitoring other environmentally unsafe cationic heavy metal ions [88–96]. Hence, this approach is introduced a new route for an efficient heavy cationic sensor probe development for the safety of environmental and healthcare fields in a broad scales.

3.2. Real environmental samples analyses by HB/Nafion/GCE sensor probe

The electrochemical sensor based on HB/Nafion/GCE was investigated to detect the Cd^{2+} ion in real environmental samples in recovery method by using electrochemical technique. The samples are collected from the underground mineral water, municipal water and read sea water. The analyzed data by electrochemical method are calculated and represented in Table 2. As it is obtained from Table 2, the outcomes are acceptable and satisfactory. Therefore, it can be concluded that the proposed Cd^{2+} ion sensor with HB/Nafion/GCE sensor probe by electrochemical technique is able

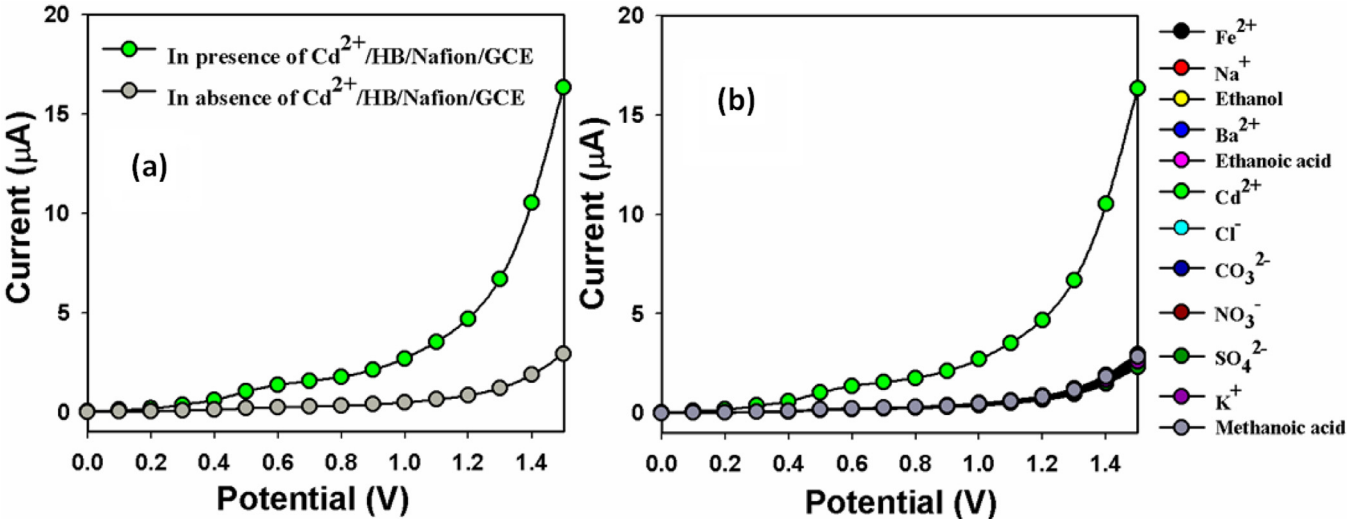


Fig. 4. Sensing performance of HB/Nafion/GCE sensor in the absence and presence of other ions by electrochemical approach. (a) Control experiment (in presence and absence of Cd^{2+} ion) and (b) Interfering effect of various inorganic and organic components.

Table 2
Analyses of real environmental samples with HB/Nafion/GCE sensor by electrochemical method.

Sample	Added Cd^{2+} ion conc. (μM)	Determined Cd^{2+}conc.[a] by HB/Nafion/GCE (μM)			Average recovery[b] (%)	RSD[c] (%) ($n = 3$)
		R1	R2	R3		
Tape water	0.01000	0.00964	0.00953	0.00969	96.20	0.85
Sea water	0.01000	0.00977	0.01018	0.01040	101.17	3.16
Mineral water	0.01000	0.00970	0.00940	0.00924	94.47	2.47

[a] *Mean of three repeated determination (signal to noise ratio 3) with by HB/Nafion/GCE.*
[b] *Concentration of Cd^{2+} ion determined/Concentration taken. (Unit: μM).*
[c] *Relative standard deviation value indicates precision among three repeated measurements(R1,R2,R3).*

to detect the selective Cd^{2+} reliably in real samples obtained from various sources.

4. Conclusion

We found that the versatile fluorine-containing building blocks such diazonium salt of 4-(trifluoromethyl)aniline or N-nitroso-N-(4-(trifluoromethyl)phenyl)acetamide (1) are useful for the synthesis of novel hydrazonoyl bromide containing a trifluoromethyl moiety (HB). The structure of the HB was confirmed via elemental and spectroscopic analyses. The proposed Cd^{2+} cation electrochemical sensor was fabricated as HB/binder/GCE and implemented to detect selective Cd^{2+} ion in phosphate buffer medium successfully. The analytical performances such as sensitivity, LDR, DL, response time, reproducibility and stability were calculated and found as satisfactory. In real time application, it showed excellent performance to detect selective Cd^{2+} ion in real environmental samples by HB/binder/GCE sensor probe in electrochemical method. It is introduced a noble route to detect the carcinogenic heavy metal ions, Cd^{2+} by using fabricated HB/binder/GCE sensor probe using electrochemical method for the safety of environmental and healthcare fields in large scales.

Declaration of Competing Interest

I declare the following states, The article is original, The article has been written by the stated authors who are ALL aware of its content and approve its submission, The article has not been published previously, The article is not under consideration for publication elsewhere, and No conflict of interest exists.

CRediT authorship contribution statement

Faisal M. Aqlan: Data curation, Formal analysis. **M.M. Alam:** Formal analysis, Validation. **Abdullah S. Al-Bogami:** Data curation. **Tamer S. Saleh:** Formal analysis. **Mohmmad Y. Wani:** Formal analysis. **Ammar Al-Farga:** Formal analysis. **Abdullah M. Asiri:** Conceptualization, Supervision. **Mohammad Razaul Karim:** Investigation, Formal analysis. **Jahir Ahmed:** Validation, Investigation. **M.A. Fazal:** Writing - review & editing. **Mohammed M. Rahman:** Writing - review & editing.

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