

Nanocomposite Based on CNT embedded in Water Soluble Conjugated Polyelectrolyte for the Electrochemical Sensing Barium(II) ion

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In this present study, CNT was embedded into the Conjugated Polyelectrolyte (CPE-K) matrix as support and used as an electrode probe material (CPE-K/CNT) for barium ion sensing with improving the current response. Prepared composite has been characterized by Scanning electron microscopy (SEM). It has been confirmed by the SEM studies that homogenous dispersion of CPEK modified CNT in a polymer matrix. The slurry of CPE-K/CNT nanocomposites in ethanol was used to coat on a glassy carbon electrode (GCE), which implemented to develop the selective barium ion (Ba^{2+}) sensor probe. The assembled sensor probe was found to respond in a linearly over large concentration range (0.1nM~0.01mM) on the current vs. Ba^{2+} ion concentration, which referred to as “calibration curve”. The sensor’s appreciable sensitivity ($12.8481\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$) is found from the slope of calibration curve by considering the GCE surface area (0.0316cm^2). The detection limit ($93.28\pm 4.66\text{pM}$) is calculated from S/N ratio at 3. In the real sample’s analysis, it is found the fabricated sensor probe effective and reliable for the detection of target cations.

Keywords: CPE-K/CNT; Barium ion (Ba^{2+}) detection; Nanostructure; Electrochemical sensing; Sensor validation

1. INTRODUCTION

Generally, hybrid materials are developed through inorganic and organic substances combination as in the abovementioned natural materials’ case; although, recently, various carbon allotropes including

graphene and CNTs, nanomaterial, and polymers types have also involved in the composite hybrid materials' broad area. Carbon nanotube's modification and functionalization are also necessary as for developing new nano-electronics and nano-phonic components it provides entirely new nano-materials that acts as starting base [1–7] as well as in bio-nanosensors and specifically for photonic applications, it offers unique spintronic properties [8–15]. Polyelectrolytes are long-chained molecules bearing charges on their backbone which dissociate in solutions as polyanions or polycations and are associated with counterions [16]. They exhibit nearly similar behaviors like polymers and salts, hence are also known as polysalts. Their properties are largely affected depending upon the dissociation nature of the ionic groups [17]. CPEs (Conjugated polyelectrolytes) that are a conjugated polymers with solubility in polar solvents like water with ionic groups have received significant properties that for basic science investigations presents interesting systems, and for devices and materials development for effective applications that includes dye-sensitized solar cells, biosensors, and fluorescence sensors. Particularly, in sensor applications, the CPEs chemical structure provides various advantages, which include water solubility and detection's increased sensitivity. CPEs are comprised of fluorene monomers, thiophene derivatives, and phenyl units [18-20], as well as not enough literature is presented on N-heterocyclic water-soluble systems. The purification and synthesis complexity can be due to this. Whereas, in the chemistry and biology field, conjugated polyelectrolytes' fluorescent sensing properties have been studied significantly, also, less reports are presented on metal ions detection in both anionic and cationic conjugated polyelectrolytes. Recently, we have reported the application of a magnesium (II) chemosensor conjugated polyelectrolyte grafted MWCNT/polypyrrole nanocomposite [21]. In addition, because of CNTs large contact area between them and extensive π -surfaces, they get strongly interacted by π -conjugated polymers [22]. Furthermore, polymers like poly (3-alkylthiophene), poly (9,9-dialkylfluorene), poly (p-/m-phenylene ethynylene) (PPE), and poly(p-phenylenevinylene) (PPV) were described forming self-assembled hybrids with CNTs [23-25]. Herein, we report the Nanocomposite Containing water-soluble Conjugated Polyelectrolyte embedded CNT composite for use as electrode material in a sensitive and selective chemical sensor.

The environmental contamination of Ba^{2+} ion is associated with the effluent of the waste of paint, nuclear, oil, gas, and barite manning industries [26-30]. In the groundwater, the barium associated with arsenic is available as a contaminant [31]. Barium has great importance in the medical industries and diagnosis due to its radioactive nature. As a result, it is found in the municipal and hospital wastes [32-33]. The toxicity of barium is depended on the solubility of its compound in water. Some reports have claimed that the soluble salts of barium in water are harmful to the animal, plants and human [34-35]. Therefore, the Environmental Protection Agency of the USA has provided a regulation that in drinking water the barium's maximum allowed levels must not be above 0.002 mg/g [U. S. Environmental Protection Agency, EPA]. This has been also stated that the Ba^{2+} ion over-concentration in human are associated with multiple neurodegenerative (tremors, cardiac irregularities, anxiety, paralysis, weakness, and dyspnea) and sclerosis diseases [36-37]. Thus, the contamination of Ba^{2+} ion in the environment is considered as an important threat to plants, humans, living organisms, as well as ecosystems [38-39]. Therefore, a reliable detection method for Ba^{2+} ions is necessary. Presently, in the I-V approach, the electrochemical methods are becoming famous for detecting several heavy toxic metal ions due to their simplicity, cost-effectiveness, reliability, and quick detection time [40-45].

As this study's essential part, fabrication of Ba²⁺ ion electrochemical sensors was done by the deposition of CNT /CPE-K on a GCE in a thin film layer with conductive Nafion binder and subjected to detect Ba²⁺ ion using I-V analysis in phosphate buffer medium. The proposed Ba²⁺ ion sensor was found as appreciable in response time, reproducibility, DL, LDR, and sensitivity terms. It was efficient in the detection of Ba²⁺ ions in the real samples of the actual environment. It is a simple but very effective and reliable method to detect Ba²⁺ ions by electrochemical approach in a room conditions.

In this study, we used a simple technique for preparing GO-CNT-POT nanocomposites with controlled morphologies. Nanocomposites can be used for metal ion detection under their electronic properties, which can be used to enhance electronic and optoelectronic materials. The concept is the development of a hierarchy of mesoporous morphologies that allow entrapment and detection of toxic metal ions which are not safe for the environmental and healthcare fields if existence with excessive amount. As a result, we utilized GO-CNT-POT nanocomposites to manufacture a straightforward as well as functional Ba²⁺ sensor. Its ability to detect barium cation at room temperature with the prepared nanocomposites. It is the only study, to our best knowledge, on Ba²⁺ detection with GO-CNT-POT nanocomposites utilizing a dependable as well as simple *I-V* procedure with short response times.

2. EXPERIMENTAL SECTION

2.1. Materials and methods

For the material's applications and synthesis, primary reagents were bought from Sigma as well as then utilized as received. Another chemical as well as reagents having analytical grades. As per the requirement of this research, the necessary materials such as Ba(NO₃)₂, SeO, HgCl₂, Tl(NO₃)₃, CrCl₃, AgNO₃, CuSO₄, SnCl₂, and AsCl₃ were acquired from the "Sigma-Andrich company". Moreover, monosodium phosphate and disodium phosphate salts are purchased from sigma Aldrich. Commercially available of 5 % ethanol suspension of nafion was obtained from Sigma-Aldrich. Since the most sensitive equipment of this electro-chemical cell, the "Keithley electrometer" was used the USA bought. The conjugated Polyelectrolyte was developed and categorized as per Bazan description [46] as well as acknowledged as a gift material.

2.2. CNT/CPE-K composites preparation

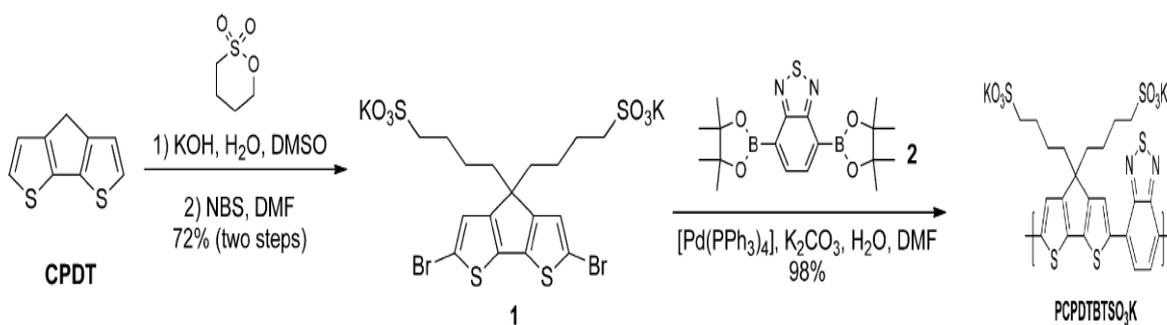
In the preparation of the CNT/CPE-K composite, CNT was synthesized from the powder of graphite with a hummer technique [47]. As the suspension of dark-colored shading, CNT was incorporated into the surfactant of SDBS solution and sonicated the solution for 12 hours for the suitable dispersion of CNT in the SDBS solution by then mixed with a ratio of 1:1 of polyelectrolyte solutions CPE-K and kept on being sonicated around an hour. The solution color changed in the green blackish precipitate was gotten and methanol and distilled water are used for washing till the point that the filtrate ended up transparent. In this way, the prepared composite was dried out at 60.0 C and performed the additional tests.

2.3. The GCE fabrication with CNT /CPE-K composite

The proposed Ba^{2+} ion sensor working electrode was produced by CPE-K/CNT composite embedded GCE. In the working electrode's fabrication process, a slurry of CNT /CPE-K composite in ethanol was prepared as well as covered GCE as a thin uniform layer. After that, this was placed in the ambient conditions of a laboratory to dry. Longtime stability of the sensor is necessary for a detailed I-V investigation. Therefore, by adding conductive nafion drop on the GCE to dry the surface, which resulted in enhancing the NCs stability onto GCE, as well as afterward, it was dry placing at 35°C inside an oven for an hour. Then, a Pt-wire and modified GCE series connection with Keithley electrometer helps in assembling the electrochemical cell. Further, Ba^{2+} ion utilized from solutions series depending on the concentration that in deionized water ranges from 0.1mM-0.1nM as well as used as the required analytes. Current vs. Ba^{2+} concentration's linear relation acknowledged as "calibration curve" was plotted and current data were collected from the I-V response of the assembled sensor to analyze Ba^{2+} ion in phosphate buffer solution. The calibration curve slope was utilized for calculating the Ba^{2+} ion sensor sensitivity. In the calibration curve, identifying the maximum linear segment is described as a "linear dynamic range (LDR)". With S/N ratio of 3, the DL (detection limit) was estimated. Also, though combining an equimolar solution of monosodium as well as disodium phosphate buffer helps in preparing 0.1M phosphate buffer solution. The proposed electrochemical sensor is consisted of a simple two electrodes system. Through the study, in the investigating beaker 10.0 mL phosphate buffer solution was taken as constant.

3. RESULTS AND DISCUSSION

The Scheme 2 is presented PCPDTBTSO3K preparation. Under basic conditions, water-soluble monomer 1 is provided with commercially available CPDT (cyclopentadithiophene) alkylation with 1,4-butanediol, afterward utilizing N-bromosuccinimide (NBS) through bromination. In a DMF/H₂O solvent mixture, commercially available bispinacolate 2 and Suzuki coupling of 1 gives PCPDTBTSO3K [46] target. PCPDTBTSO3K improving dialysis and characterization was done in a previous paper [48].



Scheme 1. Preparation of narrow-bandgap conjugated polyelectrolyte PCPDTBTSO3K [46].

PCPDTBTSO3K improving dialysis with the possible presence of polarons and characterization were done. Here, we continue chemical sensing application with embedded CNT. The acid form of these polymers has been then freeze-dried to remove the water, and electrochemical detection has been measured by the Keithley electrometer at room temperature.

3.1. Field Emission Scanning Electron Microscopy (FE-SEM)

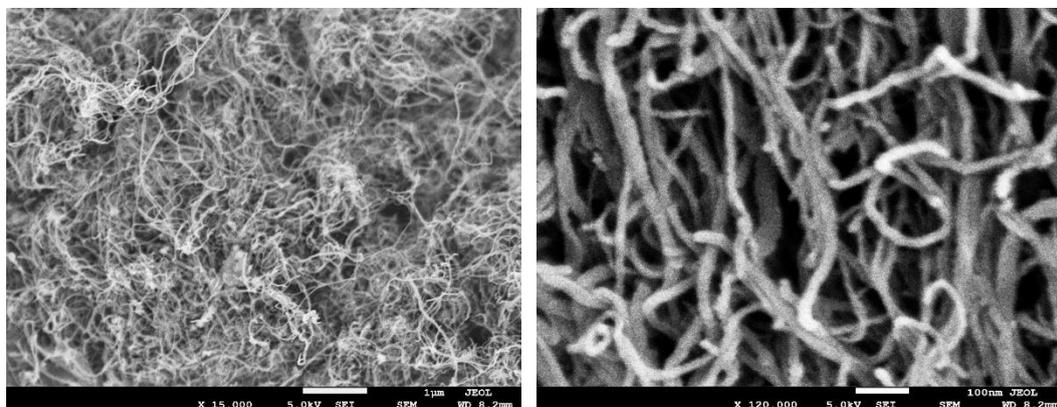
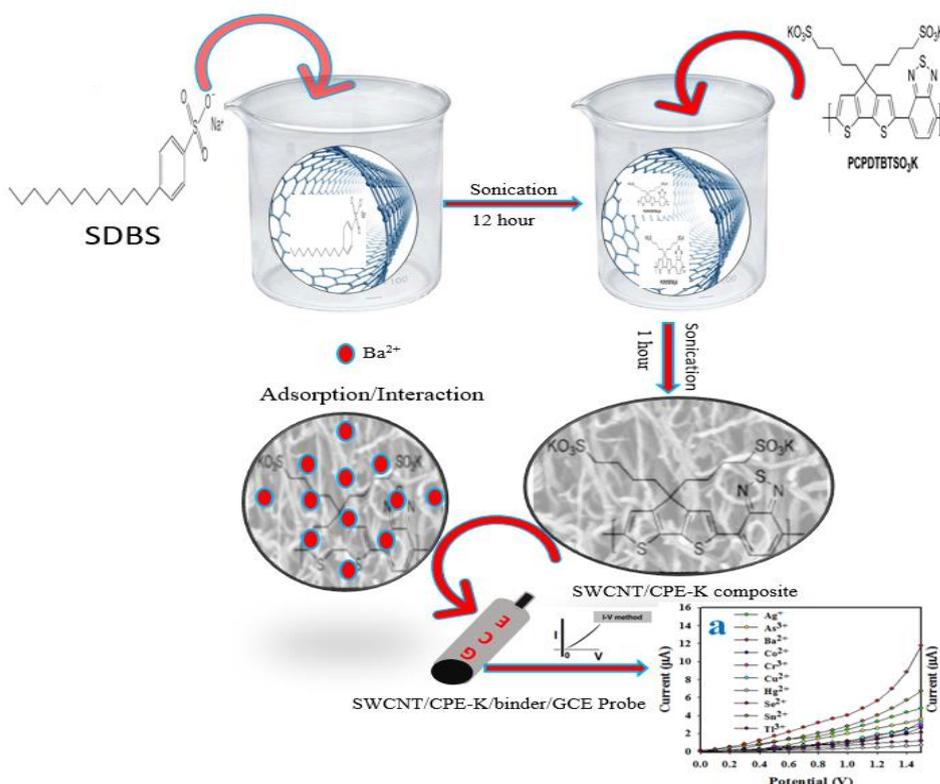


Figure 1. FESEM images of CNT /CPE-K composite



The morphological and dimensional characterization as prepared CNT/CPE-K was conducted by the FE-SEM. FE-SEM (“Field Emission Scanning Electron Microscope, ZEISS Supra 40VP,

Germany”) was utilized for obtaining SEM images under high vacuum mode operated at a range of 5 to 10 kV acceleration voltage. As far as possible the efforts were made to get images at magnifications with a bar scale of 1 μm and 100nm that has relevant for the preparation material.

Fig. 1 showed images at various magnifications which show that CNT/CPE-K composite morphology was modified in surface thickness and solid strong form when compared with pure CNTs reported [49-50]. Furthermore, the favored CPEK particle lengthening might be correlated with CPEK molecular chain's anisotropic development along the direction of the chain. The CPEK deposition mechanism occurred in the CNT/CPE-K interlayer. The CPEK molecules are believed to interact with CNTs through intermolecular forces [51]. A detailed schematic graphical is shown in Scheme 2.

3.2. Electrochemical detection of barium ions based on CNT/CPE-K/binder/GCE:

The synthesized *CNT/CPE-K* was applied on GCE as a thin film layer for fabricating the desired electrochemical sensor selective to toxic metal (Ba^{2+}) ion in phosphate buffer solution. The thin film of prepared NCs was strongly bonded on GCE by nafion. The used nafion is a conductive copolymer. Therefore, *GCE/binder/CPE-K/CNT* is fabricated sensor showed improved I-V activities as well as electrons transfer rate. Also, previously same observations were described to detect numerous metal ions [52-55]. During I-V analysis of Ba^{2+} ion, on the *CNT/CPE-K/binder/GCE* electrode surface current is calculated. The Ba^{2+} cationic sensor using *CNT/CPE-K* on GCE is the first time and regarding this, any report is not available.

At the preliminary stage of electrochemical (I-V) investigation by *CNT/CPE-K/binder/GCE* sensor, many metal ions were analyzed in a phosphate buffer solution with pH 7.0 with each concentration (0.1 μM) as well as applied potential from 0 to +1.5V. The Figure 2(a) is presented Ba^{2+} , Se^{2+} , Hg^{2+} , Tl^{3+} , Cr^{3+} , Ag^{+} , Cu^{2+} , Co^{2+} , Sn^{2+} , and As^{3+} I-V responses. The highest I-V responses are showed by Ba^{2+} ion. Depending on the greatest I-V response, for the sensor assembly, a selective metal ion is Ba^{2+} ion. After that, the proposed Ba^{2+} ion sensor was subjected to analyze based on the concentration depended Ba^{2+} ion. Ranges among 0.1nM~0.1mM as well as subsequent results from Fig. 2(b) are presented here. As Fig. 2(b) presents, there exist well defined I-V responses as well as from lower concentration to higher concentration, which are separated from one other. Similar observations similar have been reported for detecting several toxic chemicals in electrochemical (I-V) approaches reported elsewhere [56-60]. For establishing the Ba^{2+} ion sensor calibration depending on *CNT/CPE-K/binder/GCE*, a linear relation of Ba^{2+} ion current vs. concentration is plotted as illustrated in Fig. 4(c). For this exploration, from Fig. 4(b) at applied potential +1.5V the current data are isolated, which is known as a “calibration curve”. Furthermore, the online distribution of current data from Ba^{2+} ion 0.1nM-0.01mM is represented in Figure 2(c). The wider range of concentration is represented by obtained LDR. From the slope of the calibration curve in LDR, the sensor sensitivity is measured and an appreciable value of sensitivity 12.8481 $\mu\text{A}\mu\text{M}^{-1}\text{cm}^{-2}$ is obtained. The applied S/N ratio equal to 3, the DL (detection limit) is calculated. Lower limit (93.28 \pm 4.66 pM) is obtained.

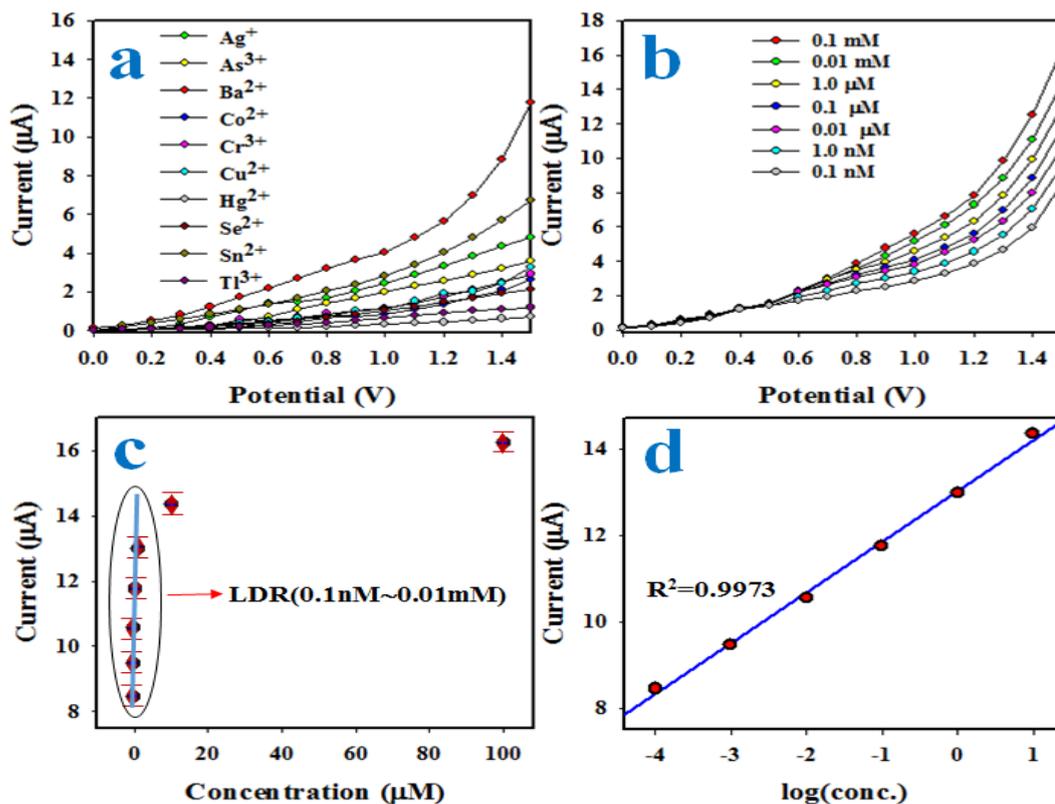


Figure 2. The I-V investigation of the “sensor based on *CNT/CPE-K/binder/GCE*. (a) The electrochemical responses of metal ions at 0.1 μM, (b) I-V responses to Ba²⁺ ion with various concentrations, (c) the calibration of Ba²⁺ ion sensor, and (d) current vs. log(conc)”.

The response time of the proposed Ba²⁺ cationic sensor with *CNT/CPE-K/binder/GCE* is described as the minimum time needed by the sensor for completing the analysis of an electrochemical. Therefore, Fig. 3(a) represented the proposed sensor is applied for response time detection using 0.1 μM of Ba²⁺ ion. As Fig. 3(a) showed that, the proposed Ba²⁺ ion sensor exhibits nearly 20.0 sec to reach the saturation level. To comparison the activity of coated and bare GCE, a control experiment has been performed in 0.1 μM Ba²⁺ ion by electrochemical analysis in potential range of 0~+1.5V in phosphate buffer medium. Fig. 3(b) is presented and demonstrated that the coated GCE shows the maximum I-V activity toward target Ba²⁺ ion.

A sensor’s reproducibility is another important analytical parameter and measured by a capability in identical conditions to produce similar I-V responses. Figure 3(c) represents the outcome of the reproducibility test of Ba²⁺ ion sensor. This experiment was done in a phosphate buffer medium in 0.1 μM of Ba²⁺ ion and potential 0~+1.5V. As it is demonstrated in Figure 3(c), replication of 7 runs are done as well as impossible for distinguishing in the each electrochemical response from other. Therefore, pieces of evidence are provided by this electrochemical test that in identical conditions, the proposed Ba²⁺ ion sensor can exhibit with a similar response. The precision of reproducibility performance is measured. In current data, the relative standard deviations terms at a potential +1.5V is calculated as 1.19%. According to the study’s requirements, the sensor’s longtime performance abilities in phosphate buffer medium are essential. Thus, longtime performance ability of this Ba²⁺ ion sensor was tested with Ba²⁺ ion in 0.1 μM, which presented in Fig. 3(d). It was a similar reproducibility test for a long time

about 7 successive days with similar conditions. This test's outcomes are the same as that of reproducibility. In a short, this has been reviewed that in the real samples proposed sensor is well enough in detecting Ba^{2+} ion. It also shows the appreciable analytical parameter including response time, reproducibility, DL, LDR, and sensitivity.

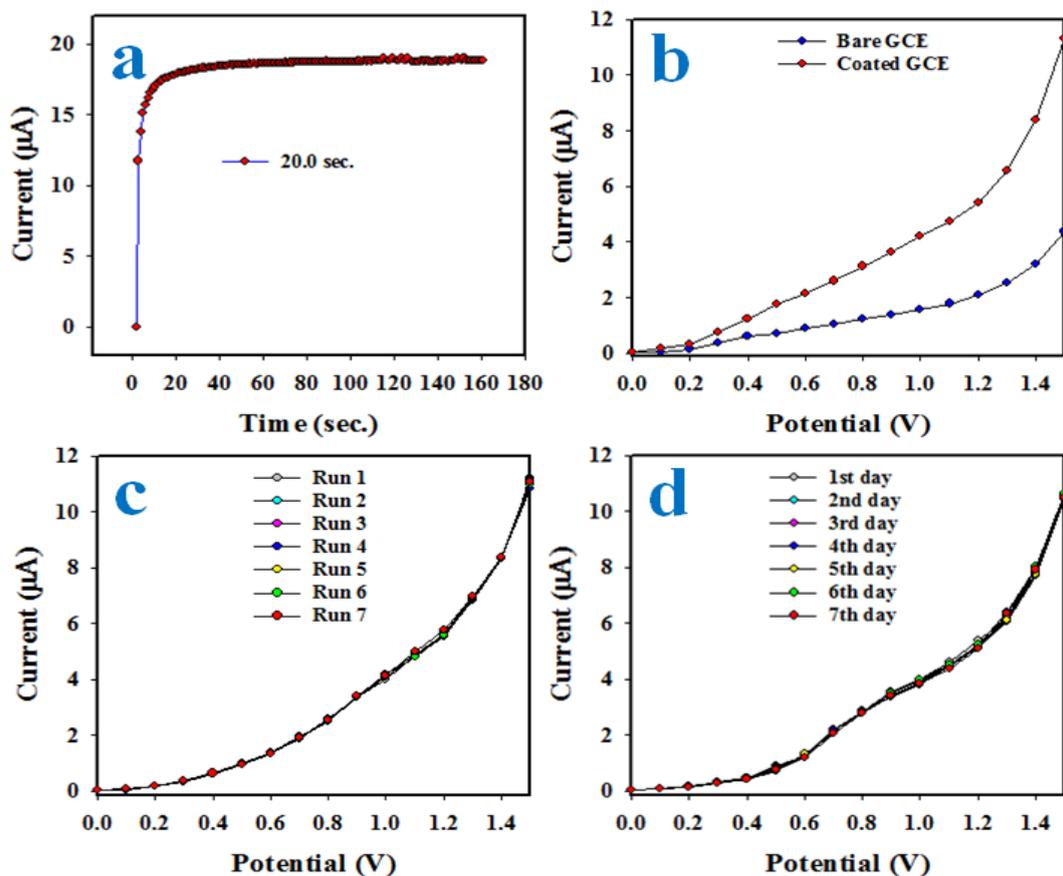


Figure 3. Optimization of barium sensor probe. (a) “The response time of Ba^{2+} ion sensor, (b) the comparison of I-V responses for coated and bare GCE in 0.1 μM of Ba^{2+} (0 to +1.5V) in phosphate buffer solution, (c) reproducibility, and (d) longtime performance of Ba^{2+} ion sensor based on CNT/CPE-K/binder/GCE

3.3. Real environmental samples Analyses

The proposed electrochemical sensor with CNT/CPE-K/binder/GCE in real environmental samples was subjected for detecting Ba^{2+} ions by utilizing the recovery approach. The actual samples are obtained from underground well-water, a supply of municipal water, seawater. It is given in Table 1. As this is clear from Table 1, the resulting outcomes are relatively good and acceptable. Hence, this can be determined that Ba^{2+} reliability can be detected by the proposed Ba^{2+} ion sensor in sample acquired from several “sources.

Table 1. Analyses of real environmental samples with *CNT/CPE-K/binder/GCE* sensor.

Sample	Added Ba ²⁺ ion concentration (μM)	Determined Ba ²⁺ conc. ^a by <i>CNT/CPE-K/binder/GCE</i> (μM)			Average recovery ^b (%)	RSD ^c (%) (n=3)
		R1	R2	R3		
Tape water	0.0100	0.0098	0.0099	0.0096	97.82	1.56
Sea water	0.0100	0.0095	0.0098	0.0097	96.67	1.58
Well water	0.0100	0.0100	0.00987	0.00976	98.76	1.22

^aMean of three repeated determination (signal to noise ratio 3) with by *CNT/CPE-K/binder/GCE*.

^bConcentration of Ba²⁺ ion determined/Concentration taken. (Unit: μM)

^cRelative standard deviation value indicates precision among three repeated measurements (R1, R2, R3).

4. CONCLUSION

The water-soluble conjugated polyelectrolyte KEP was prepared, and its CNT composites with chemical sensing properties were determined in this study. *CNT/CPE-K/binder/GCE* was found to be a Ba²⁺ cationic electrochemical sensor. The Ba²⁺ cationic electrochemical sensor fabrication is performed by applying *CNT/CPE-K* on GCE with Nafion as a thin uniform layer. The assembled sensor was exhibited a low detection limit (93.28±4.66 pM), a very wider LDR (0.1nM~0.01mM), good sensitivity (12.8481μAμM⁻¹cm⁻²), an efficient response time (20.0 sec.), and precious reproducibility. It was also effective to detect real environmental samples successively. Thus, this research works provides a glance and flavor of prospects in the field of polymer science.

CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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