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New Micro-sensor Chip Integrated with Potassium Zinc Hexacyanoferrate(II) Nano-composite for Potentiometric Determination of Cesium (I)*

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Micro-fabrication, electrochemical characterization and analytical application of nano-composite based thin-film Cs (I) micro-sensor were presented. The new microchip was realized by integration of potassium zinc hexacyanoferrate(II) (PZHCF) nano-cubes embedded in multi-walled carbon nano-tubes (CNTs) as a nano-composite sensitive layer on a treated surface of thin-film gold square planner substrate. The novel nano-composite based micro-sensor provides high sensitivity (61±0.5 mV/concentration decade) towards cesium ions covering the concentration range of 1×10^{-1}-1×10^{-5} mol L^{-1} with fast response time (< 20 s) , reasonable long-term stability and long life span (>4 months). The developed micro-sensor provides high selectivity for Cs^+ in comparison with some tested alkali, alkaline earth and transition metal cations. It was successfully applied in the determination of Cs^+ in aqueous solutions. The data obtained reveal high agreement with those obtained with ICP-AES, good accuracy (average recovery of 99.6 %) and high precision (RDS < 1.0 %).

Keywords: Nano-composite, Potassium zinc hexacyanoferrate(II) nano-cubes, Thin-film micro-sensor, Cesium (I) determination, CNT, ICP-AES.

1. INTRODUCTION

The miniaturization of bulk electrodes to micro-sensor chips or nano-wire electrodes yields dramatic enhancement in the response properties and applications versatility of the chemical sensors. Such devices have the advantages of small size, wide range of applications, high reproducibility, good accuracy and small sample volume. The micro-sensor chips play an important role in the expanding

*This paper has been presented in 5th International Conference on Materials and Applications for Sensors and Transducers, 2015, Mykonos, Greece field of modern analytical tools due to their mass production, integration and automation feasibility [1-10]. Recently, therefore, potentiometric microchips have been successfully developed for measurements of numerous species including oxygen [1], nitrite [2,3], hydrogen [4], humidity [5], hydrogen sulfide [6], nitric oxide [7], copper (II) [8,9] and pH [10]. The developments of various types of new materials as sensitive elements in the coating layers of such chemical micro-electrodes have been reviewed in the literature [11-13]. Among these, nano-particle and nano-composite materials have played a significant rule due to their unique physicochemical, mechanical and electronic properties. These materials have large effective surface area, high surface free energy and excellent electronic capability which improve the sensitivity and detection limit of the chemical sensors and microchips [1, 3-10]. On the same analog, carbon nano-tubes "CNTs" of new structure have been widely used in the chemical sensor fabrication as electrode modifier due to its high conductivity, dispersibility and wettability which increase the rate of electron transmittance [7, 14]. Therefore, CNTs of increasing interest in the sensors fabrication not only help to stabilize the sensitive materials nano-particles onto the sensor surface, but also help to ensure extremely large surface area and fast mass transport [14].

Despite the progress in the fabrication of the potentiometric microchip and nano-composite synthesis, the ability to combine both to realize new micro-sensors with enhanced properties still present a great challenge. Thus, , efforts have been done to develop nano-particle based sensitive materials in order to improve the potentiometric response properties of the microchip for biological, environmental and industrial applications [15-22]. On this context, transition metal hexacyanoferrate inorganic materials have been prepared in bulk [23-30] and nano-scale [31-35] for separation [31-33] and sensor applications [23-30, 33-35]. These materials are very interesting and promising candidates as sensitive elements in the chemical sensors fabrication due to their excellent electrochemical properties such as high stability and chemical resistivity. Among inorganic exchanger used for this purpose, potassium zinc hexacyanoferrate(II) "$K_2Zn_3[Fe(CN)_6]_2$" exhibits an ion exchange process for some alkali metals particularly, Cs^+ ions [27, 31,33]. It has been used in selective separation of Cs^+ ions [31] and consequently in fabrication of Cs^+ bulk electrode as sensitive material [28].

On the other hand, the accurate determination of Cs^+ ions particularly, in small sample volumes represent a significant challenge for environmental, industrials and radioactive strategies. For its measurements, many techniques have been developed including thermal ionization mass spectrometry [36], triple quadruple ICP-MS [37], chemically modified carbon past potentiometric electrode [28], graphite rod potentiometric sensor [38], PVC membrane electrode [39]. To the best of our knowledge, no attempt has been made till date towards the fabrication of microchips for Cesium (I) determination.

Based on the preceding facts related to the improvements of the response properties of nano-particles based micro-electrode, this paper aims to realize novel nano-composite based micro-sensor chip highly sensitive to Cesium (I). For this purpose, novel sensitive element composed potassium zinc hexacyanoferrate(II) nano-cubes "KZHCF" and carbon nano-tubes "CNTs" has been used as nano-composite coat layer. Cocktail coating membrane containing these material has been integrated on the electrochemical treated surface of silicon planer thin-film gold substrate using nebulization methodology. The novelty of this work includes realization of "KZHCF" nano-cubes/CNTs nano-composite and micro-fabrication of nano-composite based Cesium (I) microchip for the first time.

2. EXPERIMENTAL

2.1. Materials and chemicals

Purified multiwall carbon nano-tube (purity: >95%, id: 5-12 nm, od:30-50 nm, length: 10-20 μm) was purchased from Chengdu organic chemicals Company "COCC", China. Sodium dodecyl sulphate and zinc chloride were obtained from PRS Panreac chemical Company, Belgium. Non-radioactive cesium chloride was from ACROS organics, Belgium. Potassium hexacyanoferrate (II) trihydrate "$K_4[Fe(CN)_6].3H_2O$", potassium tetrakis(4-chlorophenyl) borate and 2-nitrophenyl octyl ether were purchased from Sigma-Aldrich (CH-9471 Buchs, Switzerland). THF (tetrahydrofurane) and high molecular weight (220,000) poly(vinylchloride) carboxylated were purchased from Riedel-de Haën chemical Company (Germany). Standard Cesium (I) Stock solution (Ultra grade, 1000 μg/mL, ULTRA Scientific analytical solutions, USA) was used for ICP-AES validation measurements after appropriate dilution. A thin-film gold micro-chips was used as sensor substrate. All reagents were of analytical grade, and doubly distilled water was used throughout. All measurements were carried out at ambient temperature.

2.2. Apparatus

All electrochemical measurements were conducted using Jenway (model 3510) pH/mV meter using nano-composite based microchip as working electrode responsive for cesium (I) in conjunction with Metrohum Ag/AgCl double junction reference electrode. A Thermo Scientific (iCAP 7000 series, USA) inductively coupled plasma-atomic emission spectrometer (ICP-AES) instrument supported by Qtera software and connected to a Cetac (ASX-520) auto-sampler was used in the accuracy assessment study. These measurements were performed with radial mode at 460-379 nm under optimized plasma parameters (RF power: 1150w, nebulizer gas and auxiliary gas flow: 0.5 L/min). The crystalline composition of sensitive material and the surface morphology of the thin-film substrate were analyzed using energy dispersive x-ray (EDX) attached to analytical scanning electron microscope (JEOL, model JSM-6390 LA). The diameter of the "KZHCF" nano-particles was studied by transmutation electron microscope (JEOL model JEM-1011).

2.3. Synthesis of nano-composite sensitive material

A "PZHCF" Nano-cubes material was synthesis as described elsewhere with some modifications in the type and content of surfactant [31-33]. Using sodium dodecyl sulphate (SDS) chemical surfactant reduced the surface and interfacial tension, thereby reduced the size of the particles. A solution of potassium hexacyanoferrate (II) (100 mL, 0.1 mol L^{-1}) containing an equimolar amount of potassium chloride was added gradually drop by drop into a solution of zinc chloride (100 mL, 0.1 mol L^{-1}) prepared in 8.0×10^{-3} mol L^{-1} SDS with continuous stirring. An excess of potassium salt was used to improve the coagulation of the precipitate. After complete addition, the mixture was stirred for 10 min., heated at 60 ^{o}C on water bath for 2-3 h and finally left overnight for settling at room temperature. The obtained milky precipitate was separated using centrifuge followed by subsequent washing by doubly distilled water. The last step was repeated several times to remove the excess unreacted reagents. The precipitate was collected from the centrifuge tubes in a watch glass and then dried overnight in oven at 60 ^{o}C.

As reported in table (1), three micro-sensor assemblies having different composition of sensitive material were prepared and tested as Cs^+ electrode. In the first assembly, "PZHCF" nano-particle was used solely, as sensitive element without CNTs, while "PZHCF/CNTs" nano-composite material was used as ionophore in the second assembly and in the third assembly, the microelectrode was doped in 10^{-3} mole L^{-1} after preparation by "PZHCF/CNTs" nano-composite. In each assembly, the cocktail coating mixture containing plasticized ionophore, potassium tetrakis (4-chlorophenyl) borate anion excluder and poly(vinyl chloride) support was thoroughly dissolved in THF and used as sensitive membrane coat.

Table 1. Composition of micro-sensor Cesium (I) assemblies.

No.	Ionophore, 14 mg		Anion excluder, mg	o-NPOE, mg	PVC, mg	Ag Doped
	PZHCF, %	*CNTs, %*				
1	100	0	6	114	66	-
2	95	5	6	114	66	-
3	95	5	6	114	66	10^{-3} mole L^{-1}

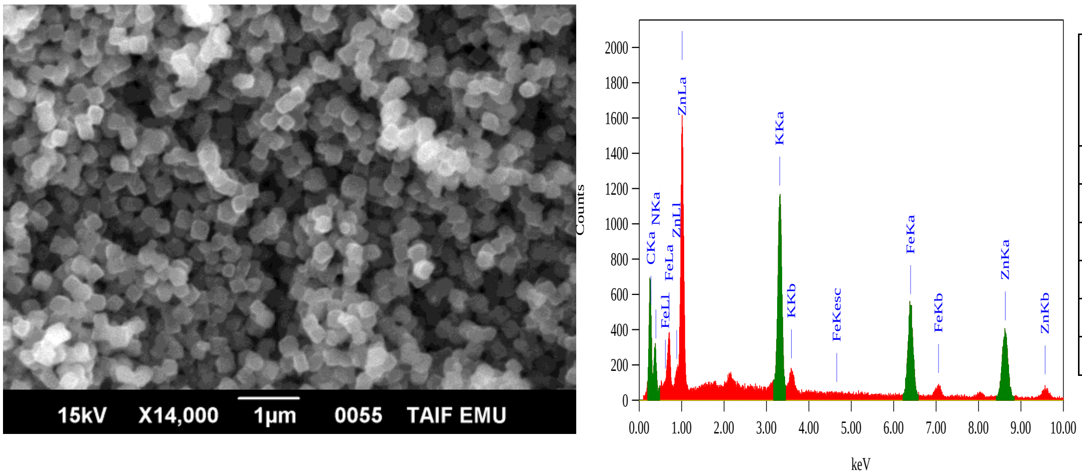
2.4. Micro-fabrication of nano-composite based Cesium (I) chip

The cocktail coating mixture containing the nano-composite sensitive element was deposited on the surface of thin-film gold silicon planer microchip using nebulization methodology recently, developed [8]. Prior to the deposition of the sensitive layer, the surface of the thin-film gold microchip substrate was treated chemically and electrochemically, respectively. In the chemical treatment, the microchip was soaked in concentrated nitric acid for 2 m., washed by doubly distilled water several times and finally, rinsed in ethanol. Immediately, the microchip was transferred into the deposition cell containing 20 mL of 1×10^{-3} mol L^{-1} Ag NO_3 to deposit a thin-layer of Ag precipitates, in an electrochemical treatment step. Using small nebulizer, minute aliquots of the cocktail coating mixture was manually, nebulized onto the treated surface of microchip substrate for few seconds in a fume hood and then left for 3-5 min., to evaporate the solvent. The nebulization step was repeated several times until a uniform layer cover the surface of the substrate was obtained. The cocktail coating mixture was sonicated for two h. before nebulization process and for 3-5 min. between each nebulization step as well. For each assembly of Cesium (I) microchip, three units were fabricated at the same time and then air dried overnight at room temperature before being characterized. The realized microchip was used as working electrode in conjunction with Ag/AgCl commercial reference electrode in Cesium (I) potentiometric measurements. The selectivity coefficient (obtained by separate solution method) and all other response properties of the realized Cs^+ microchip were performed according to IUPAC recommendations.

3. RESULTS AND DISCUSSION

3.1. Materials characterization

The synthesized "KZHCF" nano-cubes were characterized using various techniques such as scanning electron microscope (SEM), energy dispersive x-ray (EDX) and transmutation electron microscope (TEM). As shown in Fig. (1), the surface morphology study using (SEM) showed that the synthesized "KZHCF" particles were mono-dispersed nano-cubes with particles diameter ranging around 100 nm. Highly ordered crystalline structure was obtained with some agglomerated particles slightly appear. In addition, the crystalline composition of the nano-cubes investigated using energy dispersive x-ray (EDX) revealed the presence of C, N, K, Fe and Zn elements with atomic percentage of 24.58, 51.36, 6.66, 6.72 and 10.69, respectively. These results including the crystalline shape, elemental composition and the different atomic percentages come in good agreement with those obtained from similar studies reported for "KZHCF" nano-particles recently, synthesized [32].



Element	Atomic percentage (%)
C	24.58
N	51.36
K	6.66
Fe	6.72
Zn	10.69
Total	100

Figure 1. SEM image with crystalline composition (EDX) of "KZHCF" nano-cubes.

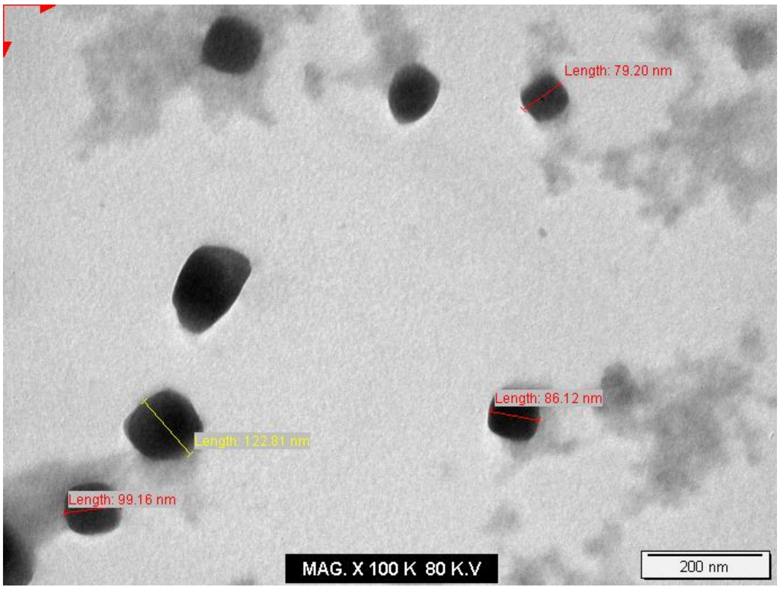


Figure 2. TEM image of "PZHCF" nano-cubes.

The exact particle size and shape of the realized "PZHCF" nano-particles were investigated using transmutation electron microscope (TEM). The results obtained presented in Fig. 2. should that a uniform mono-dispersed cubic shape nano-particles of potassium zinc hexacyano ferrate with size ranging from 80 to 100 nm. The particles shapes were similar, clear and well dispersed cubical nano-particles. Such results come in good agreements with those obtained in similar studies recently reported for 'PZHCF' nano-particles [32].

In order to improve the adhesive properties of the thin-film gold substrate towards organic membrane, a small layer of Ag precipitates was electrochemical deposited on the substrate surface using new methodology recently, developed [8]. The surface morphology characterization of the treated and untreated gold substrates were performed using SEM and the results obtained were demonstrated in Fig. 3. As can be seen, the surface of the untreated microchip substrate (a) is very smooth with poor adhesive properties towards organic membrane sensitive layer. The treated surface (b) has mountain-like morphology structure and relatively high roughness degree with good adhesive properties to organic membrane sensitive layer. The surfaces of the investigated films were fairly uniform and having no any noticeable defects. Increasing the roughness of the substrate surface dramatically improved the adhesive properties of such microchip towards the organic membrane sensitive layer and consequently modified the microelectrode stability as well as increased sensor life span.

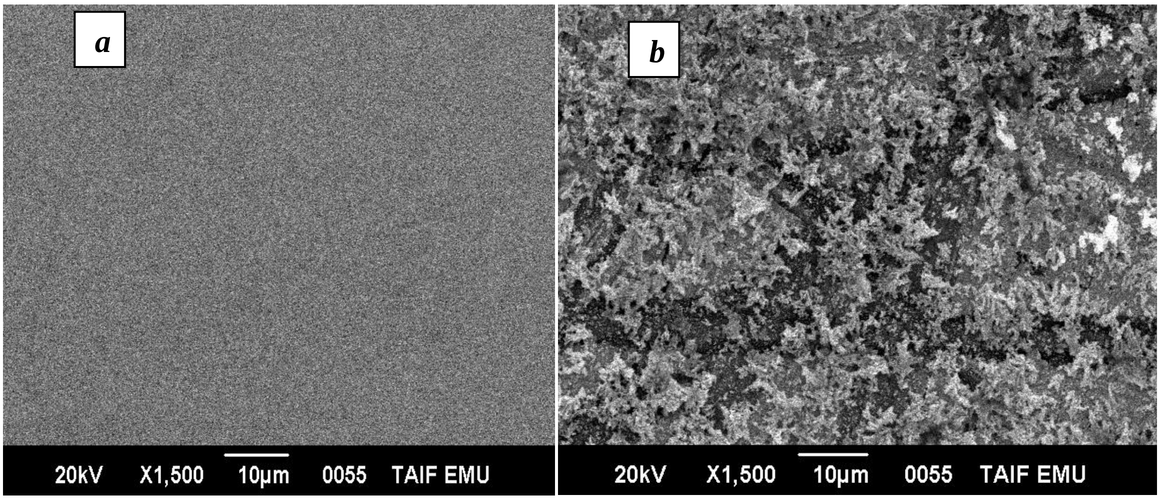


Figure 3. SEM images of untreated (*a*) and treated (*b*) surface of thin-film substrate microchip.

3.2. Electrochemical characterization of Cesium (I) microchip

New nano-composite sensitive material comprises "PZHCF" nano-cubes and "CNTs" was synthesized for the first time using new methodologies. Such material was used as a sensitive element in realization of novel thin-film microchip responsive for Cs^+ ions. The organic membrane sensitive layer was nebulized on silicon planer thin-film gold microchip after an electrochemical treatment of the substrate surface. The electrochemical properties of the new microchips were assessed by detecting standard cesium solutions with different concentrations. As summarized in Table (1), three electrode assemblies were used for this purpose in order to achieve the best response properties of the microchip towards Cs^+ ions. The results obtained were presented in figures 4, 5 and 6 for assembly 1, 2 and 3, respectively. For each microelectrode assembly, the calibration was repeated several times and only three of them were presented in each calibration graph for simplicity. The reasonable reproducibility obtained with all assemblies is attributed to the strong stability of the "PZHCF" inorganic materials used as a sensitive element. Moreover, the potentiometric response for the three assemblies were presented in fig. 7, for comparison. As can be seen, the best potentiometric response characteristics of the realized microchips were obtained with assembly 3 based on PZHCF-CNTs nano-composite as sensitive element and doped in 1×10^{-3} mol L^{-1} of Ag^+. This assembly was used in the subsequent experiments as Cs^+ microelectrode chip. All potentiometric properties of the elaborated Cs^+ microchip was summarized in Table (2). The microelectrode based on "PZHCF-CNTs" nano-composite sensitive material doped with Ag^+ provides high sensitivity (61±0.5 mV/ concentration decade) towards cesium (I) ions covering the concentration range 1×10^{-5}-1×10^{-1} mol L^{-1} with very short response time (<20 s) and long life span (>4 months). The detection limit determined as recommended by IUPAC from the intersection of the two arms of the calibration curve, was 5.0×10^{-6} mol L^{-1}. In comparison with cesium electrode previously reported, the elaborated microchip provides advantages of high sensitivity, wide linear concentration range, lower detection limit, small size and integration and automation feasibilities [28, 38, 39]. The improvements of the response properties of the elaborated Cesium (I) microelectrode particularly, sensitivity is attributed to the nano-crystalline structure of the sensitive material as well as the usage of CNTs modifier. The unique physicochemical properties of these material improve the sensitivity and detection limit of the chemical sensors and microchips [1, 3-10, 14].

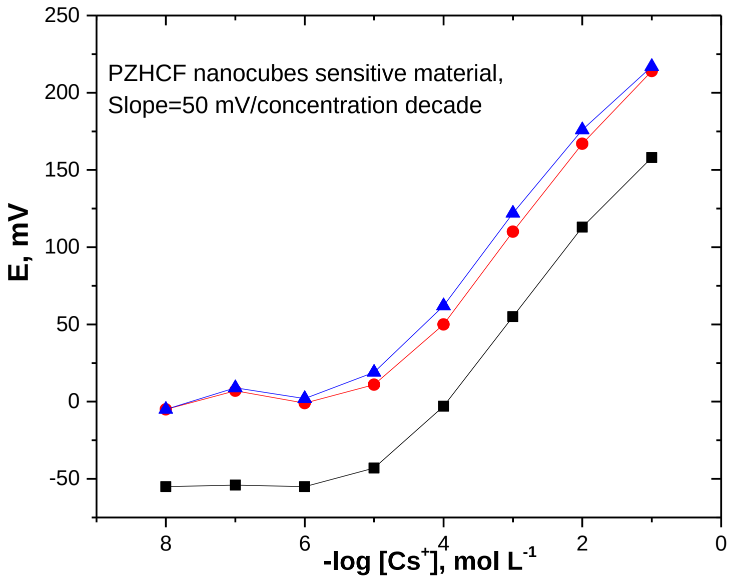


Figure 4. Potentiometric response of PZHCF based Cs^+ Microsensor.

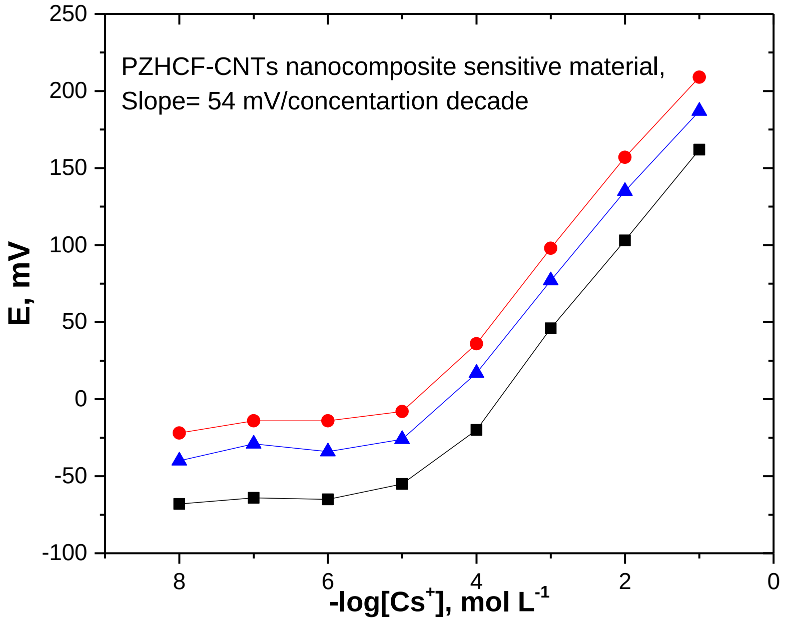


Figure 5. Potentiometric response of PZHCF-CNTs based Cs^+microsensor.

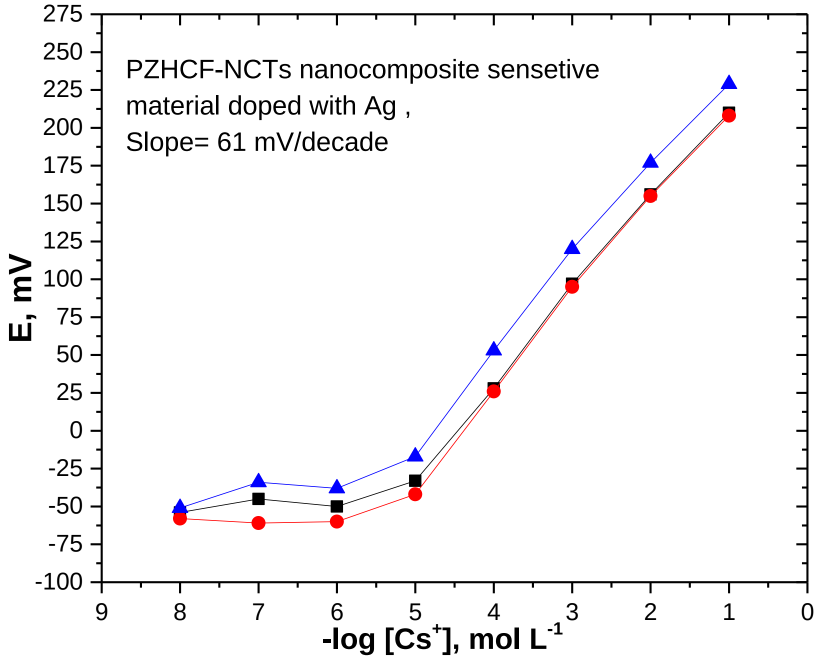


Figure 6. Potentiometric response of Ag^+ doped Cs^+microsensor.

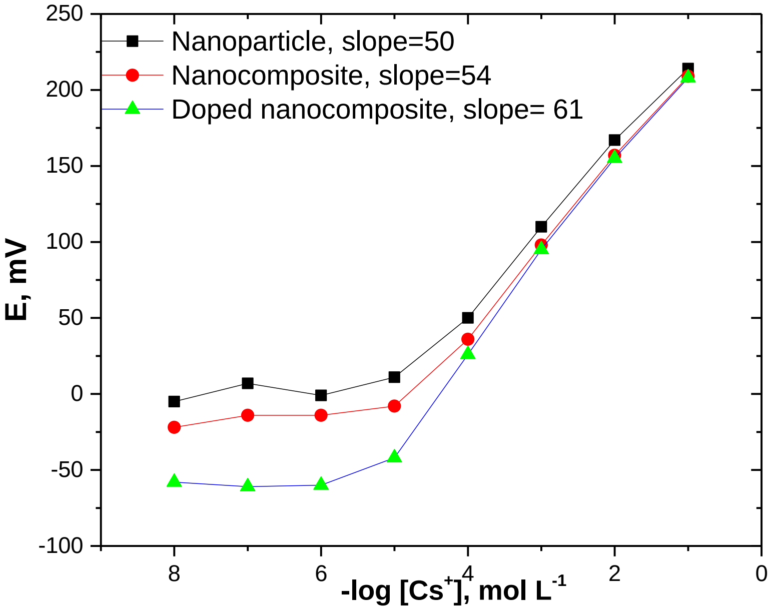


Figure 7. Potentiometric calibartion response of Cs^+ thin-film microsensors.

Table 2. Potentiometric response properties of the "PZHCF-CNTs" based Cs^+ microelectrode.

Parameters	Cesium (I) ions
Linear range, mol L^{-1}	1×10^{-5}-1×10^{-1}
Slope, mV/decade	61±0.5
Detection limit, mol L^{-1}	5.0×10^{-6}
Response time, s	<20
pH range	3-9
Life span, months	>4

In order to investigate the dynamic response time of the elaborated Cs^+ microelectrode, the potential was measured with ten-fold changes of Cesium concentration and recorded versus time in second. The results obtained illustrated in Fig. (8) revealed that the microelectrode provides very short response time (<20 s) over the linear concentration range of Cesium (I) ion.

The influence of the pH of the test solution on the response of the elaborated Cs^+ microchip was investigated for two different concentrations of Cesium (I) ion (1×10^{-2} and 1×10^{-3} mol L^{-1}) over the pH range 1-11. As shown in Fig. 9., the working pH range of the realized Cs^+ microchip is between 3 and 9. Through this pH range, the microelectrode potential is not affected by changes in pH of the test solution. At lower pH values, the microelectrode potential decreases with decreasing pH values due to the competition of H^+ ions, while at higher pH values the hetero-poly sensitive material "PZHCF" begin to de-polymerized and dissolve.

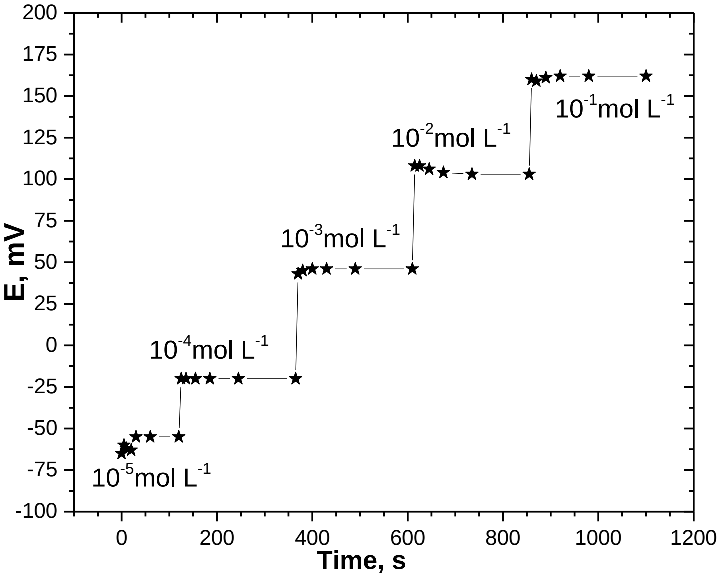


Figure 8. Dynamic response time of nano-composite Cs^+ microsensor.

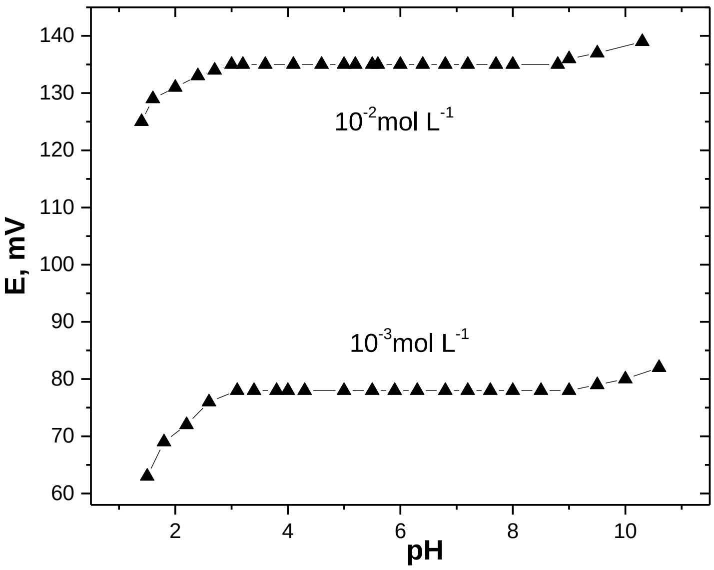


Figure 9. Effect of pH on the response of Cs^+microsensor.

The selectivity coefficient study of the realized microchip towards Cs^+ ion with respect to some monovalent, divalent and trivalent cations were assessed using separate solution method (SSM) with fixed 1×10^{-3} mol L^{-1} test solution of both Cs^+ and interfering cations. The results obtained (Table 3) showed that the elaborated microelectrode provides a good selectivity towards Cs^+ ions with respect the tested cations.

Table 3. Selectivity coefficient of nano-particle based Cs^+ micro-sensor

No.	**Ion**	$K_{Cs,M}^{pot}$
1	Li^+	1.6×10^{-2}
2	Ag^+	1.2×10^{-2}
3	NH_4^+	1.2×10^{-3}
4	Na^+	7.2×10^{-3}
5	Mg^{2+}	1.5×10^{-4}
6	Ca^{2+}	2.2×10^{-4}
7	Cu^{2+}	2.7×10^{-4}
8	Cd^{2+}	1.4×10^{-4}
9	Fe^{3+}	1.1×10^{-4}
10	Cr^{3+}	5.7×10^{-5}

3.3. Analytical application of the nano-particle based Cs^+ microchip

In order to assess the reliability and credibility of the realized Cs^+ microchip, it was successfully applied in the measurements of Cs^+ concentration in some tested aqueous samples. For comparison, these samples were also determined using independent ICP-AES standard method. The standard Cs^+ solution and the samples were introduced automatically using auto-sampler to plasma under the optimized conditions and the optical system with radial mode was detect the Cs^+ concentrations. The concentration of each sample was determined automatically using the calibration plot. The results obtained by the two methods were summarized in Table 4. As can be seen, there is a good agreement of the data obtained by the realized Cs^+ microchip with those obtained by the independent ICP-AES standard method. Thus, the microchip provides good accuracy (average recovery of 99.6 %) and high precision (RSD <1 %, n=6).

Table 4. Recovery studies on nano-particle based Cesium micro-sensor.

No	Cesium, µg/ml		Recovery %
	Microsensor	*ICP-AES*	
1	1.34	1.38	97.1
2	5.71	5.56	102.7
3	20.80	20.53	101.3
4	50.57	50.67	99.8
5	100.18	100.53	99.6
6	133.11	136.80	97.3
	Average recovery		99.6

4. CONCLUSIONS

Novel Cesium (I) microelectrode incorporated "PZHCF-CNTs" nano-composite recently, synthesized was fabricated for the first time. The Cs^+ microchip has shown sensitive, selective, fast, stable and reproducible behavior. The merits offered by the realized microelectrode over the reported Cesium electrodes include better potentiometric properties, small size, integration and automation feasibility. Moreover, the microchip has been successfully applied in the determination of Cs^+ in some tested samples with high accuracy and precision with respect to independent ICP-AES standard method.

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