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Thulium Selective Sensor based on Nanographene/RTIL/Ionophore/Graphite

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In this work, nanographene was used as a proper nano-material to modify the composition of carbon paste electrode. Because of a selective interaction between 4-methyl-1,2-bis(2-pyridinecarboxamido) benzene (MPB) and thulium ions identified by our previous work, MPB was incorporated as a sensing material into a nano-composite carbon paste electrodes. The paste is composed of graphite, sensing material MPB, nanographene (NG), and a room temperature ionic liquid namely 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4 (RTIL). The electrodes made of 50% graphite, 5% NG, 20% MPB, and 25% RTIL were found to show the most favorable behavior. The sensor shows a Nernstian response (19.9±0.3 mV decade^{-1}) in the concentration window of 1.0×10^{-6}-1.0×10^{-2} M with detection limit of 8.3×10^{-7} M. The response of the sensor was found to be stable in the pH range of 3.5-9.0 and the nano-composite based Tm(III) sensors displayed very good selectivity with respect to a number of lanthanide and transition metal ions. The proposed sensor displays a long life time (more than 12 weeks) with a short response time of about 15 s.

Keywords: sensor, ion selective electrode, potentiometry, carbon paste, nanographene, ionic liquid, thulium

1. INTRODUCTION

Recently carbon paste electrodes (CPEs) have been considered as ion selective electrodes because of their interesting advantages over membrane electrodes (e.g. renewability, stable response, low ohmic resistance, and no need for internal solution) [1–5]. Also, they have an ability to change their response behavior by modifying their composition. The carbon paste usually consists of graphite powder dispersed in a non-conductive mineral oil.

One of the new modifiers of carbon paste is grapheme. Grapheme is a carbon allotrope. Its structure is one-atom-thick planar sheets of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice [6]. Nano Graphene (NG) is similar to carbon nanotubes but have twice the surface area. NG, a single-atom-thick sheet of graphite, is a new material which combines aspects of semiconductors and metals. Graphene has been described as a carbon nanotube unrolled, and shares some of the unique properties of nanotubes. In particular, it's a so-called ballistic conductor, meaning that electrons flow through it at high speed, like photons through a vacuum, with virtually no collisions with the atoms in the crystal. This makes it a potentially outstanding conductor for wires and other elements in nanoscale electronics [7-9]. Addition of NG with special physicochemical properties of ultra-low weight, high mechanical strength, high electrical conductivities, high thermal conductivity, metallic or semi-metallic behaviors and high surface areas to CPE, has also been found to cause improvement in the response of the electrode.

Because of the fact that mineral oils used in the carbon paste have not a fixed composition, the classic CPE electrodes suffer some disadvantages caused by the oil contaminants or matrix components. Room temperature ionic liquids (RTILs) can be a suitable alternative for paraffin oil, because they have a number of interesting properties such as good solvating properties, high conductivity, non-volatility, low toxicity, good electrochemical and chemical stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity [5,10,11].

Thulium is the least abundant of the rare earths and it is never found in nature in pure form, but it is found in small quantities in minerals with other rare earths. It is principally extracted from monoazite (~0.007% thulium) ores found in river sands through ion-exchange.

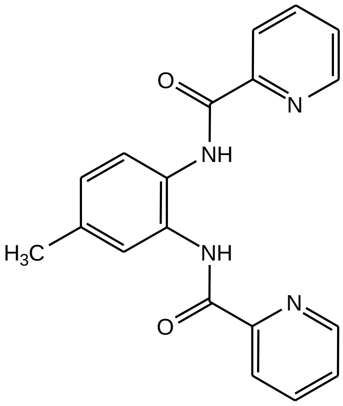

Figure 1. Chemical structure of 4-methyl-1,2-bis(2-pyridinecarboxamido) benzene (MPB)

The conventional methods for the determination of low-levels of Tm(III) ions in solutions inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), neutron activation analysis, and X-ray fluorescence spectrometry [12-16] being either time-consuming, involving multiple sample manipulations, or too cost-intensive for most analytical laboratories. On the other hand application of carrier-based ion-selective electrodes

(ISEs) can offer inexpensive and convenient analyses methods for different anions and cations [17-21] compare to instrumental and new electrochemical techniques [22].

The major problem in quantitative analysis of lanthanide family is the selectivity. Because of the similarity of these elements, finding a simple device like a sensor which can measure one of these elements selectively is of importance.

In this work a highly selective modified nano-composite carbon paste sensor based on 4-methyl-1,2-bis(2-pyridinecarboxamido) benzene (MPB), Fig. 1, as the sensing material has been developed and tested for the monitoring of Tm(III). The stability as well as the selectivity of the ionophore (MPB) complexes of some special alkali, alkaline earth, transition, and heavy metal ions was previously tested [23].

2. EXPERIMENTAL SECTION

2.1. Apparatus

The electrochemical cell used for the determination of potentials, included the Tm(III) sensor as the indicator electrode and an Ag/AgCl electrode (Azar electrode, Iran) as the reference electrode and had a format as below:

Nano-composite based sensor | sample solution | Ag/AgCl–KCl (satd.)

2.2. Reagents and materials

The sensing material, MPB was prepared as described elsewhere [24]. Graphite powder with a 1–2 μm particle size (Merck) and high-purity paraffin oil (Aldrich) were used for the construction of the carbon pastes. The ionic liquid (1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF_4) and chloride and nitrate salts of the cations were purchased from Merck Co. and were used without further treatment. The nano grapheme (xGnP®, particle thickness is about 7 nanometers, with an average surface area of about 120 to 150 m^2/g) was purchased from XG Sciences Co. Distilled deionized water was used throughout all experiments.

2.3. Carbon Paste Electrode Fabrication

The modified CPEs were prepared through a general procedure as follows: Desired amounts of MPB, graphite powder, ionic liquid or the paraffin oil and nanographene were thoroughly mixed and then transferred into a glass tube (5 mm i.d. and 3 cm in length). To avoid the formation of air gaps in the structure of the CPE, the mixture was then homogenized before being packed into the tube tip. This can help avoid unwanted increases in the electric resistance of the electrodes. Next copper wire was inserted into the opposite end act as an electrical contact and the external surface of the CPE was cleaned with soft abrasive paper, which was repeated prior to any measurement. The electrode was finally rested for 48 h by being soaked in a 1.0×10^{-3} M $TmCl_3$ solution [4,5].

3. RESULTS AND DISCUSSION

3.1. Optimization of the CPEs

The ionophore (here MPB) is the main ingredient of any ISE which determines the selectivity of such devices [26-39]. Previous solution studies in acetonitrile [23] showed the selectivity behavior of MPB toward Tm(III) (K_f : 5.25±0.21). To test the effect of the composite ingredients on electrode behavior, a series of CPEs having a variety of compositions, some of which were modified using the ionic liquid, NS and NG according to Table 1 were tested. As it can be seen from the data, the CPE lacking sensing element (composition 1), did not show any considerable response to the concentration changes of the Tm(III) ion.

Table 1. The optimization of the nano-composite based Tm(III) carbon paste ingredients

No.	**Composition (%)**					**Slope (mV decade^{-1})**	**Linear range (M)**
	Graphite	Paraffin	RTIL	MPB	NG		
1	75	25	---	-	-	3.3± 0.5	1.0×10^{-2} - 1.0×10^{-3}
2	70	25	---	5	-	11.7 ± 0.2	1.0×10^{-2} - 1.0×10^{-4}
3	65	25	---	10	-	14.8 ± 0.3	1.0×10^{-2} - 4.0×10^{-5}
4	60	25	---	15	-	16.3 ± 0.4	1.0×10^{-2} - 2.0×10^{-5}
5	55	25	---	20	-	17.5 ± 0.3	1.0×10^{-2} - 3.0×10^{-5}
6	50	25	---	25	-	17.6 ± 0.3	3.0×10^{-2} - 4.0×10^{-5}
7	55	---	25	20	-	18.5 ± 0.3	1.0×10^{-2} - 5.0×10^{-6}
8	50	---	30	20	-	18.6 ± 0.3	3.0×10^{-2} - 7.0×10^{-6}
9	54	---	25	20	1	19.0± 0.3	1.0×10^{-2} - 4.0×10^{-6}
10	52	---	25	20	3	19.2 ± 0.2	1.0×10^{-2} - 2.0×10^{-6}
11	50	---	25	20	5	19.9 ± 0.3	1.0×10^{-2} - 1.0×10^{-6}
12	48	---	25	20	7	19.6 ± 0.4	1.0×10^{-2} - 1.0×10^{-6}

Upon the addition of the ionophore, in amounts of 5-25%, to the composition of carbon paste electrodes considerable increases in the potential response of the CP electrodes (composition 2-5) was observed and presence of 20% of MPB to CP electrode was found to lead to a very good response behavior, increasing the potential response from 3.3±0.5 to 17.6±0.3 mV decade^{-1}. The response was still sub-Nernstian which was not improved by the further increase in the amount of the ionophore up to 25% wt. (no. 6). By changing paraffin oil with RTIL (no.7) the slope of the sensor increased from 17.5±0.3 to 18.5±0.3 mV decade^{-1}. This is most probably due to the excellent physicochemical properties of RTIL respect with paraffin as a neutral hydrocarbon. However, the obtained slope is not Nernstian and is near-Nernstian behavior.

Addition of 1-7% wt. of NG (Nos. 9-12) was found to improve the potential response to 19.9± 0.3 mV decade^{-1} of Tm(III) activity. There is no need to mention that this was equivalent to reducing the amount of the graphite powder in the composition. This is most probably due to the improvements in the conductivity of the CPEs. Eventually, as it can be concluded from the data in Table 1 a composition of 20% MPB, 25% [bmim]BF_4, 50% graphite powder, and 5% NG (no. 11) leading to CPEs with a Nernstian slope of 19.9±0.3 mV decade^{-1}, was chosen concluded to be optimum.

3.2. Measuring range and detection limit

The response of the CPE with the optimum composition (no. 11) was examined in a range of 1.0×10^{-1}-1.0×10^{-7} M and the results are shown in Fig. 2.

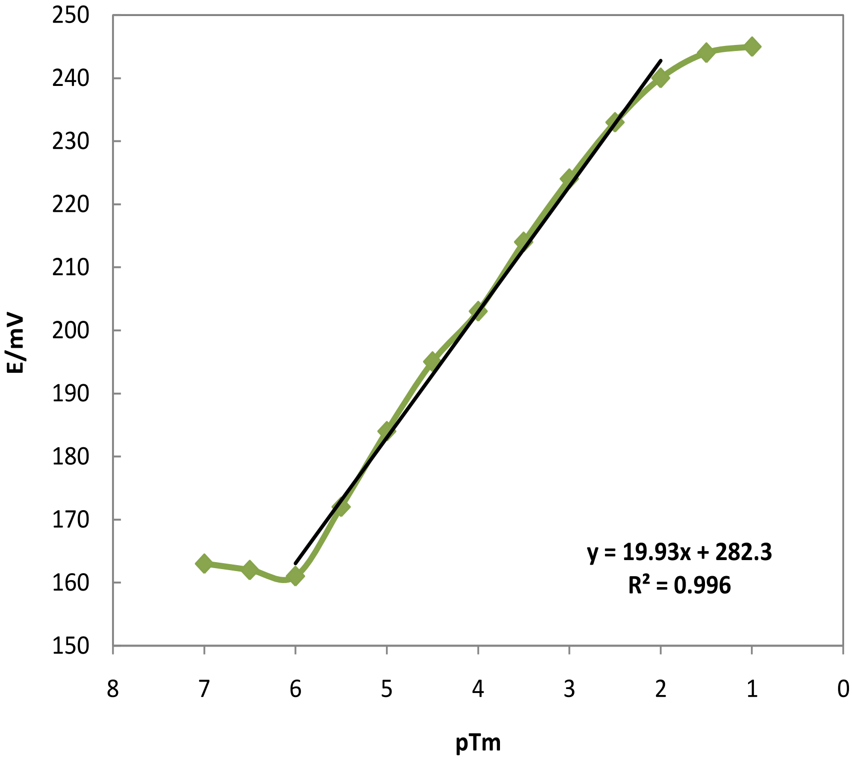

Figure 2. The calibration curve of the Tm(III) nano-composite modified CPE based on MPB (Electrode no. 11). The results based on triplicate measurments.

The results show that the CPEs have a linear response behavior in the concentration range of 1.0×10^{-2}-1.0×10^{-6} M (Fig. 2). Further, the detection limit of the CPE was evaluated by extrapolating the linear portions of the electrode’s calibration curve and was found to be 8.3×10^{-7} M.

3.3. pH effect

The pH effect of the test solution on the potential response of CPEs with the optimum composition was studied by monitoring the potential response of the sensor in 1.0×10^{-4} M and 1.0×10^{-3} M Tm(III) solution while varying the pH values in the range of 1.0-12.0 through adding concentrated HNO_3 or NaOH. The results as depicted in Fig. 3 reveal that the potential response of the Tm(III) CPE is pH independent in the range of 3.5-9.0. Potential drifts at higher pH values are attributed to the formation of soluble or insoluble Tm(III) hydroxy complexes and/or precipitates. At pH values less than 3.5 the potential drifts most probably due to partial protonation of the donor atoms in MPB.

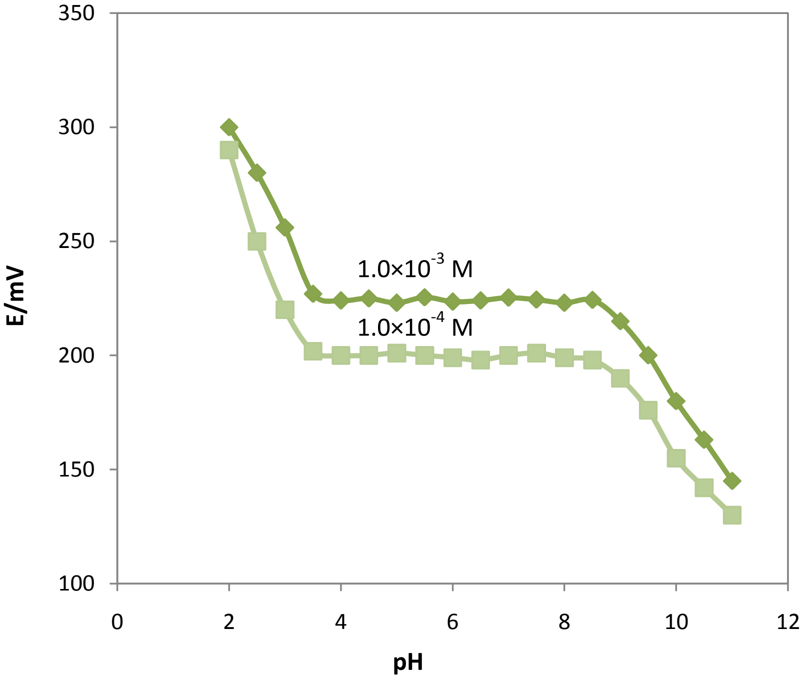

Figure 3. Effect of pH on the potential response of Tm(III) nano-composite CPE based on (Electrode no. 11) in the test solution of Tm(III) ion (10^{-3} and 10^{-4} M).

3.4. Response time and lifetime of the CPEs

The response time of the CPEs was evaluated through studying the average time the CPEs took to produce potential values within ±0.1 mV of their steady-state potentials upon their immersion in a series of solutions of Tm(III), each having a ten-fold difference in concentration [40-51]. Parameters including the temperature, type and speed of stirring, the concentration and composition of each solution, and preconditioning of the electrode are also known to influence the response time the sensors and they were hence kept at constant values throughout the experiments. The tests revealed the response time of the CPEs to be less than 15s in the whole concentration range.

Lifetime is another very imprtant issue for any sensor. We found that for most ion selective sensors the lifetime values range from 4 to 10 weeks after which the slope and detection limt of the sensor are consinderablly altered. The lifetime of the proposed Tm(III)-selective CPEs was studied for a period of 15 weeks. In this period, the sensor was used for two hours per day and the changes in its slope and detection limit were recorded (Table 2). As it is seen in Table 2, the CPEs can be used for at least 11 weeks. without significant changes in their slope and detection limits. After this peroiod, a significant decrease in the slope from 19.9±0.3 to 13.7±0.4 mV decade^{-1} and a gradual increase in the detection limit from 8.3×10^{-7} to 5.5×10^{-5} were observed. This can be attributed to the loss of the RTIL and MPB from the CPEs as a result of application over time.

Table 2. Lifetime of Tm(III) nano-composite modified CPE

Week	Slope (mV decade^{-1})	DL (M)
1	19.9 ± 0.3	8.3×10^{-7}
2	19.8 ± 0.3	9.0×10^{-7}
3	19.6 ± 0.4	9.5×10^{-7}
4	19.5 ± 0.3	1.0×10^{-6}
5	19.6 ± 0.5	2.0×10^{-6}
6	19.3 ± 0.3	3.5×10^{-6}
7	19.4 ± 0.4	5.0×10^{-6}
8	19.3 ±0.3	6.5×10^{-6}
9	19.2 ± 0.3	7.0×10^{-6}
10	19.1 ± 0.2	8.0×10^{-6}
11	19.0 ± 0.3	8.5×10^{-6}
12	18.1 ± 0.4	9.5×10^{-6}
13	16.3 ± 0.5	2.0×10^{-5}
14	15.7 ± 0.3	3.5×10^{-5}
15	13.7 ± 0.4	5.5×10^{-5}

3.5. Selectivity

As it can be conluded from the name of the sensor, selectivity behavior of ion selectyive sensors, is of determining importace.

Table 3. The selectivity coefficients of various interfering cations for electrode no. 11; concentration of the reference solution of Tm(III) ion was 1.0×10^{-6} M and the concentration of interfering ions was between 1×10^{-4} to 1.0×10^{-1} M

Cation	Selectivity Coefficient	Cation	Selectivity Coefficient
Na^+	$<10^{-5}$	Gd^{3+}	8.2×10^{-3}
K^+	$<10^{-5}$	Yb^{3+}	3.4×10^{-3}
Mg^{2+}	$<10^{-5}$	Tb^{3+}	3.0×10^{-3}
Ca^{2+}	5.2×10^{-3}	La^{3+}	7.1×10^{-4}
Ni^{2+}	7.4×10^{-4}	Sm^{3+}	6.4×10^{-4}
Cu^{2+}	8.0×10^{-4}	Dy^{3+}	7.1×10^{-4}
Pb^{2+}	6.2×10^{-4}	Pr^{3+}	3.5×10^{-3}
Co^{2+}	$<10^{-5}$	Lu^{3+}	7.3×10^{-3}
Zn^{2+}	$<10^{-5}$	Ce^{3+}	5.1×10^{-4}
Fe^{3+}	2.7×10^{-4}	Er^{3+}	4.6×10^{-3}
Ho^{3+}	8.1×10^{-3}	Nd^{3+}	6.7×10^{-3}

Hence, we included matched potential (MPM) studies of the selectivity coefficients [52-57]. The results of which are summarized in Table 3 which shows that the selectivity coefficients of CPEs for a number of mono, di and teivalents cations to be in the ranges of 2.7×10^{-4}-8.3×10^{-3}. This indicates that the tested ions do not have considerable interferences with the response of the CPEs.

4. CONCLUSION

A nano-composite carbon paste electrode were constructed for determination of Tm(III). The sensors demonstrated advanced performances with a fast response time, a lower detection limit of 2.0×10^{-7} M and potential responses across the range of 1.0×10^{-6}-1.0×10^{-2} M. MPB was employed as a sensing element in construction of both electrodes. A nano-composite carbon paste electrode was designed to improve the analytical responses. Addition of NG with special physicochemical properties of ultra-low weight, high mechanical strength, high electrical conductivities, high thermal conductivity, metallic or semi-metallic behaviors and high surface areas to CPE, has also been found to cause improvement in the response of the electrode in term of lifetime and response time. The best nano-composite electrode was composed of 5% NG, 20% MPB, 25% RTIL, and 50% graphite powder. The response of the sensor was found to be stable in the pH of 3.5-9.

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