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Long-Term Stable Fabrication of a Nanocomposite Tm(III) Sensor Containing Nanographene/Nanosilica/RTIL/Ionophore

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Given the results of our previous study indicating a relatively strong interaction between 2,2'-dianilinedisulfide (DADS) and Tm(III) ions, the ligand was incorporated as a sensing material into a nano-composite carbon paste electrodes composed of nanographene (NG), nanosilica (NS), and a room temperature ionic liquid namely 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4 (RTIL). The electrodes made of 57% graphite, 6% NG, 15% DADS, 20% RTIL, and 2%NS were found to show the optimum behavior. The sensor shows a Nernstian response (19.7±0.2 mV decade^{-1}) in the concentration window of 1.0×10^{-6}-1.0×10^{-2} M with detection limit of 2.0×10^{-7} M. The response of the sensor was found to be stable in the pH range of 4.0-8.5 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 25 s.

Keywords: Tm(III), sensor, ion selective electrode, potentiometry, carbon paste, nanographene, ionic liquid, nanosilica

1. INTRODUCTION

Thulium is the least abundant of the rare earths and its metal is easy to work, has a bright silvery-gray luster and can be cut by a knife. The element 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. Thulium-silica fiber lasers are used for soft and hard tissue ablation [1,2]. Thulium doped fiber amplifiers (TDFAs) have unique behavior in photonic networks [3], and thulium complexes are used as emitting materials in electroluminescence devices [4].

Thulium and other lanthanides are widely distributed in low concentrations throughout the earth's crust. The vapors or dusts of these elements are very toxic when inhalated. Thulium is the rarest element among the lanthanides. The need for prompt thulium determination becomes urgent when considering the risk of its penetration into humans, animals, and plants, by affecting their metabolic processes. Specifically, lanthanide ions significantly and uniquely affect the biological pathways, resulting in the alteration of physiological processes in the cells of all living organisms [5]. The biological properties of the lanthanides, primarily based on their similarity to calcium, have a high affinity for Ca^{2+} sites on biological molecules, and hence can act as either Ca^{2+} inhibitors or probes [6].

The conventional methods for the determination of low-levels of Tm(III) ions in solutions include mass spectrometry (MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution mass spectrometry, neutron activation analysis, and X-ray fluorescence spectrometry [7-11] 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 [12-15] including rare-earth ions, if the used sensors enjoy levels acceptable sensitivity and selectivity.

These devices in comparison with other advance electrochemical techniques [16] also have the benefits of being simple to use, fast, inexpensive, and capable of producing reliable responses in wide ranges of concentration. A very rough classification of the conventional ISEs divides them into the groups of PVC membrane electrodes, microelectrodes, coated wire electrodes, and carbon paste electrodes, among which carbon paste electrodes (CPEs) have currently attracted a great deal of interest due to their improved renewability, stable response, and low ohmic resistance as compared to the other members of the family [17-20].

CPE-based potentiometric sensors reported are generally based on the incorporation of the ion carrier into a carbon paste matrix, which consists of graphite powder dispersed in a non-conductive mineral oil [17-20]. Due to the fact that mineral oils do not have a fixed composition, the classic CPE electrodes suffer some disadvantages caused by the contaminants or matrix components. CPEs can be placed between membrane electrodes and all solid state electrodes, in terms of mechanical stability.

Regarding the increasing number of potentiometric sensors for Tm(III) and other ions as using different sensing materials [21-39], and in case the aforementioned problems are dealt with effectively, it would be an important breakthrough in the field to develop such sensors in the form of CPEs.

Room temperature ionic liquids (RTIL), which have a number of interesting properties including their 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 have recently been used as binders in the construction of CPEs which seems to have solved the problems of using mineral oils [40-43].

Grapheme is an allotrope of carbon, whose structure is one-atom-thick planar sheets of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice [44]. 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. From its discovery in 2004, they have showed exclusive properties. 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 [45-47].

Addition of nanographene (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 CPEs, has also been found to cause improvement in the response of such sensors.

In this work a highly selective modified nano-composite carbon paste sensor based on DADS as the sensing material has been developed and tested for the monitoring of Tm(III).

2. EXPERIMENTAL SECTION

2.1. Apparatus

The electrochemical cell used for the determination of EMF the 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

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. DADS was prepared as described elsewhere [39]. The nanosilica used was purchased from Wacker HDK®H20 and BET of the hydrophilic silica was 170-230 m^2/g. Distilled deionized water was used throughout all experiments.

2.3. Electrode Fabrication

The modified CPEs were prepared through a general procedure as follows: Desired amounts of DADS, graphite powder, nano silica, 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 [40,42].

3. RESULTS AND DISCUSSION

3.1. Optimization of the CPEs

The ionophore (here DADS) is the main ingredient of any ISE which determines the selectivity of such devices [48-55]. To test the selectivity of DADS (Fig. 1) as well as the role of the composite concentration on its behavior, the ionophore was used to fabricate a series of nano-composite CPEs having a variety of compositions, some of which were modified using the ionic liquid, NS and NG according to Table 1.

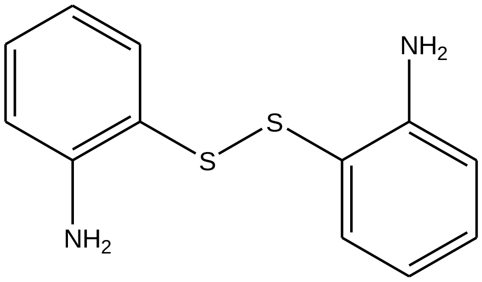

Figure 1. Chemical structure of DADS

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	DADS	NG	NS		
1	80	20	---	-	-	-	3.1± 0.2	1.0×10^{-2} - 1.0×10^{-4}
2	75	20	---	5	-	-	12.3 ± 0.1	1.0×10^{-2} - 1.0×10^{-5}
3	70	20	----	10	-	-	15.1 ± 0.1	1.0×10^{-2} - 4.0×10^{-5}
4	65	20	----	15	-	-	16.7 ± 0.3	1.0×10^{-2} - 2.0×10^{-5}
5	60	20	---	20	-	-	16.7 ± 0.1	4.0×10^{-2} - 1.0×10^{-5}
6	65	---	20	15	-	-	18.9 ± 0.3	3.0×10^{-2} - 7.0×10^{-6}
7	63	----	20	15	2	-	19.1± 0.1	1.0×10^{-2} - 4.0×10^{-6}
8	61	---	20	15	4	-	19.2 ± 0.2	1.0×10^{-2} - 2.0×10^{-6}
9	60	---	20	15	5	-	19.3 ± 0.1	1.0×10^{-2} - 1.0×10^{-6}
10	59	----	20	15	6	-	19.4 ± 0.1	1.0×10^{-2} - 1.0×10^{-6}
11	58	---	20	15	7	-	19.4 ± 0.3	1.0×10^{-2} - 1.0×10^{-6}
12	58	---	20	15	6	1	19.5 ± 0.1	1.0×10^{-2} - 1.0×10^{-6}
13	57	---	20	15	6	2	19.7 ± 0.2	1.0×10^{-2} - 1.0×10^{-6}
14	56	---	20	15	6	3	19.6 ± 0.3	1.0×10^{-2} - 1.0×10^{-6}

As can be seen from the data, the CPE lacking DADS (composition 1), did not show any considerable responses of the concentration changes of the target ion (3.1±0.1 mV decade^{-1}.

Upon the addition of the ionophore, in amounts of 5-20%, 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 15% of DADS to CP electrode was found to lead to a very good response behavior, increasing the potential response from 3.1±0.1 to 16.7±0.2 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 20% wt. (no.5).

By replacing of paraffin with RTIL (no.6) the slope of the sensor increased from 16.7±0.2 to 18.9±0.1 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 2-7% wt of NG (Nos. 7-11) was found to improve the potential response to 19.4± 0.1 mV decade^{-1} of Tm(III) activity respectively. 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.

Further addition of 1-3% wt of nanosilica (NS) to the CPEs (nos. 12-14) was found to cause increases in the sensitivity of the sensor from 19.4 to 19.7 mV decade^{-1}.

Eventually, as can be concluded from the data in Table 1 a composition of 15% DADS, 20% [bmim]BF_4, 57% graphite powder, 6% NG and 2% nanosilica (no. 13) leading to CPEs with a Nernstian slope of 19.6±0.2 mV decade^{-1}, was chosen concluded to be optimum.

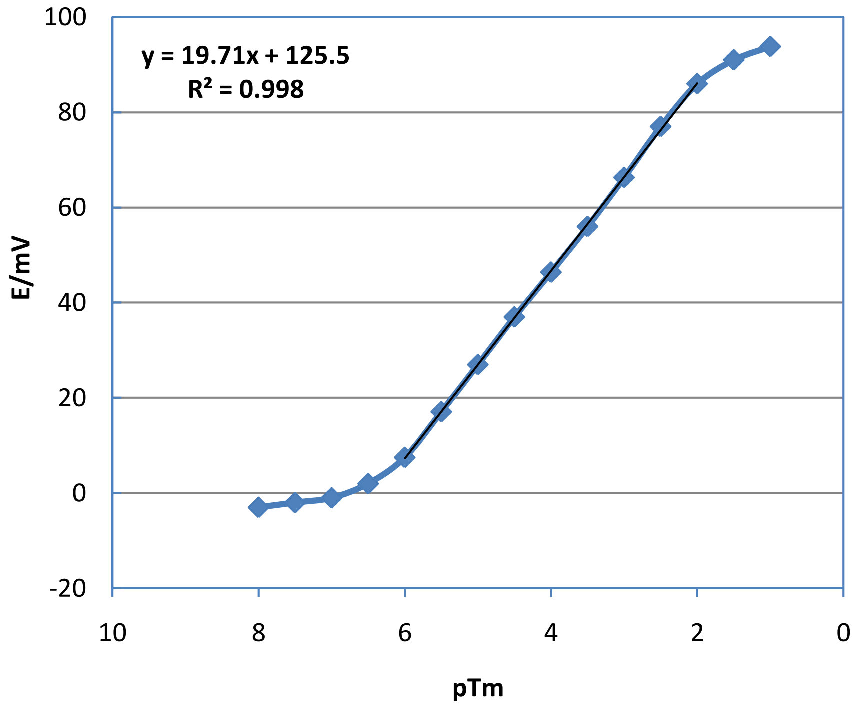

Figure 2. The calibration curve of the Tm(III) nano-composite modified CPE based on DADS (Electrode no. 13)

3.2. Measuring range and limit of detection

The response of the CPE with the optimum composition (no. 13) was examined in a range of 1.0×10^{-1}-1.0×10^{-8} M and the results are depicted in Fig. 2. 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 2.0×10^{-7} M.

3.3. pH Influence

The effect of the pH of the test solution on the response behavior of CPEs with the optimum composition was studied by monitoring the potential response of the sensor in 1.0×10^{-4} M Tm(III) solution while varying the pH values in the range of 1.0-12.0 through adding concentrated HNO_3 or NaOH.

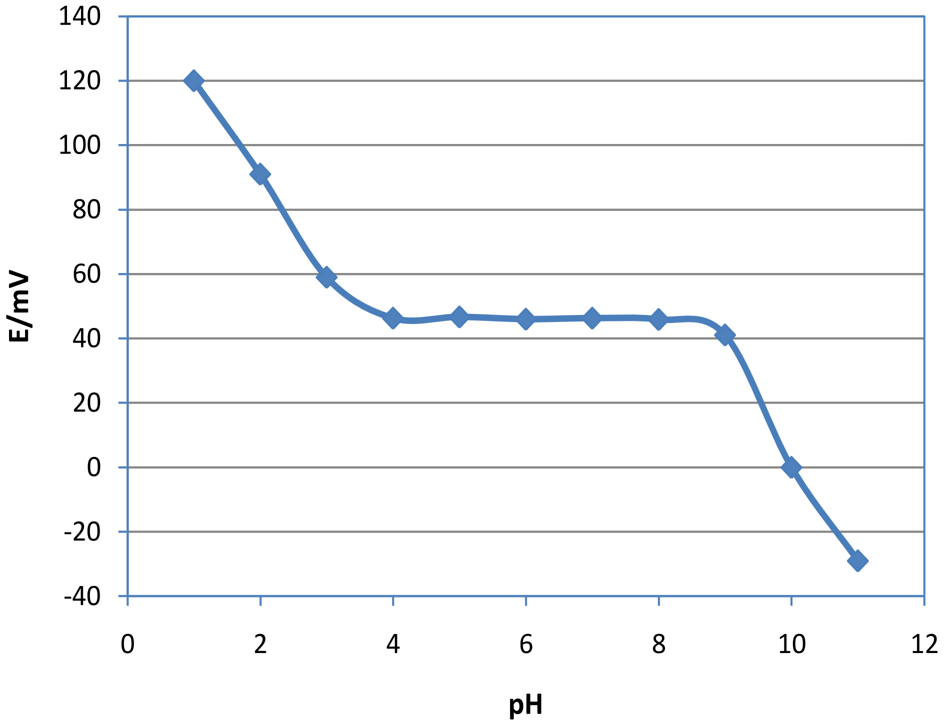

Figure 3. Effect of pH on the potential response of the Tm(III) nano-composite CPE based on (Electrode no. 13) in the test solution of Tm(III) ion (10^{-4} M)

The results as depicted in Fig. 3 reveal that the potential response of the Tm(III) CPE is pH-independent in the range of 4.0-8.5. 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 4.0 the potential drifts most probably due to partial protonation of the donor atoms in DADS.

3.4. Response time

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 [55-60]. 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 25s in the whole concentration range.

3.5. Selectivity and lifetime of the CPEs

As can be conluded from the name of the devices, selectivity behavior of ion selectyive sensors, is of determining importace. Hence we included matched potential (MPM) studies of the selectivity coefficients [61,62] the results of which are summarized in Table 2 which shows that the selectivity coefficients of CPEs for a number of mono, di and teivalents cations to be in the ranges of 1.0×10^{-2}-1.0×10^{-5}. This indicates that the tested ions do not have considerable interferences with the response of the CPEs.

Table 2. The selectivity coefficients of various interfering cations for electrode no. 13; concentration of the reference solution of Tm(III) ion was 5.0×10^{-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+}	3.9×10^{-3}
K^+	$<10^{-5}$	Yb^{3+}	1.1×10^{-2}
Mg^{2+}	2.3×10^{-5}	Tb^{3+}	2.7×10^{-3}
Ca^{2+}	4.7×10^{-3}	La^{3+}	7.3×10^{-4}
Ni^{2+}	2.4×10^{-4}	Sm^{3+}	2.7×10^{-4}
Cu^{2+}	8.5×10^{-4}	Dy^{3+}	2.1×10^{-3}
Pb^{2+}	9.1×10^{-3}	Pr^{3+}	1.1×10^{-2}
Co^{2+}	7.1×10^{-4}	Lu^{3+}	1.2×10^{-2}
Zn^{2+}	1.0×10^{-4}	Ce^{3+}	2.1×10^{-5}
Nd^{3+}	4.3×10^{-3}	Er^{3+}	1.4×10^{-2}

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 3). As seen in Table 3, the CPEs can be used for at least 12 weeks. without significant changes in their slope and detection limits. After this periood, a significant decrease in the slope from 19.7±0.2 to 16.0±0.3 mV decade^{-1} and a gradual increase in the detection limit from 2.0×10^{-7} to 4.0×10^{-6} were observed. This can be attributed to the loss of the RTIL and DADS from the CPEs as a result of application over time.

Table 3. Lifetime of Tm(III) nano-composite modified CPE

Week	Slope (mV decade^{-1})	DL (M)
1	19.7 ± 0.2	2.0×10^{-7}
2	19.7 ± 0.1	2.0 × 10^{-7}
3	19.8 ± 0.3	3.0 × 10^{-7}
4	19.8 ± 0.3	3.0 × 10^{-7}
5	19.6 ± 0.1	3.0 × 10^{-7}
6	19.7 ± 0.3	3.0 × 10^{-7}
7	19.6 ± 0.2	4.0 × 10^{-7}
8	19.6 ±0.3	4.0 × 10^{-7}
9	19.6 ± 0.3	4.0 × 10^{-7}
10	19.5 ± 0.1	5.0 × 10^{-7}
11	19.5 ± 0.3	6.0 × 10^{-7}
12	19.3 ± 0.2	7.0 × 10^{-7}
13	16.0 ± 0.2	4.0 × 10^{-6}
14	13.5 ± 0.1	9.5 × 10^{-6}
15	12.0 ± 0.1	2.5 × 10^{-5}

4. CONCLUSION

A potentiometric 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. DADS was employed as a sensing element in construction of both electrodes. A nano-composite carbon paste electrode was designed to improve the analytical responses. The carbon paste electrode incorporation of nanographene (NG) and nano-silica showed a better response especially in term of lifetime and response time. The best nano-composite electrode was composed of 2%NS, 6% NG, 15% DADS, 20% RTIL, and 57% graphite powder. The response of the sensor was found to be stable in the pH of 4.0-8.

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