

Improvement of a Lu³⁺ Carbon Paste Electrode Based on MWCNT/Nanosilica/Binder/Ionophore Nanocomposite

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A newly designed carbon paste electrode which was modified by nanocomposite structure including multi-walled carbon nanotube (MWCNT) and nanosilica (NS) was developed in order to mensuration the difference of potential versus lutetium(III) ion concentration changes. According to our previous work which introduced 2, 2'-Dithiobis (4-methylthiazole) (TMT) as an active material with strong interaction accompanied by Lu³⁺ ions, TMT was applied as a selector in construction of a nano-composite Lu³⁺-carbon paste electrode (LuCPE). The pastes were prepared by various ingredients such as MWCNT, NS, graphite powder, and paraffin oil. Pursuant to optimization stage, the best response was illustrated by Lu (III)-carbon paste electrode composed of 3% TMT, 25% paraffin oil, 3% MWCNT, 0.5% NS, and 68.5% graphite powder. The new Lu³⁺-CPE displayed a Nernstian response (19.9±0.3 mV decade⁻¹) toward Lu³⁺ ions in widish linear range of 5.0×10⁻⁸-1.0×10⁻² mol L⁻¹ with a detection limit of 1.5×10⁻⁸ mol L⁻¹. The proposed Lu³⁺-CP sensor could employ over the working pH range of 2.8 to 9.3, with a relatively fast response time (~5 s). The matched potential method (K^{M^{PM}}) was applied to assessment the selectivity coefficients for different cations toward new prepared electrode. According to obtained results this Lu³⁺ nano-composite carbon paste sensor exhibited good selectivity with respect to a number of lanthanide and transition metal ions. The constructed Lu³⁺-CPE was successfully used as an indicator electrode in analytical applications such as potentiometric titration of Lu³⁺ ions with EDTA and determination of Lu³⁺ content in various mixtures of different ions.

Keywords: Ion Selective Electrode, Lutetium(III), 2,2'-Dithiobis(4-methylthiazole), Multi-Walled Carbon Nanotubes, Sensor, Carbon Paste Electrode, PVC Membrane, Potentiometry, Nanocomposite

1. INTRODUCTION

Lutetium is the fifteenth and the last element in the lanthanide series with atomic number 71. The small amounts of lutetium are extracted in combination with other lanthanides. Since, the separation of lutetium from other rare elements in order to obtain on useful quantities are very difficult, therefore it is extremely expensive which result in very few commercial usage. Nevertheless, like the

other lanthanides which have a vast range of applications in various fields from the ceramics industry to iron and steel (metallurgy), electronics, and agriculture; lutetium also is usually employed accompanied by yttrium in metal alloys in the metallurgy industry and as a catalyst in various chemical reactions. One of the most important problems in quantitative analysis of lanthanides is choosing the methods, which show the best selectivity toward this family of elements. During different instrumental methods have been reported for determination of lutetium which most of them are costly, prolonged, involving multiple sample manipulations, and etc. such as either spectroscopic methods including inductively couple plasma mass spectrometry (ICP-MS), isotope dilution mass spectrometry, mass spectrometry (MS), X-ray, inductively couple plasma atomic emission spectrometry (ICP-AES), fluorescence spectrometry [1-3], or some electrochemical methods, the ion selective sensors based on potentiometric method due to some advantages such as portability, working fast, plainness in prepare and use, sufficient accuracy in response, low cost, widish range of responsiveness and performance, high and acceptable selectivity and sensitivity and etc. are used as an approved analytical method in analysis of a wide variety of ions [4-50]. In the meantime, in comparison of PVC membrane electrodes the carbon paste electrodes (CPEs) are one of the subgroup of potentiometric sensors which offer renewable surface, stable response, and low ohmic resistance electrodes. This kind of potentiometric sensors are mostly consisting of the ionophore into a carbon paste matrix including graphite powder dispersed in a non-conductive mineral oil. From the standpoint of mechanical stability, the CPEs can be located between membrane electrodes and all solid state electrodes. According to references and reports the addition of modifier materials such as multiwall carbon nanotubes (MWCNTs) with special physicochemical properties such as ultra-light weights, high mechanical strengths, high electrical conductivities, high thermal conductivities, metallic or semi-metallic behaviors and high surface areas to CPEs, improve the response of this type of sensor [51-54]. Multi-walled carbon nanotubes (MWCNTs) have been recently used in composition of carbon paste electrodes. Using MWCNTs in the carbon paste improves the conductivity and, therefore, conversion of the chemical signal to an electrical signal [55-58]. Literature survey revealed that only one of Lu^{3+} -CPE based on different ionophores have been reported [3]. In this work, based on our previous studies [59], a highly selective and sensitive nano-composite carbon paste composition based on TMT as the sensing material, nanosilica, multi-walled carbon nanotubes (MWCNTs) and paraffin oil has been developed and tested for the monitoring of Lu (III) ion.

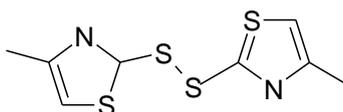


Figure 1. Structure of the ligand TMT.

2. EXPERIMENTAL

2.1. Electromotive force (EMF) measurements

To electromotive force measurement a potentiometric cell was employed including the Lu^{3+} -CPE as the working electrode, an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode

which both electrodes were placed to the glass cell containing $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Lu}(\text{NO}_3)_3$ and connected to a mili-voltmeter. All electromotive force was carried out with the membrane sensor using the following cell assembly:

Carbon paste electrode | $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Lu}(\text{NO}_3)_3$ | Ag/AgCl–KCl (satd.)

As well as, the Debye–Huckel equation $(\log \gamma = -0.511z^2 \left[\frac{\mu^{1/2}}{1 + 1.5\mu^{1/2}} - 0.2\mu \right])$ was applied to calculate the activities.

2.2. Chemicals and reagents

The nano materials such as nanosilica (NS), and multi-wall carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length, SBET: 40-600 m^2/g and with 95% purity were purchased from Research Institute of the Petroleum Industry (Iran), graphite powder with a 1–2 μm particle size (Merck), 2, 2'-Dithiobis (4-methylthiazole) and high-purity paraffin oil (Aldrich) were used for the construction of the carbon pastes. The chloride and nitrate salts of the cations were all purchased from Merck Co. Doubly distilled de-ionized water was used throughout.

2.3. Carbon paste electrode preparation

For the purpose of preparing the carbon paste electrode the following proceeding was carried out respectively: First, different amounts of the paste ingredients such as ionophore (TMT), binder (paraffin oil), graphite powder as an inert matrix, NS and MWCNTs as modifier entirely were pooled. Next, the resulting mixture was stirred to get homogenization paste about 30-40 min. Then, the final paste was transferred to the tip of a tube while a copper wire was put into the opposite side of the tube to electrical contact. It should be noted, in order to avoid possible air gaps which mostly lead to boost the electrode resistance, it is necessary to pack up the paste carefully and thoroughly into the tube tip. Last, to replace the new smoothed surface CPE by the old one, the external layer of the carbon paste was polished with soft paper. In the final stage, the electrode was conditioned for 48 h by soaking it in a $1.0 \times 10^{-3} \text{ mol L}^{-1} \text{ Lu}(\text{NO}_3)_3$ solution.

3. RESULTS AND DISCUSSION

3.1. Potential response of the electrode

To study the selectivity behavior of designed electrode by potentiometric method, TMT was employed as a sensing element in preparation of some PVC membrane electrodes for all of the lanthanide and some of other cations. Lutetium ion due to its appropriate size to the semi cavity of TMT and the rapid exchange kinetics of the resulting its complexation with ionophore, show the best Nernstian response among all other cations, Fig. 2.

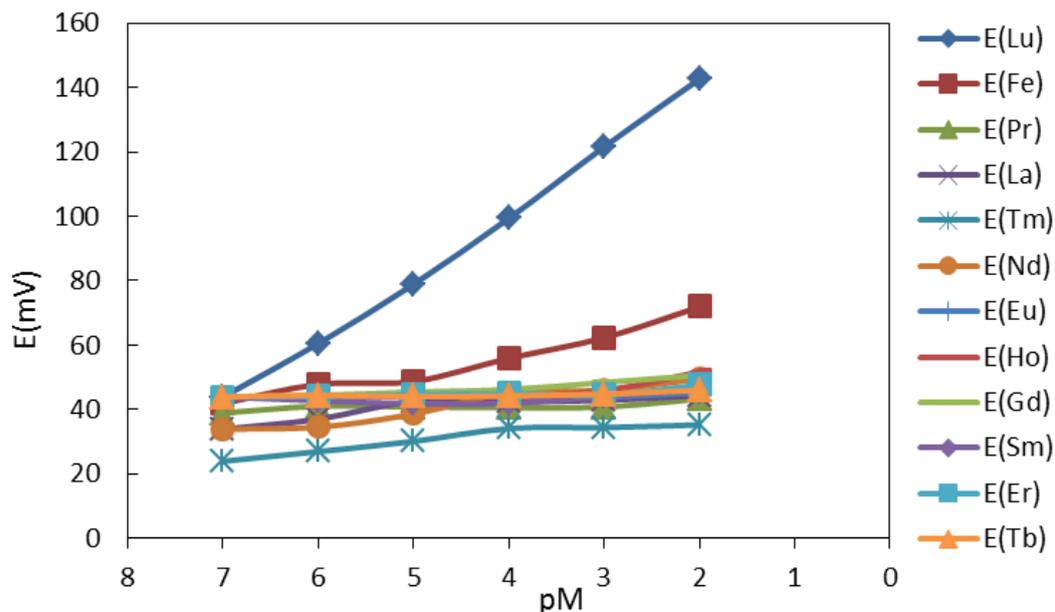


Figure 2. Potential responses of various ion-selective electrodes based on TMT.

3.2. Optimization of the LuCPE

One of the main component in ISE (ion selective electrode) which change the amount of it show the strong effect on the selectivity of electrode, is known as ionophore or ion carrier (here TMT). To evaluate the role and determine the best value of TMT in composite concentration, the diverse amount of TMT was employed to fabricate a numbers of nano-composite CPEs, according to Table. 1 addition of 3% TMT to CP displays the best response toward the other amounts (No. 2 with the slope of 19.8 ± 0.3 mV decade⁻¹). Ordinarily, the addition of ionophore to the compositions results in increasing the potential responses of the CP electrodes. One of the other ingredients in the composition of the carbon paste which cause to enhance the conductivity of the sensor, and increases the transduction of the chemical signal to electrical signal is MWCNT that adding the proper amount of this material leads to make better the dynamic working range of the sensor. The electrode compositions were modified by adding %1, %2, %3 and %5 wt. of MWCNT to the composition (No. 2 & Nos. 5-7) which led to improvements in the sensitivity of the sensor from the sub-Nernstian value of 15.0 ± 0.6 mV decade⁻¹ to 21.6 ± 0.5 mV decade⁻¹. On the other hand, it was observed that changing the amounts of the graphite powder as the filler and paraffin, does not significantly change the potential response of the sensor. Finally, the nanosilica because of its high specific surface area has a hydrophobic property that helps to extraction of the ions into the surface of the CPE, so addition of 0-1% wt. of NS (Nos. 9-12) was found to improve the potential response of Lu (III) activity. In accordance to Table 1, the best response (CPE No. 6) was put out by modified carbon paste electrode based on 0.5% nanosilica, 3% MWCNT, 3% TMT, 25% paraffin oil and 68.5% graphite powder.

Table 1. Optimization of the Lu³⁺-CPE ingredients.

Electrode No.	Composition of Carbon Paste (wt.%)					Slope (mV decade ⁻¹)	Dynamic linear range (mol L ⁻¹)
	Binder (Paraffin oil)	TMT	Graphite Powder	MWCNTs	Nano-Silicon		
1	25	2	70.5	2	0.5	22.6±0.2	1.0×10 ⁻⁶ -1.0×10 ⁻²
2	25	3	69.5	2	0.5	19.8±0.3	1.0×10 ⁻⁶ -1.0×10 ⁻²
3	25	4	68.5	2	0.5	21.0±0.8	1.0×10 ⁻⁶ -1.0×10 ⁻²
4	25	5	67.5	2	0.5	21.6±0.3	1.0×10 ⁻⁶ -1.0×10 ⁻²
5	25	3	70.5	1	0.5	21.1±0.5	1.0×10 ⁻⁶ -1.0×10 ⁻²
6	25	3	68.5	3	0.5	19.9±0.3	5.0×10 ⁻⁸ - 1.0×10 ⁻²
7	25	3	66.5	5	0.5	15.0±0.6	3.0×10 ⁻⁸ -1.0×10 ⁻²
8	20	3	73.5	3	0.5	18.6±0.8	1.0×10 ⁻⁷ -1.0×10 ⁻²
9	30	3	63.5	3	0.5	20.3±0.7	1.0×10 ⁻⁷ -1.0×10 ⁻²
10	25	3	69	3	0	22.3±0.4	1.0×10 ⁻⁷ -1.0×10 ⁻²
11	25	3	68.9	3	0.1	21.0 ± 0.6	1.0×10 ⁻⁷ -1.0×10 ⁻²
12	25	3	68	3	1	18.2±0.8	1.0×10 ⁻⁷ -1.0×10 ⁻²
13	30	3	61.5	5	0.5	16.8±0.4	5.0×10 ⁻⁸ -1.0×10 ⁻²
14	30	3	62	5	0	21.7±0.4	4.0×10 ⁻⁸ -1.0×10 ⁻²
15	30	3	61	5	1	15.9±0.2	1.0×10 ⁻⁷ -1.0×10 ⁻²
16	30	3	61.9	5	0.1	19.7 ± 0.3	5.0×10 ⁻⁸ -1.0×10 ⁻²
17	25	3	66.9	5	0.1	16.3 ± 0.3	5.0×10 ⁻⁸ -1.0×10 ⁻²
18	25	5	64.9	5	0.1	26.0 ± 0.3	1.0×10 ⁻⁶ -1.0×10 ⁻²
19	30	5	59.9	5	0.1	20.4 ± 0.2	1.0×10 ⁻⁷ -1.0×10 ⁻²

3.3. Calibration curve

The potential response of the Lu³⁺-CP electrode based on TMT, Fig. 3, which is known in terms of calibration curve displays the wide working linear range from 5.0×10⁻⁸ to 1.0×10⁻² mol L⁻¹ for optimized TMT-based lutetium (III) carbon paste electrode, while according to Nernstian equation the slope of linear part of calibration curve is 19.9±0.3 mV per decade with detection limit of 1.5×10⁻⁸ mol L⁻¹ of lutetium ions concentration which pursuant to the IUPAC recommendations is calculated by crossing of two extrapolated segments of the calibration curve [60-72]. The standard deviation for ten replicate measurements was ±0.6 mV.

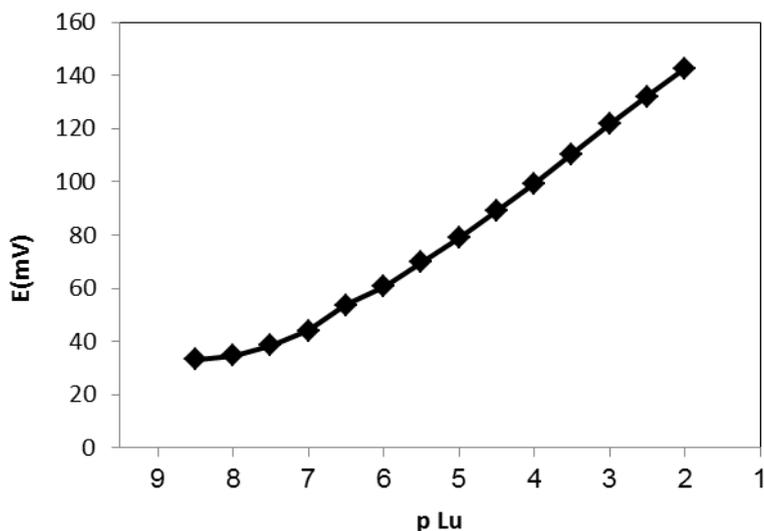


Figure 3. Calibration curves of the TMT-based Lu³⁺-CPE sensor.

3.4. pH influence

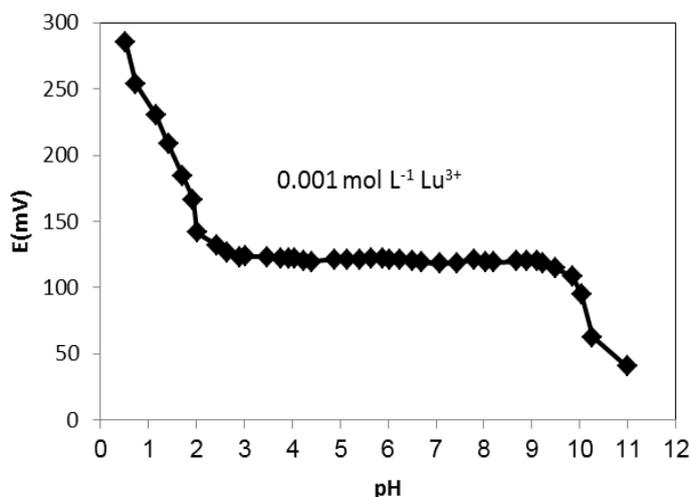


Figure 4. The effect of pH in 1.0×10^{-3} mol L⁻¹ of Lu³⁺ ion on the potential response of the Lu³⁺-CPE based on TMT.

The impact of hydronium ion concentration changes in the potential response of designed LuCPE for 1.0×10^{-3} mol L⁻¹ of test solution was assayed over the pH range of 1.0–11.0 [73-88]. Pursuant to Fig.4 which is illustrated the obtained results the operational pH range that the potential remains constant is over 2.8–9.3.

The observed drift at pH values higher than 9.3 could be attributed to formation of some hydroxyl complexes of Lu³⁺ ions which results in reduce the free lutetium ion in solution, while losing the capability of TMT to complex with lutetium ions in the solution that arising from protonation of the heteroatoms of ionophore such as nitrogen, cause to the potential drift at pH lower than 2.8.

3.5. Dynamic response time the LuCPE

One of the most important specs of ISE is the average elapsed time that the electrode shows the stable potential response at various concentrations which is known in terms of dynamic response time [89-102]. In order to assay this parameter for newly designed Lu⁺³-CP electrode the different concentration of Lu⁺³ solutions from lower to higher (0.0000001, 0.000001, 0.00001, 0.0001, 0.001 and 0.01 mol L⁻¹) was employed respectively. The results that displayed in Fig. 5 represent a very short equilibrium response time (~5 s) in the whole concentration range.

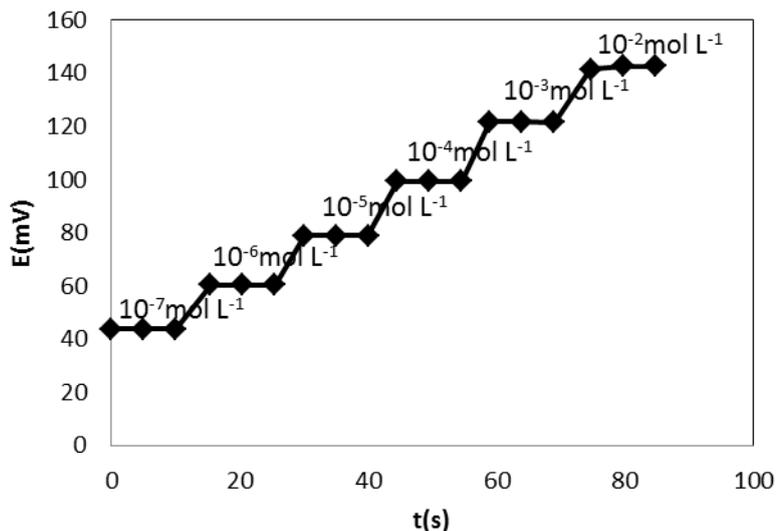


Figure 5. Dynamic response time of Lu³⁺-CP sensor based on TMT.

3.6. Selectivity studies of the LuCPE

The priority of primary ion over interfering ions (alkaline, alkaline earth, lanthanides, transition and heavy metals) is known as the selectivity coefficients which indicate the disturbance of other ions on the response of designed electrode [103-108]. This main factor of ISE was measured graphically at this work by the match potential method (MPM). to determine the selectivity coefficients by matched potential method, first, the potential of the specific activity of Lu⁺³ ions solution while adding to a reference solution was measured, next, the apparent amount of interfering ions solution was sequentially added to the same reference solution in the other experiment to obtain the potential response which matches the one acquired previously by adding Lu⁺³ ion. In the last stage, the final results getting by the following equation that is the ratio of primary ion (A) activity changes to the interfering ion (B).

$$K_{ij}^{MPM} = \frac{\Delta a_A}{a_R}$$

The resulting selectivity coefficients, which are listed in Table 2, demonstrated the negligible disturbance of various cations for the proposed electrode which bodes a good performance of the designed CPE toward the Lu^{3+} ions and specific interaction between Lu^{3+} ions and TMT.

Table 2. Selectivity coefficients ($K_{\text{Lu}^{3+}, \text{B}}^{\text{MPM}}$) of proposed Lu^{3+} -CP sensor.

Interfering Ion (B)	$K_{\text{Lu}^{3+}, \text{B}}^{\text{MPM}}$	Interfering Ion (B)	$K_{\text{Fe}^{3+}, \text{B}}^{\text{MPM}}$
Pr^{+3}	1.0×10^{-4}	Yb^{+3}	4.2×10^{-4}
La^{+3}	9.0×10^{-4}	Mg^{+2}	9.0×10^{-4}
Tm^{+3}	8.3×10^{-4}	Pb^{+2}	7.8×10^{-4}
Nd^{+3}	7.1×10^{-4}	Na^{+}	6.0×10^{-4}
Eu^{+3}	8.4×10^{-4}	K^{+}	8.7×10^{-4}
Ho^{+3}	6.8×10^{-4}	Co^{+2}	7.6×10^{-4}
Gd^{+3}	6.3×10^{-4}	Cd^{+2}	6.3×10^{-4}
Sm^{+3}	8.5×10^{-4}	Ca^{+2}	8.0×10^{-4}
Er^{+3}	7.6×10^{-4}	Fe^{+3}	9.0×10^{-3}
Tb^{+3}	8.1×10^{-4}	Cr^{+3}	8.3×10^{-4}
Dy^{+3}	7.2×10^{-4}	Ni^{+2}	8.1×10^{-4}

The priority of this lutetium-CPE in comparison of the previously reported Lu^{3+} -CP sensors in terms of selectivity, pH range, response time, detection limit and dynamic concentration range can be seen from Table 3.

Table 3. Comparison of selectivity coefficients, detection limit, linearity range, response time and pH range of the proposed Lu^{3+} -CP sensor and the formerly reported Lu^{3+} -CP sensor.

Parameters	Ref. 3	This work
Detection limit (mol L^{-1})	9.5×10^{-7}	1.5×10^{-8}
Linear range (mol L^{-1})	1.0×10^{-6} - 1.0×10^{-2}	5.0×10^{-8} - 1.0×10^{-2}
Response time (s)	~20	~5
Interfering ion (B)	Tb, Ho, Tm, Sm, Dy, Er	Fe
K_{sel}	More than 5.0×10^{-3}	
pH range	3.5-9.0	2.8-9.3

3.7. Analytical application

To assessment the practical application the proposed Lu^{3+} -CP electrode was applied as an indicator electrode to measure the lutetium (III) ion in potentiometric titration of 25ml 1.0×10^{-4} mol L^{-1} Lu^{3+} solution with 1.0×10^{-2} mol L^{-1} EDTA. The test lutetium (III) solution was adjusted by acetate

buffer in pH=6. In accordance to the titration curve which is shown in Fig. 6 the reduction in the potential values will be seen by increasing the amount of EDTA that cause to form complexation of Lu^{3+} ion with EDTA and decrease the free lutetium(III) concentration in the test solution. Ultimately, the sharp obtained titration curve bodes to ability of this electrode to play the role as an indicator electrode.

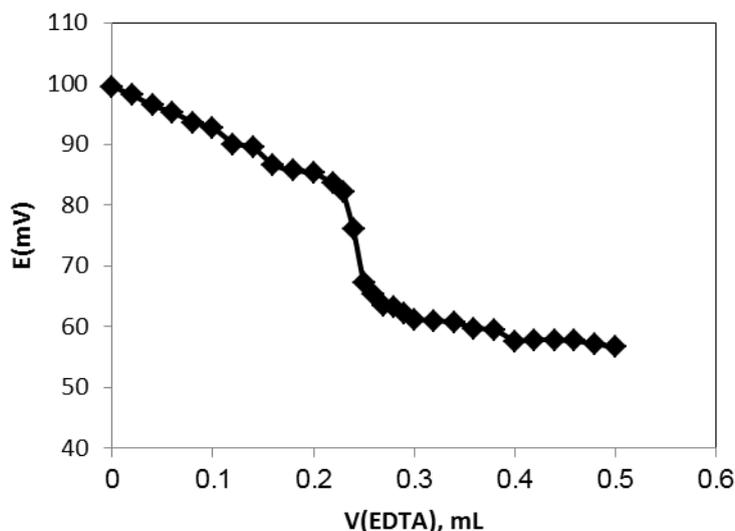


Figure 6. Potential titration curves of 25 mL 1.0×10^{-4} mol L $^{-1}$ Lu^{3+} solution with 1.0×10^{-2} mol L $^{-1}$ of EDTA.

Furthermore, Due to the high degree of lutetium selectivity, this electrode can be applied for monitoring low level lutetium ion concentrations in presence of binary mixtures containing various cations. The resulting data of Table 4 indicate that the accuracy of the Lu^{3+} ions detection in different solutions of different metal ions is almost quantitative.

Table 4. Determination of Lu^{3+} ion in presence of metal ions mixtures.

Lu^{3+} (mol L $^{-1}$)	Added cations (mol L $^{-1}$)	Found ^a (mol L $^{-1}$)	Recovery (%)
1.0×10^{-7}	(0.0001) $\text{Gd}(\text{NO}_3)_3$ & (0.0001) $\text{Pr}(\text{NO}_3)_3$	0.98×10^{-7}	98
1.0×10^{-7}	(0.0001) $\text{Eu}(\text{NO}_3)_3$ & (0.0001) $\text{Er}(\text{NO}_3)_3$	0.99×10^{-7}	99
1.0×10^{-7}	(0.0001) $\text{La}(\text{NO}_3)_3$ & (0.0001) $\text{Ho}(\text{NO}_3)_3$	1.02×10^{-7}	102
1.0×10^{-7}	(0.0001) $\text{Dy}(\text{NO}_3)_3$ & (0.0001) $\text{Yb}(\text{NO}_3)_3$	0.96×10^{-7}	96
1.0×10^{-7}	(0.0001) $\text{Tb}(\text{NO}_3)_3$ & (0.0001) $\text{Nd}(\text{NO}_3)_3$	0.98×10^{-7}	98
1.0×10^{-7}	(0.0001) $\text{Na}(\text{NO}_3)$ & (0.0001) $\text{Ca}(\text{NO}_3)_2$	0.99×10^{-7}	99
1.0×10^{-7}	(0.0001) $\text{Pb}(\text{NO}_3)_2$ & (0.0001) $\text{Ni}(\text{NO}_3)_2$	1.01×10^{-7}	101
1.0×10^{-7}	(0.0001) $\text{Cr}(\text{NO}_3)_3$ & (0.0001) $\text{Fe}(\text{NO}_3)_3$	0.94×10^{-7}	94
1.0×10^{-7}	(0.0001) $\text{K}(\text{NO}_3)$ & (0.0001) $\text{Mg}(\text{NO}_3)_2$	0.99×10^{-7}	99
1.0×10^{-7}	(0.0001) $\text{Pb}(\text{NO}_3)_2$ & (0.0001) $\text{Ca}(\text{NO}_3)_2$ & (0.0001) $\text{K}(\text{NO}_3)$	1.02×10^{-7}	101
1.0×10^{-7}	(0.0001) $\text{Fe}(\text{NO}_3)_3$ & (0.0001) $\text{Na}(\text{NO}_3)$ & (0.0001) $\text{Ca}(\text{NO}_3)_2$	0.96×10^{-7}	96

a. Results are based on three measurements

4. CONCLUSION

In this work, 2,2'-Dithiobis(4-methylthiazole) (TMT) with cyclic groups and heteroatoms including nitrogen and sulfur was employed as an active material to play the role of selector in construction of Lu(III) nanocomposite carbon paste electrode which modified by MWCNT and nanosilica. The modified Lu⁺³-CPE in comparison of recently designed PVC membrane electrode based on same ionophore to determination of lutetium (III) ion exhibited the better potentiometric response in terms of sensitivity, Nernstian slope, linear range, and response stability. The created Lu⁺³-CPE showed a Nernstian response (19.9 ± 0.3 mV decade⁻¹) in the range of 5.0×10^{-8} - 1.0×10^{-2} mol L⁻¹ with detection limit of 1.5×10^{-8} mol L⁻¹. The working pH range which the response of the sensor is independent from H₃O⁺ ion concentration changes is about 2.8-9.3. The nano-composite based Lu(III) sensor displayed good selectivity, response time (about 5 s). Further, the developed electrode can be employed successfully to analytical applications such as potentiometric titration and monitoring of Lu³⁺ ions in various mixtures of interfering ions.

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References

1. R.E. Kirk, and D.F. Othmer, *Encyclopedia of Chemical Technology*, 1982, Vol. 19, Wiley, p. 836.
2. S. Pasyar, H. A. Zamani, and M. Poorghazi-Mahmoodabadi, *Int. J. Electrochem. Sci.* 8 (2013) 4023.
3. P. Norouzi, M. Pirali-Hamedani, S.O. Ranaei-Siadat, and M.R. Ganjali, *Int. J. Electrochem. Sci.* 6 (2011) 3704.
4. H. A. Zamani, M. Masrournia, M. Rostame-Faroge, M. R. Ganjali, and H. Behmadi, *Sensor Lett.* 6 (2008) 759.
5. M. Pooyamanesh, H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, and P. Norouzi, *Anal. Lett.* 40 (2007) 1596.
6. H. A. Zamani, G. Rajabzadeh, and M. R. Ganjali, *Bull. Chem. Soc. Jpn* 80 (2007) 172.
7. K. Srinivasan, G. A. Rechnitz, *Anal. Chem.* 41 (1969) 1203.
8. M.J. Gismera, D. Hueso, J.R. Procopio, M.T. Sevilla, *Analytica Chimica Acta* 524 (2004) 347.
9. J. Růžička, E.H. Hansen, J.C. Tjell, *Analytica Chimica Acta* 67 (1973) 155.
10. M.R.Abedi, H. A. Zamani, M. R. Ganjali, and P. Norouzi, *Sensor Lett.* 5 (2007) 516.
11. M. R. Ganjali, H. Shams, F. Faridbod, L. Hajiaghababaei, and P. Norouzi, *Mater. Sci. Eng. C*, 29 (2009) 1380.
12. H. A. Zamani, M. R. Ganjali, and M. Adib, *J. Braz. Chem. Soc.* 18 (2007) 215.
13. S.L. Belli, A. Zirino, *Anal. Chem.* 65 (1993) 2583.
14. H. A. Zamani, G. Rajabzadeh, A. Firouz, and M. R. Ganjali, *J. Anal. Chem.* 62 (2007) 1080
15. H. Khani, M.K. Rofouei, P. Arab, V. Kumar Gupta, Z. Vafaeia, *Journal of Hazardous Materials* 183 (2010) 402.
16. H. A. Zamani, M. R. Ganjali, P. Norouzi, and M. Adib, *Sensor Lett.* 5 (2007) 522.
17. P. Anker, E. Wieland, D. Ammann, R.E. Dohner, R. Asper, W. Simon, *Anal. Chem.* 53 (1981) 1970.

18. H. A. Zamani, M. R. Ganjali, and N. Seifi, *Collect. Czech. Chem. Commun.* 72 (2007) 1189.
19. H. A. Zamani, M. T. Hamed-Mosavian, E. Aminzadeh, M. R. Ganjali, M. Ghaemy, H. Behmadi, and F. Faridbod, *Desalination* 250 (2010) 56.
20. R.A. Saar, J.H. Weber, *Anal. Chem.* 52 (1980) 2095.
21. H. A. Zamani, M. T. Hamed-Mosavian, E. Hamidfar, M. R. Ganjali, and P. Norouzi, *Mater. Sci. Eng. C* 28 (2008) 1551.
22. M. R. Abedi, and H. A. Zamani, *Anal. Lett.* 41 (2008) 2251.
23. P. Bühlmann, E. Pretsch, and E. Bakker, *Chem. Rev.* 98 (1998) 1593.
24. H. A. Zamani, M. R. Ganjali, P. Norouzi, A. Tajarodi, and Y. Hanifehpour, *J. Chil. Chem. Soc.* 52 (2007) 1332.
25. V. K. Gupta, R. N. Goyal, M. K. Pal, and R. A. Sharma, *Anal. Chim. Acta* 653 (2009) 161.
26. H. A. Zamani, J. Abedini-Torghabeh, and M. R. Ganjali, *Bull. Korean Chem. Soc.* 27 (2006) 835.
27. P.J.S. Smith, K. Hammar, D.M. Porterfield, R.H. Sanger, and J.R. Trimarchi, *Microscopy Research and Technique* 46 (1999) 348.
28. H. A. Zamani, A. Imani, A. Arvinfar, F. Rahimi, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Mater. Sci. Eng. C* 31 (2011) 588.
29. M. R. Abedi, H. A. Zamani, M. R. Ganjali, and P. Norouzi, *Intern. J. Environ. Anal. Chem.* 88 (2008) 353.
30. W.T. Bresnahan, C.L. Grant, J.H. Weber, *Anal. Chem.* 50 (1978) 1675.
31. H. A. Zamani, *Anal. Lett.* 41 (2008) 1850.
32. V.P.Y Gadzekpo, G.D Christian, *Analytica Chimica Acta* 164 (1984) 279.
33. H.A. Zamani, G. Rajabzadeh, and M.R. Ganjali, *Sensor Lett.* 7 (2009) 114.
34. H.K. Sharma, and N. Sharma, *E-J. Chem.* 6 (2009) 1139.
35. U. Fiedler, J. Růžička, *Analytica Chimica Acta* 67 (1973) 179.
36. H. A. Zamani, M. Nekoei, M. Mohammadhosseini, M. R. Ganjali, *Mater. Sci. Eng. C* 30 (2010) 480.
37. M.R. Ganjali, A. Ghesmi, M. Hosseini, M.R. Pourjavid, M. Rezapour, M. Shamsipur, and M. Salavati-Niasari, *Sens. Actuators B* 105 (2005) 334.
38. S. K. Mittal, S. K. A. Kumar, and H. K. Sharma, *Talanta* 62 (2004) 801.
39. H. A. Zamani, M. Mohammadhossieni, M. Nekoei, and M. R. Ganjali, *Sensor Lett.* 8 (2010) 303.
40. P. J. Milham, A. S. Awad, R. E. Paull, and J. H. Bull, *Analyst* 95 (1970) 751.
41. H.A. Zamani, M. Rohani, A. Zangeneh-Asadabadi, M.S. Zabihi, M.R. Ganjali, and M. Salavati-Niasari, *Mater. Sci. Eng. C* 30 (2010) 917.
42. Tom Lindfors, Ari Ivaska, *Analytica Chimica Acta* 437 (2001) 171.
43. H. A. Zamani, M. Masrournia, S. Sahebnaasagh, and M. R. Ganjali, *Anal. Lett.* 42 (2009) 555.
44. A. Sil, V.S. Ijeri, and A.K. Srivastava, *Sens. Actuators B* 106 (2005) 648.
45. A. K. Singh, R. P. Singh, and P. Saxena, *Sens. Actuators B* 114 (2006) 578.
46. M. Mohammadhossieni, H. A. Zamani, and M. Nekoei, *Anal. Lett.* 42 (2009) 298.
47. F. J. Sáez de Viteri, and D. Diamond, *Analyst* 119 (1994) 749.
48. H. A. Zamani, G. Rajabzadeh, A. Firouz, and A. A. Ariaii-Rad, *J. Braz. Chem. Soc.* 16 (2005) 1061.
49. S.R. Sheen, and J.S. Shih, *Analyst* 117 (1992) 1691.
50. M. Nekoei, H. A. Zamani, and M. Mohammadhossieni, *Anal. Lett.* 42 (2009) 284.
51. P.M. Ajayan, *Chem. Rev.* 99 (1999) 1787.
52. R.N. Goyal, M. Oyama, V.K. Gupta, S.P. Singh, and R.A. Sharma, *Sens. Actuators B* 134 (2008) 816.
53. L. Liu, L. Wang, H. Yin, Y. Li, and X. He, *Analytical Letters* 39 (2006) 879.
54. G.Li, H. Xu, W.J. Huang, Y. Wang, Y.S. Wu, and R. Parajuli, *Mea. Sci. & Technol.* 19 (2008) 065203.

55. M.R. Ganjali, H. Khoshshafar, F. Faridbod, A. Shirzadmehr, M. Javanbakht, P. Norouzi, *Electroanalysis* 21 (2009) 2175.
56. N. Maleki, A. Safavi, and F. Tajabadi, *Anal. Chem.* 78 (2006) 3820.
57. B. Rezaei, and S. Damiri, *IEEE Sensors* 8 (2008) 1523.
58. M. Siswana, K.I. Ozoemena, and T. Nyokong, *Sensors* 8 (2008) 5096.
59. H. A. Zamani, *Anal. Lett.* 42 (2009) 615.
60. R. De Marcol, G. Clarke, and B. Pejicic, *Electroanalysis* 19 (2007) 1987.
61. J.S. Kim, A. Ohki, R. Ueki, T. Ishizuka, T. Shimotashiro, and S. Maeda, *Talanta* 48 (1999) 705
62. M. R. Ganjali, P. Norouzi, F. Faridbod, S. Riahi, J. Ravanshad, J. Tashkhourian, M. Salavati-Niasari and M. Javaheri, *Ieee Sensors J.* 7 (2007) 544.
63. H. A. Zamani, M. S. Zabihi, M. Rohani, A. Zangeneh-Asadabadi, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Mater. Sci. Eng. C* 31 (2011) 409.
64. J.E. Harwood, *Water Research.* 3 (1969) 273.
65. H.A. Zamani, M.R. Ganjali, H. Behmadi, and M.A. Behnajady, *Mater. Sci. Eng. C* 29 (2009) 1535.
66. R.K Mahajan, I. Kaur, T.S. Lobana, *Talanta.* 59 (2003) 101.
67. M. R. Ganjali, P. Norouzi, F. S. Mirnaghi, S. Riahi and F. Faridbod, *Ieee Sensors J.* 7 (2007) 1138.
68. H. A. Zamani, G. Rajabzadeh, M. Masrornia, A. Dejbord, and M. R. Ganjali, *Desalination* 249 (2009) 560.
69. A. Craggs, G. J. Moody, and J. D. R. Thomas, *J. Chem. Educ.* 51 (1974) 541.
70. J. F. Coetzee, W. K. Istone, *Anal. Chem.* 52 (1980) 53.
71. H. A. Zamani, M. R. Ganjali, P. Norouzi, and S. Meghdadi, *Anal. Lett.* 41 (2008) 902.
72. B.T. Altura, B.M. Altura, *Magnes Trace Elem.* 10 (1991) 90.
73. H. A. Zamani, M. R. Ganjali, P. Norouzi, and M. Adib, *Mater. Sci. Eng. C* 28 (2008) 157.
74. R.J. Levins, *Anal. Chem.* 43 (1971) 1045.
75. H.A. Zamani, M.R. Ganjali, F. Faridbod, and M. Salavati-Niasari, *Mater. Sci. Eng. C* 32 (2012) 564.
76. U. Schaller, E. Bakker, U.E. Spichiger, E. Pretsch, *Anal. Chem.* 66 (1994) 391.
77. H. A. Zamani, M. Masrournia, H. Mohamadzadeh, M. R. Ganjali, M. Rahimizadeh, and P. Ziaei, *Mater. Sci. Engin. C* 29 (2009) 976.
78. A. Fitch, F.J. Stevenson, Y. Chen, *Organic Geochemistry* 9 (1986) 109.
79. H. A. Zamani, R. Kamjoo, M. Mohammadhossieni, M. Zaferoni, Z. Rafati, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Mater. Sci. Eng. C* 32 (2012) 447.
80. H. Yu Qin, S. Peper, and E. Bakker, *Electroanalysis* 14 (2002) 1375.
81. H. A. Zamani, M. Mohammadhossieni, Saeed Haji-Mohammadrezazadeh, F. Faridbod, M. R. Ganjali, S. Meghdadi, and A. Davoodnia, *Mater. Sci. Eng. C* 32 (2012) 712.
82. R. W. Cattrall, P. Chin-Poh, *Anal. Chem.* 47 (1975) 93.
83. H. A. Zamani, M. Rohani, M. Mohammadhosseini, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Sensor Lett.* 9 (2011) 1745.
84. H. A. Zamani, B. Feizyzadeh, F. Faridbod, and M. R. Ganjali, *Sensor Lett.* 9 (2011) 1767.
85. J.D.R. Thomas, *Analytica Chimica Acta* 180 (1986) 289.
86. E. Naddaf, and H. A. Zamani, *Anal. Lett.* 42 (2009) 2838.
87. K. Suzuki, H. Yamada, K. Sato, K. Watanabe, H. Hisamoto, Y. Tobe, K. Kobiro, *Anal. Chem.* 65 (1993) 3404.
88. M. Masrournia, H.A. Zamani, H.A. Mirrashid, M.R. Ganjali, and F. Faridbod, *Mater. Sci. Eng. C* 31 (2011) 574.
89. R.Y. Tsien, T.J. Rink, *Biochimica et Biophysica Acta (BBA) - Biomembranes.* 599 (1980) 623.
90. H. A. Zamani, B. Feizyzadeh, F. Faridbod, and M. R. Ganjali, *Mater. Sci. Eng. C* 31 (2011) 1379.
91. H. A. Zamani, A. Arvinfar, F. Rahimi, A. Imani, M. R. Ganjali, and S. Meghdadi, *Mater. Sci. Eng. C* 31 (2011) 307.
92. A. Craggs, L. Keil, G.J. Moody, J.D.R. Thomas, *Talanta* 22 (1975) 907.

93. H. A. Zamani, Fatemeh Naghavi-Reyabbi, M. Mohammadhossieni, Babak Feizyadeh, M. R. Abedi, F. Faridbod, and M. R. Ganjali, *Sensor Lett.* 10 (2012) 112.
94. H. A. Zamani, F. Faridbod, and M. R. Ganjali, *Mater. Sci. Eng. C* 33 (2013) 608.
95. T. Sokalski, A. Ceresa, T. Zwickl, and E. Pretsch, *J. Am. Chem. Soc.* 119 (1997) 11347.
96. H. A. Zamani, F. Naghavi-Reyabbi, F. Faridbod, M. Mohammadhosseini, M. R. Ganjali, A. Tadjarodi, and M. Rad, *Mater. Sci. Eng. C* 33 (2013) 870.
97. H.A. Zamani, A. Zanganeh-Asadabadi, M. Rohani, M. S. Zabihi, J. Fadaee, M. R. Ganjali, F. Faridbod, and S. Meghdadi, *Mater. Sci. Eng. C* 33 (2013) 984.
98. R. W. Cattrall, H. Freiser, *Anal. Chem.* 43 (1971) 1905.
99. H. A. Zamani, F. Faridbod, and M. R. Ganjali, *Mater. Sci. Eng. C* 33 (2014) 488.
100. H. A. Zamani, and F. Faridbod, *J. Anal. Chem.* 69 (2014) 1073.
101. F. Mohammadabadi, H.A. Zamani, F. Joz-Yarmohammadi, and M.R. Abedi, *Int. J. Electrochem. Sci.* 10 (2015) 2791
102. H.A. Zamani, M. Ranjkesh, and M.R. Abedi, *Int. J. Electrochem. Sci.* 9 (2014) 8435.
103. Y. Umezawa, K. Umezawa, and H. Sato, *Pure Appl. Chem.* 67 (1995) 507.
104. M. R. Ganjali, N. Motakef-Kazami, F. Faridbod, S. Khoee and P. Norouzi, *J. Hazard Mater.* 173 (2010) 415.
105. R. Zare-Dorabei, P. Norouzi and M. R. Ganjali, *J. Hazard. Mater.* 171 (2009) 601.
106. K. Alizadeh, R. Parooi, P. Hashemi, B. Rezaei and M. R. Ganjali, *J. Hazard. Mater.* 186 (2011) 1794.
107. S. Karimian, H. A. Zamani, and M. Vahdani, *Int. J. Electrochem. Sci.* 8 (2013) 2710.
108. S. Matysik, F. M. Matysik, J. Mattusch, and W. D. Einicke, *Electroanalysis* 10 (1998) 57.

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