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A Modified Ho^{3+} Carbon Paste Electrode Based on Multi-walled Carbon Nanotubes (MWCNTs) and Nanosilica

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A novel carbon paste ion selective electrode for determination of trace amount of holmium was prepared. Multi-walled carbon nanotubes (MWCNTs) and nanosilica were used for improvement of a holmium carbon paste sensor response. MWCNTs have a good conductivity which helps the transduction of the signal in carbon paste electrode. The electrode composition of 20% paraffin oil, 52% graphite powder, 20% ionophore, 5% MWCNTs, and 3% nanosilica showed the stable potential response to Ho^{3+} ions with the Nernstian slope of 19.9 (±0.3) mV $decade^{-1}$ over a wide linear concentration range of 10^{-7}-10^{-2} mol L^{-1}. The electrode has fast response time, and long term stability (more than 2 months).

Keywords: multi-walled carbon nanotubes; nanosilica; sensor; Ho^{3+} ions; carbon paste ion selective

1. INTRODUCTION

Carbon paste electrodes (CPEs) have attracted attention as ion selective electrodes mainly due to their advantages over membrane electrodes such as renewability, stable response, low ohmic resistance, no need for internal solution [1-5]. The carbon paste usually consists of graphite powder dispersed in a non-conductive mineral oil.

Now a days, carbon nanotubes (CNTs) have also been used in carbon paste electrodes [6-8]. CNTs have very interesting physicochemical properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area [9]. The facility of electron transfer between the electroactive species and the electrodes offers great promise for fabricating electrochemical sensors and biosensors. The combination of these characteristics make CNTs unique materials with the potential for diverse applications [10–19].

Silica-based materials are of interest for a number of reasons. They are robust inorganic solids displaying both high specific surface area (200-1500 m^2 g^{-1}) and a three-dimensional structure made of highly open spaces interconnected to each other. This would impart high diffusion rates of selected target analytes to a large number of accessible binding sites, which constitutes definite key factor in designing sensor devices with high sensitivity. On the other hand, a large variety of organic moieties or inorganic layers of defined reactivity can modify the silica surface. When applied in connection to electrochemistry, these properties could be advantageously exploited in electroanalysis by inducing high selectivity (either by specific binding or by preferential recognition), or enabling electrocatalysis at the modified electrode [20].

In this study, Ho^{3+} carbon paste electrode based on N'-(2-hydroxybenzylidene)furan-2-carbohydrazide (NFC) ionophore, Fig. 1, was constructed in order to determine Ho^{3+} ion concentration. Then the electrode was modified by MWCNTs and nanosilica to achieve the better electrode response.

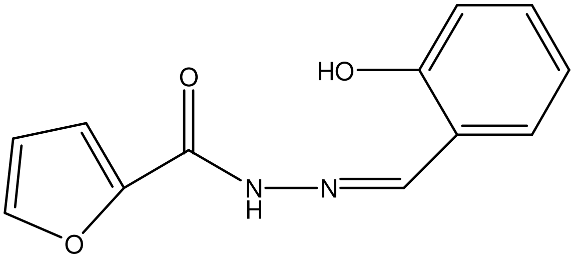

Figure 1. Chemical structure of N'-(2-hydroxybenzylidene)furan-2-carbohydrazide (NFC) ionophore

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell, where the Ho^{3+} carbon paste electrode was placed, consisted of an R684 model Analion Ag/AgCl double junction reference electrode as a reference electrode. A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0±0.1 °C.

2.2. Reagents

The graphite powder with a 1–2 μm particle size (Merck) along with the paraffin oil (Aldrich) was of high purity and was used for the preparation of the carbon pastes. The ionophore NFC was synthesized according to the previously reported procedure [21]. The multi-walled carbon nanotubes

(MWCNTs) were purchased from Research Institute of the Petroleum Industry (Iran). Nanosilica used is Wacker HDK® H20.

2.3. Carbon Paste Electrode Preparation

Different amounts of the ionophore NFC along with appropriate amount of graphite powder, nanosilica and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube. The electrode body was fabricated from a glass tube of i.d. 5 mm and a height of 3 cm. After the mixture homogenization, the paste was packed carefully into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact. The external electrode surface was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the carbon paste. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} mol L^{-1} $Ho(NO_3)_3$ solution.

2.4. Emf measurements

The electrochemical cell can be represented as follows:

Ag,AgCl(s), KCl (3 M) ‖ sample solution | carbon paste electrode

Calibration graph was drawn by plotting the potential, E, versus the logarithm of the holmium ion concentration.

3. RESULTS AND DISCUSSION

Selectivity for a certain ion selective sensor is greatly related to the ionophore used [22-24]. Due to the existence of oxygen and nitrogen donor atoms, which are intermediate properties, in the structure of NFC, its interaction with some mono, di and trivalent metal ions was studied conductometricly in acetonitrile solution [25,26]. The results showed that NFC has special interaction with Ho^{3+} ions, in comparison with other cations tested ($\log K_f = 5.51\pm0.22$) and may be acts as a suitable ion carrier in fabrication of Ho^{3+} CPE.

3.1. Electrode composition and modification

Different carbon paste compositions, as shown in Table 1, were prepared. As it can be seen, two kind of carbon paste electrode was prepared (modified and unmodified CPEs). The best unmodified CPE, with optimized composition (CPE No. 2), shows a near Nernstian slope about 14.5 mV $decade^{-1}$.

Using MWCNT in the composition of the carbon paste not only improves the conductivity of the sensor, but also increases the transduction of the chemical signal to electrical signal. By increasing the conductivity, the dynamic working range and response time of the sensor improve. If the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values. It is clearly seen from Table 1, CPE No. 5.

Using nanosilica in the composition of the carbon paste can also improve the response of the electrode. Nanosilica is a filler compound which has high specific surface area. It has a hydrophobic property that helps extraction of the ions into the surface of the CPE. Also, it enhances the mechanical properties of the electrode.

Table 1. The optimization of the carbon paste ingredients

CPE No.	Paraffin	NFC	Graphite Powder	MWCNTs	Nanosilica	Slope (mVdecade^{-1})	R^2
1	20%	15%	65%	0%	0%	13.0±0.5	0.973
2	20%	20%	60%	0%	0%	14.5±0.2	0.990
3	20%	25%	55%	0%	0%	14.1±0.4	0.987
4	25%	20%	55%	0%	0%	13.58±0.3	0.972
5	20%	20%	55%	5%	0%	15.6±0.2	0.993
6	20%	20%	55%	10%	0%	15.4±0.3	0.986
7	20%	20%	54%	5%	1%	16.7±0.4	0.995
8	20%	20%	52%	5%	3%	19.9±0.3	0.998
9	20%	20%	50%	5%	5%	18.6±0.3	0.992
10	20%	20%	57%	0%	3%	14.2±0.3	0.987

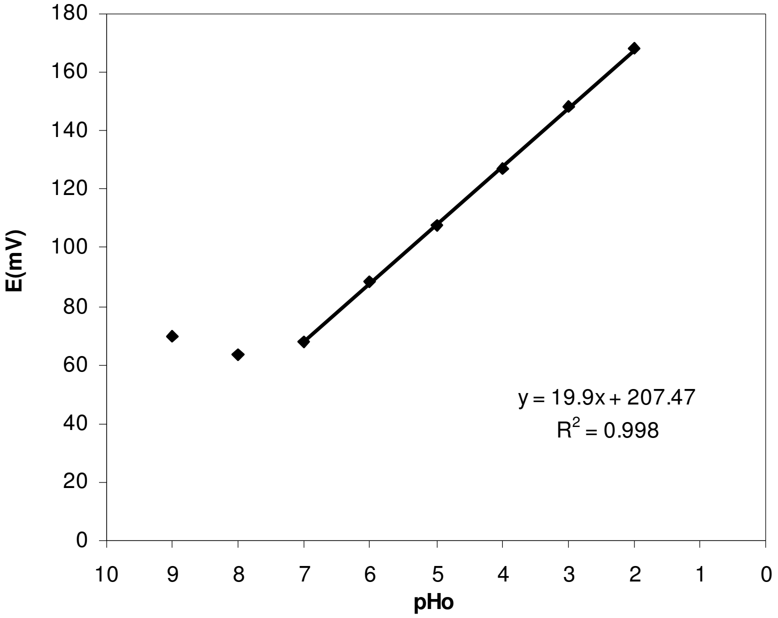

Figure 2. The calibration curve of the Ho^{3+} modified CPE (electrode no. 8)

3.2. Calibration curve

The measuring range of an ion selective electrode includes the linear part of the calibration graph as shown in Fig. 2. Measurements can be performed in this lower range. According to another definition, the measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits [27-31]. The applicable measuring range of the modified sensor as shown in Fig. 2 is between 1.0×10^{-7} and 1.0×10^{-2} mol L^{-1}.

By extrapolating the linear parts of the ion selective calibration curve, the detection limit of an ion selective electrode can be calculated [32-34].

In this work the detection limit of the modified CPE was 3.1×10^{-8} mol L^{-1} which was calculated by the extrapolating of the two segment of the calibration curve in Fig. 2.

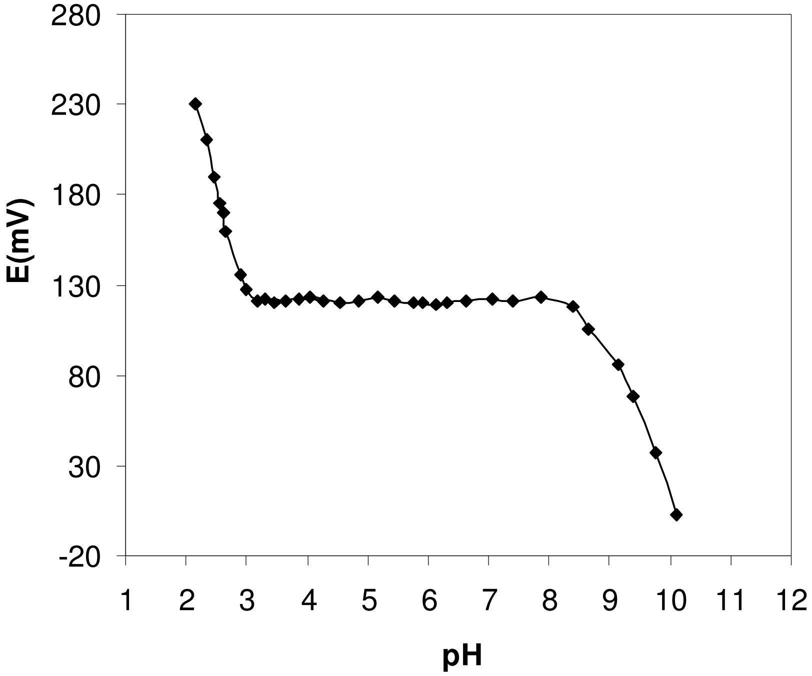

Figure 3. pH effect on the potential response of the Ho^{3+} modified CPE (electrode no. 8)

3.3. pH effect on the electrode response

In order to investigate the pH effect on the potential response of the electrode , the potentials were measured for a fixed concentration of Ho^{3+} solution (1.0×10^{-4} mol L^{-1}) having different pH values. The pH varied from (2-10) by addition of HNO_3 or NaOH. The potential variation as a function of pH is plotted in Fig. 3. The composition of the electrode was kept constant during all experiments. The results showed the potential of electrode is constant between pH (3-8). Thus the electrode works satisfactorily in the pH range 3-8, as no interference from H^+ or OH^- is observed in the range. The fluctuations above the pH value of 8.0 might be justified by the formation of the soluble and insoluble Ho^{3+} ion hydroxy complexes in the solution. And the fluctuations below the pH value of 3.0 were attributed to the partial protonation of the employed ligand [34-38].

3.4. Response time

The response time of an ion-selective electrode is also an important factor for any analytical application. In the case of all electrodes, the average response time was defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values, after successive immersions in a series of solutions, each having a 10-fold concentration difference [39-43]. The resulting potential–time responses for the mentioned electrode were obtained upon changing the Ho^{3+} concentration from 1.0×10^{-7} to 1.0×10^{-2} mol L^{-1} (by fast injection of µL-amounts of a concentrated solution of Ho^{3+}). Results showed that the potentiometric response time of the electrode was about 10s.

Table 2. The selectivity coefficients of various interfering cations for the electrode no. 8

Interference (X)	**K_{Pb}**	**Interference (X)**	**K_{Pb}**
Ca^{2+}	1.2×10^{-4}	Dy^{3+}	1.7×10^{-2}
Mg^{2+}	3.0×10^{-4}	Nd^{3+}	7.5×10^{-3}
Cu^{2+}	1.8×10^{-3}	Tm^{3+}	1.5×10^{-3}
Pb^{2+}	7.5×10^{-4}	Sm^{3+}	3.0×10^{-3}
Na^{+}	3.0×10^{-4}	Pr^{3+}	3.5×10^{-3}
K^{+}	3.0×10^{-4}	Er^{3+}	3.0×10^{-3}
Ag^{+}	2.0×10^{-4}	La^{3+}	3.0×10^{-3}

3.5. Interference studies

The potentiometric selectivity coefficients, describing the preference of the suggested electrode for an interfering ion, X, with reference to the holmium ion, Ho^{3+}, were determined by the matched potential method (MPM). The MPM is recommended by IUPAC [44] to overcome the difficulties associated with the methods based on the Nicolsky– Eisenman equation [45].

According to this method, the specified activity (concentration) of the primary ion is added to a reference solution (1.0×10^{-7} mol L^{-1} holmium nitrate, in this case) and the potential is measured. In a separation experiment, interfering ions (X) are successively added to an identical reference solution, until the measured potential matched that obtained before the addition of the primary ions. The matched potential method selectivity coefficient, $k_{Pb,X}^{MPM}$ is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $k_{Ho,X}^{MPM} = \Delta a_{Pb}/a_X$ [46-50]. The resulting values for the Pb^{2+} CPE are listed in Table 2.

3.6. Lifetime

The lifetime of the modified electrode was studied by periodically recalibrating the potentiometric response to Ho^{3+} ion in standard holmium nitrate solutions. After the conditioning step the electrode repeatedly calibrated three times during a period of one month, no significant change in the performance of the electrode was observed. This shows that the lifetime of the proposed electrode was about two months.

4. CONCLUSIONS

The results of this study show that the potentiometric method using modified carbon paste electrode provides an attractive alternative for the determination of Ho^{3+} ion. The electrode exhibited linear response over a wide concentration range with a Nernstian slope, fast response time, selective to holmium ion, and is easy to prepare. Another unique feature of the present sensor for holmium is its good long term stability (more than 2 months).

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