Evaluation of a carbon paste electrode modified with Strontium substituted bismuth and titanium oxide nanoparticles in the toxic metal chromium (VI) determination potentiometric method

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ABSTRACT

Strontium substituted bismuth and titanium oxide nanoparticles with aurivillius morphology synthesized by chemical co-precipitation method and were characterized using XRD. The nanopartcles were used in the composition of the carbon paste to improve conductivity and transduction of chemical signal to electrical signal. A procedure for the determination of chromium is described based on pre-concentration of the dichromate anion at a carbon paste electrode modified. A novel potentiometric Cr^{6+} carbon paste electrode incorporating Strontium substituted bismuth and titanium oxide nanoparticles (SSBTO). Ina acetate buffer solution of pH 5, the sensor displays a rapid and linear response for Cr^{6+} over the concentration range $1.0 \times 10\text{-}5$ to $1.0 \times 10\text{-}1mol$ L^{-1} M with an anionic slope of 54.8 ± 0.2 mV decade ' and a detection limit of the order of0.002 /µg ml '. The sensor is used for determination of Cr^{6+} by direct monitoring of Cr^{6+}.The average recoveries of Cr^{6+}at concentration levels of 0.5~40 pg/ml 'is 98.3. The electrode has a short response time (<6s) and can be used for at least twenty days without any considerable divergence in potentials and the working pH range was 4.5-6.5. The proposed electrode was successfully used as an indicator for potentiometric determination of Cr^{6+}in water sample.

Keywords: potentiometric٬nanoparticle٬Strontium substituted bismuth and titanium oxide

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INTRODUCTION

Potentiometry is an analytical technique very used for monitoring because it present a number of advantages, such as simplicity, short measurement time, low cost, selectivity, accuracy and , adequate precision as well as ability to determinate the analytes in coloured and turbid samples [1]. Also, it is possible to determine and differentiate between chemical species of one metal depending on the used compound as the sensing component of the sensor.

The potentiometric sensors must be robust to avoid the loss of their analytical characteristics when they are used for in situ measurements of complicated samples or in flow analysis. Potentiometric sensors based on carbon paste matrixes are economic and easy to construct. They present stable electrochemical responses and have lower ohmic resistance and longer functional lifetime than potentiometric sensor based on polymeric membranes. Chromium element used in industrial activities such as chrome plating and electroplating, metal smelting and metallurgy to manufacture alloys, leather tanning and wood treatment [2,3]. It exists in the environment as Cr(III) and Cr(VI) oxidation states which present different chemical properties. Cr(III) is a stable and slightly soluble cation considered an essential microelement [4], while Cr(VI) is a soluble and mobile anion, known as a toxic pollutant, with mutagenic and carcinogenic effects [5]. Due to the different toxicities of these two species, it is essential to determine hexavalent chromium rather than the chromium concentration using a rapid and simple. The major toxic effects of Cr(VI) are chronic ulcers, dermatitis, corrosive reaction in nasal septum and lung cancer. Environmental Protection Agency (EPA) has adopted up to 0.01 mg $L^{-1}$of total chromium as maximum contaminant level in community water systems. Chromium compounds extensively used in leather tanning process are not completely consumed and approximately 400 tonnes of chromium waste per year. is being discharged in India as large number of small-scale tanneries do not have access to common effluent treatment plants [6,7]. It is reported that chromium

concentration in discharged waste is up to several thousand mg L^{-1} causing serious threat to the surrounding environment and human life. Presently, sophisticated techniques, viz. atomic absorption spectroscopy (AAS), inductively coupled plasma (ICP),etc. are employed for the determination of trace amount of chromium. However, these methods are disadvantageous in terms of cost and unsuitability for routine analyses of large number of samples [8,9]. Recently, ion-sensors are being used for such analyses, as these provide a convenient, fast and 'online' method for quantification.

Several efforts have been made during the last few decades to develop a selective sensor for Cr(VI), however, the success with regard to real sample analysis is still limited [10–18].Most of the reported sensors are insensitive to chromium quantification at lower concentrations (<1 mg L-1) [9–12,14],exhibit poor selectivity [6,8–11,14].

In this study, chromium (VI) carbon paste electrode based on Strontium substituted bismuth and titanium oxide nanoparticles, was constructed in order to determine chromium (VI) ion concentration. The electrode was modified by Strontium substituted bismuth and titanium oxide nanoparticles to achieve the better electrode response. The modified electrode was successfully used as an indicator for potentiometric determination of chromium (VI)in water sample.

MATERIALS AND METHODS

Reagents and solutions
All analytical reagent grade chemicals and distilled water were used for preparing all aqueous solutions. The reagents in this experiment including $TiCl_4$, $Sr(NO_3)_2$, NaOH and $K_2Cr_2O_7$ were purchased from Merck and $Bi(NO_3)_2.5H_2O$ from Sigma-Aldrich. All solutions were prepared from distilled water. HNO_3 (65%, Merck), HCl (37%, Merck) and Ethanol (98%) were used as received.

Synthesis of $SrBi_4Ti_4O_{15}$Aurivillius oxide
Nanoparticles with $SrBi_4Ti_4O_{15}$ compositions were obtained from soft chemical method.$TiCl_4$solution was added to a mixture of $Sr(NO_3)_2$ and $Bi(NO_3)_3.5H_2O$ according to desired stoichiometries. The concentrated HNO_3 was added to the mixture of strontium and bismuth nitrate solution before adding Titanium chloride until the color of solution change from consonant to clear. 5M NaOH added to the as prepared precursor, step wisely, at room temperature and stirred for 2 hour. The resulting precipitated particles were repeatedly washed with distilled water and absolute ethanol and dried at 130^0C overnight. The samples were calcined at 500 and 700^0C for 10 h each with intermittent grinding after each heating step followed by slow cooling in air.

Electrode Preparation
General procedure to prepare the carbon paste electrode was as follows: Different amounts of nanoparticle with an appropriate amount of graphite powder, paraffin oil and plasticizer(DBP) were thoroughly mixed. After homogenization of the mixture, the paste was thoroughly packed into the teflone tube and an electrice wire was inserted into the opposite end of the CPE to set up electrical contact. The external surface of the carbon paste was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the new carbon paste. The electrode was finally conditioned for 12 h by soaking it in a $1.0×10^{-4}$mol L^{-1} chromium (VI)solution [19-21]

RESULTS AND DISCUSSION

Carbon paste electrode composition
The sensing element of a potentiometric ion-selective electrode has important role in selectivity behavior of the electrode. The influence of the percent of materials in the carbon paste composition was investigated and the results are summarized in Table 1.

Table 1. The optimization of the carbon paste ingredients

NO	Composition of Carbon Paste (wt.%)					Dynamic linear range
	Nanoparticle(SSBTO)	paraffin oil	Graphene Powder	Plasticizer	Recovery	
1	13	6	71	10	94.5	$3.0×10^{-3}$-$5.0×10^{-80}$
2	12	4	70	11	98.3	$3.0×10^{-2}$-$5.0×10^{-10}$
3	10	6	71	13	94.3	$1.0×10^{-2}$-$5.0×10^{-8}$
4	12	5	77	13	91.2	$1.0×10^{-3}$-$5.0×10^{-8}$
5	14	5	78	3	93.1	$3.0×10^{-2}$-$5.0×10^{-10}$
6	14	6	75	5	93.8	$3.0×10^{-2}$-$2.0×10^{-6}$
7	13	7	76	4	98	$2.0×10^{-2}$-$5.0×10^{-6}$
8	15	5	75	5	96.2	$3.0×10^{-2}$-$4.0×10^{-7}$
9	13	7	74	6	94.4	$3.0×10^{-2}$-$5.0×10^{-10}$
10	11	7	75	7	94.0	$8.0×10^{-4}$-$5.0×10^{-6}$

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The typical CPE with optimized composition (electrode no.2) shows a recovery%98.3. The electrode composed of 12% SSBTO, 6% paraffin oil, 70% Graphene Powder15% andPlasticizer 11% was found to be optimal for Cr^{6+} carbon paste electrode. This new carbon paste electrode was selected for further examination.

Measuring range and detection limit

The response of the optimal modified Cr^{6+} carbon paste electrode (no.2) was tested across Cr^{6+} ion concentration range of 3.0×10^{-2}–5.0×10^{-10}mol L^{-1}. The applicable range of the proposed sensor extends from 1.0×10^{-5} to 1.0×10^{-1}mol L^{-1} as seen in Fig 1.
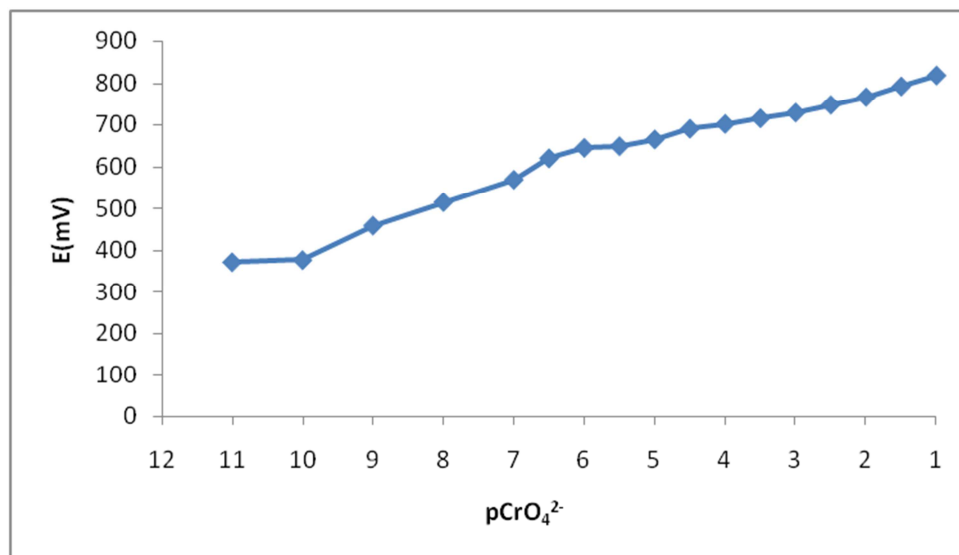

Fig. 1Calibration curve of Cr^{6+} carbon paste electrode (Electrode no. 2)

pH effect on the electrode response

In order to study the effect of pH on the response of the optimal modified Cr^{6+} sensor (no.2), the potential was measured for a fixed concentration of Cr^{6+} ion solutions at different pH values. The pH was varied from (1-13) by addition of concentrated HNO_3 or NaOH. The change in potential as a function of pH is surveyed. The potential was constant and quantitative in the pH range of 4.5–6.5. At pH<4.5, the electrode response increased rather irregularly with increasing analyte acidity. At such high acidic solutions, the observed increase in potential indicates that the protonated chromium possesses a poor response to the Cr^{6+}ions. The pH dependence of the electrode potential for the sensors is tested in presence of $1.0\times10-4$ mol.L^{-1} chromium (VI) concentration after sensor conditioning. The ionic strength in test solution is maintained constant with 0.1 mol.L^{-1} $NaNO_3$. The pH values are adjusted by adding small volumes of diluted nitric acid or sodium hydroxide solutions. The potential value is read and the solution pH is measured when the electrode response is stabilized.

The CP sensors are sensible to pH changes, in presence of Cr(VI), with as lope of 50.5mV pH^{-1} linear behaviour. This variation cannot be attributed to changes on chromium (VI) species, because at the assayed pH range (4.5–6.5), monovalent hydrogen dichromate is the predominant species.

In addition, Fluctuations at pH greater than 6.5 might be due to the formation of soluble or insoluble Cr^{6+}hydroxy complexes.

Response time

Response time is an important factor for any sensor. For electrochemical sensors, this parameter is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. The measurements of potential versus time were carried out with the chromium (VI) solutions from lower (5.0×10^{-10} M) to higher (3.0×10^{-3} M) concentrations. For the proposed modified Cr^{6+} sensor, the response time was less than 5s. The results for solutions containing chromium (VI) are shown in Fig. 2.
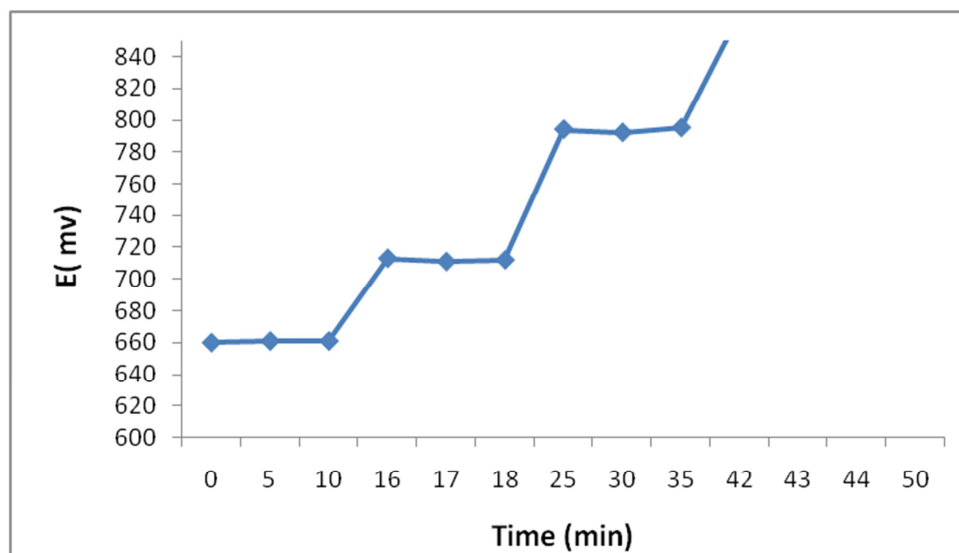
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Fig. 2Dynamic response time of the proposed carbon paste electrode (no.2)

Selectivity
Selectivity is the most important characteristic of any sensor, and describes an ion selective electrode's specificity toward the target ion in the presence of interfering ions, the potentiometric selectivity coefficients of the proposed carbon paste electrode were evaluated by separate solution method (SSM) [23] and the results are depicted in Table 2.

Table 2. Selectivity coefficients of various interfering species for proposed sensor (no.2)

| Interfering ions	K_{ij}^{pot}	Interfering ions	K_{ij}^{pot}
SO_4^{2-}	5.4×10^{-2}	F^-	2.7×10^{-3}
Cl^-	6.4×10^{-3}	SO_3^{2-}	2.6×10^{-1}
NO_3^-	4.3×10^{-2}	IO_3^-	1.1×10^{-1}

The potential of a cell comprising an ion-selective electrode and a reference electrode is measured with two separate solutions, one containing the ion (i) at the activity a_i, the other one containing the ion(j)at the same activity $a_i = a_j$. If the measured values are E_i and E_j, respectively, the value of is calculated from the equation:

$$logK_{ij}^{pot} = \left[\frac{Z_i F(E_j - E_i)}{2.303RT}\right] + log\left[\frac{a_i(i)}{a_j(j)^{Z_i/Z_j}}\right]$$

These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible.

Titration of Fe^{2+} solution with Cr(VI)
In the potentiometric measurements, the standard addition method is employed for calibration in order to avoid errors due to the presence of not well or no characterized compounds in these samples. The sensor is also investigated as indicator electrode in the titration of hexavalent chromium with Fe^{2+}. In Fig. 3, the curve for titration of 20.0mL of 3×10^{-4}mol L^{-1} Cr(VI) solution with0.072 M Fe^{2+}solution is done. When the experimental data are graphed, the titration curve exhibits the standard sigmoid shape showing the 1:6 stoichiometry of Cr(VI)–Fe(II) oxidation–reduction reaction.
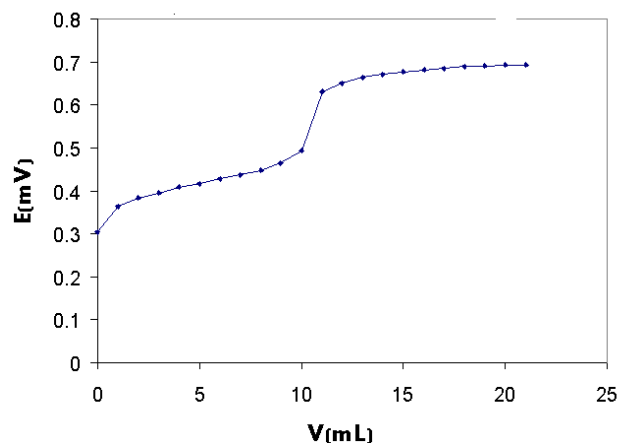
$6Fe^{2+} + Cr2O7^{2-} + 14H+ \rightarrow 6Fe3+ + Cr3+ + 7H2O$
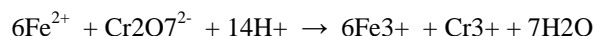
Fig. 3. Titration curve Fe2+ with Cr(VI) pcarbon paste electrode (no.2)

CONCLUSION

In this work, Cr^{6+} carbon paste electrode based on Strontium substituted bismuth and titanium oxide nanoparticles is introduced. By incorporating Strontium substituted bismuth and titanium oxide nanoparticles in composite of this electrode, high selectivity and sensitivity to Cr(VI) ion were observed. The modified CPEs show better potentiometric response than typical CPEs in terms of sensitivity, linear range, and response stability. Since the electrode shows excellent sensitivity, selectivity and stability, it may find application in the analysis of real samples. The electrode has a great potential to be used in the development of portable analyzers for monitoring Cr(VI) ions in very polluted natural waters.

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