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ORIGINAL PAPER

The use of nanocomposite approach in the construction of carbon paste electrode and its application for the potentiometric determination of iodide

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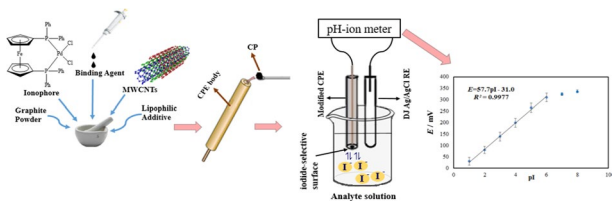
Abstract

New modified iodide-selective carbon paste electrodes based on a palladium(II) complex were prepared using multi-walled carbon nanotubes and/or metal oxide nanoparticles to demonstrate the feasibility of the nanocomposite approach to enhance the selectivity of their sensing layer. The question of whether or not the performance characteristics of the electrodes were affected by the incorporation of these materials was investigated. The linear working ranges and slopes of these electrodes were determined for comparison to specify the optimum nanosensing layer of the carbon paste electrode for better iodide sensitivity. The results showed that the introduction of multi-walled carbon nanotubes improved the Nernstian slope of the electrode from a value of 43.8 ± 0.6 to 57.7 ± 1.8 mV/pI at pH = 4.0. The response time, the detection limit, and a lifetime of the electrode were found as < 5 s, 2.9×10^{-8} mol dm^{-3}, and ≥ 4 months, respectively. Furthermore, the proposed electrode with improved selectivity was successfully employed for the determination of iodide in a pharmaceutical sample by potentiometric titration.

Graphical abstract



Keywords Anions · Electrochemistry · Iodide-selective carbon paste electrode · Carbon nanotubes · Metal oxide nanoparticles · Potentiometry

Introduction

It is of prime importance to perform the determination of any species in several samples with high accuracy, high precision, and in a very short time by using the possible cheapest method, and even without preliminary separation steps. However, common instrumental analysis methods are time consuming or difficult to accomplish, have expensive equipments, and require qualified staff. In contrast, analysis with ion-selective electrodes (ISEs) offers advantages such as wide working range, high selectivity, low cost, rapid response time, ease of preparation, and nondestructive analysis. With the emergence of ISEs, potentiometry has been applied in many research areas such as agricultural, pharmacological, environmental, clinical, industrial, biochemical, and biomedical studies [1–7]. In this case, investigations about the preparation of a large number of highly sensitive and selective electrodes, and the development of new methods for the analysis of various species in different matrix media, are still in increasing demand [8–13].

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There are fewer studies on ISEs for the anions reported in the literature when compared to that of cations due to the different molecular structures and larger sizes of the anions, toughness of the anion recognizing ionophore synthesis and their stability at narrow pH ranges. Therefore, the design of anion-selective electrodes has been of great interest as a result of anions playing a substantial role in environmental, clinical, industrial, and biological analysis [14, 15]. Poly(vinylchloride) (PVC) membrane type anion-selective electrodes with internal solution have been widespread in literature while solid-contact electrodes have been uncommon. Hence, especially carbon paste electrodes (CPEs) have come into prominence owing to many advantages such as their low ohmic resistance, ease of preparation, renewable surface, and stable potentiometric response when compared to PVC membrane electrodes [16–19]. This can also be attributed to the disadvantage of PVC membrane electrodes by means of the evaporation of internal solution resulting in undesired changes in the membrane response caused by reversible transport of species in the membrane-test solution interface [20].

The most important factor affecting the performance of ion-selective electrodes is the electrode surface in contact with the ions in the solution. Owing to complex interactions between the surface components used in the preparation of different types of ISEs, electrodes with various performance characteristics can be constructed [21–23]. Therefore, it is essential to investigate whether or not altering the carbon paste composition can affect the response properties of the electrodes. Recent studies in the literature have included the ones with the incorporation of various nanomaterials such as nanotubes [19, 24, 25], nanoparticles [26], nanowires [27], and nanorods [28] into carbon pastes to improve the performance of the electrode. However, there are few studies related to the impregnation of multi-walled carbon nanotubes (MWCNTs) and/or metal oxide nanoparticles (MONPs) in the design of anion-selective nanocomposite based carbon paste electrodes resulting in unique improvement in its potentiometric response [8, 29–37]. In this regard, much attention was dedicated to construct new anion-selective carbon paste electrodes modified with nanomaterials.

Iodine plays crucial roles in many biological activities such as thyroid gland function, neurological activities, brain functions and growth, and also serves as an antiseptic for skin lesions and for the disinfection of drinking and swimming pool waters [29, 30, 38–40]. Iodine and/or iodide are found in tap water, foods (sea products, eggs, meat, milk, and wheat) and drug compositions [41]. Due to insufficient iodine intake, several health hazards can take place such as impaired cognitive development in children, many pathological ailments, weight gain, depression, thyroid disorders, cardiovascular diseases later in life [40, 42–44]. Additionally, irritation of its vapors to the eyes and lungs is toxic, and its excess dosage can cause other health problems such as hypothyroidism, gastrointestinal irritation, ulceration, acute renal failure, hemolytic anemia, and congenital goiter [39]. Therefore, according to The World Health Organization, the permissible iodine amount per day for a healthy human was stated as 200 µg/day.

Various ionophores have been used for analytical purposes to construct carbon paste electrodes for sensitive detection of iodide. Among these, Schiff base complex of Fe(III) [44], cetyltrimethylammonium iodide [45], bis(3-phenyl-2-propenaldehydene)-1,3-propanediamine zinc(II) chloride and bis(4-nitrobenzylidene) ethylenediamine mercury(II) bromide [29], iron(II) phthalocyanine [30], bis(*trans*-cinnamaldehyde)1,3-propanediimine mercury(II) chloride and bis(*trans*-cinnamaldehyde)-1,3-propandiimine cadmium(II) chloride [46], bis(3-phenyl-2-methylpropenaldehydene)-1,2-ethanediamine mercury(II) bromide [33], 2-methoxy-6-[[3-(trimethoxysilyl)propylimino]methyl]phenol [39], copper(II)-sulphamethazine Schiff base complex [9] were successfully used. Iodide-selective carbon paste electrodes prepared by MWCNTs and MONPs lead to significant improvement in the characteristics of iodide-selective electrodes [33]. For this purpose, in this study nanomaterials as well as dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) complex (Fig. 1) as ionophore, different plasticizers and lipophilic additives were incorporated for the construction of a new sensing layer with improved selectivity of iodide. Therefore, we intended to investigate the effect of each constituent in the multicomponent composite material system on the performance of the iodide-selective carbon paste electrode. Furthermore, its application as potentiometric titration to determine the iodide content in the hypothyroidism drug samples was targeted.

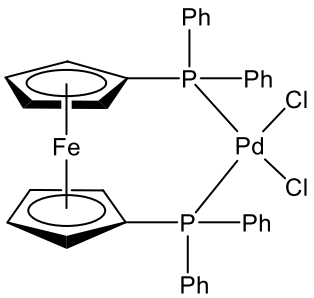

Fig. 1 The chemical structure of ionophore used in the construction of the electrode

Results and discussion

Insolubility of palladium(II) complex (Fig. 1) in water, good distribution in carbon paste, adequate lipophilicity to avoid leaching from this matrix into the test solution, and reasonable exchange kinetic properties (chloro atoms coordinated with palladium supposed to be acting as replacing groups with iodide ions) were the reason to choose this complex as an ionophore for iodide sensitivity for the preparation of nanocomposite modified iodide-selective CPEs. Several carbon paste compositions as well as the performance characteristics of the fabricated electrodes were given in Table 1.

Iodide-selective CPEs based on the same ionophore were constructed without nanomaterials in a previous study of our group and their performance characteristics were used here for comparison purposes [47]. Moreover, the effect of the amount of ionophore, various binding agents such as plasticizers, paraffin oil, and some lipophilic additives on the potentiometric response of the electrode was also investigated.

Table 1 The effect of carbon paste composition on the performance properties of the electrode

Electrode number[b]	Carbon paste composition/% (w/w)[a]					Performance characteristics		
	Ionophore	Graphite powder	Binding liquid	Lipophilic additive[c]	Nanomaterials	Slope[d]/mV/pI	LWR[e]/mol dm^{-3}	R^2 [f]
CPE1	**12**	**47.8**	**20.7 *o*-NPOE**	**18.5 TDAT*p*-ClPB**	**1.0 MWCNTs**	**57.7 ± 1.8**	**$1.0\times10^{-6} - 1.0\times10^{-1}$**	**0.9977**
CPE2	6	53.8	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 MWCNTs	56.3 ± 2.6	$1.0\times10^{-4} - 1.0\times10^{-1}$	0.9955
CPE3	17.9	41.9	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 MWCNTs	80.2 ± 1.6	$1.0\times10^{-5} - 1.0\times10^{-1}$	0.9421
CPE4	24	35.8	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 MWCNTs	78.8 ± 1.9	$1.0\times10^{-5} - 1.0\times10^{-1}$	0.958
CPE5	12.3	49.3	18.3 Paraffin oil	19.1 TDAT*p*-ClPB	1.0 MWCNTs	21.1 ± 7.8	$1.0\times10^{-6} - 1.0\times10^{-3}$	0.9734
CPE6	12.3	49	18.7 BEHA	19.0 TDAT*p*-ClPB	1.0 MWCNTs	50.8 ± 4.3	$1.0\times10^{-6} - 1.0\times10^{-1}$	0.9956
CPE7	12.3	49	18.6 BEHS	19.1 TDAT*p*-ClPB	1.0 MWCNTs	46.8 ± 4.1	$1.0\times10^{-6} - 1.0\times10^{-1}$	0.9987
CPE8	12.1	48.4	19.7 BEHF	18.8 TDAT*p*-ClPB	1.0 MWCNTs	53.1 ± 1.2	$1.0\times10^{-6} - 1.0\times10^{-1}$	0.9922
CPE9	13.6	54.3	23.5 *o*-NPOE	7.5 TDMACl	1.1 MWCNTs	46.7 ± 2.7	$1.0\times10^{-4} - 1.0\times10^{-1}$	0.9916
CPE10	13.3	53.2	23.1 *o*-NPOE	9.3 THATPB	1.1 MWCNTs	52.2 ± 0.3	$1.0\times10^{-4} - 1.0\times10^{-1}$	0.9967
CPE11	12	47.8	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 MWCNTs (–OH)	49.8 ± 2.3	$1.0\times10^{-3} - 1.0\times10^{-1}$	0.9994
CPE12	12	47.8	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 MWCNTs (–COOH)	48.4 ± 2.7	$1.0\times10^{-3} - 1.0\times10^{-1}$	0.9967
CPE13	12	47.8	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 ZnONPs	53.8 ± 1.4	$1.0\times10^{-4} - 1.0\times10^{-1}$	0.9914
CPE14	12	47.8	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 SnO_2NPs	50.9 ± 1.6	$1.0\times10^{-4} - 1.0\times10^{-1}$	0.994
CPE15	12	47.8	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 Fe_2O_3NPs	54.8 ± 3.6	$1.0\times10^{-4} - 1.0\times10^{-1}$	0.998
CPE16	12	47.8	20.7 *o*-NPOE	18.5 TDAT*p*-ClPB	1.0 Co_3O_4NPs	56.7 ± 1.6	$1.0\times10^{-4} - 1.0\times10^{-1}$	0.9924
CPE17	11.9	47.3	20.5 *o*-NPOE	18.3 TDAT*p*-ClPB	1.0 MWCNTs + Co_3O_4NPs	63.0 ± 8.0	$1.0\times10^{-4} - 1.0\times10^{-1}$	0.9913

[a]Total mass of carbon paste = 30 mg

[b]Abbreviations of carbon paste electrode names prepared with different compositions used in this study

[c]70% mole ratio relative to the ionophore

[d]95% CL $\bar{x} \pm ts/\sqrt{N}$ ($N = 5$, $t_c = 2.78$)

[e]Linear working range

[f]Regression coefficient

Optimization of the carbon paste composition

It has been reported in the literature that nanomaterials such as MWCNTs and MONPs generally improved the performance of potentiometric sensors by means of the slope, linear working range, response time, empedance, and surface area [29, 30, 46, 48–52]. According to Ref. [47], the electrode without nanomaterial showed a lower Nernstian slope (43.8 ± 0.6 mV/pI) while that of CPE1 modified with 1.0% MWCNTs was found to be increased to 57.7 ± 1.8 mV/pI in the same linear working range ($1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ mol d m^{-3}). The incorporation of MWCNTs into the carbon paste composition improved the sensitivity of the iodide-selective electrode in accordance with the literature [33, 53, 54]. In conclusion, it was decided that the addition of MWCNTs was appropriate to have an iodide-selective electrode comparable with the similar ones reported previously (Table 2) [29, 30, 46].

The most important factor affecting the potentiometric response of ISEs is the amount of ionophore on the electroactive surface. Therefore, the potentiometric response of CPE1 was compared with CPE2-CPE4. The results demonstrated that the introduction of an ionophore in the percent range of 6–24% changed the working ranges and the sensitivities of the electrodes. Applying 6% ionophore resulted in a near-Nernstian response in a narrower working range while the electrodes with other percents exhibited super-Nernstian response with low R^2 in the linear working range (LWR) of $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ mol dm^{-3} (CPE3, CPE4). That's why the best ionophore percentage content was chosen as 12% for the electrode with MWCNTs (CPE1).

Conventional carbon pastes can contain chemically inert, electroinactive organic liquids having low solubility in aqueous media, high viscosity, and low volatility. For this purpose, paraffin oil, olefin oil, nujol were employed to mechanically combine individual graphite powder particles together with other paste components [55]. In addition to these fluids, there are also studies in the literature using *o*-nitrophenyl octylether (*o*-NPOE) and other plasticizers, which are commonly considered for binding purposes to achieve a homogeneous distribution of carbon paste components [9, 51, 56–58]. By increasing the polarity of the carbon paste, these plasticizers can be thought to facilitate the dispersion of components and thus provide the mobility of the ions. Therefore, the optimization of the type of binding liquid was carried out with the introduction of paraffin oil, *o*-NPOE, bis(2-ethylhexyl) adipate (BEHA), bis(2-ethylhexyl) sebacate (BEHS), bis(2-ethylhexyl) phthalate (BEHP), respectively. As it is observed in Table 1, CPE5 showed a negligible response in the narrow working range of $1.0 \times 10^{-3} - 1.0 \times 10^{-6}$ mol dm^{-3} which may be due to the lower polarity of paraffin oil than other binding fluids. Based on the slopes of the electrodes with other four plasticizers including *o*-NPOE (CPE1), BEHA (CPE6), BEHS (CPE7), BEHP (CPE8), it can be concluded that the best binding fluid was found to be *o*-NPOE due to the Nernstian slope of CPE1. As a result, it was thought that many plasticizers used in ISEs could be used as a binding liquid in ion-selective CPEs. There are ISE studies in which *o*-NPOE was used in the preparation of carbon paste in the literature [9, 51, 57].

Since the slope of the carbon paste electrode with 12% ionophore, *o*-NPOE and MWCNTs was found as Nernstian, the effect of lipophilic additive, the type of MWCNTs and MONPs on the electrode performance was examined by keeping the same amounts of components constant for CPE1. In the literature, there are studies showing that the use of the lipophilic additive in ISEs generally enhances the electrode performance favourably. It has been stated that the inclusion of additives in the surface components of the electrode, reduces the ohmic resistance, catalyzes the ion exchange kinetics at the analyte solution-electrode interface, and improves the Nernstian response of the electrode by reducing the interference of other ions in the solution [51, 59]. As the addition of lipophilic additive results in an improvement in performance properties and serves to catalyze the phase transfer in cases where the kinetic events at the sample and carbon paste interface are limited, it was decided to apply different types of lipophilic additives as 70% mole of the ionophore [9, 59–61]. The performance of the electrode CPE1 was compared with the electrodes prepared by employing two other lipophilic additives, tridodecylmethylammonium chloride (TDMACl) (CPE9) and tetraheptylammonium tetraphenylborate (THATPB) (CPE10). Among these electrodes, the slopes of CPE9 and CPE10 were found lower in narrower working ranges than that of CPE1. It was concluded that CPE1 had shown the best iodide sensitivity due to the synergetic effect of ionophore, liphophilic additive and MWCNTs. Furthermore, it can be said that exchange equilibrium between the anionic group belonging to the tetradodecylammonium tetrakis(4-chlorophenyl)borate (TDAT*p*ClPB) in the carbon paste and the chlorides in the structure of the ionophore leads to a new palladium complex enable the iodide ions in the solution to bind more reversibly and easily to the palladium than the other new palladium complexes formed as a result of the replacement of chlorides with the anions of liphophilic additives. To confirm the contribution of lipophilic additive to the potentiometric response of the proposed CPE, ionophore free electrode with TDAT*p*ClPB was also developed. It exhibited a lower Nernstian slope (18.9 ± 6.7 mV/pI) and a narrower linear working range ($1.0 \times 10^{-3} - 1.0 \times 10^{-2}$ mo l dm^{-3}). In conclusion, the best performing MWCNT modified iodide-selective CPE was prepared by the inclusion of 18.5% TDAT*p*ClPB.

Additional optimization studies were carried out with different carbon nanotubes such as MWCNTs (-OH) and

Table 2 Comparison of MWCNT modified carbon paste iodide-selective electrode with the ones with/without MWCNTs in the literature

Ionophore	Composition	Slope/mv/pI	LWR/mol dm^{-3}	LOD[a]/mol dm^{-3}	Response time	Working pH	Lifetime	Selectivity coefficient	References
(I)	10.0 mg ionophore; 52.5 mg graphite powder; 37.5 mg paraffin oil	71.0 ± 0.3	$1.0\times10^{-6}-5.0\times10^{-1}$	6.5×10^{-7}	< 15 s	3.5–10.0	> 3 months	$I^- > SCN^- > CN^- > F^- > CH_3COO^- > NO_2^- > SO_4^{2-} > ClO_4^- > Cl^- \approx Br^-$	[44]
(II)	2.4% CTMAI; 40.6% graphite powder; 16.4% paraffin oil; 40.6% DBS	55.0 ± 0.4	$4.0\times10^{-5}-1.0\times10^{-1}$	4.0×10^{-5}	45 s	5.0–9.0	> 2 months	$I^- > SCN^- > NO_3^- > Cl^- \sim Br \sim F^- > ClO_4^- > SO_4^{2-} \sim Cr_2O_7^{2-} \sim IO_4^- > PO_4^{3-} > CH_3COO^- > NO_2^- > Br^-$	[45]
(IIIa)	27.0 mg ZnL_1Cl_2; 21.2 mg MTOACl; 150.0 mg graphite powder; 12.0 mg MWCNTs; 50.0 mg Nujol	57.3 ± 1.2	$1.0\times10^{-6}-1.0\times10^{-1}$	8.8×10^{-7}	20 s	2.5–11.0	2 months	$NO_3^- > NO_2^- > Cl^- \sim CO_3^{2-} > C_2O_4^{2-} \sim SO_4^{2-} > Br^- >$ salicylate $> PO_4^{3-} > SCN^-$	[29]
(IIIb)	20.0 mg HgL_2Br_2; 10.0 mg MTOACl; 150.0 mg graphite powder; 8.0 mg MWCNTs; 50.0 mg Nujol	59.8 ± 0.8	$1.0\times10^{-7}-1.0\times10^{-1}$	7.5×10^{-8}	15 s			$NO_3^- > Br^- > NO_2^- > Cl^- \sim CO_3^{2-} \sim SO_4^{2-} > PO_4^{3-} >$ salicylate $> C_2O_4^{2-} > SCN^-$	
(IV)	8.0 mg iyonofor, 4.8 mg MTOACl; 250.0 mg graphite powder; 60.0 mg MWCNTs; 50.0 mg Nujol	58.0 ± 0.4	$5.0\times10^{-7}-1.0\times10^{-1}$	4.0×10^{-7}	≤ 25 s	3.0–11.5	> 2 months	$NO_3^- \sim NO_2^- > MnO_4^- > C_2O_4^{2-} > SO_4^{2-} > PO_4^{3-} >$ histamine $> CO_3^{2-} > ClO_4^- \sim$ salicylate $> Br^- \sim SCN^- > Cl^-$	[30]
(Va)	26.0 mg $BCPHgCl_2$; 15.6 mg MTOACl; 150.0 mg graphite powder; 5.0 mg MWCNTs; 36.0 mg Nujol	58.5 ± 1.0	$1.0\times10^{-6}-1.0\times10^{-1}$	0.6×10^{-6}	10 s	3.0–11.0	> 2 months	$I^- > ClO_4^- > NO_3^- > SO_4^{2-} > Br^-$ > histamine $> NO_2^- \sim$ salicylate $> MnO_4^- \sim Cl^- > SCN^- > CO_3^{2}$	[46]
(Vb)	25.0 mg $BCPCdCl_2$; 17.7 mg MTOACl; 150.0 mg graphite powder; 10.0 mg MWCNTs; 45.0 mg Nujol	58.0 ± 0.7	$5.0\times10^{-6}-1.0\times10^{-1}$	2.4×10^{-6}	8 s	3.0–11.5		I^- > histamine > s salicylate > $NO_2^- > SO_4^{2-} > MnO_4^- > ClO_4^- > CO_3^{2-} > Br^- > Cl^- > NO_3^- > SCN^-$	
(VI)	40.0 mg ionophore, 12.0 mg MTOACl, 150.0 mg graphite powder ve 5.0 mg CuS-NP	59.12 ± 0.7	$1.8\times10^{-6}-1.15\times10^{-1}$	1.8×10^{-6}	> 12 s	2.5–10.0	~ 2 months	$I^- > CN^- > CO_3^{2-} > Cl^- = HS^- > HCO_3^- > SO_4^{2-} > F^- > CrO_4^{2-} > SO_3^{2-} > NO_3^- > SCN^- > Br^- > NO_2^-$	[39]
(VII)	CPE-I: 12.0 mg ZnO; 4.04 mg MTOACl; 220.0 mg graphite powder; 80.0 mg Nujol; 8.0 mg ionophore	59.1 ± 1.9	$0.06\times10^{-8}-1.0\times10^{-1}$	4.0×10^{-8}	10–15 s	2.0–9.5	2 months	$Mg^{2+} > Cr^{3+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Pb^{2+} > Cd^{2+} > Al^{3+} > Fe^{3+}$ (FIM) $Mg^{2+} > Cr^{3+} > Co^{2+} > Zn^{2+} > Ni^{2+} > > Pb^{2+} > Cd^{2+} > Al^{3+} > Fe^{3+}$ (SMM)	[33]
	CPE-II: 15.0 mg Ag; 4.03 mg MTOACl; 225.0 mg graphite powder; 80.0 mg Nujol; 8.0 mg ionophore	59.7 ± 2.1	$0.04\times10^{-8}-1.0\times10^{-1}$		5–10 s	2.0–10.5		$Cr^{3+} > Zn^{2+} > Al^{3+} > Mg^{2+} > Cd^{2+} > Co^{2+} > Pb^{2+} > Ni^{2+} > Fe^{3+}$ (FIM) $Mg^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Cr^{3+} > Pb^{2+} > Al^{3+} > Cd^{2+} > Fe^{3+}$ (SMM)	
	CPE-III: 8.0 mg ionophore; 3.75 mg MTOACl; 220.0 mg graphite powder; 25.0 mg MWCNTs; 80.0 mg Nujol	59.5	$0.04\times10^{-8}-1.0\times10^{-1}$		5–8 s	2.0–11.0		$Mg^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+} > Al^{3+} > Pb^{2+} > Cd^{2+} > Cr^{3+} > Fe^{3+}$ (FIM) $Mg^{2+} > Zn^{2+} > Ni^{2+} > Pb^{2+} > Co^{2+} > Cr^{3+} > Cd^{2+} > Al^{3+} > Fe^{3+}$ (SMM)	
(VIII)	1.0% Cu (II) complex, 49.7% graphite powder, 49.0% *o*-NPOE and 30.0% TDMACl	61.2	$1.0\times10^{-5}-1.0\times10^{-1}$	1.0×10^{-5}	1 min	4.0–8.5	1 week	$ClO_4^- > SCN^-$ > Sal > $I^- > NO_3^- > Br^- > Cl^-$	[9]
(IX)	300.0 mg AgI-NP; 15.0 mg Ag_2S-NP; 1200.0 mg graphite powder; 400.0 cm^3 paraffin oil	55.3 ± 0.5	$8.0\times10^{-9}-1.0\times10^{-3}$	7.0×10^{-9}	< 60 s	2.0–5.0		Selective against all ions found in human urine	[40]
(IIX)	6.0 mg ionophore, 24.0 mg graphite powder, 9.3 mg TDAT*p*ClPB and 0.01 cm^3 *o*-NPOE	43.8 ± 0.6	$1.0\times10^{-6}-1.0\times10^{-1}$	3.7×10^{-7}	5–10 s	4.0–7.0	3 months	$Sal > SCN^- > NO_2^- > NO_3^- > ClO_4^- >$ Benzoate $> Br^- > Cl^-$ > Citrate $> F^- > HCOO^-$	[47]

Table 2 (continued)

Ionophore	Composition	Slope/mv/pI	LWR/mol dm^{-3}	LOD[a]/mol dm^{-3}	Response time	Working pH	Lifetime	Selectivity coefficient	References
Ionophore	6.0 mg ionophore; 24.0 mg graphite powder; 9.3 mg TDAT*p*ClPB; 0.5 mg MWCNTs; 0.01 cm^3 *o*-NPOE	57.7 ± 1.8	1.0×10^{-6} – 1.0×10^{-1}	2.9×10^{-8}	< 5 s	4.0–7.0	≥ 4 months	$ClO_4^- > SCN^- \approx C_7H_5NaO_3 > C_7H_5NaO_2 > NO_3^- > NO_2^- > CrO_4^{2-} > Br^- > Cl^- > C_6H_5Na_3O_7 > CO_3^{2-} > SO_3^{2-} > F^- > HCOO^-$	This work

[a]Limit of detection; I: ionophore: Schiff base complex of Fe(III); II: CTMAI: cetyltrimethylammonium iodide; IIIa: ZnL_1Cl_2: bis(3-phenyl-2-propenaldehydene)-1,3-propanediamine zinc(II) chloride; IIIb: HgL_2Br_2: bis(4-nitrobenzylidene)ethylenediamine mercury(II) bromide; IV: Fe-FCN: iron(II) phthalocyanine; Va: $BCPHgCl_2$: bis(trans-cinnamaldehyde)-1,3-propanediimine mercury(II) chloride; Vb: $BCPCdCl_2$: bis(trans-cinnamaldehyde)-1,3-propandiimine cadmium(II) chloride; VI: MMSPIMP: 2-methoxy-6-[[3-(trimethoxysilyl)propylimino]methyl] phenol; VII: $HgLBr_2$: bis(3-phenyl-2-methylpropenaldehydene)-1,2-ethanediamine mercury(II) bromide; VIII: Cu(II): copper(II)-sulphamethazine Schiff base complex; IX: AgI + Ag_2S; IIX: Dichloro[1,1´-bis(diphenylphosphino)ferrocene]palladium(II)

MWCNTs (-COOH), and four kinds of MONPs such as ZnONPs, SnO_2NPs, Fe_2O_3NPs, and Co_3O_4NPs to investigate whether the use of nanomaterials could improve the performance of the nanocomposite based electrode CPE1 or not. As is clear from Table 1, the electrodes with different carbon nanotubes, CPE11 (MWCNTs (-OH)) and CPE12 (MWCNTs (-COOH)), displayed lower Nernstian anionic slopes in the narrow range of 1.0×10^{-3} – 1.0×10^{-1} mol dm^{-3}. This behaviour can be explained by the fact that –OH and –COOH groups in the nanotube structures might partially reduce the iodide-ionophore interaction. It was understood that only the presence of MWCNTs in the paste composition resulted in a Nernstian slope in a wide dynamic range of operation. Moreover, a set of experiments was performed by the inclusion of four different MONPs instead of carbon nanotubes in the same percentage (CPE13-CPE16). It was observed that these electrodes indicated better Nernstian slopes with a 10-fold improvement in operating range than the electrodes CPE11, CPE12. In addition, the results conducted that all the electrodes constructed with MONPs had 10^2 times narrower working ranges than CPE1. Although the electrodes fabricated with MONPs exhibited near-Nernstian slopes, the contribution of MONPs to the working ranges of the electrodes were not resulted as expected. This outcome may also be explained by the blocked interaction of iodide-ionophore to a limited extent at low iodide concentrations. However, introducing Co_3O_4NPs to the carbon paste composition resulted with an electrode displaying the highest near-Nernstian behaviour 56.7 ± 1.6 mV/pI among these MONPs (CPE16). Thus, an additional electrode using a mixture of MWCNTs and Co_3O_4NPs (CPE17) was also constructed to investigate whether these nanomaterials could have a synergetic effect on electrode response or not. It was found that CPE17 possessed a super-Nernstian slope, however, no enhancement was obtained for the linear working range. Based on these optimization studies, it can be concluded that the incorporation of MWCNTs to the carbon paste composition resulted in an improvement in the mass transfer of the analyte by changing the chemical environment of the ionophore and consequently leading to an increase in the potentiometric iodide sensitivity of the electrode in terms of both working range and slope. The healing effect of carbon nanotubes on the potentiometric response of the iodide- or other species-sensitive carbon paste electrodes was in accordance with the literature [29, 30, 33, 53, 54]. On the results discussed upto now, palladium(II) complex can be considered as a suitable ionophore for the fabrication of MWCNT modified iodide-selective carbon paste electrode (CPE1). Finally, the optimum carbon paste composition was obtained as 12.0% ionophore, 20.7% *o*-NPOE, 18.5% TDAT*p*ClPB, 1.0% MWCNTs, and 47.8% graphite powder to be utilized for further studies.

It was previously reported that the response properties of the ISEs depended on the multicomponent composite materials presented on the surface of the electrode [62]. Therefore, a scanning electron microscope (SEM) image of the surface of palladium(II) complex based MWCNT modified iodide-selective carbon paste electrode (CPE1) with optimum composition was examined and displayed in Fig. 2 together with that of the ionophore-free CPE (Fig. 2a). In this regard, the surface morphology of the carbon paste without ionophore had homogeneously distributed agglomerations while the ionophore and MWCNT incorporated morphologies in Fig. 2b, c, respectively, appeared to be having the same agglomerations together with non-uniform flake like structures (inset on the top left part of Fig. 2c) which were thought to be ionophore. MWCNTs could be observed like braided tubular entangled structures when the images were magnified (inset on the bottom left part of Fig. 2c) and it was not possible for nanotubes to be dispersed homogeneously in the paste and to be obvious within graphite powder due to their little amount.

Effect of pH and conditioning solution

The effect of pH on the electrode response depends on the structure of the ionophore. In the cases of ionophores like metal complexes or ligands containing proton binding

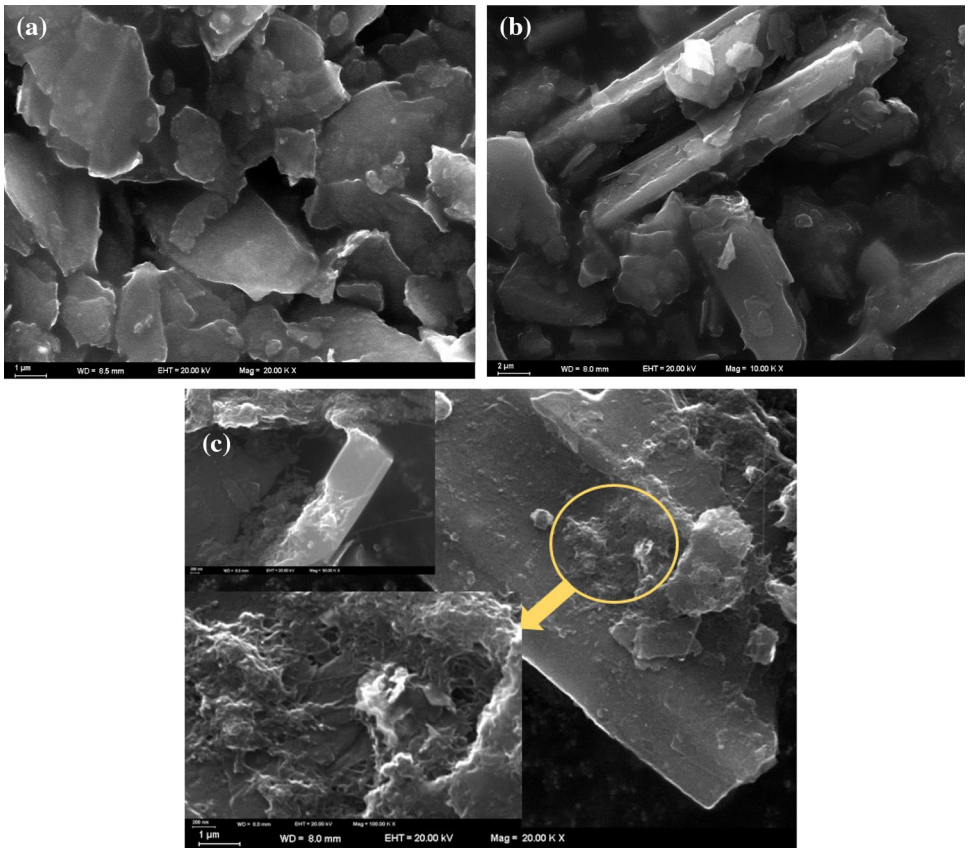

Fig. 2 SEM images for the surfaces of CPEs: **a** ionophore free; containing ionophore **b** without MWCNTs, **c** with MWCNTs

groups such as nitrogen and phosphorus, the hydronium ions in the test solution may disrupt the structure of the ionophore or the ionophore can be protonated resulting in a different interaction between analyte and the ionophore. Therefore, it is particularly significant to determine the pH of the test solution. To examine whether the palladium(II) complex was affected by the pH of the solution or not, the potentials of the BR buffer solutions containing 0.1 mol dm^{-3} NaCl were recorded with CPE1 in the pH range of 2.0–11.0. The *E*-pH graphs are shown in Fig. 3 as an inset graphic. It was observed that there was no sudden change in the potential response of the electrode in the pH range of 2.0–7.0. In the basic region pH 8.0–10.0, a negligible potential change was found towards hydronium ion as can be seen in Fig. 3. Since the electrode potential is independent of pH in the wide pH range of 2.0–7.0, this range can be accepted as the working pH range of our MWCNT modified CPE.

On the other hand, the response of the electrode was tested in different buffer solutions (MES: 4-morpholineethanesulfonic acid; TRIS: tris(hydroxymethyl)aminomethane hydrochloride) to select the optimum working pH in this range by comparing the slopes of the calibration graphs and the related linear working ranges. For this purpose, *E*-pI charts were created at pH 4.0–7.0 containing 0.1 mol dm^{-3} NaCl (Fig. 3). CPE1 possessed Nernstian slopes at pH 4.0 (57.7 ± 1.8 mV/pI), 5.0 (58.0 ± 0.4 mV/pI),

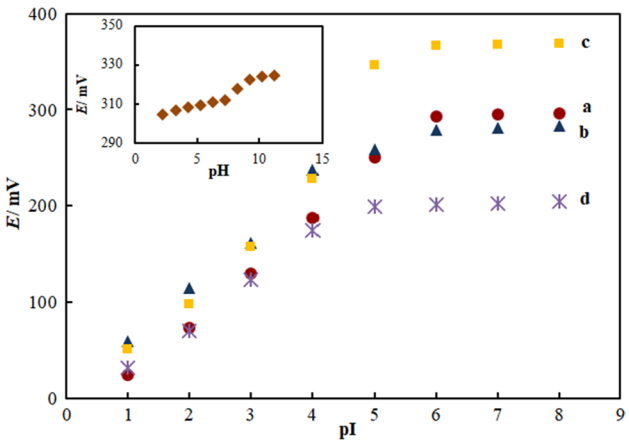

Fig. 3 Calibration curves of CPE with the optimum composition: 12.0% ionophore, 20.7% *o*-NPOE, 18.5% TDAT*p*ClPB, 1.0% MWCNTs, 47.8% graphite powder at different pHs: **a** 4.0 (acetic acid/acetate), **b** 5.0 (MES), **c** 6.0 (MES), **d** 7.0 (TRIS) inset: Effect of pH on the potentiometric response of the CPE (BR buffer solutions in the range of 2–11 without iodide)

and 6.0 (58.9 ± 0.5 mV/pI), however, at pH 7.0 the electrode showed sub-Nernstian response (47.6 ± 1.4 mV/pI).

As can be seen in Fig. 3 the largest working range was found at pH 4.0 (1.0×10^{-6} – 1.0×10^{-1} mol dm^{-3}) when compared with that of others (1.0×10^{-4} – 1.0×10^{-1} mol d

m^{-3}). Comparing the slopes and the working ranges of the electrodes, the optimum pH was selected as 4.0 due to the wide dynamic range obtained for CPE1.

The proposed electrode was conditioned in NaI solutions (1.0×10^{-3}, 1.0×10^{-4}, 1.0×10^{-5} mol dm^{-3}) and deionized water for an hour to investigate whether lower detection limits can be achieved or not. The working ranges of the electrode conditioned in 1.0×10^{-3} mol dm^{-3} sodium iodide solution and deionized water were found narrower (pI: 1–4) than that of CPE1 (pI:1–6). Conditioning in 1.0×10^{-4} mol dm^{-3} analyte solution provided a lower detection limit (2.9×10^{-8} mol dm^{-3}) in accordance with the literature [63, 64]. This situation also made an important improvement to obtain a short response time. No further contribution of conditioning to the working range and slope was observed with 1.0×10^{-5} mol dm^{-3} NaI.

EIS studies

Electrochemical impedance spectroscopy (EIS) is an effective method that provides information about the conductivity and the characterization of the electrode surface, ion exchange mechanism at the electrode-solution interface for potentiometric ISEs [65–67]. Therefore, the interaction between the analyte and modified surface of CPE1 was investigated by EIS in two sections: (i) the effect of MWCNTs, (ii) interaction between ionophore and iodide on the performance of the electrode was evaluated with the obtained Nyquist plots (Fig. 4). As is seen, at high frequencies, semicyclic curves were observed for the CPE1. It is obvious in Fig. 4A (a) that the resistance of the electrode without MWCNTs was found higher than that of CPE1 (Fig. 4A (b)). This can be interpreted as the presence of MWCNTs in the carbon paste composition reduces the resistance of the electrode surface providing faster ion transfer. To specify the interaction between ionophore and iodide to support the sensitivity of the electrode, Nyquist plots were obtained for CPE1 in solutions containing 0.1 mol dm^{-3} NaCl and different iodide concentrations at pH 4.0 (Fig. 4B). Since the existence of reduced resistances (high conductivities) belong to the ionophore-iodide interaction, this observation can be evaluated as the confirming data for high iodide sensitivity of the palladium(II) complex due to the decrease in the carbon paste resistance by the increasing iodide concentration demonstrated in impedance spectra. According to Fig. 4B, it can be concluded that the higher the iodide concentration, the lower the resistance of the electrode surface leading to the faster transfer of iodide from/to carbon paste. In addition, observing linear parts with an approximate angle of 45° in these spectra indicated the diffusion process of iodide ion from the analyte solution through the electrode surface reversibly at lower frequencies [68].

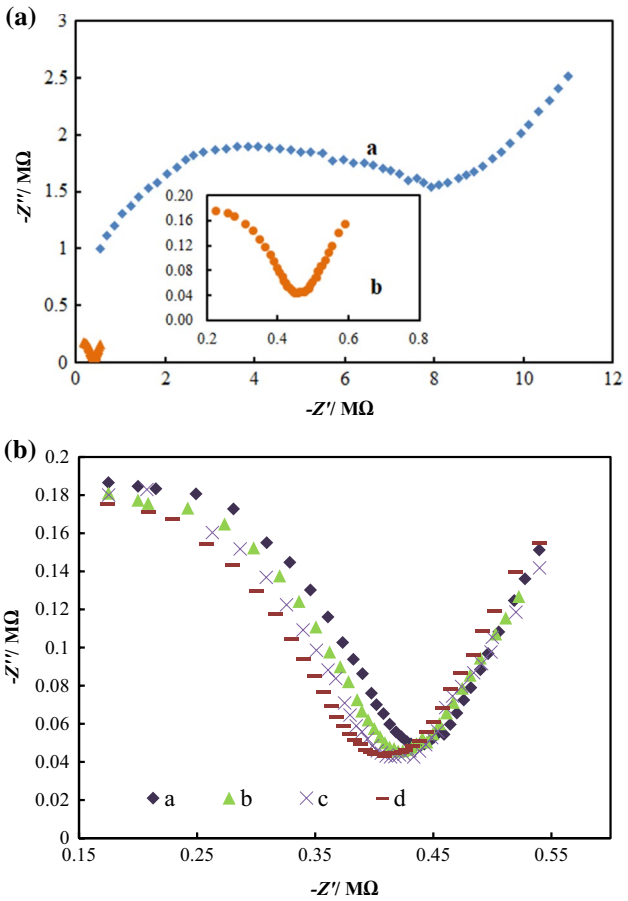

Fig. 4 Impedance plots of the carbon paste for CPE1 (**A**) **a** without and **b** with MWCNTs in 1.0×10^{-2} mol dm^{-3} NaI; (**B**) in NaI solutions of **a** 0, **b** 1.0×10^{-4}, **c** 1.0×10^{-3}, and **d** 1.0×10^{-2} mol dm^{-3} (all solutions were prepared at pH 4.0 with 0.1 mol dm^{-3} NaCl)

Performance characteristics of the electrode

The slope and the linear operating range of CPE1 were determined using the calibration curves obtained from chronopotentiometric (*E-t*) data created in iodide-containing solutions at pH 4.0 (Fig. 5). Additionally, the inclusion of MWCNTs improved the slope of the electrode with respect to the one prepared without MWCNTs (43.8 ± 0.6 mV/pI) [47]. As can be seen in Fig. 5, the linear working range was found to be 1.0×10^{-6} – 1.0×10^{-1} mol dm^{-3} with a slope of 57.7 ± 1.8 mV/pI which was acquired to be in agreement with that of the results obtained by using the potential values recorded by the pH-ion meter. LOD and the limit of quantification (LOQ) values were calculated in accordance with IUPAC recommendations reported in the literature [69–71]. LOQ was found as 9.7×10^{-8} mol dm^{-3} according to the equation of LOQ = 10*S*/slope where *S* is the standard deviation of intersection points for two linear portions providing the lowest concentration values in the

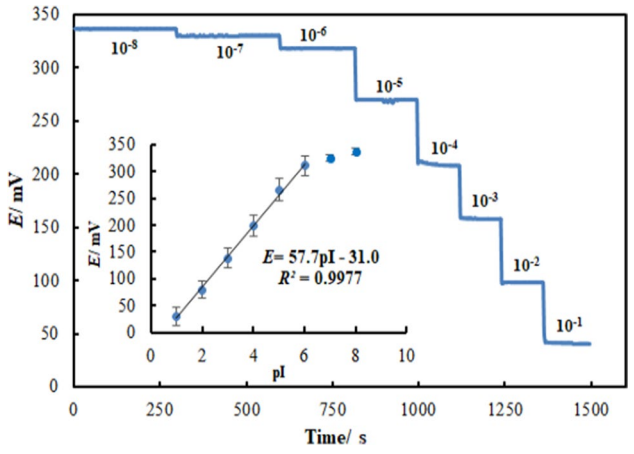

Fig. 5 Typical dynamic response of CPE1 obtained by successive additions of NaI at pH 4.0 containing 0.1 mol dm^{-3} NaCl (inset graph: calibration curve for CPE1 drawn by the chronopotentiometric data with error bars, $N=7$)

calibration curves of CPE1. Their standard deviation was multiplied by 10. The product was divided by the average slope of the calibration curves. Moreover, the LOD = 3*S*/slope equation in the above-mentioned literature was applied to find 2.9×10^{-8} mol dm^{-3} as the LOD of CPE1 which was also confirmed experimentally by considering the chronopotentiometric data in Fig. 5 due to the potential signal for iodide observed at 1.0×10^{-8} mol dm^{-3}. The performance characteristics of the proposed MWCNT modified iodide-selective CPE in Table 2 were compared with the similar ones and the ones without MWCNTs encountered in the literature. According to this table when the slopes were taken into account, CPE1 can be assumed as capable to compete with the Refs. [29, 30, 39, 46] since no significant difference was observed. On the other hand, it showed higher Nernstian slope than the electrodes reported previously [40, 45]. With regard to the working ranges, CPE1 was seen to show a wider range than the ones without MWCNTs [9, 44, 45] and a similar range with the electrode in literature [39]. In addition, it can be said that CPE1 was capable to compete with some of the CPEs with MWCNTs in terms of working ranges in literature [29, 30, 46]. Likewise, when CPE1 was compared by means of the limit of detection, it was found to have the best detection limit among all the electrodes prepared with/without MWCNTs / MONPs [9, 29, 30, 33, 39, 44–47] listed in Table 2 except [40]. This situation can be accepted as an advantage for the analytical application of the proposed electrode in a low concentration of iodide found in a pharmaceutical sample.

As is the case for all sensors, having a short response time is one of the most important factors when using an ISE for analytical purposes. Therefore, the response time of the CPE1 electrode was determined using the chronopotentiometric data given in Fig. 5 by measuring the time needed to reach the equilibrium after each successive iodide addition (starting with the necessary amount of iodide to give 1.0×10^{-8} mol dm^{-3}) to the pH 4.0 buffer solution containing 0.1 mol dm^{-3} NaCl. Based on the data, the response time of the proposed carbon paste iodide-selective electrode (< 5 s) was found to be better than most of the similar electrodes given in Table 2 [9, 29, 30, 39, 40, 44–46]. Consequently, the use of MWCNTs not only increased the speed of conversion of the chemical signal to the electrical one but also resulted in a fast response time of the sensor [54, 72, 73].

To determine the lifetime of the proposed iodide-selective electrode, calibration curves were drawn at least two times a day for a week during 4 months by using the same electrode and keeping it in 1.0×10^{-4} mol dm^{-3} NaI for an hour between each measurement. During this period it was observed that there was no significant change leading to measurable divergence change in the slopes of these calibration curves, hence the proposed electrode can be accepted as stable for a period of ≥ 4 months. Comparing this value with the lifetime of similar carbon paste electrodes based on metal complexes and MWCNTs free electrodes in literature, it can be stated that the lifetime of our electrode was quite good among these [9, 29, 30, 33, 44–46]. Therefore, MWCNTs can be considered to have an improving effect on the lifetime of the electrodes. The reason to have a quite long lifetime can be the result of homogeneously mixing the paste compositon with nanomaterials by using *o*-NPOE as a binding agent, consequently leading to effective elimination of gradual ionophore leakage from the organic phase as ion-selective surface to the aqueous phase (analyte solution). Moreover, the longevity and stability of the CPE1 can be attributed to a durable electrode surface obtained by homogeneously mixing the nanomaterial containing carbon paste for at least 30 min. The stability of the potentiometric response in this situation can be also based upon the structure of the ionophore remaining stable at pH 4.0 and the better contact area provided between the ion-selective surface and the electronically conductive nanostructured material [74].

Repeatability and reproducibility

The repeatability (with CPE1) and the reproducibility (with five different CPEs) were determined by measuring the slopes obtained from five different calibration curves of the electrode with the same optimum carbon paste composition. Then, the relative standard deviation of the slopes was calculated for each case and found to be less than 5%. This value showed that the repeatability and the reproducibility of the MWCNT modified carbon paste iodide-selective electrode were quite good.

Selectivity coefficients

The selectivity of an electrode is a significant parameter to confirm its applicability for the potentiometric determination of species in different matrix media. For this purpose, the potentiometric response of CPE1 was evaluated in the presence of bromide, salicylate, fluoride, chloride, formate, benzoate, citrate, nitrite, carbonate, sulfide, chromate, nitrate, thiocyanate, perchlorate and separate solution method was used to determine the selectivity coefficients of the electrode (log $K_{I,X}^{pot}$ where I is the analyte and X is the interfering ion). According to the data in Table 3, the selectivity order of CPE1 was found as perchlorate > thiocyanate ≈ salicylate > benzoate > nitrate > nitrite ≈ chromate > bromide > chloride > citrate > carbonate > sulphite > fluoride > acetate. The same sequence with approximately the same selectivity coefficients was obtained using the fixed interference method (C_X: 1.0×10^{-3} mol dm^{-3}). With regard to Table 3, most of the anions had no significant interfering effect except perchlorate, thiocyanate, and salicylate. A lower interfering effect of nitrate ion was found for the proposed electrode while it was the most interfering ion for some of the MWCNT modified iodide-selective carbon paste electrodes reported in the literature [29, 30]. In addition, it was observed that the selectivity coefficients found in the literature for ClO_4^-, SCN^- and salicylate were higher than that of CPE1 [9, 46]. As a result, it was decided that the proposed electrode could be successfully employed as an indicator electrode for the potentiometric determination of iodide in samples containing lower concentrations of perchlorate, thiocyanate, and salicylate or in the absence of them. Moreover, depending on the selectivity coefficients, the use of the proposed electrode as a potentiometric detector in ion chromatography for several anions such as perchlorate, thiocyanate, and salicylate is anticipated.

Analytical application

The analytical applicability of the electrode with the optimum paste composition was demonstrated in two ways: (i) Titration of standard potassium iodide solution with standard silver nitrate and (ii) determination of iodide in Jodid tablets under optimum experimental conditions. *S*-shaped titration curves with sharp end points were obtained for five replicate analyses of both ways and typical titration curves together with an inset graph of the first derivative for the titration of standard KI solution are shown in Fig. 6. In the light of sharp end points obtained in titration curves for (i), CPE1 was decided to be applied as an indicator electrode in the potentiometric determination of iodide in real samples. The patients with iodine deficiency are treated with a drug (Jodid tablet) that is used for the prevention of goiter development due to iodine deficiency in cases such as re-growth of goiter after the completion of thyroid hormone treatment or surgical intervention of goiter, during pregnancy, and in newborns, children, and adolescents. Therefore, it was chosen as a drug sample in this study.

The amount of iodide per tablet (100 µg iodide/tablet) was calculated as a result of titrating the appropriate amount taken from the Jodid tablet sample solution with the standard $AgNO_3$ solution for five replicates. The data are given in Table 4 together with the recovery values. The calculated recovery values were found to be close to 100%. In addition, the experimental t value (t_e) was compared with the critical t value ($t_c = 2.78$) at 95% confidence level (CL) by applying t test. Since $t_e < t_c$, it can be concluded that there was no systematic error and therefore no significant difference was observed between the declared value and the experimental averages calculated. Consequently, this proposed electrode can be satisfactorily used for quality control purposes of iodide-containing drugs by determining it via potentiometric titration.

Conclusion

On the basis of the results in this study, the palladium(II) complex was found to be a suitable ionophore for the proposed nanomaterial modified iodide-selective CPE. It

Table 3 The selectivity coefficients of MWCNT modified iodide-selective CPE calculated by separate solution method

Anion	Selectivity coefficients, log $K_{I,X}^{pot}$	Anion	Selectivity coefficients, log $K_{I,X}^{pot}$
Perchlorate	1.04	Bromide	− 3.21
Thiocyanate	0.52	Chloride	− 3.61
Salicylate	0.52	Citrate	− 4.15
Benzoate	− 0.13	Carbonate	− 4.38
Nitrate	− 1.81	Sulphite	− 4.51
Nitrite	− 2.58	Fluoride	− 5.55
Chromate	− 2.63	Acetate	− 6.30

Table 4 Potentiometric determination of iodide in the pharmaceutical sample (100 µg iodide/tablet) and the recovery values

Experiment	Iodide/µg	Recovery/%
1	103.6	103.6
2	99.6	99.6
3	99.6	99.6
4	103.6	103.6
5	99.6	99.6
$\bar{x} \pm ts/\sqrt{N}$[a]	101.2 ± 2.7	101.2 ± 2.7 $t_e = 1.21$

[a]$N = 5$ at 95% CL, $t_c = 2.78$

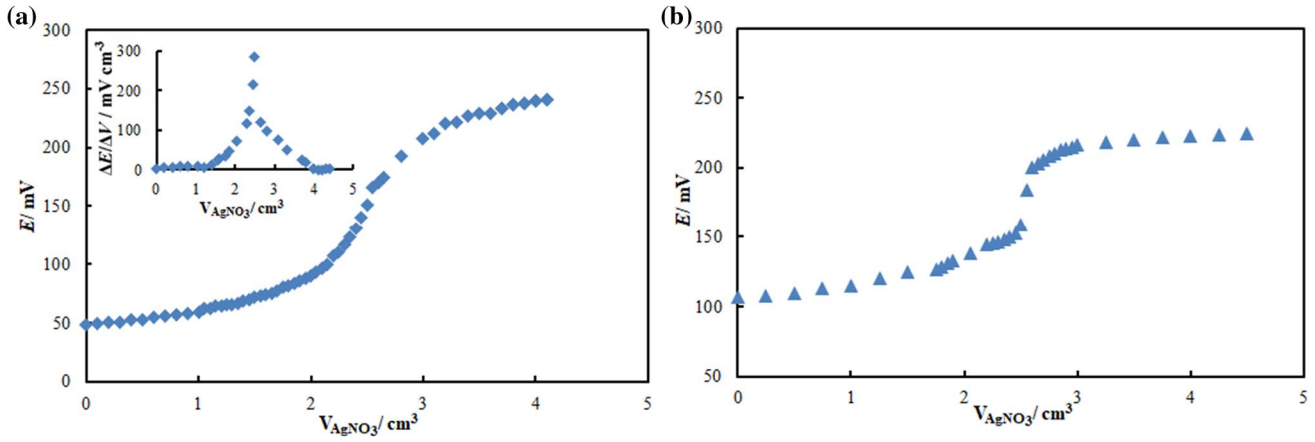

Fig. 6 Typical titration curves obtained with standard $AgNO_3$ (0.05 mol dm^{-3}) solution using CPE1 for the potentiometric determination of iodide at pH 4.0 in **A** potassium iodide (inset graph is the 1st derivative of the curve), and **B** Jodid tablet sample solution

showed better response characteristics than the previously reported CPEs without MWCNTs [47] based on the same ionophore. Addition of all nanomaterials increased the sensitivity of the electrode, however, only the use of MWCNTs resulted in a Nernstian slope of 57.7 ± 1.8 mV/pI in the range of $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ mol dm^{-3} at pH = 4.0. To the best of our knowledge, the lifetime of the electrode was the longest (≥ 4 months) among all the previously reported iodide-selective CPEs based on metal complexes in literature and the detection limit was the best except in one study [40]. Furthermore, the proposed electrode has the advantage of having a short response time (< 5 s) and a low detection limit (2.9×10^{-8} mol dm^{-3}) to be preferred for analytical applications in real samples. Since the LOD was found to be quite low, a satisfying analytical application of the proposed electrode for potentiometric iodide determination could be accomplished in a pharmaceutical sample. In addition, it was thought to be possible to employ the electrode in biological samples owing to its low detection limit as 2.9×10^{-8} mol dm^{-3}. From another analytical point of view, the proposed electrode could be a good alternative as a potentiometric detector in ion chromatography for several anions such as perchlorate, thiocyanate, and salicylate owing to its short response time and long lifetime. Finally, ease of preparation, low cost, fast response, long lifetime, high sensitivity, and renewable carbon paste electrode surface revealed that the proposed electrode could be evaluated as a contribution to the literature in terms of an alternative tool for the quality control processes of iodide containing drug samples in the future.

Apparatus

Potentiometric measurements were performed with Orion-Model 720A pH-ion meter combined with a double junction Ag/AgCl reference electrode (DJ Ag/AgCl RE, Orion 900200, containing internal and external filling solutions: AgCl and 10% KNO_3, respectively) and the proposed nanomaterial modified carbon paste iodide-selective electrode was employed as an indicator electrode. For the pH measurements, Thermo Orion 812600 combined glass electrode was used. CPE body was purchased from Bioanalytical Systems, Inc. (BASi MF-2010). EIS measurements and chronopotentiometric measurements (*E-t*) were carried out with CHi 660D Model potentiostat/galvanostat combined with BASi C3 cell stand. For this purpose, three-electrode system containing reference electrode (Ag/AgCl, (3 M NaCl), BASi MF-2052), auxillary electrode (platinum wire, BASi MW-1032) and the proposed nanomaterial-based CPE as the working electrode were used. The SEM images of the electrodes were obtained from Bruker AXS XFlash Detector 4010. Orion Model 940 automatic titrator was used for the potentiometric titrations with the electrode. Deionized water with a conductivity of 18.2 MΩ was supplied from ELGA Purelab Classic Ultra Pure Water System for the preparation of all test solutions.

Reagents and preparation of solutions

All chemicals used for the preparation of the solutions and dichloro[1,1′-bis(diphenylphosphine)ferrocene] palladium(II) complex as the ionophore in this study were purchased from Sigma-Aldrich with the highest purity available. The plasticizers such as BEHA, BEHP, BEHS, *o*-NPOE, paraffin oil and lipophilic additives such as THATPB, TDMACl, TDAT*p*ClPB were of selectophore purity supplied from Sigma-Aldrich and used as received. MWCNTs and MONPs were obtained from www.cheaptubes.com and Sigma-Aldrich, respectively. Anion solutions were prepared by dissolving sodium salt of the

corresponding ion in pH 4.0 buffer solution (acetic acid / acetate) containing 0.1 mol dm^{-3} NaCl. Other buffer solutions used in the study were MES buffer (pH 5.0; pH 6.0) and TRIS buffer (pH 7.0) containing 0.1 mol dm^{-3} NaCl. Calibration solutions for sodium iodide were freshly prepared before each experiment. Silver nitrate solutions (0.05 mol dm^{-3}) for potentiometric titrations were standardized against NaCl.

Construction of nanomaterial-modified carbon paste electrodes

The proposed nanomaterial modified carbon paste iodide-selective electrodes were set up as follows: appropriate amount of ionophore, plasticizer, graphite powder, lipophilic additive, MWCNTs, and MONPs were mixed for 30–40 min as shown in Table 1 with variable percentages until a homogeneous paste was obtained. The cavity of the commercially available CPE body (BASi MF-2010) was fully filled with the resulting composite mixture to fabricate an iodide-selective nanomaterial-based CPE. A weighting paper was preferred to polish the surface of the electrode till a shining appearance was achieved. In additon, ionophore-free electrodes with/without nanomaterial modification were constructed in similar way. 1.0×10^{-4} mol dm^{-3} NaI solution was used as a conditioning solution prior to measurements and to keep the electrodes when they were not in use.

Electrochemical measurements

All emf responses were obtained under an inert nitrogen atmosphere at 21.0 ± 2.0 °C with the electrochemical cell formed as below:

DJ Ag/AgCl RE ‖ analyte solution ǀ nanomaterial modified CPE.

Chronopotentiometric studies were performed in solutions containing 0.1 mol dm^{-3} NaCl (pH:4.0) by the addition of iodide ion to provide 10-fold concentration change to obtain *E-t* graphs.

EIS studies were operated in an alternative current impedance technique by using 0.2 V open-circuit potential with an amplitude of 0.005 V in a frequency range from 10^3 to 10^6 Hz as experimental parameters with the three-electrode system mentioned in the apparatus section. The Nyquist plots were observed for the solutions containing different concentrations of iodide at pH 4.0.

Sample preparation for analytical application

Jodid by Merck, containing 100 µg of iodide per tablet which is equivalent to 130.8 µg potassium iodide, was handled as a pharmaceutical drug sample for potentiometric determination of iodide. 50 tablets were pulverized in a ceramic mortar and then poured into a volumetric flask containing 50.0 cm^3 of ethyl alcohol. This flask was kept in an ultrasonic bath for about 3 h to accomplish the complete dissolution of iodide in a solvent. Then 100.0 cm^3 of deionized water was added and the mixture was stirred again for an hour. Finally, the solution was diluted to 250.0 cm^3 with deionized water after the filtration process to remove insoluble particles was done. Appropriate amounts were taken from this solution and their pHs were adjusted to 4.0 to prepare 50.0 cm^3 aliquot samples containing 0.1 mol dm^{-3} NaCl for the analysis.

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