

Iodide–Selective Electrodes Based on Two New Carriers: Influence of Various Nanoparticle Materials on the Response Performance of proposed electrodes

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The influence of various nanoparticles such as oxidized multiwall carbon nanotubes (MWCNTs), silver, zinc sulfide and zinc selenide loaded on the active carbon on the response properties of new iodide carbon paste electrodes based on bis(3-phenyl-2-propenaldehydene)-1,3-propanediamine zinc(II) chloride, $[\text{ZnL}^1\text{Cl}_2]$ and bis(4-nitrobenzylidene) ethylenediamine mercury(II)bromide $[\text{HgL}^2\text{Br}_2]$ as suitable carriers are described. It was seen, for both ionophores among different nanoparticle, the best response (wide linear range and low detection limit) was observed in the presence of oxidized MWCNT. The effects of various parameters such as amount of ionophores, amount of additive and role and amount of nanoparticles on the response properties of proposed electrodes were investigated. Amount of oxidized multiwall carbon nanotube (MWCNT), additives (MTOACl), ionophores and Nujol were optimized and their values are set as: carbon powder, oxidized MWCNT: Nujol, Carrier: MTOACl (0.15 g, 12 mg, 50 mg, 27 mg, 21.2 mg) and (0.15g, 8 mg, 50 mg, 20 mg, 10 mg) for $[\text{ZnL}^1\text{Cl}_2]$ and $[\text{HgL}^2\text{Br}_2]$, respectively. The electrodes based on $[\text{ZnL}^1\text{Cl}_2]$ and $[\text{HgL}^2\text{Br}_2]$ complexes exhibits Nernstian slope of 57.3 ± 1.2 and 59.8 ± 0.8 mV per decade over a wide concentration range from 1.0×10^{-6} to 1.0×10^{-1} and 1.0×10^{-7} to 1.0×10^{-1} M with detection limit of 8.8×10^{-7} and 7.5×10^{-8} M. They have relatively fast response times (20 s and 15 s), satisfactory reproducibility (± 1.2 and ± 0.8) and relatively long life times (2 months). The proposed sensors show high selectivity toward iodide ion in comparison to other common anions, while their potentiometric responses are independent of the solution pH in the pH of 2.5–11.0. The proposed electrodes especially based on mercury complex in the presence of oxidized MWCNT show very unique selectivity and low detection limits. They were used successfully as indicator electrodes in potentiometric titration and direct determination of iodide content in drug containing compound.

Keywords: Carbon paste electrode, Potentiometric sensor, iodide ion, Nanoparticle Materials

1. INTRODUCTION

Although iodine is an indispensable microelement for human, irritation of its vapors to and iodide containing compound eyes and lungs is toxic. The maximum allowable iodide concentration [1] is 1.0 mg m^{-3} . Iodine plays a key role in many biological activities such as brain functions, cell growth, neurological activities, metabolism and thyroid functions, while it is present in the composition of various drugs. Excess of iodine or iodide can cause goiter and hypothyroidism as well as hyperthyroidism. Because this bio-essential element often occurs at very low concentration, numerous analytical methods have been reported for its determination at low concentration levels. Due to its vital importance in environment, medicines and industry, there is an argent need for its determination in clinical and chemical analysis [2-4].

Most of previously reported iodide evaluation procedures suffer from drawback such as require large infrastructure backup, high operational cost and not very appropriate for analysis of large number of samples. As it is well known, potentiometric sensors offer an inexpensive and convenient method for fast analysis with high sensitivity and selectivity. Ion selective electrodes have emerged as one of the most promising tools for direct determination of various species in biological and industrial analysis. In view of such advantages, efforts have been made to make selective sensors for different anions [5]. Various types of electrodes have been suggested for determination of analyst ion. Besides conventionally constructed electrode, the carbon paste type electrode has become attracted. Therefore, there has been a growing interest in the development and application of potentiometric sensors. Most of the recently reported potentiometric sensors are carrier-based ion-selective electrode (ISEs) which presumably act on the basis of chemical recognition principles. Several iodide selective electrode based on the complexes of transition metals including Fe (III), Cu (I), Hg (II), Co (II), Ni(II) and Co(II) with various ligands as shown in Table 1 have been reported [6-16].

Table 1. Characteristics performance of some iodide sensors based on various ionophores.

Carrier	Slop (mV/decade)	L.R ($\mu\text{M-M}$)	D.L (μM)	pH	Response time	Ref
Schiff base complex of Fe(III)	-71.0	1.0-0.5	0.65	3.5-10	<15 s	[6]
Cu(I)-bathocuproine complex	-56.8	5.0-0.2	1	3-9	10 s	[7]
[Hg(CTP) ₂]	-58.4	1.0-0.1	0.6	3.5-11.5	<10 s	[8]
Thiopyrilium ion derivative	-60.2	0.8-0.1	0.2	5.5-8	15 s	[9]
Shiff base of Co(II) (salophen)	-55.8	2.0-0.06	0.7	2.5	< 1 min	[11]
Nickel(II) tetraazaannulene macrocyclic complex	-54.7	8.0-0.1	3	3-4	5 s	[13]
[Ni(L)] ²⁺	-58.6	40-0.1	16	7-10	3 s	[14]
[Co(L)] ²⁺	-53.0	40-0.1	4	7-10	3 s	[14]
[ZnL ¹ Cl ₂]	-57.3	1.0-0.1	0.88	2.5-11	20 s	Present work
[HgL ² Br ₂]	-59.8	0.1-0.1	0.075	2.5-11	15 s	

It was pointed out that impregnation of carbon nanotubes (CNTs) with high surface area, high mechanical, and chemical and thermal stability cause unique improvement in potentiometric response.

Carbon pastes electrodes (chemically modified carbon paste electrodes (CMCPEs) simply, fabricated. A stable electrochemical response can be renewed by removing an outer layer of the paste and re-smoothing the electrode surface.

They have lower ohmic resistance than ion-selective electrodes based on polymeric membranes [13-15]. Ionophores impregnated in the carbon paste matrices control the selectivity of electrode by selective binding of target ions viz strong interaction.

Therefore, there is a strong requirement to search new lipophilic character ionophores with low bleeding to sample solution [17]. The design of selective receptors for anions has been of great interest in the field of molecular recognition.

A number of molecules which are capable of displaying selective coordination and recognition with anions have been synthesized [18,19]. One of the most appealing potential applications of these anion receptors is the development of chemical sensors. The main aim of the present work was the development of highly selective carbon paste electrodes for iodide carbon paste electrode based on $[\text{ZnL}^1\text{Cl}_2]$ and $[\text{HgL}^2\text{Br}_2]$ (Scheme 1) complexes in the presence of various nanoparticles as suitable sensing material. In the present study, the carbon paste compositions were optimized. Their optimum working conditions were investigated and interference studies have been made. The proposed electrodes displays low detection limit and high selectivity and sensitivity to iodide determination.

2. EXPERIMENTAL

2.1. Reagents

Pure graphite powders and paraffin oil, methyltrioctylammonium chloride (MTOACl), tetrahydrofuran (THF) were used for the preparation of carbon paste electrode. Solutions of interferences were prepared by dissolving appropriate amounts of their potassium salts. Stock 0.5 M iodide solutions were prepared daily from potassium iodide. All other chemical were of highest purity available from Merck. The pH adjustments were made with dilute nitric acid or sodium hydroxide solutions as required.

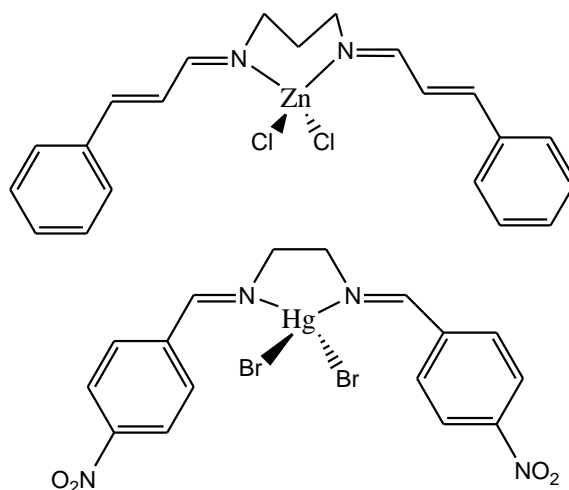
X-ray diffraction (XRD) pattern was recorded by an automated Philips X'Pert X-ray diffractometer with Cu $K\alpha$ radiation (40 kV and 30 mA) for 2θ values over 10-80°. The shape and surface morphology of the ZnO nanoparticles were investigated by field emission scanning electron microscope (FE-SEM, Hitachi S4160) under an acceleration voltage of 15 kV. For FE-SEM, it is necessary to coat the ZnO nanoparticles by gold, which was carried out by an Auto Fine Coater (JFC-1300, JEOL).

ZnO and ZNS nanoparticles were purchased from Merck Company and homogenously with a 1:5mass ration in pastel and mortar was mixed with activated carbon.

2-2. Synthesis of bis(3-phenyl-2-propenaldehyde)-1,3-propanediamine zinc(II)chloride, $[ZnL^1Cl_2]$ and bis(4-nitrobenzylidene)ethylenediimine mercury(II)bromide $[HgL^2Br_2]$

$[ZnL^1Cl_2]$ -To an ethanolic solution containing 1 mmol of 3-phenyl-1-propenal and 0.5 mmol of 1, 3- propanediamine after stirring for 4 hours, 1mmol of zinc(II) chloride was gradually added. The reaction mixture was stirred for 2 hours and then the white precipitate was filtrated, washed with ethanol twice and recrystallized form chloroform/methanol to give the complex in 85 yield. % $C_{21}H_{22}Cl_2N_2Zn$: Calculated: C, 57.49; H, 5.05; N, 6.39; Found: C, 60.4; H, 5.31; N, 6.7. IR(KBr, cm^{-1}): 3100(w), 2985(m), 1630(s), 1592(s), 1488(w), 1450(s), 1385(vs), 1350(w), 1315(w), 1287(s), 1190(w), 1180(s), 1068(m), 1035(m), 1010(s), 990(m), 750(s), 688(s), 625(w), 565(w). UV-Vis (CH_2Cl_2): 298 nm.

$[HgL^2Br_2]$ - 0.5 mmol ethylenediamine in 10 mL chloroform was gradually added to 1 mmol of 4-nitrobenzaldehyde in 10 mL chloroform and the reaction mixture was stirred severely for 4 hours. Then the result solution was added to a solution of 1mmol of mercury(II) bromide in methanol(15mL). The reaction mixture was stirred for 3-4 hours until the complex be appeared as cream white precipitate. The product was filtrated, washed with ethanol twice and recrystallized form chloroform/ethanol to give the complex in 72% yields. IR (KBr, cm^{-1}): 3465 (w), 3080 (w), 3048 (w), 2920(m), 2823(w), 2360 (m), 1641 (s), 1599 (s),1518 (Vs), 1452 (m), 1364 (w), 1343 (Vs), 1307(s), 1225(w), 1181(w), 1106 (m), 1031(m), 1009(w), 934(w), 851(s), 749(s), 696(m). UV-Vis(DMF): 284nm. $^1HNMR(DMSO-d_6)$: 8.47(s, 2H), 8.24(d, 2H, $J=8.62Hz$), 7.93(d, 4H, $J=8.63Hz$), 3.95(s, 4H). M. P.($^{\circ}C$)=210. Schematic structures of the complexes are presented in Scheme 1.



Scheme 1. Structure of Ionophores

2.3. Preparation of carbon paste electrodes

The carbon paste electrodes were prepared as follows. 150 mg of graphite powder was mixed with 50 mg of paraffin oil. Next, (27 mg of $[ZnL^1Cl_2]$ and 21.2 mg MTOACl) or (20 mg of $[HgL^2Br_2]$ and 10 mg MTOACl) (dissolved in 2 ml of THF) was incorporated into a carbon paste matrix and

blended. After evaporation of the solvent, all carbon paste compositions were packed into 5.0 mL polyethylene syringes with diameter of 2.5 mm. Copper wire was glued (imbedded into carbon paste matrices) on the end of carbon paste for electrical contact. The carbon paste was packed into the end of the syringe provided with an unmodified carbon paste-copper wire contact. The electrode surface was pressing against a filter paper to obtain an appropriate packing of the carbon paste and a smooth surface. All electrodes were stored in 0.1 M NaNO₃ solution at pH 4.0 at room temperature until use.

2.4. Apparatus and potential measurement

A cell assembly of the following type was used: CPE|Sample solution | Reference electrode.

All the emf observations were made relative to a double junction Ag/AgCl electrode with a pH/mV meter.

The performance of the electrodes was investigated by measuring the emfs of KI solutions prepared with a concentration range of 10⁻¹ to 10⁻⁸ M by serial dilution. Each solution was stirred and the potential reading was recorded when it became stable, and then plotted as a logarithmic function of iodide activity. The activities of anions were based on the activity coefficient γ , data calculated from the modified form of the Debye-Huckel equation, which is applicable to any ion $\log \gamma = -0.511 Z^2 [\mu^{1/2} / (1 + 1.5\mu^{1/2}) - 0.2\mu]$ where μ is the ionic strength and Z the valency. All measurements were carried out at 25 ± 0.1 °C.

2.4. Synthesis of Ag-NP- AC

MWNTs were treated according to the previous procedure [13]. Nano-silver coated multi-walled carbon nanotubes were prepared by chemical plating method [14]. Firstly, 1.0 g purified and functionalized MWNTs was mixed with 50mL mixture solution of 38% formaldehyde, absolute ethyl alcohol and double distilled water (volumetric ratio 3:10:10). Secondly, 50mL mixture solution of 35 g L⁻¹ silver nitrate (AgNO₃) solution and 25% ammonia solution (volumetric ratio 1:2) was dropped one by one into the mixture of MWNTs–formaldehyde–alcohol–water solution. Keeping the pH value of reacted solution is 8–9, the reaction is processed under strong stirring. After reaction, the product is centrifuged and washed by double distilled water twice, dried in vacuum oven at 60°C.

3. RESULTS AND DISCUSSION

3.1. Structural properties and amount of Ag NP- AC

Figure 1A shows the UV-Vis absorption spectra correspond to surface plasmon resonance (SPR) of Ag nanoparticle obtained at different time intervals after mixing AgNO₃ aqueous solution with soluble formaldehyde aqueous solution at 50 °C. The maximum SPR at 400 nm was achieved

after 24 h [20]. The broadband indicates a relatively high polydispersity, both in size and shape of the Ag particles.

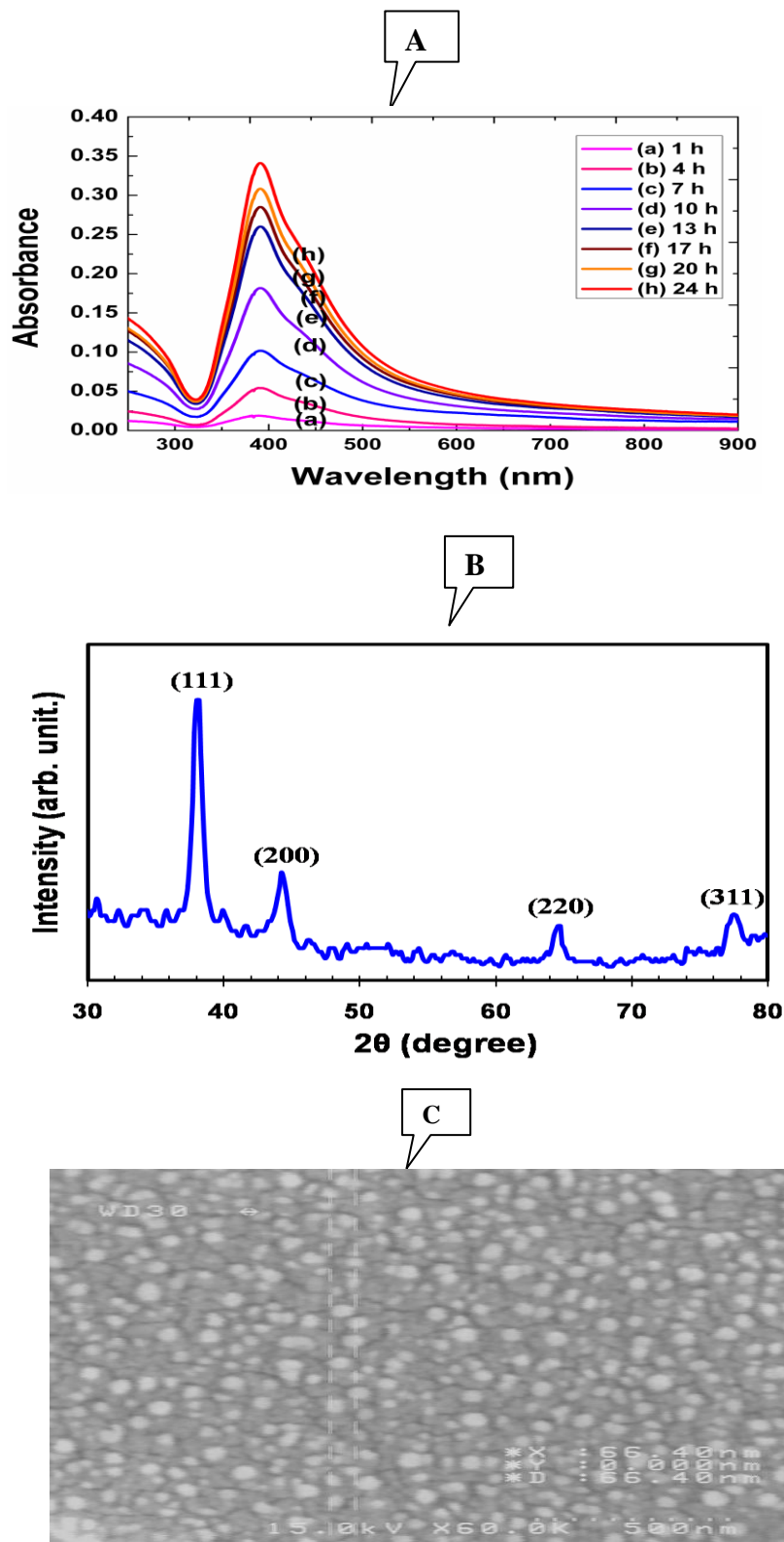


Figure 1. A (Temporal evolution of UV-visible absorption spectra after addition of AgNO₃ solution into soluble starch solution at 50 °C), B (X-ray diffraction pattern of the starch-stabilized Ag Nanoparticles), C (FESEM image of the Ag nanoparticles loaded onto activated carbon).

X-ray diffraction (XRD) pattern of silver nanoparticles powder is shown in Figure 1B. The pattern exhibits peaks at 2θ angles of 38.17, 44.21, 64.32, and 77.12 that correspond to the [111], [200], [220], and [311] crystal planes of a cubic lattice structure of silver nanoparticles, respectively [21]. From the full-width at half-maximum of diffraction peaks, the average size of the silver nanoparticles has been calculated using the Debye-Scherrer equation [22]. The calculated average size of Ag nanoparticles was around 55 nm. The FESEM image of the Ag nanoparticles is shown in Figure 1C, which reveals that the Ag nanoparticles are semi-spherical in shape and quite uniform in size distribution. The size of each Ag nanoparticles is in the range of 15–80 nm. The particle size measured directly from this FESEM image agrees with that determined by the XRD results [23].

MWCNTs powder surface was activated via stirring with 10% (v/v) hydrochloric acid solution for 2 h. Treated MWCNTs after filtering and washing with distilled deionized water dried at 80 °C for 5 h. 1 g of treated MWCNT was suspended in 250 mL of 32.5% (W/W) nitric acid solution and stirred for 36 hours at room temperature. The mixture was filtered and thoroughly rinsed with distilled deionized water until neutral pH and dried at 80 °C for 2 hours. The oxidation of MWCNTs and appearance of new functional groups was followed using FT-IR-spectroscopy as powerful and acceptable protocol. IR spectra of MWCNT and oxidized MWCNT are shown in Fig. 2 IR spectrum of chemically modified MWCNT shows some important characteristic vibration frequencies at 3400-2500(bw), 1627(w), 1155(s), 673(s), 592(s). The FESEM images of the as going and oxidized MWCNTs are shown in Fig. 3 (a, b). It can be seen that the surface morphology of the modified MWCNTs are homogeneous and relatively smooth, while the morphologies of the oxidized MWCNTs is highly disperse in the surface without any aggregation and approximately uniform in size distribution.

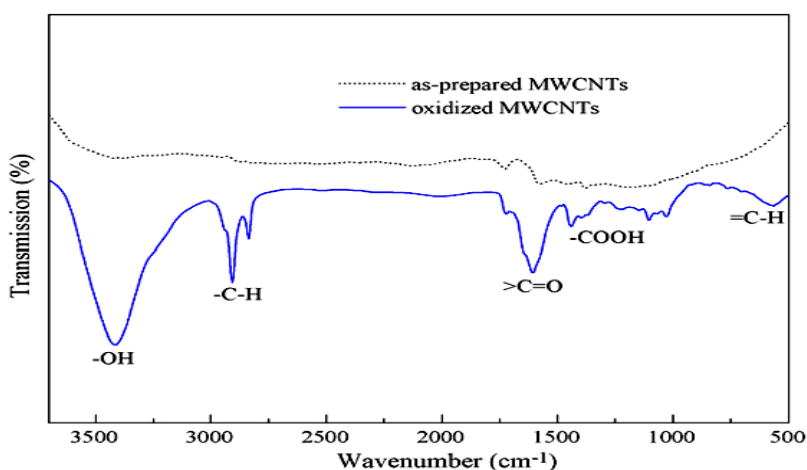


Figure 2. FT-IR spectra of as-prepared and oxidized MWCNT

Previously it has been reported that addition of carbon nanotube to the carbon paste composition improves the conductivity and transduction of the chemical signal to electrical signal. In this regard, similar CPE at optimum values of all variables and different amount of oxidized MWCNT has been prepared

As it can be seen from typical presented results for BCPHgCl_2 (Table 1) one can notice that the response properties of proposed electrodes vis. Linear range, detection limit and correlation coefficient of proposed electrode response was improved significantly by addition of oxidized MWCNTs till 30 mg.

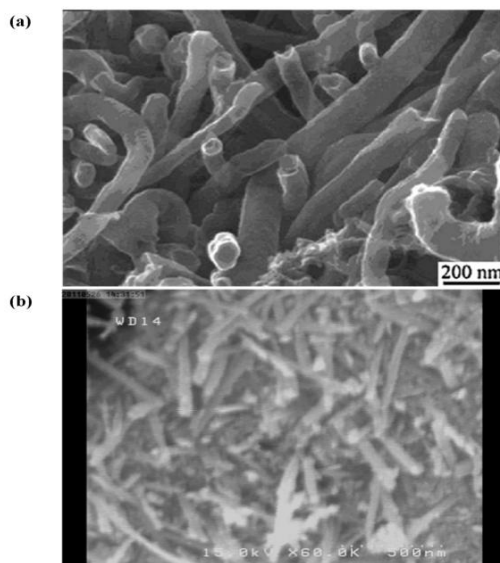


Figure 3 The FESEM images of the as-preparing and oxidized MWCNTs

3.2. Electrode composition and modification

In a set of primary experiments, two proposed ionophores were used as carriers for construction of CPEs for numerous anions. For both of electrodes it was observed clearly that the electrode response to iodide ion in a wide concentration range with a near Nernstian slope and show the poor response for the other anions. The potential response of various ion-selective electrodes based on the two proposed ionophores is shown in figure 4.

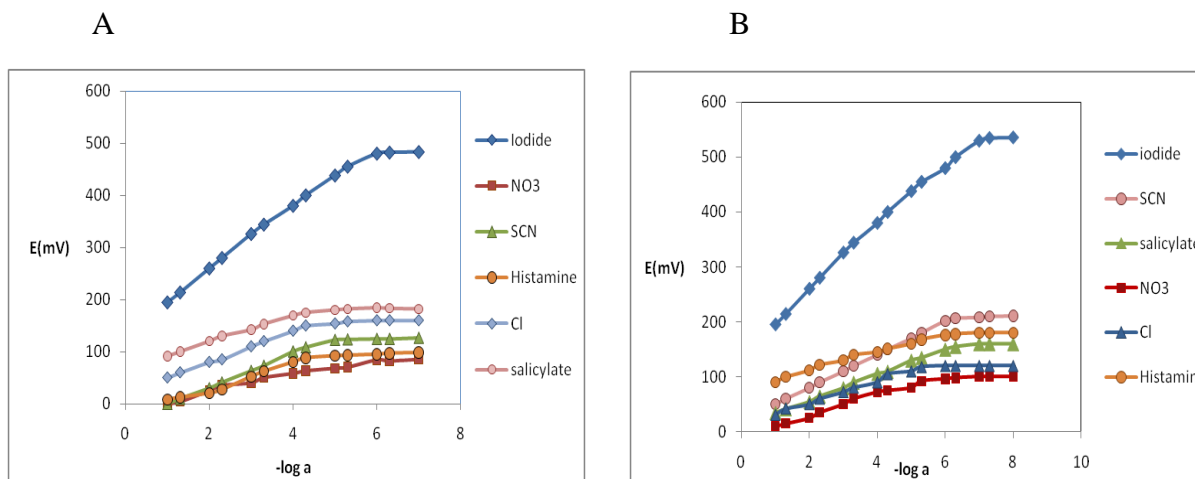


Figure 4. Potential response of various ion-selective carbon paste electrodes based on (A): $[\text{ZnL}^1\text{Cl}_2]$ and (B): $[\text{HgL}^2\text{Br}_2]$.

In order to improve the response properties of proposed electrodes different nanoparticles including Ag, ZnS and ZnO nanoparticle loaded on AC and oxidized MWCNT was added to carbon and their response properties of electrodes based on both ionophores was investigated. Response properties of proposed electrodes based on both ionophores is present in Table 2 a and b. As it can be seen, the presence of nanoparticles improve the linear range and detection limit of electrodes based on both ionophores. Using oxidized MWCNT in the composition of the carbon paste electrodes based on both ionophores, 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 was found that for both proposed electrodes, the respective ones in the presence of different oxidized MWCNT, significantly improve. Due to significant dependency of response properties to carbon paste composition the influence of carbon paste ingredients for both ionophores was investigated. Different carbon paste compositions (Table 3 and 4) were prepared and it was seen that among modified and unmodified CPEs, the best unmodified CPE with optimized composition (in the absence of complexes and nanoparticles No. 25 in Table 3 for $[ZnL^1Cl_2]$ and No. 23 in table 4 for $[HgL^2Br_2]$) shows a near Nernstian slope about 34.6 and 29.7 mV decade⁻¹.

Table 2-a. Influence of kind of nanoparticles on response of iodide selective electrode based on $[ZnL^1Cl_2]$.

N	Carrier (mg)		Kind of Nanoparticle	Amount of nanoparticle (mg)	Nujol (mg)	L. R. (μM-M)	D.L (μM)	Slope (mV/decade)
1	27	21.2	10	50	10-0.1	7.5	49.3
2			Ag			10-0.1	8.5	47.2
3			ZnS			5.0-.01	4.0	45.3
4			ZnO			5.0-0.1	3.5	48.1
5			MWCNT			1-0.1	0.9	53.1

Table 2-b. Influence of kind of nanoparticles on response of iodide selective electrode based on $[HgL^2Br_2]$

N	Carrier (mg)	MTOA CL (mg)	Kind of Nanoparticle	Amount of nanoparticle (mg)	Nujol (mg)	L. R. (μM-M)	D.L (μM)	Slope (mV/decade)
1	20	10	10	50	1.0-0.1	0.7	55.8
2			Ag			1.0-0.1	0.8	44.3
3			ZnS			0.5-.01	0.4	45.1
4			ZnO			0.5-0.1	0.4	43.2
5			MWCNT			0.1-0.1	0.08	54.5

It is well known that the sensitivity and selectivity of ISEs depend significantly on the nature of ionophore and carbon paste composition. Also, some important features of the carbon paste electrode including the nature and the amount of the additive and ionophore and the Nujol/carbon ratio significantly influence on the sensitivity and the selectivity of the carbon paste ISEs and must be optimized. The amount of modifier in the paste usually must have enough active sites in carbon paste for binding analyte ions.

Table 3. Influence of carbon paste composition based on $[\text{ZnL}^1\text{Cl}_2]$ on response of iodide selective electrode.

N	Carbon powder (mg)	Carrier (mg)	MTOAC I (mg)	Nujol (mg)	MWCN T (mg)	L. R. ($\mu\text{M-M}$)	D.L (μM)	Slope (mV/decade)
1	150	5	3.13	50	50-0.1	45	32.07
2	150	10	6.3	5	50-0.1	40	35.93
3	150	15	9.5	50	10-0.1	7.5	40.01
4	150	20	12.6	50	10-0.1	8.0	40.22
5	150	23	14.5	50	10-0.1	7.5	43.84
6	150	25	15.7	50	10-0.1	8.0	44.23
7	150	27	16.9	50	10-0.1	8.0	48.43
8	150	30	18.8	50	10-0.1	7.5	42.41
9	146	27	16.9	50	4	10-0.1	8.0	49.21
10	144	27	16.9	50	6	5.0-0.1	4.0	50.61
11	142	27	16.9	50	8	5.0-0.1	3.5	53.74
12	140	27	16.9	50	10	1.0-0.1	0.8	53.07
13	138	27	16.9	50	12	1.0-0.1	0.75	54.11
14	136	27	16.9	50	14	5.0-0.1	3.5	50.29
15	138	27	4.2	50	12	5.0-0.1	5.0	31.25
16	138	27	8.5	50	12	1.0-0.1	0.75	39.35
17	138	27	12.7	50	12	5.0-0.1	4.5	49.66
18	138	27	16.9	50	12	1.0-0.1	0.8	53.8
19	138	27	21.2	50	12	1.0-0.1	0.7	57.22
20	138	27	25.4	50	12	1.0-0.1	0.7	53.29
21	138	27	21.2	30	12	5.0-0.1	3.5	59.09
22	138	27	21.2	50	12	1.0-0.01	0.88	57.3
23	138	27	21.2	70	12.	10-0.1	8.5	35.6
24	150	27	0	50	5.0-0.1	3.5	29.6
25	150	0	21.2	50	50-0.1	40	34.6
26	150	0	0	50	100-0.1	85	47.50

Different carbon paste compositions by changing the carriers concentration in the different ratio of carbon/Nujol and MTOACI/carrier were prepared. It was observed in Table 3 and 4 that the

working range and sensitivity of the electrode response were improved by increasing the concentration of $[\text{ZnL}^1\text{Cl}_2]$ up to 27 mg and 20 mg of $[\text{HgL}^2\text{Br}_2]$.

As can be seen from Table 3 and 4, the slopes of the proposed electrodes in the absence of MTOACI is lower than the expected Nernstian value while, addition of 21.2 mg MTOACI in electrode based on $[\text{ZnL}^1\text{Cl}_2]$ and 10 mg for electrode based on $[\text{HgL}^2\text{Br}_2]$ will increase the sensitivity of the electrode response considerably. Therefore, the CPEs demonstrates a near Nernstian behavior (No. 22 for electrode based on $[\text{ZnL}^1\text{Cl}_2]$ and NO. 20 for electrode based on $[\text{HgL}^2\text{Br}_2]$).

Table 4. Influence of carbon paste composition based on $[\text{HgL}^2\text{Br}_2]$ on response of iodide selective electrode

N	Carbon powder (mg)	Carrier ^a	MTOACI ^a	Nujol ^a	MWCNT ^a	L. R. ^b	D.L. ^c	Slope ^d
1	150	5	2	50	5.0-0.1	3.8	35.43
2	150	10	4	50	5.0-0.1	4.5	40.38
3	150	15	6	50	1.0-0.1	0.8	44.05
4	150	18	7.2	50	1.0-0.1	0.75	50.24
5	150	20	8	50	1.0-0.1	0.8	53.9
6	150	22	8.8	50	1.0-0.1	0.6	47.18
7	150	25	10	50	1.0-0.1	0.7	43.1
8	146	20	8	50	4	0.5-0.1	0.08	50.84
9	144	20	8	50	6	0.5-0.1	0.075	52.9
10	142	20	8	50	8	0.1-0.1	0.08	54.4
11	140	20	8	50	10	0.1-0.1	0.08	51.35
12	138	20	8	50	12	0.5-0.1	0.5	52.02
13	142	20	2	50	8	0.5-0.1	0.35	32.98
14	142	20	4	50	8	0.1-0.1	0.075	40.78
15	142	20	6	50	8	0.1-0.1	0.06	51.15
16	142	20	8	50	8	0.1-0.1	0.075	54.5
17	142	20	10	50	8	0.1-0.1	0.08	59.7
18	142	20	12	50	8	0.50.1	0.3	54.8
19	142	20	10	30	8	0.5-0.1	0.4	62.05
20	142	20	10	50	8	0.1-0.1	0.075	59.8
21	142	20	10	70	5.0-0.01	4.5	35.6
22	150	20	0	50	1.0-0.1	0.1	31.5
23	150	0	10	50	50-0.1	50	29.7
24	150	0	0	50	100-0.1	75	47.8

a) mg b) $\mu\text{M-M}$; c) μM ; d) mv per decade concentration

For electrode based on $[\text{ZnL}^1\text{Cl}_2]$ addition of more than 21.2 mg of MTOACl to 25.4 mg the carbon paste decrease the slope from 57.2 to 53.3 mV per decade and for electrode based on $[\text{HgL}^2\text{Br}_2]$ addition of more than 10 mg of MTOACl to 12 mg the membrane causes a decrease in slope from 59.8 to 54.8 mV per decade which may be attributed to the increasing the mole ratio of MTOACl/Carrier and competitive of iodide to carriers for binding iodide ion. The amount of carrier, Nujol and graphite powder on electrode response has been optimized and their value are set as graphite powder/ MTOACl/ Nujol/ carrier/ oxidized MWCNT in the mass (mg) ratio of 150/21.2/50/27/12 for electrode based on $[\text{ZnL}^1\text{Cl}_2]$ and 150/10/50/20/8 for electrode based on $[\text{HgL}^2\text{Br}_2]$ (Table 3 and 4).

The optimized electrode composition and response characteristics of both electrodes are shown in Table 5.

Table 5. Response characteristics of the proposed iodide ion selective electrodes.

Properties	Values/range	
	$[\text{ZnL}^1\text{Cl}_2]$ complex: (0.15g: 12 mg, 50 mg: 27 mg, 21.2 mg)	$[\text{HgL}^2\text{Br}_2]$ complex (0.15g, 8 mg.: 50 mg, 20 mg: 10 mg)
Electrode type	Carbon paste electrode	
pH range	2.5-11.0	
Linear range Γ^- (M)	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$	$1.0 \times 10^{-7} - 1.0 \times 10^{-1}$
Slope (mV/decade)	57.30	59.8
Detection limit (M)	8.8×10^{-7}	0.8×10^{-7}
S.D of slope (mV/decade)	± 1.2	± 0.8
Response time (s)	≈ 20 s	≈ 15 s

3.3. Effect of pH

Generally it is necessary to find the optimum pH range where the CPEs functions without interference from the hydrogen or hydroxide ions. The influence of pH of the sample solution on the potential response of both proposed carbon paste electrode was tested over the range of 2.5-11.0 at two concentration of 1.0×10^{-3} and 1.0×10^{-2} mol L⁻¹ iodide ions (Figure 5). The pH of the solutions was adjusted by the addition of H₂SO₄ or KOH. It is clear from Figure 3 that the useful pH range is 2.5-11.0 as the pH dependence of the electrode response was not significant in this range. However, the potential of the sensor was significantly affected below pH 2.5 and above pH 11.0. In the solution with pH>11.0, the potentiometric response properties of the electrodes slightly deteriorated and the observation can be explained by hydroxide-coordinated central metal interference.

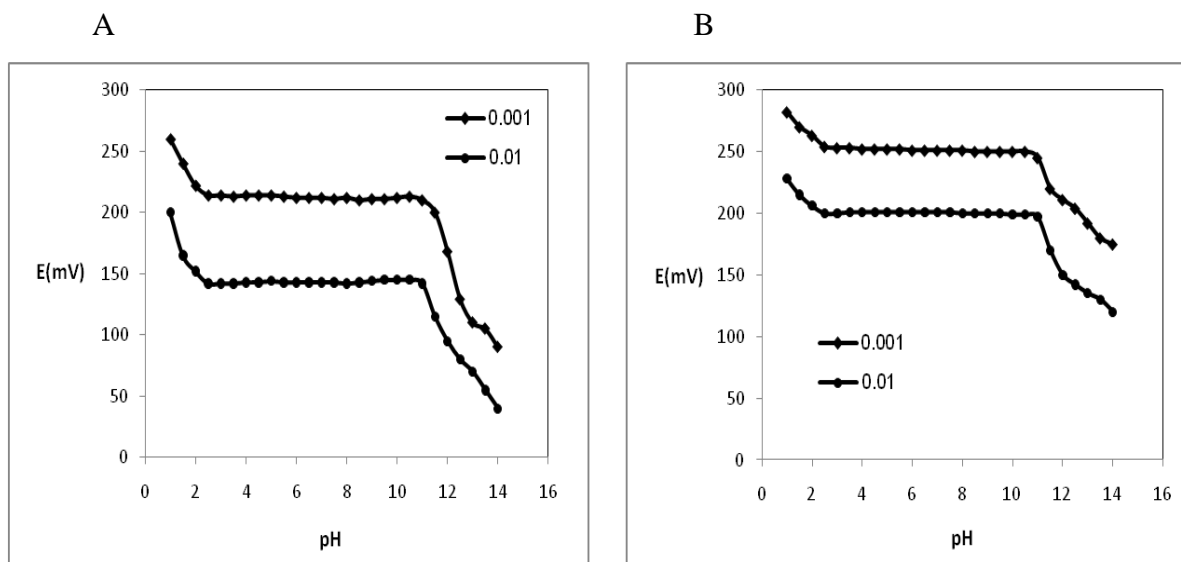


Figure 5. Effect of pH of the test solution of I^- on the potential response of the iodide ion-selective electrode based on (A) $[ZnL^1Cl_2]$ and (B) $[HgL^2Br_2]$.

3.4. Response characteristics and selectivity of the electrodes

For analytical applications the dynamic response time of a sensor is an important factor (time is the required time to reach a cell potential of 90% of the final equilibrium values). The response time was evaluated after successive immersions of proposed electrodes in a series of solutions (with 10-fold concentration difference) [24–30]. The resulting potential–time responses for the mentioned electrode were obtained upon changing the iodide concentration from 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} . Results showed that the potentiometric response time of the electrode are about 20 s for electrode based on $[ZnL^1Cl_2]$ and 15 s for electrode based on $[HgL^2Br_2]$ (Figure 6). The standard deviation of slope for several electrodes (within electrode variation), constructed by using the same carbon paste composition for $[ZnL^1Cl_2]$ and $[HgL^2Br_2]$, were -57.30 ± 1.20 and -59.80 ± 0.80 mV/decade of iodide concentration, respectively.

The potentiometric selectivity coefficients of an electrode as one of the most important characteristics is defined by its relative response for the primary ion over other ions present in the solution [31]. In this work, the potentiometric selectivity coefficients were determined graphically by the fixed interference method and separation solution methods based on the Nikolski-Eizenman equation [32,33]. In FIM from the plots of E versus $\log a_A$ and using the expression $\ln K_{A,B}^{pot} = \ln (a_A/a_B^{1/Z_B})$, the selectivity coefficients were determined. The value of a_A that is estimated by determining the iodide activity for which the linear and rising portion of the graph deviates by $2.303 RT \log Z/F$ mV from the curved part and the value of a_B^{1/Z_B} (a_B and Z_B are the activity and charge of interference ion, respectively) were used to calculate the potentiometric selectivity coefficients. In this work, the concentration of the silver ion is varied while that of the interfering ions is 1×10^{-4} mol L^{-1} . The resulting selectivity coefficients values thus obtained for the proposed iodide sensors are given in Table 6.

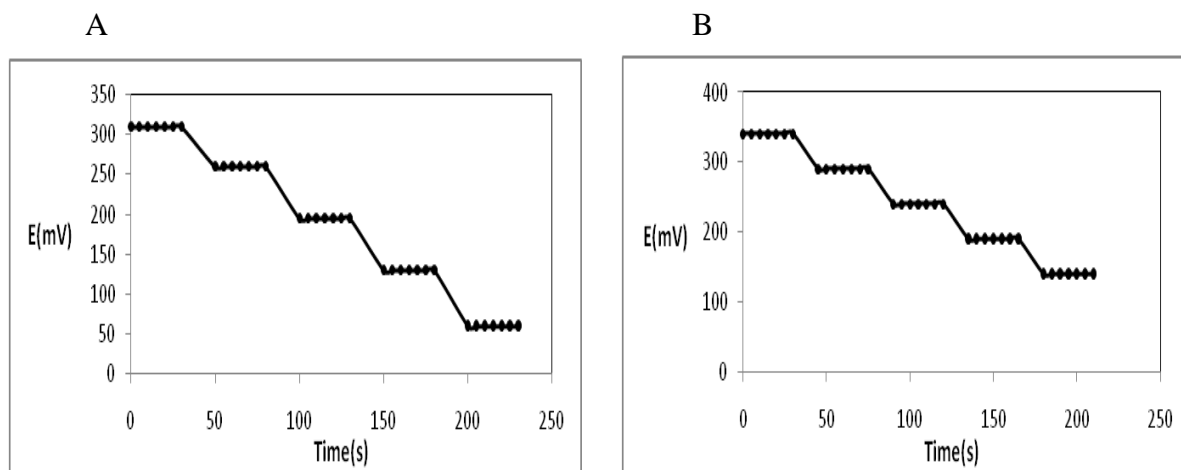


Figure 6. Response time of proposed of the iodide selective electrodes based on MWCNT-IPC in the presence of different concentrations ($1.0 \times 10^{-5} - 1.0 \times 10^{-1}$) of iodide ions based on: (A) $[ZnL^1Cl_2]$ and (B) $[HgL^2Br_2]$.

Table 6. Selectivity coefficients of the proposed carbon paste iodide selective electrodes

Ion	-LogK			
	$[ZnL^1Cl_2]$ complex		$[HgL^2Br_2]$ complex	
	FIM	SSM	FIM	SSM
Thiocyanate	2.53	2.3	2.8	2.44
Salicylate	2.9	3.1	3.5	3.6
Phosphate	3.1	3.04	3.7	3.8
Oxalate	3.6	3.42	3.88	3.28
Bromide	2.96	3.2	3.6	3.9
Chloride	3.44	3.5	3.96	3.8
Carbonate	3.2	3.5	4.0	3.8
Nitrate	3.6	3.85	4.01	3.92
Nitrite	3.44	3.6	3.8	3.83
Sulfate	3.2	3.34	3.74	3.8

3.5. Analytical applications

The resulting electrodes were applied to the determination of iodide in a drug preparation (Meglumine Compound Injection, from Darou Pakhsh Pharmaceutical Co., Iran, is an iodide-containing drug used for protection from light and secondary X-rays). The sample was prepared by refluxing 1.0 mL of the drug preparation in concentrated sodium hydroxide solution in the presence of zinc powder for 30 min [13]. After cooling, the reaction mixture was filtered and washed with water three times. The filtrate was acidified with H_2SO_4 and diluted to 1 L with water. The iodide content of the resulting solution was determined potentiometrically by the standard addition method. The results obtained by the electrode method are in agreement with those obtained by titration with standard $AgNO_3$ solution as given in Table 7.

Table 7. Application of the Electrodes Based on $[ZnL^1Cl_2]$ and $[HgL^2Br_2]$ for Determination of Iodide Added to well and river Water and a Drug Preparation samples

Sample	Iodide added (M)	Iodide found (M) $[ZnL^1Cl_2]$ complex	Iodide found (M) $[HgL^2Br_2]$ complex
1.(Well water)	-	ND	ND
"	3.0×10^{-4}	$(3.3 \pm 0.14) \times 10^{-4}$	$(3.1 \pm 0.10) \times 10^{-4}$
2. (River water)	-	ND	ND
"	1.8×10^{-4}	$(2.5 \pm 0.13) \times 10^{-4}$	$(2.3 \pm 0.07) \times 10^{-4}$
2. (Meglumine Compound)	$(2.78 \pm 0.12) \times 10^{-3}$ *	$(2.95 \pm 0.16) \times 10^{-3}$	$(2.9 \pm 0.11) \times 10^{-3}$

The electrodes were also applied for the determination of iodide added to water samples and as indicator electrodes for potentiometric titration of silver and iodide ions. The direct potentiometric measurement was carried out using the standard addition technique. The results for the determination of iodide ion at several concentrations are in agreement with the known iodide content as given in Table 7. The electrodes were also found useful for the potentiometric titration of Ag^+ with iodide and vice versa. Typical titration plots are shown in Figure 7.

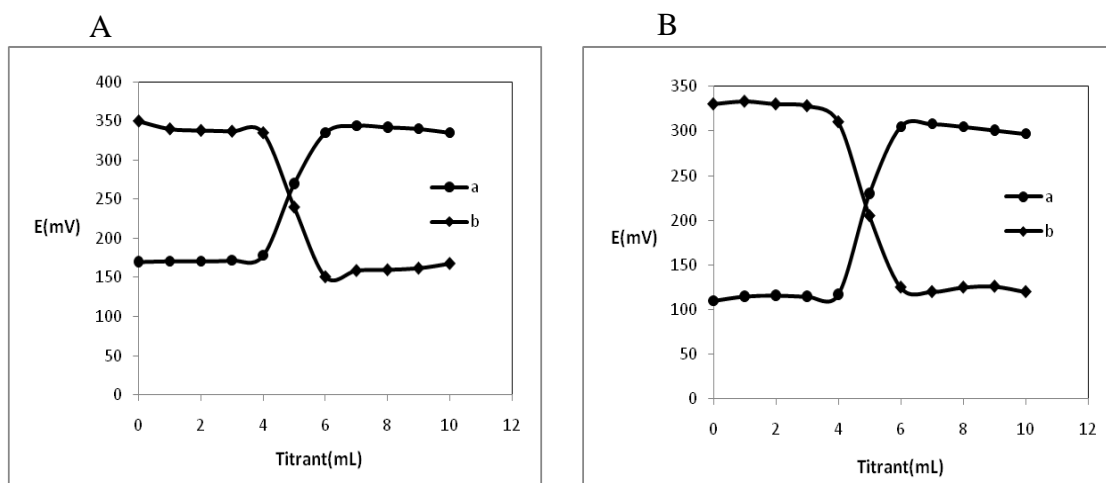


Figure 7. Application of the electrode based on (A) $[ZnL^1Cl_2]$ and (B) $[HgL^2Br_2]$ for potentiometric titration of (a) 50 mL of 1×10^{-2} M I^- with 0.1 M mL of Ag^+ and (b) 50 mL mL of 1×10^{-2} M Ag^+ with 0.1 M mL of I^-

4. CONCLUSIONS

New carbon paste iodide-selective electrodes have been prepared using these new ionophores complexes. Influence of various nanoparticles on the electrode responses of proposed electrode was investigated and best responses was obtained via addition of oxidized MWCNT. The electrodes have been shown to have good operating characteristics (Nernstian response; reasonable detection limit;

relatively high selectivity, especially with respect to the highly lipophilic anions; wide dynamic range; fast response; applicability over a wide pH range). These characteristics and the typical applications presented in this paper, make the electrode suitable for measuring the iodide content in a wide variety of samples, without a significant interaction from concomitant anionic species. The results show coordination of iodide to the central atom of carriers played an important role in the response characteristics and selectivity of the electrodes. The proposed sensors exhibit wide working concentration range, shorter response time, greater tolerance to pH variations and high selectivity towards the target ions over other anions.

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