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ORIGINAL PAPER

Silica gel/gold nanoparticles/$(NS)_2$ ligand nanoporous platform-modified ionic liquid carbon paste electrode for potentiometric ultratrace assessment of Ag(I)

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Abstract A novel ionic liquid carbon paste electrode has been developed using sol–gel/Au nanoparticle (SGAN) involving $(NS)_2$ compound of N,N′-di-(cyclopentadienecarbaldehyde)-1,2-di(o-aminophenylthio) ethane (CCAE) as an appropriate neutral ion-carrier for ultrahigh-sensitive potentiometric determination of Ag(I). Colloidal gold nanoparticles (AuNPs) also well dispersed self-assembly into the 3-(mercaptopropyl)-trimethoxysilane (MPTS)-derived sol–gel network through Au–S covalent bond engendering continuous and super-conductive nanoporous three-dimensional array. The room-temperature ionic liquid, 1-n-butyl-3-methylimidazolium tetrafluoroborate ($BMIM.PF_6$), was applied as a super-conductive pasting agent (binder). The SGAN/CCAE/IL-CPE exhibited a significantly enhanced sensitivity and preferential selectivity toward Ag(I) over a wide concentration range of 2.4×10^{-9} to 2.2×10^{-2} mol L^{-1} ($R^2 = 0.9996$) with a lower limit of detection of 7.9×10^{-10} M and a Nernstian slope of 58.5 (±0.3) mV $decade^{-1}$. The electrode has a short response time of ~5 s and long-time durability of about 2 months without any considerable divergence in potentials. Moreover, the potentiometric examinations could be carried out within the wide pH range of 3.5–9.5. Eventually, the practical utility of the proposed Ag(I)-sensor was evaluated by volumetric titration of $AgNO_3$ solution by sodium chloride and recovery of silver content in some real samples using flame atomic absorption spectroscopy as a confident reference.

Keywords Gold nanoparticles · Silica sol–gel · Carbon paste electrode · Room-temperature ionic liquid · Silver ion · Potentiometric sensor

Introduction

Silver is utilized for a wide range of applications, such as in medicine, electronics, optics, photography, and the production of jewelry, coins, batteries, photovoltaic cells, bearings, and catalysts. Because of their antibacterial properties, silver salts and silver nanoparticles are used for the disinfection of drinking water and the preparation of topical gels, specialty bandages, implantable prostheses, and catheters. As a result, about 2500 tons of silver are released into the environment annually, and approximately 80 tons end up in surface waters (Ratte 1999; Mashhadizadeh et al. 2013). Silver is not as toxic to humans as many other heavy metals, but the U.S. Environmental Protection Agency reported that a concentration higher than 1.6 nM is toxic to fish and microorganisms (Lai et al. 2010) and the maximum contaminant level for total silver in drinking water was set to 0.9 µM, according to the Environmental Protection Agency in Washington DC of USA (1991).

While other methods for the determination of silver are available, atomic absorption spectrometry and the use of inductively coupled plasma in combination with atomic emission or mass spectrometry are recommended methods (Kilinc et al. 2009; Hu et al. 2002; Karadjova et al. 2000; Krachler et al. 2002; Guo and Khoo 1999; Anderson et al. 1996).

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These and many other techniques often require quite extensive and time-consuming sample pretreatment, including preconcentration and matrix separation. In comparison, ion-selective electrodes (ISEs) require little sample preparation and manipulation while still permitting very wide ranges of linear response, low limits of detection, high selectivities, and the possibility to distinguish between the free metal ion and its complexes (Ramezani et al. 2014). Carbon paste electrodes (CPEs) are one of the most interesting ISEs. These kinds of electrodes are inexpensive and possess many advantages such as low background current, easy fabrication and rapid renewal, broad potential window (−1.40 to +1.30 V), chemical modifiability and suitability for various sensing and detecting applications (Ramezani et al. 2015; Mashhadizadeh et al. 2012, 2015). The main reason of modification of CPEs is to improve sensitivity, selectivity, durability, and stability of response of the electrochemical measurements by preconcentrating the target analyte from a dilute solution on the electrode surface (Hu et al. 2016). The operation mechanism of such CMCPEs depends drastically on the properties of the modifier materials used to enhance durability, selectivity, and sensitivity toward the target species (Mashhadizadeh et al. 2012, 2015).

In order to prepare a CPE with high electrical conductivity and therefore high sensitivity and low response time, room-temperature ionic liquids (RTILs) are the best replacement to the conventional non-conductive reagents, such as mineral oil or paraffin oil (PO) (Lin et al. 2009). RTILs are gaining wide recognition as novel solvents in chemistry. Their application in analytical chemistry is merited because they have some unique properties, such as high electrical conductivity, negligible vapor pressure, good thermal and chemical stability, and tunable viscosity (Liu et al. 2005; Anderson et al. 2006). Moreover, the negligible vapor pressure and robust thermal and chemical stability of ILs warrant IL-based electrochemical sensors operating in terms of long-term stability. The liquid status of ILs at room temperature and also its high electrical conductivity provide fast diffusion of analytes, so the IL-modified sensor exhibits a rapid response time (Liu et al. 2005; Anderson et al. 2006).

Based on the chemical recognition principle, several types of carriers of suitable size and specific metal–carrier interaction have been successfully utilized for the construction of Ag(I)-ISEs. In recent years, several ISEs modified with some synthetic compounds containing nitrogen and sulfur atoms as coordinative sites for quantitative determination of silver(I) ion based on reasonable interaction between nitrogen and sulfur atoms have been reported (Mashhadizadeh et al. 2013; Mohadesi and Taher 2007; Abu-Shawish et al. 2013; Zhang et al. 2012; Javanbakht et al. 2009). The silver ion recognition with most of these carriers relies on the hard–soft acid base (HSAB) concept of Pearson (Pearson 1968).

It should be pointed out that, among the various modifying additives of electrochemical sensors and biosensors, nanomaterials including nanotubes, nanowires, nanoparticles, and nanospheres have attracted particular interest owing to their unparalleled catalyzing, stabilizing, and reinforcing effects toward modified sensors (Mashhadizadeh et al. 2010; Singh et al. 2013). Owing to their small dimensional size, good conductivity, excellent biocompatibility, and catalytic activity, gold nanoparticles (AuNPs) have potential applications in the construction of electrochemical sensors and biosensors where it functions as “electronic wire” efficiently channeling electrons between the electrode and the electroactive species promoting better electron transfer through electrode/electrolyte interface (Mashhadizadeh et al. 2010, 2011; Singh et al. 2013). As is well known, among the various metal nanoparticles, AuNPs and partially AgNPs have relatively profound interest to bind covalently to the –CN, $-NH_2$, and specially –SH functional groups (Jia et al. 2002). Therefore, encapsulation of AuNPs in thiol (–SH) functionalized sol–gel network via S–Au covalent linkage paved the way for the construction of new-generation electrochemical sensors and catalytic systems. This technology will combine the benefits of high electrical conductivity, high durability and robustness, self-assembly, nanoparticles, and increased surface area of three-dimensional electrodes (Jia et al. 2002; Maduraiveeran and Ramaraj 2007).

This research article focuses on the application of RTIL compound of BMIM.PF_6 as an appropriate pasting agent (Fig. 1) and AuNPs encapsulated within sol–gel matrix as to facilitate assembly of AuNPs on CPE surface. The

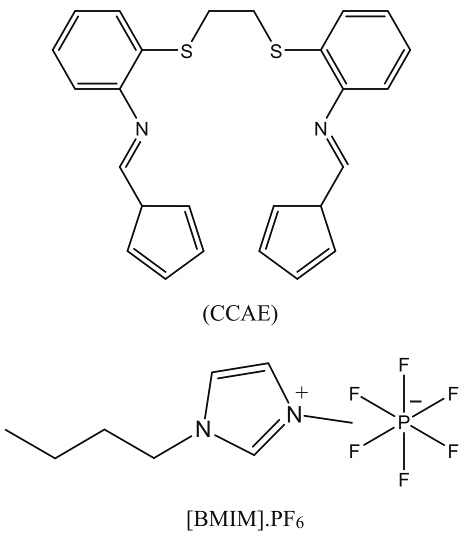


Fig. 1 Chemical structure of the CCAE and BMIM.PF_6 used in the Ag(I)-CPE composition

modified electrode AuNP–sol–gel (SGAN) designed was used to construct potentiometric sensor for Ag(I) quantity estimation using CCAE $(NS)_2$ ligand as a neutral carrier (Fig. 1). Effects of paste ingredients and their amounts, pH of the test solution, and interfering species on the potentiometric response of the SGAN/CCAE/IL-based CPE were also scrutinized in detail.

Materials and methods

Reagents and chemicals

All reagents for synthesis were commercially available and used as-received, and aqueous solutions were prepared with double-distilled water. 1,2-Di-(o-aminophenylthio)ethane (DAPTE) was prepared using the reported procedure (Ramezani et al. 2014). Carbon graphite powder, paraffin oil, and room-temperature ionic liquid were purchased from the Fluka (USA). Hydrogen tetracholoroaurate ($HAuCl_4 \cdot 3H_2O$), trisodium citrate, and 3-(mercaptopropyl) trimethoxysilane (MPTS) were supplied from Merck (Germany). The silver(I) nitrate, and nitrate salts of other metals (all from Merck) were of the highest purity available and used without any further purification to prepare all of the metallic ions stock solutions. Stock solution of 0.1 M $AgNO_3$ was prepared with double-distilled water and stored in the dark place. Buffer solutions were prepared from HNO_3, H_2SO_4, NaOH and its salts for pH range of 1.0–12.0 adjusted by pH/mV meter in order to avoid some personally and random errors that may occur during the process. All other chemicals used were of the analytical reagent grade (from Merck, Aldrich or Fluka). Prior to any experiments, all glassware used in all the experiments were washed with freshly prepared aqua regia (HNO_3/HCl 1:3 v/v) and rinsed thoroughly in tap water first and then in double-distilled water.

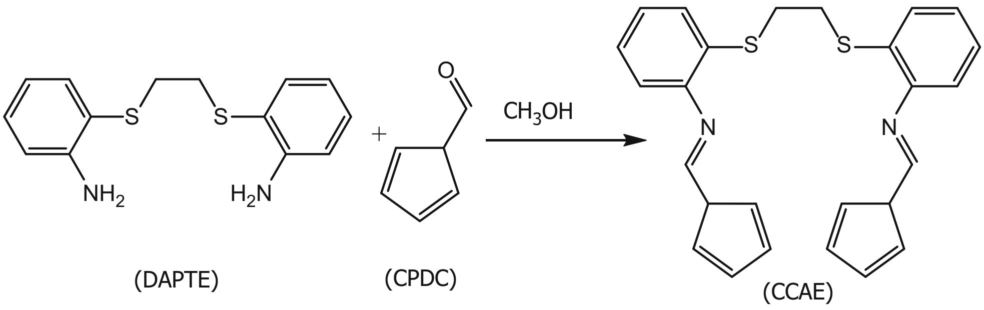
Apparatus

All potentiometric measurements were fulfilled using a pH/mV meter (Metrohm-827, Switzerland) using proposed MCPE as indicator electrode in conjunction with a double-junction Ag/AgCl (Azar electrode, Iran) reference electrode. UV–Vis absorption spectra were recorded with a (Perkin-Elmer model Lambda 25, USA) spectrophotometer. Some solutions were homogenized by ultrasonic homogenizer (Bandelin UW 3200, Germany) whenever they were required. Melting points were determined by a digital melting point apparatus (Barnstead Electrothermal, 9200) and are uncorrected. IR spectra were recorded on a Fourier transform infrared spectrometer (Perkin-Elmer RX1, USA). The ^{1}HNMR and ^{13}CNMR spectra were obtained using Bruker Avance DPX 300-MHz apparatus. Mass spectra were obtained by the Fisons Trio 1000 (70 eV). Elemental analysis was performed by a CHN-O-Rapid elemental analyzer (Perkin-Elmer 2400 series II, USA).

Preparations

Synthesis of the ionophore

The (CCAE) $(NS)_2$ Schiff base ligand was prepared according to the reaction presented in Scheme 1 (Morshedi et al. 2009). Succinctly, 0.228 g (2.4 mmol) of cyclopenta-2, 4-diene-1-carbaldehyde (CPDC) was added dropwise to the 20 ml of ethanolic solution of 1, 2-bis-(aminophenylthio)ethane (APTE) (0.276 g, 1 mmol) under continuous stirring. The obtained mixture was then stirred for about 30 min to give a pale yellow product of (CCAE) ligand, the formed sediment was filtered off and washed with excess EtOH, the resulting product was dried in oven, and then the pure product was isolated very well with surplus ethanol solutions. Yield: 0.298 g (70 %). IR (KBr



Scheme 1 Synthesis pathway of the ionophore (CCAE) used in the present study

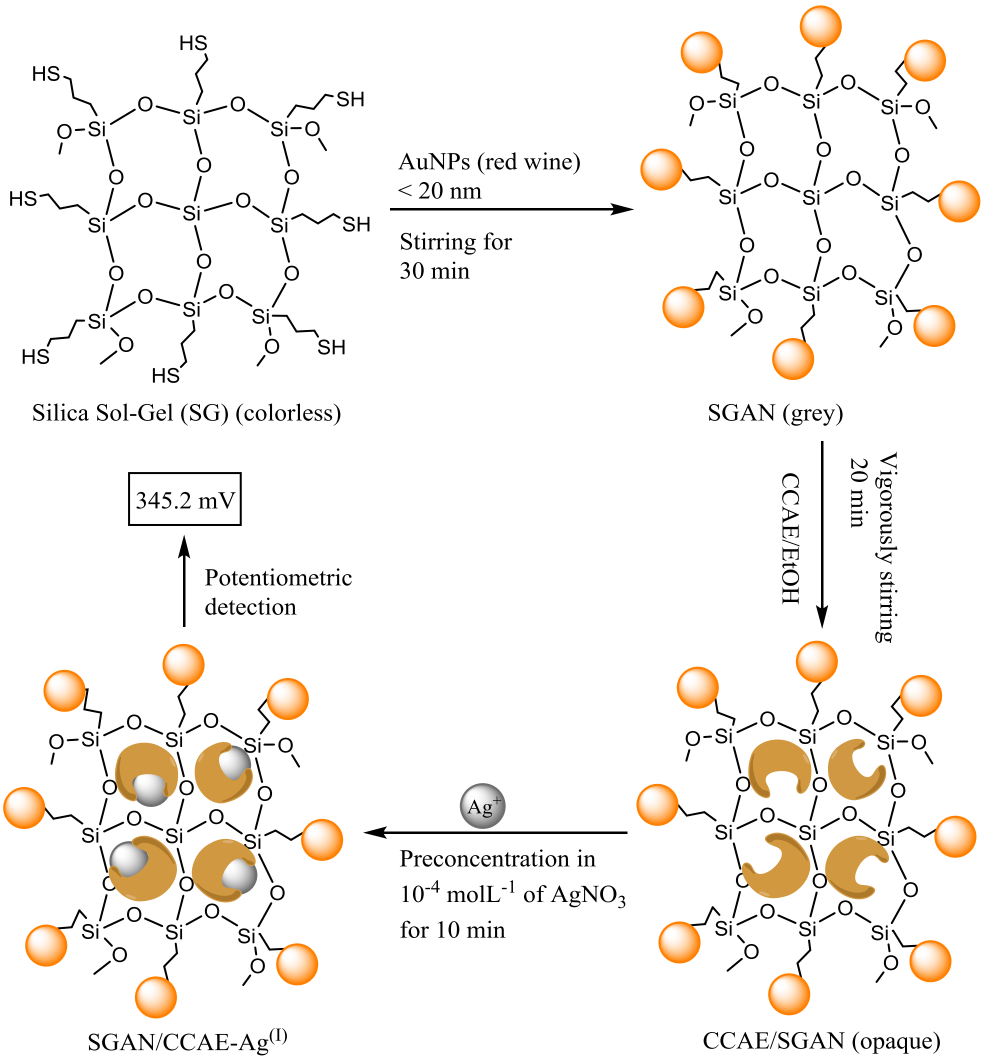
pellet, υ/cm^{-1}): C=N 1650 s, 1512 m, 1575 m. ^{1}HNMR (DMSO-d$_6$, 300 MHz): $\delta = 3.42$ (s, 4H), 7.06 (d, 2H), 7.10–7.31 (m, 4H), 6.79 (t, 2H), 7.37 (d, 2H), 6.04 (d, 2H), 6.50 (d, 2H), 8.50 (s, 2H) ppm. ^{13}CNMR (DMSO-d$_6$, 300 MHz): $\delta = 36.8$, 130.5, 127.4, 137.6, 117.0, 151.4, 124.9, 163.7, 37.0, 133.6, 132.8, ppm. Anal. Calc. for $C_{26}H_{22}N_2S_2$: C, 73.2; H, 5.1; N, 6.5. Found: C, 73.0; H, 5.0; N, 6.3 %.

Preparation of silica gel nanoporous matrix

The MPTS-derived thiol-functionalized sol–gel (SG) silica network was provided according to the Jena et al. (2006, 2008) reports. Briefly, the tricomponent mixture of MPTS/MeOH/H_2O was provided with the 1:3:3 molar ration in the form of 0.1 M HCl in a small beaker (5 ml). The as-prepared sol mixture was then stirred incessantly for about 30 min at the ambient conditions until a clear and homogeneous solution resulted and subsequently left at room temperature for about 30 min to form gel nanoporous network. The resulting solution of SG was characterized by FT-IR (Bharathi et al. 2001). FT-IR spectra of the as-prepared SG solution (Supporting Information) have shown the presence of strong bands in the 1000–1100 cm^{-1} region characteristic of Si–O–Si stretching modes and a weak band around 920 cm^{-1} corresponding to Si–OH groups. Also, a broad band in the region of 3000–3500 cm^{-1} comes from hydrogen bonds between silanol group (Si–OH) and H_2O molecules. These observations confirm the existence of an extensive silicate network in the bulk of the solution.

Preparation of AuNPs and SGAN

Colloidal gold nanoparticles were firstly prepared and then densely dispersed into the sol–gel network (SGAN) closely



Scheme 2 Figurative representation of CCAE/SGAN sensing platform preparation pathway

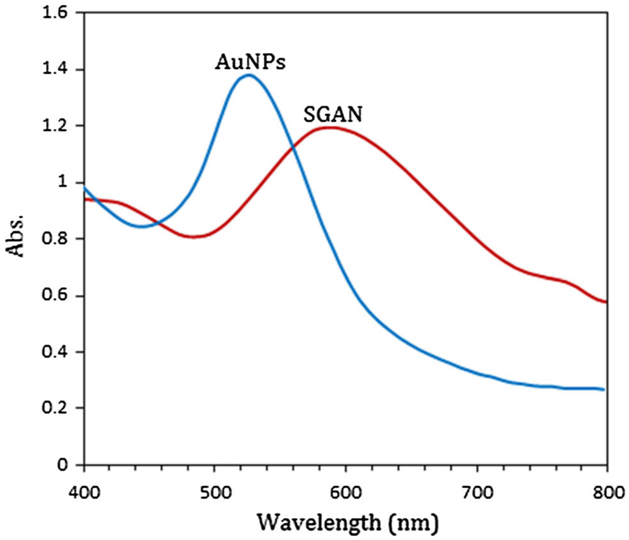


Fig. 2 UV–Vis absorption spectra of AuNPs ($\lambda_{max} = 527.1$ nm) and SGAN ($\lambda_{max} = 590.6$ nm) in ethanol solution

as discussed previously (Mashhadizadeh et al. 2010, 2012, 2013). Preparation of AuNPs/sol–gel process was concisely depicted in Scheme 2. The UV–Vis spectrum shows a peak at 527 nm which is indicative of the formation of AuNPs in the colloidal solution (Ramezani et al. 2015; Mashhadizadeh et al. 2012). Also the UV–Vis absorption spectrum of SGAN shows a wide peak at the maximum wavelength of about 590.6 nm implying on the dispersion and self-assembling of AuNP in MPTS sol–gel texture (Fig. 2).

Preparation of unmodified and modified CPE

Bare CPE was fabricated by hand-mixing graphite powder (GP) with ionic liquid (IL) in the weight percentage ratio of 66:34 with a mortar and pestle. The modified carbon paste electrodes were prepared in a similar way, except that the graphite powder was mixed thoroughly with a certain amount of ligand CCAE in a mortar and pestle, and then, to enhance the uniformity of the mixture, it was dissolved in surplus acetone and sonicated for 5 min. The produced mixture was finally left at room temperature to evaporate the used solvent completely. Eventually, the CCAE-modified paste was mixed thoroughly with an appropriate amount of SGAN besides IL for about 5 min to get different composition (Scheme 2). Both unmodified and modified pastes were packed into a polyethylene tube (2.5 mm id), the tip of which had been cut off. Electrical contact to the paste was established via inserting a copper wire through flank. For each new use, a fresh electrode surface of paste was cut out with a glass rod and the exposed-end polished on a soft paper until the paste surface showed shiny appearance. At the end of this process, there will be four types of electrode including IL-CPE, CCAE/IL-CPE, SG/CCAE/IL-CPE, and SGAN/CCAE/IL-CPE and will be distinguished through some supplemental experiments.

General procedure

All electromotive force (emf) were measured on a Metrohm-827 pH/mV meter, using proposed CMCPE versus a double-junction Ag/AgCl reference electrode by the following cell assembly:

$$\text{Ag}\,||\text{AgCl (sat'd), KCl (3.5 M)}\,||\,\text{Sample solution}\,|\,\text{CPE}$$

The calibration graph was drawn by plotting the potential, E, versus the logarithm of the various copper ion concentration. The performance of the electrodes was investigated by measuring the emfs of silver nitrate solution which was prepared with a concentration range of 2.2×10^{-1} to 4.0×10^{-11} mol L^{-1} by serial dilution. All measurements were implemented at ~25 °C (more details are exactly similar to the previously reported works) (Ramezani et al. 2015; Mashhadizadeh et al. 2012, 2013, 2015).

Results and discussion

Preliminary assessments

Potentiometric study

The separate and synergetic effects of the modifying additives including IL binder, CCAE ionophore, SG, and SGAN matrix on the selectivity, sensitivity, and durability of the CPE were scrutinized through potentiometric preliminary assessments. To do so, some electrodes modified by various above-hinted modifying additives were fabricated and their potentiometric response and sensitivity were surveyed toward Ag(I) and Pb(II) (as a most likely interfering species) and the results are represented in Fig. 3 and Table 1. As can be seen clearly from Fig. 3, among different tested electrodes modified by various additives, potentiometric response of the SGAN/CCAE/IL-CPE seems to be suitably most sensitive and selective toward silver ion. In view of this fact, the IL with high electrical conductivity instead of non-conductive PO gives an acceptable sensitivity and uniformity to the modified paste. Besides, the $(NS)_2$ CCAE ligand possessing N and S atoms as coordinative sites forms exclusively stable complex with Ag(I) ion that largely guarantees the selectivity and sensitivity of the modified electrode. Finally, the SGAN nanoporous matrix with high surface to volume ratio, high

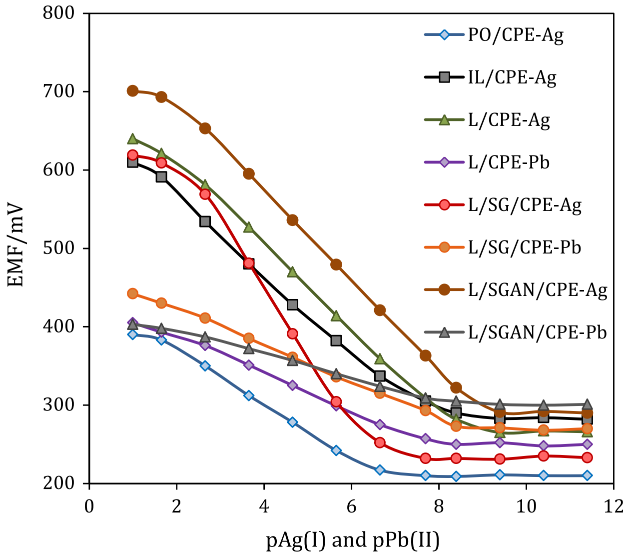


Fig. 3 Potentiometric response of the various modified electrodes toward silver (I) and lead (II)

stability, and conductivity gives such valuable figure of merits on the modified electrode. Consequently, adverting to the data presented in Fig. 4 and Table 1, the potentiometric response of the SGAN/CCAE/IL-modified CPE (no. 5) is completely distinguished from the other sensors in terms of sensitivity, selectivity, response time, and durability.

Spectrophotometric study

Necessarily, the UV–Vis spectrophotometric method was used for more appraisal of the CCAE ligand interaction with different cations in methanol solution. In this way, a spectrophotometric titration of 3 ml of 2.6×10^{-5} mol L^{-1} methanolic solution of the CCAE by 1.7×10^{-3} mol L^{-1} of Ag(I) is shown in Fig. 5a. As can be overtly seen, by adding silver ions to the ligand solution, the absorbance band of the CCAE at $\lambda_{max} = 340.8$ nm assigned to the $\pi \rightarrow \pi^*$ transition (C=N, Schiff base bond) vanishes gently and a new band at 405.0 nm attributed to the ligand to metal charge transfer (LMCT) appears simultaneously indicating formation of CCAE-Ag(I) complex during titration process.

Besides, the mole ratio plot (absorbance versus [Ag(I)]/[CCAE]) at the maximum wavelengths of 340.8 and 405.0 nm was attained using nonlinear least-squares curve fitting (KINFIT) program (inset of Fig. 5b) (Nicely and Dye 1971). As shown, the absorbance–mole ratio plot revealed a level off at a [Ag(I)]/[CCAE] molar ratio of exactly 1.0, emphasizing the formation of the 1:1 (metal/ligand) complex in the methanol solution.

On supplementation of this discussion, a complexometric study of the CCAE ligand with some of the metal ions was also fulfilled and the formation constants of the resulting 1:1 complexes were evaluated by KINFIT program. It was found surprisingly that the CCAE ligand forms the most stable complex with the Ag(I) ion ($\log \beta = 8.56 \pm 0.01$) compared to the other interfering species. The most probable metal ion based on HSAB concept was Pb(II) with the nearest formation constant of ($\log \beta = 4.23 \pm 0.02$). Therefore, all the obtained results were unanimously consistent with the fact that the CCAE compound can be an appropriate Ag(I)-sensitive carrier (ionophore) in the carbon paste bulk of the electrode.

Optimal paste composition

As is well known, sensitivity, selectivity, and other analytical figure of merits of the electrochemical sensors and biosensors depend significantly on the electrode

Table 1 Influence of the modifying additives on the CPE performance

No.	Carbon paste ingredients						Observed results			
	L (mg)	GP (mg)	PO (mg)	RTIL (mg)	SG (µL)	SGAN (µL)	NS[a] (mV decade^{-1})	LR (mol L^{-1})	LOD (mol L^{-1})	DU (day)
1	–	67	33	–	–	–	33.7(±0.3)	5.4×10^{-7} to 2.2×10^{-2}	3.1×10^{-7}	14
2	–	–	33	67	–	–	47.9 (±0.1)	4.6×10^{-8} to 2.2×10^{-2}	1.9×10^{-8}	20
3	6	32	–	62	–	–	53.0 (±0.2)	7.6×10^{-9} to 2.2×10^{-2}	5.5×10^{-9}	35
4	6	32	–	62	100	–	88.5 (±0.2)	6.2×10^{-7} to 2.2×10^{-3}	3.9×10^{-7}	45
5	6	32	–	62	–	100	58.5 (±0.3)	2.4×10^{-9} to 2.2×10^{-2}	7.9×10^{-10}	60

[a] Values in parentheses are SDs based on three replicate analyses; *L* ligand (CCAE) used as ion carrier, *GP* graphite powder, *PO* paraffin oil, *RTIL* room-temperature ionic liquid, *SG* sol–gel, *SGAN* thiol-protected Au nanoparticles in the sol–gel network, *NS* Nernstian slope, *LR* linear range, *LOD* limit of detection, *DU* durability

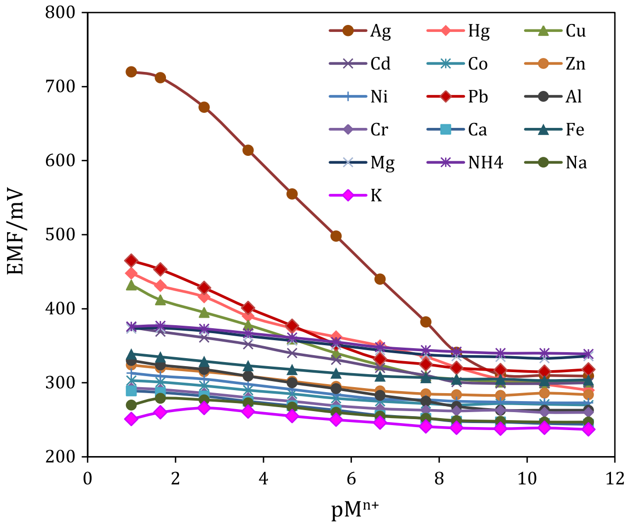


Fig. 4 Potentiometric response of the CCAE/SGAN/IL-CPE toward some multivalent metal ions

composition (Mashhadizadeh et al. 2007, 2010a, b, 2011). Hence, influence of nature and amounts of modifiers on the potentiometric response of the modified electrodes were carefully investigated, and the results are summarized in Table 2. From Table 2, it was obvious that in the absence of IL, the response of the recommended electrode was decreased (nos. 1 and 2). Because, applying IL, with higher dielectric constant than PO as a binder, in the composition of the carbon paste improves the polarity of the sensor and increases the mobility of the Ag(I) ions. If the polarity of the sensor increases, Ag(I) ions as a monovalent species can be extracted from aqueous solution to the sensor easier and the potential response attains to its Nernstian value (Ratte 1999). In addition, replacement of PO by RTIL causes an increase in conductivity of the sensor and reduces the response time and improves the dynamic working range. It should be also pointed out that CCAE ligand can be easily dissolved in the RTIL and therefore the mobility of ionophore in the carbon paste can be adjusted, which will lead to fast exchange kinetics of the metal–ligand complexation–decomplexation at the electrode/electrolyte interface (nos. 6 and 7). Also, the electrodes without CCAE modifier show a poor potentiometric response toward Ag(I) (nos. 1–3 than 4–6), indicating determinative role of CCAE ligand as ionophore. The sensitivity of the electrode response enhanced with increasing ionophore until the value of 6.0 % (w/w) (No. 4–8). Furthermore, using SGAN leads to the expanding of the surface of paste by fabrication of three-dimensional nanostructures, as well as diminishing the Ohmic resistance of the paste, these properties redound to the high linear concentration range and the low limit of detection of the recommended electrode (nos. 3 and 8). Nevertheless, exorbitant addition of the modifying additives including SGAN and CCAE leads to somewhat worsen slopes, linearity, and sensitivity, most probably due to some inhomogeneities and possible saturation of the paste; in addition, the excess amount of ionophore can decrease the conductivity of the carbon paste seriously owing to imbalance of the GP/L ratio (nos. 9–12) (Shamsipur et al. 2003). As seen, the SGAN/CCAE/IL-modified CPE with the GP/IL/CCAE percentage ratio of 62/32/6

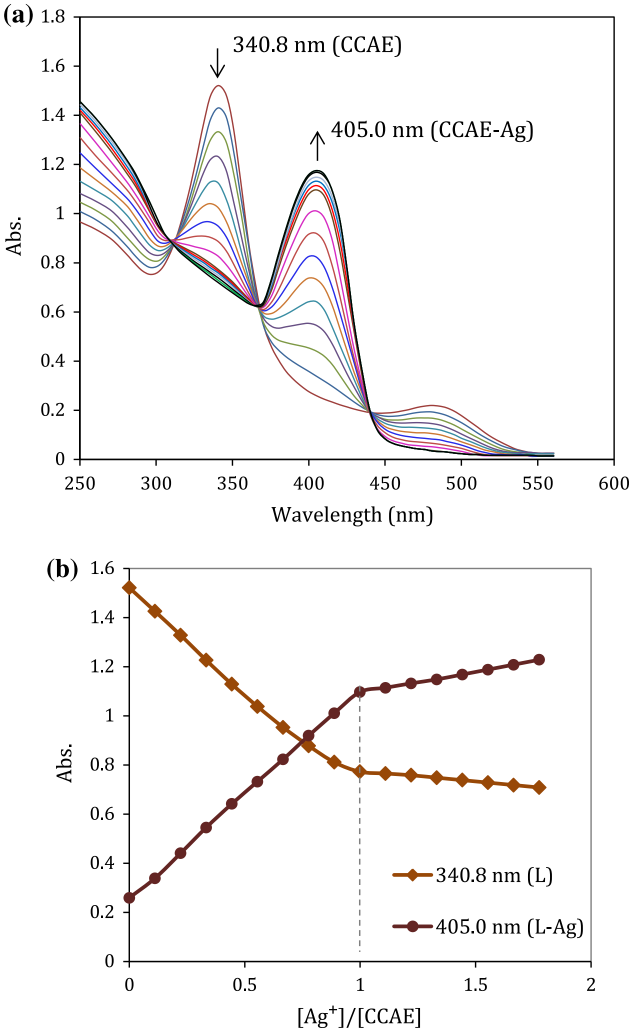


Fig. 5 **a** UV–Vis absorption spectra of the ligand (CCAE) in methanol (2.6 × 10^{-5} mol L^{-1}) in the ascending trend of Ag(I) ion concentration and **b** absorbance versus [Ag(I)]/[CCAE] molar ratio plots in the maximum wavelengths of 340.8 and 405.0 nm

Table 2 Optimization of the CPE composition and its potentiometric characteristics (optimized values were bolded, no. 8)

No.	Carbon paste ingredients				Electrode characteristics				
	L (mg)	GP (mg)	Binder (mg)	SGAN (μL)	NS (mV $decade^{-1}$)	LR (mol L^{-1})	LOD (mol L^{-1})	RT (s)	R^2
1	–	66	34, PO	–	37.4	8.7×10^{-5} to 2.2×10^{-3}	8.2×10^{-5}	15	0.97
2	–	66	34, IL	–	44.0	3.2×10^{-6} to 3.0×10^{-2}	1.5×10^{-6}	9	0.95
3	–	66	34, IL	100	48.1	2.2×10^{-7} to 2.5×10^{-2}	2.0×10^{-7}	7	0.97
4	3	65	32, PO	–	51.0	7.2×10^{-7} to 2.2×10^{-3}	7.0×10^{-7}	–	0.98
5	4	64	32, IL	–	55.0	2.2×10^{-8} to 2.2×10^{-3}	2.0×10^{-8}	–	0.99
6	5.5	62.5	32, PO	–	56.3	8.5×10^{-8} to 2.2×10^{-3}	8.0×10^{-8}	10	0.97
7	5.5	62.5	32, IL	–	58.0	2.0×10^{-8} to 2.2×10^{-2}	2.0×10^{-8}	5	0.99
8	6	62	32, IL	100	58.5 (±0.3)[a]	2.4×10^{-9} to 2.2×10^{-2}	7.9×10^{-10}	5	0.99
9	6.5	62	31.5, IL	100	57.7	2.0×10^{-8} to 2.0×10^{-3}	1.5×10^{-8}	7	0.99
10	7	62	31, IL	100	56.2	2.2×10^{-7} to 2.0×10^{-4}	2.0×10^{-7}	14	0.97
11	8	61	31, IL	100	51.5	2.2×10^{-6} to 2.2×10^{-4}	2.0×10^{-6}	30	0.98
12	6	62	32, IL	150	56.0	2.5×10^{-9} to 2.2×10^{-5}	2.0×10^{-9}	11	0.99

[a] Value in parenthesis is SD based on three replicate analyses

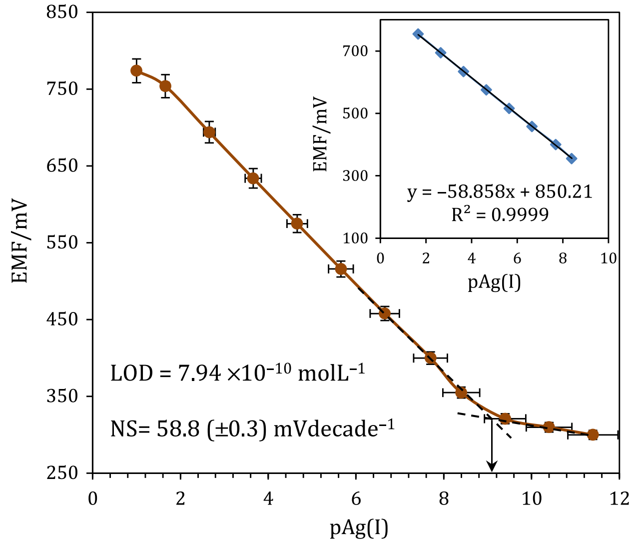


Fig. 6 Calibration curve obtained by the modified silver(I)-CPE at pH ~ 5.0

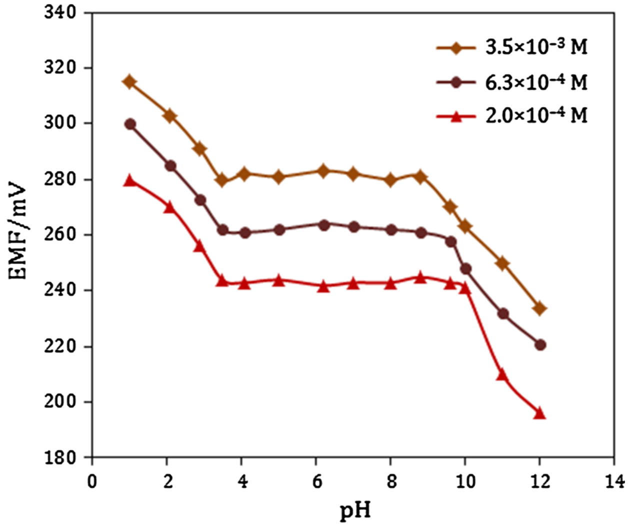


Fig. 7 Influence of pH variations on the cell potential of the SGAN/CCAE/IL-CPE (No. 8) in the different Ag(I) ion concentrations (mol L^{-1})

beside 100 μL SGAN was selected as an optimal ingredient composition (no. 8), and it exhibited a Nernstian slope of 58.5 ± (0.3) mV $decade^{-1}$ in a wide silver ion concentration range of 2.4×10^{-9} to 2.2×10^{-2} mol L^{-1} with a lower limit of detection of 7.9×10^{-10} mol L^{-1} (Fig. 6). These results show that the CCAE is an excellent ionophore for silver(I) ion, and also, addition of SGAN improves satisfactorily the linear range, detection limit, and response time of the modified electrode.

Effect of pH of the test solution

The influence of pH on the electrode performance in the 3.0×10^{-3}, 6.3×10^{-4}, and 2.0×10^{-4} mol L^{-1} of $AgNO_3$ solutions was surveyed over the pH range of 1.0–12.0 (Fig. 7). As can be seen, in the pH range of 3.5 to about 9.0, the observed potential is almost independent of the pH variations. However, the observed potential decrease at the pH values higher than 9.0 is because of the

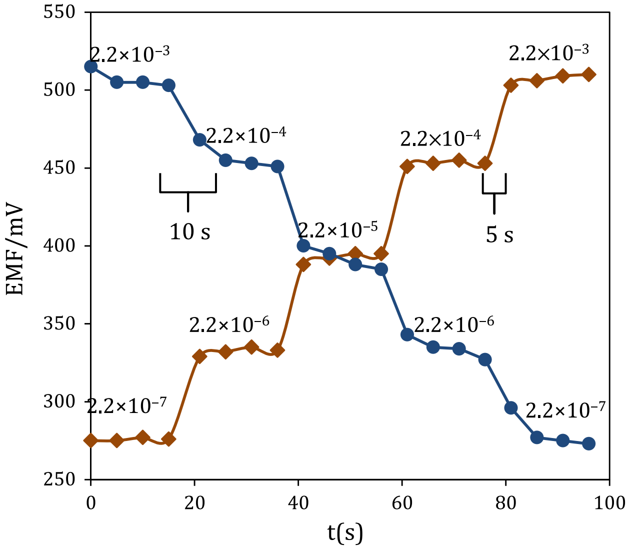


Fig. 8 Dynamic response of the proposed SGAN/CCAE/IL-CPE (No. 8) for step changes of Ag(I) ion concentration from low (2.2×10^{-7} M) to high (2.2×10^{-3} M) and vice versa

formation of AgOH complexes in solution that reduces the density of the Ag^+ ions accessible to the electrode surface and consequently makes a negative error. As can be seen from Fig. 7, this phenomenon depends on the initial concentration of Ag^+ ion based on the related Ksp. On the other hand, at the pH values lower than 3.0, the electrode potential rises. This likely arises from simultaneous response of the electrodes to H_3O^+ and Ag^+ ions; as a result, a positive error appears in the electrode response.

Dynamic response, reversibility, reproducibility, and life time of the proposed CPE

In this study, the practical response time was recorded by changing the Ag^+ ion concentration in solution, over a range of 2.2×10^{-7} to 2.2×10^{-3} mol L^{-1} and vice versa, and the actual potential (mV) versus time(s) was traced (Fig. 8). A very fast response time of 5 s was observed to achieve a 90 % steady potential by tenfold change of concentration of silver nitrate (according to the IUPAC definition) (Buck and Lindner 1994), and the final potential was steady to within ±1 mV for at least 10 min.

To evaluate the reversibility of the electrode, the emf measurements were performed in the sequence high-to-low sample concentrations as shown in Fig. 8. The results illustrated that the response of the electrode was reversible, although the time needed to reach equilibrium values (10 s) was longer than that for low-to-high sample concentrations

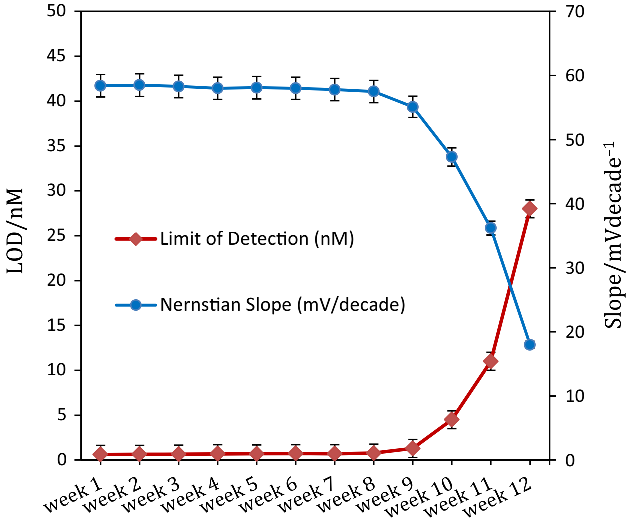


Fig. 9 Durability of the proposed MCPE in terms of limit of detection and Nernstian slope within 12 weeks

(5 s), because residual silver will still be adsorbed on the surface of the CPEs, which will lead to less response time.

The reproducibility was investigated using five similar electrodes provided exactly in the equal way and conditions by dipping the electrodes consecutively with minimum interval into Ag(I) ion solution of 1.0×10^{-3} mol L^{-1}. The experiments exhibited a SD of 3.7 mV ($n = 5$) implying no significant difference between the sensors fabricated in equal conditions, on the other word, indicating acceptable reproducibility of the proposed sensor.

In terms of lifetime, the modified electrode was studied by periodically measuring the calibration graph of Ag^+ over the concentration range of 2.2×10^{-3} to 2.2×10^{-9} mol L^{-1} during 12 weeks (week by week) (Fig. 9). It was found that the electrode works well over the period of about 60 days without showing any significant divergence in the limit of detection, calibration curve slope, and response time. During non-usage, the electrodes should be stored within distilled water at refrigerator. In light of the experiments, we can conclude that the proposed electrode has good stability, reproducibility, reversibility, and fast response time.

Selectivity studies

In view of the fact that, at the impressively low concentration levels, interfering ions strongly compete with primary ions to generate the potentiometric response,

Table 3 Selectivity coefficients of the proposed sensor over silver (I) ion, estimated by FIM and MPM in the presence of some interfering species

Interfering species	$K^{\mathrm{FIM}}_{\mathrm{Ag,M}}$	$k^{\mathrm{MPM}}_{\mathrm{Ag,M}}$
Pb^{2+}	3.98×10^{-3}	1.7×10^{-2}
Cu^{2+}	7.01×10^{-4}	5.0×10^{-3}
Cd^{2+}	1.20×10^{-4}	1.7×10^{-3}
Zn^{2+}	3.16×10^{-4}	5.6×10^{-4}
Hg^{2+}	2.51×10^{-4}	1.4×10^{-4}
Co^{2+}	2.10×10^{-6}	1.8×10^{-5}
Ni^{2+}	2.60×10^{-6}	2.2×10^{-5}
Al^{3+}	1.07×10^{-7}	1.8×10^{-5}
Cr^{3+}	1.35×10^{-7}	2.1×10^{-5}
Ca^{2+}	1.20×10^{-7}	3.5×10^{-5}
Fe^{3+}	8.57×10^{-6}	6.0×10^{-5}
Mg^{2+}	5.01×10^{-6}	8.2×10^{-5}
NH_4^+	1.58×10^{-6}	8.1×10^{-5}
Na^+	3.16×10^{-6}	6.0×10^{-5}
K^+	3.16×10^{-5}	1.5×10^{-5}
Ga^{3+}	1.9×10^{-6}	7.4×10^{-5}
La^{3+}	5.2×10^{-6}	3.2×10^{-6}
Cysteine	–	NR
Urea	–	NR
Glucose	–	NR
Glutamine	–	NR
Ascorbic acid	–	NR

NR no response

detection limits are often determined by equilibrium selectivity (Hu et al. 2016). Therefore, addressing the quality of the proposed electrode selectivity is entirely indispensable. In this work, selectivity coefficients of the electrode toward different cationic species (M^{n+}) were evaluated by using both of the matched potential method (MPM) and the fixed interference method (FIM) adverting to the IUPAC definition (Umezawa et al. 2000). Based on the MPM, the activity of Ag(I) was increased from $a_A = 2.2 \times 10^{-7}$ to $a_A = 4.0 \times 10^{-7}$ mol L^{-1} as reference solution, and the corresponding changes in potential (E, mV) were measured. Afterward, a solution of an interfering ion of concentration a_B, in the range 2.2×10^{-7} to 2.2×10^{-2} mol L^{-1}, was added to a new 2.2×10^{-7} mol L^{-1} (reference solution) until a same potential change (ΔE) was recorded. The selectivity coefficient $k^{\mathrm{MPM}}_{A,B}$ for each species was calculated using the following equation:

$$k^{\mathrm{MPM}}_{A,B} = \frac{a'_A - a_A}{a_B}$$

Furthermore, the selectivity coefficients of interfering species were evaluated by the fixed interference method (FIM). In this method, the CPE and the reference electrode was placed in 25.0 mL of 1.0×10^{-2} mol L^{-1} interfering ion solution. Various volumes of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} of silver nitrate solutions were added by microsyringe. The solution was stirred magnetically throughout, and after each addition the cell potential was recorded. In this manner, the interference ion (M^{n+}) concentration was kept constant without having to transfer the electrodes to new solutions. The pH of whole solutions was constant about 5.0. And then, the fixed interference method selectivity coefficient is given by:

$K^{\mathrm{FIM}}_{A,B} = \frac{a_A(\mathrm{DL})}{(a_B)^{Z_A/Z_B}}$, where a_A (DL) is the primary ion activity in detection limit and a_B is the interference ions activity

Table 4 Analytical performance of the proposed sensor as compared to some of the formerly reported Ag(I)-sensor electrodes

References	NS	LOD (mol L^{-1})	LR (mol L^{-1})	RT ($t_{\%90}$)	pH range	Selectivity (FIM)
Mashhadizadeh et al. (2013)	60.0	2.5×10^{-9}	4.0×10^{-9} to 2.2×10^{-2}	<5	3.0–9.0	Good
Zhang et al. (2012)	58.5	1.0×10^{-5}	2.7×10^{-7} to 1.0×10^{-1}	~15	3.0–9.0	Admissible
Zhao et al. (2012)	60.8	8.0×10^{-8}	8.6×10^{-8} to 1.0×10^{-1}	~20	4.0–9.0	Good
Badr (2005)	60.3	–	8.3×10^{-7} to 9.4×10^{-4}	60	2.0–7.5	Very good
Mashhadizadeh et al. (2006)	58.4	4.2×10^{-7}	9.0×10^{-7} to 3.1×10^{-7}	5	3.5–7.0	Good
Yan et al. (2007)	60.2	2.3×10^{-7}	1.0×10^{-6} to 1.0×10^{-3}	<20	2.0–8.0	Good
Kim et al. (2005)	60.0	1.3×10^{-9}	1.0×10^{-9} to 1.0×10^{-3}	<20	–	Good
Ngeontae et al. (2008)	59.7	5.0×10^{-7}	1.0×10^{-6} to 1.0×10^{-2}	<5	2.0–8.0	Very good
Zhang et al. (2006)	54.8	–	5.1×10^{-6} to 1.0×10^{-1}	<30	4.0–8.0	Good
Goldcamp et al. (2005)	59.5	1.0×10^{-5}	1.0×10^{-5} to 1.0×10^{-2}	30–90	6.2–6.3	Good
Ibrahim (2005)	59.3	$2.5 \times 10^{--7}$	5.0×10^{-7} to 1.0×10^{-3}	3–7	2.0–8.0	Good
Mahajan et al. (2003)	59.0	7.1×10^{-6}	1.0×10^{-5} to 1.0×10^{-1}	20	1.0–6.5	Good
Hassouna et al. (2010)	59.3	2.0×10^{-7}	1.0×10^{-6} to 1.0×10^{-1}	<5	4.0–10	Very good
This study	58.5[a]	7.9×10^{-10}	2.4×10^{-9} to 2.2×10^{-2}	5	3.5–9.5	Very good

[a] SD based on three replicate analyses was ±0.3, *RT* response time (s)

Table 5 Determination of silver contents in some real samples using proposed Ag(I)-CPE

Samples	Ag^+ (mgL^{-1})[a]			Recovery (%)	
	Added (SAM)	Found (MCPE)	Found (AAS)	MCPE	AAS
Urine	0	Nd.	Nd.	–	–
	15.0	14.7(±0.2)	15.1(±0.1)	98.0	100.6
Blood serum	0	Nd	Nd	–	–
	15.0	14.8 (±0.1)	15.2 (±0.1)	98.6	101.3
Burning ointment (SSD)	0	9.1 (±0.3) (mg g^{-1})	9.5 (±0.3) (mg g^{-1})	–	–
	10.0	19.5 (±0.3) (mg g^{-1})	19.7 (±0.1) (mg g^{-1})	104.0	102.0
Radiology film	0	1.6 (±0.1) (mg g^{-1})	1.9 (±0.2) (mg g^{-1})	–	–
	10.0	12.3 (±0.2) (mg g^{-1})	12.8 (±0.2) (mg g^{-1})	107.0	109.0

SAM standard addition method, *Nd* not detected, *SSD* silver sulfadiazine topical

[a] Values in parentheses are SDs based on three replicate analyses

(1.0×10^{-2} mol L^{-1}). All results are summarized in Table 3. As can be seen, the selectivity coefficient of some ions such as Hg(II), Cu (II), and especially Pb(II) as relatively soft Lewis acids is relatively high, which tend to bind to the donor atoms applied in the ionophore structure (N and S) as soft Lewis bases based on HSAB rule of Pearson (Mashhadizadeh et al. 2011). Even more surprising, based on the CCAE-Pb(II) complex formation constant, the selectivity coefficient obtained for Pb(II) was highest among the other interfering species indicating partial interference of Pb(II) against silver ion. In the contrary, some hard Lewis acids of Al^{3+}, Cr^{3+}, and Fe^{3+} have no tendency to bind to the ligand via coordinative interaction that leads to low selectivity coefficients representing slight disturbance of this species. Also, as can be seen, other mono-, di-, and trivalent ions can't disturb the electrode response significantly based on its low selectivity coefficients. The effect of some biological species such as cysteine, uric acid, glucose, glutamine, and ascorbic acid on the response of the proposed electrode has also been studied using MPM. Luckily, the obtained result in Table 3 indicated that the proposed electrode has an acceptable applicability for determination of Ag(I) in biological environments.

Comparative study

The response characteristics and selectivity coefficients for some potentially interfering ions of the proposed CMCPE were compared with those of the best recently reported Ag(I) ion-selective electrodes employing different neutral carriers (Table 4). It is clear that the proposed electrode is well comparable with the most of the existing electrodes with regard to working concentration range, Nernstian slope, response time, pH range, and lower limit of detection. Furthermore, the proposed electrode exhibits better selectivity coefficients over most of metal ions, especially for the common interfering Pb^{2+} ion, which is a valuable preferential property of the proposed electrode. Without exaggeration, in many aspects, performance of the proposed electrode is of utmost priority compared with those reported previously. This preferential superiority undoubtedly owes to the applied modifying additives with unparalleled traits in the carbon paste composition.

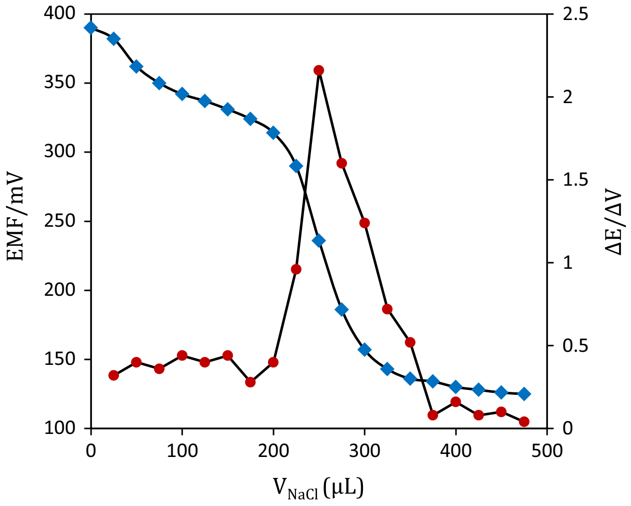


Fig. 10 Potentiometric titration of 25 ml of 10^{-4} M $Ag(NO_3)$ solution by 0.02 M NaCl solution and its first-order derivative, using the proposed SGAN/CCAE/IL-CPE at pH ∼ 5.0

Practical efficiency

Recovery detection of silver(I) in some real samples

To evaluate the practical applicability of the proposed sensor, it was applied as an indicator electrode to potentiometric recovery of Ag(I) quantity in some real samples of silver sulfadiazine (%1 SSD) topical burning ointment (IranNajo Pharmaceutical Hygienic & Cosmetic Co. Tehran, Iran), radiology film, human blood serum and urine samples, using standard addition method (Table 5). Pretreatment of the SSD burning cream and radiology film samples was fulfilled adverting to the literatures (Ibrahim 2005; Abbaspour et al. 2004) for quantitative analysis. Likewise, the human blood serum and urine samples were collected from the clinical laboratory and diluted to 10 and 25 times, respectively, using 0.1 M phosphate buffer solution (PBS) at pH 5.5. To certify the reliability of the potentiometric method, the silver ion concentration in the samples were also quantified by flame atomic absorption spectroscopy (FAAS). The tabulated data suggest that the results attained by potentiometric recovery are completely in consistence with those obtained by FAAS reference method signifying the acceptable performance of the proposed electrode in the practical conditions.

Titration of silver nitrate solution with NaCl

In order to assay the performance of the proposed electrode, it was used as an indicator electrode in conjunction with Ag/AgCl reference electrode to potentiometric titration of 25 ml of 1.0×10^{-4} mol L^{-1} silver nitrate applying 1.0×10^{-2} mol L^{-1} of NaCl solution, at pH 5.5 (Fig. 10). Sharp inflection breaks (~236 mV), showing perfect stoichiometry, are observed in all titration plots.

Conclusion

In conclusion, the non-conductive binder (paraffin oil) in traditional CPE was replaced by an appropriate highly conductive room-temperature ionic liquid ($BMIM.PF_6$), which is substantially viscous, water immiscible, and chemically inert. Coupling of AuNPs with MPTS-derived sol–gel leads to the high-performance SGAN nanoporous matrix. The sensitivity, selectivity, and long-term stability of the proposed electrode were successfully guaranteed by coexistence of SGAN, IL, and $(NS)_2$ CCAE neutral carrier with synergetic reinforcing effects as an appropriate preferential signal booster. The introduced sensor has capability of preferential detection of silver ion with an ultrahigh selectivity over wide range of the most likely mineral and biological interfering species. Eventually, the mentioned sensor has a satisfactory performance in detection and quantification of silver ion contents in some biological, pharmaceutical, and industrial real samples.

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