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# New nano-composite potentiometric sensor composed of graphene nanosheets/thionine/molecular wire for nanomolar detection of silver ion in various real samples



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## ABSTRACT

A novel nanographene carbon composite potentiometric sensor for the determination of trace amounts of silver(I) ion was fabricated. Its sensing layer was prepared with the addition of graphene nanosheets into the matrix consisting of graphite powder, diphenylacetylene “a typically molecular wire (MW) as the conductive binder” and thionine as an efficient ionophore. For investigation of the ion-to-electron transducing ability of graphene nanosheets and molecular wire on the electrode surface, the electrochemical impedance spectroscopy measurements were done and the morphology and properties of the electrode surfaces were characterized by scanning electron microscopy. Under the optimized experimental conditions, the suggested potentiometric silver(I) sensor exhibited an excellent Nernstian slope of 59.70 mV decade<sup>-1</sup> with a rapid response to silver(I) ion within ~6 s. The response was linear in the range  $8.00 \times 10^{-9}$  to  $1.00 \times 10^{-2}$  mol L<sup>-1</sup> and calculated detection limit was  $4.17 \times 10^{-9}$  mol L<sup>-1</sup>. The suggested sensor was successfully applied to the determination of silver in radiological film, environmental and drug samples with satisfactory results.

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## 1. Introduction

Due to strict environmental legislations and to protect natural resources, it is now necessary to develop a new techno-economical process for recycling treatment of industrial effluents [1,2]. The presence of soluble silver species in waste waters is one of the problems shared by many industrial processes. Silver is an important element that is mainly used in electroplating, photographic and imaging industries, graphic arts, dental and medical products, electrical and electronic equipments [3–5]. Also, it is an important ion in some drugs like silver sulfadiazine cream that has been a standard treatment for burns over the past decades and silver deposition has been found in the skin, gingival, cornea, liver, and kidney of patients [6]. In addition, silver is the most ancient metal and finds numerous applications in other fields like jewelry, coins, mirrors, anti-corrosive alloys and in the production of light sensitive devices [7]. It is reported that the concentration of silver in water sources higher than  $1.6 \text{ nmol L}^{-1}$  is toxic for fish and microorganisms. It has also been found that silver is toxic for humans at a concentration higher than  $0.9 \text{ } \mu\text{mol L}^{-1}$  in drinking water [8–10].

With attention to these cases, determination of trace amount of silver ions in environmental and industrial samples has great importance. Various instrumental techniques have been employed for the determination of silver species in different real samples, including atomic absorption spectroscopy (AAS) [11,12], inductively coupled plasma-mass spectrometry (ICP-MS) [13,14], inductively coupled plasma optical emission spectrometry (ICP-OES) [15] and flow injection analysis [16]. However, these techniques are too expensive that are not applicable for in-situ analysis. So, the development of convenient and direct methods for the assay of silver in different real samples is an urgent need. Electrochemical sensors have been widely used to determine various species due to their high sensitivity and desirable selectivity in their responses [17–30]. Among these sensors, potentiometric carbon paste electrodes (CPEs), due to the ease of their construction, easy renewability of the surface, inexpensive techniques, chemical inertness, robustness, stability of response, low ohmic resistance, no need of internal solution and compatibility with various types of modifiers have been widely used as simple tools for detecting various analytes. Further, their modification can improve the surface state of the electrode, which may lead to increase target signals significantly [18–26]. The ion-sensing properties of potentiometric CPEs largely depend on the nature of the employed sensing materials. In recent years, research activities are related to the optimization and rational design of both ionophores

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and matrices targeted to particular applications [21–26]. At the same time, the search for novel matrices became the subject of increasing interest. Graphene has attracted in electrochemical sensing field in recent years [31] due to its unique physicochemical properties such as high specific surface area, chemical stability and electrical conductivity [32], excellent thermal conductivity [33] and strong mechanical strength [34]. Furthermore, in comparison to carbon nanotubes (CNTs), graphene compounds provide the advantages of low production cost and low metallic contamination levels [35]. For the potential application of a certain kind of carbon materials in electrochemical studies, their basic electrochemical behaviors should be first studied to determine several important parameters of sensors [36,37], e.g., electrochemical potential window, heterogeneous electron transfer rate, etc. For these reasons, graphene has begun to be exploited as an alternative choice for electrical sensors, especially during the fabrication of electrochemical sensing devices [38]. Herein, we report application of a novel sensing composite that act as a matrix and ionophore for improving response of the sensor. It is based on graphene nanosheets (GNS), diphenylacetylene (DPA), and thionine and was fabricated for the determination of Ag(I). Thionine (TH) showed good behaviour as an efficient ionophore due to the excellent interactions with silver(I) ion [39]. The results showed that the sensor response was enhanced by replacing paraffin oil with a conductive binder agent (DPA). Also, combination of GNS and Th into the paste could amplify the signal significantly. Moreover, the sensor could also be renewed easily by mechanical polishing whenever needed.

## 2. Experimental

### 2.1. Apparatus

The constructed Ag(I) selective CPE, as the working electrode, and a double junction Ag/AgCl (Azar electrode, Iran) as the reference electrode, were placed in a glass cell and used for the potentiometric measurements. Both the electrodes were connected to a digital milli-voltmeter (HIOKI 3256.50). Electrochemical impedance spectroscopy (EIS) was performed using an Autolab PGSTAT 302 N potentiostat/galvanostat. A Metrohm pH-meter with a combined glass electrode was used for pH controlling, and a Heidolph type of (MR 2000) stirrer was used for stirring the solutions. Scanning electron microscopy (SEM) was performed to survey the electrode surface (SEM-EDX, XL30, Philips Netherland). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was used as its manual. An Agilent 8453 diode array UV–vis spectrophotometer (Agilent, USA) equipped with a 1.0 cm path length quartz cell was used to obtain absorbance spectra and absorbance curves.

### 2.2. Reagents and materials

Natural graphite powder (98%, 50 mesh, and 2–5 mm in lateral size) was obtained from Hyundai Coma Ind. Co., Korea. DPA (Merck), and high-purity paraffin oil (Aldrich) were used for the preparation of carbon pastes. Chloride and nitrate salts of the cations were purchased from Merck and TH was purchased from Sigma-Aldrich. Distilled deionized water was used throughout all experiments.

### 2.3. Preparation of graphene nanosheets

For synthesis of graphene nanosheets first, the graphene oxide (GO) was prepared with a modified Hummer's method [40]. GNS was prepared by the reduction of GO according to the literature [41] as follow: about 100 mg of GO was loaded in a 250 mL round

bottom flask and then 100 mL of water was added, yielding an inhomogeneous yellow–brown dispersion. This dispersion was sonicated until it became clear with no visible particulate matter. Then 1.00 mL, 32.1 mmol, hydrazine hydrate was added and the solution was heated in an oil bath at 100 °C under a water-cooled condenser for 24 h over which the reduced GO gradually precipitated out as a black solid. This product was filtrated and isolated, washed copiously with appropriate volume of water and methanol, and dried on the funnel under a continuous air flow through the solid product cake.

### 2.4. Preparation of working electrodes

The unmodified CPE (Table 1, No. 1) was prepared by hand-mixing of graphite powder with paraffin oil at a ratio of 70:30 (w/w) in an agate mortar and grounded homogeneously for about 25 min. For fabrication of CPEs modified with ionophore, the pastes were prepared by hand-mixing of graphite powder with paraffin oil and different ratio of TH (Table 1, No. 2–4). The GNS modified pastes (Table 1, No. 5, 6) were prepared by hand-mixing of the graphite powder, GNS, TH and paraffin oil with an appropriate ratio in an agate mortar to form a homogeneous paste. Eventually, the (GNS/TH/MW)-CPEs (Table 1, No. 7, 8) were prepared by mixing the appropriate amounts of graphite powder, TH, GNS and DPA together in an agate mortar. The mixture should be heated in an oven at 65 °C for 3 min, which is higher than the melting point of DPA (m.p.=62.5 °C). It was then left to cool to room temperature [42]. By this procedure graphite powder and graphene nanosheets could be totally mixed with DPA to get a stable modified carbon paste.

The resulting mixtures (prepared by the above-mentioned method) were transferred into an insulin syringe with an internal diameter of 2.5 mm and a height of 3 cm as an electrode body. After the homogenization of each mixture, a portion of the prepared paste was carefully packed into the tube tip to avoid possible air gaps, which often enhance the electrode resistance. A copper wire was inserted into the opposite end of the CPE to establish electrical contact. Prior to use, the external surface of the carbon paste was smoothed with a soft paper. A new surface was produced by scraping out the old surface and replacing the new carbon paste.

Finally, the electrodes were conditioned for 24 h by soaking in a  $1.00 \times 10^{-3}$  mol L<sup>-1</sup> silver(I) nitrate solution. The pH of the solution was adjusted at 5.5.

**Table 1**  
Optimization of the carbon paste compositions.

Electrode no	Binder	Ionophore (TH) (%)	Graphite powder (%)	GNS (%)	Slope (mV decade <sup>-1</sup> )
1	30%-Paraffin	0.0	70	0.0	9.87 ± 0.14
2	30%-Paraffin	5.0	65	0.0	36.72 ± 0.13
3	30%-Paraffin	7.0	63	0.0	41.32 ± 0.22
4	30%-Paraffin	.0	62	0.0	40.91 ± 0.31
5	30%-Paraffin	7.0	58	5.0	48.71 ± 0.31
6	30%-Paraffin	7.0	53	10.0	54.89 ± 0.31
7	<b>30%-MW (DPA)</b>	<b>7.0</b>	<b>53</b>	<b>10.0</b>	<b>59.70 ± 0.10</b>
8	30%-MW (DPA)	7.0	48	15.0	59.23 ± 0.11

## 2.5. Preparation of real samples

In order to demonstrate the applicability and reliability of the suggested silver sensitive sensor, for five real samples including mineral water, river water and industrial manufactory waste water samples, silver sulphadiazine burning cream and radiological film were prepared and analyzed by the method.

The river water sample was collected in polyethylene bottle and acidified with nitric acid. This sample was filtered to remove any solid particles before the analysis. Standard Ag(I) solution was spiked into appropriate of the mineral water. The pH of the water samples was adjusted at pH 5.5.

Industrial manufactory waste water sample was taken from Hamedan industrial zone. This water sample was acidified with  $1.0 \text{ mol L}^{-1} \text{ HNO}_3$  and heated for 1 h until its volume reach to one tenth. Then, the pH of the water sample was adjusted at pH 5.5 via dilute NaOH.

For the preparation of cream sample, about 2 g of silver sulphadiazine cream was weighed and dissolved in  $\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{O}_2$  as described in the literature [43].

The radiological film sample was prepared as follows [44]: radiology films (2 g) were dry ashed in a muffle furnace at  $450^\circ\text{C}$  for 90 min. The residue was dissolved in nitric acid, boiled for 3 h and evaporated to dryness at low heating rate. The residue was dissolved in 80 mL of distilled water and filtered. The filtrate was adjusted to pH 5.5 using NaOH solution and then quantitatively diluted with appropriate double distilled water.

## 2.6. Spectrophotometric studies

TH with a sulfur atom and two amine groups donating ligand is insoluble in water. Consequently, we investigated the complexation of silver ion in ethanol solution. A typical spectrum was depicted in Fig. S1 (Supplementary data). As it can be observed, significant apparent changes in the peaks intensity and appearance of a new peak for Th after adding of analyte ions indicate that, the ligand has strong interaction with Ag(I) ions. Therefore, it may be used as an efficient ionophore for detecting of Ag(I). Further analyzing the absorbance at maximum absorbance wavelength, using a nonlinear least-squares curve-fitting program (Kinfit program), provided the stoichiometry and stability constant of Th complex with the Ag(I) [27]. From the results observed for analyte at a mole ratio of 0.5, it can be immediately concluded that a 2:1 complex of  $[\text{ML}_2]$  with the stability constant of  $\log K_f = 6.10$  is formed in the ethanol solution. Furthermore, we decided to use TH as a suitable ionophore for the selective determination of silver ion using potentiometric carbon paste electrode because of its excellent metal-binding properties and water insolubility.

## 3. Results and discussion

The obtained results from some experimental works revealed that the performance of the suggested Ag(I) potentiometric carbon paste sensor based on nanographene composite can be highly improved by adding GNS and TH into paste and application of DPA instead of paraffin oil. For this purpose, the potentiometric responses of the unmodified CPE and modified CPE with the new nano-composite towards Ag(I) ions were studied in terms of linear range, detection limit, selectivity coefficients, response time, lifetime and response stability, which are important characteristics of every ion selective CPEs, and compared with some previously reported Ag(I) potentiometric sensors based on different compositions [45–50].

## 3.1. Electrode composition and modification

It is well known that the sensitivity, linear dynamic range and selectivity obtained for an ion selective electrode (ISE) depend significantly on the composition of the electrode [17–26]. Thus, it is necessary to investigate the influence of the paste composition on the potential responses of the modified CPEs. For this purpose, several electrodes with different compositions were investigated in this study. Unmodified CPE was prepared by mixing 70% of graphite powder with 30% of paraffin oil in a mortar and pestle. Modified pastes were prepared in a similar fashion, except that the graphite powder was mixed with a desired weight of TH, GNS and DPA to get different compositions as given in Table 1. As can be seen, the electrode without the ionophore (sensor No. 1) showed poor sensitivity to silver cation. Also, an increase at the TH level in the CPE (sensor No. 2, 3) caused a slope increase of the calibration curve, whereas, in the presence of the ionophore, the electrode showed remarkable selectivity for Ag(I). It is possible that the presence of S and N atoms in TH generate a great affinity between the ionophore and the Ag(I) ion. This indicated that ionophore is the most important component in the proposed carbon paste electrodes for sensing silver ion. Further addition of the ionophore (sensor No. 4), however, resulted in a little decrease in the response of the electrode. This phenomenon can arise from the decrease of graphite powder/TH ratio, thereupon decreases of paste homogeneities and conductivity [51].

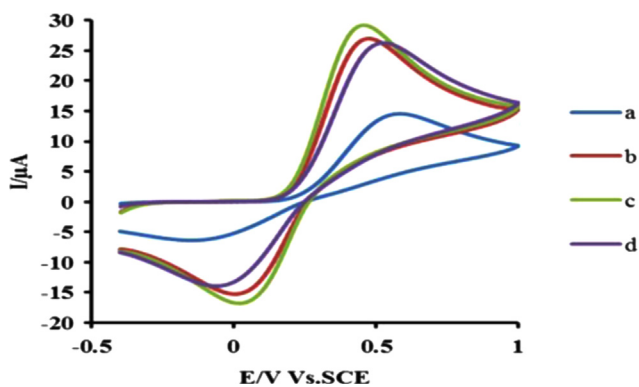
According to Table 1, the electrode composed of 30% DPA, 7% TH, 53% graphite powder, 10% GNS, (No. 7) has optimum composition for sensing Ag(I). This new composition was selected for further examinations.

Recent years MWs have aroused great attention due to their specific characteristics such as good chemical and thermal stability, high conductivity and wide electrochemical windows [52–54]. They are molecular scale compounds that have been exhibited excellent electrical conductivity. DPA is the smallest conjugated oligomer and can be used as a conducting binder in CPEs. Safavi et al. fabricated a DPA based MW modified carbon paste electrode (MW-CPE) and investigated its electrochemical behavior, which exhibited better performances than the prepared CPE using paraffin oil [42]. In this study we used DPA as the conductive binder instead of paraffin oil in the carbon paste, provides higher sensitivity in the determination of Ag(I). Due to the effects of conjugated system of DPA and its  $\pi$ - $\pi$  interaction with graphene and graphite powder, with their combination, a stable modified carbon paste electrode and a higher sensitivity for the target analyte detection was achieved (Table 1) [55–57].

Also, for improving the electrochemical performance of the sensor, the GNS can be used as an excellent candidate of conventional modifier for the modification of CPE owing to its superior electrical conducting ability and high specific surface area [32]. So, we used GNS into the carbon paste that increased the available surface area and improved the conductivity property of the electrode surface and, therefore, conversion of the chemical signal to an electrical one.

## 3.2. Effect of the GNS/graphite ratio on the performance of the suggested modified CPE

As an electrical conducting modifier, the amount of GNS mixed in the carbon paste would influence the performance of the suggested modified electrode. The redox couple of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  was chosen to characterize the electron transfer properties of different amount of GNS added into the carbon pastes. According to the literature [58] the electron transfer property of the redox couple is strongly dependent on the surface chemistry and microstructure as well as the density of electronic states of electrode



**Fig. 1.** CVs of  $1.0 \text{ mmol L}^{-1}$   $[\text{Fe}(\text{CN})_6]^{4-}$  at the unmodified CPE (a) and different GNS mixed CPEs with GNS/graphite ratios of 5/58% (b), 10/53% (c), 15/48% (d), respectively. Scan rate:  $100 \text{ mV s}^{-1}$ .

materials near the Fermi level. Fig. 1 shows CVs of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  at the unmodified CPE and CPE modified with different amounts of GNS. It was evident that  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  exhibited a poor electrochemical behavior on unmodified CPE (curve a), with a larger peak-to-peak potential separation ( $\Delta E_p$ ) than others, and relatively broadened wave shape. However, by increasing the GNS ratio up to about 10% into the pastes the electrochemical response of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  was improved. With increasing the GNS/graphite ratio (from curve a to curve c), both cathodic and anodic peak current increased, and the  $\Delta E_p$  values for the suggested modified CPEs (curves b to d) were 425, 402 and 518 mV, respectively. It is obvious that the GNS mixed CPE at the weight ratio of 10/53% exhibited the relatively smallest  $\Delta E_p$  and highest peak currents (curve c). The excellent conducting property of GNS could contribute to the improved electrochemical response of the modified CPEs toward  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ . However, increasing the amount of the GNS higher than 10% in the composition of the paste may lead to undesirable mechanical properties of the suggested CPE, which correspondingly decreased the electron transfer rate of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  (curve d). Accordingly, an optimized GNS/graphite ratio for the preparation of suggested CPE was selected as 10/53% (c).

### 3.3. Electrochemical behavior of Ag(I) at the surface of various electrodes

The CVs were obtained for the unmodified CPE, TH-CPE, (GNS/TH)-CPE and (GNS/TH/MW)-CPE in the absence and presence of analyte in  $\text{KNO}_3$   $0.1 \text{ mol L}^{-1}$  solution. The results are summarized in Fig. S2. There is no observable peaks for an unmodified CPE in the absence of Ag(I) (curve a). Curves of b, c, d and e show CVs of unmodified CPE, TH-CPE, (GNS/TH)-CPE and (GNS/TH/MW)-CPE in the presence of  $1.00 \times 10^{-3} \text{ mol L}^{-1}$  Ag(I), respectively. Concerning Ag reversible wave with oxidation peak on the forward scan at about 0.38 V vs. SCE and cathodic peak on the reverse scan at 0.22 V vs. SCE. A comparison of oxidation and reduction peak currents for Ag at the unmodified CPE, TH-CPE, (GNS/TH)-CPE and (GNS/TH/MW)-CPE indicate an enhancement with each step of modifications, which are due to the increase in the surfaces area and functionality of (GNS/TH/MW)-CPE, as compared with unmodified CPE. Therefore, as expected for a modified process, GNS/TH/MW composite caused an increase in the sensitivity of the sensor.

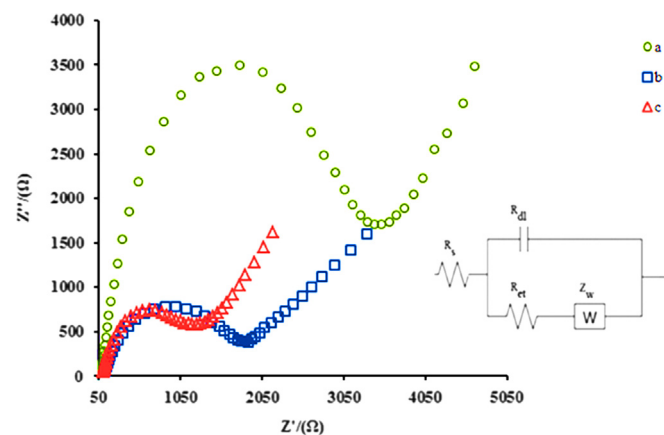
### 3.4. EIS studies

EIS is a powerful technique to study the conductivity properties of the modified sensor surface. The curve of the EIS includes a semicircular part and a linear part. The semicircular part at higher frequencies corresponds to the electron-transfer limited process

and its diameter is equal to the electron transfer resistance, which controls the electron transfer kinetics of the redox probe at the electrode interface [28]. For investigation of the effects of GNS and DPA on the conductivity property of the prepared potentiometric sensors surface, EIS measurements were done. Nyquist diagrams of  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  solution containing  $0.1 \text{ mol L}^{-1}$   $\text{KNO}_3$  at different electrodes (unmodified CPE and modified CPEs) are shown in Fig. 2. To obtain the detailed information of the EIS, a simple equivalent circuit model was used to fit the results. In this circuit,  $R_s$ , C and  $R_{et}$  represent solution resistance, a capacitance for the double-layer and electron transfer resistance, respectively. W is a finite-length Warburg short-circuit term coupled to  $R_{et}$ , which accounts for the Nernstian diffusion.  $R_{et}$  at the electrode surface is equal to the semicircle diameter, which can be used to describe the interface properties of the electrode. Fig. 2, curve a represents impedance spectrum at unmodified CPE. Curves b and c show impedance spectra at CPE modified with GNS and with GNS and DPA, respectively. As can be seen from this figure, the semicircle diameter decreases from curves a to c. So, semicircle diameter comparison of these curves clearly shows that charge transfer resistance decreased by adding 10% GNS into the paste and also by using DPA as conducting binder instead of paraffin oil. By increasing the conductivity, the dynamic working range, sensitivity 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.

### 3.5. The surface morphology of the prepared CPEs

The surface morphology of the prepared electrodes plays a key role in the selective and sensitive detection of the analytes. So, the SEM measurements were carried out to investigate the surface morphologies of two electrodes (unmodified CPE and new suggested nano-composite modified CPE), as shown in Fig. 3. The unmodified CPE (Fig. 3A) is characterized by a surface formed by irregularly shaped of graphite powder that were isolated with each other and a closer look of the film reveals a broken surface. After the modification of the carbon paste with GNS and DPA, it can be seen that materials were distributed on the surface of electrode with relatively uniform which shows the good adherence of DPA to graphite and GNS (Fig. 3B). Significant improvement in the available high specific surface area of the suggested composite CPE is observed.



**Fig. 2.** Impedance plots for different electrodes in  $[\text{Fe}(\text{CN})_6]^{3-/4-}$ -containing  $0.1 \text{ mol L}^{-1}$   $\text{KNO}_3$ : (a) unmodified CPE (b) modified CPE with GNS (c) modified CPE with GNS and DPA.

### 3.6. Emf measurements

All emf measurements were carried out with the following cell assembly:



All of the emf observations were made relative to a double junction Ag/AgCl electrode with a digital milli-voltmeter. Calibration graph was drawn by plotting the potential,  $E$ , versus the logarithm of the Ag(I) ion concentration. All measurements were carried out at 25 °C.

### 3.7. Response of the electrode to various cations

In preliminary experiments, the suggested modified Ag(I) carbon paste sensor was examined for the wide variety of metal ions. The potential obtained for the most sensitive ion selective electrode based on the new nano-composite (Table 1, No. 7) are shown in Fig. 4A. As can be seen, the proposed modified CPE exhibited a Nernstian behavior and the most sensitive response toward Ag(I) among different tested cations over a wide concentration range.

### 3.8. Measuring range and detection limit

Measuring range and detection limit (DL) of the optimal modified Ag(I) carbon paste sensor (Table 1, No. 7) was evaluated using linear curve fitting based on IUPAC recommendations. The suggested Ag(I) selective electrode exhibited linear response to the logarithm of the concentration of Ag(I) ions with the calibration

equation of  $y=59.70x+785.49$  and correlation coefficient of  $r=0.998$  within the concentration range of  $8.00 \times 10^{-9}$  to  $1.00 \times 10^{-2} \text{ mol L}^{-1}$  of silver(I) nitrate with Nernstian slope of  $59.70 \pm 0.10 \text{ mV decade}^{-1}$  at  $25 \pm 1 \text{ }^\circ\text{C}$ . The DL for the determination of Ag(I) by the suggested sensor was  $4.17 \times 10^{-9} \text{ mol L}^{-1}$ , which was calculated by the extrapolating of the two segments of the calibration curve in Fig. 4B.

### 3.9. Effect of pH on the sensor response

The most important factor on the performance of the most ISEs is the pH value of the test solution. The pH influence of the solution on the response of the suggested modified electrode was studied on  $1.00 \times 10^{-5} \text{ mol L}^{-1}$  silver(I) ion having different pH values. The pH varied from 2 to 12 by the addition of dilute solutions of HNO<sub>3</sub> or NaOH. The potential variation as a function of pH is plotted in Fig. 5A. The composition of the electrode was kept constant during all experiments. The results obtained indicated that the working range of the suggested modified electrode to be between pH 3.5 and 10.5. The increase in the potential below the pH value of 3.5 could be attributed to the partial protonation of the employed ionophore. Moreover, above pH 10.5 the measured potential decreased, due to the generation of silver hydroxides.

### 3.10. Response time and reversibility of the proposed Ag(I) CPE

The response time is a significant factor for any sensor in analytical applications. The practical response time (the time required to achieve a 90% of final steady potential value of the electrodes after successive immersion of Ag(I) ion solutions, each having a 10-fold difference in

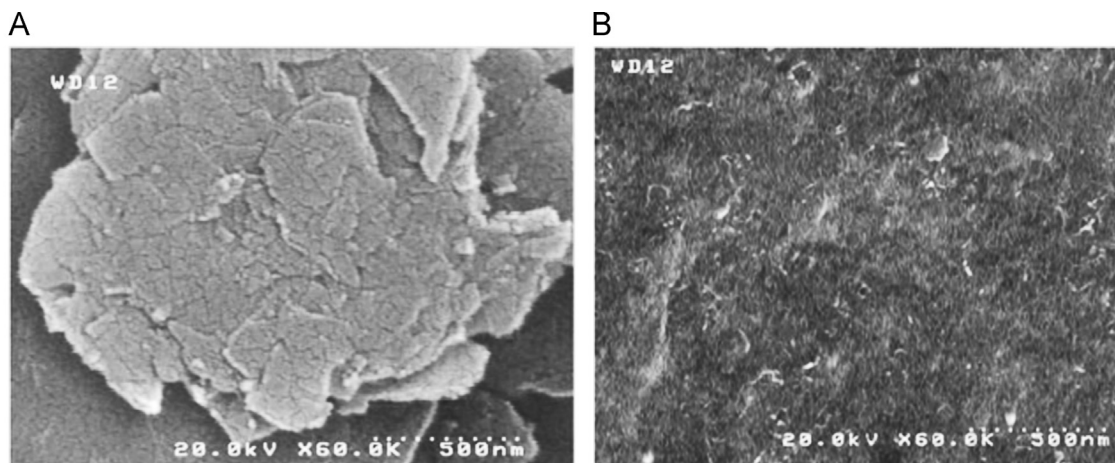


Fig. 3. SEM images of unmodified CPE (A) and suggested modified CPE with GNS and DPA (B).

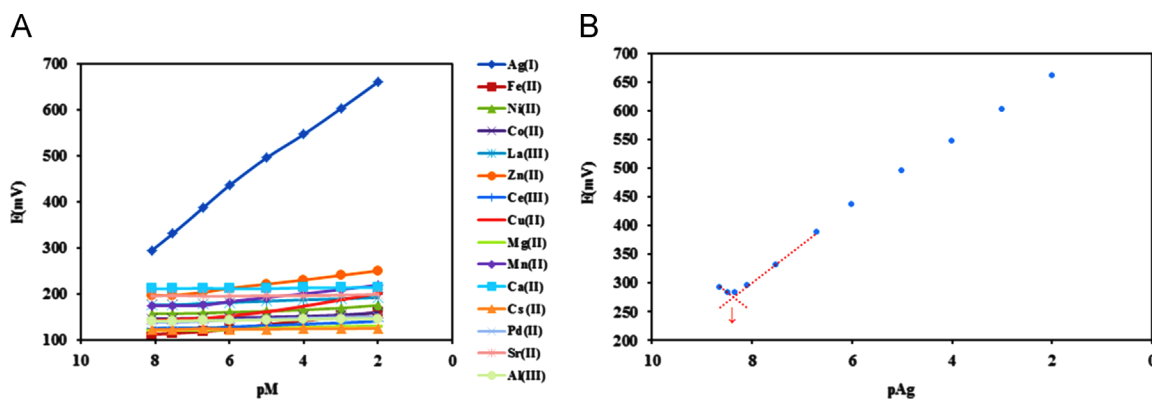


Fig. 4. (A) Schematic diagram of the electrode (Table 1, No. 7) response to various cations. (B) Calibration curve of the Ag(I) modified CPE (Table 1, No. 7).

concentration) has been recorded at different Ag(I) concentrations. In this study, the practical response time (for sensor No. 7) was recorded by changing the Ag(I) ion concentration in the range  $1.00 \times 10^{-6}$  to  $1.00 \times 10^{-3}$  mol L<sup>-1</sup> (Fig. 5B). As it is seen, the electrode reached the equilibrium response in a very short time of about 6 s. To evaluate the reversibility of the electrode a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low ( $1.00 \times 10^{-3}$  to  $1.00 \times 10^{-6}$  mol L<sup>-1</sup>) concentrations as shown in Fig. 5B. The results showed that the response of the electrode was reversible; although the time needed to reach equilibrium values (about 18 s) was longer than that for low-to-high sample concentrations (about 6 s), because residual silver will still be adsorbed on the surface of the CPEs, and cause to occupy the site of surface of the indicator electrode significantly, therefore the proposed electrodes don't can sense the silver ions that exist in the bulk of the solution promptly, which will lead to less response time [59,60].

### 3.11. Selectivity of the electrode

An important characteristic of any ISE is its response to the primary ion in the presence of other ions in the solution, which is expressed in terms of the potentiometric selectivity coefficient.

The potentiometric selectivity coefficients of the suggested modified Ag(I) sensor were evaluated by the matched potential method (MPM) [61]. According to this method, the potentiometric selectivity coefficient is defined as the activity (concentration) ratio of primary (A) and interfering (B) ions that give the same potential change under identical conditions. At first, a known activity of the primary ion ( $a'_A$ ) solution is added into a reference solution that contains a fixed activity ( $a_A$ ) of primary ion, and the corresponding potential change ( $\Delta E$ ) is recorded. Next, a solution of an interfering ion (B) is added to the reference solution until the same potential change ( $\Delta E$ ) is recorded. The change in potential produced at the constant background of the primary ion must be the same in both cases. The selectivity coefficient ( $K$ ) is given by the expression:

$$K_{A,B}^{pot} = \frac{a'_A - a_A}{a_B}$$

The resulting values of the selectivity coefficients are given in Table 2. According to this table, all the investigated cations would not affect the response of the suggested sensor, and had very small value of selectivity coefficients. Table 2 also shows that the obtained selectivity coefficients for the proposed sensor for most of the investigated cations are smaller than those for the previously

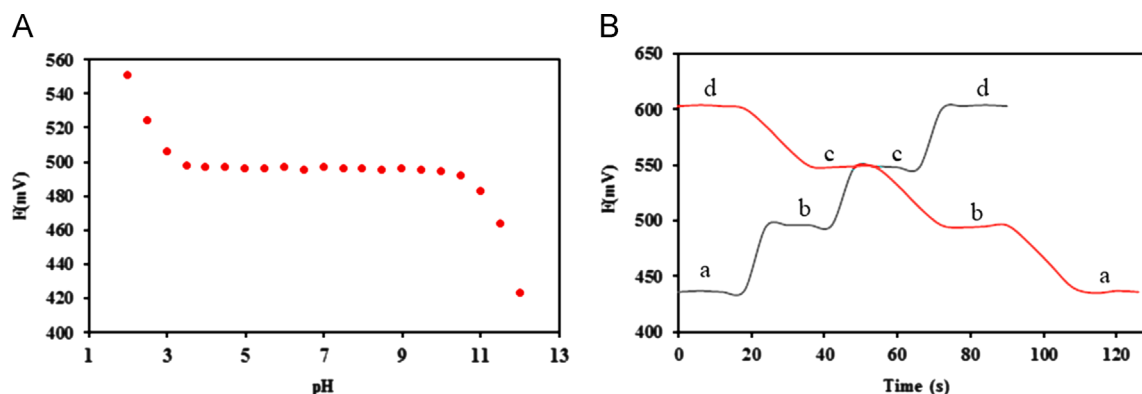


Fig. 5. (A) Effect of pH on the potential response of the proposed Ag(I) modified CPE (No. 7). (B) Dynamic response of the proposed Ag(I) modified CPE for step changes in Ag(I) concentration (from low to high and vice versa): (a)  $1.00 \times 10^{-6}$  (mol L<sup>-1</sup>), (b)  $1.00 \times 10^{-5}$  (mol L<sup>-1</sup>), (c)  $1.00 \times 10^{-4}$  (mol L<sup>-1</sup>), (d)  $1.00 \times 10^{-3}$  (mol L<sup>-1</sup>).

**Table 2**  
Selectivity coefficient ( $K_{i,j}$ ) for various interfering cations for Ag(I) selective carbon paste electrode.

Interference (j)	$K_{Ag,j}$						
	[45]	[46]	[47]	[48]	[49]	[50]	This work (MPM)
Pb <sup>2+</sup>	$3.98 \times 10^{-5}$	$1.48 \times 10^{-5}$	$2.45 \times 10^{-5}$	$4.70 \times 10^{-3}$	$1.50 \times 10^{-4}$	$6.10 \times 10^{-3}$	$2.81 \times 10^{-3}$
Mg <sup>2+</sup>	$7.94 \times 10^{-6}$	$1.66 \times 10^{-5}$	$6.76 \times 10^{-6}$	$3.90 \times 10^{-6}$	$2.00 \times 10^{-4}$	$1.70 \times 10^{-4}$	$1.23 \times 10^{-6}$
Fe <sup>2+</sup>	–	–	–	–	–	–	$3.49 \times 10^{-4}$
Mn <sup>2+</sup>	–	$2.14 \times 10^{-5}$	$5.37 \times 10^{-6}$	–	–	–	$3.86 \times 10^{-6}$
Al <sup>3+</sup>	$1.26 \times 10^{-5}$	$5.50 \times 10^{-3}$	$2.14 \times 10^{-4}$	$2.20 \times 10^{-5}$	$1.60 \times 10^{-3}$	$7.80 \times 10^{-6}$	$9.81 \times 10^{-6}$
Sr <sup>2+</sup>	$6.31 \times 10^{-6}$	$1.58 \times 10^{-5}$	$8.13 \times 10^{-6}$	–	–	–	$4.76 \times 10^{-6}$
Cr <sup>3+</sup>	–	$7.94 \times 10^{-4}$	$7.56 \times 10^{-5}$	–	–	$1.40 \times 10^{-5}$	$5.17 \times 10^{-5}$
Cu <sup>2+</sup>	$6.31 \times 10^{-6}$	$7.76 \times 10^{-4}$	$4.90 \times 10^{-5}$	$2.16 \times 10^{-2}$	$2.50 \times 10^{-3}$	$8.10 \times 10^{-4}$	$4.37 \times 10^{-6}$
Ni <sup>2+</sup>	$1.00 \times 10^{-5}$	$1.05 \times 10^{-5}$	$1.23 \times 10^{-5}$	–	$1.50 \times 10^{-4}$	$4.10 \times 10^{-4}$	$1.13 \times 10^{-5}$
Ca <sup>2+</sup>	$6.31 \times 10^{-6}$	$1.23 \times 10^{-5}$	$6.03 \times 10^{-6}$	$1.80 \times 10^{-5}$	–	$2.40 \times 10^{-6}$	$5.92 \times 10^{-6}$
Ba <sup>2+</sup>	$1.00 \times 10^{-5}$	$1.32 \times 10^{-5}$	$7.76 \times 10^{-6}$	$1.80 \times 10^{-6}$	–	–	$1.63 \times 10^{-6}$
Hg <sup>2+</sup>	$3.98 \times 10^{-4}$	–	–	$2.10 \times 10^{-2}$	$2.50 \times 10^{-2}$	$2.20 \times 10^{-4}$	$2.41 \times 10^{-3}$
Zn <sup>2+</sup>	$1.00 \times 10^{-5}$	$1.23 \times 10^{-5}$	$7.41 \times 10^{-6}$	$3.20 \times 10^{-5}$	$1.10 \times 10^{-3}$	$4.30 \times 10^{-4}$	$9.86 \times 10^{-4}$
Na <sup>+</sup>	$2.00 \times 10^{-4}$	$2.82 \times 10^{-6}$	$8.13 \times 10^{-7}$	$8.80 \times 10^{-3}$	$1.10 \times 10^{-4}$	$4.30 \times 10^{-4}$	$2.27 \times 10^{-6}$
Cs <sup>+</sup>	$1.58 \times 10^{-4}$	–	–	–	–	–	$9.41 \times 10^{-5}$
K <sup>+</sup>	$6.31 \times 10^{-5}$	$2.19 \times 10^{-6}$	$3.31 \times 10^{-7}$	$2.30 \times 10^{-4}$	–	–	$1.11 \times 10^{-6}$
Cd <sup>2+</sup>	$1.00 \times 10^{-5}$	$1.78 \times 10^{-5}$	$1.23 \times 10^{-5}$	$6.30 \times 10^{-6}$	$4.00 \times 10^{-3}$	$2.10 \times 10^{-5}$	$8.94 \times 10^{-4}$
Co <sup>2+</sup>	$6.31 \times 10^{-6}$	$4.37 \times 10^{-6}$	$8.13 \times 10^{-6}$	$3.10 \times 10^{-6}$	$1.20 \times 10^{-4}$	$4.30 \times 10^{-3}$	$2.84 \times 10^{-6}$
Fe <sup>3+</sup>	$1.00 \times 10^{-4}$	–	–	–	$1.00 \times 10^{-3}$	$3.60 \times 10^{-5}$	$6.71 \times 10^{-5}$
Tl <sup>+</sup>	$5.01 \times 10^{-4}$	–	–	–	–	–	$9.26 \times 10^{-5}$
La <sup>3+</sup>	–	$4.47 \times 10^{-5}$	$1.91 \times 10^{-5}$	–	–	–	$8.76 \times 10^{-6}$
NH <sub>4</sub> <sup>+</sup>	$2.51 \times 10^{-5}$	$3.31 \times 10^{-6}$	$3.72 \times 10^{-7}$	$5.20 \times 10^{-3}$	$3.10 \times 10^{-4}$	$3.30 \times 10^{-5}$	$4.71 \times 10^{-7}$

**Table 3**  
Comparison of the proposed Ag(I) selective electrode with the some previously reported electrodes.

DL (mol L <sup>-1</sup> )	Linear range (mol L <sup>-1</sup> )	Slope (mV decade <sup>-1</sup> )	Life time (Weeks)	Response time (s)	Ref.
4.17 × 10 <sup>-9</sup>	8.00 × 10 <sup>-9</sup> –1.00 × 10 <sup>-2</sup>	59.70	19	~6	Proposed electrode
4.00 × 10 <sup>-7</sup>	1.00 × 10 <sup>-6</sup> –1.00 × 10 <sup>-1</sup>	56.40	4	30	[45]
9.50 × 10 <sup>-7</sup>	1.00 × 10 <sup>-6</sup> –1.00 × 10 <sup>-1</sup>	60.40	12	50	[46]
8.00 × 10 <sup>-8</sup>	8.60 × 10 <sup>-8</sup> –1.00 × 10 <sup>-1</sup>	60.80	4	~20	[47]
7.00 × 10 <sup>-8</sup>	1.10 × 10 <sup>-7</sup> –1.00 × 10 <sup>-3</sup>	61.20	N. R. <sup>a</sup>	~3	[48]
6.30 × 10 <sup>-8</sup>	8.20 × 10 <sup>-8</sup> –1.50 × 10 <sup>-2</sup>	58.60	N. R.	8	[49]
5.00 × 10 <sup>-8</sup>	2.20 × 10 <sup>-7</sup> –2.20 × 10 <sup>-2</sup>	59.54	~8	< 10	[50]

<sup>a</sup> N. R.: Not reported.

**Table 4**  
Determination of Ag(I) recovery by the suggested electrode in the different real samples.

Samples	Ag(I) added	Ag(I) found <sup>a</sup>	Recovery (%)	Ag(I) found <sup>a</sup> by ICP-OES	t <sub>exp</sub> <sup>b</sup>	F <sub>exp</sub> <sup>b</sup>
Mineral water (mg L <sup>-1</sup> )	–	N.D. <sup>c</sup>	–	N.D.	–	–
	5.00	4.88 ± 0.41	97.6	5.02 ± 0.24	0.71	2.92
	20.00	19.78 ± 0.29	98.9	19.95 ± 0.11	1.33	6.95
River water (mg L <sup>-1</sup> )	–	< LOD	–	3.14 × 10 <sup>-4</sup> ± 0.24	–	–
	5.00	4.91 ± 0.31	98.2	5.09 ± 0.26	1.07	1.42
	20.00	20.21 ± 0.28	101.1	20.32 ± 0.19	0.79	2.17
Industrial manufactory waste water (mg L <sup>-1</sup> )	–	0.14 ± 0.42	–	0.31 ± 0.27	0.84	2.42
	5.00	5.08 ± 0.24	98.8	5.19 ± 0.16	0.95	2.25
	20.00	20.58 ± 0.22	102.2	20.72 ± 0.13	1.34	2.86
Silver sulphadiazine burning cream (mg g <sup>-1</sup> )	–	0.076 ± 0.018	–	0.093 ± 0.010	1.95	3.24
	1.50	1.62 ± 0.13	102.7	1.65 ± 0.10	0.47	1.69
	–	2.12 ± 0.33	–	2.18 ± 0.21	0.37	2.47
Radiology film (mg g <sup>-1</sup> )	1.50	3.64 ± 0.20	101.3	3.77 ± 0.17	1.25	1.38

<sup>a</sup> Average of six replicate measurements ± standard deviation.

<sup>c</sup> N.D. not detected.

<sup>b</sup> The critical value of F<sub>5,5</sub>=7.146 and the critical value of t<sub>10</sub>=2.23 for P=0.05

reported sensors for silver(I) determination [45–50]. This sensor displays significantly high selectivity for Ag(I) ion.

### 3.12. Stability and lifetime of the electrode

The long terms stability and lifetime of the suggested silver sensor were investigated by periodically recalibrating in standard solution and calculating the slope of the optimized sensor over a period of 25 weeks in working concentration range of 8.00 × 10<sup>-9</sup> to 1.00 × 10<sup>-2</sup> mol L<sup>-1</sup> silver nitrate solutions. During this period, the sensor was used weekly. The proposed sensor was gently washed with distilled water, dried and stored at room temperature when not in use. The results exhibited that the slope of the electrode responses before 19 weeks was reproducible and no significant drift and also no significant change in the performance of the sensor was observed for this period of time. After this time, there was a slight gradual decrease in the slopes from 59.70 to 58.89 mV decade<sup>-1</sup>. This shows that the lifetime of the proposed silver selective sensor was about 5 months.

### 3.13. Comparison study

In Table 3, some important characteristics of the proposed electrode are compared with the corresponding values for some previously reported Ag(I)-selective electrodes based on different composites [45–50]. It is evident from this table that in most cases, the performance of the proposed electrode show superior behavior in comparison with some previously reported Ag(I) sensors.

### 3.14. Analytical applications

The suggested (GNS/TH/MW)–CPE was applied to the determination of trace amounts of silver ions in a wide variety of real

samples. Mineral water, river water and industrial manufactory waste water samples, silver sulphadiazine burning cream and radiological film were analyzed. The analysis was performed by the standard addition method. As Table 4 shows, the results were comparable with those obtained by ICP-OES [62]. Thus the sensor provides a good alternative for the determination of Ag(I) in different real samples.

The suggested electrode was also successfully applied as an indicator electrode for the titration of 9.0 mL of 1.00 × 10<sup>-3</sup> mol L<sup>-1</sup> Ag(NO<sub>3</sub>) with a 1.00 × 10<sup>-3</sup> mol L<sup>-1</sup> NaCl solution. Typical results of titration of Ag(I) is shown in Fig. S3. The results show that the amount of silver ions in the solution can be accurately determined with the proposed electrode.

### 3.15. Statistical treatment of results

For comparing the results of the suggested method with those obtained by ICP-OES, the *F*-test and *t*-test were applied. *F*-test was used for comparing the precisions of the two methods and *t*-test was used for comparing the accuracy. It can be concluded from Table 4 that there is no significant difference between the results obtained by the two methods for P=0.05. The results confirm applicability of the suggested method for precise and accurate determination of the Ag(I) ions in the different real samples with different complex matrices.

## 4. Conclusions

A novel nano-composite potentiometric sensor for the determination trace amounts of Ag(I) ion based on (GNS/TH/MW)–CPE was fabricated successfully. The performance of modified (GNS/TH/MW)–CPE in comparison to the unmodified CPE was dramatically

improved due to the excellent electrical conductivity of both MW and GNS and also large specific surface area of GNS. This study indicated that after the modification of the carbon paste with GNS and DPA, the electrode surface was relatively uniform which shows the good adherence of DPA to graphite and GNS. High sensitivity, reproducibility and selectivity, and very low detection limit with the ease of preparation and surface regeneration make the proposed modified electrode as a very useful sensor for accurate determination of target analyte in various real samples in nanomolar levels.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2014.08.004>.

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