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Fabrication of new carbon paste electrodes based on gold nano-particles self-assembled to mercapto compounds as suitable ionophores for potentiometric determination of Copper ions

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Abstract

In the present study, we investigate the potentiometric behavior of Cu^{2+} carbon paste electrodes based on two mercapto compounds 2-Ethylmino-5-Mercapto-1,3,4-Thiadiazole (EAMT) and 2-Acetylamino-5-mercapto-1,3,4-thiadiazole (AAMT) self-assembled on gold nano-paricle (GNP) as ionophore. Then, the obtained results from the modified electrodes are compared. The self-assembled ionophores exhibit a high selectivity for Copper ion (Cu^{2+}),in which the sulfur and nitrogen atoms in their structure play a significant role as the effective coordination donor site for the Copper ion. Among these electrodes, the best performance was obtained with the sensor with a EAMT/graphite powder/paraffin oil weight ratio of 4.0/68/28 with 200 μL of GNP which exhibits the working concentration range of 1.6×10^{-9} to 6.3×10^{-2} M and a Nernstian slope of 28.9±0.4 mVdecade^{-1} of copper (II) activity. The detection limit of electrode was $2.9(\pm0.2)\times10^{-10}$M and potential response was pH , in other words, it was independent across the range of 2.8–6.3. The proposed electrode presented very good selectivity and sensitivity towards the Cu^{2+} ions over a wide variety of cations including alkali, alkaline earth, transition and heavy metal ions. Moreover, the proposed electrode was successfully applied as an indicator electrode in the potentiometric titration of Cu (II) ions with EDTA and also the potentiometric

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determination of copper ions in spiked water samples.

Keywords: Gold nano-particle, self-assembly, potentiometric determination, carbon paste electrode, cupper ions

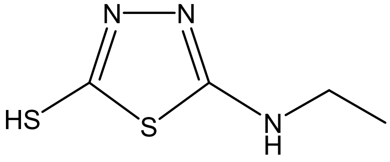
Introduction

Potentiometric ion selective sensors are known to have an anexcellent low cost tool for the selective, sensitive and rapid determination of a vast variety of analytes in different fields of application. They are extremely versatile tools to chemical sensing science in which selectivity can be chemically adjusted by incorporating different ionophore into the membrane phase. Solid electrodes based on carbon materials are commonly used in electroanalysis due to their broad potential window, low background current, rich surface chemistry, low cost, chemical inertness and suitability for various sensing and detection applications [1,2]. Among what was mentioned, carbon paste electrodes (CPEs) combine a carbon powder with a pasting liquid (an organic binder). The advantages of carbon paste electrodes drew the attention of researchers in recent years where these advantages were exploited for various measurements including their potentiometric [3–7]. However the exact behavior of carbon paste electrodes is not fully understood. In recent years, much attention has been directed towards the synthesis and applications of metal nano-particles because of their various applications in several areas including materials science, catalysis and biology [8]. Among the different metal nano-particles, AuNPs are widely used for various studies due to their chemical stability and ease in preparation [9,10]. The preparation of a thin film of AuNPs on different conducting substrates is more important for a wide range of applications such as chemical, electrochemical and biological sensing [11–15]. Until now a large number of Cu^{2+}-selective electrode has been reported [16–25]. However, most of these Cu^{2+}-selective electrodes suffer from the interfering effects of Co^{2+}, Ni^{2+}, Cd^{2+}, and Ag^{+} ions as well as limited linear ranges and high detection limits. In this work, two novel sensors for potentiometric determination of Cu (II) which were constructed by GNPs were self-assembled onto two mercapto compounds (Figure 1) as an ionophore. These electrodes were applied as indicator electrodes for potentiometric determination of trace amounts of Cu (II) ions.

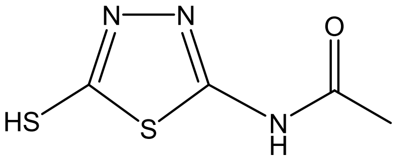
Experimental

Reagents

All analytical reagent grade chemicals and distilled water were used for preparing all aqueous solutions. Hydrogen tetracholoroaurate ($HAuCl_4 \cdot 3H_2O$), trisodium citrate and copper nitrate were obtained from Merck (Germany), carbon graphite powder and paraffin oil were purchased from Fluka (Switzerland). Salts of metal nitrates (all from Merck) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5.



(AAMT)



(EAMT)

Figure1. Structures of mercapto compounds used as ionophore in the proposed electrodes

Apparatus

All potentiometric measurements were made with a pH/mV meter (Metrohm-827, Switzerland) using proposed sensors in conjunction with a double junction Ag/AgCl (Azar electrode, Iran) reference electrode. UV–vis absorption spectrum was recorded with a UV–vis spectrometer (Philips-PU8750, Netherlands).

Preparation

Preparation of gold nano-particle

Colloidal gold nano-particles were prepared according to the literature [26-28] by adding 0.5mL of 1% (w/v) sodium citrate solution to 50 mL of 0.01% (w/v) $HAuCl_4 \cdot 3H_2O$. All glassware used in this procedure was cleaned in freshly prepared 1:3 HNO_3–HCl and rinsed thoroughly by our distilled water. The two solutions were heated up to 60 ◦C. The final mixture of red color was boiled for 15 min. The preparation was stored in dark glass bottles at 4 ◦C.

Electrode preparation and modification

Bare CPEs were prepared by mixing 0.700 g of graphite powder, which had been heated at 700 ◦C in a muffle furnace for 15 second, with 0.300 g of paraffin oil with a mortar and pestle. A modified paste was prepared in a similar fashion, except that the graphite powder was mixed with a desired weight of ligand and gold nano-particle to get different composition as given in Table 1.

Both unmodified and modified pastes were packed into a polyethylene tube (2.5

mmdiameter), the tip of which had been cut off. Electrical contact to the paste was established via inserting a copper wire thorough flank. The surface of fresh modified carbon paste electrode were preconditioned by exposure to a 1.0×10^{-4} MCu^{2+} ion solution for30 min, then the electrode was rinsed with deionized water. A fresh electrode surface of paste was cut out with a glass rod and the exposed-end polished on a paper until the surface showed shiny appearance.

Table 1. Formation constants of complexation of different metal ions and AAMT ligands in acetonitrile[a].

Ion	**Log K_f (AMT)**	**Log K_f (AAMT)**
Na^+	< 2.0	< 2.0
NH_4^+	< 2.0	< 2.0
Mg^{2+}	2.15 ± 0.10	2.19 ± 0.19
Al^{3+}	2.18 ± 0.16	2.25± 0.31
Fe^{3+}	2.16 ± 0.15	2.31 ± 0.28
Cr^{3+}	2.29 ± 0.25	2.41 ± 0.17
Cu^{2+}	6.11 ± 0.33	5.31 ± 0.16
Ni^{2+}	3.22 ± 0.22	2.98 ± 0.17
Co^{2+}	3.07 ± 0.37	2.94 ± 0.22
Hg^{2+}	4.18 ± 0.24	3.99 ± 0.21
Zn^{2+}	3.13 ± 0.11	3.01 ± 0.44
Cd^{2+}	3.41 ± 0.21	3.31 ± 0.11
Pb^{2+}	3.27 ± 0.32	3.12 ± 0.17
Ag^+	4.51 ± 0.14	4.14 ± 0.19

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

Emf measurements

The electrochemical cell can be represented as follows:

Ag,AgCl(s), KCl (3M) || sample solution | carbon paste electrode

Calibration graph was drawn by plotting the potential, E, versus the logarithm of the copper ion concentration. The activities of metal ions were based on the activity coefficient (μ), where calculated from the modified form of the Debye–Huckel equation, which is applicable to any ion in which μ is the ionic strength and Z is the valency. All measurements were carried out at 25±0.1 ◦C.

$$\log\lambda = -0.511Z^{2}\left[\frac{\mu^{1/2}}{\left(1+1.5\mu^{1/2}\right)-0.2\mu}\right]$$

UV–Vis spectroscopic measurements

In all measurements, a 2 mL of ligand solution (5.0×10^{-5} mol L−1) is placed in a quartz cell with 1 cm pass length. Then, a known amount of a metal ion solution (5.0×10^{-3} mol.L^{-1}) is added in a stepwise manner, using a calibrated micropipette. The absorbance of the solution is measured after each addition. The ion addition is continued until the desired ionophore-to-ion mole ratio is achieved.

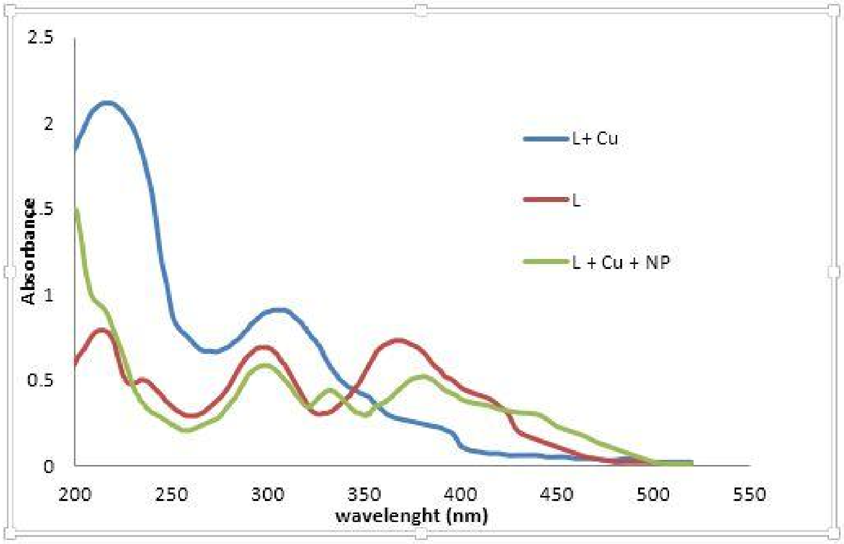


Figure 2. UV–Vis absorption spectra of EAMT, EAMT-Cu and EAMT-GNP-Cu.

Results and discussion

UV-Vis spectroscopy can explain the interaction between gold nano-particle and -S-H group of ligands. Figure 2 shows the UV-Vis spectrum of EAMT ligand along with a mixture of ligand-Cu ions and ligand gold nano-particles-Cu metal ions. As can be seen, in the absence of gold nano-particle the -S-H group of ligand can interact with Cu metal ions. Accordingly, the charge transfer peak appears in 220 nm and this peak disappears when the gold nano-particle is added to the mixture, this is so because–S-H group of lagand interact with gold nano-particles.

Complexation study

Complexation can actually be defined as a simple interaction between a donor (ligand) and an acceptor (substrate) [29]. The interaction of the proposed ligands with some metal ions was studied by spectroscopic method. For the evaluation of the formation constant from absorbance– mole ratio data, again the non-linear least-squares curve-fitting program KINFIT was used [30]. The formation-constant values (K_f) of the resulting 1:1 complexes were reported in Table 1. As can be seen from table 1 both Ligands EAMT and AAMT formed the most stable complex with Cu (II) ions which is expected to act as suitable ionophores for the fabrication of Cu (II) Selective carbon paste electrodes.

Composition and characteristics of the electrodes

Some important features of the carbon paste electrode, such the binder/graphite powder ratio, the nature and amount of ionophore, and especially, the nature and amount of the nano-material used, have been reported in order to significantly influence the sensitivity and selectivity of the ion-selective electrodes [31].

Thus, the influence of the type and amount of modifier, amount of gold nano-particle and the amount of oil on the potential response of the electrodes to Cu^{2+} ion activity were investigated and the results are summarized in Table 2.

Table 2. Optimization of the carbon paste ingredients (optimized values are **bold**).

Electrode No.	Ligand (mg)	Graphite powder (mg)	paraffin oil. (mg)	Nano-particle (µL)	Slope (mV/dec)	Linear range (mol l^{-1})	R^2
1	-	70	30	-	16.6	8.0×10^{-6}-3.1×10^{-2}	0.997
2	-	70	30	200	15.0	2.5×10^{-6}-1.5×10^{-2}	0.996
3	3 (1)	68	29	200	25.0	2.0×10^{-8}-2.2×10^{-2}	0.992
4	4 (1)	68	28	200	28.9	1.6×10^{-9}-6.3×10^{-2}	0.997
5	4 (1)	68	28	-	25.9	6.3×10^{-8}-1.6×10^{-2}	0.996
6	5 (1)	67	28	200	31.4	2.5×10^{-8}-1.8×10^{-2}	0.996
7	4 (2)	68	28	200	25.1	1.0×10^{-7}-2.0×10^{-2}	0.997
8	5 (2)	67	28	200	28.3	1.0×10^{-8}-2.1×10^{-2}	0.996
9	5 (2)	67	28	-	25.1	3.0×10^{-8}-2.0×10^{-2}	0.992
10	6 (2)	67	27	200	33.3	2.5×10^{-8}-5.0×10^{-2}	0.991

As seen, in the absence of mercapto compounds and gold nano-particle modifiers the electrodes have no response or low response towards copper ion (nos. 1 and 2). In addition, the electrodes without gold nano-particle and in the presence of non-self-assembled mercapto compound gave a limited working concentration range and relatively high detection limit (nos. 5 and 9). It is probably due to the self-assembled of the ionophores from –SH group to the gold nano-particles.

Besides, the gold nano-particles may lead to the expanding of the surface of paste by fabrication of three-dimensional nanostructures; besides, it may also diminish the Ohmic resistance of the paste. Accordingly, The obtained results– indicate that the best sensitivity, detection limit, and therefore, linear ranges can be reached for pastes with the following compositions (Figure 3). Number 4 with a EAMT/graphite powder/paraffin oil weightratio of 4.0/68.0/28.0 with 200µL of GNP have a slope of 28.9mVdecade^{-1} of activity and linear range 1.6×10^{-9} to 6.3×10^{-2}Mwith a detection limit of 2.9×10^{-10} M. Number 8 with a AAMT/graphite powder/paraffin oil weight ratio of 5.0/67.0/28.0 with 200µL of GNP have a slope of 28.3 mVdecade^{-1} of activity and linear range 1.0×10^{-8} to 2.1×10^{-2} M with a detection limit of 3.0×10^{-9} M.The equation line for nos. 4 and 8 elctrodes are:

$y= -28.898x + 291.17$

$R^2= 0.9996$ and $y= -28.228x + 239.03$ $R^2= 0.9961$

respectively, where in these equations y is cell potential in mV x is pCu and R^2 is regression coeeficient of line.All detection limits mentioned above are calculated from 3S/m equation, where S is blank standard deviation and m is calibration curve slope.

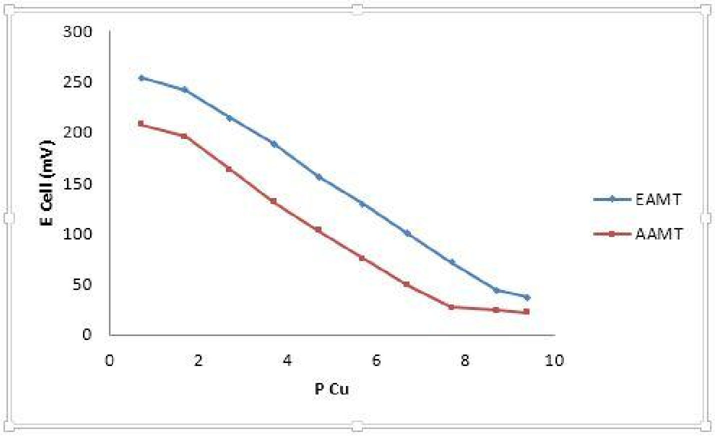


Figure 3. Calibration curves for Cu (II)–carbon paste electrode based on EAMT and AAMT at pH~ 4.0.

Selectivity studies

The selectivity behavior is obviously one of the most essential characteristics of an ion selective electrode, determining the feasibility of a reliable measurement in the target sample. In this work selectivity coefficients of the electrode towards different cationic species (M^{n+}) were evaluated by using of the matched potential method (MPM) [32, 33]. According to this method, a specified activity (concentration) of primary ion (A, 1.0×10^{-2} mol L^{-1} of Cu ions) is added to a reference solution (1.0×10^{-7} mol L^{-1} of Cu ions) and the potential is measured. In a separate experiment, interfering ions (B, 1.0×10^{-2} mol L^{-1}) are successively added to an identical reference solution, until the measured potential matches the one obtained before the primary ions addition.

Table 3. Selectivity coefficients of various interfering species for proposed sensors, calculated by MPM method.

Interference ion	$-LogK_{Cu,M}^{MPM}(EAMT)$	$-LogK_{Cu,M}^{MPM}(AAMT)$
Na^+	5.2	5.1
NH_4^+	4.9	4.9
Mg^{2+}	4.7	4.6
Al^{3+}	4.8	4.8
Fe^{3+}	4.7	4.6
Cr^{3+}	4.7	4.7
Ni^{2+}	3.6	3.2
Co^{2+}	3.9	3.0
Hg^{2+}	3.2	2.3
Zn^{2+}	3.5	3.1
Cd^{2+}	3.3	2.8
Pb^{2+}	3.8	3.1
Ag^+	3.0	2.1

The matched potential method selectivity coefficient, K_{MPM}, is then given by the resulting primary ion to interfering ions activity (concentration) ratio, $K_{A,B}^{MPM} = \dfrac{\Delta A_A}{\Delta A_B}$.

The resulting selectivity coefficients values are shown in Table 3.

The dependence of sensor's potential response was investigated over the pH range 2.0–8.5 for 1.0×10^{-4} M Cu (II) solution (Figure 4). The operational range was studied by varying the pH of the test solution with nitric acid or sodium hydroxide (0.1M). As can be seen from Figure. 3, the potential is independent of pH in the range 2.8-6.1 and 2.5–6.0 for sensor nos.4 and 8 based on EAMT and AAMT, respectively. Therefore, the same was taken as the working pH range of the sensor assemblies. The increase in potential below pH 2.5 is mainly due to the contribution of H^+ ions in transport mechanism over the Cu (II) ions. Similarly, when the pH is above 6.1, the contribution of OH^- ions which was observed as a precipitation of $Cu(OH)_2$, results in the reduction of potential.

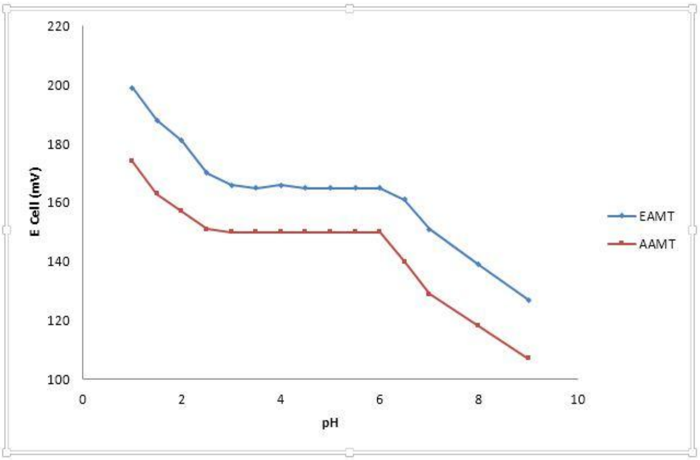


Figure 4. The pH effect of the test solution on the potential response of the proposed Cu^{2+} carbon paste electrodes.

Response time of the electrode

Generally, dynamic response time is an important factor for any sensor. The critical emf response of the electrode was assessed according to IUPAC recommendations. The average time required for the mentioned electrode to reach a potential within ±1mV of the final equilibrium value after successive immersion of Cu (II) ion solutions, each having a10-fold difference in concentration, was investigated. The measurements of potential versus time were carried out with the Cu (II) nitrate solutions from lower (1.0×10^{-7} M) to higher (1.0×10^{-3} M) concentrations (Figure 5).

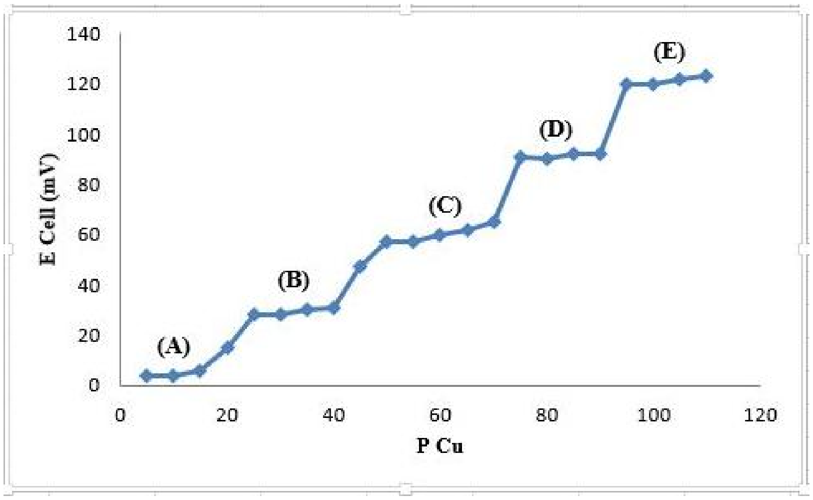


Figure 5. Dynamic response of the AMT-GNP carbon paste electrode for step changes in Cu^{2+} concentration: (A) 10^{-7} M, (B) 10^{-6} M, (C) 10^{-5} M, (D) 10^{-4} M, and (E) 10^{-3} M.

The electrode reaches equilibrium in about 5–10 s. As shown in Figure. 5, the response time increased to 10 s when the concentration was lowered to1.0×10^{-6}M because of the longer equilibration time. Whereas higher concentrations ($\geq5.0\times10^{-5}$ M) have response times of less than 5s due to fast exchange kinetics of the metal–ligand complexation-decomplexation at the surface of the paste.

Analytical applications

To further determine the analytical utility of the proposed sensor (no. 4), as an indicator electrode, the quantification of Cu^{2+}, has been carried out by potentiometric titration using EDTA as a titrant. Figure 6 shows a typical titration curve of Cu $(NO_3)_2$ solution with EDTA as titration reagent, which indicates that the end-point can be accurately determined by the proposed ISE.Furthermore, the proposed electrodes were utilized to extract and determine Cu^{2+} concentration in laboratory and tap water samples.Each sample was analyzed in triplicate and the analysis by sensors was repeated under identical conditions.The copper (II) concentration of the samples was determined using modified electrode based AMT ligand by the calibration plot method. The obtained results are given in Table 4.As could be seen, the relative recoveries for the spiked samples are in acceptable range (97.50–108.00%).

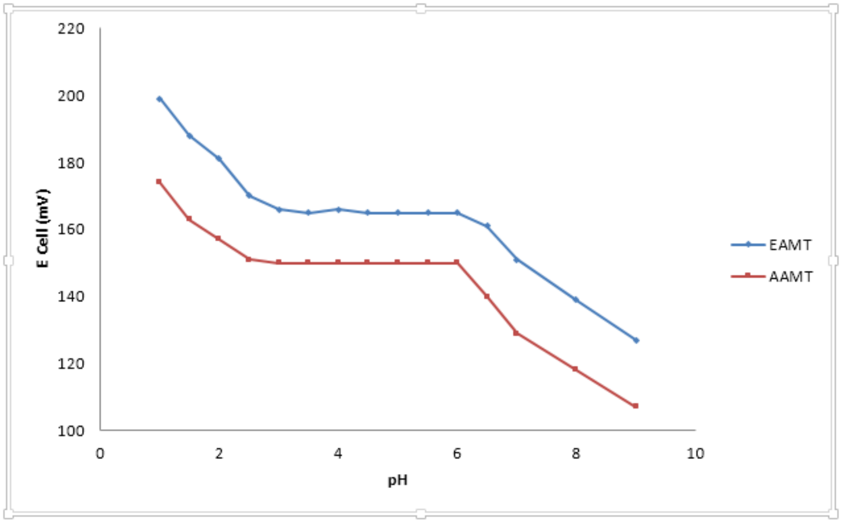


Figure 6. Potential titration curves of 25.0mL 1.0×10^{-4}M Cu (NO_3)solution with 1.0×10^{-2}M of EDTA.

Table 4. Recovery of copper ions from different water samples[a].

Sample		**Added Cu^{2+} (M)**	**Found (M)**	**Recovery %**
Lab. Water	1.	1.00×10^{-6}	$1.05(\pm0.04)\times10^{-6}$	105.00
	2.	1.00×10^{-5}	$9.75(\pm0.04)\times10^{-6}$	97.50
Tap water	1.	1.00×10^{-6}	$1.08(\pm0.04)\times10^{-6}$	108.00
	2.	1.00×10^{-5}	$1.02(\pm0.04)\times10^{-5}$	102.00

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

Conclusion

The proposed work describes the comparative study of 2-Ethylmino-5-Mercapto-1,3,4-Thiadiazole (EAMT) and 2-Acetylamino-5-mercapto-1,3,4-thiadiazole (AAMT) self assembled on gold nano-particle for construction of Cu^{2+} carbon paste sensors. The sensor no. 4 based on AMT ligand found to be more selective for Cu^{2+}. In the working range of 2.5×10^{-7} to 1.0×10^{-2} M copper (II), performs satisfactorily over wide pH range of 2.5–7.5 with a fast response time (10 s). The proposed sensor (no. 4) successfully used as an indicator electrode in the potentiometric titration of Cu $(NO_3)_2$with EDTA and finally was successfully employed to detect Cu^{2+} ion in some real sample.

Comparison study

In Table 5, some important characteristics of the proposed electrodes are compared with the corresponding values previously reported for Cu (II)-selective electrodes based on different modifiers [26,27, 34-36]. It is evident from this table that in many cases, the performances of the proposed electrode show superior behavior if compared with the best previously reported Cu (II) sensors.

Table 5. Comparison of the proposed Cu (II) selective electrode with the previously reported electrodes.

Refs.	Slope (mV Decade-1)	Detection limit (M)	Linear range (M)	pH range
26	31.0	4.1×10^{-9}	$7.9 \times 10^{-9} – 7.9 \times 10^{-4}$	2.5-7.0
27	29.1	4.0×10^{-7}	$4.3 \times 10^{-7} – 1.0 \times 10^{-2}$	3.5-6.0
34	28.7	1.0×10^{-9}	$4.0 \times 10^{-9} – 7.0 \times 10^{-2}$	3.0-6.5
35	30.0	1.6×10^{-7}	$1.0 \times 10^{-7} – 1.0 \times 10^{-1}$	3.0-9.0
36	28.8	6.3×10^{-7}	$2.0 \times 10^{-6} – 5.0 \times 10^{-3}$	3.0-8.0
This work	28.9	2.9×10^{-10}	$1.6 \times 10^{-9} – 6.3 \times 10^{-2}$	2.8-6.1
This work	28.3	3.0×10^{-9}	$1.0 \times 10^{-8} – 2.1 \times 10^{-2}$	2.5-6.0

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