Short communication

Direct electrochemical detection mechanism of ammonia in aqueous solution using Cu-decorated Si microelectrodes

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Abstract

Most of the reports on electrochemical ammonia detection with copper electrodes have been performed at pH 10 or higher. However, according to phase diagrams, no reactions take place between copper and ammonia under those conditions, qualifying such detection of ammonia as indirect. This short paper deals with the detection of ammonia concentration in the micromolar range through a direct mechanism at pH 9, using a Cu-decorated microstructured Si electrode. The reaction mechanism is thoroughly studied.

Keywords

Ammonia detection; electrochemical sensing; silicon nanowalls; copper nanoparticles; Cu complex

Introduction

Ammonia (NH_3) is a substance that can be found in aqueous systems and determining its presence and/or change in its concentration could be of vital importance to establish the state of a system. For example, low NH_3 concentration in urine may be indicative of kidney disease [1], while high concentrations of NH_3 in the blood of COVID-19 patients may indicate pre-existing liver damage [2], and high concentrations of NH_3 in saliva could be related to *Helicobacter pylori* infection [3]. For this reason, many reports have been devoted to developing technology for detecting and determining the concentration of NH_3 [4].

Electrochemical methods have received special interest due to the possibility of miniaturizing the equipment used in this method [5], which would allow testing at the sampling site. Among the electrochemical devices proposed to detect NH_3 in an aqueous solution, ones quite attractive because of their performance are electrodes containing copper nanoparticles (Cu NPs) [6-8]. Manufacturing Cu-based materials is easy [9], which favors the optimization of sensors, while a high exposed surface area resulting from nanostructures confers a good sensitivity. Also, one of the most important features is that Cu is a common material, significantly reducing fabrication costs [9].

Although Cu NPs-based electrodes can be used to detect NH_3 in an aqueous solution, little research has been devoted to exploring this possibility [6-8]. This may be because it is still unclear which electrochemical reactions allow the detection of NH_3 [6,7].

Mayo's group detected NH_3 with a Cu/graphite paste electrode using the cyclic voltammetry technique [8]. In that research, the change of current intensity corresponding to extreme values of potential of a voltammogram of an NH_3-containing solution was related to a change in its concentration. This was attributed to the oxidation of the cuprous complex (formed by NH_3 and Cu^+ ion), although the exact reaction is not shown [8]. In that report, the pH of the solution was not mentioned, which is important to establish the current species in the system.

In more recent works, such as that of Valentini's group, ammonia has been detected with copper nanoparticles in a linear concentration range (3-100 µM) [7]. The detection mechanism was attributed to the electrochemical oxidation of copper in the presence of ammonia. This work emphasized a need to oxidize the copper particles since the oxide layer favors this reaction, although the report did not show the chemical and/or electrochemical reactions in the system.

On the other hand, Yang's group detected ammonia with copper particles with a limit of detection of 1.25 µM [6]. The detection mechanism was attributed to the formation of a stable copper-ammonia complex by an electrodissolution process of copper. According to the reactions shown in that report, the electrochemical signal used for ammonia detection was attributed to the oxidation of copper to form the cupric hydroxide, which is chemically dissolved by ammonia to form the cupric complex.

Both Yang's and Valentini's groups mentioned that the competition between $Cu-NH_3$ and $Cu-OH^-$ reactions could be avoided if the ammonia solution pH was 10 [6,7]. According to phase diagrams for NH_3 concentration 10^{-3} M [10], $Cu-OH^-$ reactions are the most favorable at that pH. This means that even when the studies of the aforementioned groups have been successful in quantifying ammonia, the voltammetric and thermodynamic data indicate that at pH 10 no electrochemical reactions occur between Cu and ammonia [6,10]. Thus, the detection of ammonia at pH 10 can be qualified as indirect detection. This situation, however, could cause a misinterpretation of measured data because other substances present in the fluids to be analyzed (*e.g.,* sodium carbonate in saliva) can cause the same effect that ammonia has on the oxidation of copper to form cupric oxide [11].

In previous works, it was reported that at pH value of about 9 and NH_3 concentration of 10^{-3} M, $Cu-NH_3$ species (such as $[Cu(NH_3)_2]^+$ and a $Cu(NH_3)OH_{ads}$ layer) are formed electrochemically [10]. Thereby in this short work, we are focused on the possibility of detecting ammonia at pH 9 through linear sweep voltammetry (LSV) employing an electrode made of copper nanoparticles deposited on silicon nanowalls (Cu NPs/Si NW electrode). This new ammonia detection mechanism is based on the Pourbaix diagram calculated for ammonia concentrations in the micromolar range and involves a direct interaction between Cu and NH_3 with Cu nanoparticle-based electrodes. In addition, the effect of LSV scanning rate and ionic strength of the aqueous ammonia solution has been elucidated.
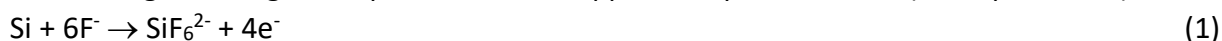
Experimental

Materials

For electrode fabrication, the following reagents were used: single-side polished p-type Si wafer with resistivity 15-25 Ω·cm and orientation (100), hydrofluoric acid (HF, 48 %, EMSURE), silver nitrate (AgNO_3, 99.8 %, Riedel-Härm), hydrogen peroxide (H_2O_2, 30 %, J. T. Baker), deionized water (18.2 MΩ·cm), polyethylene glycol (PEG, Aldrich Chemistry), and copper sulphate pentahydrate (CuSO_4·5H_2O, J.T.

Baker). The following reagents were employed to execute the voltammetry experiments: NaOH (Sigma-Aldrich), 2 M NH_3 solution in ethanol (Sigma-Aldrich), and deionized water (18.2 MΩ·cm).

Preparation of Cu NPs/Si NW electrode

Si nanowalls were prepared by metal-assisted chemical etching (MACE), as previously reported by our group [12]. First, a rectangular piece of Si wafer (1×2 cm) was rinsed with acetone in an ultrasonic bath. The Si sample was then rinsed with deionized water and dried with N_2. Subsequently, the Si sample was introduced into a solution composed of 25 ml $AgNO_3$ 0.005 M and 0.5 ml HF for 10 s at 30 °C to carry out the deposition of Ag NPs on the Si surface. Si sample was then placed in a solution of $HF : H_2O : H_2O_2$ with a 4 : 35 : 1 v/v composition for 5 min at 30 °C to etch the wafer and form Si nanowalls. Based on previous experiments in our laboratory, under these synthesis conditions, the silicon nanowalls layer has a thickness of approximately 5 µm. The thickness of the Si nanowalls must be less than 24 µm since there are reports about diffusion limitation of aqueous electrolytes into nanostructures when the depth is around 24 µm [13].

For the Cu NPs chemical deposition [14], the Si nanowalls sample was placed in a solution composed of 0.11875 g $CuSO_4 \cdot 5H_2O$, 0.5 ml HF, 99.5 ml deionized water and 2 g PEG for 5 min at 30 °C. Then it was rinsed with deionized water and dried with N_2 at room temperature. In this method, the fluoride ions (F^-) react with Si, causing Si to release electrons that reduce Cu^{2+} ions present on the Si surface, thus generating the deposition of the copper nanoparticles on Si (see Eqs. 1 and 2) [14].

$$Si + 6F^- \rightarrow SiF_6^{2-} + 4e^- \tag{1}$$
$$2Cu^{2+} + 4e^- \rightarrow 2Cu \tag{2}$$

Electrochemical detection

Linear sweep voltammetry experiments were performed in four different aqueous solutions: 0.01 mM NH_3 solution (pH 9), 6 mM NaOH solution (pH 10), 3 mM NaOH solution (pH 9) and a 0.006 mM NH_3 + 2 mM NaOH solution (pH 9).

NaOH solution pH 10 and NaOH solution pH 9 were used to distinguish the effect of pH on the electrochemical processes because, in the copper-ammonia-water system, the main reactions are associated with the interaction of copper and hydroxyl ions (OH^-) to form copper oxides and hydroxides. On the other hand, the NaOH solution pH 9 and the NH_3 solution pH 9 were used to discern the electrochemical processes involving NH_3 at this pH value and thus determine the peak of the voltammogram that allows the detection of NH_3. Finally, the NH_3/NaOH solution was used to study the effect of the supporting electrolyte on the peak voltammogram used for NH_3 detection.

Electrochemical experiments were controlled by a potentiostat/galvanostat (Zennium), interfaced with a PC running ThalesXT software. An electrochemical setup composed of a Teflon cell (as a container of the NH_3 solution) and a three-electrode system was used to obtain voltammograms (Figure 1).
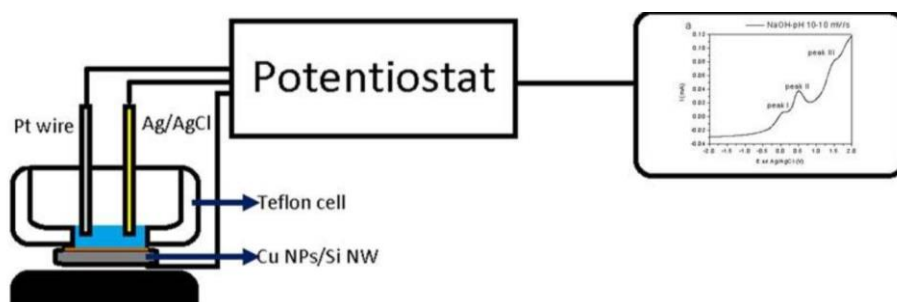

Figure 1. *Diagram of the electrochemical setup used for the experiments. The figure shows the cross-section view of the Teflon cell, having a container for the electrolyte of 0.78 cm³*

The counter electrode was a platinum wire (with a diameter of *ca*. 0.003 cm), and the potential of the working electrode was measured *vs*. the Ag/AgCl (sat. KCl) electrode (with a diameter of 0.2 cm). The Cu NPs/Si NW electrode was employed as the working electrode. Because of the design of the Teflon cell, the surface of the working electrode in contact with the ammonia solution was 0.78 cm^2 and the depth of the container was 1 cm.

To perform LSV experiments, 0.5 ml of solution was measured and put directly into the Teflon cell. Subsequently, the LSV experiment was started. The cell was washed with water after measuring each solution.

LSV was performed from -2.0 V to 2.0 V in NaOH solution at pH 10 and from -1.5 V to 1.5 V in the rest of the solutions, at sweep rates of 2, 5 and 10 mV s^{-1}. All potentials in this work were reported *vs*. the Ag/AgCl reference electrode. The intensity of the peaks in the voltammograms was measured by taking the intensity reading of the peak base (I_1) and peak tip (I_2) (Figure 2) and then subtracting these values (eq. 3).
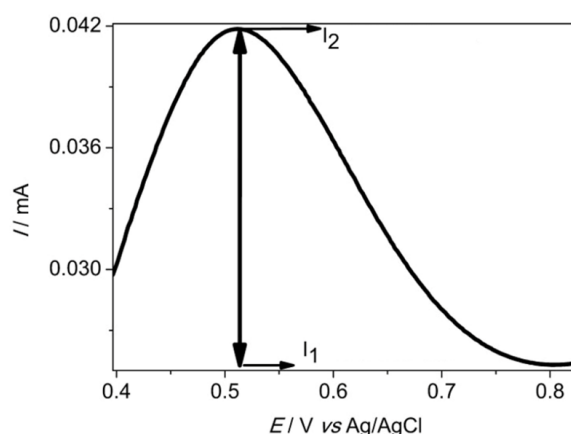
Peak intensity = $I_2 - I_1$ (3)

Figure 2. *Determination of LSV peak intensity*

Results and discussion

Figure 3 a-c shows linear sweep voltammograms (LSVs) of the Cu NPs/Si NW electrode in NaOH solutions, in which the effects of sweep rate and pH on the electrochemical reactions taking place in the Cu/NaOH system are analyzed.

At pH 10 and 10 mV s^{-1} (Figure 3a), three clear peaks are observed. Based on the shape of the voltammogram, these peaks can be associated with the following oxidation processes: peak I is related to the oxidation of metallic copper (Cu) to form cuprous oxide (Cu_2O) (see eq. 4 and 5) [15]. Peak II is attributed to the production of cupric oxide (CuO) from either oxidation of Cu or Cu_2O (see Eqs. 6-8) [15]. Peak III is assigned to the formation of soluble Cu species (see Eqs. 9-11) [15].
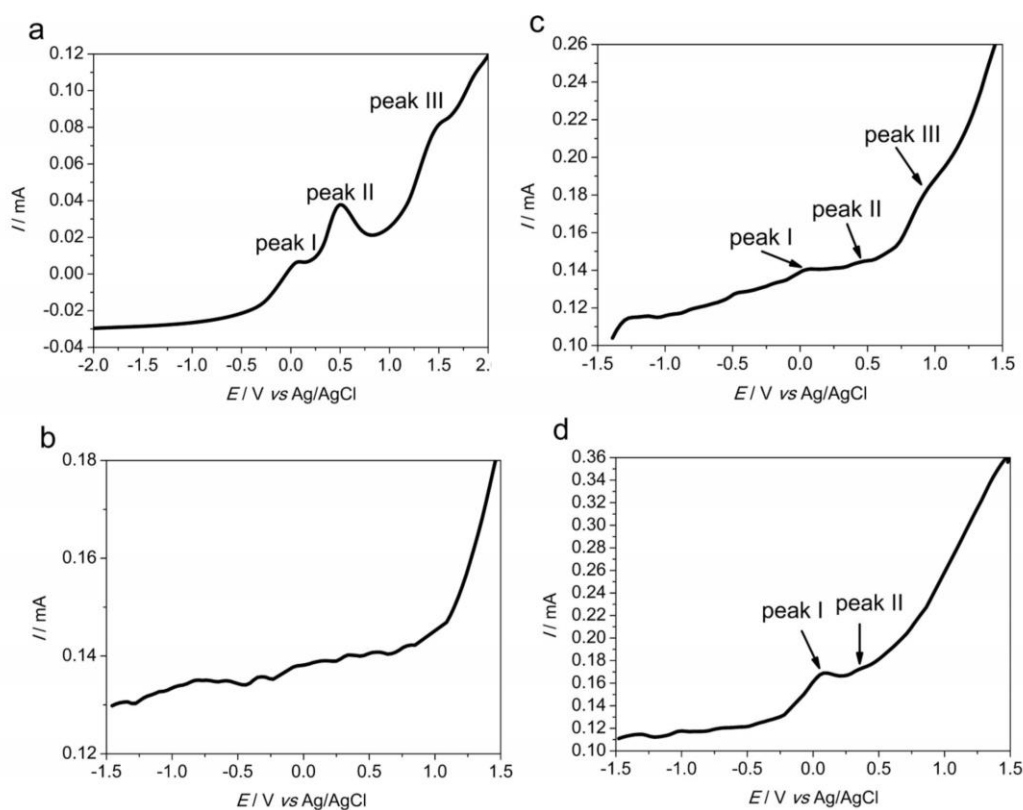
$Cu + OH^- \rightarrow CuOH + e^-$ (4)

$2CuOH \leftrightarrow Cu_2O + H_2O$ (5)

$Cu + 2OH^- \rightarrow Cu(OH)_2 + 2e^-$ (6)

$Cu_2O + 2OH^- + H_2O \rightarrow 2Cu(OH)_2 + 2e^-$ (7)

$Cu(OH)_2 \leftrightarrow CuO + H_2O$ (8)

$Cu + 3OH^- \rightarrow HCuO_2^- + H_2O + 2e^-$ (9)

$Cu(OH)_2 + 2OH^- \rightarrow CuO_2^- + 2H_2O + e^-$ (10)

$2CuO + 2OH^- \rightarrow Cu_2O_3 + H_2O + e^-$ (11)

Figure 3. *Linear sweep voltammogram of Cu/NaOH system (a) pH 10, sweep rate 10 mV s^{-1}, (b) pH 9, sweep rate 10 mV s^{-1}, (c) pH 9, sweep rate 5 mV s^{-1}, (d) Cu/NH$_3$ system, pH 9, sweep rate 5 mV s^{-1}*

In the study of the effect of sweep rate on electrochemical reactions in the Cu/NaOH system (Figures 3b and 3c), it is observed that peak III re-appears when the sweep speed is reduced. On the other hand, peak II is more intense than peak I at pH 10 compared with peaks I and II at pH 9 (see Table 1). This fact could be the evidence that at pH 10 two electrochemical reactions associated with peak II are contributing to the intensity of this peak (see Eqs. 6-8), while at pH 9 only one reaction is contributing to the intensity. It should be noted that these trends have been observed by other research groups [15]. Figure 3d shows the voltammogram of the Cu NPs/Si NW electrode in NH$_3$ solution at pH 9 and a sweep rate of 5 mV s^{-1}. In this voltammogram, two peaks are noted. According to previous work on NH$_3$ detection in aqueous solution [6], these peaks could be associated with the oxidation of Cu to form Cu$_2$O (see Eqs. 4 and 5), while peak II is assigned to two processes: the oxidation of Cu and Cu$_2$O to produce CuO (see Eqs. 6-8) [6].

In the comparison of the results of the Cu/NH$_3$ and Cu/NaOH systems, it is observed that in the Cu/NH$_3$ system, peak I increases its intensity by an order of magnitude compared to all the experiments of the Cu/NaOH system, while peak II has approximately the same intensity in both systems at pH 9 (see Table 1).

Table 1. *Experimental details and results produced by LSV analyses*

Solution	pH	Sweep rate, mV s^{-1}	Potential, V		Current intensity, mA	
			Peak I	Peak II	Peak I	Peak II
NaOH	10	10	0.0863	0.5047	0.00019	0.01660
NaOH	9	5	0.0799	0.4703	0.00016	0.00036
NH$_3$	9	5	0.0959	0.3519	0.00261	0.00034
NH$_3$	9	2	0.1236	0.4549	0.01010	0.00028
NH$_3$+NaOH	9	2	0.0198	0.4554	0.00008	0.0003
NH$_3$+NaOH	9	5	0.0626	0.5419	0.00149	0.00016

The significant increase in the intensity of peak I in the Cu/NH$_3$ system compared to the Cu/NaOH system could have two explanations: the first one is that this peak originated from more than one electrochemical reaction [10]. In addition to the formation of Cu$_2$O from the reaction between Cu and OH$^-$ ions (see Eqs. 4 and 5), reactions take place to form Cu-NH$_3$ complexes and a Cu(NH$_3$)OH$_{ads}$ layer (Eqs. 12 to 15), the latter being also reactive for the formation of Cu$_2$O (see eq. 14) [10]. This assumption is based on the phase diagram for NH$_3$ concentrations of 10^{-3} M. In this diagram, at pH close to 9, Cu-NH$_3$ species are stable.

$$Cu + NH_3 + H_2O \rightarrow Cu(NH_3)OH_{ads} + H^+ + e^- \tag{12}$$

$$Cu(NH_3)OH_{ads} + NH_3 \leftrightarrow [Cu(NH_3)_2]^+ + OH^- \tag{13}$$

$$Cu + Cu(NH_3)OH_{ads} \rightarrow Cu_2O_{ads} + NH_3 + H^+ + e^- \tag{14}$$

$$Cu + 2NH3 \rightarrow [Cu(NH_3)_2]^+ + e^- \tag{15}$$

Another possibility could be that NH$_3$ reacts chemically with Cu$_2$O after it is formed (eq. (16)) [16]. This fact favors electron transfer increasing the peak intensity, a similar effect to that reported by Yang's group [6].

$$Cu_2O + 4NH_3 + 2H^+ \rightarrow 2[Cu(NH_3)_2]^+ + H_2O \tag{16}$$

At pH 9 the intensity of peak II is similar in the Cu/NH$_3$ and Cu/NaOH systems. From these results, it could be proposed that this peak originated only by reactions between Cu and OH$^-$ ions (Eqs. (6) to (8)), ruling out any direct or indirect interaction between NH$_3$ and Cu, as has been reported in the Cu/NH$_3$ system at pH 10 [6,7].

The effect of the voltage sweep rate on the electrochemical reactions of the Cu/NH$_3$ system was also analyzed (Figure 4). It can be observed that peak I increases in intensity by one order of magnitude while peak II maintains approximately the same intensity as the sweep rate is reduced from 5 to 2 mV s^{-1} (Table 2). The reduction in the intensity of peak I as the sweep speed increases may indicate that the electrochemical reaction between Cu and NH$_3$ is diffusion controlled due to the low concentration of NH$_3$.
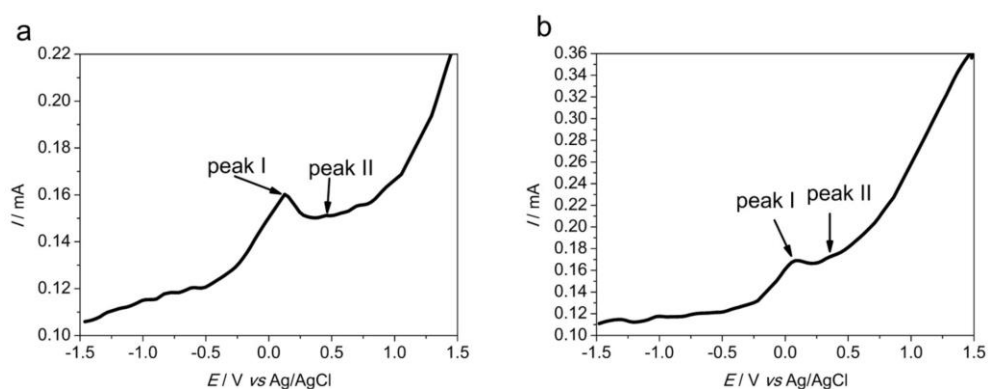

Figure 4. *Voltammogram of Cu/NH$_3$ system at pH 9 and (a) 2 mV s^{-1} and (b) 5 mV s^{-1}*

The increase in the intensity of peak I was not observed in the Cu/NH$_3$ system at pH 10 [6] because increasing the concentration of OH$^-$ ions favors the formation of CuOH (see eq. 4) over the generation of Cu(NH$_3$)OH$_{ads}$ layer (see eq. 12) [10].

Figure 5 shows the voltammograms of the Cu NPs/Si NW electrode in the NH$_3$+NaOH solution at pH 9, which has a higher ionic strength than NH$_3$ solutions due to the presence of Na$^+$ ions. It is noted that as the sweep speed decreases, the intensity of peak I (associated with the formation of the Cu(NH$_3$)OH$_{ads}$ layer) is reduced. This phenomenon may be caused by the presence of Na$^+$ cation in the solution since this cation is solvated by NH$_3$ molecules [17], which generates that NH$_3$ is part of a

complex whose mobility in the solution is lower compared to the mobility of the individual NH_3 molecule due to the size difference [18]. This phenomenon was observed in previous reports in which carbonate and borax buffer solutions (both solutions containing Na^+ cations) were used as supporting electrolytes [8,9], but in these reports, the phenomenon was related only to chemical reactions between the NH_3 molecules and the carbonate and borate anions. In this work, the supporting electrolyte (NaOH) does not contain anions that can react with NH_3 or ammonium ions NH_4^+, although the same phenomenon is observed. Future research should analyze the use of supporting electrolytes that do not contain cations that form complexes with NH_3 or are solvated by NH_3.
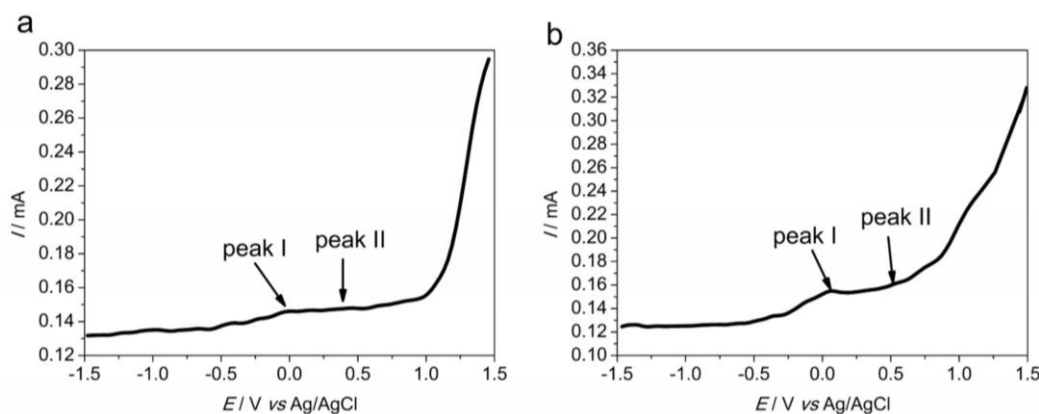

Figure 5. *Voltammogram of Cu NPs /Si NW electrode in NH_3+NaOH solution at pH 9 at (a) 2 mV s^{-1} and (b) 5 mV s^{-1}*

Conclusions

In this work, the electrochemical detection of ammonia, present in the micromolar concentration range in an aqueous solution at pH 9, was carried out using an electrode made of copper nanoparticles deposited on silicon nanowalls. At pH 9, the signal that could be used for detecting NH_3 is associated with the electrochemical reactions between Cu-NH_3 to form Cu-NH_3 complexes and $Cu(NH_3)OH_{ads}$ layer. This signal is more reliable than the one used in the usual detection of NH_3 at pH 10, where signal increment is related to the chemical reaction between Cu and NH_3. In other words, the electrochemical detection of NH_3 at pH 10 is indirect, whereas at pH 9 the detection is the result of the direct electrochemical interaction between Cu and NH_3. According to LSV at different voltage sweep rates, it was observed that at speeds larger than 2 mV s^{-1}, the intensity of the signal that could be used for NH_3 detection reduces because the electrochemical reaction between Cu and NH_3 is diffusion-controlled due to the low concentration of NH_3. Finally, the reduction of the intensity of the signal in the presence of NaOH is related to the interaction between Na^+ and NH_3 in the solution.

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