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ARTICLE

GOLD CLUSTERS BASED ELECTROCATALYTIC SENSOR FOR THE DETECTION OF FORMALDEHYDE

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The development of an electrochemical sensor for the analysis of formaldehyde, based on the use of a screen printed carbon electrode modified with gold clusters, is reported in this work. The electrocatalytic properties of the gold clusters enabled the voltammetric detection of formaldehyde, taking place at potentials around +0.3 V (vs. Ag pseudo-reference electrode), at concentration levels down to 1mM in 0.1 M NaOH electrolyte solution. A two-step oxidation process was observed, which could be ascribed to the oxidation of this chemical species to produce gem-diol ion and formate. The effect of the gold cluster density on the electrode surface was evaluated. The sensor responded to formaldehyde in a concentration range from 1mM to 10mM, the estimated limit of detection being 0.9 mM. The developed sensor was eventually applied to the detection of formaldehyde in tap water. No interference from glucose, formic acid, methanol or ethanol in the analytical sensor signal was observed.

Introduction

For over 30 years there have been studies where formaldehyde has been considered a hazardous contaminant[1], but it was not until 2006 that the International Agency for Research on Cancer (IARC) classified it as carcinogenic to humans[2]. Since then, numerous research reports have shown new results about the adverse effects of formaldehyde in human health[3,4].

Formaldehyde is present in the aquatic system because of its high water solubility. In fact, it has been detected in rain water, fog and ice samples, for which classical methods of analysis were used. Those most widely applied are UV-Vis spectroscopy, and gas and liquid chromatographic techniques [5,6]. However, in recent years analytical devices that yield results more quickly and without using large and costly equipment have been developed. Among them, chemical sensors based on electrochemical transduction modes have shown the potential to be applied in the detection of this hazardous species. Besides, combining the versatility of electrochemical techniques with the implementation of screen printed electrodes, results in the development of low-cost devices for the in-situ analysis of a wide variety of target analytes[7].

Most of the electrochemical sensors for airborne and waterborne formaldehyde detection, reported so far make use of biomolecules[8] or electrocatalysts such as platinum, palladium, or gold as recognition elements[9–11]. Platinum sensors have been made for this purpose by using monocrystals, polycrystalline disks and nanoparticles[12–15]. Nanoparticles have also been used to elaborate palladium sensors by incorporating them onto different supports like carbon nanotubes or titanium oxide [16,17]. Other sensor approaches combine Pd and Pt catalysts [18] because of the well-known synergistic catalytic activity of both metals. A common drawback of all these sensor approaches is the surface fouling and in turn passivation that they easily undergo[12,16,19,20]. In an investigation accomplished by Enyo et al. [21], a comparative study of the catalytic activity of Pt, Pd and Au for the formaldehyde oxidation, concluded that Au showed the highest catalytic activity and was less affected by surface fouling processes.

Gold electrodes were applied in the 1980's by Beltowska [22] and Avramov-Ivic et al. [23], and more recently by Yan and Jin in 2013[24] to elucidate the oxidation mechanism of formaldehyde. One of the earliest studies conducted on gold nanostructures was performed by Yahikozawa et al. in 1992. They found a higher catalytic activity than that reported with the bulk material[25]. Besides, more recent reports showing the size dependent catalytic activity of gold are drawing the attention to the synthesis and study of even smaller particles, such as nanocluster arrangements[26,27]. In this context, the catalytic properties of gold clusters have been exploited in the fabrication of an electrochemical sensor for the ultra-trace determination of mercury[28].

In this work we present the development of an electrochemical sensor that incorporate catalytic gold clusters readily deposited on a screen printed carbon electrode, and its thorough analytical characterization for the detection of formaldehyde in aqueous samples.

Experimental

Sodium hydroxide of analytical grade was purchased from Sigma Aldrich. Formaldehyde 37% solution stabilized with 10-

15% of methanol was obtained from J.T. Baker. Formaldehyde standard solutions were prepared by using 0.1 M NaOH as background electrolyte solution and deionized water. Tap water samples from Barcelona (Spain) municipal water system were spiked with 5 mM formaldehyde and its ionic conductivity adjusted with NaOH in order to get a 0.1 M NaOH in the final solution.

In order to test the sensor chemical cross reactivity, solutions of 5 mM glucose, 5 mM methanol, 5 mM ethanol and 5mM formic acid were prepared.

DRP-110 screen printed electrochemical cells were from DropSens, S.L. (Oviedo, Spain). They comprise a 4-mm diameter carbon working electrode, a carbon counter electrode, and a silver pseudo-reference electrode, all of them printed on a ceramic substrate.

Gold cluster suspensions containing 0.02 mg/mL Au, stabilized using a polyelectrolyte (proprietary information), were provided by Goldemar Solutions S.L.[29] The gold clusters were deposited by drop casting on the screen printed working electrode. 15μL drops were deposited with the aid of a micropipette and the process was repeated several times in order to get the desired Au quantity (0.6, 1.2, 1.8 and 3 μg) on to the working electrode surface. Drops were allowed to dry in air between every deposition.

Electrochemical measurements were performed using a μStat 400 DropSens potentiostat. Cyclic voltammetric experiments were carried out in a potential window from -0.2 V to 0.8V at a scan rate of 0.05V/s. All potentials were measured against the integrated Ag pseudo-reference screen printed electrode.

The surface analysis was carried out in a cross-beam workstation Zeiss Neon 40, Scanning Electron Microscope (SEM). Finally HRTEM images were acquired using a JEOL JEM-2011 microscope operated at 200 kV.

Results and Discussion

The SEM image of a screen printed sensor surface is presented in Figure 1. Figure 1a presents the image of the working electrode after deposition of 1.8 μg of gold cluster.
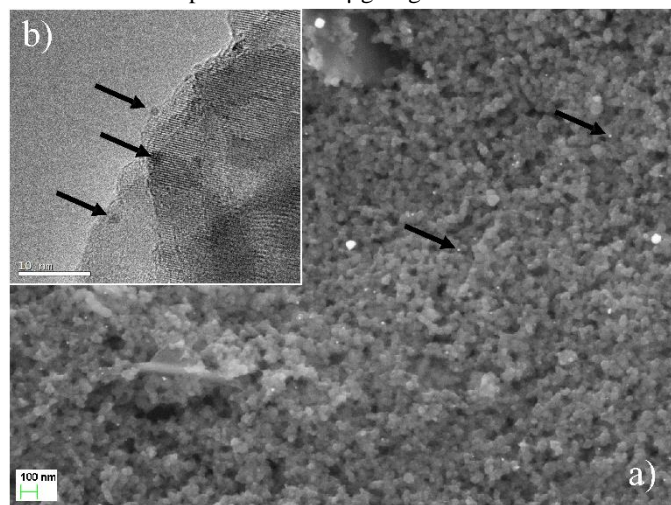

Figure 1. SEM image of the sensor decorated with gold clusters (1a), TEM image of the clusters (1b).

Little shiny points of clusters agglomerated particles are clearly observed. Such clusters are better appreciated in the TEM image of Figure 1b, in which a cluster size of about 2-3 nm is shown over a TiO_2 surface used as a support.
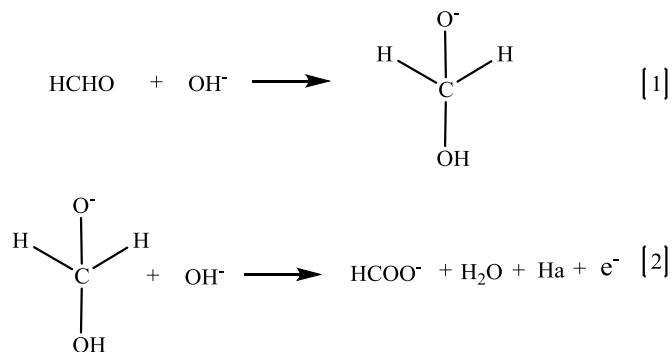
The sensor voltammetric responses to different concentrations of formaldehyde are shown in Figure 2. Two anodic peaks are
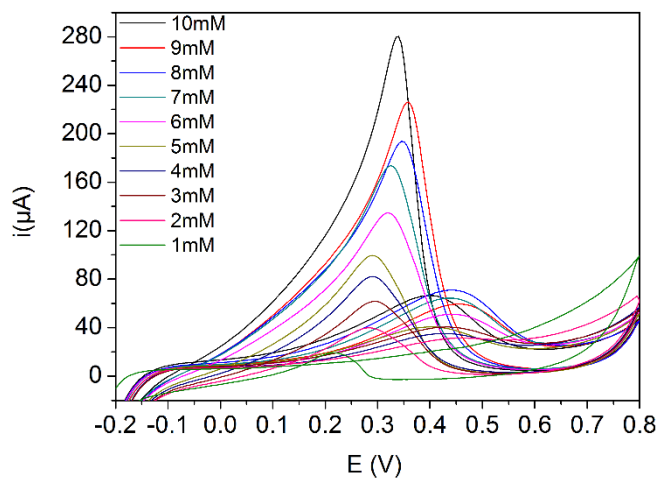
clearly visible, one at + 0.43 V in the forward scan and another one at +0.3 V in the reverse scan.

Figure 2. Cyclic voltammetry responses of an electrochemical sensor fabricated by depositing 1.2 μg of gold clusters, recorded in 0.1 M NaOH solutions

The electrochemical oxidation of formaldehyde has widely been studied. Adzic et al. proposed a pathway involving the formation of a gem-diol anion in solution, which undergoes an electrochemical oxidation to produce a formate ion[30]. Adzic's study was based on the report by Barnes and Zuman, which shows the detection of the presence of the gem-diol in a formaldehyde solution using polarography technique [31]. Also, this was supported by other authors using other analysis techniques, such as in situ rapid-scan time-resolved IR spectroelectrochemistry[24]. Later, in 1999 Yang et al. proposed a subsequent oxidation of the formate species to CO_2 on the surface of an Au electrode[32]. Following these reports, the reactions that may take place on the electrode surface and are electrocatalyzed by the gold clusters are the following:

$$HCHO + OH^- \rightarrow \underset{OH}{\overset{O^-}{\underset{|}{\overset{|}{C}}}}\overset{H}{\underset{H}{}} \quad [1]$$

$$\underset{OH}{\overset{O^-}{\underset{|}{\overset{|}{C}}}}\overset{H}{\underset{H}{}} + OH^- \rightarrow HCOO^- + H_2O + Ha + e^- \quad [2]$$

Thus, the peak observed in the forward scans can be ascribed to the gem-diol oxidation (equation 1) whereas that one recorded in the reverse scan can be due to the formate oxidation (equation 2).

Also is shown in Figure 2 the increase in the peak current response when the formaldehyde concentration in solution was increased from 1 mM to 10mM. By using the peak current of the anodic peak recorded at + 0.3 V as the sensor analytical signal, a calibration curve was plotted that showed a linear concentration range of 1-10mM, with the sensitivity and the estimated limit of detection (LOD) being 28µA/mM and 0.93mM, respectively.

The same study was repeated with electrochemical sensors containing different amounts of gold clusters (i.e. 0.6, 1.2, 1.8 and 3 µg of the stock solution were deposited on the carbon electrode) respectively. All of them showed an electrocatalytic response to formaldehyde. Figure 3 shows the corresponding calibration curves.
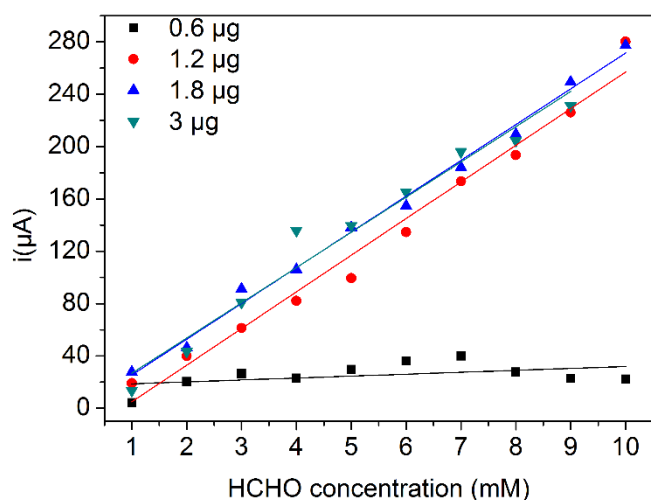

Figure 3. Plot of the maximum oxidation current against the concentration of formaldehyde solution.

The sensor fabricated using 0.6 µg of gold clusters shows a poor sensitivity for the detection of the target analyte. On the other hand, it is also shown that those sensors fabricated with 1.2, 1.8, and 3 µg of gold clusters exhibit a very similar analytical performance. This could be attributed to some aggregation issues that may have taken place during the electrode performance. It is well known that the gold catalytic activity is very size dependent[26]. When the gold concentration present on the electrode increases, an aggregation phenomenon

can occur, and thus the particle size increases upon the application of the potential scan during the analysis.

Therefore, the use of 1.2 µg of the gold stock solution was set to be optimum to get the desired sensing response. Formaldehyde concentrations above 10 mM were also tested (Figure 2). Although the sensor was able to detect them, the oxidation peaks shifted to more positive potentials and were considered to be not reliable for analytical purposes. The

Table 1. **Analytical characteristics of the elaborated sensors.**

Amount of Au (µg)	Sensitivity (µA/mM)	R^2	LOD (mM)
0.6	2.27	0.2828	8.283
1.2	28.01	0.9776	0.93
1.8	27.34	0.9930	0.518
3	26.91	0.9638	1.15

analytical characteristics of the sensors are shown in Table 1.

The lowest limit of detection achieved with this Au cluster-screen printed electrochemical device, is similar to that previously reported using a palladium screen printed microelectrode, which was presented by Metter in 2013, and showed a LOD of 1.6mM but no lineal response to this target analyte [9]. Also, there are some reports of other non-enzymatic sensor approaches for the detection of formaldehyde in aqueous media, that showed lower LOD, but whose architectures or fabrication methods appeared to be more complex and not that straightforward as the one shown in this work [10,17,18]. In Table 2, the analytical parameters of these previously reported devices together with the electrode architecture are given. , the sensor that exhibits the smaller LOD, involves fabrication process with multiple steps, which is a disadvantage for escalation to a mass production.

To the best of our knowledge, the LOD values presented in this work have not been achieved with other non-enzymatic nanostructured gold based electrochemical sensors. Moreover this sensor is capable to perform up 160 analyses without losing sensitivity.

The selectivity of the sensor was evaluated in solutions containing 5 mM concentrations of formic acid, ethanol, methanol, and glucose. Figure 4 shows the voltammetric responses recorded with the sensor. The response is negligible in all cases and just for the case of glucose a small signal in the reverse scan could be seen. From these results, it can be affirmed that the here reported sensor show no interference with this known interfering analyte.

Table 2. Non-enzymatic electrodes for formaldehyde sensing in aqueous media

| Electrode composition	Electrolyte (M)	Lineal range (mM)	LOD (mM)	Reference
Pd nanoparticles /TiO₂	0.1 NaOH	0 to 17.7	0.015	[17]
Pd nanoparticles/Carbon ionic liquid composite electrode.	0.1 NaOH	20 to 100	-	[33]
Pd nanowire/GCE.	0.1 KOH	$2.0e^{-3}$ to 1	0.0005	[10]
Pt/PANI/MWCNT/Ch/WGE.	0.5 H₂SO₄	$1e^{-6}$ to 1	$4.6e^{-8}$	[34]
Pt-Pd/Nafion/GCE.	0.1 H₂SO₄	0.01 to 1	0.003	[18]
Pd/Screen Printed Electrode.	0.1 KOH	2.5 to 6.5	1.6	[9]
This work	0.1 NaOH	1 to 10	0.9	
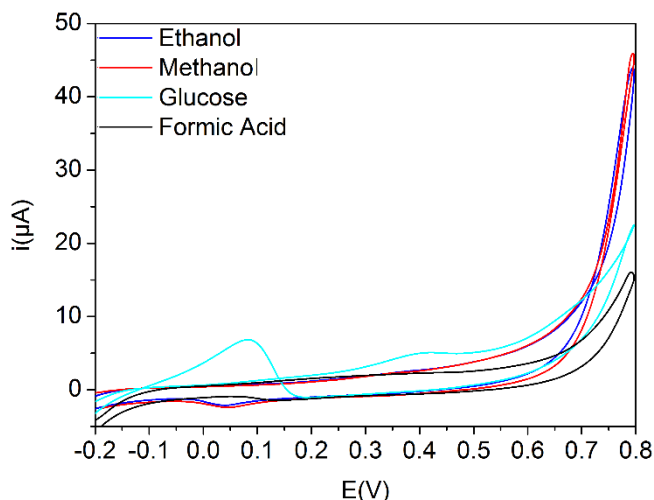
Figure 4. Cyclic voltammetry signals recorded with the electrochemical sensor prepared with 1.2 µg of the gold clusters against different possible interfering agents.

As an approach to a real sample assay, the sensor was tested with two different solutions containing formaldehyde 5mM, one prepared with deionized water and the other one with tap water. Figure 5 shows the sensor voltammetry response recorded in each solution. A shift of the peak potential to more negative values may be related to the matrix composition that also has an effect on the potential set when using a pseudo-reference electrode. Nevertheless, the peak currents are nearly the same, which indicates that the sensor was not affected by the tap water composition.
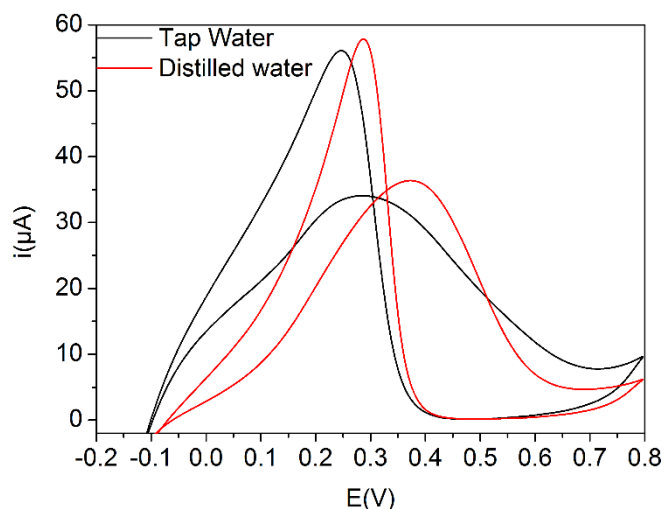

Figure 5. Voltammetry response of the 1.2 µg sensor to two solutions containing formaldehyde 5mM, one prepared with tap water and another with distilled water.

Conclusions

Based on the catalytic properties of gold clusters and using a simple synthesis technique, a gold cluster modified screen-printed sensor was fabricated. The sensor is able to detect formaldehyde in aqueous solutions with a detection limit of 0.9mM. The sensor response did not show any interferences from other organic compounds such as methanol, ethanol, formic acid and glucose. The low cost and simplicity of this technology make it suitable for the fabrication of electrochemical sensors, which could be implemented in automatic analysis systems and be applied to the in situ analysis of this hazardous species.

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Notes and references

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