

Research Article

Modification of Gold Surface with Gold Nanoparticles and Cyclohexyl Dithiocarbamate as a Selective Sensor for Cysteine

Ehab AlShamaileh,^{1,2} Haytham Saadeh,¹ and Valerie Favry²

¹ Department of Chemistry, Faculty of Science, The University of Jordan, Amman 11942, Jordan

² Faculty of Sciences and Humanities, Salman bin Abdulaziz University, Al-Kharj 11942, Saudi Arabia

Correspondence should be addressed to Ehab AlShamaileh; ehab@ju.edu.jo

Received 21 November 2012; Accepted 5 December 2012

Academic Editor: Concha Gimeno

Copyright © 2013 Ehab AlShamaileh et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The self-assembly of cyclohexylamine dithiocarbamate (C₆DTC) on gold (Au) and gold nanoparticles (AuNPs) was studied electrochemically using cyclic voltammetry (CV). Cyclic voltammetry was used to study the system Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ at the electrode surface of (C₆DTC/Au) and (C₆DTC/AuNPs). The application of the resulting chemically modified surface as a selective sensor for cysteine, among other amino acids, was investigated. Linear oxidative desorption technique was used to characterize the modified electrode that consists of the self-assembled monolayer of cyclohexylamine dithiocarbamate on gold nanoparticles deposited on Au electrode (C₆DTC/AuNPs/Au). The results showed an enhancement in the oxidation peak of cysteine on the modified electrode and hence a greater sensitivity.

1. Introduction

Dithiocarbamate derivatives have been extensively studied due to their antimicrobial activity [1] and the various applications in industrial and chemical processes, such as vulcanization accelerators [2], flotation agents, fungicides [3], pesticides [4], and corrosion inhibitors [5]. One of the most interesting properties of dithiocarbamates is their strong metal-binding ability and the ease to form self-assembled monolayers (SAMs) on gold surfaces making them useful to many applications. The structural features of SAMs on gold surfaces are dictated by two major factors: the sulfur-gold interaction and the organic interchain interaction. It has been shown that both sulfur atoms in the headgroup of a dithiocarbamate chemically bond to the surface of gold [6].

Owing to their large surface area and biocompatibility, many nanostructured materials represent a powerful detection platform for a broad range of sensors including biological, electrochemical, gas, optical, pH, and molecular orientation. The sensing devices may include individual nanostructured sensors, multi-nanostructured sensors, nanostructured film sensors, and others. These nanosensors have a number of key features, including high sensitivity,

exquisite selectivity, fast response and recovery, and potential for integration of addressable arrays on a massive scale, which set them apart from other sensors technologies [7, 8]. Many researchers agree that more development is needed at the molecular level of detection to improve miniature and nanosensor devices.

Cysteine (2-amino-3-mercaptopropionic acid) is a biologically important substance in living systems and its oxidized form (cysteine) is utilized as a model of the thiol group in proteins. Cysteine, mainly the L-enantiomer, is a precursor in the food, pharmaceutical, and personal care industries. One of the largest applications is the production of flavors. For example, L-cysteine is used as a processing aid for baking while the reaction of cysteine with sugars yields meat flavors [9].

Very little research targeted the selective sensing of cysteine due to difficulties arising from the structural similarity with α -amino acids and peptides (carboxylic and amino groups). The need to improve the sensing selectivity of cysteine is therefore obvious. Dithiocarbamates attached to gold nanoparticles have already been tested in the electrochemical sensing for dopamine and ascorbic acid [10].



FIGURE 1: A photograph showing the three-electrode setup where the visible light red color electrode is the surface of the nanogold electrode (AuNPs/Au).

In this paper, cyclohexylamine dithiocarbamate is self-assembled onto gold (Au) and nanogold (gold electrode with adsorbed gold nanoparticles; AuNPs/Au) and the chemically modified electrode was tested as a sensor for several aminoacids including cysteine.

2. Experimental

2.1. Chemicals. Cyclohexylamine was purchased from Aldrich (99%), sodium hydroxide NaOH (Aldrich), carbon disulfide CS₂ (97%) and ethanol, absolute (99%), sulfuric acid H₂SO₄ (98%), potassium ferrocyanide (K₃Fe(CN)₆) (99.0%), potassium chloride (99.9%), HAuCl₄ (99.9%) and ammonium peroxydisulfate (NH₄)₂S₂O₈ (99%) were all of analytical grade and used as received. All solutions were prepared with triply distilled water.

2.2. Instrumentation. Cyclic voltammetry experiments were carried out with a VoltaLab PGZ 100 potentiostat in a double-wall three-electrode glass cell under nitrogen (Figure 1). Solutions were degassed with ultrapure nitrogen for about 20 minutes before electrochemical measurements. The working electrode (WE) was a gold polycrystalline electrode embedded in a glass tube with a surface diameter of 3.0 mm. Prior to measurements, the surface of the working electrode was carefully polished with alumina slurry, rinsed several times, and then sonicated for about 1 minute. Afterwards, the electrode was electrochemically cleaned in 0.5 M H₂SO₄ until a stable and acceptable gold oxidation/reduction CV was obtained.

All reported potential values are versus the SCE reference electrode and all measurements were carried out at around 20°C. A platinum wire was used as the auxiliary electrode. Solutions' pH values were measured with a Hanna calibrated digital pH meter (Switzerland).

All glassware for electrochemical experiments were carefully cleaned by immersion in a solution of concentrated sulfuric acid containing ammonium peroxydisulfate (NH₄)₂S₂O₈ for 10 hours followed by copious rinsing with deionised and triply-distilled water.

2.3. Synthesis of Cyclohexyl Dithiocarbamate (C₆DTC). The sodium salt of cyclohexyl dithiocarbamate (C₆DTC) was synthesized as reported in the literature with modification [11]. To summarize, the C₆DTC was prepared by reacting cyclohexylamine with an equimolar ratio of CS₂ and NaOH solutions in an ice bath. To 0.1 M of NaOH, dissolved in minimum water, cyclohexylamine in 50 mL of ethanol (0.1 M) was added. After thorough stirring, an ethanolic solution of 0.1 M CS₂ was added drop wise. The reaction was stirred for 1 hour at 0–5°C followed by another hour at ambient temperature (~22°C). The solid product was filtered and washed with cold water/ethanol solution giving a white product which is then recrystallised from ethanol (yield = 60%, m.p ~ 130°C). IR/cm⁻¹: 3350 (–OH), 3200 (–NH), 1480 (C–N), and 990 (C=S).

2.4. Preparation of the Nanogold Electrode (AuNPs/Au). The Au electrode surface was freshly polished prior to use with 0.05 μm α-Al₂O₃ slurry, and rigorously rinsed with doubly distilled water. The electrode was successively ultrasonically rinsed with 98% H₂SO₄ and 95% ethanol and distilled water for 10 minutes, dried with nitrogen gas, and then electrochemically cycled in 1.0 M H₂SO₄ until a stable gold oxide formation/reduction CV was obtained (Figure 2(a)). The electrode was then immersed into 3 mM HAuCl₄ solution containing 1.0 M H₂SO₄ solution as an electrolyte, and electrochemical deposition of gold nanoparticles was conducted by the electrochemical scanning the electrode between a potential of –200 mV and –190 mV (versus SCE) for a selected number of times at a scan rate of 10 mV/s. The electrode surface showed a very visible light red color indicating the presence of gold nanoparticles as shown in the photograph in Figure 1. We call the resulting surface the nanogold electrode (AuNPs/Au). After experiments, the electrode was regenerated by soaking it in piranha solution (a mixture of 3 : 7, v/v of 30% H₂O₂ and 98% H₂SO₄) overnight and then rinsing it with 95% ethanol and distilled water followed by drying in a stream of nitrogen gas.

2.5. Preparation of C₆DTC-SAMs on the Gold Electrode (C₆DTC/Au). The electrode was initially cleaned in the same way described in 2.4 above. The C₆DTC/Au were prepared by immersing the gold electrode in freshly prepared aqueous solutions of 1.0 mM of cyclohexyl dithiocarbamate (C₆DTC) solution at ambient temperature for 6 hours followed by another 6 hours in triply distilled water to remove any physically adsorbed molecules. The electrode was then rinsed with water and dried in a stream of nitrogen gas.

2.6. Preparation of the C₆DTC-Modified Nanogold Electrode (C₆DTC/AuNPs/Au). The electrode was cleaned and nanogold was deposited as described in 2.4 above. The self-assembly of C₆DTC was accomplished with the immersion of the electrode into a freshly prepared 1 mM C₆DTC aqueous solution for 24 h in the dark at room temperature. The modified electrode was then taken out, soaked in triply distilled water for 6 h, and finally dried in a stream of nitrogen gas.

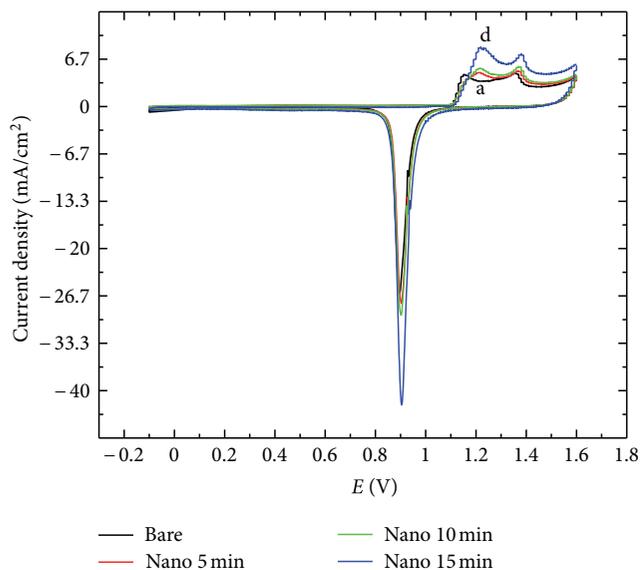


FIGURE 2: Cyclic voltammograms of (a) bare gold electrode, (b) nanogold electrode with deposition time of 5 min, (c) nanogold electrode with deposition time of 10 min, and (d) nanogold electrode with deposition time of 15 min. Electrolyte: aqueous 1.0 M H_2SO_4 solution. Scan rate = 50 mV/s.

3. Results and Discussion

This section is divided into three parts. In the first part, the $(\text{C}_6\text{DTC}/\text{Au})$ and $(\text{C}_6\text{DTC}/\text{AuNPs}/\text{Au})$ are investigated using cyclic voltammetry. The redox system of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ is studied on both electrodes using cyclic voltammetry in the second part. Finally, the C_6DTC -modified nanogold electrode, $\text{C}_6\text{DTC}/\text{AuNPs}/\text{Au}$, is tested for the electrooxidation of cysteine.

3.1. Cyclic Voltammetry of the Electrode Surface of $(\text{C}_6\text{DTC}/\text{Au})$ and $(\text{C}_6\text{DTC}/\text{AuNPs}/\text{Au})$. Figure 2 shows cyclic voltammograms (CVs) of the bare gold electrode and nanogold electrodes in deoxygenated 1.0 M H_2SO_4 solution. The nanogold particles were deposited at 5, 10, and 15 minutes. We noticed that further deposition (over 15 minutes) resulted in CVs different from that for the polycrystalline gold mainly with extra and sharper peaks. We chose the 5-minute modification time in all experiments to eliminate any complications that may result from producing different surfaces at different deposition times. We also noticed that more deposition deepens the color of the electrode and makes it more difficult to regenerate to a clean gold electrode afterwards. Previous studies showed that small deposition times give reasonable and acceptable modification of the gold electrode with gold nanoparticles [12]. The relative surface area of the electrode could be estimated from the coulombic integration of the reductive waves of gold oxide [13]. By analyzing Figure 2, the ratio of the surface area of the nanogold electrode to that of the bare gold electrode is around 1.1 : 1 for the 5-minute deposition time and 1.8 : 1 for the 15-minute deposition time. Studying the electrochemical behavior of the electrode as a function of gold nanoparticles deposition time, we conclude

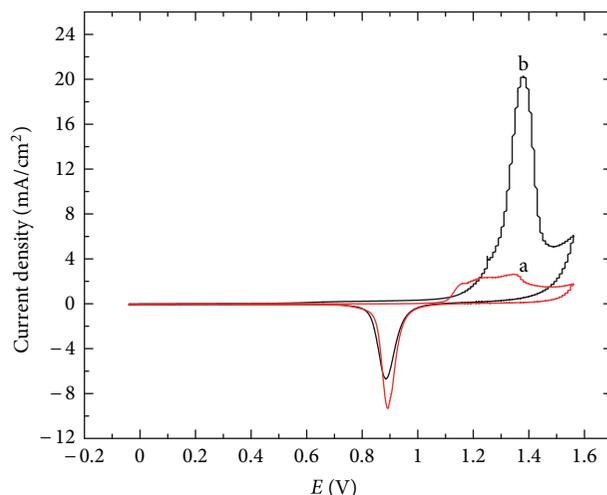


FIGURE 3: CV of (a) bare gold and (b) $\text{C}_6\text{DTC}/\text{Au}$ electrodes in aqueous 0.5 M H_2SO_4 solution. Scan rate = 50 mV/s.

that there is no significant change in the main reduction peak potential as a function of gold nanoparticles deposition time.

Figure 3 shows the cyclic voltammograms of bare Au and $\text{C}_6\text{DTC}/\text{Au}$ electrodes in 0.5 M H_2SO_4 solution at a potential scan rate of 50 mV/s. A more diluted H_2SO_4 solution was used here and onwards to increase the pH value and therefore avoid any interference with the organic molecule: C_6DTC . When the potential was scanned above +800 mV, a C_6DTC desorption peak was noticed. Therefore, all following experiments involving the C_6DTC molecule were limited to a maximum potential of +600 mV. We found that when the scanning is continued to higher potentials (>+800 mV), the peaks' intensity decreased and the CV became very similar to the bare gold electrode CV (not shown here).

Figure 4 shows the cyclic voltammograms of AuNPs and $\text{C}_6\text{DTC}/\text{AuNPs}$ electrodes in 0.5 M H_2SO_4 at a potential scan rate of 50 mV/s. The oxidation behavior is similar to that of the bare polycrystalline gold except that the C_6DTC desorption peak is much broader. In a similar manner to the bare surface, all following experiments were performed at potential values under +600 mV.

3.2. Cyclic Voltammetry of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ at the Electrode Surface of $(\text{C}_6\text{DTC}/\text{Au})$ and $(\text{C}_6\text{DTC}/\text{AuNPs})$. Figure 5 shows the cyclic voltammograms of bare Au and $\text{C}_6\text{DTC}/\text{Au}$ electrodes in 5 mM potassium ferrocyanide with 0.1 M KCl as the supporting electrolyte at a potential scan rate of 50 mV/s. We notice from the figure that the bare Au electrode (Figure 5(a)) shows a reversible voltammogram for the redox couple indicating that the electron transfer reaction is mainly diffusion controlled. On the other hand, the absence of major peaks in the CVs of the $\text{C}_6\text{DTC}/\text{Au}$ electrode (Figure 5(b)) shows that the redox reaction has been somehow inhibited.

As illustrated in Figure 5(b), the CV exhibits perfect blocking behavior which means that a highly ordered, compact monolayer is formed on the Au surface. This is also proven by the EIS measurements where the modified

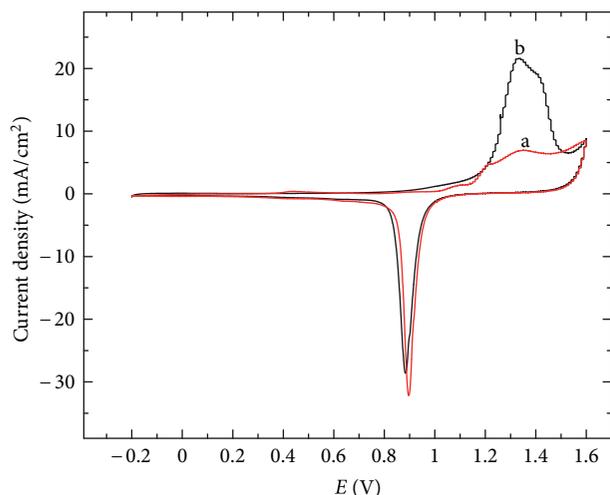


FIGURE 4: CV of (a) AuNPs electrode and (b) C₆DTC/AuNPs in aqueous 0.5 M H₂SO₄ solution. Scan rate = 50 mV/s.

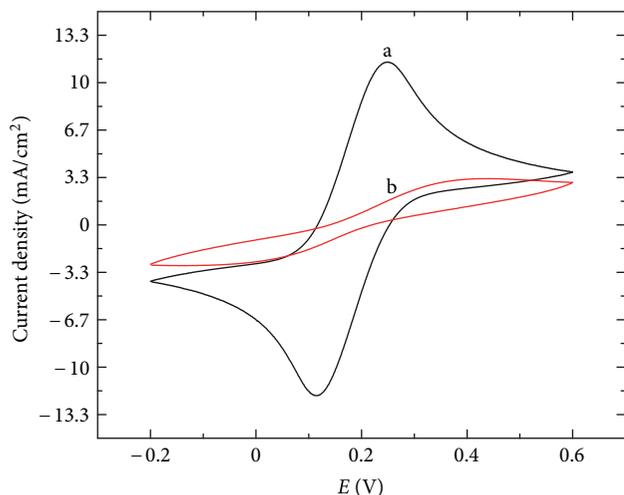


FIGURE 5: Cyclic voltammograms of (a) bare Au and (b) C₆DTC/Au electrodes in 5 mM potassium ferrocyanide with 0.1 M KCl as the supporting electrolyte at a potential scan rate of 50 mV/s.

interface displays a much higher resistance compared to that of the bare surface [14].

Figure 6 shows the cyclic voltammograms obtained for the nanogold modified electrode in 5 mM potassium ferrocyanide in 0.1 M KCl as the supporting electrolyte at a potential scan rate of 50 mV/s.

The bare Au electrode witnessed a pair of well-defined redox peaks with the anodic (E_{pa}) and cathodic (E_{pc}) peak potential of 0.236 V and 0.124 V, respectively, and a peak potential difference of 112 mV (curve a). These peaks are attributed to the redox behavior of the [Fe(CN)₆^{3-/4-}] electrochemical system. The self-assembly of C₆DTC monolayer on electrode surface induced a small decrease of peak current, which was invoked by the diffusion inhibition of [Fe(CN)₆^{3-/4-}] to the electrode surface (curve c). The modification with gold nanoparticles increased the effective electrode surface area and enhanced the rate of electron

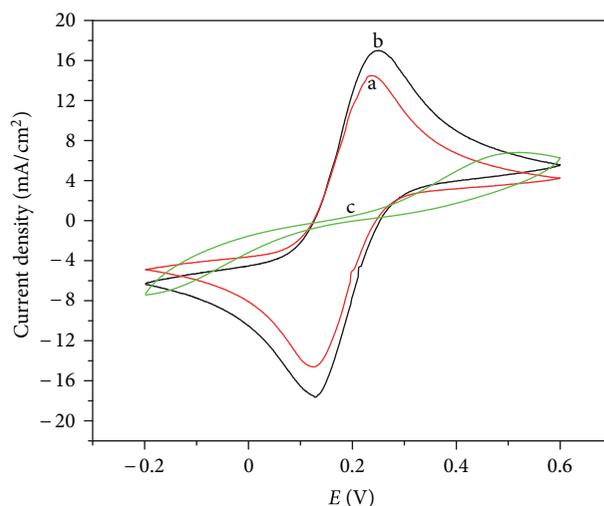


FIGURE 6: Cyclic voltammograms of (a) C₆DTC/AuNPs electrode (red curve), (b) nanogold AuNPs electrode (black curve) and (c) bare Au electrode (green curve) in 5 mM potassium ferrocyanide with 0.1 M KCl as the supporting electrolyte at a potential scan rate of 50 mV/s.

transfer, which was evidenced by a slight increase in the voltammetric responses of [Fe(CN)₆^{3-/4-}] compared to that of the bare electrode (curve b).

3.3. Linear Oxidative Desorption of Cysteine on the C₆DTC-Modified Nanogold Electrode. The linear oxidative desorption of an aqueous solution of 1 mM cysteine was performed on bare gold electrode (Figure 7(a)). No oxidation peaks were detected under a potential of 600 mV. Upon the deposition of gold nanoparticles on Au producing the AuNPs electrode, a slight increase in the measured current was seen in the region of 300 mV and above (Figure 7(b)) compared to the bare Au electrode (Figure 7(a)). C₆DTC was assembled on both bare Au and AuNPs electrodes. The linear oxidative desorption curve was measured. For the C₆DTC/Au, a desorption broad peak started to appear below 200 mV and peaked at around 500 mV (Figure 7(c)). Some C₆DTC desorption might be attributed to this curve in addition to the oxidation of cysteine. The curve in Figure 7(d) is a linear desorption of 1 mM cysteine on the C₆DTC-modified nanogold electrode (C₆DTC/AuNPs/Au). The curve shows the presence of two major peaks in the regions -100 to -50 mV and 300 to 400 mV. It is clear that the modified electrode has better sensitivity compared to the other electrodes. The 400 mV peak potential is more negative than that in the C₆DTC/Au electrode which indicates that nanogold plays an important role in lowering the peak potential. The two peaks in curve d can be employed as a basis in the fabrication of a selective sensor for cysteine in aqueous solutions due to their high current values. In addition, the combination of gold nanoparticle and C₆DTC modification clearly increased the bonding of C₆DTC to the gold surface and enhanced the self-assembly stability (compare curve d with c). When a C₆DTC-modified nanogold electrode was stored in a buffer solution (pH 7.0) for at least 1 month at ~5°C, the electrode retained

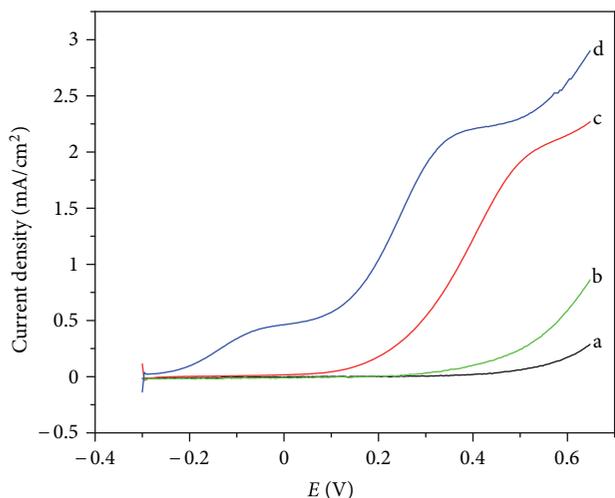


FIGURE 7: Linear oxidative desorption of 1 mM aqueous solution of cysteine in a buffer pH = 7 on (a) bare Au, (b) AuNPs, (c) C₆DTC/Au, and (d) C₆DTC/AuNPs/Au electrodes. Scan rate = 50 mV/s.

about 95% of its initial response provided that the potential is kept below 600 mV.

4. Conclusions

An electrochemical method for sensing cysteine has been tested. It consists of a self-assembled monolayer of cyclohexylamine dithiocarbamate on gold nanoparticles deposited on Au electrode. Cyclic voltammetry (CV) and linear oxidative desorption were used to characterize the modified electrode. We also conclude that gold nanoparticle modification increased the bonding of C₆DTC to the gold surface and enhanced its stability.

Acknowledgments

The authors thank the Faculty of Scientific Research at the University of Jordan for their financial support.

References

- [1] L. Ronconi, C. MacCato, D. Barreca, R. Saini, M. Zancato, and D. Fregona, "Gold(III) dithiocarbamate derivatives of N-methylglycine: an experimental and theoretical investigation," *Polyhedron*, vol. 24, no. 4, pp. 521–531, 2005.
- [2] P. J. Nieuwenhuizen, A. W. Ehlers, J. G. Haasnoot, S. R. Janse, J. Reedijk, and E. J. Baerends, "The mechanism of zinc(II)-dithiocarbamate-accelerated vulcanization uncovered; theoretical and experimental evidence," *Journal of the American Chemical Society*, vol. 121, no. 1, pp. 163–168, 1999.
- [3] K. W. Weissmahr, C. L. Houghton, and D. L. Sedlak, "Analysis of the dithiocarbamate fungicides ziram, maneb, and zineb and the flotation agent ethylxanthogenate by ion-pair reversed-phase HPLC," *Analytical Chemistry*, vol. 70, no. 22, pp. 4800–4804, 1998.
- [4] M. A. Kamrin, *Pesticide Profiles: Toxicity, Environmental Impact, and Fate*, CRC Press, New York, NY, USA, 1997.
- [5] A. E. Al-Rawajfeh and E. M. Al-Shamaileh, "Inhibition of corrosion in steel water pipes by ammonium pyrrolidine dithiocarbamate (APDTC)," *Desalination*, vol. 206, no. 1–3, pp. 169–178, 2007.
- [6] R. Colorado, R. J. Villazana, and T. R. Lee, "Self-assembled monolayers on gold generated from aliphatic dithiocarboxylic acids," *Langmuir*, vol. 14, no. 22, pp. 6337–6340, 1998.
- [7] X. J. Huang and Y. K. Choi, "Chemical sensors based on nanostructured materials," *Sensors and Actuators B*, vol. 122, no. 2, pp. 659–671, 2007.
- [8] R. N. Goyal, A. Ali Umar, and M. Oyama, "Comparison of spherical nanogold particles and nanogold plates for the oxidation of dopamine and ascorbic acid," *Journal of Electroanalytical Chemistry*, vol. 631, no. 1–2, pp. 58–61, 2009.
- [9] A. Asghar and A. R. Bhatti, "Advances in food research," in *Advances in Food and Nutrition Research*, O. . Chichester, Ed., vol. 31, p. 410, Academic Press, Boston, Mass, USA, 1986.
- [10] M. Li, F. Gao, P. Yang, L. Wang, and B. Fang, "Conveniently assembling dithiocarbamate and gold nanoparticles onto the gold electrode: a new type of electrochemical sensors for biomolecule detection," *Surface Science*, vol. 602, no. 1, pp. 151–155, 2008.
- [11] H. Gilman and A. H. Blatt, *Organic Synthesis, Collective*, vol. 1, John Wiley & Sons, New York, NY, USA, 1958.
- [12] E. Spain, B. Miner, T. E. Keyes, and R. J. Forster, "Regio selective functionalisation of gold nanoparticles with DNA," *Chemical Communications*, vol. 48, no. 6, pp. 838–840, 2012.
- [13] S. F. Liu, X. H. Li, Y. C. Li, Y. F. Li, J. R. Li, and L. Jiang, "The influence of gold nanoparticle modified electrode on the structure of mercaptopropionic acid self-assembly monolayer," *Electrochimica Acta*, vol. 51, no. 3, pp. 427–431, 2005.
- [14] E. AlShamaileh, A. Al-Rawajfeh, and V. Favry, in preparation.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

