Colloids and Surfaces B: Biointerfaces 88 (2011) 362–365

Contents lists available at ScienceDirect

Colloids and Surfaces B: Biointerfaces

journal homepage: www.elsevier.com/locate/colsurfb

# PDMS-based gold electrode for sensing ascorbic acid

Qin Xu[a], Lianhua Bi[a,b], Huxiang Zheng[b], Dahe Fan[b], Wei Wang[b,*]

[a] School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China
[b] School of Chemical and Biological Engineering, Yancheng Institute of Technology, Yancheng 224051, China

ARTICLE INFO

*Article history:*
Received 23 March 2011
Received in revised form 10 May 2011
Accepted 5 July 2011
Available online 12 July 2011

*Keywords:*
Flexible gold electrode
Poly(dimethylsiloxane)
Electrochemical sensing
Ascorbic acid

ABSTRACT

Electrode with optical shapes is appreciated in microfluidics. In this article, we reported a flexible poly(dimethylsiloxane) (PDMS)-based gold electrode for ascorbic acid detection. Gold nanoparticles were chemically deposited on PDMS and the composite film was applied as working electrode. The electrode could undergo deformation and display good response performance without damage. This biosensor could give quick response to ascorbic acid (AA) (<5 s) and the currents were linear with concentrations of AA in range of 0.023–7.00 mM and 30–100 mM, respectively. Limit of detection was 0.008 mM (S/N = 3). This biosensor has been applied to determine ascorbic acid content in vitamin C tablets and the results were consistent with traditional iodometric method.



## 1. Introduction

Ascorbic acid (AA, vitamin C) is a vital water-soluble substance in human bodies, fruits, pharmaceuticals, vegetables, etc. It plays an important role in preventing diseases like scurvy and scavenging free radicals. AA is widely used as an anti-oxidant in food processing, pharmaceutical formulations, and clinical applications. Many analytical methods have been developed for determination of AA, including titrimetry [1], enzymatic methods [2,3], spectrophotometry [4,5], chemiluminescence [6] and electroanalysis [7–11]. Point-of-care detection of AA is of great interest. Carvalhal et al. reported a low-cost and simple electrochemical detection method in paper-based device [12]. This research implied us that developing a flexible, biocompatible and disposable electrode would be popular among point-of-care devices.

Poly(dimethylsiloxane) (PDMS) is an attractive polymeric matrix due to its many favorable properties such as chemical inertness, biocompatibility, mechanical flexibility, nontoxic, stability, high dielectric constant, optical clarity in the visible and ultraviolet region and importantly, ease of processing [13]. It has been applied in many fields including biomedical implants and devices, chemical separation, microstructure fabrication and it also has been widely used in lab-on-chip and microfluidic devices. Chen group [14,15] prepared PDMS-AuNPS composite films and patterned Au/PDMS substrate with chemical gold plating method on native PDMS. Wu et al. [16] demonstrated the gold layer could be applied as electrode for electrochemical application.

This article describes fabrication and performance of flexible PDMS-based gold electrode for sensing AA. Working electrode is PDMS-gold film which can be bent or folded into different shapes and other two electrodes are Pt (counter electrode) and Ag/AgCl (reference electrode). We characterize the electrode and demonstrate the application on AA quantification, the results show high sensitivity, the detection limit of AA is 0.008 mM, which is the approximately to the results of traditional modified gold electrodes [17,18]. Linear range is 0.023–7.00 mM and 30–100 mM. This electrochemical sensor is simple and flexible for quantitative detection of analytes in aqueous solutions.

## 2. Experimental

### 2.1. Chemical reagents

Poly(dimethylsiloxane) (PDMS) was obtained from Dow Corning (midland, MI, USA). $HAuCl_4{\cdot}4H_2O$ was from Shanghai Chemical Reagent Company (Shanghai, China). Ascorbic acid (AA), $K_3[Fe(CN)_6]$, KCl was from Yizheng Second Chemical Reagent Company (Yangzhou, China). Sodium acetate, vitamin C tablets were purchased from Northeast Pharmaceutical Group Co., Ltd., acetic and $KHCO_3$ were obtained from Shanghai Shenxiang Chemical Reagent Company (Shanghai, China). Supporting electrolyte was 0.1 M acetate buffer. All solutions were prepared with deionized water. All reagents were of analytical grade, and triple distilled water was used throughout.

* Corresponding author. Tel.: +86 515 83102110; fax: +86 515 88298191.
*E-mail address:* wangw@ycit.edu.cn (W. Wang).

0927-7765/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfb.2011.07.014

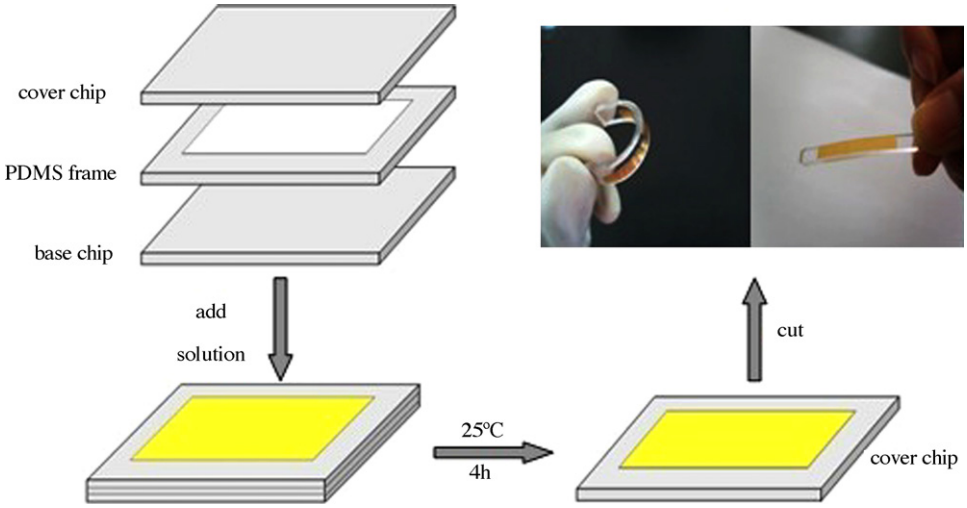


**Fig. 1.** Production process of flexible PDMS-based working electrode.

### 2.2. Instrumentation

All the electrochemical experiments were performed with a CHI840c electrochemical workstation (Shanghai Chenhua Company, Shanghai, China).

### 2.3. Design and fabrication of PDMS based flexible electrochemical sensing device

PDMS film was prepared similar as the described procedure in Refs. [15,16]. Briefly, PDMS monomer and the curing agent were firstly mixed in a proportion of 1:0.1 and cured at 120 °C for 30 min. Chemical gold plating solution containing 0.03 M $HAuCl_4$, 2 M $KHCO_3$, and 9.9 M glucose (v/v, 2:1:1) was prepared just before use. Plexiglass frame with inner area 3 cm × 4 cm was sandwiched between two native 2-mm-thick PDMS films named 'cover chip' and 'base chip', and then the solution for chemical gold plating was injected into this sandwich architecture. It was then incubated at room temperature for 4 h to ensure the elemental gold deposit completely. All resulting PDMS-gold films were washed with deionized water for three times, and stored at room temperature when not in use. A piece of PDMS-gold film of 2.5 cm × 0.4 cm was cut as working electrode, working electrode area was defined as 1.5 cm × 0.4 cm controlled by transparent adhesive tape and connected by indium tin oxide (ITO) conductive glass. The counter electrode is Pt and reference electrode is Ag/AgCl. The Production process of flexible PDMS-based working electrode was shown in Fig. 1

## 3. Results and discussion

### 3.1. Fabrication and connection of PDMS-based gold electrode

The growth of gold on PDMS was considered to follow a two-step as reported [15] as follows: residual Si–H in PDMS can start to reduce $HAuCl_4$ directly as soon as they contact to each other, so that gold nanoparticles were imbedded into PDMS matrix or adhere to the PDMS surface firstly. Then these gold nanoparticles acted as cores for subsequent gold metal deposition orderly, which led to the formation of a compact and continuous gold layer on PDMS films.

PDMS-based gold electrode was soft and flexible, the electrode and wire should be connected via a hard ITO glass, this connection method insured the stability of long lifetime of working electrode.

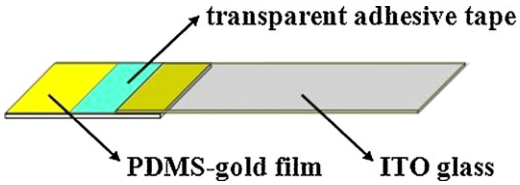


**Fig. 2.** Schematic connection method of PDMS-based gold electrode with ITO glass, and the working electrode area defined with transparent adhesive tape.

Working electrode area was defined with transparent adhesive tape. The schematic connection was shown in Fig. 2.

### 3.2. Characterization of PDMS-based gold electrode

Electrochemical behavior of PDMS-gold working electrode was investigated by cyclic voltammetry in 0.5 M $H_2SO_4$ solution. As shown in Fig. 3, the CV profile exhibited a typical redox peaks of gold, which corresponds to the surface gold oxidation and the consequent reduction of gold oxides, respectively.

$K_3[Fe(CN)_6]$ aqueous solution was employed as a model redox-active compound to characterize electrochemical behavior of our PDMS-gold film (Fig. 4). The insert showed anodic and cathodic

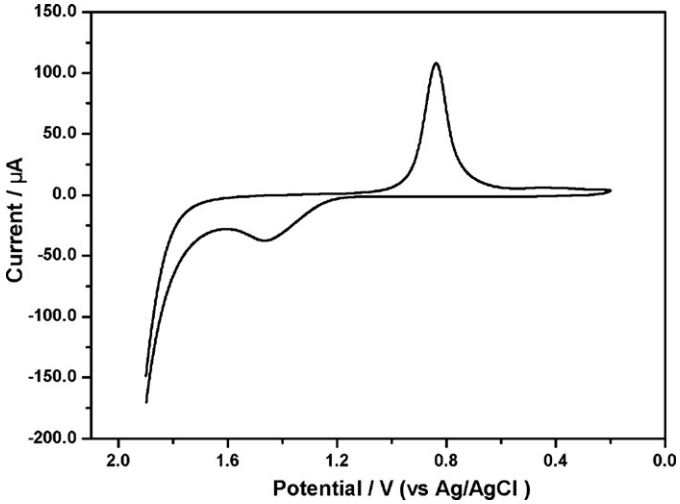


**Fig. 3.** Cyclic voltammogram with flexible PDMS-gold working electrode sensor in 0.5 M $H_2SO_4$. Scan rate is 100 mV $s^{-1}$.

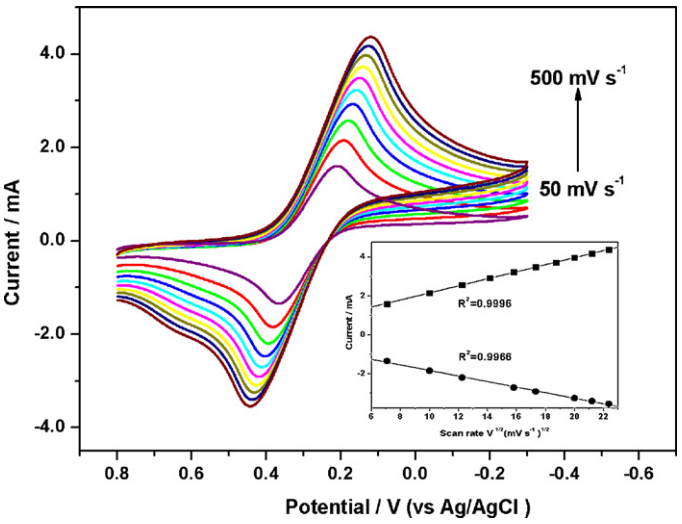


**Fig. 4.** Cyclic voltammograms of 0.01 M $K_3[Fe(CN)_6]$ aqueous solution at various scan rates (ascending along *Y*-axis): 50, 100, 150, 200, 250, 300, 350, 400, 450 and 500 mV $s^{-1}$. The insert is the relationship of redox currents and the square root of the scan rates. Solid lines represent a linear fit to both oxidation current and reduction current with the regression equation: upper data, $Y = 0.3397 + 0.1812X$ ($R^2 = 0.9996$); lower data, $Y = -0.417 - 0.1424X$ ($R^2 = 0.9966$).

peak currents were directly proportional to the square root of the scan rate between 50 and 500 mV $s^{-1}$. The solid lines represented a linear fit to both oxidation current and reduction current with the regression equation: upper data, $Y = 0.3397 + 0.1812X$ ($R^2 = 0.9996$); lower data, $Y = -0.417 - 0.1424X$ ($R^2 = 0.9966$). The linearity indicated the mass transfer in this system was a diffusion controlled process. The peak shape of CVs showed a typical reversible electrochemical reaction in which the rate of reaction was governed by diffusion of the electroactive species to the surface of a planar electrode.

To understand the electrochemical behavior of gold electrode with different shapes, 0.01 M $K_3[Fe(CN)_6]$ aqueous solution was applied as model for testing. Electrochemical response of the flexible PDMS-gold working electrode was measured upon bending inward to angles of 90°, 180°, twist for 360°, 90° and straight, CV profiles were consistent, as shown in Fig. 5. The results showed

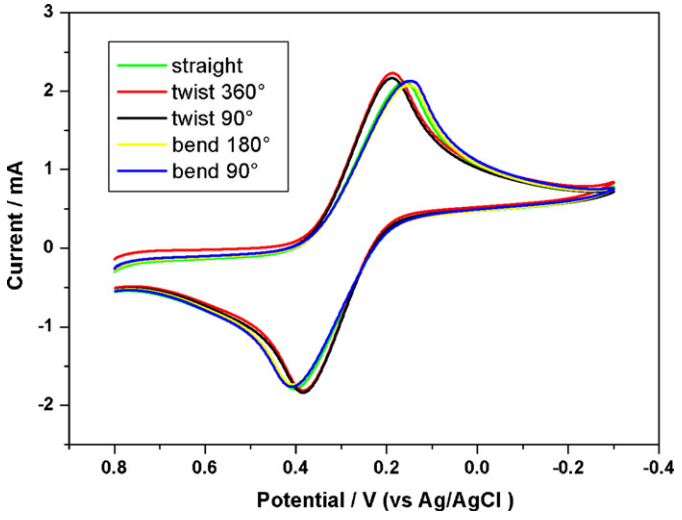


**Fig. 5.** Cyclic voltammograms of PDMS-gold working electrode with various shapes of straight, twisting 360°, 90° and bending 90°, 180° in 0.01 M $K_3[Fe(CN)_6]$ aqueous solution. Scan rate is 100 mV $s^{-1}$.

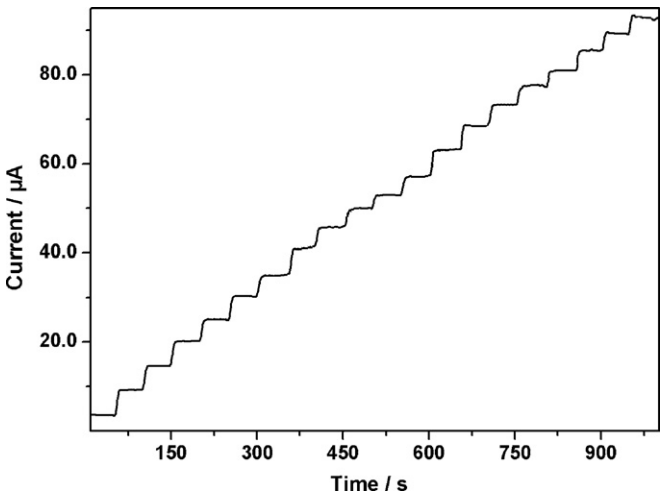


**Fig. 6.** Current–time plot of subsequent spiking of 0.1 mM AA on PDMS-based gold electrode.

that the PDMS-gold working electrode can be bent and folded to different shapes to adapt to various situations.

### 3.3. Amperometric response of AA

Our home-made PDMS-based gold electrode was used to construct an amperometric sensor for AA. The parameters of AA detection with common Au gold electrode [12,19] were applied. Current–time response curves were observed at 0.4 V (vs. Ag/AgCl) with subsequent spiking of 0.1 mM AA in 0.1 M HAc–NaAc (pH 4.5). The *i*–*t* calibration curve and relationship between catalytic current and concentration of AA were shown in Figs. 6 and 7, respectively. The linear relationship between catalytic current and concentration was observed in the range of 0.023–7.00 mM and 30–100 mM. The linear regression equation were expressed as $Y = 14.3823 + 33.6262X$ ($R^2 = 0.9972$, $n = 11$) and $Y = 372.9091 + 1.0527X$ ($R^2 = 0.9962$, $n = 8$), with the detection limit of 0.008 mM at a signal to noise ratio of 3. The response time was about 5 s, which indicated a generally fast electron-transfer process in this PDMS-based gold electrode. Stability of the electrode was investigated after it was stored in refrigerator (4 °C) for two

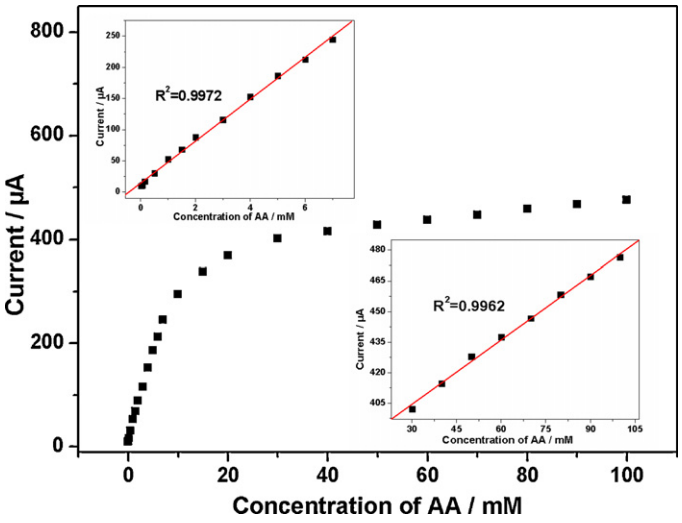


**Fig. 7.** Calibration plots for AA in 0.1 M HAc–NaAc (pH 4.5) at applied potential of 0.4 V (vs. Ag/AgCl).

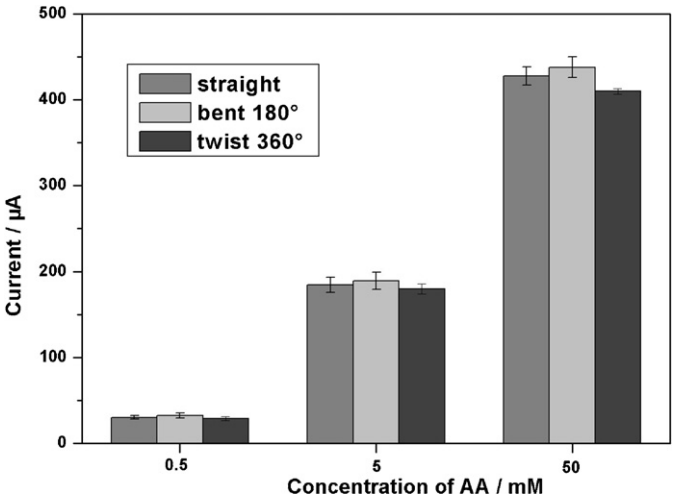


**Fig. 8.** Detection of AA by PDMS-AuNPs electrode with different shapes.

**Table 1**
Detection of AA in vitamin C tablet[a] with provided electrochemical method and iodometric method.

| Vitamin C tablet sample | Provided electrochemical method ($g\,L^{-1}$) | Iodometric method ($g\,L^{-1}$) | Labeled content ($g\,L^{-1}$) |
|---|---|---|---|
| S1 | 1.0029 ± 0.0863 | 1.0205 ± 0.0508 | 1.0 |
| S2 | 0.5105 ± 0.0445 | 0.4997 ± 0.0573 | 0.5 |
| S3 | 0.0982 ± 0.0107 | 0.0964 ± 0.0085 | 0.1 |

[a] Five repetitive measurements, mean value ± expanded uncertainty.

weeks, amperometric response signal was equal to that of freshly prepared PDMS-based gold electrode.

Electrochemical detection integrated in the microfluidics has been widely applied. In order to match the detection cell, the electrode needs to be deformed. Especially, the electrode with optional shapes is appreciated in the case of in vivo detection. AA is an important biomolecules in living beings. Detection of AA by PDMS-AuNPs electrode with different shapes was shown in Fig. 8, the results were consistent.

## 4. Detection of AA in tablets of vitamin C

Ten tablets of vitamin C (labeled net content of 100 mg vitamin C per tablet with total weight 120 mg) were completely ground and homogenized, 330 mg of which was accurately weighed and dissolved with ultrasonication in 20 mL of triple distilled water, then was diluted with water in a 50 mL flask. Pipette a certain volume of the solution into 10 mL buffer solution. The results from provided method were consistent with that from traditional iodometric method and labeled content (shown in Table 1).

## 5. Conclusions

We described a flexible PDMS-based gold electrode for sensing AA, the electrode could withstand mechanical deformation without damage and showed stable electrochemical properties. PDMS has many advantages such as chemical inertness and flexibility, especially biocompatible. It can be applied as implantable sensing devices for in situ diagnosis. And the gold surface is bioaffinity, it also has the potential to be modified with enzyme or aptamers even cells for further biosensing. The electrode has the property of ease-of-fabrication will enable mass production.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (20875080, 20705030), Jiangsu Foundation for International Cooperation (BZ2010053) and Scientific Project of Yancheng Institute of Technology (XKY2009010, XKY2009016).

## References

[1] R.A. Verdini, C.M. Lagier, J. Agric. Food Chem. 48 (2000) 2812.
[2] T.N. Shekhovtsova, S.V. Muginova, J.A. Luchinina, A.Z. Galimova, Anal. Chim. Acta 573 (2006) 125.
[3] X. Wang, H. Watanabe, S. Uchiyama, Talanta 74 (2008) 1681.
[4] M.R. Moghadam, S. Dadfarnia, A.M.H. Shabani, Anal. Biochem. 410 (2011) 289.
[5] W. Zeng, F. Martinuzzi, A. Macgregor, J. Pharm. Biomed. Anal. 36 (2005) 1107.
[6] H. Dai, X. Wu, Y. Wang, W. Zhou, G. Chen, Electrochim. Acta 53 (2008) 5113.
[7] A.A. Ensafi, M. Taei, T. Khayamian, Colloids Surf., B 79 (2010) 480.
[8] R. Hosseinzadeh, R.E. Sabzib, K. Ghasemlu, Colloids Surf., B 68 (2009) 213.
[9] J.R.L. Guerreiro, A.H. Kamel, M.G.F. Sales, Food Chem. 120 (2010) 934.
[10] A. Ambrosi, A. Morrin, M.R. Smyth, A.J. Killard, Anal. Chim. Acta 609 (2008) 37.
[11] R. Thangamuthu, S.M.S. Kumar, K.C. Pillai, Sens. Actuators 120 (2007) 745.
[12] R.F. Carvalhal, M.S. Kfouri, M.H.D. Piazetta, A.L. Gobbi, L.T. Kubota, Anal. Chem. 82 (2010) 1162.
[13] M.L. Van Poll, F. Zhou, M. Ramstedt, L. Hu, W.T.S. Huck, Angew. Chem. Int. Ed. 46 (2007) 6634.
[14] Q. Zhang, J.J. Xu, Y. Liu, H.Y. Chen, Lab Chip 8 (2) (2008) 352.
[15] H.J. Bai, M.L. Shao, H.L. Gou, J.J. Xu, H.Y. Chen, Langmuir 25 (2009) 10402.
[16] W.Y. Wu, X.Q. Zhao, W. Wang, J.J. Zhu, Electrochem. Commun. 12 (2010) 1600.
[17] R. Dhanusuraman, I.G. Anantha, Sens. Actuators B 143 (2010) 696.
[18] R.A.A. Muoz, R.C. Matos, Talanta 55 (2001) 855.
[19] Y. Wang, W. Zheng, Chemical Sensors 28 (3) (2008) 53.