

Urchin-like Ag Nanowires as Non-enzymatic Hydrogen Peroxide Sensor

Wei-Han Hsiao,^a Hsin-Yu Chen,^b Ta-Ming Cheng,^a Ting-Kai Huang,^a Yu-Liang Chen,^a Chi-Young Lee^b and Hsin-Tien Chiu^{a*}^aDepartment of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050, R.O.C.^bDepartment of Materials Science and Engineering and Center for Nanotechnology, Materials Science and Microsystems, National Tsing Hua University, Hsinchu, Taiwan 30043, R.O.C.

(Received Aug. 16, 2011; Accepted Oct. 25, 2011; Published Online Nov. 7, 2011; DOI: 10.1002/jccs.201100500)

Urchin-like Ag nanowires were prepared by reacting AgNO₃(aq) with Cu metal in the presence of cetyltrimethylammonium chloride and HNO₃(aq) on a screen printed carbon electrode at room temperature. The diameters of the nanowires were about 100 nm, while the lengths were up to 10 μm. Cyclic voltammetric experiments using the Ag nanowires as the working electrode showed electrocatalytic H₂O₂ reduction. The electrode exhibited a high sensitivity of 4705 μA mM⁻¹ mg⁻¹ cm⁻² from 50 μM to 10.35 mM and a measurable detection limit of 10 μM in amperometric detection. This is the first report on Ag NWs for non-enzymatic H₂O₂ sensing.

Keywords: H₂O₂; Ag nanowire; Amperometric sensor.

INTRODUCTION

H₂O₂ is not only widely used in paper, cleaning product, and food industries,¹ but also generated as a by-product in several enzyme-catalyzed reactions.²⁻⁵ A lot of analytic techniques have been developed to detect minute quantities of H₂O₂ such as titrimetry,⁶ spectrophotometry,^{7,8} chemiluminescence,⁹⁻¹¹ and electrochemistry.¹²⁻¹⁴ Among them, electrochemical analysis has been considered as a low-cost and effective method due to its simplicity and high sensitivity. Until now, a great deal of H₂O₂ sensors have been developed based on electrocatalysis of H₂O₂ reduction by immobilized enzymes.¹⁵⁻¹⁷ However, these electrodes showed many disadvantages related to their stability and activity degradations of immobilized enzymes.^{18,19} Therefore, there are more and more attempts to develop non-enzymatic sensors constructed from nanostructured materials. For example, in recent years, electrodes modified with metal nanoparticles (NPs) such as Pt NPs,^{20,21} Au NPs,²² Pd NPs²³ and Ag NPs,²⁴ have been extensively used for non-enzymatic H₂O₂ sensors. They usually showed large specific surface areas, excellent conductivities, and outstanding electrocatalytic activities. Because Ag is a relatively inexpensive noble metal of all, several kinds of Ag nanostructures have been fabricated for non-enzymatic H₂O₂ sensing applications.²⁵⁻²⁷ Previously, we have reported the non-enzymatic glucose sensors such as Cu nanobelt²⁸ and Au nanocoral²⁹ on screen-printed carbon (SPC) electrodes via several heterogeneous reactions. We discovered that surfactant-as-

sisted galvanic reductions provide low cost, one step, and near room temperature growth routes. By using this strategy, recently, we demonstrated the growth of urchin-like Ag NWs on screen-printed carbon (SPC) electrodes.³⁰ Using the new electrode, we wish to report the first case of using Ag NWs for non-enzymatic H₂O₂ sensing. Our discoveries are discussed below.

EXPERIMENTAL SECTION

Reagent

Silver nitrate (Mallinckrodt), cetyltrimethylammonium chloride (CTAC, Taiwan Surfactant), hydrogen chloride (TEDIA), nitric acid (Showa), sodium phosphate dibasic dihydrate (Aldrich), sodium phosphate monobasic monohydrate (JT-Baker), D-(+)-glucose (Aldrich), L-ascorbic acid (AA, Aldrich), uric acid (UA, Aldrich), sodium chloride (Aldrich), sodium bicarbonate (Aldrich), and hydrogen peroxide (Aldrich) were used without further purification.

Preparation of Growth Substrate

We used 0.1 N HCl_(aq) to clean a Cu foil (5 × 5 × 0.2 mm³) for 3 min and rinsed it by deionized water. Then, the foil and a commercial SPC electrode (Zensor R&D SE100, 0.196 cm²) were stuck together with conductive silver (Ted Pella). The whole substrate was put into an oven for 30 min at 353 K.

Preparation of Urchin-like Ag NWs

AgNO₃ (0.064 g, 0.375 mmol), CTAC (0.89 M, 0.3

* Corresponding author. E-mail: htchiu@faculty.nctu.edu.tw

mL) and HNO_3 (0.312 M, 0.8 mL) were added into a constantly stirred aqueous solution (50 mL) in a glass beaker. Instantly, the solution turned white and opaque. The colloidal suspension was stirred for 15 min and allowed to stand for 15 min more. Then, the as-prepared growth substrate was immersed into the solution at 303 K. After 6 h, the substrate was removed and rinsed by deionized water. To avoid oxidation, the as-prepared Ag NWs electrodes were stored in a N_2 filled glove box to prevent excessive surface oxidation.

Preparation of Ag Microparticles

A glass vial containing AgNO_3 electrolyte (10 mL, 10 mM) was placed in a water bath controlled at 303 K. A two-electrode electrochemical cell composed of a DC power supply and two carbon electrodes. Ag microparticles were grown on the cathode, which was an SPC electrode purchased from Zensor R&D with a geometric area of 0.196 cm^2 . The anode was fabricated by painting carbon paste uniformly on a transparent projection slide followed by drying it on a hotplate at 353 K for 3 h under air. After the cathode and the anode were immersed in the electrolyte for 2 min, a fixed DC voltage of 1.0 V was supplied across the electrodes. At 303 K without stirring, the cathode surface turned into gray color gradually. After 1 h, a total charge of ca. 0.24 C (corresponding to Ag 0.268 μg) was supplied. The cathode was removed and rinsed with deionized water. To avoid oxidation, the as-prepared Ag microparticles were stored in a N_2 filled glove box to prevent excessive surface oxidation.

Characterizations and Spectroscopic Measurements

The scanning electron microscopic (SEM) and energy dispersive spectroscopic (EDS) data were taken from a Hitachi S-4000 (25 keV) and a JEOL JSM-7401F (15 keV). Transmission electron microscopic (TEM) and selected area electron diffraction (SAED) images were captured by a JEOL JEM-2010 at 200 kV. The X-ray diffraction (XRD) patterns were acquired by using a Bruker AXS D8 Advance. Cyclic voltammetric (CV) and amperometric experiments were carried out on a CHI 6081C (CH Instruments) electrochemical analyzer. A three electrode system was employed for the measurements. It contained a working electrode, which is an Ag electrode fabricated in this study, a counter electrode composed of a Pt wire, and an Ag/AgCl (in KCl 3.00 M) reference electrode, with a potential of 0.200 V vs. standard hydrogen electrodes (SHE). Amperometric curves of hydrogen peroxide were recorded at -0.28 V and -0.4 V for Ag NW and Ag microparticle

electrodes, respectively. Before carrying out the electrochemical experiments, all of the solutions employed were de-oxygenated by $\text{N}_{2(\text{g})}$. Various amounts of hydrogen peroxide were added every 100 s into a stirring PBS solution (0.01 M, pH 7.4) in air.

RESULTS AND DISCUSSION

Figure 1 shows the SEM data of the as-prepared Ag NWs and Ag micro-particles. As displayed in Fig. 1A, lots of Ag urchin-like NWs grow on the electrode surface. Based on the EDS (Fig. 1B), we conclude that the NWs are composed of Ag only. The inset in Fig. 1A shows an enlarged view of the urchin-like morphology. The diameters of the NWs are estimated to be about 100 nm while the lengths are found to be in the range 3–10 μm . For further characterizations, the XRD pattern shown in Fig. 2 indicates that the NWs had a face-centered-cubic (fcc) structure. From the pattern, the lattice parameter a was estimated to be 0.409 nm, consistent with the value reported for Ag.³¹ Figure 1C displays the image of the microparticles. They are about 20 μm in diameters and composed of Ag (Fig. 1D).

Cyclic Voltammetric Studies

Figure 3 shows the CV responses of different H_2O_2 concentrations on an Ag NW electrode. It indicates that the reduction current (at -0.28 V) gradually increases with the increasing of H_2O_2 concentration. Figure 4 displays the CVs in the absence (black line) and presence (red line) of H_2O_2 (6 mM) in deaerated PBS (pH 7.4, 0.01 M) using Ag

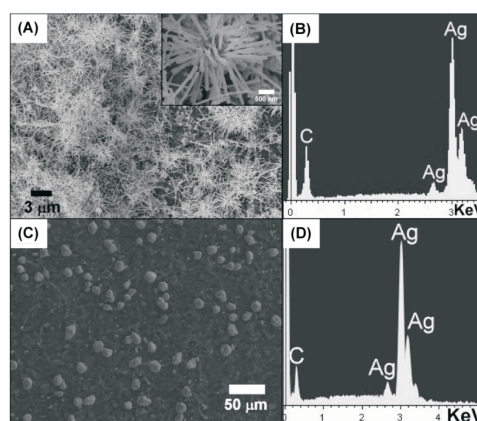


Fig. 1. (A) SEM image of Ag urchin-like NWs on an SPC electrode (inset: enlarged view of a single cluster of urchin-like Ag NWs). (B) EDS of an area in part A. (C) SEM image of Ag microparticles on an SPC electrode. (D) EDS of an area in part C.

NW, Ag microparticle, and SPC electrodes. We notice that the reduction current response from using the Ag NW is slightly larger than using the Ag microparticle electrode. Furthermore, the reduction potential of using the Ag NW electrode (-0.28 V) is also smaller than the value of using Ag microparticle electrode (-0.4 V). These results indicate that the Ag NW electrode possesses a relatively notable catalytic ability towards H_2O_2 reduction. It is known that the electrocatalytic properties of Ag nanoparticles depend on their dimension, density and amount deposited on electrode surfaces.^{32,33} Since the Ag NWs on a SPC electrode had smaller size and higher density than the Ag micro-

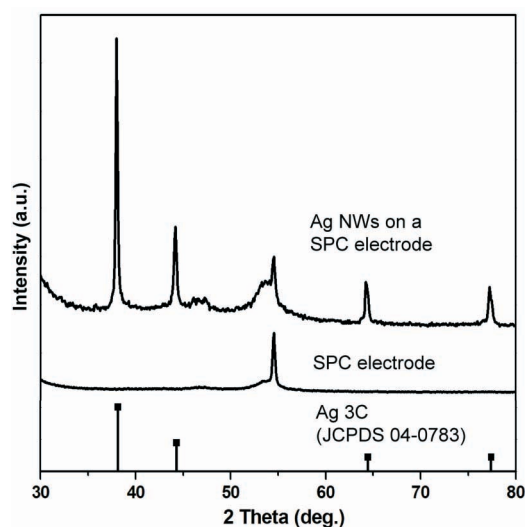


Fig. 2. XRD patterns of Ag NWs on a SPC electrode.

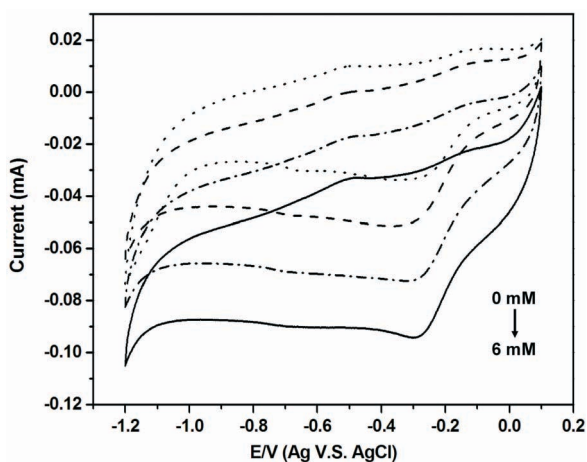


Fig. 3. CVs of different H_2O_2 concentrations in deaerated PBS (pH 7.4, 0.01 M) using an Ag NW electrode as the working electrode. The H_2O_2 concentrations are 0 mM (dot), 2 mM (dash), 4 mM (dash dot), and 6 mM (solid). The scan rate is 50 mV/s.

particles on the electrode did, the reduction potential of using the Ag NW electrode displayed better electrocatalytic

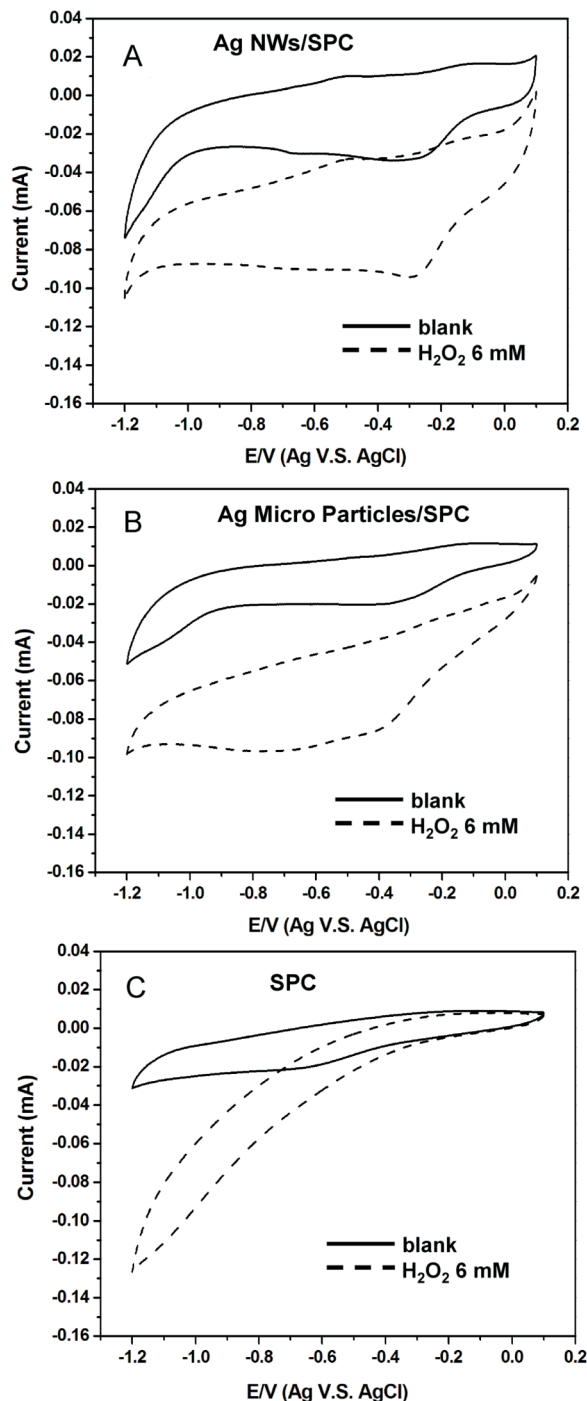


Fig. 4. Comparison of CV scans before (solid) and after (dashed) addition of H_2O_2 (6 mM) in deaerated PBS (pH 7.4, 0.01 M). The working electrodes are (A) Ag NWs, (B) Ag microparticles and (C) screen printed carbon electrodes. The scan rate is 50 mV/s.

property and lower reduction potential for H_2O_2 reduction than the other electrode showed.

Amperometric Studies of H_2O_2 Sensing

Figure 5 illustrates amperometric measurements of H_2O_2 in PBS (0.01 M) using the Ag NW electrode (-0.28 V) and Ag microparticle electrode (-0.4 V). The former electrode provides higher reduction current response than the second one does. The inset in Fig. 5 shows that the detection limit of H_2O_2 is 10 μM . A sensitivity of $257 \mu\text{A mM}^{-1} \text{cm}^{-2}$ with a linear dependence (R^2 value, 0.998) of the reduction current to the H_2O_2 concentration (50 μM - 10.35 mM) is observed for the Ag NW electrode, which is slightly higher than the data observed for Ag microparticle electrode ($138.4 \mu\text{A cm}^{-2} \text{mM}^{-1}$). The calibration curves are derived from the amperometric tests in Fig. 5 and showed in Fig. 6A. When we take the Ag masses into account, normalized calibration curves of the amperometric measurements are obtained and shown in Fig. 6B. The mass of Ag NWs is determined by using stripping voltammetry³⁴ (Fig. 7). It can be seen clearly that the sensitivity of the Ag NW electrode ($4705 \mu\text{A mM}^{-1} \text{mg}^{-1} \text{cm}^{-2}$) is much superior to the Ag microparticle one ($540 \mu\text{A mM}^{-1} \text{mg}^{-1} \text{cm}^{-2}$). Based on this evidence, we conclude that the Ag NWs have better electrocatalytic property than the Ag microparticles do. We also noticed that for a given morphology, the electrodes with the same amount of deposited Ag showed identical H_2O_2 sensing capability. Performances of various nanostructured non-enzymatic Ag electrodes reported previ-

ously are summarized in Table 1.^{22-27,33,35-41} In general, our NW electrode performed equally or better than the reported cases did. Although the amount of Ag micro-spheres (25.6 μg) on glass carbon (GC) electrode²⁵ is less than the Ag NWs (54.6 μg) we made, the linear range of our electrode (0.05-10.35 mM) is much higher than the other one (0.25-2 mM). The applied potential of our Ag NW electrode is also lower than the Ag micro-sphere electrode (-0.5 V). For other electrodes, most of them did not show the amount of Ag on the electrodes. This makes quantitative comparisons difficult. We anticipate that the performance of our NW electrode could be enhanced further by adjusting the amount of Ag deposited and the geometric area employed. Other noble metal based non-enzymatic H_2O_2 sensors such as Au²² and Pd²³ are usually expensive and require multiple

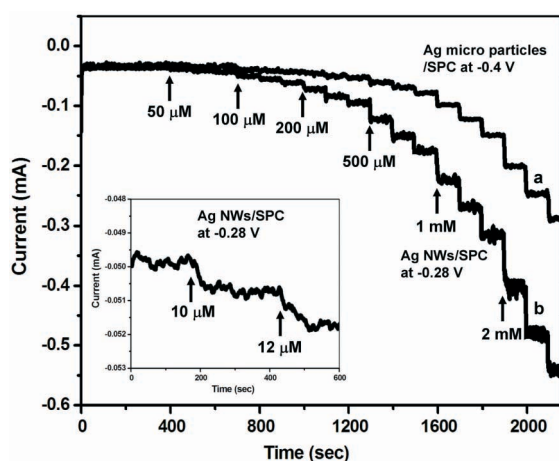


Fig. 5. Amperometric current responses to successive additions of H_2O_2 in deaerated PBS (pH 7.4, 0.01 M) on (a) Ag microparticle electrode (black) at -0.4 V and (b) Ag NW electrode (red) at -0.28 V. Inset shows the lowest concentration to be detected at 10 μM .

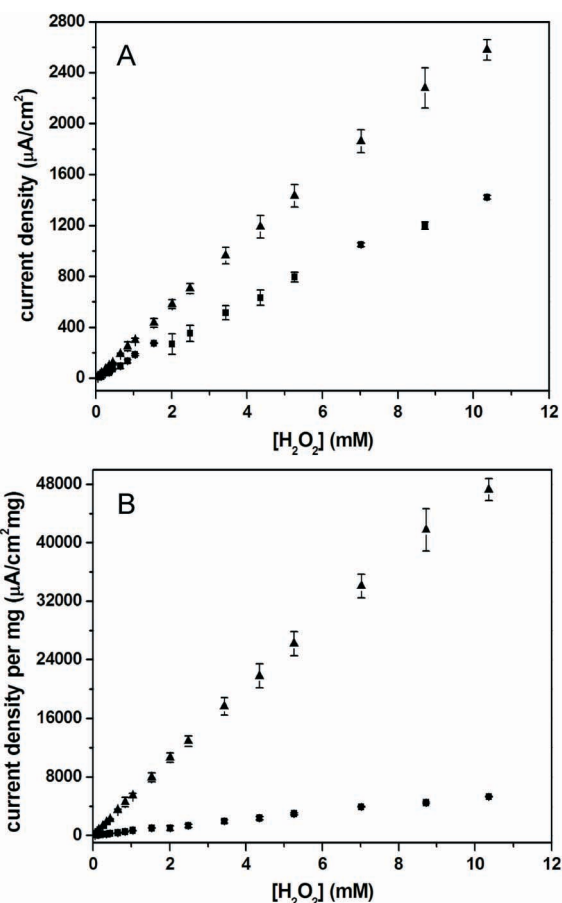


Fig. 6. (A) Calibration curves of amperometric tests in Fig. 5. (B) Calibration curves (current density normalized by mass) of amperometric tests in Fig. 5. The working electrodes are Ag NWs (black triangle) and Ag microparticles (black square). The error bars indicate the standard deviations of three successive measurements.

Table 1. Comparison of various non-enzymatic H₂O₂ sensors

Electrode	Applied potential	Mass (μg)	Sensitivity (μA mM ⁻¹ cm ⁻²)	Linear range (mM)	Detection limit (μM)	Ref.
Ag NPs/type I collagen/GC	-0.300 V ^a	-	-	0.005-40.6	0.7 ^b	33
Ag-DNA hybrid NPs/GC	-0.45 V ^a	-	773	0.002-2.5	0.6 ^b	24
Ag NPs/DNA network/GC	-0.400 V ^a	-	-	0.004-16	1.7 ^b	35
MWNTs/Ag nanohybrids on Au electrode	-0.2 V ^c	-	1.42 ^d	0.05-17	0.5 ^b	36
Ag micro-spheres/GC	-0.5 V ^a	25.6	-	0.25-2	1.2 ^b	25
Roughened Ag	-0.30 V ^a	-	-	0.01-22.5	6 ^b	37
Ag NPs-NFs/GC	-0.30 V ^c	-	-	0.1-80	62 ^b	38
Ag nano-sieve/GC	-0.44 V ^c	-	-	0.04-900 ^e	10 ^b	27
AgNP-decorated PMPD micro-particle/GC	-0.300 V ^c	-	-	0.1-30	4.7 ^b	39
AgNPs/ZnO NRs/FTO	-0.55 V ^c	-	152.1	0.008-0.983	0.9 ^b	40
AgNPs/PVA/Pt	-0.500 V ^a	-	4090	0.04-6	1 ^b	41
Ag dendrite/GC	-0.2 V ^c	-	104.53	0.005-12	0.5 ^b	26
Pd/CNF-CPE	-0.2 V ^c	-	4.15 ^f	0.2-20	0.2 ^b	23
Au NPs/OMC/GC	-0.15 V ^c	-	-	0.002-3.92	0.49 ^b	22
Ag Urchin-like NWs/SPC	-0.28 V ^c	54.6	257	0.05-10.35	10 ^f	This work
Ag microparticles/SPC	-0.40 V ^c	268	138.4	0.05-14.20	50 ^f	This work

^a referred to a saturated calomel electrode (SCE) (0.242 V versus SHE)

^b theoretical detection limit (estimated from three times of the standard deviation of the blank signal)

^c referred to an Ag/AgCl (in KCl 3.00 M) electrode (0.200 V versus SHE)

^d the unit is μA mM⁻¹

^e acidic media

^f smallest additive

synthetic steps. To our knowledge, our study is the first report on Ag NWs for non-enzymatic H₂O₂ sensor application.

For interference test, we choose five common species L-ascorbic acid (AA), uric acid (UA), glucose, chloride ion (Cl⁻), and hydrogen carbonate ion (HCO₃⁻) found commonly in real physiological samples.⁴² We used concentra-

tions comparable to the ones reported for our experiments. Amperometric responses of the Ag NW electrode towards the additions of these species (AA: 2 mM, UA: saturated, glucose: 6 mM, Cl⁻: 150 mM, HCO₃⁻: 27 mM) followed by H₂O₂ (1 mM successively) were examined. As shown in Fig. 8, AA, UA, and glucose do not produce significant responses. Moreover, the anions of Cl⁻ and HCO₃⁻ have no obvious interference in the reduction of H₂O₂. The observations reveal the application potential of Ag NWs electrode for sensing H₂O₂ in real samples.

CONCLUSION

In conclusion, we have demonstrated a simple low-cost galvanic displacement process to grow urchin-like Ag NWs on SPC electrodes for H₂O₂ sensing. Our results indicate that the Ag NW electrode shows higher electrocatalytic ability of H₂O₂ reduction than the Ag microparticle electrode does. The Ag NW electrode shows that its sensitivity for H₂O₂ reduction at an applied potential -0.28 V in PBS is 4705 μA mM⁻¹ mg⁻¹ cm⁻². The detection limit is observed at 10 μM. This is the first report on using Ag NWs for non-enzymatic H₂O₂ sensing application. The electrode

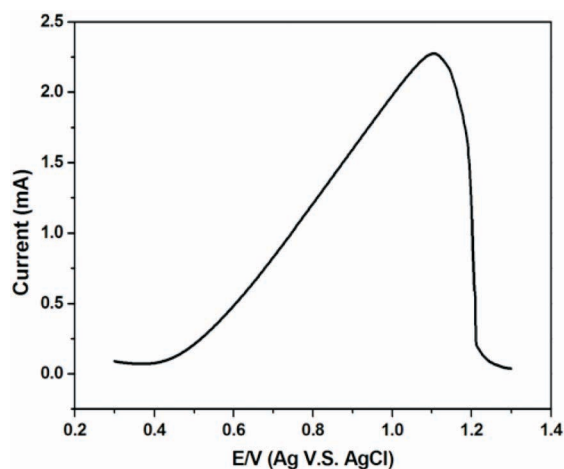


Fig. 7. Stripping voltammetry of Ag NWs in a 0.1 M NaClO₄ solution at a scan rate $\nu = 20$ mV/s.

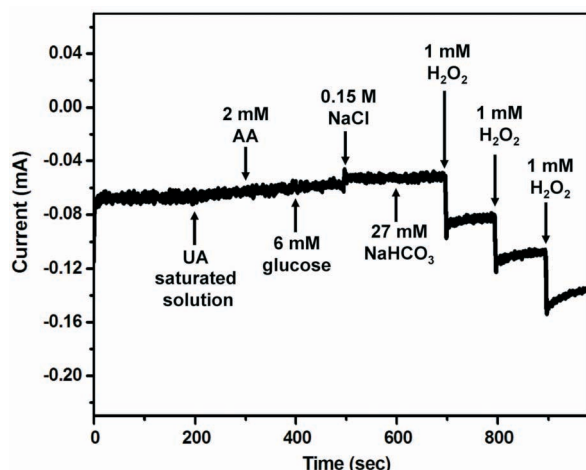


Fig. 8. Interference analysis by amperometry at -0.28 V. The injection sequences are UA (saturated), AA (2 mM), glucose (6 mM), NaCl (0.15 M), NaHCO₃ (27 mM), followed by H₂O₂ (1 mM) additions in deaerated PBS (pH 7.4, 0.01 M).

can detect H₂O₂ easily and resists many interfering species commonly found in real physiological samples.

ACKNOWLEDGMENTS

We are thankful for support from the National Science Council, "Aim for the Top University Plan" of the National Chiao Tung University, and the Ministry of Education of Taiwan, Republic of China.

REFERENCES

- Prodrromidis, M. I.; Karayannis, M. I. *Electroanalysis* **2002**, *14*, 241.
- Guilbault, G. G. *Handbook of Enzymic Methods of Analysis*; Dekker: New York, 1976.
- Darder, M.; Takada, K.; Pariente, F.; Lorenzo, E.; Abruña, H. D. *Anal. Chem.* **1999**, *71*, 5530.
- Masullo, M.; Raimo, G.; DelloRusso, A.; Bocchini, V.; Banister, J. V. *Biotechnol. Appl. Biochem.* **1996**, *23*, 47.
- Jiang, Y.; Miles, P. W. *Phytochemistry* **1993**, *33*, 29.
- Brestovisky, A.; Kirowaeisner, E.; Osteryoung, J. *Anal. Chem.* **1983**, *55*, 2063.
- Rinsland, C. P.; Coheur, P. F.; Herbin, H.; Clerbaux, C.; Boone, C.; Bernath, P.; Chiou, L. S. *J. Quant. Spectrosc. Radiat. Transf.* **2007**, *107*, 340.
- Fernandes, K. F.; Lima, C. S.; Lopes, F. M.; Collins, C. H. *Process Biochem.* **2005**, *40*, 3441.
- Yamashiro, N.; Uchida, S.; Satoh, Y.; Morishima, Y.; Yokoyama, H.; Satoh, T.; Sugama, J.; Yamada, R. *J. Nucl. Sci. Technol.* **2004**, *41*, 890.
- Janasek, D.; Spohn, U. *Sens. Actuator, B* **1997**, *39*, 291.
- Pehrman, R.; Amme, M.; Cachoir, C. *Czech. J. Phys.* **2006**, *56*, D373.
- Shao, M. W.; Shan, Y. Y.; Wong, N. B.; Lee, S. T. *Adv. Funct. Mater.* **2005**, *15*, 1478.
- Qiao, Y. B.; Yang, G.; Jian, F. F.; Qin, Y. Q.; Yang, L. R. *Sens. Actuator, B* **2009**, *141*, 205.
- Shen, Y.; Trauble, M.; Wittstock, G. *Anal. Chem.* **2008**, *80*, 750.
- Song, Y.; Wang, L.; Ren, C.; Zhu, G.; Li, Z. *Sens. Actuators, B* **2006**, *114*, 1001.
- Guo, C.; Song, Y.; Wei, H.; Li, P.; Wang, L.; Sun, L.; Sun, Y.; Li, Z. *Anal. Bioanal. Chem.* **2007**, *389*, 527.
- Ferapontova, E.; Schmengler, K.; Borchers, T.; Ruzgas, T.; Gorton, L. *Biosens. Bioelectron.* **2002**, *17*, 953.
- Willner, I.; Katz, E. *Angew. Chem. Int. Ed.* **2000**, *39*, 1180.
- Xiao, Y.; Patolsky, F.; Katz, E.; Hainfeld, J. F.; Willner, I. *Science* **2003**, *299*, 1877.
- Polsky, R.; Gill, R.; Kaganovsky, L.; Willner, I. *Anal. Chem.* **2006**, *78*, 2268.
- Li, J. P.; Yu, Q. L.; Peng, T. Z. *Anal. Sci.* **2005**, *21*, 377.
- Wang, L.; Bo, X.; Bai, J.; Zhu, L.; Guo, L. *Electroanalysis* **2010**, *22*, 2536.
- Huang, J.; Wang, D.; Hou, H.; You, T. *Adv. Funct. Mater.* **2008**, *18*, 441.
- Wu, S.; Zhao, H. T.; Ju, H. X.; Shi, C. G.; Zhao, J. W. *Electrochem. Commun.* **2006**, *8*, 1197.
- Zhao, B.; Liu, Z. R.; Liu, Z. L.; Liu, G. X.; Li, Z.; Wang, J. X.; Dong, X. T. *Electrochem. Commun.* **2009**, *11*, 1707.
- Qin, X.; Wang, H. C.; Wang, X. S.; Miao, Z. Y.; Fang, Y. X.; Chen, Q.; Shao, X. G. *Electrochim. Acta* **2011**, *56*, 3170.
- Singh, R. P.; Pandey, A. C. *Anal. Methods* **2011**, *3*, 586.
- Huang, T.-K.; Lin, K.-W.; Tung, S.-P.; Cheng, T.-M.; Chang, I.-C.; Hsieh, Y.-Z.; Lee, C.-Y.; Chiu, H.-T. *J. Electroanal. Chem.* **2009**, *636*, 123.
- Cheng, T.-M.; Huang, T.-K.; Lin, H.-K.; Tung, S.-P.; Chen, Y.-L.; Lee, C.-Y.; Chiu, H.-T. *ACS Appl. Mater. Interfaces* **2010**, *2*, 2773.
- Hsiao, W.-H.; Chen, H.-Y.; Yang, Y.-C.; Chen, Y.-L.; Lee, C.-Y.; Chiu, H.-T. *ACS Appl. Mater. Interfaces* **2011**, ASAP. doi: 10.1021/am2007239.
- Joint Committee for Power Diffraction (JCPDS) File No. 04-0783, International Center for Diffraction Data (ICDD), 1982.
- Welch, C. M.; Banks, C. E.; Simm, A. O.; Compton, R. G. *Anal. Bioanal. Chem.* **2005**, *382*, 12.
- Yonghai, S.; Kang, C.; Li, W.; Shouhui, C. *Nanotechnol.* **2009**, *20*, 105501(8 pp.).
- Jones, S. E. W.; Campbell, F. W.; Baron, R.; Xiao, L.; Compton, R. G. *J. Phys. Chem. C* **2008**, *112*, 17820.

35. Cui, K.; Song, Y. H.; Yao, Y.; Huang, Z. Z.; Wang, L. *Electrochem. Commun.* **2008**, *10*, 663.
36. Zhao, W.; Wang, H. C.; Qin, X.; Wang, X. S.; Zhao, Z. X.; Miao, Z. Y.; Chen, L. L.; Shan, M. M.; Fang, Y. X.; Chen, Q. *Talanta* **2009**, *80*, 1029.
37. Lian, W. P.; Wang, L.; Song, Y. H.; Yuan, H. Z.; Zhao, S. C.; Li, P.; Chen, L. L. *Electrochim. Acta* **2009**, *54*, 4334.
38. Tian, J. Q.; Liu, S.; Sun, X. P. *Langmuir* **2010**, *26*, 15112.
39. Tian, J. Q.; Li, H. L.; Lu, W. B.; Luo, Y. L.; Wang, L.; Sun, X. P. *Analyst* **2011**, *136*, 1806.
40. Lin, C. Y.; Lai, Y. H.; Balamurugan, A.; Vittal, R.; Lin, C. W.; Ho, K. C. *Talanta* **2010**, *82*, 340.
41. Guascito, M. R.; Filippo, E.; Malitesta, C.; Manno, D.; Serra, A.; Turco, A. *Biosens. Bioelectron.* **2008**, *24*, 1057.
42. These concentrations of common species in blood can be found at the Web site: http://en.wikipedia.org/wiki/Reference_ranges_for_blood_test (Accessed April 20, 2011)