

Supporting Information

The synthesis of high-aspect-ratio Au microwires with a biomolecule for electrochemical sensing

Lili Lv,^{a,c} Xiangsheng Han,^a Xiaochen Wu^{a,b*} and Chaoxu Li^{a,c*}

^aCAS Key Lab of Bio-based materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Songling Road 189, Qingdao 266101, P. R. China

^bDepartment of Pharmacy, College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

^cCenter of Material and Optoelectronics Engineering, University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, P.R. China

Corresponding Authors: (X. Wu) wuxc@qibebt.ac.cn and (C. Li) licx@qibebt.ac.cn

Experimental Section

Materials

L-Tyrosine was purchased from Beijing Solarbio Science & Technology Co., Ltd. (Beijing, China). Tetrachloroauric acid (HAuCl_4 , 48% Au basis) and tannic acid were brought from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Other reagents were brought from Sinopharm Chemical Reagent Co. Ltd., China. All reagents are commercially available and used without further purification. Ultrapure water (resistivity: $18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$) was used to prepare aqueous solutions and dispersions.

Synthesis of Au microwires

L-Tyrosine was dissolved in H_2O (pH=1, adjusted by HCl) to reach a concentration of 1 mg/mL. 5 mL of L-tyrosine solution (1 mg/mL) was mixed with 5 mL of HAuCl_4 (5 mM), and then 1.17 g of NaCl was added to make a concentration of 2 M. The mixture was sealed and incubated at $80 \text{ }^\circ\text{C}$ for 5 days. After cooling down to room temperature, the products were washed with H_2O for 3 times and then incubated in 20 mL of NaOH (1 M) at $60 \text{ }^\circ\text{C}$ for 2 h to remove the organic shell of L-tyrosine. Au microwires were obtained by thoroughly washing and purifying *via* filtration.

Yields of Au microwires

The yield of the Au microwires was calculated directly by a weighing method. Au microwires were dried and weighed after thoroughly washing and purifying, Au microwires yield (wt%) = W_1/W_0 , where W_0 referred to the initial Au weight in the precursor, W_1 referred to the weight of obtained Au microwires.

Fabrication of Au microelectrode

A 10-cm-length copper wire was dipped in a conductive silver solution (Guangzhou Yingxun electronic trading co. Ltd, China) as conductive adhesive. After removing the organic shell by alkaline hydrolysis and thoroughly washing, Au microwires were free-dried for fabricating Au microelectrode. In brief, Au microwires were carefully inserted halfway into the conductive silver layer using a Dumont tweezer under optical microscope. Epoxy resin was used to wrap the copper wires firmly before thermal incubation in an oven at 65 °C for 600 min.

Modifying glassy carbon electrode with Au microwires

Electrochemical measurements were carried out at room temperature on a CHI 660E electrochemical workstation (CH Instrument, Shanghai, China) with a three-electrode cell, in which a saturated calomel electrode was the reference electrode and platinum slice (10 mm *10 mm *0.1 mm) served as the counter electrode. Glassy carbon electrode (GCE, diameter: 3 mm) was polished with alumina powder slurry for 10 min, sonicated in ethanol and ultrapure water each for 10 min, and flowing dried by N₂. After removing the organic shell by alkaline hydrolysis and thoroughly washing, the Au microwires were drop-casted directly onto GCE and conducted electrochemical sensing experiments. The suspension of Au microwires (10 mg/mL, 5 μL) was casted onto the surface of the pre-polished GCE and dried in air for 12 h to get the modified GCE (Au microwires/GCE). The modified electrode was activated in 1 M of H₂SO₄ by subjected to cyclic voltammetry (CV) scanning with potential range from -0.1 V to 1.7 V, scanning rate of 50 mV/s. CV were then carried out to

characterize the electrochemical performance of the modified GCE and bare GCE.

Electrochemical sensing.

The detection of glucose was conducted in N₂-saturated 0.2 M NaOH at a scanning rate of 50 mV/s in a potential range from -0.7 V to 0.7 V. For the detection of Hg²⁺, a pre-concentration step was conducted with a depositing time of 200 s and a deposited potential at -0.5 V. Then the stripping step was carried out using differential pulse voltammetry (DPV) method (4 mV step increment, 50 mV amplitude, 0.1 s pulse period) in 0.1 M of KCl (pH=1 with 0.1 M of HNO₃), with positive-going potential scan from -0.2 V to 0.7 V and different concentrations of Hg²⁺ (2.2-40 μM) in electrolyte. After the stripping test, a disposed process at the potential of 0.9 V was conducted for 200 s to remove the residual metal.

Characterization

Transmission electron microscopy (TEM, Hitachi H-7650) was used to characterize the morphologies. Samples were prepared by putting a drop of their aqueous suspension on a copper grid, followed by removal of the solvent through tilting the grid on a piece of filter paper. Emission scanning electron microscopic measurements (FESEM, JEOL 7401) equipped with an X-ray energy dispersive spectrometer (EDS) was performed at an acceleration voltage of 10 kV. The suspension of Au microwires was dropped onto a square aluminum foil, and air-dried under room temperature to acquire the SEM samples. Microscopic images were acquired with a fluorescence microscope (Olympus BX51). Fourier transform infrared (FT-IR) analyses were performed on a Nicolet 6700 FT-IR spectrometer. X-ray diffraction (XRD)

measurements were carried out on the X-ray diffractometer (Bruker D8 ADVANCE) using Cu-K α ($\lambda = 1.5406 \text{ \AA}$) radiation. UV-vis spectrophotometric analyses were performed using a DU800 UV-vis spectrophotometer. Electrical measurements were carried out using a semiconductor parameter analyzer. Before conductivity tests, the Au microwires were incubated in NaOH (1 M) at 60 °C for 2 h to remove the organic shell, thoroughly washed by H₂O, drop-casted directly onto a glass substrate, and air-dried for 24 h. The Keithley 4200 SCS system (Tektronix Company, America) and the H100 series probe station in a clean and shielded box were used for the I-V characterization at room temperature. I-V measurements were performed by sweeping the voltage from -0.6 V to 0.6 V.

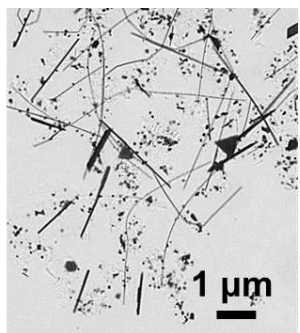


Fig. S1 Microscopic image of the as-formed Au microwires together with Au particles. Conditions: 0.5 mg/mL of tyrosine, 2.5 mM of H₂AuCl₄, 2 M of NaCl, 80 °C, 5 days.

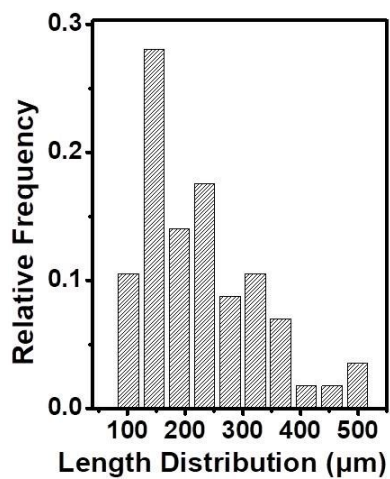


Fig. S2 Length distribution of Au microwires.

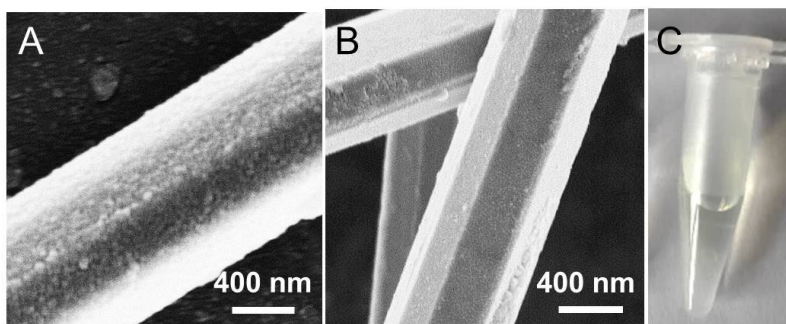


Fig. S3 SEM images of Au microwires when incubating in NaOH (1 M) for (A) 1 h and (B) 2 h. (C) Supernatant of Au microwires incubating in NaOH.

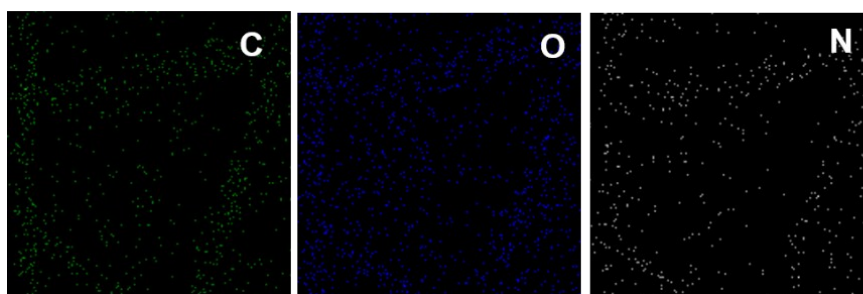


Fig. S4 EDS mapping of C, O, and N elements in Au microwires shown in Fig. 1F.

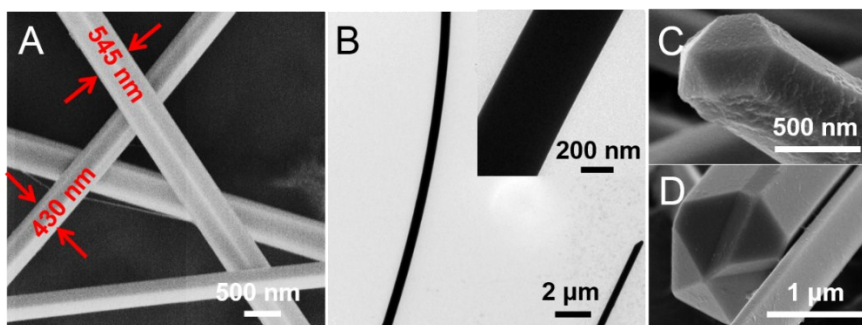


Fig. S5 (A) SEM and (B) TEM images of Au microwires after removing the organic shells. (C-D) SEM images showing polyhedral cross-sections of Au microwires.

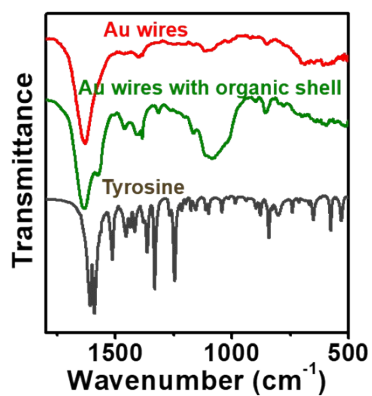


Fig. S6 FTIR spectra of L-tyrosine, Au microwires with organic shell, and Au microwires without organic shell.

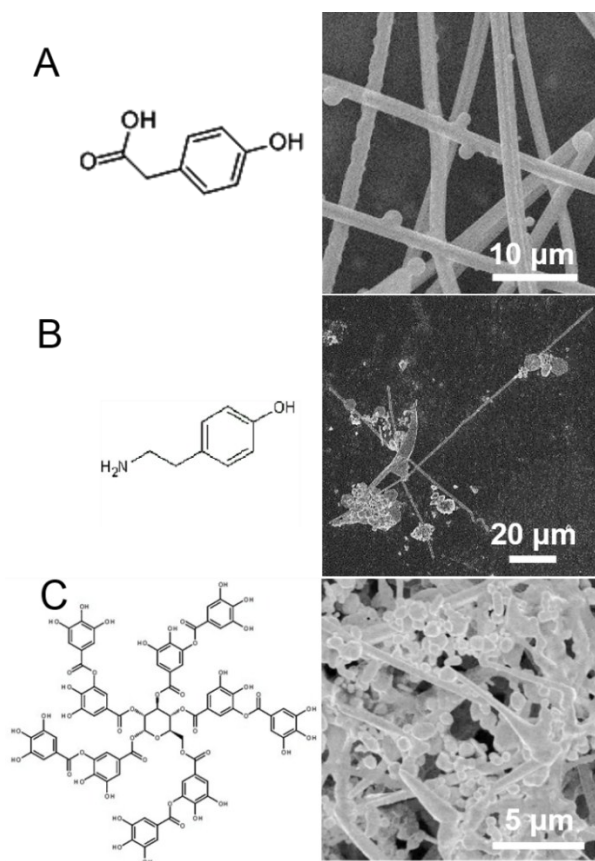


Fig. S7 SEM images of Au crystals synthesize with (A) 4-hydroxyphenylacetic acid (0.5 mg/mL), (B) 4-hydroxyphenylethylamine (0.5 mg/mL), and (C) tannic acid (0.5 mg/mL). Reaction conditions: 2.5 mM of HAuCl_4 , 2 M of NaCl, 80 °C, 5 days.

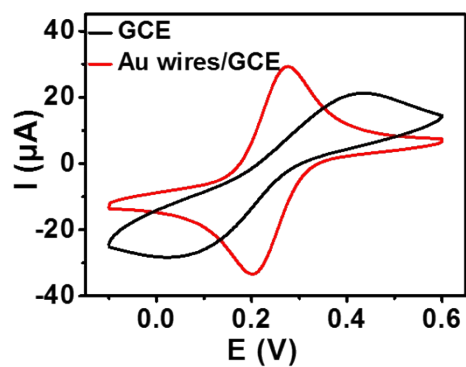


Fig. S8 CV curves of GCE modified with Au microwires and bare GCE in 0.1 M KCl containing 5 mM of $\text{Fe}(\text{CN})_6^{3-/4-}$ with the positive-going potential scan from -0.1 V to 0.6 V. The scanning rate was 50 mV/s.

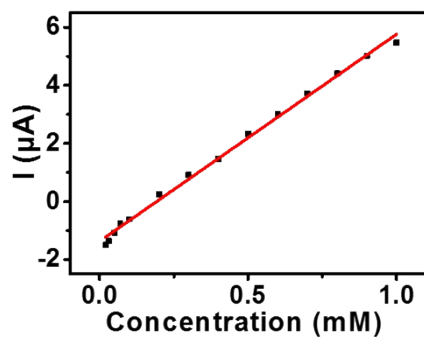


Fig. S9 Linear calibration plot of peak current at 0.032 V of modified GCE with successive addition of glucose corresponding to Fig. 3C.

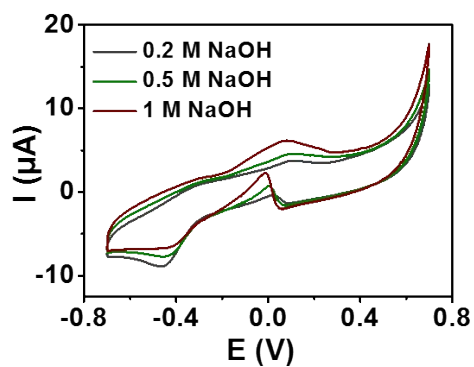


Fig. S10 CV curves of GCE modified with Au microwires in different concentration of NaOH. Glucose concentration: 0.1 mM; scanning rate: 50 mV/s.

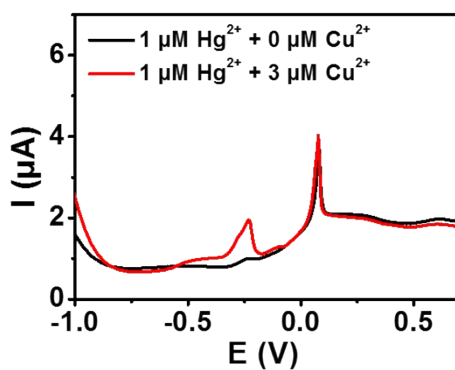


Fig. S11 DPV response of GCE modified with Au microwires to 1 μM of Hg²⁺ with or without 3 μM of Cu²⁺.

Table S1. Comparison of the analytical performances for glucose oxidation using Au structures based electrode materials.

Electrode Materials	Linear Range	Sensitivity ($\mu\text{A mM}^{-1} \text{cm}^{-2}$)	Reference
Au microwires	0.01-1 mM	100.9	This work
Au microwires	1-10 mM	46.2	This work
Au nanowire Array	0.4-10 mM	79.97	1
Au nanowire array	0.1-20 mM	41.9	2
Au nanoparticles decorated ternary Ni-Al layered double hydroxide/single-walled carbon nanotubes/graphene nanocomposite	0.01-6.1 mM	1989	3
Au nanoparticles/BSA/RGO	0.02-1.6 mM	11.5	4
Au nanoparticles/BSA/RGO	1.6-16.6 mM	3.8	4
three-dimensional gold film	0.005-10 mM	46.6	5
Au/NiAu multilayered nanowire arrays	0.005-25 mM	257	6
Hierarchical porous Au networks	1-500 μM	1253.8	7
Hierarchical porous Au networks	4-12 mM	138.9	7
Block-copolymer-assisted synthesis of mesoporous Au	0.01-10 mM	291.6	8
Au nanoparticles	0.5-8 mM	160	9
Au (111)-Like Nanoparticle Array/ Indium Tin Oxide	0.03-45 mM	67.2	10
poly(5-hydroxyl-1,4-naphthoquinone) stabilized gold nanoparticles	0.5-50 mM	183	11
cathodized Au nanoparticle-modified graphite pencil electrode	0.05-5 mM	52.61	12

Reference

- 1 Y. Zhao, J. Chu, S. H. Li, W. W. Li, G. Liu, Y. C. Tian and H. Q. Yu, *Electroanal.*, 2014, **26**, 656-663.
- 2 S. Cherevko and C. H. Chung, *Sensors Actuat. B-Chem.*, 2009, **142**, 216-223.
- 3 S. Fu, G. Fan, L. Yang and F. Li, *Electrochim. Acta*, 2015, **152**, 146-154.
- 4 Y. Liu, Y. Dong, C. X. Guo, Z. Cui, L. Zheng and C. M. Li, *Electroanal.*, 2012, **24**, 2348-2353.

- 5 Y. Bai, W. Yang, Y. Sun and C. Sun, *Sensors Actuat. B-Chem.*, 2008, **134**, 471-476.
- 6 L. F. Wang, W. Q. Zhu, W. B. Lu, X. F. Qin and X. H. Xu, *Biosens. Bioelectron.*, 2018, **111**, 41-46.
- 7 S.-L. Zhong, J. Zhuang, D.-P. Yang and D. Tang, *Biosens. Bioelectron.*, 2017, **96**, 26-32.
- 8 A. S. Nugraha, C. L. Li, J. Bo, M. Iqbal, S. M. Alshehri, T. Ahamad, V. Malgras, Y. Yamauchi and T. Asahi, *Chemelectrochem*, 2017, **4**, 2571-2576.
- 9 F. Kurniawan, V. Tsakova and V. M. Mirsky, *Electroanal.*, 2006, **18**, 1937-1942.
- 10 J. Wang, X. Cao, X. Wang, S. Yang and R. Wang, *Electrochim. Acta*, 2014, **138**, 174-186.
- 11 M. C. D. Cooray, Y. Liu, S. J. Langford, A. M. Bond and J. Zhang, *Anal. Chim. Acta*, 2015, **856**, 27-34.
- 12 A. N. Kawde, M. A. Aziz, M. El-Zohri, N. Baig and N. Odewunmi, *Electroanal.*, 2017, **29**, 1214-1221.