Electronic Supplementary Information for

A Novel Photoelectrochemical Sensor Based on SiNWs@PDA for Efficient Detection of Myocardial Infarction

Hui-Jun Li,[ab1] Shibo Zhi,[a1] Shen Zhang,[b] Xiaoyu Guo,[b] Yueyi Huang,[a] Ling Xu,[c] Xianying Wang,[c] Ding Wang,[a] Minfang Zhu [b]* and Bin He [b]*

a. School of Materials and Chemistry, University of Shanghai for Science and Technology, 516 Jungong Road, Shanghai 200093, China.

b. Department of Critical Care Medicine, Shanghai Chest Hospital, Shanghai Jiao Tong University, Shanghai, 200092, China.

c. School of Microelectronics, Fudan University, Shanghai 200093, China

d. CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), Shanghai 200050, China.

* Correspondence: zhuminfang@shsmu.edu.cn (M. Z.); bin_he@sjtu.edu.cn (B. H.)

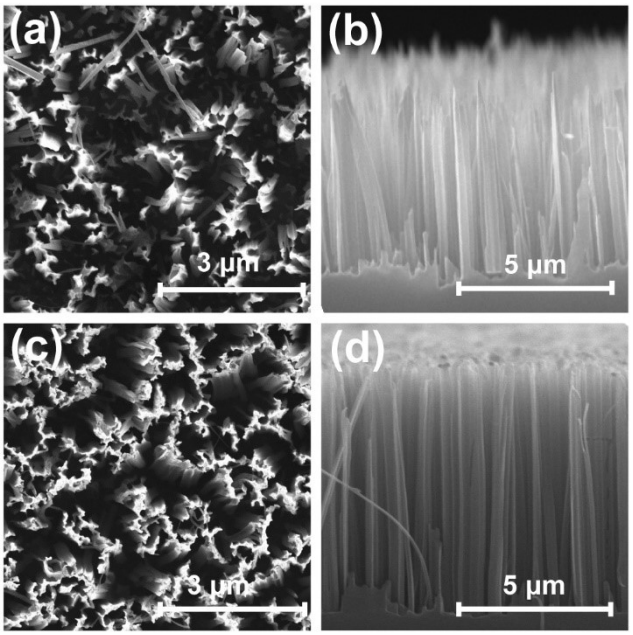


Figure S1 The SEM images of SiNWs arrays obtained via (a,b) One-step and (c,d) two-step MACE.

(1) One-step MACE

The etching solution containing HF (5 mol/L) and $AgNO_3$ (0.04 mol/L) was prepared. The cleaned silicon wafer was placed horizontally in the etching solution and etched at room temperature for 30 min. After etching, the etching waste on the surface of the silicon wafer was washed away by concentrated nitric acid. Then the substate was soaked in nitric acid for 30 min to remove the residual silver nanoparticles.

(2) Two-step MACE

Two etching solutions were prepared. Solution I contain HF (5 mol/L) and $AgNO_3$ (0.04 mol/L), while solution II contain H_2O_2 (0.3 mol/L) and HF (5 mol/L). Firstly, the cleaned silicon wafer was placed horizontally in etching solution I for 1 min, of which the purpose is to deposit a uniform film of silver nanoparticles on the surface of silicon wafers. The excess silver ions on the surface of the silicon wafer were then washed with deionized water. Then, the wafer deposited with silver ions was etched in solution II for 1 h. Afterwards, the etching wastes on the wafer surface were removed by nitric acid. The wafter was then soaked in nitric acid for 30 min to remove the residual silver nanoparticles.

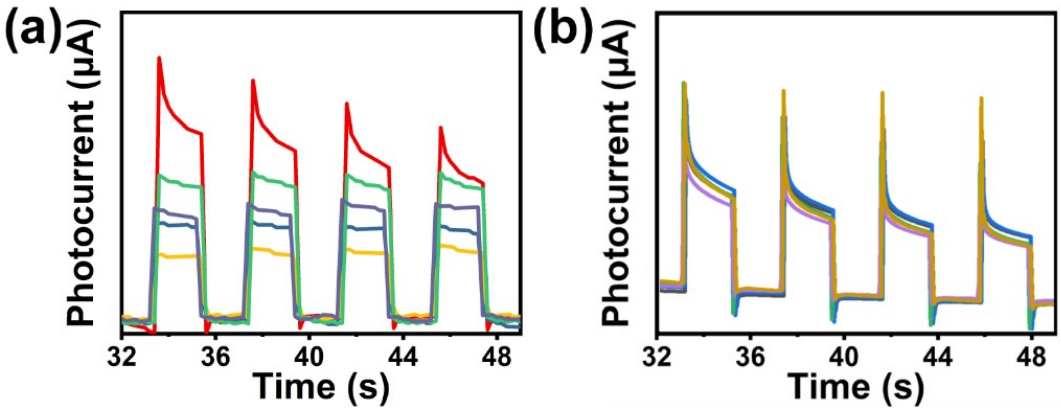


Figure S2 (a) One-step and (b) two-step photocurrent-time plots of the same batch of SiNWs arrays.

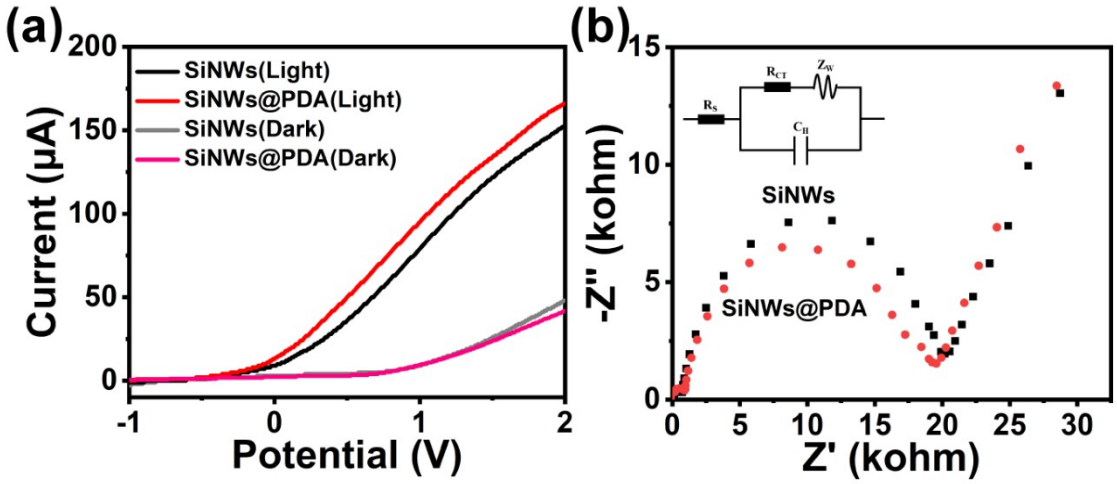
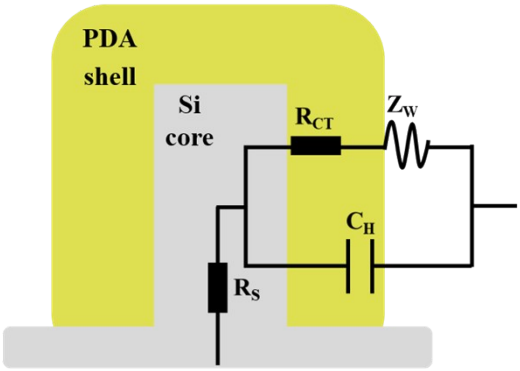


Figure S3 (a) The photocurrent-time curves and (b) EIS Nyquist plots of SiNWs and SiNWs@PDA.

EIS fitting data during working electrode assembly

Sample	R_{ct} (kohm)
a	15.64
b	13.11
c	30.76
d	41.08
e	84.64



EIS fitting data of different concentrations of cTnI

Sample	R_{ct} (kohm)
a	40.92
b	60.25
c	72.08
d	84.49
e	103.8
f	126.3

Figure S4 The equivalent circuit model and corresponding fitted EIS data.

In this model, R_S represents the bulk series resistance from the electrode and electrolyte, C_H describes the Helmholtz capacitance, Z_W refers to the Warburg impedance originated from the diffusion process, and R_{CT} stands for the charge transfer resistance across the electrode/electrolyte interface. The arcs in the EIS Nyquist plot at high frequency represents the charge transfer resistance across electrode/electrolyte interface, whereas the straight line at the low frequency is ascribed to the control of charge transfer and diffusion processes. Smaller radii suggests smaller R_{CT} at the interface, and the smallest R_{CT} is consistent with the highest photocurrent density, indicative of most effective separation of the photogenerated carriers and fastest interfacial charge carrier transfer.

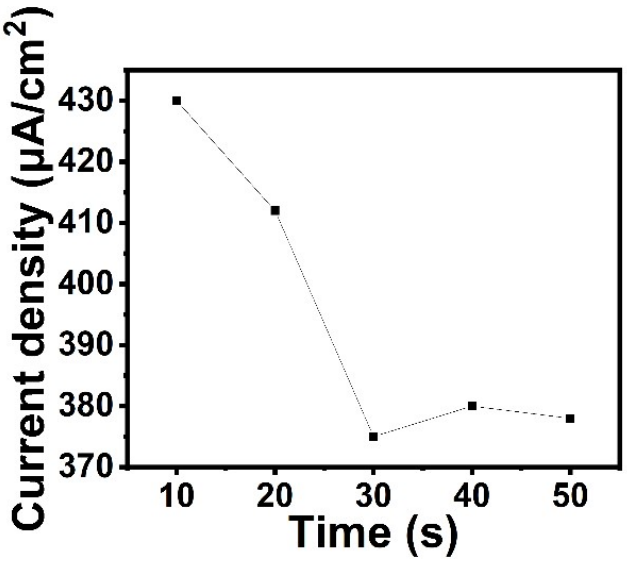


Figure S5 The photocurrent changes with time when the electrode was immersed in 2 mg/mL BSA solution for different time.

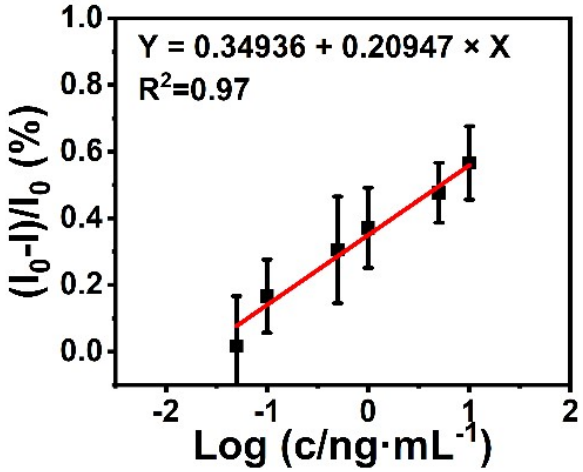


Figure S6 Relationship between photocurrent change and antibody concentration of APTES-functionalized SiNWs.

Preparation of APTES-SiNWs electrode

Firstly, the prepared SiNWs array was placed in a solution containing H_2SO_4:H_2O_2 (3:1/V:V) for hydroxylation treatment (30 min). Then the hydroxylated SiNWs array was transferred to a mixture containing APTES and ethanol and water (ethanol: water =V:V=95:5), and placed on a shaker for a certain time. After the reaction, the APTES-modified SiNWs array (APTES-SiNWs) was obtained by cleaning it with anhydrous ethanol for three times.

Construction of PEC immune sensor

cTnI antibody (anti-cTnI) covalently bound to the electrode surface through the reaction between carboxyl group and amino group. Firstly, EDC (10 mg/mL) and NHS (10 mg/mL) were added into anti-cTnI (0.1 mg/mL) solution and placed on a shaker for 15 min to activate the carboxyl groups on the surface of the antibody. Then, the activated anti-cTnI solution was dropped onto the surface of the APTES-SiNWs electrode (the electrode was placed in a wet box to avoid drying) and reacted at 37 °C for 1 h. After the reaction, phosphoric acid buffer (PBS, 0.01 M) was used to clean the electrode, and 1 mg/mL bovine serum protein was dropped onto the surface of the electrode (APTES-SiNWs/Ab), and the active site on the electrode surface was closed after incubation for 30 min to reduce the non-specific adsorption of non-target protein. Finally, the unbound BSA was washed with phosphoric acid buffer to obtain an APTES-SiNWs PEC immune sensor.

Table S1 Performance of different cTnI detection methods

Methods	Linear ranges (ng/mL)	LOD (pg/mL)	Reference
Electrochemical Immunoassay	0.5 ~ 100	40	[1]
ELISA	0.1 ~ 10	27	[2]
Photoelectrochemical	50 ~ 500000	8.0	[3]
Differential Pulse Voltammetry	1.25 ~ 125	67.5	[4]
Electrochemical Impedance Spectroscopy	0.25 ~ 2.50 × 104	30	[5]
Enzymatic Chemiluminescence	0.1 ~ 50	100	[6]
Fluorescent Aptasensor	0.1 ~ 6	0.07	[7]
Photoelectrochemical	0.005 ~ 10	1.47	This work

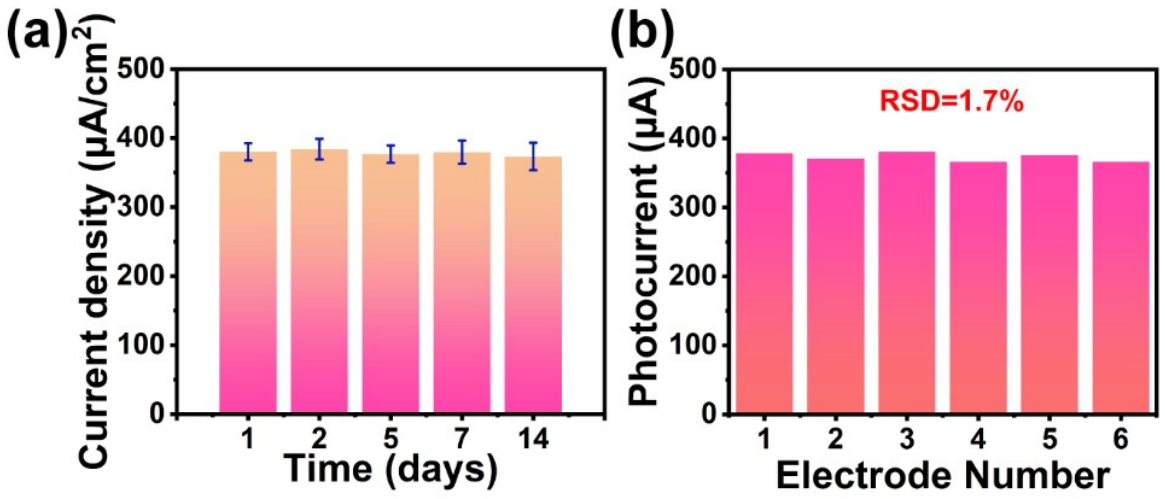


Figure S7. Stability of the electrodes stored in vacuum for different days.

1. B. Rezaei, A.M. Shoushtari, M. Rabiee, L. Uzun, W.C. Mak and A.P. Turner, Talanta, 2018, **182**, 178-186.

2. I.H. Cho, E.H. Paek, Y.K. Kim, J.H. Kim and S.H. Paek, Anal. Chim. Acta, 2009, **632**, 247-255..

3. M. Negahdary, Biosens. Bioelectron., 2020, **152**, 112018.

4. J. Zuo, X. Zhao, X. Ju, S. Qiu, W. Hu, T. Fan and J. Zhang, Electroanalysis, 2016, **28**, 2044-2049

5. X. Qiao, K. Li, J. Xu, N. Cheng, Q. Sheng, W. Cao, T. Yue and J. Zheng, Biosens. Bioelectron., 2018, **113**, 142-147.

6. J. Liu, L. Zhang, Y. Wang, Y. Zheng, S. Sun, Measurement, 2014, **47**, 200-206.

7. D. Liu, X. Lu, Y. Yang, Y. Zhai, J. Zhang and L. Li, Anal. Bioanal. Chem., 2018, **410**, 4285-4291.