Insights into the Mechanism of Bipolar Electrodeposition of Au Films and Its Application in Visual Detection of Prostate Specific Antigens

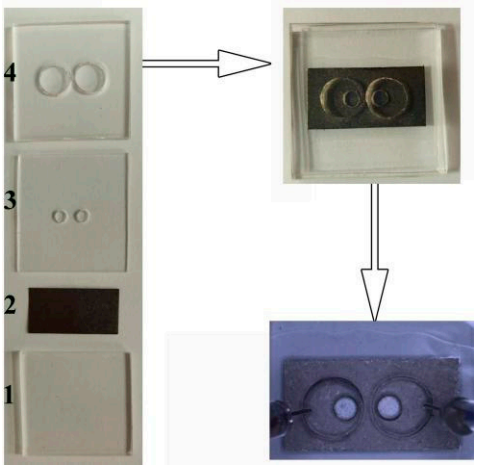
Daoyuan Zhao[a], Yujing Liu[b], Hong Jiang[b], Haijian Yang[a], Huihui Yu[a], Jingtang Qiao[a], Zhiwen Li[a], Bing Jin[a]*, and Meisheng Wu[a]*

[a]Department of Chemistry, College of Sciences, Nanjing Agricultural University, 1 Weigang, Nanjing 210095, P.R. China.

[b]College of Life Sciences, Nanjing Agricultural University, 1 Weigang, Nanjing 210095, P.R. China.

Correspondence: wumeisheng@njau.edu.cn (M. S. Wu.); jinbing@njau.edu.cn (B. Jin)

Contents



Scheme S1 Closed bipolar deposition device.

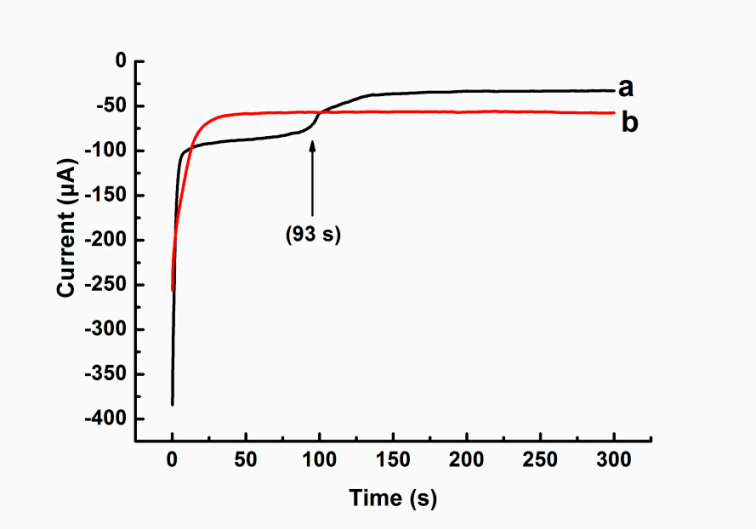


Figure S1 Amperometric i-t plots obtained on bare GP (cathode)-Au modified GP (anode) BPE when the anode was immersed into 10 mM PBS (a) and 5 mM $HAuCl_4$ (b), respectively. The cathode was immersed into 5 mM $HAuCl_4$. The external voltage was 4.5 V.

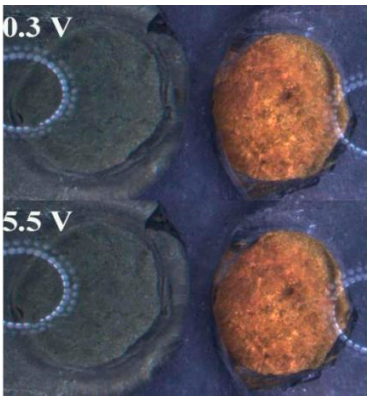


Figure S2 Optical images recorded during the second deposition of Au under linear sweep voltage. The left reservoir was filled with 5 mM $HAuCl_4$ and the right reservoir was filled with water. The voltage was applied from 0 to 5.5 V at a scan rate of 0.005 V/s.

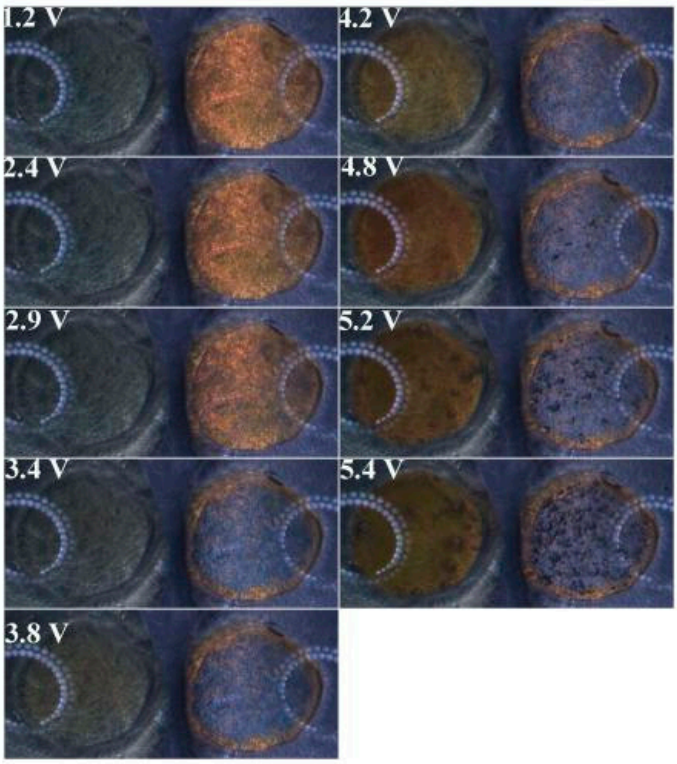


Figure S3 Optical images recorded during the second deposition of Au under linear sweep voltage. The left reservoir was filled with 5 mM $HAuCl_4$ and the right reservoir was filled with 10 mM PBS. The applied voltage was from 0 to 5.5 V at a scan rate of 0.005 V/s.

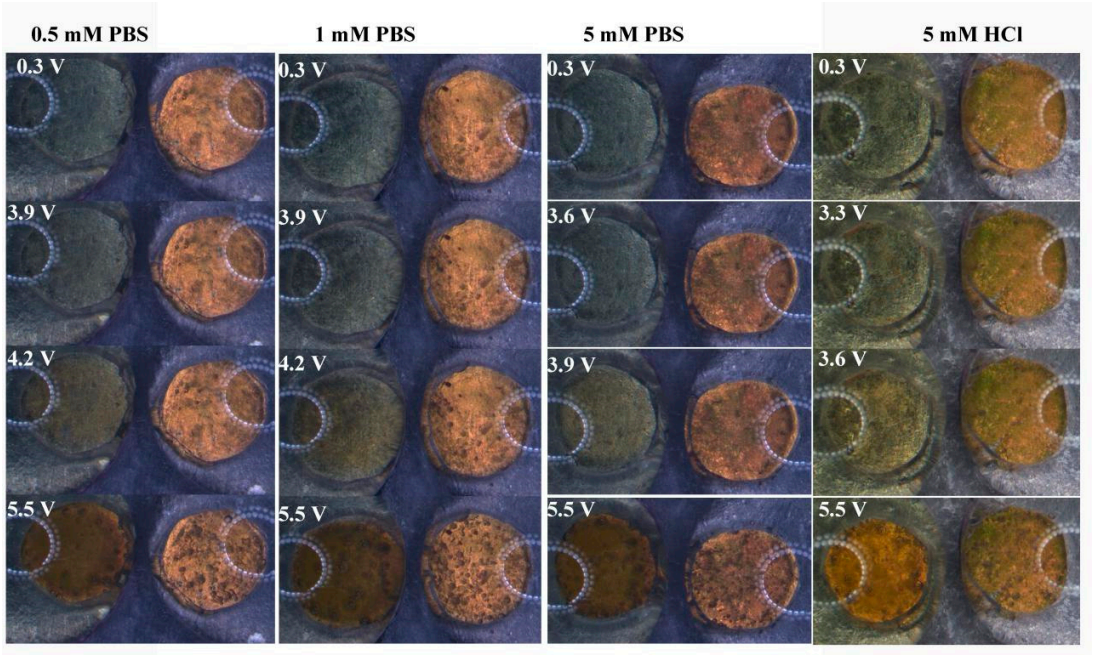


Figure S4 Optical images recorded during the second deposition of Au under linear sweep voltage. The left reservoir was filled with 5 mM $HAuCl_4$ and the right reservoir was filled with 0.5 mM PBS, 1 mM PBS, 5 mM PBS, and 5 mM HCl. The applied voltage was from 0 to 5.5 V at a scan rate of 0.005 V/s.

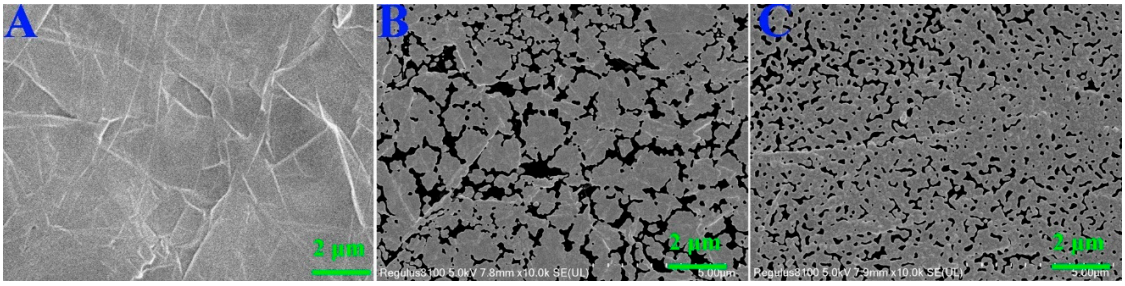


Figure S5 SEM images of (A) GP, (B) Au-1 film modified GP, and (C) Au-2 film modified GP.

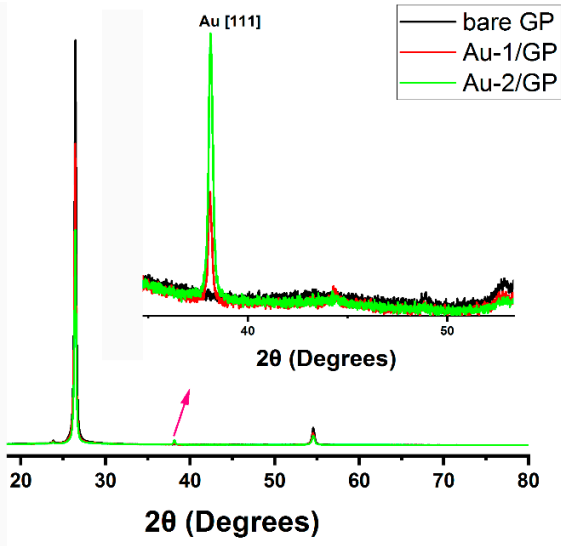


Figure S6 XRD patterns of GP substrate, Au-1 film modified GP (Au-1/GP), and Au-2 film modified GP (Au-2/GP).

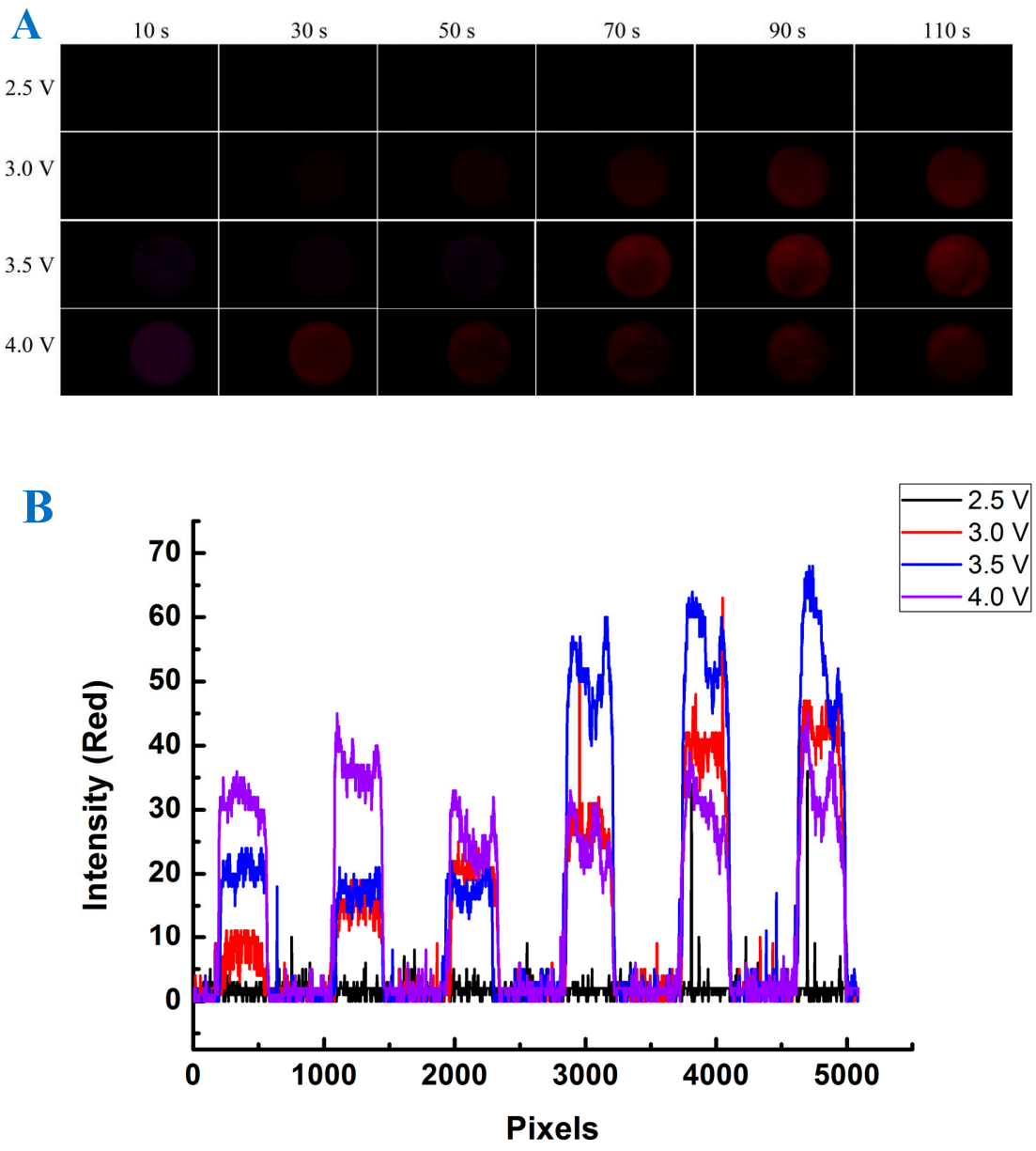


Figure S7 ECL images (A) and corresponding red channel intensity (B) obtained on Au modified (cathode)-Au modified (anode) GP BPE under different external voltages.

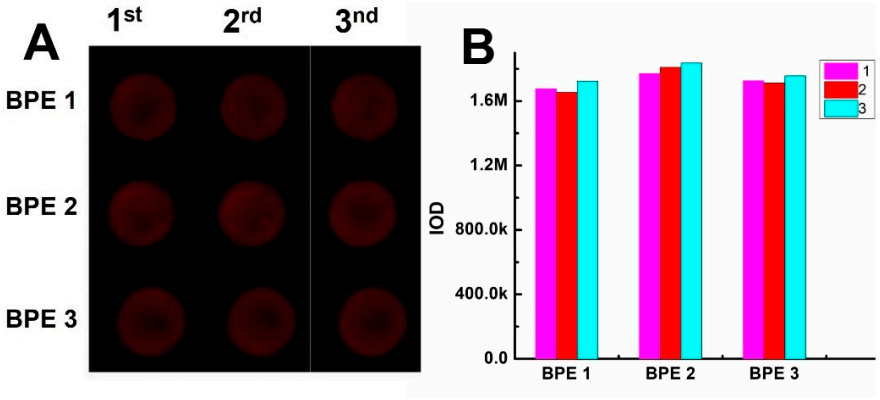


Figure S8 ECL images (A) and corresponding IOD (integrated optical intensity, B) obtained on four Au modified (cathode)-Au modified (anode) GP BPEs for three consecutive measurements.

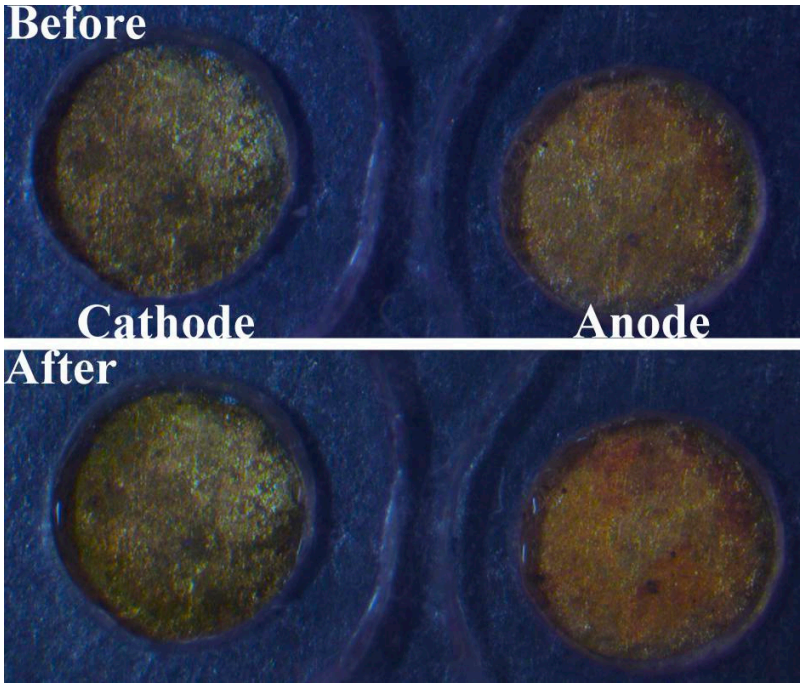


Figure S9 Images of BPE before and after three consecutive ECL detections.

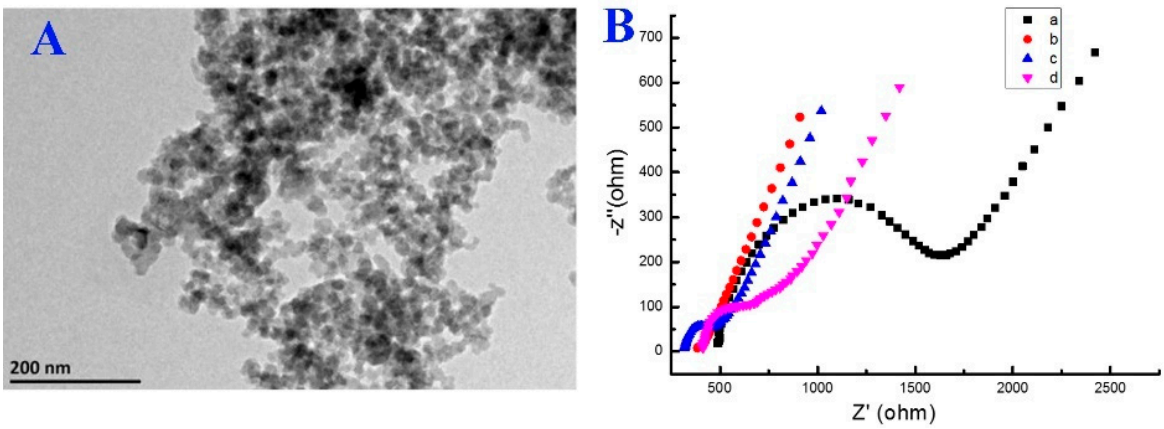


Figure S10 (A) TEM image of SiO_2 NPs. (B) Electrochemical impedance spectrum of various electrodes. Electrode was immersed in 5.0 mM $[Fe(CN)_6]^{3-/4-}$ solution containing 0.1 M KCl. Frequency range: 0.1-10^5 Hz. (a) Bare GP, (b) Ab_1/Au/GP, (c) PSA/Ab_1/Au/GP, (d) Ab_2-SiO_2/PSA/Ab_1/Au/GP.

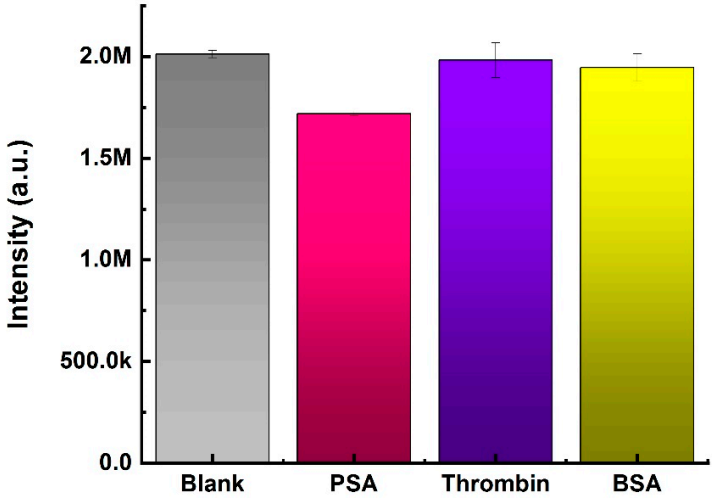


Figure S11 Selectivity of the designed biosensor towards thrombin and BSA. The concentration of PSA was 1 ng/mL. The concentration of thrombin and BSA were 10 ng/mL.

Table S1 Conductivity of solutions

Solution	Conductivity (μS/cm)
10 mM PBS	Out of range
5 mM PBS	8280
5 mM $HAuCl_4$	2340
5 mM HCl	2000
1 mM PBS	1779
0.5 mM PBS	923
H_2O	1.70

Table S2 Performance of the proposed biosensor compared with other biosensors

Analytical method	Linear range (ng/mL)	LOD (ng/mL)	Refs
ECL	1.0 to 1000	0.5	[1]
ECL	0.5 to 50	0.031	[2]
Colorimetric assay	0.1 to 100	0.02	[3]
Electrochromic assay	0.1 to 50	0.03	[4]
Photothermal imaging assay	1 to 200	0.2	[5]
ECL	0.1 to 1000	0.071	Our work

References:

[1] Lu, H.-J., Zhao, W., Xu, J.-J., and Chen, H.-Y. Visual electrochemiluminescence ratiometry on bipolar electrode for bioanalysis, *Biosensors and Bioelectronics* **2018**, *102*, 624-630.

[2] Cao, J.-T., Wang, Y.-L., Zhang, J.-J., Dong, Y.-X., Liu, F.-R., Ren, S.-W., and Liu, Y.-M. Immuno-Electrochemiluminescent Imaging of a Single Cell Based on Functional Nanoprobes of Heterogeneous Ru(bpy)32+@SiO2/Au Nanoparticles, *Analytical chemistry* **2018**, *90*, 10334-10339.

[3] Shayesteh, O. H., and Ghavami, R. A novel label-free colorimetric aptasensor for sensitive determination of PSA biomarker using gold nanoparticles and a cationic polymer in human serum, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2020**, *226*, 117644.

[4] Lei, Q., Wang, Y., Dong, W., Sun, H., Lv, J., and Li, H. Self-powered electrochromic sensing for visual determination of PSA in serum using PB as an indicator, *Journal of Electroanalytical Chemistry* **2019**, *839*, 108-115.

[5] Lv, S., Zhang, K., and Tang, D. A new visual immunoassay for prostate-specific antigen using near-infrared excited CuxS nanocrystals and imaging on a smartphone, *The Analyst* **2019**, *144*, 3716-3720.