

Sensitive photoelectrochemical immunoassay of *Staphylococcus aureus* based on one-pot electrodeposited ZnS/CdS heterojunction nanoparticles

Hui Yang, Xiao Zhao, Hui Wang, Wenfang Deng,* Yueming Tan,* Ming Ma, and Qingji Xie

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

Email: dandy3-3@163.com (W. Deng); tanyueming0813@hunnu.edu.cn (Y. Tan)

Sodium dodecyl sulfate polyacrylamide gel electrophoresis

In the experiment, 2 μL of sample was mixed with 8 μL of Milli-Q water and 2 μL of 6 \times loading buffer, and then the mixture was loaded into sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) gel. A 0.5 M Tris/boric acid buffer was used as the running buffer. The gel was run for 1 h at a voltage of 120 V.

Bacterial growth

S. aureus, *E. coli* O157:H7, *E. coli* K12, and *Salmonella typhimurium* grew in sterile Luria-Bertani (LB) media (2.0 g bacto-tryptone, 1.0 g bacto-yeast extract powder, 2.0 g NaCl dissolving in 200 mL distilled water, and adjusted to pH 7.4 with 3.0 M NaOH) in an incubator-shaker at 37 °C to reach the growing stationary phase. After overnight incubation, 1 mL of bacterial cells was centrifuged (6000 rpm, 10 min) to remove the supernatant and washed 3 times with PBS (0.1 M, pH 7.4), and resuspended in 1 mL of PBS. The bacterial concentration was adjusted to an appropriate level by measuring the optical density (OD) at 600 nm. By plating bacteria on LB plates, the amount of bacteria per milliliter can be acquired by counting related colony forming units (CFU) after incubation overnight at 37 °C.

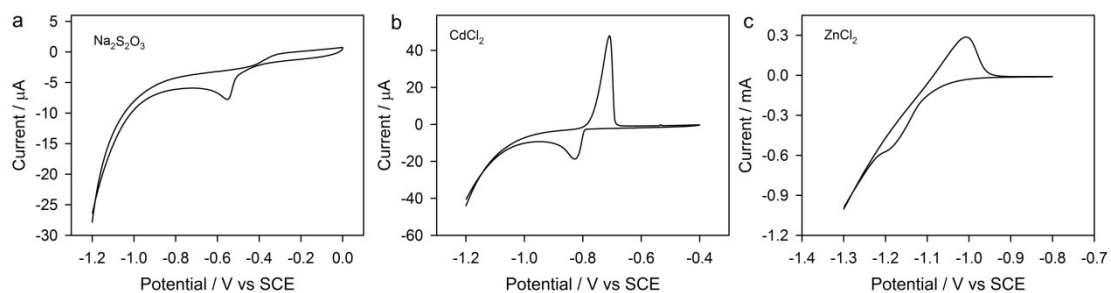


Fig. S1 Cyclic voltammograms on the ITO electrode in citrate buffer solution (pH 3.0) containing 8 mM $\text{Na}_2\text{S}_2\text{O}_3$ (a), 0.05 mM CdCl_2 (b), and 0.05 mM ZnCl_2 (c) at a scan rate of 40 mV s^{-1} .

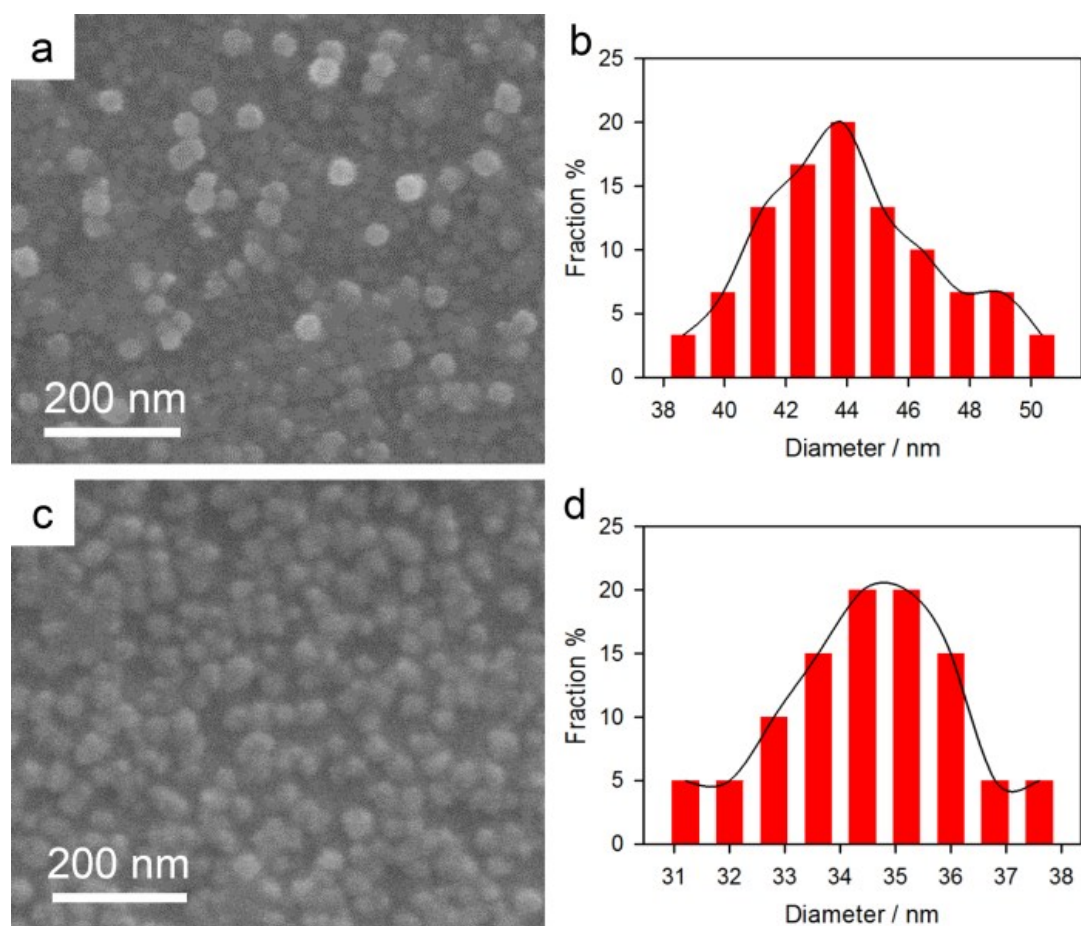


Fig. S2 SEM image (a) and size distribution (b) of ZnS nanoparticles deposited on ITO electrode. SEM image (c) and size distribution (d) of CdS nanoparticles deposited on ITO electrode.

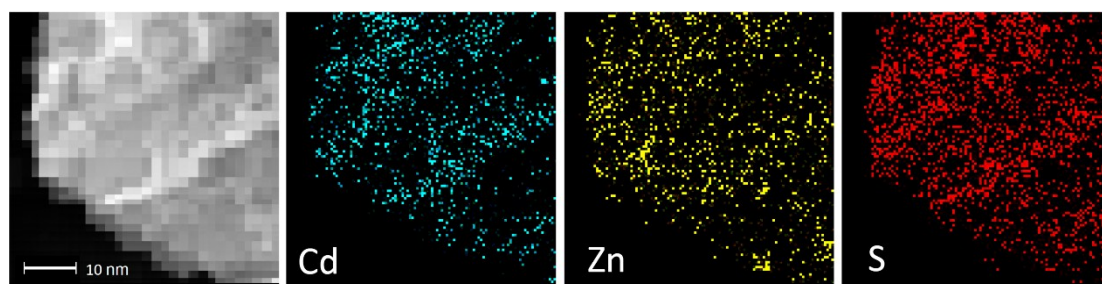


Fig. S3 High angle annular dark field scanning image and energy-dispersive X-ray elemental mapping of a ZnS/CdS nanoparticle.

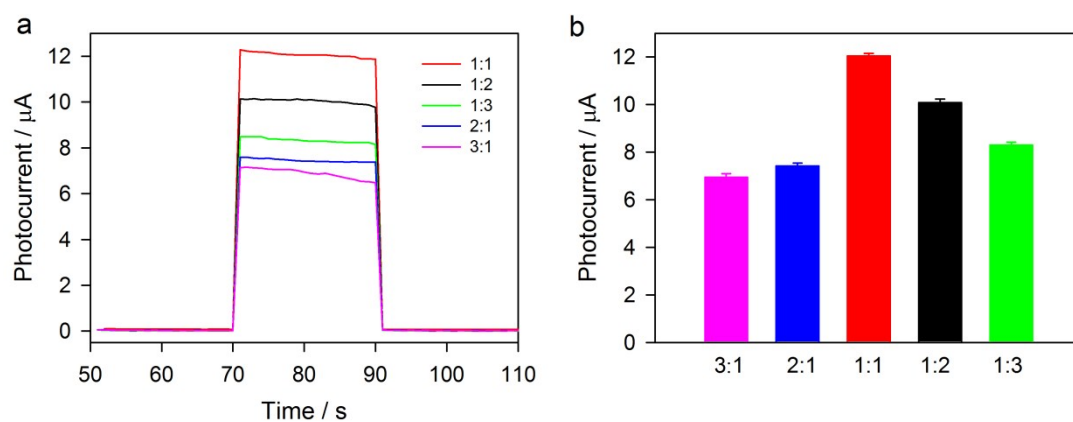


Fig. S4 Photocurrent curves (a) and measured photocurrents (b) of ZnS/CdS/ITO with different Zn/Cd atomic ratios in 0.1 M Na_2SO_4 aqueous solution containing 50 μM L-cysteine at 0.1 V.

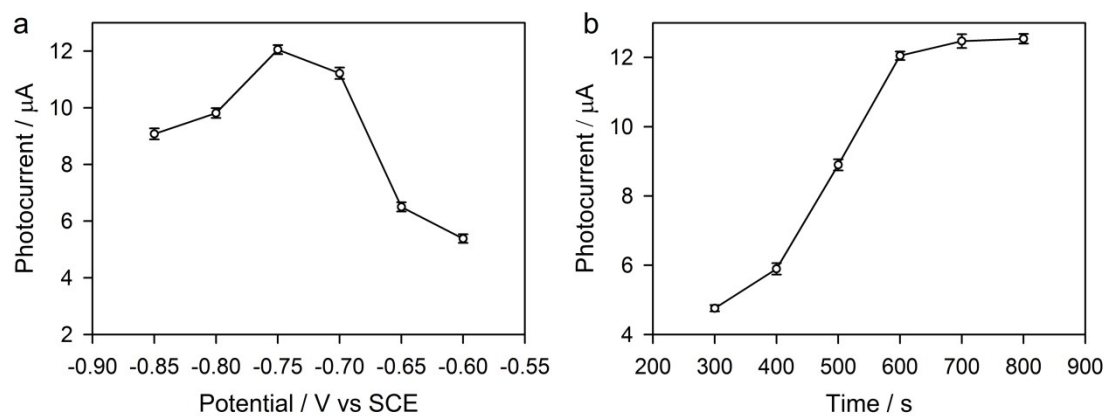


Fig. S5 The effects of deposition potential (a) and deposition time (b) on the photocurrent responses of the as-prepared ZnS/CdS/ITO in 0.1 M Na_2SO_4 aqueous solution containing 50 μM L-cysteine.

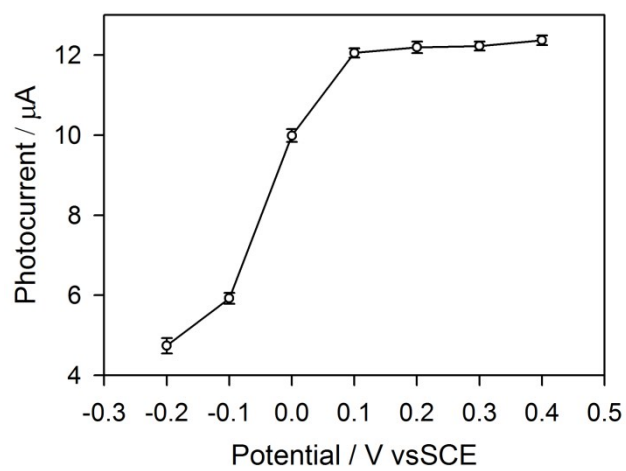


Fig. S6 The effect of bias potential on the photocurrent responses of the ZnS/CdS/ITO in 0.1 M Na₂SO₄ aqueous solution containing 50 μM L-cysteine.

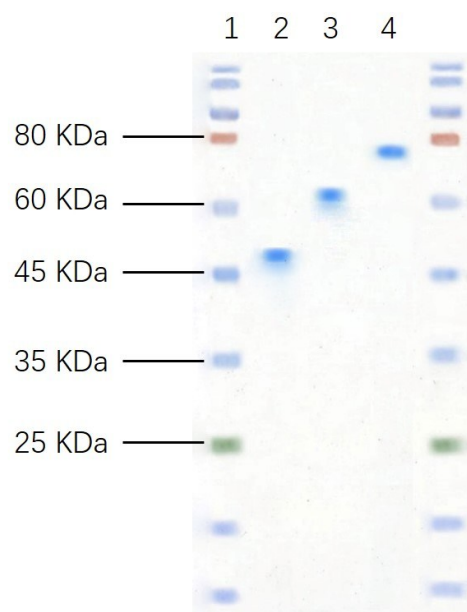


Fig. S7 SDS-PAGE results for 120-kDa protein marker (Lane 1), anti-*S. aureus* antibody (Lane 2), cysteine@liposome immunonanocapsules (Lane 3), and immunomagnetic nanoparticles (Lane 4).

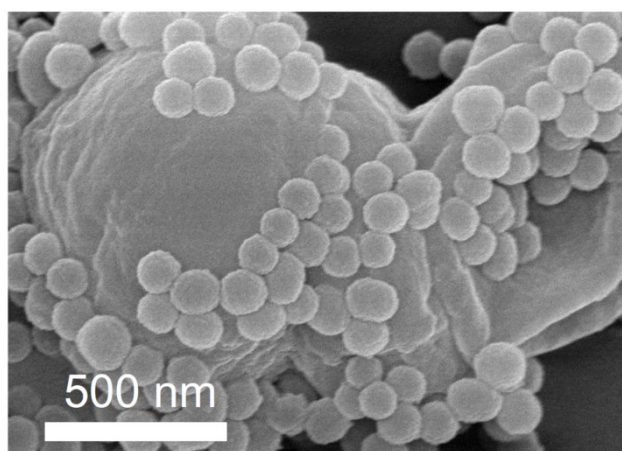


Fig. S8 SEM images of *S. aureus* cells labeled with cysteine@liposome immunonanocapsules.

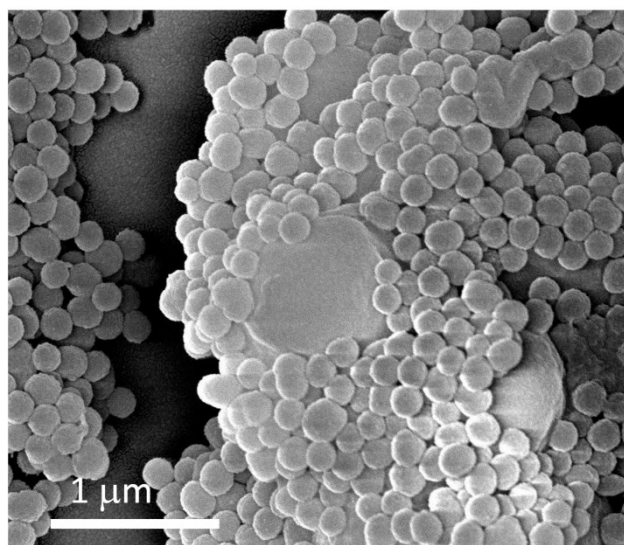


Fig. S9 SEM image of *S. aureus* cells separated from the samples by immunomagnetic nanoparticles.

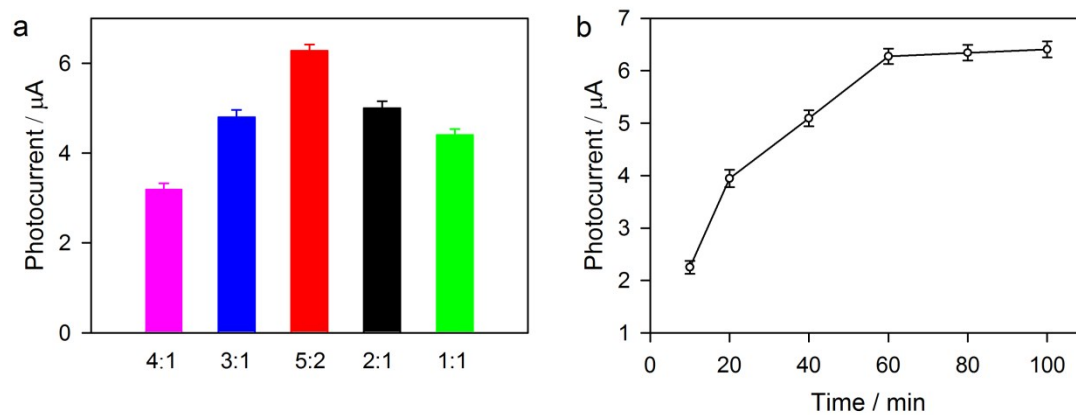


Fig. S10 (a) Effect of the weight ratio of cysteine@liposome immunonanocapsules and immunomagnetic nanoparticles on the photocurrent responses for the detection of 1000 CFU mL^{-1} *S. aureus*. (b) Effect of incubation time on the photocurrent responses for the detection of 1000 CFU mL^{-1} *S. aureus*.

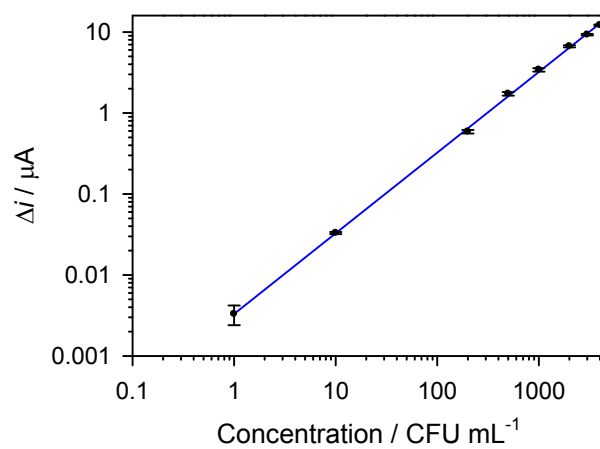


Fig. S11 Calibration curve (a log scale presentation) for photoelectrochemical detection of *S. aureus*. Error bars represent the standard deviation.

Table S1. The effects of metal ion concentrations in the electrodeposition bath on the composition of the prepared ZnS/CdS heterojunction nanoparticles.

Sample	Concentration ratio of Cd ²⁺ and Zn ²⁺ in electrolyte	Cd/Zn atomic ratio measured by EDS
1	1 : 1	52.0 : 48.0
2	2 : 1	67.8 : 32.2
3	3 : 1	76.3 : 23.7
4	1 : 2	34.6 : 65.4
5	1 : 3	26.2 : 73.8

Table S2. The comparison of the determination of pathogen in the literature.

Technique	Target	Linear range (CFU mL ⁻¹)	Detection limit (CFU mL ⁻¹)	Ref.
Surface plasmon resonance	<i>Salmonella</i>	10 ² - 10 ⁶	100	1
Colorimetry	<i>S. aureus</i>	1.5×10 ³ - 1.5×10 ⁵	1.5×10 ³	2
Fluorescent spectrometry	<i>S. aureus</i>	1.0×10 ³ - 1.0×10 ⁹	2.9×10 ²	3
Electrochemical	<i>E. coli</i> O157:H7	3.0×10 ² - 3.0×10 ⁸	100	4
Surface plasmon resonance	<i>E. coli</i> O157:H7	0.25×10 ⁴ - 4×10 ⁴	1.87 × 10 ³	5
Fluorescent spectrometry	<i>S. typhimurium</i>	50-10 ⁷	50	6
Positive dielectrophoresis driven and fluorescence	<i>S. aureus</i>	93-270	93	7
Fluorescence	<i>E. coli</i> O157:H7	5×10 ² - 5×10 ⁶	500	8
Colorimetry	<i>S. aureus</i>	4.0×10 ³ - 10 ⁶	4.0×10 ³	9
Photoelectrochemical	<i>S. aureus</i>	1 - 4000	30	This work

References

1. Z. Farka, T. Juřík, M. Pastucha and P. Skládal, *Anal. Chem.*, 2016, **88**, 11830-11836.
2. Y. J. Sung, H.-J. Suk, H. Y. Sung, T. Li, H. Poo and M.-G. Kim, *Biosens. Bioelectron.*, 2013, **43**, 432-439.
3. W. Kong, J. Xiong, H. Yue and Z. Fu, *Anal. Chem.*, 2015, **87**, 9864-9868.
4. H. Huang, M. Liu, X. Wang, W. Zhang, D.-P. Yang, L. Cui and X. Wang, *Nanoscale Res. Lett.*, 2016, **11**, 507-515.
5. S. Wang, J. Xie, M. Jiang, K. Chang, R. Chen, L. Ma, J. Zhu, Q. Guo, H. Sun and J. Hu, *Sensors*, 2016, **16**, 1856-1865.
6. P. Zhang, H. Liu, X. Li, S. Ma, S. Men, H. Wei, J. Cui and H. Wang, *Biosens. Bioelectron.*, 2017, **87**, 1044-1049.
7. J. Shanguan, Y. Li, D. He, X. He, K. Wang, Z. Zou and H. Shi, *Analyst*, 2015, **140**, 4489-4497.
8. R. Chen, X. Huang, J. Li, S. Shan, W. Lai and Y. Xiong, *Anal. Chim. Acta*, 2016, **947**, 50-57.
9. J. Yu, Y. Zhang, Y. Zhang, H. Li, H. Yang and H. Wei, *Biosens. Bioelectron.*, 2016, **77**, 366-371.