## Ultramicro and Ultrasensitive Detection of Lipopolysaccharide Based on Triple-Signal Amplification via Ultrafast ATRP and Ultramicroelectrode

Shipeng Jiang, Mingyang Sun, Peiran Meng, Xiaoyu Zhang, Yue Sun\*

School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, China

\*Corresponding author:

Email: yuesun@lnnu.edu.cn

Postal address: Yue Sun, School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, China



Fig. S1 FTIR characterization of CQDs

FTIR analysis showed that there were abundant surface groups on the surface of N-CQDs (Fig. S1).The wide band at 3310-3550 cm<sup>-1</sup> is caused by the stretching vibrations of O-H and N-H. The peak at 2928 cm<sup>-1</sup> is attributed to the C-H bond. The peak at 1639 cm<sup>-1</sup> can be attributed to C=O tensile vibration. The peaks at 1271, 1402, 1582 and 1621 cm<sup>-1</sup> belong to the tensile vibrations of C-O-C, C-N, C=C and C=N, respectively<sub>o</sub>



Fig. S2 CD of Apt in buffer (a) and polymeric solution and irradiate for 2.5 min(b).



Fig. S3 Device diagram of ultramicro system



**Fig. S4** CV (A) and DPV (B) results of using different reference electrodes in different volumes of electrolyte (PBS containing 5 mM [Fe(CN)<sub>6</sub>]<sup>3-/4-</sup> and 0.1 M KCl). 1-SCE in 10 mL; 2-PME in 10 mL;

## 3-PME in 5 µL

## Table S1 The properties of PME characterized by DPV

	1	2	3	4	5	RSD%
$I_{\rm p}({\rm nA})$	906.4	909.5	904.3	903.7	911.8	0.54
$E_{\rm p}\left({ m V} ight)$	0.004	0.004	0.003	0.004	0.005	0.01



Fig. S5 (A)Effect of the Initiator link time on the BPA/LPS/Apt/nAu/Au UME; (B) Effect of the polymerization time on the PMLA/LPS/Apt/nAu/Au UME; (C) Effect of the silver ammonia solution concentration on the AgNPs/PMLA/LPS/Apt/nAu/Au UME.

Table S2 Comparison between AgNPs/PMLA/LPS/Apt/nAu/Au UME and similar sensors for LPS

detection								
Strategy	Detection Methods	Linear response range (pg/mL)	LOD (pg/mL)	Detection volumes (µL)	Ref.			
Base on Cu <sup>2+</sup> -modified metal- organic framework	DPV	1.5-7.5×10 <sup>5</sup>	6.10×10 <sup>-1</sup>	10	[1]			

Base on dsDNA-templated					
fluorescent copper nanoparticles	fluorescence	10 <sup>3</sup> -10 <sup>8</sup>	9.50×10 <sup>2</sup>	105	[2]
Base on logical circuit by CRISPR/Cas12a-driven guanine nanowire assisted non-cross-linking hybridization chain reaction	RRS	10 <sup>3</sup> -10 <sup>5</sup>	0.17	600	[3]
mediated dual recognition coupled with a CRISPR/Cas12a system	fluorescence	5.0×10 <sup>1</sup> -5.0×10 <sup>6</sup>	44.86	80	[4]
Base on Raw264.7 cells	DPV	10-3000	3.50	50	[5]
Base on collaboration of dual enzymes	EIS	2.5-10 <sup>3</sup>	1.00	50	[6]
Based on boronate affinity and (4- (ferrocenylacetamido)phenyl)b oronic acid	SWV	1.0-10 <sup>3</sup>	0.34	10	[7]
Base on LAL	LAL	0.1-3.0	0.10	200	[8]
Based on UATRP and UME	SWV	10 <sup>-4</sup> -10 <sup>8</sup>	7.99×10 <sup>-2</sup>	5	This
	2				work



Fig. S6 Stability of the sensor (0-16 days).

## References

[1] Z. Li, G. Dai, F. Luo, Y. Lu, J. Zhang, Z. Chu, P. He, F. Zhang, Q. Wang, An electrochemical sensor for bacterial lipopolysaccharide detection based on dual functional Cu<sup>2+</sup>-modified metal-organic framework nanoparticles, Microchim. Acta, 2020, **187**, 415.

[2] N. K. Radhika, S. Gorthi, dsDNA-templated fluorescent copper nanoparticles for the detection of lipopolysaccharides, Anal. Methods, 2021, **13**, 186-191.

[3] Z. Gao, L. Zheng, L. Dong, J. Li, Y. Shen, P. Chen, F. Xia, Label-Free resonance rayleigh scattering amplification for lipopolysaccharide detection and logical circuit by CRISPR/Cas12a-Driven guanine nanowire assisted non-crosslinking hybridization chain reaction, Anal. Chem., 2022, 94, 6371-6379.

[4] A. Sheng, J. Yang, L. Cheng, J. Zhang, Boronic Ester-Mediated dual recognition coupled with a CRISPR/Cas12a system for lipopolysaccharide analysis, Anal. Chem., 2022, **94**, 12523-12530.

[5] H. Jiang, J. Yang, K. Wan, D. Jiang, C. Jin, Miniaturized paper-supported 3D cell-based electrochemical sensor for bacterial lipopolysaccharide detection, ACS Sens., 2020, **5**, 1325-1335.

[6] Y. Huang, L. Wang, L. Sha, Y. Wang, X. Duan, G. Li, Highly sensitive detection of lipopolysaccharide based on collaborative amplification of dual enzymes, Anal. Chim. Acta, 2020, **1126**, 31-37.

[7] Q. Hu, W. Feng, Y. Liang, Z. Liang, X. Cao, S. Li, Y. Luo, J. Wan, Y. Ma, D. Han, L. Niu, Boronate affinityamplified electrochemical aptasensing of lipopolysaccharide, Anal. Chem., 2022, 94, 17733-17738.

[8] T. J. NOVITSKY, Limitations of the limulus amebocyte lysate test in demonstrating circulating lipopolysaccharides, Ann. N. Y. Acad. Sci., 1998, **851**, 416-421.