

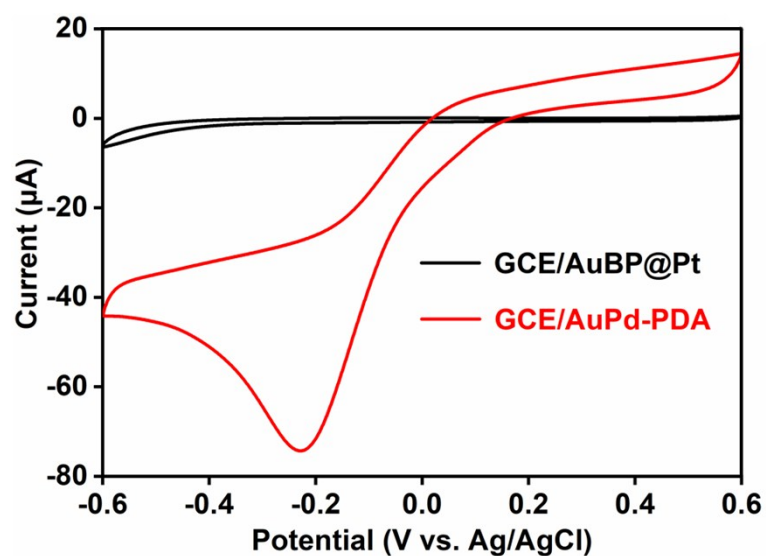
## Electrochemical immunosensor based on AuBP@Pt nanostructure and AuPd-PDA nanozyme for ultrasensitive detection of APOE4

Yibiao Liu\*, Guangli He, Huili Liu, Hang Yin, fengli Gao, Jian Chen\*, Shouren Zhang, Baocheng Yang

Henan Key Laboratory of Nanocomposites and Applications, Institute of Nanostructured Functional Materials, Huanghe Science and Technology College, Zhengzhou 450006, China.

\*Address correspondence: E-mail: [liuyibiao12345@126.com](mailto:liuyibiao12345@126.com);

[jianchen@infm.hhstu.edu.cn](mailto:jianchen@infm.hhstu.edu.cn);

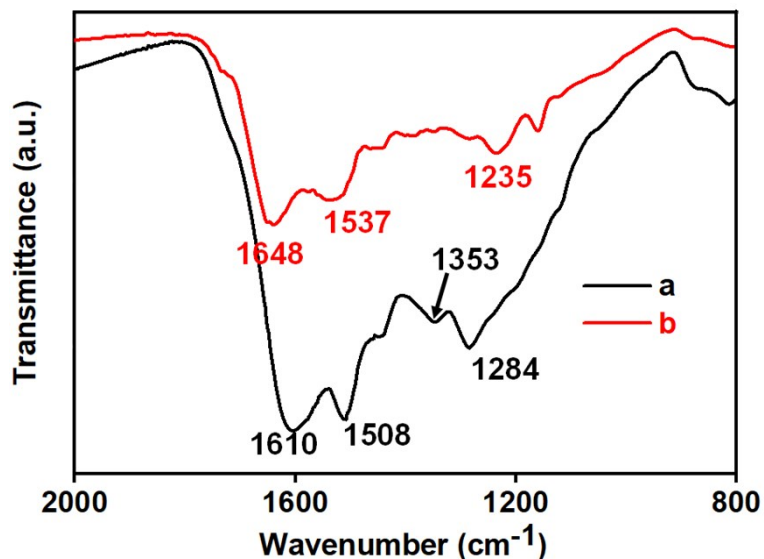


**Figure S1.** CV curves of GCE/AuBP@Pt and GCE/AuPd-PDA electrodes in Ar-saturated PBS (0.1 M, pH 7.4) buffer containing 2 mM H<sub>2</sub>O<sub>2</sub>.

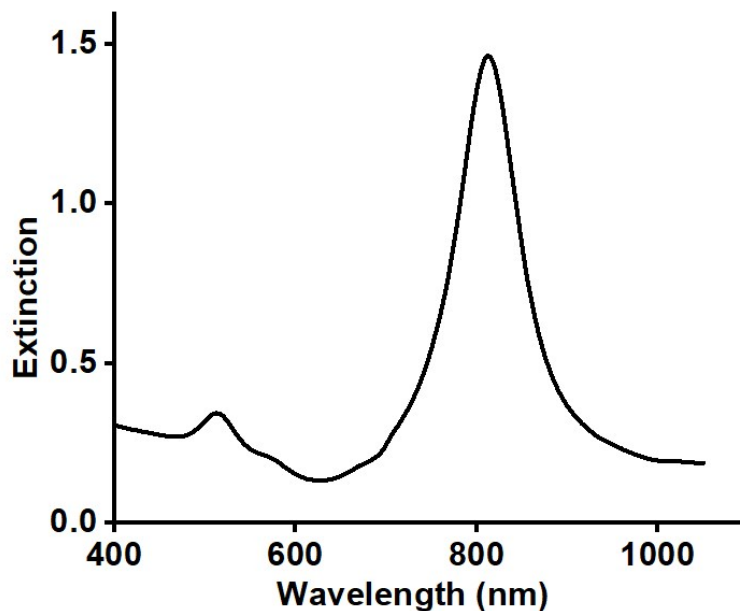
### The FTIR characterization of AuPd-PDA-Ab<sub>2</sub>.

The characteristic peaks of AuPd-PDA are at 1508 cm<sup>-1</sup> (scissoring vibration of N-H), 1353 cm<sup>-1</sup> (bending vibration of O-H), and 1284 cm<sup>-1</sup> (stretching vibration of phenolic C-O).

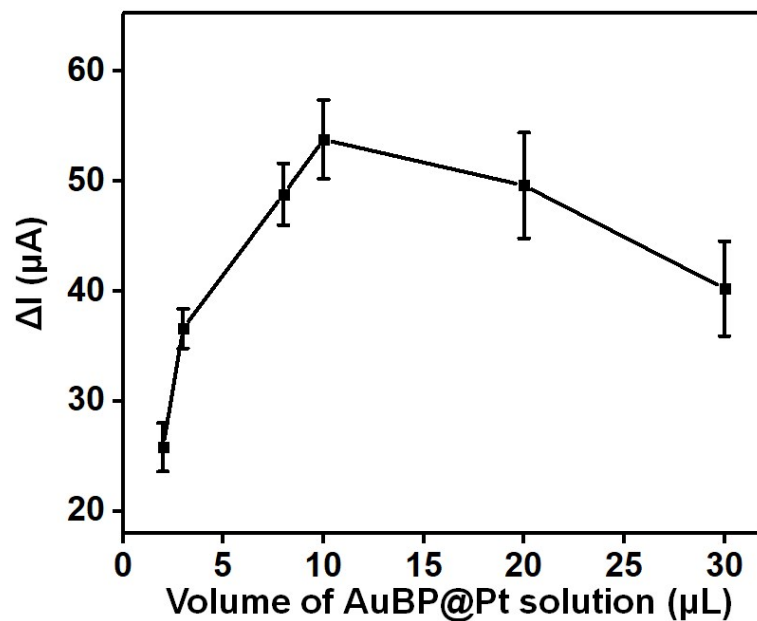
After the Ab<sub>2</sub> conjugation, the amide I (1648 cm<sup>-1</sup>, C=O stretching) and amide II (1537 cm<sup>-1</sup>, overlap of N-H bending and C-N stretching) bands of the Ab<sub>2</sub> are observed, which indicates that the human APOE4 detection antibody is successfully attached on the AuPd-PDA.



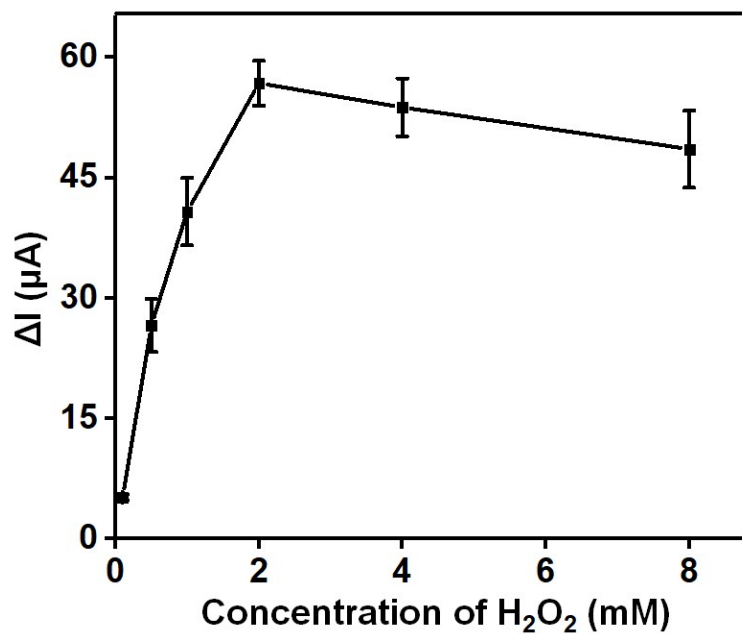
**Figure S2.** The FT-IR spectrum of AuPd-PDA (a) and AuPd-PDA-Ab<sub>2</sub> (b).



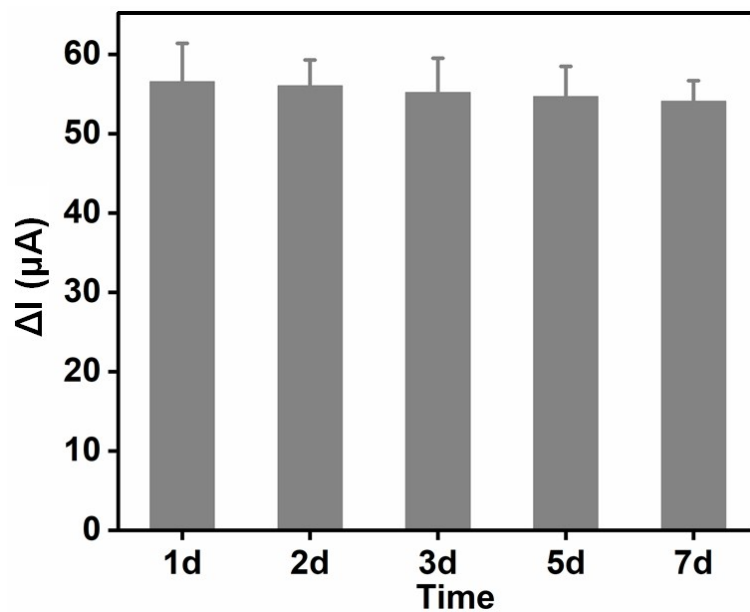
**Figure S3.** The characterization of Au BPs by extinction spectrum.



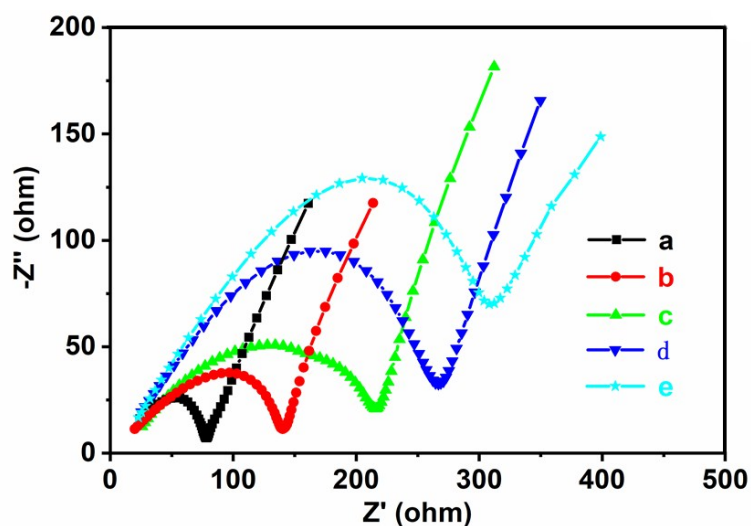
**Figure S4.** Optimization of AuBP@Pt volume when the concentration is constant. error bar = RSD (n = 5).



**Figure S5.** Optimization of  $\text{H}_2\text{O}_2$  concentration. Error bar = RSD (n = 5).



**Figure S6.** The stability study of the electrochemical immunosensor based on AuBP@Pt nanostructures and AuPd-PDA nanozyme. Error bar = RSD (n = 5)



**Figure S7.** The characterization of surface-modification on GCE/Au/AuBP@Pt electrode: EIS of the GCE/Au/AuBP@Pt electrode (a) modified with Ab<sub>1</sub> (b), Ab<sub>1</sub> + BSA (c), Ab<sub>1</sub> + BSA + APOE4 (d) Ab<sub>1</sub> + BSA + APOE4 + Ab<sub>2</sub> label (e). The EIS was carried out in 5 mM [Fe(CN)<sub>6</sub>]<sup>3-</sup>/[Fe(CN)<sub>6</sub>]<sup>4-</sup> at scan rates of 50 mV·s<sup>-1</sup>.

**Table S1.** Comparison between different methods for APOE or APOE4 detection.

Methods	Linear range (ng/mL)	LOD (ng/mL)	Target	Reference
Magneto-immunoassay	10~200	12.5	APOE	1
Nanobiosensor based on porous magnetic microspheres (PMM)	0.1~12.5	0.08	APOE	2
Electrochemical sandwich sensor	1~10000	0.3	APOE4	3
colorimetric immunosensor based on nanobody	0.001-10	0.00042	APOE	4
Electrochemical immunosensor	0.05-2000	0.015	APOE4	This work

**Table S2.** Determination of human APOE4 protein in goat serum.

Added APOE4 concentration (ng/mL)	Average $\Delta I$ ( $\mu A$ , n=5)	Measured concentration (ng/mL)	RSD (%, n=5)	Recovery (%, n=5)
1	36.83	0.97	3.47	97.00
10	55.62	10.48	5.46	104.80
100	73.66	102.78	5.31	102.78

## References

1. M. Medina-Sánchez, S. Miserere, E. Morales-Narváez and A. Merkoçi, *Biosensors and Bioelectronics*, 2014, **54**, 279-284.
2. A. de la Escosura-Muñiz, Z. Plichta, D. Horák and A. Merkoçi, *Biosensors and Bioelectronics*, 2015, **67**, 162-169.
3. Y. Liu, L.-P. Xu, S. Wang, W. Yang, Y. Wen and X. Zhang, *Biosensors and Bioelectronics*, 2015, **71**, 396-400.
4. X. Ren, J. Yan, D. Wu, Q. Wei and Y. Wan, *ACS Sensors*, 2017, **2**, 1267-1271.

