Supporting Information

Dual-mode label-free electrochemical immunosensor for ultrasensitive detection

of procalcitonin based on g-C₃N₄-NiCo₂S₄-CNTs-Ag NPs

Xiaoting Xu, Xuan Li, Juncong Miao, Lei Liu*, Xinyi Huang, Qin Wei, Wei Cao*

Key Laboratory of Interfacial Reaction & Sensing Analysis in Universities of

Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan

250022, PR China

*Corresponding author.

E-mail address: jn_chm302@163.com (W. Cao), chm_liul@ujn.edu.cn (L. Liu).

1.Experimental section

1.1Reagents and apparatuses

CNTs was purchased from China Chemical Reagent Co., Ltd. nickel acetate tetrahydrate (Ni(Ac)₂•4H₂O) and Cobalt acetate tetrahydrate (Co(Ac)₂•4H₂O) were purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Isopropanol was obtained from fuyu Fiine Chemical Co., Ltd (Tianjin,China). BSA was purchased from Sigma-Aldrich (Beijing, China). AgNO₃ was purchased from Aladdin Reagent Database Inc. (Shanghai, China). PCT and antibody-PCT was purchased from Nanjing Jinrui Technology Co., Ltd. (Nanjing, China).

Scanning electron microscope (SEM) was obtained from a field emission SEM (Zeiss, Germany). Energy dispersive X-ray spectroscopy (EDX) obtained from QuantaFEG 50 (FEI, USA). Electrochemical measurements were performed on a CHI760D electrochemical workstation (Chenhua Instrument Shanghai Co., Ltd., China).

2. Real sample analysis

To evaluate the accuracy and feasibility of the immunosensor, the recovery of P CT in the serum sample was assessed by standard addition method. Firstly, the human blood was pretreated by centrifugation to remove the blood cells and other blood sedi ment. Then, the human serum was taken out and the samples were diluted with PBS (pH=7.38) until a level that was during the calibration range.

Electrochemical technique	Analysis scope	LOD	References
automated immunoassays	0.02 ng/mL -50 ng/mL	0.06 ng/mL	1
multicenter comparison of automated procalcitonin immunoassays	0.02 ng/mL -50 ng/mL	0.05 ng/mL	2
fluorescence immunoassay	25 pg/mL -100 ng/mL	0.04 ng/mL	3
label-free competitive electrochemical immunosensor	0.05 ng/mL-50 ng/mL	16.7 pg/mL	This work
dual-mode label-free electrochemical immunosensor	1 pg/mL-10 ng/mL	0.33 pg/mL	This work

Table.S1 Comparison of different electrochemical technique used to detect PCT



Fig. S1 (A) stability of the sensor: DPV (a), i-t (b), Error bar = SD (n=5); (B)selectivity of the sensor: (1) 1 ng/mL PCT+10 ng/mL Aβ, (2) 1 ng/mL PCT+10 ng/mL PSA, (3) 1 ng/mL
PCT+10 ng/mL BNP, (4) 1 ng/mL PCT+10 ng/mL CEA, (5) 1 ng/mL PCT+10 ng/mL insulin; (C) reproducibility of the sensor;

References

1. P. Schuetz, M. Christ-Crain, A. R. Huber, B. Muller, Long-term stability of procalcitonin in frozen samples and comparison of Kryptor and VIDAS automated immunoassays. *Clin Biochem* 2010, **43** (**3**), 341-4.

2. M. Dipalo, L. Guido, G. Micca, S. Pittalis, M. Locatelli, A. Motta, V. Bianchi, T. Callegari, R. Aloe, G. Da Rin, G. Lippi, Multicenter comparison of automated procalcitonin immunoassays, Pract Lab Me: 2015, **2**, 22-28.

3. D. Rascher, A. Geerlof, E. Kremmer, P. Kramer, S. Michael, A. Hartmann, M. Rieger, Total internal reflection (TIRF)-based quantification of procalcitonin for sepsis diagnosis-a point-of-care testing application, Biosens Bioelectron 2014, **59**, 251-258.