Supporting Information

Ratiometric Electrochemical strategy for Sensitive Determination of Furin Activity Based on Dual Signal Amplification and Anti-fouling Nanosurface

Dazhi Yao, Wenqi Zhao, Limin Zhang* and Yang Tian*

School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, P.R. China.

*Corresponding author.
E-mail: lmzhang@chem.ecnu.edu.cn; ytian@chem.ecnu.edu.cn
Tel: +86-21-54345031; Fax: +86-21-54341041.

1. Ultraviolet-Visible absorption spectrum of GBFs.

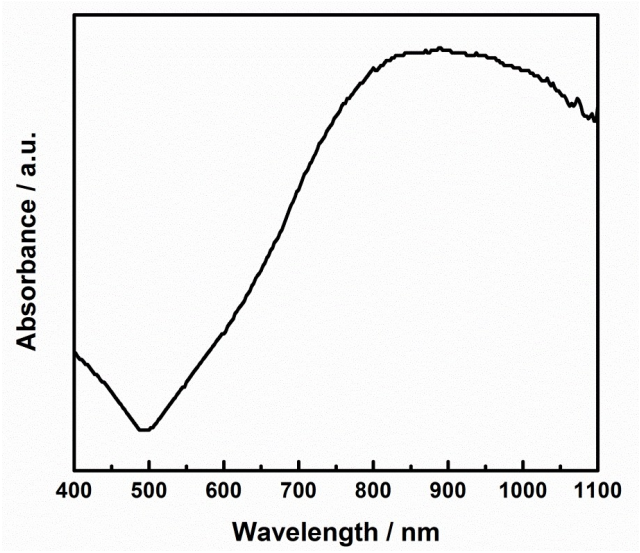

Figure S1. Ultraviolet-Visible absorption spectrum of GBFs.

2. XPS characterization of modification process of electrodes

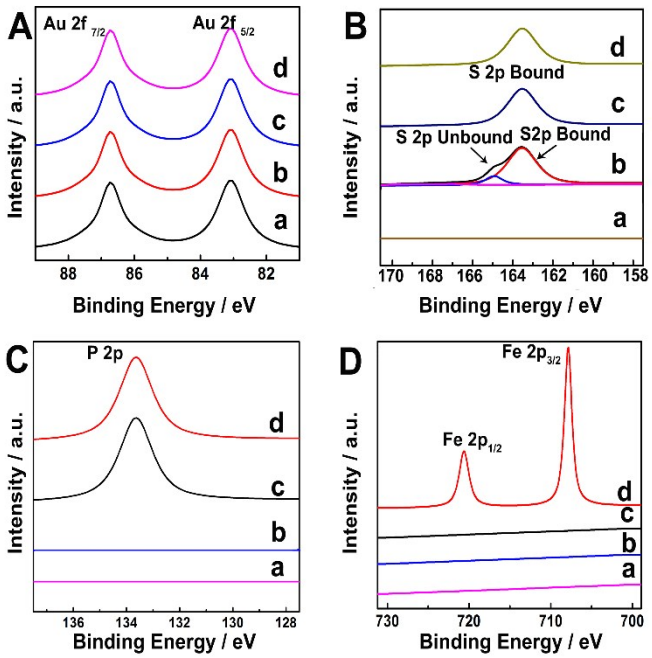

Figure S2. XPS spectra of (A) Au 4f7/2 and Au 4f5/2, (B) S 2p, (C) P 2p, (D) Fe 2p3/2 and Fe 2p1/2 for (a) Au, (b) Au/GBF, (c) Au/GBF/MB+P3 and (d) GBF/MB+P3/Fc, respectively.

3. Stability test.

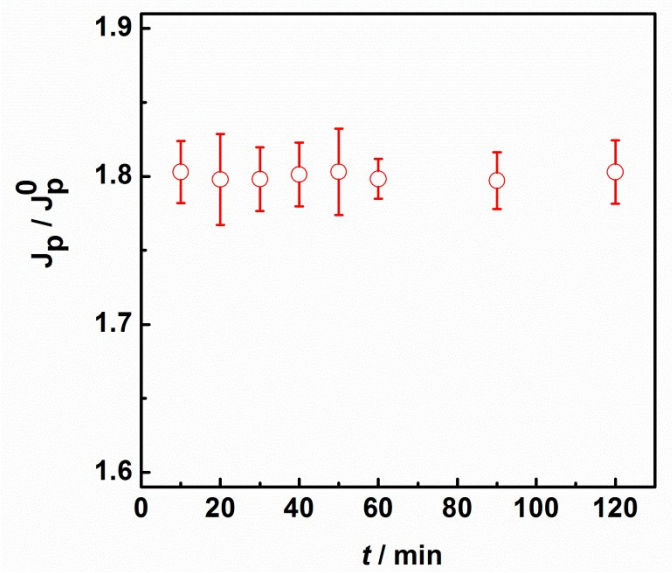

Figure S3. Stability test for GBF/MB+P3/Fc in 10 mM PBS (pH 7.4).

4. HPLC traces of P3 alone, P3 with Furin, or P3 incubated with the inhibitor before addition of Furin for 30 minutes

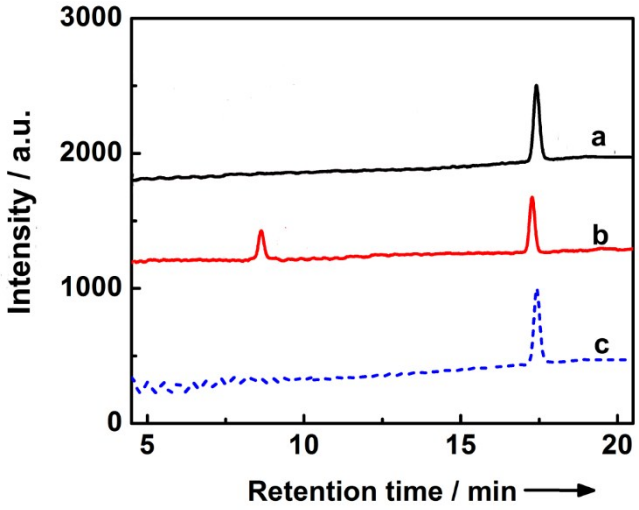

Figure S4. HPLC traces of (a) P3 alone, (b) P3 with Furin, or (c) P3 incubated with the inhibitor before addition of Furin for 30 minutes.

5. Relationship between peak current density ratio and incubation time.

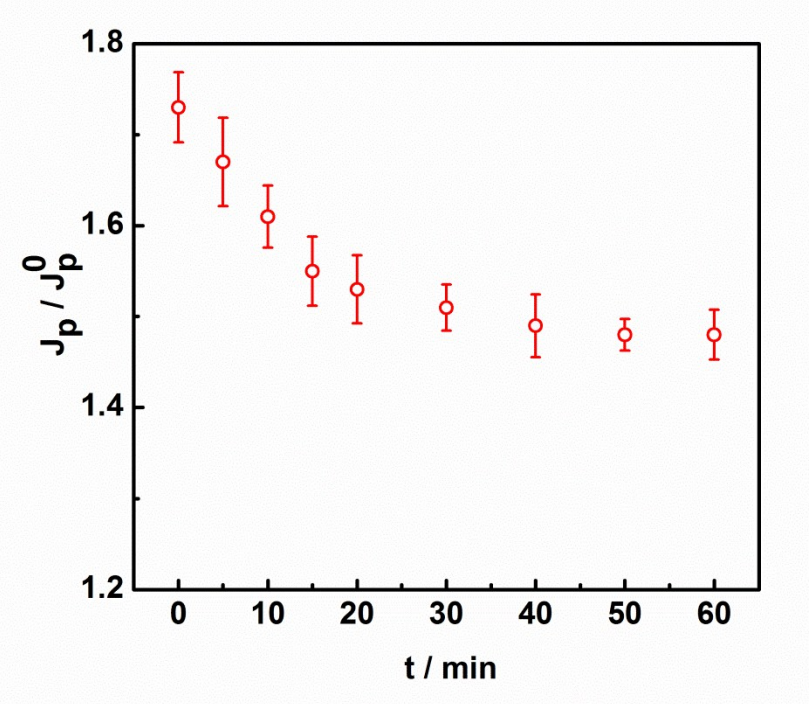

Figure S5. J_p/J_p^0 values obtained at GBF/MB+P3/Fc electrode under different time after addition of 5 U/L Furin in 10 mM PBS buffer solution (pH 7.4).

6. Optimization of volume ration of SH-DBA-MB and P3 on electrode modification

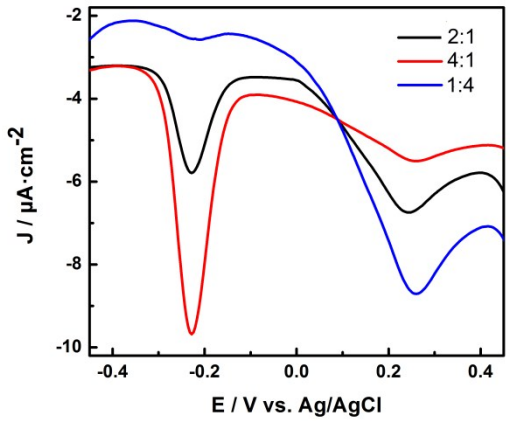

Fig. S6. DPV responses obtained at GBF/MB+P3/Fc modified with different C_{MB} to C_{P3}.

7. Sensitivity comparison between GBF/MB+P3/Fc electrode and Au/MB+P1/Fc electrode.

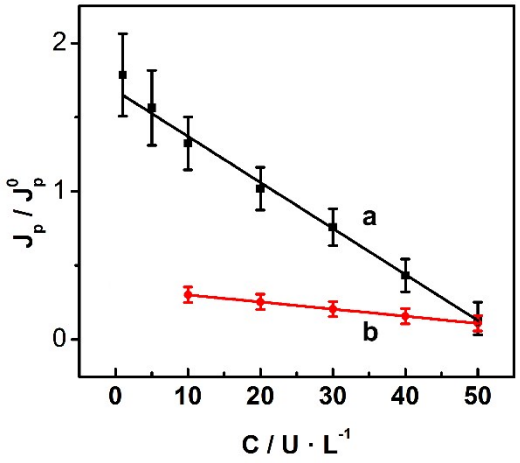

Figure S6. The linear plots of J_p/J_p^0 with Furin activity obtained at (a) GBF/MB+P3/Fc and (b) Au/MB+P1/Fc electrodes.

8. Performance comparison of PEGlysated Gold Bellflowers (GBFs) to antifouling

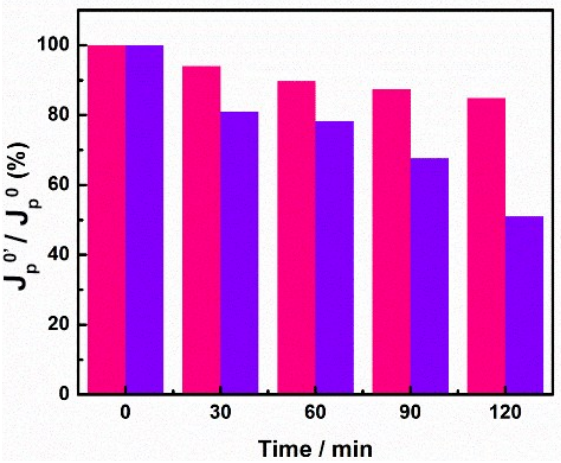

Fig. R8. $J_p^{0'}/J_p^{0}$ values obtained at GBF/MB+P3/Fc (red column), and Au/MB+P3/Fc without PEGlysated gold bellflowers (blue column), where $J_p^{0'}$ stands for the current density of MB dipped in cell lysate for different time, J_p^{0} is the initial current density of MB.

9. Selectivity test

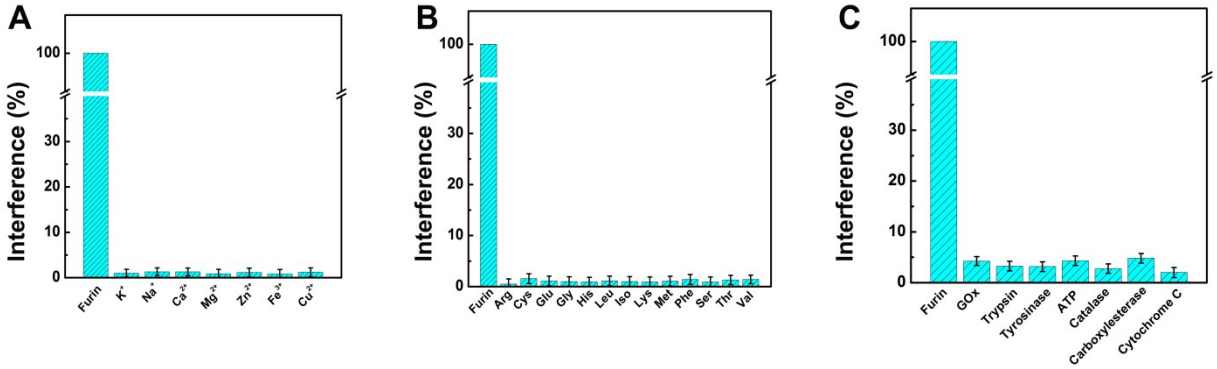

Figure S9. Selectivity test: Interference on peak current density ratio obtained at 190 mV and -220 mV in addition of (A) metal ions: (a) 20 U/L Furin, (b) K^+ (150 mM), (c) Na^+ (150 mM), (d) Ca^{2+} (2.5 mM), (e) Mg^{2+} (2.5 mM), (f) Zn^{2+} (1 mM), (g) Fe^{3+} (10 μM) and (h) Cu^{2+} (10 μM) ; (B) amino acids: (a) 20 U/L Furin, (b) Arg, (c) Cys, (d) Glu, (e) Gly, (f) His, (g) Leu, (h) Iso, (i) Lys, (j) Met, (k) Phe, (l) Ser, (m) Thr, and (n) Val (10 μM for b to n) and (C) Enzyme and biological molecules: (a) Furin (20 U/L), (b) Glucose Oxidase (GOx, 20 U/L), (c) Trypsin (20 U/L), (d) Tyrosinase (20 U/L), (e) Catalase (1 mg/mL), (f) ATP (1 mM), (g) Carboxylesterase(1 mg/mL) and (h) Cytochrome C (10 μM). Herein, the interference % was estimated according to $(J_p/J_p^0)/(J_p/J_p^0)_{I,}$ in which $(J_p/J_p^0)_I$ means the J_p/J_p^0 value after addition of various interferences.

10. Determination of Furin activity in cell lysates by the present method and by Elisa method.

Table S1. Determination of Furin activity in cell lysates by the present method and by Elisa method.

Cells	Number of cell	Our developed Method (U/ L)	Elisa Method (U/ L)
U251	10^3	2.53±0.59	N.A.
	10^4	27.78±6.38	27.53±4.35
MDA-MB-468	10^3	1.89±0.57	N.A.
	10^4	16.92±4.94	17.04±3.31
Lovo cell	10^3	N.A.	N.A.
	10^4	N.A.	N.A.