

Supporting Information

Combination of Hematin and PEDOT via 1-Pyrenebutanoic acid: A new platform for direct electrochemistry of hematin and biosensing applications

Xuehua Yu¹, Jinming Kong^{1*}, Xiaojun Han² and Xueji Zhang^{1,3*}

¹School of Environmental and Biological Engineering

Nanjing University of Science & Technology

No. 200 Xiaolingwei, Xuanwu District, Nanjing, P. R. China 210094

²State Key Laboratory of Urban Water Resource and Environment,

School of Chemical Engineering and Technology,

Harbin Institute of Technology, Harbin 150001, China.

³Chemistry Department, College of Arts and Sciences

University of South Florida, 4202 East Fowler Ave, Tampa, FL, 33620

Corresponding Author: Jinming Kong, Xueji Zhang

Email: j.kong@njust.edu.cn, xueji@usf.edu

Experimental Section

Apparatus

The electrochemical experiments were performed on CHI660D (CH Instruments, Shanghai, China). Electrochemical impedance Spectroscopy (EIS) was measured by Autolab PGSTAT302N (Metrohm, Switzerland). Field emission scanning electron microscope (FE-SEM) and X-ray photoelectron spectroscopy (XPS) were carried out

with S-4800 (Hitachi Co., Ltd., Japan) and PHI Quantera II (Japan). Electrochemical experiments were performed with a three-electrode system, with bare GCE ($d=3$ mm) as the working electrode, a platinum wire as the auxiliary electrode, and an Hg/HgCl/Saturated KCl as the reference electrode.

Materials

3,4-Ethylenedioxythiophene and Poly(4-styrenesulfonate) sodium was obtained from Aladdin reagents. PBA was purchased from J&K (Shanghai, China). $ZrOCl_2$ and hematin were purchased from Sigma (USA). H_2O_2 , N,N-Dimethylformamide (DMF) and absolute alcohol were all obtained from Sinopharm Chemical Reagent (Beijing, China). All reagents used were of analytical grade.

Electrode preparation

GCEs were carefully polished to a mirror like surface by polishing by $0.05\ \mu\text{m}$ alumina slurry first, followed by ultrasonication in anhydrous ethanol and double distilled deionized water for 3 min, respectively. After drying the electrode with nitrogen, the EDOT was polymerized on the GCE by CV with 8 potential cycles from -0.1 - 1.0 V at a scan rate of $100\ \text{mV}\cdot\text{s}^{-1}$, in PBS containing $10\ \text{mmol}\cdot\text{L}^{-1}$ EDOT and $0.3\ \text{mg}\cdot\text{mL}^{-1}$ PSS under magnetic stirring and N_2 degassing [Fig. S1];^[1] then the treated GCEs were cleaned in $0.5\ \text{mL}$ ultrapure water by stirring 1 min and dried with N_2 . After that, the GCEs were incubated in $0.5\ \text{mL}$, $2.3\ \text{mg}\cdot\text{mL}^{-1}$ solution of PBA in DMF for 2 h. Then the GCE was rinsed with $1\ \text{mL}$ DMF and $1\ \text{mL}$ ultrapure water successively. After drying with N_2 , the GCE was immersed in $1\ \text{mg}\cdot\text{mL}^{-1}$ $ZrOCl_2$ solution (Water: ethanol=2:3) for 30 min, then $4\ \mu\text{L}$ $0.1\ \text{mmol}\cdot\text{L}^{-1}$ hematin in DMF

was deposited on GCE surface for other 30 min, then GCE was cleaned with DMF and ultrapure water respectively.

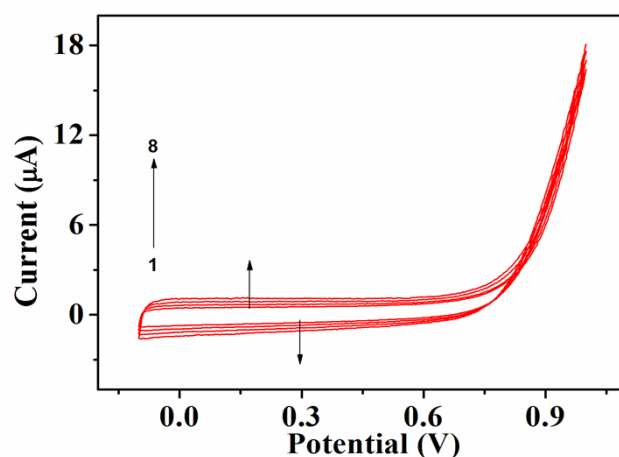


Fig. S1 CVs of GCE in 0.01 mol·L⁻¹ EDOT at a sweep rate of 100 mV·s⁻¹ in the potential range between -0.1 and 1.0 V.

The effect of different amount of hematin on catalysis of H₂O₂

Amount of hematin is an important factor to catalyze H₂O₂. The current response of H₂O₂ is different with altering of concentration of hematin (Fig. s2). We have prepared a series of GCE/PEDOT/PBA/Hematin sensors with different amount of hematin from 0.01 μmol·L⁻¹~5 mmol·L⁻¹, and the volume is 4 μL. From Fig. s2, we can determine the optimal concentration of hematin is 0.1 mmol·L⁻¹, the volume of modification is 4 μL.

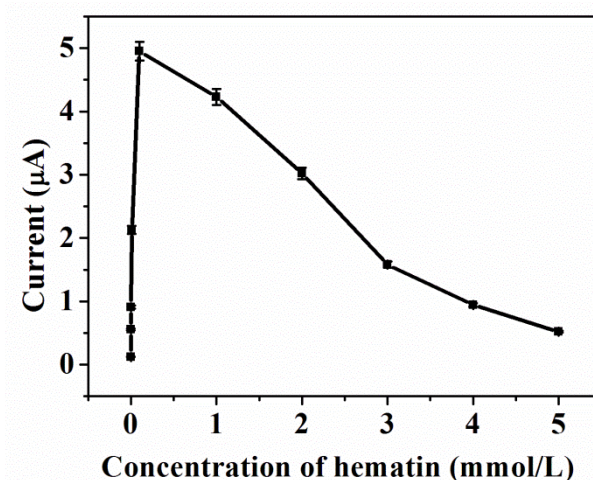


Fig. s2 Different current response of H₂O₂ (0.08 mmol·L⁻¹) on GCE/PEDOT-PBA-Hematin sensors with a series

of amount of hematin from $4 \times 10^{-14} \sim 2 \times 10^{-8}$ mol. (The scan rate is $100 \text{ mV} \cdot \text{s}^{-1}$. pH of PBS is 7.0.)

References

1. W. M. Si, W. Lei, Y. H. Zhang, M. Z. Xia, F. Y. Wang and Q. L. Hao, *Electrochimica Acta*. 2012, 85, 295