

Electronic Supporting Information

A Multiporous Electrochemical Sensor for Epinephrine Recognition and Detection Based on molecularly imprinted polypyrrole

Hong Zhou^a, Guilin Xu^a, Anhong Zhu^a, Zhe Zhao^a, Chengcheng Ren^a, Linlin Nie^a, Xianwen Kan^{a,b*}

^a College of Chemistry and Materials Science, Anhui Key Laboratory of Chemo-Biosensing, Anhui Normal University, Wuhu 241000, P.R. China.

^b State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P.R. China.

In order to construct an efficient sensor, different influencing factors including pH value of electropolymerization solution, scan cycles of electropolymerization process, template molecule/monomer ratio, and extraction solution were investigated.

Corresponding author: Prof. Xianwen Kan

Tel: +86-553-3883513

Fax: +86-553-3869303

Email: kanxw@mail.ahnu.edu.cn

Optimization of experimental conditions

1. Effect of pH value of electropolymerization solution

Imprinted sensor and non-imprinted sensor were tested by DPV at constant concentration of EP ($1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$) in PBS with the pH value range from 5.0 to 9.0. The current intensity difference of EP on imprinted sensor and non-imprinted sensor was observed before and after immersing the sensor into EP solution, as shown in Fig. S1. It was obvious that the current intensity difference increased with the increase of pH at the beginning and then decreased as the pH increased further. And the highest current intensity difference was obtained at pH 7.0. Therefore, pH 7.0 PBS was used in the present work.

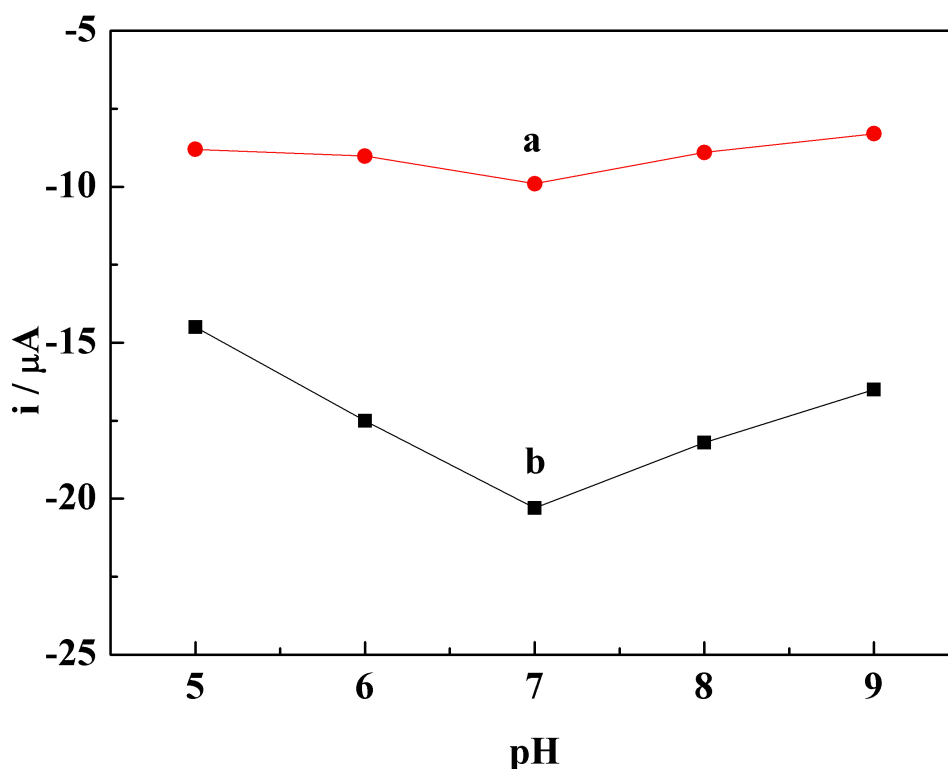


Fig. S1 pH influence on the imprinted sensor and non imprinted sensor in PBS containing $1.0 \times 10^{-5} \text{ mol L}^{-1}$ CAF.

2. Effect of electropolymerization cycles

The thickness of the polymer film would increase with the increase of scan cycles

of electropolymerization, which should affect the sensitivity of the sensor. The effect of scanning cycles with different numbers on the multiporous MIPs/MWNTs/GCE and the multiporous NIPs/MWNTs/GCE was tested by using the DPV measurements. In Fig. S2A, a maximum current response difference of EP on imprinted sensor and non-imprinted sensor was observed by applying 5 cycles in the electropolymerization process, indicating that the optimum electropolymerization cycles should be 5 cycles. Polymer films that formed less than 5 cycles were found to be unstable and the template molecule would not be adequately embedded. On the other hand, higher cycles led to more extensive electropolymerization, which would cause the formation of a thicker sensing film with less accessible imprinted sites.

3. Effect of electropolymerization scan rate

The electropolymerization scan rate also has a significant influence on the peak current of EP on the multiporous MIPs/MWNTs/GCE, as shown in Fig. S2B. The multiporous MIPs/MWNTs/GCE produced at a slower scan rate was found to form a tight film to decrease the number of accessible imprinted sites. However, a faster scan rate formed a loose film with a low recognition capacity. The current response of EP on the multiporous MIPs/MWNTs/GCE was found to increase with an increase in the scan rate up to 80 mV s^{-1} and decrease as the scan rate increased above that value. Thus, the optimum scan rate was 80 mV s^{-1} .

4. The use of SiO_2NPs

In the present study, SiO_2NPs played an important role because it was expected to occupy the space in the polymer during the electropolymerization process and leave many pores after the etch by HF to facilitate the transfer of template molecules. Different concentration of SiO_2NPs ethanol solution, including 0.3, 0.5, and 0.7 mg mL^{-1} , were prepared and the same volume ($6 \mu\text{L}$) of SiO_2NPs solution was introduced into the imprinted film to fabricate three multiporous MIPs/MWNTs/GCE. The current responses of EP on the multiporous MIPs/MWNTs/GCE prepared by using the different amount of SiO_2NPs could be seen in Fig. S2C. It's obvious that the highest current was obtained on the imprinted sensor prepared by using 0.5 mg mL^{-1} of SiO_2NPs .

The prepared MIPs/SiO₂NPs/MWNTs/GCE was immersed into 5% HF for different time to etch off SiO₂NPs, obtaining the multiporous MIPs/MWNTs/GCE. The current responses of EP on the above mentioned imprinted sensors were compared, as shown in Fig. S2D. The current response of EP increased remarkably as the incubation time prolonged. And a maximum current value was observed when the electrode was immersed in HF solution for 25 min, indicating the completely removal of SiO₂NPs, which also could be demonstrated by SEM test (Fig. 2D). Based on these results, 6 μ L 0.5 mg/mL SiO₂NPs and immersing MIPs/SiO₂NPs/MWNTs/GCE in 5% of HF solution for 25 min could be used as the optimum amount of SiO₂NPs and incubation time, respectively.

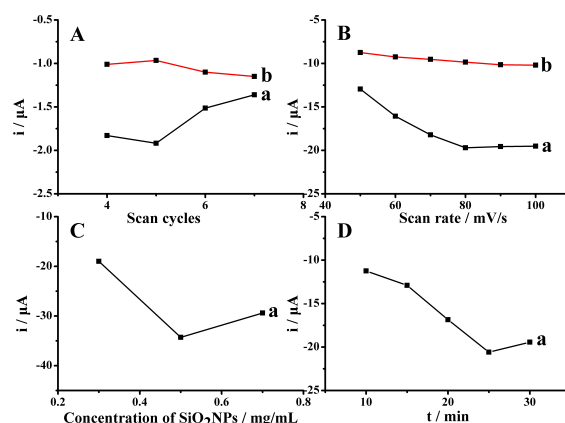


Fig. S2 Effect factors of the electropolymerization cycles (A), scanning rate (B), the amount of SiO₂NPs (C), and the incubation time in HF solution (D) for the preparation of the multiporous MIPs/MWNTs/GCE (a) and the multiporous NIPs/MWNTs/GCE (b), respectively.