Supporting Information

An electrochemical chlorpromazine sensor based on gold-copper bimetal synergetic molecularly imprinted interface on acupuncture needle electrode

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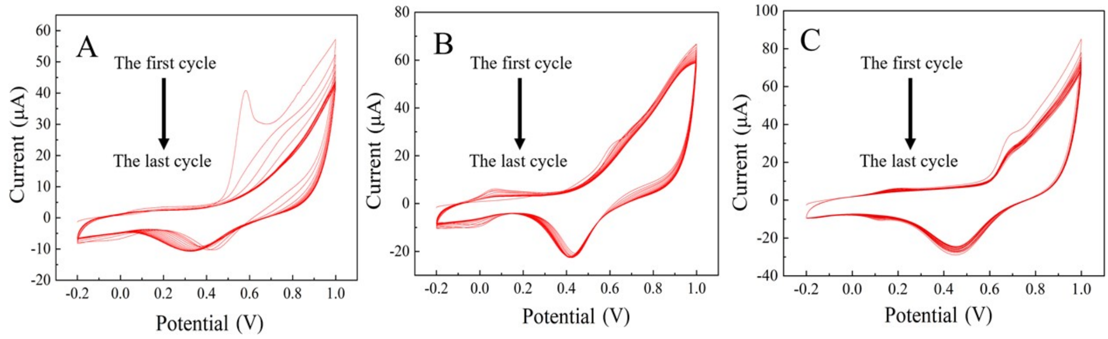

Fig. S1 CVs of electropolymerized 3-APBA with (A) or without (B) CPZ as template molecule, (C) CV of CPZ within the electropolymerization potential.

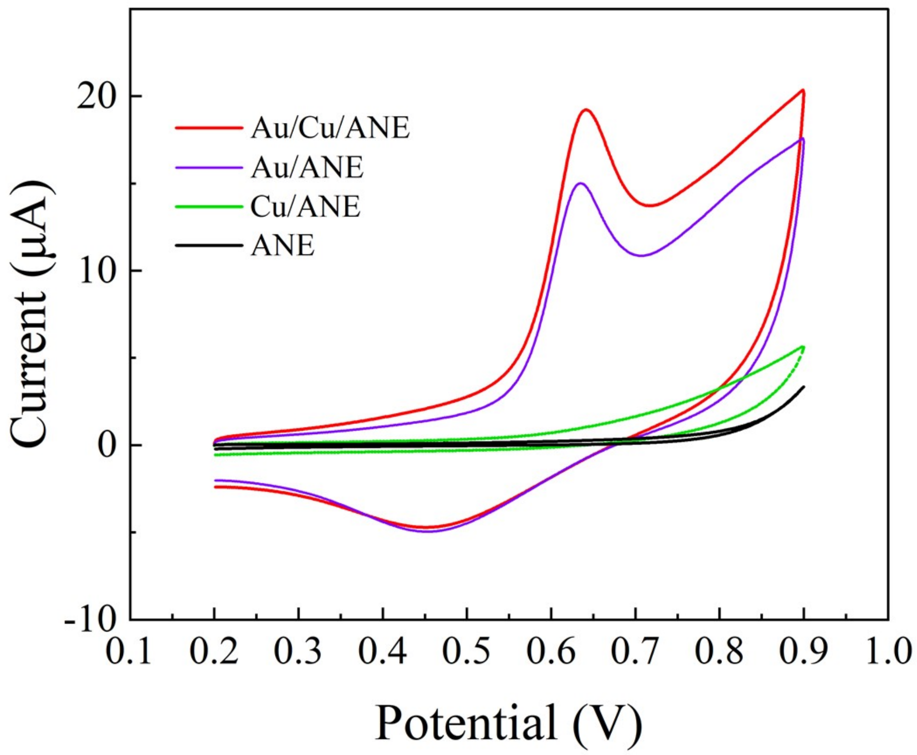

Fig. S2 CV responses of Au/Cu/ANE, Au/ANE, Cu/ANE and ANE in 0.1 mM PBS (pH=7.4) containing 0.5 mM CPZ at the scan rate of 100 mV/s.

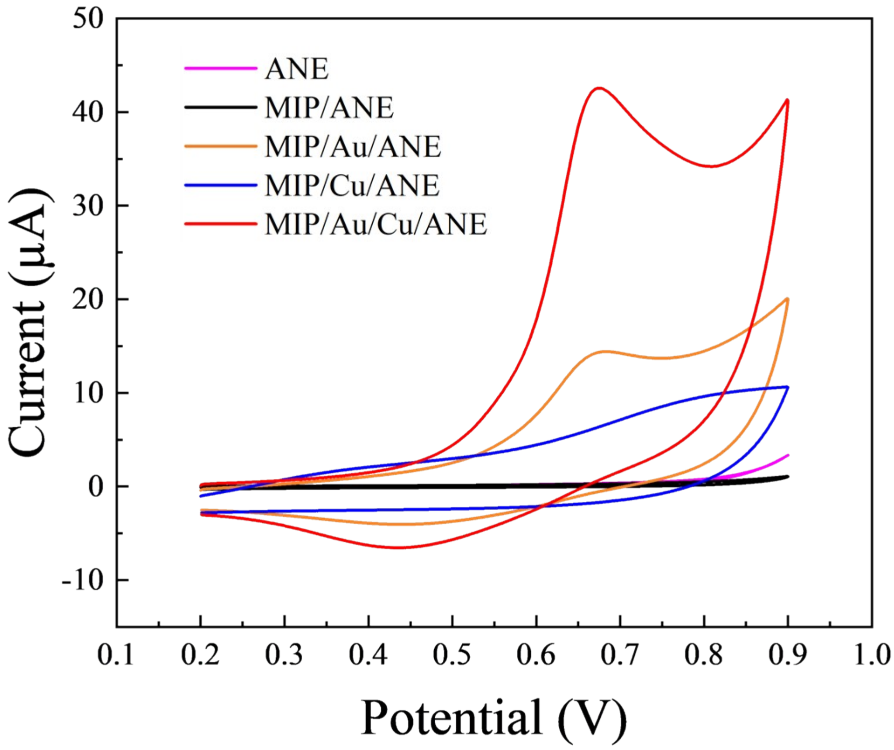

Fig. S3 CV responses of MIP/Au/Cu/ANE, MIP/ANE, and ANE in 0.1 mM PBS (pH=7.4) containing 0.5 mM CPZ at the scan rate of 100 mV/s.

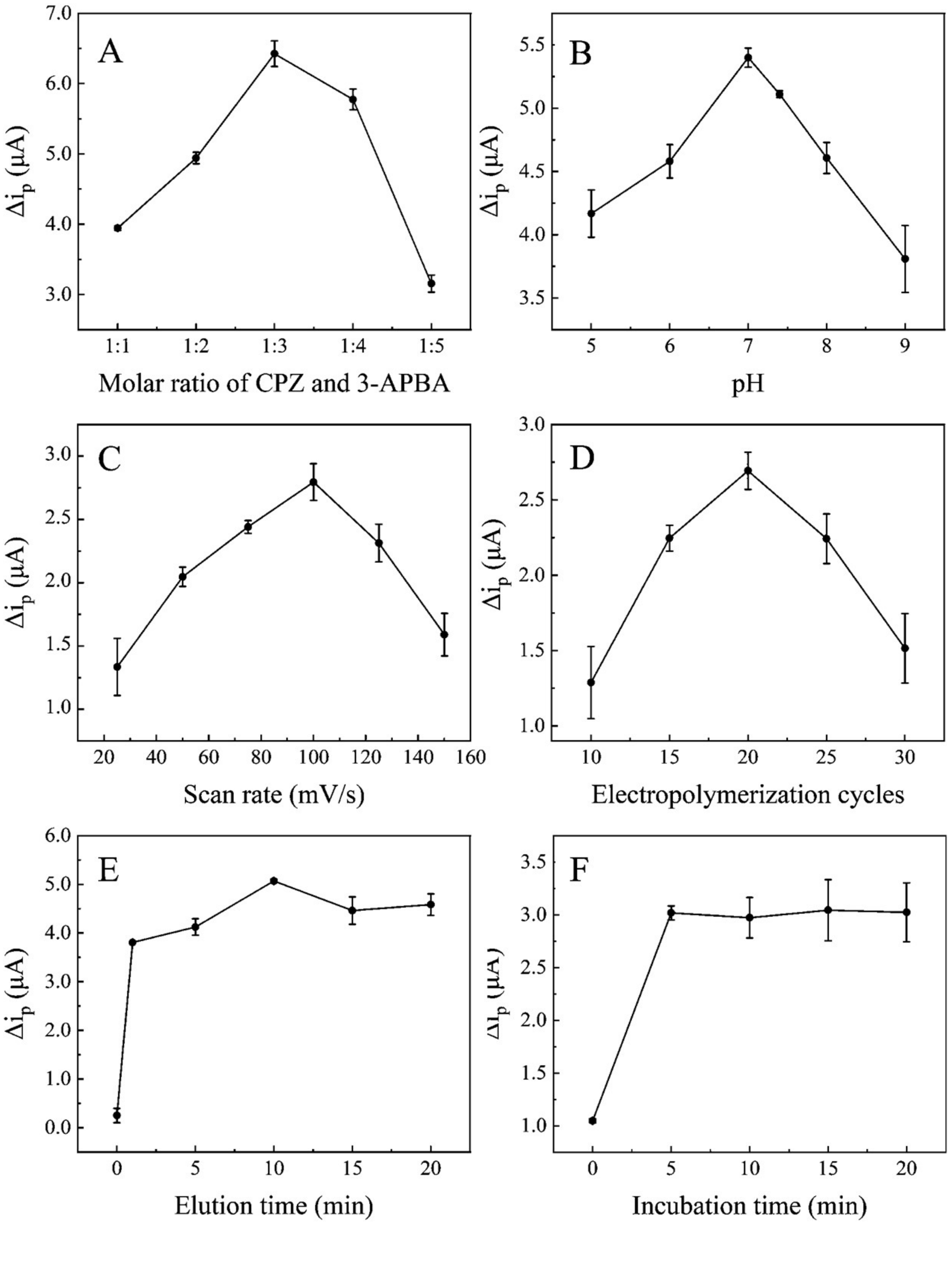

Fig. S4 The Δi_p of MIP/Au/Cu/ANE under different template molecular/mole ratio (A), polymerization solution pH value (B), polymerization rate (C), number of cycles (D), template molecular elution times (E), incubation time (F).

Experimental condition optimization

1. Optimization of the molar ratio of template to monomer

When making MIP films, the molar ratio of the template to the monomer is important since it determines how many imprinted sites there are on the film [1]. The parameter is changed within 1:1, 1:2, 1:3, 1:4, 1:5, respectively. And the current responses of modified electrode performance to CPZ were recorded. The results are shown in Fig.S4A, the greatest current value, indicating the optimum electrochemical performance, occurred when the molar ratio was 1:3. This was because when the monomer concentration was low, the number of monomers combined with template molecules was limited, and the imprinted film formed by electropolymerization had fewer sites. However, when the monomer concentration was high, the imprinted film formed was thicker, which led to the overembedding of template molecule and made it difficult to remove template molecule by elution.

2. Optimization of pH

The pH of the polymerization environment was a key element affecting the fabrication of MIP sensors. Between 5.0 and 9.0, the effect of pH on the sensing response was discussed. As shown in Fig. S4B, there was a considerable rise in Δi_p from 5.0 to 7.0, while the Δi_p dropped as the pH was raised from 7.0 to 9.0. One possible reason for the observed phenomenon is that in an acidic environment, there are many H^+ ions present which can react with the alkaline nitrogen atoms in CPZ molecules, resulting in the protonation of CPZ. Conversely, in an alkaline environment with a high pH value, CPZ may partially dissociate into CPZ^{2+}, which could then undergo free radical reactions, leading to changes in the molecular structure and oxidative degradation [2]. After experimentation, the optimal pH value for CPZ stability was ultimately determined to be 7.0.

3. Optimization of scan rate

The scan rate of electropolymerization affected the density of the polymer film, and the influences of different scan rates on the electrode performance were investigated. The result shows as Fig. S4C that the polymer film was rather loose when the electropolymerization scan rate was too small, making it challenging for the template molecules to adhere to the loose polymer film, which was not conductive to the formation of imprinted sites. On the contrary, when the scan rate was too high, the polymer film became too tight, which was unbeneficial to the elution of template molecules. Finally, the optimum scan rate was selected at 100 mV/s.

4. Optimization of electropolymerization cycles

The thickness of the MIP film varied depending on how many electropolymerization cycles were used. The electrode performances were compared when the electropolymerization cycles were 10, 15, 20, 25 and 30. When the number of cycles were too less, the thickness of the polymer film was smaller, which led to fewer imprinting sites and reduced stability of the polymer film. However, when the number of electropolymerization cycles were too large, the thickness of the polymerization film was larger, which made the template molecules embedded deeply in the polymerization film, and the template molecules cannot be completely remove in the elution process, resulting in the reduction of the imprinting cavity. Fig. S4D shows that the maximum current value and the best performance of the electrode are obtained when the number of cycles is 20.

5. Optimization of elution time

The elution time of the template molecule affects the elution effect of the MIP, consequently, affecting the ability of the interface to recombine with the detection molecule. The difference of the electrode detection results was compared when the elution time was 0, 1, 5, 10, 15, and 20 min. When the elution time was insufficient, the template molecules in the imprinted cavities are not completely removed, which reduces the ability of the electrode to recombine with CPZ molecules. When the elution time was too long, the elution solution with high polarity would damage the structure of imprinted polymer membrane. According to the experimental data in Fig. S4E, the ideal time for template molecule elution was determined to be 10 minutes.

6 Optimization of incubation time

The incubation time affected the number of specific recognize and binding CPZ molecules of cavities, the influence of the incubation time of 0, 5, 10, 15 and 20 min on the detection results was tested. As shown in Fig.S4F, within 0-5 min, the current value increased, but the current changed little after 5 min. The results indicate that the interface was nearly saturated with CPZ molecules after their adsorption, and five minutes was ultimately decided upon as the ideal incubation time.

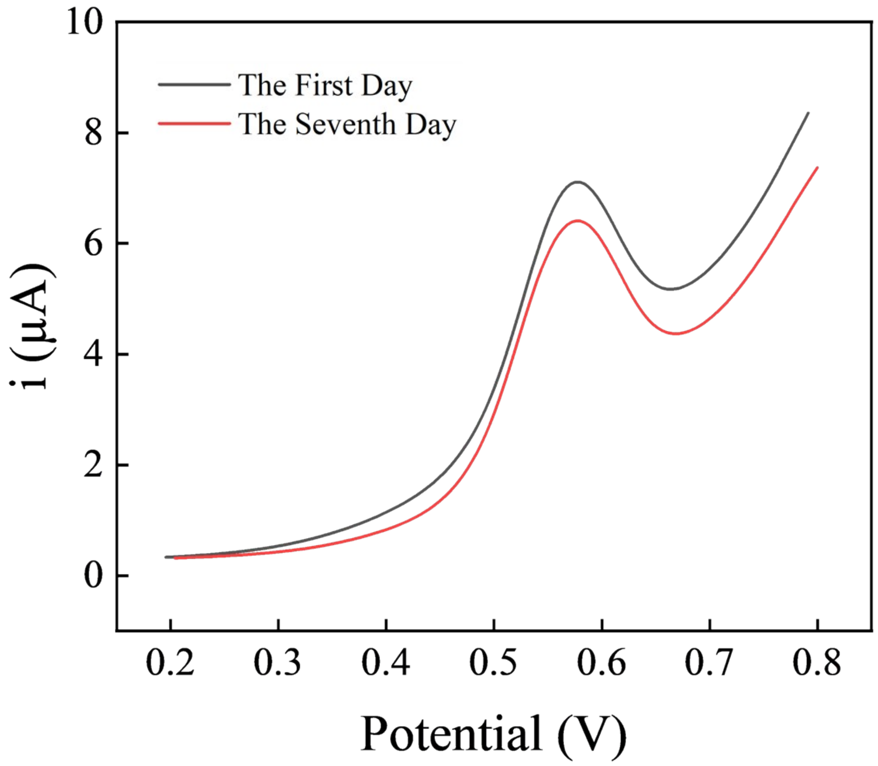

Fig. S5 DPV responses of MIP/Au/Cu/ANE in 0.1 mM PBS (pH=7.4) containing 0.1 mM CPZ at the scan rate of 100 mV/s.

References:

1 Y. Liu, X. Hu, Y. Xia, F. Zhao and B. Zeng, *Anal. Chim. Acta*, 2022, **1190**, 339245.

2 V. N. Palakollu, R. Karpoormath, L. Wang, J. N. Tang and C. Liu, *Nanomaterial*, 2020, **10**, 1513.