Electronic supplementary information

Interface engineering of microelectrodes toward ultrasensitive monitoring of β-amyloid peptides in cerebrospinal fluid in Alzheimer's disease

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Abstract

This supporting information includes Zeta-potentials of gold nanoparticles, UV-vis absorption spectra and DLS analysis of Cu^{2+}-PEI/AuNPs-hemin nanoprobes, EDX spectra and XPS spectra to characterize the molecular assembly on electrode surface, optimization of electrochemical detection conditions, reproducibility test of GME/cys/hemin.

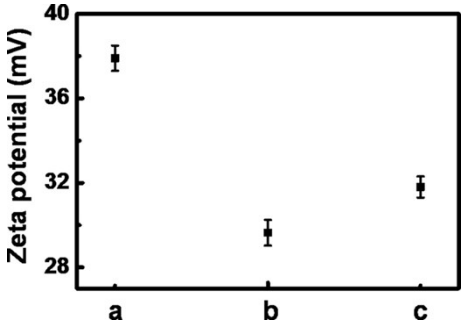

Figure S1. Zeta-potentials of (a) PEI/AuNPs, (b) PEI/AuNPs-hemin and (c) Cu^{2+}-PEI/AuNPs-hemin.

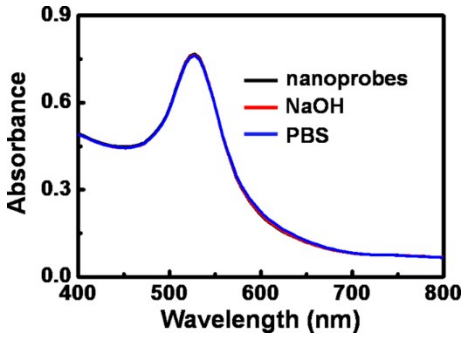

Figure S2. UV-vis absorption spectra of Cu^{2+}-PEI/AuNPs-hemin nanoprobes with addition of PBS (10 mM, pH =7.4) and 10 mM NaOH.

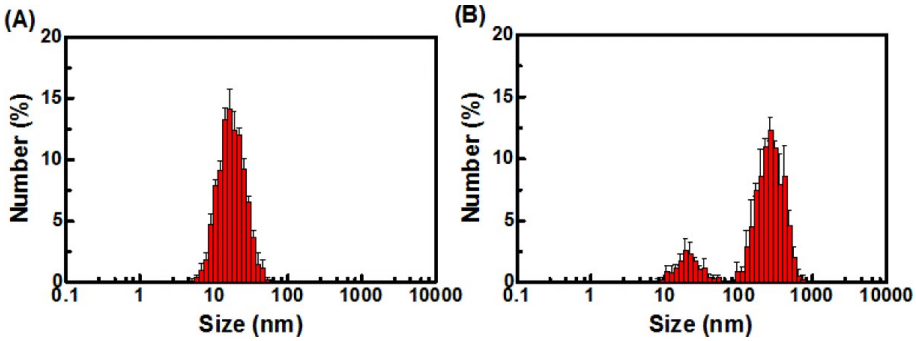

Figure S3. DLS analysis for Cu^{2+}-PEI/AuNPs-hemin nanoprobes (A) in the absence and (B) presence of 1 μM Aβ monomers.

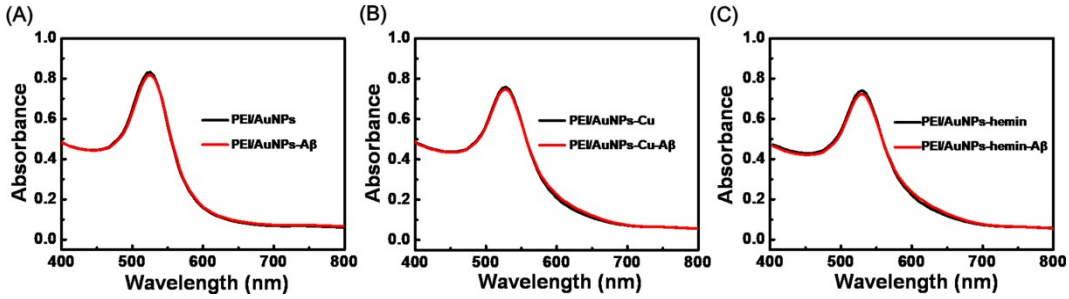

Figure S4. UV-vis absorption spectra of PEI/AuNPs, PEI/AuNPs-Cu^{2+}, and PEI/AuNPs-hemin with addition of 1μM Aβ monomers.

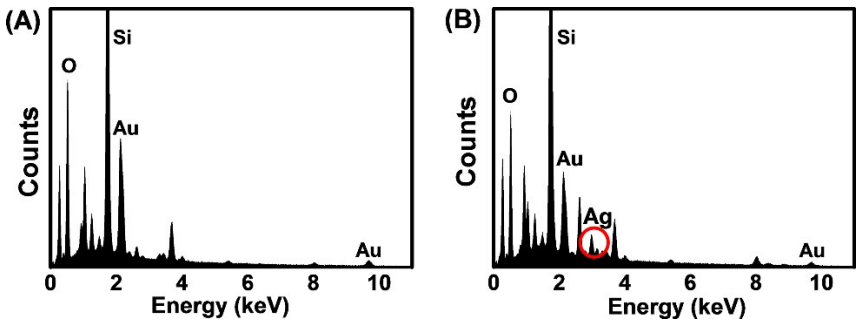

Figure S5. EDX spectra of GME/cys/hemin surface (a) before and (b) after silver deposition on Cu^{2+}-PEI/AuNPs-hemin-based architecture.

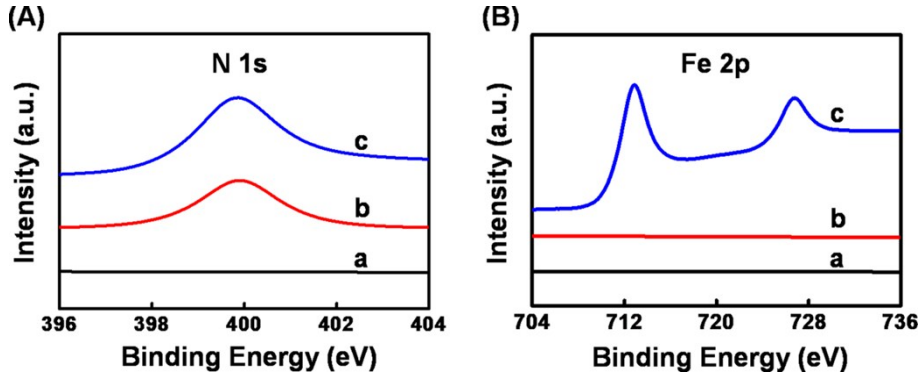

Figure S6. High-resolution XPS spectra of (A) N 1s, (B) Fe 2p for (a) GME, (b) GME/cys, (c) GME /cys/hemin.

As shown in Fig. S6, obvious peak of N 1s was obtained after the electrode was treated with cysteamine. Subsequently, new Fe 2p peak generated upon treatment with hemin. These results further demonstrated the successful construction of functional electrode.

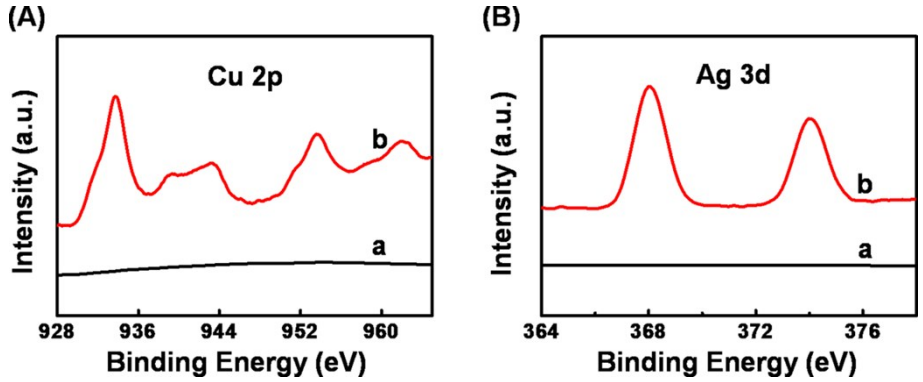

Figure S7. (A) High-resolution XPS spectra of Cu 2p for GME/cys/hemin (a) before and (b) after treated with 50 nM Aβ monomers in the presence of Cu^{2+}-PEI/AuNPs-hemin nanoprobes. (B) High-resolution XPS spectra of Ag 3d for GME/cys/hemin surface (a) before and (b) after silver deposition on AuNPs archietecture.

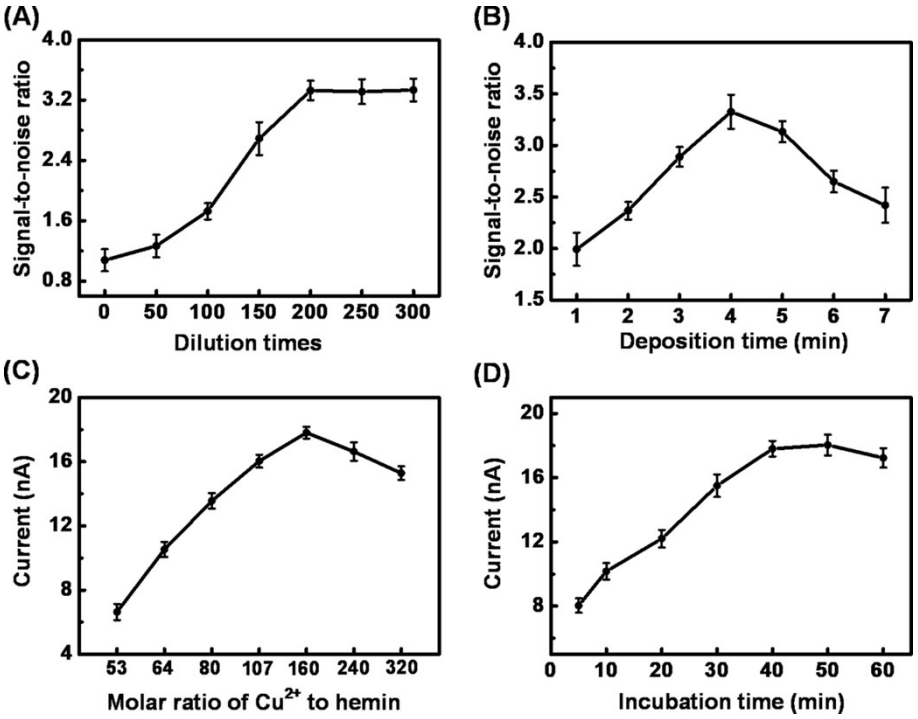

Figure S8. Optimization of electrochemical detection conditions. (A) Different dilution times of silver enhancer solutions, (B) silver deposition times, (C) molar ratio between Cu^{2+} and hemin and (D) incubation time of the Cu^{2+}-PEI/AuNPs-hemin.

The concentration of silver enhancer solutions and deposition time were explored based on background current, which was measured in the absence of Cu^{2+}-PEI/AuNPs-hemin nanoprobes through the direct reduction of Ag^{+} by the reducing reagent in silver enhancer solutions. We used the ratio of signal to noise to optimize the deposition conditions. Upon successive dilution of silver enhancer solutions, the signal to-noise ratio increased quickly and trended to a maximum value at 200-fold dilution (Figure S8A). Thus, the silver enhancer solutions with 200-fold dilution were used. In addition, 4 min was selected as the optimal deposition time due to the highest detection signal (Figure S8B). Considering the dual molecule recognition ability of Cu^{2+}-PEI/AuNPs-hemin nanoprobes, the molar ratio between Cu^{2+} and hemin to construct the nanoprobe was investigated. As shown in Figure S8C, the peak current for Aβ monomers detection increased with the increasing molar ratio and reached maximum at 160:1, indicating an equilibrium between the two recognition elements coexisting in the nanoprobe to reach a high determination sensitivity. Figure S8D displayed the effect of incubation time of

Cu^{2+}-PEI/AuNPs-hemin nanoprobes on analytical performance. With the increasing incubation time, the peak current increased and trended to a constant value after an incubation time of 40 min, which showed saturated binding between the Aβ and nanoprobes. Therefore, the incubation time of 40 min was selected.

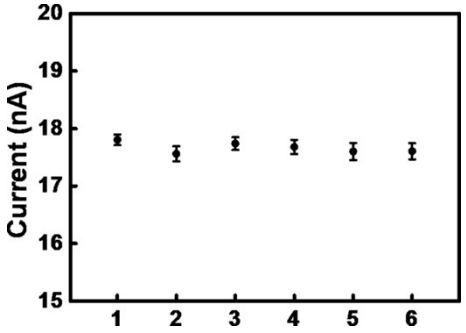

Figure S9. Reproducibility test of GME/cys/hemin toward 50 nM Aβ monomers.