Supporting Information

Combined determination of Copper ion and β-Amyloid peptide by a Single ratiometric Electrochemical Biosensor

Yanyan Yu,*a,† Peng Wang,b,† Xiaodan Zhu,b,† Qiwen Peng,a Yi Zhou,b Tianxiao Yin,a Yixin Liang c and Xiaoxing Yin *a

† Jiangsu Key Laboratory of New Drug Research and Clinical Pharmacy, Xuzhou Medical University, 209 Tongshan Road, Xuzhou 221004, Jiangsu, P.R.China
‡ Department of Pharmaceutical Analysis, School of Pharmacy, Xuzhou Medical University, 209 Tongshan Road, Xuzhou 221004, Jiangsu, P.R.China
§ School of Liberal Arts and Science, Shanghai University of Medicine & Health Sciences, 279 Zhouzhu Highway, Shanghai 201318, P.R.China
† These authors contributed equally to this work.

Electronic Supplementary Material (ESI) for Analyst. This journal is © The Royal Society of Chemistry 2017
Fig. S1 Raman spectrum of CNTs and ABTS-PDDA/CNTs.
Fig. S2 FT-IR spectrum of CNTs and ABTS-PDDA/CNTs.
As demonstrated in Fig. S3, after the modification of PDDA/CNTs, two obvious peaks belonging to C 1s and O 1s located at 284.7 and 532.5 eV respectively were observed and the intensity of them gradually increased along with the modification of ABTS and NKB. What’s more, the presence of N 1s and S 2p peaks located at 403.1 and 166.3 eV in the ABTS-PDDA/CNTs and ABTS-PDDA/CNTs-NKB composites also demonstrated that ABTS and NKB have both immobilized onto electrode.

![XPS spectra of (A) C 1s, (B) O 1s, (C) N 1s and (D) S 2p for samples of PDDA/CNTs, ABTS-PDDA/CNTs and ABTS-PDDA/CNTs-NKB composites.](image-url)
Fig. S4 Cyclic voltammograms of bare GC, and PDDA/CNTs, ABTS-PDDA/CNTs, ABTS-PDDA/CNTs-NKB modified electrodes in 0.1M KCl solution containing 1mM $\text{K}_3\text{Fe(CN)}_6$. 
Fig. S5 The UV-vis absorption spectra of the formed Cu²⁺ - Aβ₁₋₄₂ complex prepared by incubating them with three different concentrations of Cu²⁺ and Aβ₁₋₄₂ at 37°C. The peroxide activity of Cu²⁺ - Aβ₁₋₄₂ complex was tested by the catalytic oxidation of ABTS (0.15 mM) in the presence of H₂O₂ (100 mM).
Fig. S6 Selectivity investigations of Cu\(^{2+}\) and Aβ\(_{1-42}\) determination by ABTS-PDDA/CNTs-NKB modified electrode in the presence of other metal ions (A), amino acids (B) and several endogenic species (C). “Cu\(^{2+}\) + interferences” experiments were carried out by adding Cu\(^{2+}\) into PBS containing other metal ions, amino acids and other endogenic species. The Cu\(^{2+}\) concentration was 9 \(\mu\)M. Concentrations of the tested metal ions are 1 mM for Ca\(^{2+}\) (1), Mg\(^{2+}\) (6), Na\(^{+}\) (7) and 10 \(\mu\)M for Cd\(^{2+}\) (2), Co\(^{2+}\) (3), Cu\(^{+}\) (4), Fe\(^{3+}\) (5), Mn\(^{2+}\) (8), Ni\(^{2+}\) (9), Pb\(^{2+}\) (10), Zn\(^{2+}\) (11). The twelve amino acids are all 5 \(\mu\)M for cysteine (1), phenylalanine (2), methionine (3), glycine (4), glutamic acid (5), arginine (6), lysine (7), leucine (8), serine (9), threonine (10), valine (11), histidine (12). Concentrations of the tested endogenic species are 10 \(\mu\)M for ascorbic acid (1), dopamine (2), uric acid (3) and 1 mM for glucose (4) and lactate (5). Concentrations of the aggregated Aβ form were 0.1 \(\mu\)g/mL for Aβ\(_{1-38}\) and Aβ\(_{1-42}\) by incubating them at 37°C for three days.
**Table S1.** Results of detection of Aβ$_{1-42}$ in hippocampus homogenates from normal and AD groups by the present electrochemical method (Cu$^{2+}$ concentration: 0.95 μM).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Added amount (μg/mL)</th>
<th>Detected amount (μg/mL)</th>
<th>Recovery (%)</th>
<th>RSD (n = 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>0.05</td>
<td>0.05</td>
<td>100</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.11</td>
<td>110</td>
<td>7.2</td>
</tr>
<tr>
<td></td>
<td>0.30</td>
<td>0.33</td>
<td>110</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>0.02</td>
<td>100</td>
<td>5.6</td>
</tr>
<tr>
<td>AD</td>
<td>0.04</td>
<td>0.04</td>
<td>100</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>0.12</td>
<td>0.11</td>
<td>91.7</td>
<td>8.1</td>
</tr>
</tbody>
</table>