Electronic supplementary information

A high precision MUA-spaced single-cell sensor for cellular receptor assay based on bifunctional Au@Cu-PbCQDs nanoparticles

Dongping Long*, Chengchi Chen*, Chenyu Cui, Zheng Yao and Peihui Yang*

Department of Chemistry, Jinan University, Guangzhou 510632, China.
E-mail: typh@jnu.edu.cn; Tel/Fax: +86-20-85223039

S1.1 UV–vis spectra of Au@Cu-PbCQDs nanoparticles

The fabrication of Au@Cu-PbCQDs nanoparticles was demonstrated by UV-vis absorbance spectra. As shown in Fig. S1, compared with the spectrum of AuNPs (Fig. S1A), the L-cysteine-modified AuNPs exhibited a new absorption band at 700 nm, which was attributed to L-cysteine modification. The absorption peak of Au@Cu nanoparticles was redshifted correspondingly, because Cu^{2+} was connected to the L-cysteine-modified AuNPs. Moreover, compared with the CQDs, the PbCQDs exhibited a large absorption at 280 nm, which was due to the π-π* transition of the C=C bonds. The Au@Cu-PbCQDs nanoparticles (Fig. S1B) had Au@Cu nanoparticles and PbCQDs as absorption bands, indicating that the Au@Cu-PbCQDs nanoparticles was successfully fabricated.

Fig. S1 UV–vis spectra of (A) Au@Cu; (B) Au@Cu-PbCQDs nanoparticles.

S1.2 Characterization of single-cell capturing

When carrying out the single-cell assay, the single cell was captured on the interface under the inverted microscopy using a pipet by dilution of cell concentration. Fig S2 showed the process of 3 single cells being captured one by one.
Fig. S2 Inverted microscope images of (A) control, (B) single-cell, (C) 2 cells and (D) 3 cells captured on the interface one by one.

S1.3. Optimization of the concentration of MA-C_{11}

The concentration of MA-C_{11} had an important effect on improving the detection sensitivity of single cell in Fig. S3. As the concentration of MA-C_{11} progressively increased, the ECL signal increased after 0.6 μmol/L and then tended to level off, indicated that the optimum of the concentration of MA-C_{11} was 0.6 μmol/L. These optimal experiment parameters were used in subsequent measurements.

Fig. S3 ECL intensity of MA-C_{11} with different concentration (A) and relationship curves of MA-C_{11} with different concentration (B).
S1.4. Effect of MA-C\textsubscript{n} on electronic-transfer rate

As shown in Table S1, the electron-transfer rate decreased as the carbon number in MA-C\textsubscript{n} increased because the nonconductive MA with long carbon chain could hinder electron transfer while providing interspace on the electrode surface. The electron-transfer rate test indicated that MA-C\textsubscript{n} could to some extent hinder the electron transfer of the sensing interface, which explained why MA-C\textsubscript{16}-spaced sensor showed inferior performance to the MA-C\textsubscript{11} counterpart.

<table>
<thead>
<tr>
<th>group</th>
<th>α</th>
<th>k ( / ) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA(MA-C\textsubscript{0})</td>
<td>0.723</td>
<td>0.268</td>
</tr>
<tr>
<td>MAA(MA-C\textsubscript{2})</td>
<td>0.472</td>
<td>0.171</td>
</tr>
<tr>
<td>MSA(MA-C\textsubscript{4})</td>
<td>0.615</td>
<td>0.127</td>
</tr>
<tr>
<td>MHA(MA-C\textsubscript{6})</td>
<td>0.672</td>
<td>0.051</td>
</tr>
<tr>
<td>MUA(MA-C\textsubscript{11})</td>
<td>0.501</td>
<td>0.023</td>
</tr>
<tr>
<td>MHDA(MA-C\textsubscript{16})</td>
<td>0.248</td>
<td>0.017</td>
</tr>
</tbody>
</table>

S1.5. Analytical performance of MUA-spaced single-cell sensor for CD44 receptor

As shown in Fig. S4, the average ECL intensity without MA-C\textsubscript{11} was calculated to be 387.3 ± 59.2 a.u. (\(\bar{x} \pm s, n = 20\)) with an RSD of 15.3%. And the average ECL intensity with MA-C\textsubscript{11} was calculated to be 619.2 ± 61.6 a.u. (\(\bar{x} \pm s, n = 20\)) with an RSD of 9.9%. The average current intensity was 2.48 ± 0.19 μA (\(\bar{x} \pm s, n = 10\), RSD = 7.7%) and 4.03 ± 0.25 μA (\(\bar{x} \pm s, n = 10\), RSD = 6.2%) with and without MA-C\textsubscript{11}, respectively. The results implied the heterogeneity of the single cells as well as the improvement of the accuracy for single-cell analysis.
Fig. S4 Histograms of MCF-7 cell capturing without and with MA-C_{11}, respectively by ECL analysis (A, B) and DPV analysis (C, D). Each bar represents one cell.