Supporting information

Electrochemical Sensor for Detection of \( p \)-Nitrophenol Based on Cyclodextrin Decorated Gold Nanoparticles-Mesoporous Carbon Hybrid

Yongying Zhou, Jin Zhao, * Shenghua Li, Minjie Guo and Zhi Fan, *

\(^{a}\) Tianjin Key Laboratory of Brine Chemical Engineering and Resource Eco-utilization, College of Chemical Engineering and Materials Science, Tianjin University of Science & Technology, Tianjin 300457, P.R. China

zhaoj@tust.edu.cn
Content

Scheme S1. Synthesis of per-6-deoxy-per-6-(2-carboxy-methyl)thio-β-cyclodextrin.........................1

Figure S1. The ¹H-NMR spectrum of per-[6-deoxy-6-bromo]-β-cyclodextrin .................................2

Figure S2–3. The ¹H-NMR and mass spectrometry of per-6-deoxy-per-6-(2-carboxy-methyl)-thio-β-cyclodextrin.............................................................................................................................3

Figure S4. (a) TEM image of AuNPs; (b) TEM image of AcSCD-AuNPs; (c) SEM image of AcSCD-AuNPs-MC; (d) TEM image of AcSCD-AuNPs-MC. .................................................................4

Figure S5–6. CV and DPV response for 100 μM p-nitrophenol at bare GC electrode, MC/GC, AcSCD/GC, AcSCD-AuNPs/GC, AcSCD-AuNPs-MC/GC electrodes..............................................5

Figure S7. (a) CVs of bare GC electrode in 0.1 M PBS electrolyte containing 100 μM p-NP with different scan rate values (scan rate:20, 40, 60, 80, 100, 120, 150, 200, 250 mV s⁻¹) at pH=6.5; (b) A Plot of peak current against square root of scan rate .............................................6

Figure S8. A plot of potential against logarithm of scan rate ............................................................6

Figure S9. Differential pulse voltammograms response for the different concentrations of p-nitrophenol at four individual AcSCD-AuNPs-MC electrodes .........................................................7

Table S1. Supplementary datum of the reduction peak currents at four individual AcSCD-AuNPs-MC electrodes ............................................................................................................................7

Table S2. Comparison of the different methods for p-nitrophenol determination...............................8

Figure S10. Normalized current of AcSCD-AuNPs-MC electrode for 100 μM p-nitrophenol in the presence of the high concentrations of possible interferents .....................................................8

Table S3. Determination of p-nitrophenol in real samples by standard addition method at AcSCD-AuNPs-MC electrode ..................................................................................................................9

Reference ........................................................................................................................................9
Scheme S1. Synthesis of per-6-deoxy-per-6-(2-carboxy-methyl)thio-β-cyclodextrin

**Synthesis of per-(6-deoxy-6-bromo)-β-cyclodextrin**

Triphenylphosphine (28 g, 106 mmol) was dissolved in anhydrous DMF (60 mL) and placed in a three-necked flask, and bromine (2.8 mL, 106 mmol) was placed in a constant pressure dropping funnel, and drip into the solution at a rate of 3 to 4 seconds per drop. The temperature was controlled below 15 °C. When the addition was completed, the reaction solution was stirred for 30 min, and then β-cyclodextrin (6.8 g, 6 mmol) was dissolved in 30 mL of DMF solution and placed in a constant pressure dropping funnel. The temperature was adjusted to 70 °C for 14 hours, and nitrogen gas was continuously supplied during the reaction until the reaction was completed. After the reaction is completed, the reaction solution is stirred in an ice water bath at 0 to 5 °C and the sodium methoxide solution is added dropwise to adjust the pH to 8, and then 1000 mL of methanol is added to stir to precipitate a solid, which is filtered to obtain a crude product. DMF/H₂O was recrystallized twice and vacuum dried to give per-[6-deoxy-6-bromo]-β-cyclodextrin. (product weight: 7.13 g; yield: 75%)

**1H NMR** (400 MHz, DMSO) δ 6.02 (d, J = 6.7 Hz, 7H), 5.89 (d, J = 1.9 Hz, 7H), 4.98 (d, J = 3.4 Hz, 7H), 4.00 (d, J = 9.9 Hz, 7H), 3.82 (t, J = 9.0 Hz, 7H), 3.74 – 3.56 (m, 14H), 3.39 (dd, J = 12.8, 6.4 Hz, 14H).

**Synthesis of per-6-deoxy-per-6-(2-carboxy-methyl)thio-β-cyclodextrin**

Sodium hydroxide (4.0 g, 100 mmol) was dissolved in 30 mL of distilled water, and mercapto acetic acid (3.68 g, 40 mmol) was added and reacted for 8 h. Then 20 mL of dissolved per-[6-deoxy-6-bromo]-β-cyclodextrin (3.16 g, 2 mmol) in DMF was added, pass nitrogen protection, and raise the temperature to 60 °C with stirring. When the initial addition, a white solid precipitated, but as the reaction progressed, the white solid disappeared and the solution became transparent. At this time, heating was stopped, and the reaction was completed. The reaction solution was cooled to room
temperature and poured into 900 mL of methanol. Solids were precipitated, filtered under reduced pressure, and the obtained solid was dissolved with as little water as possible. The pH of the solution was adjusted to 2 with 3 mol/L hydrochloric acid, and the solid was slowly precipitated and centrifuged. The solid was obtained and washed three times with distilled water, and recrystallized twice in a mixed solvent of C$_2$H$_5$OH/H$_2$O to give a white product per-6-deoxy-per-6-(2-carboxy-methyl)thio-β-cyclodextrin sodium salt. (product weight: 2.04 g; yield: 62%) $^1$H NMR (400 MHz, D$_2$O) δ 5.07 (d, J = 3.5 Hz, 7H), 4.09 – 3.95 (m, 7H), 3.89 (t, J = 9.5 Hz, 7H), 3.67 (t, J = 9.2 Hz, 7H), 3.60 (dd, J = 10.0, 3.4 Hz, 7H), 3.33 (q, J = 15.3 Hz, 14H), 3.11 (d, J = 13.8 Hz, 7H), 3.03 – 2.71 (m, 14H); LC-MS: m/z 1651.4 [M-H].

![Figure S1. The $^1$H-NMR spectrum of per-(6-deoxy-6-bromo)-β-cyclodextrin](image)

Figure S1. The $^1$H-NMR spectrum of per-(6-deoxy-6-bromo)-β-cyclodextrin
Figure S2. The $^1$H-NMR of per-6-deoxy-per-6-(2-carboxy-methyl)thio-β-cyclodextrin

Figure S3. The mass spectrometry of per-6-deoxy-per-6-(2-carboxy-methyl)thio- β-cyclodextrin
Figure S4. (a) TEM image of AuNPs; (b) TEM image of AcSCD-AuNPs; (c) SEM image of AcSCD-AuNPs-MC; (d) TEM image of AcSCD-AuNPs-MC
**Figure S5.** CVs of 100 μM p-nitrophenol at bare GC electrode, MC/GC, AcSCD/GC, AcSCD-AuNPs/GC, AcSCD-AuNPs-MC/GC electrodes

**Figure S6.** DPV response for 100 μM p-nitrophenol at bare GC electrode, MC/GC, AcSCD/GC, AcSCD-AuNPs/GC, AcSCD-AuNPs-MC/GC electrodes
Figure S7. (a) CVs of bare GC electrode in 0.1 M PBS electrolyte containing 100 μM p-NP with different scan rate values (scan rate: 20, 40, 60, 80, 100, 120, 150, 200, 250 mV s⁻¹) at pH=6.5; (b) A Plot of peak current against square root of scan rate

Figure S8. A plot of potential against logarithm of scan rate on bare GC electrode
Figure S9. Differential pulse voltammograms response for the different concentrations of p-nitrophenol at four individual AcSCD-AuNPs-MC electrodes

Table S1. Supplementary datum of the reduction peak currents (μA) for the different concentrations of p-nitrophenol (μM) at four individual AcSCD-AuNPs-MC electrodes

<table>
<thead>
<tr>
<th></th>
<th>Electrode 1</th>
<th>Electrode 2</th>
<th>Electrode 3</th>
<th>Electrode 4</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>−70.77</td>
<td>−70.44</td>
<td>−67.71</td>
<td>−69.18</td>
<td>−73.27</td>
</tr>
<tr>
<td>300</td>
<td>−63.83</td>
<td>−63.26</td>
<td>−66.22</td>
<td>−66.50</td>
<td>−68.28</td>
</tr>
<tr>
<td>250</td>
<td>−54.75</td>
<td>−62.17</td>
<td>−35.90</td>
<td>−60.35</td>
<td>−64.64</td>
</tr>
<tr>
<td>200</td>
<td>−47.34</td>
<td>−53.30</td>
<td>−38.57</td>
<td>−61.82</td>
<td>−54.88</td>
</tr>
<tr>
<td>150</td>
<td>−37.95</td>
<td>−46.73</td>
<td>−32.35</td>
<td>−51.07</td>
<td>−44.64</td>
</tr>
<tr>
<td>100</td>
<td>−38.55</td>
<td>−41.15</td>
<td>−27.49</td>
<td>−46.91</td>
<td>−40.29</td>
</tr>
<tr>
<td>50</td>
<td>−23.39</td>
<td>−32.63</td>
<td>−20.71</td>
<td>−35.09</td>
<td>−31.04</td>
</tr>
<tr>
<td>10</td>
<td>−14.94</td>
<td>−21.47</td>
<td>−13.19</td>
<td>−24.03</td>
<td>−19.74</td>
</tr>
<tr>
<td>5</td>
<td>−13.42</td>
<td>−19.48</td>
<td>−9.98</td>
<td>−21.81</td>
<td>−17.71</td>
</tr>
<tr>
<td>1</td>
<td>−12.00</td>
<td>−18.27</td>
<td>−0.00</td>
<td>−18.99</td>
<td>−18.21</td>
</tr>
<tr>
<td>0.5</td>
<td>−11.37</td>
<td>−16.71</td>
<td>−10.46</td>
<td>−18.22</td>
<td>−15.97</td>
</tr>
<tr>
<td>0.1</td>
<td>−11.65</td>
<td>−18.65</td>
<td>−7.76</td>
<td>−18.71</td>
<td>−15.05</td>
</tr>
</tbody>
</table>
### Table S2. Comparison of the different methods for p-nitrophenol determination

<table>
<thead>
<tr>
<th>Electrode materials</th>
<th>Methods</th>
<th>Linear range (μM)</th>
<th>LOD (μM)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMC</td>
<td>DPV</td>
<td>2–90</td>
<td>0.1</td>
<td>[2]</td>
</tr>
<tr>
<td>rGO</td>
<td>DPV</td>
<td>50–800</td>
<td>42</td>
<td>[3]</td>
</tr>
<tr>
<td>AgNWs-PANI</td>
<td>DPV</td>
<td>0.6–32</td>
<td>0.052</td>
<td>[4]</td>
</tr>
<tr>
<td>DTD/AgNP</td>
<td>CV</td>
<td>1–100</td>
<td>0.25</td>
<td>[5]</td>
</tr>
<tr>
<td>AuNPs/RGO</td>
<td>SWV</td>
<td>0.05–2</td>
<td>0.01</td>
<td>[6]</td>
</tr>
<tr>
<td>NMP/Gr</td>
<td>Amperometry</td>
<td>0.5–5.6</td>
<td>0.15</td>
<td>[7]</td>
</tr>
<tr>
<td>AcSCD-AuNPs-MC</td>
<td>DPV</td>
<td>0.1–10</td>
<td>26.1</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-350</td>
<td></td>
<td>(3.63 μg/mL)</td>
</tr>
</tbody>
</table>

**Figure S10.** Normalized current of AcSCD-AuNPs-MC electrode for 100 μM p-nitrophenol in the presence of the high concentrations of possible interferents
Table S3. Determination of p-nitrophenol in real samples by standard addition method at AcSCD-AuNPs-MC electrode

<table>
<thead>
<tr>
<th>Samples</th>
<th>Added (μM)</th>
<th>Average found (μM)</th>
<th>Recovery(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Water1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tap Water 2</td>
<td>30</td>
<td>30.94</td>
<td>103.15</td>
</tr>
<tr>
<td>Tap Water 3</td>
<td>100</td>
<td>103.94</td>
<td>103.94</td>
</tr>
<tr>
<td>Shangde Lake1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Shangde Lake2</td>
<td>50</td>
<td>47.62</td>
<td>95.25</td>
</tr>
<tr>
<td>Shangde Lake3</td>
<td>100</td>
<td>86.48</td>
<td>86.48</td>
</tr>
</tbody>
</table>

References