Supplementary information for

Entrapment of alkaloid within silver: from enantioselective hydrogenation to chiral recognition

Hengpan Yang, Dinghui Chi, Qilong Sun, Wenwen Sun, Huan Wang* and Jiaxing Lu**

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China.
*Corresponding Author: Dr. Huan Wang (Tel: +8621-52134935, E-mail: hwang@chem.ecnu.edu.cn).
**Corresponding Author: Prof. Jia-Xing Lu (Tel: +8621-62233491, E-mail: jxlu@chem.ecnu.edu.cn).

1. Materials and Instruments

All reagents were used as received.

Galvanostatic electrohydrogenation was performed using a direct current-regulated power supply (HY3002D, HYelec®, China).

Linear sweep voltammetry was performed with a CHI 660c electrochemical Station (Shanghai Chenhua Instruments Company).

The product yield, the ee value and alkaloid amount in filtrate were determined by a high performance liquid chromatography (HPLC) instrument (DIONEX Ultimate 3000 pump) equipped with a UV (RS Variable Wavelength) detector and a chiralcel OD-H column [DAICEL Chiral technologies (China) CO., LTD.].

Microstructure and morphology of alkaloid@Ag were analyzed using Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM).

X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu Kα radiation (k= 1.5406 Å).

N₂ adsorption was carried out at 77 K on a BELSORP-MAX instrument after outgassing the samples for 10 h under vacuum at 573 K.

Infrared spectra were achieved by a Fourier transform infrared spectrometer (FT-IR,
2. Structure of alkaloids

![Fig. S1 Structures of alkaloids](image)

3. General methods

**Synthesis of alkaloid@Ag and pure Ag:** 0.05 g of CN was dissolving in 15 mL EtOH and added into 50 mL deionized water. 0.1 g AgNO₃ was dissolved in 150 mL deionized water. Then, those two solutions were mixed. After 10 min stirring, 1.5 g of NaH₂PO₂ was slowly added, and the mixture was stirred at 25 °C for 4h. Precipitation of CN@Ag began immediately. The precipitate was filtered, washed with 10 mL water 5 times, and dried for 12 h at 50 °C under vacuum. Powder with metallic luster was achieved after filtration and drying (Fig. S2A). The filtrate was detected by HPLC. CD@Ag, QN@Ag and QD@Ag were prepared the same method. Pure Ag was prepared in the same way except for the absence of alkaloids in reducing solution.

![Fig. S2 CN@Ag before (A) and after (B) press.](image)

**Electrohydrogenation procedure:** Powder of alkaloid@Ag was pressed into coin
(Fig. S2B) and used as cathode for the enantioselective electrohydrogenation of MB. A typical galvanostatic electrohydrogenation was carried out in a mixture of 50 mM MB, 0.1 M tetraethylammonium iodide (TEAI) in an undivided glass cell, with a CN@Ag composite cathode and sacrificial magnesium (Mg) anode. Current density: 3 mA cm\(^{-2}\), electric quantity: 300 C.

**LSV procedure:** Linear sweep voltammetry was carried out in a mixture of 20 mM substrate (or blank), 0.1 M tetraethylammonium tetrafluoroborate (TEABF\(_4\)) dissolving in 20 mL MeCN in an undivided glass cell, with an alkaloid@Ag composite cathode (or pure Ag), a Pt counter electrode and an Ag/AgI/I\(^-\) reference electrode at a sweep rate of 10 mV\(^{-1}\).

4. **Characterization of CD@Ag, QN@Ag and QD@Ag**

**FE-SEM patterns:**

![FE-SEM patterns of CD@Ag (a), QN@Ag (b) and QD@Ag (c).](image)

According to Fig. S3, CD@Ag (a) is in the ~100 nm size range, which is close to CN@Ag. QN@Ag (b) and QD@Ag (c) are in the ~200 nm size range.

**Linear sweep voltammograms:**

Linear sweep voltammograms recorded at QN@Ag and QD@Ag cathode were the same as CN@Ag and CD@Ag. According to Fig. S4, QN@Ag after extraction and
QD@Ag after extraction were demonstrated to also retain some chirality.

Fig. S4 Linear sweep voltammograms recorded at a sweep rate of 10 mV\(^{-1}\) in 0.1 M TEABF\(_4\) dissolving in 20 mL MeCN at pure Ag electrode (A), QN@Ag after extraction electrode (B) and QD@Ag after extraction electrode (C). Blank solution: a, d, g; 20 mM (S, S)-tartrate: c, f, h; 20 mM (R, R)-tartrate: b, e, i.

5. Expansion of substrates

Under similar reaction conditions, certain ee value and yield could also be achieved with these substrates, which was presented as following and added into supplementary information (Table S1). So, this kind of electrodes has some generality for enantioselective hydrogenation.

| Table S1 Enantioselective electrohydrogenation of several substrates\(^a\). |
|---|---|---|---|---|
| Entry | Substrate | Product | Yield\(^b\) (%) | ee\(^b\) (%) | Charge efficiency\(^b\) (%) |
| 1 | ![Image](image1.png) | ![Image](image2.png) | 72 | 43(S) | 69 |
| 2 | ![Image](image3.png) | ![Image](image4.png) | 14 | 56(S) | 14 |
Cathode: CN@Ag, anode: Mg, 20 mL co-solvent (MeCN/H₂O=9/1), 50 mM substrate, 0.1 M TEA, current density: 3 mA cm⁻², electric quantity: 200 C. b Determined by HPLC with a chiral column.

6. Differences between physical adsorption and entrapment

We presented herein the evidences that this kind of entrapment was fundamentally different from physical adsorption. Pure Ag was prepared in the same way as alkaloid@Ag expect for the absence of alkaloids in reducing solution. The reducing solution would not be filtered and 0.05 g CN was added immediately for 4 h physical adsorption. Alkaloid concentration before and after the entrapment or adsorption were determined by HPLC. The adsorption or entrapment amount of alkaloids was calculated from alkaloids concentration differences. It is obvious that the entrapment amount is far more than adsorption amount, so this kind of entrapment is fundamentally different from physical adsorption.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkaloid</th>
<th>Adsorption amount (%)</th>
<th>Entrapment amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CN</td>
<td>&lt;1</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>CD</td>
<td>&lt;1</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td>QN</td>
<td>&lt;1</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>QD</td>
<td>&lt;1</td>
<td>98</td>
</tr>
</tbody>
</table>

a The adsorption amount of alkaloids was calculated from alkaloids concentration differences before and after the entrapment or adsorption. b Determined by HPLC.

FT-IR (Fig. S5) further explored the difference between entrapment and adsorption. After 4 h physical adsorption in CN solution, FT-IR spectra of pure Ag (d) was almost identical to pure CN (c). However, if washed with MeCN, there was no trace of CN in FT-IR spectra (b). In contrast, even after being reused for 10 times, CN could also be detected by XRD (Fig. 1e), although there was no trace of CN in FT-IR spectra (a). In summary, entrapment was fundamentally different from adsorption and much more stable.
**Fig. S5** FT-IR spectra of CN@Ag reused for 10 times (a), pure CN (c), pure Ag after physical adsorption (d), (d) after washed with MeCN (b).