

Supplementary information for
**Enantioselective hydrogenation of methyl
benzoylformate on Ag electrode electrosorbed with
cinchonine**

Hengpan Yang, Ting Lv, Wenwen Sun, Yanfang Du, 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.

Electrodeposition was performed with a CHI 660c electrochemical Station (Shanghai Chenhua Instruments Company) on carbon paper (CP, TGP-H-060, Toray). Galvanostatic electrohydrogenation and electroadsorption of CN were performed using a direct current-regulated power supply (HY3002D, HYElec®, China).

The product yields, the ee values and adsorption amounts 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.].

Infrared spectra were achieved by a Fourier transform infrared spectrometer (FT-IR, NEXUS 670, Nicolet).

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

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.

2. Structure of inducer

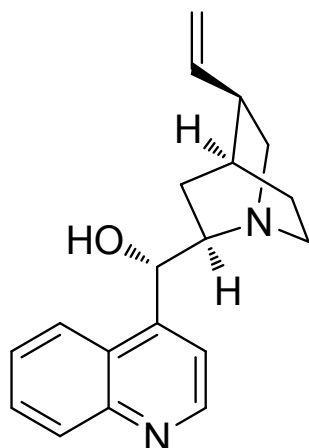


Fig. S1 Structure of cinchonine

3. General methods

Electrodeposition and electrohydrogenation procedure: The ED Ag electrode was prepared by potentiostatic reduction of 20 mM AgNO₃ and 0.1 M polyethylene glycol (400) aqueous solution on CP (4.0 cm²) at -1.6 V (vs saturated calomel electrode) for 300 s. After electrodeposition, the electrode was dried for 12 h at 50 °C under vacuum. A typical galvanostatic electrohydrogenation was carried out in a mixture of 50 mM MB, 0.1 M tetraethylammonium iodide (TEAI), 1.0 mM CN in 20 mL co-solvent in an undivided glass cell under a N₂ atmosphere, with an ED Ag cathode and sacrificial magnesium (Mg) anode. Each experiment condition was performed for 4 times and the average values were listed in Table 1.

Electrosorption procedure: The selective adsorption of L- and D-amino acids on calcite could be detected by gas chromatography¹. In our work, a similar method was used for quantitative determination of adsorption of CN on ED Ag electrode. The electrosorption of CN on an ED Ag electrode, to perform an adsorbed Ag (AD Ag) electrode, was conducted in a mixture of 0.1 M TEAI, certain concentration CN in 20 mL MeCN, MeOH or DMF in an undivided glass cell under a N₂ atmosphere for 30 mins. The adsorption amount of CN was calculated from CN concentration differences before and after the electrosorption, which was detected by HPLC. Each experiment condition was performed for 4 times and the average values were listed in Table 2.

4. Graph of ee value of MM versus CN adsorption amount.

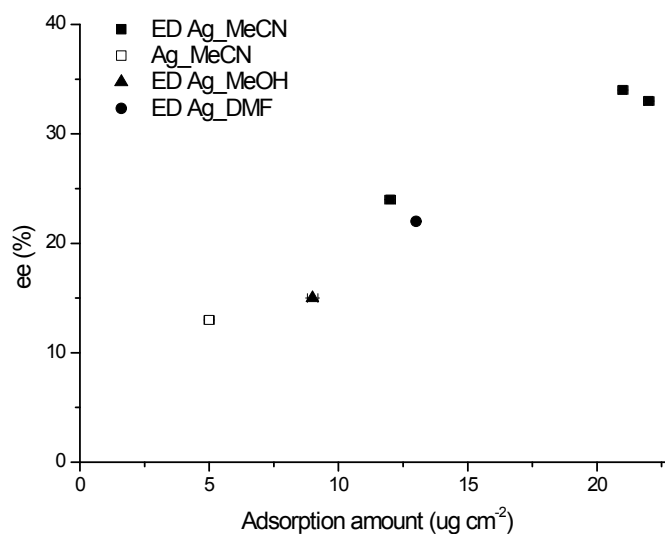


Fig. S2 ee value of MM versus CN adsorption amount.

According to Fig. S2, if we plot the ee value versus the adsorption amount, a straight line could be achieved, although the points show some scatter around this trend.

5. Influence of MM concentration on adsorption amount of CN and ee value.

Certain concentration of MM was added into electrolyte to characterize the competitive adsorption. It was obvious that both the adsorption amount of CN and ee value (Table S1) would decrease with the addition of MM.

Table S1 Influence of MM concentration on adsorption amount of CN^a and ee value^b.

Entry	C_{MM} (mM)	Adsorption amount ^c ($\mu\text{g cm}^{-2}$)	Conv ^c (%)	Sel ^c (%)	ee ^c (%)
1	5	20 \pm 0.2	57	91	33
2	10	20 \pm 0.2	60	93	32
3	20	19 \pm 0.2	57	92	29
4	30	16 \pm 0.2	59	94	26
5	50	13 \pm 0.2	58	93	23

^a Electrosorption carried out in an undivided cell, cathode: ED Ag, anode: Mg, solvent: MeCN,

supporting electrolyte: 0.1 M TEAI, CN concentration: 1 mM, current density: 3 mA cm⁻², time: 30 mins, temperature: 25 °C.

^b Electrolyses carried out in an undivided cell, anode: Mg, cathode: ED Ag, co-solvent: MeCN/H₂O (9/1), supporting electrolyte: 0.1 M TEAI, CN concentration: 1 mM, MB concentration: 50 mM, current density: 3 mA cm⁻², Charge 2 F mol⁻¹, temperature: 25 °C.

^c Determined by HPLC with a chiral column.