# **Electronic Supplementary Information**

# **Bromine-Mediated Electrochemical Refinery Towards Tartaric Acid**

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# **Experimental Section**

#### Chemicals

Ammonium molybdate tetrahydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O,  $\geq$ 99%), dopamine hydrochloride (C<sub>8</sub>H<sub>11</sub>NO<sub>2</sub>·HCl,  $\geq$ 98%), potassium bromide (KBr,  $\geq$ 99%), potassium chloride (KCl,  $\geq$ 99.5%), potassium sulfate (K<sub>2</sub>SO<sub>4</sub>,  $\geq$ 99%), potassium hydroxide (KOH,  $\geq$ 95%), maleic acid (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>,  $\geq$ 99%), *cis*-epoxysuccinic acid (C<sub>4</sub>H<sub>4</sub>O<sub>5</sub>,  $\geq$ 97%), *trans*-epoxysuccinic acid (C<sub>4</sub>H<sub>4</sub>O<sub>5</sub>,  $\geq$ 97%), and ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O,  $\geq$ 98%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. 5-Nitrosalicylic acid (C<sub>7</sub>H<sub>5</sub>NO<sub>5</sub>,  $\geq$ 99%) and chloroacetic acid (C<sub>2</sub>H<sub>3</sub>ClO<sub>2</sub>,  $\geq$ 99%) were purchased from J&K Scientific Co., Ltd. Tartaric acid (C<sub>4</sub>H<sub>4</sub>Br<sub>2</sub>O<sub>4</sub>,  $\geq$ 98%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All the chemicals were purchased and used without further purification. Deionized water was prepared with a Milli-Q purification system, and used throughout all the experiments.

## Preparation of Mo<sub>2</sub>C NF

For the preparation of Mo<sub>2</sub>C NF, 370 mg of  $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$  was dissolved in a mixture of 18 mL of deionized water and 8 mL of ethanol. The pH was adjusted to ~8 with 0.4 mL of NH<sub>3</sub>·H<sub>2</sub>O. Subsequently, the solution was added with 10 mL of 20 mg mL<sup>-1</sup> dopamine solution, and further reacted under continuous magnetic stirring for 12 h at room temperature. The resulting solid product was collected, repetatively washed with a mixture of ethanol and acetone, and lyophilized to yield PDA-Mo. Finally, the as-prepared PDA-Mo was annealed under Ar at 750 °C for 3 h with a heating rate of 2 °C min<sup>-1</sup> to yield Mo<sub>2</sub>C NF.

#### **Structural characterizations**

XRD patterns were collected on a PANalytical X-ray diffractometer with monochromatic Cu Ka

radiation. SEM images were obtained on a Zeiss G500 scanning electron microscope. TEM images were carried on an FEI Tecnai TF20 transmission electron microscope operating at an accelerating voltage of 200 kV. Liquid <sup>1</sup>H NMR was performed on a Bruker AVANCE NEO 400 MHz NMR spectrometer. UV-Vis spectroscopy was conducted on a Perkin-Elmer Lambda 950 spectrophotometer. ICP analysis was carried out on an Aurora M90 inductively coupled plasma optical emission spectrometer.

### **Electrochemical measurements**

To prepare the working electrodes, 1 mg of  $Mo_2C$  NF, 0.5 mg of Ketjenblack carbon, and 6.5 µL of 5 wt% Nafion solution were dispersed in 250 µL of ethanol. The mixture was sonicated for 30 min to form a uniform catalyst ink. This ink was then dropcast onto a 1×1 cm<sup>2</sup> carbon fiber paper (HCP020P) and dried at room temperature. All the electrochemical measurements were conducted in an H-cell using a three-electrode configuration controlled by a CHI 660E potentiostat. The Mo<sub>2</sub>C NF-loaded working electrode and a saturated calomel reference electrode (SCE) were located in the anodic compartment, and a graphite rod counter electrode was placed in the cathodic compartment. The two compartments were each filled with 25 mL of electrolyte, and separated by a Nafion 117 membrane.

#### Electrochemical BER, CER, and OER

BER, CER, and OER measurements were carried out in 0.1 M KBr, 0.1 M KCl and 0.1 M  $K_2SO_4$ , respectively. All the potential readings were recorded against SCE and compensated for 90% of the ohmic loss. Polarization curves were recorded at a scan rate of 10 mV s<sup>-1</sup>.

### Bromine-mediated electrochemical conversion of MA to ESA

Bromine-mediated electrochemical conversion was conducted in the solution of 0.1 M KBr and 20 mM MA with its pH adjusted to ~5 with KOH. Chronoamperometric experiments were conducted at the selected working potentials between 0.97 V to 1.13 V versus SCE. At the end of electrolysis, the anolyte was collected, and added with 5 mL of 1 M KOH to facilitate the dehydrohalogenation of BHSA to ESA.

Liquid products (*cis*-ESA, *trans*-ESA, and DBSA) in the solution were quantified using <sup>1</sup>H NMR spectrometer with dimethyl sulfoxide (DMSO,  $\geq$ 99.9%) as the internal standard. The apparent Faradaic efficiency (FE) for each product was calculated as follows:

$$FE(\%) = \frac{N \times c \times V_a \times F}{Q_{tot}} \times 100\%$$

where *N* is the number of electrons transferred for the formation of the target product, *c* is the molar concentration of the liquid product determined by <sup>1</sup>H NMR based on the calibration curve,  $V_a$  is the anolyte volume, F (= 96485 C mol<sup>-1</sup>) is the Faraday constant, and  $Q_{tot}$  is the total charge passing the electrode during the chronoamperometric experiments.

The production rate (r) of ESA was calculated as follows:

$$r = \frac{c \times V_a}{t \times S}$$

where *t* is the electrolysis time, and  $S (= 1 \text{ cm}^2)$  is the electrode area.

#### Direct electrochemical oxidation of MA

The direct electrochemical oxidation of MA was carried out in the solution of  $0.1 \text{ M K}_2\text{SO}_4$  and 20 mM MA. Chronoamperometric experiments were conducted at the selected working potentials between 1.37 V and 1.61 V. No oxidation products from MA were detected under these conditions.

## Acidic hydrolysis of ESA to TTA

To prepare TTA, the ESA-containing solution from the bromine-mediated conversion was added with 5 mL of 1 M HCl, and magnetically stirred at 80 °C for 10 h. The concentration of TTA was determined by a colorimetric method using UV-Vis as detailed in the following. First, an indicator solution was prepared by mixing 16 mL aqueous solution of 0.036 M Fe(NO<sub>3</sub>)<sub>3</sub> and 40 mL methanol/water (3:7, v/v) solution of 0.01 M 5-nitrosalicylic acid. Its pH was adjusted to 2.6~2.7 with 0.1 M chloroacetic acid before dilution to 500 mL. For TTA quantification, 1 mL of its reaction solution was added with 5 mL of the indicator solution, and then diluted to 10 mL with chloroacetic acid. Its UV-Vis absorbance at 492 nm was measured, and its concentration was determined based on the comparison with the calibration curve.

### **Chemical reaction equations**

The chemical equations involved in the bromine-mediated conversion are listed as follows:

Electrochemical BER:  $2Br \rightarrow Br_2 + 2e^2$ Disproportionation:  $Br_2 + H_2O \rightleftharpoons HBr + HOBr$ Electrophilic addition:  $C_4H_4O_4 + HOBr \rightarrow C_4H_5O_5Br$ Side reaction:  $C_4H_4O_4 + Br_2 \rightarrow C_4H_4O_4Br_2$ Dehydrohalogenation:  $C_4H_5O_5Br \rightarrow C_4H_4O_5 + HBr$ Hydrolysis:  $C_4H_4O_5 + H_2O \rightarrow C_4H_6O_6$ 

The possible reaction mechanisam is listed as follows:





Fig. S1 SEM images of PDA-Mo at different magnifications.



Fig. S2 SEM images of  $Mo_2C$  NF prepared with (a) 10 mL of 40 mg mL<sup>-1</sup> and (b) 10 mL of 400 mg mL<sup>-1</sup> of dopamine under otherwise identical conditions.



Fig. S3 SEM images of  $Mo_2C$  NF after the stability test at different magnifications.



Fig. S4 Chronoamperometric curves of bromine-mediated conversion of MA on  $Mo_2C$  NF in 0.1 M KBr and 20 mM MA.



Fig. S5 Calibration curves of (a) *cis*-ESA, (b) *trans*-ESA, and (c) DBSA for the <sup>1</sup>H NMR analysis. To plot the calibration curves, a series of *cis*-ESA (1~10 mM), *trans*-ESA (1~10 mM), and DBSA (1~5 mM) standard solutions were prepared by dissolving a calculated amount of each compound in 0.1 M KBr solution containing 20 mM MA. 500  $\mu$ L of the standard solution was then mixed with 100  $\mu$ L of D<sub>2</sub>O solution containing 200 ppm DMSO as the internal standard. <sup>1</sup>H NMR spectra were obtained in the water suppression mode. The relative peak area of each compound over that of DMSO was plotted against the concentration of the standard solution to construct the calibration curves. For the quantification of liquid products in our experiments, 500  $\mu$ L of the reaction solution was mixed with 100  $\mu$ L of D<sub>2</sub>O solution containing 200 ppm DMSO. Its concentration was determined by comparison with the calibration curve.



**Fig. S6** <sup>1</sup>H NMR analysis of the anolyte after the direct electrochemical oxidation of MA at 1.61 V for 60 min.



**Fig. S7** (a) UV-Vis absorbance of standard TTA solutions. (b) TTA calibration curve. To plot the calibration curve, a series of TTA standard solutions (1~5 mM) were prepared by dissolving a calculated amount of TTA in 0.1 M KBr solution containing 20 mM MA. 1 mL of the above solution was added with 5 mL of the indicator solution, and then diluted to 10 mL with chloroacetic acid buffer solution. Its UV-Vis absorbance at 492 nm was measured, and plotted against the TTA concentration to construct the calibration curve.