† Electronic Supplementary Information (ESI)

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1. Measurement of temperature coefficient for HWCE

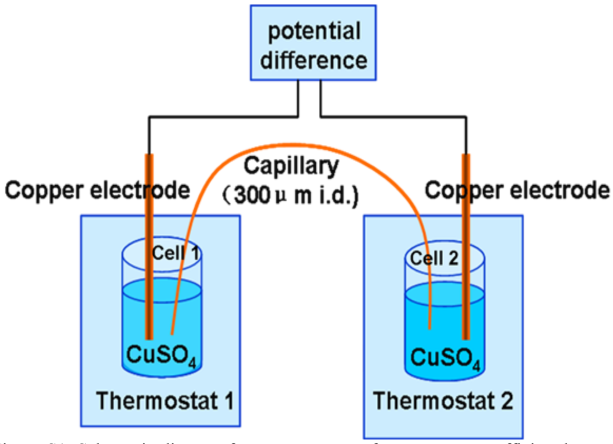

Figure S1. Schematic diagram for measurement of temperature coefficient by open circuit electrode potentials measured between two 360μm diameter Cu electrodes in two similar cells. Cell 1: 0.1 M $CuSO_4$ + 0.1 M H_2SO_4 at 25 ± 0.1℃; cell 2: the same solution with variable temperature.

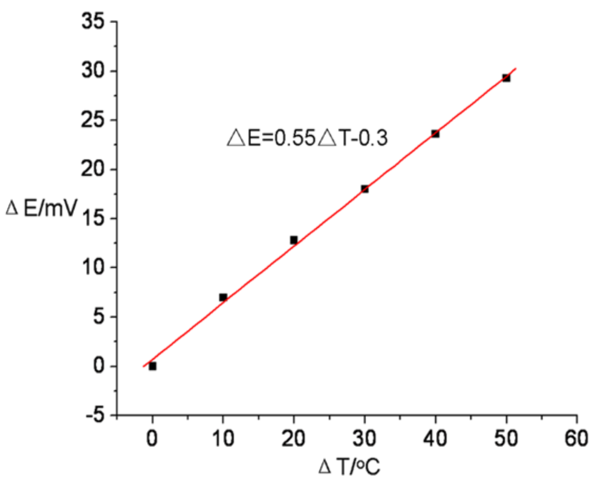

Figure S2. Relationship between ΔE and ΔT; ΔE is the potential difference between two Cu electrode surfaces; ΔT is the temperature difference between the two cells.

The temperature coeffiecient of Cu/Cu^{2+} was measured by dipping two copper wire to a separate container filled with 0.1 M $CuSO_4$ and 0.1 M H_2SO_4 as shown in Figure S1. The container was kept in a separate thermastat, and electrical connected by a capillary which was full of 0.1 M $CuSO_4$ and 0.1 M H_2SO_4 solution. The potential difference was measured after a equilibration time of 30 mins. Figure S2 shows the potential differece vs the elevated temperature. The temperature coeffiecient of Cu/Cu^{2+} is 0.55mV/℃.

2. Cyclic voltammograms (CVs) of three carbohydrates and shikimic acid (SA) at HCME

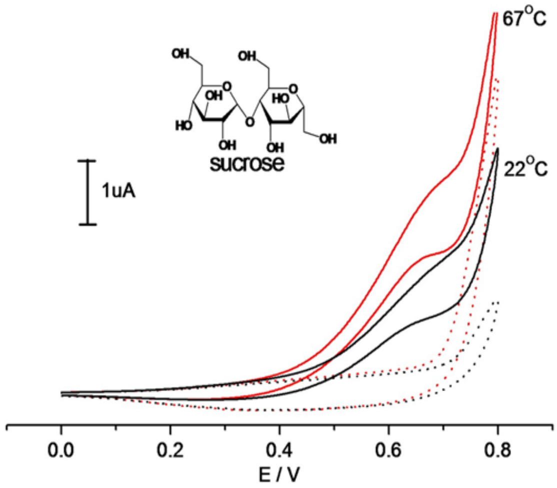

Figure S3. CVs of HCME in 0.02 M NaOH before (dashed line) and after (solid line) addition of 3 mM sucrose at two electrode temperature: 22 ℃ (black line) and 67 ℃ (red line). Scan rate: 100 mV·s^{-1}

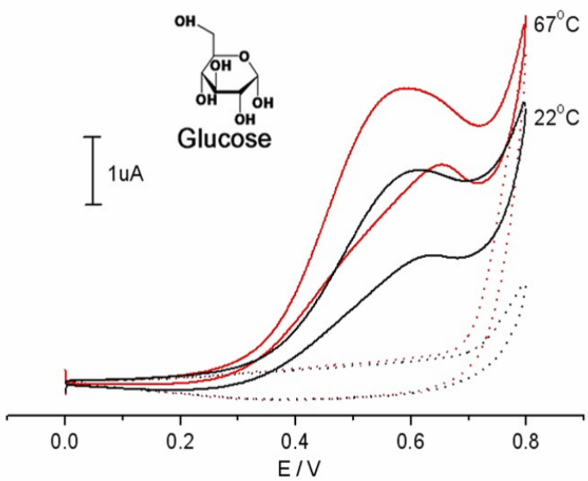

Figure S4. CVs of HCME in 0.02 M NaOH before (dashed line) and after (solid line) addition of 3 mM glucose at two electrode temperature: 22 ℃ (black line) and 67 ℃ (red line). Scan rate: 100 mV·s^{-1}

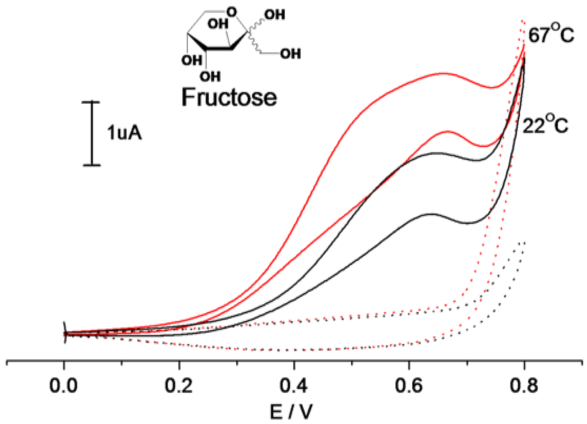

Figure S5. CVs of HCME in 0.02 M NaOH before (dashed line) and after (solid line) addition of 3 mM fructose at two electrode temperature: 22 ℃ (black line) and 67 ℃ (red line). Scan rate: 100 mV·s^{-1}

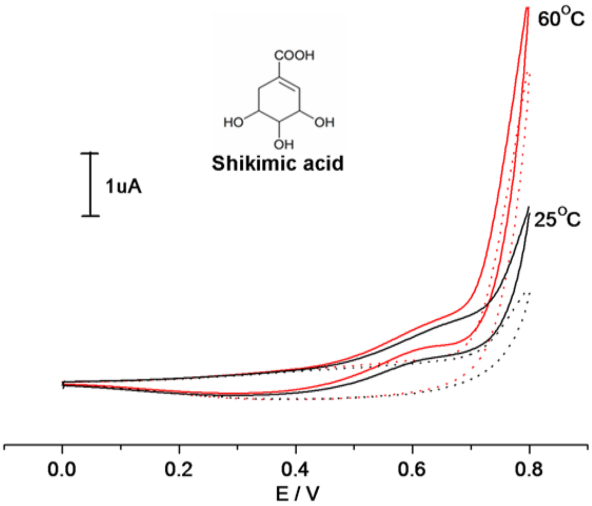

Figure S6. CVs of HCME in 0.02 M NaOH before (dashed line) and after (solid line) addition of 3 mM skikimic at two electrode temperature: 25 ℃ (black line) and 60 ℃ (red line). Scan rate: 100 mV·s^{-1}

3. The Optimization of CE-ECD conditions.

Effect of detection potential, NaOH concentration and seperation Voltage

The potential applied to the HCME directly affects the sensitivity, detection limits. Thus, the potential was investigated towards three carbohydrates by changing from 0.6 V to 1.0 V (versus SCE). When the potencial was less than 0.6V, no obvious amperometric signal was observed. With increasing potential from 0.6V to 0.8V the amperometric signal increased rapily. When the potential was higher than 0.8V, there was a significant increase in the background current due to the onset of oxygen evolution. Thus, an operating potential of 0.8 V gave the best compromise between signal and background, and therefore was selected for subsequent CE amperometric detection in NaOH solution.

In an attempt to optimize the separation of carbohydrates, the composition of the electrophoresis medium was changed with 10, 20, 30, 40 and 50 mM NaOH. Because the NaOH concentration affects their resolution. When the NaOH concentration less than 20mM, it is diffcult to distinguish glucose and fructose. When NaOH buffer concentration was further increased above 20 mM, the migration time became too long, and the separation did not improve with increasing the current intensity too much. Thus, the optimum concentration was fixed at 20 mM, which gave short migration time and good resolution.

The amperometric signal increased with the increase of injection time from 6 to 12 s, or with the increase of injection voltage from 9 to 18 kV. However, the resolution was improved at lower injection voltage and injection time. Therefore, 15 kV for 10 s was chosen as the suitable injection parameters. The separation voltage also was investigated; In view of the Joule heating problem and the generation of high background, a separation voltage of 15 kV was employed.

4. The Optimization of CE-Chip-ECD conditions.

Effect of detection potential , NaOH concentration and seperation Voltage

Electrochemical response of SA at oxide covered copper electrode was investegated. The response can hardly be observed when the applied potential is lower than 0.6V, and increases with higher potential. However, it goes down when the potential is higher than 0.8V. This can be ascribed to the thicker oxide layer formed at higher potential, which hinders the electron transfer[S1]. The baseline also becomes instable at high potential. Thus, 0.8V was adapted for detection.

The concentration of NaOH can also influence the separation time, current and efficiency. It was found that, the efficiency is low when the concentration is less than 20 mmol/L, and higher concentration would result in the instability of baseline. Therefore, 20 mmol/L was considered as the best.

Regarding the separation voltage, we investigated it in the range of 1000~1800 V, the best voltage is 1500 V. Sampling through the fracture is in the advantage of shorter time and lower injection voltage requirement, as well as less zone broadening[S2-S4]. It was found that, more time was consumed when the injection voltage is less than 300V. This would result in the zone broadening and lower separation efficiency. We finally chose 300V-3s (an optimum injection voltage of 300 V at the injection time of 3 s) as the optimized condition.

Reference

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