

Supporting Information

Electrochemical reduction of the simplest monosaccharides: dihydroxyacetone and glyceraldehyde

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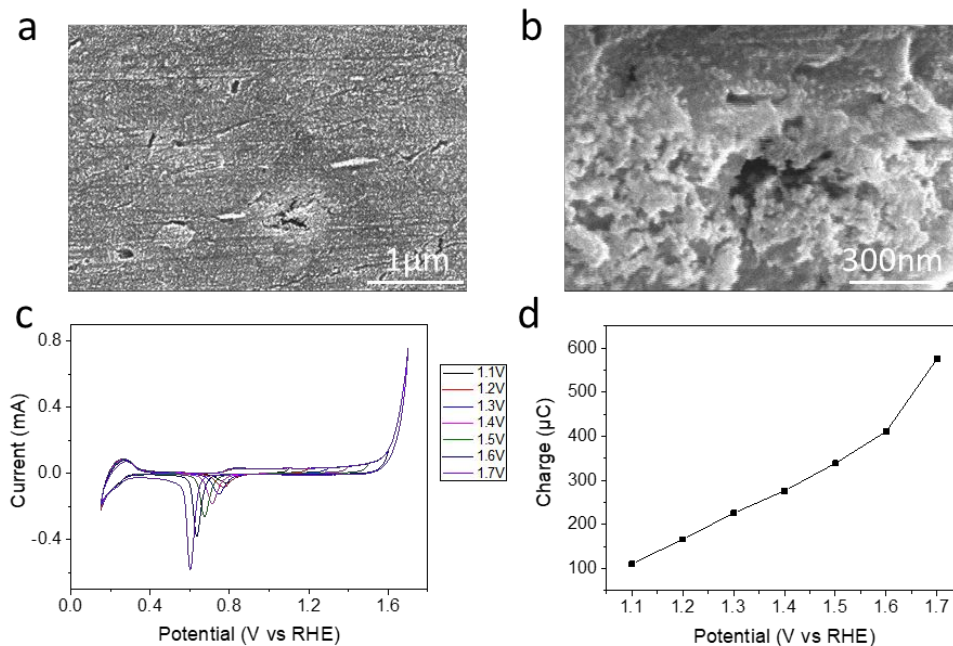


Figure S1. Characterization of Pd electrode after the mechanical polishing. (a-b) SEM images at (a) 50000 \times and (b) 150000 \times magnification. (c) Cyclic voltammetry (CV) scans with different upper potential limit (1.1 V – 1.7 V vs.RHE) in 0.1 M H₂SO₄. The scan rate is 50 mV/s. (d) Integrated charge for the reduction of Pd oxide as a function of the upper potential limit.

The potential where the straight line in Figure S1d changes its slope corresponds to the formation of a complete PdO monolayer. At higher potentials, a further oxidation proceeds, leading to a higher valence state of Pd oxides. So we chose the charge at the potential of 1.6 V vs. RHE to get the active surface area of 0.98 cm².

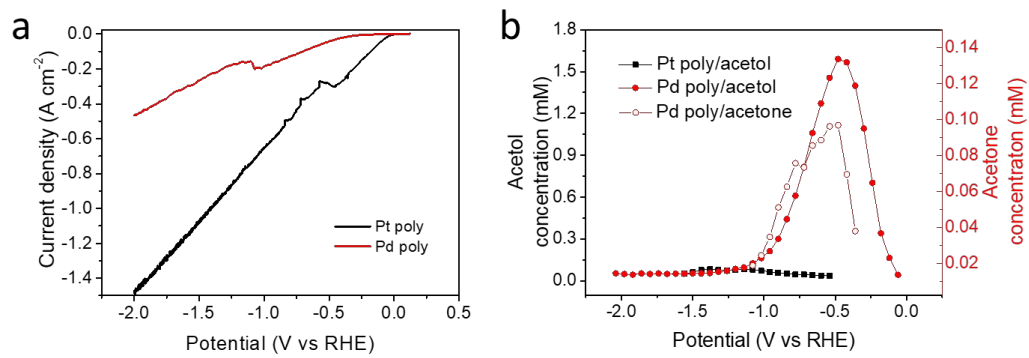


Figure S2. Electrode effect on dihydroxyacetone (DHA) electroreduction. (a) The linear sweep voltammetry (LSV) of Pt and Pd electrodes from 0 to -2.0 V vs. RHE at 1 mV s⁻¹ in 0.1 M H₂SO₄ electrolyte with 100 mM of DHA. Current density is normalized by the geometric surface area. (b) Product distribution of DHA reduction detected from HPLC during the voltammetry in (a).

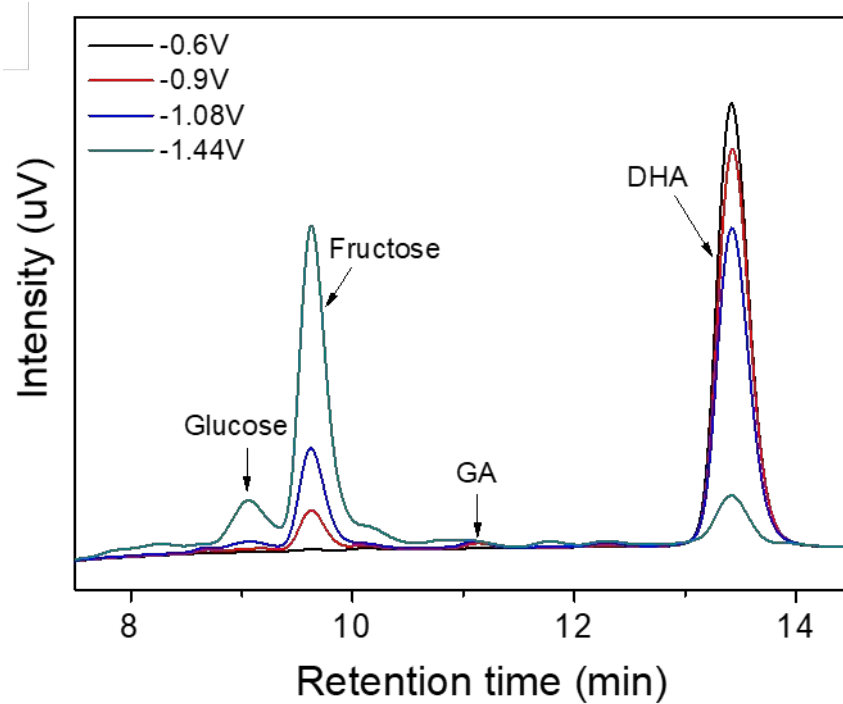


Figure S3. Chromatograms from HPLC analysis with collected online samples during voltammetry for DHA reduction at pH=6.

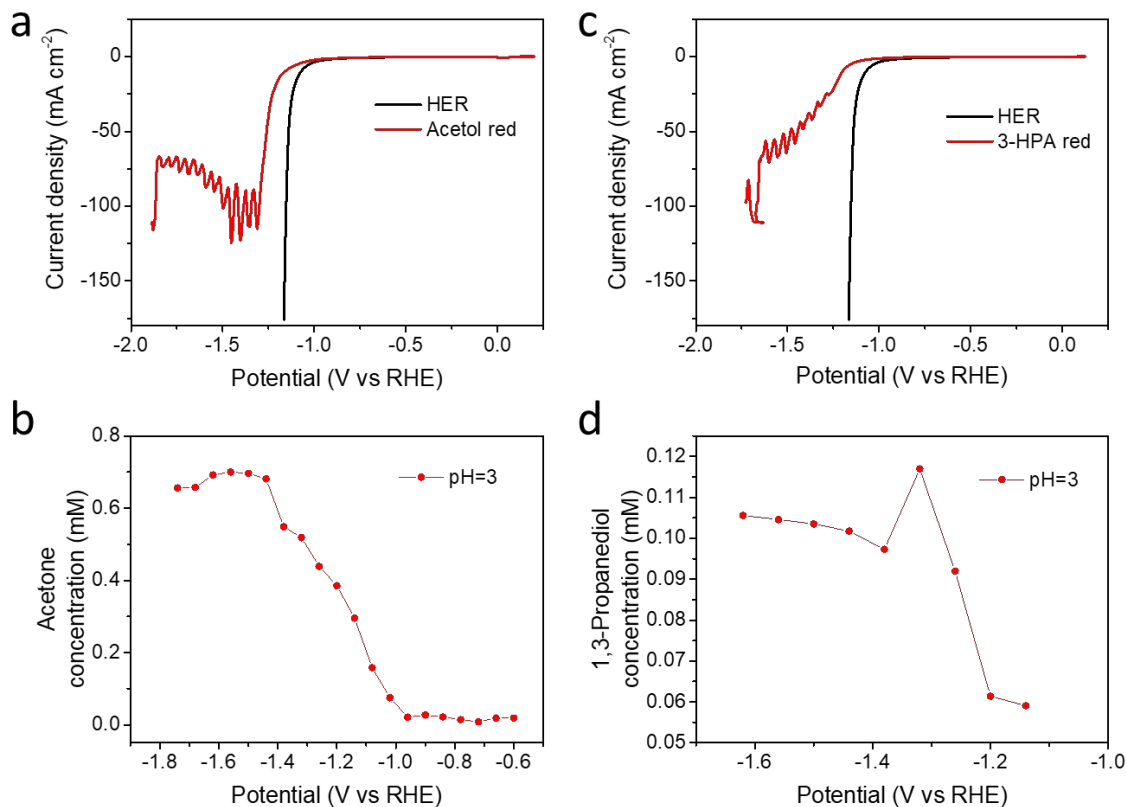


Figure S4. The reduction of acetol and 3-hydroxypropionaldehyde (3-HPA) on Pd electrode and their corresponding product identification. (a, c) LSV scans for the reduction of (a) 50 mM acetol and (c) 50 mM 3-HPA in pH=3: 0.001 M HClO₄ + 0.099 M NaClO₄. The scan rate is 1.0 mV s⁻¹. (b, d) Reduction products of (b) acetone corresponding to (a), and (d) 1,3-propanediol (1,3-PD) corresponding to (c).

To determine the involved intermediates, we investigated the reduction of acetol and 3-HPA, respectively. Figure S4 presents the voltammetry and the corresponding reduction products at pH=3. Acetol is reduced to acetone (Figure S4b), and 3-HPA is reduced to 1,3-PD (Figure S4d), and their onset potentials are consistent with the results in Figure 1d and 3d in the main text, corroborating their role as the intermediates in the reaction pathways of DHA and glyceraldehyde (GA) reduction.

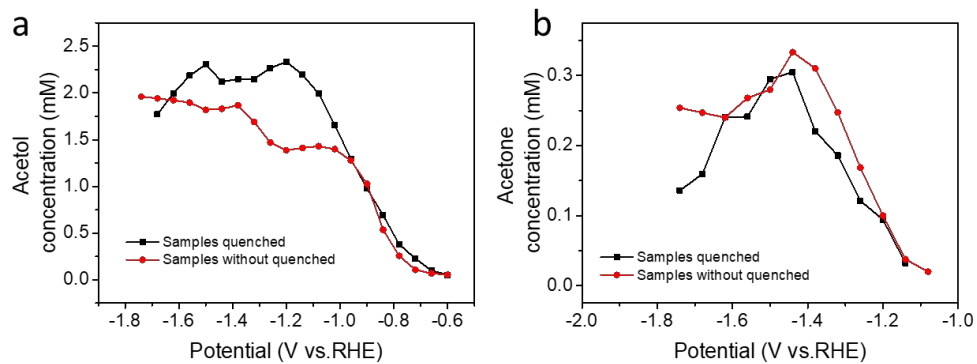


Figure S5. The products of DHA reduction (50 mM) on Pd electrode at pH=6 measured by online HPLC with and without quenching samples by 0.1 M HClO₄ after sample collection: (a) acetol production, and (b) acetone production.

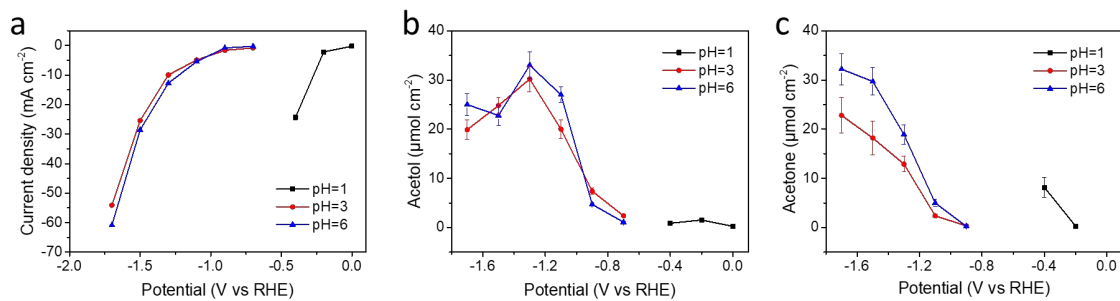


Figure S6. Bulk electrolysis for DHA reduction. (a) Total current density. (b-c) The yields of (b) acetol and (c) acetone.

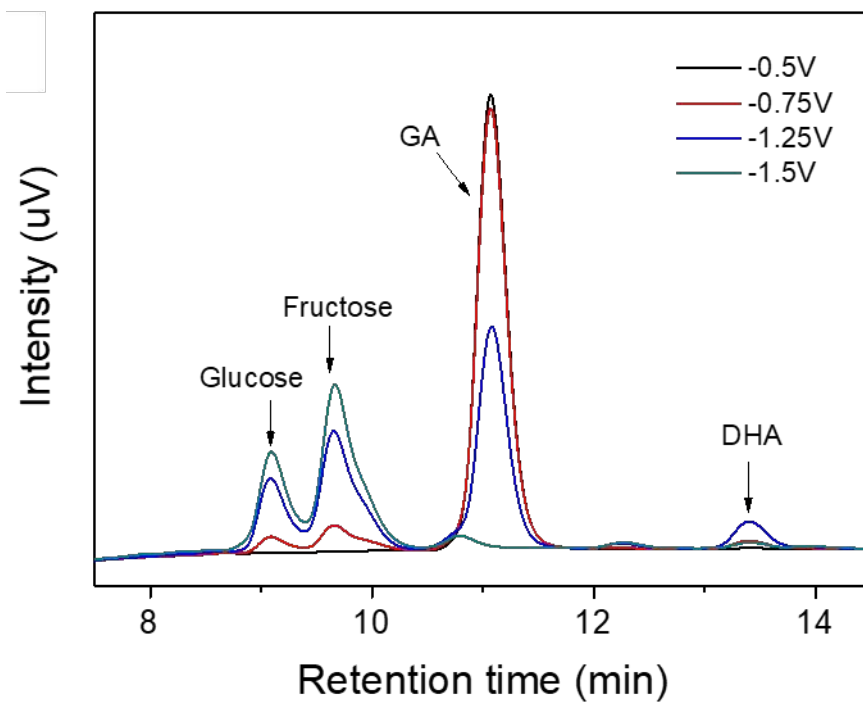


Figure S7. Chromatograms from HPLC analysis with collected online samples during voltammetry for GA reduction at pH=6.

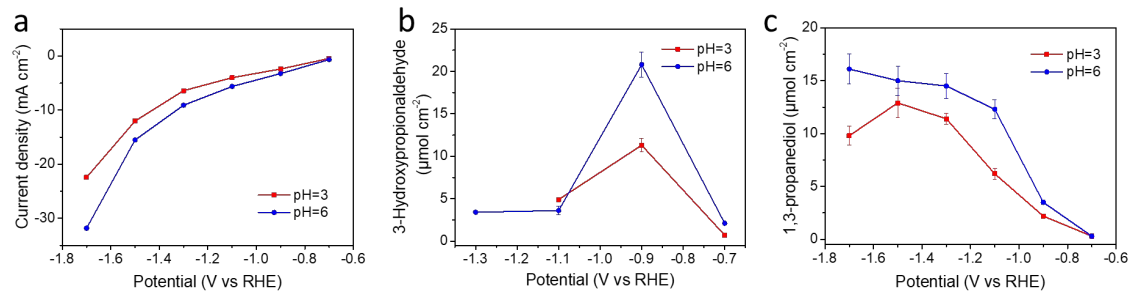


Figure S8. Bulk electrolysis for GA reduction. (a) Total current density. (b-c) The yields of (b) 3-HPA and (c) 1,3-PD.

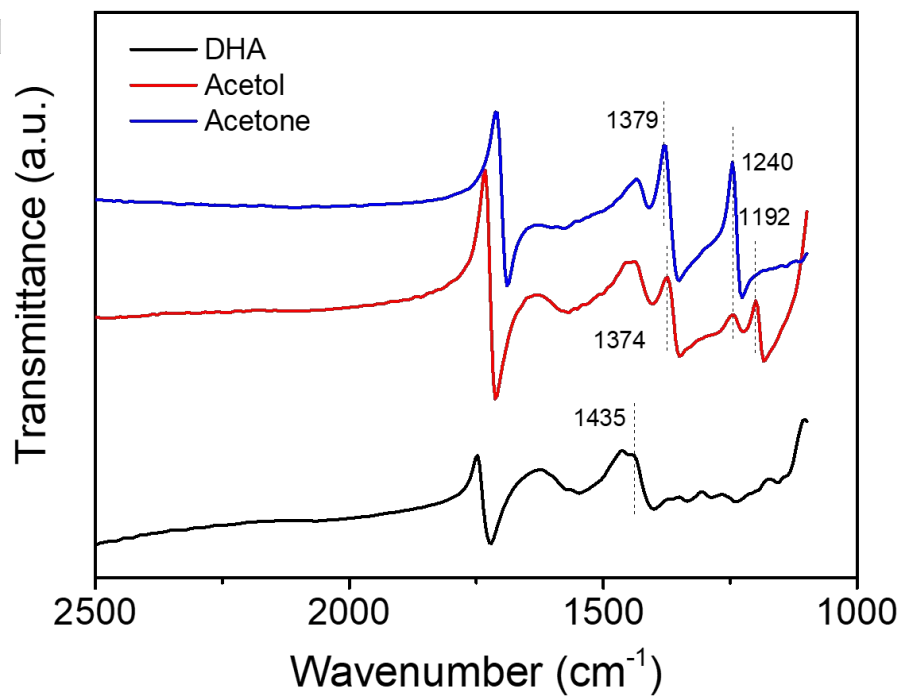


Figure S9. Transmission spectra of DHA, acetol, and acetone. Background was obtained at pH=3 solution: 0.001 M HClO₄ + 0.099 M NaClO₄.

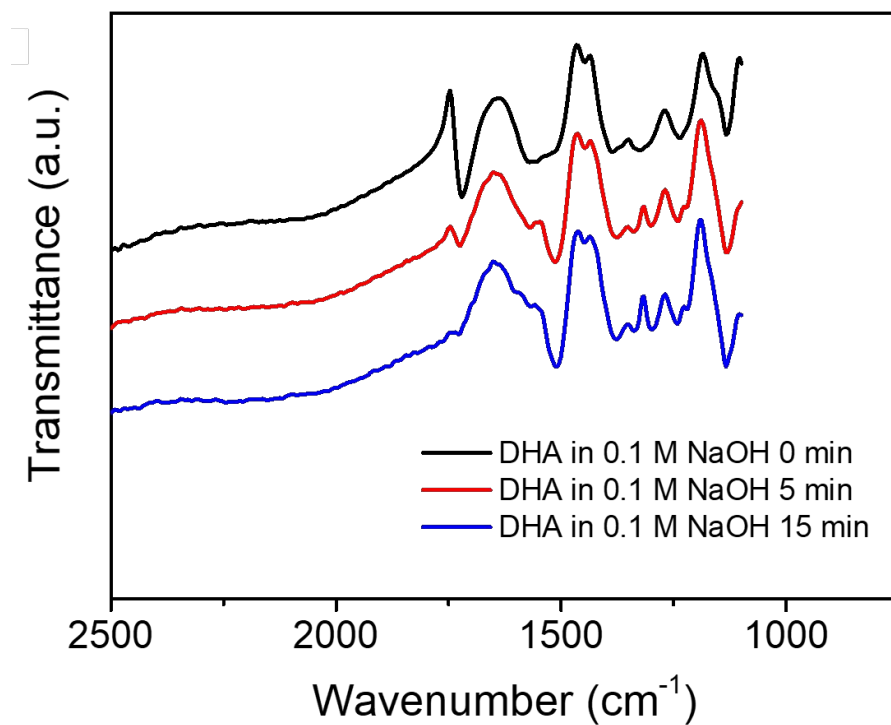


Figure S10. Transmission spectra of 50 mM DHA in 0.1 M NaOH solution for different standing time. Background was obtained in 0.1 M NaOH.

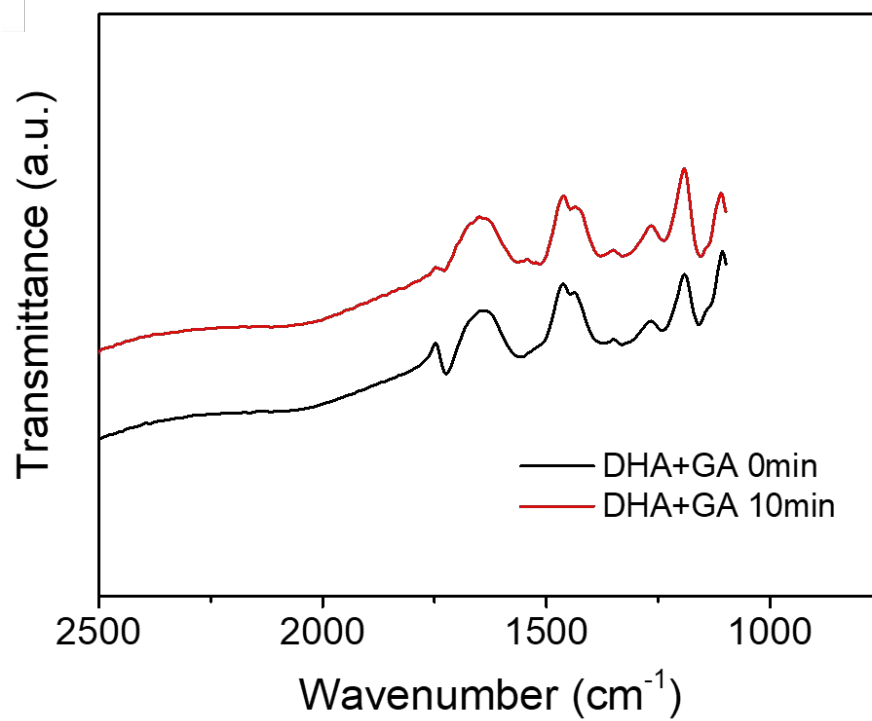


Figure S11. Transmission spectra of 50 mM DHA + 50 mM GA in 0.1 M NaOH solution for different standing time. Background was obtained in 0.1 M NaOH.

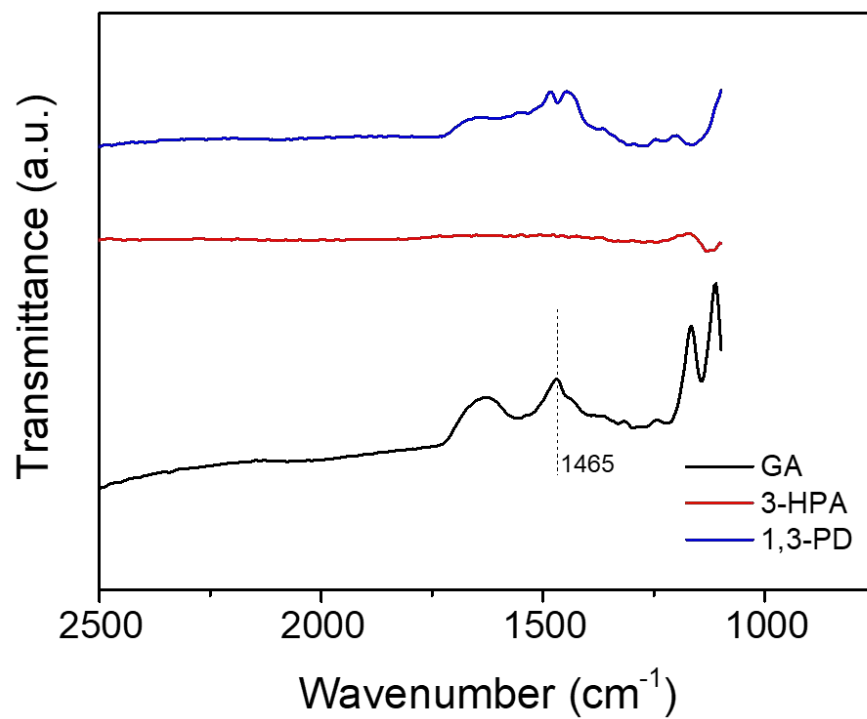


Figure S12. Transmission spectra of GA, 3-HPA, and 1,3-PD. Background was obtained at pH=3 solution: 0.001 M HClO₄ + 0.099 M NaClO₄.

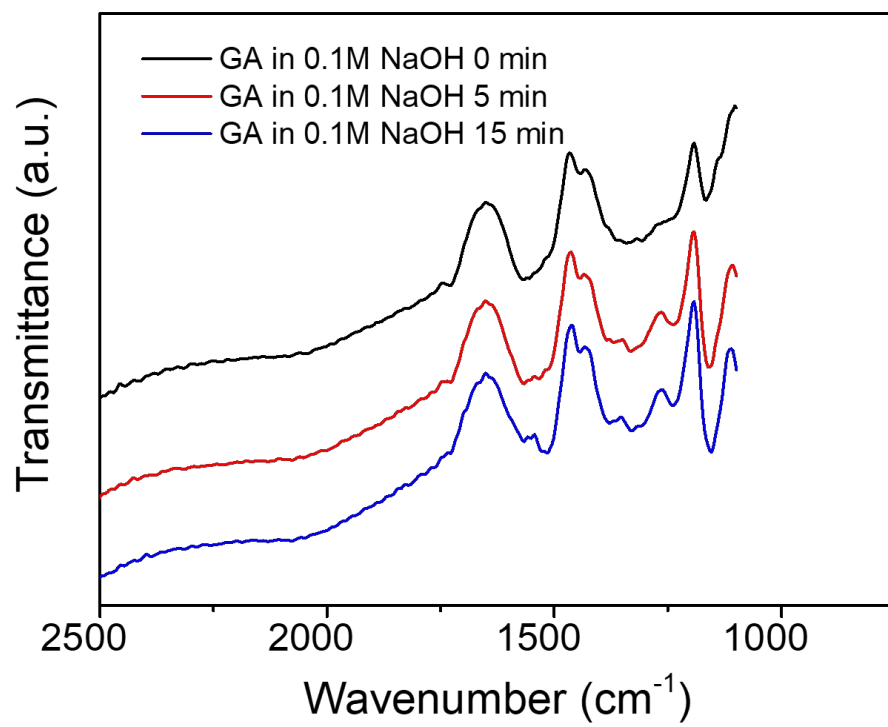


Figure S13. Transmission spectra of 50 mM GA in 0.1 M NaOH solution for different standing time. Background was obtained in 0.1 M NaOH.

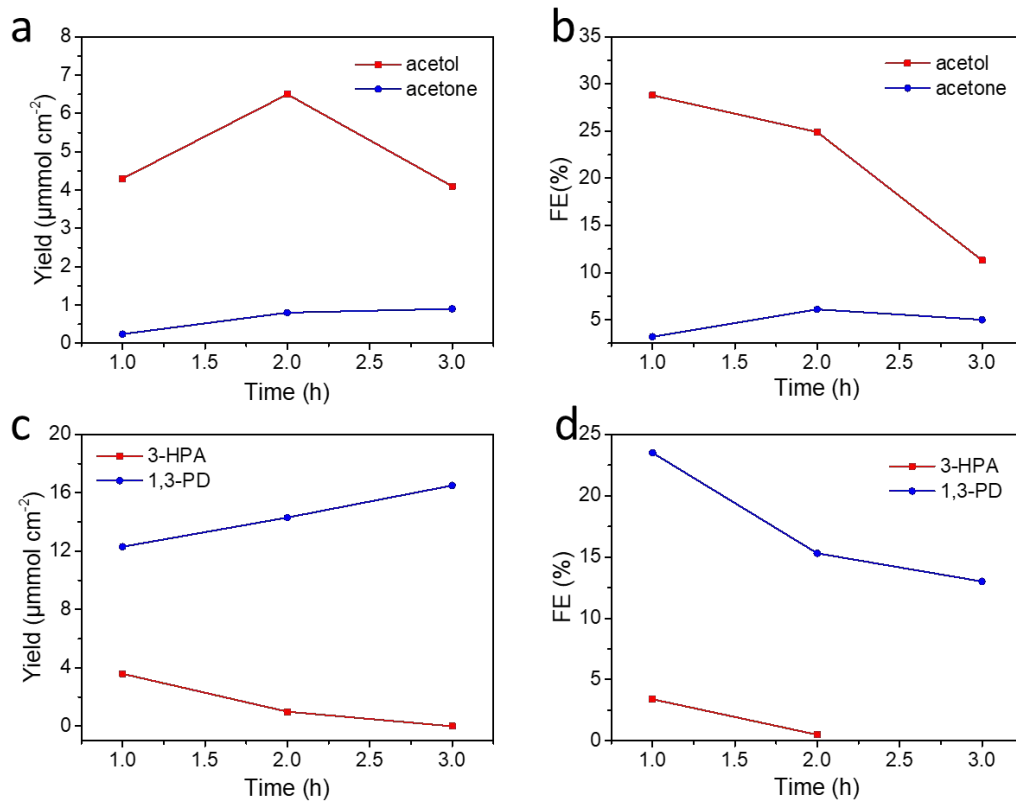


Figure S14. (a) The yield and (b) the corresponding faradaic efficiency of the products for DHA reduction with increasing the reaction time. (c) The yield and (d) the corresponding faradaic efficiency of the products for GA reduction with increasing the reaction time.

Table S1. Composition of the buffer electrolytes and their solution resistance

Bulk pH	Electrolyte solution	Resistance (Ω)
5.8	0.1 M NaH_2PO_4 +0.01 M Na_2HPO_4	71.873
7.8	0.01 M NaH_2PO_4 +0.1 M Na_2HPO_4	38.804
9.7	0.1 M Na_2HPO_4 +0.001 M Na_3PO_4	38.102
11.4	0.1 M Na_2HPO_4 +0.1 M Na_3PO_4	20.797

Table S2. pH of the sample solution before and after reaction for DHA reduction.

DHA reduction	Before reaction	After reaction
0.1M HClO_4	1	1
0.001M HClO_4 +0.099M NaClO_4	3	9.1
0.1M NaClO_4	6	10.3

Table S3. pH of the sample solution before and after reaction for GA reduction.

GA reduction	Before reaction	After reaction
0.1M HClO_4	1	1
0.001M HClO_4 +0.099M NaClO_4	3	8.9
0.1M NaClO_4	6	10.7

Table S4. Faradaic efficiency of DHA reduction products at different pH condition.

pH=3						
	-0.7 V vs.RHE	-0.9 V vs.RHE	-1.1 V vs.RHE	-1.3 V vs.RHE	-1.5 V vs.RHE	-1.7 V vs.RHE
FE (acetol/%)	16.1±1.4	24.8±2	21.9±2	16.3±1.4	5.3±0.4	2±0.2
FE (acetone/%)	N/A	2.2±0.3	5.2±0.6	13.9±1.7	7.7±1.4	4.5±0.7
pH=6						
	-0.7 V vs.RHE	-0.9 V vs.RHE	-1.1 V vs.RHE	-1.3 V vs.RHE	-1.5 V vs.RHE	-1.7 V vs.RHE
FE (acetol/%)	24.5±1.1	31.5±2	26.7±1.6	13.8±1.1	4.3±0.4	2.2±0.2
FE (acetone/%)	N/A	3.2±1.3	10±1.6	15.9±1.7	11.2±1	5.7±0.6
pH=1						
	0V vs.RHE		-0.2V vs.RHE		-0.4V vs.RHE	
FE (acetol/%)	6±0.6		3.8±0.1		0.2	
FE (acetone/%)	N/A		1.4		3.6±0.9	

Table S5. Faradaic efficiency of GA reduction products at different pH condition.

pH=3						
	-0.7 V vs.RHE	-0.9 V vs.RHE	-1.1 V vs.RHE	-1.3 V vs.RHE	-1.5 V vs.RHE	-1.7 V vs.RHE
FE (3-HPA/%)	8.4±0.4	25.2±1.8	6.6±0.1	N/A	N/A	N/A
FE (1,3-PD/%)	7.2±0.1	9.8±0.5	16.6±1.3	19±0.8	11.5±1.2	4.7±0.4
pH=6						
	-0.7 V vs.RHE	-0.9 V vs.RHE	-1.1 V vs.RHE	-1.3 V vs.RHE	-1.5 V vs.RHE	-1.7 V vs.RHE
FE (3-HPA/%)	17.1±0.8	34.4±2.5	3.4±0.5	2±0.04	N/A	N/A
FE (1,3-PD/%)	4.9±1	11.6±0.7	23.4±1.7	17.1±1.4	10.3±1	5.4±0.5