Supporting Information

Experimental section

ASD purification: A large amount of deionized water was added to the product of oxidative depolymerization of Zhaotong lignite, and it was fully stirred for 2 hours. After stirring, the solution to be mixed is allowed to stand for layering, and the solid is separated at the rotating speed of 1000 rpm. Wash the separated solid with deionized water, and repeat the above operation for 4-5 times. After the supernatant was washed to a colorless state, the separated solids were collected and dried in a vacuum drying oven at 80℃ for 24 hours to obtain the required ASD.

Electro-catalytic performance characterization:

(1) MA electrolysis

For MA electrolysis, ion chromatography is used directly to determine the residual MA and the main product benzoic acid (BA) in the electrolyte. MA conversion (**C_{MA}**) and BA selectivity (**S_{BA}**) are calculated according to the following formulas:

$$C_{MA} = \Delta n_{MA} / n_{MA}$$
$$S_{BA} = n_{BA} / \Delta n_{MA}$$

Here, n_{BA}: molar mass of BA before reaction; n_{MA}: molar mass of BA produced after the reaction.

(2) ASD electrolysis

Due to the complex structure of ASD and FA, it is impossible to calculate their accurate molar masses. We introduce the concepts of apparent conversion (**AC_{ASD}**) and apparent selectivity (**AS_{FA}**) as follows:

$$AC_{ASD} = \Delta m_{ASD} / m_{ASD} \times 100\%$$

$$AS_{FA} = m_{FA} / \Delta m_{HA} \times 100\%$$

Here, m_{ASD}: mass of ASD before reaction; Δm_{ASD}: mass change of ASD before and after reaction; m_{FA}: mass of FA generated after reaction.

Elemental content of electrocatalyst:

The approximate elemental composition of Nico-LDH@NiC_2O_4/NF surface was determined by scanning electron microscopy (SEM) mapping method, and the composition of Co and Ni after catalyst stripping was analyzed by ICP-AES. According to these measurements, the Co/Ni ratios obtained by the two methods are 1.63 and 1.23, respectively. We believe these results are reasonable, considering that the peeled samples may contain Ni-based components such as nickel oxalate and even foam nickel.

Table S1 Elemental Composition from SEM Mapping.

Element	C	O	Co	Ni
Weight %	28.71	35.90	21.97	13.42
Atomic %	45.65	42.86	7.12	4.37

Table S2 Co/Ni Ratio from ICP-AES Analysis (Powder sample)

Element	Co	Ni
Concentration (ppm)	12.09	9.81

Ion chromatography analysis:

As an example, Figure S1 shows that the residual MA and generated organic acids, such as benzoic acid (BA), acetic acid, formic acid, etc. can be effectively detected by ion chromatography.

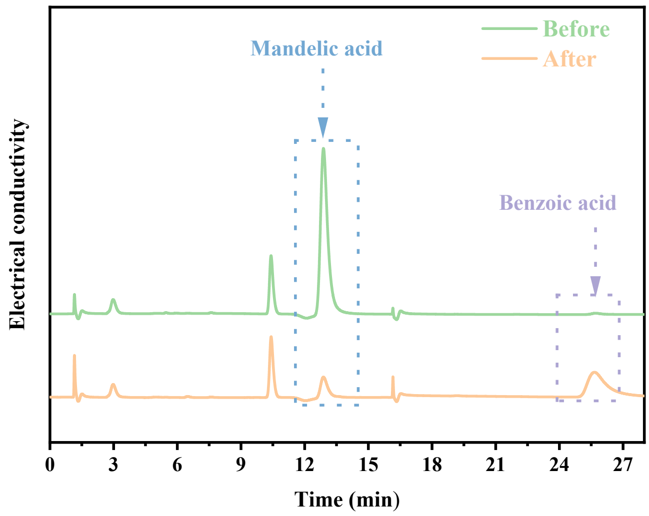


Fig. S1 Ion chromatography of MA electrolyte.

To quantitatively determine BA and MA in the electrolyte, the external standard curve method was used. The calibration curves for MA and BA were established and are shown in Fig. S2. These calibration curves enable accurate quantification of the concentrations of MA and BA in the electrolyte, facilitating the calculation of conversion rates and selectivity.

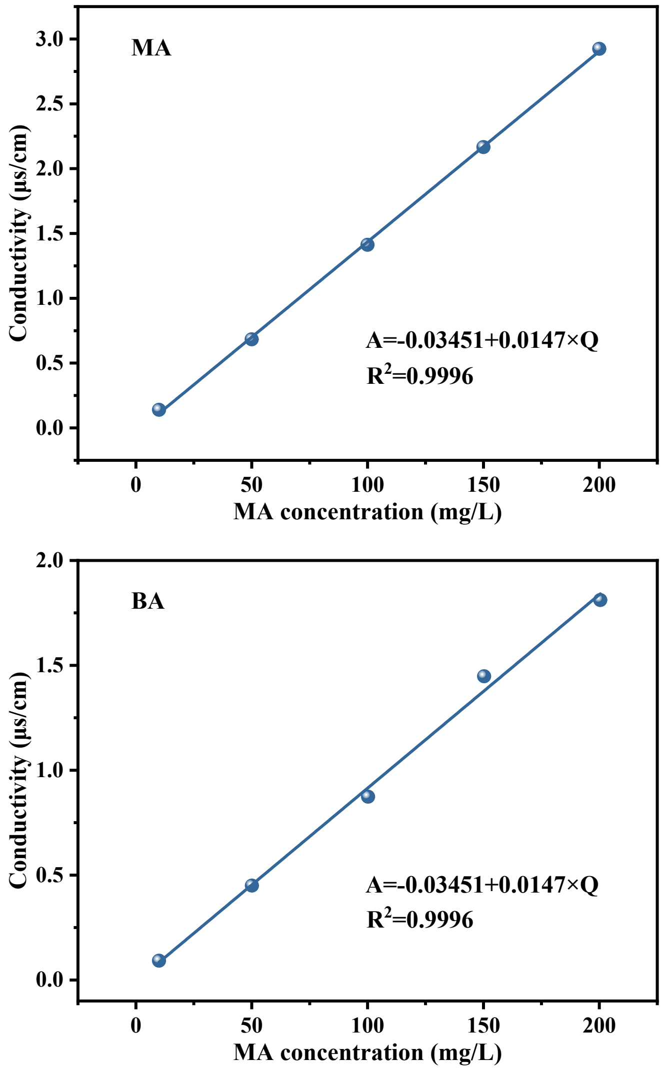


Fig. S2 Calibration curves for MA and BA determination, respectively.

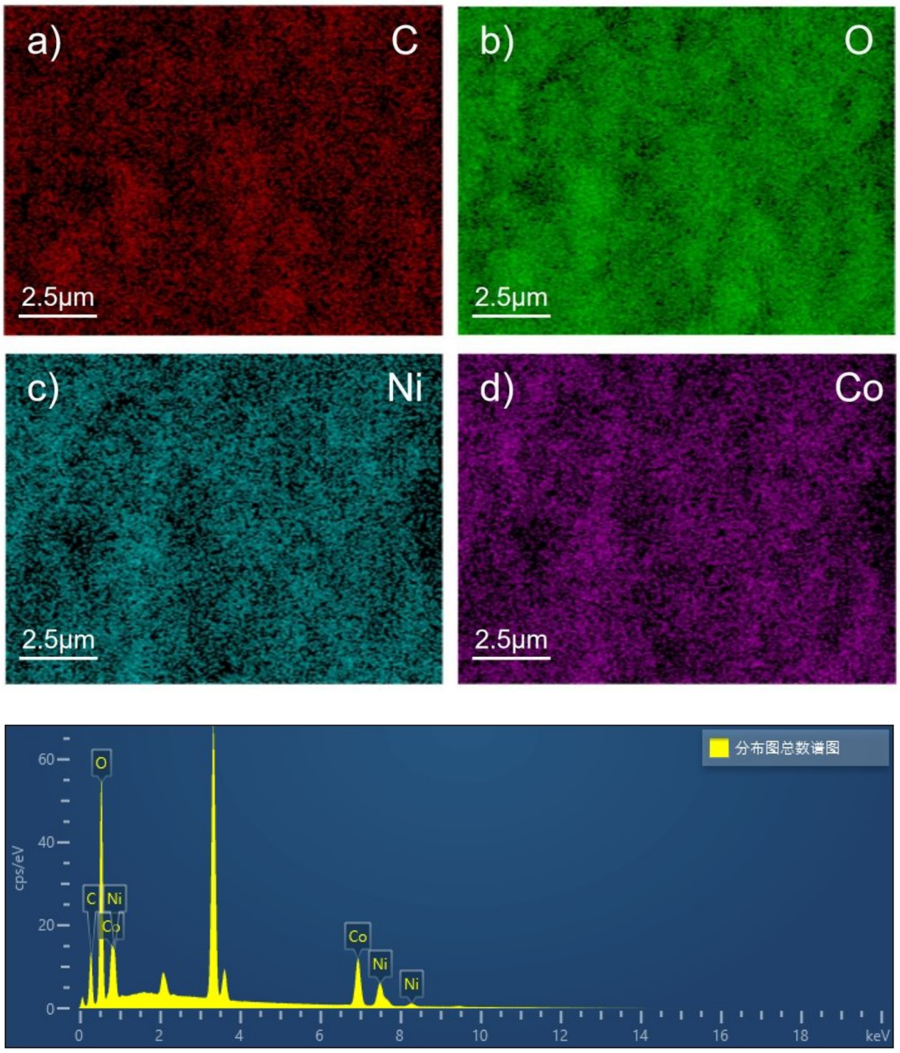


Fig. S3. EDS mapping of NiCo-LDH@NiC_2O_4/NF.

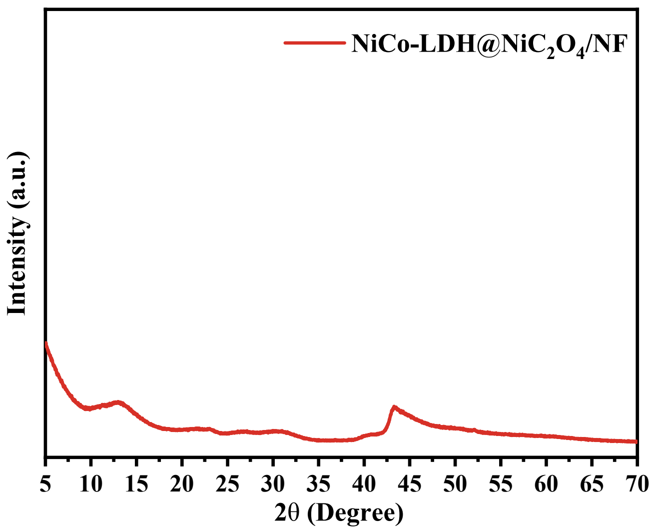


Fig. S4. XRD patterns of NiCo-LDH@NiC_2O_4/NF.

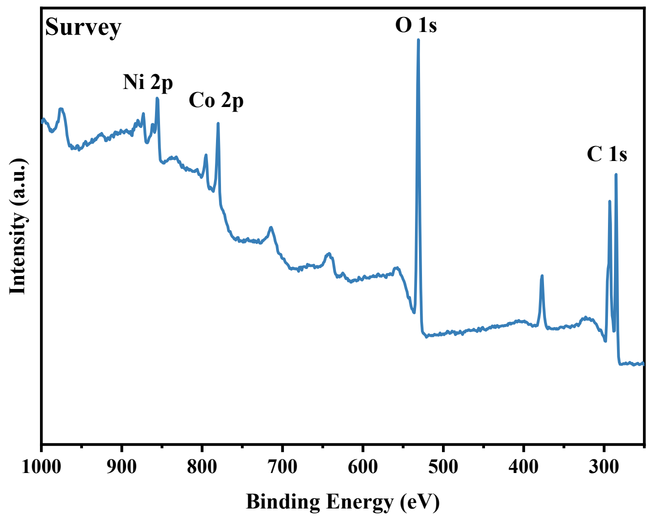


Fig. S5. XPS Spectra of NiCo-LDH@NiC_2O_4/NF Electrode.

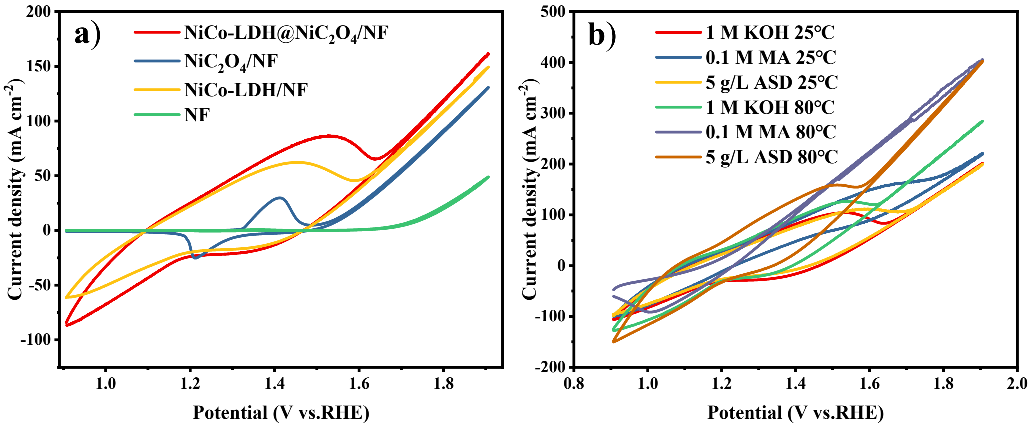


Fig. S6. (a) CV curves of different electrocatalysts in 1M KOH solution; (b) CV curve of NiCo-LDH@NiC_2O_4/NF electrode under different substrate conditions.

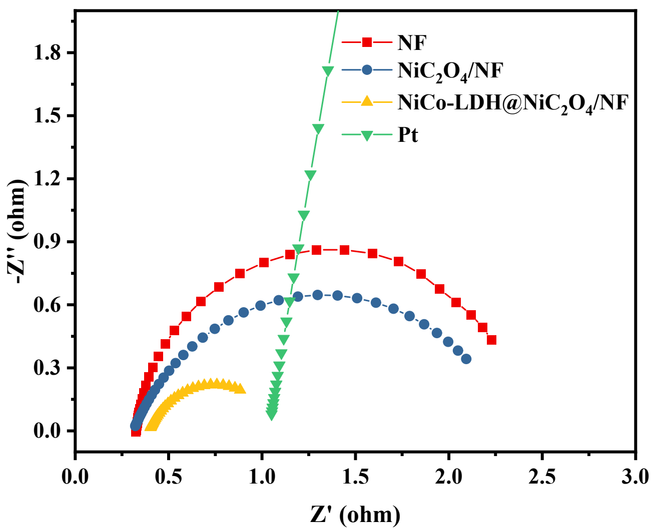


Fig. S7. Electrochemical impedance spectroscopy spectra of NiCo-LDH@NiC_2O_4/NF, NiC_2O_4/NF, NF and Pt.

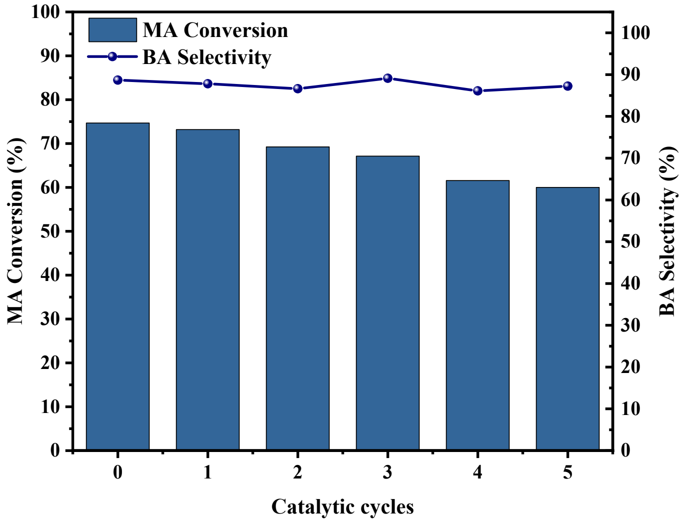


Fig. S8. Experimental results of batch cyclic electrolysis of NiCo-LDH/NF electrode in MA solution.

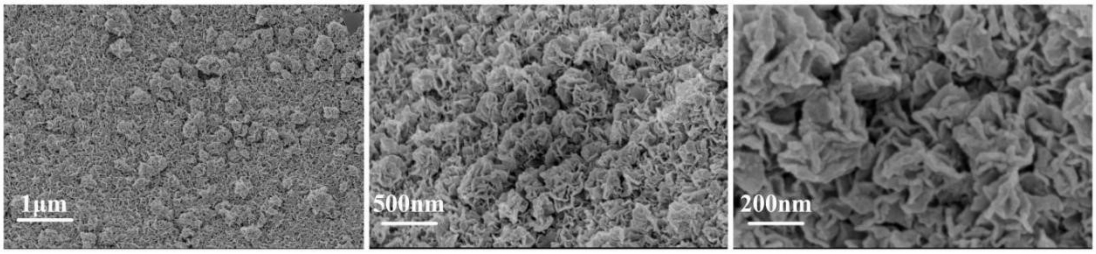


Fig. S9. SEM image of NiCo-LDH@NiC_2O_4/NF electrode surface after multiple electrolysis.

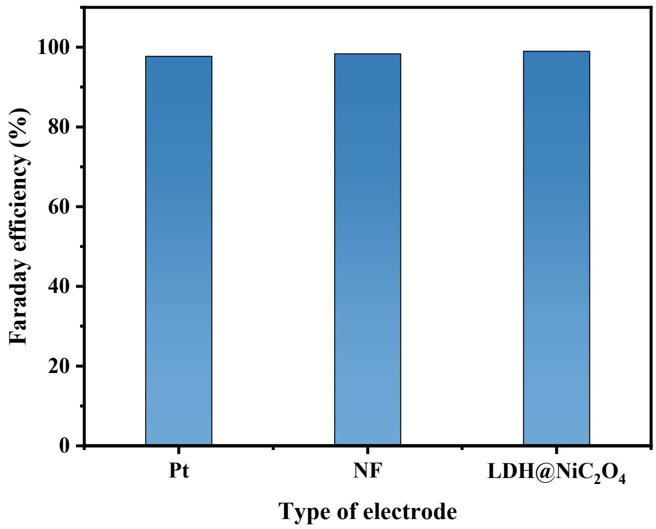


Fig. S10. Faraday efficiency under different counter electrode conditions in the process of electrolytic ASD.

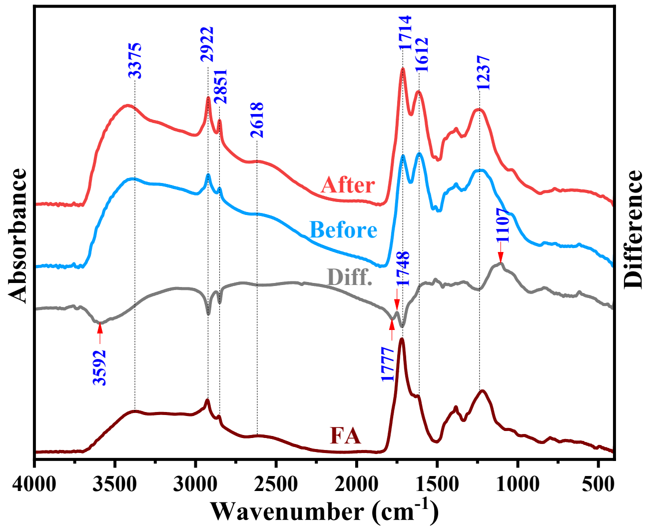


Fig. S11. Infrared spectra of FA and ASDs before and after reaction.

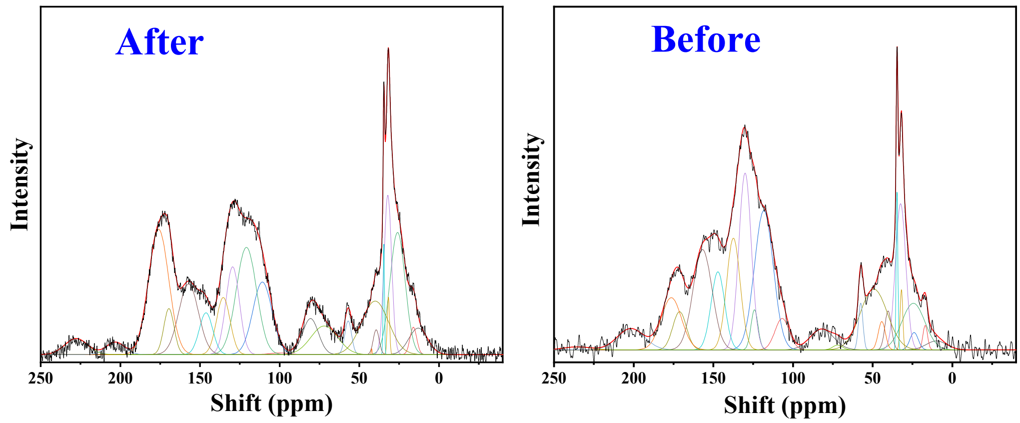


Fig. S12. Fitting curves of ^{13}C-NMR spectra of ASDs before and after electrolysis.

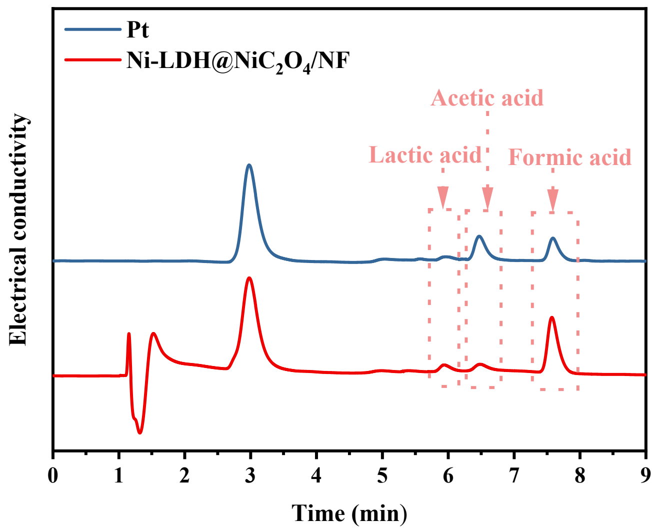


Fig. S13. IC characterization of the electrocatalytic oxidized ASD products**.**

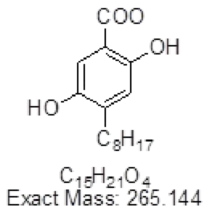
Table S3. Fitting parameters and results of ASD and ASDr [13]C-NMR spectra.

No	Carbon structure	Symbol	Peak	FWHM	Area percent (%)	
					After	Before
1	$-CH_3$	$f^{(1)}_{al}$	10.00-13.05	13.81-15.00	2.71	0.98
2	$-CH_3$	$f^{(1)}_{al}$	16.08-17.00	3.39-5.00	1.01	0.60
3	$-CH_2CH_3$	$f^{(2)}_{al}$	24.00	6.14-20.00	0.00	0.78
4	$-CH_2CH_3$	$f^{(2)}_{al}$	24.45-26.00	11.22-16.96	10.15	5.77
5	$-CH_{2n}CH_2$	$f^{(3)}_{al}$	32.12-32.48	5.58-7.66	6.58	8.17
6	$-(CH_2)_nCH_2CH_3$	$f^{(3)}_{al}$	31.73-31.96	1.66-2.00	0.70	0.88
7	$ArCH_2CH_2$		34.60-34.73	0.97-1.26	0.80	1.45
8	$ArCH_2CH_2$	$f^{(a2)}_{al}$	39.41-40.31	4.33-4.86	0.80	1.38
9	$ArCH_2$	$f^{(a2)}_{al}$	40.05-49.31	20.00	7.92	8.89
10	other CH	$f^{(4)}_{al}$	42.27-44.28	0.65-5.28	0.03	1.09
11	$-OCH_3$	$f^{(O1)}_{al}$	56.98-57.51	3.24-5.00	1.24	1.11
12	$-OCH_2CH_3$	$f^{(O2)}_{al}$	72.00	7.21-19.88	4.21	0.25
13	$-OCH_2CH_3$	$f^{(O2)}_{al}$	80.61-81.93	11.63-17.42	3.10	2.65
	Total	f_{al}	0-100		39.25	33.98
14	Car-H(O)	$f^{(H(O))}_{a}$	100.00-106.80	10.53-15.00	0.18	2.42
15	Car-H(O)	$f^{(H(O))}_{a}$	110.85-118.31	13.85-14.17	7.60	14.10
16	Car-H(O)	$f^{(H(O))}_{a}$	120.87-124.18	5.21-14.98	11.89	1.53
17	Car-H	$f^{(H)}_{a}$	129.51-130.10	9.14-10.00	6.49	11.81
18	Bridge	$f^{(B)}_{a}$	135.39-137.41	10.00	4.22	8.16
19	C Substituted	$f^{(S)}_{a}$	146.23-147.15	9.89-10.00	3.06	5.70
20	O substituted	$f^{(O)}_{a}$	156.78-157.18	14.01-14.54	7.59	10.27
	Total	f_a	100-160		41.04	53.98
21	carboxyl(COO)	$f^{(1)}_{c}$	169.49-171.22	7.60-10.00	2.59	2.79
22	carboxyl(COO)	$f^{(1)}_{c}$	175.95-176.40	14.95-15.00	13.86	5.71
23	carboxyl(C=O)	$f^{(2)}_{c}$	201.74-203.12	13.64-20.00	1.26	3.12
24	carboxyl(C=O)	$f^{(2)}_{c}$	227.70-235.34	16.96-20.00	2.01	0.42
	Total	f_c	160-210		19.72	12.04

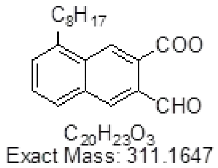
Table S4. Average molecular weight and dispersion coefficient of ASD before and after electrolysis detected by MALD-TOF MS.

Sample	Mn	Mw	PD
ASD	818	951	1.16
ASDr	720	824	1.14

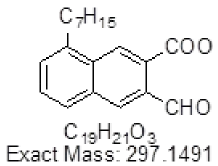
Table S5. Possible structure of all components with RE>10% in FA detected by ESI FT-ICR MS



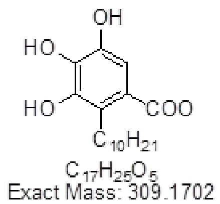
m/z=265.1440(100%)



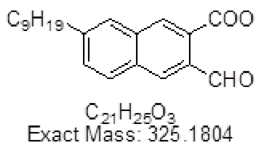
m/z=311.1647(97.1%)



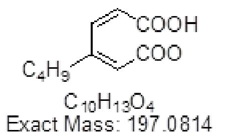
m/z=297.1491(70.5%)



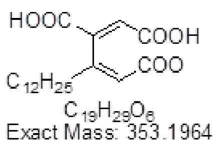
m/z=309.1702(58.9%)



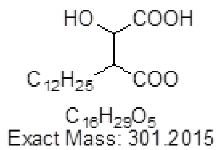
m/z=325.1804(54.4%)



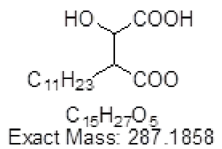
m/z=197.0813(43.5%)



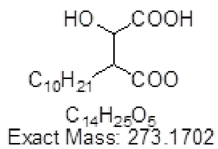
m/z=353.1964(42.2%)



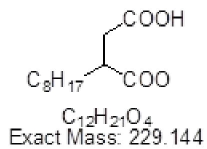
m/z=301.2014(41.4%)



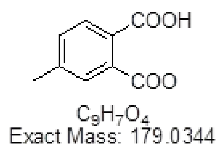
m/z=287.1857(39.3%)



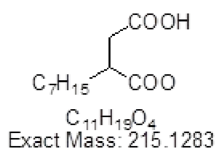
m/z=273.1701(33.2%)



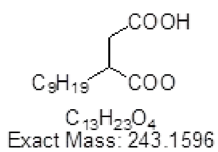
m/z=229.1439(28.9%)



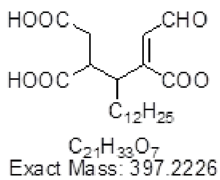
m/z=179.0344(27.6%)



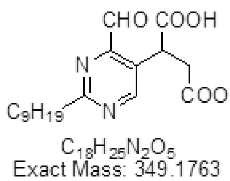
m/z=215.1283(26.8%)



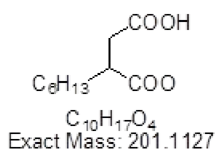
m/z=243.1595 (26.8%)



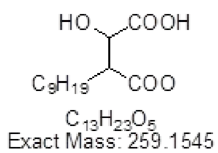
m/z=397.2225(22.9%)



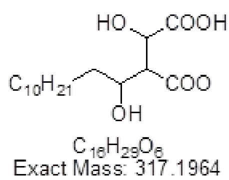
m/z=349.1763(21.9%)



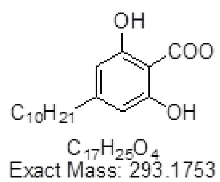
m/z=201.1126(21.8%)



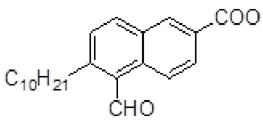
m/z=259.1545(20.5%)



m/z=317.1964(20.3%)

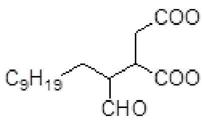


m/z=293.1752(19.8%)



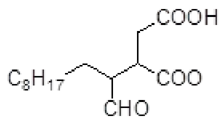
$C_{22}H_{27}O_3$
Exact Mass: 339.196

m/z=339.1959(19.1%)



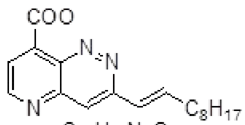
$C_{16}H_{27}O_5$
Exact Mass: 299.1858

m/z=299.1858(18.7%)



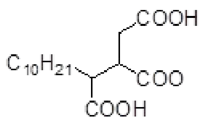
$C_{15}H_{25}O_5$
Exact Mass: 285.1702

m/z=285.1701(17.8%)



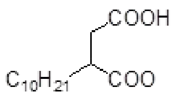
$C_{18}H_{22}N_3O_2$
Exact Mass: 312.1712

m/z=312.1714(17.4%)



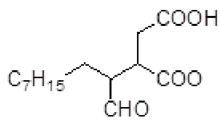
$C_{16}H_{27}O_6$
Exact Mass: 315.1808

m/z=315.1807(16.3%)



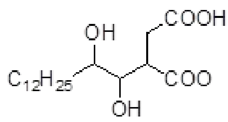
$C_{14}H_{25}O_4$
Exact Mass: 257.1753

m/z=257.1752(15.5%)



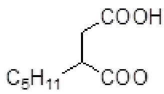
$C_{14}H_{23}O_5$
Exact Mass: 271.1545

m/z=271.1545(15.5%)



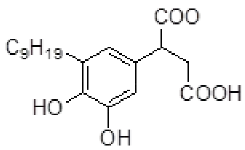
$C_{18}H_{33}O_6$
Exact Mass: 345.2277

m/z=345.2277(14.9%)



$C_9H_{15}O_4$
Exact Mass: 187.097

m/z=187.0970(14.0%)

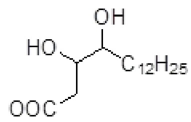


$C_{19}H_{27}O_6$
Exact Mass: 351.1808

m/z=351.1807(13.4%)

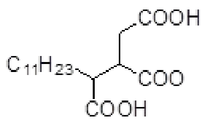
$C_9H_{13}O_2$
Exact Mass: 153.0916

m/z=153.0915(13.0%)



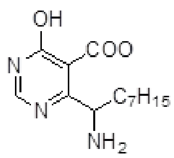
$C_{16}H_{31}O_4$
Exact Mass: 287.2222

m/z=287.2222(12.8%)



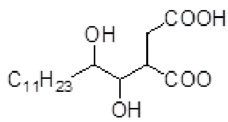
$C_{17}H_{29}O_6$
Exact Mass: 329.1964

m/z=329.1964(12.6%)



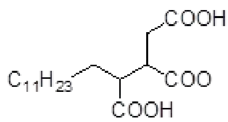
$C_{13}H_{20}N_3O_3$
Exact Mass: 266.1505

m/z=266.1506(12.3%)



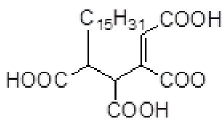
$C_{17}H_{31}O_6$
Exact Mass: 331.2121

m/z=331.2120(12.1%)



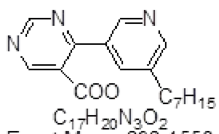
$C_{18}H_{31}O_6$
Exact Mass: 343.2121

m/z=343.2120(12.0%)



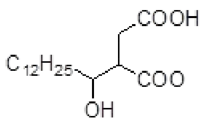
$C_{23}H_{37}O_8$
Exact Mass: 441.2488

m/z=441.2488(11.8%)



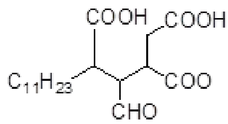
$C_{17}H_{20}N_3O_2$
Exact Mass: 298.1556

m/z=298.1557(11.8%)



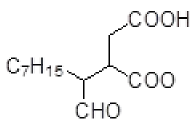
$C_{17}H_{31}O_5$
Exact Mass: 315.2171

m/z=315.2171(11.6%)



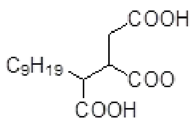
$C_{19}H_{31}O_7$
Exact Mass: 371.207

m/z=371.2069(10.5%)



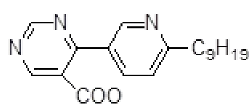
$C_{13}H_{21}O_5$
Exact Mass: 257.1389

m/z=257.1388(10.4%)



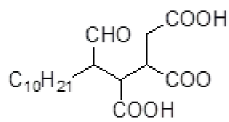
$C_{15}H_{25}O_6$
Exact Mass: 301.1651

m/z=301.1651(10.3%)



$C_{19}H_{24}N_3O_2$
Exact Mass: 326.1869

m/z=326.1870(10.2%)



$C_{18}H_{29}O_7$
Exact Mass: 357.1913

m/z=357.1913(10.1%)

The positions of substituents and alkyl number and chain length are uncertain, but the total alkyl carbon number is accurate.