Supporting Information

Green Closed-Loop Process for Selective Recycling of Lithium from Spent Lithium-ion Batteries

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15 pages,6 Figures and 6Tables

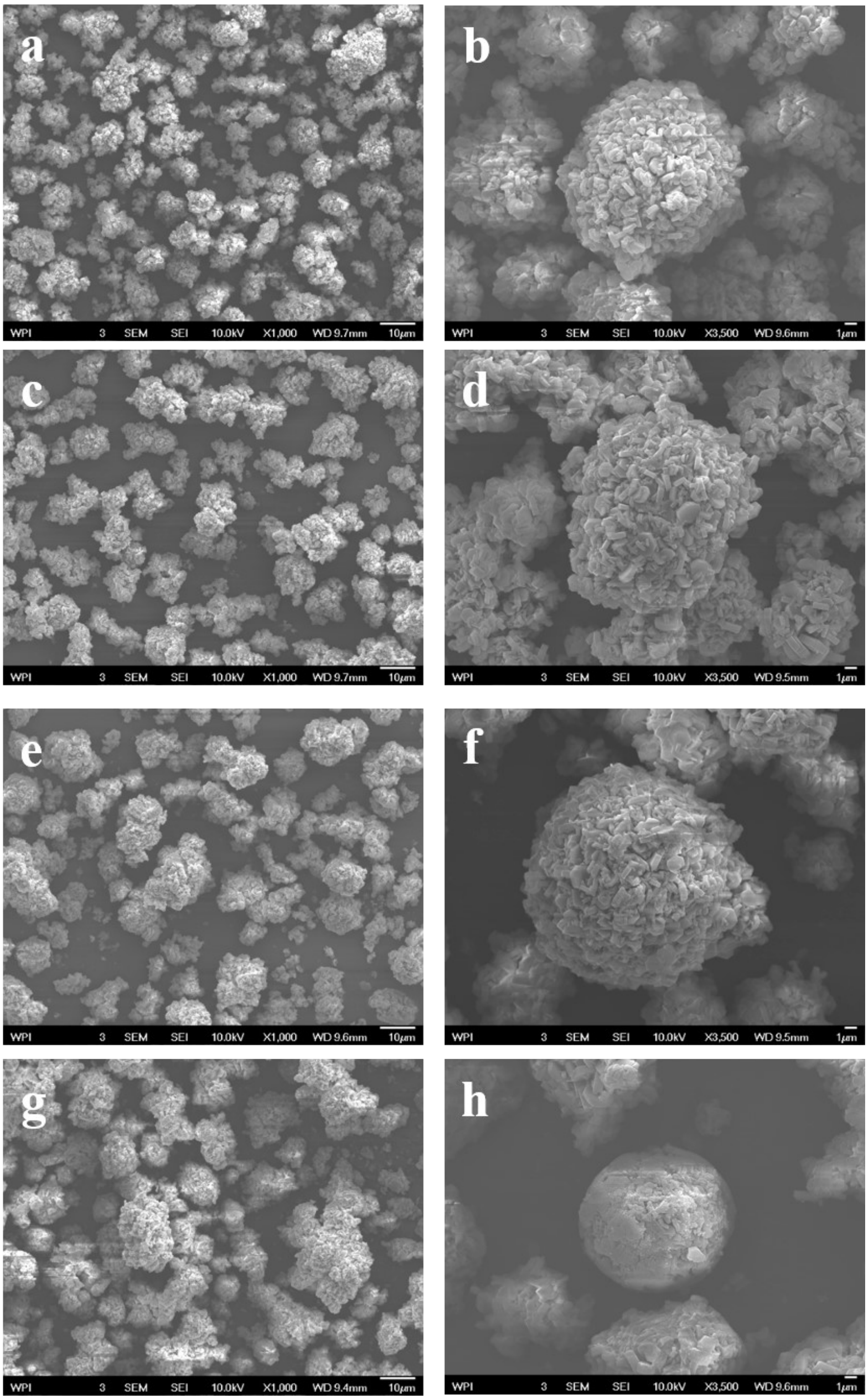

Figure S1. Insoluble salt shell formed on the surface of particles as temperature increases; (a) the aggormeration of leached particles at 50°C for 1 hr, (b) the insoluble salt shell formed on the surface of the particles at 50°C for 1 hr, (c) the aggormeration of leached particles at 60°C for 1 hr, (d) the unsoluable salt shell formed on the surface of the particles at 60°C for 1 hr, (e) the aggormeration of leached particles at 70°C for 1 hr, (f) the insoluble salt shell formed on the surface of the particles at 70°C for 1 hr, (g) the aggormeration of leached particles at 80°C for 1 hr, and (h) the insoluble salt shell formed on the surface of the particles at 80°C for 1 hr.

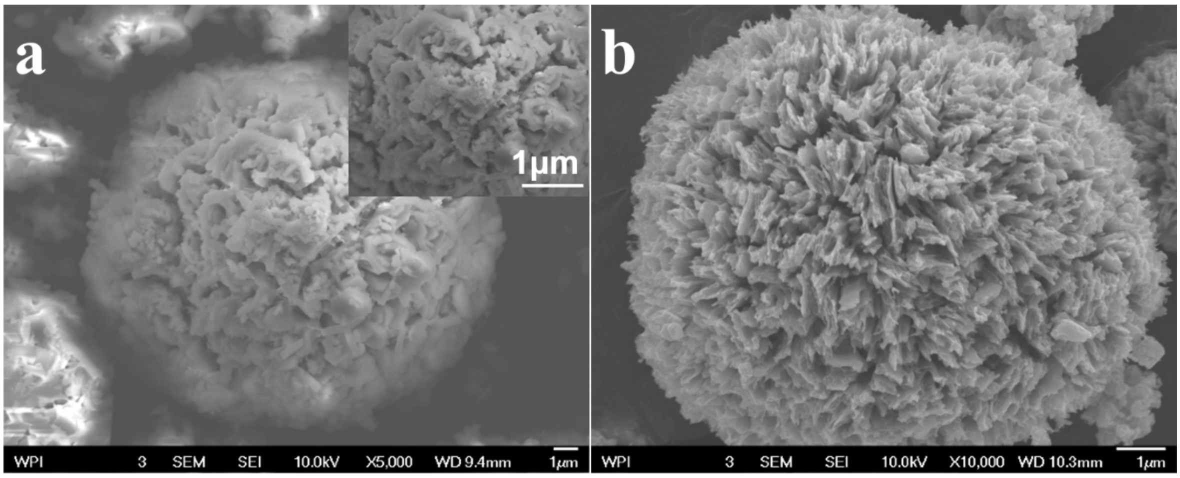

Figure S2. The porous structure of particles after leaching treatment; (a) the leached particle after formic acid washed, and(b) the particle after water washed.

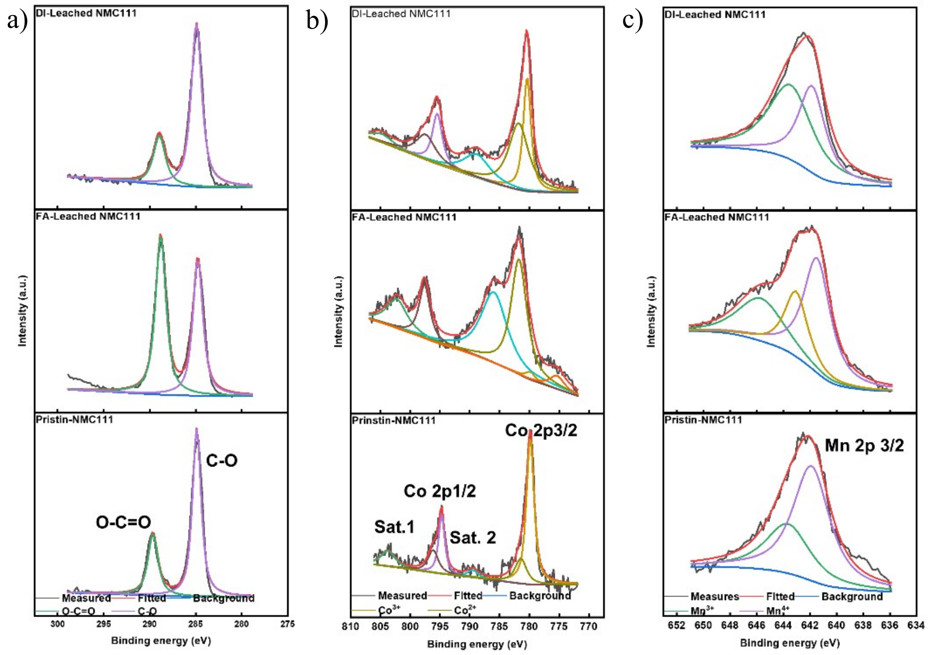

Figure S3. (a) C1s valance bind for Pristine-NMC111, FA-Leached NMC111, and DI-Leached NMC111, (b)Mn 2p valance bind for pristine-NMC111, FA-Leached NMC111, and DI-Leached NMC111, (c) Co 2p valance bind for pristine-NMC111, FA-Leached NMC111, and DI-Leached NMC111

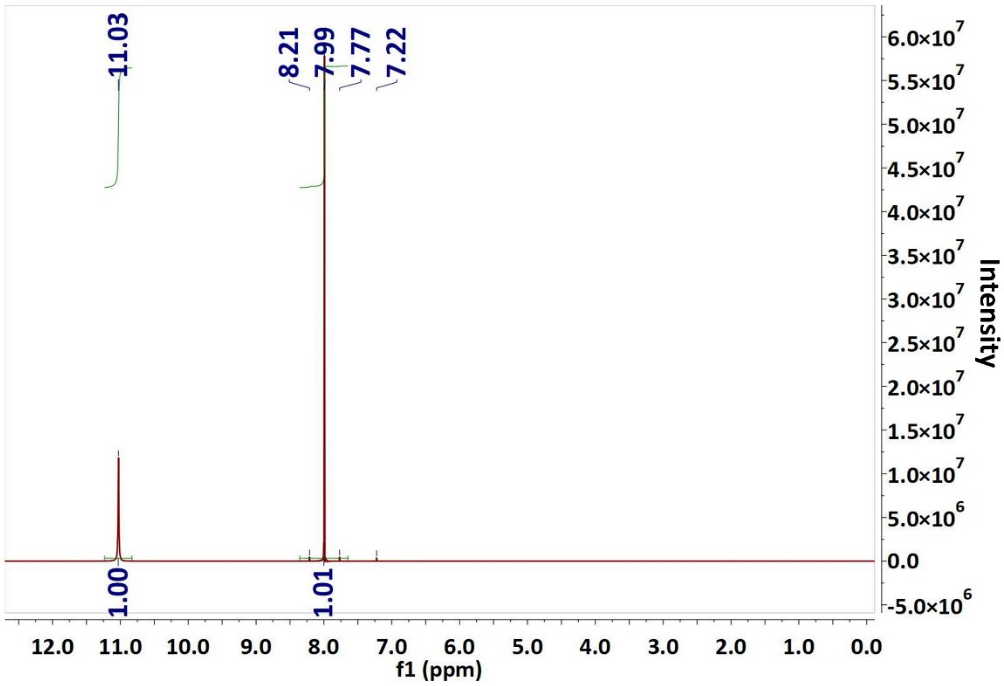

Figure S4. H^1 NMR spectra for pure formic acid.

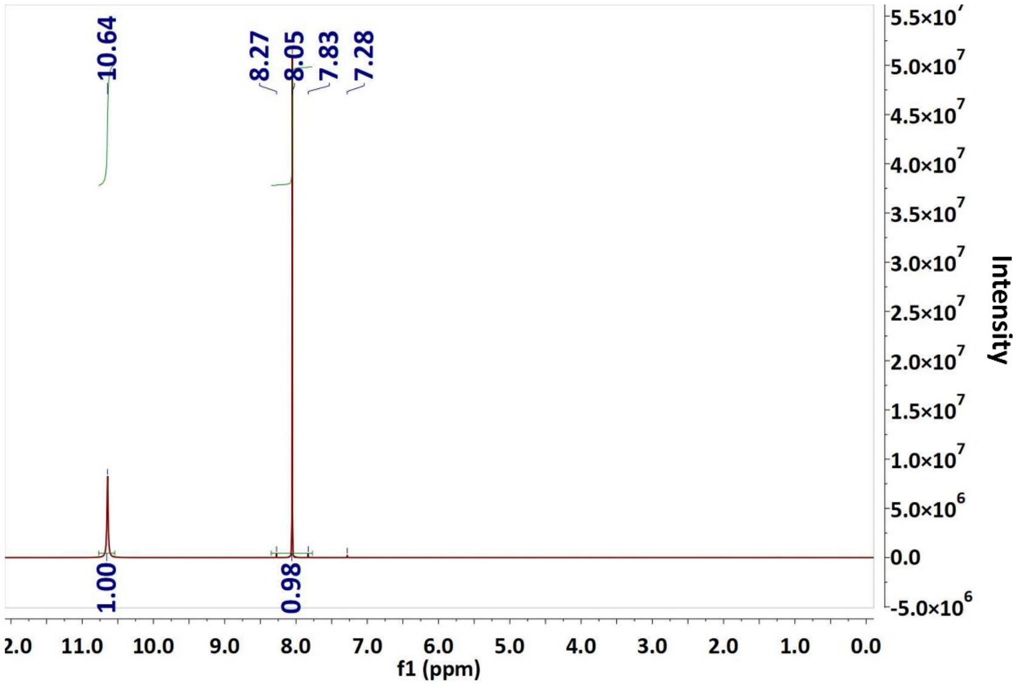

Figure S5. H^1 NMR spectra for recycled formic acid

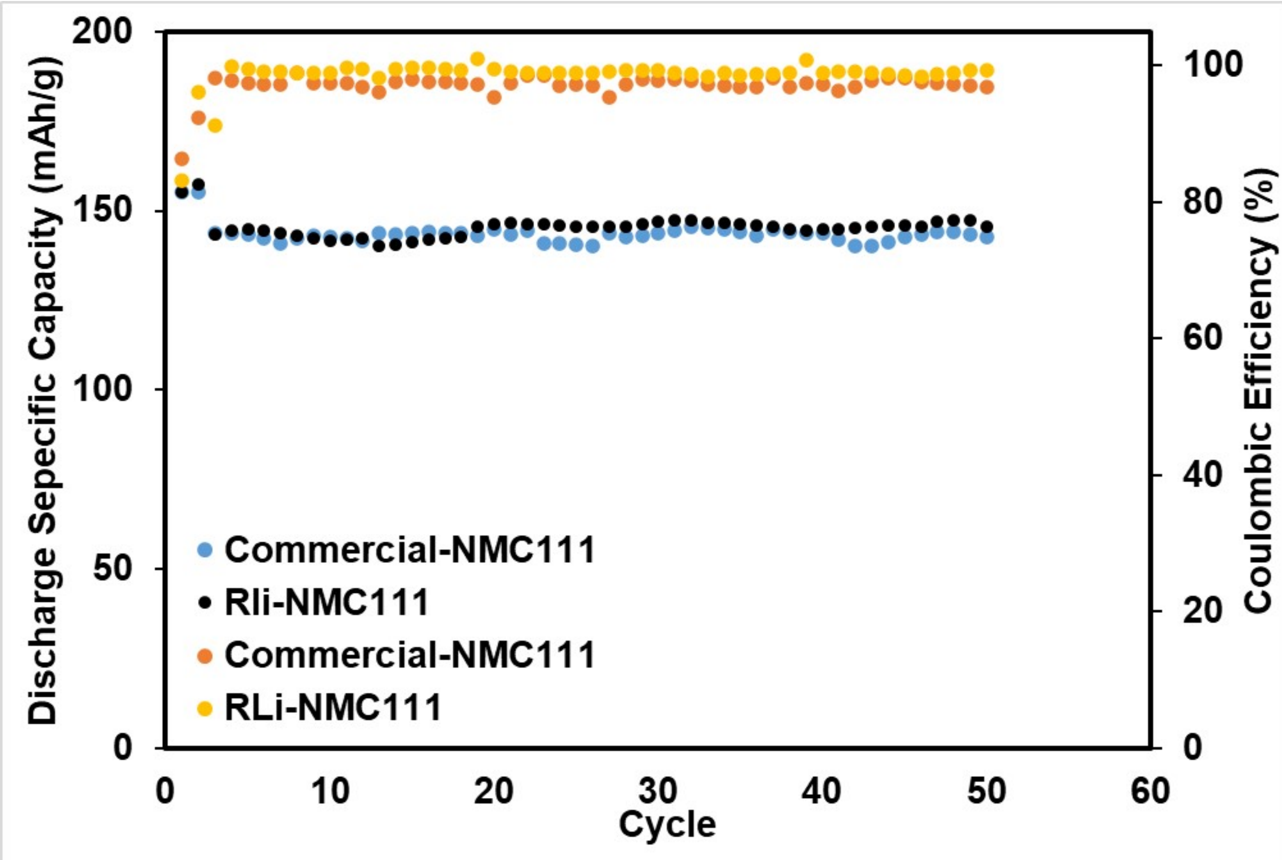

Figure S6. Half-cell cycling performance of Rli-NMC111 and TODA-NMC111 at a current density of 1C (1C=155mAh g-1)

Table S1. Summarized stoichiometric elemental ratio obtained from ICP-OES analysis for different raw materials

Materials	**Li**	**Ni**	**Mn**	**Co**
NMC111	1	0.38	0.27	0.35
NMC622	1	0.63	0.18	0.19
NMC811	1	0.84	0.048	0.11
Black mass	0.87	0.17	0.61	0.22

70°C	89.70%	2.78%						
	90.06%	2.91%						

NMC111			NMC622			NMC811		
	Li	TMs		Li	TMs		Li	TMs
20°C	67.50%	2.09%	50°C	38.01%	1.30%	50°C	49.20%	1.53%
	65.83%	1.94%		37.51%	1.29%		48.53%	1.59%
	68.51%	2.06%		39.12%	1.16%		50.12%	1.50%
Mean	67.28%	2.03%	Mean	38.21%	1.25%	Mean	49.28%	1.54%
Standard Deviation	1.35%	0.08%	Standard Deviation	0.82%	0.08%	Standard Deviation	0.80%	0.05%
Standard Error	0.78%	0.31%	Standard Error	0.48%	0.04%	Standard Error	0.46%	0.03%
30°C	76.80%	2.23%	60°C	66.51%	1.52%	60°C	86.55%	2.97%
	75.91%	2.53%		65.73%	1.46%		88.51%	2.87%
	77.03%	2.03%		67.16%	1.64%		85.03%	3.13%
Mean	76.58%	2.26%	Mean	66.47%	1.54%	Mean	86.70%	2.99%
Standard Deviation	0.59%	0.25%	Standard Deviation	0.72%	0.09%	Standard Deviation	1.74%	0.13%
Standard Error	0.34%	0.29%	Standard Error	0.41%	0.05%	Standard Error	1.01%	0.08%
40°C	82.90%	2.48%	70°C	60.41%	1.10%	70°C	81.42%	2.59%
	81.79%	2.59%		58.61%	1.01%		80.43%	2.51%
	83.03%	2.31%		61.26%	1.22%		82.65%	2.66%
Mean	82.57%	2.46%	Mean	60.09%	1.11%	Mean	81.50%	2.59%
Standard Deviation	0.68%	0.14%	Standard Deviation	1.35%	0.11%	Standard Deviation	1.11%	0.08%
Standard Error	0.39%	0.35%	Standard Error	0.78%	0.06%	Standard Error	0.64%	0.04%
50°C	95.00%	3.14%	80°C	45.60%	1.27%	80°C	55.63%	1.98%
	96.06%	3.43%		44.09%	1.21%		54.16%	1.92%
	94.25%	2.94%		46.16%	1.35%		56.03%	2.06%
Mean	95.10%	3.17%	Mean	45.28%	1.28%	Mean	55.27%	1.99%
Standard Deviation	0.91%	0.25%	Standard Deviation	1.07%	0.07%	Standard Deviation	0.98%	0.07%
Standard Error	0.53%	0.43%	Standard Error	0.62%	0.04%	Standard Error	0.57%	0.04%
60°C	100.00%	3.44%						
	100.01%	3.36%						
	100.03%	3.51%						
Mean	100.01%	3.44%						
Standard Deviation	0.02%	0.08%						
Standard Error	0.01%	0.04%						

Table S2. The detaild leaching effiency and calculated uncertainties for NMC111, NMC622, and NMC811

	88.95%	2.69%						
Mean	89.57%	2.79%						
Standard Deviation	0.57%	0.11%						
Standard Error	0.33%	0.06%						
80°C	87.10%	2.60%						
	88.05%	2.65%						
	86.56%	2.53%						
Mean	87.24%	2.59%						
Standard Deviation	0.75%	0.06%						
Standard Error	0.44%	0.03%						

Table S3. Summarized elemental concentration obtained from ICP-MS analysis for FA-NMC111, DI-NMC111, commercial lithium carbonate, recovered lithium carbonate, and recycled formic acid.

Materials (ppm)	Li	Ni	Mn	Co	Al	Cu	Fe	Mg
FA-NMC111	2.513	131.94	109.93	94.54				
DI-NMC111	0	115.15	107.53	70.26				
NMC111-leaching solution	1447.76	16.16	124.03	10.14				
NMC622-leaching solution	1432.18	41.42	61.21	0.17				
NMC811-leaching solution	1427.01	38.61	17.17	4.85				
Mixed-leaching solution	2021.85	98.47	67.21	9.85				
Black mass-leaching solution	1299.69	133.85	47.04	89.53				
Commercial Li2CO3	875.5	30.5	14.2	10.4	0.5	1.3	6.3	1.5
Recovered Li2CO3	887.3	1.6	0.3	1.7	0.4	0.2	0.1	0.0
Commercial formic acid	0.087	0.063	0.0	0.0	0.103	0.084	0.0	0.0
Recycled formic acid	0.164	0.173	0.148	0.105	0.226	0.141	0.332	0.884

Table S4. Refinement data of XRD patterns in Fig. 7 using FullProf Suite software with $LiTMO_2$ as structural model.

Sample	A-axis (Å)	C-axis (Å)	Volume (Å3)	Rwp(%)	χ2
TODA-NMC111	2.862	14.236	100.71	4.35	1.91
Rli-NMC111	2.861	14.234	100.31	5.55	2.67

Table S5. Detailed cost for general hydrometallurgical and closed-loop lithium recovery[1]

Cost items	General Hydrometallurgical	A closed-loop lithium recovery
① Direct cost ($/year)[2]	35,566,971	20,222,430
A. Equipment	13,028,194	7,145,735
B. Buildings, process and auxiliary	3,257,049	1,786,434
C. Service facilities and yard improvements	6,514,097	4,287,441
D. Land	1,042,256	571,659
② Indirect cost ($/year)[3]	7,113,394	4,044,486
A. Engineering and supervision	3,556,697	2,022,243
B. Construction expense and contractor's fee	3,556,697.05	2,022,243.04
C. Contingency	-	-
③ Fixed capital Investment ($/year)	42,680,365	24,266,916
④Working capital ($/year)	-	-
⑤Total capital investment ($/year)	42,680,365	24,266,916.5
⑥Manufacturing costs ($/year)[4]	18,376,514	21,278,087.88
A. Direct product costs	9,729,701	16,363,966
B. Fixed charges	8,646,813	4,914,122
C. Plant overhead costs	-	-
⑦General expenses ($/year)	-	-
⑧Total product cost ($/year)[5]	18,376,514	21,248,088
⑨Battery fee ($/kg black mass)	0.2	0.2
⑩Total Cost of recipient ($/kg black mass)	2.25	2.45

Table S6. Summary of condition and result of lithium recycling of waste LIBs investigated in the literature

Spent materials	**Efficiency**	**Purity**	**Chemicals**	**Referenes**
LIB scraps	90.00%	99.95%	HNO_3, Na_2CO_3	[6]
Electrode materials	80.00%	98.00%	C, CO_2	[7]
LIB scraps	80.00%	＞98%	H_2SO_4, glucose, Na_2CO_3	[8]
NMC111	94.00%	/	H_2SO_4, H_2O_2, Na_2CO_3	[9]
LIB scraps	72.00%	99.70%	H_2SO_4, H_2O_2, Na_2CO_3	[10]
LCO	86.20%	74.20%	HCl, Na_2CO_3	[9]
NMC532	81.20%	＞99.5%	$NH_3.H_2O$, NH_4HCO_3, Na_2CO_3	[11]
LIB scraps	96.30%	/	Oxalic acid, Na_2CO_3	[12]
LIB scraps	91.23%	99.00%	H_2SO_4, NaS_2O_8	[13]
LIB scraps	99.8%	99.994%	HCOOH	This work

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