Efficient Recovery of End-of-Life NdFeB Permanent Magnets by Selective Leaching with Deep Eutectic Solvents

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Number of Tables: 6

Chemicals and Materials. Guanidine hydrochloride (99.0%), 1-aminoguanidine hydrochloride (99%), 1,3-diaminoguanidine hydrochloride (99%), choline chloride (99%), glycolic acid (99.0%), ethylene glycol (99.5%), malic acid (99.5%), L-lactic acid (90% in water), and glycerol (99%) were purchased from Shanghai Macklin Biochemical Co., Ltd. Neodymium(III) oxide (Nd_2O_3, 99.99%) and iron(III) oxide (Fe_2O_3, 99.99%) were purchased from Shanghai Aladdin Biochemical Co., Ltd. Neodymium(III) chloride ($NdCl_3$, 99.99%) were purchased from Shanghai Yuanye Biochemical Co., Ltd. All chemicals were used as received. The standard solutions of Nd and Fe bought from Guobiao (Beijing) Testing & Certification Co., Ltd. Working solutions ranging from 1 to 10 mg L^{-1} of Nd and Fe were prepared via diluting the standard solution. The neodymium lactate ($NdLAC_3$) was prepared by dissolving the Nd_2O_3 into the aqueous lactic acid solution. Then the solution was concentrated by rotary evaporation and settled for the precipitation of the light purple solid. The roasted NdFeB permanent magnet was composed of Nd_2O_3 and Fe_2O_3 with a molar ratio of 1:7, as the same in the $Nd_2Fe_{14}B$.

Characterization Methods. The viscosity of DESs was determined using a Universal Rheometer (HAAKE RheoStress 6000, Thermo Fisher Scientific Inc., Germany). The glass transition temperature of DESs was achieved by differential scanning calorimetry (DSC), which was performed with a heating rate of 10 $^{o}C \cdot min^{-1}$ by the instrument (Q200, TA Instrument Company, America). All the DESs were run in aluminum hermetic crucibles, which were cooled to −90 ^{o}C before heated up to room temperature. Thermal gravimetric analysis (TGA) was conducted by the instrument (Q600, TA Instrument Company, America) from room temperature to 400 ^{o}C at a heating rate of 10 $^{o}C \cdot min^{-1}$ in a nitrogen atmosphere to get the DESs' onset decomposition temperature. ^{1}H NMR spectra were recorded on an NMR spectrometer (Bruker Avance III 500, Bruker Corporation, America) with dimethyl sulfoxide-d_6 as the solvent. Fourier transform infrared (FT-IR) spectra were recorded on an FT-IR spectrometer (Thermo iS50, Thermo Fisher Scientific Inc., Germany) in the range of 400 to 4000 cm^{-1}. The UV-vis spectra of Nd loaded DESs was recorded by a UV-Vis-NIR spectrophotometer (UH5300, Hitachi High-Tech Corporation, Japan). The concentrations of Nd and Fe dissolved in the DESs were analyzed by an inductively coupled plasma optical atomic emission spectrometry (ICP-OES,730-ES, Varian Inc., America). Before analysis, all the samples were digested in concentrated nitric acid using a microwave digestion system (MARS 6, CEM Corporation, America) and diluted by deionized water. Each analysis was repeated three times. The particle size was recorded by a laser diffraction particle sizing analyzer (LS13320, Beckman Coulter Inc., USA). Powder X-ray diffraction (PXRD) measurements were done with a Rigaku 114 Ultima IV diffractometer (Rigaku Corporation, Japan) using Cu Kα radiation (λ=1.54184 Å). Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS) were measured on a Field Emission Scanning Electron Microscope (SU8000, Hitachi High-Technologies Corporation, Japan).

Calculation of Oxalic Acid Amount. The solid-liquid ratio of oxalic acid to DES was chosen based on the fact that the oxalic acid is generally reacted with Nd^{3+} with a molar ratio of 3:2. The roasted NdFeB permanent magnet powders was composed of Nd_2O_3 and Fe_2O_3 with a molar ratio of 1:7. It was reacted with GUC-LAC in a mass ratio of 1:10 and the dissolution ratio was about 85%. Taking the molar mass of Nd, Nd_2O_3, GUC-LAC, and oxalic acid into consideration, it could be easily calculated the mass ratio of oxalic acid and the DES was 1:100.

Calculation of Acids Consumption. We only considered the reaction between acids and Nd, Fe, in the theoretical acids consumption. An ideal NdFeB magnets has a formula of $Nd_2Fe_{14}B$. After been totally oxidized, it would reacted with acids following the equations:

$$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O$$

$$Nd_2O_3 + 6H^+ = 2Nd^{3+} + 3H_2O$$

In solvent extraction process, the Nd and Fe were completely dissolved into the leaching liquor, 48 mole H^+ was needed to treat 1 mole NdFeB. In selective leaching process, only Nd was dissolved into the leaching liquor, 6 mole H^+ was needed to treat 1 mole NdFeB. The acids consumed in the selective leaching was only 1/8 of the complete leaching.

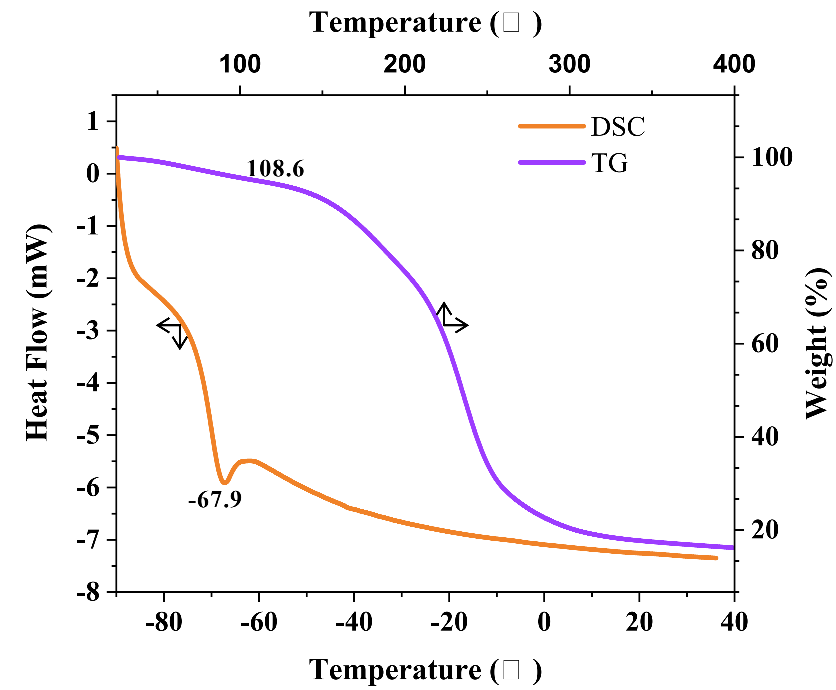

Figure S1. TG and DSC curves of GUC-GA

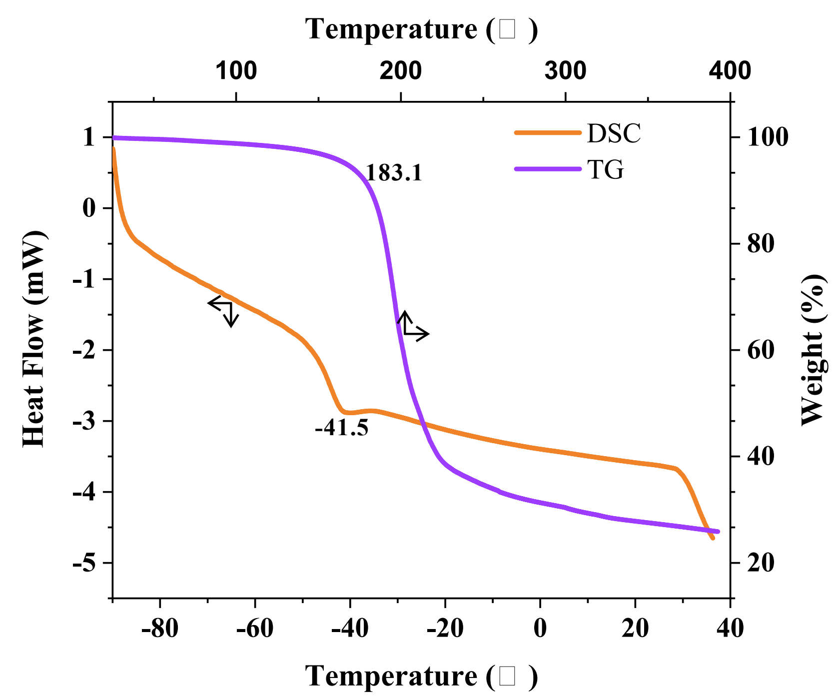

Figure S2. TG and DSC curves of GUC-MA

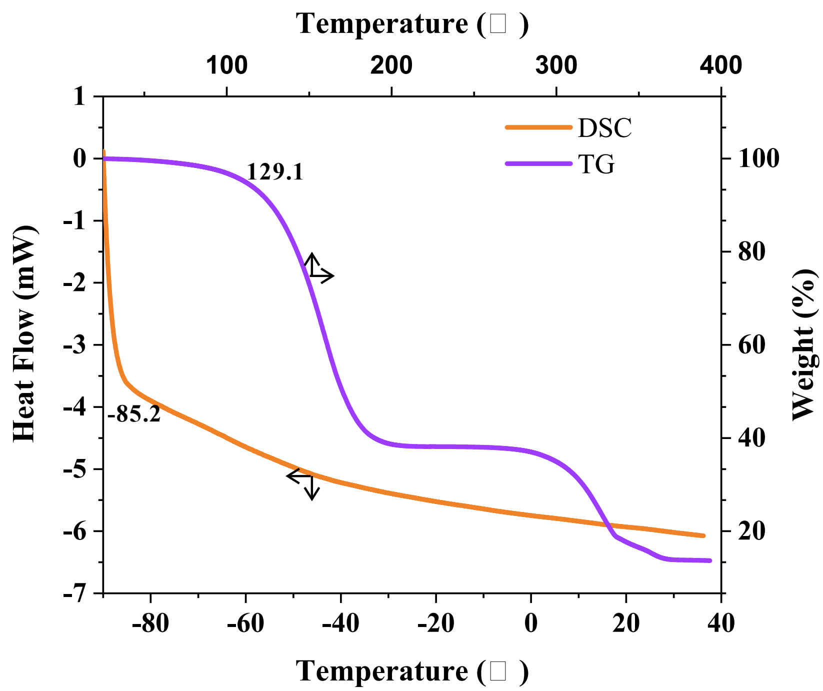

Figure S3. TG and DSC curves of GUC-EG

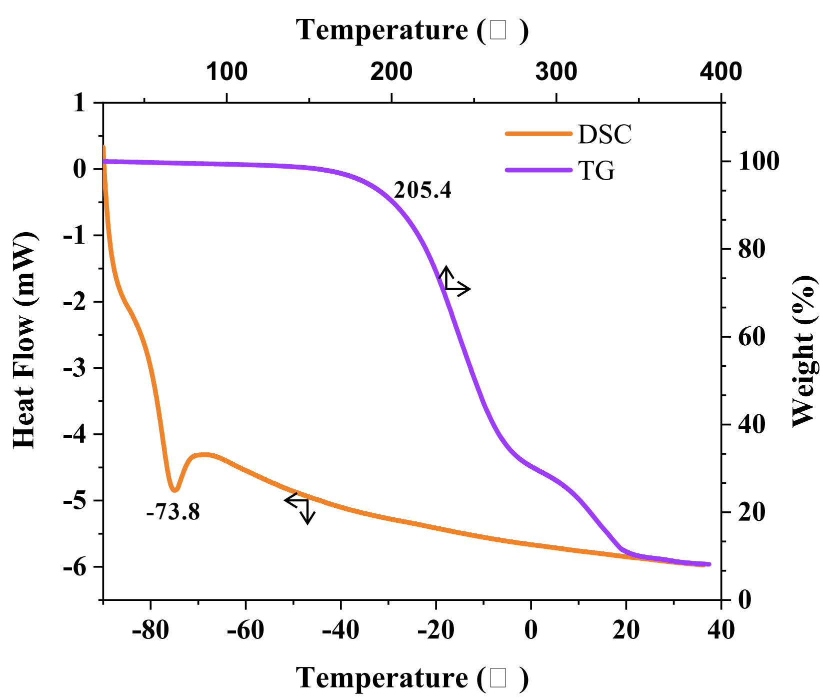

Figure S4. TG and DSC curves of GUC-GLY

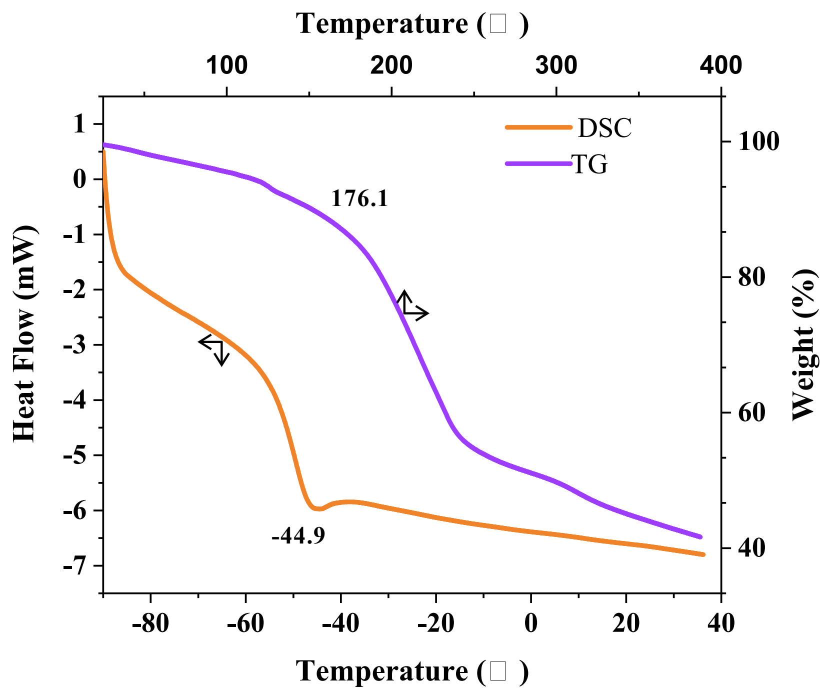

Figure S5. TG and DSC curves of AGU-GA

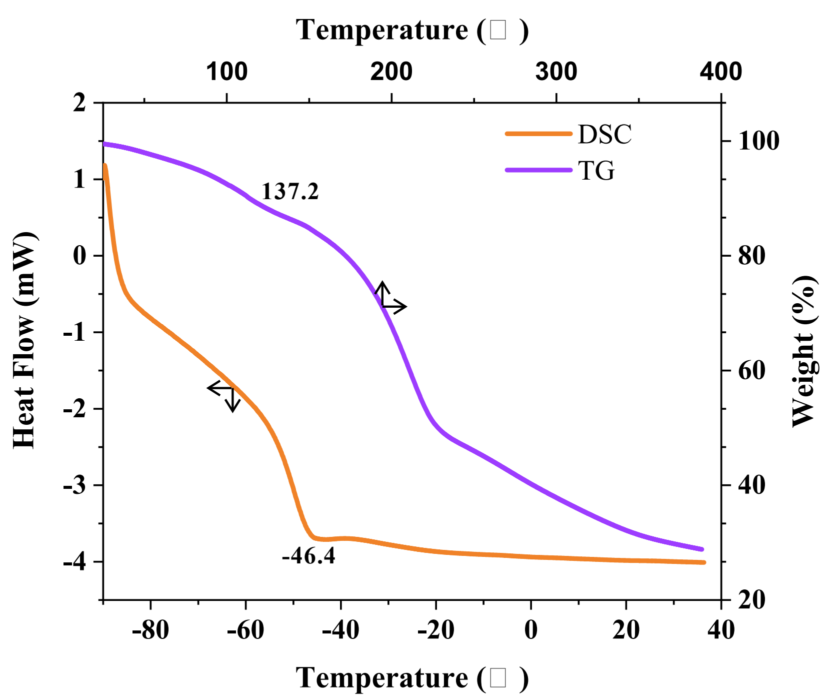

Figure S6. TG and DSC curves of AGU-LAC

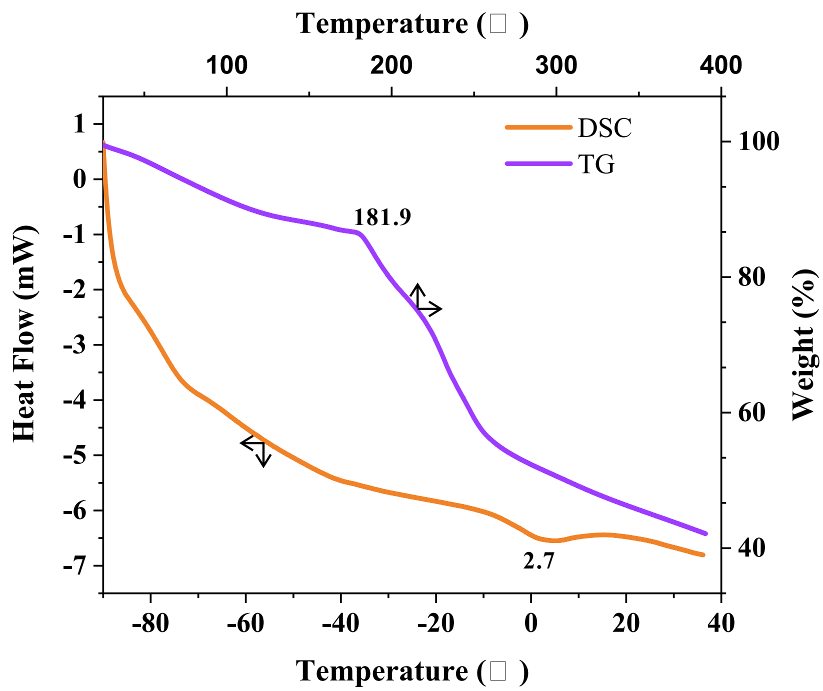

Figure S7. TG and DSC curves of DAG-GA

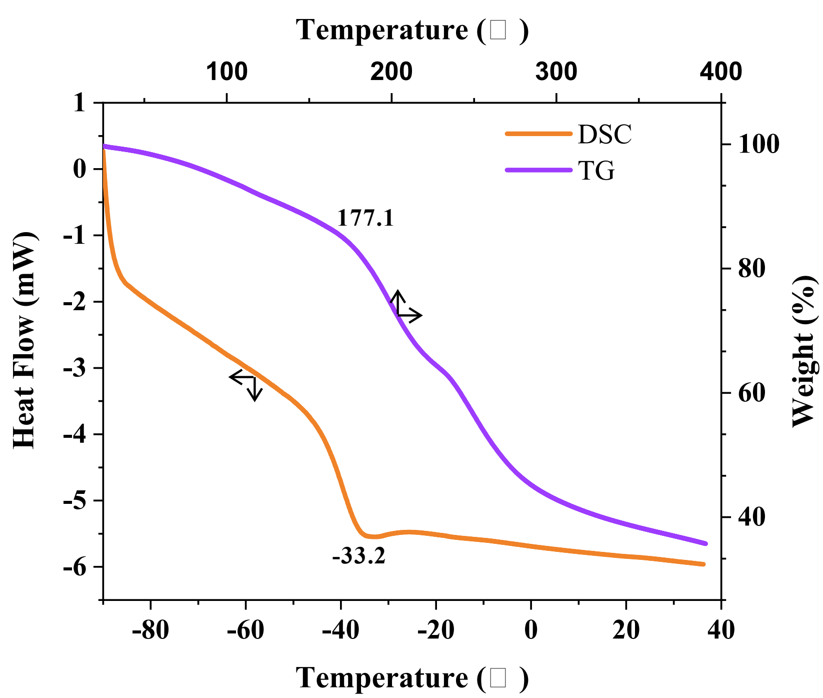

Figure S8. TG and DSC curves of DAG-LAC

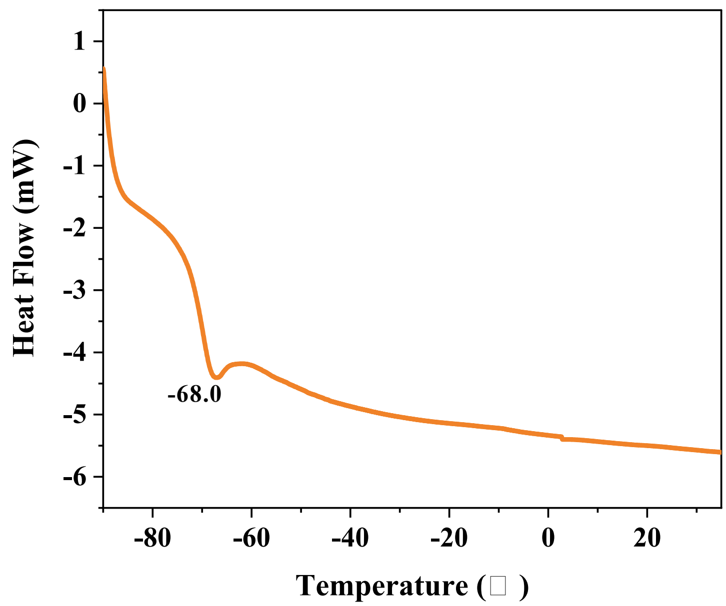

Figure S9. DSC curve of GUC-LAC (HBA:HBD = 1:3)

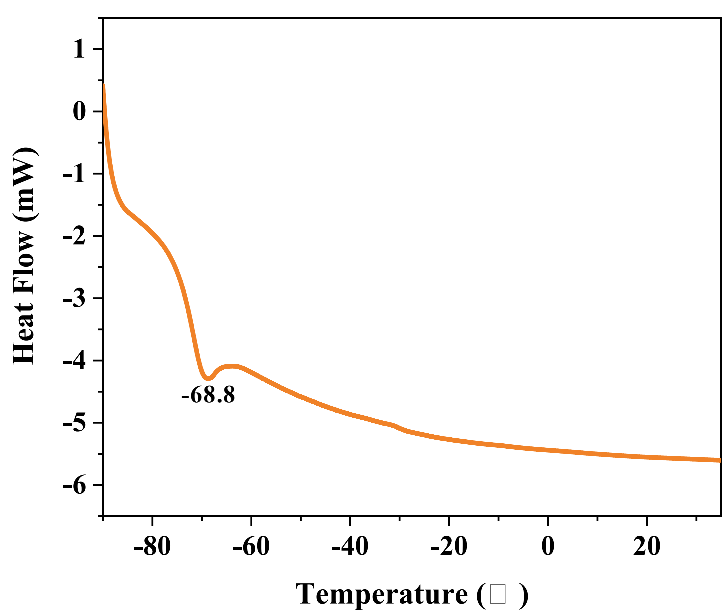

Figure S10. DSC curve of GUC-LAC (HBA:HBD = 1:5)

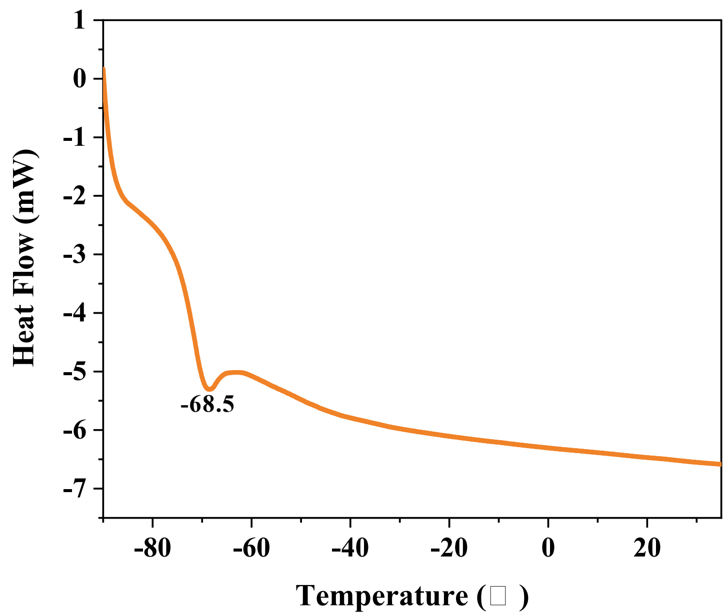

Figure S11. DSC curve of GUC-LAC (HBA:HBD = 1:7)

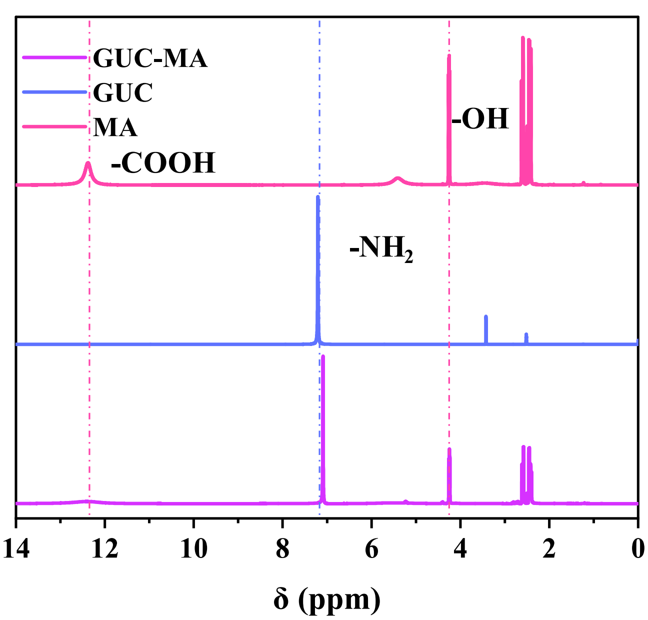

Figure S12. ^1H NMR spectra of GUC-MA and its corresponding HBA and HBD

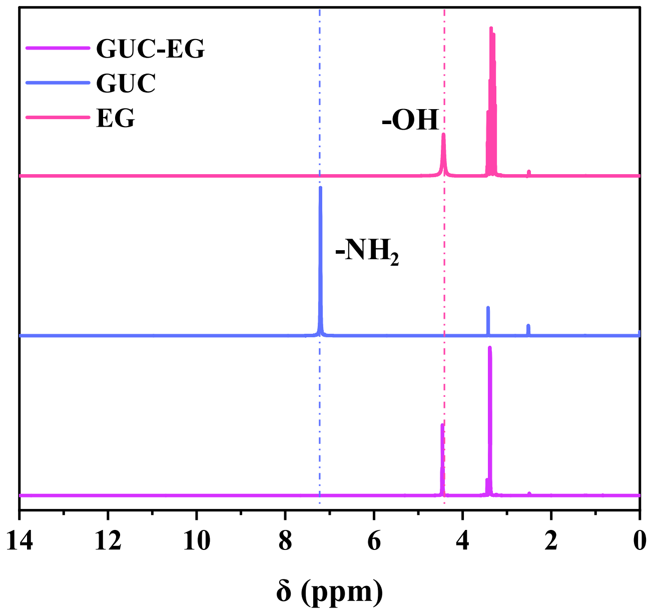

Figure S13. [1]H NMR spectra of GUC-EG and its corresponding HBA and HBD

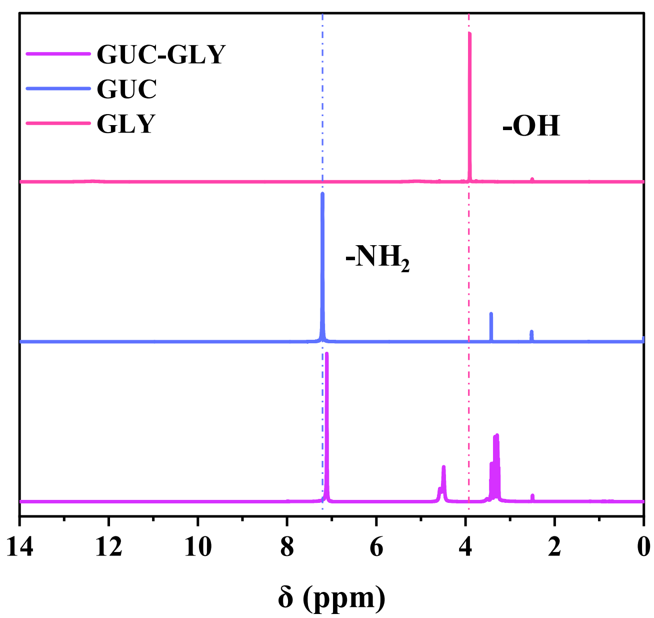

Figure S14. [1]H NMR spectra of GUC-GLY and its corresponding HBA and HBD

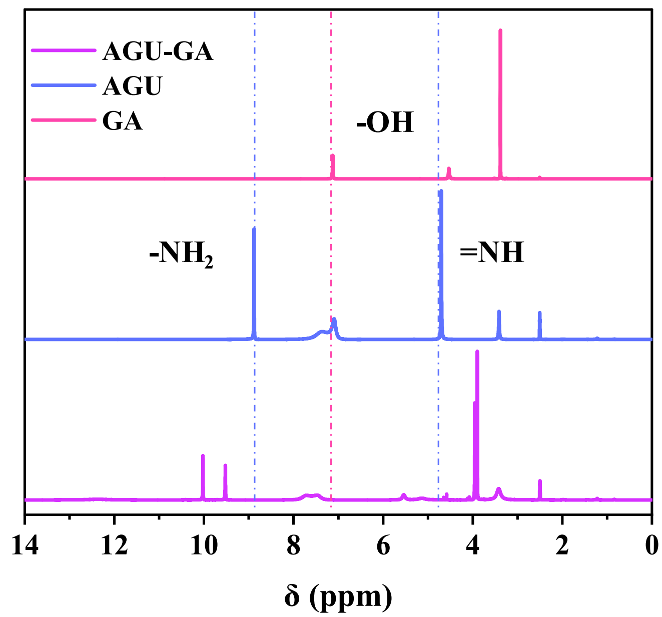

Figure S15. ^{1}H NMR spectra of AGU-GA and its corresponding HBA and HBD

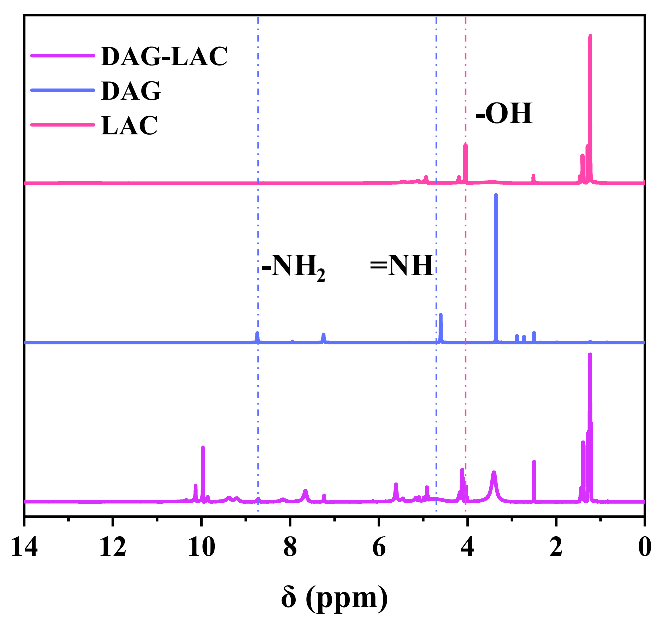

Figure S16. ^{1}H NMR spectra of DAG-LAC and its corresponding HBA and HBD

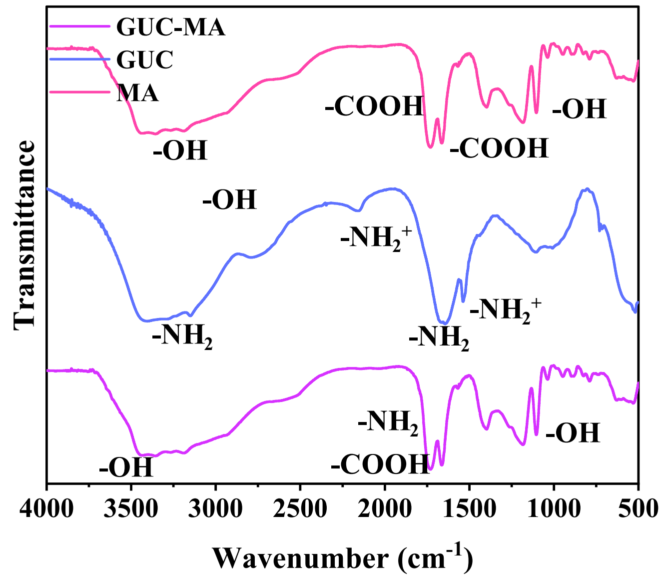

Figure S17. FT-IR spectra of GUC-MA and its corresponding HBA and HBD

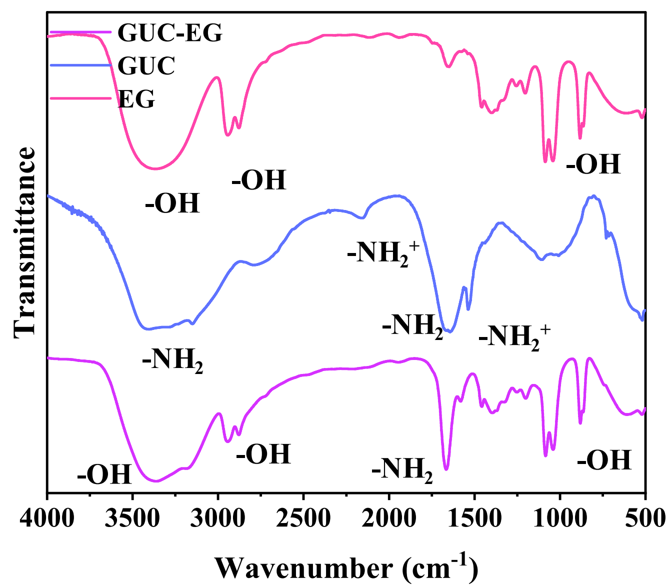

Figure S18. FT-IR spectra of GUC-EG and its corresponding HBA and HBD

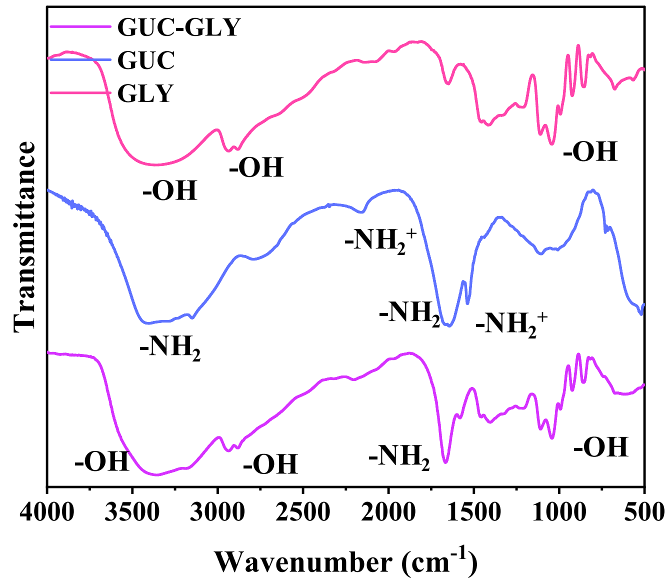

Figure S19. FT-IR spectra of GUC-GLY and its corresponding HBA and HBD

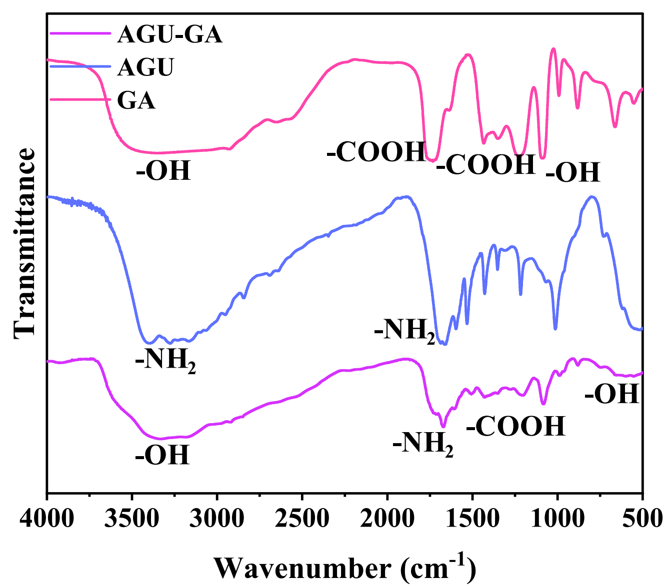

Figure S20. FT-IR spectra of AGU-GA and its corresponding HBA and HBD

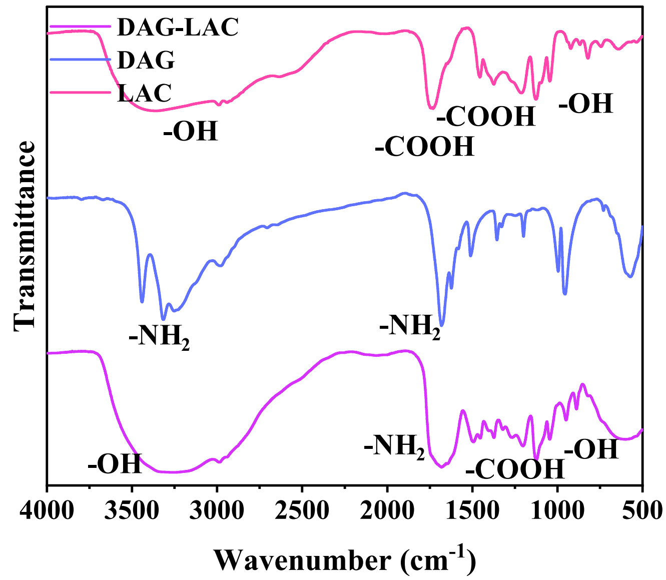

Figure S21. FT-IR spectra of DAG-LAC and its corresponding HBA and HBD

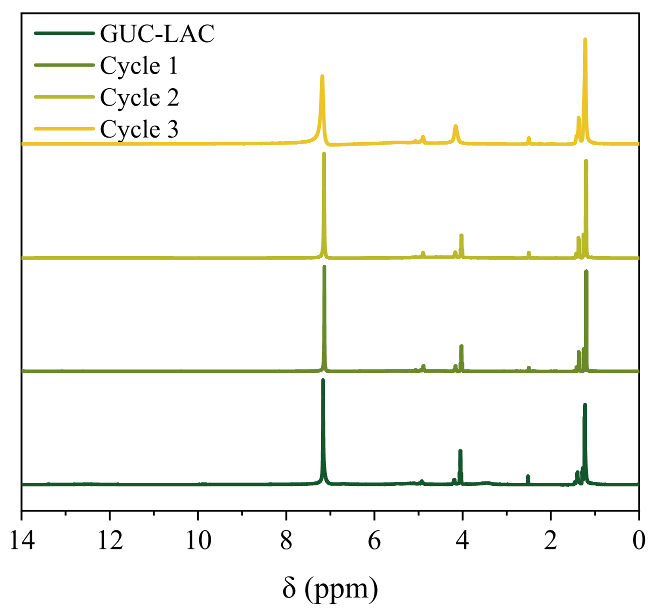

Figure S22. 1H NMR spectra of recycled GUC-LAC

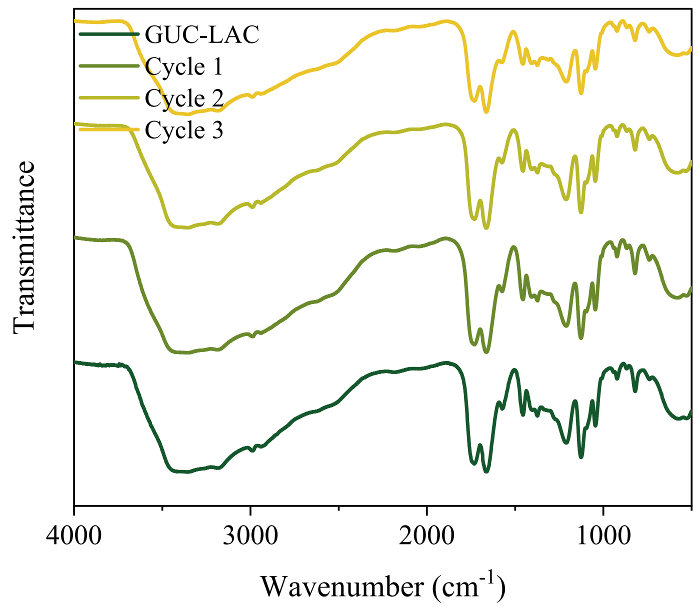

Figure S23. FT-IR spectra of recycled GUC-LAC

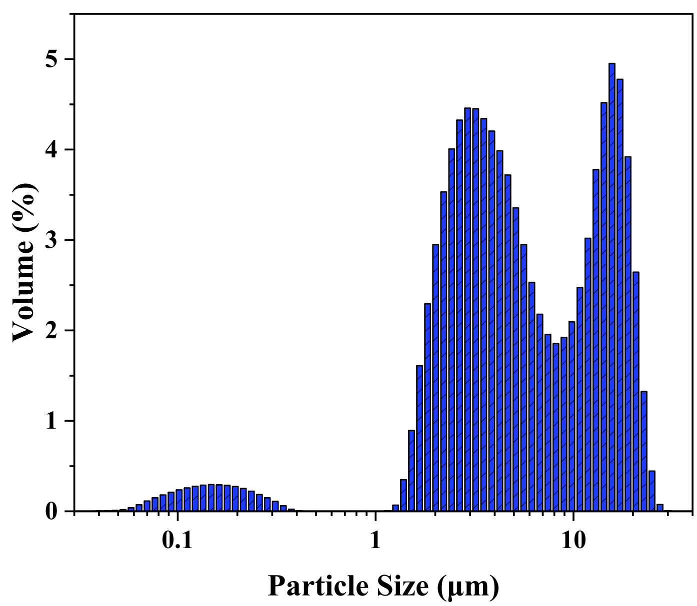

Figure S24. Particle Size distribution of $Nd_2(C_2O_4)_3$

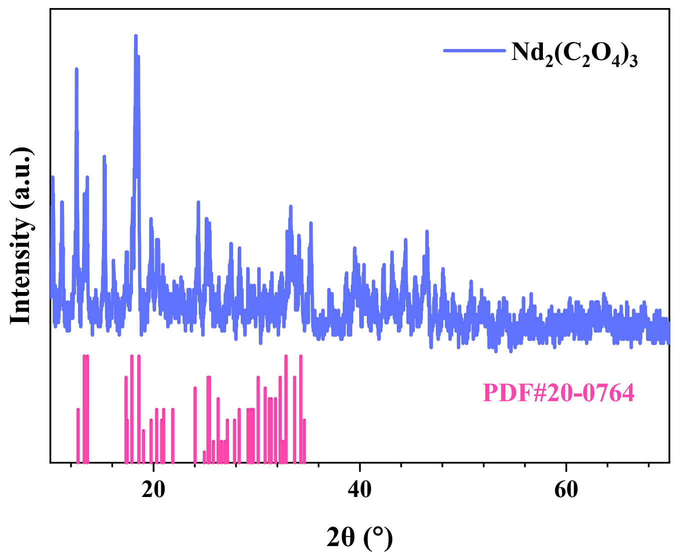

Figure S25. PXRD pattern of $Nd_2(C_2O_4)_3$

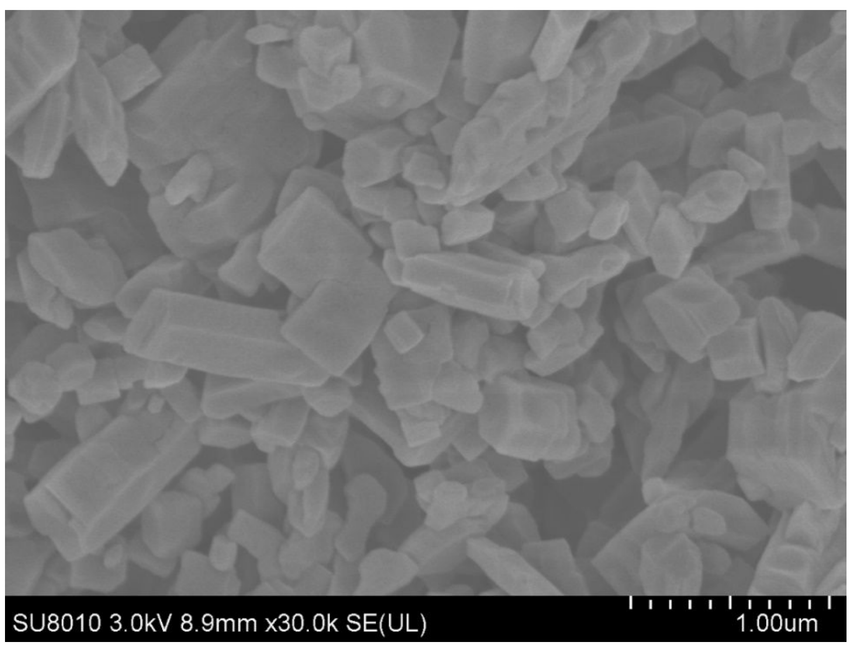

Figure S26. SEM image of $Nd_2(C_2O_4)_3$

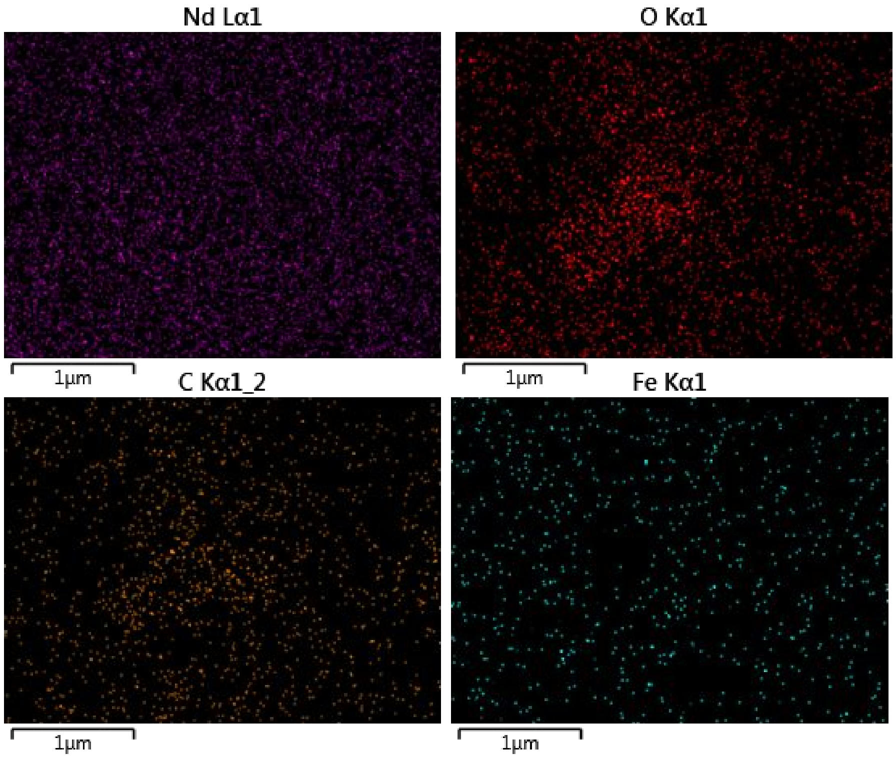

Figure S27. EDS elemental mapping of $Nd_2(C_2O_4)_3$

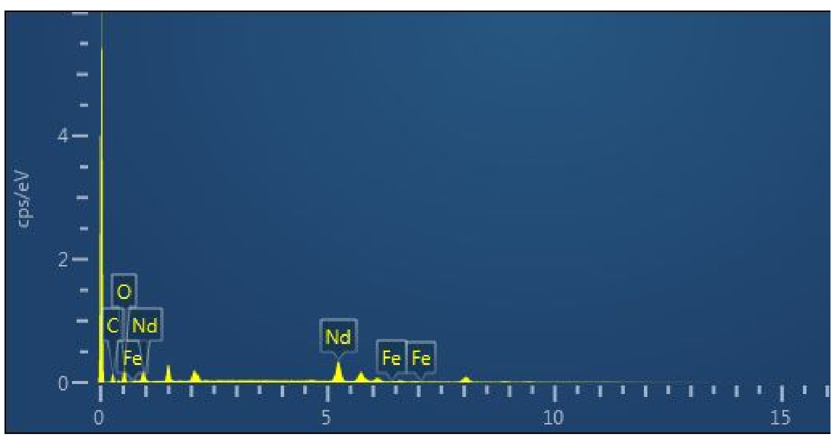

Figure S28. EDS spectrum of $Nd_2(C_2O_4)_3$

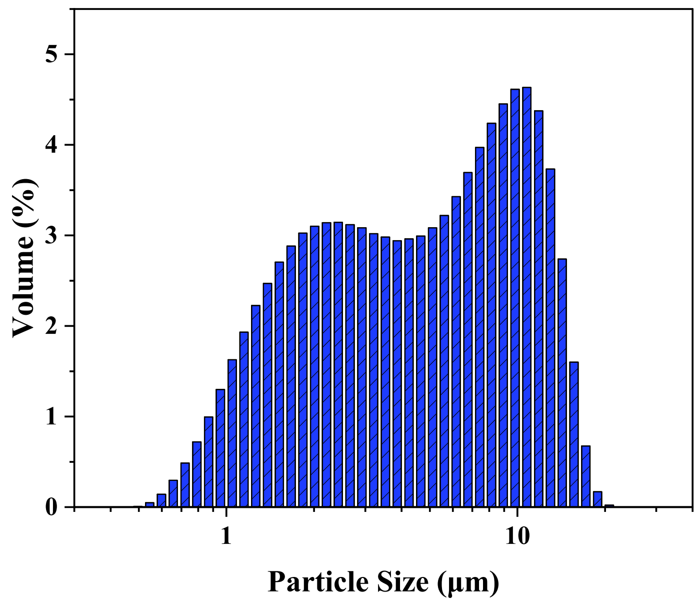

Figure S29. Particle Size distribution of Nd_2O_3

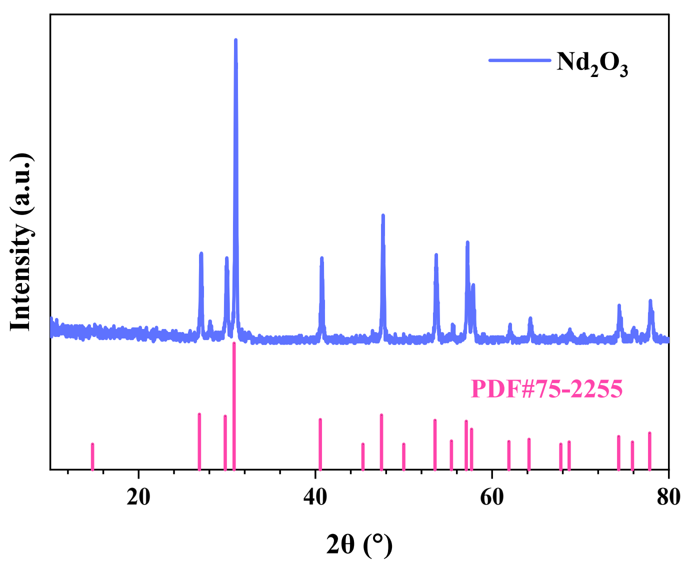

Figure S30. PXRD pattern of Nd_2O_3

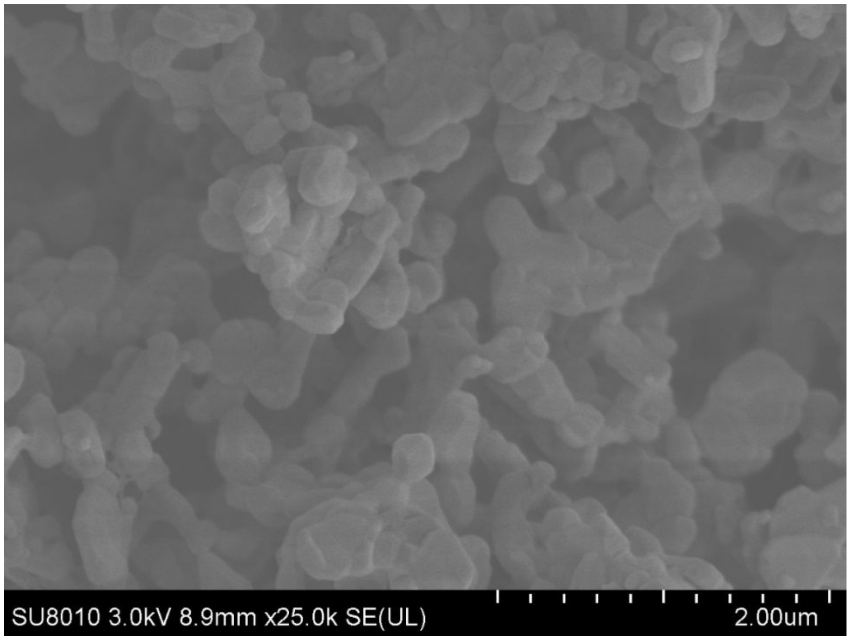

Figure S31. SEM image of Nd_2O_3

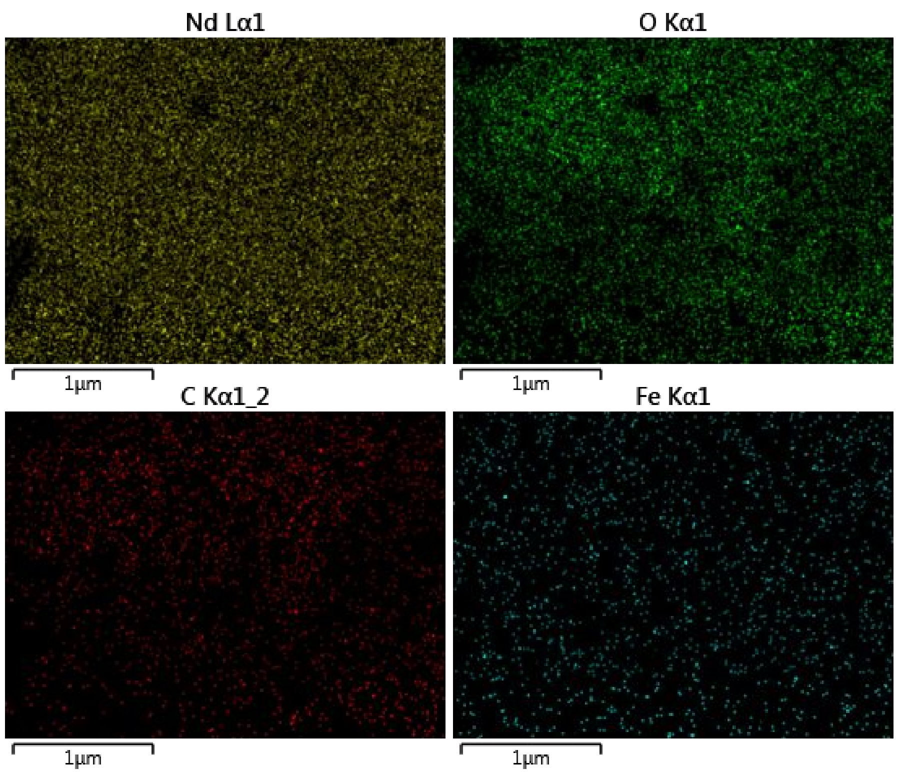

Figure S32. EDS elemental mapping of Nd_2O_3

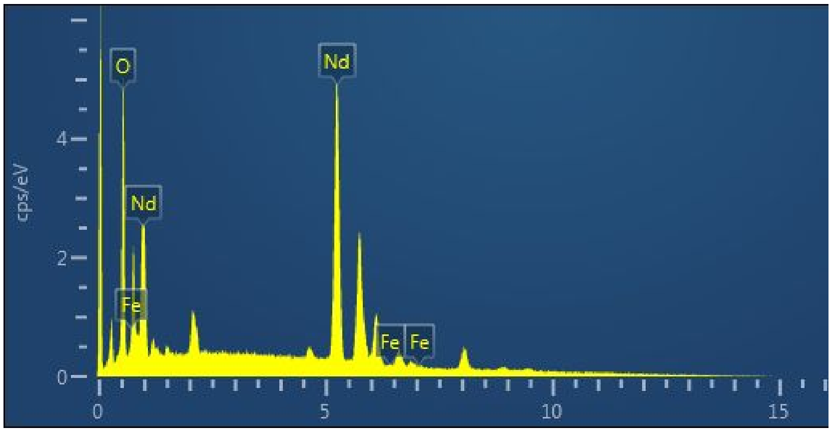

Figure S33. EDS spectrum of Nd_2O_3

Table S1. The standard deviation of dissolution ratio

Variables	Condition	D_{Nd}	$STDEV_{Nd}$	D_{Fe}	$STDEV_{Fe}$
Time (h)	1	62.67%	0.064892	0.13%	0.028826
	3	72.13%	0.068211	0.28%	0.024895
	6	84.23%	0.071772	1.10%	0.040449
	12	86.60%	0.066807	1.84%	0.039739
	24	86.20%	0.051373	1.43%	0.028262
Temperature (°C)	20	62.64%	0.068668	0.20%	0.029175
	25	75.22%	0.066317	0.42%	0.029588
	30	83.57%	0.065285	0.29%	0.01953
	35	81.93%	0.068843	0.47%	0.024852
	40	84.39%	0.069026	0.41%	0.029281
	50	86.20%	0.051373	1.43%	0.028262
	60	87.87%	0.05627	3.86%	0.030765
Solid to liquid ratio	0.1	86.20%	0.051373	1.43%	0.028262
	0.2	86.43%	0.05403	1.51%	0.023864
	0.3	84.51%	0.05006	1.59%	0.025901

	0.4	85.70%	0.058118	0.73%	0.029118
	0.5	86.27%	0.067892	0.60%	0.026616
	0.7	85.57%	0.056596	0.85%	0.028496
HBD ratio	0	0.49%	0.047006	0.19%	0.032757
	2/3	86.20%	0.051373	1.43%	0.028262
	4/5	85.27%	0.043186	2.26%	0.006186
	8/9	81.29%	0.044524	1.98%	0.018355
	1	12.16%	0.041271	0.66%	0.03712
DESs	AGU-LAC	34.45%	0.055276	0.53%	0.039092
	GUC-LAC	86.20%	0.051373	1.43%	0.028262
	GUC-GA	10.50%	0.039489	1.24%	0.01537
	GUC-GLY	0.23%	0.041539	0.07%	0.012755
	CC-EG	0.01%	0.079747	0.09%	0.028903
	CC-LAC	7.71%	0.042455	0.34%	0.35706
Recycle of GUC-LAC	Cycle 0	96.37%	0.074227	1.51%	0.011265
	Cycle 1	95.24%	0.073564	1.85%	0.013819
	Cycle 2	96.61%	0.079899	1.44%	0.011445
	Cycle 3	95.61%	0.072636	1.68%	0.015534

Table S2. The loaded metal in GUC-LAC after dissolution in practical leaching and recycle

Element	Cycle 0 (ppm)	Cycle 1 (ppm)	Cycle 2 (ppm)	Cycle 3 (ppm)
Nd	20466.95	21869.74	20358.87	21480.04
Fe	913.40	1081.8	777.42	955.82

Table S3. The residual metal in GUC-LAC after stripping in practical leaching and recycle

Element	Cycle 0 (ppm)	Cycle 1 (ppm)	Cycle 2 (ppm)	Cycle 3 (ppm)

Nd	1460.38	2113.64	3642.27	3714.55
Fe	727.51	447.02	753.57	992.046

Table S4. The metal composition of the Nd_2O_3 product

Element	Nd	Fe
Mass fraction (%)	99.56	0.44

Table S5. Elemental composition of $Nd_2(C_2O_4)_3$ by EDS spectrum

Element	Line	Apparent concentration	K	wt%	Sigma	Standerd Sample
C	K	3.28	0.03281	16.73	0.69	C Vit
O	K	11.86	0.03990	14.64	0.43	SiO_2
Fe	K	0.00	0.00000	0.00	0.35	Fe
Nd	L	58.84	0.58840	68.63	0.72	Nd (v)
Total:				100.00		

Table S6. Elemental composition of Nd_2O_3 by EDS spectrum

Element	Line	Apparent concentration	K	wt%	Sigma	Standerd Sample
O	K	27.53	0.09263	16.57	0.24	SiO_2
Fe	K	0.00	0.00000	0.00	0.17	Fe
Nd	L	127.14	1.27143	83.43	0.24	Nd (v)
Total:				100.00		