Supplement Material

An acid-free process for selective REEs recovery from spent NdFeB magnets by room-temperature electrolysis

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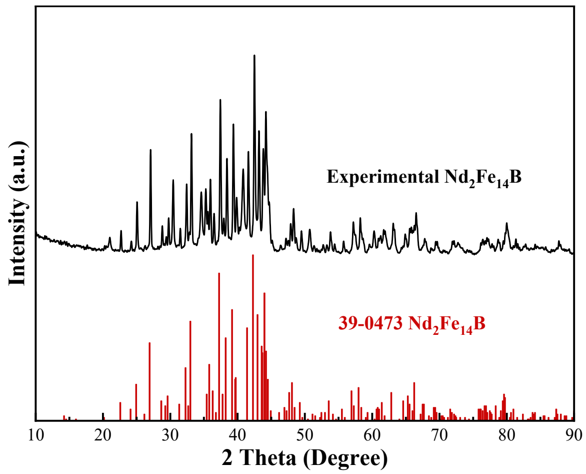
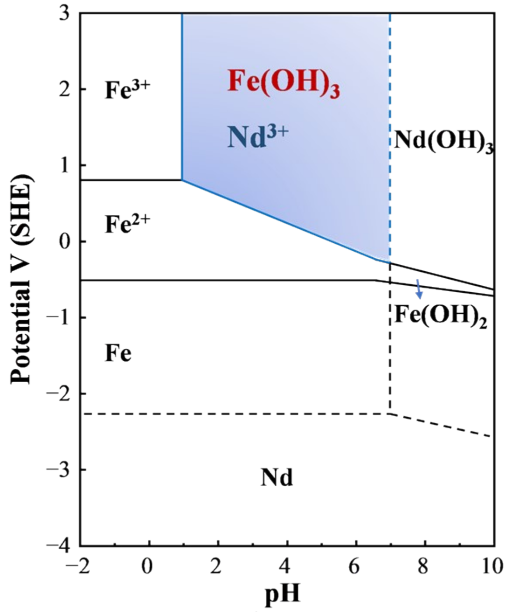


Fig. S1 Analysis of XRD spectra of EOL NdFeB mangets used in experiments.



$\alpha_{Fe^{2+}}/\alpha_{Fe^{3+}}=10^{-4}$, $\alpha_{Nd^{3+}}=1$, T=25 °C

Fig. S2 E -pH of Nd - H_2O and Fe - H_2O systems. (Based on reference data and using HSC to plot [1].)

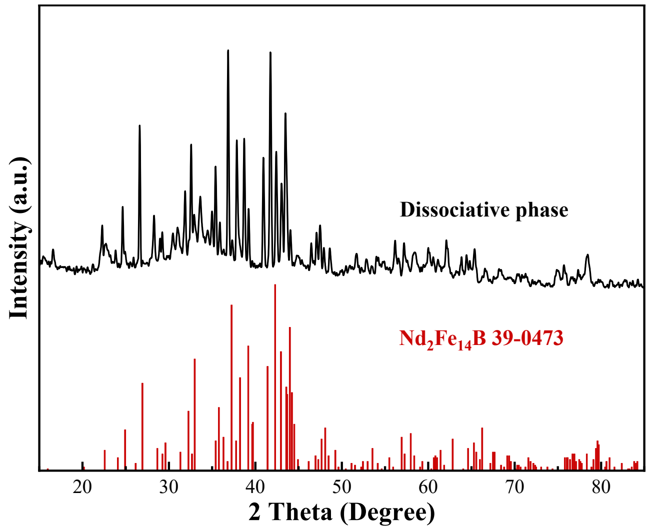


Fig. S3 Electrolytic dissociative phase XRD analysis.

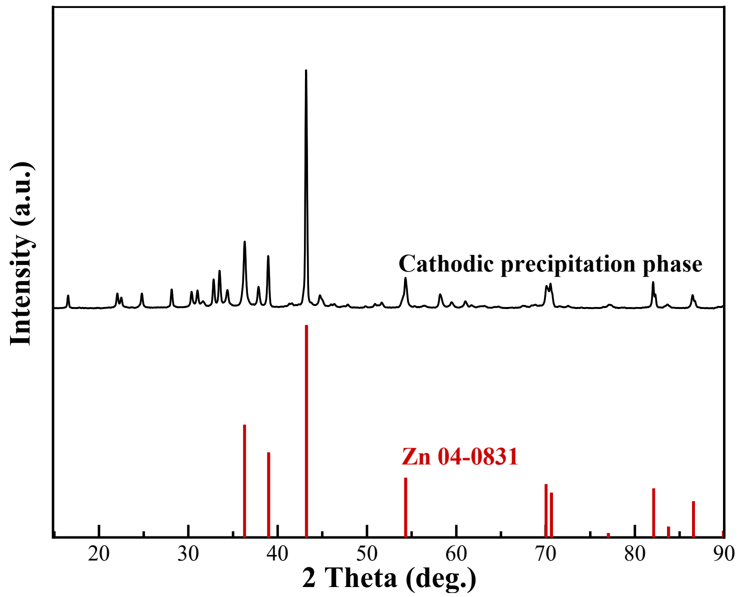


Fig. S4 XRD analysis of cathodic deposition products.

Table S1. PH of $ZnCl_2$ solution at different temperatures.

Temperature (℃)	25	40	50	60
pH	4.69	4.21	3.89	3.63

Table S2. The effect of adding different amounts of Na_2SO_4 on the pH value of electrolytes.

Na_2SO_4:Nd^{3+} (mol)	0	2:1	4:1	6:1	8:1
pH of electrolytes	4.72	4.77	4.75	4.76	4.75

Table S3. Analysis of ICP-OES testing for obtained every 1g REOs.

Element	Nd	Pr	Dy	Fe
Wt (%)	77.16	11.17	11.67	0.1

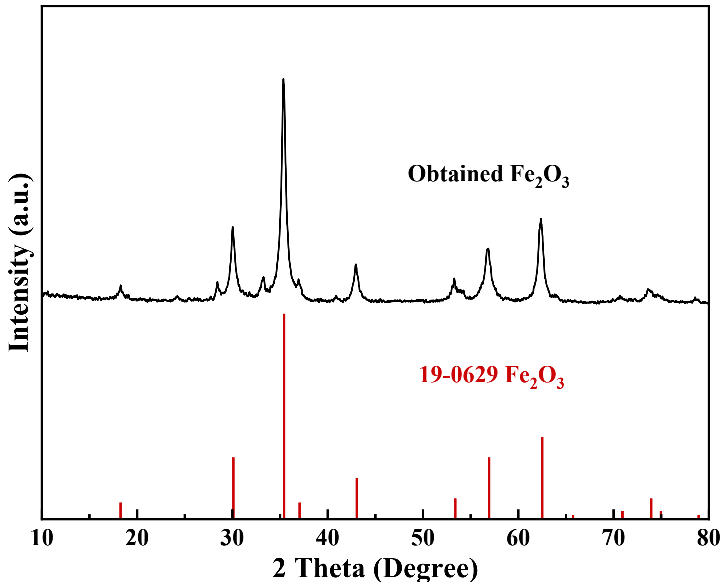


Fig. S5 XRD analysis of obtained Fe_2O_3 products.

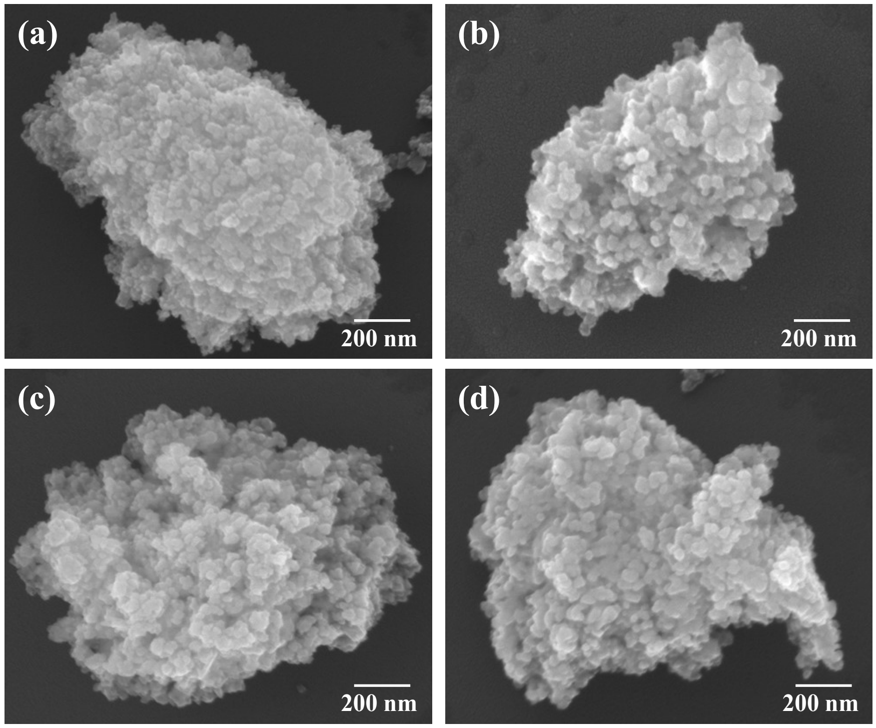


Fig. S6 SEM analysis of obtained Fe_2O_3 products.

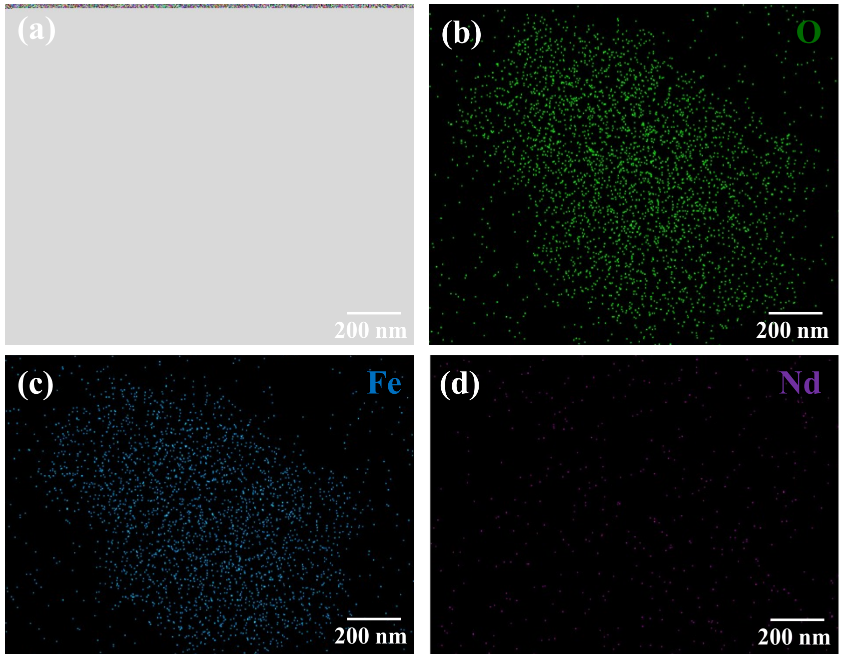


Fig. S7 SEM-Mapping analysis of obtained Fe_2O_3 products.

Table S4. Elements quantitative analysis of Fe_2O_3 SEM-Mapping.

Element	Wt %
O	28.45
Fe	71.55
Nd	0.00
Total	100.00

Table S5. ICP-OES analysis of Fe_2O_3.

Element	Wt %
Fe (theoretical value)	69.90
Fe (actual value)	69.55
Nd	0.46
Pr	0.03

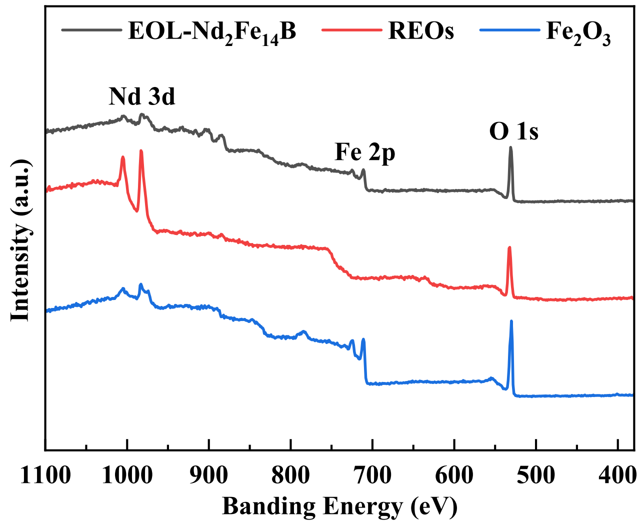


Fig. S8 The XPS survey spectra of the EOL-$Nd_2Fe_{14}B$, REOs, and Fe_2O_3.

EOL-NdFeB, REOs, and obtained Fe_2O_3 was characterized by XPS to analyze its elemental composition (Fig. S8). In the obtained REOs mainly composed of Nd_2O_3, almost no XPS peak of Fe 2P appeared, indicating that they almost didn‘t contain Fe element,, which is consistent with the results of ICP (Table S3). There are still peaks of Nd element present in the XPS full spectrum analysis of Fe_2O_3, which is consistent with its icp test results (Table S5). Subsequently, high-resolution XPS analysis was performed on Fe 2P and Nd 3d of Fe_2O_3 (Fig. S9). The binding energies of Fe in Fe 2P are 709.68 eV, 711.17 eV, 718.18 eV, 723.19 eV, and 724.88 eV, respectively, which are similar to the previously reported binding energies of Fe_2O_3 [2,3]. The binding energies of Nd in Nd 3d are 1008.77 eV, 1006.39 eV, 1002.95 eV, 995.17 eV, 983.71 eV, 980.35 eV, and 975.43 eV, respectively, which are similar to previous study [4,5].

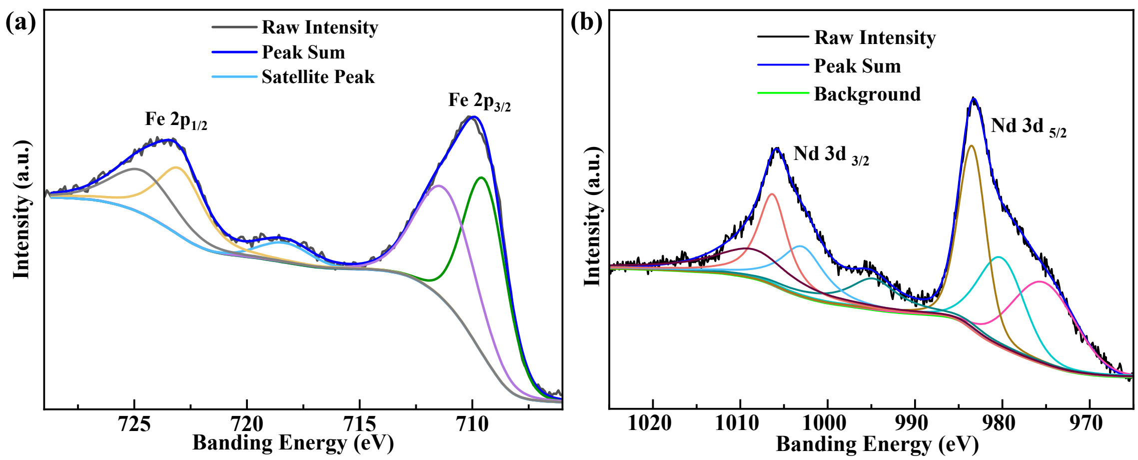


Fig. S9 The XPS spectra for (a) Fe 2p and (b) Nd 3d of obtained Fe_2O_3.

Table S6. Comparison of present work and other similar work

Scheme	Major Chemical Inputs	Energy Consumption	References
Leaching with HCl and solvent extraction using NaCyanex 302	1 mol Nd_2O_3: 15.6 mol HCl 9.4 mol NaCyanex 302	1.98 kwh/kg Nd_2O_3	Padhan et al. [6]
Anion exchange membrane combined with dual electrolysis chamber	1 mol Nd_2O_3: 384 mol NaCl	15.00 kwh/kg REOs	Prakash et al. [7]
Electrochemical dissolution of NdFeB followed by deposition of Fe and Nd, respectively	1 mol Nd_2O_3: 2.4 mol H_2SO_4 2mol Na_2SO_4	4.85 kwh/kg REOs	Xu et al. [8]
Extraction of REEs and Fe from NdFeB by co-leaching stepwise precipitation method	1 mol Nd_2O_3: 13 mol HCl 8 mol $H_2C_2O_4$	–	Liu et al. [9]
After roasting at 350 °C, leaching Nd with inorganic acid precipitation	1 mol Nd_2O_3: 144.42 mol H_2SO_4	0.028 kwh/kg Nd_2O_3	Lee et al. [10]
Demagnetized and roasted Leached with Citic/Maleic acid	1 mol Nd_2O_3: 22.86 mol Citic/Maleic acid	8.14 kwh/kg Nd_2O_3	Reisdorfer et al. [11]
$ZnCl_2$ solution as electrolyte combined with dual anode system	1 mol Nd_2O_3: 4 mol Na_2SO_4 8 mol NaOH	2.67 kwh/kg REOs	Present work

Electricity consumption: The calculation method for energy consumption is as follows: According to the equation 5: P= (0.3 V * 0.15 A) + (3.3 V * 0.06 A) = 0.243 w. W=P*t=0.000243 kwh. The electrolysis process adopted constant current electrolysis, and the voltage was calculated by taking the average value. Under this condition, 0.28 g NdFeB magnets can be electrolyzed. Then for every 1 kg of NdFeB magnets electrolyzed, 0.8678 kwh of electricity is required. Previously mentioned that 1.8678 kwh of electricity is required for processing 1 kg of NdFeB. The remaining 1 kwh of electricity is the energy consumption for roasting $Nd(OH)_3$ in a muffle furnace. By fully utilizing the volume of the muffle furnace, this part of energy consumption can be further saved. The size of the muffle furnace used is 15 * 15 * 15 cm, which can process 5 kg of $Nd(OH)_3$ in a single operation, and the energy consumption is 1 kwh. Calculated based on the production of 0.2 kg $Nd(OH)_3$/kg of NdFeB magnets. So processing 1 kg NdFeB required an additional 0.04 kwh of electrical energy.

To sum up, taking into account the energy consumption of both parts, the required electrical energy for each 1 kg of NdFeB magnets processed by electrolysis is 0.9078 kwh. According to the calculation of producing 0.34 kg of REO per kg of NdFeB, the power consumption of 1kg REOs is 2.67 kwh.

Table S7. Current density of each electrode.

NAA Current (A)	NAA Current Density (A/cm^2)	PIA Current (A)	PIA Current Density (A/cm^2)
0	0	0	0
0.05	0.025	0.01	0.005
0.10	0.050	0.02	0.010
0.15	0.075	0.03	0.015
0.20	0.100	0.04	0.020
0.25	0.125	0.05	0.025
-	-	0.06	0.030
-	-	0.07	0.035

Reference

[1] Mikiya T., Tatsuya O., Kazuya K., etal. Recycling of Rare Earths from Scrap. Handbook on the Physics and Chemistry of Rare Earths, 2013, 43, 159-211.

[2] L. Niu, G. Zhang, G. Xian, et al., Tetracycline degradation by persulfate activated with magnetic γ-Fe_2O_3/CeO_2 catalyst: Performance, activation mechanism and degradation pathway, Separation and Purification Technology. 259 (2) (2020), 118156.

[3] Pavel K., Dinara S., Rashid D., and et al. Characterization of Fe_2O_3 thin film on highly oriented pyrolytic graphite by AFM, Ellipsometry and XPS. 2019, 493, 673-678.

[4] G.J. Gao, M.Q. Zeng, E.L. Zhang, et al., Dealloying corrosion of anodic and nanometric Mg41Nd5 in solid solution-treated Mg-3Nd-1Li-0.2Zn alloy. Journal of Materials Science and Technology. 83 (9) (2021) 161-178

[5] John P. Baltrus, Murphy J. Keller. Surface Science Spectra. Rare earth oxides Eu_2O_3 and Nd_2O_3 analyzed by XPS. 2019, 26, 014001.

[6] Padhan E., Nayak A. K., Sarangi K. Recovery of neodymium and dysprosium from NdFeB magnet swarf. Hydrometallurgy. 2017, 174, 210-215.

[7] Prakash V., Tom V. H., Koen B., et al. Selective Extraction of Rare-Earth Elements from NdFeB Magnets by a Room-Temperature Electrolysis Pretreatment Step. ACS Sustainable Chemistry Engineering. 2018, 6, 9375-9382.

[8] Xu, X., Sturm S., Samardzija, Z., et al. A facile method for the simultaneous recovery of rare-earth elements and transition metals from Nd-Fe-B magnets. Green Chemistry. 2020, 22, 1105-1112.

[9] Liu Z., Zhou H., Li W. Separation and coextraction of REEs and Fe from NdFeB sludge by co-leaching and stepwise precipitation[J]. Separation and Purification Technology, 2022, 282, 119795, 2-9.

[10] Lee, C. H., Chen, Y. J., Liao, C. H., et al. Selective leaching process for neodymium recovery from scrap Nd-Fe-B Magnet. Metall. Mater. Trans. A 2013, 44, 5825-5833.

[11] Reisdorfer, G., Bertuol D., Tanabe E. H. Recovery of neodymium from the magnets of hard disk drives using organic acids. Miner.Eng. 2019, 143, 105938.