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PNNL-38593

Understanding Mechanisms of Selective Crystal Nucleation and Growth Using In Situ Electron Microscopy

October 2025

Dongsheng Li

U.S. DEPARTMENT of ENERGY

Prepared for the U.S. Department of Energy
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Abstract

Separation processes are essential for purifying and isolating critical materials, but are challenging due to the natural tendency of systems to mix. This project explores far-from-equilibrium separation methods using external electric and magnetic fields to drive selective nucleation and crystal growth. Using *in situ* electrochemical transmission electron microscopy (TEM), we observed ion transport and crystallization behavior under applied electric fields. We found that ions migrate toward the working electrode, where nucleation preferentially occurs. These findings advance our understanding of non-equilibrium separation mechanisms and support the development of efficient, sustainable methods for extracting critical materials from unconventional domestic sources.

Summary

Separation processes are essential but inherently challenging due to the natural tendency of substances to mix. Separations play a critical role in purifying, refining, and isolating materials—such as recovering metals from waste and producing high-purity rare earth elements. While analytical techniques like chromatography are effective at small scales, industrial applications rely on large-scale methods like distillation, which are energy-intensive and often struggle to achieve high purity.

This project seeks to overcome these limitations by applying far-from-equilibrium conditions through external stimuli, such as electric and magnetic fields. Combined with *in situ* transmission electron microscopy (TEM), these approaches enable real-time observation of selective nucleation and growth processes. In FY 2025, we investigated the influence of electric fields on crystal formation and observed that ion transport follows the direction of the electric field, with nucleation occurring preferentially at the working electrode rather than the reference or counter electrode.

These findings advance our understanding of non-equilibrium separation mechanisms and support the development of efficient, sustainable methods for extracting critical materials from unconventional sources. Ultimately, this work contributes to building a robust domestic supply chain and accelerating the transition to energy dominance.

Acknowledgments

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Acronyms and Abbreviations

Abbreviation/Acronym	**Full Form**
Ca	Calcium
CO_2	Carbon Dioxide
CV	Cyclic Voltammetry
Dy	Dysprosium
$DyCl_3$	Dysprosium(III) Chloride
EC	Electrochemical
EDS	Energy Dispersive X-ray Spectroscopy
FY	Fiscal Year
HAADF	High-Angle Annular Dark-Field
LPTEM	Liquid-Phase Transmission Electron Microscopy
Na	Sodium
NaOX/Na oxalate	Sodium Oxalate
Nd	Neodymium
$NdCl_3$	Neodymium(III) Chloride
RE	Reference Electrode
REE	Rare Earth Element
SEM	Scanning Electron Microscopy (or Microscope)
TEM	Transmission Electron Microscopy (or Microscope)
WE	Working Electrode

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1.0 Introduction

Separations are among the most challenging processes in science and engineering, as naturally occurring systems tend to favor mixing. Separation techniques—including purification, refining, and isolation—are critical to both chemists and chemical engineers.[1] For example, separation processes are employed to recover manganese metal from recycled battery waste.[2]

There is increasing demand for rare earth elements (REEs) of high purity and in large quantities. A series of ion-exchange processes has been developed to separate adjacent rare earth elements at the macroscale.[3] Small-scale analytical separation techniques, such as chromatography,[4] are widely used to analyze complex mixtures, quantify component concentrations, and recover or purify chemicals. However, industrial-scale chemical manufacturing requires cost-effective, large-scale separation methods that differ significantly from laboratory techniques—for instance, the use of distillation for hydrocarbon separation and solvent extraction for purification of critical minerals.[5]

A key challenge in current separation processes lies in achieving both high purity and large-scale production of critical materials. In this study, we introduced external stimuli—such as external electric and magnetic fields—to induce far-from-equilibrium conditions favorable for selective nucleation and crystal growth.

These innovative approaches, combining non-equilibrium environments with *in situ* transmission electron microscopy (TEM), enabled us to advance conventional separation methodologies and probe the kinetics and dynamics of nucleation and growth. This knowledge paves the way for robust extraction of critical materials from abundant, unconventional, and domestically available feedstocks.

This work establishes selection principles for precipitation from multicomponent solutions. It contributes to the development of a sustainable supply chain for critical materials, accelerating the transition to energy dominance. In parallel, it builds foundational molecular-level understanding of far-from-equilibrium separation processes applicable to critical materials and beyond.

2.0 Methodology

Using *in situ* liquid-phase transmission electron microscopy (LPTEM), we investigated the mechanisms of element-specific nucleation in mixed solutions. Our focus was on crystal nucleation and growth under far-from-equilibrium conditions—particularly in the presence of externally applied electric and magnetic fields—as a means of selectively controlling nucleation behavior. Specifically, we aimed to induce selective nucleation of pure Nd and Dy particles from aqueous $NdCl_3$/$DyCl_3$ mixtures.

In FY 2025, we examined how electric fields influence selective nucleation and growth. By applying external electric fields, we introduced far-from-equilibrium conditions that modify the driving forces for transport, speciation, and crystal formation. We hypothesized that electric fields influence nucleation dynamics by affecting ion transport and interfacial energies.

The electric fields were applied using an electrochemical (EC) *in situ* LPTEM system with external voltage control *via* a potentiostat. This setup allowed real-time observation of nucleation sites and crystal growth as a function of electric field strength.

3.0 Results

3.1 Control Experiments without Electric Fields

3.1.1 Morphology and Composition of Precipitates

We mixed 10 mM $NdCl_3$, 10 mM $DyCl_3$, and 20 mM Na oxalate with 1:1:1 volume ratio. Both fresh and 3-month-old solutions produced precipitates with average compositions of ~55 atomic percent (at%) Nd and ~45 at% Dy. Using HAADF-STEM imaging, we found that particle morphologies and compositions varied widely.

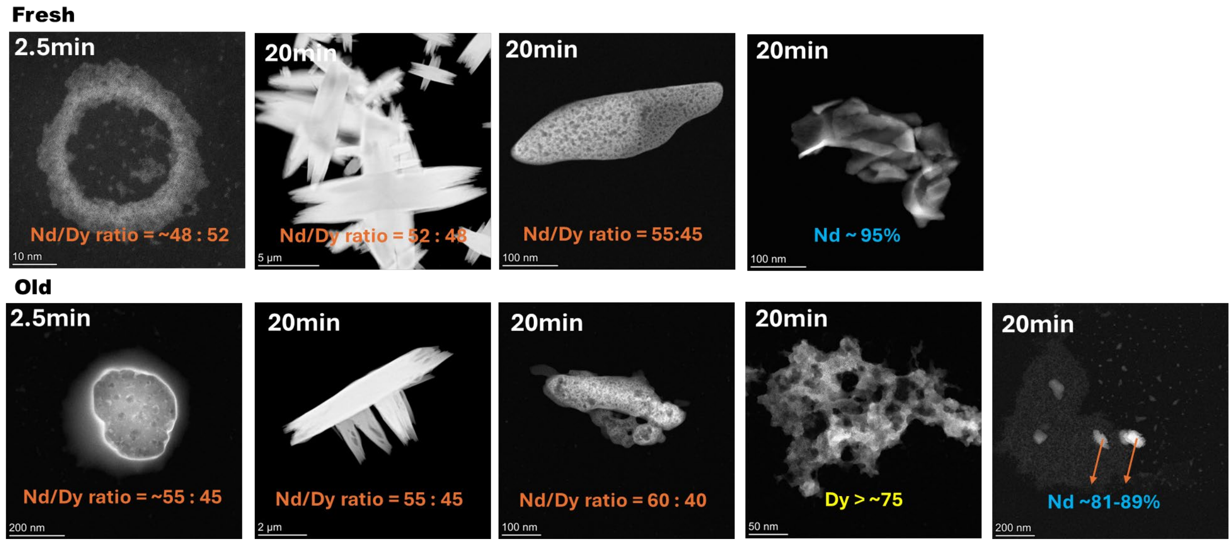

Figure 1. HAADF STEM images and EDS results of precipitates from fresh and aged solutions.

3.1.2 Effect of pH on Precipitation

We observed interesting phenomena. Besides precipitates with average compositions of ~55 at% Nd and ~45 at% Dy, fresh solutions also yielded Nd-rich particles (80–90% Nd), while aged solutions produced both Nd-rich and Dy-rich particles (>75%), indicating time-dependent changes in solution chemistry (**Figure 2**).

To investigate the underlying mechanisms, we measured the pH values of fresh and aged solutions. While $NdCl_3$ and $DyCl_3$ showed slight pH drops (~2%), Na oxalate exhibited a larger decrease (~11%), likely due to CO_2 absorption from air, causing gradual acidification through the formation of carbonic acid. This shift in pH may explain the increased Dy-rich precipitation in aged solutions through formation of carbonates rather than oxalates. Further analysis will explore the separation mechanisms and phases of precipitates with various shapes.

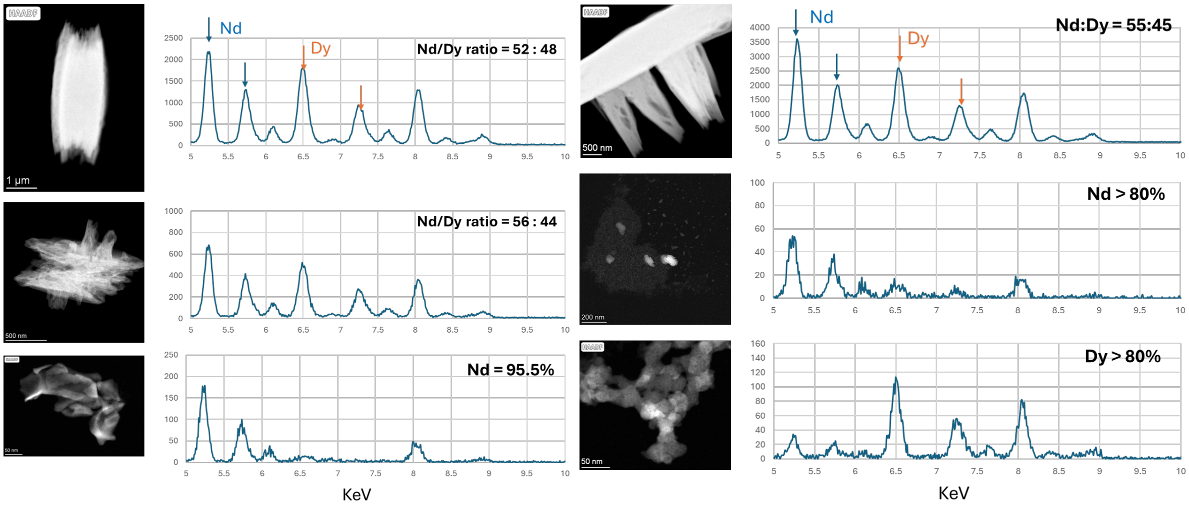

Figure 2. HAADF STEM images and EDS spectra of precipitates from fresh (left) and aged (right) solutions.

Table 1. pH values of solutions, comparing theoretical, fresh, and 3-month-aged conditions.

Solution	Theoretical pH	Fresh solution	Aged solution
10 mM $NdCl_3$	**~5.2**	**5.8**	**5.67**
10 mM $DyCl_3$	**~5.15**	**6.24**	**6.08**
20 mM Na oxalate	**~8.78**	**8.69**	**7.73**

3.2 EC-LPTEM Study of Nucleation and Growth Under External Electric Fields

3.2.1 Voltage Range Determination

We first performed both *ex situ* and *in situ* experiments to determine appropriate voltage and current ranges that induce electromigration while avoiding unwanted redox reactions.

Cyclic voltammetry (CV) measurements were conducted on $NdCl_3$, sodium oxalate, and their mixture (**Figure 3**) using glassy carbon electrodes to define the electrochemical stability window. All electrolytes exhibited a stability range between –0.2 V and 0.8 V *vs.* an Ag/AgCl reference electrode. This voltage range is suitable for probing the effects of applied electric fields on ion transport and chemical precipitation without electroreduction.

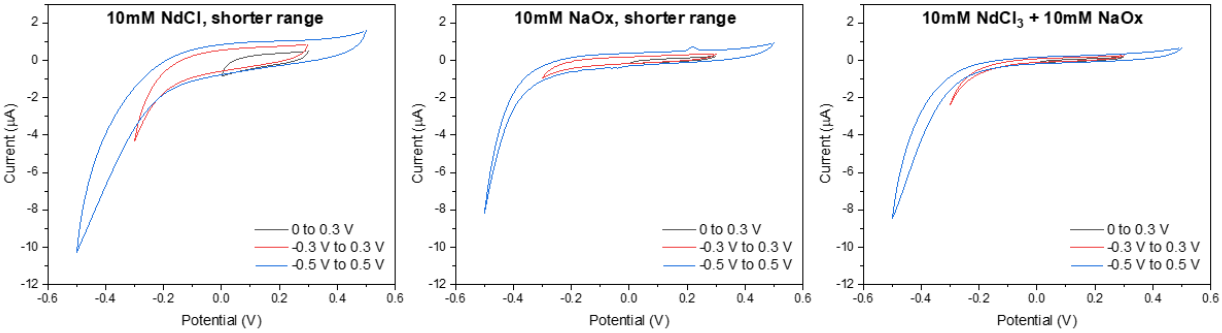

Figure 3. CV measurements of $NdCl_3$, sodium oxalate, and their mixture.

We performed CV measurements using the EC-LPTEM setup on a mixed solution of 1 mM $NdCl_3$, 1 mM $DyCl_3$, and 2 mM sodium oxalate (**Figure 4**). Based on these results and *ex situ* measurements, a voltage range of 0.1–0.5 V was selected for subsequent experiments.

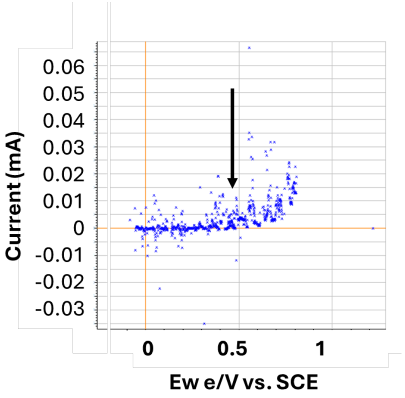

Figure 4. CV of a mixed solution of $NdCl_3$, $DyCl_3$, and sodium oxalate, over a voltage range of 0 to 0.8 V.

3.2.2 Effect of Electric Fields on Ion Transport and Crystal Growth

In the EC-LPTEM system, we swept the voltage from 0 to 0.5 V and maintained it at 0.5 V for 50 seconds. Precipitates were observed to accumulate on the working electrode (WE), with visible tracks leading toward it, indicating ion transport along electric field lines (Figure 5).

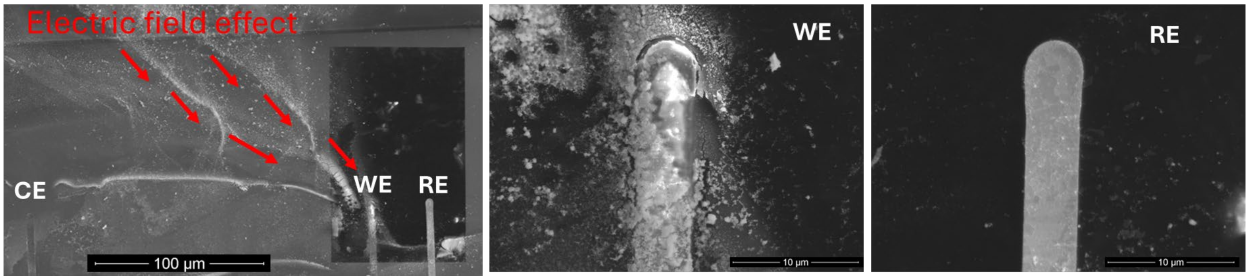

Figure 5. SEM images of EC liquid cell chips showing nucleation and growth of precipitates near the WE from a mixed solution of 1 mM $NdCl_3$, 1 mM $DyCl_3$, and 2 mM sodium oxalate.

EDS analysis revealed that Nd/Dy oxalate co-precipitates formed near the working electrode (WE) had a slightly higher average Nd content (~57 at%, Figure 5) compared to those in the bulk solution (~55 at%), in contrast with the initial 1:1 molar ratio. This suggests that the electric field selectively enhances the ion transport of Nd over Dy.

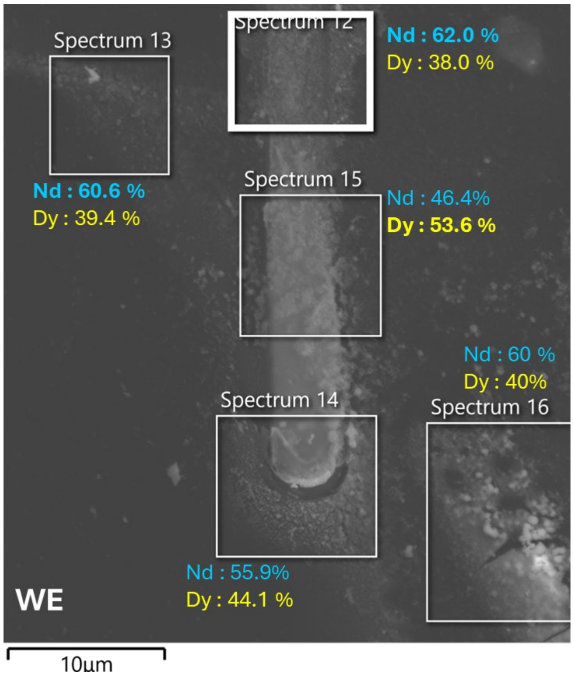

Figure 6. SEM and EDS analysis of precipitates near the WE on the EC liquid cell chip.

To further investigate, we conducted *in situ* EC-LPTEM experiments at 0.35 V to focus on early-stage nucleation. A significantly higher density of precipitates was observed near the WE (**Figure 7)** compared to the reference electrode (RE), indicating electric-field-directed nucleation.

EDS analysis showed that precipitates near the WE had a composition of approximately 46 at% Nd and 54 at% Dy—slightly lower in Nd content than under the 0.5 V condition (57%). However, at the tip of the WE (**Figure 8**)—where the electric field is strongest—Nd concentration reached 68 at%, indicating a strong influence of field distribution on local composition.

Preliminary results indicate that the electric field influences both ion transport and the composition of the precipitates. Further precise EDS analysis will confirm these findings.

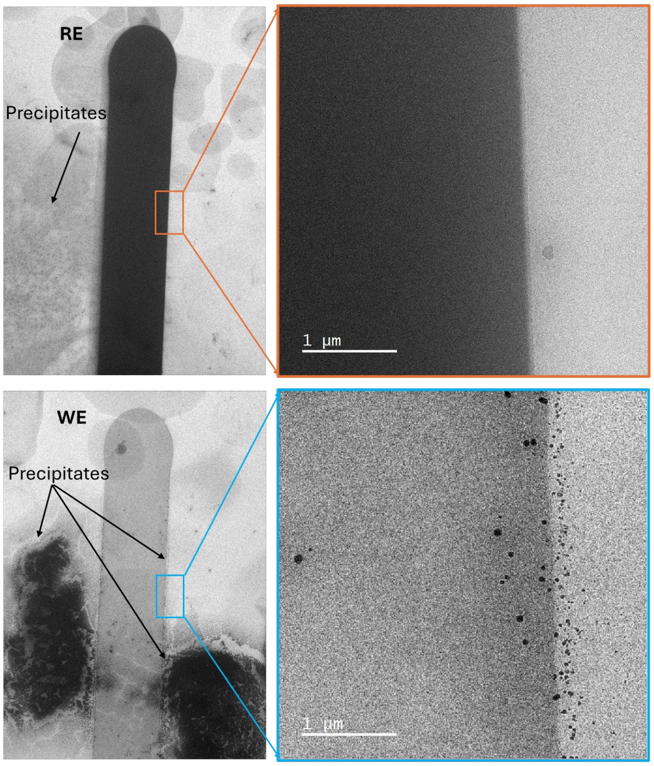

Figure 7. TEM images showing a higher density of precipitates near the WE compared to the RE.

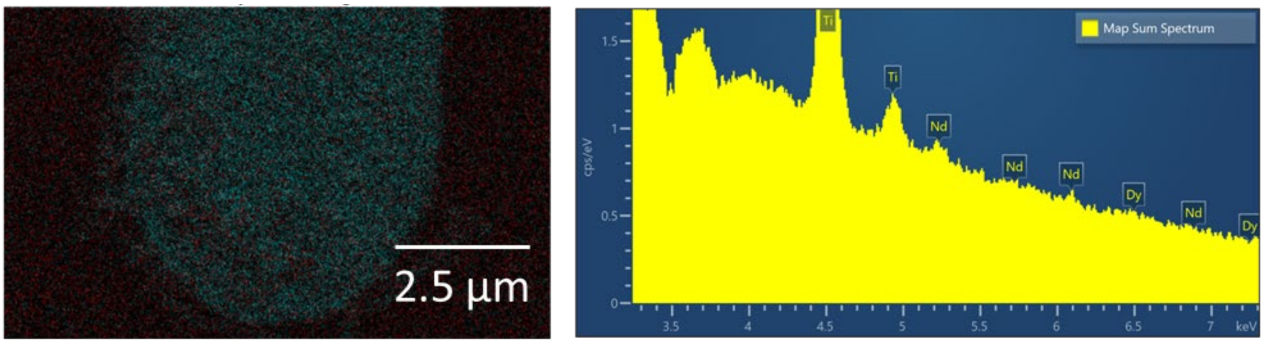

Figure 8. SEM image and EDS spectrum from the tip of the WE, showing Nd enrichment in the precipitates.

3.2.3 The Role of Metal Ion Valence in Selective Precipitation

To explore the influence of metal ion valence on nucleation under an external electric field, we first examined precipitation from mixed solutions of Ca^{2+} and Nd^{3+} at various concentrations. At both initial Ca:Nd atomic ratios of 1:1 and 2:1, particles with approximately 1:1 Ca:Nd ratios were observed. However, at a 1:1 starting ratio, additional particles enriched in either Ca or Nd also formed. In contrast, with a 2:1 Ca:Nd ratio, only Ca-rich particles were observed (**Figure 9**).

The effect of the electric field on ion transport and crystal precipitation was not investigated, as the TEM was unavailable and *in situ* TEM experiments could not be conducted until the end of the fiscal year.

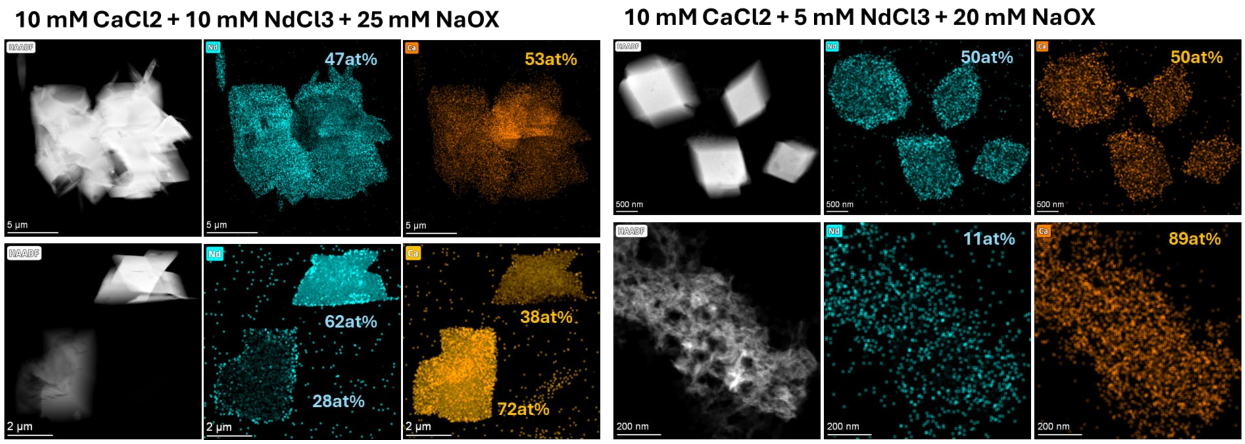

Figure 9. HAADF images of particles precipitated under two different Ca/Nd ratio conditions, with corresponding EDS maps showing Ca and Nd distributions.

4.0 References

1. Spedding, F. H., Large-scale separation of rare-earth salts and the preparation of the pure metals. *Discussions of the Faraday Society* **1949,** *7* (0), 214-231.
2. Keller, A.; Hlawitschka, M. W.; Bart, H. J., Manganese recycling of spent lithium-ion batteries via solvent extraction. *Sep. Purif. Technol.* **2021,** *275*, 119166.
3. Moore, B. W., Selective separation of rare earth elements by ion exchange in an iminodiacetic resin. *US6093376A, a continuation-in-part of U.S. patent application Ser. No. 08/686,263, filed Jul. 25, 1996,* .
4. Kanu, A. B., Recent developments in sample preparation techniques combined with high-performance liquid chromatography: A critical review. *J. Chromatogr. A* **2021,** *1654*, 462444.
5. Khaled A. M. GasemRobert L. Robinson, J. C. J. S. A. T., Separation of hydrocarbons by extractive distillation. *WO2002022528A1*.

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