

Electronic Supplementary Information

A sustainable approach to separate and recover indium and tin from spent indium-tin oxide targets

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Composition of the spent ITO target

The spent ITO target was ground carefully into fine powder as shown in Figure S1. Then, a certain amount of the ITO powder was dissolved completely by fresh aqua regia. The bulk density of the spent ITO powder is 2.06 g/mL. The grain diameter distribution map is shown in Figure S2. The size of the spent ITO powder was mainly in the range of 1~100 μm with the D50 being 6.781 μm . After the leaching process, all the leaching solution was transferred into a volumetric flask and analyzed with a Perkin Elmer[®] Optima 5300 DV ICP-OES. Table S1 shows the detailed mass determined by ICP-OES for the species In^{3+} , Sn^{4+} , and Zn^{2+} for three spent ITO powder samples.



Figure S1 A photograph for the ground ITO target powder.

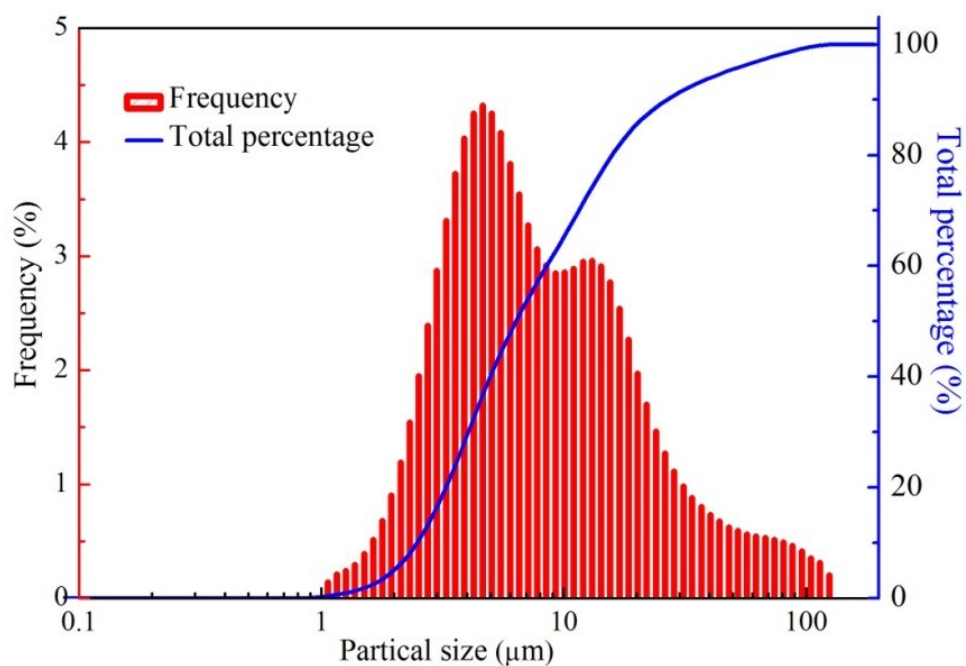


Figure S2 Size distribution of the spent ITO powder.

Table S1 The mass of In^{3+} , Sn^{4+} , and Zn^{2+} determined by ICP-OES for the three ITO powder samples with different masses after dissolving by aqua regia with a solid to liquid ratio of 1g to 100 mL and at a leaching temperature of 40°C, a stirring rate of 500 rpm, and a leaching time of 2 h.

ITO powder (g)	In^{3+}		Sn^{4+}		Zn^{2+}	
	g	wt%	g	wt%	g	wt%
3.275	2.5710	95.17	0.1274	4.71	0.003147	0.12
3.158	2.478995	17	0.1228	4.71	0.003041	0.12
3.098	2.4318	95.16	0.1206	4.72	0.002979	0.12

Distillation of the leaching solution

After the leaching process, the acidity of the leaching solution was around 3.8 mol/L HCl. The leaching solution was then transferred to a rotary evaporator equipped with an oil bath and vacuum pump to distill HCl for reuse. The hydrate of indium chloride and tin chloride was left at the bottom of the flask. A rotary evaporator was utilized in the lab scale for the reduced pressure distillation, while for an industrial distillation a large HCl recovery setup will be needed. According to a survey on the internet, a 9000L waste HCl recovery setup only cost around \$40000, which is relatively cheap.

Analysis of the hydrate metal chlorides

For some reason, we cannot access the standard card info of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ which makes it impossible to analyze the exact composition of the hydrate obtained in the distillation step. In order to confirm the co-existence of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in the crystal, a similar process was adopted to obtain a mixed hydrate crystal of 94.5wt% $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and 5.5wt% $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ using analytical pure $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ (99.99%) and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (99.9%) as the starting materials. First, $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ were accurately weighed and then transferred into a 5M HCl solution. Next, the solution was distilled to obtain the crystal of InCl_3 and SnCl_4 hydrates. Since we do not have the standard pattern of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, an additional experiment was carried out to prove that the crystal produced in the distillation step was tin chloride pentahydrate. The SnCl_4 hydrate was prepared by adding a certain amount of analytical pure $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ into 5M HCl solution for distillation. The obtained SnCl_4 hydrate was coated with a layer of Vaseline to avoid the exposure to air and analyzed by XRD. The XRD patterns for the standard $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and the SnCl_4 hydrate are shown in Figure S3.

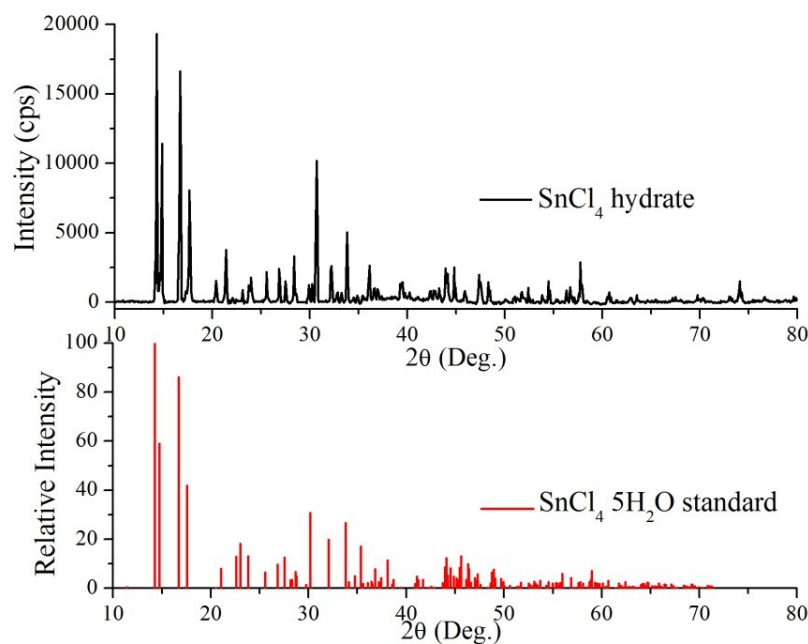


Figure S3 XRD patterns of the hydrate obtained from the distilled SnCl_4 -HCl solution and the standard $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ crystal.

At the meantime, the crystals recovered from the three spent ITO targets were also analyzed with ICP-OES, and the data are shown in Table S2. The content of the crystals was calculated based on the assumption that all InCl_3

and SnCl_4 hydrates were $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, respectively. This assumption makes sense due to the high similarity of XRD patterns shown in Figure S3 and the fact that the amounts of crystal water in InCl_3 and SnCl_4 have little influence on the products shown in equations (2) and (3). The crystals were determined to consist of 94.4wt% $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and 5.53wt% $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$.

Table S2 The content of the crystals obtained from the spent ITO targets assuming that InCl_3 and SnCl_4 hydrate was $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, respectively.

Targets (g)	Crystals (g)	$\text{InCl}_3 \cdot 4\text{H}_2\text{O}$		$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	
		Mass (g)	Mass percentage (%)	Mass (g)	Mass percentage (%)
1.098	2.328	2.196	94.33	0.1288	5.53
1.103	2.339	2.208	94.39	0.1293	5.53
1.056	2.240	2.115	94.42	0.1239	5.53

Figure S4 shows a photograph for the crystal obtained from an ITO target. The crystal is white powder which fumes on contact with air. The fuming of the crystal was mainly caused by $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, which would easily decompose upon exposure to moist air according to the MSDS.

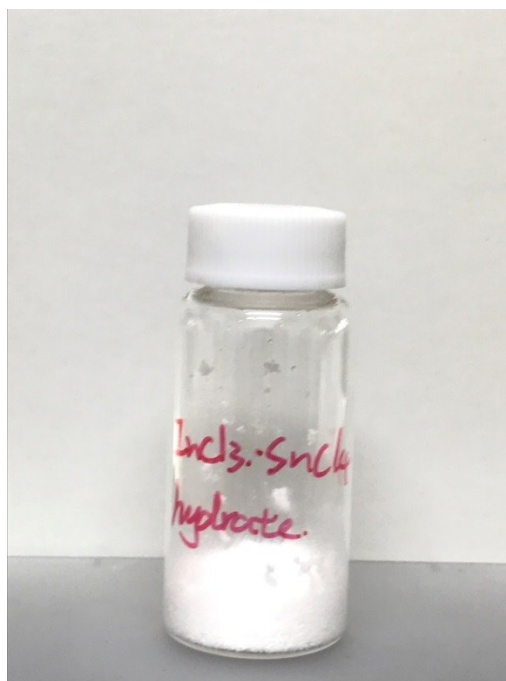


Figure S4 A photograph for the recovered mixed crystal hydrates of InCl_3 and SnCl_4 .

Table S3 Calculated secondary wastes produced in solvent-extraction, ion-exchange, and DDDF processes.

Methods	Processes	Secondary wastes	Amount
Solvent extraction with D2EHPA	H ₂ SO ₄ leaching	–	–
	pH adjustment	–	–
	Extraction (twice)	1M H ₂ SO ₄ solution	1000L
	Stripping (twice)	20% D2EHPA kerosene 1.5M HCl solution	250L 250L
Solvent extraction with TBP	HCl leaching	–	–
	pH adjustment	–	–
	Extraction (once)	1M HCl solution 1M TBP kerosene	1000L 1000L
Ion-exchange with DODGAA-IL	HNO ₃ leaching	–	–
	pH adjustment	–	–
	Adsorbent synthesis	Acetone with IL and DODGAA	151L
	Adsorption	pH=2 HNO ₃ solution	1570.1 L
	In ³⁺ elution	2.5M HNO ₃ solution	130.8L
	Sn ⁴⁺ elution	5M HNO ₃ solution DODGAA-IL resin	130.8L 45kg
DDDF and handling of HCl and SO ₂ mixed gas	HCl leaching	–	–
	Vacuum distillation	–	–
	Dehydration	SO ₂	117.8 M SO ₂
		HCl	235.5M HCl
	Fractionation	–	–
	Vacuum heating	–	–
	Reuse and collection	Sodium sulfite. Byproducts: HCl solution, SO ₂ , and 7.268L of SOCl ₂	10L of Na ₂ SO ₃ solution
	Or disposal with Ca(OH) ₂	CaSO ₃ , CaCl ₂ , and H ₂ O	8.72kg CaSO ₃ , 8.72kg CaCl ₂ , and 6.36kg H ₂ O

Dehydration and fractionation

During the dehydration process, a simulated indium and tin chloride solution was prepared, which has an actual ratio of indium and tin in the spent ITO target. Indium chloride and tin chloride were dissolved in 5M HCl solution and then distilled under a reduced pressure to obtain the crystal of indium and tin chloride hydrates. Next, the crystal was finely ground and put into a flask of freshly distilled SOCl_2 with a ratio of crystal to SOCl_2 of 1 g to 1.2 mL. Sulfur dioxide and hydrogen chloride immediately bubbled out of the solution. After bubbling stopped, the flask was heated to 90 °C to reflux the slurry for 2h. Figure S5 shows the setup for dehydrating process. Then the flask was cooled down and equipped with a Vigreux fractionating column to separate SOCl_2 and anhydrous tin chloride. Anhydrous InCl_3 , SnCl_4 , and SOCl_2 co-exist in the flask. As can be seen from Figure S6, anhydrous InCl_3 is insoluble in both SnCl_4 and SOCl_2 solution and the solubility does not change with the temperature. This indicates that the appearance of anhydrous InCl_3 would not affect the fractionation of SnCl_4 and SOCl_2 . The fractionation of SnCl_4 and SOCl_2 was processed according to Figure3 when the purity of SnCl_4 at the bottom of the flask is high enough ($>99\%$), SOCl_2 (Density: 1.64g/ml) can be distilled out of the flask with 5 theoretical plates to reach 99.9% purity. The consumption and recovery rate of SOCl_2 is shown in Table S4. The average recovery rate of SOCl_2 is around 91%. Figure S7 shows the setup for the fractionation process.



Figure S5 The setup of dehydrating process.

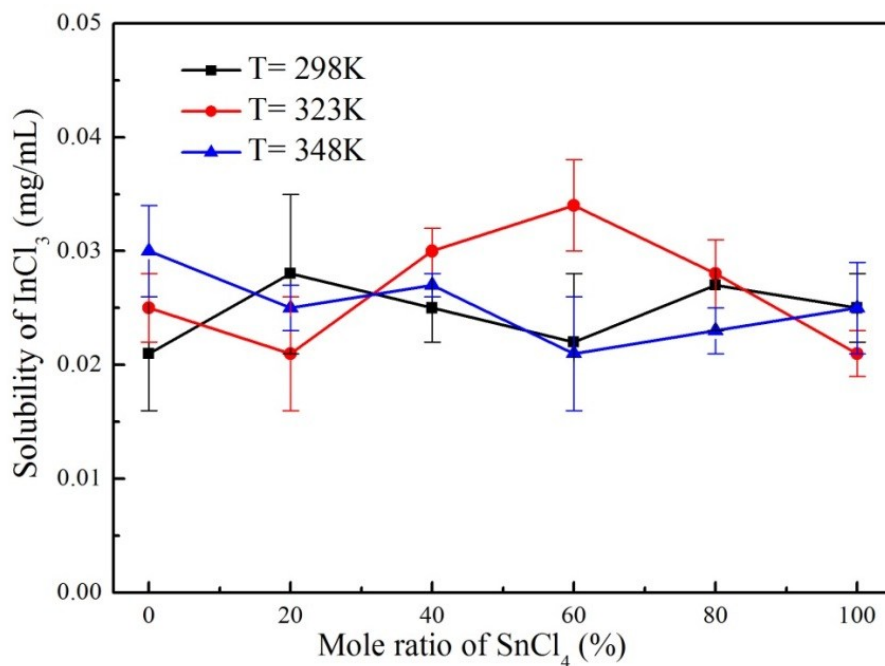


Figure S6 The solid-liquid equilibrium of anhydrous InCl_3 with SnCl_4 and SOCl_2 at different temperatures.

Table S4 Consumption and recovery rate of SOCl_2 in the DDDF process.

ITO	Hydrate (g)	SOCl_2 added (ml)	SOCl_2 consumed (mL)	SOCl_2 recovered (g)	Recovery rate (%)
5.079	10.77	13.00	10.67	3.515	91.99
5.018	10.64	13.00	10.54	3.676	91.12
5.027	10.66	13.00	10.56	3.628	90.66



Figure S7 The setup of fractionation process.

Characterization of anhydrous InCl_3 and SnCl_4

Figure S8A shows a photograph for the anhydrous InCl_3 obtained after fractionation, which is white powder. The anhydrous powder was washed with SOCl_2 solution for three times to wash away the residual SnCl_4 . After that, the white powder remained in the flask was filtered out of the solution and moved to a vacuum drier at 90°C to get rid of the excess SOCl_2 . The as-obtained anhydrous InCl_3 was then transferred into a dry box and kept in a suitable container that can be sealed. The anhydrous InCl_3 was analyzed with XRD in an air-sensitive sample holder to avoid any contact with air. The purity of InCl_3 was calculated according to the XRD pattern shown in Figure 3. In^{3+} concentration in a certain amount of InCl_3 was determined by ICP-OES. The recovery rate of indium was calculated by dissolving all the InCl_3 obtained in this process and measuring the concentration of In^{3+} with ICP-OES, and the data are shown in Table S5.

Table S5 The purity of InCl_3 and SnCl_4 measured by ICP-OES.

InCl_3 (g)	SnCl_4 (g)	Measured In^{3+} (g)	Measured Sn^{4+} (g)	Purity of InCl_3 (%)	Purity of SnCl_4 (%)
1.056	1.102	0.5472	0.4987	99.82	99.71
1.013	1.089	0.5250	0.4927	99.83	99.68
1.071	1.054	0.5548	0.4770	99.79	99.72

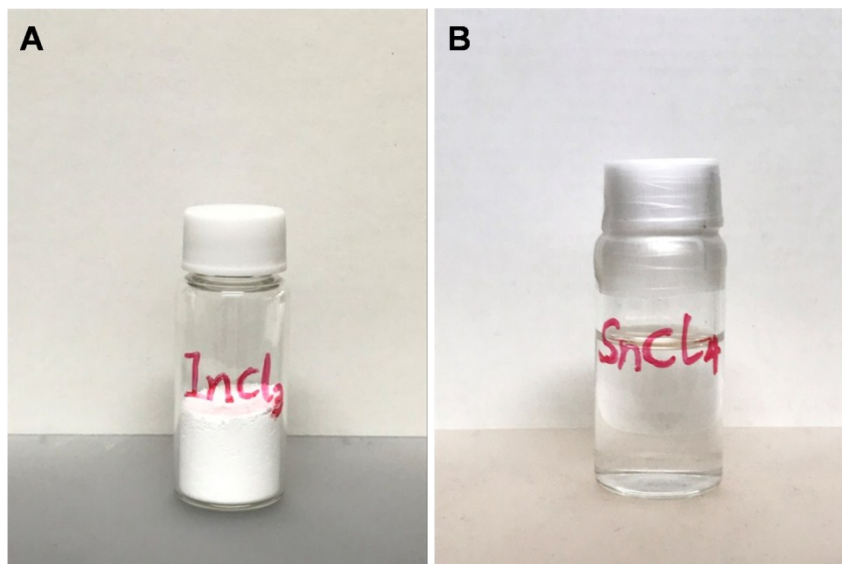
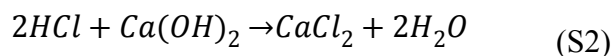
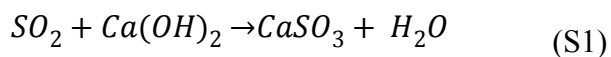


Figure S8 A photograph for the as-filtrated anhydrous InCl_3 (A) and SnCl_4 (B).

After the fractionation process, SnCl_4 was collected and moved into a vacuum drying machine and heated at 100°C for 24 h to get rid of any remaining SOCl_2 in the solution. Figure S8B shows the anhydrous SnCl_4 obtained after this process. The purity of SnCl_4 obtained in this process was calculated by measuring the concentration of Sn^{4+} in a certain amount of SnCl_4 obtained, while the recovery rate of tin was determined by dissolving all the SnCl_4 obtained in this process and measuring the concentration of Sn^{4+} with ICP-OES. The data for the purity of SnCl_4 are also shown in Table S5.

The reuse and disposal of the hazardous gases produced in the dehydration process

As can be seen from equations (2) and (3), HCl and SO_2 gases were emitted during the dehydration process, and this mixed gas can either be reused or disposed with alkali. Because the solubility of SO_2 in H_2O is highly dependent on temperature resulting in enormous solubility difference between HCl and SO_2 , HCl gas can be separated from SO_2 gas by scrubbing with hot water. By scrubbing the mixed gas with hot water (e.g., 40°C), HCl can be dissolved with high selectivity, while the majority of SO_2 discharged from hot water. The obtained solution may still contain a little amount of SO_2 , which can be purified if needed. After the dissolution with hot water, a small amount of HCl may still remain in the SO_2 gas due to its relatively high vapor pressure and incomplete dissolution. A cold saturated solution of sulfurous acid can then be used to further dissolve the remaining HCl . After which, the gas can finally be dried with desiccant (e.g., CaCl_2), so that a purified SO_2 gas stream can be obtained and collected for sale. The other option is to dispose the mixed gas with lime as shown in equations (S1) and (S2). The hazardous gases emitted from the flask during the dehydration process in lab scale were bubbled in a saturated $\text{Ca}(\text{OH})_2$ solution to remove SO_2 and HCl gas, as shown in Figure S5.



The comparison of recycling 1 kg spent ITO target between solvent-extraction, ion-exchange, and DDDF processes

To demonstrate the superiority of DDDF process, a calculation has been done according to the experiments done by Virolainen and Schaeffer. 1kg of spent ITO target with a mass ratio of In_2O_3 to SnO_2 around 95:5 was used as the recycling target. ITO powder was first dissolved by 3M HCl/ H_2SO_4 / HNO_3 , with a solid-liquid ratio of 1g/10mL, temperature of 40°C, stirring rate of 500 rpm, and leaching time of 2h. The leaching solution was then used as the source for the separation and recycling of indium and tin. In the solvent extraction with D2EHPA process, both indium and tin can be extracted into the organic phase from H_2SO_4 solution. After extraction, the organic phase was selectively stripped with 1.5M HCl solution to strip indium from the organic phase, and thus separate indium from tin. In the solvent extraction with TBP process, 3M HCl was used as the leaching solution, and after the dissolution the leaching solution was then diluted with distilled water to adjust the pH value. Afterwards, 1M TBP in kerosene was used to extract tin into the organic phase, while the majority of indium remained in the aqueous phase. In the ion-exchange process, a solvent impregnated resin (SIR) was used to separate indium from tin. DODGAA and the ionic liquid $[\text{C}_4\text{min}][\text{Tf}_2\text{N}]$ with a ratio of 1:1 was mixed with Amberlite XAD-7 resin in acetone solution to synthesize the SIR. This resin can adsorb both indium and tin in HNO_3 solution. After the adsorption, indium and tin were eluted with 2.5M HNO_3 and 5M HNO_3 , respectively. Table S3, S5, S6, and S7 shows the calculated secondary wastes, energy consumptions, products, and reagent consumptions in solvent-extraction, ion-exchange, and DDDF processes, respectively. In the DDDF process, 7.268 L of SOCl_2 was recovered (recovery rate: 91.9%). Energy consumptions were calculated by the power of the equipment used and the duration of which was used. The reuse or disposal of the mixed gas was not calculated in the energy consumption part. Secondary wastes produced in these processes only concerns about the extractions, diluents, stripping reagents, and eluents. The washing, regeneration, resin-pretreatment processes were not considered.

Table S6 Calculated energy consumptions in solvent-extraction, ion-exchange, and DDDF processes.

Methods	Processes	Equipment	Power(kW/h)	Time(h)	Work(kW)
Solvent extraction with D2EHPA	H ₂ SO ₄ leaching	Stirring hotplate×2	1.2	2	4.8
	pH adjustment	Stirring×2	1	0.5	1
	Extraction (twice)	Water bath shaker×40	2	0.2	16
	Stripping (twice)	Water bath shaker×40	2	0.2	16
Solvent extraction with TBP	HCl leaching	Stirring hotplate×2	1.2	2	4.8
	pH adjustment	Stirring×2	1	0.2	1
	Extraction (once)	Water bath shaker×40	2	0.2	16
Ion-exchange with DODGAA-IL	HNO ₃ leaching	Stirring hotplate×2	1.2	2	4.8
	pH adjustment	Stirring×2	1	0.5	1
	Adsorbent synthesis	Water bath shaker×20	2	12	480
		Rotary evaporator×30	1.5	3	135
	Adsorption	Water bath shaker×30	2	0.5	30
	In ³⁺ elution	Peristaltic pump×645	0.02	2	25.8
	Sn ⁴⁺ elution	Peristaltic pump×645	0.02	2	25.8
DDDF	HCl leaching	Stirring hotplate×2	1.2	2	4.8
	Vacuum distillation	Rotary evaporator×5	1.5	2	15
	Dehydration	Mandarin heater×25	0.25	2	12.5
	Fractionation	Mandarin heater×25	0.25	2	12.5
	Vacuum heating	Vacuum oven×1	2	3	6

Table S7 Calculated products in solvent-extraction, ion-exchange, and DDDF processes.

Methods	Solvent extraction with D2EHPA		Solvent extraction with TBP		Ion-exchange with DODGAA-IL		DDDF	
	In ³⁺ in 250L of 1.5M HCl	Sn ⁴⁺ in D2EHPA	In ³⁺ in 1000L of 1M HCl	Sn ⁴⁺ in TBP	In ³⁺ in 130.8L of 2.5M HNO ₃	Sn ⁴⁺ in 130.8L of 5M HNO ₃	Anhydrous InCl ₃	Anhydrous SnCl ₄
Recovery rate (%)	97.4	–	99.3	–	92.2	87.3	99.6	98.6
Purity (%)	99.8	–	96.5	–	96.9	48.9	99.8	99.7

Table S8 Calculated reagent consumption in solvent-extraction, ion-exchange, and DDDF processes.

Methods	Processes	Other reagents	H ₂ O (L)	HCl (L)	H ₂ SO ₄ (L)	HNO ₃ (L)
Solvent extraction with D2EHPA	H ₂ SO ₄ leaching	–	8.37	–	1.63	–
	pH adjustment	–	937.3	–	52.7	–
	Extraction (twice)	D2EHPA: 50L Kerosene: 200L	–	–	–	–
Solvent extraction with TBP	Stripping (twice)	–	218.75	31.25	–	–
	HCl leaching	–	7.5	2.5	–	–
	pH adjustment	–	909.17	80.83	–	–
	Extraction (once)	TBP: 273L Kerosene: 727L	–	–	–	–
Ion-exchange with DODGAA-IL	HNO ₃ leaching	–	7.5	2.5	–	–
	pH adjustment	NaOH: 0.8468 kg	1560	–	–	–
	Adsorbent synthesis	XAF-7 resin: 30.2 kg	–	–	–	–
		DODGAA: 7.55 kg	–	–	–	–
		[C ₄ mim][Tf ₂ N]: 7.55kg Acetone: 151L	–	–	–	–
	Adsorption	–	–	–	–	–
	In ³⁺ elution	–	108.25	–	–	22.55
Sn ⁴⁺ elution	–	85.7	–	–	45.1	
DDDF and handling of HCl and SO ₂ mixed gas	HCl leaching	–	7.5	2.5	–	–
	Vacuum distillation	–	–	–	–	–
	Dehydration	SOCl ₂ : 10L	–	–	–	–
	Fractionation	–	–	–	–	–
	Vacuum heating	–	–	–	–	–
	Reuse and collection	Na ₂ SO ₃ : 10L	16.39	–	–	–
Or disposal with Ca(OH) ₂	Ca(OH) ₂ : 17.45kg	–	–	–	–	