

Supplementary Information

Efficient and sustainable recycling for waste gallium arsenide semiconductors based on triiodide ionic liquids

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Supplementary Text

Text S1 Materials and characterization

Waste GaAs were provided by Alibaba Group Holding Ltd. 1-Iodomethane (98%), 1-iodobutane (99%), 1-iodooctane (98%), 1-iododecane (98%), 1-iodododecane (98%), iodohexadecane (95%) and 1-iodooctadecane (98%) were sourced from Shanghai Titan Co., Ltd. Tri-n-butylphosphine (98%) were purchased from Shanghai Bide Pharmatech Ltd. Iodine (99.8%) and heptane (99%) were purchased from Macklin Co., Ltd. Acetonitrile (97%) and ethyl acetate (99.5%) were obtained from Aladdin Chemical Co., Ltd. All reagents were used directly without further purification.

¹H NMR (Avance 400, Bruker, Germany) and Raman spectra (DXR, 633 nm, Thermo Fischer, USA) were employed to analyze triiodide ILs. The analysis of the viscosity properties, water solubility, and thermal stability of these ILs was conducted through the utilization of the viscometer (DV-2 pro, Brookfield, USA), ICP-MS (NexION 300X, PerkinElmer, USA) and gravimetric analyzer (TGA5500, TA, USA), respectively. Detailed water solubility measurements can be found in Text S2. The characterization of WGASs involved X-ray diffractometer (XRD, Empyrean, Netherlands), scanning electron microscopy, and element mapping (Gemini SEM 300, Zeiss, Germany), respectively. The content of As and Ga in aqua regia-digested IL-WGAS phase was determined by ICP-OES (ICP 5800, Agilent, USA). To investigate the mechanism, thermogravimetric mass spectrometry (TG-MS, thermo plus EVO₂, USA) and UV-vis spectrometer (Lambda 750, PerkinElmer, USA) were

utilized. The valence states of As, Ga and I were identified through X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, USA). The XPS binding energy was calculated based on the C1s peak at 284.8 eV, and the data analysis was performed employing the Avantage software.

Text S2 Synthesis of triiodide ILs

A specific synthetic procedure for the preparation of tributyl(octyl)phosphonium triiodide ($[P_{444,8}][I_3]$) is elucidated as a representative example (Fig. S1). Initially, iodooctane (0.11 mol) and acetonitrile (40 mL) were introduced into a 100 mL three-necked round-bottomed flask, purged with N_2 for 1 h to eliminate O_2 and H_2O . Subsequently, tributylphosphine (0.10 mol) was added dropwise to the flask. The reaction mixture was stirred and heated to 85°C for 24 h. Upon completion of the reaction, heptane (40 mL) was added and rinsed four times to remove any residual phosphine oxide and unreacted iodooctane. Ultimately, the intermediate tributyl(octyl)phosphonium iodide ($[P_{444,8}][I]$) was obtained through acetonitrile evaporation with 96.2% yield.

Triiodide ILs ($[P_{444,n}][I_3]$, $n = 1, 4, 8, 10, 12, 16, 18$) were prepared following the methodology illustrated in Fig. 1b. The synthesis of the deep purple $[P_{444,n}][I_3]$ involved the combination of $[P_{444,8}][I]$ and I_2 with a 1:1 molar ratio. And the mixture was stirred at 60°C for 2 h under dark atmosphere. And remaining six triiodide ILs with distinct chain lengths were synthesized using identical procedures as those for $[P_{444,8}][I_3]$. The triiodide ILs obtained were utilized without further post-treatment.

The specific ^1H NMR characterization was found in Text S3, Fig. 1d, S2 and S4.

Text S3 ^1H NMR of $[\text{P}_{444,n}]\text{I}$ and $[\text{P}_{444,n}][\text{I}_3]$

(1) $[\text{P}_{444,n}]\text{I}$ ($n = 1, 4, 8, 10, 12, 16, 18$)

We synthesized seven types of monoiodo-quaternary phosphonium-based ILs $[\text{P}_{444,n}]\text{I}$ ($n = 1, 4, 8, 10, 12, 16, 18$) with yields of 76.94%, 58.58%, 96.22%, 54.20%, 83.57%, 82.87%, and 77.03%, respectively. The ^1H NMR spectra of $[\text{P}_{444,n}]\text{I}$ ($n = 1, 4, 8, 10, 12, 16, 18$) are shown in Figure S2, with specific details shown below:

$[\text{P}_{444,1}]\text{I}$: (400 MHz, CDCl_3 , ppm): $\delta=2.45$ (m, 9 H, 3 CH_2 , CH_3), 1.53 (m, 12 H, 6 CH_2), 0.96 (m, 9 H, 3 CH_3).

$[\text{P}_{444,4}]\text{I}$: (400 MHz, CDCl_3 , ppm): $\delta=2.37$ (m, 8 H, 4 CH_2), 1.49 (m, 16 H, 8 CH_2), 0.93 (m, 12 H, 4 CH_3).

$[\text{P}_{444,8}]\text{I}$: (400 MHz, CDCl_3 , ppm): $\delta=2.42$ (m, 8 H, 4 CH_2), 1.54 (m, 16 H, 8 CH_2), 1.27 (m, 8 H, 4 CH_2), 0.98 (m, 9 H, 3 CH_3), 0.86 (m, 3 H, CH_3).

$[\text{P}_{444,10}]\text{I}$: (400 MHz, CDCl_3 , ppm): $\delta=2.37$ (m, 8 H, 4 CH_2), 1.50 (m, 16 H, 8 CH_2), 1.20 (m, 12 H, 6 CH_2), 0.91 (m, 9 H, 3 CH_3), 0.80 (m, 3 H, CH_3).

$[\text{P}_{444,12}]\text{I}$: (400 MHz, CDCl_3 , ppm): $\delta=2.01$ (m, 8 H, 4 CH_2), 1.12 (m, 16 H, 8 CH_2), 0.81 (m, 16 H, 8 CH_2), 0.53 (m, 9 H, 3 CH_3), 0.42 (m, 3 H, CH_3).

$[\text{P}_{444,16}]\text{I}$: (400 MHz, CDCl_3 , ppm): $\delta=2.43$ (m, 8 H, 4 CH_2), 1.55 (m, 16 H, 8 CH_2), 1.25 (m, 24 H, 12 CH_2), 0.98 (m, 9 H, 3 CH_3), 0.87 (m, 3 H, CH_3).

$[\text{P}_{444,18}]\text{I}$: (400 MHz, CDCl_3 , ppm): $\delta=2.45$ (m, 8 H, 4 CH_2), 1.56 (m, 16 H, 8 CH_2), 1.26 (m, 28 H, 14 CH_2), 0.99 (m, 9 H, 3 CH_3), 0.88 (m, 3 H, CH_3).

(2) $[P_{444,n}][I_3]$ ($n = 1, 4, 8, 10, 12, 16, 18$)

The 1H NMR spectra of $[P_{444,n}][I_3]$ ($n = 1, 4, 8, 10, 12, 16, 18$) were shown in Figure 1d and S3, with specific details provided as follows:

$[P_{444,1}][I_3]$: (400 MHz, $CDCl_3$, ppm): $\delta=2.32$ (m, 9 H, 3 CH_2 , CH_3), 1.63 (m, 12 H, 6 CH_2), 1.05 (m, 9 H, 3 CH_3).

$[P_{444,4}][I_3]$: (400 MHz, $CDCl_3$, ppm): $\delta=2.29$ (m, 8 H, 4 CH_2), 1.64 (m, 16 H, 8 CH_2), 1.06 (m, 12 H, 4 CH_3).

$[P_{444,8}][I_3]$: (400 MHz, $CDCl_3$, ppm): $\delta=2.29$ (m, 8 H, 4 CH_2), 1.62 (m, 16 H, 8 CH_2), 1.34 (m, 8 H, 4 CH_2), 1.05 (m, 9 H, 3 CH_3), 0.89 (m, 3 H, CH_3).

$[P_{444,10}][I_3]$: (400 MHz, $CDCl_3$, ppm): $\delta=2.27$ (m, 8 H, 4 CH_2), 1.62 (m, 16 H, 8 CH_2), 1.31 (m, 12 H, 6 CH_2), 1.05 (m, 9 H, 3 CH_3), 0.88 (m, 3 H, CH_3).

$[P_{444,12}][I_3]$: (400 MHz, $CDCl_3$): $\delta=2.28$ (m, 8 H, 4 CH_2), 1.62 (m, 16 H, 8 CH_2), 1.31 (m, 16 H, 8 CH_2), 1.05 (m, 9 H, 3 CH_3), 0.89 (m, 3 H, CH_3).

$[P_{444,16}][I_3]$: (400 MHz, $CDCl_3$, ppm): $\delta=2.28$ (m, 8 H, 4 CH_2), 1.62 (m, 16 H, 8 CH_2), 1.27 (m, 24 H, 12 CH_2), 1.05 (m, 9 H, 3 CH_3), 0.89 (m, 3 H, CH_3).

$[P_{444,18}][I_3]$: (400 MHz, $CDCl_3$, ppm): $\delta=2.27$ (m, 8 H, 4 CH_2), 1.60 (m, 16 H, 8 CH_2), 1.26 (m, 28 H, 14 CH_2), 1.04 (m, 9 H, 3 CH_3), 0.88 (m, 3 H, CH_3).

Text S4 The viscosity of triiodide ILs

The viscosity of $[P_{444,n}][I_3]$ ($n = 8, 10, 12, 16$) was measured across a temperature range of 273-333K, and the data were fitted using the Arrhenius model (Equation (S1)).

$$\eta = \eta_0 \exp\left(-\frac{E_a}{RT}\right) \quad (\text{S1})$$

where η_0 (cP) represents the viscosity at infinite temperature. E_a is the activation energy. R (8.314 J/(mol·K)) and T (K) refer to the idea gas constant and temperature, respectively.

Figure 1e showed that the Arrhenius model exhibited an excellent non-linear fit to the temperature-viscosity relationship ($R^2 > 0.990$). Thus, the viscosity of triiodide ILs could be accurately predicted at various temperatures using Arrhenius model. Notably, [P_{444,16}][I₃] exhibited solid-state behavior below 40°C due to strengthened intermolecular forces caused by elongated carbon chains, yet it transitioned to a liquid state with small viscosity after heating. Additionally, the investigation revealed a positive relationship between viscosity and carbon chain length among the four triiodide ILs, with the sequence of [P_{444,16}][I₃] > [P_{444,12}][I₃] > [P_{444,10}][I₃] > [P_{444,8}][I₃].

Text S5 Water solubility of triiodide ILs

Based on the content of iodine, the water solubility of triiodide ILs was obtained. The specific method involved mixing 1.0 g of triiodide ILs with 5 mL of water, stirring at 80°C for 2 h, centrifuging, and measuring the content of element iodine in the supernatant by ICP-MS. Then, the water solubility of triiodide ILs was calculated based on the iodine content.

Text S6 Stability analysis of triiodide ILs

The stability of ionic liquids ILs is of particular concern to us. Thermal stability, acid-base stability, long-term placement stability, and the stability after several cycles of usage are all potential stability concerns arising from the recycling process.

(1) Acid-base stability of triiodide ILs

The stability regarding thermal stability and recyclability of ILs has been described in the main text. The acid-base stability of triiodide ILs is of vital importance in the process of recovering waste GaAs, as most stripping experiments may be conducted in acidic or alkaline environments. Perform acid and alkali resistance tests using $[P_{444,8}][I_3]$ as an example. Remarkably, no changes were detected in the Raman and 1H NMR spectra of the $[P_{444,8}][I_3]$ following soaking in 2-4 mol·L⁻¹ HCl or NaOH solutions for 6 h (Fig. S5), indicating their exceptional acid resistance and is suitable for a broad range of acidity and basicity.

(2) The stability of triiodide ILs during long-term storage

In this study, we aim to investigate the stability of triiodide ILs, particularly when it is subjected to prolonged use or storage. Initially, $[P_{444,8}][I_3]$ was subjected to three different storage conditions for evaluation. ① It was kept at 80 °C in an oven for 20 days. Analysis of its 1H NMR and Raman spectra, as illustrated in Fig. S5, revealed no change in its structures. Furthermore, the leaching efficiencies of $[P_{444,8}][I_3]$ on As and Ga from waste GaAs were found to 95.1% and 51.2%, respectively. These results suggest that this particular storage condition does not impact the performance of $[P_{444,8}][I_3]$. ② $[P_{444,8}][I_3]$ was stored at room temperature for a duration of 12 months. Remarkably, both the structure of $[P_{444,8}][I_3]$ and its metal

leaching efficiency remained stable. Based on the aforementioned investigations, it can be concluded that $[P_{444,8}][I_3]$ is a stable triiodide ILs that is this is resistant to the effects of time.

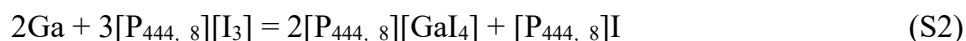
Text S7 FTIR spectra

Comparison of the FTIR spectra of $[P_{444,8}][I_3]$ and the $[P_{444,8}][I_3]$ -As product phases in the spectral range of 400-4000 cm^{-1} demonstrated remarkable similarity, as depicted in Fig. S6. This could be because $[P_{444,8}]^+$ is primarily responsible for the peaks in this range (C-H: 2912 cm^{-1} ; C-P: 1096 cm^{-1}), yet is not involved in the reaction.

Text S8 Leaching mechanism of Ga

As observed in the XPS spectra in Figure S5, the peak belonged to Ga^{3+} (20.5 eV). The valence of Ga changed from 0 to +3, while the I in $[P_{444,8}][I_3]$ was reduced from 0 to -1. The variations in oxidation states demonstrated the occurrence redox reactions. To investigate the by-products, UV-vis spectra study was conducted. As shown in Figure S6, the characteristic peaks at 291.3 and 359.7 nm were attributed to $[P_{444,8}][I_3]$, while the characteristic peaks of $[P_{444,8}]I$ were located at 210.8 and 244.7 nm. Upon introducing elemental Ga into the IL phase (S/L ratio of 120 g/kg), the peak of $[P_{444,8}][I_3]$ significantly decreased, whereas the peak of $[P_{444,8}]I$ noticeably increased, indicating the continuous consumption of $[P_{444,8}][I_3]$ during the leaching process leading to the generation of $[P_{444,8}]I$. Based on the aforementioned study, the

leaching mechanism of Ga was proven as illustrated in Equations S1 and S2.



Simplifying the equation yields:



Text S9 Life Cycle Assessment

The environmental impact of recycling WGASs with $[\text{P}_{444,8}][\text{I}_3]$ was analyzed using the Life Cycle Assessment (LCA) approach. LCA is a systematic tool used to determine the environmental impacts of a product or process throughout its entire life cycle or part of its life cycle (ISO 14040, ISO 14044). Utilizing Simapro software (version 9.3) and the Ecoinvent database to construct a life cycle environmental impact model. The recovery procedure consisted of three major stages: (1) synthesis of $[\text{P}_{444,8}][\text{I}_3]$, (2) leaching of WGASs, and (3) stripping to obtain the products. The functional unit for the recovery process was set at 1.0 kg of WGASs. The life cycle inventory (LCI) was obtained by collecting inventory data on laboratory logs, analyzing processes, and material energy balances. The relevant results of the evaluation were presented in Tables S4 and S5.

Text S10 The details of economic feasibility

(1) Costs

Using optimized leaching conditions, 33.3 kg of triiodide ionic liquids (ILs) were needed to recover 1.0 kg of GaAs. Notably, the triiodide ILs can undergo six cycles of

recycling, thereby reducing the actual ILs needed to 5.55 kg. Additionally, labor costs are determined at 20.6 USD per day in adherence to local standards. The recycling process for 1.0 kg of waste GaAs involves two workers over a span of four days. And the electricity cost is set at 0.13 USD/kWh. Further cost breakdown is available in Table S7.

(2) Benefits

The end products derived from the recycling of waste GaAs consist of As_2O_3 , Ga^{3+} solution, and Ga residue (Table S8). The market value of As_2O_3 is directly influenced by its various applications. With a purity exceeding 99.9%, recycled As_2O_3 can be utilized in the pharmaceutical field. Its transformation into an injectable formulation for cancer therapy significantly elevates the market price of As_2O_3 compared to its conventional industrial uses. In this study, the price of As_2O_3 is determined to be 1.37 USD/g based on the raw materials of injectable formulations used for cancer treatment.

Additionally, the value of a 1 L solution with a concentration of 1 g/L of Ga^{3+} is 137.17 USD, which is determined by the average market selling price. Specifically, the selling prices for a 1g/L Ga^{3+} solution are recorded at 156.4 USD by Shanghai Macklin Co., Ltd, 163.9 USD by Beijing MREDA Technology Co., Ltd, and 91.2 USD by Alibaba Group Holding Ltd. Upon computing the average price of these aforementioned items, the composite value stands at 137.17 USD per 1 L of Ga^{3+} solution with a concentration of 1 g/L.

The Ga residue exhibits a purity of 95.6%, a value inferior to that found in

commercially accessible elemental Ga at 99.9%. Consequently, pricing is determined at 80% of the elemental Ga value. Elemental Ga is obtainable from Macklin Co., Ltd, Mayer Biochemical Technology Co., Ltd and Alibaba Group Holding Ltd at prices of 3.14 USD/g, 2.94 and 2.43 USD/g, yielding an average price of 2.27 USD/g at 80% of the elemental Ga value.

(3) Profits

The profit from recycling 1.0 kg of waste GaAs is computed according to the Equation S4.

$$\text{Profits} = \text{Total costs} - \text{Total benefits} \quad (\text{S4})$$

Supplementary Figures

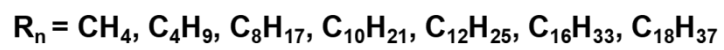
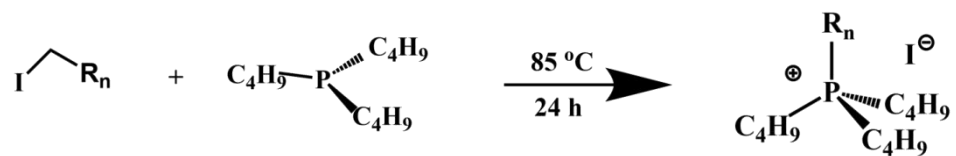


Fig. S1 The synthesis process of $[\text{P}_{444,n}]\text{I}$ ($n=1, 4, 8, 10, 12, 16, 18$).

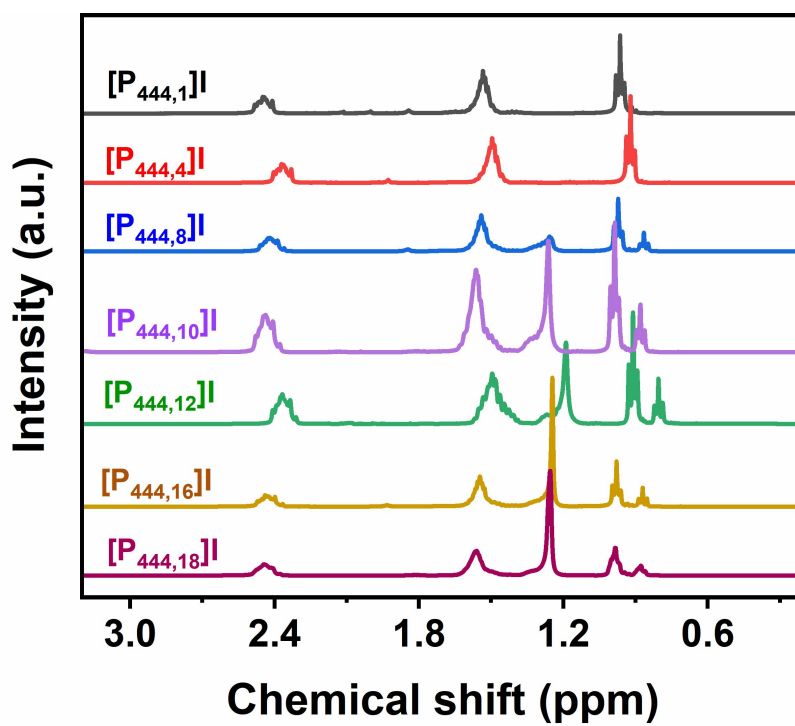


Fig. S2 ¹H NMR spectra of [P_{444,n}]I ($n = 1, 4, 8, 10, 12, 16, 18$).

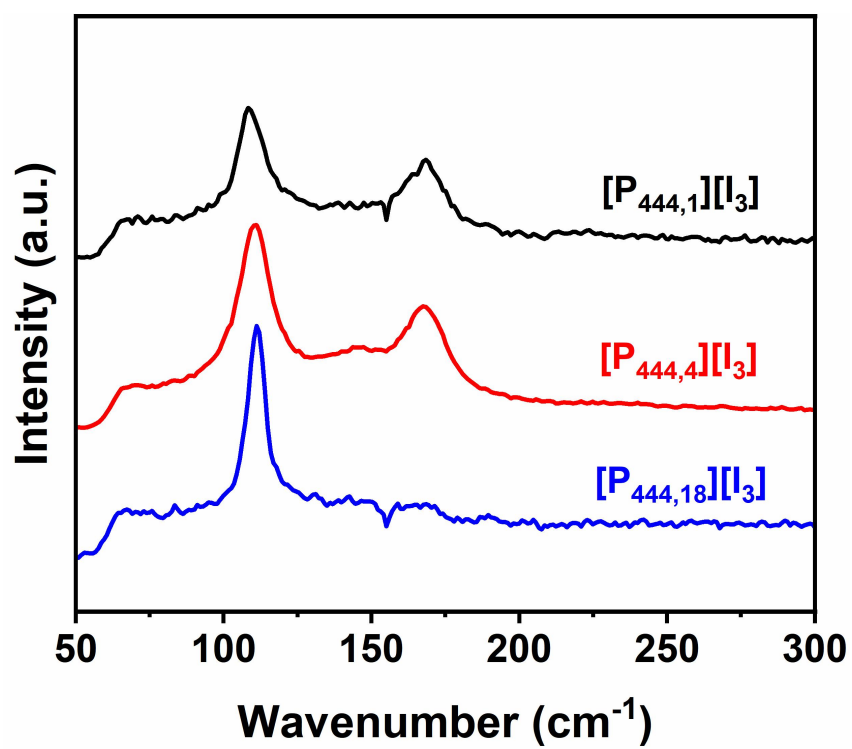


Fig. S3 Raman spectra of $[P_{444,n}][I_3]$ ($n=1, 4, 18$).

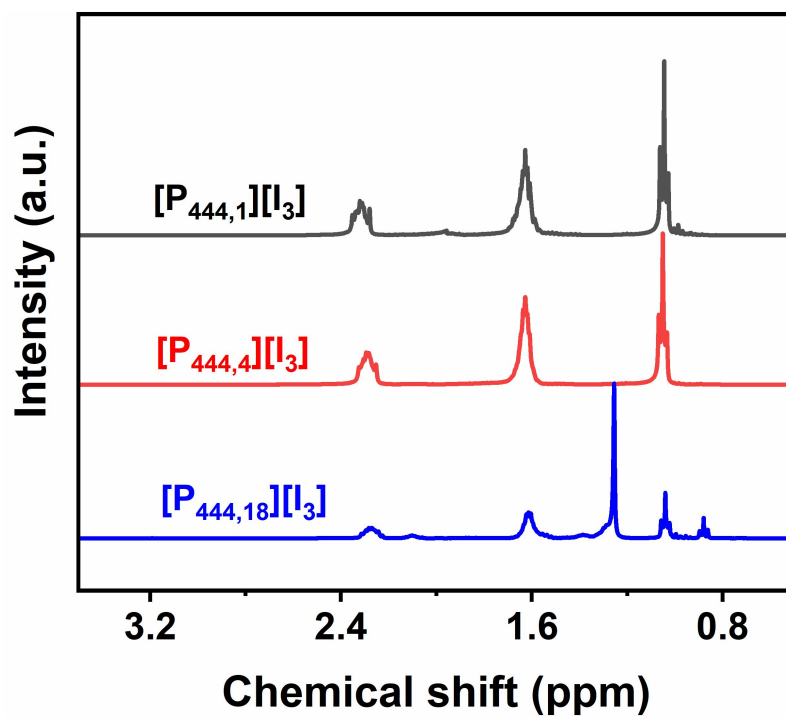


Fig. S4 ¹H NMR spectra of [P_{444,n}][I₃] (*n* = 1, 4, 18).

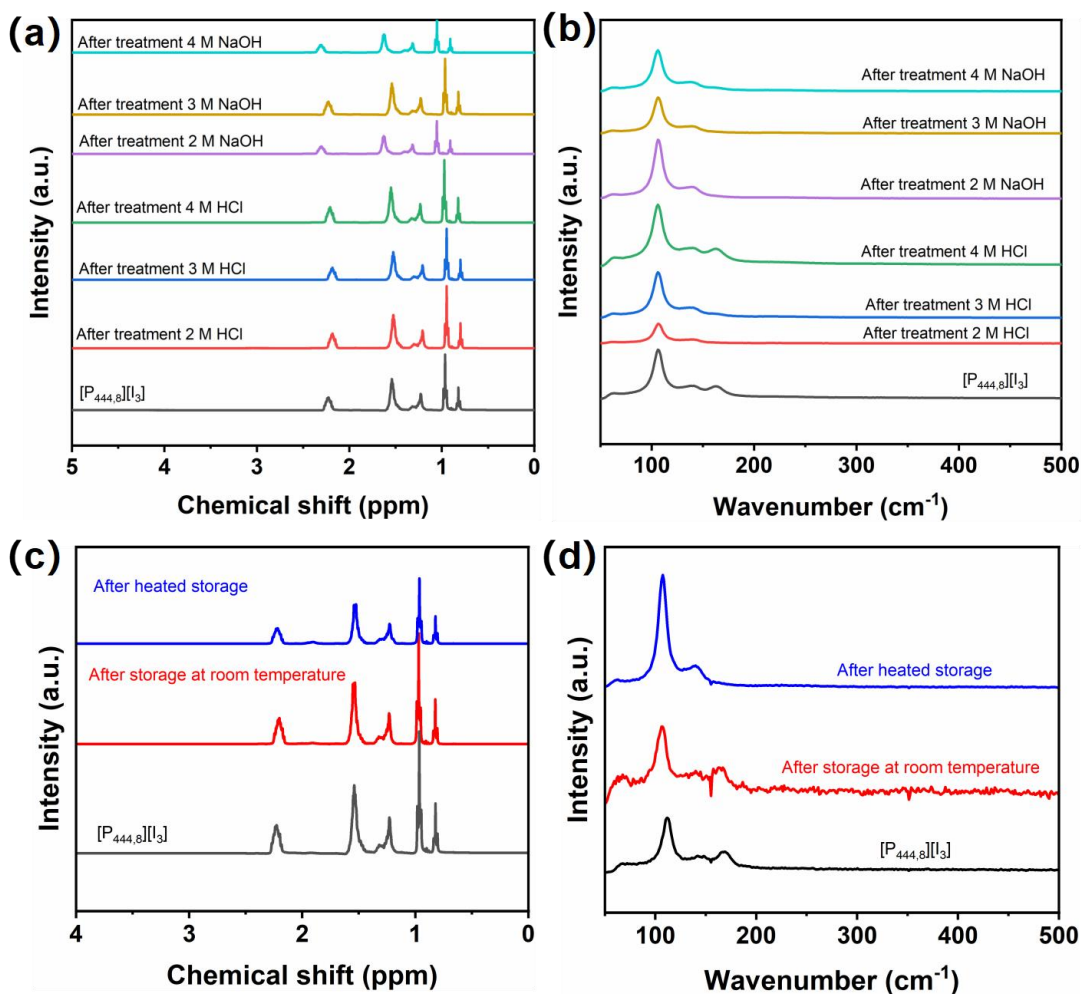


Fig. S5 Acid-base resistance test of [P_{444,8}][I₃]: (a) Raman and (b) ¹H NMR spectra of [P_{444,8}][I₃] at various acid (2-4 mol·L⁻¹ HCl) and (2-4 mol·L⁻¹ NaOH) conditions. Stability of storage: (c) Raman and (d) ¹H NMR spectra of [P_{444,8}][I₃] at various storage conditions. Condition 1: Oven storage at 80 °C for 20 days. Condition 2: Storage at room temperature for 12 months.

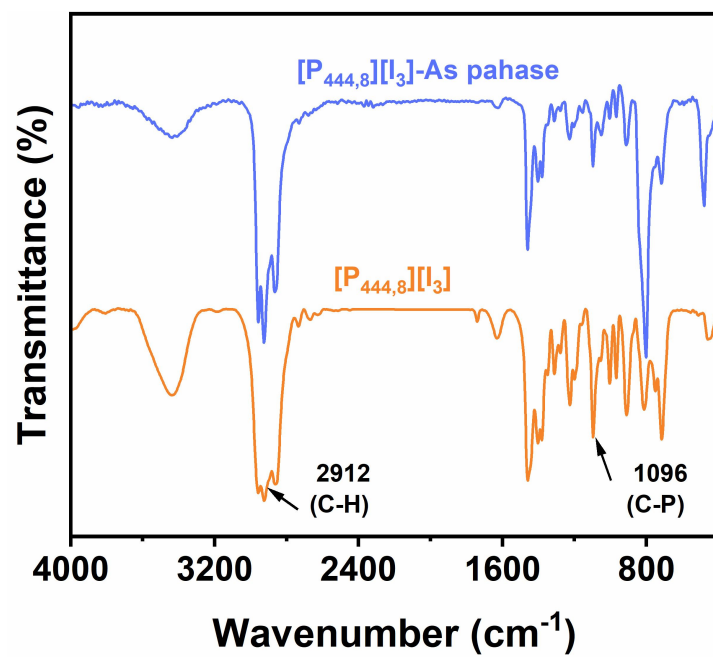


Fig. S6 FTIR spectra of [P_{444,8}][I₃] and [P_{444,8}][I₃]-As phase in the range of 400-4000 cm⁻¹.

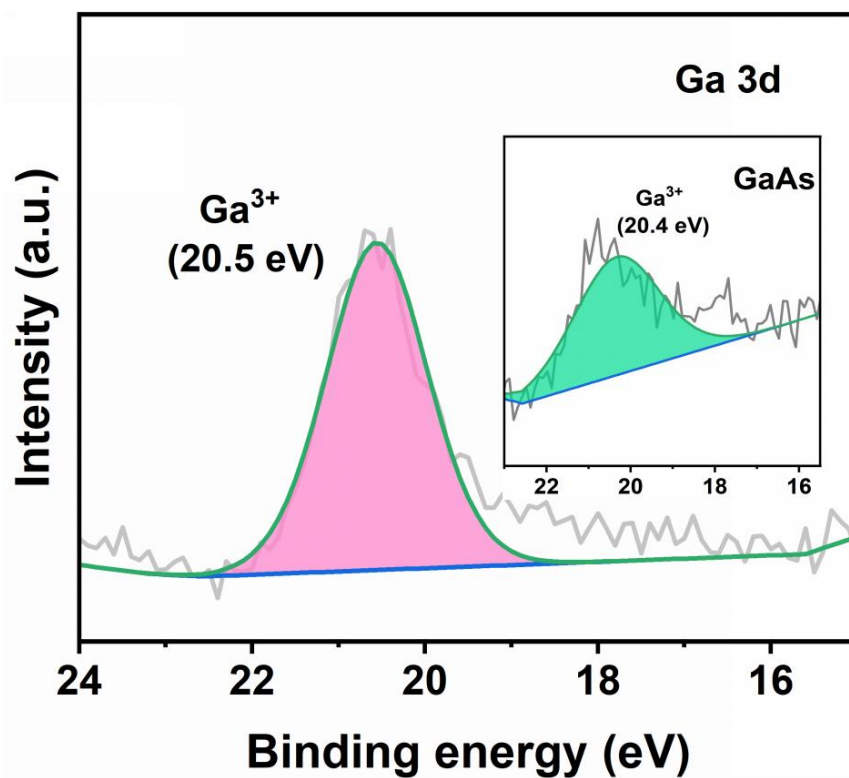


Fig. S7 XPS spectra of Ga 3d after leaching of Ga particles and waste GaAs by triiodide ionic liquids.

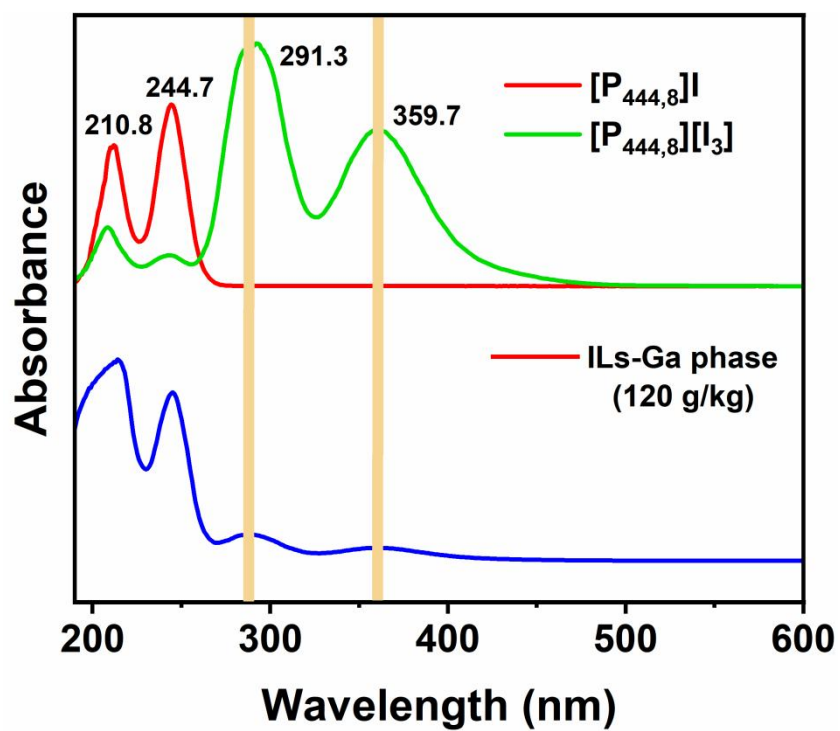


Fig. S8 UV-vis spectra of $[P_{444,8}]I$, $[P_{444,8}][I_3]$, $[P_{444,8}][I_3]$ -Ga phase (S/L=120 g/kg).

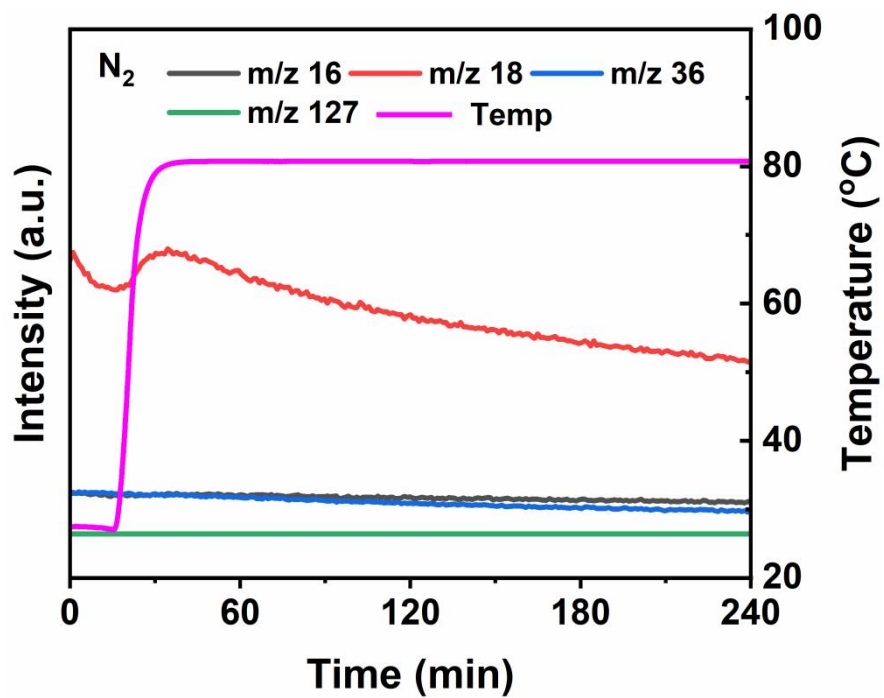


Fig. S9 Thermogravimetric analysis along with mass spectra data (TG-MS) of [P_{444,8}][I₃] under N₂ atmosphere.

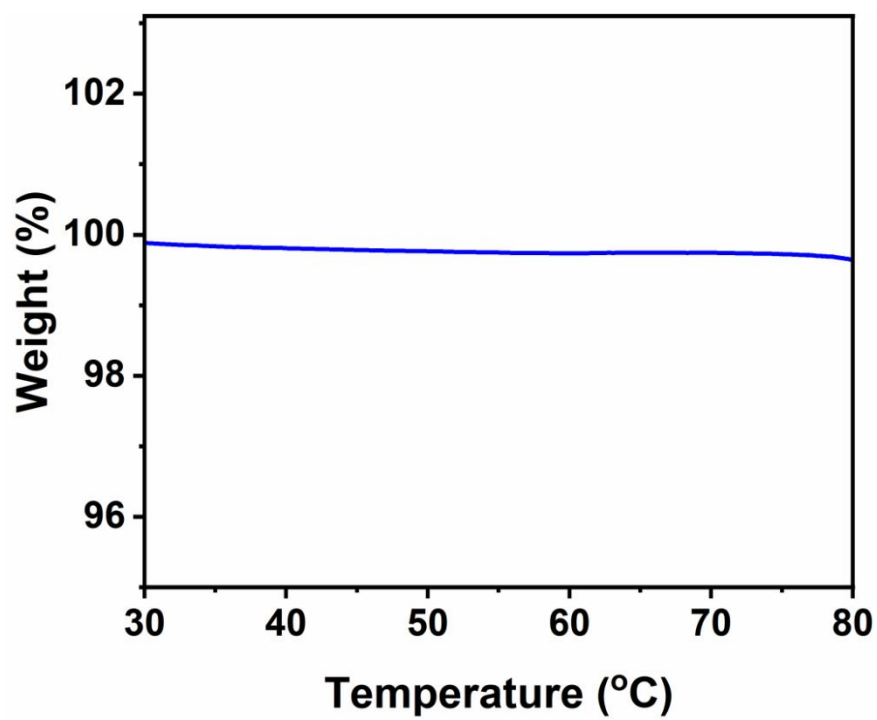


Fig. S10 Thermogravimetric analysis of [P_{444,8}][I₃].

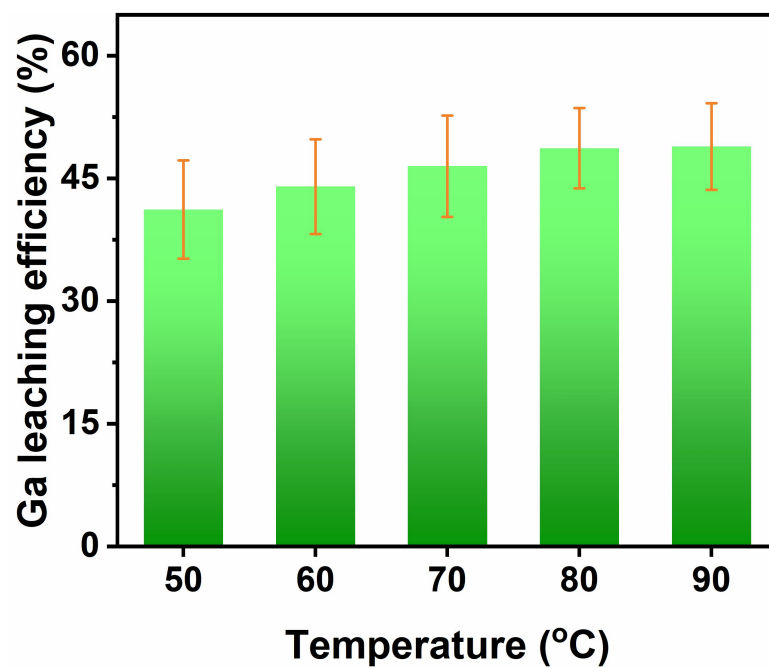


Fig. S11 The impact of treating waste GaAs with 1.0 mol/L HCl at different temperatures on the leaching efficiency of Ga.

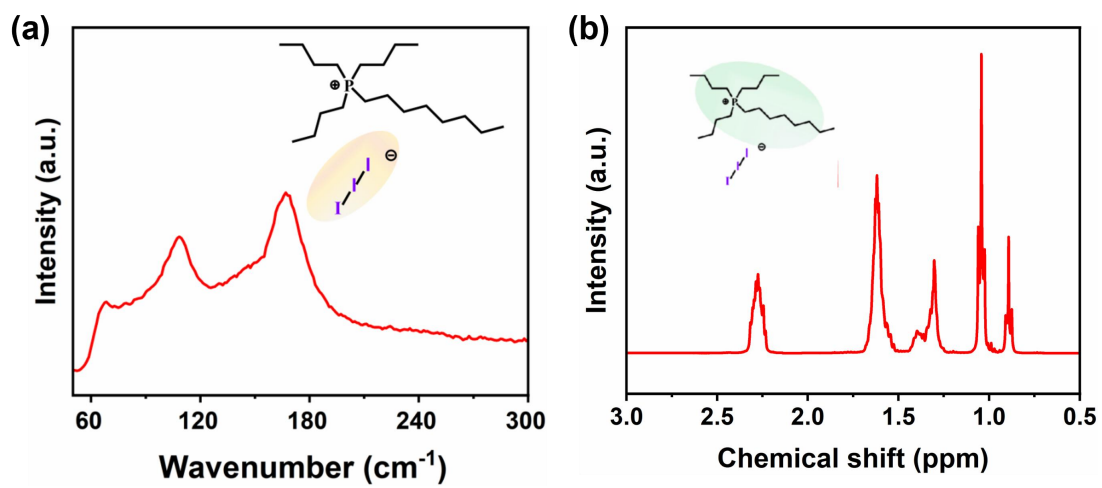


Fig. S12 (a) Raman and (b) ¹H NMR spectra of [P_{444,8}][I₃] after 6 cycles.

Supplementary Tables

Table S1 Comparison of current Ga and As recycling technologies.

Waste materials	Leaching agents	Condition	As recovery efficiency (%)	Ga recovery efficiency (%)	Processing capacity (g/L)	h_o (g/(L·h))	References
Waste GaAs	2 M HNO ₃ , Diaion CR-11	30 °C, 1 h	98	98	20	20	27
Waste GaAs	33.3 g/L NaOH, H ₂ O ₂	150 rpm, 1 h	-	90.46	25	25	32
Waste light emitting diode	Acidithiobacillus ferrooxidans, Fe ³⁺	mineral salt solutions, 29 °C, 15 days	-	84	20	0.02	11
Waste light emitting diode	subcritical water, 3% H ₂ O ₂	300 °C, 300 r/min, 6.7 h	98.4	80.5	10	1.49	28
Waste light emitting diode	4 M HCl	1100 °C oxidation, HCl, 93°C, 2 h	-	91.4	3	1.5	29
Waste light emitting diode	Siderophore desferrioxamine E	pH 4, 14 days	-	12	5	0.03	30
Waste light emitting diode	Acidithiobacillus ferrooxidans	18 days	-	60	20	0.046	31
Waste GaAs	This work	80 °C, 4 h	94.1	97.1	30	7.5	/

Table S2 Fukui indices for electrophilic attack (Fukui (-)) of $[P_{444,n}][I_3]$ ($n = 8, 10, 12, 16$).

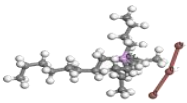
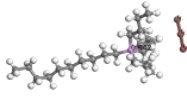
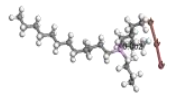
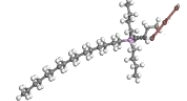
Triiodide IIs	Fukui(-)		
	0.227	0.140	0.243
	0.310	0.204	0.342
	0.209	0.129	0.217
	0.358	0.260	0.241

Table S3 Obtained parameters from three control models for As and Ga leaching.

Samples	Temperature (°C)	Interfacial chemistry-controlled		Diffusion-controlled		Mixed-controlled	
		R^2	k_1	R^2	k_2	R^2	k_3
As	60	0.971	0.0212	0.960	0.0216	0.945	0.0073
	70	0.994	0.0258	0.992	0.0270	0.972	0.0105
	80	0.996	0.0337	0.988	0.0383	0.948	0.0178
	90	0.984	0.0386	0.977	0.0465	0.947	0.0248
Ga	60	0.957	0.0010	0.987	0.0003	0.990	0.00006
	70	0.976	0.0013	0.998	0.0004	0.998	0.00009
	80	0.988	0.0014	0.990	0.0006	0.986	0.0001
	90	0.956	0.0016	0.986	0.0007	0.990	0.0002

Table S4 Types of oxides and the proportions of various oxides

Compound	Content
As ₂ O ₃	49.754
Ga ₂ O ₃	49.696
Al ₂ O ₃	0.267
SiO ₂	0.218
SO ₃	0.065

Table S5: Life cycle inventory for recycling 1.0 kg WGASs.

Items	Items	Amount	Unit	Corresponding LCI	Database	Comment
Input	Synthesis of [P _{444,8}]I					
	Iodoctane	2.54	kg	Self-built model products		/
	tri-n-butyl phosphine	1.95	kg	Self-built model products		/
	N ₂	0.78	kg	Nitrogen fertiliser, as N {GLO} market for Cut-off, U	Ecoinvent 3	
	Acetonitrile	4.49	kg	Acetonitrile {GLO} market for Cut-off, U	Ecoinvent 3	
	Heptane	13.47	kg	Heptane {GLO} market for Cut-off, U	Ecoinvent 3	
	Electricity I	4.80	kW·h	Electricity, low voltage {CN} market group for Cut-off, U	Ecoinvent 3	
	Synthesis of [P _{444,8}][I ₃]					Actual consumption
	I ₂	2.35	kg	Iodine {GLO} market for Cut-off, U	Ecoinvent 3	
	Electricity II	1.20	kW·h	Electricity, low voltage {CN} market group for Cut-off, U	Ecoinvent 3	
	Grinding and Leaching					
	Electricity III	2.00	kW·h	Electricity, low voltage {CN} market group for Cut-off, U	Ecoinvent 3	
	Electricity IV	2.40	kW·h	Electricity, low voltage {CN} market group for Cut-off, U	Ecoinvent 3	
	Stripping					
	Ethyl acetate	11.11	kg	Ethyl acetate {GLO} market for Cut-off, U	Ecoinvent 3	Cycle 6 times, average dosage per
	Water	33.33	L	Water, cooling, surface	Ecoinvent 3	
	Electricity V	1.20	kW·h	Electricity, low voltage {CN} market group for Cut-off, U	Ecoinvent 3	
[P _{444,8}][I ₃] regeneration						
Electricity VI	1.2	kW·h	Electricity, low voltage {CN} market group for Cut-off, U	Ecoinvent 3		
Output	As ₂ O ₃	669.24	g	Gallium, semiconductor-grade {GLO} market for Cut-off, U	Ecoinvent 3	Avoided product
	Ga ³⁺ solution	66.66(251)	L(g)	Gallium, semiconductor-grade {GLO} market for Cut-off, U	Ecoinvent 3	Avoided product
	Remaining Ga	234.0	g	Gallium, semiconductor-grade {GLO} market for Cut-off, U	Ecoinvent 3	Avoided product

Table S6 LCA data source for recycling 1.0 kg GaAs semiconductor.

Impact category	GGE	SOD	IR	FPMF	ME	TE	FE	HCT	MRS	WC	RC
Unit	kg CO ₂ eq	kg CFC11 eq	kBq Co-60 eq	kg PM2.5 eq	kg N eq	kg 1,4-DC B	kg 1,4-DC B	kg 1,4-DC B	kg Cu eq	m ³	kg ore
Synthesis of [P _{444.8}][I ₃]	95.704	6.337E-05	2.943	0.034	0.021	109.721	2.515	0.022	20.450	0.803	63.829
Leaching	6.088	6.705E-07	0.074	0.002	5.832E-05	2.535	0.163	0.0007	0.003	0.012362098	0.967
Stripping Ga	5.627	6.196E-07	0.068	0.002	5.390E-05	2.343	0.151	0.0006	0.002	0.126	1.008
Stripping As	39.018	9.315E-06	1.110	0.013	0.0006	51.634	1.222	0.010	0.084	0.489	17.572
Regeneration	1.637	1.803E-07	0.020	0.0007	1.568E-05	0.682	0.044	0.0002	0.0007	0.003	0.260
As ₂ O ₃	-138.248	-5.234E-05	-3.958	-0.045	-0.062	-137.496	-3.364	-0.843	-76.894	-1.227	-112.938
Ga ³⁺ solution	-37.069	-1.403E-05	-1.061	-0.012	-0.017	-36.868	-0.902	-0.225	-20.618	-0.329	-30.283
Residual Ga	-64.771	-2.452E-05	-1.854	-0.021	-0.029	-64.419	-1.576	-0.394	-36.026	-0.575	-52.913
Total	-92.012	-1.674E-05	-2.657	-0.024	-0.086	-71.867	-1.746	-1.429	-112.999	-0.697	-112.499

Table S7 Costs of recycling 1.0 kg waste GaAs under optimal conditions (30 g/kg, 4 h, 80°C).

Entries	Unit prices (USD/kg)	Amounts (kg)	Costs (USD)	Total costs (USD)
Spent raw materials	80.0	1.0	80.0	
Iodoctane	164.6	2.54*	418.0*	
Acetonitrile	5.5	4.5*	24.8*	
tri-n-butyl phosphine	274.4	1.95*	535.1*	
N ₂	0.34 USD/L	4.1* L	1.4*	2246.8
Heptane	14.2	13.5*	191.4*	
I ₂	336.9	2.35*	791.7*	
Ethyl acetate	2.74	11.1	30.5	
Water	0.00045	66.7	0.03	
Energy	0.13	70 h	9.1	
Labour	20.6	8	164.8	

Note *: The reagent costs for synthesizing [P_{444,8}][I₃] were all split by 6 to obtain the numbers above because [P_{444,8}][I₃] could be cycled at least 6 times.

Table S8 Benefits of recycling 1.0 kg waste GaAs under optimal conditions (30 g/kg, 4 h, 80°C).

Products	Unit prices (USD/g)	Amounts (g)	Benefits (USD)	Total benefits (USD)
As ₂ O ₃	1.37	669.2	918.0	
Ga ³⁺ solution	137.17	C=3.76g/L, V=66.7 L	34402.2	35853
Ga residue	2.27	234.0	532.8	