Electronic supplementary information

Green palladium and platinum recovery by microwave-assisted aluminum chloride solution

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Supplementary Texts

Text S1. Hammett Acidity Experiments. UV-vis was used to analyzed the Hammett acidity of different chloride solutions. Indicator 4-nitroaniline (pK_{BH+} =0.99, peak wavelength at 377.5 nm) was dissolved at a concentration of 8.5 mg/L in ethanol (to make an all-alkali-type solution), 98% H_2SO_4 (to prepare an all-proton-type solution), and five chloride solutions. Following complete mixing, the solutions were left to sit at room temperature in the dark for 2 h before UV-vis measured. Proton transfer reaction occurs in the solution between indicator basic type B and its conjugated acid (proton type BH^+):

$$B + H^+ \leftrightarrow BH^+ \quad \text{(S1)}$$

Ion balance defines Hammett acidity as follows:

$$H_0 = pK_{BH^+} - \lg(c_{BH^+})/c_B \quad \text{(S2)}$$

where pK_{BH^+} is the ion equilibrium constant of 4-nitroaniline (0.99), and the indicator's proton-type concentration to its base-type concentration is expressed as c_{BH^+}/c_B. According to Lambert-Beer law, c_{BH^+}/c_B at a fixed wavelength is as follows:

$$(c_{BH^+})/c_B = (A_B^\lambda - A^\lambda)/(A^\lambda - A_{BH^+}^\lambda) \quad \text{(S3)}$$

where A_B^λ is the indicator's all-alkali-type absorbance of the same concentration at a fixed wavelength degree, $A_{BH^+}^\lambda$ is its all-proton-type absorption of the same concentration at the same wavelength degree, and A^λ is the indicator's absorbance in the medium being measured at the same conditions as A_B^λ and $A_{BH^+}^\lambda$.

Text S2. Calculation of Energy Consumption and Chemical Inputs. In the scale-up recovery process of Pd/C catalysts with seven cycles, the total chemicals consumption contained 7.84 g $NaBH_4$ (0.98 g for each cycle), 200 g $AlCl_3 \cdot 6H_2O$ and 200 g H_2O. After 30 min of microwave-assisted leaching at 100 °C, the leachate was reduced by $NaBH_4$. The total mass of leached Pd was calculated as:

$$M = m \sum_{i=0}^{7} D_i \tag{S4}$$

where M represents the total mass of leached Pd, m represents the mass of Pd in the catalysts put into each cycle (g), D_i represent the dissolution ratio in each cycle. The mass of leached Pd was calculated to be 8.648 g.

The total energy consumption contains the electricity utilization during the microwave-assisted leaching. The powder of the microwave reactor is 1800 W. Therefore, the energy consumption during the seven cycles was calculated as

$$\frac{1800\ W \times 1800\ s \times 8}{3600000\ J/kW \cdot h} = 7.2\ kW \cdot h$$

The cost of chemical inputs of 200 g $AlCl_3 \cdot 6H_2O$, 7.84 g NaBH4 (the cost of 200 g H_2O was negligible) could be calculated according to the materials cost in **Table S7** as

$$200\ g \times \frac{\$12.64}{kg} \times 10^{-3} + 7.84 \times \frac{\$780.21}{kg} \times 10^{-3} = \$8.64$$

In total, 0.83 kW·h of energy and $1.00 in material consumption were utilized per gram of Pd leached from spent Pd/C catalysts.

Supplementary Figures

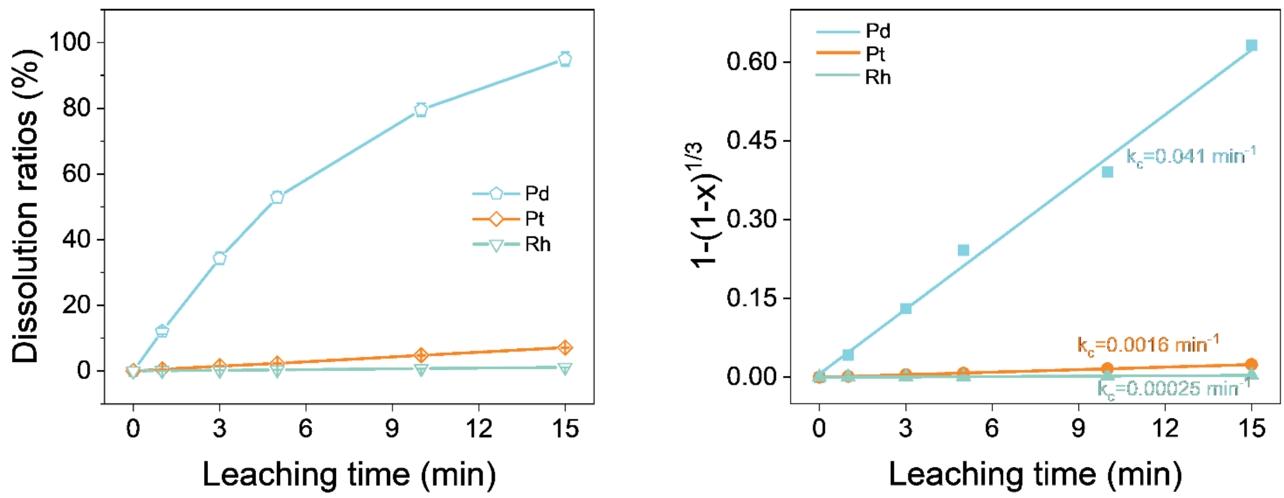

Figure S1. Dissolution ratios and leaching efficiencies of PGMs in $AlCl_3 \cdot 6H_2O$ solution (100 °C).

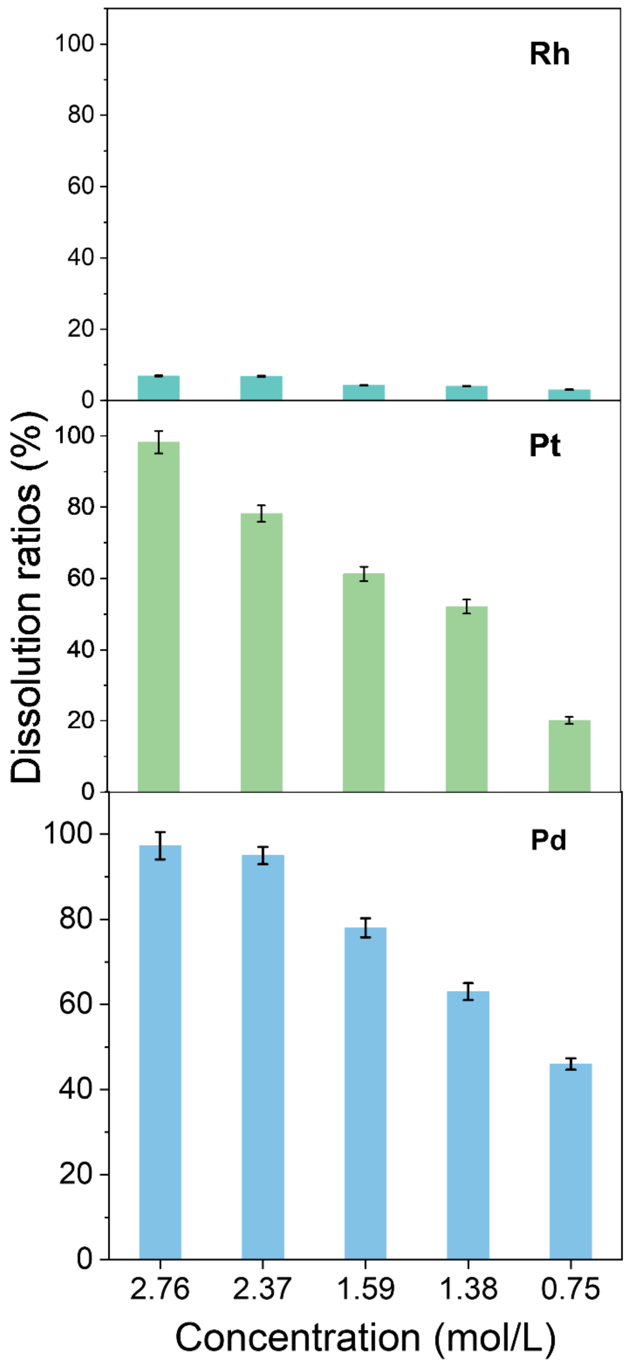

Figure S2. Dissolution ratios of PGMs with varied concentrations of $AlCl_3 \cdot 6H_2O$ solutions (120 °C, 120 min).

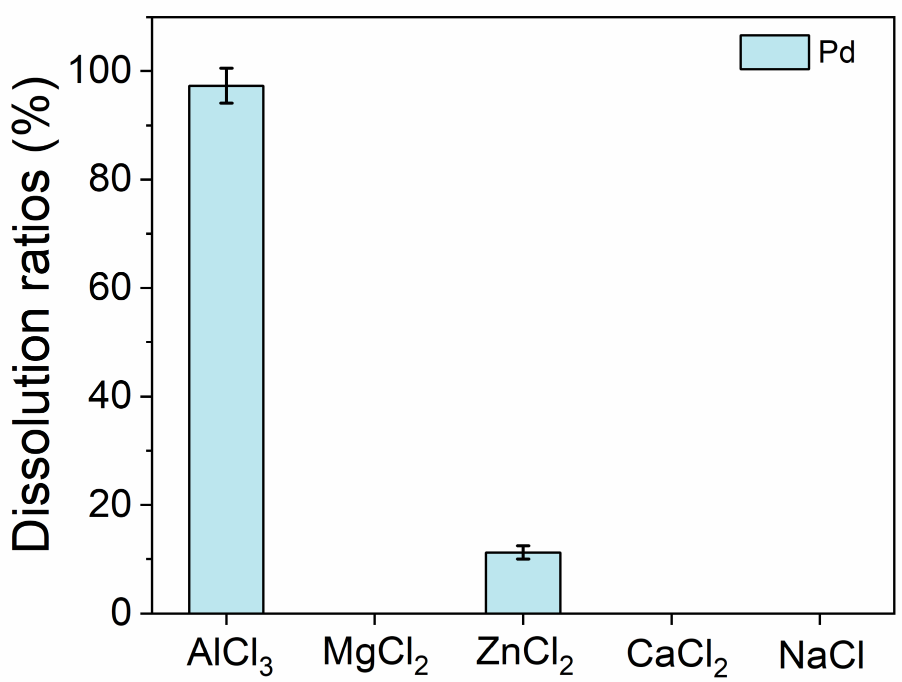

Figure S3. Dissolution ratios of Pd in five chloride salts with microwave-assisted (120 °C, 120 min).

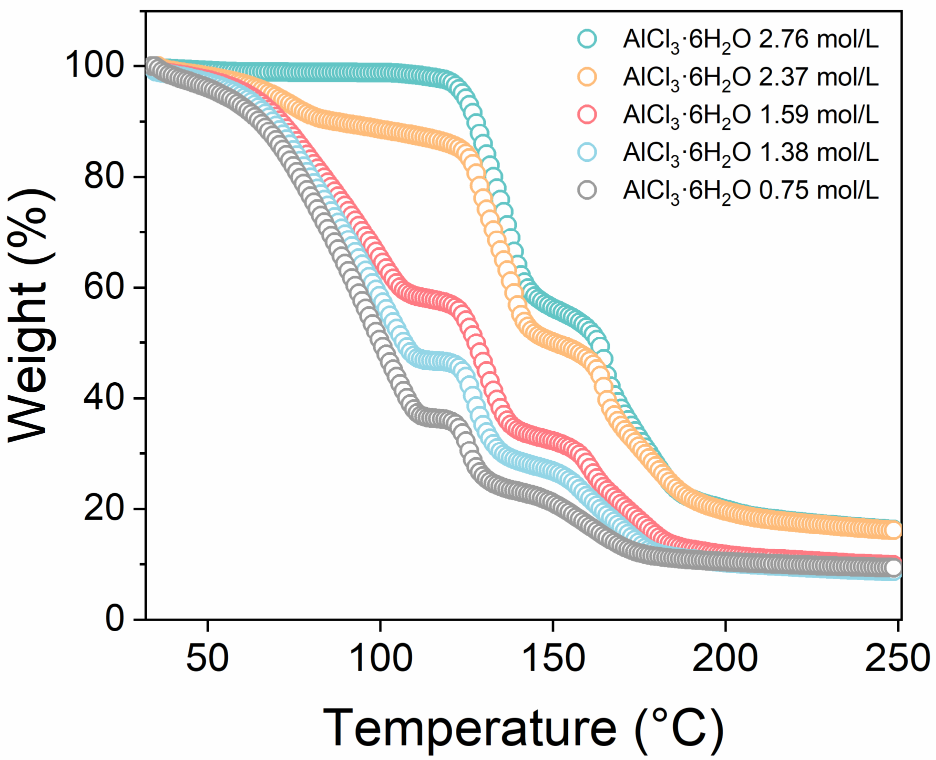

Figure S4. TG curves of $AlCl_3 \cdot 6H_2O$ solutions with different concentrations.

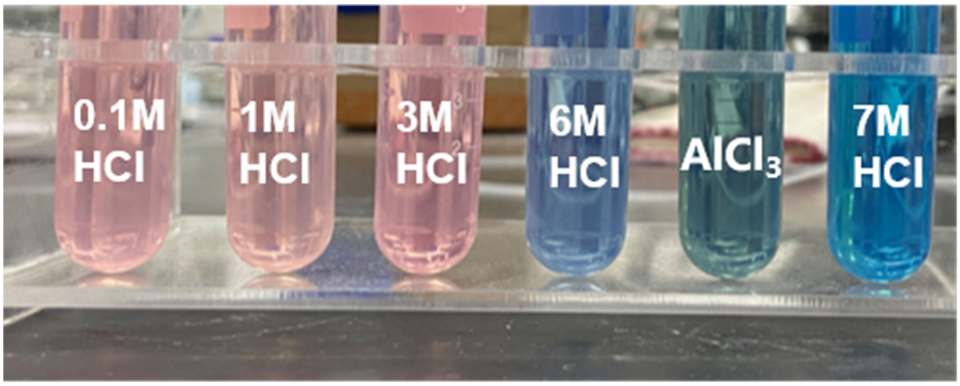

Figure S5. Photo of $CoCl_2$ in HCl and $AlCl_3$ solutions.

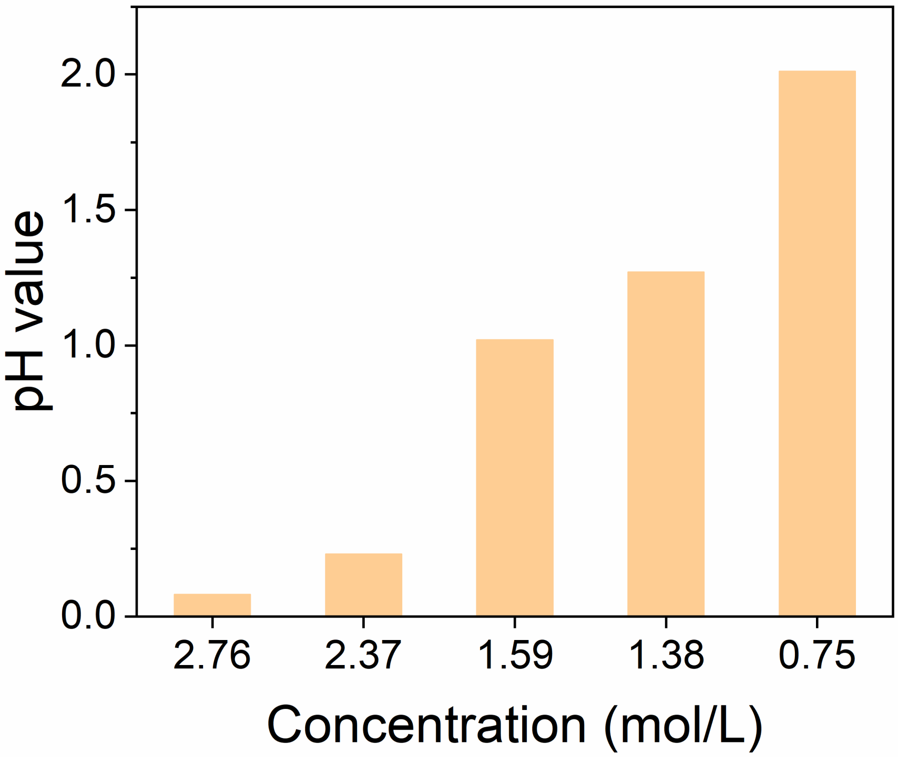

Figure S6. pH values of $AlCl_3$ solutions with varied concentrations.

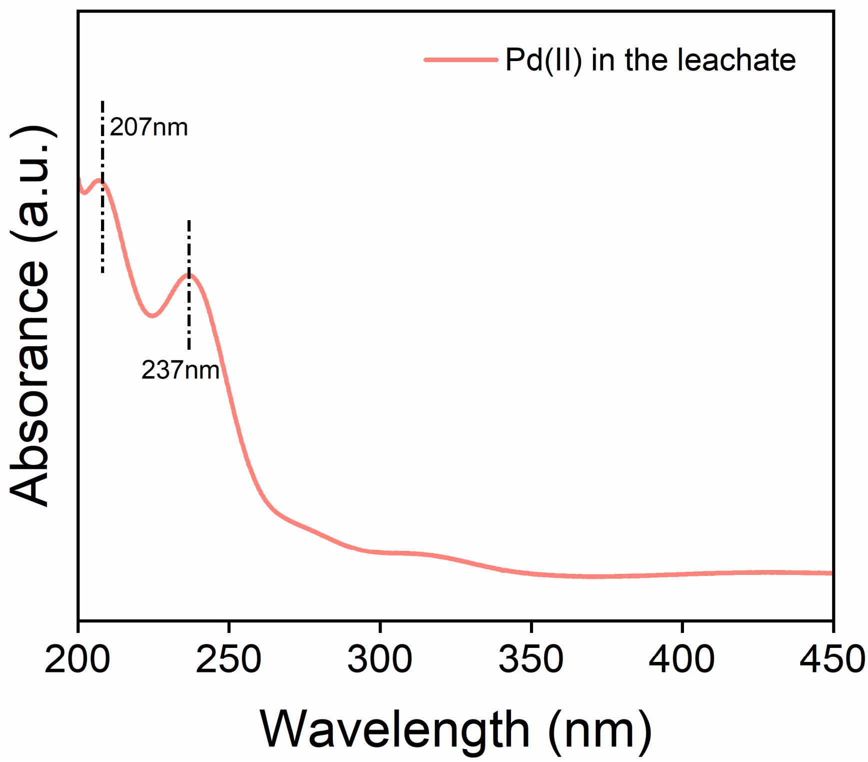

Figure S7. UV-vis spectra of Pd(II) in the leachate.

Supplementary Tables

Table S1. Comparison of this work with other methods in the precious metal recovery reaction reported in literature

Lixiviant	Treatment	PMs	Energy consumption kWh/g PM	Chemicals consumption $/g PM	Secondary waste	Ref.
NaCN/NaOH	leaching (20 °C 24 h)	Au Ag	N/A	56.3	cyanide/NaOH	1
thiourea/$FeCl_3$	leaching (25 °C 2 h)	Au Ag	N/A	32.1	thiourea/$FeCl_3$	2
acetonitrile/Ph_3PCl_2/H_2O_2	leaching (3 min)	Au	N/A	79.2	acetonitrile/ Ph_3PO	3
HCl/H_2O_2	leaching (25 °C 45 min)	Au	N/A	18.9	HCl/Cl_2(aq)	4
I_2/I^-/H_2O_2	leaching (25 °C 4 h)	Au	N/A	18.2	I_2(aq)/I^-	5
H_2SO_4/H_2O_2	leaching (25 °C 4 h)	Au	N/A	21.3	H_2SO_4	6
HCl/Cl_2	leaching (30 °C 90 min 1250 rpm)	Au	69.6	30.7	HCl/Cl_2(aq)	7
DMF/$CuCl_2$/$CaCl_2$	leaching (75 °C 10 min)	Au	35.2	45.6	DMF/Cu^{2+}/ Ca^{2+}/Cl^-	8
CH_3CN/TiO_2	photocatalyst leaching (24 h)	Au Ag	480	45.3	CH_3CN	9
trihexyl(tetradecyl)phosphonium trihalide ionic liquids	leaching (65 °C 24 h 100 rpm)	Au	78.3	88.3	[P_{66614}][Cl_3]	10
NH_4Br/TiO_2	photocatalyst leaching (120 min)	Pd Au	400	15.4	NH_4Br/Br_2(aq)	11
$Al(NO_3)_3$/$AlCl_3$	leaching (80 °C 15 min 350 rpm)	Pd Pt Rh	42.8	21.3	Al^{3+}/NO_3^-/Cl^-	12

$Al(NO_3)_3/NaCl$	leaching (80 °C 180 min 500 rpm)	Pd Au	65.3	22.8	$Al^{3+}/NO_3^{-}/Cl^{-}$	13
$CH_3CN/FeCl_3$	leaching (70 °C 180 min)	Pd Pt Rh	38.2	24.1	$CH_3CN/Fe^{3+}/Cl^{-}$	14
HNO_3/aqua regia	leaching (80 °C 1.5 h)	Pt	35.6	20.4	HNO_3/aqua regia	15
$H_2SO_4/NaCl/NaClO_3$	leaching (40 °C 2 h)	Au	8.9	19.8	$H_2SO_4/Na^{+}/Cl^{-}/ ClO_3^{-}$	16
$(NH_4)_2S_2O_3/CuSO_4$	leaching (25 °C 8 h 250 rpm)	Au	46.2	25.2	sulfer dioxide/ Cu^{2+}/SO_4^{-}	17
$AlCl_3$	Microwave-assisted leaching (100 °C 30 min)	Pd Pt	0.83	1.0	Al^{3+}/Cl^{-}	this work

Table S2. Mass composition in the spent three-way automobile catalyst.

Element	Al	Pd	Pt	Rh	Si
wt%	35.21	1.544	0.101	0.063	10.22

Table S3. The summary of the correction of Gibbs free energy (G_{corr}), delta G and the single point energy (E_{sp}).

Filename	G_{corr} (a.u.)	SP Energy (a.u.)	G (a.u.)	ΔG (a.u.)	ΔG (kcal/mol)
R	0.417239	-1691.336845	-1690.919606		
TS	0.41151	-1691.316885	-1690.905375	0.014231218	8.93023167
P	0.347457	-1691.303596	-1690.956139	-0.036533408	-22.9250787
H_3O+3H_2O	0.070528	-305.5815246	-305.5109966		
$AlOH(H_2O)_5^{2+}$9H2O	0.309456	-1385.691495	-1385.382039		

Table S4. Mass composition of recovered Pd product.

Element	Pd	Pt	Rh	Na	Al	Si	B	Total
wt%	99.1	0.6	0	0	0.3	0	0	100

Table S5. Mass composition of recovered Pt product.

Element	Pt	Pd	Rh	Na	Al	Si	B	Total
wt%	98.8	0.89	0.04	0	0.27	0	0	100

Table S6. Mass composition of recovered Pd product in scale-up experiments (cycle 0).

Element	Pd	C	Al	Na	B	Total
wt%	99.86	0	0.11	0.03	0	100

Table S7. The cost in bulk for leaching reagents.

Method	Material	Source	Cost	Minimum Cost
Microwave-assisted Dissolution	$AlCl_3·6H_2O$	Sigma-Aldrich Co. General Reagent Co. Macklin Biochemical Technology Co.	17.39 $ kg^{-1} 12.64 $ kg^{-1} 13.98 $ kg^{-1}	12.64 $ kg^{-1}
	$NaBH_4$	Adamas Reagent Co. Runjing Chemical Reagent Co. Macklin Biochemical Technology Co.	800.23 $ kg^{-1} 780.21 $ kg^{-1} 813.77 $ kg^{-1}	780.21 $ kg^{-1}
Note: Due to regional variations in personnel costs, operating processes, reagent prices, and environmental expenses, there are certain mistakes in the economic assessment of the dissolution of precious metals.				

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