Supplementary Information

Unlocking Value from Waste: Peroxymonosulfate Oxidation for the Valorization of Precious Metals into High-Value Products

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Supplementary Notes

Supplementary Note 1. Chemicals and materials. All reagents were obtained from commercial sources and used as received without further purification. KCl (AR, FuChen Chemistry), NaCl (AR, FuChen Chemistry), potassium peroxymonosulfate (PMS, 42-46%, $KHSO_5$ basis, Innochem), NaF (AR, MACKLIN), NaBr (AR, MACKLIN), NaI (AR, MACKLIN), NaSCN (AR, Xilong Chemistry), sodium persulfate (PDS, AR, Aladdin), H_2O_2 (≥30%, Beijing Tongguang Reagent), $NaClO{\cdot}5H_2O$ (≥40%, RHAWN Reagent), HCl (≥33%, Beijing Tongguang Reagent), HNO_3 (≥68%, Beijing Tongguang Reagent), Na_2SO_3 (AR, 3AChem), $NaBH_4$ (AR, Xilong Chemistry), absolute ethanol (GR, Beijing Tongguang Reagent), , L-histidine (99%, MACKLIN), MeOH (AR, Fuchen Chemistry), tert-butanol (AR, MACKLIN), p-Benzoquinone (p-BQ, AR, Aladdin), 2,2,6,6-Tetramethylpiperidine (TEMP, GC ≥98%, Aladdin), 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, ≥97%, Aladdin), N-tert-butyl-α-phenylnitrone (PBN, AR, Shanghai Dibai Biotechnology Co., Ltd.), Au foil (99.99%, PtLab), Pt foil (99.99%, PtLab), Pd (99.99%, PtLab), Ir foil (99.99%, PtLab), Ag foil (99.99%, PtLab), Acetonitrile (AR, Fuyu Reagent).

Supplementary Note 2. Characterizations. The morphology and corresponding energy-dispersive X-ray spectroscopy (EDX) and mapping of Au powder and E-waste were examined by field-emission scanning electron microscopy (FESEM, Zeiss SUPRA 55). The crystal structure of the reduction products was examined by X-ray diffraction (XRD, Bruker D8) with Cu Kα radiation (λ = 0.154178 nm). Raman spectra were recorded on a LabRAM ARAMIS Raman spectrometer (HORIBA) with an excitation wavelength of 633 nm. The metal concentration was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Electron paramagnetic resonance (EPR) measurements were performed on a Bruker EMX-500 10/12 spectrometer. UV-visible absorption spectra of the samples were obtained using a UV-vis spectrophotometer (UV-2550, Shimadzu).

Supplementary Note 3. Au dissolution reaction

Comparative gold dissolution experiments were carried out using 0.4 M PDS, H_2O_2, PMS, HClO, and NaCl solutions. Specifically, 2 mg of Au was placed in 0.5 mL of NaCl solution (0.4 M), after which 0.5 mL of PDS, H_2O_2, or PMS solution (0.4 M) was added. The mixture was stirred at 30 °C, and the samples were analyzed after 10 min. The other comparative experiments shown in Fig. 2 were conducted under the same conditions unless otherwise specified.

The dissolution-time curve of the gold foil was obtained under the optimized PMS/Cl^- conditions. The concentrations of PMS and NaCl were 0.4 M and 1.6 M, respectively, in a total solution volume of 1 mL, and the mass of the gold foil was 5.7 mg. Samples were collected every 1 min for analysis.

To evaluate the dissolution performance of the PMS/Cl^- system toward different precious metals, 2 mg of each metal (Au, Pd, Pt, Ag, and Rh) was added to 0.5 mL of NaCl solution (0.4 M). Then, 0.5 mL of PMS solution (0.4 M) was introduced at 30 °C under stirring. After 10 min of reaction, the samples were collected for analysis.

To investigate the effect of different anions on Au dissolution, NaCl was replaced with equimolar NaF, NaBr, NaI, or NaSCN solutions, while all other experimental conditions were kept the same as described above.

For large-scale Au recovery experiments, 6 M HNO_3 was used to remove base metals from waste CPU, and the dissolution of the waste CPU was conducted in a fume hood, followed by filtration. PMS (14.33 g) and KCl (5.97 g) were separately dissolved in 50 mL of deionized water. The two solutions were then combined to prepare the PMS/KCl leaching solution, which was used to leach Au from the pretreated CPU residues. After filtration, purification, and recrystallization, $KAuCl_4$ was obtained. Alternatively, by adding Na_2SO_3 (10 g) into the Au-containing solution, Au powder could be recovered.

Supplementary Note 4. Technoeconomic analysis of the recovery process.

In the recovery process of Au in waste CPUs to **$KAuCl_4$**, the total chemicals consumption contained 14.33 g PMS, 5.97 g KCl, 51.5 ml HNO_3, 150 ml EtOH and 398.5 ml H_2O. The total mass of $KAuCl_4$ was 332.1 mg. The total energy consumption included the electricity consumed during base metal removal, Au leaching, filtration, purification, and recrystallization. A power converter was used to calculate the power of each process. The chemicals involved in techno-economic analysis for recovery was listed in Table S5.

(1) Material costs. The prices of all the raw chemicals and regents were based on the prices on varied regent companies. The purchase price of Waste CPU is \$13.92. The total prices were calculated as:

PMS: \$5.58 / 500 g × 14.33 g = \$0.16

KCl: \$2.37 / 500 g × 5.97 g = \$0.029

HNO_3: \$5.3 / 500 ml × 51.5 ml = \$0.55

EtOH: \$2.37 / 500 ml × 150 ml = \$0.72

H_2O: \$3.63 / 19000 ml × 348.5 ml = \$0.067

Total cost = \$0.16 + \$0.029 + \$0.55 + \$0.72 + \$0.067 + \$13.92 = \$15.464

(2) Consumption costs. Energy consumption costs. The price of electricity in Beijing, China is \$ 0.075 per kWh. The total prices were calculated as:

(Vacuum pump) \$0.075 × 0.06 kW × 3 h + (Oven) \$0.075 × 1.3 kW × 8.667 h + (Heating magnetic stirrer) \$0.075 × 0.6 kW × 5.5 h = \$1.11

(3) Operating costs. Glass reactor, digital hot plate, filtration devices and oven all have a certain service life. By calculating the direct ratio of the use time to the service life and multiplying it by the purchase price, the loss value of the equipment can be calculated. The total prices are calculated as follows:

\$5.99/1000 h × 9.5 h (\$0.057, glass reactor) + \$1562.4/8760 h × 3.5 h (\$0.624, digital hot plate) + \$16.88/1000 h × 2 h (\$0.034, filter bottle) + \$44.36/1000 h × 3 h (\$0.133, vacuum pump) + \$3172.93/8760 h × 8.667h (\$3.14, oven) = \$3.988

(4) Post-treatment costs. The spent acid liquor generated after the extraction of base metals from waste CPUs was regarded as an acidic metal-bearing wastewater. Therefore, its post-treatment cost was approximately estimated with reference to reported treatment costs for acid mine drainage. Reported operating costs for acid mine drainage treatment are in the range of \$ 1.59-3.18 /m^3.[1] For a conservative techno-economic

assessment, the upper-bound value of \$ 3.18 /m^3 was adopted in this work. After crushing the waste CPU and removing base metals, the remaining solid residue mainly consists of residual fiber glass and plastic, which require further disposal. As a literature-based approximation, a disposal fee of \$ 28 /t was adopted in this study. The total cost was calculated as follows:

(wastewater costs)\$ 3.18/m^3 x 250 ml + (solid residue costs) \$ 28/t x 200 g = \$0.0064

In the recovery process of Waste CPU to **Au powder**, the total chemicals consumption contained, 14.33 g PMS, 5.97 g KCl, 51.5 ml HNO_3, 10 g Na_2SO_3 and 348.5 ml H_2O. The total mass of Au powder was 193.2 mg. The total energy consumption included the electricity consumed during base metal removal, Au leaching, filtration, reduction and calcination. A power converter was used to calculate the power of each process.

(5) Material costs. The prices of all the raw chemicals and regents were based on the prices on varied regent companies. The purchase price of Waste CPU is \$13.92. The total prices were calculated as:

PMS: \$5.58 / 500 g × 14.33 g = \$0.16

KCl: \$2.37 / 500 g × 5.97 g = \$0.029

HNO_3: \$5.3 / 500 ml × 51.5 ml = \$0.55

Na_2SO_3: \$1.90 / 500 g × 10 g = \$0.038

H_2O: \$3.63 / 19000 ml × 348.5 ml = \$0.067

Total cost = \$0.16 + \$0.029 + \$0.55 + \$0.038 + \$0.067 + \$13.92 = \$14.764

(6) Energy consumption costs. The price of electricity in Beijing, China is \$ 0.075 per kWh. The total prices were calculated as:

(Vacuum pump) \$0.075 × 0.06 kW × 3 h + (Oven) \$0.075 × 1.3 kW × 8 h = \$0.80

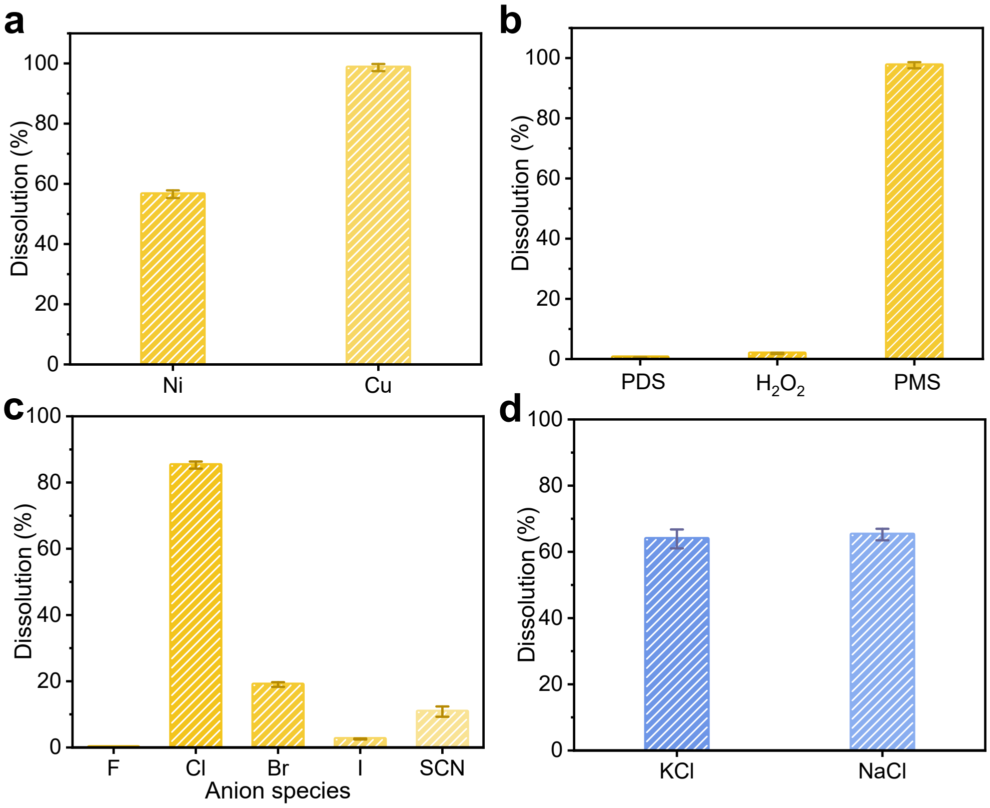
(7) Operating costs. Glass reactor, digital hot plate, filtration devices and oven all have a certain service life. By calculating the direct ratio of the use time to the service life and multiplying it by the purchase price, the loss value of the equipment can be calculated. The total prices are calculated as follows:

\$5.99/1000 h × 9.5 h (\$0.057, glass reactor) + \$16.88/1000 h × 2 h (\$0.034, filter bottle) + \$44.36/1000 h × 3 h (\$0.133, vacuum pump) + \$3172.93/8760 h × 8h (\$2.9, oven) = \$3.124

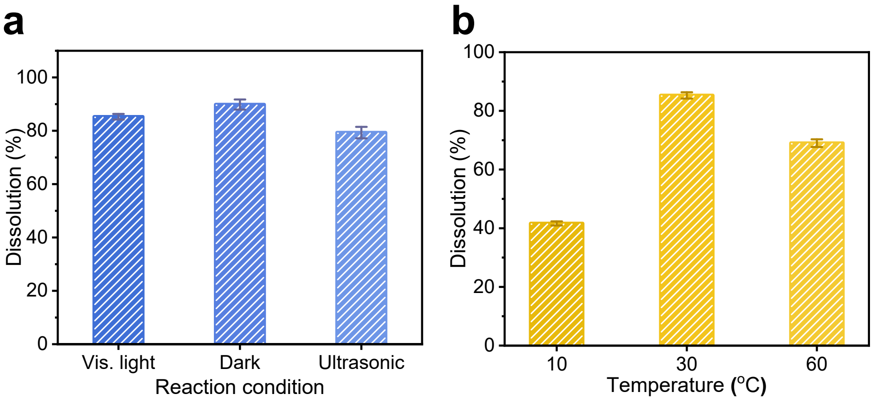
(8) Post-treatment costs. The spent acid liquor generated after the extraction of base metals from waste CPUs was regarded as an acidic metal-bearing wastewater. Therefore, its post-treatment cost was approximately estimated with reference to reported treatment costs for acid mine drainage. Reported operating costs for acid mine drainage treatment are in the range of \$ 1.59-3.18 /m^3. For a conservative techno-economic assessment, the upper-bound value of \$ 3.18 /m^3 was adopted in this work. After crushing the waste CPU and removing base metals, the remaining solid residue mainly consists of residual fiber glass and plastic, which require further disposal. As a literature-based approximation, a disposal fee of \$ 28 /t was adopted in this study. The total cost was calculated as follows:

(wastewater cost)\$ 3.18/m^3 x 250 ml + (solid residue cost) \$ 28/t x 200 g = \$0.0064

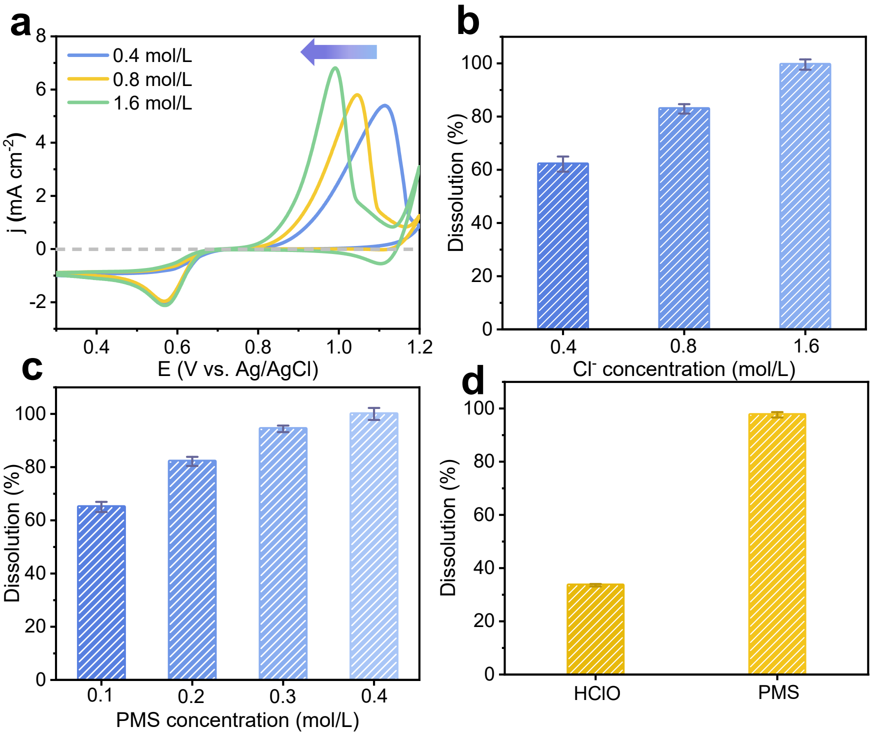
Supplementary Figures



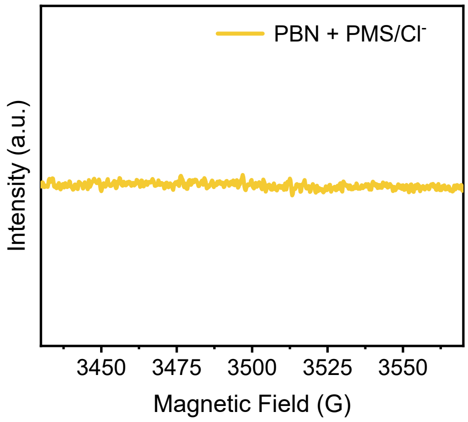
Supplementary Fig. 1. (a) Dissolution efficiencies of Ni and Cu. (b) Dissolution efficiency of Au in Cl^- solution under different oxidants. (c) Au Dissolution ratio in the presence of different anions. (d) Dissolution ratio of Au in PMS/KCl or PMS/NaCl solutions.



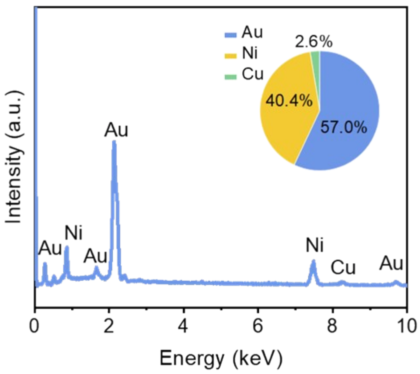
Supplementary Fig. 2. Au Dissolution ratio under different (a) reaction conditions, or (b) temperatures.



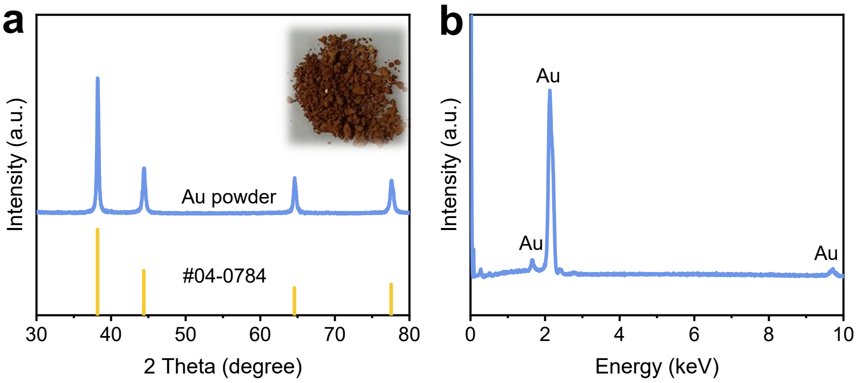
Supplementary Fig. 3. (a) Changes in the redox potential of Au at different chloride concentrations. (b) Dissolution efficiency of Au as a function of Cl$^-$ concentration. (c) Au Dissolution ratio under different PMS concentrations. (d) Au dissolution in a Cl$^-$ solution using equimolar HClO and PMS.



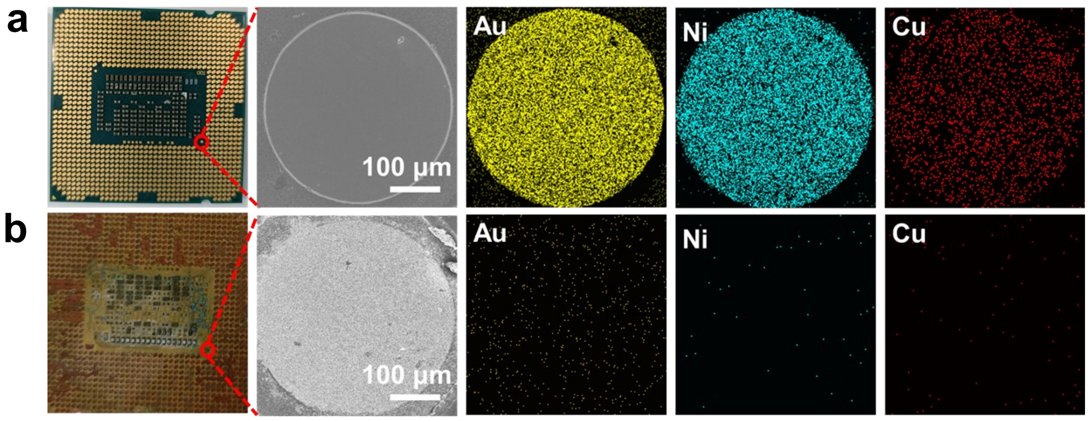
Supplementary Fig. 4. EPR spectrum of PBN in the PMS/Cl^- solution.



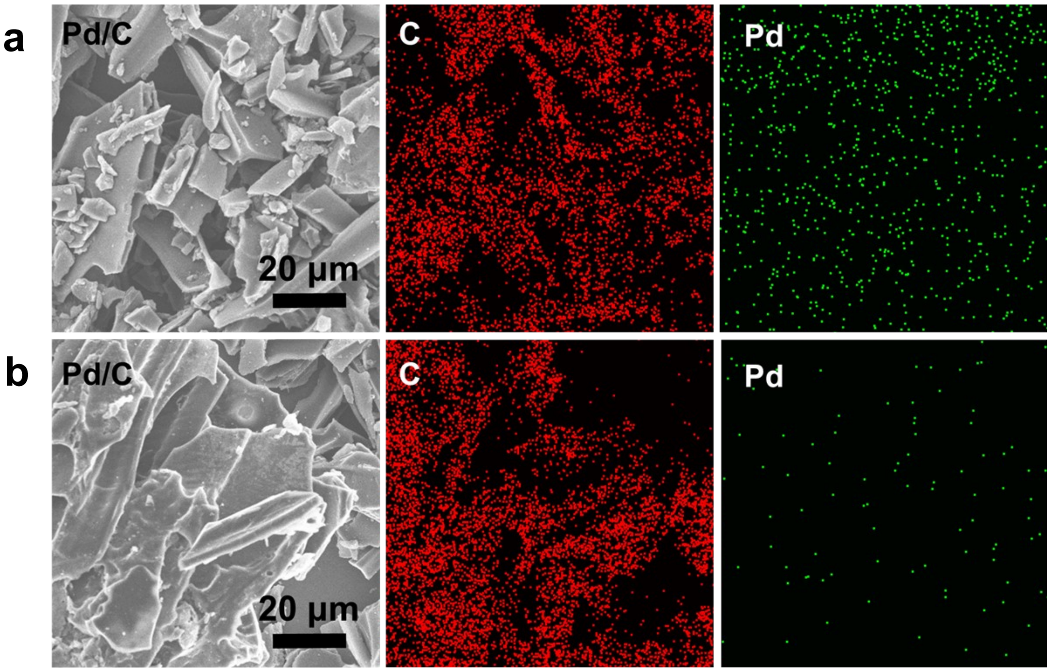
Supplementary Fig. 5. EDS spectrum of the gold-plated contacts of the waste CPU.



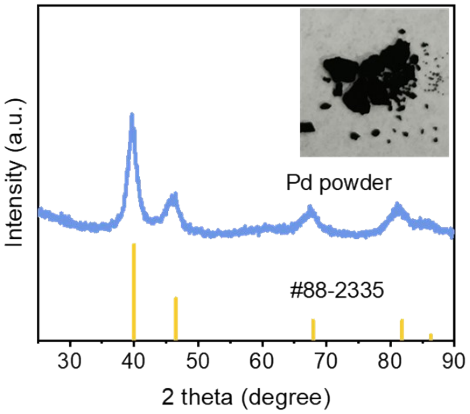
Supplementary Fig. 6. (a) XRD pattern of the Au powder obtained after reduction, with the inset showing an optical photograph of the powder. (b) EDS spectrum of the Au powder.



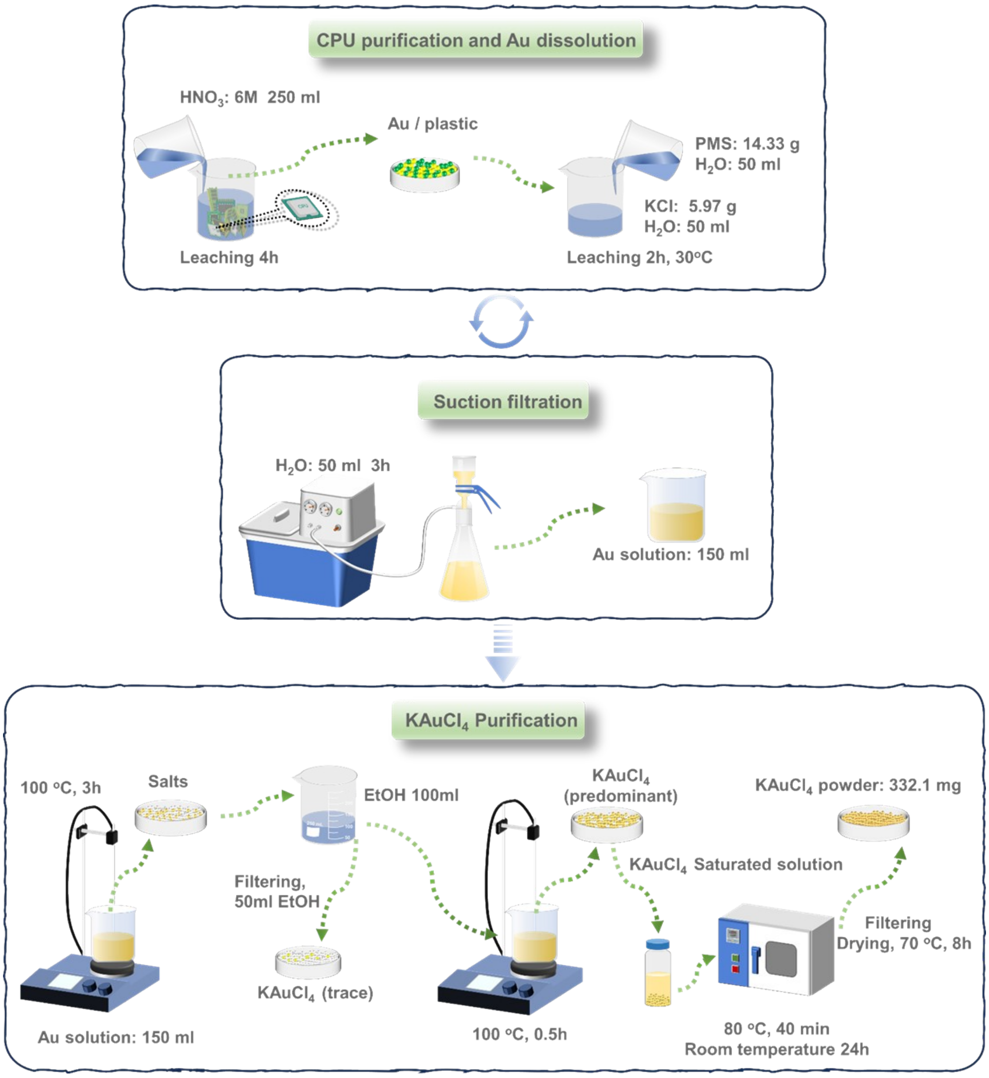
Supplementary Fig. 7. Elemental mappings of wasted-CPU before (a) and after (b) dissolution.



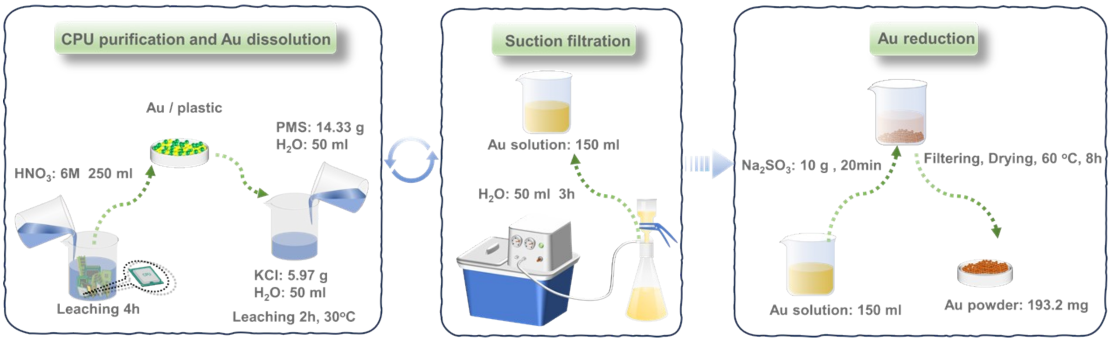
Supplementary Fig. 8. Elemental mappings of Pd/C before (a) and after (b) dissolution.



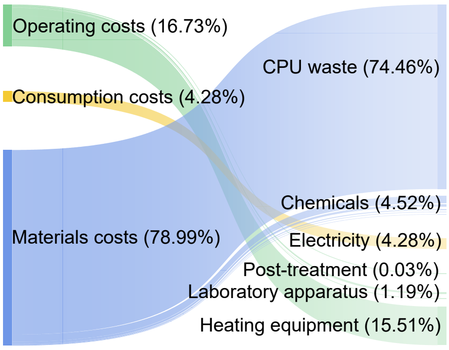
Supplementary Fig. 9. XRD patterns of Pd powder, with the inset showing an optical photograph of the powder.



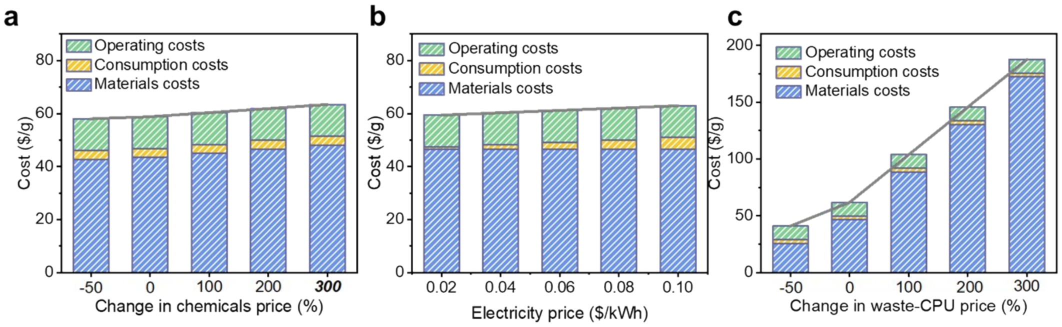
Supplementary Fig. 10. Schematic diagram of Au recovery from waste CPUs and subsequent preparation of $KAuCl_4$.



Supplementary Fig. 11. Schematic diagram of Au recovery from waste CPUs.



Supplementary Fig. 12. The subdivided coat of the Au recovery.



Supplementary Fig. 13. Effects of (a) chemical price variation, (b) electricity price fluctuation, and (c) waste CPUs price on the cost of converting Au from waste CPUs to $KAuCl_4$.

Supplementary Tables

Supplementary Table 1. Metal composition analysis of waste CPU and recovered products.

	HNO_3 pretreatment	Au	Cu	Ni	Purity
Gold-plated contacts of waste CPU	Before	0.6 wt%	92.4 wt%	7.0 wt%	
	After	95.2 wt%	4.6 wt%	0.2 wt%	
Recovered Au	--	99.2 wt%	--	--	99.2%
Recovered $KAuCl_4$	--	51.1 wt%	--	--	98.0%

Supplementary Table 2. The subdivided items of the $KAuCl_4$ recovery in Fig. 4e.

Items			Proportion
Materials costs	CPU waste		67.71%
	Chemicals	PMS	0.77%
		KCl	0.14%
		EtOH	3.50%
		HNO_3	2.67%
		H_2O	0.37%
Consumption costs	Electricity		5.40%
Operating costs	Post-treatment	Wastewater/CPU residue	0.03 %
	Laboratory apparatus	Vacuum pump	0.65%
		Glass reactor	0.28%
		Filter bottle	0.17%
	Heating equipment	Digital hot plate	3.04%
		Oven	15.27%

Supplementary Table 3. The subdivided items of the Au recovery in Fig. S17.

Items			Proportion
Materials costs	CPU waste		74.46%
	Chemicals	PMS	0.86%
		KCl	0.16%
		Na_2SO_3	0.21%
		HNO_3	2.94%
		H_2O	0.36%
Consumption costs	Electricity		4.28%
Operating costs	Post-treatment	Wastewater/CPU residue	0.03 %
	Laboratory apparatus	Vacuum pump	0.71%
		Glass reactor	0.30%
		Filter bottle	0.18%
	Heating equipment	Oven	15.51%

Supplementary Table 4. Comparison of this work with other methods in the Au recovery reaction reported in literature.

Lixiviant	Energy consumption kWh/g	Chemicals consumption $/g
$CH_3CN/BaTiO_3$[2]	2.4	22.51
$DMF/CuCl_2/CaCl_2$ [3]	35.2	45.6
CH_3CN/TiO_2 [4]	480	45.3
trihexyl(tetradecyl) phosphonium trihalide ionic liquids [5]	78.3	88.3
NH_4Br/TiO_2 [6]	400	15.4
$Al(NO_3)_3/NaCl$ [7]	65.3	22.8
$H_2SO_4/NaCl/NaClO_3$ [8]	8.9	19.8
$(NH4)_2S_2O_3/CuSO_4$ [9]	46.2	25.2
$PDS/FeCl_2{\cdot}4H_2O$ [10]	22.3	7.9
This work	4.64	3.34

Supplementary Table 5. The chemicals involved in TEA for Au recovery.

chemicals	brand	package size	price
PMS	Innochem	500 g	$ 5.58
potassium chloride	FuChen chemistry	500 g	$ 2.37
sodium chloride	FuChen chemistry	500 g	$ 0.98
nitric acid	Beijing Tongguang Reagents	500 ml	$ 5.30
ethanol	Beijing Tongguang Reagents	500 ml	$ 2.37
sodium sulfite	3AChem	500 g	$ 1.90
deionized water	Wahaha	19 L	$ 3.63

Supplementary References

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