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闪光焦耳加热城市采矿

Urban mining by flash Joule heating

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从电子废物中回收贵金属，称为城市采矿，对于循环经济。目前的城市采矿方法，主要是冶炼和浸出，受到来自漫长的净化过程和负面的环境影响。这里，一种无溶剂的、可持续的过程通过闪光焦耳加热回收贵金属和在一秒钟内清除电子废物中的有害重金属。样品温度通过超快的电热过程，温度在毫秒内上升到3400 K左右。这样的高温可使贵金属与载体蒸发分离，基质，Rh、Pd、Ag的回收率>80%，Au的回收率>60%。重金属在电子废物中，包括Cr、As、Cd、Hg和Pb在内的一些剧毒废物移除后，留下金属含量最低的最终废物，即使对于农业也是可以接受的土壤水平。采用焦耳闪光加热的城市采矿将减少80×至500×能源消耗，比使用传统熔炼炉进行金属成分回收和更多环保。

Precious metal recovery from electronic waste, termed urban mining, is important for a circular economy. Present methods for urban mining, mainly smelting and leaching, suffer from lengthy purification processes and negative environmental impacts. Here, a solvent-free and sustainable process by flash Joule heating is disclosed to recover precious metals and remove hazardous heavy metals in electronic waste within one second. The sample temperature ramps to ~3400 K in milliseconds by the ultrafast electrical thermal process. Such a high temperature enables the evaporative separation of precious metals from the supporting matrices, with the recovery yields >80% for Rh, Pd, Ag, and >60% for Au. The heavy metals in electronic waste, some of which are highly toxic including Cr, As, Cd, Hg, and Pb, are also removed, leaving a final waste with minimal metal content, acceptable even for agriculture soil levels. Urban mining by flash Joule heating would be 80× to 500× less energy consumption than using traditional smelting furnaces for metal-component recovery and more environmentally friendly.

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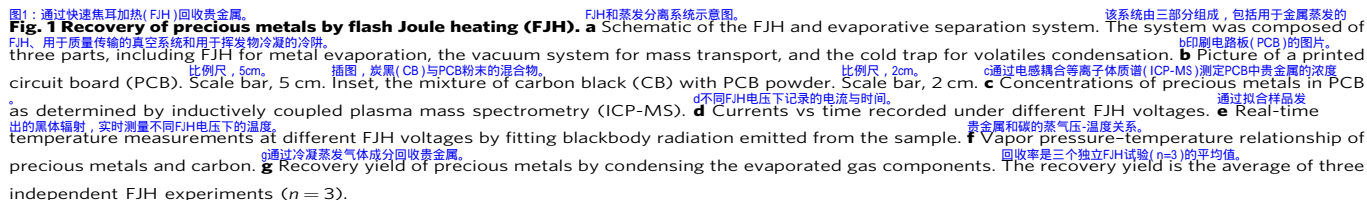
全球每年产生4000多万吨电子废物, 1.2由于个人电气和电子设备的快速升级, 电子废物是固体废物中增长最快的组成部分^{3,4}。电子废物被生产出来, 每年约1.2, 这是最快的-growing component of solid wastes due to the rapid upgrade of personal electrical and electronic equipments^{3,4}。Most of e-waste are landfilled with only ~20% being recycled⁵, which could lead to negative environmental impact due to the broad use of heavy metals in electronics⁶⁻⁸. E-waste could become a sustainable resource because it contains abundant valuable metals⁹. The concentrations of some precious metals in e-waste are higher than those in ores⁹. Precious metals recovery from e-waste, termed urban mining, is becoming more cost-effective than virgin mining² and important for a circular economy⁸. Similarly, due to the broad use of heavy metals in electronics, including Cd, Co, Cu, Ni, Pb, and Zn, e-waste could lead to significant health risks and negative environmental impact⁶⁻⁸. The heavy metal leakage due to improper landfill disposal leads to environmental disruption^{1,8}. The release of hazardous components during the recycling processes in the form of dust or smoke⁶ deteriorates the health of recycling workers and local residents. For example, in the blood of e-waste workers^{7,10}. The lack of high-yielding and environmentally friendly recovery processes are the main obstacles to urban mining⁹. The traditional method for e-waste recycling is based on a pyrometallurgy process¹¹, where metals are melted by heating at high temperature. Pyrometallurgy is energy-intensive, lacks selectivity, and requires high-grade precursors¹². Pyrometallurgical processes also produce hazardous fumes containing heavy metals, especially for those with low melting points such as Hg, Cd, and Pb⁹. The hydrometallurgical process is more selective and done by leaching the metals using acid, base, or cyanide¹³. The leaching kinetics are usually slow. The use of highly concentrated leaching agents renders the hydrometallurgical process difficult for large-scale applications, and large amounts of liquid waste and sludge are produced that could result in secondary pollution¹⁴. Biomining could be highly selective and environmentally sustainable, yet it is still in its infancy¹⁵. The separation of valuable metals from various materials matrices, including plastics, glass, and ceramics, are based upon their differences in physical or chemical properties. For example, the gravity separation technique relies on differing specific densities¹⁶. Magnetic separation is used to separate magnetic metals from non-ferrous waste¹⁷. Hydrometallurgical separation is based upon the chemical reactivity of metals with leaching agents¹⁸. Here, we show that the different vapor pressure of metals compared to that of substrate materials (carbon, ceramics, and glass) enables the separation of metals from e-waste. This is termed evaporative separation. The high vapor pressure of precious metals is obtained by an ultrafast flash Joule heating (FJH) process under vacuum. A subsecond current pulse is passed through the precursors, which brings the sample to an ultrahigh temperature of ~3400 K, enabling the evaporative separation of precious metals. Halide additives are used to improve the recovery yield of Au to the recovery rate to 60% for Au that is abundant in the tested e-waste. Alternatively, compared with directly leaching e-waste raw materials, by leaching the residual solids after FJH, the recovery yield is significantly improved with tens of times increase for Ag and few times increase for Rh, Pd, and Au. The toxic heavy metals, including Cd, Hg, As, Pb, and Cr, could also be removed and collected, minimizing the health risks and environmental impact of the recycling process.

Results

FJH从电子废物中蒸发分离贵金属。Evaporative separation of precious metals from e-waste by FJH. FJH从电子废物中回收贵金属的过程包括三个阶段(图1a)。The FJH process to recover precious metals from e-waste involves three stages (Fig. 1a). The metals in e-waste were heated and

通过超高温FJH蒸发, 然后在真空下传输金属蒸汽并通过冷凝收集。evaporated by ultrahigh-temperature FJH, then the metal vapors were transported under vacuum and captured by condensation. A printed circuit board (PCB) from a discarded computer, a representative e-waste, was used as the starting material (Fig. 1b and Supplementary Fig. 1). The PCB was ground to small powder and mixed with carbon black (CB), which served as the conductive additive (Fig. 1b, inset). To establish baseline concentrations, the PCB was digested using dilute aqua regia¹⁹, and the concentration of precious metals was determined by inductively coupled plasma mass spectrometry (ICP-MS). Among the precious metals, Rh, Pd, Ag, and Au are abundant with concentrations of several to tens of parts per million (ppm) (Fig. 1c). In a typical FJH process, the mixture of PCB powder and ~30 wt% CB was slightly compressed inside a quartz tube between two sealed electrodes (Fig. 1a and Supplementary Fig. 2). One electrode was a porous Cu electrode to facilitate gas diffusion, and the other was a graphite rod (Supplementary Fig. 3). The resistance of the sample was tunable by adjusting the compressive force on the two electrodes. The two electrodes were connected to a capacitor bank with a total capacitance of 60 mF (Supplementary Fig. 3). The detailed separation conditions are shown in Supplementary Table 1. The high-voltage discharge of the capacitor bank brings the reactant to a high temperature. With the fixed sample resistance of ~1 Ω , the current passing through the sample was measured under different FJH voltages (Fig. 1d). The real-time temperature of the sample was estimated by fitting the blackbody radiation in the 600–1100 nm emission (Supplementary Fig. 4). The temperature varied according to the FJH voltage, reaching ~3400 K at 150 V in <50 ms (Fig. 1e). Since the resistance of the sample is much larger than that of the graphite and porous Cu electrode, the voltage drop was mainly imposed on the sample. Hence, the high-temperature region was limited to the sample and the FJH setup has good durability even though it can achieve a high temperature of >3000 K (Supplementary Fig. 5). Numerical simulations showed that the temperature was relatively uniform along both the longitudinal and radial directions of the sample (Supplementary Note 1, temperature simulation, Supplementary Fig. 6), demonstrating the homogeneous heating ability of the FJH process. Such a high temperature (>3000 K) volatilizes most of the non-carbon components. According to the calculated vapor pressure-temperature relationships (Fig. 1f), the precious metals have a higher vapor pressure than carbon, the latter not subliming until ~3900 K²⁰. As a result, the metals are evaporated, and the major carbon-containing components such as plastics were carbonized^{21,22}. The evaporated metal vapors were captured by condensation in a cold trap (Fig. 1a and Supplementary Fig. 2). Some of the vapor remained gaseous even at the liquid N₂ temperature (77 K) (Supplementary Fig. 2); these gases were presumed to be H₂ and CO²². The content of the precious metals in the condensed solid was measured and the recovery yield was calculated (Fig. 1g and Supplementary Note 2). The recovery yield of Ag was ~40%, while Rh, Pd, and Au had a relatively low recovery yield of ~3%. This is because Ag has a high vapor pressure and relatively low boiling point (Supplementary Fig. 7). The concentration of precious metals in the starting commercial CB is 1–2% of the concentration in PCB, hence their presence in CB will not introduce significant errors (Supplementary Fig. 8). Moreover, the precious metals tend to not form stable carbide phases even at high temperature due to their extremely low C solubility²³ (Supplementary Fig. 9). Hence, the use of CB as a conductive additive will not affect the evaporative behavior of precious metals.

卤化物有助于提高回收率。Halide assisted improvement of recovery yield. The high-recovery yield of the evaporative separation relies on the



即使使用F和Cl添加剂,金的回收率也小于10%。有趣的是,当使用碘化钠(NaI)作为添加剂时,Even with the use of F and Cl additives, the recovery yield of Au is less than 10%. Interestingly, the recovery yields of all four precious metals were improved when sodium iodide (NaI) was used as the additive; the recovery yield of Au was improved to >60% (Fig. 2e). 在氯化物中,添加剂的金回收性能最好。The I additive has the best performance among halides for Au recovery. According to the hard and soft acids and bases (HSAB) theory, Au⁺ is a soft Lewis acid, and I⁻ is a soft Lewis base while F⁻ and Cl⁻ are harder than I⁻ favoring AuI. By using an NaCl and NaI的添加剂混合物,贵金属都具有良好的回收率, Rh>60%, Pd>60%, Ag>80%, Au>40% (图2f)。有利于Au⁺通过使用NaF, NaCl, and NaI, the precious metals all had a good recovery yield, >60% for Rh, >60% for Pd, >80% for Ag, and >40% for Au (Fig. 2f). 通过X射线光电子能谱(XPS)对原材料和F/H后剩余固体的成分分析表明, F/H过程中蒸发了10-40%的氯化物添加剂(补充图13), 可经过水洗和沉淀过程回收和再利用。photoemission spectroscopy (XPS) showed that 10–40% of the halide additives were evaporated during the F/H process (Supplementary Fig. 13), which could be recovered and reused by a water washing and precipitation process.

我们对冷阱中收集的金属进行了总成分分析(补充图3)。We conducted a total composition analysis of the collected metals in the cold trap (Supplementary Note 3). In both cases 在有化学添加剂的两种情况下, 除贵金属外, 最丰富的金属是铜, 质量比>60 wt%。其次是电子废物中的其他主要金属, 包括钨、钼、铁和锌(补充图14)。In addition to the precious metals, the most abundant metals were Cu with mass ratio >60 wt %, followed by other prominent metals in e-waste including Al, Sn, Fe, and Zn (Supplementary Fig. 14). 进一步的提纯和精炼可以通过选择性沉淀、溶剂萃取和固相萃取来完成, 这些都是商业上公认的做法²⁶。Further purification and refining could be done by selective precipitation, solvent extraction, and solid-phase extraction, which are commercially well-established practices²⁶.

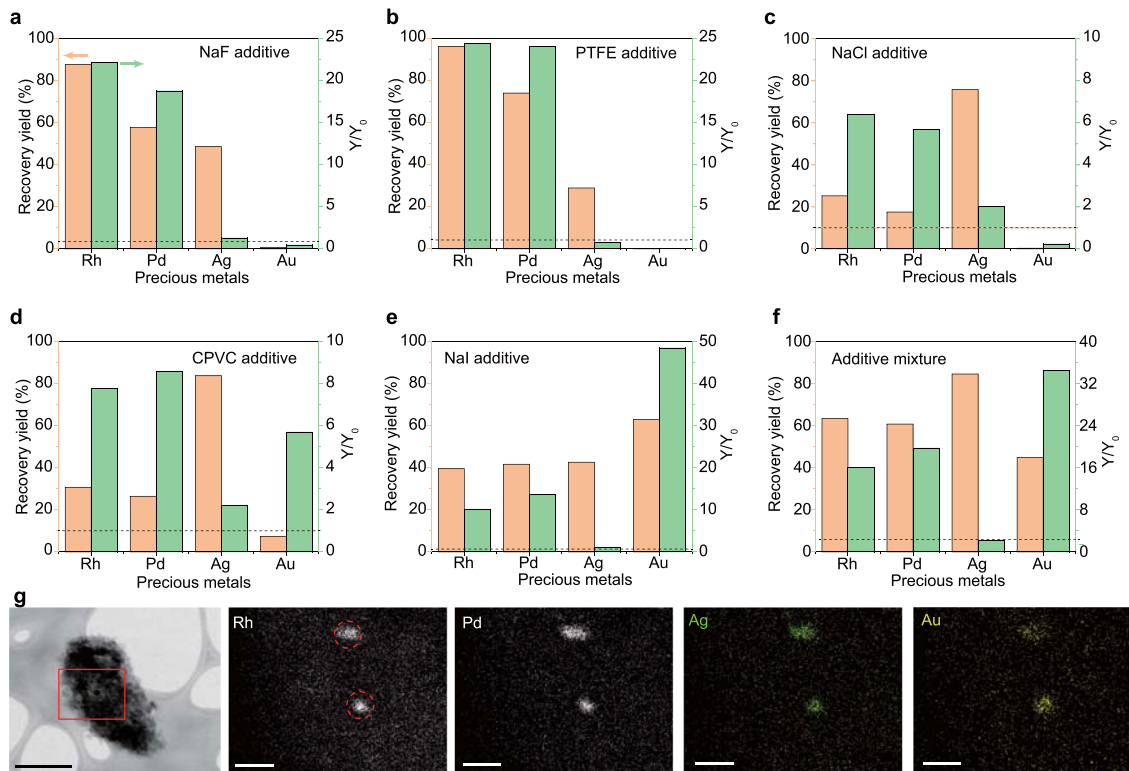


Fig. 2 Halide assisted improvement of recovery yield. (a) NaF, (b) PTFE, (c) NaCl, (d) CPVC, (e) NaI, and (f) NaF, NaCl and NaI mixture as additives, recovery yield of precious metals by using (a) NaF, (b) PTFE, (c) NaCl, (d) CPVC, (e) NaI, and (f) mixture of NaF, NaCl, and NaI, as additives. Y_0 and Y mean the recovery yield of precious metals without and with additives, respectively. The dashed line denotes $Y/Y_0 = 1$, meaning that there is no advantage of the additive if $Y/Y_0 \leq 1$. The recovery yields were the average of three independent flash Joule heating (FJH) experiments ($n = 3$). **g** Scanning transmission electron microscopy (STEM) image of the collected solids, and energy dispersive spectroscopy (EDS) maps of Rh, Pd, Ag, and Au at the rectangular region. Scale bar in STEM image, 0.5 μm ; scale bars in EDS maps, 100 nm. The dashed circles in Rh show the clustered alloys.

使用扫描透射电子显微镜 (STEM) 和能量色散光谱 (EDS) 对凝聚固体的形态和化学成分进行了表征。The morphology and chemical composition of the condensed solids were characterized using scanning transmission electron microscopy (STEM) and energy dispersion spectroscopy (EDS). The elemental maps showed the clustered alloy particles of Rh, Pd, Ag, and Au (Fig. 2g), which were formed by the ultrafast heating and rapid cooling of the FJH process. This is similar to the case of the carbothermic shock synthesis of high-entropy alloy nanoparticles, which could be potentially used in catalysts²⁷. In other regions, the precious metals spreading over the entire product were also observed (Supplementary Fig. 15). Moreover, the XPS analysis of the collected volatiles showed that Ag and Au were mainly in the elemental state, while elemental state and higher oxidation state coexisted for Rh and Pd, presumably due to their different chemical reactivity (Supplementary Note 3 and Supplementary Fig. 16).

提高了FJH对贵金属的浸出效率。Improved leaching efficiency of precious metals by FJH. Apart from the condensation of the volatile composition, the other pathway to recover the precious metals was by leaching the residual solids obtained by FJH (Supplementary Fig. 17a). Different from the use of a vacuum to facilitate the metal volatilization in the evaporative separation scheme (Fig. 1a), a pressurized setup was built to trap the metals in the reactor (Fig. 3a). An inert gas (N_2) cylinder was connected to the FJH reactor, where the pressure was monitored by a pressure gauge. The inner pressure (P_0) during FJH was estimated to be ~ 5 atm according to the amount of collected gas (Supplementary Fig. 2 and Supplementary Note 1). 根据FJH燃烧室的压强和尺寸, 模拟了FJH燃烧室中气体的扩散过程。The size of the FJH chamber, the gas diffusion was simulated under

不同压力 (P_{out}) (图3b, 补充图)。When different pressures (P_{out}) (Fig. 3b, Supplementary Fig. 18). 当使用真空 (Pout=0 atm) 时, 正如在蒸发分离中一样 (图1a), 气体速度高达800 m s^{-1} 。如此高的气体速度有助于挥发性成分迅速扩散到冷阱中, 并防止管侧壁处的冷凝损失。相反, 随着压力的增加, 气体速度大大降低 (图3b)。结果, 更多原本易挥发的成分被困在反应器中的残余固体中。加压FJH的详细反应条件见补充表2。The detailed reaction conditions for the pressurized FJH are shown in Supplementary Table 2. 我们从使用稀酸 (1 M HCl, 1 M HNO_3) 在120 V和大气压下FJH (表示为PCB-Flash) 后的残余固体浸出开始 (补充图17a)。We started from leaching the residual solids after FJH (denoted as PCB-Flash) at 120 V and atmospheric pressure using dilute acids (1 M HCl, 1 M HNO_3) (Supplementary Fig. 17a). The leachable content of Rh, Pd, and Ag in PCB-Flash was substantially higher than that in the PCB raw materials (Fig. 3c). The ratio of the recovery yield by leaching the PCB-Flash (Y) and leaching the PCB raw materials (Y_0) was calculated. FJH浸出比单独浸出有效得多。Rh, Pd, Ag的回收率分别提高了 4.17 ± 0.48 , 2.90 ± 0.31 , 分别为56.0 \pm 18.1 times, respectively (Fig. 3c). 这些偏差可能与电子废物中贵金属的不均匀分布有关。有趣的是, FJH工艺后, 金回收率降低。原因可能是Au和carbon28之间形成共价键, 这会显著增加酸浸的难度。The thermogravimetric analysis (TGA) of the PCB-Flash showed that the carbon could be removed in the air at $\sim 700^\circ\text{C}$ (Supplementary Fig. 17b). 因此, PCB-Flash固体在700 $^\circ\text{C}$ 下煅烧1h (表示为PCB-Flash-Calcination, Supplementary

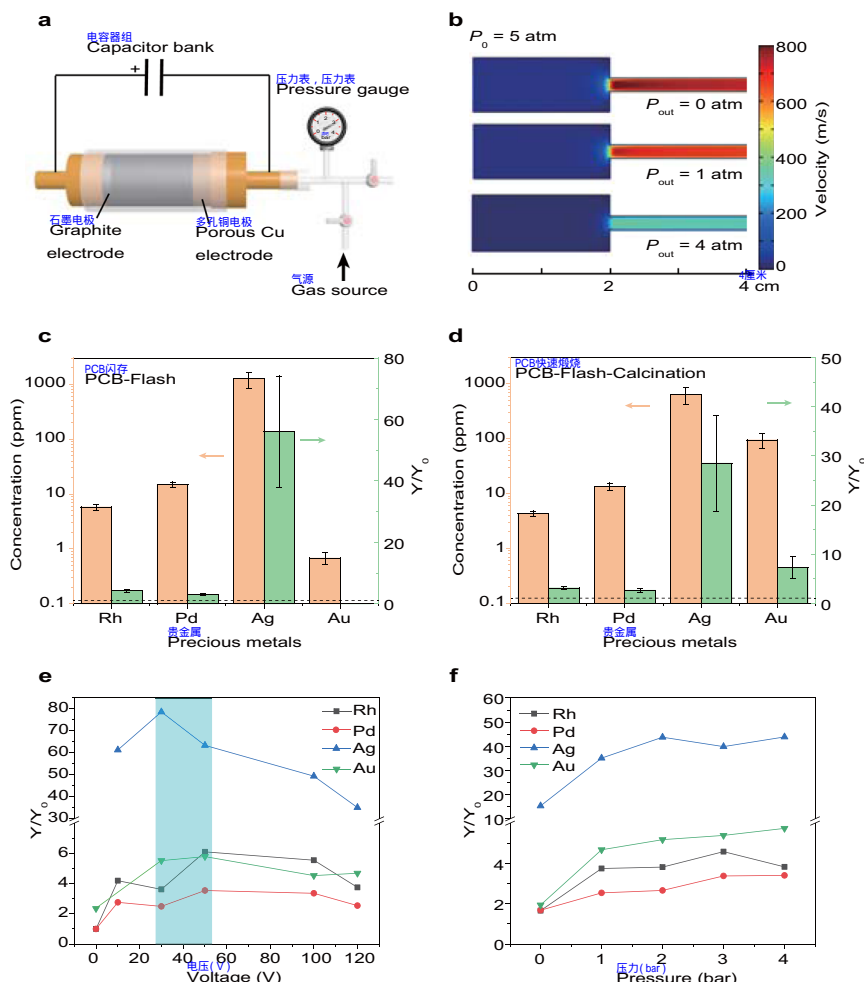


Fig. 3 | Leaching efficiency improvement of precious metals by the flash Joule heating (FJH) process. **a** Schematic of the pressurized setup for FJH. **b** Gas flow simulation under different pressures. The inner pressure (P_0) during the FJH was calculated to be $\sim 5 \text{ atm}$. P_{out} of 0 atm, 1 atm, and 4 atm correspond to the FJH under vacuum, atmospheric pressure, and 3 atm of positive pressure. **c** Concentration of precious metals and improvement of recovery yield by FJH. Y_0 and Y mean the recovery yield by leaching printed circuit board (PCB) and PCB-Flash, respectively. The dashed line denotes $Y/Y_0 = 1$. The error bars denote the standard deviation where $n = 3$. **d** Concentration of precious metals and improvement of recovery yield by FJH and calcination. Y_0 and Y mean the recovery yield by leaching PCB and PCB-Flash-Calcination, respectively. The dashed line denotes $Y/Y_0 = 1$. The error bars denote the standard deviation where $n = 3$. **e** Improvement of recovery yield varied with FJH voltages under atmospheric pressure. The highlighted region is the approximate optimal voltage for all metal recovery. **f** Improvement of recovery yield varied with pressure. For **e** and **f**, the recovery yields of Rh, Pd, and Ag are calculated from PCB-Flash, and the recovery yield of Au is calculated from PCB-Flash-Calcination.

Fig. 17b). PCB原材料也作为对照进行煅烧(表示为PCB煅烧, 补充图17c). Fig. 17b). The PCB raw materials were also calcined as a control (denoted as PCB-Calcination, Supplementary Fig. 17c). The XPS analysis showed the efficient removal of carbon by calcination (Supplementary Fig. 17d). With the FJH and calcination process, the recovery yields of Rh, Pd, Ag, and Au were increased by 3.11 \pm 0.37, 2.64 \pm 0.39, 28.5 \pm 9.8, 7.24 \pm 2.22 times, respectively (Fig. 3d). The values are larger than those achieved with the calcination-only process (Supplementary Figs. 17e, f). The presumable mechanism of the improved leaching efficiency by FJH is shown in Supplementary Fig. 19. Modern electronics are fabricated and packaged by a planar process and have a laminated configuration, where the useful metals are embedded into the polymer or ceramic matrices (Supplementary Fig. 19a)¹³. Even after the pulverization, the particle size was large $\sim 5 \mu\text{m}$ (Supplementary Fig. 19b). The laminated structure hinders the extraction of metals in a typical hydrochemical process, resulting in elongated leaching times and low leaching efficiencies¹³. During the FJH process, the matrix was rendered

作为超高温下的超细粉末(补充图). as an ultrafine powder at the ultrahigh temperature (Supplementary Figs. 19c, d), and the metals were exposed (Supplementary Fig. 19e), which greatly accelerated the leaching rate and extent of metal extraction.

研究了FJH电压和压力对回收率的影响。 The effects of the FJH voltage and pressure on the recovery yield were studied. It was found that the modest FJH voltages between 30 and 50 V led to the best recovery yield (Fig. 3e). Too low voltage did not provide enough energy to thermally decompose the matrix, while too high voltage presumably resulted in the evaporative loss. It was found that a higher surrounding pressure was beneficial (Fig. 3f). This is because the volatile components were trapped in the residual solid, as we projected by the gas-flow simulations (Fig. 3b). The mild acid-leaching condition (1 M HCl, 1 M HNO₃) used in our process is more cost-effective and environmentally friendly compared to other hydrometallurgical processes, which use highly concentrated mineral acids such as aqua regia^{13,29}, or toxic cyanides^{18,30} as extractants for achieving a high-recovery yield.

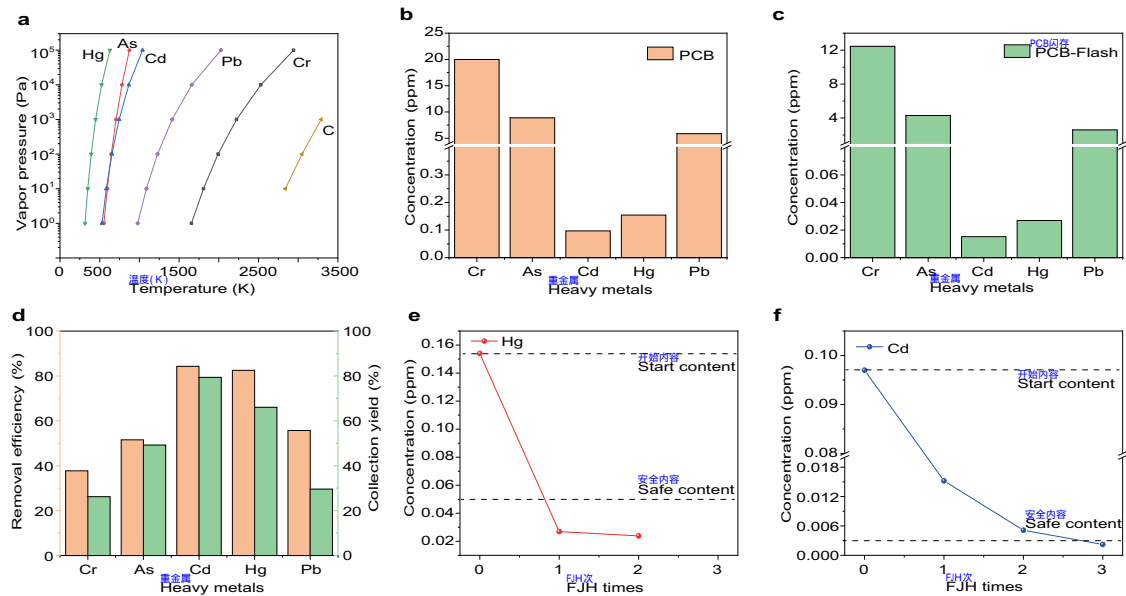


Fig. 4 Removal of heavy metals in e-waste by flash Joule heating (FJH) process. **a** Vapor pressure-temperature relationships of toxic heavy metals and carbon. **b** Concentrations of toxic heavy metals in the printed circuit board (PCB). **c** Concentrations of toxic heavy metals in PCB after FJH. **d** Removal efficiency and collection yield of heavy metals. The efficiency and yield were the average of three independent FJH experiments ($n = 3$). **e** Concentration of Hg in the residues after multiple FJH reactions. **f** Concentration of Cd in the residues after multiple FJH reactions. The dashed lines in **(e, f)** represent the starting contents and the approved World Health Organization (WHO) level for safe limits of agricultural soils.

Removal and collection of toxic heavy metals in e-waste.

Removal of toxic components is another major concern for e-waste processing^{3,6,7,31}. The heavy metal removal capability of the FJH process was evaluated. Compared to precious metals, heavy metals, including Cr, Pb, Cd, As, and Hg, have much higher vapor pressures and lower boiling points (Fig. 4a and Supplementary Fig. 7b). Especially for the most toxic Cd, As, and Hg, the separation factors between them and precious metals could achieve $\sim 10^5$ based on the theoretical analysis (Supplementary Note 4). The levels of heavy metals in PCB waste are in the range of 0.1–20 ppm (Fig. 4b). These values are above the safe limits of heavy metals in soils for agriculture as recommended by the world health organization (WHO)³². After one FJH, the heavy metal contents in the remaining solid (PCB-Flash) were greatly reduced (Fig. 4c). The removal efficiencies of As and Cd were calculated to be $>80\%$, followed by Pb and As ($>50\%$), and Cr ($>35\%$) (Fig. 4d and Supplementary Note 2). These efficiencies were consistent with their vapor pressure values (Fig. 4a). The heavy metals were collected by condensation in the cold trap, as we did for the evaporative separation, and the collection yields were calculated (Fig. 4d). The collection yield matched well with the removal efficiency, demonstrating that most of the evaporated heavy metal was trapped by the cold trap, minimizing the leakage of heavy metals into the environment during the recycling process.

The concentration of heavy metals in the residue solids could be further reduced by multiple FJH reactions. After one FJH reaction, the concentration of Hg was reduced to below the safe limit of Hg in soils for agriculture (0.05 ppm) (Fig. 4e). For Cd, the highest standard for waste disposal. As for Cd, three consecutive FJH cycles reduced the concentration to below the safe limit (0.003 ppm) (Fig. 4f). The concentration of As, Pb, and Cr were all reduced with an increase in the number of FJH reactions (Supplementary Fig. 20). Since each FJH only takes 1 s, multiple flashes are easily accomplished.

Discussion

The proposed evaporative separation scheme is mainly targeted to the recovery of metals from e-waste. Nevertheless, it could exhibit

the capability for the separation of metals. Theoretical calculation shows that large separation factors up to $\sim 10^5$ could be realized for most metals with large vapor pressure differences (Supplementary Note 4, theoretical separation factors of the evaporative separation process based on the vapor pressure difference, Supplementary Fig. 21, Supplementary Table 3). The theoretical separation factors are calculated based on the vapor pressure of pure metals. They represent practical values for trace metal separation even with the melt alloy formation (Supplementary Note 4, the effect of melt alloy formation on the separation factors, Supplementary Fig. 22). The different recovery yields of the FJH process (Fig. 1g) already demonstrated the separation feasibility of the FJH process based on the vapor pressure difference (Supplementary Note 4, the achieved separation ability by the evaporative separation, Supplementary Table 4). The chemical additives (Fig. 2a–f) also regulated the precious metals separation presumably due to their different chemical reactivity (Supplementary Note 4, the metal separation ability from the chemical additives, Supplementary Tables 5–7). The separation ability of the evaporative separation scheme could be further improved by progressively increasing the FJH temperature (Supplementary Note 4, the evidence-based predictions on the practices to increase the separation factors). The cost and benefit of the FJH processing were evaluated since economic incentives are the main driver for waste recycling (Supplementary Note 5). FJH is a highly efficient heating process due to the ultrafast heating/cooling rate, the direct sample heating feature, and the short reaction duration, compared to traditional smelting furnaces where large amounts of energy are used to maintain the temperature of the whole chamber³³. The FJH method has an energy consumption of ~ 939 kWh ton⁻¹, which is $\sim 1/500$ of that for a lab-scale tubular furnace³⁴, and $\sim 1/80$ of that for a commercially used Kaldofurn in industrial scale³⁵ (Supplementary Note 5). Hence, the FJH process for e-waste processing could have advantages over traditional pyrometallurgical processes. The FJH process is scalable. According to the scaling rule revealed by the theoretical analysis, we could increase the FJH

放大样品质量时电容器组的电压和/或电容(补充注释6和补充图。voltage and/or the capacitance of the capacitor bank when scaling up the sample mass (Supplementary Note 6 and Supplementary Figs. 23 and 24). By using a homemade automation system integrated with the FJH setup, our research lab has already realized a production rate of $>10\text{ kg day}^{-1}$. Further commercial scaling up of the FJH process is underway (Supplementary Note 6). Considering the diminishing easily accessible ores of precious metals and the toxicity of several metal elements, the proposed FJH process to recover metals in e-waste could be a harbinger for near-future recovery methods.

方法
Methods
Materials. CB (Cabot, Black Pearls 2000, 平均直径10 nm)用作导电添加剂。PCB废料来自一台废弃的计算机。使用镊子将PCB切割成小块,然后使用镊子磨粉机(Dade, DF-15)研磨成微米粉末。以该粉末的PVC、CPVC和聚偏二氟乙烯(PVDF)塑料颗粒。塑料废料用镊子切成小块,然后用镊子磨粉机(Dade, DF-15)研磨成微米。using a hammer grinder (Dade, DF-15). The salt additives were NaCl (J. T. Baker), NaF (Acros Organics), and NaI (Aldrich, 99.5%). The precious metals chlorides were RhCl_3 (Aldrich, 38–40% Rh), PdCl_2 (Aldrich, 99%), AgCl (Allied Chemical), and AuCl_3 (Aldrich, >99.9%). Polytetrafluoroethylene (PTFE) powder was purchased from Runaway Bike. PVC, CPVC, and polyvinylidene fluoride (PVDF) plastic tubes from plumbing pipes were used as raw materials. The plastic waste products were cut into small pieces using a saw, and then ground into powders by using a hammer grinder (Dade, DF-15).

FJH system and evaporative separation process. The electrical diagram of the FJH reactor is shown in Supplementary Fig. 3. There is a risk of electrocution so all safety measures should be obeyed carefully, as we listed in detail in the Supplementary Information. CB, PCB powders, and additives were mixed by using ball milling (MSE Supplies, PMV1-0.4 L). The reactants were loaded into a quartz tube with an inner diameter of 8 mm and an outer diameter of 12 mm. Copper wool was used as the porous electrode on one side to facilitate the gas diffusion, and a graphite rod was used as the electrode on the other side of the quartz tube. The resistance was controlled by compressing the electrodes. The quartz tube was sealed by an O-ring. A vessel with a volume of ~40 mL was used as the cold trap. The vessel should withstand negative pressure (~10 Pa). A mechanical pump was used to pump the vessel to vacuum; then the trap was immersed into the liquid N_2 . Dewar. This sequence must be followed to avoid condensation in the N₂ Dewar since O_2 has a higher boiling point than N_2 . A capacitor bank with a total capacitance of 60 mF was charged by a direct current (DC) supply that can reach voltages up to 400 V. A relay with programmable ms-level delay time was used to control the discharge time. The high-voltage discharging brings the sample to a high temperature. The detailed conditions for the FJH are listed in Supplementary Table 1. For each condition, three FJH experiments were conducted to collect the total volatiles for sample digestion and ICP-MS measurement. Hence, the measured recovery yield is the average of three independent experiments using the same circuit board. After the FJH reaction, the FJH apparatus was allowed to cool to room temperature while the cold trap remained immersed in the liquid N_2 . Then, the trap was taken out from the liquid N_2 while the apparatus remained under vacuum. After the trap warmed to room temperature, the vacuum was released.

FJH under atmospheric and positive pressure. The FJH reaction is similar to the evaporative separation except with the following changes. The quartz tube was sealed by an O-ring to hold pressure. The porous Cu electrode side was connected to an inner gas (N_2) cylinder by tubing that withstands pressure up to 5 bar. The pressure was adjusted to the desired values (1–4 atm) using a regulator and was monitored by a pressure gauge. Once the pressure was set, the FJH system was charged and then discharged for reaction. The detailed conditions for the FJH are shown in Supplementary Table 2. After the FJH reaction, the pressure was released, and the sample was removed for further analysis.

Characterization. SEM图像是在5 kV电压下使用FEI Helios NanoLab 660双光束SEM系统获得的。使用配置有Cu K α 辐射(=1.5406 Å)的Rigaku D/Max II XRD系统收集XRD。Ultima II system configured with a Cu K α radiation ($\lambda = 1.5406\text{ Å}$). XPS spectra were taken using a PHI Quantera XPS system under the base pressure of 5×10^{-9} Torr. Elemental XPS spectra were collected using a step size of 0.1 eV with a pass energy of 26 eV. All of the XPS spectra were calibrated by using the standard C 1 s peak at 284.8 eV. STEM images and EDS maps were taken on a JEOL 2100 Field Emission Gun Transmission Electron Microscope under the voltage of 200 kV. TGA was conducted in air at a heating rate of $10^\circ\text{C min}^{-1}$ up to 1000°C by using a Q-600 Simultaneous TGA/DSC from TA instruments. Calculation was conducted using the Mafu furnace in the air (NEY 6-160 Å).

Sample digestion and ICP-MS measurement. The standards were purchased from Millipore-Sigma. Three periodic table mixtures and Hg standard were used,

其中成分列于补充表中。样品消解使用 HNO_3 (67–70 wt%, TraceMetal™级, 费希尔化学)。HCl (37 wt%, 99.99% where the composition is listed in Supplementary Table 8. HNO_3 (67–70 wt%, TraceMetal™ Grade, Fisher Chemical), HCl (37 wt%, 99.99% trace metals basis, Millipore-Sigma), and water (Millipore-Sigma, ACS reagent for ultratrace analysis) were used for sample digestion. The samples were digested by using a diluted aqua regia method^{14,19}. The samples were soaked in HNO_3 /HCl (1 M each) solution at 45°C for 24 h. The acidic solution was filtered to remove any undissolved particles. The solution was then diluted to the appropriate concentration range using 2 wt% HNO_3 or HCl within the calibration curve. ICP-MS was conducted using a Perkin Elmer Nexion 300 ICP-MS system. The PCB raw powder, the condensed solid from the cold trap, the PCB-Flash powder, the PCB-Flash-Calcination powder, and the PCB-Calcination powder were leached using the same protocol.

数据可用性
Data availability
支持本研究结果的数据可在文章及其Supplementary Information. Other relevant data are available from the corresponding author upon reasonable request. Source data generated in this study are provided in the Source Data file. The Source Data file is also uploaded to the Zenodo repository <https://doi.org/10.5281/zenodo.5293516>. Source data are provided with this paper.

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