

## Supporting Information

### Selective recovery of Cr from electroplating nanosludge via crystal modification and dilute acid leaching

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Includes 9 pages, 7 figures and 13 tables

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## 1. Characterization of the electroplating sludges

### 1.1. The apparent characteristics of the samples

The four electroplating sludges used in this work are labeled as ES-A, ES-B, ES-C and ES-D, respectively. ES is the abbreviation of electroplating sludge. Their optical photos and moisture contents were shown in Fig. S1 below. The original electroplating sludges were green, brown, grey or cyan due to the species and content of heavy metals. The moisture content ranged from 30% to 70%.

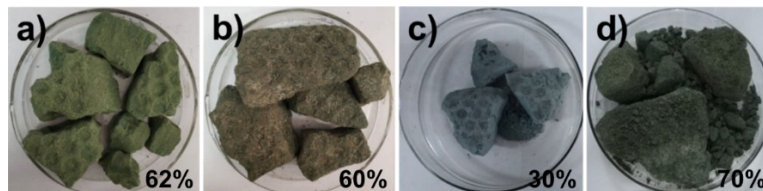


Fig. S1 Photos of the electroplating sludges: (a) ES-A, (b) ES-B, (c) ES-C, (d) ES-D.

### 1.2. Semi-quantification of element contents

X-ray fluorescence (XRF) test was conducted to roughly determine the relative content of the elements with atomic number larger than 8 (oxygen not included). XRF results (Table S1) showed that Al, Cr, Fe, Ni, Cu, and Zn are the major heavy metals.

Table S1 Relative element content of the electroplating sludge obtained by XRF

Mass%	Cr	Ni	Cu	Al	Zn	Fe	Ca	Si
ES-A	1.97	12.86	13.46	5.81	4.42	5.78	31.83	1.86
ES-B	26.54	1.91	1.01	5.17	5.94	5.63	31.95	0.57
ES-C	29.26	28.43	11.09	5.28	0.01	1.33	13.62	1.55
ES-D	38.60	8.48	11.10	9.12	1.17	7.73	7.99	2.82
Mass%	P	S	Na	Mg	Cl	Sn	F	Others
ES-A	12.85	2.29	1.12	0.87	0.51	0.93	2.39	1.05
ES-B	13.55	4.51	0.31	0.75	-	0.06	-	2.10
ES-C	0.51	6.63	0.29	0.16	0.47	0.70	-	0.67
ES-D	3.85	7.07	0.26	0.24	0.34	-	-	1.23

### 1.3. Morphology and element distribution

The microscopic morphology of ES-A, ES-B, ES-C and ES-D was observed via scanning electron microscope (SEM) (Fig. S2-S5). The particles without specific shape were in the scale of less than 100 nm, or even less than 50 nm. The distribution of the elements was observed via energy disperse spectrum (EDS) mapping. It was shown that the distribution of each element was even and in keeping with the overall particles in SEM images, which means the heavy metals coexist with other elements in the nanosized particles homogeneously.

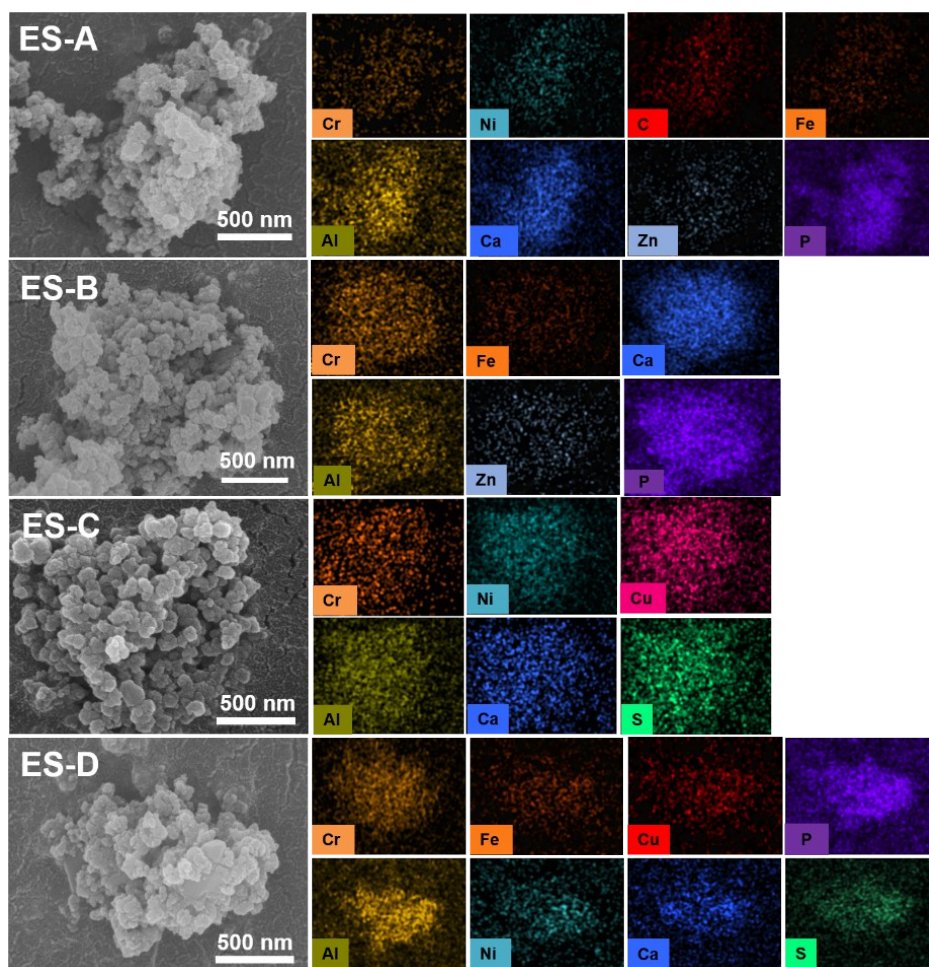


Fig. S2 SEM image and element mapping of (a) ES-A, (b) ES-B, (c) ES-C, (d) ES-D.

#### 1.4. Recovery of heavy metals through acid leaching

For evaluating the extraction rate through traditional hydrometallurgy, these four electroplating sludge samples were leached with  $\text{H}_2\text{SO}_4$  at different concentration. 1.00 g of dried ES sample and 10 mL of  $\text{H}_2\text{SO}_4$  solution (0.05 mol/L or 0.5 mol/L) were added in a conical flask and shaken for 24 hours. Then the leachate was extracted by a syringe and filtered through a 0.22  $\mu\text{m}$  syringe filter for pH and ICP-OES (inductively coupled plasma-optical emission spectroscopy) analysis. The concentration of the heavy metals in the leachate was recorded in Table S1 and Table S2.

Table S2 Concentration of heavy metals in the leachate through diluted acid leaching ( $\text{H}_2\text{SO}_4$ , 0.05 mol/L).

Sample	Conc. of Al (mg/L)	Conc. of Cr (mg/L)	Conc. of Fe (mg/L)	Conc. of Ni (mg/L)	Conc. of Cu (mg/L)	Conc. of Zn (mg/L)
ES-A	0.01	1.79	5.28	72.05	1.79	2.71
ES-B	0.11	11.45	0.06	7.72	0.59	0.54
ES-C	0.16	0.54	0.02	346.79	1.44	2.44
ES-D	73.93	8.28	5.85	767.81	481.01	138.2

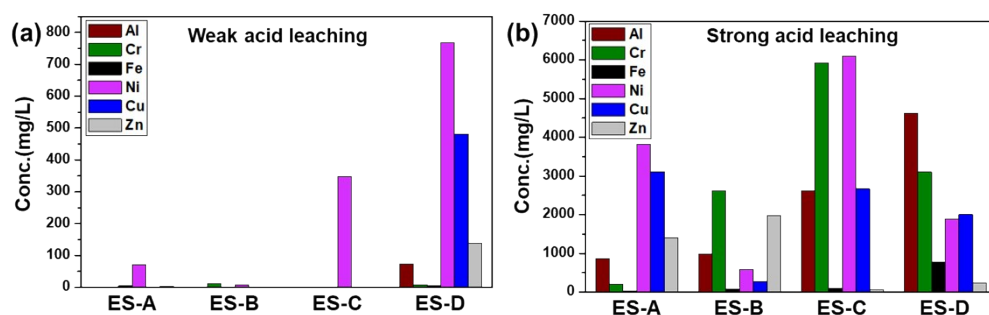
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40 Table S3 Concentration of heavy metals in the leachate through concentrated acid leaching

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Sample	(H <sub>2</sub> SO <sub>4</sub> , 0.5 mol/L)					
	Conc. of Al (mg/L)	Conc. of Cr (mg/L)	Conc. of Fe (mg/L)	Conc. of Ni (mg/L)	Conc. of Cu (mg/L)	Conc. of Zn (mg/L)
ES-A	865.9	205.1	28.5	3820.1	3113.6	1403.0
ES-B	980.2	2619.7	84.9	583.7	263.1	1972.8
ES-C	2626.4	5918.0	89.5	6096.7	2669.1	61.3
ES-D	4616.6	3106.1	767.0	1892.2	2004.1	238.9

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44 Fig. S3 Concentration of heavy metals in leachate after (a) diluted acid leaching (H<sub>2</sub>SO<sub>4</sub>, 0.0545 mol/L), or (b) concentrated acid leaching (H<sub>2</sub>SO<sub>4</sub>, 0.5 mol/L) of different electroplating samples.

## 2. Screening of the additive for selective extraction of Cr

### 2.1. Comparison of different additives

In this experiment, 2.000 g of dried (under 105°C) ES-A sample was calcinated with 0.01 mol of specific additive under 700°C for 8 hours. Then 1.00 g of the calcinated sample was ground and leached with 10 mL of H<sub>2</sub>SO<sub>4</sub> (0.05 mol/L). The volume of the leachate is about 9 mL rather than 10 mL. The extraction rate of the heavy metal (HM) is calculated as following.

$$\text{extraction rate} = \frac{\text{concentration of HM in the leachate} \times 9 \text{ mL}}{\text{content of HM in the calcinated ES sample} \times 1.00 \text{ g}}$$

Table S4 Mass of the additive and the concentration of each heavy metal in the leachate.

Additive	Mass of the additive /g	Conc. of Al (mg/L)	Conc. of Cr (mg/L)	Conc. of Fe (mg/L)	Conc. of Ni (mg/L)	Conc. of Cu (mg/L)	Conc. of Zn (mg/L)
Control	0.000	16.29	345.11	5.27	532.96	570.21	317.42
CaO	0.561	4.66	119.43	0.01	0.27	0.32	0.95
KCl	0.754	13.06	570.15	4.06	217.90	1165.40	261.60
NaCl	0.584	228.01	331.99	5.38	144.02	455.58	95.83
K <sub>2</sub> CO <sub>3</sub>	1.382	189.66	463.98	2.18	0.35	3.02	0.98
Na <sub>2</sub> CO <sub>3</sub>	1.060	267.07	604.53	4.44	0.20	1.68	0.77
KOH	0.561	60.55	721.63	4.47	0.05	0.01	0.71
NaOH	0.400	25.22	779.95	4.92	0.41	0.48	0.94

Content of the heavy metal in a calcinated sample was simply calculated according to (i) the content of heavy metal in the original ES-A sample (content<sub>1</sub>) and (ii) the mass change after calcination. Content of Al, Cr, Fe, Ni, Cu and Zn in the original ES-A sample was 27.6, 8.1, 22.7, 50.0, 55.4 and 18.2 mg/g, respectively. The mass change is mainly due to the mass loss of the sludge sample and the addition of the additive (m<sub>a</sub>). The mass of the control sample without additive changed from 2.000 g to 1.417 g after calcination, so the mass of the calcinated sample is 1.417g+m<sub>a</sub>. Therefore, the following formula is proposed.

$$\text{content of HM in 1 g of a calcinated ES sample} = \text{content}_1 \times 2.00 \text{ g} \times \frac{1 \text{ g}}{1.417 \text{ g} + m_a}$$

Table S5 Content of HM in 1g of a calcinated ES-A sample.

Additive	Content of Al (mg/g)	Content of Cr (mg/g)	Content of Fe (mg/g)	Content of Ni (mg/g)	Content of Cu (mg/g)	Content of Zn (mg/g)
Control	38.94	11.39	31.97	70.50	78.14	25.70
CaO	27.90	8.16	22.90	50.51	55.98	18.41
KCl	25.41	7.43	20.86	46.01	50.99	16.77
NaCl	27.57	8.06	22.63	49.92	55.32	18.20
K <sub>2</sub> CO <sub>3</sub>	19.71	5.77	16.18	35.69	39.56	13.01
Na <sub>2</sub> CO <sub>3</sub>	22.28	6.52	18.29	40.33	44.70	14.70
KOH	27.90	8.16	22.90	50.51	55.98	18.41
NaOH	30.37	8.88	24.93	54.98	60.94	20.04

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66 The extraction rate of heavy metal can be calculated via the formula proposed in the  
 67 beginning of this section and the data in Table S3 and Table S4.

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69 Table S6 Extraction rate (ER) of each heavy metal after leaching the calcinated ES-A sample with  
 70  $\text{H}_2\text{SO}_4$  (0.05 mol/L).

Additive	ER of Al /%	ER of Cr /%	ER of Fe /%	ER of Ni /%	ER of Cu /%	ER of Zn /%
Control	0.38	27.27	0.15	6.80	6.57	11.11
CaO	0.15	13.17	<0.01	<0.01	0.01	0.05
KCl	0.46	69.03	0.18	4.26	20.57	14.04
NaCl	7.44	37.05	0.21	2.60	7.41	4.74
$\text{K}_2\text{CO}_3$	8.66	72.42	0.12	0.01	0.07	0.07
$\text{Na}_2\text{CO}_3$	10.79	83.50	0.22	<0.01	0.03	0.05
KOH	1.95	79.59	0.18	<0.01	<0.01	0.03
NaOH	0.75	79.02	0.18	0.01	0.01	0.04

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## 72 2.2. Selective extraction of Cr from four ES samples with NaOH

73 Concentration of each heavy metal in the leachate of four ES samples calcinated with and  
 74 without NaOH were recorded in Table S6.

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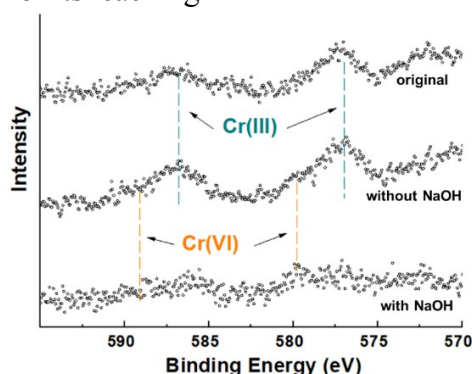
76 Table S7 Concentration of each heavy metal in the leachate of the sample calcinated with and  
 77 without NaOH and leached with  $\text{H}_2\text{SO}_4$  (0.05 mol/L).

Sample	Conc. of Al (mg/L)	Conc. of Cr (mg/L)	Conc. of Fe (mg/L)	Conc. of Ni (mg/L)	Conc. of Cu (mg/L)	Conc. of Zn (mg/L)
ES-A-control	16.29	345.11	5.27	532.96	570.21	317.42
ES-B-control	9.44	107.18	0.33	61.19	22.00	13.23
ES-C-control	644.55	550.13	0.10	500.04	705.97	5.36
ES-D-control	2494.23	13.14	16.31	46.33	578.21	5.84
ES-A-NaOH	25.22	779.95	4.92	0.41	0.48	0.94
ES-B-NaOH	0.02	9367.60	0.05	3.02	0.34	1.25
ES-C-NaOH	0.51	12299.75	0.20	7.28	0.99	0.65
ES-D-NaOH	0.05	6253.75	0.14	10.67	2.32	0.78

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### 79 3. Mechanism analysis

#### 80 3.1. Oxidation of Cr(III) for its leaching



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82 Fig. S4 XPS spectra of the original sample (top), the calcinated sample (middle), and the sample  
83 calcinated with NaOH (bottom) of ES-A. The binding energy of Cr(III) is 577.0 eV (2p 3/2) and  
84 586.8 eV (2p 1/2), the binding energy of Cr(VI) is 579.8 eV (2p 3/2) and 589.1 eV (2p 1/2).

85 (Reference: E. Desimoni, C. Malitesta, P.G. Zamboni, J.C. Riviere, An X-ray photoelectron  
86 spectroscopic study of some chromium-oxygen systems, Surf. Interface Anal., 13 (1988) 173-179.)

87  
88 Table S8 The binding energy (B.E.) of Cr(III) and Cr(VI) in the reference; the fitting parameters  
89 (B.E., peak area and mass ratio of different valence of Cr) of the samples.

	B.E. of Cr(III) / eV (2p3/2; 2p1/2)	Peak area of Cr(III) peaks	B.E. of Cr(VI) / eV (2p3/2; 2p1/2)	Peak area of Cr(VI) peaks	Mass ratio of Cr(III) and Cr(VI)
Reference	577.0 eV; 586.8 eV	-	579.8 eV; 589.1 eV	-	-
ES-B	577.25 eV; 587.05 eV	-	-	-	100%; 0%
ES-B-control	576.39 eV; 586.79 eV	-	-	-	100%; 0%
ES-B-NaOH	-	-	579.35 eV; 589.05 eV	-	0%; 100%
ES-C	577.08 eV; 586.88 eV	-	-	-	100%; 0%
ES-C-control	576.83 eV; 586.63 eV	39468	579.42 eV; 588.72 eV	4372	90.03%; 9.97%
ES-C-NaOH	576.8 eV; 586.6 eV	933	579.65 eV; 588.95 eV	22636	3.96%; 96.04%
ES-D	577.28 eV; 587.08 eV	-	-	-	-
ES-D-control	576.25 eV; 586.85 eV	-	-	-	100%; 0%
ES-D-NaOH	576.81 eV; 586.31	8465	579.57 eV; 589.07 eV	106014	7.39%; 92.61%



The ratios of NaOH consumed in oxidation of Cr in samples ES-C and ES-D were calculated, which is the proportion of the practical amount of consumed NaOH and the amount of added NaOH (0.010 mol). The former one was calculated via multiplying the theoretical total amount of required NaOH with the oxidation ratio of Cr.

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Table S9 Theoretical amount of required NaOH and the practical consumed NaOH for Cr oxidation in ES-C and ES-D.

Sample	Theoretical total amount of required NaOH /mol	Oxidation ratio of Cr /%	Practical amount of consumed NaOH /mol	Ratio of consumed NaOH /%
ES-C	0.0095	96.0	0.00912	91.2
ES-D	0.0115	92.6	0.010649	106.5

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### 3.2. Nanocrystal growth of NiO and CuO for their retaining

2.00 g of ES-C and 5 mL of NaOH solution (2 mol/L) were mixed in a porcelain boat and well stirred. The sample was then dried at an oven for removing the water. After crushing, it was calcinated in the muffle furnace under different temperature for 2 hours. 1.000 g of calcinated sample was leached with 10 mL of H<sub>2</sub>SO<sub>4</sub> solution (0.05 mol/L) and shaken for 24 hours. The concentration of each heavy metal in leachate was analyzed via ICP-OES, and the selectivity of Cr was calculated.

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Table S10 Concentration of Cr, Ni, Cu, and Al in the leachate of the ES-C sample calcinated under different temperature for 2 hours; selectivity of Cr in each leachate. (pH=6)

Calcination temperature /°C	Conc. of Cr (mg/L)	Conc. of Ni (mg/L)	Conc. of Cu (mg/L)	Conc. of Al (mg/L)	Relative conc. of Cr /%
200	722.3	395.4	13.4	1.32	63.78
300	5082.4	427.6	18.3	1.75	91.91
400	8516.1	374.2	15.9	0.83	95.61
500	9727.6	14.98	0.46	1.09	99.83
600	10014.8	14.69	0.47	0.44	99.84

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NiO and CuO remained in the residue after leaching the calcinated sample. Subsequently, the crystalline sizes of NiO and CuO before and after leaching were calculated via Debye-Scherrer formula. Enlarged XRD patterns were shown in Fig. S5.

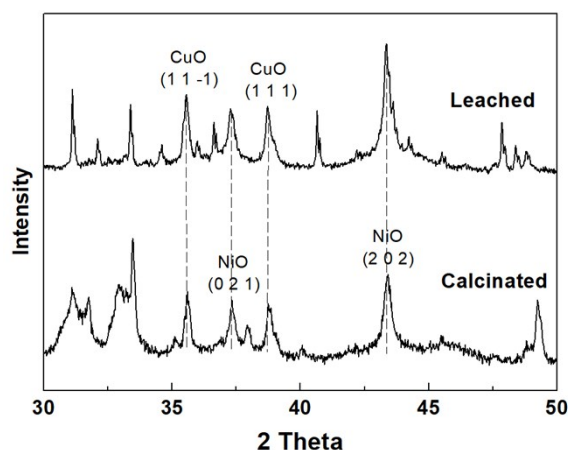


Fig. S5 XRD patterns of the calcinated sample and the leached residue.

The formula and parameters were shown below.

$$\text{Crystallite size} = \frac{\text{Scherrer factor} \times \text{wavelength}}{(\text{observed FWHM} - \text{structural FWHM}) \times \cos \theta}$$

Here, Scherrer factor = 0.9; Wavelength of the X-ray generated from Cu target = 0.15406 nm;  
Structural FWHM = 0.072 (2 $\theta$ ).

Table S11 Crystallite sizes of NiO in ES-C after calcination with NaOH and the one after calcination and leaching.

Sample and crystal face	Peak position / 2 Theta	Observed FWHM / 2 Theta	Crystallite size / nm
Calcinated (0 2 1)	37.323	0.192	69.1
Calcinated (2 0 2)	43.403	0.192	70.5
Leached (0 2 1)	37.297	0.206	62.6
Leached (2 0 2)	43.338	0.142	120.8

Table S12 Crystallite sizes of CuO in ES-C after calcination with NaOH and the one after calcination and leaching.

Sample and crystal face	Peak position / 2 Theta	Observed FWHM / 2 Theta	Crystallite size / nm
Calcinated (1 1 -1)	35.595	0.186	72.4
Calcinated (1 1 1)	38.751	0.192	69.4
Leached (1 1 -1)	35.551	0.142	117.9
Leached (2 0 2)	38.708	0.178	78.6

## 4. Application and environmental implication

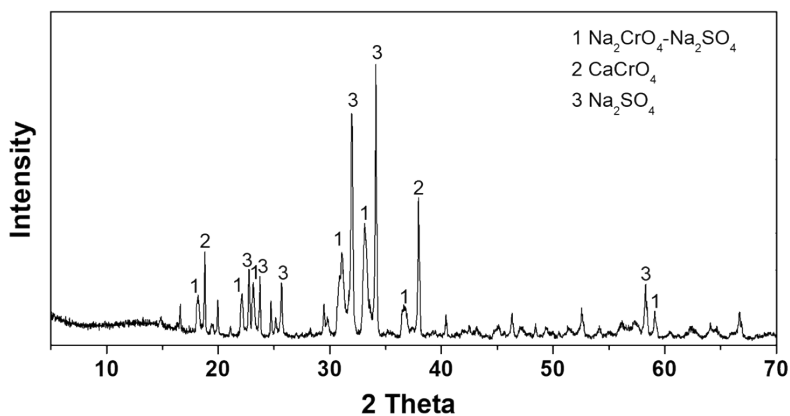
2.000 g of ES-C samples was calcinated with 0.01 mol of NaOH under 600°C for 3 hours, following the process described above. The leaching process was modified. 1.000 g of the calcinated sample was mixed with 10 mL of H<sub>2</sub>SO<sub>4</sub> solution (0.05 mol/L) and treated with ultrasonic for 15 min, then shaken for 30 min. After centrifugation, the supernatant was extracted with a syringe. This procedure was repeated for 5 times for sufficiently extracting Cr in the residue, and pH of the leachate was kept in 4~5. The amount of the heavy metals in the leachate was recorded in Table S11. After that, the leachate was simply evaporated for obtaining the recovered Cr products. Both of the products and the residue were identified via XRD, as shown in Fig. S6 and S7.

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Table S13 Volume of the leachate and concentration of each heavy metal in the leachate.

Batch	Volume (mL)	Conc. of Cr (mg/L)	Conc. of Ni (mg/L)	Conc. of Cu (mg/L)	Conc. of Al (mg/L)
No. 1	9.5	15623.95	70.75	54.25	51.75
No. 2	10	1597.74	73.28	16.82	11.66
No. 3	10	529.74	61.42	5.98	4.82
No. 4	10	234.28	74.94	121.28	51.09
No. 5	10	50.21	18.02	14.26	14.42
Summary	49.5	172.5 mg	2.95 mg	2.10 mg	1.31 mg

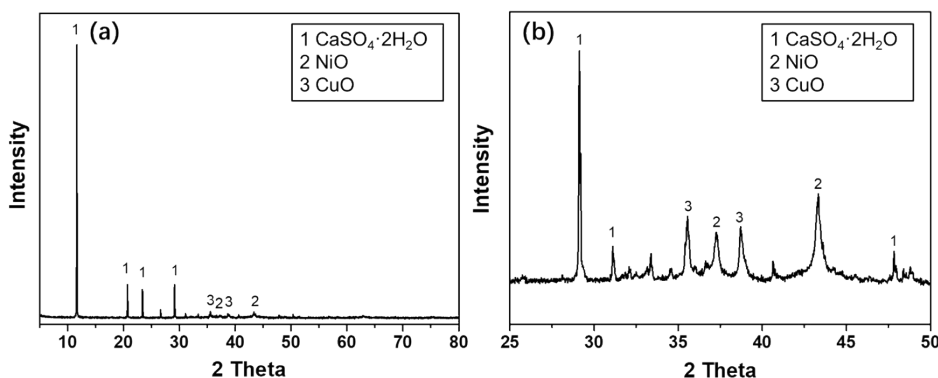
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Fig. S6 XRD pattern of the crystals obtained after evaporation of the leachate.

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Fig. S7 (a) XRD pattern of the residue after calcination and acid leaching; (b) the enlarged XRD