Supplementary Information

Precise reduction of spent Li-ion battery cathode and new phase transition mechanism by self-generated H_2 to achieve dual-recycling of resources and energy

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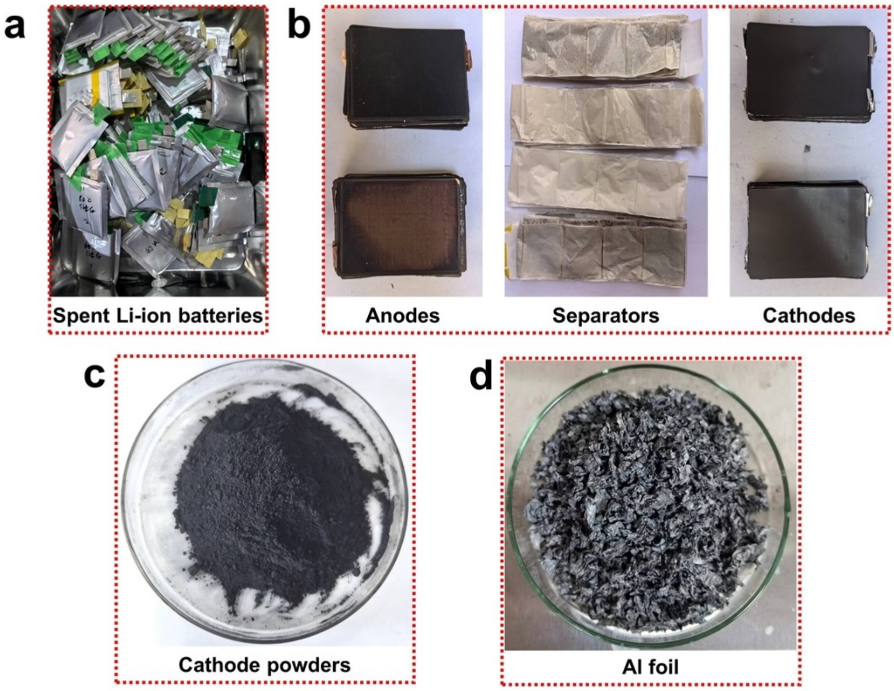

Figure S1. Dismantling process of spent LCO batteries. The digital photos: (a) spent LCO batteries, (b) the main components of spent LCO batteries, (c) cathode powders, (d) Al foil.

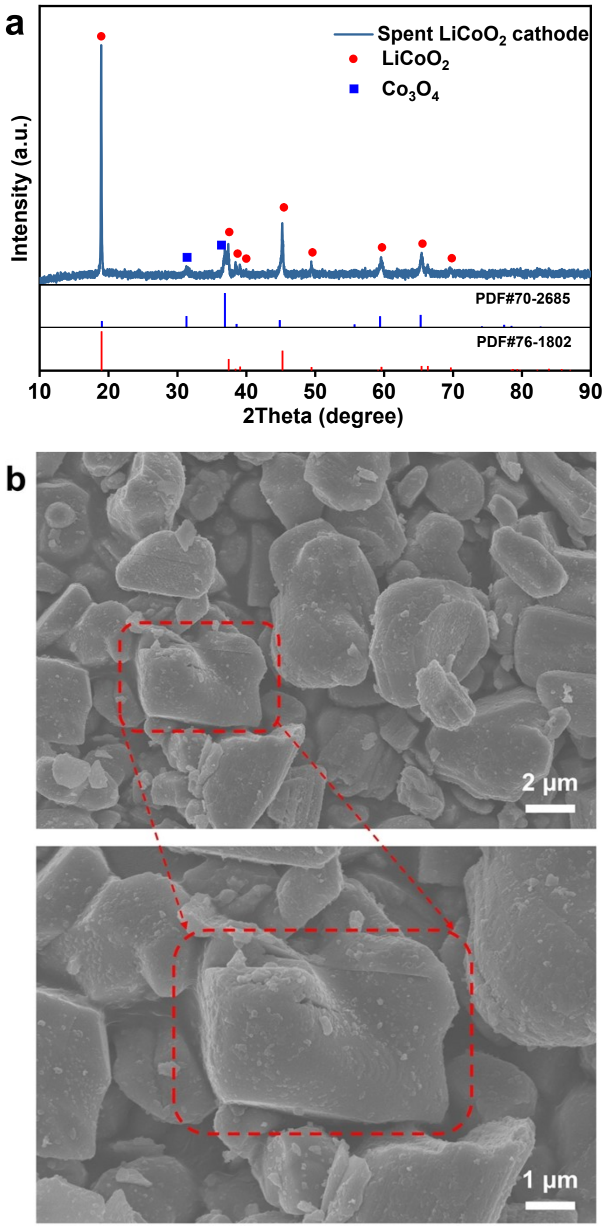

Figure S2. (a) XRD pattern of spent LCO material; (b) SEM images of spent LCO material.

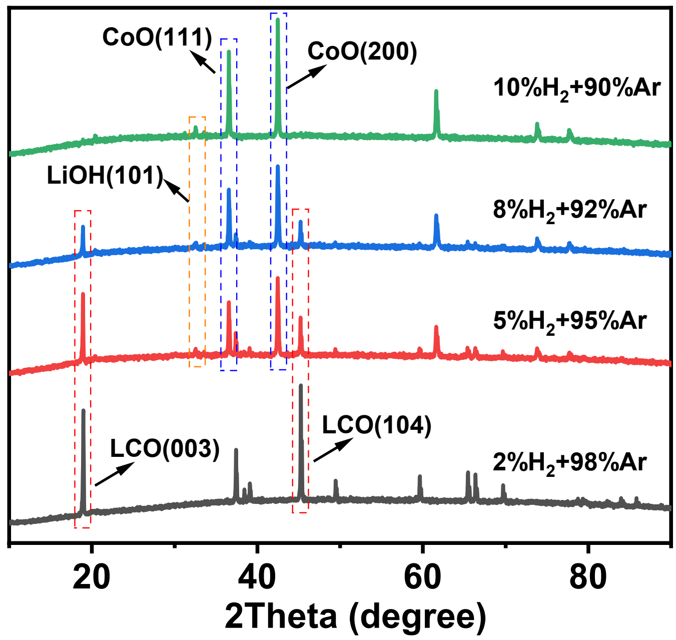

Figure S3. XRD patterns of reduction products at different hydrogen concentrations.

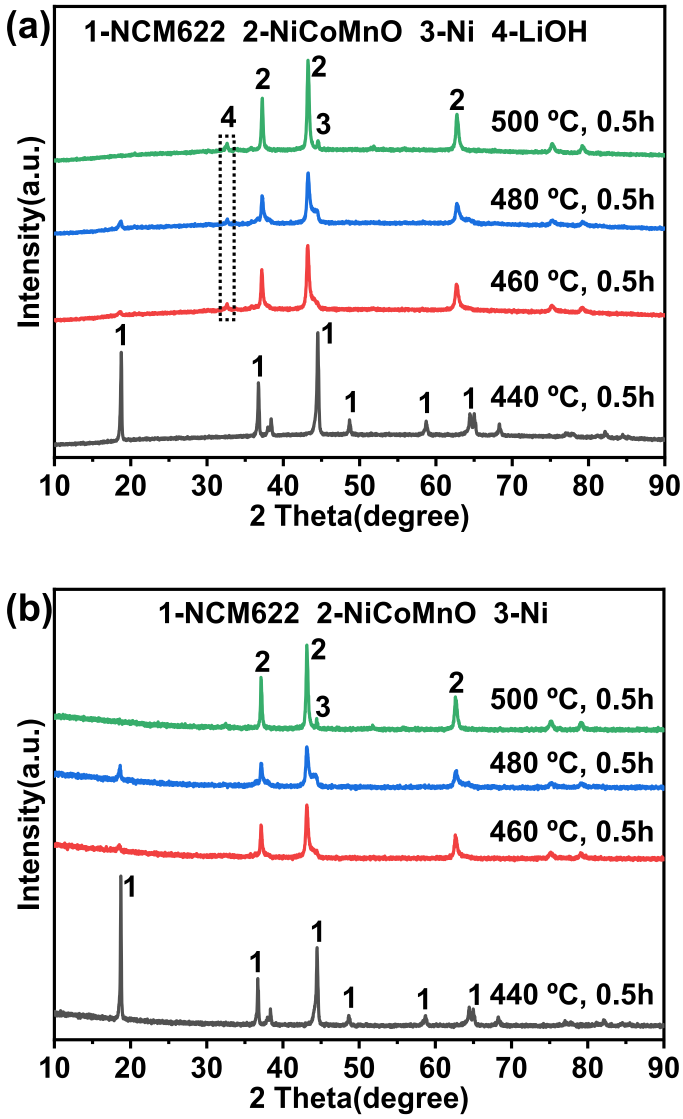

Figure S4. XRD patterns of the H_2 reduction product (a) and the leaching residue (b) of spent $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM622).

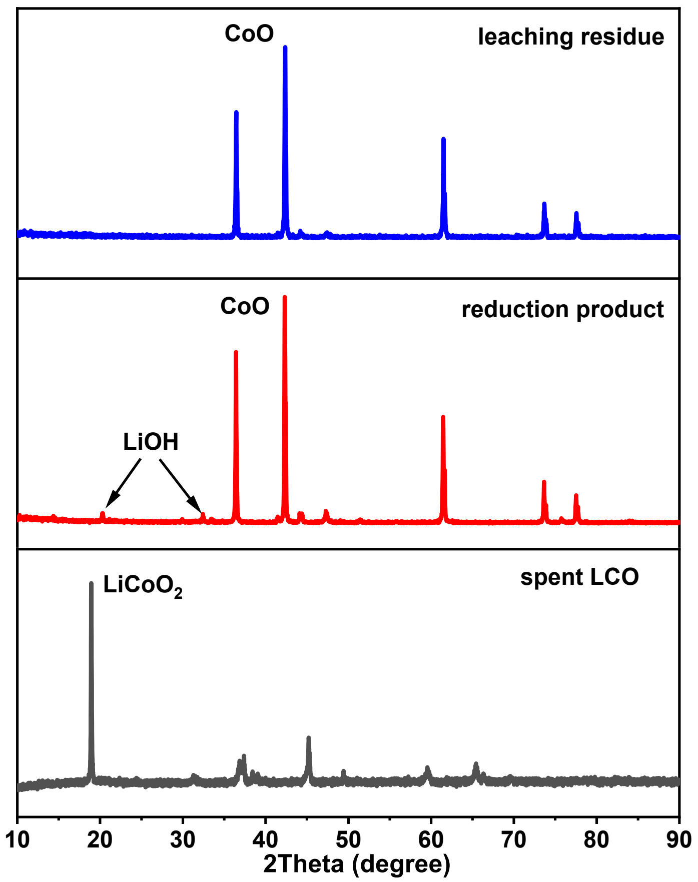

Figure S5. XRD patterns of spent LCO, the reduction product, and the leaching residue.

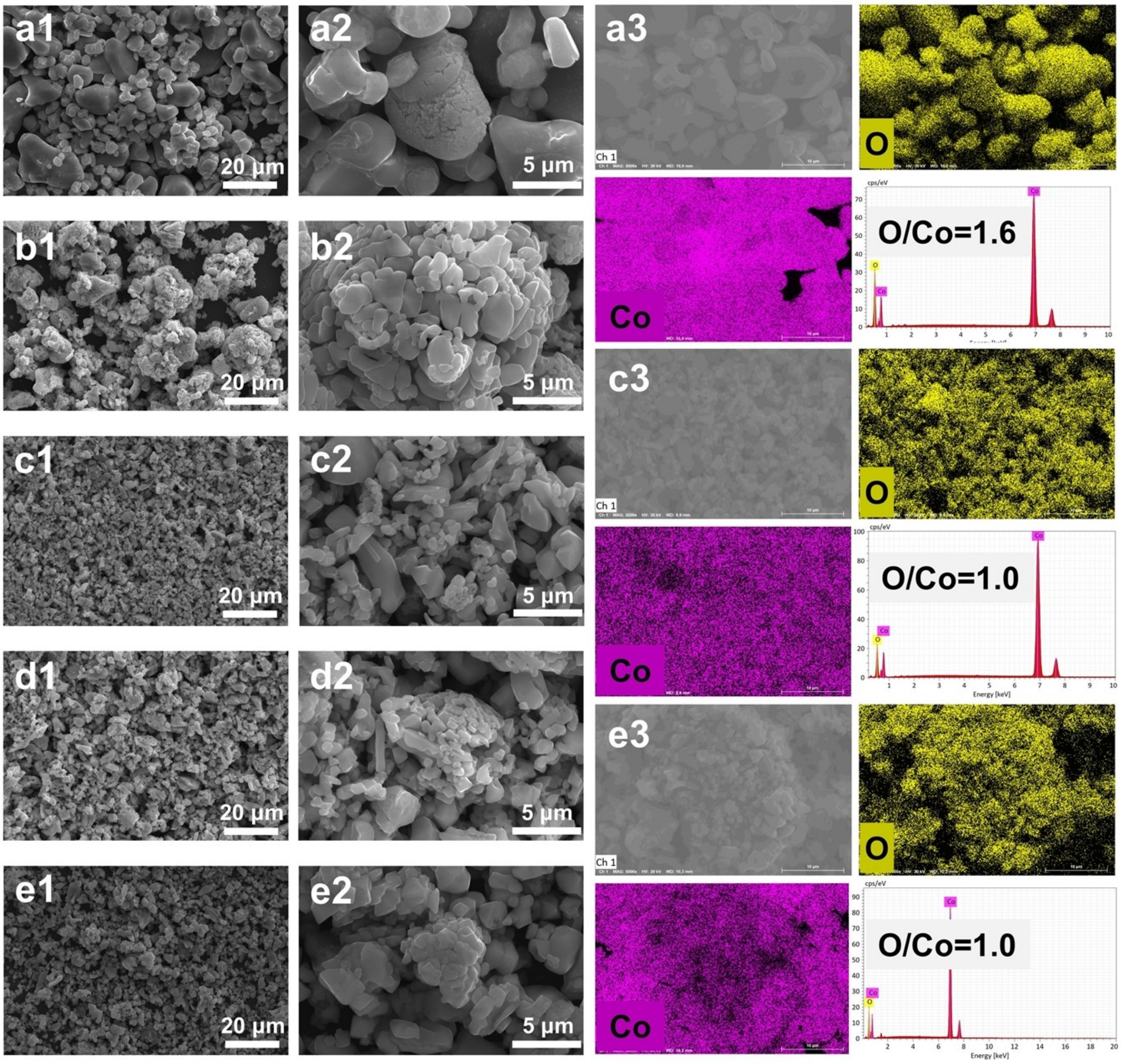

Figure S6. SEM images of leaching residues at different reduction temperatures. (a1, a2) 450 ºC, (b1, b2) 470 ºC, (c1, c2) 490 ºC, (d1, d2) 500 ºC, and (e1, e2) 510 ºC. EDS-mapping results at (a3) 450 ºC, (c3) 490 ºC, and (e3) 510 ºC.

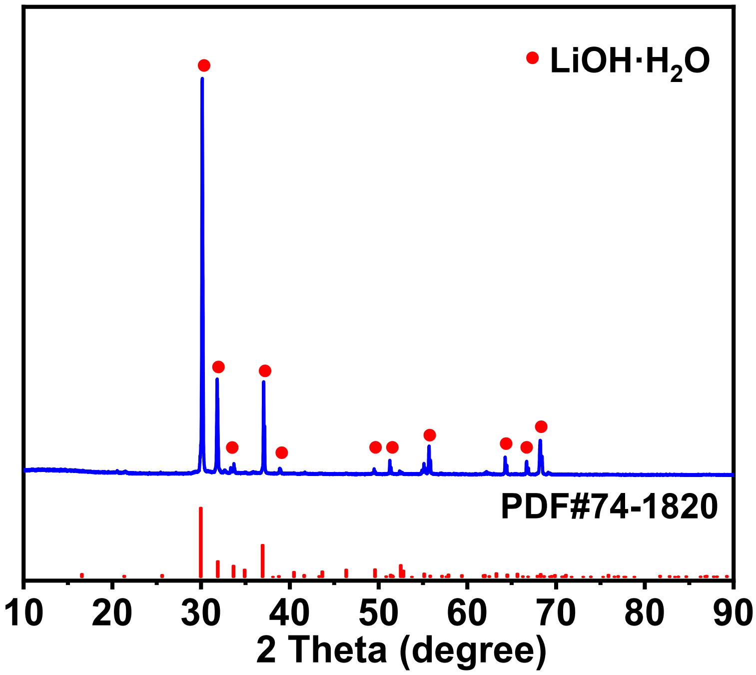

Figure S7. XRD pattern of $LiOH \cdot H_2O$ recovered by evaporation crystallization.

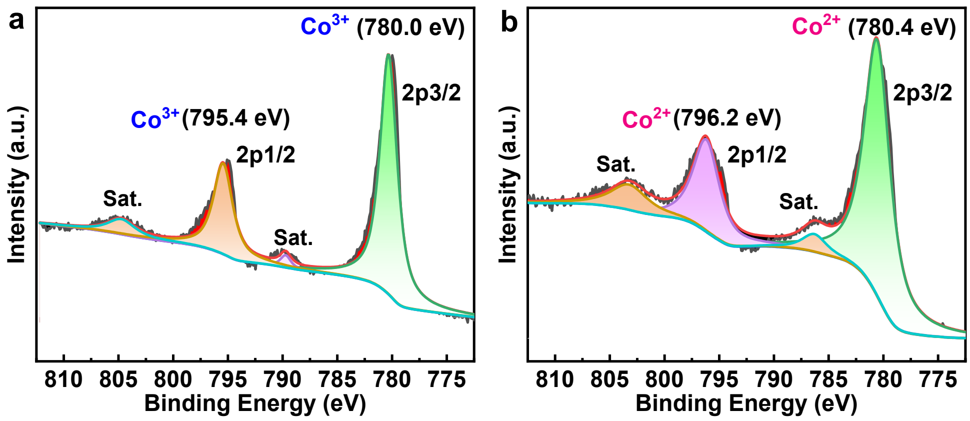

Figure S8. XPS survey spectra of Co2p of (a) spent LCO and (b) reduction product.

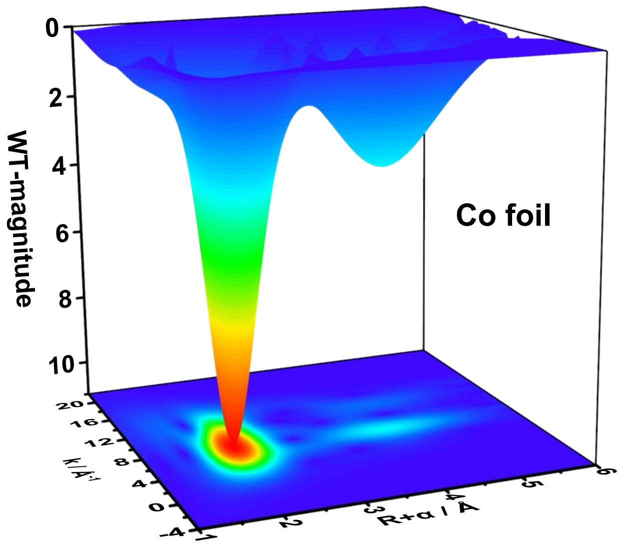

Figure S9. k^3-weighted Co K_3-edge WT-EXAFS contour plots of Co-foil.

Table S1. Lattice parameters (a, c) and lattice volume (V) of LCO and LCO (at 500 ºC in Ar) powders given with reliability factors of weighed (R_{wp}) profiles and goodness of fit (χ^2) values.

	LCO	LCO at 500 ºC in Ar
a (Å)	2.813848	2.866973
c/a	4.992	4.954
V (Å^3)	96.325	101.098
Li at Co site	1.884%	7.872%
$I_{(003)}/I_{(104)}$	1.745	1.094
$(I_{(006)}+I_{(012)})/I_{(101)}$	0.417	0.477
R_p (%)	5.3%	4.9%
R_{wp} (%)	6.8%	6.3%
Gof (χ^2)	1.27	1.53

Table S2. Possible chemical reactions during H_2 reduction process.

	Reactions	ΔH (kJ/mol)	ΔG (kJ/mol)
(1)	$2LiCoO_2 + H_2 (g) = Li_2O + 2CoO + H_2O (g)$	40.81	11.78
(2)	$Li_2O + H_2O (g) = 2LiOH$	-130.09	-88.11
(3)	$2LiCoO_2 + H_2 (g) = 2LiOH + 2CoO$	-89.28	-76.33
(4)	$CoO + H_2 (g) = Co + H_2O (g)$	-3.88	-14.38
(5)	$2LiCoO_2 + 3H_2 = Li_2O + 2Co + 3H_2O (g)$	33.04	-16.99

Table S3. Main materials used in different recycling processes*.

Materials	Price ($/t)	Usage for Pyro-(t)	Usage for Hydro-(t)	Usage for This work (t)
Recycled LCO battery powder (Co=27.5%, Li⩾3.5%)	5000	1	1	1
HCl	11.6	1.255	/	/
H_2O_2	118.7	/	0.159	/
H_2SO_4	56.3	/	0.705	/
NaOH	343.4	0.353	0.353	/
Na_2CO_3	242.3	0.267	0.267	/
H_2O	0.373	29.85	29.85	7.06

*The prices of other metallic compounds are referenced from China Metals Network (www.cbcie.com) and https://www.100ppi.com; The prices of recycled LCO black powder are referenced from Mysteel Network (www.mysteel.com).

Table S4. Main products of different recycling processes*.

Materials	Price ($/t)	Yield for Pyro-(t)	Yield for Hydro-(t)	Yield for This work (t)
Cu	6600	0.205	0.205	0.205
Al	1300	0.103	0.103	0.103
Spent graphite	197	/	0.236	0.236
$CoOH_2$	11050	0.410	0.410	/
Li_2CO_3	10552	0.186	0.186	/
LiOH	12960	/	/	0.121
CoO	17610	/	/	0.35

*The price of Li_2CO_3, $CoCO_3$, LiOH, and CoO are referenced from Shanghai Nonferrous Metals Network (https://hq.smm.cn/).

Table S5. Energy consumption of different recycling methods.

Methods	Energy consumption (MJ/t)
Pyrometallurgy	5312
Hydrometallurgy	396
This work	2656

The energy consumption of pyrometallurgical and hydrometallurgical recycling was primarily derived from the EverBatt 2020 database. The dominant pyrometallurgical method usually requires a temperature of over 1000 °C, while this work requires a temperature of 500 °C and a shorter heating time, so we estimate that the energy consumption of this work is only 50% of the pyrometallurgical method.

Table S6. Calculation of total cost and possible profit of different recycling methods (1t LCO).

Methods	Materials cost ($)	Process cost ($)		Income ($)	Profit ($)
		Chemical cost ($)	Energy cost ($)		
Pyrometallurgy	5000	211.68	132.8	7980.07	2635.59
Hydrometallurgy	5000	255.68	9.9	8026.56	2760.98
This work	5000	2.63	66.4	9265.05	4196.02

[1] B. Ravel, M. Newville, *J. Synchrotron Radiat.* **2005**, *12*, 537-541.

[2] S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, M. J. Eller, *Phys. Rev. B* **1995**, *52*, 2995-3009.

[3] Z. Xia, H. Zhang, K. Shen, Y. Qu, Z. Jiang, *Phys. Rev. B Condens. Matter* **2018**, *542*, 12-19.