

# **Directly upgrading spent graphite anodes to stable CuO/C anodes by utilizing inherent Cu impurity from spent lithium-ion batteries**

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## **S1 Experimental**

### ***S1.1 Confirmation of air oxidation temperature***

The spent anode was initially immersed into deionized water and subjected to continuous ultrasonication to separate SG and Cu foil. To ascertain the suitable oxidation temperature, the TGA curves of individual SG and Cu foil were both recorded under air and N<sub>2</sub> atmospheres. The TGA curve of the SG sample tested under a N<sub>2</sub> atmosphere (refer to Fig. S9a) shows a weight loss of ~7 wt.% as the temperature increases to 800 °C. In contrast, the TGA curve tested under an air atmosphere (refer to Fig. S9b) displays two distinct platforms. The initial weight loss below 530 °C (~7 wt.%) corresponds to the evaporation of adsorbed water and decomposition of organic impurities, whereas the weight loss between 530 °C and 800 °C (~93 wt.%) can be attributed to the combustion of graphite. As indicated in Fig. S9c, the Cu undergoes effective oxidation at ~400°C. In order to ensure the thorough oxidation of Cu without combusting the graphite phase, the final oxidation temperature was ultimately determined to be 530°C.

### ***S1.2 Proportion optimization of CuO/RG hybrids***

The electrochemical performance of CuO/RG hybrids is greatly influenced by the proportions of CuO and SG. Insufficient CuO content may result in relatively low capacity, whereas excessive CuO content is likely to cause inferior cycling stability. To check the most optimal proportion, different proportions of CuO/RG hybrids were prepared by mechanical blend of extra SG with the CuO/RG-40% sample, and then their cycling performance was measured at a current density of 372 mA/g, as shown in

Fig. S10. It is evident that the 40 wt.% sample, despite initially exhibiting a notably high discharge-specific capacity, displays poor cycling stability and experiences significant deterioration after approximately 150 cycles. This is attributed to an excessive CuO content, which exceeds the capacity of the available graphite to mitigate the volume expansion of CuO. In contrast, the 10–30 wt.% CuO samples consistently demonstrate stable cycling performance. Hence, taking into account both specific capacity and cycling stability, we selected the 30 wt.% CuO samples as the target materials for all subsequent experiments.

### ***S1.3 Material characterizations***

X-ray diffraction (XRD, D 8 Advance, Bruker, Germany) was employed to analyze the oxidation of Cu in CuO/SG and CuO/RG–30% samples and the change of graphitization of graphite. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD, UK) was used to analyze the binding of CuO to graphite. Fourier Transform infrared spectroscopy (FT-IR, BRUKER VERTEX7, Germany) was used to analyze the binding of CuO to graphite in CuO/RG–30% samples. Raman spectra (Raman, Renishaw inVia, UK) was utilized to explore the disorder degree of different samples. Scanning electron microscope (SEM, JEOL JSM 7401, Japan) were used to analyze the distribution of elements in Cu/SG and CuO/RG–30% and the removal of impurities from Cu/SG. Transmission electron microscope (TEM, TalosF200X, USA) was used to analyze the binding of CuO to graphite. Inductive coupled plasma emission spectrometer (ICP, OPTIMA 8300, Thermo Scientific, USA) was used to analyze the metal impurities in Cu/SG and CuO/RG–30%. The thermal stability of SG and Cu foil

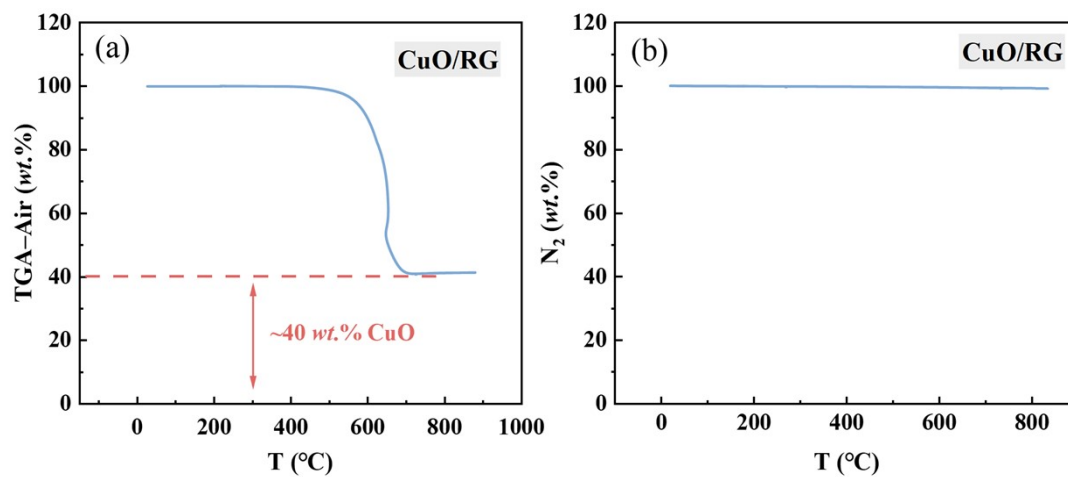
were tested by thermogravimetric analysis (TGA, Diamond TG, Japan).

#### ***S1.4 Electrochemical tests***

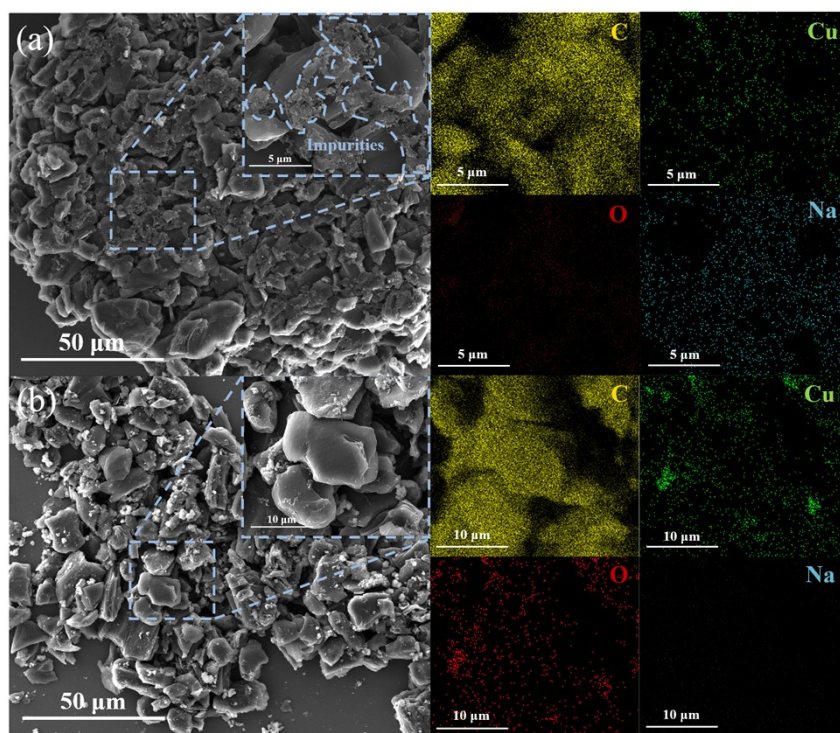
The electrochemical performance of the obtained samples was studied by coin cells (CR 2025) using lithium foil and microporous polypropylene membrane as counter electrode and separator, respectively. The working electrode was made by casting the mixed slurry (80 wt.% active material, 10 wt.% acetylene black, 5 wt.% styrene–butadiene rubber and 5 wt.% carboxymethylcellulose sodium) onto a cleaned Cu foil and dried in vacuum overnight. The size of each electrode was controlled as a circular disk with an average diameter of 12 mm, and the mass loading of active material on each electrode was set as  $\sim 1.0 \text{ mg cm}^{-2}$ . The electrolyte used in this work was made of  $\text{LiPF}_6$  (1 M) dissolved into a mixed solvent of ethylene carbonate, dimethylcarbonate and ethylmethyl carbonate (1:1:1 by volume). The cell was assembled inside an Ar–filled glove box with both  $\text{H}_2\text{O}$  and  $\text{O}_2$  below 0.1 ppm. Galvanostatic charge/discharge measurement was conducted on a multichannel battery testing system (CT3002A, China) between 0.01 and 3.0 V (*vs.*  $\text{Li}^+/\text{Li}$ ). Cyclic voltammetry (CV) test was carried out on an electrochemical workstation (CHI 760E, China) at a scan rate of  $0.2 \text{ mV s}^{-1}$ . Electrochemical impedance spectroscopy (EIS) plots were recorded on the open circuit potential within the frequency range from 0.01 Hz to 100 kHz.

In the context of full–cell tests, anodes comprised CuO/RG–30% electrodes, while cathodes consisted of commercial  $\text{LiCoO}_2$  electrodes. The CuO/RG–30% anode electrodes were prepared through a process involving the casting of a slurry mixture

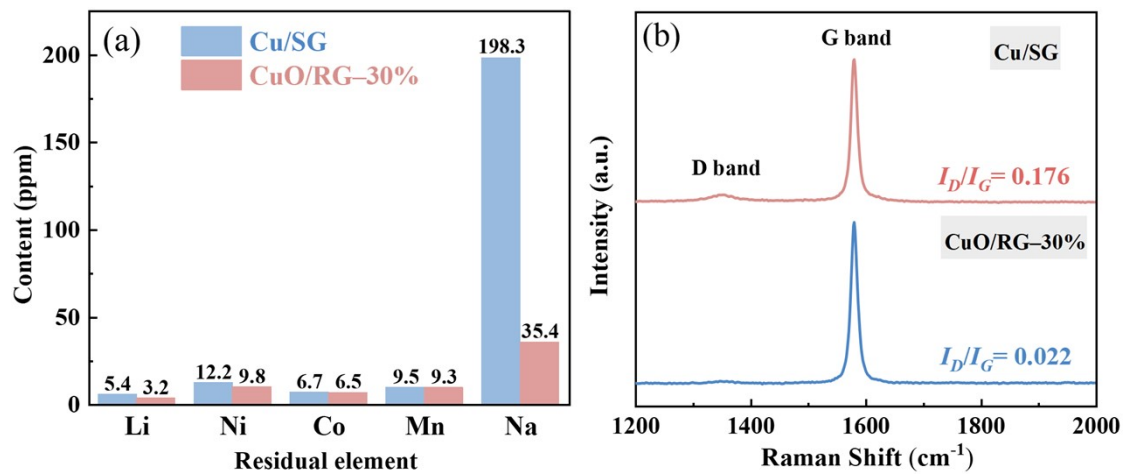
(comprising 80 wt.% active material, 10 wt.% acetylene black, 5 wt.% styrene-butadiene rubber, and 5 wt.% sodium carboxymethylcellulose) onto pristine Cu foil, followed by an overnight drying phase within a vacuum environment. Similarly, LiCoO<sub>2</sub> electrodes were crafted by casting a slurry mixture (consisting of 80 wt.% active material, 10 wt.% Super-P, and 10 wt.% PVDF) onto clean Al foil, which was also subjected to an overnight drying process within a vacuum. The dimensions of each electrode were precisely controlled to adopt a disk-like configuration with an average diameter of 12 mm, and the active material loading on each electrode was maintained at approximately ~1.0 mg/cm<sup>2</sup>. Notably, the capacity ratio between the anode and cathode electrodes (referred to as the N/P ratio) was preconfigured at 1.1:1. Full cells use the same electrolyte as half cells. The cell was assembled inside an Ar-filled glove box with both H<sub>2</sub>O and O<sub>2</sub> below 0.1 ppm. Galvanostatic charge/discharge measurement was conducted on a multichannel battery testing system (CT3002A, China) between 2.8 and 4.3 V.



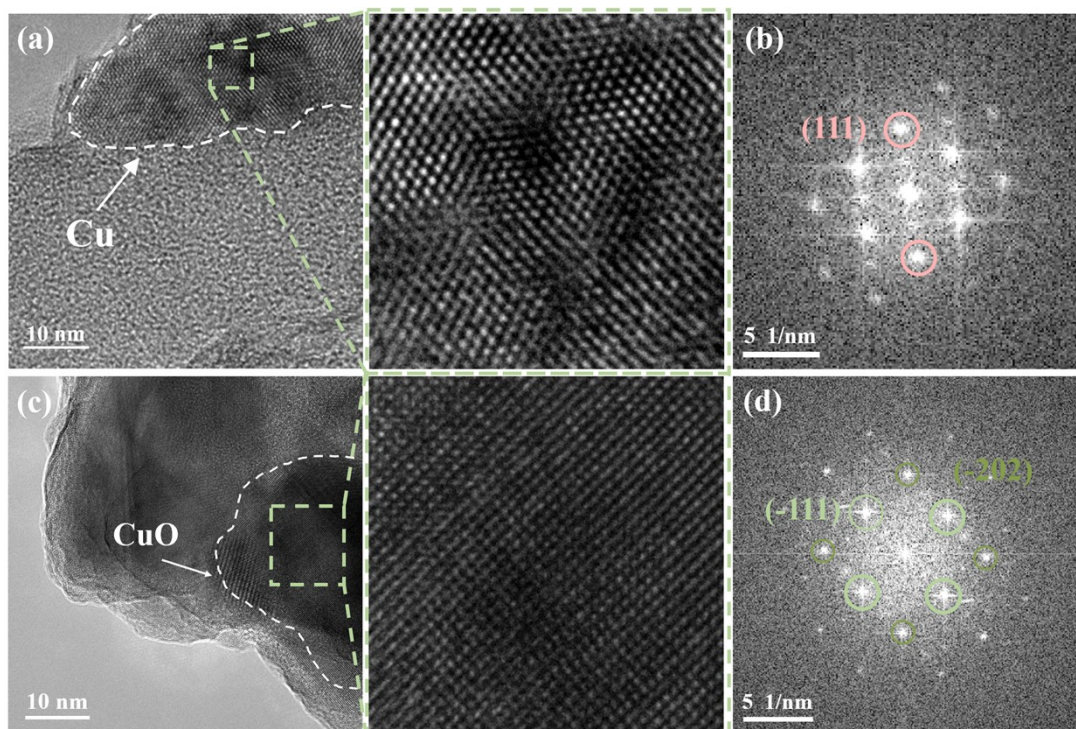
**Fig. S1** (a, b) TGA curves of CuO/RG in air and N<sub>2</sub> atmosphere



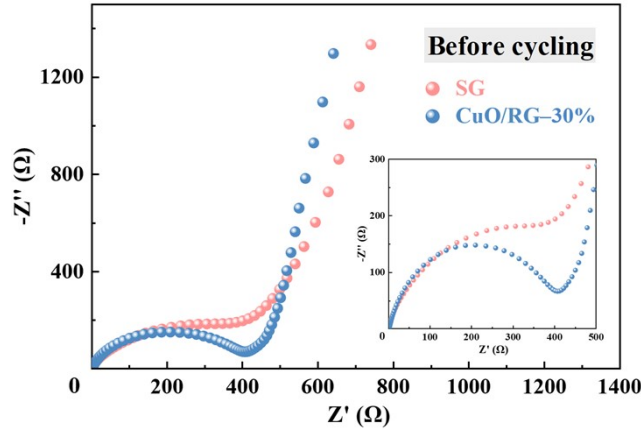
**Fig. S2** (a) SEM images of Cu/SG; (b) SEM images of CuO/RG-30%



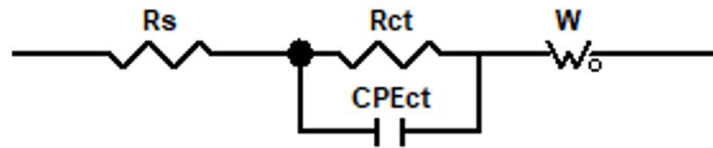
**Fig. S3** (a) ICP result of Cu/SG and CuO/RG-30%; (b) Raman spectra of Cu/SG and CuO/RG-30%



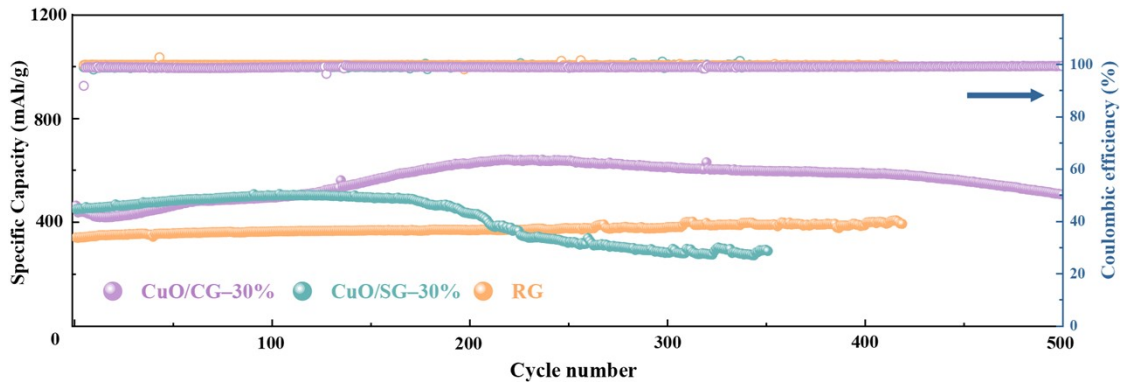
**Fig. S4** (a, c) HRTEM images of Cu/SG and CuO/RG-30%; (b, d) The corresponding selected area electron diffraction (SAED) patterns of Cu/SG and CuO/RG-30%



**Fig. S5** Nyquist plots of SG and CuO/RG-30% electrode before cycling



**Fig. S6** Equivalent circuit diagram

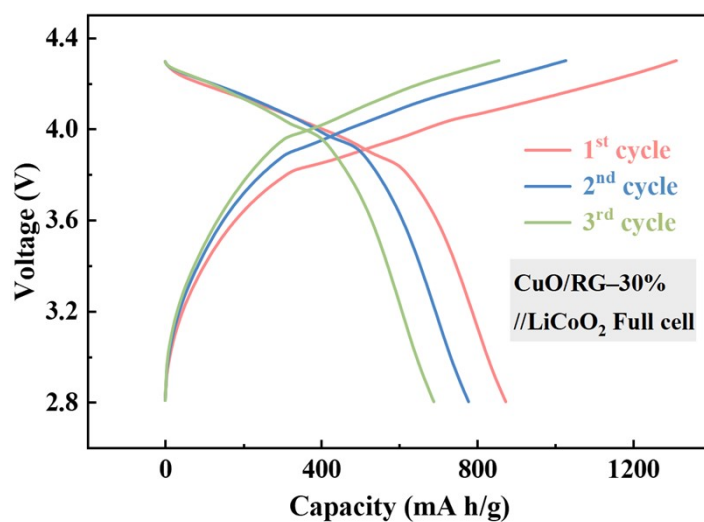


**Fig. S7** Cycling performance of RG, CuO/SG-30% and CuO/CG-30% electrodes at 372 mA/g

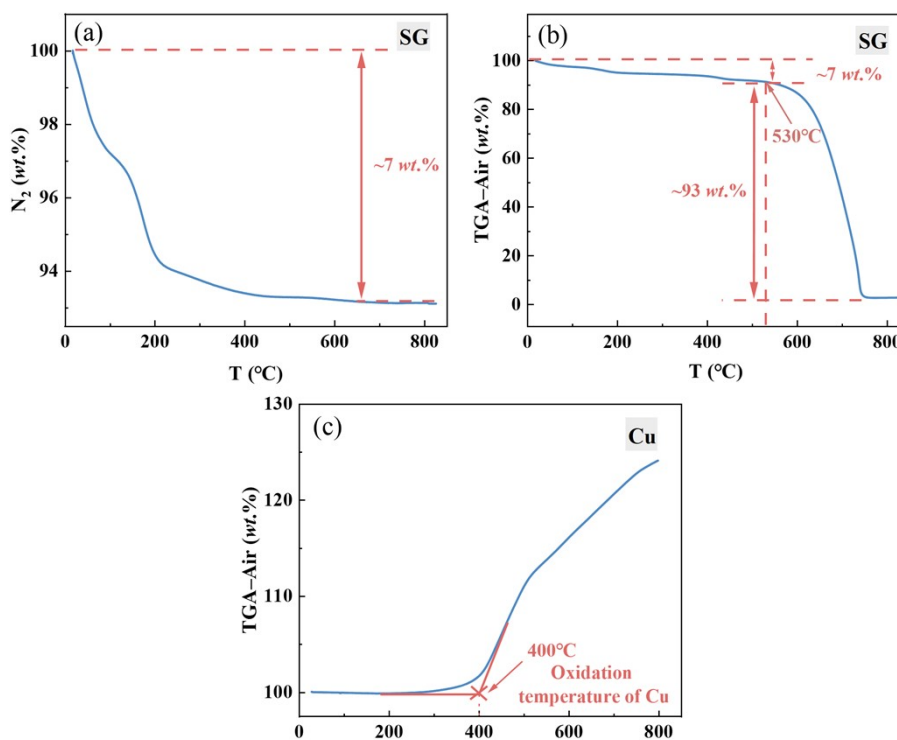
**Note:** The preparation of CuO/CG-30% sample was as follows. Firstly, the Cu current collector was separated from the spent anode, and then crushed through an 800-mesh screen. Subsequently, the crushed Cu was mixed with CG by ball-milling and finally calcined at 530°C under an air atmosphere for 3 h to obtain CuO/CG-30%. By contrast,



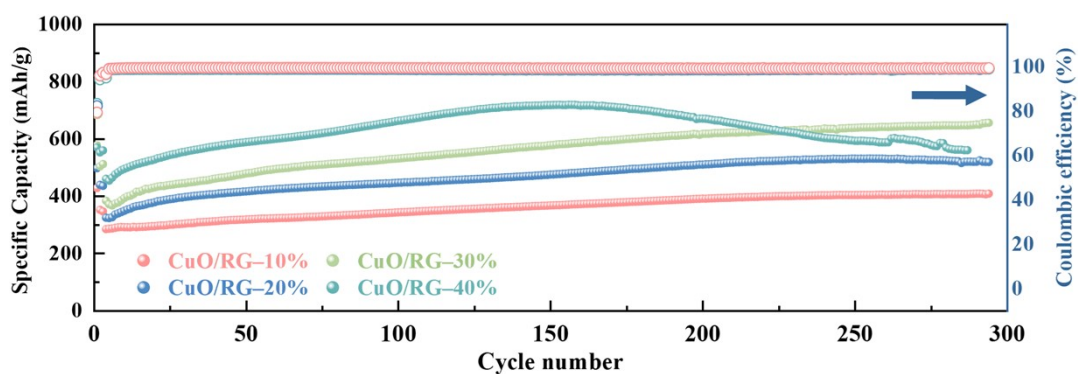
the preparation of CuO/SG-30% sample was little different. The crushed Cu was firstly calcined at 530°C in air for 3 h to make CuO, which was then mixed with SG to obtain CuO/SG-30% sample. RG is obtained by calcining SG at 530°C for 3h in air.



**Fig. S8** Charge/discharge curves of CuO/RG-30%//LiCoO<sub>2</sub> full cell



**Fig. 9** (a, b) TGA curves of SG in air and N<sub>2</sub>; (c) TGA curves of Cu in air



**Fig. S10** Cycling performance of the electrodes with different CuO contents at 372 mA/g

**Table S1** The EIS fitting parameters of different electrodes before cycling

Samples	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$W_o$ ( $\Omega$ )
SG	2	337	253
CuO/RG-30%	3	318	25

**Table S2** The EIS fitting parameters of CuO/RG-30% electrode for different cycles

Cycle number	$R_s$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$W_o$ ( $\Omega$ )
0	3	318	25
5	4	91	186
10	4	49	166

**Table S3** Environmental–economic relevant data of the proposed process in this work

Technology	Raw material	CO <sub>2</sub> (g)	NO <sub>x</sub> (g)	SO <sub>x</sub> (g)	Total energy (MJ)	Water (L)	Profit (\$)
Shredding	Spent anode 1 kg	24.67	0.08	0.07	1.08	–	-0.02
Calcination	Cu/SG 1 kg	1233.29	4.20	3.33	54.00	–	-1.24
Product	CuO/RG– 30% 1 kg						+8.96
Total		1257.96	4.28	3.40	55.08		+7.70

1. This program is based on the work done by the existing battery recycling plant industry line, so the dismantling part of the battery is not included in the calculation.
2. Shredding: The spent graphite anode electrode is crushed as a whole with a pulverizer with a power of 1.5 kW and a handling capacity of 5 kg/h. Crushing 1kg of graphite anode electrode requires about 1.08 MJ of energy.
3. Calcination: The crushed spent graphite anode powder was calcined in a tube furnace at a temperature of 530 °C for 3 h. Assuming 100 g of calcination per batch, it takes 54 MJ of energy to calcine 1 kg of waste graphite negative electrode crushed powder. The CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, energy and water consumed from the process and the preparation of the raw material are available by searching in the GREET software, as shown in Table S3 (GREET is a traditional multidimensional model that provides a comprehensive, life–cycle–based approach to compare the energy

use and emissions of conventional and advanced vehicle technologies. It includes Vehicle–Cycle Model evaluates the energy and emission effects associated with vehicle material recovery and production, vehicle component fabrication, vehicle assembly, and vehicle disposal/recycling).

4. The total energy consumed by the above process is combined and converted into electrical energy consumption, and the energy consumption cost is calculated according to the Chinese commercial electricity consumption of 0.15 \$(/kWh), and the total expenditure is calculated by combining the cost of reagents used (query in GREET software).
5. Finally, the above components are summed to obtain the total gas emissions, energy and water consumption, and total benefits, as shown in Table S3.

**Table S4** Environmental–economic relevant data of the proposed process in other work

Technology	Raw material	CO <sub>2</sub> (g)	NO <sub>x</sub> (g)	SO <sub>x</sub> (g)	Total energy (MJ)	Water (L)	Profit (\$)
Mixing	Cu(OH) <sub>2</sub> @RC 1 kg	–	–	–	–	3.85	-463.19
Washing	Cu(OH) <sub>2</sub> @RC 1 kg	–	–	–	–	18.00	-26.42
Carbonization	Cu@C 1 kg	2466.58	8.40	6.66	108.00	–	-2.50
Oxidation	CuO@C 1 kg	3699.86	12.60	10.00	162.00	–	-3.72
Product	CuO@C 1 kg						+8.96

Total	6166.44	21	16.66	270.00	-486.87
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In order to better assess the economic, energy, and carbon emission benefits of the scheme proposed in this work, we compared the scheme with previously reported schemes for the preparation of CuO/C <sup>S1</sup>.

1. **Mixing:** Cotton liner pulp was dissolved in a solution of ammonium copper hydroxide at a concentration of 6 *wt.* %. A mixed suspension containing 100 mL of trimethylpentane and 10 mL of Span 85 was dispersed in a reactor. The resulting suspension was stirred at 800 rpm for 40 min and then 20 mL of copper ammonium cellulose solution was added dropwise to the suspension over a period of 5 min. The suspension was stirred continuously at 1000 rpm for 40 min at 0 °C. The suspension was then mixed with 2.5 mL of copper cellulose ammonium solution over a period of 10 min. Subsequently, 2 mL of ECH was dropped into the suspension over 10 min and the mixture was stirred at the same speed and temperature for an additional 30 min. The mixture was heated to 35 °C for 2 h at the same stirring rate to form a cellulose gel <sup>S1</sup>.
2. **Washing:** After removing the trimethylpentane, the obtained Cu(OH)<sub>2</sub>@regenerated cellulose (RC) microspheres were washed by ethyl alcohol and diluted water successively to obtain a neutral aqueous suspension. RC microspheres were obtained by washing the Cu(OH)<sub>2</sub>@RC microspheres with a 10 *wt.*% H<sub>2</sub>SO<sub>4</sub> aq. and diluted water successively to fully removed the Cu(OH)<sub>2</sub>. Finally, all the microspheres were freeze-dried <sup>S1</sup>.

3. Carbonization: Cu@C microspheres were obtained by carbonizing Cu(OH)<sub>2</sub>@RC microspheres under an Ar atmosphere at 800 °C for 2 h. The Cu@C microspheres were then oxidized in the air at 300 °C for 3 h with a heating rate of 2 °C/min to form CuO@C microspheres <sup>S1</sup>.
4. Oxidation: The Cu@C microspheres were sintered in the air at 400 °C for 3 h with a heating rate of 2 °C/min to form bare CuO microspheres <sup>S1</sup>.
5. Finally, the above components are summed to obtain the total gas emissions, energy and water consumption, and total benefits, as shown in Table S4.

**Table S5** Environmental–economic relevant data of Partially–recovery technology

Technolog y	Raw material	CO <sub>2</sub> (g)	NO <sub>x</sub> (g)	SO <sub>x</sub> (g)	Total energy (MJ)	Water (L)	Profit (\$)
Burning	Spent anode 1 kg	2466.57	8.40	6.66	108.00	–	-2.50
Product	CuO 0.4 kg						+2.76
Total		2466.57	8.40	6.66	108.00		+0.26

1. Burning: 1 kg of spent graphite anode was heated in air at 750 °C for 3 h. According to the TGA results (Fig. S1), the weight ratio of CuO remaining after calcination is 40 wt.%, so the product of this step is 0.4 kg CuO. The CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>x</sub>, energy consumed, and water produced by this process can be found by searching in the GREET software, as shown in Table S5 <sup>S2</sup>.

2. Finally, the above components are summed to obtain the total gas emissions, energy and water consumption, and total benefits, as shown in Table S5.

### **Reference**

- S1 Y. Dong, X. Y. Jiang, J. H. Mo, Y. Z. Zhou and J. P. Zhou, *Chem. Eng. J.*, 2020, **381**, 122614.
- S2 Y. K. Li, W. G. Lv, H. Zhao, Y. B. Xie, D. S. Ruan and Z. Sun, *Green Chem.*, 2022, **24**, 9315-9328.