

Electronic Supplementary Information

The Thermal Expansion Exfoliation Technology and Lithium Promoter

Assistant Enables CuO_x/graphene as a High-Performance Anode for

Lithium-Ion Batteries

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Experimental Section

Preparation Procedure

In a typical procedure, 140 mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added into 10 mL of 20 $\text{mg} \cdot \text{mL}^{-1}$ GO suspension under ultrasonic condition and mixed continuously for 30 min. The precursor slurry was dried at 65 °C for 12 h and then heated in a thin quartz tube under an air atmosphere at the heating rate of 10 °C \cdot min $^{-1}$ until popping occurred. The as-obtained samples were collected and labeled as CuO_x/PGO . In addition, the $\text{CuO}_x/\text{Li-PGO}$ samples were prepared through similar procedures, except for the addition of an amount of LiNO_3 to the precursor.

Characterization Techniques

The phases were identified using X-ray diffraction (XRD, Panalytical Empyrean, Holland). The scanning electron microscopy (SEM, Zeiss Gemini SEM 300, Germany), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM, Philips-FEI Tecnai F30, Holland), and atomic force microscopy (AFM, Bruker Multimode 8, USA) were carried out to observe the morphologies. Nitrogen adsorption-desorption isotherms were obtained using a Beishide 3H-2000PS2 analyzer. Raman spectra in the range 800-2000 cm^{-1} were collected on a Raman spectrometer with a 514.5 nm Ar^+ laser as the excitation source. X-ray photoelectron spectroscopy (XPS) was performed using Scientific K-Alpha $^+$ (Thermo, England). The Cu content was measured by inductive coupled plasma (ICP) analysis on the device Thermo iCAP6300.

Electrochemical Measurements

The lithium storage performance of as-prepared anodes was measured in CR2025 type coin cells assembled by the anode electrode (the mass ratio of active material: Super P: PVDF binder was 7:2:1), Li foil, electrolyte of 1.0 M LiPF_6 in EC/DMC (volume ratio of 1:1, 5wt% FEC as electrolyte additive), and polypropylene (PP) film (Celgard 2400), in an Ar-filled glove box ($\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm). The loading mass of active material was 2.0 $\text{mg} \cdot \text{cm}^{-2}$ for all of as-prepared samples. The cycling and rate performance was tested by Land electric test system (CT3001A). The cyclic voltammetry (CV) curves were collected from electrochemical workstation

(CHI1000C) at 0.01-3V. Electrochemical impedance spectroscopy (EIS) was performed on electrochemical workstation (CHI660E) with an amplitude voltage of 5 mV and frequency range from 0.1 Hz to 100 kHz.

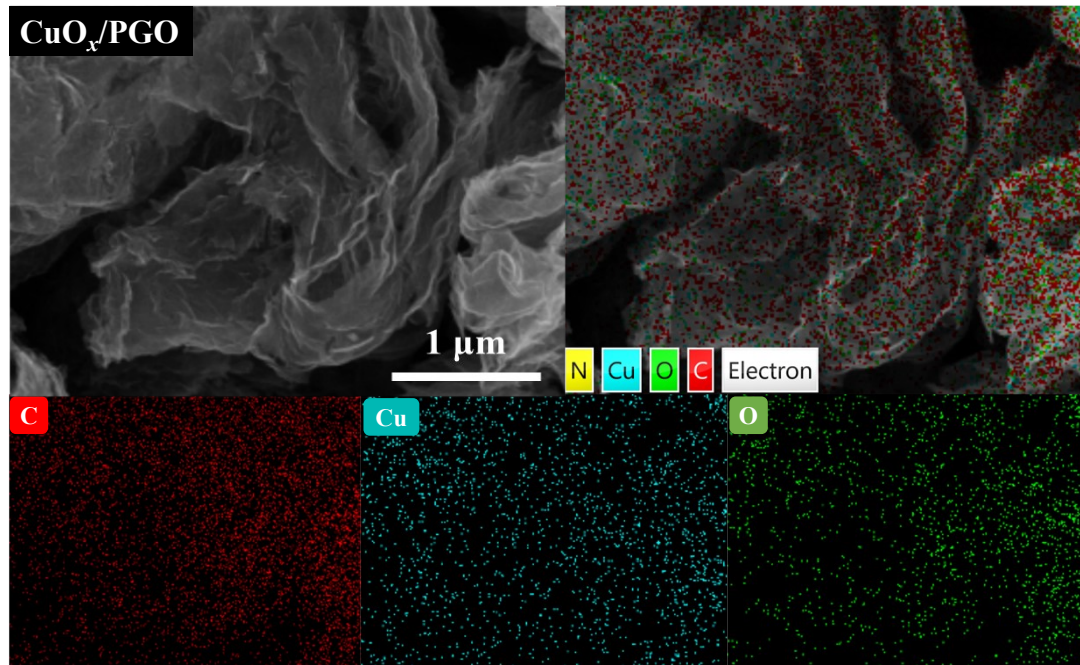


Figure S1 SEM and the corresponding EDS elemental mapping images of CuO_x/PGO

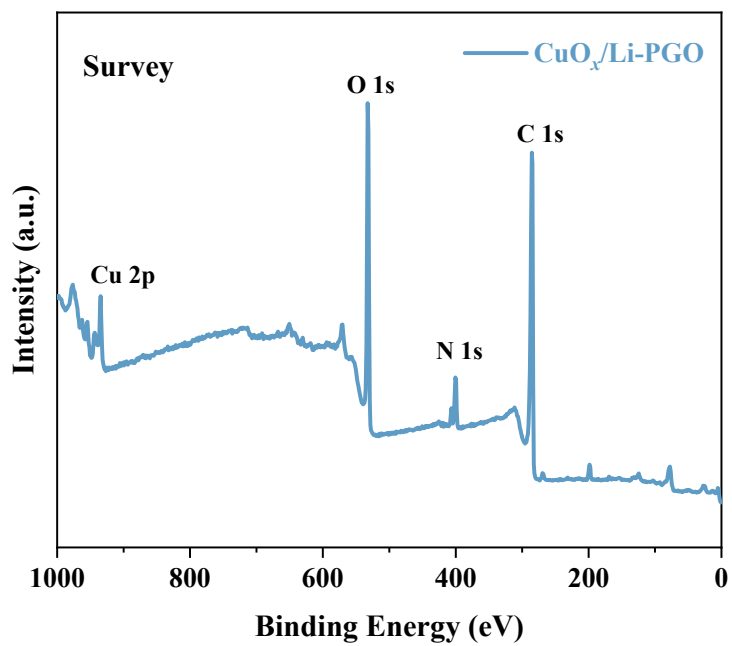


Figure S2 XPS full survey spectra of CuO_x/Li-PGO.

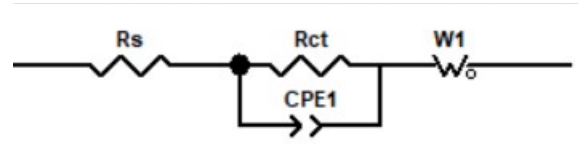


Figure S3. Fitted circuit of EIS analysis

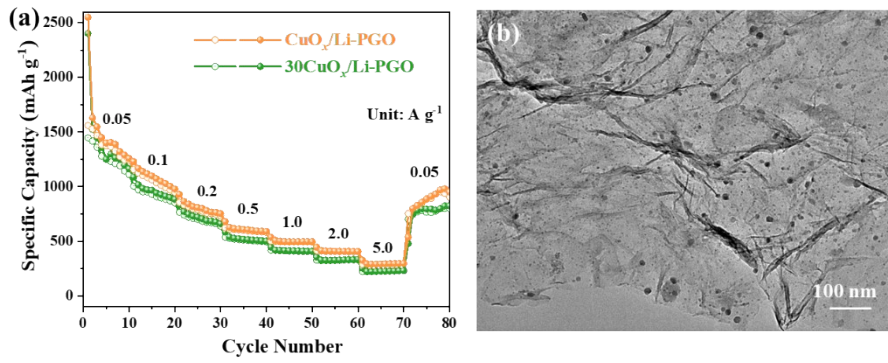


Figure S4 (a) rate performance of CuO_x/Li-PGO and 30CuO_x/Li-PGO electrodes;
TEM image of 30CuO_x/Li-PGO.

The samples showed better electrochemical properties with the increasing copper content. However, as shown in Figure S4a, the 30CuO_x/Li-PGO electrode with higher copper content (29.6 wt% determined by ICP) delivers worse rate capacities compared with CuO_x/Li-PGO (21.7 wt% determined by ICP). The TEM images (Figure S4b) of 30CuO_x/Li-PGO sample show that the copper oxide nanoparticles on the graphene surface increase in size and exhibit uneven distribution due to the high copper content, which may be the main reason for the decrement in the rate performance. In conclusion, the CuO_x/Li-PGO sample (with 21.7 wt% copper content) possessed the best proportion between GO and Cu(NO₃)₂, and showed the best electrochemical performance.

Table S1 Physicochemical properties of the GO, CuO_x/PGO, and CuO_x/Li-PGO samples

Sample	S _{BET} (m ² ·g ⁻¹) ^a	V _{total} (cm ³ ·g ⁻¹) ^b	d (nm) ^c
GO	60	0.2	3.7
CuO _x /PGO	171	1.0	3.8
CuO _x /Li-PGO	208	1.3	3.8

^a specific surface area was calculated by BET modelling;

^b specific pore volume was measured by single point adsorption at P/P₀ = 0.99;

^c the most probable apertures which was calculated by BJH.

Table S2 The percentages of various elements in the samples

Sample	C ^a (at%)	O ^a (at%)	Li ^a (at%)	Cu ^a (at%)	Cu ^b (wt%)
CuO _x /PGO	71.75	20.82	-	2.72	20.8
CuO _x /Li-PGO	68.91	17.65	6.56	2.85	21.7

^a Determined by XPS;

^b Determined by ICP.

Table S3 Comparison of rate performance of CuO_x/Li-PGO anode in this work with recently reported CuO_x-based electrodes for lithium-ion batteries

Materials	Electrochemical performance (mAh g ⁻¹)	References
CuO/C-5%-400	826 and 462 at 0.067 and 0.67 A g ⁻¹	[1]
Porous CuO@C	1024 and 389 at 0.1 and 1.2 A g ⁻¹	[2]
CuO@PCNF/GN	665 and 443 at 0.1 and 0.8 A g ⁻¹	[3]
CuO@Cu-BTC (20 h)	845.1 and 489.3 at 0.1 and 2.0 A g ⁻¹	[4]
Cu ₂ O/Cu@C	265.3 at 2.0 A g ⁻¹	[5]
polygonal-stacked Cu ₂ O	506 at 0.2 C (1 C=374 mAh g ⁻¹)	[6]
dumbbell-like CuO	757 and 559 at 0.2 C and 2 C (1 C=674 mAh g ⁻¹)	[7]
CuO _x /Li-PGO	1258.2 and 512.1 at 0.05 and 2.0 A g ⁻¹	in this work

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