

Electronic Supplementary Information

Identification of cathode stability in Li-CO₂ batteries with Cu nanoparticles highly dispersed onto N-doped graphene

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Materials Preparation: All the reagents were analytical grade without further purification. Few-layered graphene was purchased from Nanjing XFNANO Materials Tech Co.,Ltd. In a typical synthesis process, 0.1907 g Cu(CH₃COO)₂·H₂O, 30 mg graphene, and 0.7628 g urea were mixed with 35 mL ethylene glycol (EG) through intense agitation for 1 h, and ultrasonically treated for 1 h homogeneously. Next, the mixed solution was transferred into 50 mL Teflon-lined stainless steel autoclave and kept at 200 °C for 1 h. After cooling down, the mixture was washed with ethanol for six times, and dried at 60 °C in a vacuum oven. The Cu-NG composite was obtained by annealing the above mixture at 600 °C in an Ar/H₂ atmosphere (volume ratio=9:1) for 8 h. Individual N-doped graphene was prepared without adding Cu(CH₃COO)₂·H₂O at the same conditions for comparison.

Materials Characterization: X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex-600 X-ray diffractometer with Cu K α radiation ($\lambda=1.5406$ Å). Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 field-emission scanning electron microscope equipped with an energy-dispersive spectrometer (EDS). Transmission electron microscopy (TEM) images and high-resolution TEM (HRTEM) images were obtained on a FEI Tecnai G2 F20 electron microscope operated at 200 kV. Fourier-transform infrared (FTIR)

spectroscopy was conducted on a NicoletMAGNA-560 FTIR spectrometer with KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Scientific ESCALAB 250Xi X-ray Photoelectron Spectrometer. Thermogravimetric-differential thermal analysis was performed on a Rigaku PTC-10 A TG-DTA analyzer. ¹H nuclear magnetic resonance (NMR) spectroscopy was recorded on a Bruker AV400 spectrometer. A Vario EL CUBE elemental analyzer was used to quantitatively confirm the contents of C and N. AFM was performed on a Dimension Icon instrument.

Electrochemical Tests: The electrochemical behaviors were measured in Swagelok cells with a 1.0 cm² hole placed on the cathode which enabled CO₂ to flow in. The cells were assembled in a glove box filled with high-purity argon (O₂ and H₂O < 1 ppm). To prepare the cathodes, a slurry was obtained by mixing graphene and polyvinylidene fluoride (PVDF) in a mass ratio of 9:1. The slurry was uniformly deposited onto a circular piece of carbon paper (12 mm, 0.3–0.5 mg), and then dried in an oven at 80°C. Li foil (14 mm) was used as the anode, and polytetrafluorethylyene (PTFE) membrane (18 mm) was used as the separator. The electrolyte was 1 mol L⁻¹ lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) dissolved in tetraethylene glycol dimethyl ether (TEGDME). Discharge/charge tests were conducted on a LAND-CT2001A tester, and the cells were discharged to 2.2 V and then recharged to 4.5 V. Cyclic tests were controlled with a cut-off capacity of 1000 mAh/g at a current density of 200 mA/g and 400 mA/g (i.e., the cells were discharged and charged for 5 h and 2.5 h, respectively).

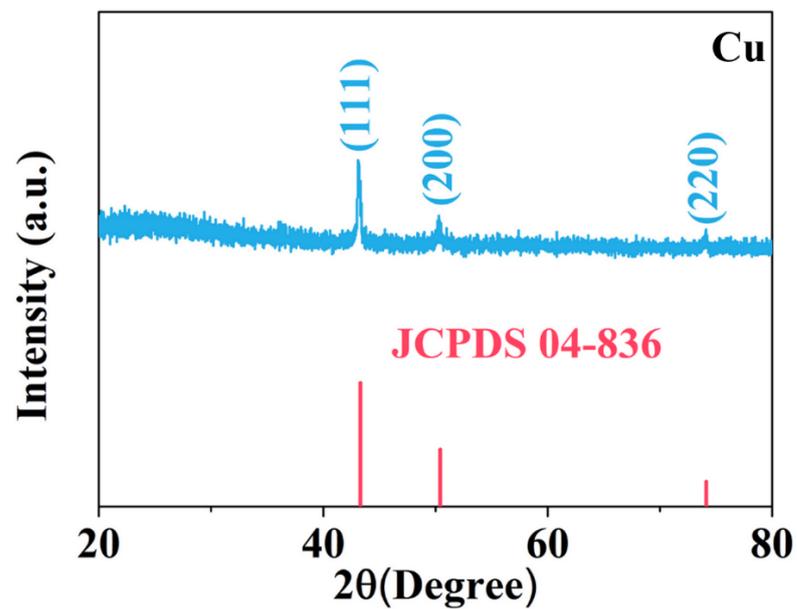


Fig. S1. XRD pattern of Cu-NG composite.

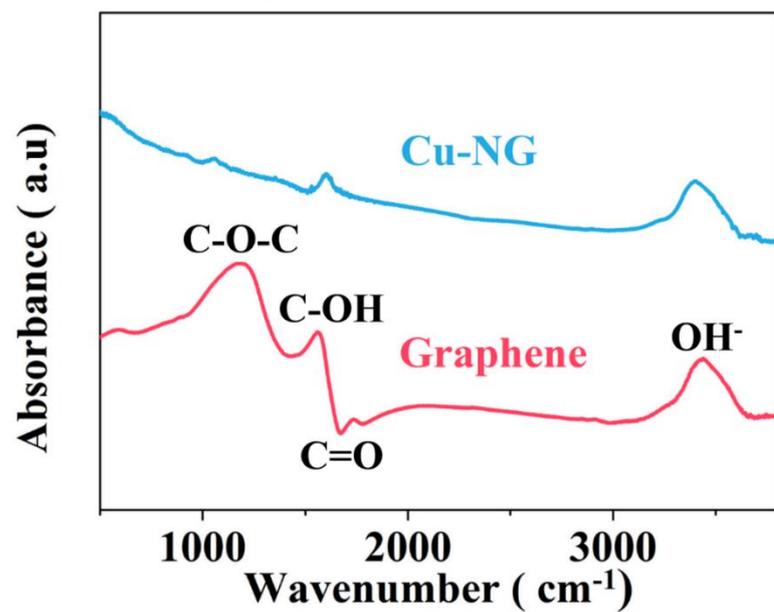


Fig. S2. FTIR spectra of the Cu-NG.

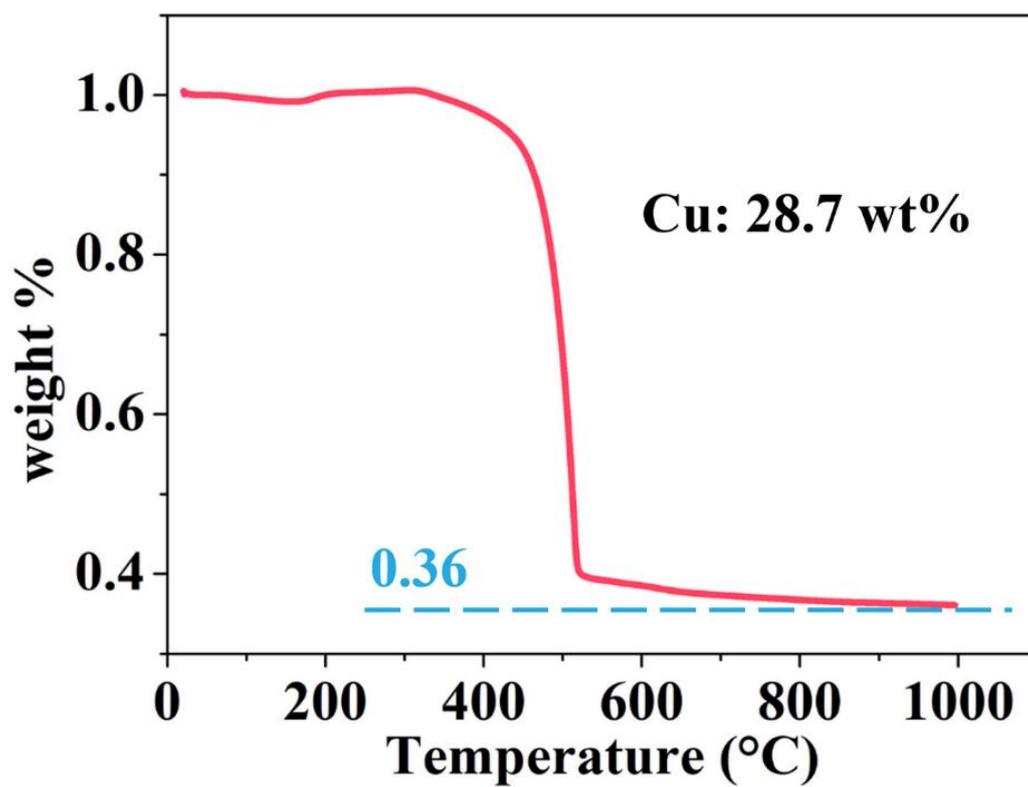


Fig. S3. TG-DTA curve of Cu-NG.

Element	C	N
Amount	65.3 wt%	1.36 wt%

Table S1. Element analysis of Cu-NG.

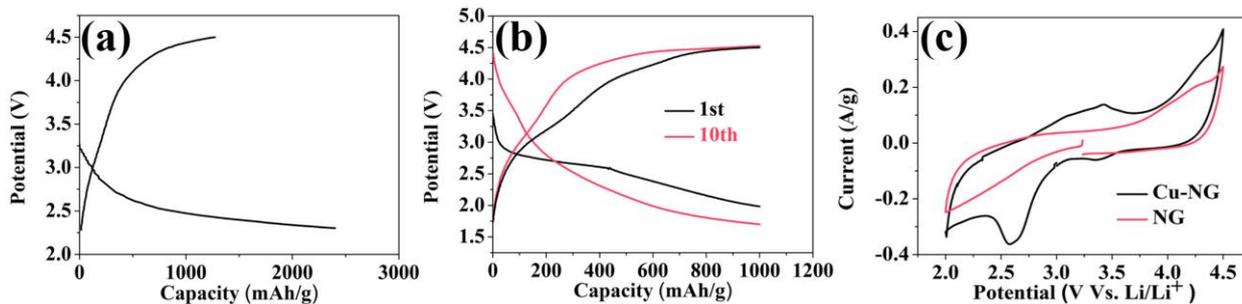


Fig. S4 (a) The discharge-charge profiles of NG cathodes at current densities of 200 mA g⁻¹. (b) Curtailing capacity of 1000 mA h g⁻¹ at a current density of 200 mA g⁻¹. (c) CV curves of Li-CO₂ batteries with NG or Cu-NG cathodes at a scan rate of 0.2 mV s⁻¹.

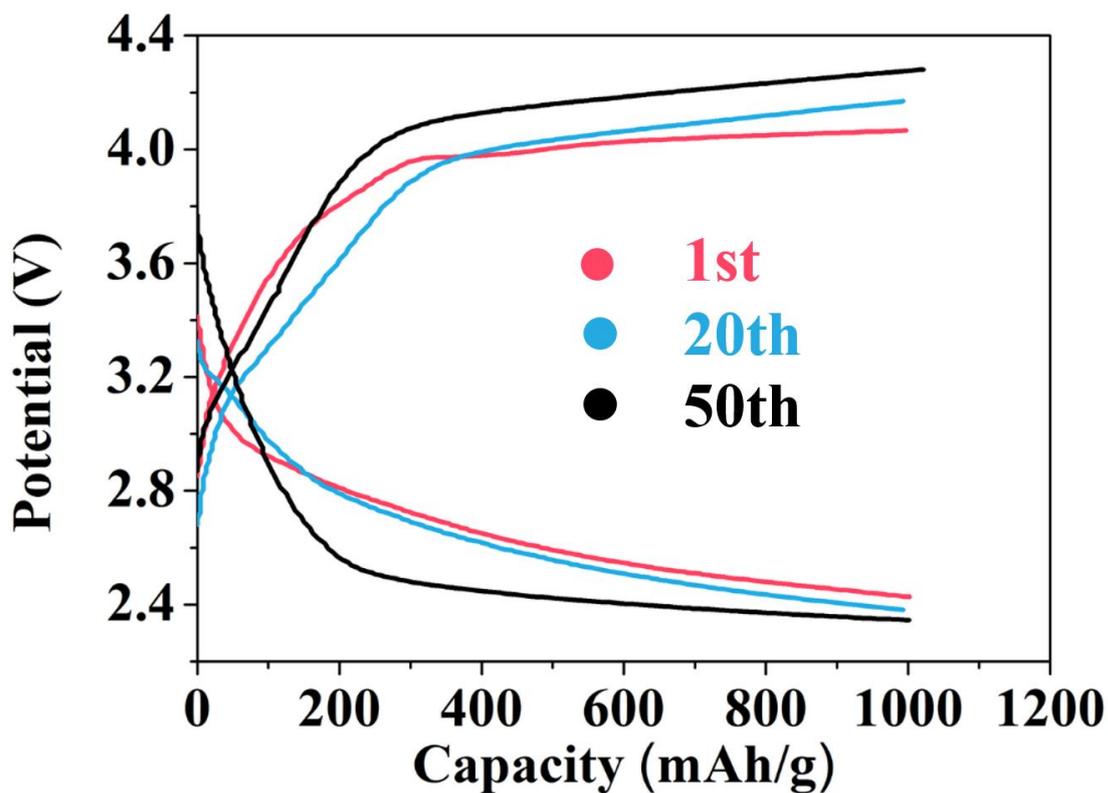


Fig. S5. Curtailing capacity of 1000 mA h g⁻¹ at a current density of 400 mA g⁻¹.

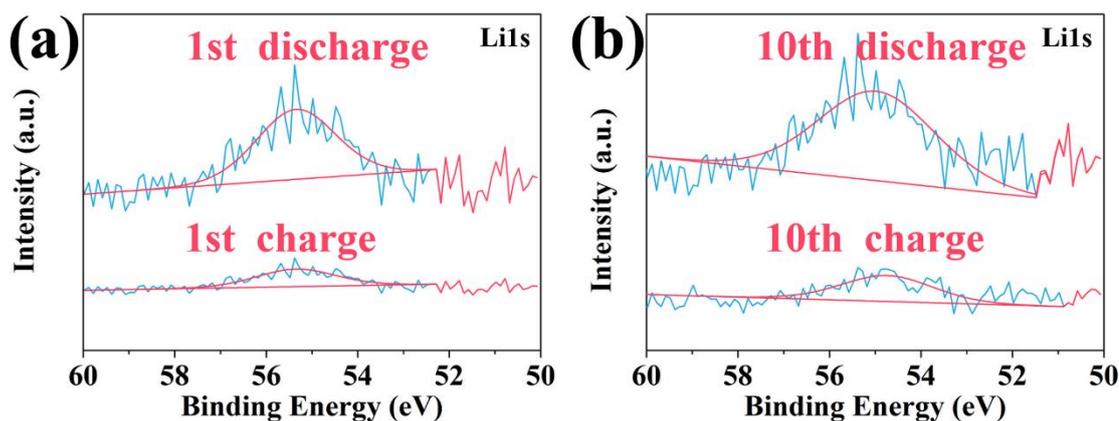
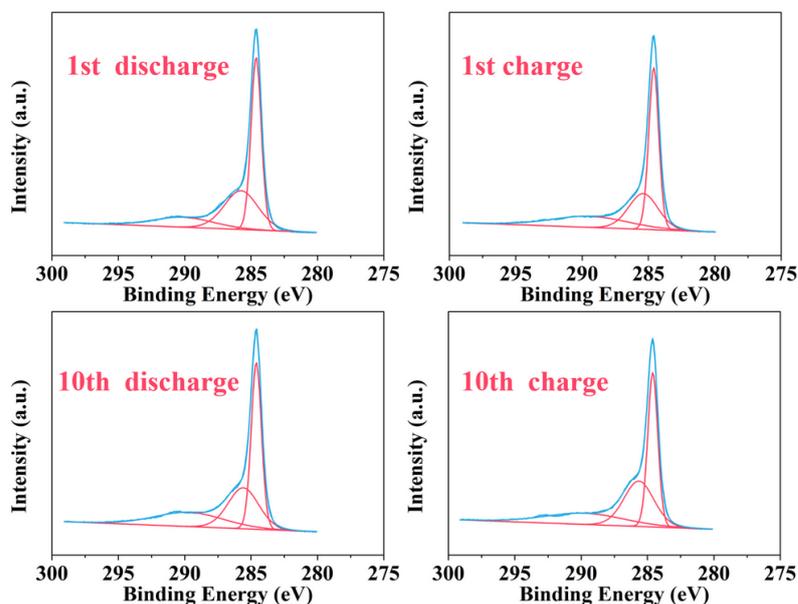


Fig. S6. Li1s XPS of the cathode after (a) 1st, (b) 10th discharge-charge process.



Area%	C=C	C-O	C=O
Initial state	42.62	30.85	26.53
1st discharge	45.00	38.73	16.28
1st charge	45.86	30.03	24.11
10th discharge	43.21	31.89	24.9
10th charge	42.68	33.88	24.43

Fig. S7. C1s XPS of the cathode after discharge-charge process and corresponding area proportion of characteristic peaks .

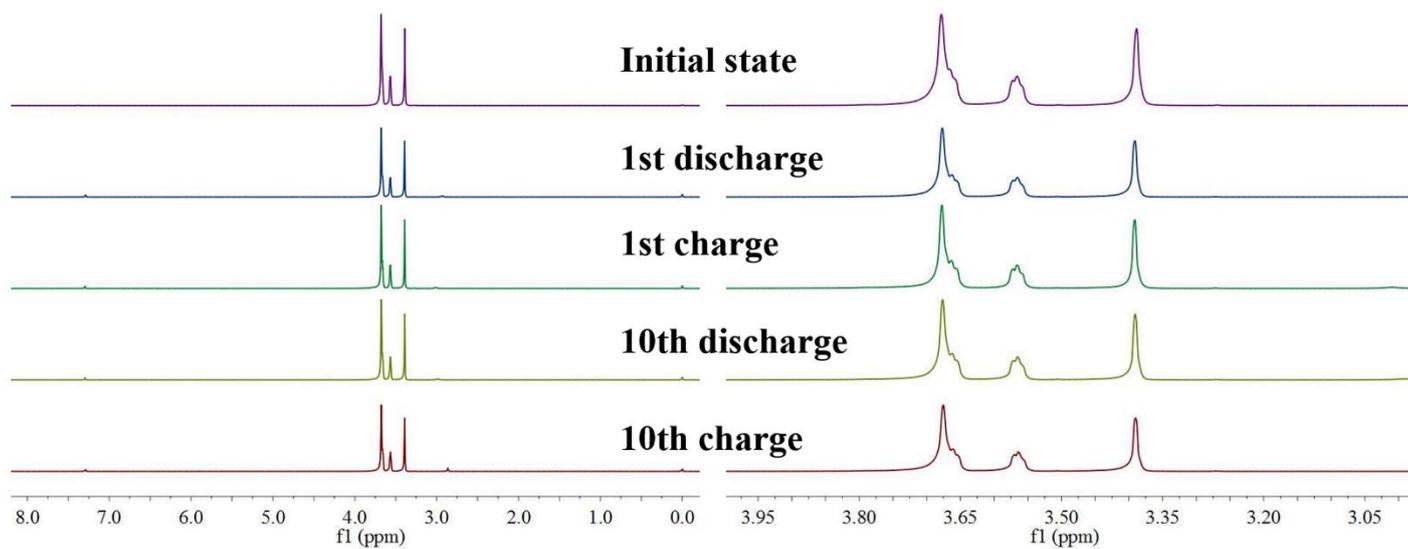


Fig. S8. ^1H NMR analysis of electrolyte after each cycle.

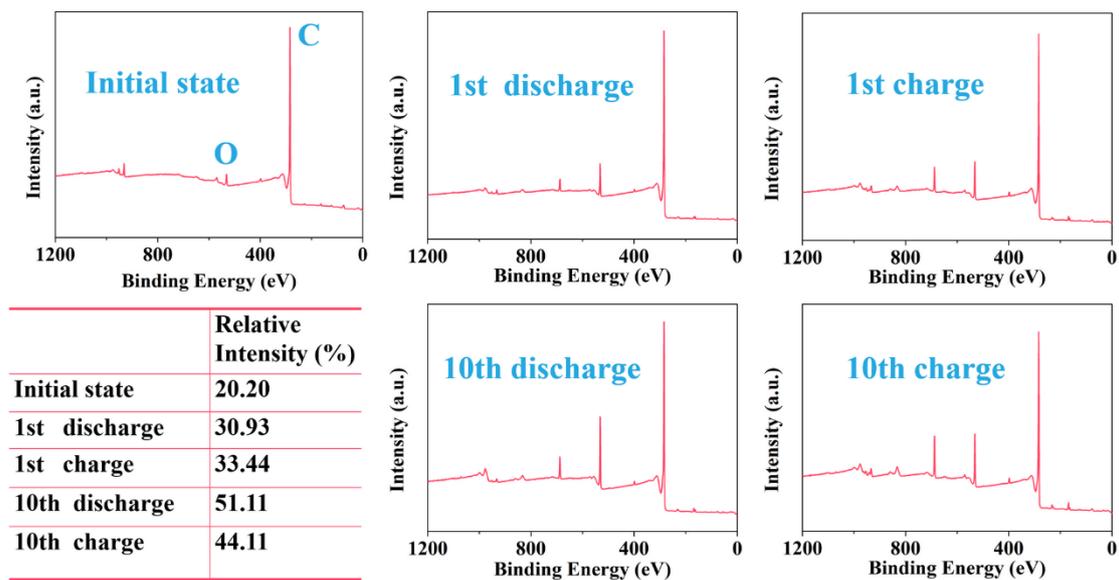


Fig. S9. XPS survey spectrum of Cu-NG and relative intensity of C/O content.

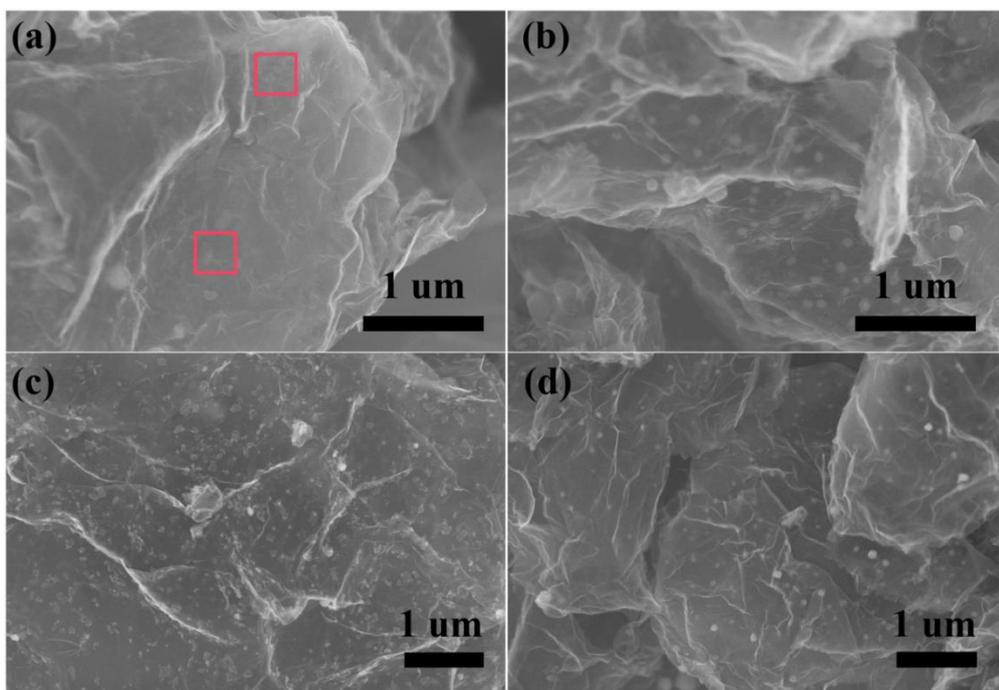


Fig. S10. SEM images of (a) 1st discharge. The mark place represents Li_2CO_3 . (b) 1st charge. (c) 10th discharge. (d) 10th charge.

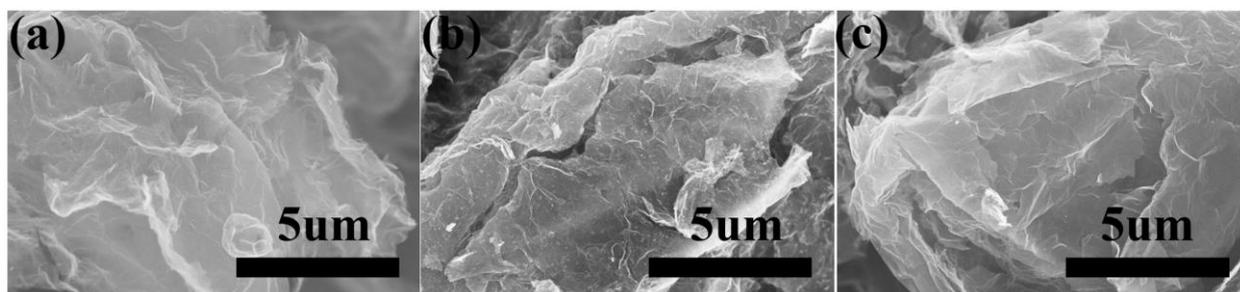


Fig. S11 (a) SEM image of NG. SEM images of the NG cathode after (b) 1st discharge, (c) 1st charge.

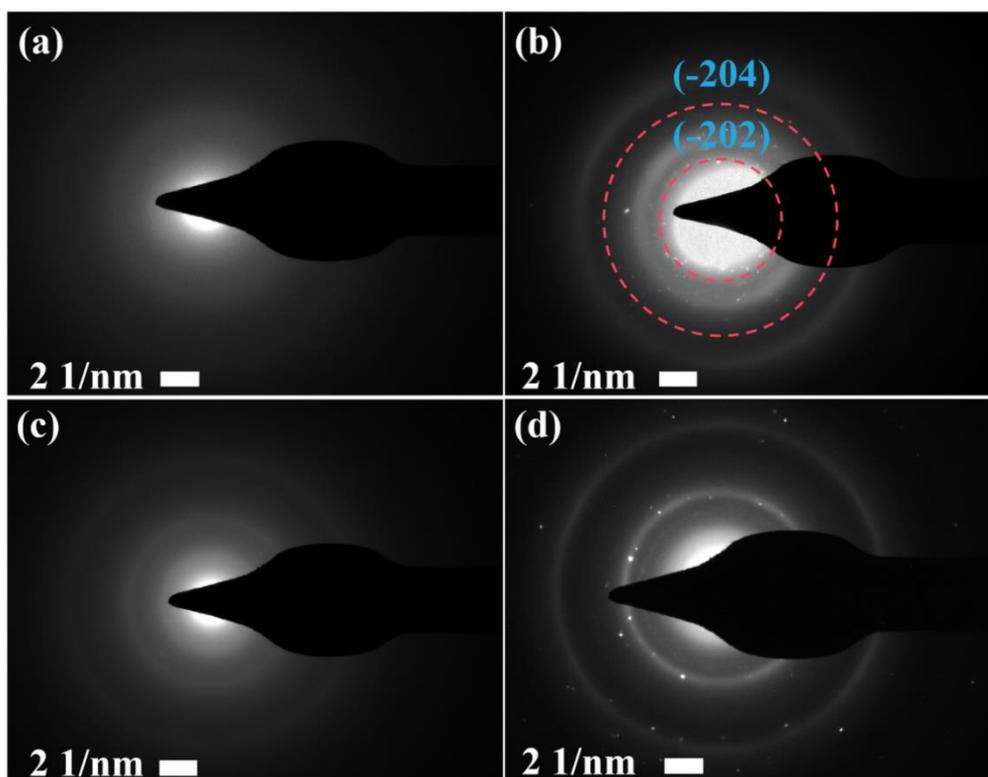


Fig. S12. SAED patterns of Cu-NG in different regions after the discharge process (a) and (b). SAED image of Cu-NG after the charge process (c) and (d).

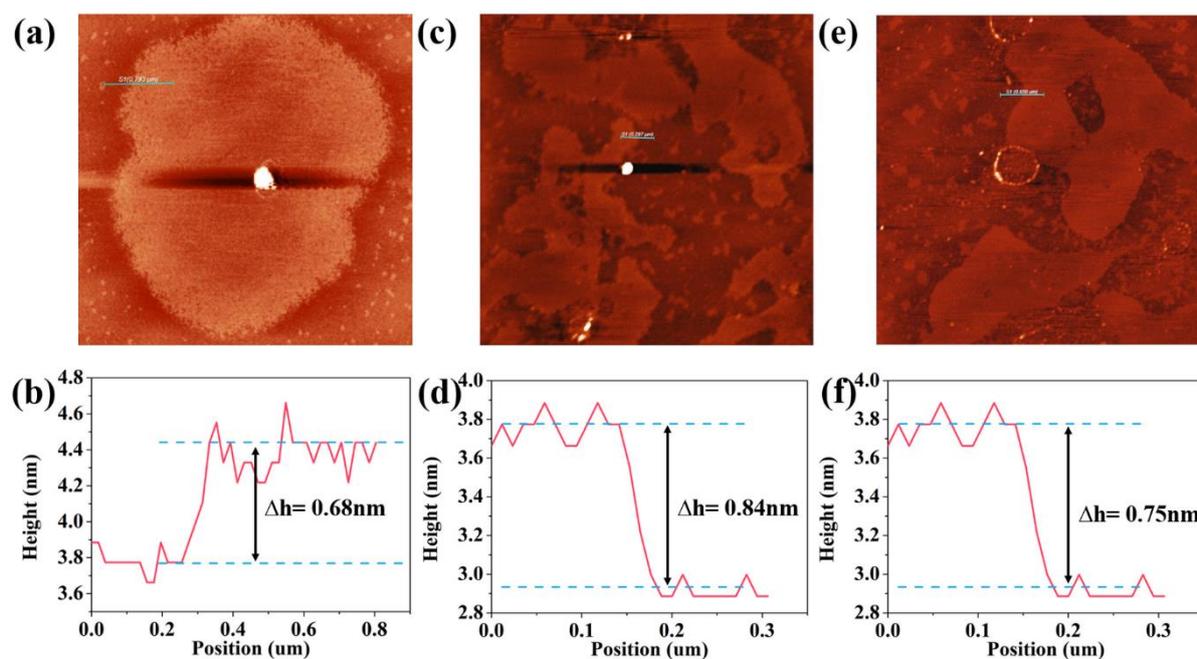


Fig. S13. AFM images of Cu-NG cathode (a, b) pristine state. (c, d) After 10th discharge cycle. (e, f) After 10th charge cycle.