Electronic Supplementary Information

An elastic Germanium/Carbon nanotubes/Copper foam monolith as anode for rechargeable lithium batteries

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Experimental:

Preparation of CNTs coated Cu foam:

Thin copper foam with an area of 0.25 cm^2 were employed as substrates for CNTs film growth and served as cathode for nanoparticle catalyst deposition. The electrolyte consisted of a mixing aqueous solution of 1.5 M $CuSO_4$ and 1 M H_2SO_4, and the galvanic deposition process was carried out at a current density of 4 mA cm^{-2} for 10 minute. For preparation of CNTs film, Cu substrate with catalyst coated were moved in a tube furnace for CVD process under H_2/C_2H_2 (v:v=1:1) atmosphere at 600□ for 1 hour.

Preparation of Ge precursor:

Ge precursor was prepared by a modified wet-chemistry route at room temperature as reported by Jing et al..[1] Specifically, 1 g GeO_2 commercial powder (99.999%) was dissolved in 30 ml aqueous ammonia solution which was pre-heated to 70 □ with stirring for 30 minutes to obtained a transparent solution. After cooling to room temperature, 1.8 g $NaBH_4$ powder was added to the germanate ion

solution and reaction proceed for 24 hours. The Ge precursor was collected by centrifugation and dried at 100 □ for another 24 hours.

Preparation of Ge/CNTs/Cu monolith anode:

0.1 g as-prepared Ge precursor was loaded in an alumina boat and covered with CNTs coated Cu foam. Ge particles were evaporated to directly grow on the CNTs film under H_2 atmosphere at 600□ for 1 hour.

Materials characterization:

X-ray diffraction (XRD) patterns of samples were recorded on a Bruker-AXS Micro-diffractometer (D8 ADVANCE) with Cu Kα radiation (λ =1.5406 Å) from 25° to 90° at a scanning speed of 4° min^{-1}. Resonance Raman spectra were recorded on a JY HR800 Raman spectrophotometer (Horiba Jobin Yvon, France) with 532 nm diode laser excitation. Morphology details and lattice structural information were examined on field emission scanning electron microscopy (FESEM, HITACHI S-4800). Elemental mapping was carried out using the characteristic Ge and C K edges, respectively.

Electrochemical measurements:

Two-electrode Swagelok cell assembled in an argon-filled glove box was used for electrochemical test. Lithium foil was used as counter electrode and separated with the monolith anode by a glass-fiber separator. The electrolyte was 1.0 mol L^{-1} $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). Electrochemical impedance spectroscopy (EIS) measurements were carried out using a ZHANER ZENNIUM electrochemical workstation by applying an AC voltage of 5 mV amplitude in the frequency range of 0.1 to 100 kHz at room temperature. The cells were charged and discharged over a voltage range of 0.05–1.5 V (vs Li^+/Li) at different rates using a LAND battery testing system.

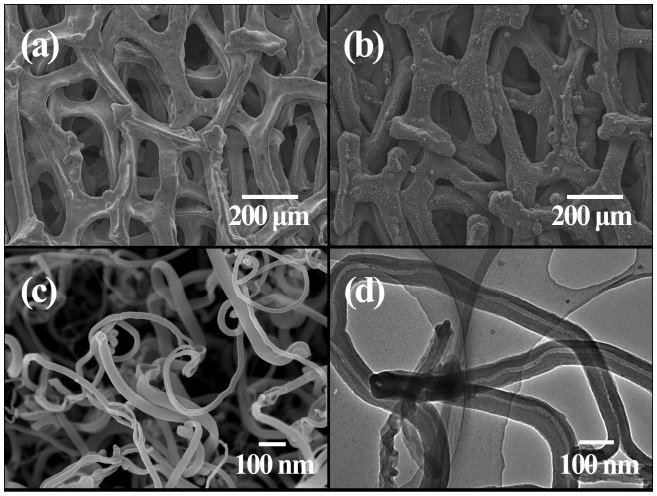

Fig. S1 SEM images of Cu foam before (a) and after CNTs coating (b). (c) and (d) are the typicalSEM and TEM images of CNTs obtained by scrape from the surface of CNTs coated Cu foam.

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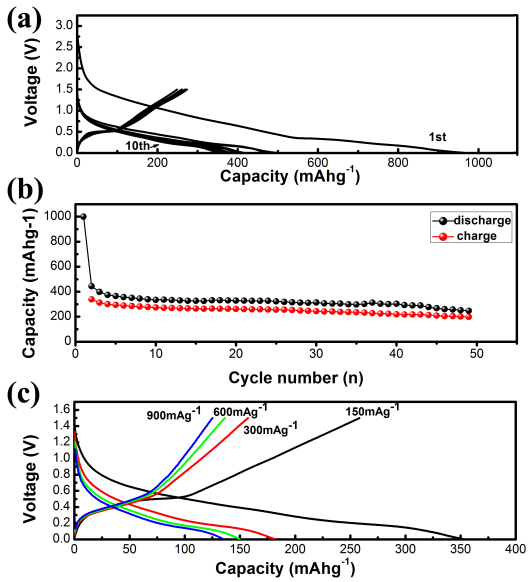


Fig. S2 The first ten discharge/charge profiles (a) and cycle performances (b) of Ge/Cu anode between 0.005 and 1.5 V at a current density of 150 mA g^{-1}; (c) Rate capability of Ge/Cu anode.

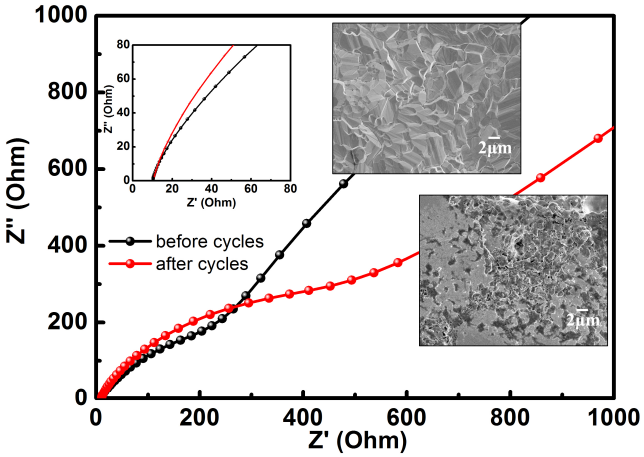
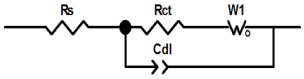


Fig. S3 Electrochemical impedance spectra of Ge/Cu anode before and after 10 discharge/charge cycles at a current density of 150 mA g^{-1}. Insets are the enlarged curve in the high frequency range and corresponding ex-situ SEM images.

Table S1. RC equivalent circuit and corresponding fitting values of the Ge/CNTs/Cu monolith anode and Ge/Cu anode.

Electrode	RC equivalent circuit model	Rs [Ohm]	R` [Ohm]	Rct [Ohm]	C1 [Farad]	Cdl [Farad]
Ge/CNTs/Cu monolith anode before cycles		6.146	35.48	160.1	3.404E-6	1.555E-5
Ge/CNTs/Cu monolith anode after 10 cycles		7.212	7.899	40.77	1.357E-4	4.727E-5
Ge/ Cu anode before cycles		9.598	------	292.8	------	1.248E-5
Ge/ Cu anode after 10 cycles		9.813	------	487.3	------	6.247E-6

Reference

1. C.B. Jing, X. D. Zang, W. Bai, J. H. Chu, A. Y. Liu, *Nanotechnology*, 2009, **20**, 505607