Electronic Supplementary Information (ESI)

An Artificial Sea Urchin with Hollow Spines: Improved Mechanical and Electrochemical Stability in High-Capacity Li-Ge Batteries

Jinyun Liu,[*,a] Xirong Lin,[b] Tianli Han,[a] Qianqian Lu,[b] Jiawei Long,[a] Huigang Zhang,[c] Xi Chen,[d] Junjie Niu,[*,d] and Jinjin Li*[,b]

[a] *Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, Key Laboratory of Electrochemical Clean Energy of Anhui Higher Education Institutes, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, P.R. China. E-mail: jyliu@iim.ac.cn*

[b] *Key Laboratory of Thin Film and Micro Fabrication, Ministry of Education, Department of Micro/Nano Electronics, Center for High-Performance Computing, Shanghai Jiao Tong University, Shanghai 200240, P.R. China. E-mail: lijinjin@sjtu.edu.cn*

[c] *National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P.R. China*

[d] *Department of Materials Science and Engineering, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53211, United States. E-mail: niu@uwm.edu*

Experimental Section

Preparation of 3D ZnO nanorod array: At first, 2.24 g KOH (Sinopharm Chemical Reagent Co., Ltd) was dissolved in 10 mL H_2O to form solution A. Then 1.48 g $ZnNO_3 \cdot 6H_2O$ (Sinopharm Chemical Reagent Co., Ltd) was dissolved in another 10 mL H_2O

to form solution B. Solution B was added dropwise to solution A, and stirred to form mixed solution C. Consequently the cleaned nickel foam (thickness: 1.7 mm; area: 1.13 cm^2) was placed vertically in solution C, reacted at 50 °C for 6 h in a Teflon-lined stainless steel autoclave. At last, the foam was taken out, ultrasonically washed with de-ionized water and ethanol, and dried at 50 °C for 3 h.

Preparation of ZnO@TiO_2 nanorod array: TiO_2 was prepared through a sol-gel method. Typically, 10 mL butyl titanate (Sinopharm Chemical Reagent Co., Ltd), 75 mL ethanol, 1 mL acetylacetone were mixed to form solution A. 25 mL ethanol and 1 mL deionized water were mixed to form solution B. Then solution B was slowly added to the solution A under magnetic stirring, forming a yellow TiO_2 solution. The nickel foam with ZnO nanorods obtained above was immersed in the TiO_2 solution for 1 min, then taken out, dried at room temperature. The sample was transferred into a muffle furnace to treat under 500 °C for 1 h at a ramp rate of 5 °C min^{-1}.

Preparation of TiO_2 nanotube array: The nickel foamed coating with ZnO@TiO_2 nanorod array was immersed in a 5 wt% aqueous solution of acetic acid to etch ZnO. After 10 min, the sample was taken out, washed with water and ethanol, and dried at 60 °C for 2 h.

Preparation of TiO_2@Ge nanotube composite: The nickel foam with TiO_2 nanotubes was immersed into a 0.01 M $GeCl_4$ ethanol solution. It was taken out after 1h, and dried at 60 °C for 3 hours. Then the sample was placed in a tube furnace and calcined for 4 h at 650 °C with a ramp rate of 5 °C min^{-1} under H_2/Ar (H_2: vol 5%).

Characterizations: Scanning electron microscopy (SEM, FEI Quanta 200 FEG, operating voltage 5.0 kV), High resolution transmission electron microscopy (HRTEM, JEOLJEM-2010, operating voltage 200 kV), X-ray diffractometer (XRD, Philips X'Pert, Cu target Kα radiation λ=1.54187Å) were used to characterize the structure and morphology. Element mapping was performed on a HRTEM equipped with an Oxford INCA energy dispersive X-ray (EDX) analyzer device. The elemental states and chemical composition were determined by an X-ray photoelectron spectroscopy (XPS, Thermo-VG Scientific ESCALAB 250) and an X-ray fluorescence spectrometer (XRF-1800, SHIMADZU).

Electrochemical tests: A CR2032 coin cell system was used to evaluate the electrochemical performance of the samples. The cells were assembled in a glove box (Mikrouna Super 1220/750; O_2 and $H_2O< 0.01$ ppm) using the 3D Ge-THC as the working electrode with a loading of about 2.14 mg cm^{-2}, a metallic Li foil was used as the counter electrode. The electrolyte was formed by mixing 1:1 volume ratio of ethylene carbonate (EC) and diethyl carbonate dissolved 1 M $LiPF_6$. The Celgard 2400 microporous polypropylene film was applied as the separator. The electrochemical performance was measured via a galvanostatic discharge/charge method on a Neware battery tester. Electrochemical impedance spectra and cyclic voltammogram curves were measured on an electrochemical workstation (Shanghai Cheng Hua CHI660D). Low temperature tests were conducted using a high-low temperature chamber (Shanghai Munee Instruments Co., Ltd, HTM22). The tester clips holding the coin cells in the chamber were connected to the Neware battery system through extended lines. Before each measurement, the coin cells were stored in the –5 °C chamber for 24 hours.

***In-situ* TEM characterization:** For the *in-situ* TEM observation, a micro-battery system was fabricated. A lithium foil with a thin Li_2O layer on the surface was used instead of the ionic liquid as a solid electrolyte to solve the wetting problem of liquid electrolyte. At first, the Li_2O-coated Li flake was connected with a W tip as a counter electrode. Then, the composite was attached to an Al tip via a conductive resin as a working electrode. The two electrodes were mounted on a sample stage holder of a Nanofactory STM-*in situ* TEM. Real-time observations of the changes of the morphology and structure were conducted on a TEM (FEI Titan S 80-300 TEM/STEM, operating voltage: 300 kV) equipped with a Gatan image filter (Quantum-865) through potentiostatic lithiation under an applied voltage.

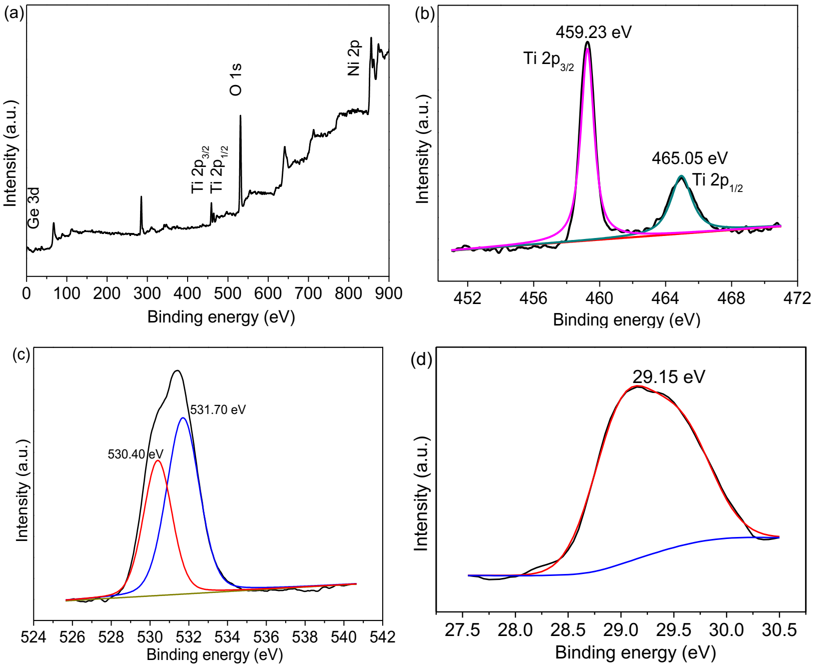

Fig. S1 (a) Survey spectrum of the TiO_2@Ge composites. High-resolution XPS spectra of (b) Ti 2p, (c) O 1s, and (d) Ge 3d.

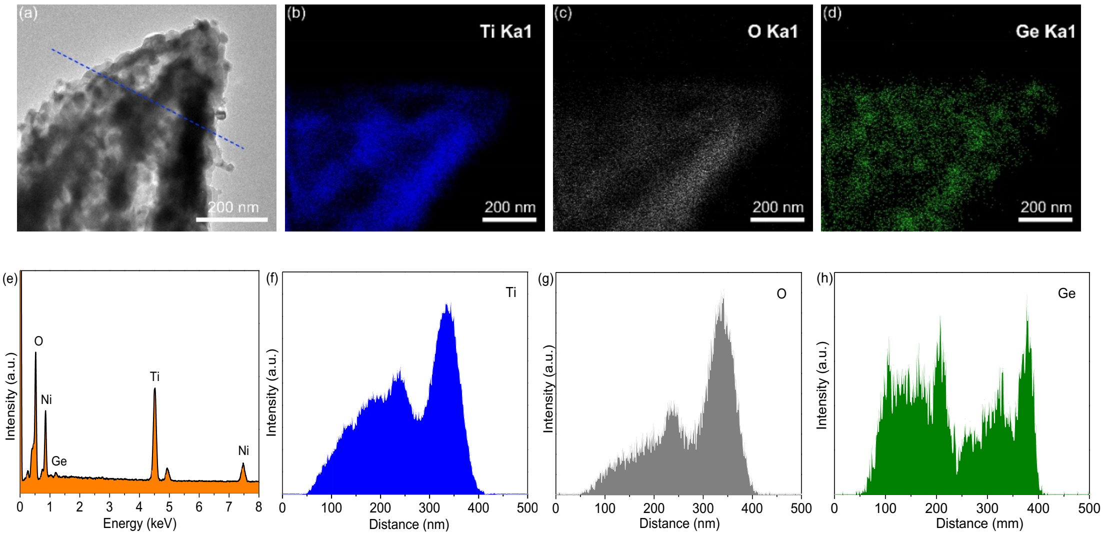

Fig. S2 (a) TEM image and elemental mappings of (b) Ti, (c) O, and (d) Ge. (e) The EDS spectrum and distribution of elements (f) Ti, (g) O, and (h) Ge from the line-scanning in (a).

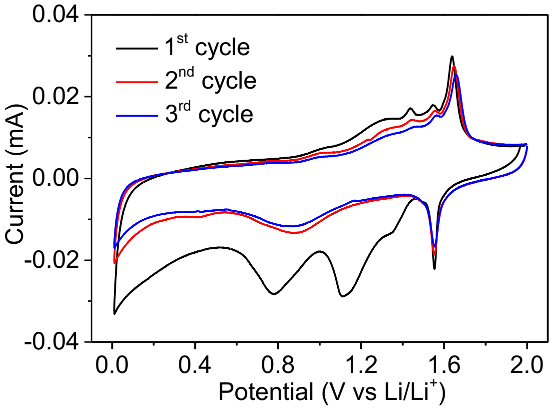

Fig. S3 Cyclic voltammogram curves of the Ge-THC anode.

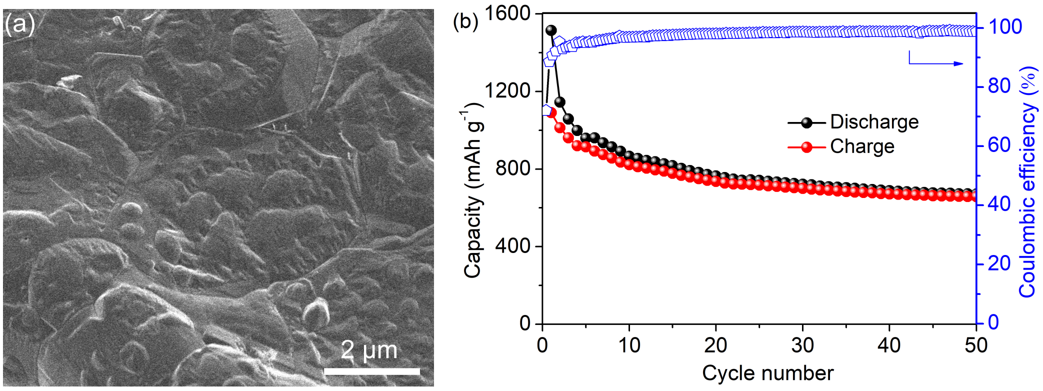

Fig. S4 (a) SEM image of pure Ge on nickel foam prepared by dip-coating and heat-treatment under H_2/Ar (H_2: 5 vol%) gas. (b) Cycling performance of the pure Ge anode at 0.1 C.

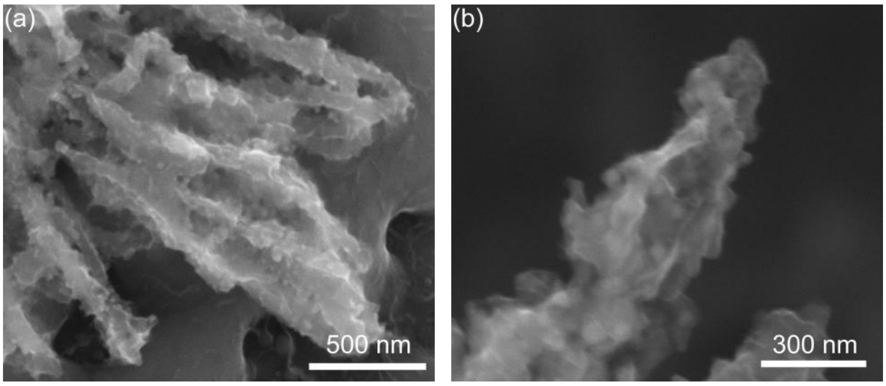

Fig. S5 SEM images of the Ge-THC electrode after 130 cycles at 0.1 C.