Supporting information for

Electrochemical storage mechanism of In$_2$S$_3$/C nanofiber anode for high-performance Li-ion and Na-ion Batteries

Yiting Yuan [a], Min Yang [a, &], Li Liu [a, b*], Jing Xia [a], Hanxiao Yan [a], Junfang Liu [a], Jiaxin Wen [a], Yue Zhang [a], Xianyou Wang [a]

(a National Base for International Science & Technology Cooperation, National Local Joint Engineering Laboratory for Key materials of New Energy Storage Battery, Hunan Province Key Laboratory of Electrochemical Energy Storage and Conversion, School of Chemistry, Xiangtan University, Xiangtan 411105, China

b Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, China)

Experimental section

Preparation of materials : The In$_2$S$_3$/C nanofibers were fabricated by a simple electrospinning method. Firstly, 0.3 g polyacrylonitrile (PAN, average Mw=150000, Macklin, China) and 0.2 g polyvinylpyrrolidone (PVP, average Mw=1300000, Alfa Aesar, US) were dissolved in 5 mL N,N-dimethylformamide (DMF, anhydrous, 99.9%, Sinopharm Chemical Reagent Co. Ltd, China) solvent with vigorous stirring at 60°C for 4 h. Then 3 mmol indium(Ⅲ) chloride (InCl$_3$, anhydrous, 99.9%, Macklin, China) was dissolved in the PAN-PVP-DMF mixed solution with vigorous stirring at 60°C for 4 h. The obtained mixture was used as the work solution for electrospinning.

& Co-first author: contributed equally to this work.

* Corresponding author at : School of Chemistry, Xiangtan University, Xiangtan 411105, China.
E-mail addresses: liulili1203@126.com (L. Liu)

The work solution was loaded into a 5 mL plastic syringe equipped with a 22-gauge flat-needle. The flow rate of the solution was controlled by a single channel syringe pump to be 0.3 mL h^{-1}. The flat-needle was connected to a high voltage power supply that applies a voltage of 16 kV. A grounded aluminum foil was placed 15 cm below the flat-needle to collect the nanofibers.

The as-collected precursor fibers were preliminary oxidized firstly, the tube furnace was heated to 200°C and held for 2 h in the air. The heating rate in all heating processes is 2°C min^{-1}. Then, the oxidized precursor fibers were sulfuretted in a tube furnace where high-purity nitrogen (N$_2$) circulated. The sulfidation method is similar to our previous work.[1] Specifically, the precursor fibers and thiourea (CN$_2$H$_4$S, 99%, Aladdin, China) in a mass ratio of 1:3 were placed in two different porcelain boats. The porcelain boat containing thiourea was placed upstream of the N$_2$ atmosphere, and the porcelain boat containing the precursor fibers was placed downstream of the N$_2$ atmosphere. The tube furnace was heated to 250°C and held for 2 h. In this process, thermoplastic PAN and PVP were converted to non-plastic compound.[2] Besides, thiourea was decomposed and produces the gas phase product dominated by CS$_2$ and NH$_3$. Therefore, InCl$_3$ was sulfuretted by CS$_2$ into In$_2$S$_3$. After the vulcanization was completed, the glass tube naturally cooled down to room temperature then removes the porcelain boat containing thiourea residue. Finally, the fibers were carbonized in tube furnace at N$_2$ atmosphere. The temperature was raised to 700°C for 4 h. After the glass tube naturally cooled down to room temperature, In$_2$S$_3$/C nanofibers were obtained.

Materials characterization: The crystal structure of samples was studied by X-ray diffraction (XRD, Bruker D8 ADVANCE, Cu Kα radiation, λ = 1.54439 Å) at a scanning rate of 2 ° min^{-1}. Raman spectrum was measured on a confocal Raman microscope (Renishaw 2000) with a 532 nm wavelength argon-ion laser. X-ray photoelectron spectroscopy (XPS, K-Alpha$^+$, Thermo fisher Scientific) equipped with a monochromatic Al-Kα X-ray source (hν = 1486.6eV) was used to investigate the surface elemental states. The morphology and microstructure were observed using field-emission scanning electron microscopy (FE-SEM, SIGMA HD-01-61, Carl Zeiss) and transmission electron microscopy (TEM, FEI-Tecnai G2 TF20). Brunauer-Emmett-Teller (BET) method was implemented to investigate the specific surface area and pore size distribution of the samples by N_2 adsorption-desorption isotherms on a Micromeritics ASAP 2020 HD88 apparatus. The content of In_2S_3 and carbon in the In_2S_3/C nanofibers was detected by a thermogravimetry analyzer (TG, Labsys Evo, Setaram) from room temperature to 800°C with a heat rate of 10 °C min^{-1} in air. The content of In_2S_3 in In_2S_3/C nanofibers was calculated based on the following formula:

$$In_2S_3 \text{ (wt. \%)} = 100 \times \frac{\text{molecular weight of } In_2S_3}{\text{molecular weight of } In_2O_3} \times \frac{\text{final weight}}{\text{initial weight}}$$

Electrochemical tests: The lithium/sodium storage performance of In_2S_3/C nanofiber anode was tested in the CR2025 coin-type cells, which were assembled in a glovebox (H_2O and O_2 value < 0.1 ppm). The slurries of working electrodes were fabricated by using the In_2S_3/C nanofibers (active material), carbon black (conductive agent) and polyvinylidene fluoride (PVDF, binder) with a weight ratio of 70:20:10

mingled in N-methyl pyrrolidinone (NMP, solvent), and continuously stirred for 8 h. The as-prepared slurries were uniformly coated on the Cu foil current collector, and dried under vacuum at 80 °C for 12 hours. After the drying was completed, the Cu foil was cut into disks with a diameter of 1 cm as the working electrodes. Metallic Li and metallic Na were employed as the counter/reference electrode for LIBs and SIBs, respectively. 1 M $LiPF_6$ added in a commixture solution of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, vol. %) was applied as the lithium-ion battery electrolyte. The sodium-ion battery electrolyte was composed of 1 M $NaClO_4$ added in a commixture solution of propylene carbonate (PC) and ethylene carbonate (EC) (1:1, vol. %) and 5 % fluorinated ethylene carbonate (FEC) additive. The lithium-ion battery separator and the sodium-ion battery separator were employed the Whatman GF/A and GF/D glass microfiber film, respectively. The cycling performance and rate capability were tested by using the CT-3008 battery tester (Neware BTS, China). The voltage test ranges in LIBs and SIBs are set at 0.01-3.0 V and 0.01-2.5 V, respectively. The discharge and charge specific capacities in this work were calculated based on the full weight of In_2S_3/C nanofiber composite. Cyclic voltammetry (CV) measurements and electrochemical impedance spectroscopy (EIS) were performed on the CHI660e electrochemical workstation. The scan rate of CV measurement was set to 0.1 mV s^{-1}. The EIS tests were implemented a sine wave with an AC amplitude of 5 mV in 0.01 Hz to 100kHz. The obtained EIS results were simulated by an equivalent circuit model (the inset in Fig. S8). In the equivalent circuit model, the R_s represent the ionic resistance of the electrolyte, the CPE is linked

4

with the interfacial resistance, the W_o is concerned with the diffusion of ions into the bulk of the electrode material, the R_{sei} is related to the resistance caused by SEI film, the R_{ct} is relevant to the charge transfer resistance.
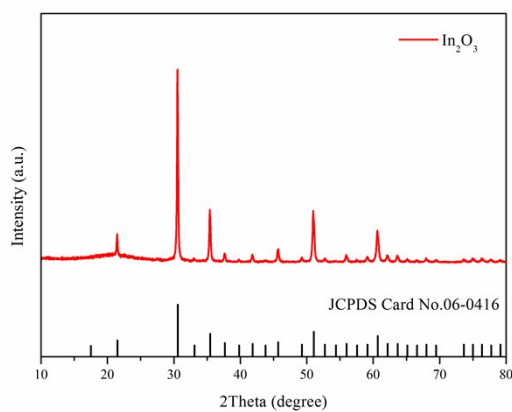
Supplementary figures

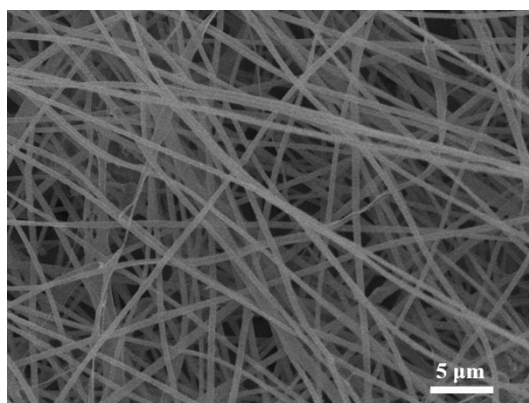Fig. S1 XRD pattern of the combustion products after TG test.
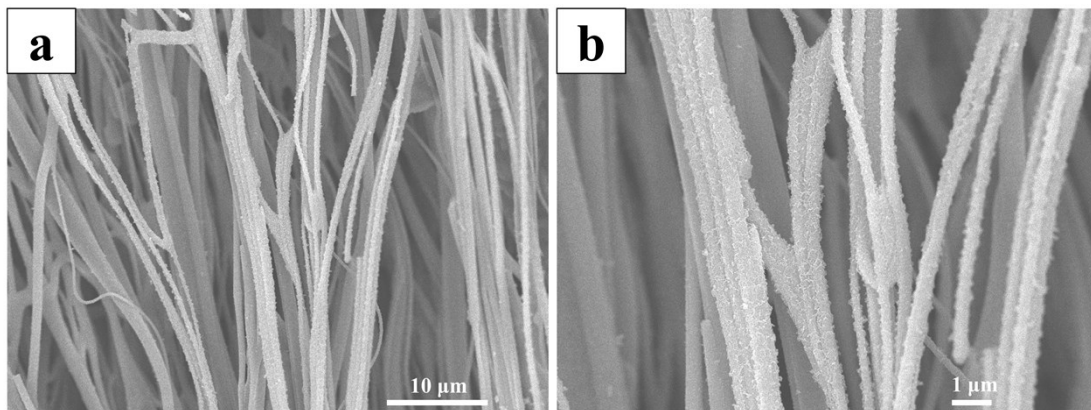

Fig. S2 SEM image of the precursor nanofibers.

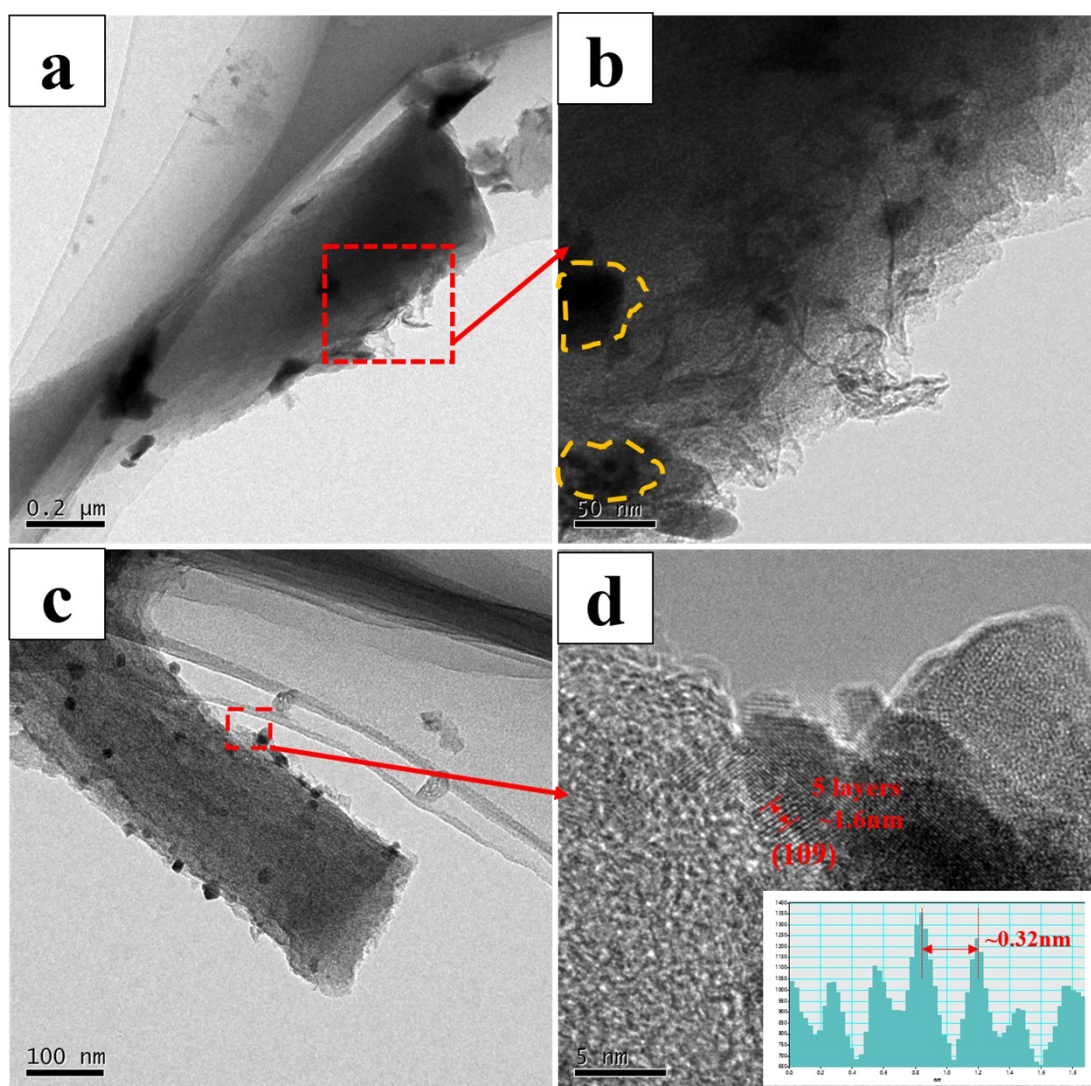Fig. S3 (a, b) FE-SEM images of the In$_2$S$_3$ nanofibers.

Fig. S4 (a, b, c) TEM images of In$_2$S$_3$/C nanofibers; (d) HR-TEM image and the interplanar crystal spacing statistical tables (inset) of In$_2$S$_3$/C nanofibers.
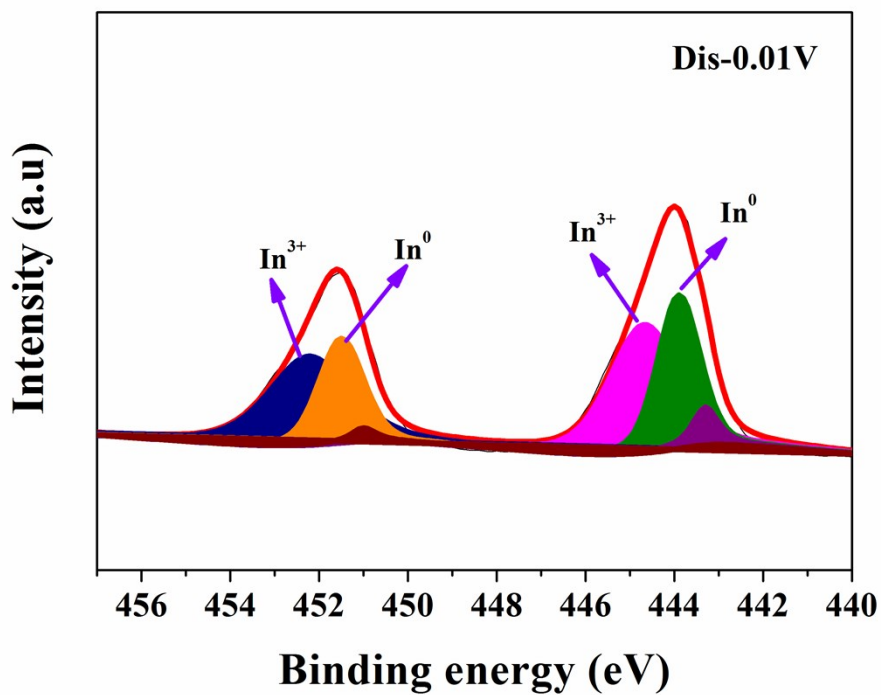
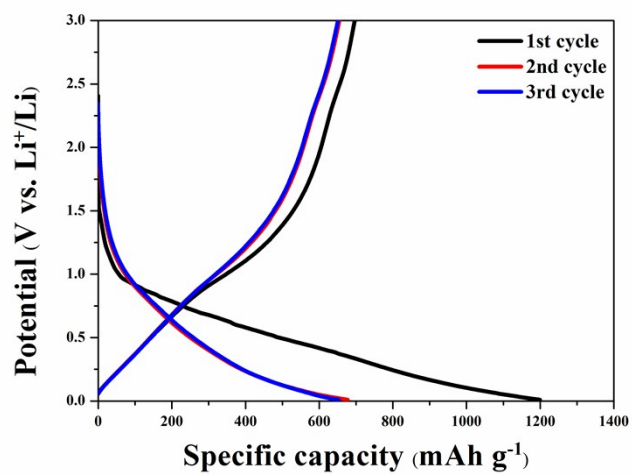Fig. S5 the high resolution In3d spectrum at dis-0.01V.

Fig. S6 Galvanostatic charge/discharge voltage profiles of In_2S_3/C nanofiber anode at
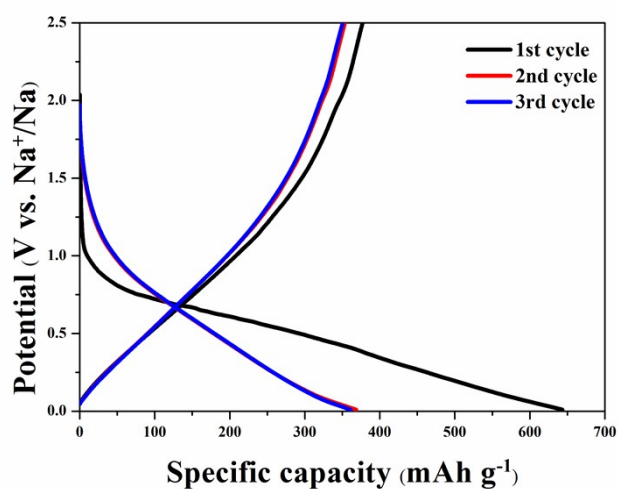
50 mA g^{-1} in LIBs.

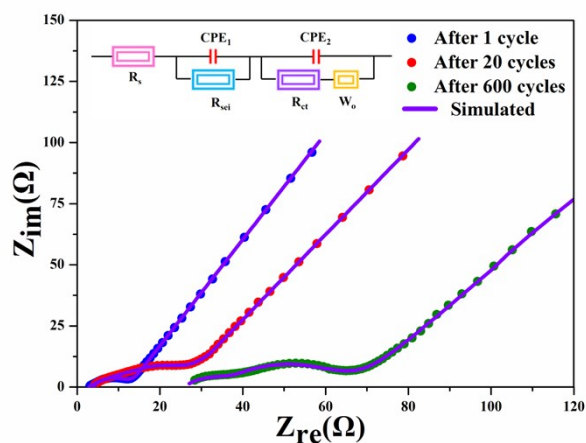Fig. S7 Galvanostatic charge/discharge voltage profiles of In_2S_3/C nanofiber anode at

50 mA g^{-1} in SIBs.

Fig. S8 Electrochemical impedance spectra (EIS) and equivalent electric circuit
(inset) of the In_2S_3/C nanofiber anode in LIBs after 1 and 20 cycles at 50 mA g^{-1} and
after 600 cycles at 1000 mA g^{-1}.

Table S1 Simulated impendence parameters (R_s, R_{sei} and R_{ct}) of In_2S_3/C nanofiber
electrode in LIBs.

Cycle number	$R_s(\Omega)$	$R_{sei}(\Omega)$	$R_{ct}(\Omega)$

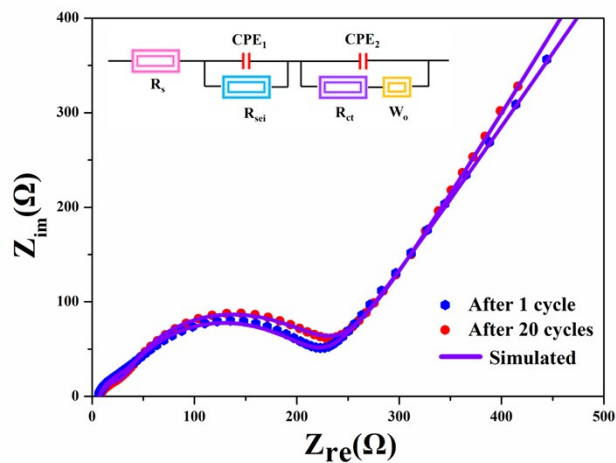|			
1	2.9	1.2	7.1
20	4.2	4.6	12.6
600	25.9	12.9	20.3

Fig. S9 Electrochemical impedance spectra (EIS) and equivalent electric circuit (inset) of the In_2S_3/C nanofiber anode in SIBs after 1 and 20 cycles at 50 mA g^{-1}.

Table S2 Simulated impendence parameters (R_s, R_{sei} and R_{ct}) of In_2S_3/C nanofiber electrode in SIBs.

Cycle number	$R_s(\Omega)$	$R_{sei}(\Omega)$	$R_{ct}(\Omega)$
1	7.2	27.9	150.6
20	7.4	28.0	162.6

Supplementary references

1. J. Xia, L. Liu, S. Jamil, J. Xie, H. Yan, Y. Yuan, Y. Zhang, S. Nie, J. Pan, X. Wang and G. Cao, Energy Storage Mater., 2019, **17**, 1-11.
2. Y. Liu, N. Zhang, L. Jiao and J. Chen, Adv. Mater., 2015, **27**, 6702-6707.