Supporting information for:

In situ TEM Tracking Sodium Migration in TiS_2

Bo Han[a,b], Shulin Chen[b,c], Jian Zou[d], Ruiwen Shao[b], Zhipeng Dou[b,e], Chen Yang[f,g], Xiumei Ma[b], Jing Lu[f,g], Kaihui Liu[f,h], Dapeng Yu[b,f,h,i], Liping Wang[d,*], Haicheng Wang[a,*], and Peng Gao[b,h,j*]

a *National Center for Materials Service Safety, University of Science and Technology Beijing, Beijing 100083, China*
b *Electron Microscopy Laboratory, School of Physics, Peking University, Beijing 100871, China*
c *State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin 150001, China*
d *School of Materials and Energy, State Key Laboratory of Electronic Thin Film and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China*
e *Key Laboratory for Micro-/Nano-Optoelectronic Devices of Ministry of Education, School of Physics and Electronics, Hunan University, Changsha 410082, China*
f State Key Laboratory for Artificial Microstructure & Mesoscopic Physics, School of Physics, Peking University, Beijing 100871, China
g Academy for Advanced Interdisciplinary Studies, Peking University, Beijing 100871, China
h Collaborative Innovation Center of Quantum Matter, Beijing 100871, China
i Shenzhen Key Laboratory of Quantum Science and Engineering, Shenzhen 518055, China
j International Center for Quantum Materials, School of Physics, Peking University, Beijing 100871, China

E-mail: lipingwang@uestc.edu.cn (Liping Wang),
hcwang@mater.ustb.edu.cn (Haicheng Wang),
p-gao@pku.edu.cn (Peng Gao)

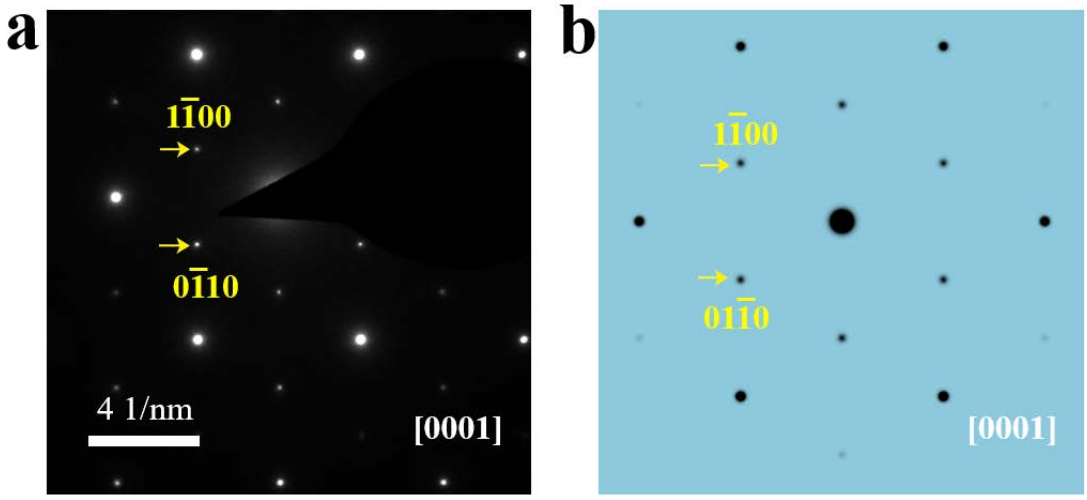

Figure S1. Electron diffraction pattern of (a) pristine TiS_2 and (b) simulated TiS_2 single crystal. Simulated pattern is calculated by theoretical atomistic model (PDF#15-0853, *a*=3.397 Å, *b*=3.397 Å, *c*=5.691 Å).

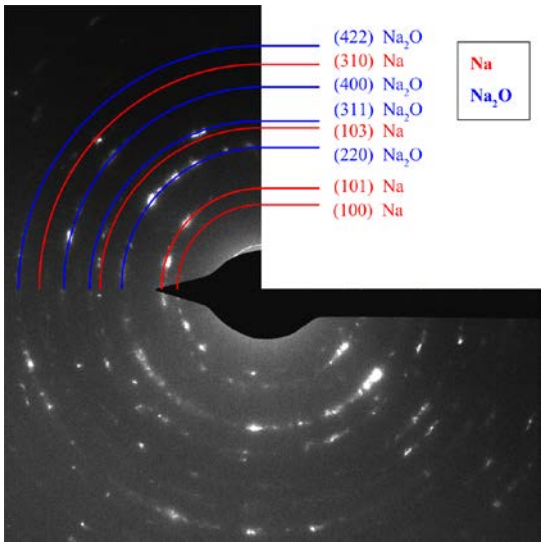

Figure S2. The electron diffraction pattern of Na_2O/ Na probe.

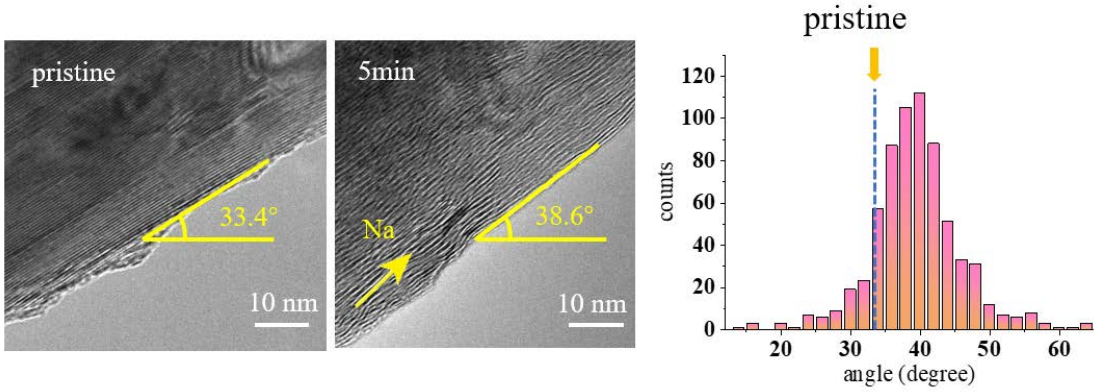

Figure S3. Nanometer-sized domains generate after sodium inserted into TiS_2. The angles of domains are 38.6±6.6 degree, compared with the pristine 33.4 degree. The change results from the in-homogenous lattice expansion during sodiation.

In order to calculate the average angle of sodiated TiS_2 domains, 740 domains were measured. The measurement was based on a frame of TEM image at 5 min.

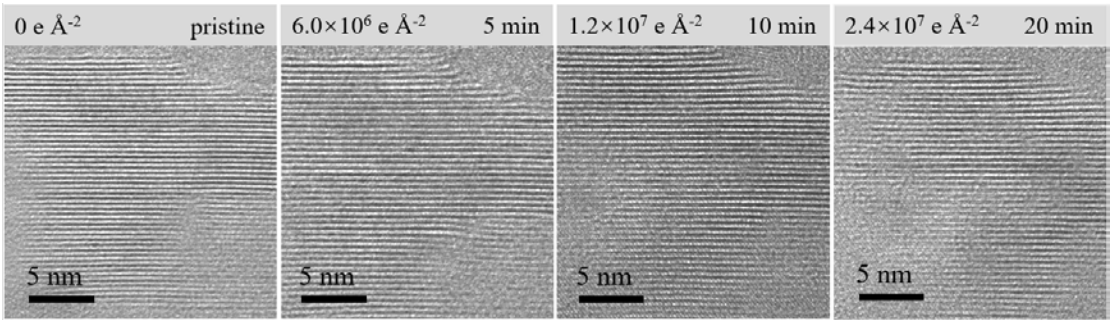

Figure S4. TiS_2 nanosheet exposed under electron beam irradiation.

Under long time irradiation in TEM column environment, TiS_2 remains its layered structure. TiS_2 nanosheets were intentionally exposed under electron beam in TEM column environment. The dose rate was kept at 2.0×10^4 e $Å^{-2}$ s^{-1}. After 20 mins exposure under electron beam (total dose 2.40×10^7 e $Å^{-2}$), no lattice expansion observed. As our in-situ sodiation experiments were carried out in less than 10 mins at a dose rate 4.7×10^3 e $Å^{-2}$ s^{-1} (total dose is 2.8×10^6 e $Å^{-2}$ that is far below the tested one), the effects of these environmental factors in column (beam damage effects, possible oxygen and water vapor, heating etc.) can be ruled out.

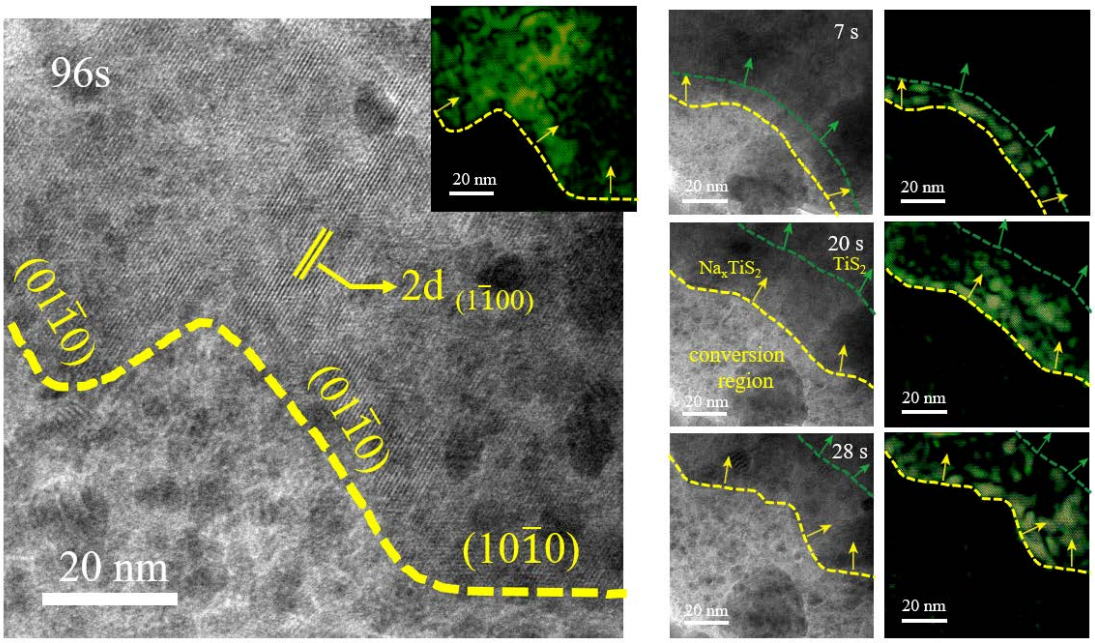

Figure S5. The inverse Fast Fourier Transformation (iFFT) images to show boundaries between different phases. The iFFT images are acquired only including superstructure FFT spot of TEM images to judge the position of the boundary.

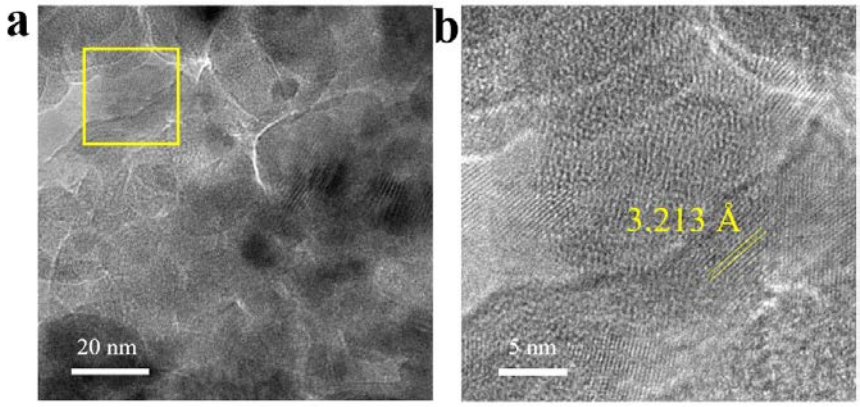

Figure S6. Na_2S in fully sodiated TiS_2 discharged to 0 V. (a) A TEM image of the fully sodiated TiS_2. (b) An enlarged view of showing the spacing between lattice is 3.213 Å, corresponding to the Na_2S (200) plane (PDF#23-0441).

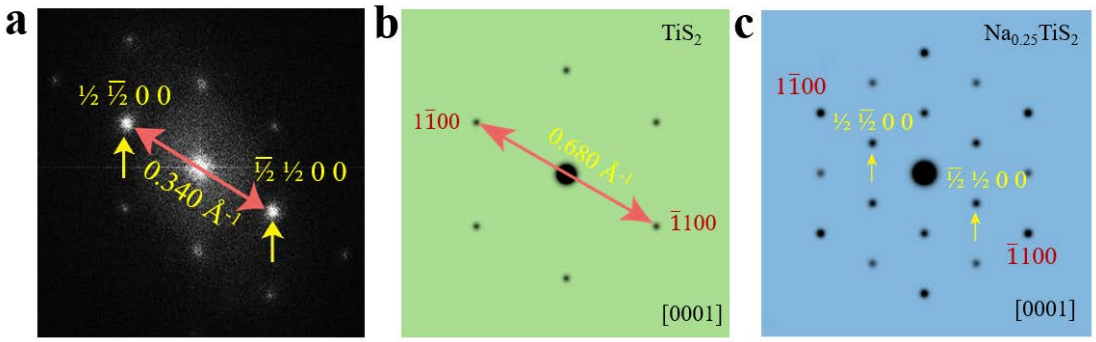

Figure S7. Superstructure of Na-intercalated TiS_2. (a) FFT pattern of the TEM image at 28 s during sodiation (see also Figure 4b). (b) A simulated electron diffraction pattern of pristine TiS_2 single crystal. (c) A simulated electron diffraction pattern of $Na_{0.25}TiS_2$.

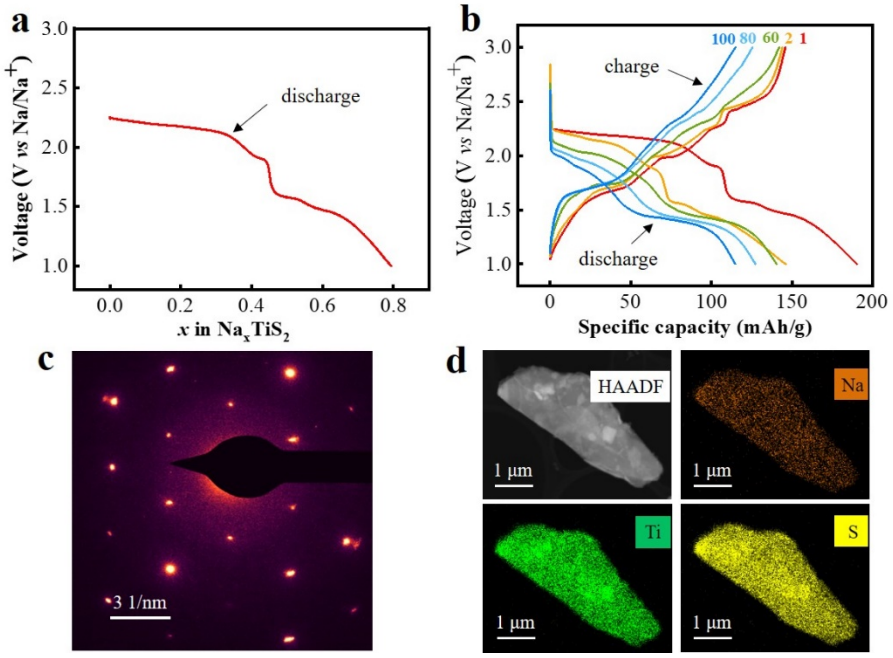

Figure S8. Structure of *ex situ* electrochemical Na-intercalated TiS_2. (a) The first galvanostatic discharge curve of Na-TiS_2 half battery. The x-axis indicates the mole ratio (*x*) of Na in the Na_xTiS_2 composition which is calculated from discharge capacity of the battery based on the Na/TiS_2 theoretical capacity. (b) Charge-discharge curves with 100 cycles. (c) The SAED pattern of TiS_2 electrode discharged to the end of first platform (2.1 V) in a half coin cell. The orange dash rhombus shows the basic geometry of original TiS_2 crystal. (d) Elements distribution maps of a TiS_2 single powder from battery electrode discharged to 2.1 V.

On the first galvanostatic discharge curve of Na-TiS_2 half battery, the discharge profile contains a platform at low Na concentration, which corresponds to an intercalation reaction with Na_xTiS_2 generation. From the SAED pattern of TiS_2 discharged to 2.1 V, although the sodium ion has intercalated into TiS_2 nanosheets based on the elements distribution maps, there is no 2×2 superstructure diffraction spots ($Na_{0.25}TiS_2$) observed. As for Na-TiS_2 battery, the first coulombic efficiency is 76.6% with 44.6 mAh g^{-1} capacity loss. Besides, the capacity decreases in the following cycles and after 100 cycles the discharge capacity decreases to 115.0 mAh g^{-1} from the first 190.5 mAh g^{-1}. The degraded capacities may be related to the irreversible structure fracture with the formation of nanosized domains (in Figure 2) of TiS_2 during soidum insertion. Moreover, the sodiation process undergoes a large volume expansion, leading to the formation of defects and fracture in the active material TiS_2 and losing contact with the electronic binder, which also contributes to the capacity decay.

Movie S1: (corresponding to Figure. 2) This video is made up of series of HRTEM images and shows the structural evolution of TiS_2.

Movie S2: (corresponding to Figure. 3) This video shows the phase propagation of conversion region and 2×2 superstructure region in TiS_2.