Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Construction of Bi-based Amorphous/Crystalline Heterostructures for Efficient Potassium Ion Storage

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Characterization of the materials:

The crystal structure of the was examined by X-ray diffraction (XRD, Rigaku, Ultima IV with D/teX Ultra with CuKα radiation). The morphological and detailed structure characterization was investigated by scanning electron microscopy (SEM, JSM-6610L, Japan) and transmission electron microscopy (TEM, FEI TECNAI G2 F20, America). The surface elemental states of as-synthesized materials were characterized by X-ray photoelectron spectra (XPS, Kratos Axis Ultra DLD, Japan).

Electrochemical Measurements:

The CR2032-type cells were assembled in the glove box fulfilled by argon. The working electrodes were prepared by mixing the as-prepared products, super P, and PVDF at a weight ratio of 7:2:1. The slurry was casted onto the Cu foil and completely

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dried in a vacuum oven at 50 °C overnight. The average mass loading was about 1.2-1.4 mg cm^{-2}. For half-cell testing, K slice was used as the counter electrode, the glass fiber film (Whatman GF/D) was employed as a separator and the electrolyte was composed of 3.0 M KFSI in DME. The galvanostatic discharge-charge tests were measured on the battery testing systems (Neware, Shenzhen). Cyclic voltammetry (CV) and EIS measurements were performed on a CHI660E electrochemical workstation (ChenHua, Shanghai).

Theoretical Computation:

The Vienna Ab Initio Simulation Package was used to implement all the DFT calculations.[1] The exchange-correlation interaction between electrons was described by the generalized gradient approximation (GGA) in the strategy of Perdew-Burke-Ernzerhof (PBE) functional. A cutoff energy of 520 eV was applied for the plane-wave expansion of the electronic wave functions. The self-consistency field calculations were conducted with an energy convergence of 10^{-4} eV and force convergence of 10^{-2} eV/Å.[2] For all of the surfaces explored, the Brillion-zone integration was sampled by adopting a 3×3×1 Gamma-centered k-point mesh. Bi_2S_3 (211), and Bi_2O_3 (200) surfaces were applied as stable surfaces for adsorption calculations.

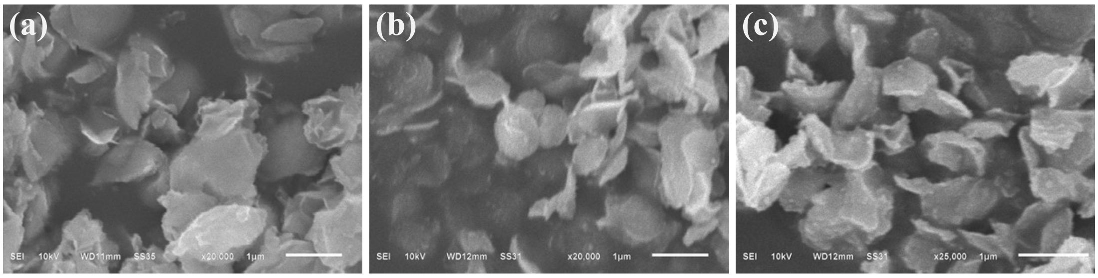

Figure S1. SEM image of a) c-Bi_2O_3, b) c-Bi_2S_3/c-Bi_2O_3, and c) a-Bi_2S_3/c-Bi_2O_3.

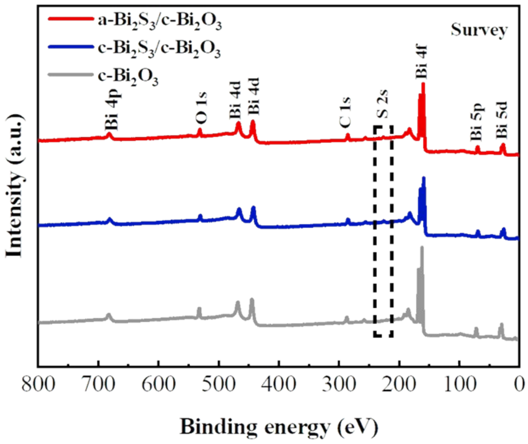

Figure S2. XPS survey spectrum of a-Bi_2S_3/c-Bi_2O_3, c-Bi_2S_3/c-Bi_2O_3, and c-Bi_2O_3.

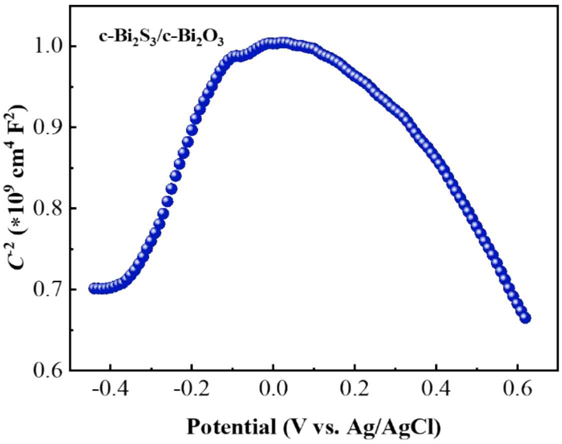

Figure S3. Mott–Schottky plot.

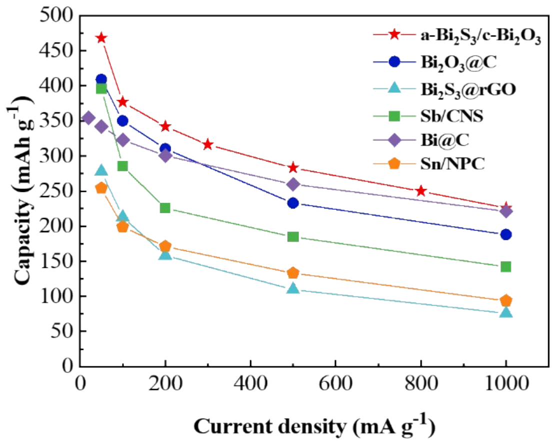

Figure S4. Rate performance of a-Bi_2S_3/c-Bi_2O_3 electrode compared with those of the previously reported alloy anodes for KIBs.

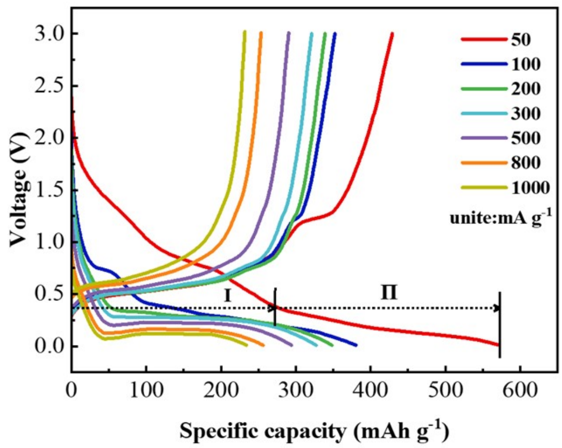

Figure S5. Discharge capacity from the embedding/conversion plateau (denoted as I), alloying plateau (denoted as Π).

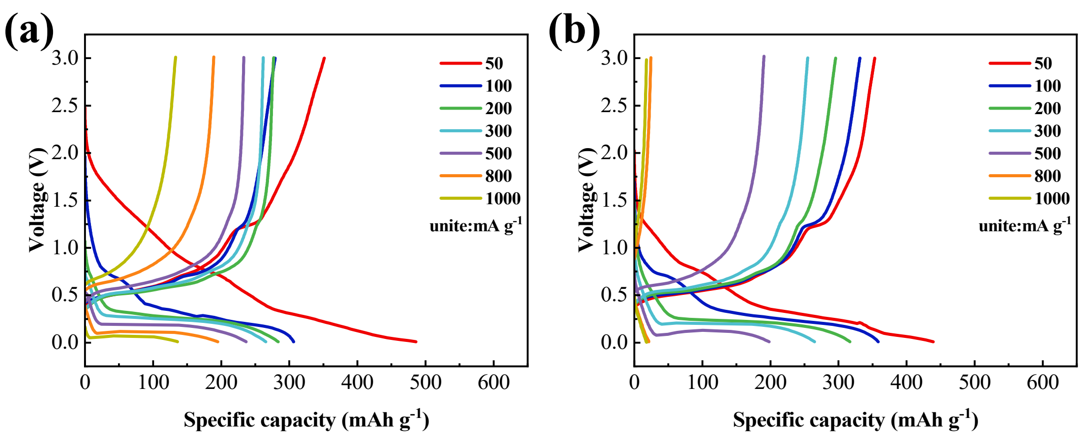

Figure S6. Galvanostatic charge–discharge profiles of a) c-Bi_2S_3/c-Bi_2O_3 and b) c-Bi_2O_3 at various rates.

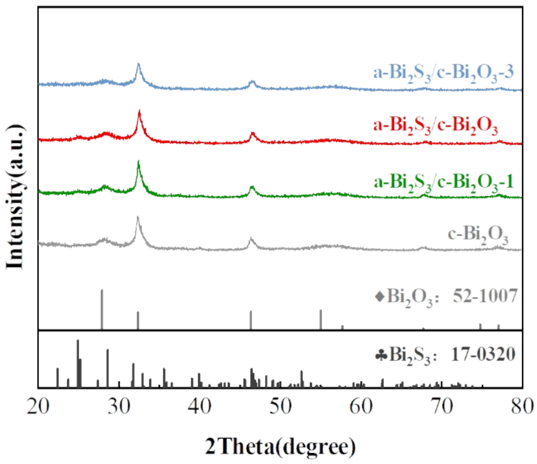

Figure S7. XRD pattern with different degrees of sulfidation.

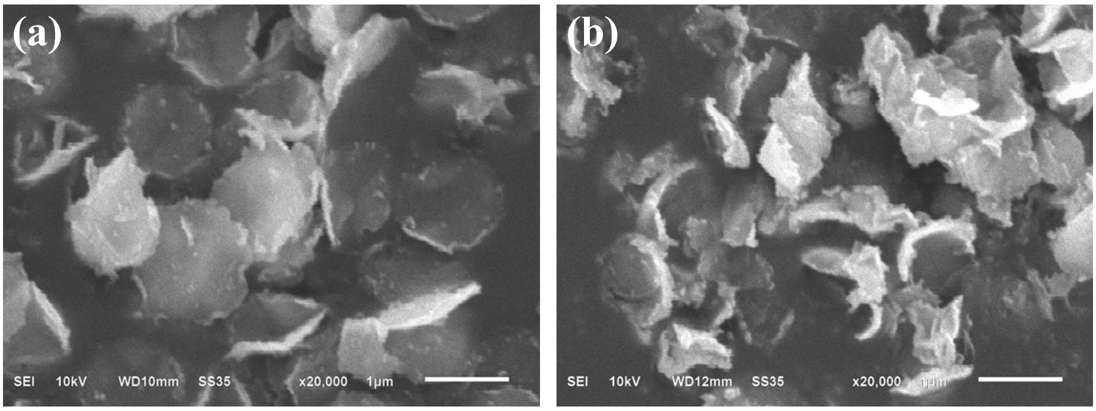

Figure S8. SEM image of a,b) a-Bi_2S_3/c-Bi_2O_3-1 and a-Bi_2S_3/c-Bi_2O_3-3.

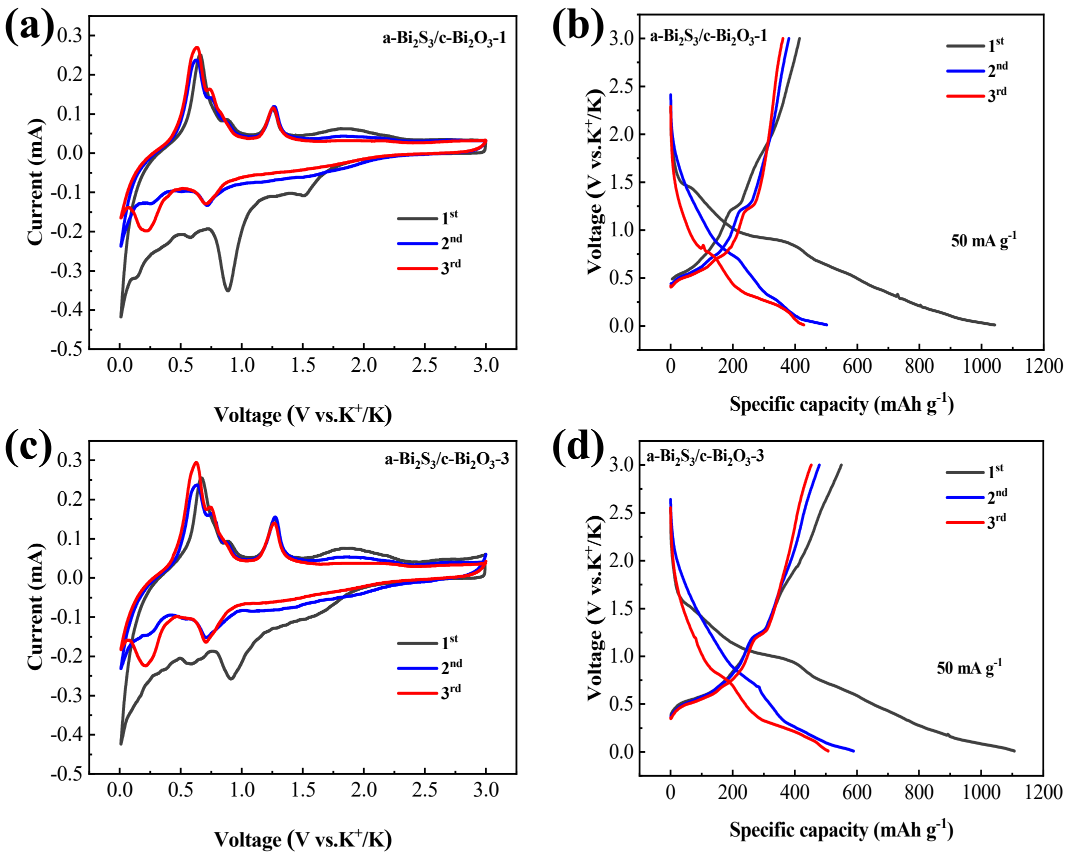

Figure S9. a,c) CV curves of a-Bi_2S_3/c-Bi_2O_3-1 and a-Bi_2S_3/c-Bi_2O_3-3 at 0.1mV s^{-1}. b,d) Charge/discharge profiles of a-Bi_2S_3/c-Bi_2O_3-1 and a-Bi_2S_3/c-Bi_2O_3-3 at 50 mA g^{-1}.

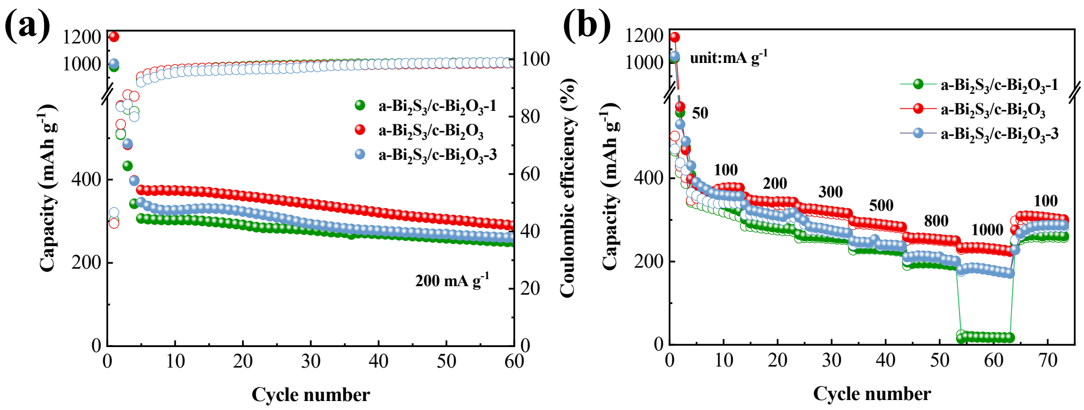

Figure S10. a) Cycling performance at 200 mA g^{-1}. b) Rate capability.

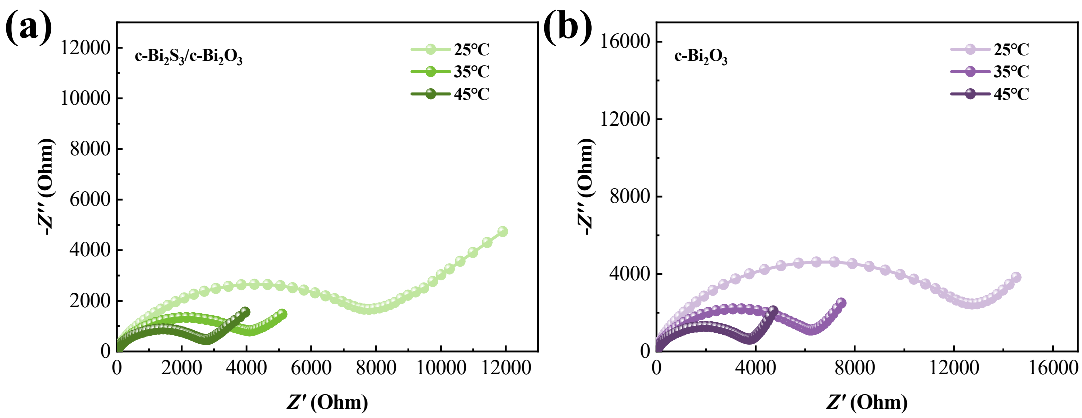

Figure S11. EIS curves of a) c-Bi_2S_3/c-Bi_2O_3 and b) c-Bi_2O_3 at different temperatures.

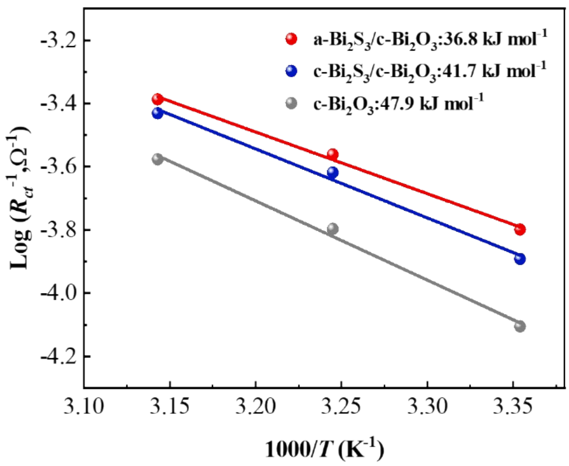

Figure S12. The comparison of activation energies.

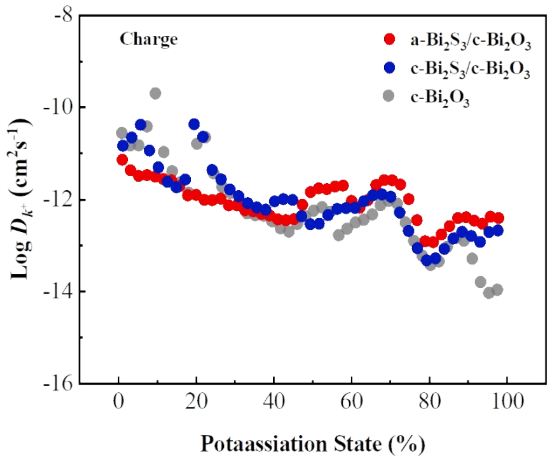

Figure S13. Calculated K^+ diffusion coefficient at different potassiation states during the charging

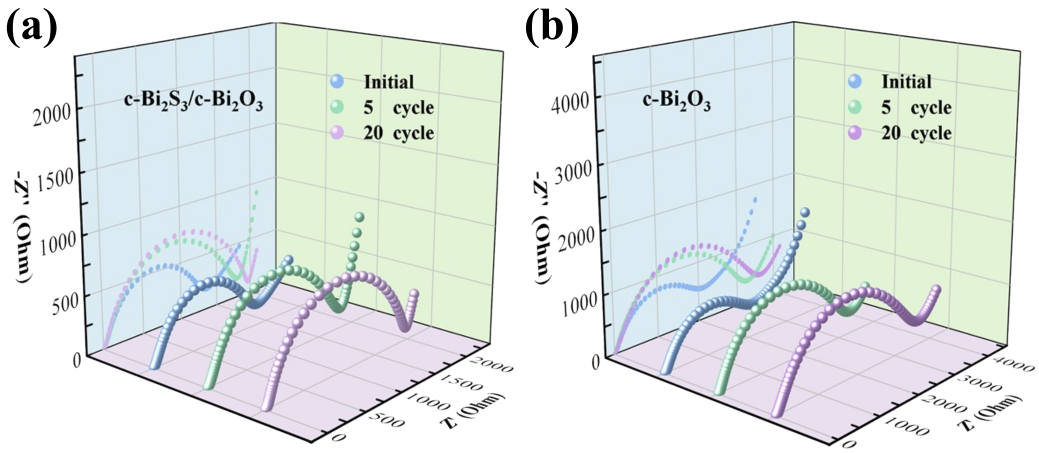

Figure S14. EIS curves of a) c-Bi_2S_3/c-Bi_2O_3 and b) c-Bi_2O_3 electrodes after different cycles at 300 mA g^{-1}.

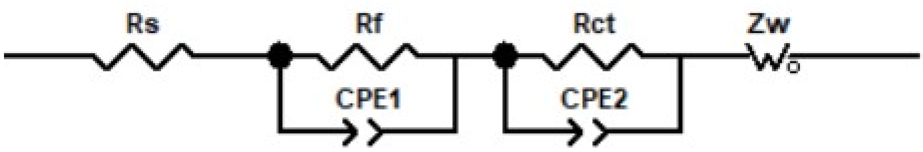

Fig S15. The equivalent circuit of Nyquist.

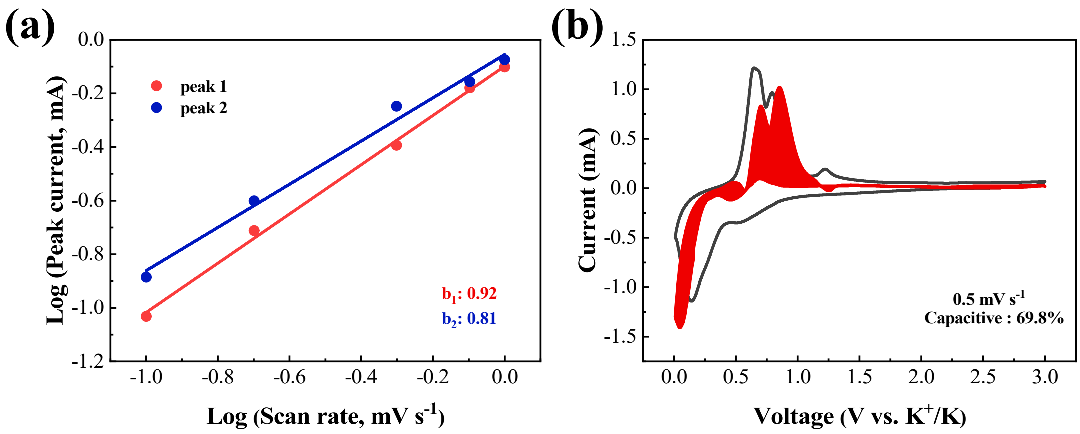

Figure S16. a) The corresponding b values in linear regression. b) The composition of pseudocapacitive characteristics in the CV curve at a scan rate of 0.5 mV s^{-1}.

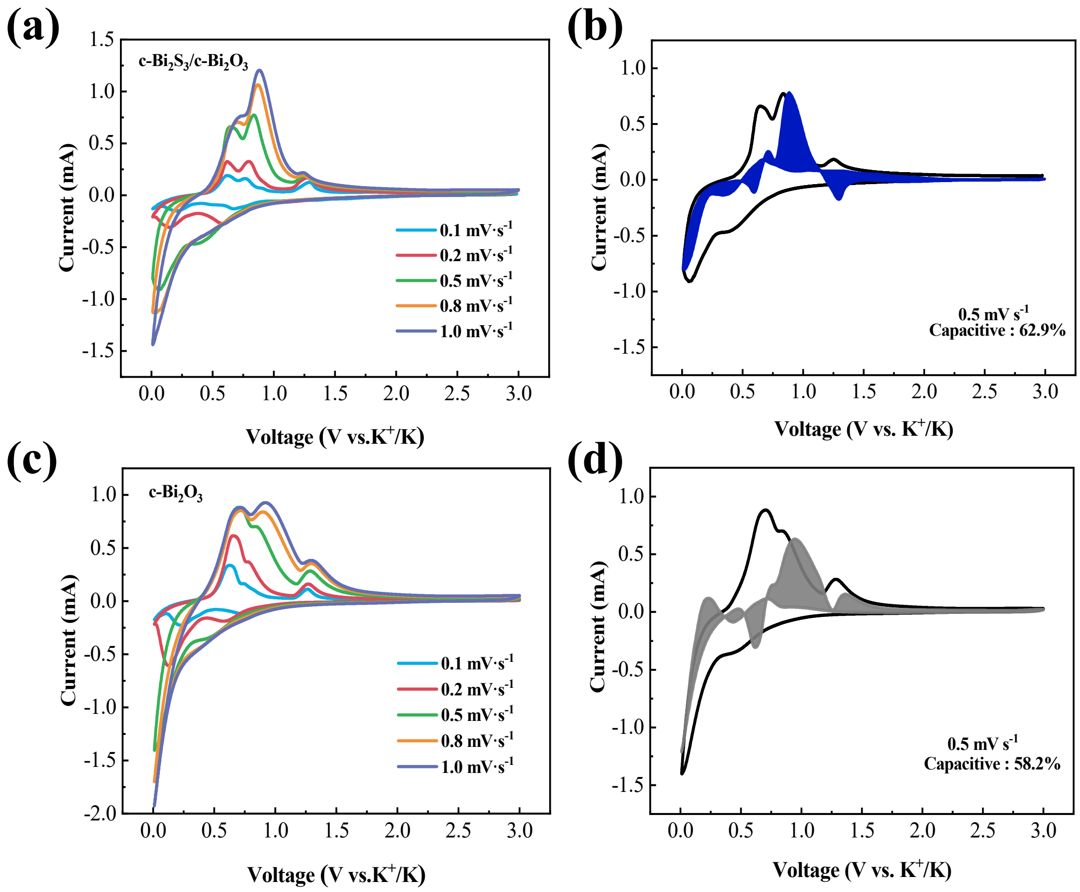

Figure S17. a,c) CV curves of c-Bi_2S_3/c-Bi_2O_3 and c-Bi_2O_3 at different sweeping rates. b,d) The contribution ratio of pseudocapacitive characteristics of c-Bi_2S_3/c-Bi_2O_3 and c-Bi_2O_3 in the CV curve at a scan of 0.5 mV s^{-1}.

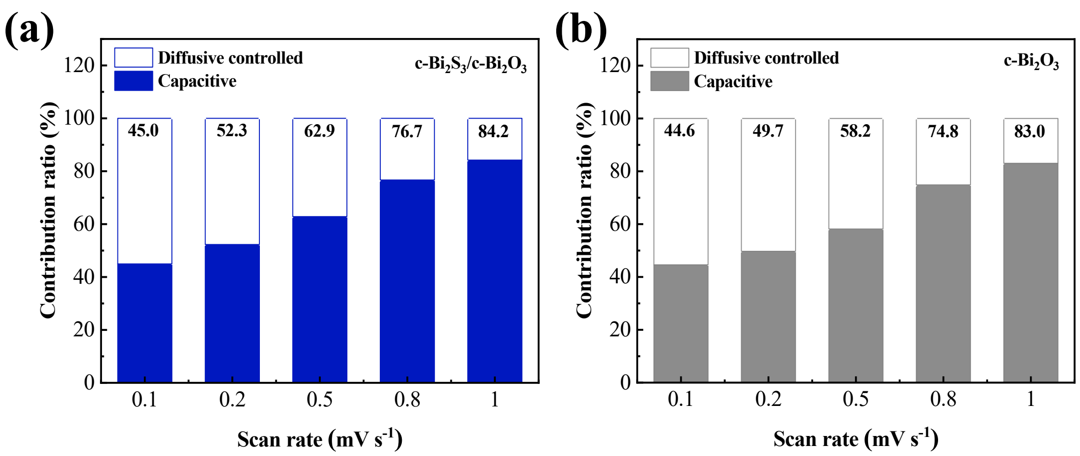

Figure S18. a,b) The contribution ratio of surface-controlled and diffusion-controlled behaviors of c-Bi_2S_3/c-Bi_2O_3 and c-Bi_2O_3 at different scan rates.

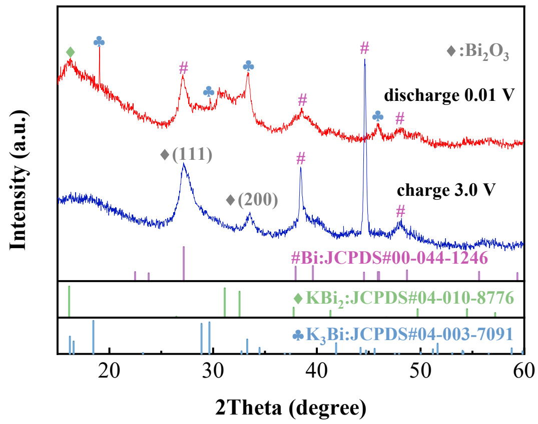

Figure S19. Ex-situ XRD patterns of a-Bi_2S_3/c-Bi_2O_3 electrode during the first discharge and charge.

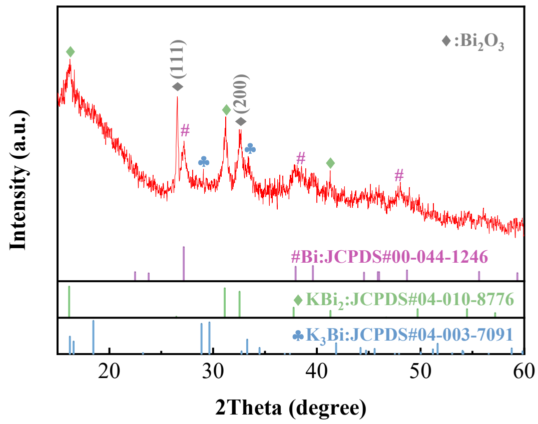

Figure S20. XRD patterns of a-Bi_2S_3/c-Bi_2O_3 electrode after 300 cycles.

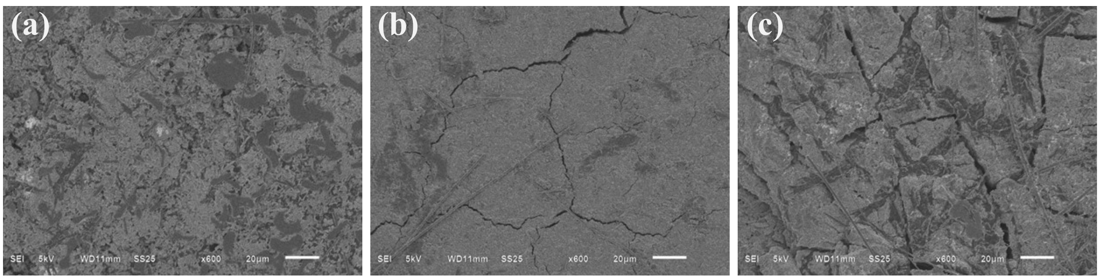

Figure S21. The post-mortem SEM images of a) a-Bi_2S_3/c-Bi_2O_3, b) c-Bi_2S_3/c-Bi_2O_3 and c) c-Bi_2O_3.

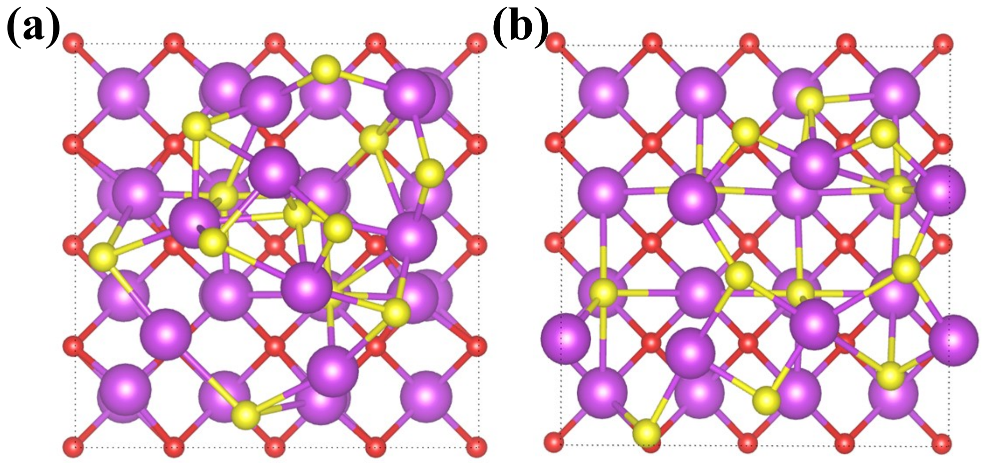

Figure S22. Top views of the optimized structure a) a-Bi_2S_3/c-Bi_2O_3 and b) c-Bi_2S_3/c-Bi_2O_3.

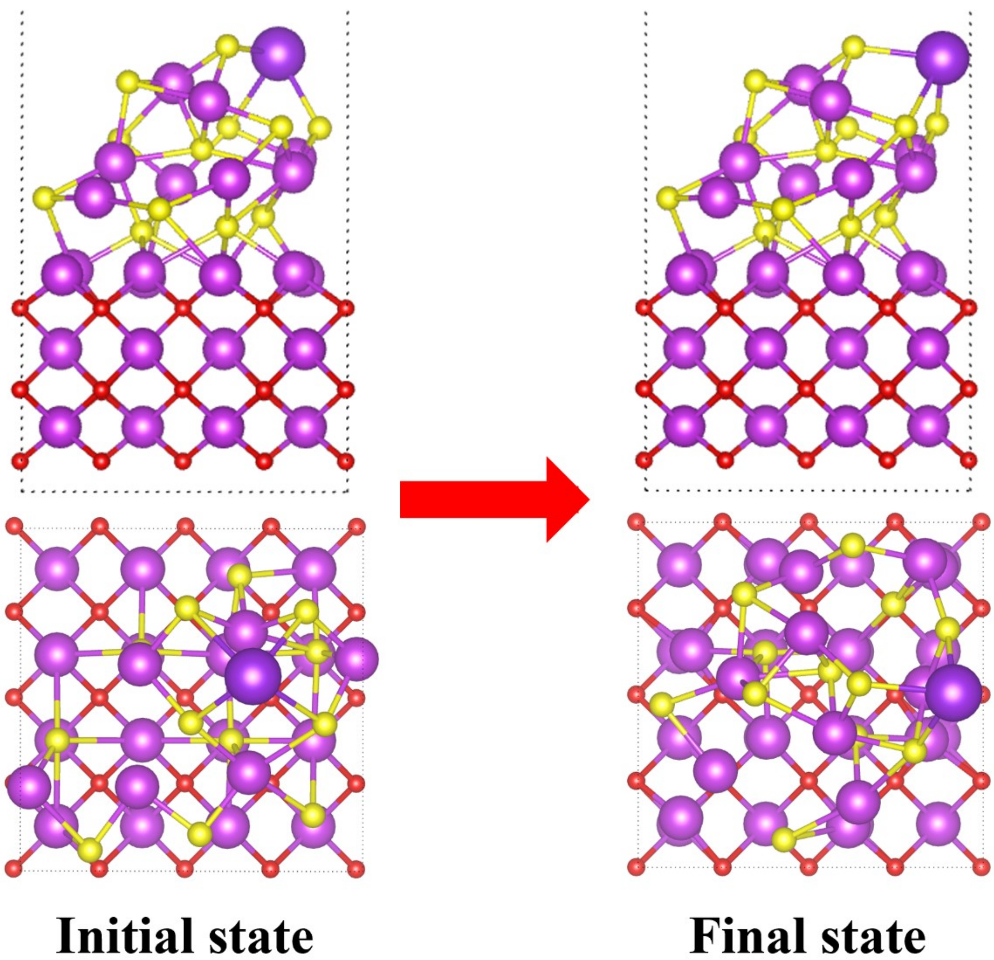

Figure S23. The initial and final state of K-atom diffusion in a-Bi_2S_3/c-Bi_2O_3.

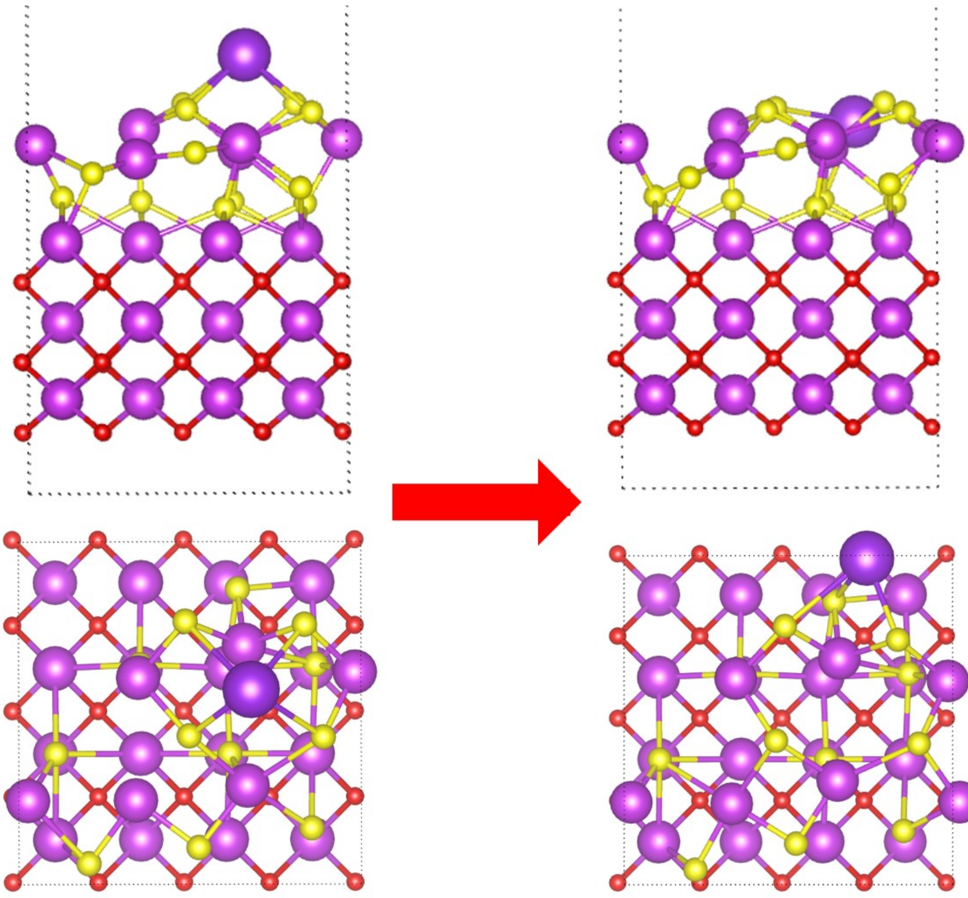

Figure S24. The initial and final state of K-atom diffusion in c-Bi_2S_3/c-Bi_2O_3.

References

1. P. E. Blochl, *PHYSICAL REVIEW B*, 1994, **50**, 17953-17979.
2. M. Yu and D. R. Trinkle, *JOURNAL OF CHEMICAL PHYSICS*, 2011, **134**.