Electronic Supplementary Material (ESI) for Nanoscale.
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Electronic Supplementary Information:

N-doped Carbon Coated Bismuth Nanorod with Hollow Structure as Anode for Superior-Performance Potassium-Ion Batteries

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Experimental Section:

Materials Synthesis: A simple hydrothermal method was used to prepare the Bi_2S_3 nanorods. $Na_2S{\cdot}9H_2O$, $Bi(NO)_3{\cdot}5H_2O$, and urea were dissolved in deionized water, glycol, and deionized water, respectively. Subsequently, the solution was mixed and transferred to stainless steel autoclave with Teflon-liner at 120 °C for 24 h. The product was washed with deionized water and alcohol. For carbon coating, as-prepared Bi_2S_3 nanorods, sodium dodecyl sulfate and pyrrole were added into deionized water with stirring and ultrasound. Then, $(NH_4)_2S_2O_8$ solution was added into the mixture and complete reacted. After that, the product was washed by water and dried overnight. Finally, Bi@N-CT was prepared by annealing under N_2 atmosphere at 650 ℃ for 2 hours. Nickel-based Prussian White ($K_{1.74}Ni[Fe(CN)_6]_{0.95}\square_{0.05}{\cdot}1.45H_2O$ (note as KNF) was synthesized via a co-precipitation of potassium ferrocyanide and nickel salt.

Materials characterization: XRD patterns of the samples were characterized by the X-ray diffractometer (Empyrean, PANalytical) with Cu Kα radiation (0.154 nm). TGA data were measured using a thermal analyzer (STA409PC, NETZSCH) from 50 °C to 800 °C at a heating rate of 5 °C·min^{-1} under an oxygen atmosphere. The morphologies of the samples were observed using FESEM (Zeiss Ultra Plus). The internal structure of sample was analyzed by TEM (Talos F200S, FEI). For *in-situ* XRD analysis (D8 Advance, Bruker), the electrode was placed on an iron net near a beryllium window. The XRD signals were collected by the planar detector in a still mode.

Electrochemical measurements: To test the electrochemical performance, a slurry was prepared by mixing Bi@N-CT, super-p, and a binder sodium polyacrylate with a weight ratio of 70: 20: 10 in deionized water. The slurry was spread onto the aluminum foil and dried in a vacuum oven at 60 °C. The electrodes were assembled into CR2032 coin cells with the potassium metal as the counter electrode in an argon-filled glove-box. The electrolyte solution was 1 M KPF_6 in 1, 2-dimethoxyethane (DME). Cells were tested on a Land Battery Testing System and Neware Testing System with galvanostatic charge and discharge in the voltage range of 0.01~1.5 V. Cyclic voltammogram (CV) tests were performed with an Autolab PGSTAT30 electrochemical workstation (Metrohm).

DFT calculations of K_3Bi_2 parameters: The structure of K_3Bi_2 is based on the Cs_3Bi_2 (COD: 4116198) with the element replacement from Cs to K. The general gradient approximation was employed in the form of a Perdew-Burke-Ernzerhof solid (PBEsol) exchange-correlation functional using CASTEP program. The plane wave cutoff was set to 600 eV. Self-consistency tolerance is set as 1.0×10^{-8} eV. The force convergence criterion on the atoms is 0.02 eV $Å^{-1}$.

Supporting Figures:

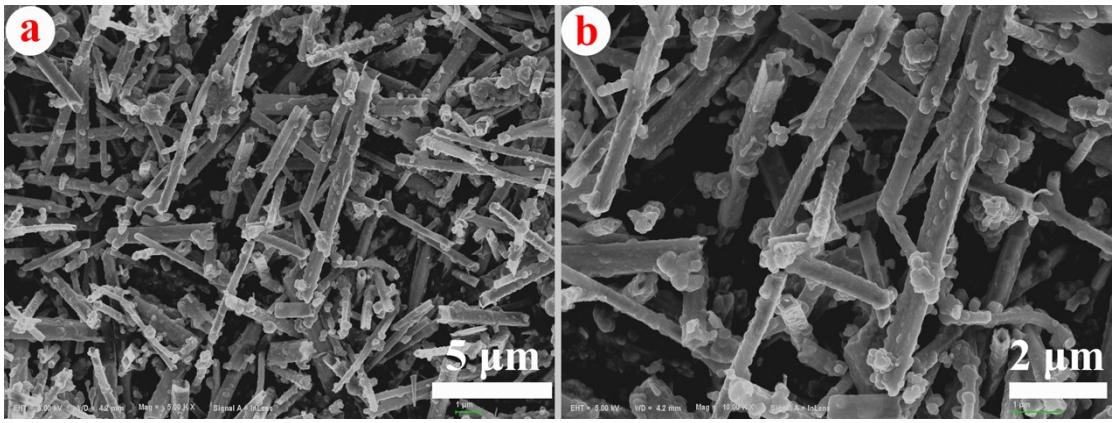

Fig. S1. FESEM images of Bi_2S_3@PPy.

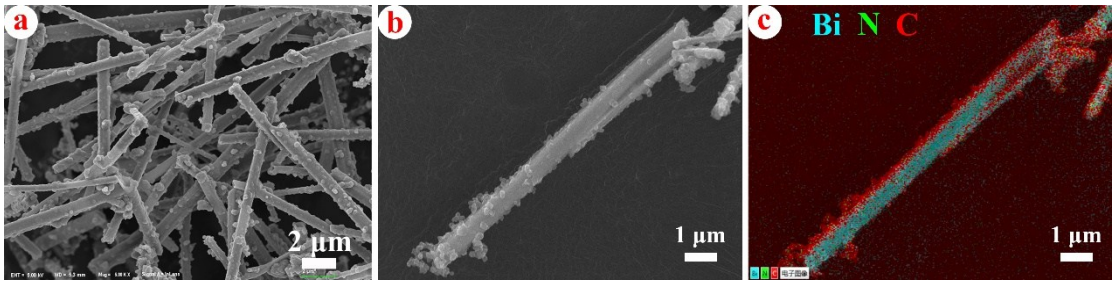

Fig. S2. FESEM image of Bi@N-CT.

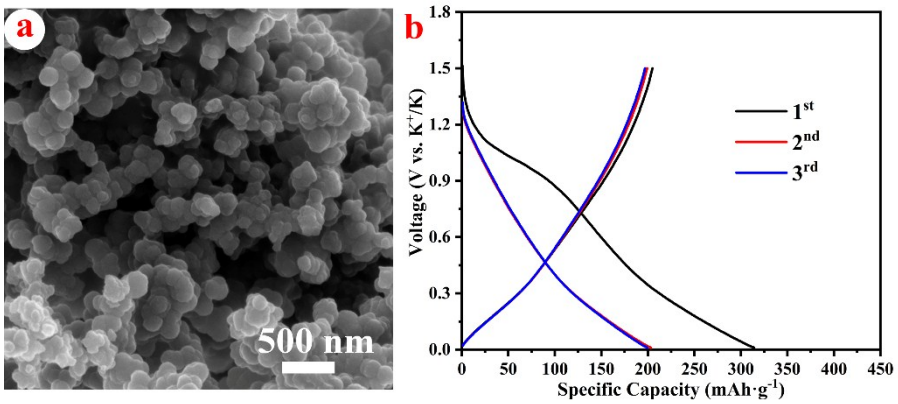

Fig. S3. a) FESEM image of N-C. b) Discharge/charge curves of N-C.

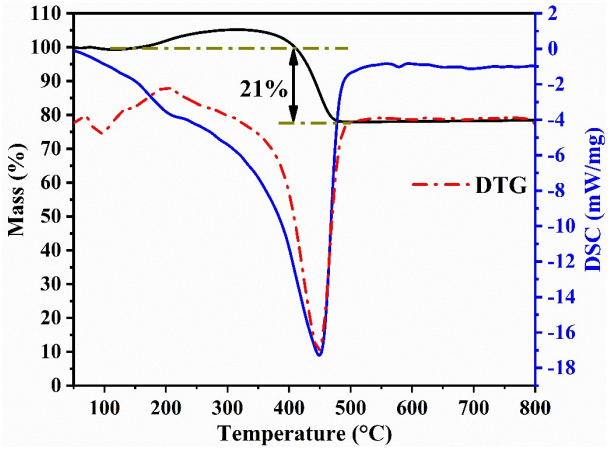

Fig. S4. TGA curves of Bi@N-CT under oxygen atmosphere.

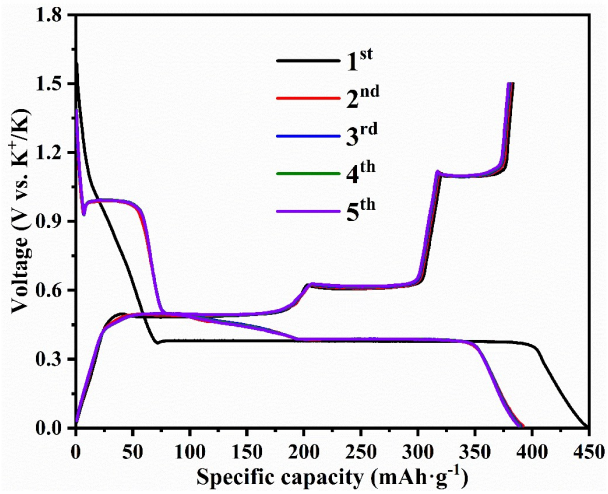

Fig. S5. First five discharge/charge curves of Bulk Bi for PIBs.

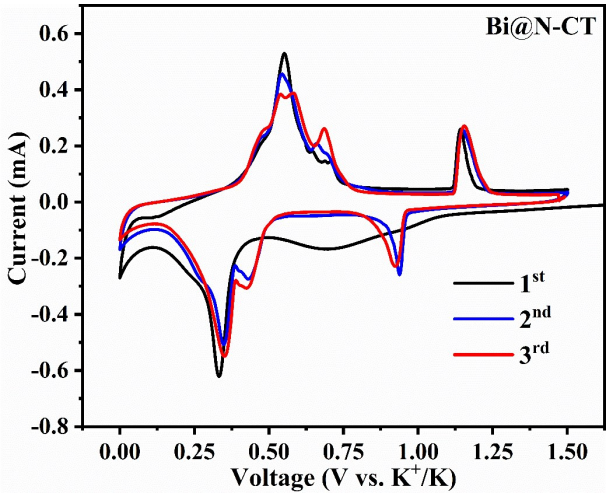

Fig. S6. CV curves of Bi@N-CT for PIBs.

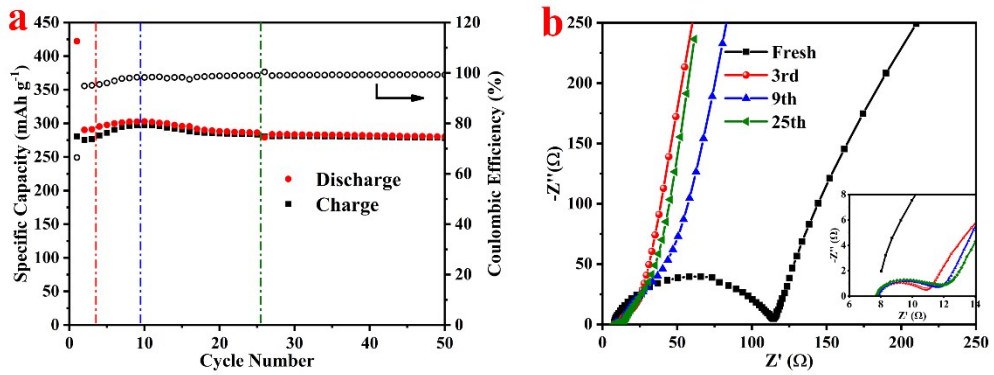

Fig. S7. a) Cycling performance of Bi@N-CT as anode for PIBs at 1C. b) The corresponding EIS spectra over different cycles.

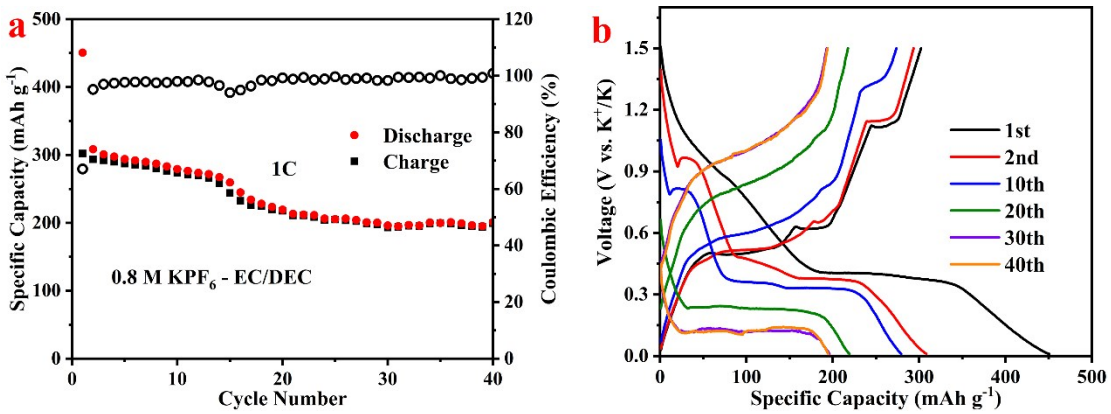

Fig. S8. The cycling performance of Bi@N-CT for PIBs with a KPF_6-EC/DEC electrolyte.

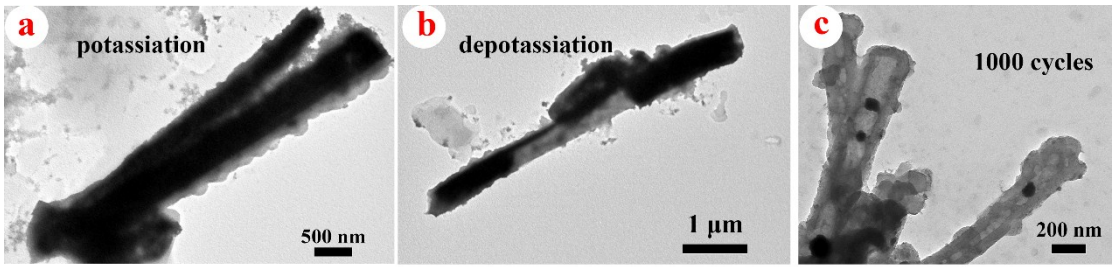

Fig. S9. TEM images of the Bi@N-CT at a) first fully discharged state and b) first charged state at 1C; c) cycled over1000 cycles.

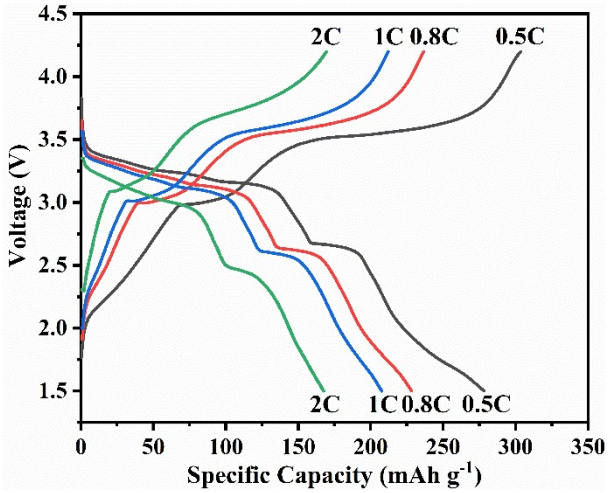

Fig. S10. Potassium storage performance of the $K_{1.74}Ni[Fe(CN)_6]_{0.95}\square_{0.05}\cdot 1.45H_2O$ //Bi@N-CT coin type full cells. a) Cycling performance. b) Rate capability.

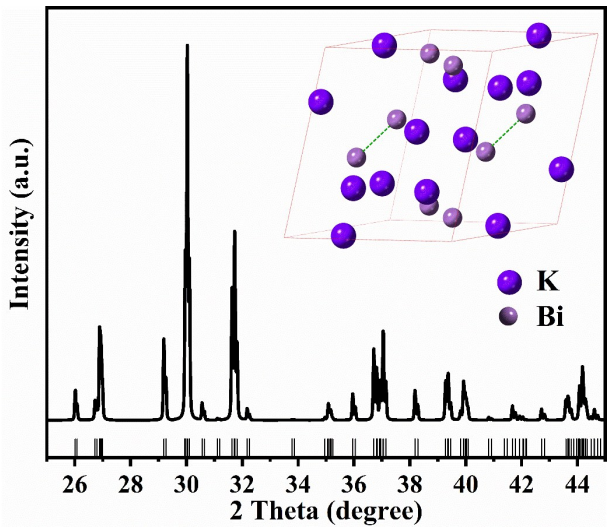

Fig. S11. Crystal structure and XRD pattern of K_3Bi_2 simulated by DFT calculation.

$$Bi_2S_3 \xrightarrow[C]{650\ ^\circ C} Bi \quad \text{(S1)}$$

$$Bi + C \xrightarrow{O_2} Bi_2O_3 + CO_2 \quad \text{(S2)}$$

Table S1. Capacity retentions of previous bismuth-based materials for PIBs.

Sample	Current Density ($A\ g^{-1}$)	Cycle Number	Capacity Retention (%)	Reference
This Work	3.8	1000	88	
Bi/rGO	0.05	50	66	Ref. 1
Bi@3DGF	1	400	71	Ref. 2
UCF@ CNs@BiN	0.1	600	76	Ref. 3
Bi@N-C	10	1000	76	Ref. 4
Bi@C	0.2	600	85	Ref. 5

Reference:

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