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Supplementary Information

Advanced arrayed bismuth nanorod bundle anode for sodium-ion batteries

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Experimental Section

1. Material synthesis

$Al_{30}Bi_{70}$ (at%) alloys were prepared from pure Al block (99.99 wt%) and pure Bi block (99.99 wt%). High-frequency induction heating was employed to melt the Al and Bi in a quartz crucible (at a temperature of 1200 °C for 5 min), and then the Al-Bi melt was cast into ingots in an iron chill mold. By using a single roller melt spinning apparatus (Model No. SP009A) (as shown in Fig. S2), the Al-Bi ingots were remelted in a quartz tube by high-frequency induction heating and melt-spun onto a copper roller at a circumferential speed of about 18.3 m s^{-1}. The Al-Bi ribbons obtained were typically 20-50 μm in thickness，2-6 mm in width, and several centimeters in length. The

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dealloying of the melt-spun Al-Bi ribbons was performed in a 20 wt% NaOH aqueous solution with water bath at 60 °C for 12 h. The magnetic stirring was at a rate of 600 r/min. Abundant gas bubbles generated on the surface of the ribbons at the beginning of the dealloying reaction which finished when no bubbles emerged in the NaOH solution. After dealloying, the precipitation was filtered with filter paper and rinsed with distilled water for several times, followed by drying for 24 h at 80 °C under vacuum. The as-prepared samples were kept in a glove box with water/oxygen content lower than 1 ppm to avoid oxidation.

2. Sample Characterization

The microstructure of the as-prepared materials were characterized by scanning emission microscope (SEM, HITACHI SU-70), high resolution transmission electron microscope (HRTEM, JEOL JEM-2100). The structure was characterized using X-ray diffraction (XRD, Rigaku Dmax-rc diffractometer). The actual content of Al in the sample was determined by inductive coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer 7300DV).

3. Electrochemical Measurement

The as-prepared arrayed Bi nanorod bundles or commercial Bi nanoparticles (No. B109175-5g, Purity⩾99.9%, Aladdin Industrial Co., Ltd., as shown in Fig. S6) was mixed with super P (purchased from lzy battery sale department in China) and a carboxymethyl cellulose (CMC) binder (70:15:15 in weight) in deionized water to form a homogenous slurry, which was painted on a copper foil (purchased form lzy battery sales department in China) and then dried at 100 °C under vacuum for 12 h to form the electrodes. Na sheet (home-made) was used as the counter electrodes, and Celgard 2400 was used as the saparator. The electrolyte was a mixture of 1 M $NaClO_4$ in propylene carbonate with 5% fluoroethylene carbonate (FEC) additive. All the cells (CR2016 coin-type) (purchased from lzy battery sales department in China) were assembled in a glove box with water/oxygen content lower than 1ppm and tested at room temperature. Cyclic voltammetric measurements were carried out with the coin cells at a scan rate of 0.1 mv s^{-1} between 0.1 V and 2.0 V (vs. Na^+/Na) on a CHI 660E electrochemical workstation (Shanghai, China). Galvanostatic discharge/charge cycles were performed between 0.1 and 0.9 V (vs Na^+/Na) on a Neware-CT-3008 test system (Shenzhen, China). Electrochemical impedance spectroscopy (EIS) was also performed on a CHI 660E electrochemical workstation with a frequency of 100 kHz to 0.01Hz.

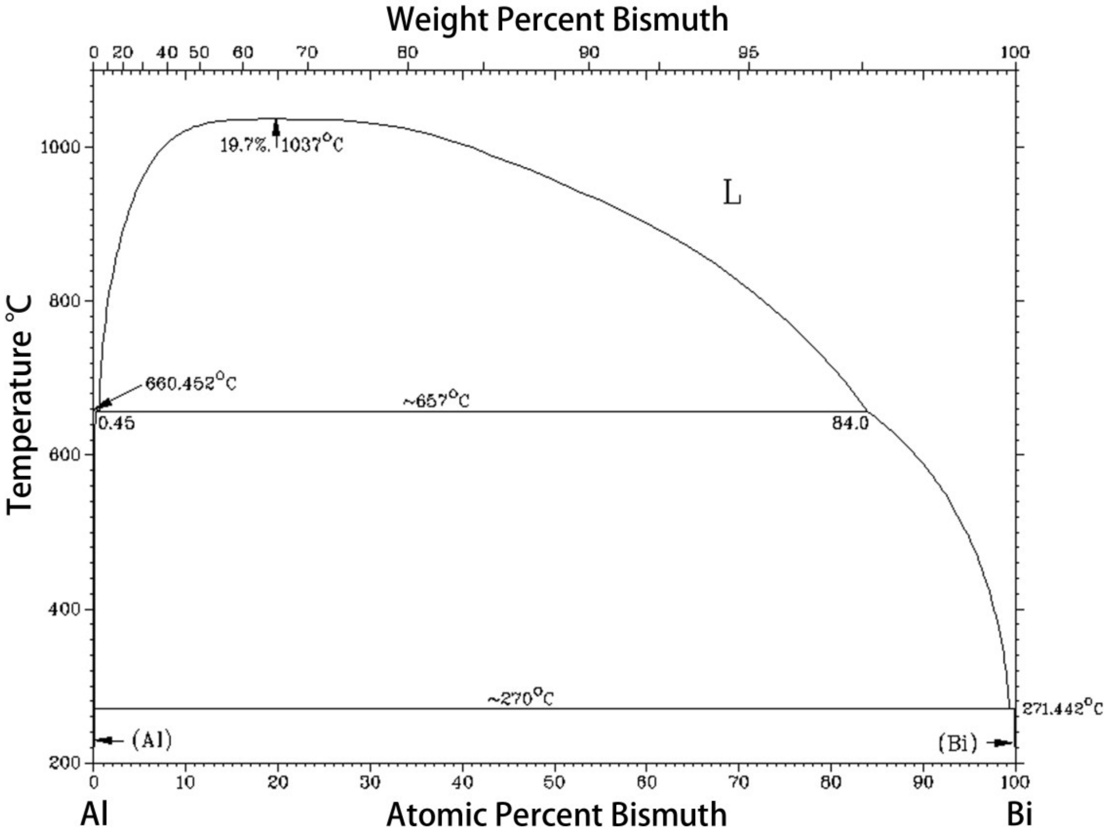

Fig. S1. Al-Bi phase diagram[1, 2]

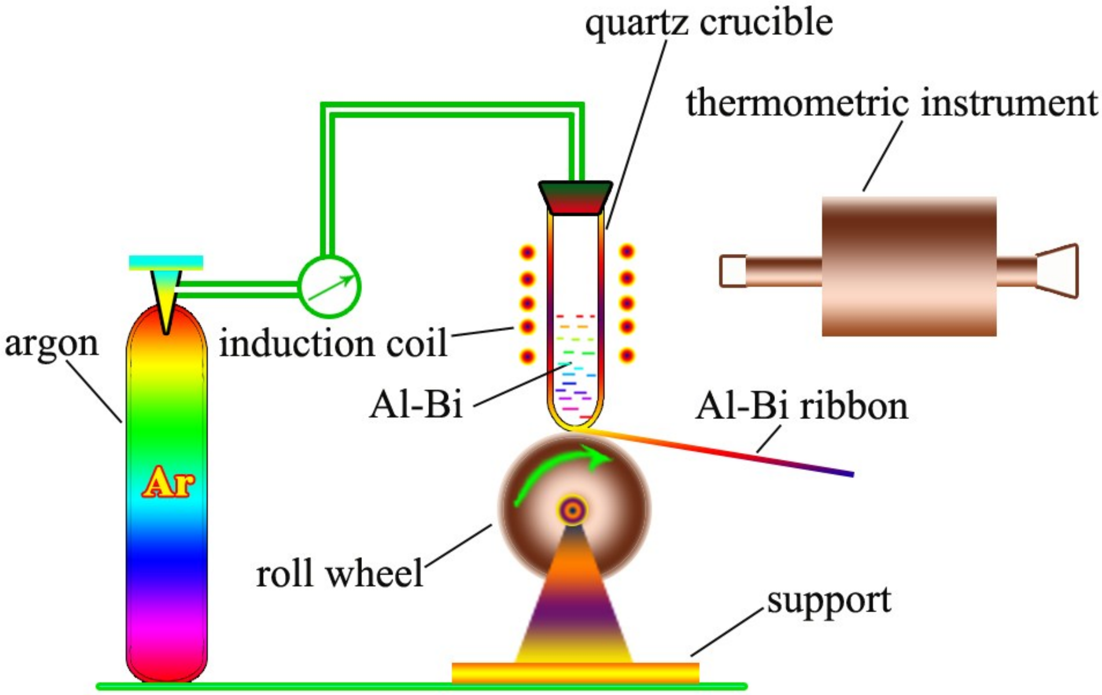

Fig. S2. Schematic diagram of single roller melt spinning apparatus

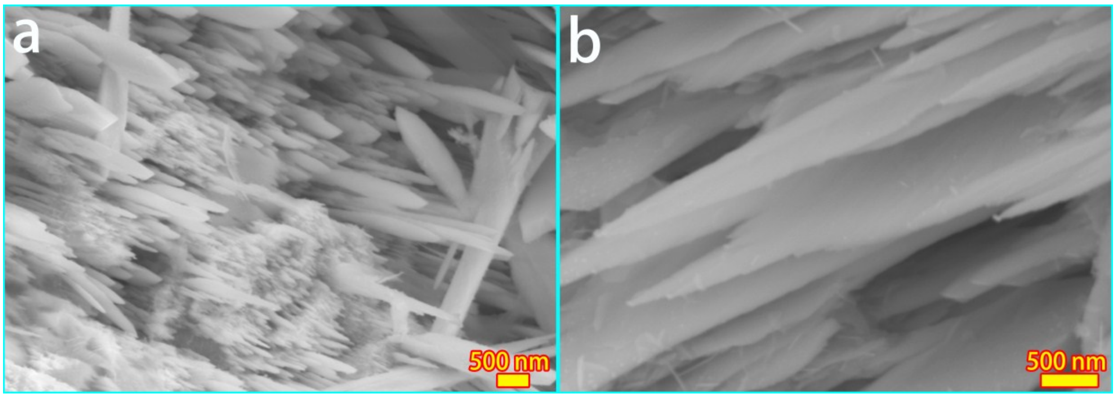

Fig. S3. (a) SEM image (tilted view) of the arrayed Bi nanorod bundles with a higher magnification on the right (b)

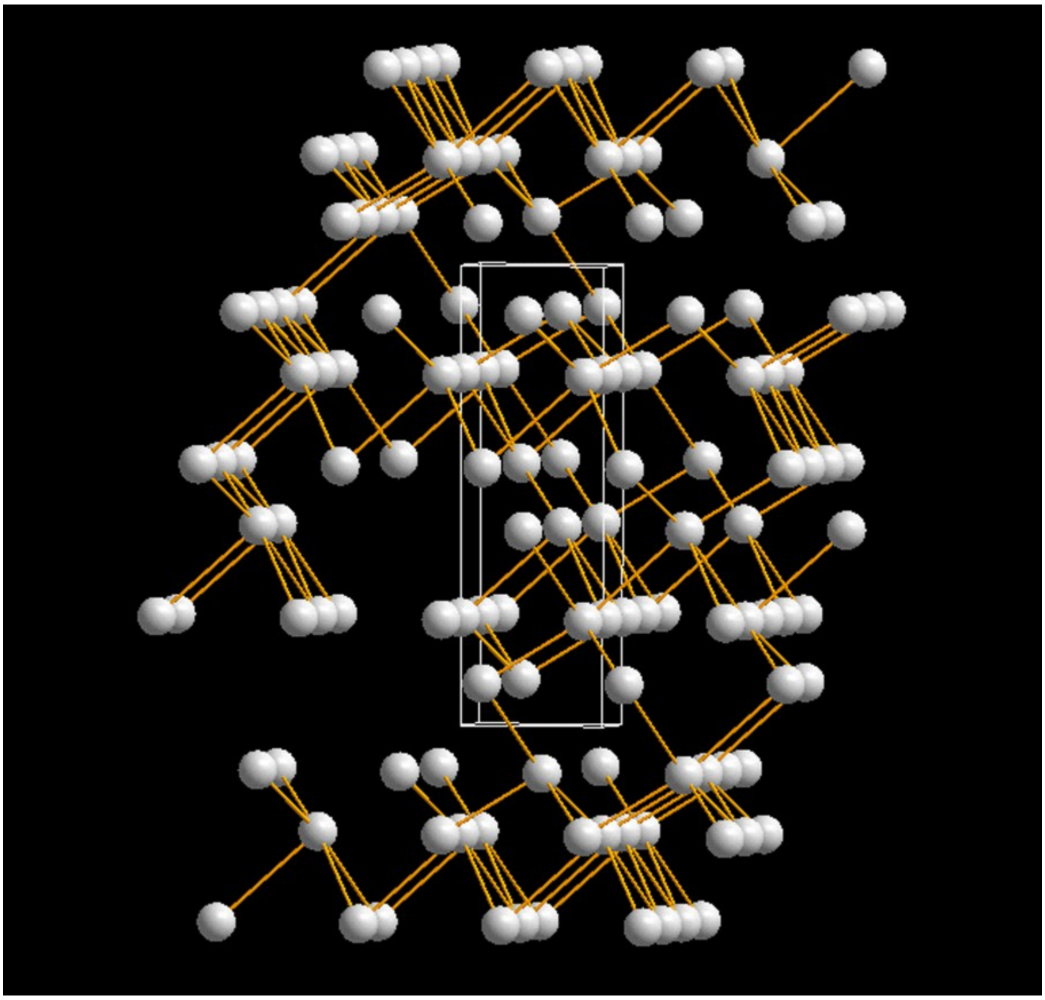

Fig. S4. Atomic arrangement in the Bi crystal. The lattice parameter values are given as follows: a=4.546 Å, b=4.546 Å, c=11.862 Å, α=90°，β=90°，γ=120°

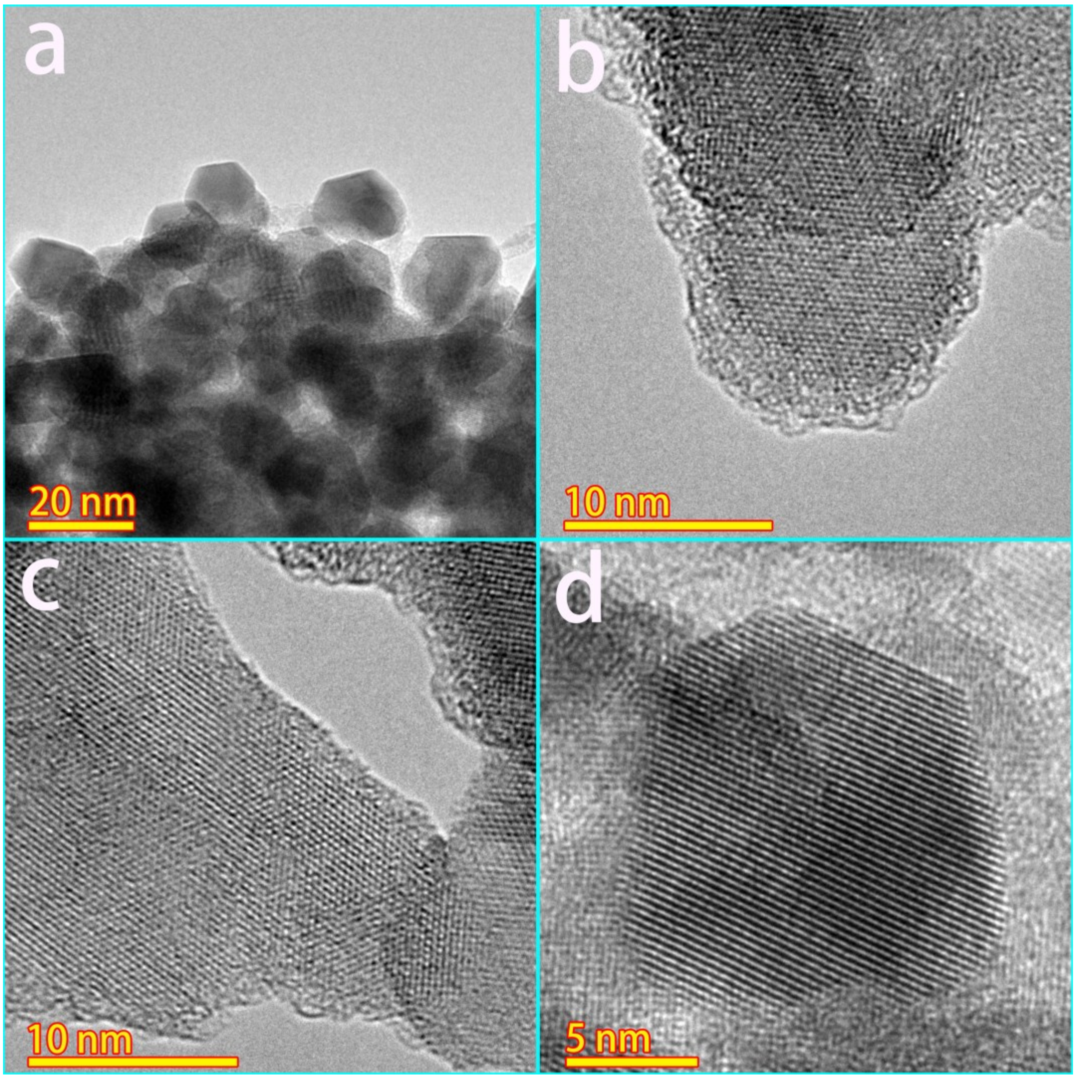

Fig. S5. TEM image (a) and HRTEM images (b-d) of arrayed Bi nanorod bundles.

Fig. S6 SEM image of commercial Bi nanoparticles (No. B109175-5g, Purity≥99.9%, Aladdin Industrial Co., Ltd.)

Table S1 electrochemical performance comparison of the as-prepared arrayed Bi nanorod bundles with some previously reported SIB anodes.

Materials	Current density ($A\ g^{-1}$)	Discharge capacity ($mAh\ g^{-1}$)		Rate capability, $mAh\ g^{-1}$ (Current density, $A\ g^{-1}$)
		2nd cycle	50th cycle	
CuVOH-NWs/CFs[3]	0.5	~399	~288	~207 (5)
FN-CNF[4]	0.05	~170	~140	~121 (2)
b-Mo-4Al[5]	0.2	~300	~230	~123.3 (1)
Ordered Ni-TiO_2 Nanoarrays[6]	0.05	~292	~218	~132 (1)
Bi@C microsphere[7]	0.1	~264.7	~130	~130.4 (1)
WS_2/graphene nanocomosite[8]	0.32	~300	~260	~140 (0.64)
Na 4,4′-stilbene-dicarboxylate[9]	0.05	~305	~200	~72 (10)
Arrayed Bi nanorod bundles	0.05	~358.3	~315	~159 (1)

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