Experimental Sections:

Synthesis

Polyacrylonitrile (1g, PAN, Mw = 1 300 000 g mol^{-1}) was melted in N, N-dimethyformatide (10 g, DMF) with ultrasonic stirring applied in drum wind drying oven at 60 °C for overnight. Then, a certain amount of bismuth (iii) citrate (1.90, 2.86, or 4.44 g, which correspond with 50 60, 70 wt. % of Bi in total mass of Bi and PAN) was added into the mixed solution and stirring continued for 12 h to acquire the homogeneous precursor solution for electrospun (Figure S1b). During electrospun (Figure 1b), the suspension was transferred to a plastic syringe and extruded through stainless steel needle with a flow rate of 0.8 mL h^{-1} at 20 kV. The electrospinning fiber webs gathered on a roller covered by aluminum foil. The rotation speed was 1000 rpm, and keep 15 cm from the needle to the roller. Finally, the electrospun PAN/ bismuth (iii) citrate fiber webs were heated at 600 °C (heating rate of 3 °C min^{-1}) for 2 h in nitrogen atmosphere. According to the content of bismuth (iii) citrate in the precursor solutions, the as-prepared samples with 50, 60 and 70 wt % denoted as Bi/CNFs-1, Bi/CNFs-2, and Bi/CNFs-3.

Material characterization

Morphologies and composition of samples were detected and evaluated by a wide angle X-ray diffraction (WAXD, D8 Advance, Brucker, Cu Kα, λ=0.154 nm), field emission scanning electron microscope(FE-SEM, Supra55, Carl Zeiss), high resolution transmission electron microscope (HRTEM, JEM-3010, JEOL), X-ray photoelectron spectrometer (XPS, EscaLab 250, Thermo Fisher Scientific). TGA instrument (TA-Q50, America) at a heating rate of 10 ^{o}C min^{-1} from 25 to 900 ^{o}C in air to measure the amounts of components. The Raman spectrum performed via a Renishaw system (Ar laser, wavelength: 633 nm, RM2000).

Electrochemical characterization

The electrochemical test was measured through CR2025 cell. Bi/CNFs fiber webs were punched into circular electrodes (12 mm diameter). For lithium ion battery, the counter electrode is lithium metal. Celgard 2300 membrane was used as the separator and electrolyte is 1 M LiPF6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v). The batteries were assembled in argon-filled glove-box (OMNI-LAB). For sodium ion battery, the counter electrode is sodium metal. Whatman glass fiber membrane (GF/D) was served as separator and electrolyte is 1 M NaPF6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 v/v). The batteries were assembled in argon-filled glove-box (OMNI-LAB). The cycle performance of the battery was estimated though a LANDCT2001A system. Cyclic voltammetry (CV) measurements were used an Autolab PGSTAT 302 N (Metrohm) workstation with scan rate of 0.1 mV s^{-1} between 0.005 and 3V (LIBs) or between0.01 and 2V (SIBs). Electrochemical impedance spectra (EIS) measurement data were obtained using the same electrochemical workstation with 10 mV and frequency between 10 kHz and 0.1 Hz.

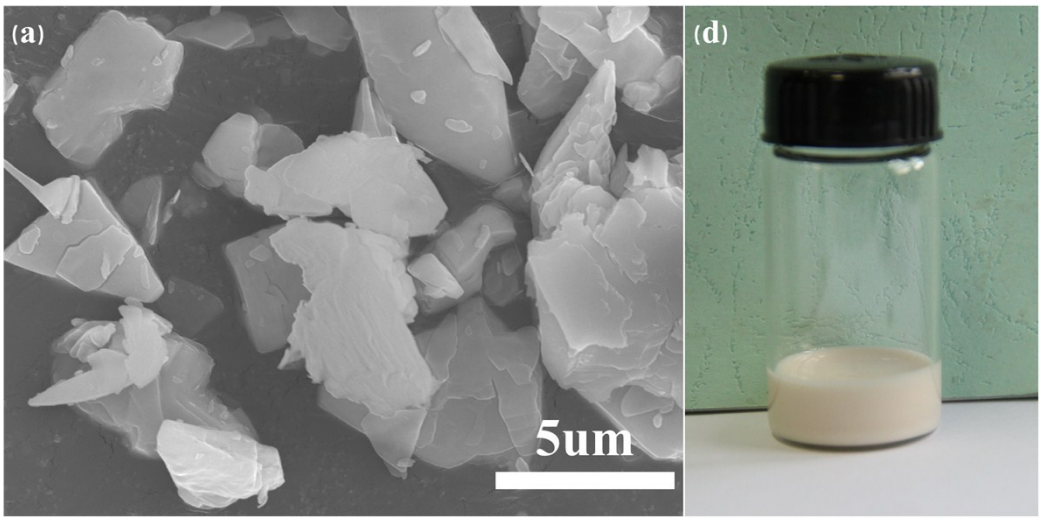

Fig. S1(a) SEM image of commercial bismuth (iii) citrate, (b) precursor solutions of Bi/CNFs-1.

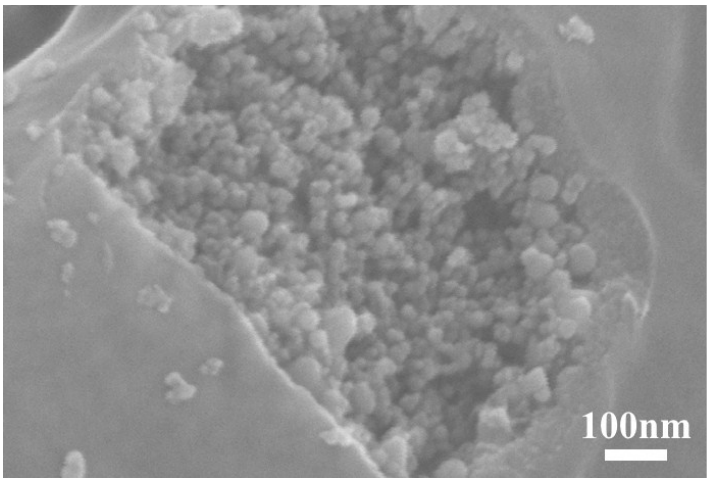

Fig. S2 SEM image of the crack for Bi/CNFs-1.

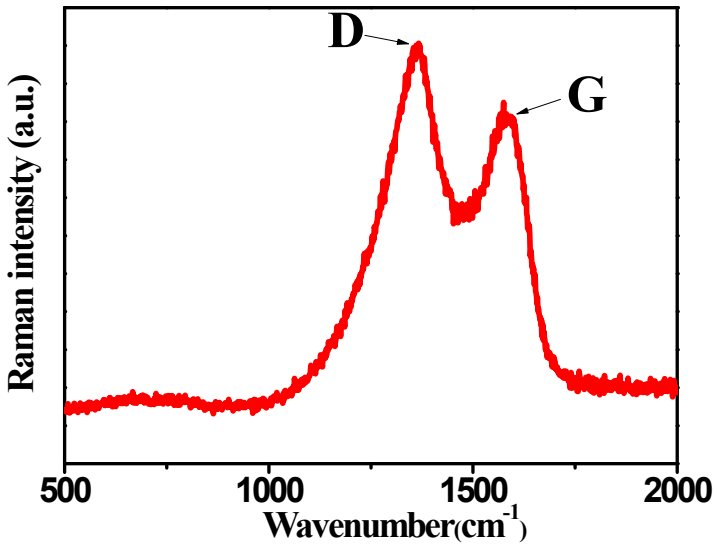

Fig. S3 Raman spectra for Bi/CNFs-1.

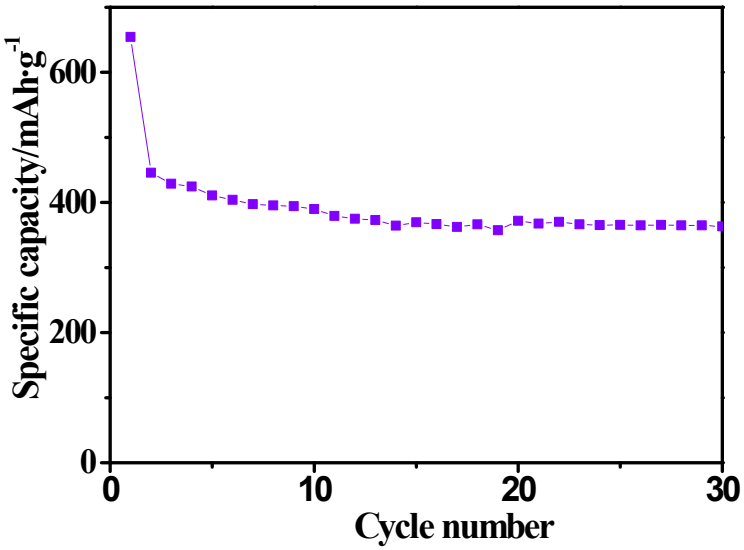

Fig. S4 Cycle performance of Bi/CNFs (the theoretical calculation 40 wt. % of elementary Bi in total of elementary Bi and PAN) at a current density of 100 mA g^{-1} for LIBs.

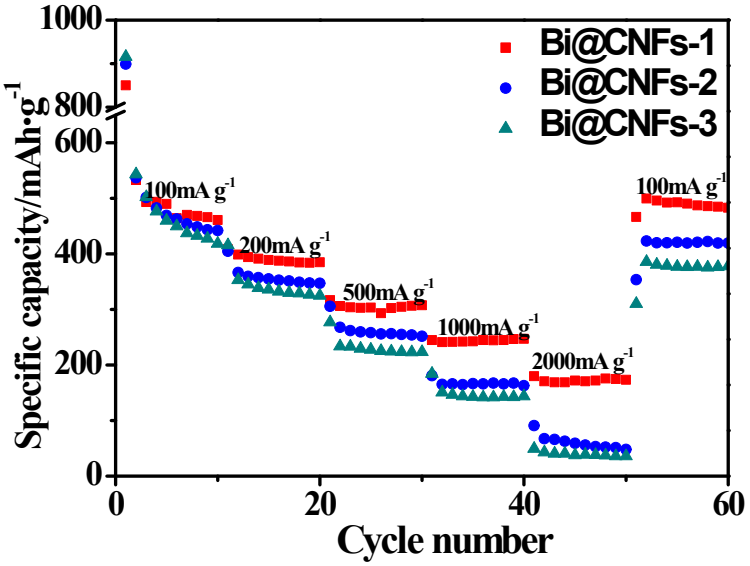

Fig. S5 Rate performances of the Bi/CNFs-1, Bi/CNFs-2 and Bi/CNFs-3 for LIBs at various current densities.

Table S1 Comparison of our Bi@CNFs-1 with other Bi materials reported by previous related works for LIBs and SIBs

	Materials	Current density (mA g^{-1})	Cycle numbers	Capacity (m Ah g^{-1})	Reference
LIBs	Bi@C microspheres	100	100	290	[29]
	Bi@C core–shell nanowires	100	100	408	[28]
	Bi/Al2O3/C composites	100	100	310	[16]
	N-doped graphene/Bi nanocomposite	50	10	390	[30]
	Bi@CNFs	**100**	200	483.8	**This work**
SIBs	Bi@C microspheres	100	100	123.5	[29]
	bismuth nanorod bundle	50	100	319	[32]
	Bi@graphene nanocomposite	40	50	198	[31]
	Bi-NS@C	200	2000	106	[26]
	Bi@CNFs	**50**	100	186	**This work**

Table S2 Data for Bi@CNFs anode cycled at 100 mA g^{-1} (for LIBs) and 50 mA g^{-1}(for SIBs).

	Item	Capacity (mAh g^{-1})	Areal loading (mg cm^{-2})	Thickness (μm)	Areal capacity (m Ah cm^{-2})	Volumetric capacity (m Ah cm^{-3})
LIBs	Bi@CNFs-1	483.8	2.26	72	1.093	151.8
	Bi@CNFs-2	421.3	3.05	92	1.285	139.7
	Bi@CNFs-3	400	4.73	138	1.892	137.1
SIBs	Bi@CNFs-1	186	2.26	72	0.42	58.3

Calculation method (take Bi@CNFs-1 as an example):

The thickness of the Bi@CNFs-1 was estimated by thickness gauge to be ~0.072 mm, mass loading of electrode is 2.26 mg cm^{-2}

The mass density of the Bi@CNFs-1 electrode is calculated:

$$\rho = m\ (mg)/v\ (cm^3) = 2.26\ mg\ cm^{-2} / 72\ \mu m = 0.3139\ g\ cm^{-3}$$

Therefore, the volumetric capacity (C_v) is calculated:

$$C_v = C_g \times \rho = 483.8\ mA\ h\ g^{-1} \times 0.3139 g\ cm^{-3} = 151.8\ mA\ h\ cm^{-3}\ (200th\ cycles)$$

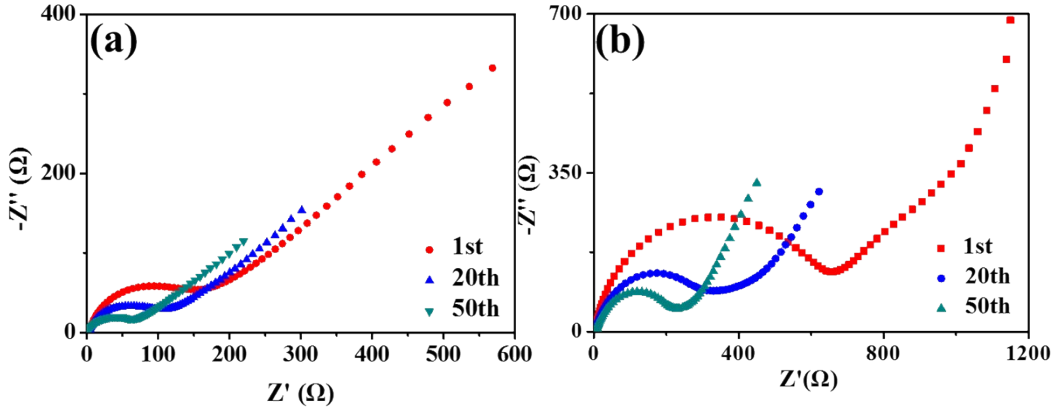

Fig. S6 Electrochemical impedance spectroscopy plots of Bi@CNFs-1 after different cycles for LIBs (a) and SIBs (b).