Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Self-Standing Bi_2O_3 Nanoparticles/Carbon Nanofiber Composite Film as a Binder-Free Anode for Flexible Sodium Ion Batteries

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The carbon nanofibers are prepared by paralyzing the PAN fibers at 700 ℃ for 6h in Ar.

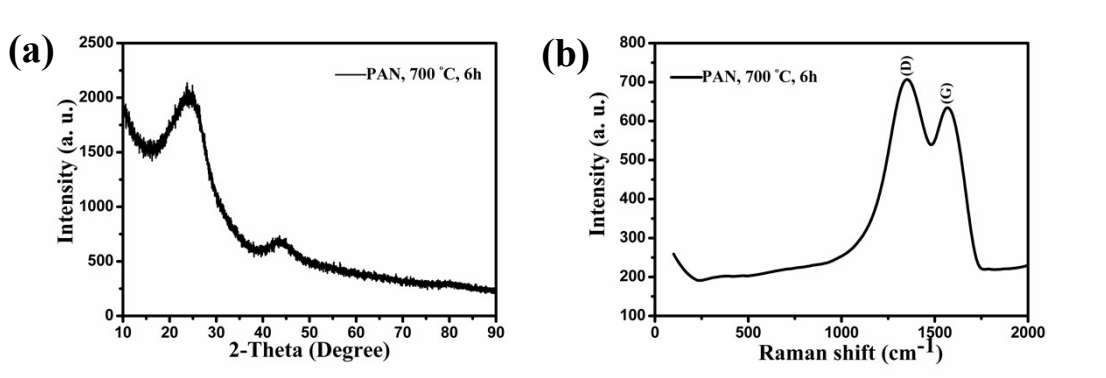


Fig. S1 (a) XRD patterns of the carbon nanofibers. (b) Raman spectra of the carbon nanofibers.

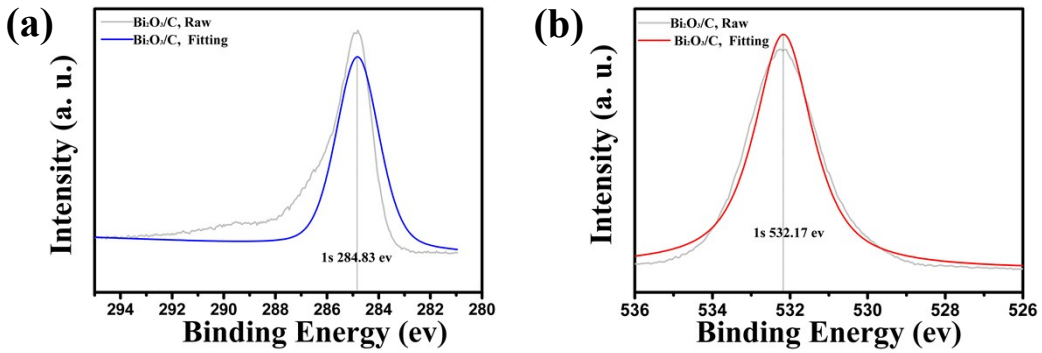


Fig. S2 (a) and (b) XPS spectra of carbon and oxygen for Bi_2O_3/C, respectively.

The Bi_2O_3/C (Bare) was prepared by pyrolyzed the PAN/$Bi(NO_3)_3$ precursor at 700 ℃ for 6 h in Ar and then oxidation at 350 ℃ for 3 h in Air. The Bi_2O_3 nanoparticles stick on the surface of carbon nanofibers and few nanoparticles embed in the carbon nanofibers (**Figure S3 a, b**).

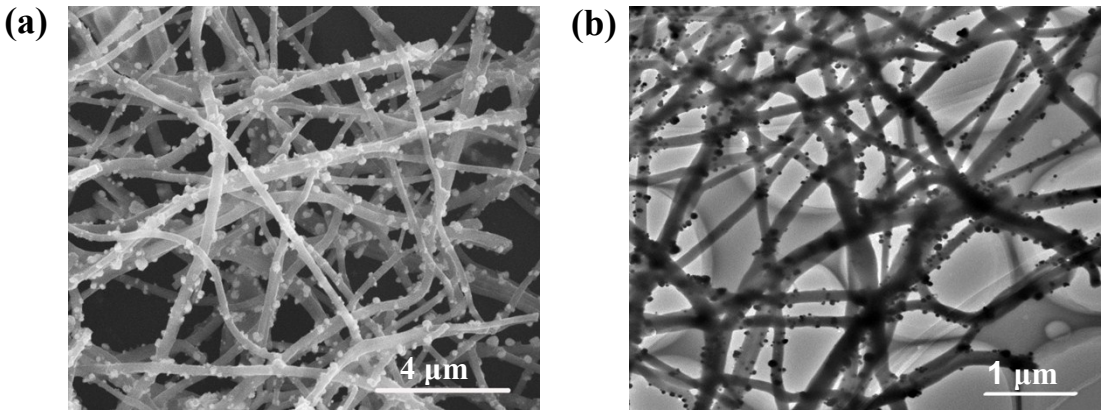


Fig. S3 (a) and (b), SEM and TEM images of Bi_2O_3/C (Bare).

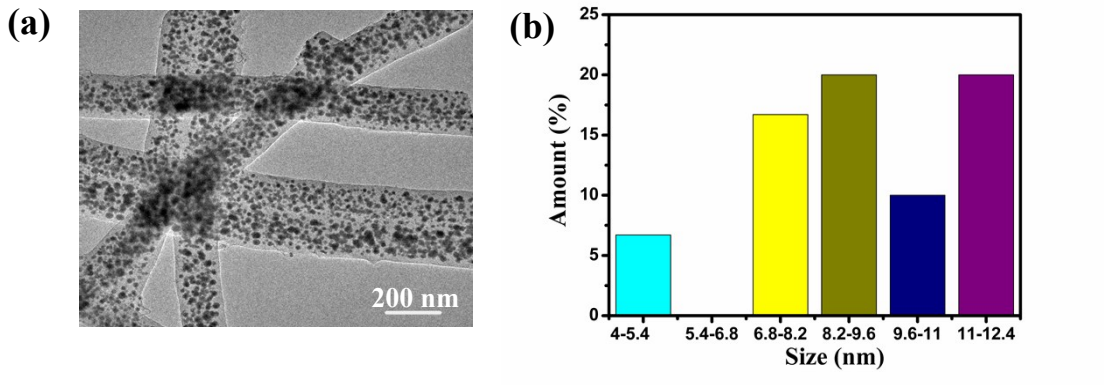


Fig. S4 (a) TEM image of Bi_2O_3/C. (b) The size distribution of Bi_2O_3 in carbon nanofibers.

The Bi nanoparticles embedded in carbon nanofibers is about 18 wt% by the TGA-DSC curves (**Fig. S5** a). The Bi_2O_3 nanoparticles embedded in carbon nanofibers is about 48 wt% by the TGA-DSC curves (**Fig. S5** b).

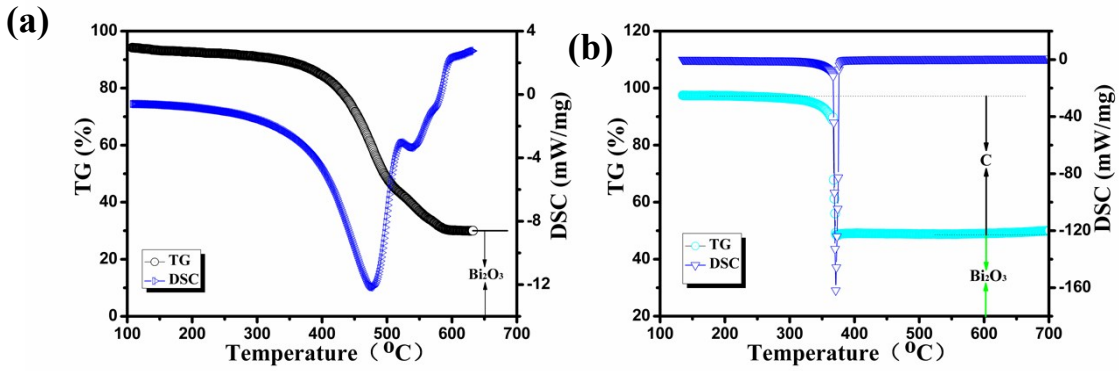


Fig. S5 (a) TGA-DSC curves of Bi/C in air. (b) TGA-DSC curves of Bi_2O_3/C in air.

The Bi_2O_3 nanoparticles content vs. different concentration in precursor solution ($BiCl_3$, PAN and DMF).

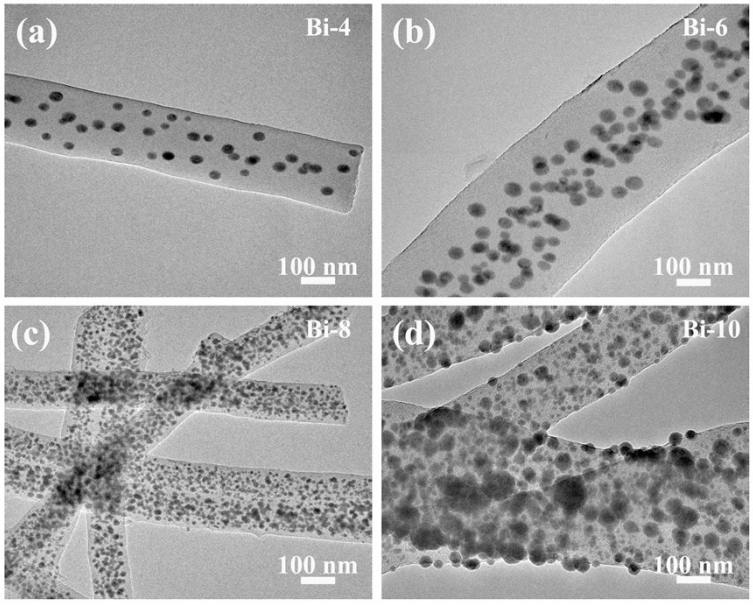


Fig. S6 TEM images of Bi_2O_3/C nanofibers at $BiCl_3$ feed concentration of (a), Bi-4, (b) Bi-6, (c) Bi-8 and (d) Bi-10.

Table S1 Bi_2O_3 nanoparticles content vs. different **$BiCl_3$** concentration.

$BiCl_3$ concentration	4 %	6 %	8 %	10 %
Bi_2O_3 nanoparticles content	20 wt%	35 wt%	48 wt%	59 wt%

The Bi_2O_3/C (Bare) was prepared by paralyzing the PAN/$Bi(NO_3)_3$ precursor at 700 ℃ for 6h in Ar and then oxidation at 500 ℃ for 3h in Air. The length of the as-prepared Bi_2O_3/C (Bare) is short (about 10 μm) and could not form a bind-free and flexible film (**Fig. S7** a). The size of the Bi_2O_3 is also exceeding 100 nm (**Fig. S7** b).

For the preparation of anode sheets, a slurry was formed by mixing the active material (80 wt%), acetylene black (10 wt%) and binder (10 wt% polyvinylidene fluoride, PVDF, dissolved in *N*-methyl-2-pyrrolidone, NMP). Then the slurry was coated onto a copper foil current collector. The electrodes were dried under vacuum at 120 ℃ for 12 h and then punched and weighed. The mass loading of the electrode is about 2.98 mg/cm^2 and the area of electrode is 0.50 cm^2. The batteries were assembled in a glove box under a high purity argon atmosphere. 1 M $NaPF_6$ in a mixture of ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 by volume) with 5% fluoroethylene carbonate (FEC) as the electrolyte, and Celgard®3501 (Celgard, LLC Corp., USA) as the separator.

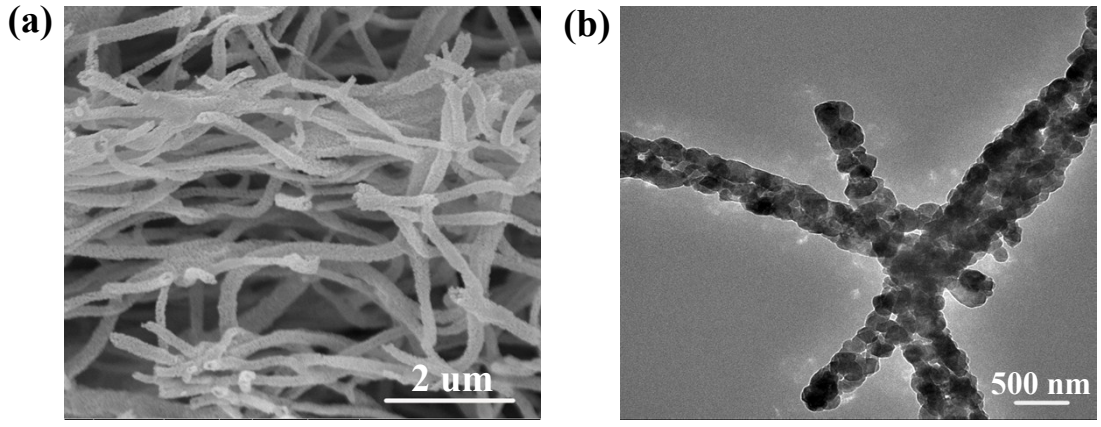
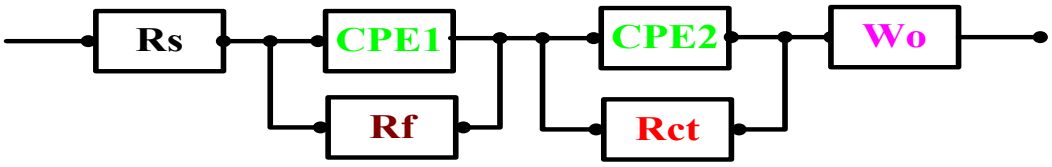


Fig. S7 (a) and (b), SEM and TEM images of Bi_2O_3/C (Macroparticle).

Depiction 1



Where *Rs* is the solution resistance of the bulk electrolyte, *CPE* is Constant Phase Element, *Rf* is Na-ion migration resistance, *Rct* is charge transfer resistance, *Wo-R* is Warburg Open Circuit Terminus impedance, *Wo-T* is Open Circuit Terminus T parameter values, *Wo-P* is Open Circuit Terminus P parameter values.

Depiction 2 Electric conductivity & sodium ion diffusion coefficient at open circuit state,

$$D = R^2T^2/2A^2n^4F^4C^2\sigma^2 \cdots\cdots (1) \qquad Z_{Re} = K + \sigma\omega^{-1/2} \cdots\cdots (2)$$

where *D* is the diffusion coefficient ($cm^2\ s^{-1}$), *R* is the gas constant (8.31 J $mol^{-1}\ K^{-1}$), *T* is the absolute temperature (298 K), *A* is the surface area of the cathode (0.5 cm^2), *n* is the number of electrons transferred in the half-reaction for the redox couple, *F* is the Faraday constant (96485 C mol^{-1}), *C* is the is the molar concentration of Na-ions in Bi_2O_3/C, *K* is a constant, ω is frequency, and σ is the Warburg factor which corresponds to the slope of the curve shown in **Fig. 3**b.

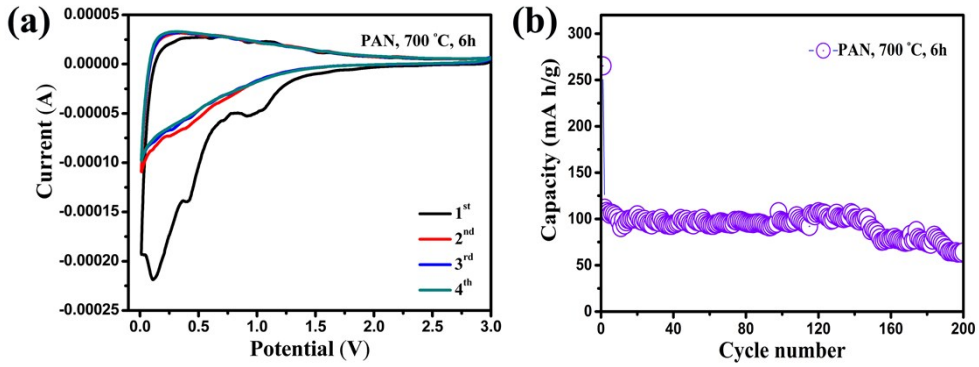


Fig. S8 (a) CV curves of CNF anodes from 0.01 V to 3 V at a scan rate of 0.1 mV s^{-1}.

(b) cycling performance of CNFs at a cycling rate of 100 mA g^{-1}.

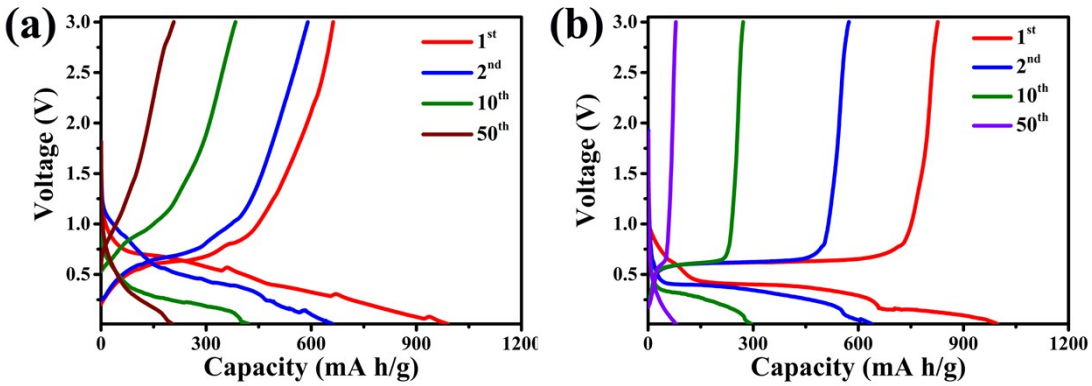


Fig. S9 The charge and discharge voltage profiles of Bi_2O_3/C (Bare) and Bi_2O_3 (Macroparticle).