Supporting information

Galvanic Replacement Preparation of Spindle-Structured Sb@C@NC as Anode for Superior Lithium-Ion Storage

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Experimental section

1. Synthesis of uniform Fe@C@NC precursors

First, fumaric acid ($C_2H_4O_4$, 0.672 g) and $Fe(NO_3)_3 \cdot 9H_2O$ (2.56 g) were dissolved in N,N-dimethylformamide (DMF, 128 mL) at room temperature with stirring for 3 hours, and then the mixture was placed in 200 mL reactor and treated at 110°C for 1 h. After cooling to room temperature, the brown product Fe-MOFs were collected by centrifuging and washing three times with ethanol. After drying, Fe-MOFs (0.5 g) were uniformly dispersed in a methanol solution (300 mL). Tris(hydroxymethyl)aminomethane was added to adjust the pH value to 8.5 and then adding dopamine (0.1 g) with stirring for another 20 hours. The products were collected by suction filtration and were completely dried in a blast drying oven. After that, the sample was transferred to an Al_2O_3 boat and placed in a tube furnace treated at 600°C for 2 hours under the atmosphere of H_2/Ar with a heating rate of 5 °C min^{-1} to attain the Fe@C@NC.

2. Synthesis of spindle-structured Sb@C@NC

After the Fe@C@NC precursor was prepared, the final product Sb@C@NC was obtained by a simple method of galvanic replacement. The prepared Fe@C@NC (0.5 g) precursor and $SbCl_3$ (4 g) were dispersed in 70 mL of ethanol sonicating for 10 minutes. Then, the mixture solution was poured into a 100 mL PTFE tank. The stainless steel reactor was placed in a blast drying oven at 100 °C for 24 hours. After cooling to room temperature, the samples were collected by centrifugation and washed with ethanol three times. The product was dried at 80°C for 24 hours to obtain the robust

spindle-structured Sb@C@NC.

3. Material characterization

The X-ray diffraction (XRD) characterization was used to analyze the material structure using an Empyrean X-ray diffractometer from PANalytical B. V., the Netherlands. The scan angle is 10~90° and the scan rate is 2° min^{-1}. The powder microstructure was characterized by a scanning electron microscope (SEM, Zeiss Spura 40/VP, Carl Zeiss AG, Germany) and transmission electron microscope (TEM, JEOL JEM-2100F, Japan Electronics Co., Ltd.). Quantitative analysis of the relative content of carbon in the material by the thermogravimetric analyzer (TGA, TG 209 F3 Tarus, NETZSCH (Shanghai) Machinery Instrument Co., Ltd.). The Raman spectrum results were obtained by Renishaw Invia Raman microscope, England.

4. Electrochemical measurements

The electrode was prepared with 80 wt% active material, 10 wt% carbon black (Super P), and 10 wt% polymer binder (polyvinylidene fluoride, PVDF), which were mixed in N-Methylpyrrolidone (NMP) solution and then dried under vacuum at 80℃ for 12 hours on the surface of copper foil. After that, the electrodes coated on cooper foil were cut into 12mm diameter round pieces with a material loading of 1.0mg cm^{-2}. The electrochemical performance of the Sb@C@NC for lithium-ion batteries was tested by assembling the CR2016 coin cells in an argon atmosphere at room temperature (argon-filled glovebox, 25 ℃). And the electrolyte consisted of 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) and the lithium foil was used as the counter electrode. At the same time, the electrochemical of the

Sb@C@NC anode for sodium-ion batteries (SIBs) was tested by assembling the CR2032 coin cells. And the electrolyte consisted of NaClO$_4$ (1M) in propylene carbonate (PC) with a 5 vol% addition of FEC and the sodium foil was used as the counter electrode. Cyclic voltammetry (CV) measurements were tested by Gamry electrochemical workstation with scan rates of 0.1, 0.2, 0.4, 0.7, 1.0, and 1.5 mV s^{-1} in a voltage range of 0.01~2.0 V. The galvanostatic charge/discharge experiments were tested on the LAND-CT2001A battery-testing system in the voltage range of 0.01 0.01~2.0 V.

5. Pseudocapactive calculation

In addition, the total current contribution could be divided into the diffusion-controlled contribution $(k_1v^{1/2})$ and the pseudocapacitive contribution (k_2v), which is according to the following equation [1, 2]:
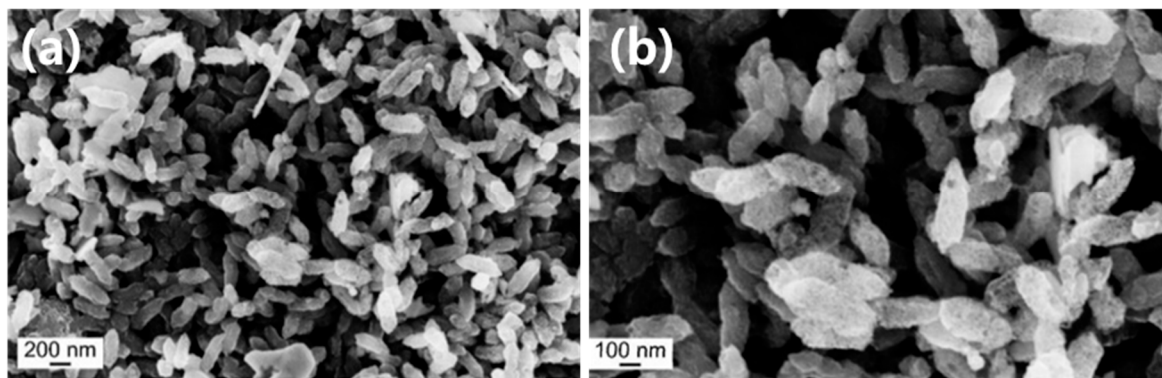
$$i(V) = k_1v^{1/2} + k_2v \tag{1}$$

At the same time, equation (1) could be described as:
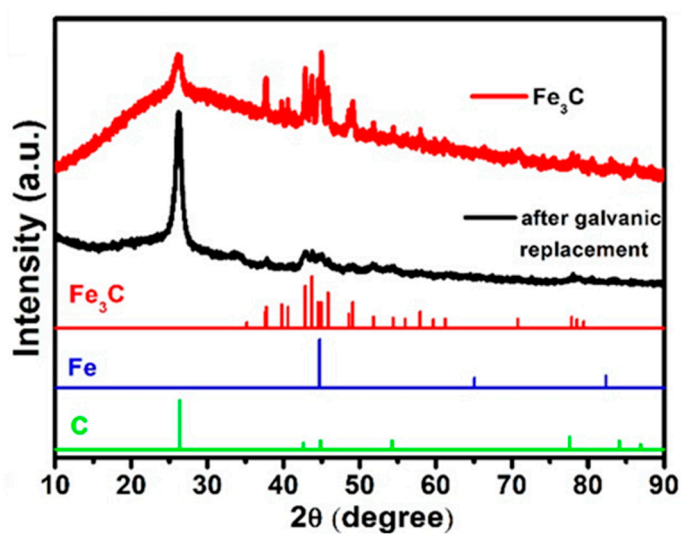
$$i(V)/v^{1/2} = k_1 + k_2v^{1/2} \tag{2}$$

After fitting linear $i(V)/v^{1/2}$ vs. $v^{1/2}$, k_1 and k_2 can be facilely achieved. If we have the value of k_1 and k_2, the $k_1v^{1/2}$ and k_2v will be facilely calculated by equation (1).
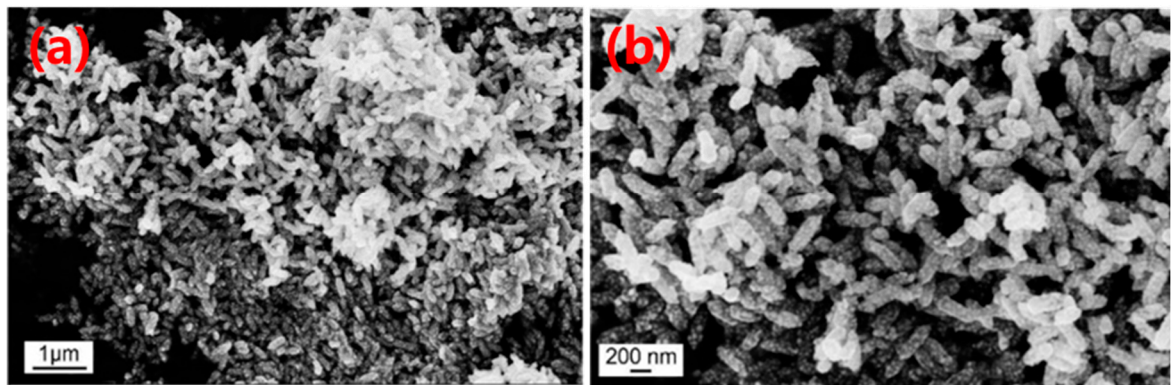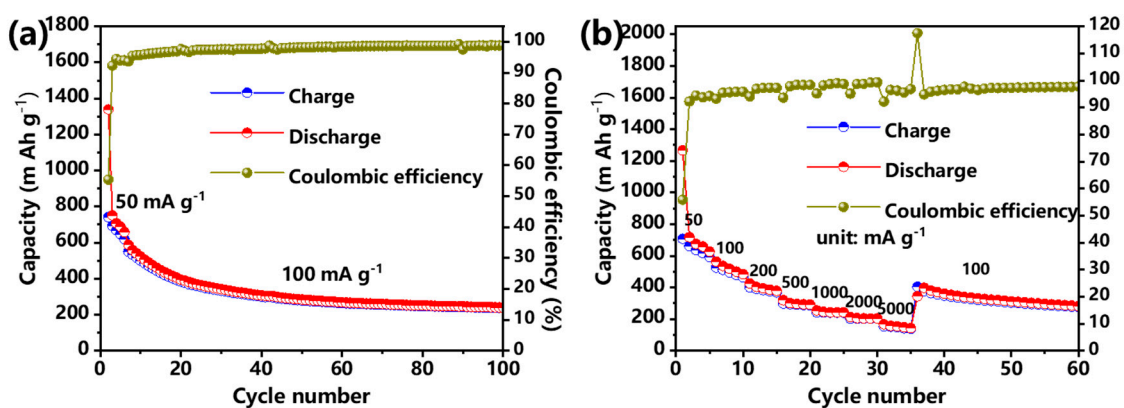

Figure S1. Low-magnification (a) and high-magnification (b) SEM images of Fe@C.

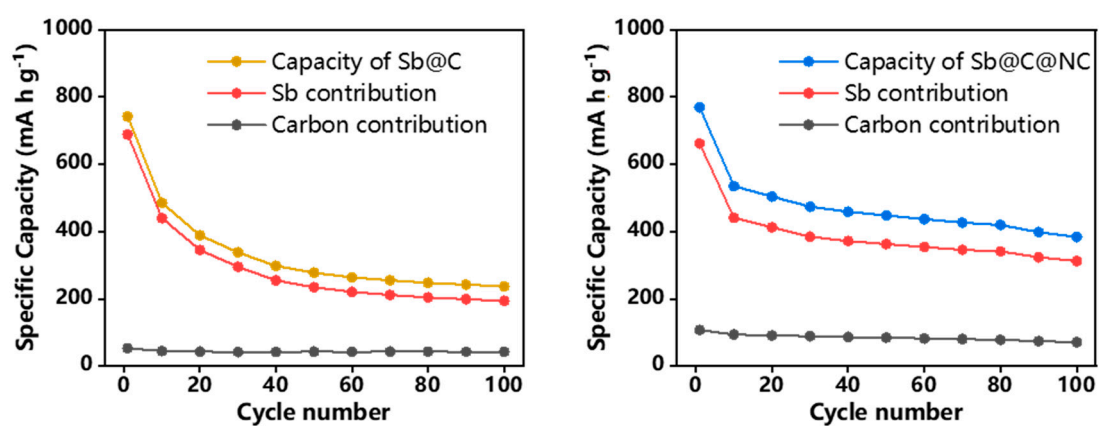**Figure S2.** Low-magnification (a) and high-magnification (b) SEM images of Sb@C.

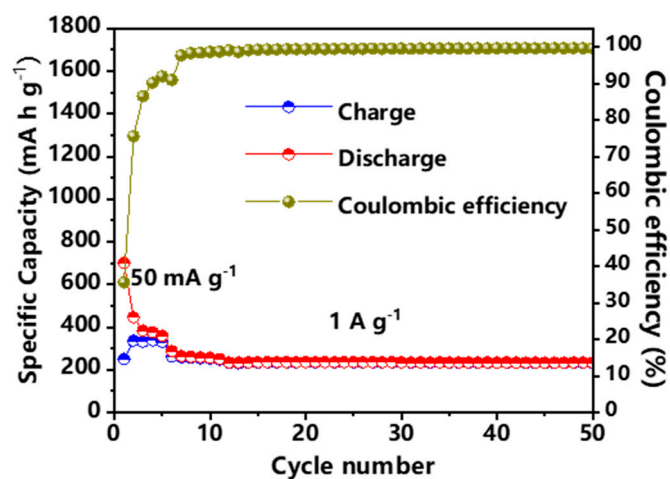**Figure S3.** XRD pattern of Fe₃C and Fe₃C with galvanic replacement

Figure S4. (a) Cyclic performance of Sb@C at 100 mA g^{-1}. (b) The rate capability of
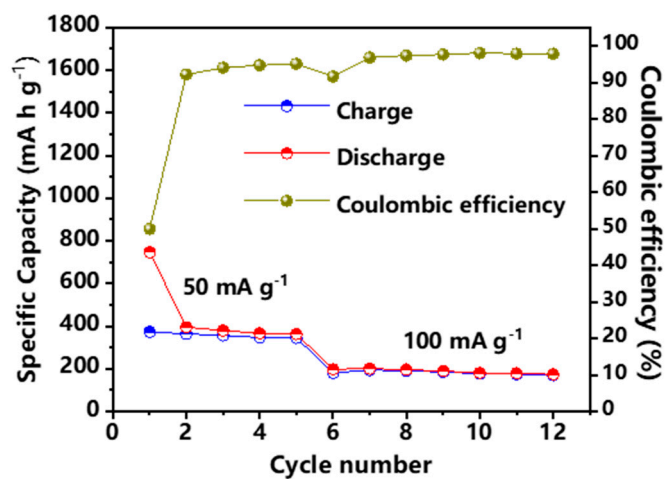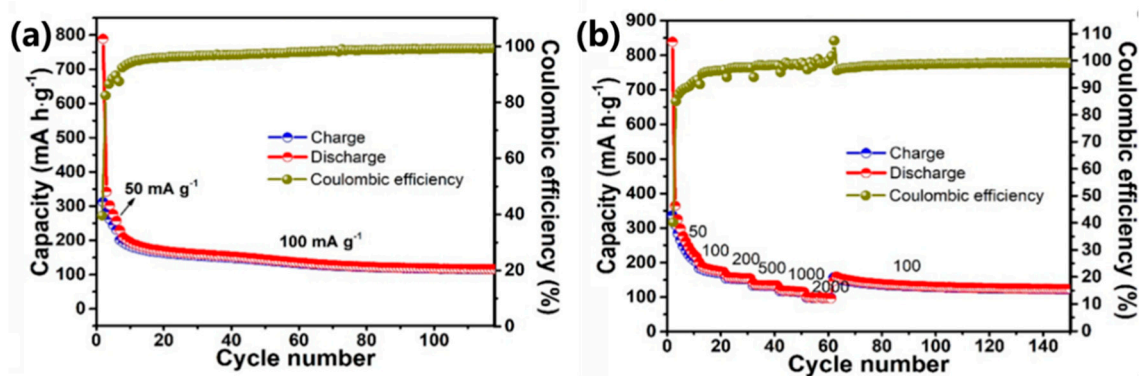
Sb@C.

Figure S5. (a) The carbon and Sb contribution of specific capacity of Sb@C and
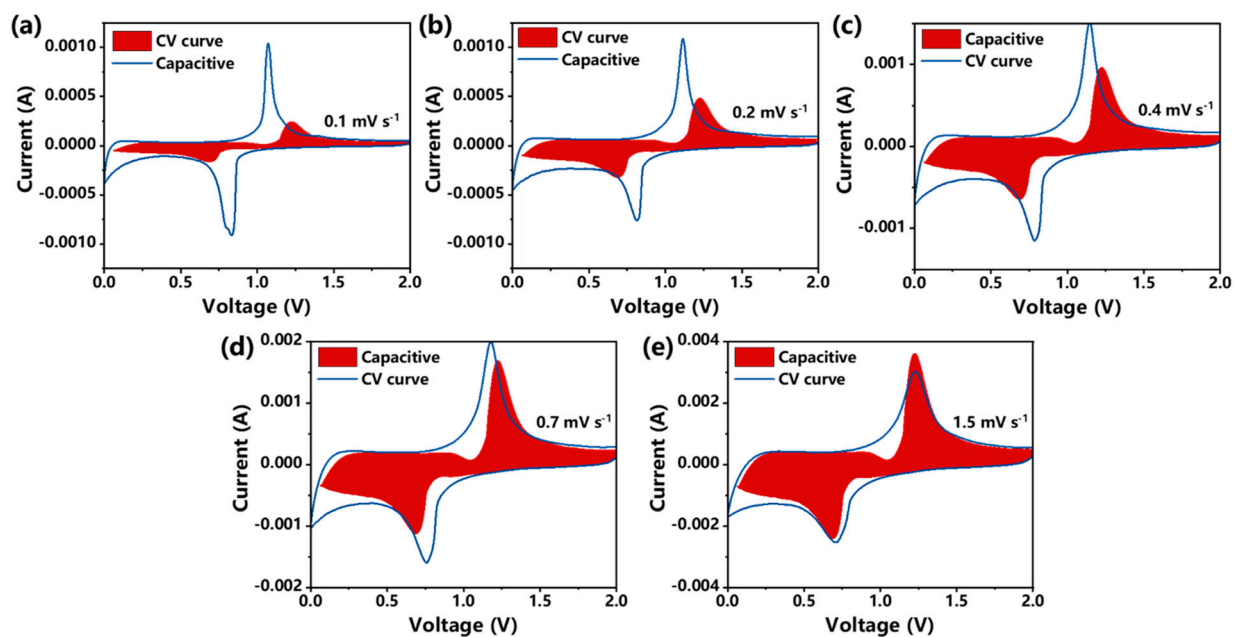
Sb@C@NC composites.

Figure S6. Cyclic performance of Sb@C@NC anodes with a high loading of 3.2 mg

cm^{-2} at 1 A g^{-1}.

Figure S7. Cyclic performance of Sb@C at 100 mA g^{-1} for SIBs.

Figure S8. (a) Cyclic performance of Sb@C@NC at 100 mA g^{-1} for SIBs. (b) The

rate capability of Sb@C@NC for SIBs.

Figure S9. The capacitive capacity contribution to the total current contribution at 0.1

mV s^{-1} (a), 0.2 mV s^{-1} (b), 0.4 mV s^{-1} (c), 0.7 mV s^{-1} (d), and 1.5 mV s^{-1} (e).

Table S1. Comparison of the rate performances of Sb@C@NC with various Sb-based anode materials

Materials	Morphology	Rate performances
Sb@C@NC composite (This work)	Robust spindle-structure	343 mA h g^{-1} (2000 mA g^{-1})
Sb–C composite[3]	Rod-like	369.7 mA h g-1 (500 mA g-1)
Sb/C composite[4]	Spherical	416 mA h g^{-1} (600 mA g^{-1})
Sb@C/expanded graphite composite[5]	Sandwich structure	274 mA h g^{-1} (2000 mA g^{-1})
Sb@C composite[6]	Spherical	336.8 mA h g^{-1} (500 mA g^{-1})
Sb-hard carbon composite[7]	Irregular	213 mA h g^{-1} (400 mA g^{-1})
Sb@C[8]	Rod-like	213 mA h g^{-1} (2000 mA g^{-1})
NiSb@C[9]	Nanosheets	305 mA h g^{-1} (2000 mA g^{-1})

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