Electronic Supplementary Information

Sn@Ni₃Sn₄ embedded in nanocable-like carbon hybrids for stable lithium-ion batteries

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**Experimental Section**

1.1 Synthesis of Sn@Ni<sub>3</sub>Sn<sub>4</sub>/C hybrids

1.1.1 FSP process

In a typical FSP experiment, 0.5 mol/L SnCl<sub>4</sub>·5H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (molar ratio 2:1) dissolved in pure ethanol (100 mL) were employed as precursor solution. The precursor solution was fed at 5 ml/min through a spray nozzle and dispersed by external 5 L/min O<sub>2</sub> forming fine spray with a diffuse pressure of 0.15 MPa. Then the spray was ignited and reacted in the flame high temperature zone. The combustion atmospheres were controlled by adjusting the flammable gas flow of 0.38 m<sup>3</sup>/h H<sub>2</sub> and the assisted-oxide gas flow of 1.5 m<sup>3</sup>/h Air. The fresh productions were collected by glass fibers filter (ADVTECH/GA55, Toyo Roshi Kaisha Ltd. Japan) in the downstream of FSP equipment with the aid of vacuum pump.

1.1.2 CVD process

In a typical CVD experiment, 0.2 g SnO<sub>2</sub>/NiO powders were put into furnace. The furnace temperature was heated to 650 °C for 2h with heating rate of 5 °C/min. The atmosphere was composed of 0.6 L/min 99.99% Ar and 30 mL/min C<sub>2</sub>H<sub>2</sub>. After cooling down to the room temperature, the final products were obtained.

1.2 Characterizations

The samples were characterized by Field emission scanning electron microscopy (FE-SEM: HITACHI S-4800) with energy dispersive X-ray spectroscopy (EDS), Transmission electron microscope (TEM: JEOL JEM-1400), High resolution Transmission electron microscope (HRTEM: JEOL JEM-2100), X-ray diffraction (XRD: D/max 2550V) and Thermogravimetric Analysis (TG: NETZSCH STA409PC). Nitrogen adsorption–desorption (ASAP 2010N) was determined by the Brunauer–Emmett–Teller (BET) method. X-ray photoelectron spectroscopy (XPS) experiments were carried out by Thermo Fisher (ESCALAB 25). The Raman spectrum (Raman) was characterized by Renishaw inVia/Reflex.

1.3 Electrochemical measurements

The working electrode was composed of active materials (Sn@Ni<sub>3</sub>Sn<sub>4</sub>/C hybrids), conductive material (acetylene black, AB) and binder (polyvinylidifluoride, PVDF) with a weight ratio of 80:10:10. The three components were stirred into slurry with assistance of N-methyl-2-pyrrolidone.
(NMP) and uniformly pasted on Cu foils (19 μm) with a controllable membrane thickness of 50 μm. Thin Li foils (φ16×1.2 mm) and polypropylene membrane (Celgard 2400) were employed as the counter electrode and separator, respectively. The electrolyte was 1 M LiPF₆ dissolved in ethylene carbonate/diethyl carbonate (EC-DEC, 1:1 w/w). The half-cells (CR2016 coin type) were employed and assembled in a high-purity argon filled glove box (Mikrouna Advanced Series) where moisture and oxygen levels were under 1 ppm. Cyclic voltammograms (CV) and electrochemical impedance spectroscopy (EIS) of the working electrode had been characterized by electrochemical workstation (Autolab PGSTAT302N). Galvanostatic cycle performance of coin cells were tested using on a LAND-CT2001C test system at several different current densities (from 100 mA h g⁻¹ to 2000 mA h g⁻¹) in the voltage range from 0.01 V to 2.5 V.

**Figure S1.** Schematic diagram of FSP route for preparation of SnO₂/NiO
Figure S2 (a) TEM and (b) HRTEM of SnO₂/NiO nanoparticles made by FSP (inset of S1a was particle size distribution)

Figure S3 XRD pattern of flame-made SnO₂/NiO
Figure S4. (a) EDS, (b) XPS, (c) TGA/DSC, (d) Raman, (e) BET, (f) Pore size distribution of Sn@Ni$_3$Sn$_4$/C hybrids

Selected area EDS affirmed that no trace of O was found, ensuring no existence of metal oxides (Fig. S4a). The X-ray photoelectron spectroscopy (XPS) spectrum of the Sn@Ni$_3$Sn$_4$/C hybrids was studied, further confirming the existence of Sn, Ni and C elements, and the valence of Sn and Ni was 0 (484.7 eV for 3d$^{5/2}$ of metal Sn, 852.2 eV for 2p$_{3/2}$ of metal Ni), which matched the metal state of Sn and intermetallic state of Ni$_3$Sn$_4$ (Fig. S4b). The carbon content of the as-prepared sample was calculated to be 44.0% by thermogravimetric analysis (TGA) (Fig. S4c). The Raman spectrum...
showed that $I(D)/I(G)$ was equal to 0.9, indicating that the nanocable carbon layers had many defects (Fig. S4d). Besides, adsorption–desorption isotherms were carried out and the BET surface area of the Sn@Ni$_3$Sn$_4$/C hybrids was 36.1 m$^2$ g$^{-1}$ with a bimodal pore size distribution of 3.8 nm and 9.1 nm (Fig. S4e and f).

Figure S5 TEM images of (a) Sn@C nanowires catalyzed by SnO$_2$, (b) Sn@Ni$_3$Sn$_4$/C hybrids catalyzed by sintered SnO$_2$/NiO, (c) Sn/C nanocomposites catalyzed by mixed of SnO$_2$ and NiO nanoparticles.

Figure S6 (a) TEM; (b) XRD (c) rate performance of contrast sample with Sn/Ni in 1:1 ratio.

Figure S7. Cycling performance of flame-made SnO$_2$/NiO nanoparticles in the current density of 0.2
Figure S8. Charge/discharge vs. voltage of Sn@Ni₃Sn₄/C hybrids electrode

The CV curve of the cell after 800 cycles had been tested to identify the electrochemical process after cycling, as shown in Fig. S9. Two separated broad peaks around 0.4–0.7 V and 1.1–1.3 V were ascribed to the characteristic peaks of deintercalation of LiₓSn and LiₓC, respectively, revealing that the capacity was still attributed to Sn and the carbon layer.