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**A Novel Tin Hybrid Nano-Composite with Double Nets of Carbon Matrixes as a Stable Anode in Lithium Ion Batteries**

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Experimental Section

Synthesis of SnO$_2$/C precursors: The SnO$_2$/C microspheres were prepared using a hydrothermal method. Typically, 20 mmol of SnCl$_4$·5H$_2$O and 20 mmol of fructose (Sinopharm Chemical Reagent Co., Ltd) were dissolved in 60 mL deionized Millipore water. The mixture was stirred and ultrasonicated until a transparent solution was obtained. Subsequently, the solution was transferred to a Teflon-lined stainless steel autoclave with a capacity of 100 mL, and heated at 170 °C for 12 h. After cooling down to room temperature, the SnO$_2$/C precursors were washed with ethanol and de-ionized water followed by drying in a vacuum oven at 60 °C for 5 h.

Preparation of GO sheets: GO sheets were prepared using a modified Hummer's method. Firstly, 5.0 g of graphite powders (Nanjing Geruifa Carbon Material Co., Ltd.) were mixed with 3.75 g of NaNO$_3$ (Sinopharm Chemical Reagent Co., Ltd). Subsequently, 150 mL of concentrated H$_2$SO$_4$ was slowly added into the solution under the mechanical stirring. Afterwards 20.0 g of KMnO$_4$ (Sinopharm Chemical Reagent Co., Ltd) was slowly added within 0.5 h. After stirring for 20 h, the mixture was stored for 5 days. Then 30 mL of H$_2$O$_2$ (30%, Sinopharm Chemical Reagent Co., Ltd) was injected into the mixture, which leads to the color change from puce to brilliant yellow. The mixture was then centrifuged, rinsed, and dialyzed over 5 days using de-ionized water to remove metal ions and acid, thus finally forming the GO sheets.

D-net Sn composite synthesis: A hydrothermal method and a thermally reducing treatment were conducted for the synthesis of D-net Sn composites. In a typical experiment, 30 mg of GO sheets, 270 mg of SnO$_2$/C precursor, and 10 mL of oxalic acid (Sinopharm Chemical Reagent Co., Ltd) were uniformly dispersed into 4 mL of de-ionized water. Then the solution was transferred to a 10 mL glass beaker. Thereafter, the beaker was placed in a Teflon-lined stainless steel autoclave with a capacity of 100 mL and heated at 140 °C for 3 h. When it cooled down to room temperature, the columnar product was collected, and rinsed with ethanol and de-ionized water followed by freeze-drying. Finally, the freeze-dried samples were reduced in Ar/H$_2$ (5 vol.% H$_2$) gas at 550 °C (a ramp rate of 5 °C min$^{-1}$) for 4 h.
**Characterization:** The morphology and structure were characterized using SEM (FEI Corporation, QUANTA 200FEG), high-resolution TEM (JEOL 2010 LaB₆) equipped with an Oxford INCA energy dispersive X-ray analyzer operating at 200 kV, and XRD with Cu Kα radiation (1.5418 Å) (X’Pert Pro, PANalytical). Raman spectra were recorded on a laser confocal Raman spectrometer (Horiba Jobin Yvon, LabRAM HR800). XPS (Thermo-VG Scientific, ESCALAB 250) was used for identifying the chemical composition. The component weight ratio was measured using TGA (Perkin-Elmer, Pyris 1) at a ramp rate of 10 °C min⁻¹ in air. The thickness of the GO sheet was performed on a Atomic Force Microscope (AFM, Veeco MultiMode V).

**DFT-based first principle modeling:** The geometry optimization, DOS, and electron density of pure Sn and Sn@C were investigated using DFT calculations performed on a DMol3 package. All the calculations were carried out using Perdew-Bruke-Frnzerhof exchange-correlation functions in the framework of general gradient approximation with all the atoms fully relaxed. All the structures were calculated without symmetry constraints or spin polarizations. Double numerical basis sets with polarization functions were performed to describe the valence orbitals of all the atoms. A thermal broadening of 0.05 eV to the band occupations was applied. The convergence criteria applied for the geometry optimizations were 1.0×10⁻⁵ au, 2.0×10⁻³ au Å⁻¹, and 5.0×10⁻³ Å for energy change, maximum force, and maximum displacement, respectively. *K* point was set to 6×6×6 and 6×6×1 for bulk Sn and the Sn (100) surfaces, respectively. The orbital cutoff was 4.9 Å. The threshold for self-consistent field density convergence was set to 1.0×10⁻⁶ eV. The PDOS was obtained with a *K*-point of 3×4×2.

**In-situ TEM observations:** For the in-situ TEM, a nanoscale battery system in which the D-net Sn composite as working electrode was checked. A Li foil with a thin Li₂O layer on the surface was used as a solid electrolyte instead of an ionic liquid to minimize the wetting problems. First, a Li₂O-coated Li flake was connected to a tungsten wire as the counter electrode. Subsequently, the composites were attached to the tip of an aluminum wire using conductive
silver epoxy as the working electrode. The two electrodes were installed on a Nanofactory STM-TEM \textit{in-situ} holder. The \textit{in-situ} observations were performed on an aberration-corrected FEI Titan S 80-300 TEM/STEM equipped with a Gatan Image Filter Quantum-865 operated at 300 kV. The composites were checked by performing potentiostatic discharge at different voltages ranging from 0 to 2.0 V versus the counter electrode. During the discharge process, TEM images and movies were recorded to monitor the morphology evolution of the composites.

\textbf{Electrochemical measurements:} The electrochemical performance was measured using a CR2032 coin cell system. The working electrode was fabricated by 70\% D-nets Sn composites, 20\% conductive carbon black (Super P), 9\% carboxymethyl cellulose binder (CMC) and 1\% styrene-butadiene rubber (SBR) by weight, which were mixed into a homogeneous slurry. The slurry was then coated onto an Al current collector and dried in a vacuum at 110 °C for 12 h. The electrodes were tailored into 12 mm-diameter circular pieces. The loading of the active material was approximately 1.965 mg cm$^{-2}$. A lithium foil (Sinopharm Chemical Reagent Co., Ltd) was employed as the counter/reference electrode; whereas porous polypropylene film (Celgard Co., 2400) was used as the separator. The coin cell was assembled in an Ar-filled glovebox (H$_2$O < 0.01 ppm and O$_2$ < 0.01 ppm, Mikrouna, Super (1220/750/900)) with 1.0 M LiPF$_6$ in a mixture of ethylene carbonate/dimethylene carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1 by volume) as the electrolyte. The electrochemical properties were measured via a galvanostatic discharge-charge technique on a battery tester (Shenzhen Neware Technology Co., Ltd, CT-4008). The cut-off voltage window was 0.01–2.0 V. The battery cycling at 50 °C was performed after placing the cells in a high-low temperature chamber (Shanghai Munee Instruments Co., Ltd, HTM22). The CVs (0.01–2.0 V, 0.1 mV s$^{-1}$) and EIS from 100 KHz to 0.01 Hz were conducted on an electrochemical work station (Shanghai Chenhua Instruments Co., Ltd, CHI-660E).
ESI Figures

In Fig. S1a, the SnO$_2$@C precursors prepared via the hydrothermal route show a solid and spherical morphology. However, after annealing the precursors at a high temperature of 500 °C in air, a multi-layered, hollow structure was observed (Fig. S1b-e).

Fig. S1 (a) TEM image of the SnO$_2$@C precursors. (b, c) SEM (d, e) TEM images of the samples obtained after annealing the SnO$_2$@C precursors in air at 500 °C for 2 h.

Fig. S2 Low-magnification SEM image of the D-net Sn composite.
Fig. S3 (a, b) Cross-sectional SEM images of the Sn@C obtained by the focused ion beam.

Fig. S4 EDS spectrum of the D-net Sn composite.

Fig. S5 (a) AFM image and the (b) height profile of the GO sheet in (a).
In Fig. S6a, the peaks located at 1328 and 1585 cm\(^{-1}\) are indexed to the D and G bands of graphene, respectively. The G band represents the crystal structure; whereas the D band is attributed to the disorders or defects. Thermogravimetric analysis (TGA) was carried out to quantify the carbon and Sn components of the D-net Sn composite, as shown in Fig. S6b. The weight increase when the temperature increases from 50 to 450 °C, which is ascribed to the oxidization of Sn to SnO\(_2\). Beyond 450 °C, the weight loss is own to the decomposition of rGO and the carbon within the Sn/C composites. When the temperature exceeds 600 °C, the weight remains constant. The percentage of SnO\(_2\) was calculated as approximately 52.3%, indicating that the Sn in the composite is 41.2 wt%.

![Raman spectra and TGA curve](image)

**Fig. S6** (a) Raman spectra of the (A) D-net Sn composite and (B) GO sheets. (b) TGA curve of the D-net Sn composite.
Fig. S7a shows the survey spectrum of the D-net Sn composite, which confirms the existence of C, O, and Sn elements. The spectrum of C 1s (Fig. S7b) shows two peaks located at 284.6 and 285.6 eV, which are attributed to C–O and O–C=O, respectively. Fig. S7c shows the spectrum of O 1s wherein the peak at 530.6 eV corresponds to the O in SnO₂. In Fig. S7d, the binding energies of Sn3d₃/₂ and Sn3d₅/₂ are located at 495.3 and 486.7 eV, respectively, which are attributed to the Sn⁴⁺ cation. The presence of Sn⁴⁺ is due to the residuals of SnO₂ or the exposure of samples in air.

Fig. S7 XPS spectra of (a) survey spectrum, (b) C 1s, (c) O 1s, and (d) Sn 3d of the D-net Sn composite.
Fig. S8 The charge/discharge profiles of the D-net Sn composite anode at 0.5C.

Fig. S9 shows the EIS curves of the D-net Sn composite anode before and after 160 cycles. The impedance profiles consist of a semicircular high-frequency region and a fastigiated low-frequency region. The high-frequency region represents the solid electrolyte interphase (SEI) resistance and the contact resistance; whereas the semicircle of the intermediate-frequency region indicates the charge transfer resistance of the electrode/electrolyte interface. Inset is the equivalent circuit used for fitting which contains the surface film ($R_s$) and charge transfer ($R_{ct}$) resistances, a constant phase element involving a double layer capacitance, and a Warburg impedance ($Z_w$) related to solid-state diffusion of lithium in the anode. The semicircle in the high-frequency region after cycling is slightly larger than that before cycling, indicating a stable SEI formation with a relatively low contact resistance. The $R_{ct}$ of the cell consisting of the fresh D-net Sn anode was about 53.3 $\Omega$, which increased to $\sim 92.5 \Omega$ after 160 cycles.

Fig. S9 Nyquist plots of the battery with D-net Sn composite as anode before and after charging/discharging for 200 cycles at 0.5C. The inset shows the fitted equivalent circuit.
Fig. S10 Schematic illustration of the in-situ TEM set-up.

Table S1. Calculation results of different Sn atoms in Sn@C.

<table>
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<th>Parameters</th>
<th>Sn₁</th>
<th>Sn₂</th>
<th>Sn₃</th>
</tr>
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<tr>
<td>Original</td>
<td>0.5, 0.25, 0.31</td>
<td>0, 0.38, 0.31</td>
<td>0.5, 0.75, 0.31</td>
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<tr>
<td>Relaxed</td>
<td>0.5, 0.36, 0.3</td>
<td>0, 0.51, 0.32</td>
<td>0.5, 0.86, 0.3</td>
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<tr>
<td>Sn bonded with C</td>
<td>0.53, 0.18, 0.32</td>
<td>0.01, 0.41, 0.32</td>
<td>0.51, 0.71, 0.32</td>
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<tr>
<td>Sn–C bond length (Å)</td>
<td>2.169</td>
<td>2.174</td>
<td>2.186</td>
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<tr>
<td>Population</td>
<td>0.63</td>
<td>0.62</td>
<td>0.6</td>
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Table S2. Mulliken charges of the Sn atoms bonding with C.

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<th>Species</th>
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<th>Orbit p (e)</th>
<th>Total (e)</th>
<th>Charge (e)</th>
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<tbody>
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<td>Sn₁</td>
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<tr>
<td>Sn₃</td>
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