Supplementary Information for:

SnO_2/α -MoO₃ core-shell nanobelts and their extraordinarily high reversible capacity as lithium-ion battery anodes

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SI-1. Experimental materials

All chemicals were of analytical grade and used as purchased without further purification. Ammonium heptamolybdate tetrahydrate (AHM, (NH₄)₆Mo₇O₂₄·4H₂O), Nitric acid (HNO₃), Stannous chloride (SnCl₂·2H₂O), hydrochloric acid (HCl) were all supplied by Sinopharm Chemical Reagent Co. Ltd.

SI-2. Materials synthesis

Synthesis of α -MoO₃ nanobelts: 1 g AHM was dissolved in 33 ml distilled water under continually stirring. Then, 6 ml HNO₃ (65%) was slowly added under vigorous stirring. After fully dissolved, the mixture was transferred into a Teflon-lined stainless steel autoclave (50 ml) and heated at 180 °C for 24 h. After cooling down to room temperature, the light gray products were collected by centrifugation and washed with ethanol and distill water. Finally, the products were dried at 60 °C under vacuum for 12h.

Synthesis of α -MoO₃ nanobelts with SnO₂ nanoparticles: 0.95 mg α -MoO₃ nanobelts were

ultrasonically dispersed into 50 ml distilled water for 30 minutes. 0.875 ml HCl and 1.5 g $SnCl_2 \cdot 2H_2O$ were added into the above solution. After ultrasonically treatment for 10 minutes and vigorously stirring for 4 h, the resulting precipitates were collected and washed with ethanol and distilled water. Then, the light blue products were dried at 60 °C under vacuum for 12h.

SI-3. XRD patterns of as-synthsized products



Figure S1 XRD patterns of α -MoO₃ nanobelts (pattern 1) and SnO₂/ α -MoO₃ core-shell nanobelts (pattern 2).

The crystal phase of α -MoO₃ nanobelts and SnO₂/ α -MoO₃ core-shell nanobelts was identified by X-ray power diffraction (XRD; D/max 2550V, Cu K α Radiation, λ =1.5416 Å). Fig. S1 is XRD patterns of α -MoO₃ nanobelts and SnO₂/ α -MoO₃ core-shell nanobelts. Both of them exhibit sharp diffraction peaks, which indicate the well crystallization of α -MoO₃ nanobelts and SnO₂/ α -MoO₃ core-shell nanobelts. All the peaks in pattern 1 can be indexed to the orthorhombic α -MoO₃ (JCPDS File No. 05-0508; space group: Pbnm (62); lattice constants: a = 3.962 A°, b = 13.858 A°, c = 3.697 A°). In

pattern 2, three new peaks at 26.6, 38.9 and 51.8 can be indexed to (110), (111), (211) planes of SnO₂ crystal (JCPDS card No. 41-1445; space group: P4₂/mnm (136); lattice constants: a = 4.738 A°, c = 3.187 A°). There are no other clear sharp peaks coincident with those peaks of other impurities. These results confirm that SnO₂/ α -MoO₃ core-shell nanobelts with relatively high crystal purity are obtained.

SI-3. EDS spectrum of SnO₂/α-MoO₃ core-shell nanobelts



Figure S2 EDS spectrum of SnO_2/α -MoO₃ core-shell nanobelts.

Fig. S2 is one of EDS spectrum taken from one single SnO_2/α -MoO₃ core-shell nanobelts by a finely focused electron probe. Presence of the Cu peaks in the spectrum comes from the copper grids used as a support in TEM observations. It is clearly seen that the core-shell nanobelts are composed from three elements: Sn, Mo and O. By analyzing the EDS results obtained from more than 20 different areas, the molar ratio of SnO₂ and MoO₃ is about 1:10. These results above confirm that single-crystal α -MoO₃ nanobelts are uniformly coated with a thin SnO₂ nanoparticle layer.

SI-4. Electrode preparation and electrochemical measurements

The samples were mixed with acetylene black and carboxymethyl cellulose (CMC) at a weight ratio of 8: 1: 1. The mixture was painted onto a copper foil with a diameter of 15 mm. The 2016 coin-type cells were assembled in an argon-filled glove box, and pure Li foils were used as the counter electrodes. The electrolyte was made of 1 M LiPF₆ in the mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with the volume ratio 1:1. The cells were galvanostatically charged and discharged between 0.001 and 2.75 V versus Li⁺/Li at room temperature on a program-controlled test system. It should be pointed that the specific capacity are based on total weights of SnO₂/ α -MoO₃ core-shell nanobelts.



SI-5. SEM image analysis of SnO₂/α-MoO₃ core-shell nanobelts before and after cycling test

Figure S3 SEM image of SnO_2/α -MoO₃ core-shell nanobelts (a) before cycling test, (b) after discharge process and (c) after charge process.

Fig. S3a, b & c are SEM images of SnO_2/α -MoO₃ core-shell nanobelts before cycling test, after discharge process and after charge process, respectively. The cycling measurement is performed for 20 times. As shown in Fig. S3a, before cycling test, SnO_2/α -MoO₃ core-shell nanobelts have the average

diameter of 220 nm. As shown in Fig. S3b, after discharge process, the samples are still dominated by 1D nanostructures and the diameters increases to 280 nm. As shown in Fig. S3c, after charge process, their average diameter is 240 nm. These results demonstrate that 1D nanostructures can accommodate the strain during cycles and have high stability.



SI-6. Coulombic efficiency analysis

Figure S4 The coulombic efficiency of (a) α -MoO₃ nanobelts and (b) SnO₂/ α -MoO₃ core-shell nanobelts.

Fig. S4 shows coulombic efficiency of α -MoO₃ nanobelts and SnO₂/ α -MoO₃ core-shell nanobelts. The initial coulombic efficiency of α -MoO₃ nanobelts and SnO₂/ α -MoO₃ core-shell nanobelts is 70.8 % and 69.7 %, respectively. The low initial coulombic efficiency is probably attributed to the formation of solid electrolyte interphase (SEI) layer (coincidence with the differential capacity curves in Fig. S3). Such a behavior has been reported in many literatures, and can not be avoided. In the following cycles, both α -MoO₃ nanobelts and SnO₂/ α -MoO₃ core-shell nanobelts show high coulombic efficiency (>96.0 %).

SI-7. Confirmation of reversible capacity



Figure S5 Reversible capacity of α -MoO₃ nanobelts (pattern 1) and SnO₂/ α -MoO₃ core-shell nanobelts (pattern 2) measured from 20 different LIBs at C/10 rate.

To confirm the extraordinarily high reversible capacity, 20 different LIBs are fabricated from α -MoO₃ nanobelts and SnO₂/ α -MoO₃ core-shell nanobelts, respectively. As shown in Fig. S5, the reversible capacity of SnO₂/ α -MoO₃ core-shell nanobelts is ~2200 mAh/g, much higher than that of pure α -MoO₃ nanobelts (~1400 mAh/g).

SI-8. XRD analysis of SnO₂/α-MoO₃ core-shell nanobelts during the cycling test



Figure S6 XRD patterns of SnO_2/α -MoO₃ core-shell nanobelts after (a) Li insertion and (b) Li extraction.

Fig. S6 shows XRD patterns of SnO₂/ α -MoO₃ core-shell nanobelt electrodes after Li insertion and extraction. As shown in Fig. S6a, after Li insertion, the sharp diffraction peaks can be indexed to Li₂₂Sn₅ (JPCDS File No. 18-0753), Li₂O (JPCDS File No. 12-0254), Mo (JPCDS File No. 65-7442), Cu (JPCDS File No. 04-0836) and C (JPCDS File No. 41-1487), Li_xMoO₃, respectively. The diffraction peak of Li_xMoO₃ almost coincides to that of Li_{1,3}Mo₃O₈ (JPCDS File No. 37-0249), which probably arises from phase-transition process of α -MoO₃ nanobelts after Li insertion. As shown in Fig. S6b, after Li extraction, the diffraction peaks can be indexed to Cu and C. The diffraction peaks of Sn and MoO₃ can not be observed because Sn and MoO₃ are of amorphous phase. It should be noted that the diffraction peaks of Li₂O can not be observed, which confirms that Mo metal clusters make Li₂O reversibly convert to Li⁺.

SI-9. Differential capacity curves (dC/dV vs. voltage) analysis



Figure S7 The derivative relation of the galvanostatic voltage vs. the capacity for the 1st, 2nd and 30th cycle of (a) α -MoO₃ nanobelts and (d) SnO₂/ α -MoO₃ core-shell nanobelts.

Fig. S7a & b are differential capacity curves (dC/dV vs. voltage) for the 1st, 2nd and 30th cycles of α -MoO₃ nanobelts and SnO₂/ α -MoO₃ core-shell nanobelts, respectively, showing their structural and electrochemical information during lithiation/delithiation process. For pure α -MoO₃ nanobelts (Fig. S7a), during the first lithiation process, three peaks can be observed at 2.25, 0.4 and 0.07 V. The peak at 2.25 V, only observed in the first discharge process, is probably ascribed to the formation of SEI layer. The other two peaks can be attributed to the lithiation process. In the subsequent lithiation processes, all the peaks (at 0.07, 0.3, 0.53, 1.29 and 1.48 V) are reversible, which can be attributed to the lithiation process of α -MoO₃ nanobelts. For SnO₂/ α -MoO₃ core-shell nanobelts (Fig. S7b), during the first lithiation process, the irreversible peak, also observed at 2.25 V, can be ascribed to the formation of SEI layer. In the following lithiation processes, a new and reversible peak at ~0.7 V is observed, corresponding to the formation of Li₂₂Sn₅ alloys. No other irreversible peaks can be observed, which further confirms that all Li₂O reversibly converts to Li⁺.