Electrochemical properties of SnO$_2$ nanoparticles immobilized within a metal-organic framework as anode material for lithium-ion battery

Buxue Wang, Ziqi Wang, * Yuanjing Cui,* Yu Yang, Zhiyu Wang and Guodong Qian*

State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027 P. R. China. E-mail: cuiyj@zjuedu.cn, gdqian@zju.edu.cn.

Experimental Details

Synthesis
1. MIL-101(Cr). A mixture of 1.86 g CrCl$_3$·6H$_2$O, 1.16 g terephthalic acid (BDC), 50 ml H$_2$O was loaded into a 100 ml autoclave with a Teflon cup and heated at 210 °C for 24 h. Upon cooling down, the green suspension of nano MIL-101(Cr) was centrifuged and washed with hot DMF and EtOH. Then it was dispersed in NaOH solution (pH=12, 20 ml) and stirred overnight at 60 °C. After it was centrifuged and washed with deionized water, MIL-101(Cr) was obtained by drying at 120 °C in vacuum.

2. SnO$_2$@MIL-101(Cr). 0.2 g MIL-101(Cr) and 1.0 g SnCl$_4$·5H$_2$O were dispersed in 15 ml H$_2$O and stirred for 24 h in room temperature. Then it was centrifuged and washed once with 10 ml H$_2$O. After that it was dispersed in 100 ml NaOH solution (pH=12) and stirred overnight at room temperature. Then the suspension was centrifuged and washed with deionized water (four times, 20 ml each time) to remove free ions in MIL-101(Cr). After drying at 180 °C in vacuum, SnO$_2$@MIL-101(Cr) was obtained. Bare SnO$_2$ was synthesized following the similar procedure in the absence of MIL-101(Cr) by adding NaOH solution into SnCl$_4$ solution.

3. Battery assembling. SnO$_2$@MIL-101(Cr) (bare SnO$_2$) was mixed with 10% acetylene black and 10% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) separately. The slurry was coated on copper foil as anode (~0.3 mg-SnO$_2$/cm$^2$, whole carbon content 41.6 wt%). 2025 batteries were assembled with electrolyte of 1 M LiPF$_6$ in 1,3-dioxolan-2-one/dimethylcarbonate (EC/DMC, v:v=1:1), Celgard 2400 membrane and lithium foil counter electrode.

Characterization

PXRD patterns were recorded on a PANalytical X'Pert PRO diffractometer at 40 kV, 25 mA for Cu Kα, (λ=1.541 Å). SEM morphologies were investigated using a Hitachi S4800 field-emission scanning electron microscopy. TEM morphologies and EDS mappings were taken on a Hitachi HT7700 transmission electron microscopy. ICP-MS was performed on a Thermo Scientific XSERIES 2 ICP-MS system to determine SnO$_2$ content in SnO$_2$@MIL-101(Cr). The FTIR spectra were measured with a Nicolet Thermo Scientific Nicolet iS10 spectrometer. N$_2$ sorption properties were studied with a Quantachrome 20-E high speed gas sorption analyzer. The CV curves were collected with an Arbin electrochemical workstation at a scan rate of 0.1 mV s$^{-1}$ between 0.02 and 2.5 V. The EIS data were collected with an Arbin electrochemical workstation. The charge/discharge profiles, cyclability, rate capability and Coulombic efficiency were recorded with
a LAND battery cycler between 0.02 and 2.5 V.

Fig. S1. N\textsubscript{2} adsorption/desorption isothermal of SnO\textsubscript{2}@MIL-101(Cr) at 77 K.

Fig. S2. FTIR spectra of SnO\textsubscript{2}@MIL-101(Cr).

Fig. S3. EIS spectra for the half cell with SnO\textsubscript{2}@MIL-101(Cr) anode after 1\textsuperscript{st} cycle and 100\textsuperscript{th} cycle.
Fig. S4. (a) Galvanostatic charge/discharge profiles and (b) cycle performance at 0.1 C of bare SnO$_2$. 