An inorganic-organic hybrid supramolecular nanotube as high-performance anode for lithium ion batteries

Shubiao Xia \textsuperscript{a}, Fushao Li \textsuperscript{a}, Xue Li \textsuperscript{c,d}, Feixiang Cheng \textsuperscript{a}, Chengke Sun \textsuperscript{a}, Jian-Jun Liu \textsuperscript{a,*}, Guo Hong \textsuperscript{b,*}

\textsuperscript{a} Center for Yunnan-Guizhou Plateau Chemical Functional Materials and Pollution Control, Qujing Normal University, Qujing 655011, China

\textsuperscript{b} School of Materials Science and Engineering, Yunnan University, Kunming, 650091, China

\textsuperscript{c} State and Local Joint Engineering Laboratory of Lithium Ion Battery and Material Preparation Technology, Kunming 650093, China

\textsuperscript{d} Faculty of Materials Science and Engineering, Kunming University of Science and Technology, Kunming 650093, China;

E-mail: jianjun_liu@mail.qjnu.edu.cn; E-mail: guohongcom@126.com
Experimental

Materials and measurements

All chemical materials were purchased from commercial sources and used without further purification. The Na$_9$[A-α-PW$_{9}$O$_{34}$]$\cdot$nH$_2$O (PW9) were prepared by literature method (A. P. Ginsberg, Inorganic Syntheses, John Wiley & Sons: New York 27 (1990) p85). Fourier transform infrared spectra were taken on a Nicolet iS50 spectrometer from KBr pellets in the range of 4000-400 cm$^{-1}$. Powder X-ray diffraction (PXRD) patterns were collected on Rigaku Ultima IV diffractometer with Cu Kα (λ = 1.5418 Å) radiation in the range of 2–50° at a rate of 10°/min. X-ray photoelectron spectra (XPS) were carried out using a Kratos AXIS Ultra DLD spectrometer with Al Kα X-ray source. Thermogravimetric analyses (TGA) were carried out on a TG-209 system analyzer under nitrogen atmosphere from room temperature to 800°C at a ramp rate of 10 °C/min. SEM images were taken using FEI Nova Nano SEM 230 with an accelerating voltage of 10 kV. The cyclic voltammograms measurements were carried out and recorded on a Chenghua 660C electrochemical workstation with scan rate 0.1 mV/second.

Synthesis of Ni-POM

The Ni-POM was synthesized following the reported process (Chem. Commun. 2015, 51, 2048–2051). Typically, a mixture of PW9 (0.600 g), Ni(NO$_3$)$_2$$\cdot$6H$_2$O (0.700 g) and 1H-1,2,4-triazole-3-thiol (0.100 g) was added into 8 mL of a 0.5 M sodium acetate buffer (pH 4.8). Further, 0.40 mL ethanediamine was added to this solution and stirred for half an hour, transferred into a Teflon-lined stainless steel autoclave
(50 mL) and kept at 170 °C for 72 hours, and then cooled to room temperature, which was washed with water and then immersed in EtOH to stand for 3 days. The resulting solids were filtered and dried in vacuum at 150 °C.

**Fabrication of Li-ion battery and electrochemical measurements**

The working electrode of Ni-POM was obtained by mixing the active material (60%) with carbon black (Super-P, 30%) as conductive additive and polyvinylidene difluoride (PVDF, 10%) as binder by weight in N-methyl pyrrolidone (NMP) to form a well-dispersed slurry, which was subjected to ultrasonication for 1 h and then coated onto an copper foil substrate. The copper foil was cut into the discs with a diameter of 12 mm after drying in vacuum at 100 °C for overnight to use as working electrodes. The batteries were assembled using a conventional CR2025 coin cell in a glove box (Mikrouna Universal 24401750) under ultrapure argon. Lithium foil was used as reference and counter electrode, a Celgard 2400 membrane was used as the separator, and 1 M LiPF₆ in dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylene carbonate (EC) (volume ratio of 1:1:1) was the electrolyte. Cyclic voltammetry of the Ni-POM electrode were conducted on two-electrode cells with lithium dish as the counter electrode and cycled between 0.01 V and 3.00 V at a rate of 0.1 mV s⁻¹ (vs. Li/Li⁺). Galvanostatic charge/discharge was tested on a programmable testing system (LAND-2001A, Wuhan) in the voltage range of 0.01-3 V (vs. Li/Li⁺) for the Ni-POM electrode at varies current densities.
Figure S1. Gas sorption isotherms of $N_2$ at 77 K for Ni-POM. The BET surface area evaluated by $N_2$ adsorptions are 31.4 m$^2$/g.

Figure S2. PXRD patterns of the Ni-POM electrode and immersed in electrolyte.
Figure S3. PXRD patterns of the Ni-POM electrode after 1 and 50 cycles performed.

Figure S4. TEM images of Ni-POM electrode after different cycles (a. initial; b. after 1 cycle; c. after 50 cycles); d. EDX spectrum of Ni-POM after 50 cycles.
Figure S5. TEM images of raw Ni-POM material (a, b) and initial Ni-POM electrode (c, d).