

Supporting Information

Synthesis of Sn-Co@PMMA nanowire arrays by electrodeposition and in situ polymerization as a high performance lithium-ion battery anode

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Experimental section

Materials

The anodic alumina template (AAO, ANODISC 13) were purchased from WHATMAN which had an average pore diameter of around 200 nm. The electrodepositions were carried out in a three electrode cell consisting of a Pt counter electrode, Ag/AgCl reference electrode and alumina template working electrode. A film of gold was sputtered on one side of the alumina membrane through ultra high vacuum magnetron sputtering coating machine (JGP-800). The thickness of gold layer is about 90 nm. This side was then glued by a conductive paste to a suitable holder for deposition of the Cu current collector. The gold layer is sputtered to ensure the conductive contact between AAO and Cu foil so that the Sn-Co NWs could be deposited on to the Cu current collector in the pore of AAO template. Methyl methacrylate (MMA, 99% assay) was washed with dilute alkali and distilled water, dried over calcium chloride, and distilled under reduced pressure. Sodium dodecyl sulfate (SDS), ammonium persulfate and sodium hydrogen sulfite were used as the emulsifier, initiator and reducing agent, respectively. A 20 mL aqueous solution of 0.30 M Na_2SnO_3 , 0.02 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.50 M $\text{C}_4\text{O}_6\text{H}_4\text{KNa}$ and 0.06 M $\text{K}_4\text{P}_2\text{O}_7$ was prepared for the electrodeposition of Sn-Co NWs. All the reagents were used without further purification.

Preparation of the Sn-Co@PMMA nanowire arrays

The Sn-Co NWs were electrodeposited using a galvanostatic method at a current density of 5 mA cm^{-2} , typically for 60 minutes. After that, the pores of the alumina

templates were widened chemically using 0.10 M NaOH for 40 minutes. The processed alumina templates were then rinsed several times with deionized water. A 1 wt% PMMA solution in methylene chloride was used to wet the walls of the widened alumina template. The solution was dropped onto the surface of the template and the extra liquid was wiped off using soft tissue paper for five times. After that, the sample was immersed in 1 M NaOH solution for two hours to dissolve the AAO templates and finally cleaned with deionized water (as Sn-Co@PMMA NWs 1).

The widened templates were put into 100 mL aqueous solution containing of 0.01 g SDS, 0.01 g ammonium persulfate and 5 ml purified MMA monomer. Then 0.05 g sodium hydrogen sulfite was added and the mixture was stirred for an additional 2 h. The polymerization was carried out at 75°C for 2 h. After cooling, the products were precipitated by the addition of saturated NaCl and then washed with dichloromethane and acetonitrile to remove the redundant PMMA on the surface of arrays. The resulting products were also immersed in NaOH solution to dissolve the AAO templates (as Sn-Co@PMMA NWs 2).

To validate the role of PMMA during the development of the nanowire array architecture, a synthesis of the Sn-Co nanowire arrays were attempted without PMMA, while all other synthetic parameters remained identical to those for Sn-Co@PMMA nanowire arrays.

Structure characterizations

The morphology and structure of the obtained samples were examined by a Hitachi S-4800 field-emission scanning electron microscope (FE-SEM) at an

accelerating voltage of 5 kV and a high-resolution transmission electron microscope (HR-TEM, JEM-2100F) operated at 200 kV. Genesis XM2 energy dispersive X-ray spectroscopy (EDS, USA) was used to determine the composition of the Sn-Co NWs. An X-ray diffraction spectrometer (Scintag PAD5) with Cu Ka radiation (1.54056 Å) was used to record the XRD patterns. Thermal analysis of the composite was performed by thermal gravimetric analysis (TG) (ModelQ50, TA, USA) under an air atmosphere, with a heating rate of 10°C/min.

Electrochemical characterizations

Electrochemical performance was investigated directly using coin cells (type CR2032) assembled in an argon-filled glovebox by directly using the as-synthesized samples as the anodes. The counter and reference electrodes were lithium metal foils (15 mm diameter), and the electrolyte solution was a 1 M solution of LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume). Each cell was aged for 24 h at room temperature before the electrochemical tests. Cyclic voltammetry (CV) was performed on a CHI 660B electrochemical workstation at a scan rate of 0.1 mV s⁻¹ in the potential window of 0.001-3.0 V. The galvanostatic charge/discharge measurements were carried out in a LANHE battery testing system at room temperature with cutoff voltage of 0.01 to 3.0 V (vs Li⁺/Li). The impedance of the cells after 1 and 100 cycles were determined with CHI 660D (Shanghai, China). The frequency was varied from 10⁶ Hz to 1 Hz and the amplitude was set at 5 mV. The impedance data were analyzed using ZSimpWin Version 3.1 software.

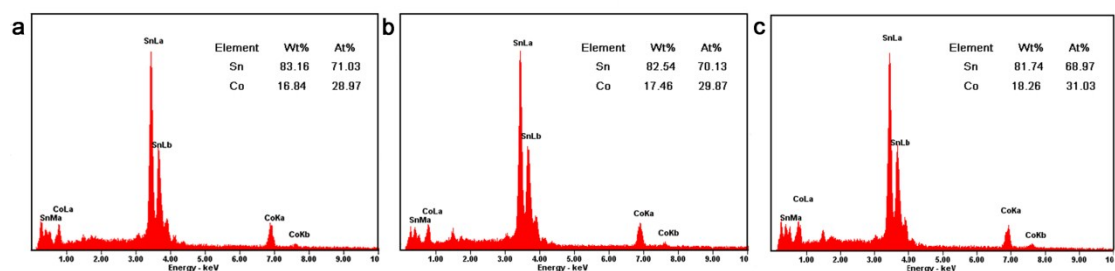


Figure S1. EDS microanalysis with corresponding element mass and atomic percentages of (a) Sn-Co NWs, (b) Sn-Co@PMMA NWs 1 and (c) Sn-Co@PMMA NWs 2.

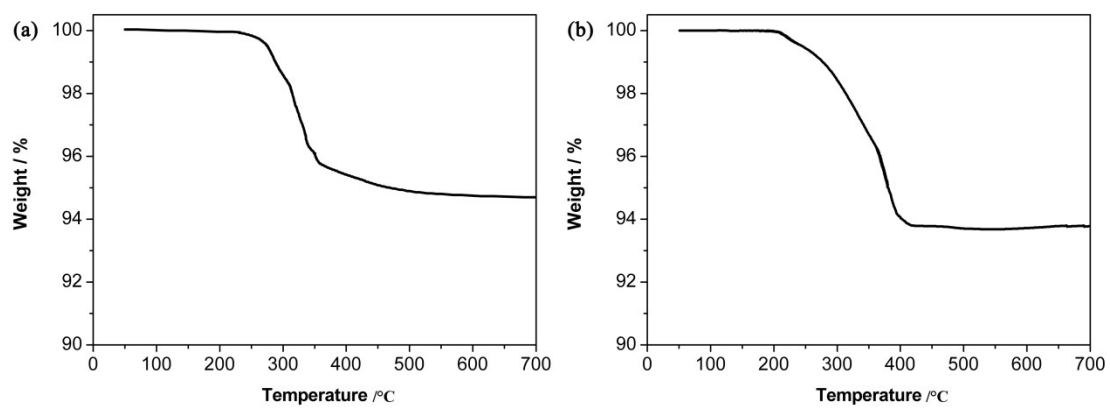


Figure S2. TG curves of (a) Sn-Co@PMMA NWs 1 and (b) Sn-Co@PMMA NWs 2.

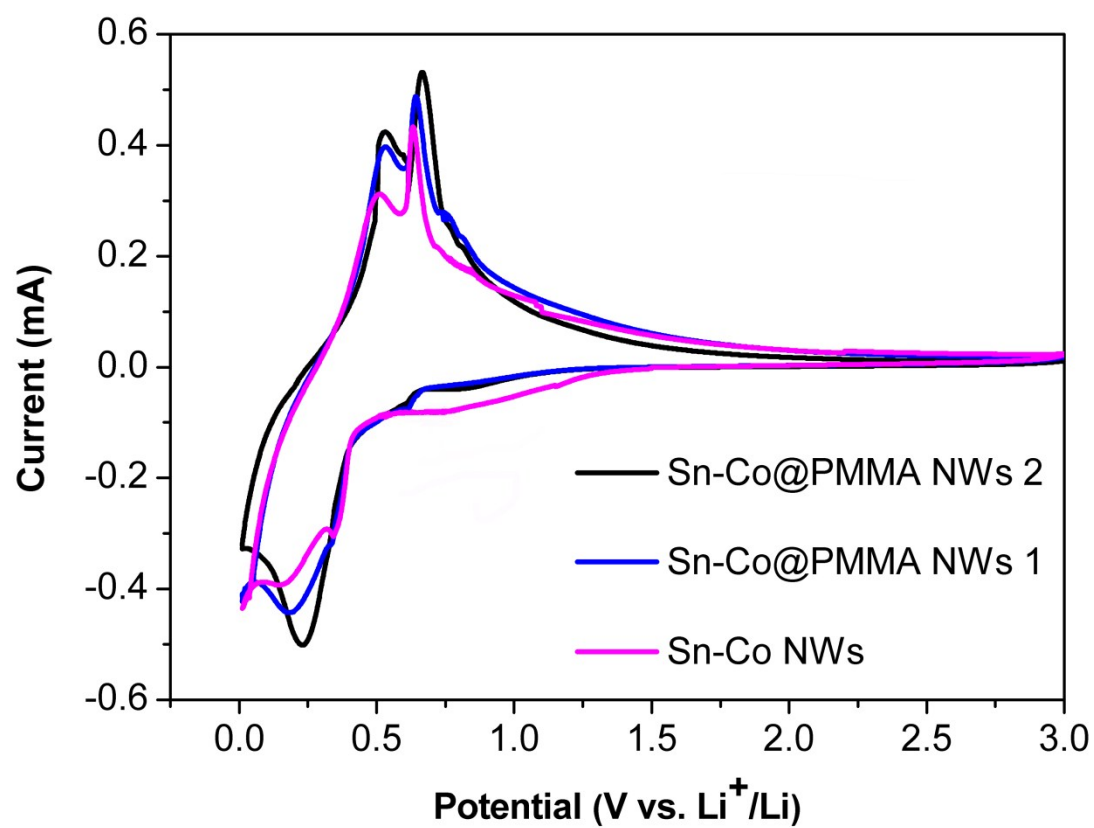


Figure S3. Cyclic voltammetric curves of Sn-Co NWs electrode, Sn-Co@PMMA NWs 1 electrode and Sn-Co@PMMA NWs 2 electrode for the first cycle.

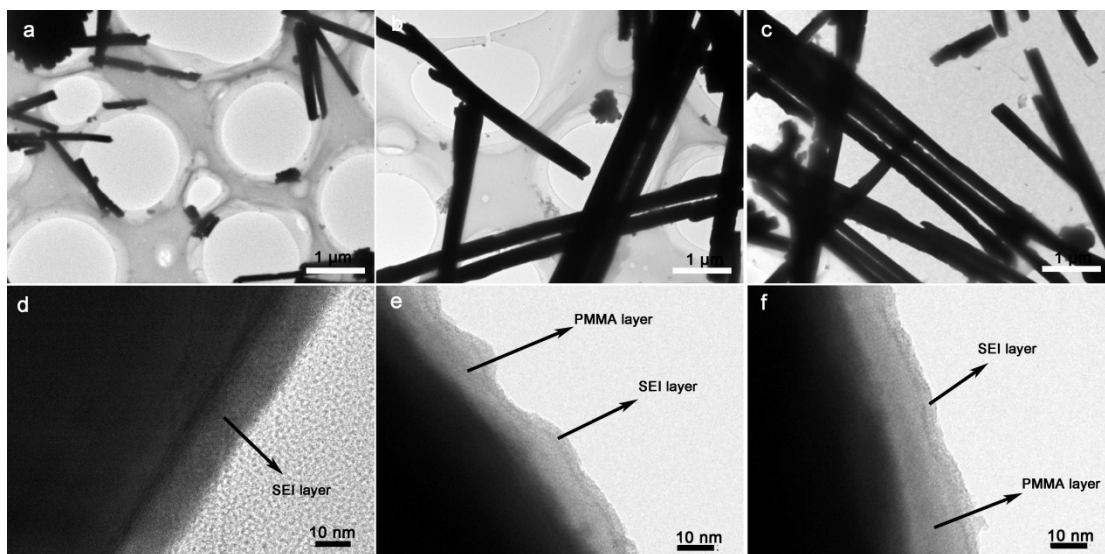


Figure S4. (a, b, c) Low and (d, e, f) high TEM images of electrodes after 100 cycles:

(a, d) Sn-Co NWs, (b, e) Sn-Co@PMMA NWs 1, (c, f) Sn-Co@PMMA NWs 2.