

# Convenient Fabrication of Core-Shell Sn@TiO<sub>2</sub> Anode for Lithium Storage From Tinplate Electroplating Sludge

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## Experimental

### Method

Pretreatment of the electroplating sludge: The electroplating sludge comes from Fujian Zhongrida Metal Co. Ltd. First, the electroplating sludge was dried at 80°C for 12 h and the dried solid was ground to a small powder. Then 10 g dried sludge powder was stirred with 100 ml 0.7 M NaOH solution. Subsequently, the mixture was transferred to a 200 ml Teflon-lined stainless steel autoclave and heated at 230 °C for

2 h. The extracting solution was obtained by filtration.

Preparation of Al@TiO(OH)<sub>2</sub> precursor: Specifically, 0.5 g of TiOSO<sub>4</sub> (reagent grade, Sigma-Aldrich) and 30 g of H<sub>2</sub>SO<sub>4</sub> (ACS grade, 1.0 N, Guangzhou Chemical Reagent Factory) were dissolved in 1000 ml deionized water. Then, 0.135 mg of Al powder (approximately 150 nm in diameter, 99.9%, Hongwu New Material) was added to the saturated TiOSO<sub>4</sub> solution. After vigorously agitating the solution using an ultrasonic cleaner for 30 min, it was stirred for 10/60/120 min to form TiO<sub>2</sub> shell and partial etch Al. The obtained powders were filtered and washed with deionized water and ethanol three times and dried at 80 °C overnight.

Preparation of Sn@TiO<sub>2</sub>: Typically, 0.2g Al@TiO(OH)<sub>2</sub> precursor was added in 100 ml extraction solution and impregnated for 6 h until there is no more bubble in the solution. The resulting solution was then filtered in a vacuum system and washed three times with ethanol. After drying in a vacuum oven at 80°C for 7 h, the Sn@TiO<sub>2</sub> was synthesized by annealed at 450 °C for 2 h with a temperature rate of 2 °C min<sup>-1</sup> at N<sub>2</sub> atmosphere.

### **Material characterization**

X-ray diffraction patterns were performed on a Rigaku D/max 2500 using Cu Ka radiation in the 2θ range of 10°–90° with a scan step of 0.12° s<sup>-1</sup>. Raman and X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Renishaw

RM1000 microspectrometer and a Thermo K-Alpha XPS spectrometer, respectively. Brunauer–Emmett–Teller (BET) specific surface areas were obtained using a Micromeritics ASAP 2020 analyzer at the liquid-nitrogen boiling point (77 K). Material morphology was measured by FESEM (Hitachi S-4800) and TEM (JEM-2010 JEOL, 200 kV).

### **Electrochemical measurements**

The sodium-storage properties of all the samples were characterized by making CR2032 coin-type cell in an Ar glove box. Porous polypropylene based membrane (Celgard) ( $\Phi$ 19 mm) was used as separator, and Li foil ( $\Phi$ 15 mm) as the anode. The working electrode ( $\Phi$ 13 mm) was prepared by mixing the Sn@TiO<sub>2</sub> composite, acetylene black, and the polyvinylidene fluoride bond (PVDF) with a mass ratio of 8:1:1 in N-methyl-2-pyrrolidone solvent. Generally, the active material has a mass load of approximately 1.5~1.7 g cm<sup>-2</sup>. The electrolyte was a solution containing 1.0 M LiPF<sub>6</sub> in EC/DEC/EMC (1/1/1 by volume), and the used amount of electrolyte is about 30  $\mu$ L in each cell. The CV measurements were conducted using a CHI660E electrochemical workstation. The responses of the test cycle performance and rated capacity were recorded by the LAND-BT2013A Measurement System at 25°C.

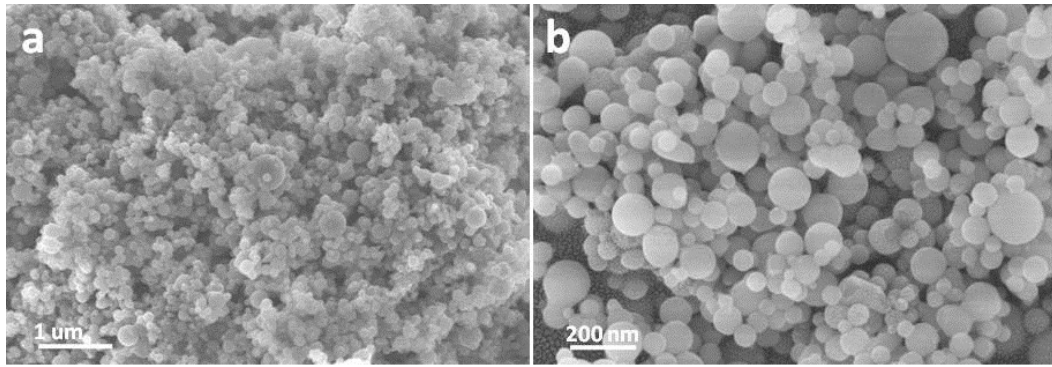


Fig. S1. SEM imaged of pure Al powder.

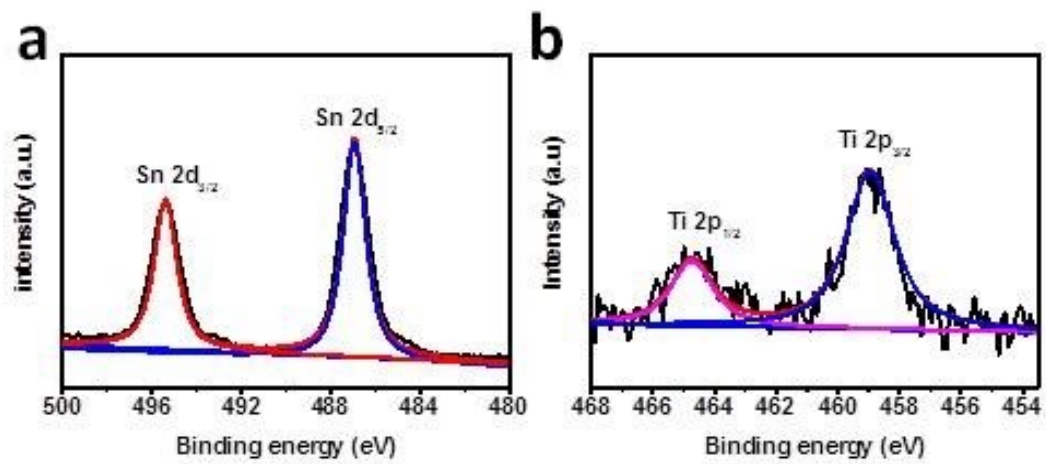


Fig. S2. (a) High resolution XPS spectra of Sn 2d and (b) High resolution XPS spectra of Ti 2p of Sn@TiO<sub>2</sub>.

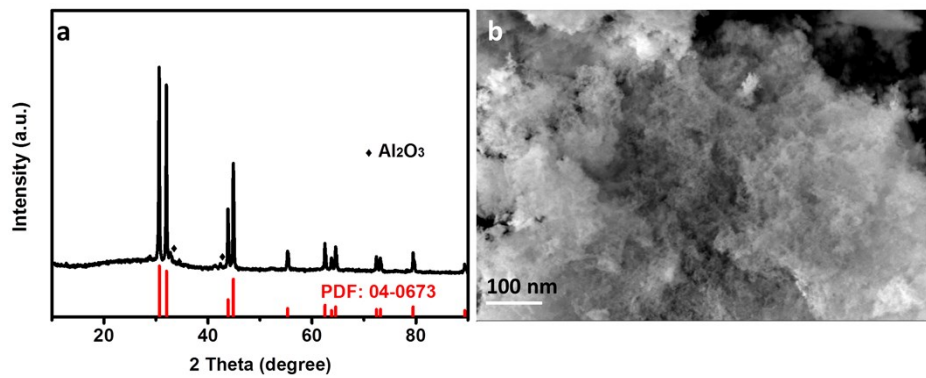


Fig. S3. (a) XRD patterns and (b) SEM image of Sn electrode without TiO<sub>2</sub> coating.

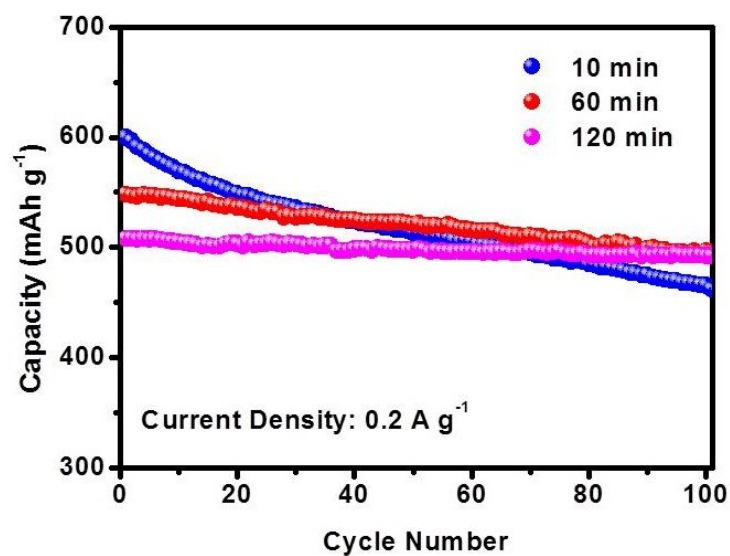


Fig. S4. Cycling performance at 0.2 A g<sup>-1</sup> of Sn@TiO<sub>2</sub> with different reaction time.

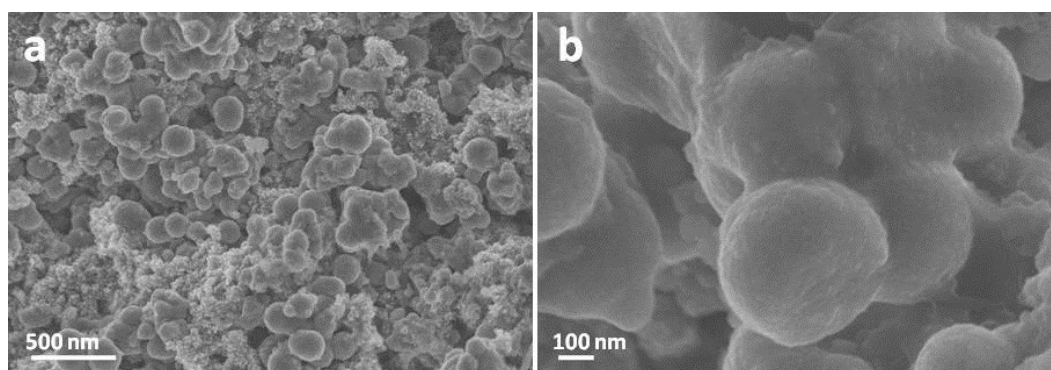


Fig. S5. SEM of Sn@TiO<sub>2</sub> after 100 cycles at 0.2 A g<sup>-1</sup>.

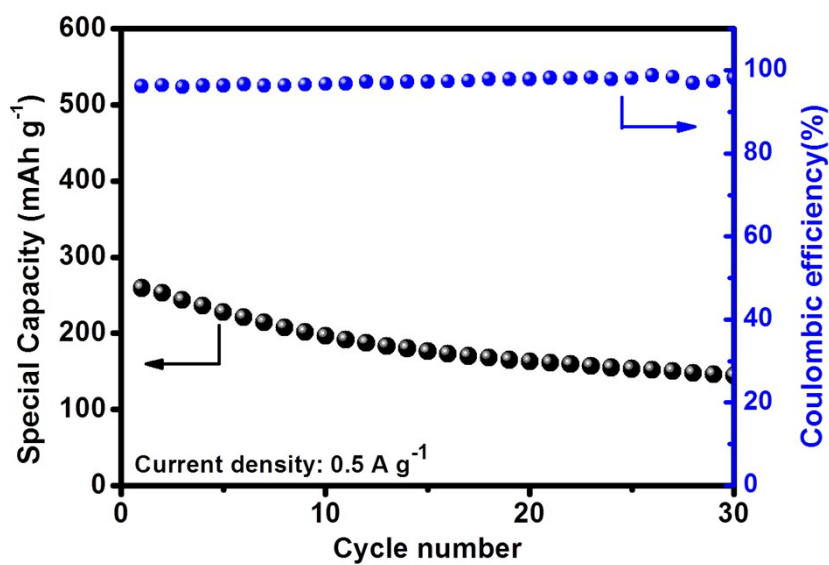


Fig. S6. Cycling performance at 0.5 A g<sup>-1</sup> of Sn electrode without TiO<sub>2</sub> coating.