

Electronic Supplementary Information

Nanocrystalline tin disulfide coating of reduced graphene oxide produced by the peroxostannate deposition route for sodium ion battery anodes

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Experimental Details

Synthesis protocols

Preparation of GO. GO was synthesized from exfoliated graphite by a modified Hummers method^{1,2} and a detailed protocol is described in our previous articles^{3,4}. First, exfoliated graphite powder⁵ (1 g) was added to a solution of $K_2S_2O_8$ (1.67 g) and P_2O_5 (1.67 g) in 8 mL concentrated H_2SO_4 . The mixture was kept at 80 °C for 4.5 h on a hot plate. After the mixture was cooled to room temperature, it was diluted with 0.35 L of deionized water (DIW) and filtered. Then the preoxidized material was washed with DIW and dried at 60-70°C overnight. Next, preoxidized carbon was redispersed in 40 mL of concentrated H_2SO_4 with the mixture kept in an ice bath. Subsequently, 5 g of potassium permanganate were added gradually under constant stirring to avoid overheating. The mixture was stirred at 35°C for 2 h and then slowly diluted with 80 mL of DIW upon cooling in the ice bath. The mixture was stirred for an additional 2 h and then 250 mL more DIW were added, followed by the addition of 6 mL of 30% H_2O_2 to react with the excess of permanganate. The color of the solution changed to yellow after addition of the peroxide. The oxidized product was filtered and washed with 100 mL HCl (1:10) to remove metal ion impurities, followed by washing with 300 mL of DIW and by dialysis to remove the acid. A dispersion of GO in water was prepared by dispersing the oxidized material in DIW in an ultrasound bath for 2 h. Aqueous GO dispersions were stable for at least a few months.

Preparation of hydroxostannate precursor solutions. 10 mL of $SnCl_4$ (0.086 mol) was dissolved in a few mL of deionized water (DIW) and neutralized with ammonia until pH 7. The precipitate was washed several times with DIW and dissolved in 31 mL of 25% aqueous tetramethylammonium hydroxide (0.086 mol). After full dissolution, DIW was added to achieve 1.4 M tin concentration.

Hydroperoxostannate supported GO. Typically, 2.8 g of aqueous GO dispersion (2% wt.) were dispersed in 15 mL of hydrogen peroxide (30%) by sonication. Then 0.7 mL of hydroxostannate solution (1.4 M) was added. Precipitation of peroxostannate onto the GO surface was accomplished by addition of 80 mL of ethyl alcohol. The coated GO was washed with ethyl alcohol and subsequently with diethyl ether and dried under vacuum at room temperature. The coated material was stored in a refrigerator.

Sulfurization of peroxostannate supported GO. Sulfurization was carried out by bubbling hydrogen sulfide for 2 h through a 100 mL stirred alcohol suspension of 500 mg peroxostannate supported GO. The peroxostannate-GO was taken wet after centrifugation

and contained some ethanol with residual hydrogen peroxide. Hydrogen sulfide gas was produced in a Kipp's apparatus from concentrated HCl and iron sulfide. At the end of the reaction the excess H₂S gas was collected by an alkali trap.

Preparation of GO-Sn-S-RT. After the sulfurization step the material was washed with alcohol, centrifuged, and dried in vacuum.

Preparation of GO-SnS₂-300. Heat treatment at 300°C for 5h of the GO-Sn(IV)-S powder was carried out in a tube furnace at 10⁻⁵ Pa pressure. Heating to the set point was conducted at a rate of 0.8 °C min⁻¹ to prevent loss of the products by carryover.

Characterization

High Resolution Transmission Electron Microscope. We used FEI Technai F20 G2 (Eindhoven, Holland) High Resolution Transmission Electron Microscopes. HRTEM imaging was performed at 200 kV. A drop of the suspension of the sample in ethanol was deposited onto 400 mesh copper grids covered with a lacy carbon net.

Scanning Transmission Electron Microscope. STEM imaging was performed at 20kV using a FEI Extra High Resolution Scanning Electron Microscope, MagellanTM 400L (Eindhoven, Holland). The specimen was prepared by deposition of a drop of the ethanol suspension of the sample onto 400 mesh copper grid.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra X-ray photoelectron spectrometer (Manchester, UK). High resolution spectra were acquired with a monochromated Al K α (1486.6 eV) X-ray source with 0° takeoff angle. The pressure in the test chamber was maintained at 1.7·10⁻⁹ Torr during the acquisition process. Data analysis was performed with Vision processing data reduction software (Kratos Analytical Ltd.) and CasaXPS (Casa Software Ltd.).

X-ray powder diffraction (XRD) measurements were performed on a D8 Advance Diffractometer (Bruker AXS, Karlsruhe, Germany) with a goniometer radius 217.5 mm, Göbel Mirror parallel-beam optics, 2° Sollers slits and 0.2 mm receiving slit. The powder samples were carefully filled into low background quartz sample holders. The specimen weight was approximately 0.5 g. XRD patterns from 5° to 65° 2 θ were recorded at room temperature using CuK α radiation ($k=1.5418\text{\AA}$) under the following measurement conditions: tube voltage of 40 kV, tube current of 40 mA, step scan mode with a step size 0.02° 2 θ and counting time of 1 s/step. XRD patterns were processed using Diffrac Plus software.

Gravimetric analysis of Sn content. A weighted amount of the graphene oxide supported material was heated in air to a temperature of 900°C in the TGA instrument. The fraction remained is only SnO₂ which allowed accurate (<3%) calculation of the tin loading.

Electrochemical Studies

Electrochemical evaluation was conducted for a sample annealed at 300°C in vacuum for 5 hours (rGO-SnS₂-300). In the following, we use the same nomenclature for the active electrode material and the anode that was made from it.

Electrochemical evaluation. Each of the different materials was mixed with acetylene black and carboxymethylcellulose sodium salt (CMC, Sigma-Aldrich) in a weight ratio of 6:2:2 with deionized water as the medium to form a slurry. The slurry was then coated on roughened copper foil as a current collector using a doctor's blade. The electrode was then dried at 80°C and pressed in a roll press. The electrodes were cut into 16 mm diameter discs and further dried at 110°C for 4 hrs in vacuum before being introduced into an argon-filled glove box. The electrodes were assembled with Na metal as counter electrodes in a 2016 coin cell. 1 M sodium perchlorate (NaClO₄) in propylene carbonate (PC) with 5% fluorinated ethylene carbonate (FEC) additive was used as electrolyte. Specific capacities recorded in this paper are calculated with respect to the mass of the SnS₂/GO composite (i.e. 60% of the electrode mass).

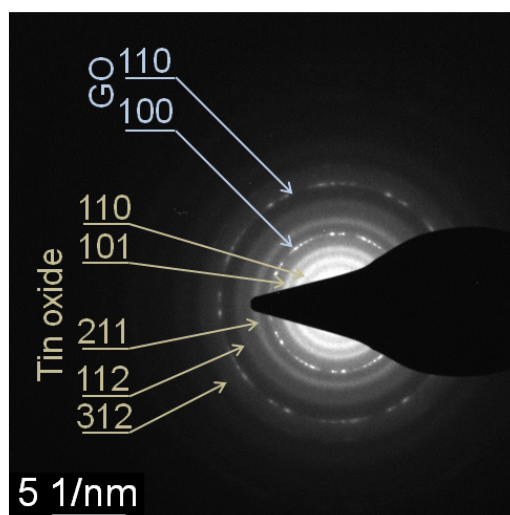


Figure S1. SAED of GO supported tin oxide (hydroperoxostannate coated graphene oxide before sulfidization).

Ex-situ XRD studies of NIB anodes at different potentials.

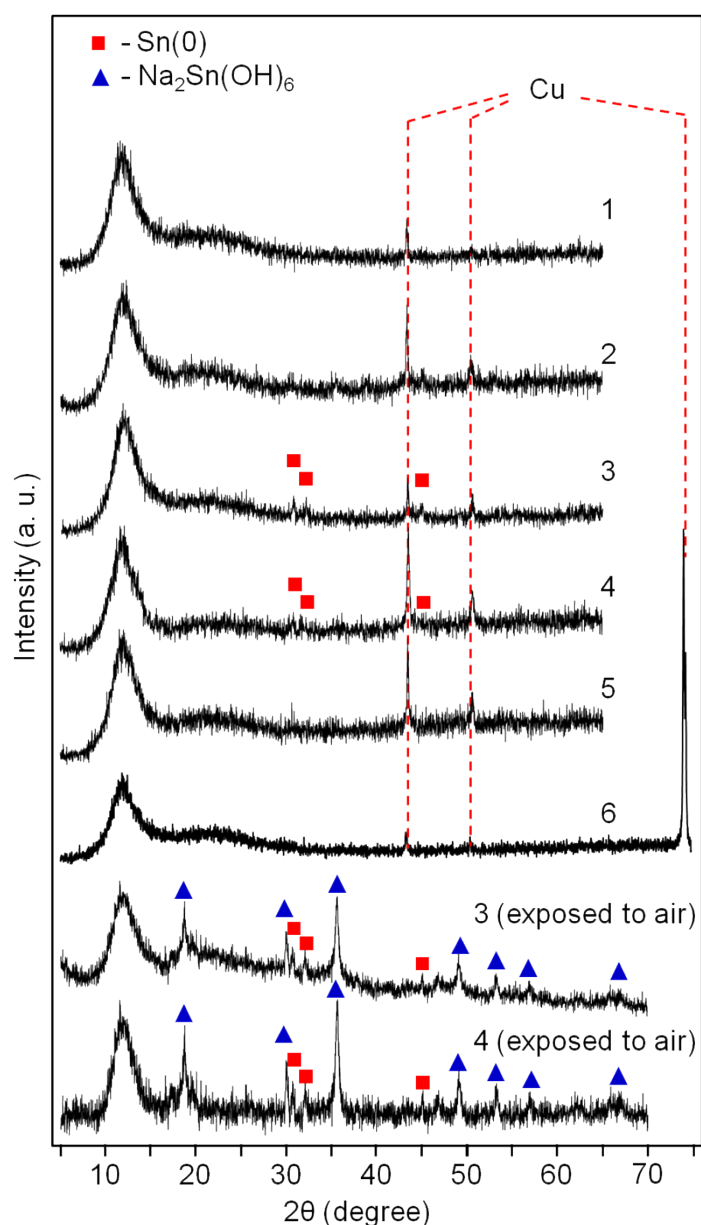


Fig. S2. XRD diffractograms of GO-SnS₂-300 anodes taken under the following electrochemical conditions: 1) First discharge at 0.5 V; 2) First discharge at 0. V; 3) After two cycles and discharge to 0 V; 4) After three cycles and then discharge to 0.5V; 5) After three cycles and then discharge to 2.5 V; 6) After 50 cycles and charging at a potential of 2 V (all voltages are vs Na/Na⁺). The cells were then disassembled in a glove box and the electrodes were immersed in Vaseline. XRD studies were carried out within less than 1 hr after removal from the glove box in order to minimize exposure to ambient humidity and oxygen.

The XRD did not show any sulfur containing crystalline phase in all electrodes. Electrodes 2 and 4 (at 0.5 V) show elemental tetragonal Sn crystallites.

The diffractograms marked by the labels "exposed to air" correspond to electrodes 3 and 4 after being taken off the copper support and exposure to air. Blue triangles correspond to sodium tin hydroxide, $\text{Na}_2\text{Sn}(\text{OH})_6$ space group R-3 (148). And the red squares correspond to tetragonal tin.

STEM Images of the cycled electrodes

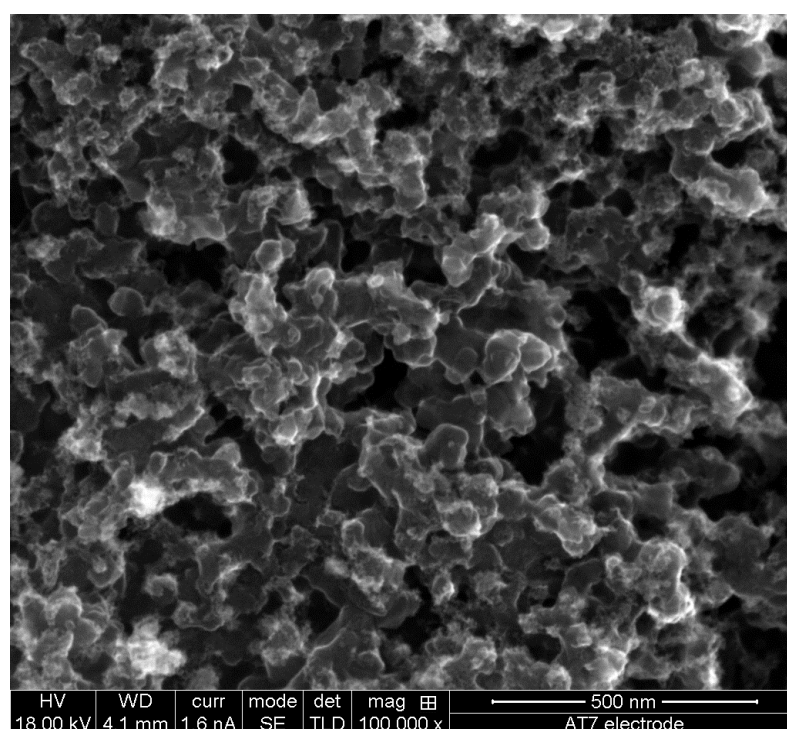


Fig. S3. STEM images of SnS_2 coated electrode after 30 cycles and charging at $E= 2. \text{ V}$. The images that dendrite growth does not take place.

Resistance Studies:

Table S1: Specific resistivity of the active anode materials.

Sample	Specific Resistivity, $\text{Ohm}\cdot\text{m}$
GO-Sn-S-RT	2.39
GO-SnS ₂ -300	0.028
GO-80	157.
GO-300	0.005

Specific resistivity values of graphene oxide supported tin sulfide before and after heat treatments at 300°C and bare graphene oxide exposed to 80°C and 300°C for 5 hrs are depicted in Table S1. The resistivity was measured on 100 mg of the different anode materials that were pressed at 6×10^6 Pa in a 20 mm² press (the results are corrected to the exact thickness of the different samples). The table shows that the GO in rGO-SnS₂-300 are reduced. The somewhat lower resistivity of the tin containing electrodes compared to the bare GO and rGO electrodes is attributed to the presence of the resistive coating.

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