Supplementary Information

Binder-free 3D SnO_2-based nanocomposites anode with high areal capacity for advanced sodium-ion batteries

Yangang Zhang, Zewei Wang, Yaohui Zhang, Kai Wang, Jiangchun Chen, Xuxu Guo, Jinlei Wu, Yuqi Xu, Jian Zhu, Hewei Zhao, Junfei Liang * and Hua Wang*

Materials and Methods

Synthesis of SnO_2 NSs/HGF.

Graphene oxide (GO) was prepared by oxidation of natural graphite flakes following a modified Hummers' method, and the solution-processable holey graphene oxide (HGO) was prepared using our reported approach.[1] Briefly, 5 mL of 30% H_2O_2 aqueous solution was mixed with 50 mL of 2 mg mL^{-1} GO aqueous dispersion and then heated at 100 °C under stirring for 2.0 hours. The as-prepared HGO was purified by centrifuging and washing to remove the residual H_2O_2 and then re-dispersed in deionized (D.I.) water. The HGO along with pristine GO sheets were used as building blocks for the synthesis steps described below.

The 3D SnO_2 NSs/HGF composites were prepared using a two-step process. Firstly, the SnO_2 NSs/graphene composites was synthesized using our reported approach with minor modification.[2] In a typical synthesis, a glycinesodium hydroxide buffer solution with pH ~2.2 was prepared by dispersing 0.188 g (2.5 mmol) glycine and 183 μL (2.2 mmol) concentrated hydrochloric acid in 8 mL deionized water and 42 mL ethylene glycol (EG). Then, GO sheets (5 mg) and tin chloride pentahydrate (0.25 mmol) were added and dispersed by ultrasound for 15 min. This solution was then incubated at 70 °C for 4 h under vigorously stirring. The precipitate was collected after centrifugation and carefully washed to clean out remnant salt and subsequently dried in a freezer dryer for 24 h. Next, the dried product was thermos treatment at 500 °C for 2 h under argon flow for two hours. Secondly, the resulting powder sample (SnO_2 NSs/graphene) was dispersed into HGO aqueous solution with magnetic stirring. Excess sodium ascorbate was added into this aqueous mixture and heated at 100°C for 2 hours to reduce the composites. The as-prepared 3D SnO_2 NSs/HGF composites were washed by D.I. water for six times to remove any impurities and cut into thin slices. After freeze-drying, the samples were annealed at 500°C under argon flow for two hours. As a comparison, the SnO_2 NSs/GF electrodes without nanopores on graphene sheets was obtained using the same two-step process by replacing holey graphene oxide (HGO) with GO aqueous solution.

Material Characterization.

The morphology and structure of materials were characterized by a SIGMA HD scanning electron microscopy (Carl Zeiss, Germany), transmission electron microscopy (TEM, Titan S/TEM FEI) and X-ray diffraction (XRD) (Panalytical X'Pert Pro X-ray Powder Diffractometer). Raman spectra were recorded on a RM 2000 Microscopic confocal Raman spectrometer (Horiba LABHR) using a 488 nm laser beam. Thermogravimetric analysis (TGA, PerkinElmer instruments Pyris Diamond TG/DTA) was conducted in air atmosphere from room temperature to 700 °C at a heating rate of 6°C min^{-1}.

Electrochemical Characterization.

The free-standing and binder-free SnO_2 NSs/HGF electrode composites were mechanically compressed and assembled into coin cells. These electrodes served as the working electrodes without any binders or conductive additives. The electrochemical properties were carried out by assembling 2025 coin cells in an argon filled glove box with water and oxygen content kept below 0.1 ppm, using sodium tablets as the counter and reference electrodes, and Whatman GF/F glass microfiber filters as the diaphragm. The LAND CT2001A battery test system was used for evaluating the rate and cycle performance of the prepared coin cells. Cyclic voltammetry (CV) was performed on the coin cells through the IVIUMSTAT electrochemical workstation from the Netherlands.

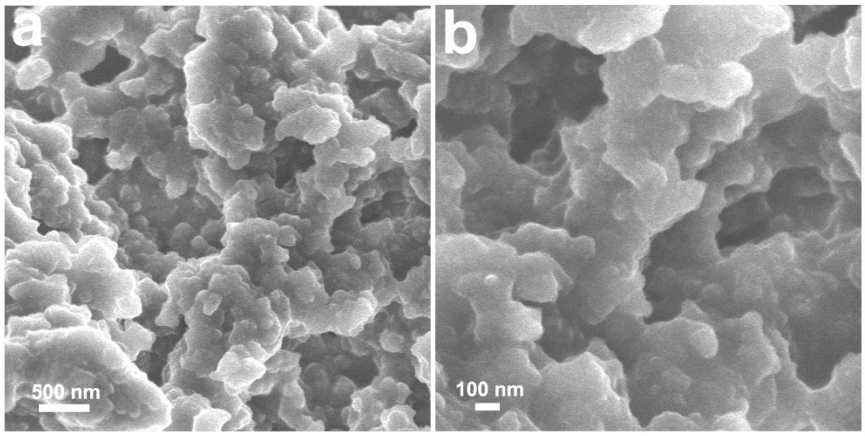

Fig. S1 Low-magnification (a) and high-magnification (b) SEM images of the SnO_2 NSs/HGF electrodes after charge/discharge cycles.

References

1 H. Sun, L. Mei, J. Liang, Z. Zhao, C. Lee, H. Fei, M. Ding, J. Lau, M. Li, C. Wang, X. Xu, G. Hao, B. Papandrea, I. Shakir, B. Dunn, Y. Huang and X. Duan, *Science,* 2017, **356,** 599.

2 H. Zhao, Y. Zhu, F. Li, R. Hao, S. Wang and L Guo, Angew. Chem. Int. Ed., 2017, 56, 8766.