

Supplementary Information:

Corn-like Graphene-SnO₂-carbon nanofibers composite as high-performance Li-storage material

Youlan Zou, Xiangyang Zhou, Jing Xie, Qunchao Liao, Bin Huang, Juan Yang*

Experimental section

Graphite oxide was first synthesized by a modified Hummers' method^{S1}. Then, 120mg of graphite oxide was dispersed into 150mL pure water by ultrasonication for 2h to get an exfoliated yellow-brown GO suspension A.

Typically, 0.5 mL of pyrrole monomer (Py) and 3.6 g of cetrimonium bromide (CTAB) were added into 100 mL 0.1 M HCl solution under ice bath. After being magnetically stirred for 0.5 h and cooled down to 0 °C, the ammonium persulfate (APS, 3.4 g) was added. The reaction was carried out at 0 °C for 5 h. A black precipitate was generated, rinsed and marked as B.

2.4g of tin (IV) chloride pentahydrate (SnCl₄·5H₂O) and product B were dissolved in suspension A and dispersed by ultrasonication for 0.5 h. Then, the solution was transferred to an airtight reactor and kept in an oven at 160 °C for 2.5 h. The black precursor was collected, rinsed, and vacuum-dried at 0 °C for 2 days. Then, the precursor was heat-treated at 600 °C for 2 h under Ar atmosphere with a temperature ramp of 5 °C min⁻¹. The as-prepared sample was designated as GSCN. For comparison, the bare SnO₂ sample was synthesized without the above-mentioned A and B added.

Scanning electron microscopy (SEM, JSM-6360LV, Japan) and transmission

electron microscopy (TEM, JEM-2100F, Japan) images were taken to characterize the morphologies and structures of the sample. X-ray diffraction (XRD) patterns were recorded on RigakuD/max-2550V X-ray diffractometer with Cu K α radiation. Laser Raman spectroscopy (OLYMPUS, BX41) with an excitation wave length of 488 nm by a KAr matrix was used to observe the type of carbonized sucrose. Fourier transform infrared spectra (FTIR, NICOLET6700) of powder samples diluted with KBr were recorded. The content of SnO₂ in the composite was determined using thermogravimetric analysis (TGA, SDTQ600) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) was introduced to determine the element content of the sample.

The GSCN electrode was prepared by mixing 80% sample, 10% carbon black, and 10% polyvinylidene fluoride (PVDF) and dissolving into N-methylpyrrolidinone (NMP) to form slurry, which was then coated onto a copper foil and dried overnight at 120 °C in a vacuum for 12 h. The coin cell was assembled in a glove box filled with pure argon (Super 1220/750, Shanghai Mikrouna Co. Ltd.). Metallic lithium was used as the negative electrode and counter electrode, 1mol/L LiPF₆/ethylene carbonate (EC)/diethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1, by volume) was used as electrolyte. Galvanostatic discharge/charge experiments were performed over a potential range of 3 V~0.01 V vs. Li⁺/Li using a LAND testing (CT-2001A, Wuhan Jinnuo Electron Co. Ltd.). Electrochemical workstation (Solartron 1470E, Solartron Metrology Co. Ltd.) was taken to measure the electrochemical impedance spectra (EIS) and the cyclic voltammograms (CV). CV experiment was

performed in the range of 3 V ~ 0.01 V vs. Li⁺/Li at a scanning rate 0.2 mVs⁻¹. Here the total weight of the samples were used to calculate the capacity values.

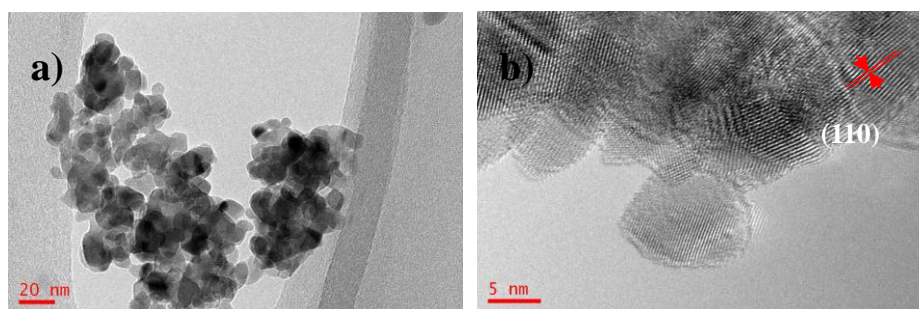


Fig. S1 TEM and HETEM images of SnO₂

Table S1. Elemental composition of GSCN

Element	Sn	O	C	N
Atomic %	7.01	15.07	71.48	6.44

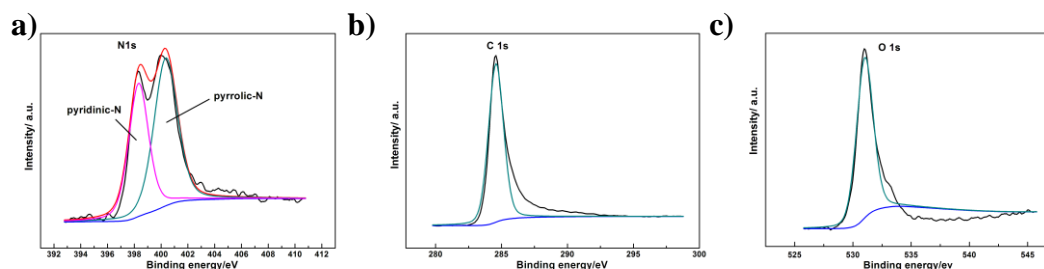


Fig S2. a) N1s , b) C1s and c) O1s, XPS spectra for GSCN.

Two peaks of GSCN(Seen in Fig. S2a) located in the interval 399.98 and 398.28eV are attributed to the pyrrolic-N and hexagonal pyridinic-N, respectively. The peak of C1s is mainly attributed to the graphene and carbon nanofibers. The O/Sn atomic ratio of the is 2.15 in this composite, which is a litter higher than the theoretical value of 2 for SnO₂. This observation indicates that most of oxygenated functional groups have

been removed after the hydrothermal process and subsequent thermal treatments, But a few residual functional groups are reported to be useful in obtaining stable, highly dispersed SnO₂ particles^{S2}.

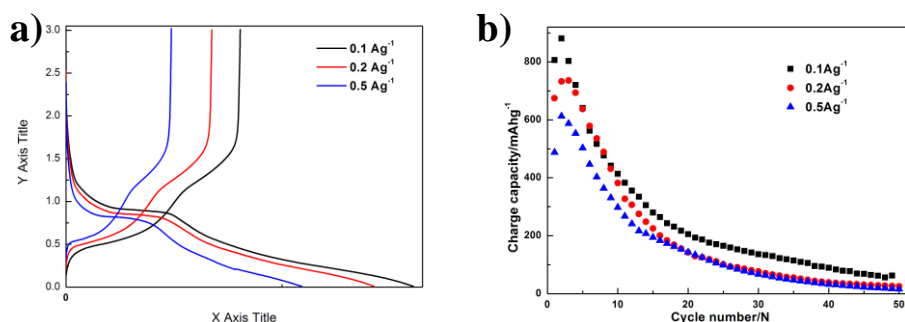


Fig.S3 a) Charge/discharge curves, b) cycle and rate performance of SnO₂ electrode at current densities of 0.1, 0.2 and 0.5Ag⁻¹.

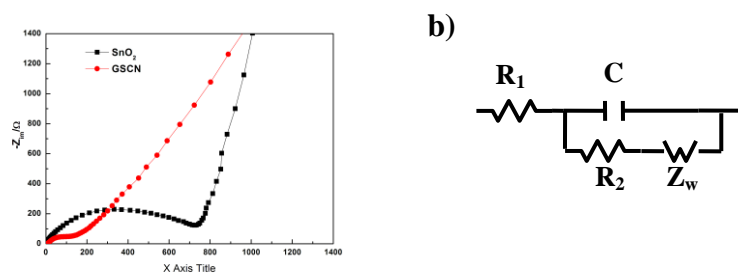


Fig.S4 a) Electrochemical impedance spectra and b) the corresponding equivalent circuit of the SnO₂ and GSCN anodes.

Fig.S4 shows the comparison of electrochemical impedance spectra (EIS) between the SnO₂ and GSCN electrodes. The measured impedance data were analyzed using the equivalent circuit, as shown in the inset of the figure. The data points from 100 kHz to 0.1 Hz were selected. The symbols R_s, R_{ct}, C_d and Z_w denote the solution resistance, charge transfer resistance, double layer capacitance and Warburg

impedance, respectively. The charge transfer resistance (R_{ct}) represents the kinetic resistance of charge transfer at the electrode-electrolyte boundary. The R_{ct} value is 122.6Ω for the GSCN electrode, which is much lower than 700.1Ω for the SnO_2 electrode. The 1D structure of the carbon nanofibers facilitate fast electronic conduction through the formation of 3D conductive networks. The presence of carbon nanofibers could also improve the capacity of graphene by expanding the distance between graphene sheets.

S1. L. Noerochim, J. Z. Wang, S. L. Chou, D. Wexler and H. K. Liu, *Carbon*, 2012, **50**, 1289.

S2 L.S. Zhang, L.Y. Jiang, H.J. Yan, W.D. Wang, W. Wang and W.G. Song, *J. Mater. Chem.*, 2010, **20**, 5462.