Supporting information

Porous silicon nano-aggregate from silica fume as anodes for highenergy lithium-ion battery

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Experimental section Material Synthesis

Synthesis of Mg₂Si: Mg₂Si was prepared following a literature (*Chem. Commun.* 2015, 51, 7230). Typically, 2.0 g of Mg and 1.0 g of bulk Si were mixed and moved into a tube furnace. Subsequently, the tube furnace was maintained at 500 °C for 5 hours under an Ar atmosphere and cooled to room temperature to obtain the Mg₂Si.

Synthesis of SNC: the as- prepared Mg₂Si powder and silica fume ($\sim 96\%$ SiO₂) with a molar ration of 1:1 were mixed and moved into a tube furnace. The tube furnace was heated to 650 °C with a heating rate of 5 °C min⁻¹ under an Ar atmosphere. And then, the as-obtained sample was immersed in hydrochloric acid (2M) for several hours. Subsequently, the khaki precipitate was collected by centrifugation, washed with deionized water and ethanol and dried at 70 °C for 12 h in a vacuum oven.

Materials Characterization

The product morphology was examined using scanning electron microscopy (SEM, JEOL-JSM-6700F), Transmission electron microsocopy (TEM, Hitachi H7650 and HRTEM, JEOL 2010). Crystallographic information of the product was performed on a Philips X' Pert Super diffract meter with Cu K α radiation (λ =1.54178 Å). The pore size and specific surface area of the sample were measured by Brunauer-Emmett-Teller analyzer (BET; Micromeritics ASAP 2020) at 77 K. The information of Raman spectrum was collected using a Spex 1403 Raman spectrometer. The surface composition of the sample was examined by X-ray photoelectron spectroscopy (XPS; ESCA-Lab MKII X-ray photoelectron spectrometer), using Mg K α X-ray as the excitation source. The conductivity of the PSNA is measured by voltammetry (Keithley 2410).

Electrochemical measurements

The electrochemical properties of PSNA electrodes were measured under ambient temperature with coin-type half cells (CR2016) which were assembled under an argon-filled glove box (H₂O, O₂ < 1 ppm). The working electrode was prepared by mixing the PSNA material, Carboxyl Methyl Cellulose (CMC) and super P carbon black in a 6:2:2 weight ratio in water solvent. The mixture slurry was pasted onto a Cu foil and then dried at 80 °C for 10 h in a vacuum oven. The mass loading of nanosilicon active material for each electrode was determined to be 0.6-0.8 mg/cm². The counter electrode was metallic Li sheet, and the electrolyte used was 1 M LiPF6 in a mixture of ethylene carbonate and dimethylcarbonate (1:1 by Volume, Zhuhai Smoothway Electronic Materials Co., Ltd (China)). Cyclic voltammetry (CV) was performed on a electro-chemical workstation (CHI660D), with a scanning rate of 0.1 mV s⁻¹ at room temperature. The charge-discharge measurements were performed using a LAND-CT2001A instrument at room temperature that was cycled between 0.005 V and 1.50 V (vs. Li⁺/Li).



Figure S1. The SEM images of silica fume and Mg₂Si.



Figure S2. The XRD pattern of Mg₂Si.



Figure S3. The voltammetric curve of the specimen.

$R = \Delta E / \Delta I$	(1)

 $\rho = R A / b$ (2)

(3))
3	

 $\sigma = \Delta I b / \Delta E A$ (4)

$$E_1 = -5 V$$
, $I_1 = -1.61 \times 10^{-4} A$; $E_2 = 5 V$, $I_2 = 1.62 \times 10^{-4} A$;

$$b = 1.02 \times 10^{-3} \text{ m}; \text{ A} = 8.41 \times 10^{-6} \text{ m}^2$$

R is the electrical resistance of a uniform specimen of the material (measured in ohms, Ω)

b is the thickness of the specimen (measured in metres, m)

A is the cross-sectional area of the specimen (measured in square metres, m²).

ρ is the electrical resistivity

 σ is the conductivity

The conductivity of the PSNA is as follows:

$$\sigma = (1.62 \times 10^{-4} \text{ A} + 1.61 \times 10^{-4} \text{ A}) \times 1.019 \times 10^{-3} \text{ m} / (5 \text{ V} + 5 \text{ V}) \times 8.41 \times 10^{-6} \text{ m}^2$$

$$= 3.92 \times 10^{-3} \text{ S} / \text{m}$$