Supplemental Information

Self-Assembled Porous-Silica within N-Doped Carbon Nanofibers as Ultra-flexible Anodes for Soft Lithium Batteries

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Figure S1. Morphology and particle size distribution of the synthesized p-SiO$_2$ NPs, related to Figure 1(b).

(a-c) SEM and TEM images of the synthesized p-SiO$_2$ NPs in different magnifications and, (d) the particle diameter distribution histogram. The particles had well-distributed nano-pores and uniform particle sizes. The average particle size was calculated as 108 nm.
Figure S2. Pore size distribution of the synthesized p-SiO$_2$ NPs and p-SiO$_2$ @N-CNFs, related to Figure 2(b) and Table S1.

Testing curves of pore size distributions and pore volumes in the synthesized p-SiO$_2$ NPs and p-SiO$_2$ @N-CNFs. Analyses were based on the method of 2-D nonlocal density functional theory (2D-NLDFT). Two models of (a) NLDFT and (b) BJH were used to calculate the pore volumes and the total pore volumes, as summarized in Table S1.
Figure S3. TG analysis of the p-SiO$_2$@N-CNF in air atmosphere, related to Figure 3.

The test started from room temperature to 650 °C at a heating rate of 5 °C min$^{-1}$. The content of SiO$_2$ was calculated as follows: wt.% = $\frac{36.12}{95.75} = 37.7\%$.

Figure S4. p-SiO$_2$@N-CNF under various deforming states, related to Figure 3.

(a) Digital photos of the anodes of p-SiO$_2$@N-CNF under various bending, rolling and deforming states. (b) The corresponding cross-sectional SEM images with diverse angles of the nanofibrous membranes. There were not obvious cracks after deforming.
Figure S5. SEM images of the different anodes, related to the figure 3(a).

SEM images of (a) the pure CNFs, (b) the SiO$_2$@N-CNFs and (c) the p-SiO$_2$@N-CNFs with digital photo images under bending states; (d-f) statistical analysis of their corresponding NF diameter histograms.
Figure S6. FTIR spectra of indicating the CTAB removal and p-SiO$_2$ loadings on the N-CNFs, related to Figure 3.

FTIR spectra of the p-SiO$_2$ NPs without calcination, p-SiO$_2$@N-CNF and the pure N-CNFs. The peaks at 460, 967, 1107 cm$^{-1}$ were assigned for the Si-O rocking vibration, Si-O bond stretching and internal Si-O-Si stretching vibrations, respectively. The twin peaks at 2331, 2361 cm$^{-1}$ were attributed to the presence of SiO$_2$ on the N-CNFs, which were not observed in the pure CNFs. For the pure N-CNFs, the obvious peak at 1620 cm$^{-1}$ was attributed to C=C and C-O bonds, and the peak at 3440 cm$^{-1}$ was assigned for the primary and/or the secondary N-H stretch and O-H stretch. It is worthy note that the disappearance of the absorption peak at 2922 cm$^{-1}$ in p-SiO$_2$@N-CNF revealed that CTAB was completely removed (Hao et al., 2016; Jing et al., 2011).
Figure S7. The cross-section morphology and TEM of the fabricated anodes, related to Figure 3(e).

(a) The cross-section FE-SEM images of the SiO$_2$@N-CNF, in which most of the NPs located out of the NFs. (b-d) TEM images of the p-SiO$_2$@N-CNF to show the in-situ formed graphitic and amorphous carbon domains over p-SiO$_2$ NPs.
Figure S8. The 1st voltage profiles of the p-SiO$_2$@N-CNF, related to Figure 5(c).

The low initial Coulombic Efficiency was probably caused by the irreversible reactions between Li-ions and SiO$_2$ to form silicon as follows (Guo et al., 2008):

1st Lithiation reactions with different proportions (irreversible reactions)

\[ \text{SiO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow 2\text{Li}_2\text{O} + \text{Si} \]

Or

\[ 2\text{SiO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Li}_4\text{SiO}_4 + \text{Si} \]

While; from the 2nd cycle, the lithiation reactions are as follows

\[ \text{Si} + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li}_x\text{Si} \]
Figure S9. Postmortem analysis of the anodes of SiO$_2$@N-CNF, related to Figure 5(c).

The FE-SEM images of the anodes of SiO$_2$@N-CNF (a) before and (b) after 500 cycles at 1 C; (c, d) the corresponding NF diameter histograms. The commercial SiO$_2$ NPs caused a large NF diameter change from 305 nm to 529 nm, corresponding to 1.73 times of expansion.
Figure S10. Postmortem analysis of the anodes that were fabricated by physically mixing p-SiO$_2$ NPs with N-CNF, related to Figure 5(c).
Characterizations of the anodes comprising 38 wt.% of p-SiO$_2$, 52 wt.% of CNFs and 10 wt.% percent of PVDF binder. After 500 cycles, multiple large cracks were formed on the surface of the anodes due to volume changes of SiO$_2$ during the lithiation and delithiation processes.
Figure S11. Performance of the anodes of SiO$_2$@N-CNF, related to Figure 5.

Cycling performance of batteries (Li/SiO$_2$@N-CNF) at (a) 0.1 C and (b) 1 C. The batteries had a fast capacity fade rate and a low Coulombic efficiency.
Figure S12. Performance of the anodes of p-SiO$_2$@N-CNFM that were assembled in soft batteries, related to Figure 5(e).

The 2$^{\text{nd}}$ and the 500$^{\text{th}}$ Galvanostatic charge-discharge profiles of the composite anodes of p-SiO$_2$@N-CNFM under a bending state of 90 degrees at a discharge rate of 1 C.
Figure S13. Scalable fabrication of the membranes, related to Figure 5.

(a) The digital photo of the as-spun membrane with a size of 70 cm x 55 cm. Before heating these membranes to carbon, we cut the membranes into small pieces due to the limited furnace space in our lab. (b) The divided membrane of p-SiO$_2$@N-CNF and (c) the corresponding punched free-standing anodes.

Figure S14. Robust flexibility of the anodes of p-SiO$_2$@N-CNF, related to Figure 5.

SEM images of the composite anode of p-SiO$_2$@N-CNF under applied bending forces with two different magnifications
Supplementary Table

Table S1. The pore texture parameters of SiO$_2$ NPs and p-SiO$_2$ @N-CN, related to Figure 2(b).

| Samples       | $(V_t)$ (cm$^3$/g) | $(V_{meso})$ (cm$^3$/g) | $(PVF_{meso})$ (%) |
|---------------|--------------------|-------------------------|---------------------|
| p-SiO$_2$ NPs | 0.8678             | 0.4887                  | 56.31               |
| p-SiO$_2$@N-CN | 0.3457             | 0.106                   | 30.66               |

$(V_t)$: the total pore volume
$(V_{meso})$: the Mesoporous pore volume,
$(PVF_{meso})$: the fraction ratio of the mesopore volume to the total pore volume;
calculation based on Barret-Joyner-Halenda (BJH) model (Ge et al., 2016).

Transparent Methods

Materials

Polyacrylonitrile (PAN, Mw = 90000) was purchased from Spectrum Chemicals & Laboratory Products Co., Ltd, USA. N,N-Dimethyl formamide (DMF), absolute ethanol (EtOH, 99.5%), hydrochloric acid (HCl, 37%) and Sodium Hydroxide (NaOH) were obtained from the Shanghai Chemical Reagents Co., Ltd, China. Tetraethoxysilane (TEOS) and cetyltrimethyl ammonium bromide (CTAB) were supplied by Macklin Biochemical Co., Ltd, China. Commercial SiO$_2$ NPs (particles diameter ~100 nm) was provided from Aladdin Chemistry Co. Ltd, China. Deionized (DI) water produced by a Water Purification System (UPT-11-20T) was used during this work. All chemicals possess an analytical grade and were used without further purification.

Synthesis of p-SiO$_2$ NPs

Typically, as described previously, 1 mg of CTAB was stirred in 480 ml of DI H$_2$O and then 3.5 ml of 2 molar solution of NaOH were added and stirred vigorously at 80ºC. Subsequently, TEOS (5 ml) was drop-wise added to the mixture and the
resultant was then kept under stirring for 2 hours. Subsequently, a white precipitate was separated via the vacuum filtration. Finally, a white precipitate of p-SiO$_2$ NPs containing CTAB template was obtained and then dried at 100 °C overnight under vacuum. For comparative analysis, to get the non-containing CTAB porous particles, the obtained dried white precipitate was washed for several times with EtOH and DI-H$_2$O alternatively, and a step of calcination to remove the CTAB template was done in a muffle furnace at 550 °C for 5 hours in air atmosphere.

**Fabrication of self-interlocked p-SiO$_2$@N-CNF membranes**

An appropriate amount of p-SiO$_2$ NPs was dispersed homogenously in Dimethyl formamide (DMF) for 2 h by using a powerful ultrasonic bath. Next, PAN powder (10 wt %) was added to the suspensions and was stirred for 8 hours and then was ultra-sonicated for 2 hours at room temperature. The electrospinning process was then carried out with a rate of 1.2 mL/h, a voltage of 25 kV and a distance of 20 cm between the needle head and the rotating collector. The temperature and humidity in the electrospinning chamber were controlled at 25±5 °C and 50±5%, respectively. The as-spun PAN NFs were dried at 70 °C for 1 hour under vacuum to completely remove the remaining DMF. The films were then thermally treated at 280 °C for 2 hours with air cycling to remove CTAB while simultaneously pre-oxidizing PAN. Lastly, the films were annealed under high purity nitrogen (99.999%) at 800 °C for 2 hours. Similarly, the pure CNFs and commercial SiO$_2$@N-CNF were prepared with the same procedures.

**Material Characterizations**

Morphology and element distribution of the samples were checked by SEM (S-4800) and TEM (JEM-2100F), while crystallographic structures were tested by Bruker XRD (with Cu K$_\alpha$, $\lambda=1.5406$ Å) and Raman (inVia-Reflex). The specific surface areas, the mesopore sizes and the pore volumes were examined by an automatic adsorption system analyzer (ASAP 2020, Micromeritics Co., USA) with both Brunauer-Emmett-Teller (BET) model and Barrett-Joynes-Halenda (BJH) model. Moreover, bonding spectrum in the NFs was tested by FTIR (Nicolet iS8). X-ray
photoelectron spectroscopy (XPS) was tested in a vacuumed chamber using (X-ray ThermoFischer, ESCALAB 250 Xi) with a monochromatic source Al-Kα (1486.6 eV). SiO₂ contents were determined by TGA (SDT Q600) heated from room temperature to 650 °C with a ramp rate of 5 °C min⁻¹. The softness of the NF membranes was assessed by a softness tester (RRY-1000) according to the standard of ASTM D 2923-06. The tensile mechanical properties of the NF membranes were measured by a tensile tester (XQ-1A) according to the international standard (ISO 1798:2008).

**Soft battery assembly and electrochemical measurements**

CR2025-type coin cells were assembled with the ring Li-foils (thickness of 20 μm and a diameter of 1.65 cm) or LiFePO₄ (containing 80 wt. % of LiFePO₄, 10 wt. % of PVDF and 10 wt. % of carbon black) as counterpart electrodes and Cellgard 2400 microporous membranes as separator. Soft batteries with a transparent PET (as battery cases) were also assembled. In both types of batteries, 1M LiPF₆ in ethylene carbonate, diethyl carbonate and ethyl methyl carbonate (EC: DEC: EMC = 1: 1: 1 v/v) was used as an electrolyte. All the cells were assembled within an Ar-filled Mikrouna lab glove box. For post-mortem examinations, the batteries disassembled in the Ar-filled gloves box and the electrodes were saved in Ar-filled bottles before testing. Electrochemical measurements were performed galvanostatically for charging and discharging between 0 and 3.0 V at various current densities using LAND-CT2001A battery testing system. Cyclic voltamograms (CV) were conducted using an electrochemical workstation (Chenhua, CHI 660E, Shanghai) at a scan rate of 0.1 mV/s. Meanwhile, the electrochemical impedance spectroscopy (EIS) was carried out employing the same electrochemical workstation in a frequency range between 100 kHz and 100 m Hz at potentiostatic signal amplitude of 10 mV. All experiments were conducted at room temperature.

**Supplementary References**
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