

## Supporting Information

### **Direct construction interconnected Si<sub>3</sub>N<sub>4</sub> nanowires networks for enhancing thermal conductivity and mechanical performance of flexible composite films**

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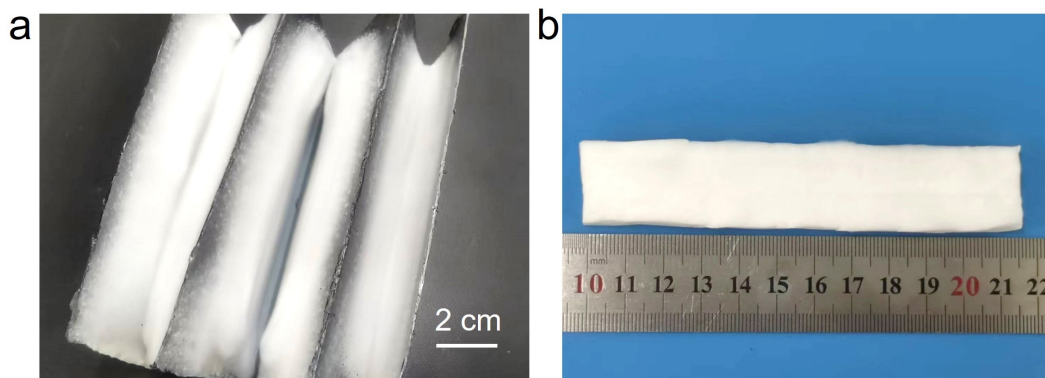
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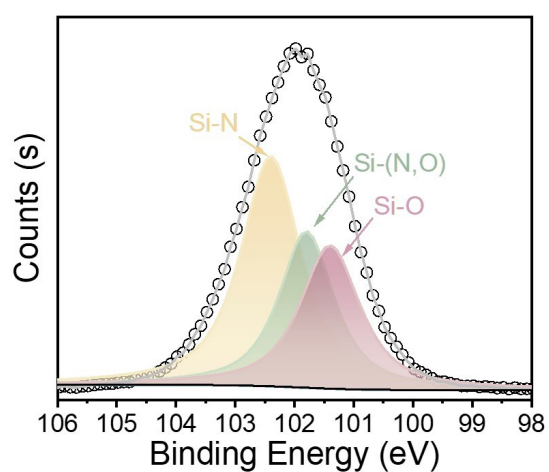
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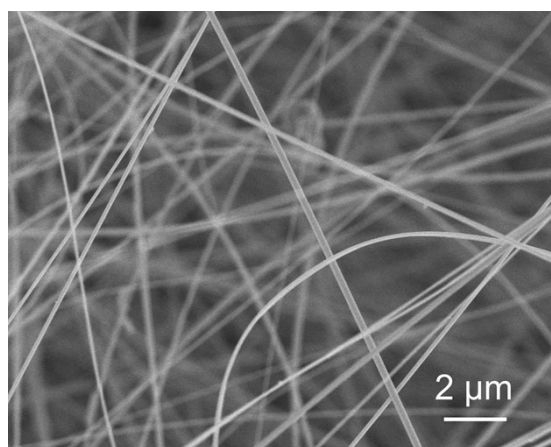
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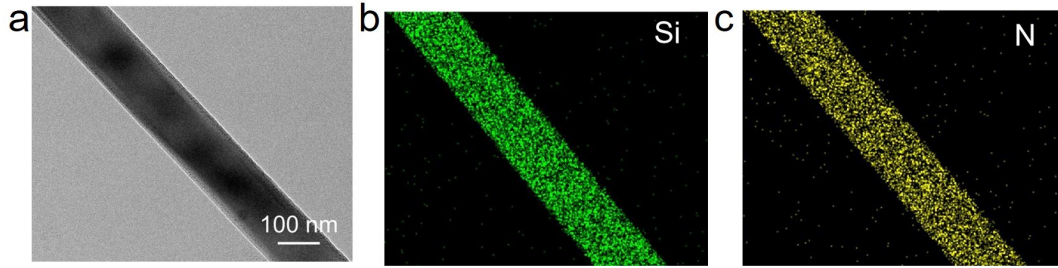
**Fig. S1** (a) Digital pictures showing the Si<sub>3</sub>N<sub>4</sub>NWs grown on the substrate of carbon paper; (b) digital picture of a large piece of Si<sub>3</sub>N<sub>4</sub>NWs paper after detaching.



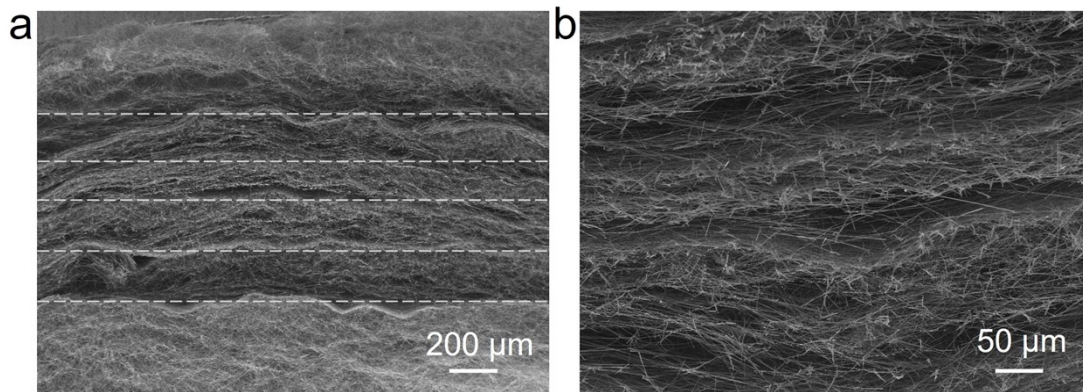
**Fig. S2** High-resolution XPS spectrum of Si 2p.



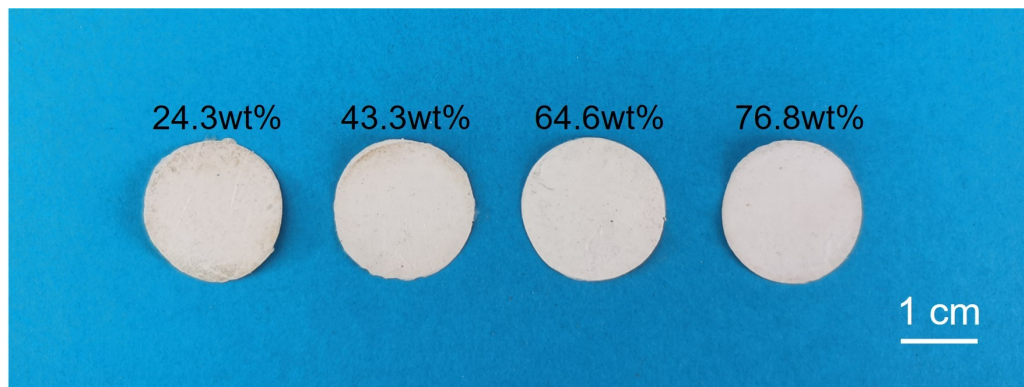
**Fig. S3** SEM image of the as-synthesized Si<sub>3</sub>N<sub>4</sub>NWs paper.



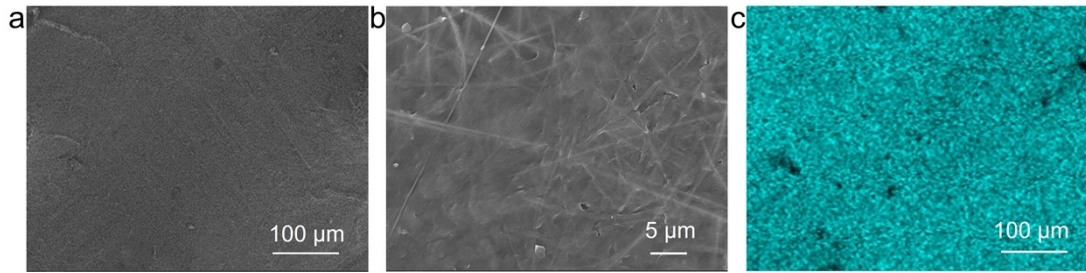
**Fig. S4** (a) TEM image of single Si<sub>3</sub>N<sub>4</sub>NW; corresponding EDS mapping images of (b) Si and (c) N elements.



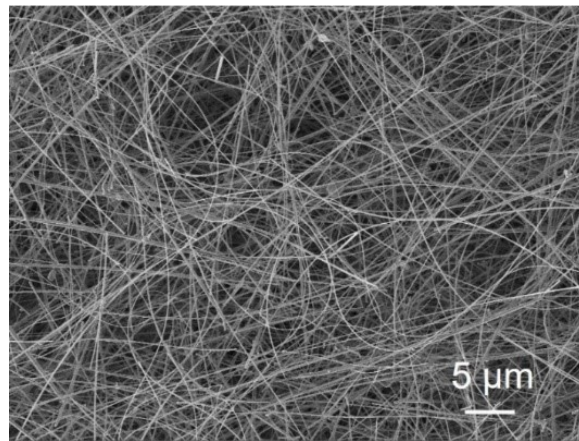
**Fig. S5** Cross-sectional SEM image of the six-layer stacked Si<sub>3</sub>N<sub>4</sub>NWs paper under different magnifications: (a) 100×, (b) 500×.



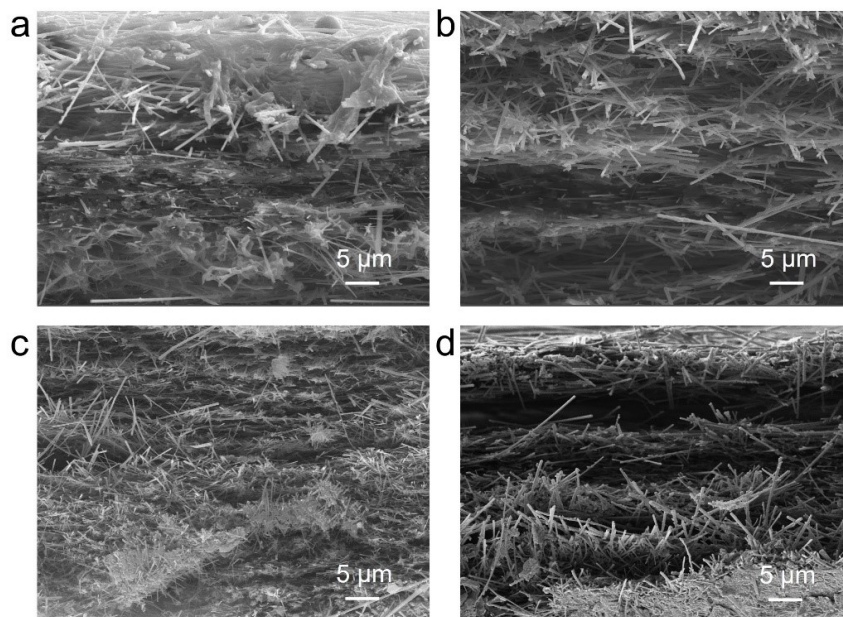
**Fig. S6** Digital pictures of various Si<sub>3</sub>N<sub>4</sub>NWs/EP composite films with different filling fractions.



**Fig. S7** (a-b) SEM images at different magnifications and (c) Si elemental distribution on the surface of the 64.6L-Si<sub>3</sub>N<sub>4</sub>NWs/EP composite film.

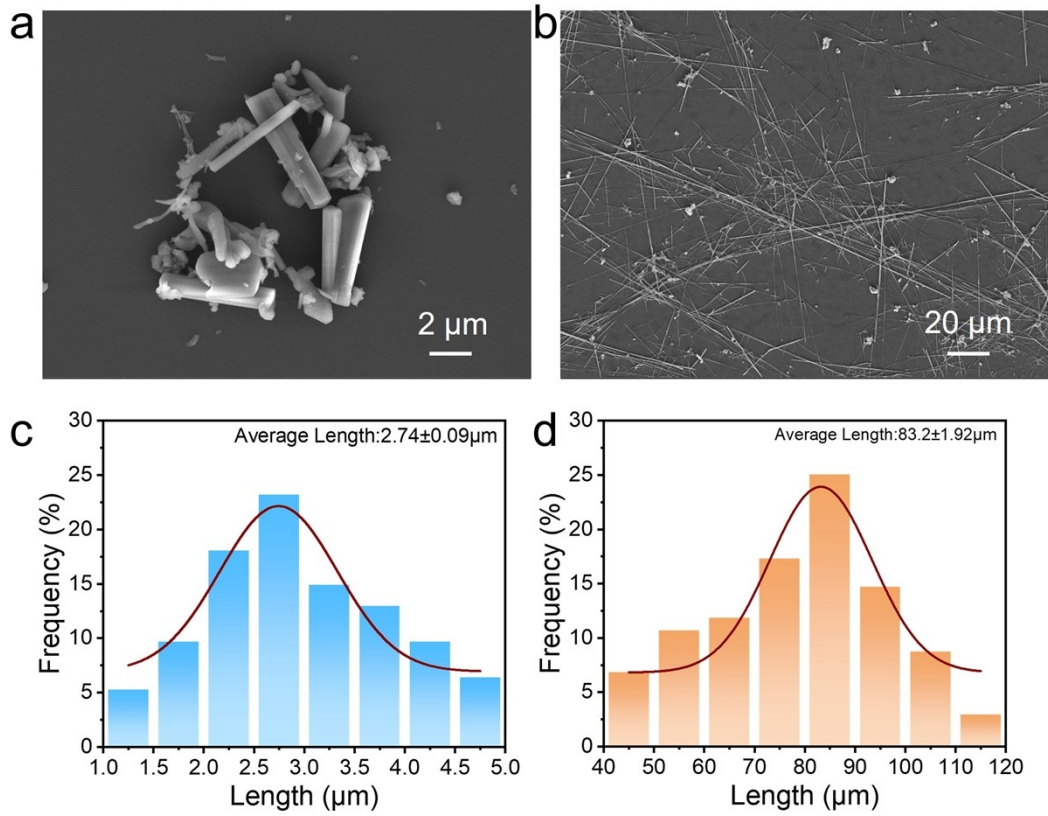


**Fig. S8** SEM image of the residual Si<sub>3</sub>N<sub>4</sub>NWs skeleton of the composite film after heat treatment at 800 °C for 2 h in air atmosphere.



**Fig. S9** SEM images of fracture surfaces of composite films with different Si<sub>3</sub>N<sub>4</sub>NWs filling fraction: (a) 24.3 wt%; (b) 43.3 wt%; (c) 64.6 wt%; (d) 76.8 wt%.





**Fig. S10** SEM images and length distribution of Si<sub>3</sub>N<sub>4</sub>Ps and S-Si<sub>3</sub>N<sub>4</sub>NWs:

(a,c) Si<sub>3</sub>N<sub>4</sub>Ps; (b,d) S-Si<sub>3</sub>N<sub>4</sub>NWs.

**Tab. S1** Density and porosity of *x*L-Si<sub>3</sub>N<sub>4</sub>NWs/EP composite films

Composite films samples	Calculated density (g/cm <sup>3</sup> )	Measured density (g/cm <sup>3</sup> )	Porosity (vol%)
24.3L-Si <sub>3</sub> N <sub>4</sub> NWs/EP	1.4255	1.3778	3.14
43.3L-Si <sub>3</sub> N <sub>4</sub> NWs/EP	1.7052	1.5521	8.97
64.6L-Si <sub>3</sub> N <sub>4</sub> NWs/EP	1.9244	1.7341	9.89
76.8L-Si <sub>3</sub> N <sub>4</sub> NWs/EP	2.3455	1.4246	39.11

**Tab. S2** Comparison of the comprehensive performance between the as-prepared 64.6L-Si<sub>3</sub>N<sub>4</sub>NWs/EP composite film and some previously reported composite films.

Composites	In-plane TC (W·m <sup>-1</sup> ·K <sup>-1</sup> )	Through-plane TC (W·m <sup>-1</sup> ·K <sup>-1</sup> )	Tensile stress (Mpa)	Tensile strain (%)	Volume resistivity (Ω·cm)	References
AlN/ UHMWPE	7.12	1.93	16.8	/	/	2023 <sup>[S1]</sup>
PVDF/BN/PW	0.52	/	/	/	1.89×10 <sup>5</sup>	2024 <sup>[S2]</sup>
NH <sub>2</sub> -rGO/ PI	7.13	0.74	35.7	/	/	2021 <sup>[S3]</sup>
Si <sub>3</sub> N <sub>4</sub> NWs/PVA	15.4	1.52	3.4	/	/	2023 <sup>[S4]</sup>
Si <sub>3</sub> N <sub>4</sub> NWs/EP	16.02	2.21	37.3	10.17	6.68×10 <sup>9</sup>	This work

[S1] S. Wan, X. Hao, C. Yu, M. Li, Z. Zhao, L. Zhu, W. Xuan, M. Yue, W. Cao and Q. Wang, *Ceram. Int.*, 2023, 49, 35094-35103.

[S2] K. Ruan, Y. Guo, C. Lu, X. Shi, T. Ma, Y. Zhang, J. Kong and J. Gu, *Research*, 2021, 2021: 8438614.

[S3] X. Zhang, K. Sun, H. Liu, J. Chen, X. Yan, Y. Kou and Q. Shi, *Nano Energy*, 2024, 121, 109256.

[S4] S. Wan, X. Hao, L. Zhu, C. Yu, M. Li, Z. Zhao, J. Kuang, M. Yue, Q. Lu, W. Cao, and Q. Wang, *ACS Appl. Mater. Interfaces*, 2023, 15, 32885-32894.