Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary Information

Nucleation-density-regulated dimensional evolution of growth unit from 2D nanosheets to 1D nanoneedles in self-assembled hierarchical $NiCo_2O_4$ for enhanced lithium storage

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Table S1 The pore volume, pore average diameter and surface area of 1D-Nanoneedles Self-Assembled Hierarchical flower (1D-Nanoneedles-SAHF) and 2D-nanosheets Self-Assembled Hierarchical flower (2D-Nanosheets-SAHF).

Materials	Pore volume ($cm^3\ g^{-1}$)	Pore average Diameter (nm)	Surface Area ($cm^3\ g^{-1}$)
1D-nanoneedles-SAHF	0.323	12.606	53.578
2D-nanosheets-SAHF	0.171	12.467	40.797

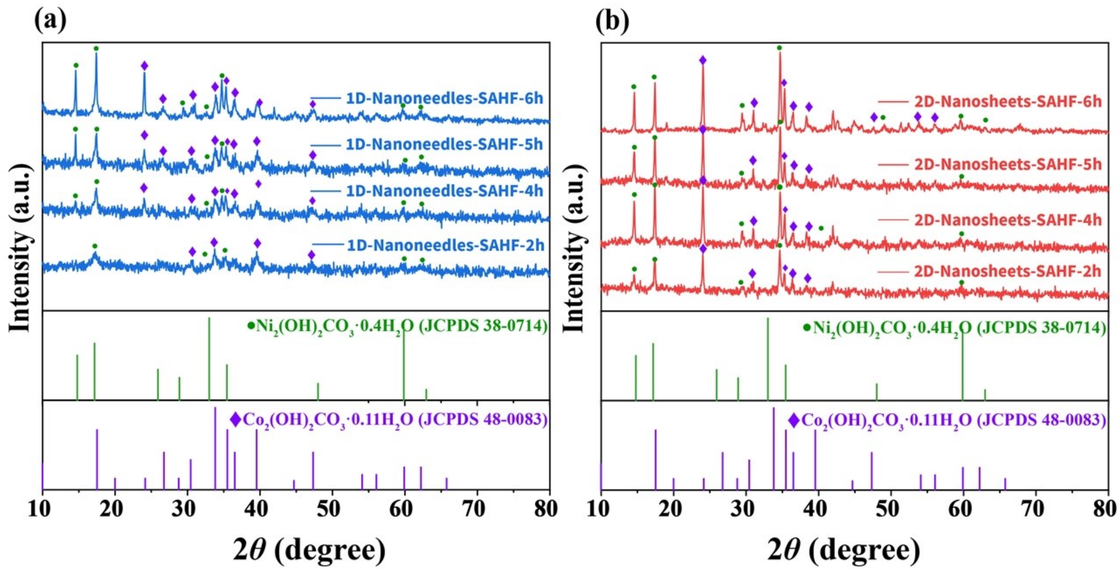

Fig. S1 XRD patterns of precipitated products before calcination for 1D-Nanoneedles-SAHF (a) and 2D-Nanosheets-SAHF (b) with different hydrothermal reaction times (2h, 4h, 5h, 6h).

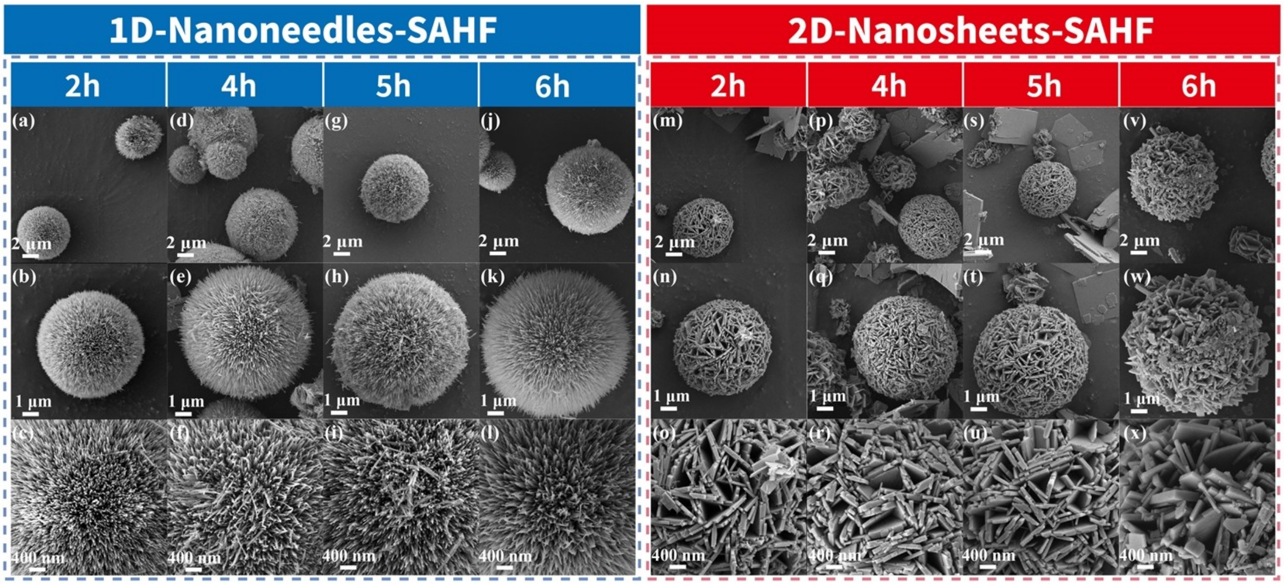

Fig. S2 SEM characterizations of precipitated products before calcination for 1D-Nanoneedles-SAHF(a-c)2h;(d-f)4h;(g-i)5h;(j-l)6h, and 2D-Nanosheets-SAHF(m-o)2h; (p-r) 4h; (s-u) 5h; (v-x) 6h.

Table S2 Comparison of reported cycling performance of Ni-Co oxides.

Materials	Material morphology	Current Density ($A\ g^{-1}$)	Cycle Number	Specific Capacity ($mAh\ g^{-1}$)	Capacity Retention (%)
This work	1D-Nanoneedles-Self-Aseembled Hierarchical Flower	0.2	200	1660.93	116.46
$NiCo_2O_4$	Nanorods	0.1	100	1046.7	68.73
$NiCo_2O_4$	Hollow multishelled	0.15	100	1550	35.76
$NiCo_2O_4$	Nanofibers	0.1	120	926.2	77.87
$NiCo_2O_4$	Nanocage	0.2	200	793	87.81
$NiCo_2O_4$/Carbon	Nanoclusters	0.1	200	1103	76.76
NiCo- $NiCo_2O_4$/C	Nanoparticles	0.1	100	720	87.34
$NiCo_2O_4$/NiO	Hollow microspheres	0.1	100	659	83.97
$NiCo_2O_4$/Carbon	Nanowires	0.1	200	1016.7	99.19
$CoSnO_3$@ $NiCo_2O_4$	Multi-shell hollow structure	0.1	100	992	64.08
$NiCo_2O_4$/Carbon	Mesoporous	0.05	120	473.7	93.17
$NiCo_2O_4$/V_2O_3	3D micro nanostructured porous	0.1	200	1155.6	106.3
Mo-doped $NiCo_2O_4$	Porous spheres	0.1	200	1360	101.6
$NiCo_2O_4$/g-C_3N_4	Porous nanoparticles	0.1	100	1252	77.52

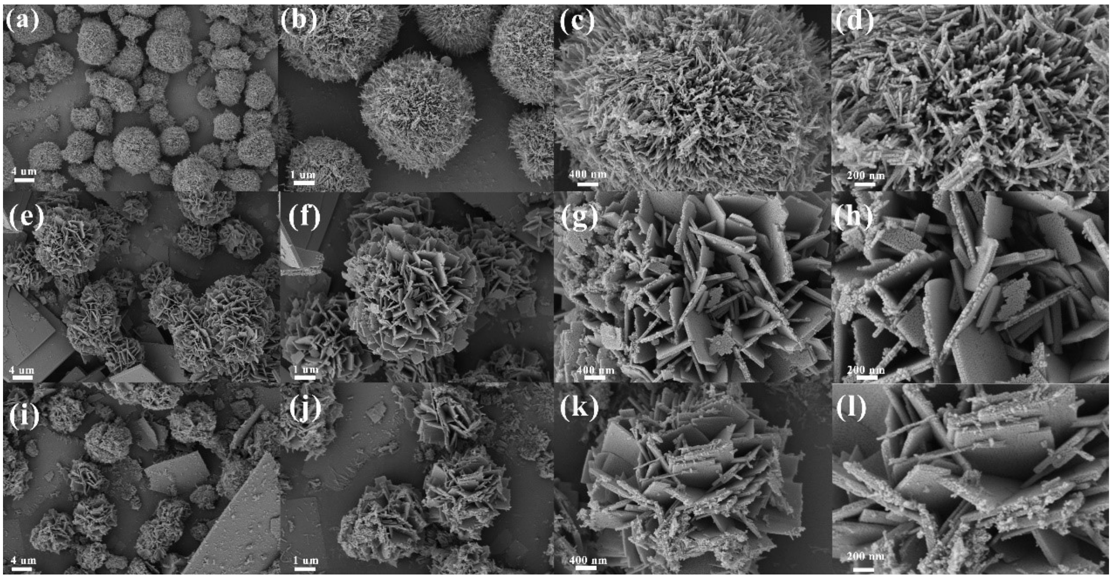

Fig. S3 SEM images of different urea concentrations: (a-d) 0.2 mol L^{-1}, (e-h) 0.6 mol L^{-1}, (i-l) 1.0 mol L^{-1}.

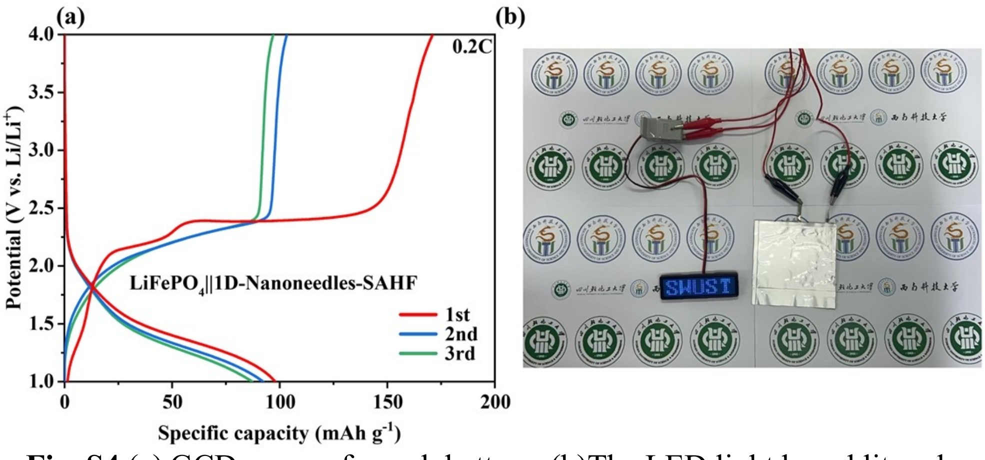

Fig. S4 (a) GCD curve of pouch battery. (b)The LED light board lit up by the $LiFePO_4$||1D-Nanoneedles-SAHF pouch battery.

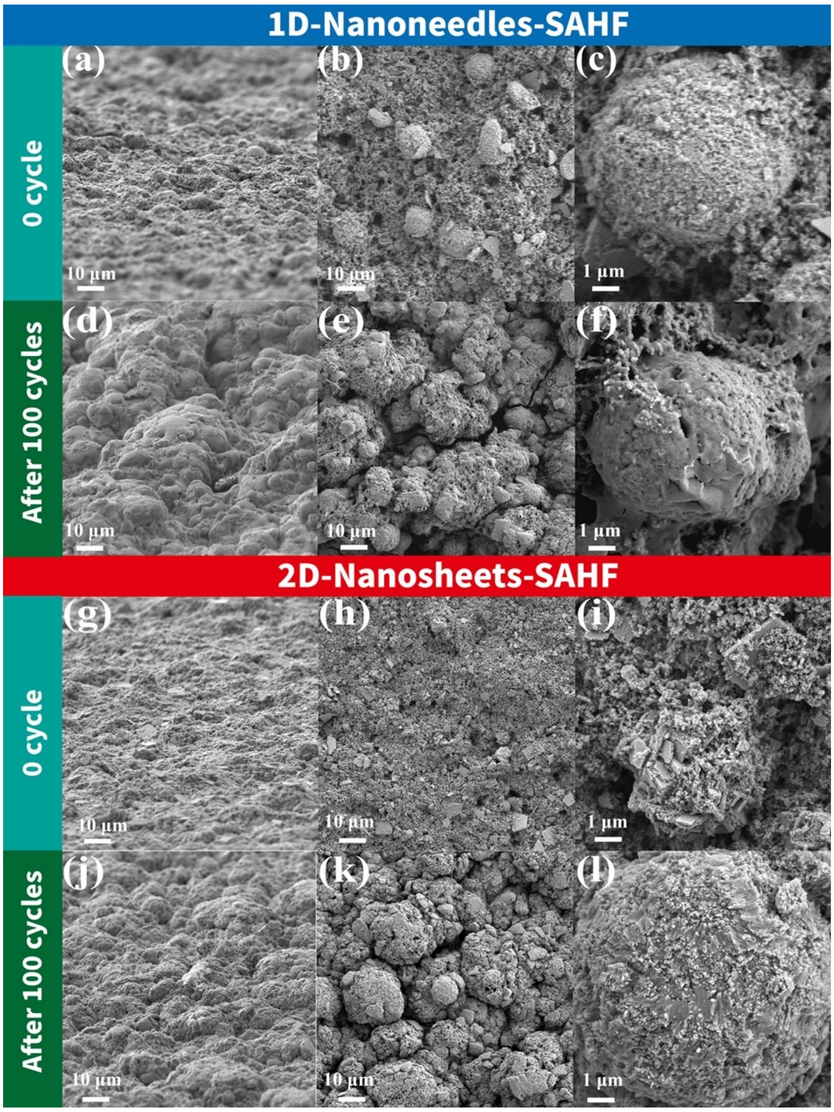

Fig. S5 (a-c) SEM images of fresh 1D-Nanoneedles-SAHF electrodes. (d-f) SEM images of 1D-Nanoneedles-SAHF after 100 cycles @1000 mA g^{-1}. (g-i) SEM images of fresh 2D-Nanosheets-SAHF electrodes. (j-l) SEM images of 2D-Nanosheets-SAHF after 100 cycles @1000 mA g^{-1}.

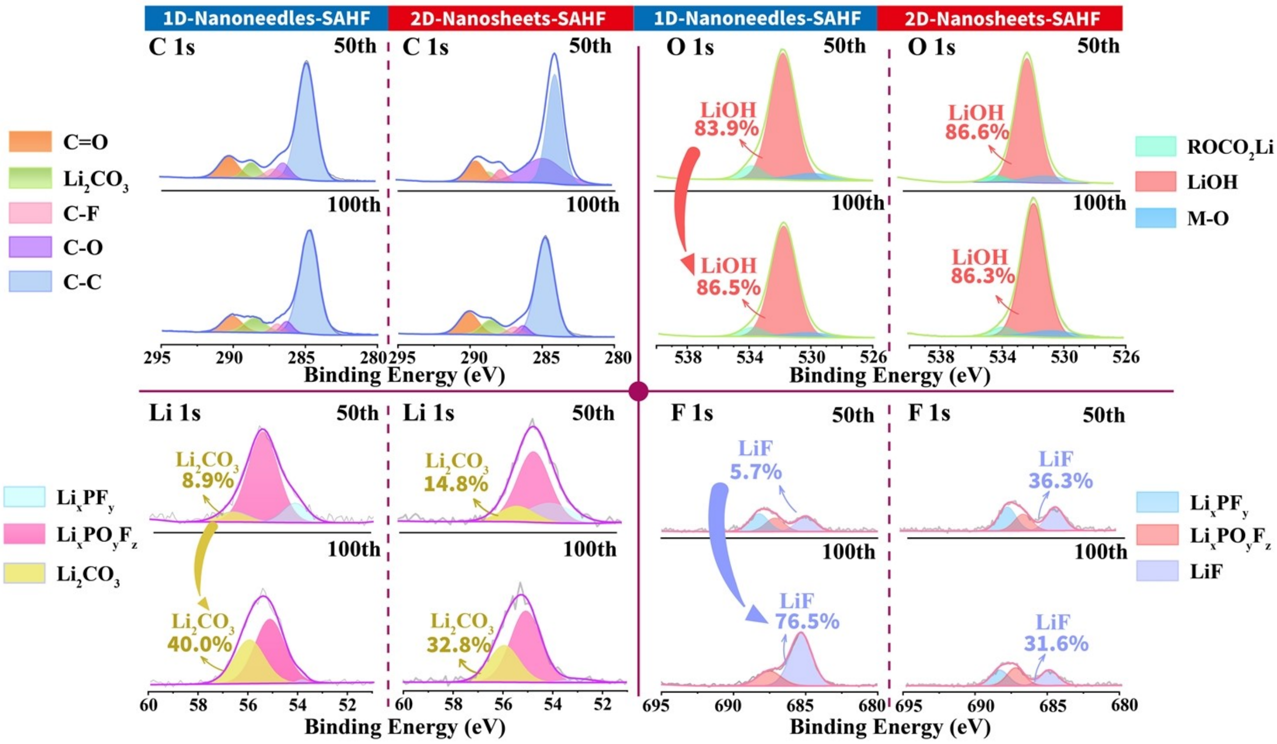

Fig. S6 High-resolution X-ray photoelectron spectroscopy (XPS) C 1s, F 1s, Li 1s and O 1s spectra of 1D-Nanoneedles-SAHF and 2D-Nanosheets-SAHF electrodes after 50 and 100 cycles at 1000 mA g^{-1}.

As shown in Fig. S6, X-ray photoelectron spectroscopy (XPS) characterization on the surface SEI layer from cycled samples reveals distinct chemical states in C, F, Li, and O spectra. Apart from characteristic graphitic carbon (284.8 eV) and oxygen-containing decomposition products (C-O/C=O at 286-288 eV), the dominant features correspond to electrolyte residues or decomposition products (Li_xPF_y, $Li_xPF_yO_z$) and lithium-containing species of the SEI, such as Li_2CO_3, LiOH, LiF. Specifically, the Li1s peak at 56.02 eV confirms the formation of Li_2CO_3, while the F1s peak at 685.29 eV and O1s peak at 531 eV are attributed to LiF and LiOH, respectively. [1,2]

Importantly, it can be clearly observed that, with increased cycling, 1D-Nanoneedles-SAHF exhibits significantly greater accumulation of lithium-containing species than 2D-Nanosheets-SAHF, particularly in the amounts of Li_2CO_3, LiF and LiOH, suggesting a possible link between Li-containing film growth and increased cycling capacity.

References

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2 L. Yang, Y. Wang, J. Wang, Y. Zheng, E. H. Ang, Y. Hu and J. Zhu, *Angew Chem Int Ed*, 2024, 63, e202402827.