## **Supporting Information**

## Hollow Sphere Formation by Self Aggregation of Nanocrystals Perovskite Fluoride NaNiF<sub>3</sub> and Ultrahigh Performance Asymmetric Supercapacitor

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**Fig. S1** Adsorption-desorption isotherm and Pore size distribution of as prepared hollow spheres Perovskite fluoride NaNiF<sub>3</sub>.



Fig. S2 TGA curve obtained from 10 to 700 °C in air of as prepared hollow spheres Perovskite fluoride  $NaNiF_3$ 



Fig. S3 Ni 2p XPS spectra of NaNiF3 at charged state in three-electrode system.



Fig. S4 Nyquist plots of perovskite fluorides NaNiF<sub>3</sub> measured at open circuit potential.



**Fig. S5** (a) CV curves of AC at different scan rates (10-100 mV s<sup>-1</sup>) within the voltage window from -1 to 0 V. (b) Galvanostatic charging/discharging curves of activated carbon at different current densities within voltage window  $-1\sim0$  V



Fig. S6 CV curves of AC and NaNiF<sub>3</sub> hollow spheres at scan rate of 20 mV s<sup>-1</sup> in a mixture of KOH and LiOH (3M+0.5M).



**Figure S 7 Electrochemical performance of NaNiF**<sub>3</sub>**//AC ASC device using carbon paper as current collector.** (a) CV curves at different scan rates (5-80 mV s<sup>-1</sup>) within the voltage window 0-1.7 V. (b) Galvanostatic charging/discharging curves at different current densities within voltage window 0-1.7 V.

Table S1. Three electrode performance Comparison of hollow sphere perovskite fluorides  $NaNiF_3$  with reported perovskite fluorides, perovskite oxides and other state of art electrode materials.

Electrode material	Electrolyte	Specific Capacitance	Current density	Stability	Ref.					
NaNiF <sub>3</sub>	3 M KOH + 0.5 M LiOH	1342 F g <sup>-1</sup>	5 A g <sup>-1</sup>	90 % after 8,000 cycles	This work					
PerovskiteFluorieds										
KNi <sub>0.8</sub> Co <sub>0.2</sub> F <sub>3</sub>	3 M KOH + 0.5 M LiOH	1530 F g <sup>-1</sup>	1 A g <sup>-1</sup>	-	1					
K-Co-Mn-F	3 M KOH + 0.5 M LiOH	226 F g <sup>-1</sup>	1 A g <sup>-1</sup>	118 % after 5,000 cycles	2					
Perovskite Oxides										
SrC00.9Nb0.1O3-8	6 M KOH	786.1 F g <sup>-1</sup>	1 A g <sup>-1</sup>	95.7 % after 3000 cycles	3					
$SrRuO_{3};\\La_{0.2}Sr_{0.8}Mn_{0.2}Ru_{0.8}O$	6 М КОН	270 F g <sup>-1</sup> ; 160 F g <sup>-1</sup>	20 mV s <sup>-1</sup>		4					
BiFeO <sub>3</sub>	1 M NaOH	81 F g <sup>-1</sup>	20 mV s <sup>-1</sup>		5					
TiO <sub>2</sub> /BiFeO <sub>3</sub>	0.5 M Na <sub>2</sub> SO <sub>4</sub>	440 F g <sup>-1</sup>	1.1 A g <sup>-1</sup>		6					
LaNiO <sub>3</sub> ; MnO /LaNiO	1 M Na <sub>2</sub> SO <sub>4</sub>	6.2; 160 F g <sup>-1</sup>	10; 0.01 V s <sup>-1</sup>		7					
LaNiO <sub>3</sub> /NiO	7 M KOH	213.2 F g <sup>-1</sup>	1 A g <sup>-1</sup>		8					
La <sub>0.85</sub> Sr <sub>0.15</sub> MnO <sub>3</sub> ;LaM	1 М КОН	198;187 F g <sup>-1</sup>	0.5 A g <sup>-1</sup>		9					
$(La_{0.75}Sr_{0.25})_{0.95}MnO$	1 M Na <sub>2</sub> SO <sub>4</sub>	56 F g <sup>-1</sup>	2 mV s <sup>-1</sup>		10					
$La_{x}Sr_{1-x}NiO_{3-\delta}$	1 M Na <sub>2</sub> SO <sub>4</sub>	719 F g <sup>-1</sup>	2 A g <sup>-1</sup>		11					
$\begin{array}{c} La_{x}Sr_{1-}\\ {}_{x}Co_{0.1}Mn_{0.9}O_{3-\delta}\end{array}$	1 М КОН	485 F g <sup>-1</sup>	1 A g <sup>-1</sup>		12					

LaMO <sub>3</sub>	106.58, 56.78,	1 A g <sup>-1</sup>	13
(M=Ni, Mn, Fe, Cr)	16.43, 24.40	-	
	F g <sup>-1</sup>		

Non perovskite materials								
Ni <sub>0.67</sub> Co <sub>0.33</sub> Se	6 M KOH	535 F g <sup>-1</sup>	1 A g <sup>-1</sup>	82 % after 2,000 cycles	14			
Ni-Co-P	3 M KOH + 0.5 M LiOH	1448 F g <sup>-1</sup>	1 A g <sup>-1</sup>		15			
Ni-Co-F	3 M KOH + 0.5 M LiOH	564 F g <sup>-1</sup>	1 A g <sup>-1</sup>		16			
NiCo <sub>2</sub> O <sub>4</sub>	6 M KOH	351 F g <sup>-1</sup>	1 A g <sup>-1</sup>		17			
Ni-P@NiCo <sub>2</sub> O <sub>4</sub>	3 M KOH + 0.5 M LiOH	1240 F g <sup>-1</sup>	1 A g <sup>-1</sup>		18			
NixCo <sub>2-x</sub> P	6 M KOH	571 F g <sup>-1</sup>	1 A g <sup>-1</sup>		19			
CoMoO4- NiMoO4•xH2O	2 M KOH	1039 F g <sup>-1</sup>	1 A g <sup>-1</sup>		20			
$NiCo_2S_4@Ni_3V_2O_8$	6 M KOH	512 C g <sup>-1</sup>	1 A g <sup>-1</sup>		21			
NiCo <sub>2</sub> S <sub>4</sub> /Co <sub>9</sub> S <sub>8</sub>	6 M KOH	749 F g <sup>-1</sup>	4 A g <sup>-1</sup>		22			
NiCo <sub>2</sub> O <sub>4</sub> @NiWO <sub>4</sub>	6 M KOH	1384 F g <sup>-1</sup>	1 A g <sup>-1</sup>		23			
Co-Ni-W-B- O/20rGO	6 M KOH	1189.1 F g <sup>-1</sup>	1 A g <sup>-1</sup>		24			
OMC/MoO <sub>2</sub>	$1 \text{ M H}_2\text{SO}_4$	37 mA h g <sup>-1</sup>	0.2 A cm <sup>-2</sup>		25			

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