Supporting Information (SI)

NiF_2 Nanorod Arrays for Supercapattery Applications

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Table S1. A data presenting electrochemical energy storage performance of self-grown nanostructured electrode materials**.**

Sr. No.	Product and Morphology	Supercapacitor configuration						Ref.
		Three-electrode system		Two electrode system				
		SCs	Cyclability (cycle)	SCs	ED	PD	Stability (cycle)	
[1]	$Ni(OH)_{2}$- Nanoflakes	1228 $F\ g^{-1}$ (3 M KOH)	100 % (1000)	-	-	-	-	[1]
[2]	$Ni(OH)_{2}$-	1100	---------	-	-	-	-	[2]

	Nanosheet	F g^{-1} (2M KOH)	--					
[3]	$Ni(OH)_2$- Hexagonal nanoplate	2534 F g^{-1} (2 M KOH)	97 % (2000)	-	-	-	-	[3]
[4]	$Ni(OH)_2$- Nanobrush	5.59 F cm^{-2} (5 M KOH)	94.9 % (10^4)	16.74 F cm^{-3}	4.56 mW cm^{-3}	100. mWh cm^{-3}	96.5 % (10^4)	[4]
[5]	Ni_3S_2- Hierarchical dendrites	710 F g^{-1} (1 M KOH)	(2000)	-	-	-		[5]
[6]	Ni_3S_2-Nest like	1293 F g^{-1} (1MNaOH)	69 % (2000)	-	-	-	-	[6]
[7]	Ni_3S_2- Graphene like	1.342 F g^{-1} (2M KOH)	93.6 % (3000)	-	-	-	-	[7]
[8]	Ni@NiO - Numerous ravines	2.0 F cm^{-2} (6 M KOH)	170 (100 000)	1.38 (F cm^{-3})	1.06 mWh cm^{-3}	0.42 W cm^{-3}	100%	[8]
[9]	β-NiS - Nanorods	1158 F g^{-1} (6 M KOH)	97.4 (2000)	113 F g^{-1}	55.1 W h kg^{-1}	925.9 W kg^{-1}	97 % (2000)	[9]

[10]	Ni_3Se_2Nano sheets	854 F g^{-1} (3 M KOH)	87.23 (5000)	131.1	23.3 W h kg^{-1}	398.1 W kg^{-1}	91.11 % (5000)	[10]
[11]	NiSe-Microspheres	492 F g^{-1} (2 M KOH)	84.6 (200)	-	-	-	-	[11]
[12]	NiTe/NiSe-Flakes	1868 F g^{-1} (3 M KOH)	81.2 % (1000)	94.9 F g^{-1}	33.7 W h kg^{-1}	4000 W kg^{-1}	86.2 % (5000)	[12]
[13]	NiTe-Flakes	603.6 F g^{-1} (3M KOH)	93.2 (1000)	131.1	42.7 Wh kg^{-1}	800.6 W kg^{-1}	76.4 % (10,000)	[13]
[14]	Ni-P@NiCo LDH	3470.5 F g^{-1}(KOH)	96 (1000)	94.9 F g^{-1}	35.1 W h kg^{-1}	770.8 W kg^{-1}	70 % (5000)	[14]
[14]	**NiF_2@Ni**	**51 F cm^{-2} (1 M KOH)**	**94 (1000)**	**15.84 F g^{-1}**	**31 W h kg^{-1}**	**797 W kg^{-1}**	**70 % (5000)**	**Current work**

Reaction mechanism

The formation of NiF_2@Ni NAs in a 1:50 mL (v/v) HF solutionin ethanol occurs as follows under hydrothermal conditions. When ethanolic HF solution is hydrothermally heated it produces ethoxy and fluoride ion radicals and protons. At the same time, Ni foam in the solution oxidizes to provide nickel ions and electrons in to solution reduce fluoride ions to nucleate on the Ni foam surface as shown in Scheme S1. In this reaction, hydrothermal displacement occurs between Ni and F, causing deposition ofNiF_2@Ni.

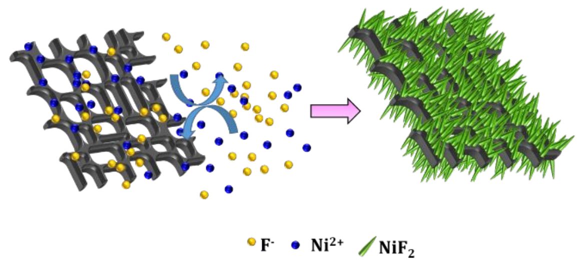

Figure S1. Schematic image illustrating the possible formation mechanism of the NiF_2@Ni during hydrothermal method. The black 3D network represents the Ni-foam surface, blue and yellow spheres are $Ni^{2+}$and F^{+} ions and on the right hand side we show a schematic sketch of the nanorod array (NA) of NiF_2.

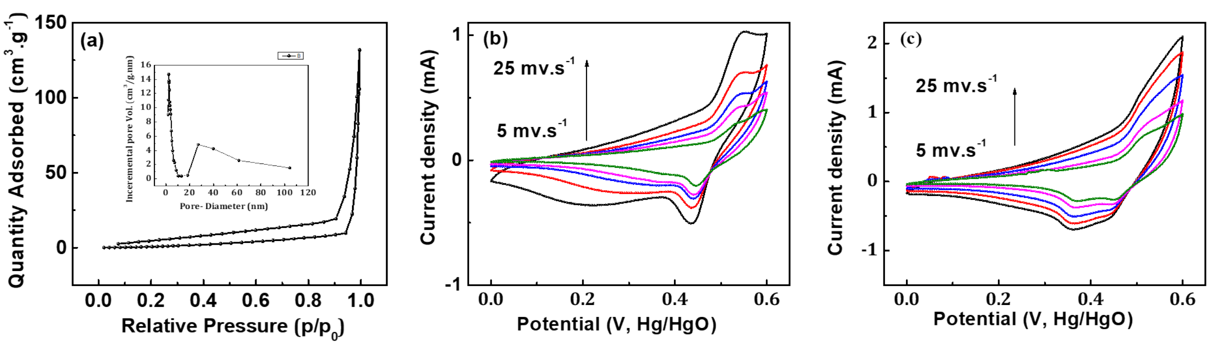

Figure S2. (a and b) BET (inset shows pore size distribution) and CV curves of NiF, and (c) CV curves of NiF_2@NiF at different scan rates in the range 5-25 mV s^{-1}.

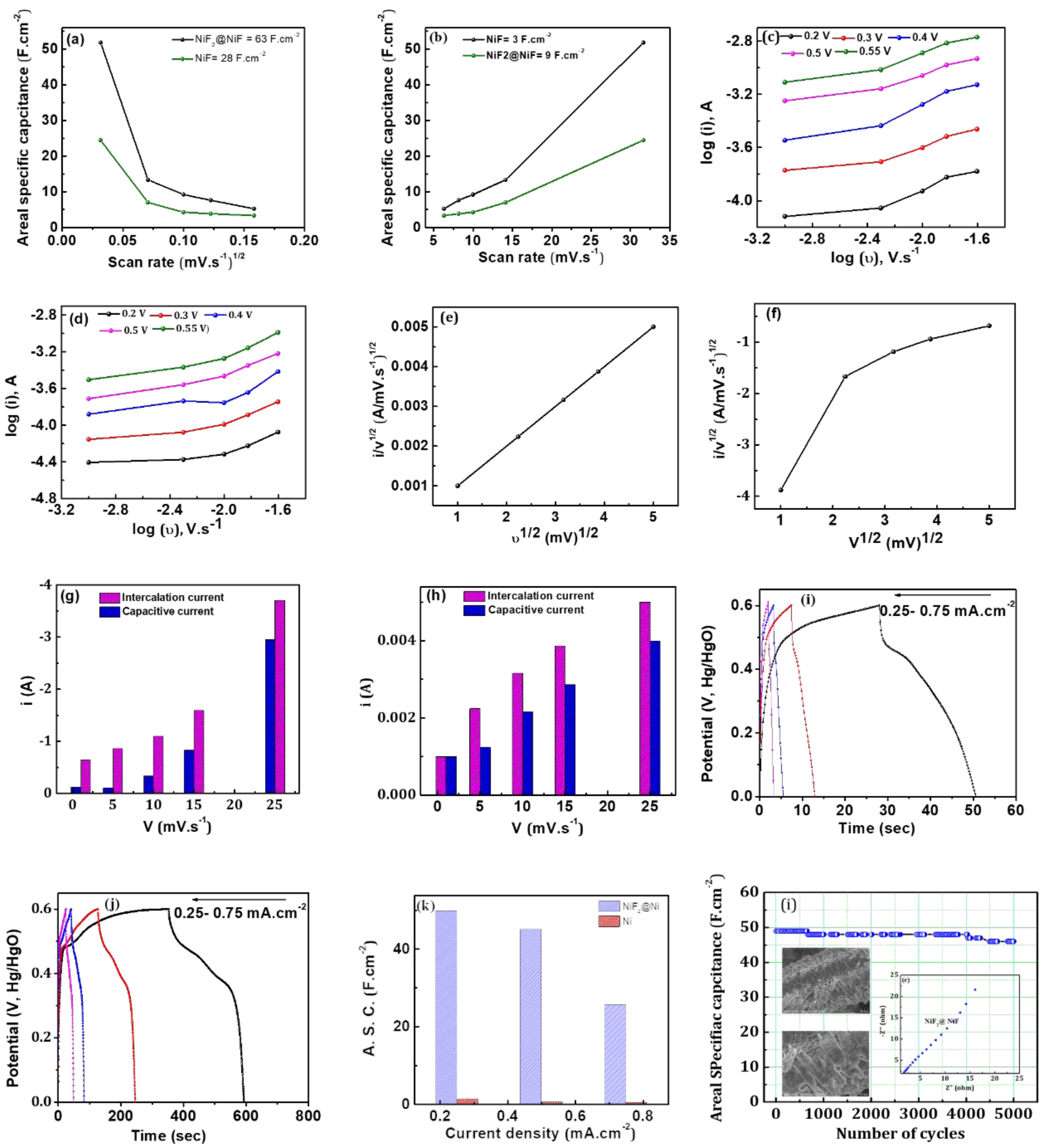

Figure S3. Trasatti plots: (a and b) areal capacitance *vs.* $1/(\mathrm{mv})^{1/2}$ and areal capacitance vs. $1/(\mathrm{mV})^{1/2}$ for NiF_2@NiF and Ni. (c and d) log I *vs.* log v plots for the NiF_2@Ni and NiF used for estimating slope 'b'. (e and f) $i/v^{1/2} vs. v^{1/2}$ plot to determinea_1 and a_2 (@ 0.2 V), with (g and h) showing the share of the capacitive and battery contribution for the NiF_2@Ni and Ni.(i and j) GCD curves and (k) ASC of the NiF_2@Ni and Ni at different current densities.(l) Stability of the NiF_2@Ni NA over 5000 cycles (inset shows FE-SEM image and EIS graph 5000 cycles NiF_2@Ni electrode after 5000th cycle).

Device fabrication process

The NiF_2@Ni//NiF_2@Ni device fabricated using NiF_2@Ni electrodes (a) and separated by a sheet of separator was mounted in a plastic cell(b) (see digital photograph in Figure S3 c) with 1 M KOH of electrolyte solution. Two wires from both electrodes were carefully drawn before sealing the pencil plastic cell for electrical processing.

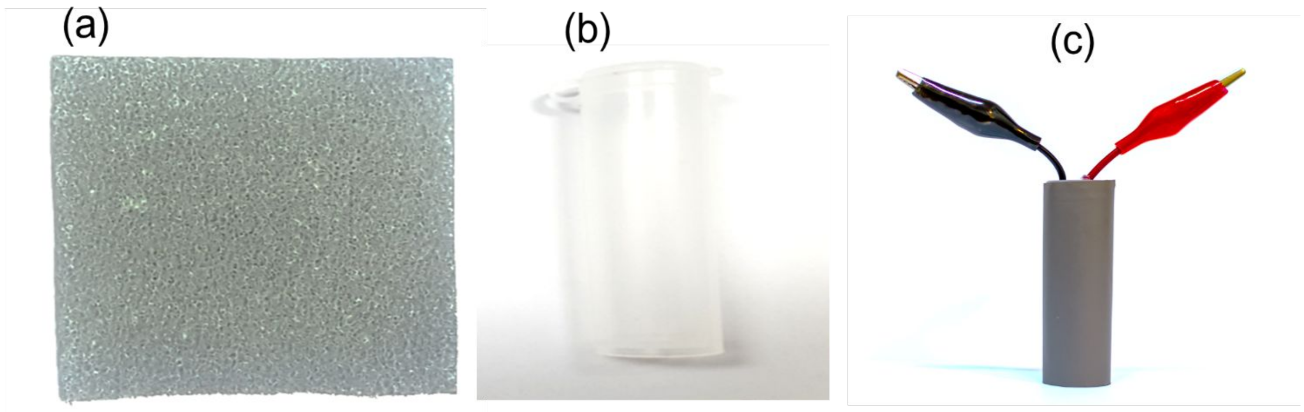

Figure S4. (a) Photoimage of the NiF_2@Ni form used in the supercapattery device. (b) the outer plastic casing used to house the supercapattery. (c). The final assembled device with connection leads. (Photograph courtesy of 'Nanasaheb M Shinde).

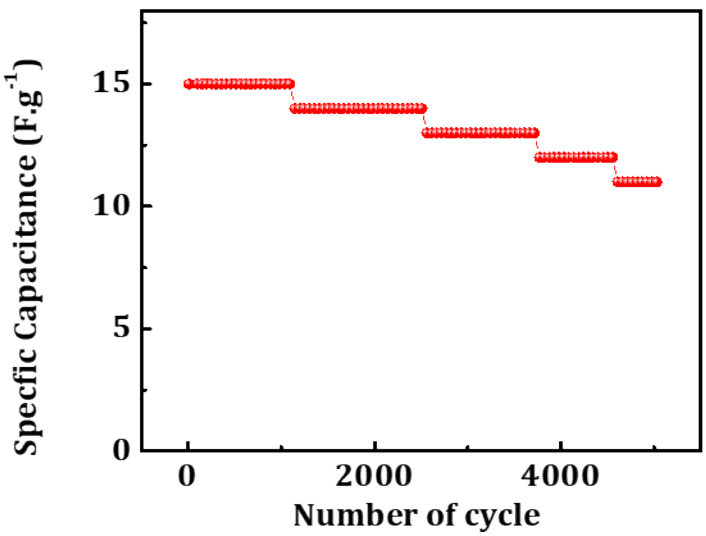

Figure S5. Stability of the NiF_2@Ni//NiF_2@Ni symmetric ESS devicefor 5000 redox cycles. The cell maintains ~11 F g^{-1} from an initial specific capacitance of 15 F g^{-1}.

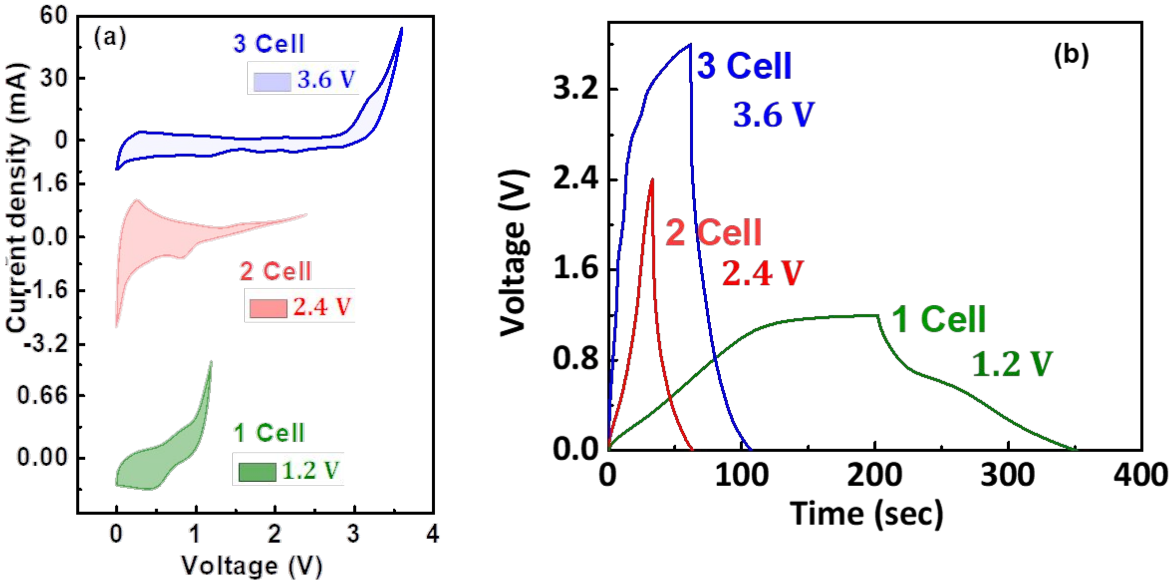

Figure S6. (a and b) CV and GCD curves of series combination of NiF_2@Ni//NiF_2@Ni symmetric electrochemical device.

REFERENCES

(1) Hu, B.; Qin, X.; Asiri, A. M.; Alamry, K. A.; Al-Youbi, A.O.; Sun, X. Fabrication of $Ni(OH)_2$ Nanoflakes array on Ni foam as a Binder-free Electrode Material for High Performance Supercapacitors, *Electrochim. Acta*, **2013**, *107*, 339–342.

(2) Xu, J. M.; Ma, K. Y.; Cheng, J. P. Controllable in Situ Synthesis of $Ni(OH)_2$ and NiO Films on Nickel Foam as Additive-free Electrodes for Electrochemical Capacitors, *J. Alloy. Compd.,* **2015**, *653*, 88–94.

(3) Li, L.; Xu, J.; Lei, J.; Zhang, J.; McLarnon, F.; Wei, Z.; Li, N.; Pan, F. A One-step, Cost-Effective Green Method to in Situ Fabricate $Ni(OH)_2$Hexagonal Platelets on Ni foam as Binder-free Supercapacitor Electrode Materials, *J. Mater. Chem. A,***2 015**, *3*, 1953–1960

(4) Li, X. X.; Chen, G. F.; Xiao, K.; Li, N.; Ma, T. Y.; Liu, Z. Q. Self-supported Amorphous-Edge Nickel Sulfide Nanobrush for Excellent Energy Storage, *Electrochim. Acta*, **2017,** *255***,** 153–159.

(5) Zhang, Z.; Huang, Z.; Ren, L.; Shen, Y.; Qi, X.; Zhong, J.; One-pot Synthesis of Hierarchically Nanostructured Ni_3S_2 Dendrites as Active Materials for Supercapacitors. *Electrochim. Acta*, **2014**, *149*, 316–323.

(6) Krishnamoorthy, K.; Veerasubramani, G. K.; Radhakrishnan, S.; Kim, S. J. One Pot Hydrothermal Growth of Hierarchical Nanostructured Ni_3S_2 on Ni foam for Supercapacitor application, *Chem. Eng. J. Chem***.**, **2014**, *251***,**116–122.

(7) Zhuo, M.; Zhang, P.; Chen, Y.; Li, Q.; Facile Construction of Graphene-like Ni_3S_2 Nanosheets Through the Hydrothermally Assisted Sulfurization of Nickel foam and Their Application as Self-supported Electrodes for Supercapacitors, *RSC Adv.,* **2015**, *5*, 25446–25449.

(8) Yu, M.; Wang, W.; Li, C.; Zhai, T.; Lu, X.; Tong, Y. Scalable Self-growth of Ni@NiO Core-shell Electrode with Ultrahigh Capacitance and Super-long Cyclic Stability for Supercapacitors, *NPG Asia materials*, **2014**, *6,* e129–e136.

(9) Li, W.; Wang, S.; Xin, L.; Wu, M.; Lou, X. Single-crystal β-NiS Nanorod Arrays with a Hollow-structured Ni_3S_2 Framework for Supercapacitor Applications, *J. Mater. Chem. A*, **2016,** *4*, 7700–7709.

(10) Jiang, S.; Wu, J.; Ye, B.; Fan, Y.; Ge, J.; Guo, Q.; Huang, M. Growth of Ni_3Se_2Nanosheets on Ni foam for Asymmetric Supercapacitors, *J. Mater. Sci. Mater. Electron.,* **2018**, *29*, 4649–4657.

(11) Guo, K.; Yang, F.; Cui, S.; Chen, W.; Mi, L., Controlled Synthesis of 3D Hierarchical NiSeMicrospheres for High-performance Supercapacitor Design, *Rsc Adv.,* **2016,** *6*, 46523–46530.

(12) Ye, B.; Huang, M.; Bao, Q.; Jiang, S.; Ge, J.; Zhao, H.; Fan, L.; Lin, J.; Wu, J.Construction of NiTe/NiSe Composites on Ni Foam for High-Performance Asymmetric Supercapacitor, *ChemElectroChem*, **2018**, *5,* 507–514.

(13) Ye, B.; Huang, M.; Jiang, S.; Fan, L.; Lin, J.; Wu, J.; In-situ growth of Se-doped NiTe on Nickel foam as Positive Electrode Material for High-performance Asymmetric Supercapacitor, *Mater. Chem. Phys.,* **2018**, *211*, 389–398.

(14) Xing, J.; Du, J.; Zhang, X.; Shao, Y.; Zhang, T.; Xu, C. A Ni-P@ NiCo LDH Core–shell Nanorod-decorated Nickel foam with Enhanced Areal Specific Capacitance for High Performance Supercapacitors, *Dalton Trans,* **2017**, *46*, 10064–10072.