

Two-step synthesis of a-NiCu(OH)₂CO₃/Na₃NiCuCO₃PO₄: A battery-type electrode for pseudocapacitor applications

Nishchith B S^a, Yogesh Kalegowda^{a*}Ashoka S^b, Ganesan Sriram^c, Mahaveer D Kurkuri^c, Manjunatha Channegowda^{d,e}

^aDepartment of Physics, School of Engineering, Dayananda Sagar University, Bengaluru, India-560068

^bDepartment of Chemistry, School of Applied Sciences, REVA University, Bengaluru, India-560064

^cCentre for Nano and Material Sciences, JAIN University, Jain Global Campus, Bengaluru, India-562112

^dDepartment of Chemistry, RV College of Engineering, Bengaluru, India-560059

^eVisvesvaraya Technological University, Belagavi, India-590018

*Corresponding author.

E-mail address: yogesh-phy@dsu.edu.in

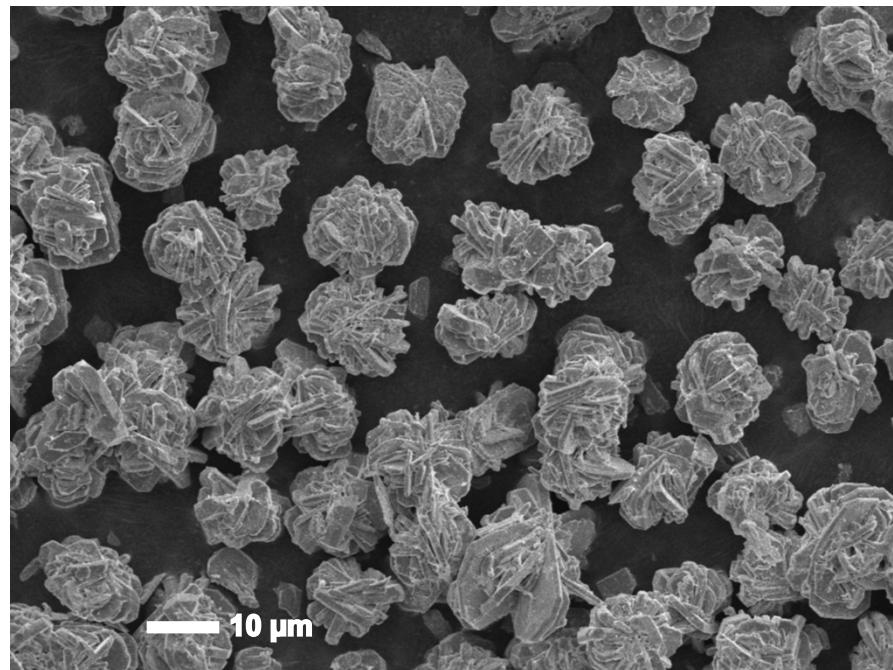


Fig. S1. FESEM image of a sample Ni:Cu-100:0 (Na₃NiCO₃PO₄).

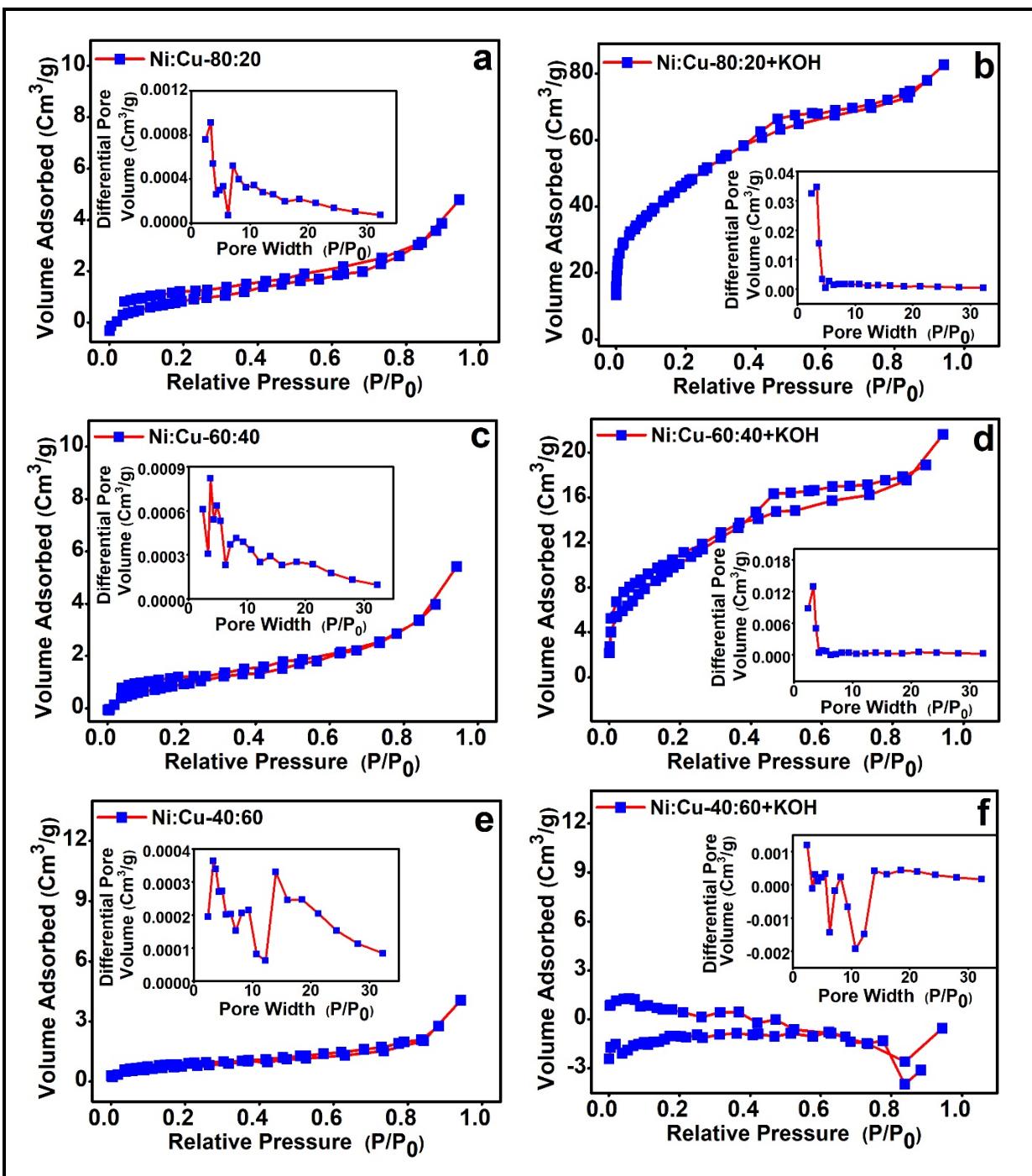


Fig. S2. N_2 adsorption-desorption isotherms of the $\text{Na}_3\text{NiCuCO}_3\text{PO}_4$ samples before and after KOH etching.

Table S1. Specific surface area, pore size and pore volume of the as-prepared and surface modified $\text{Na}_3\text{NiCuCO}_3\text{PO}_4$ particles.

Compound	pore size (nm)		pore volume (cm^3/g)	
	As prepared	Surface modified	As prepared	Surface modified
Ni:Cu-100:0	15.02	4.09	0.010679	0.1301
Ni:Cu-80:20	7.02	2.99	0.007775	0.0958
Ni:Cu-60:40	8.19	3.37	0.008703	0.0292
Ni:Cu-40:60	9.10	0.00	0.006260	0.0000

Table S2. The concentration of analyte in 1 M KOH electrolyte solution after $\text{Na}_3\text{NiCuCO}_3\text{PO}_4$ (Ni:Cu-80:20) electrode immersed in KOH solution for different time.

Technique	Element (in ppm)	Interaction with 1 M KOH solution		
		20 min	60 min	120 min
ICP-OES	P	34.7	37.3	41.1
	Na	500	543	587
	Ni	0.66	0.89	0.93
	Cu	2	2.3	2.7
IS 3025 (P- 51) 2001 titration technique	C	1100	1318	1212

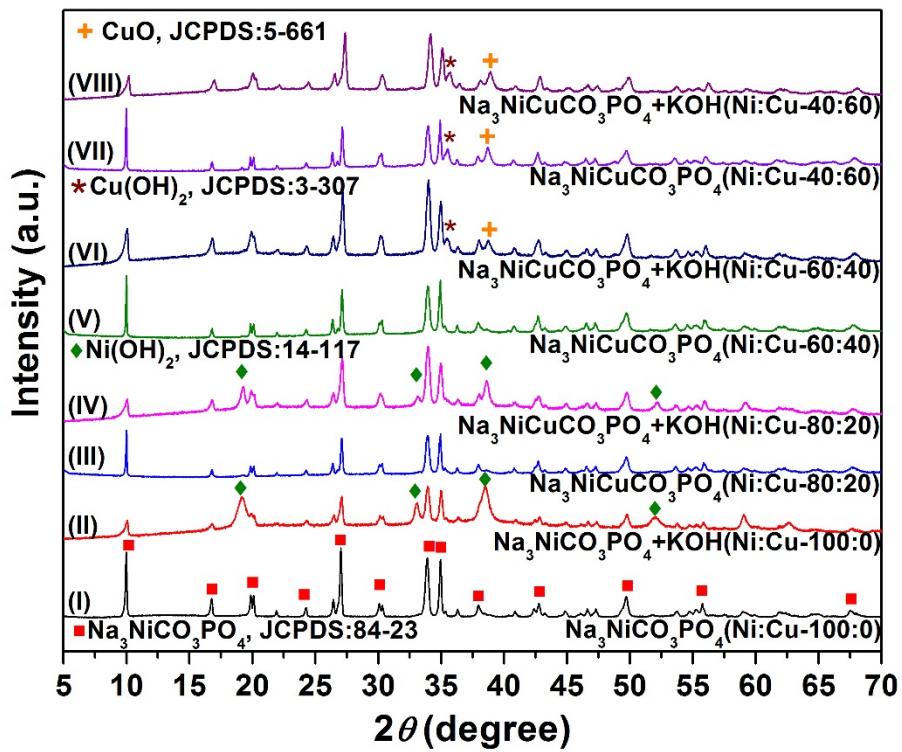


Fig. S3. Comparison of the XRD patterns of the $\text{Na}_3\text{NiCuCO}_3\text{PO}_4$ before and after KOH etching.

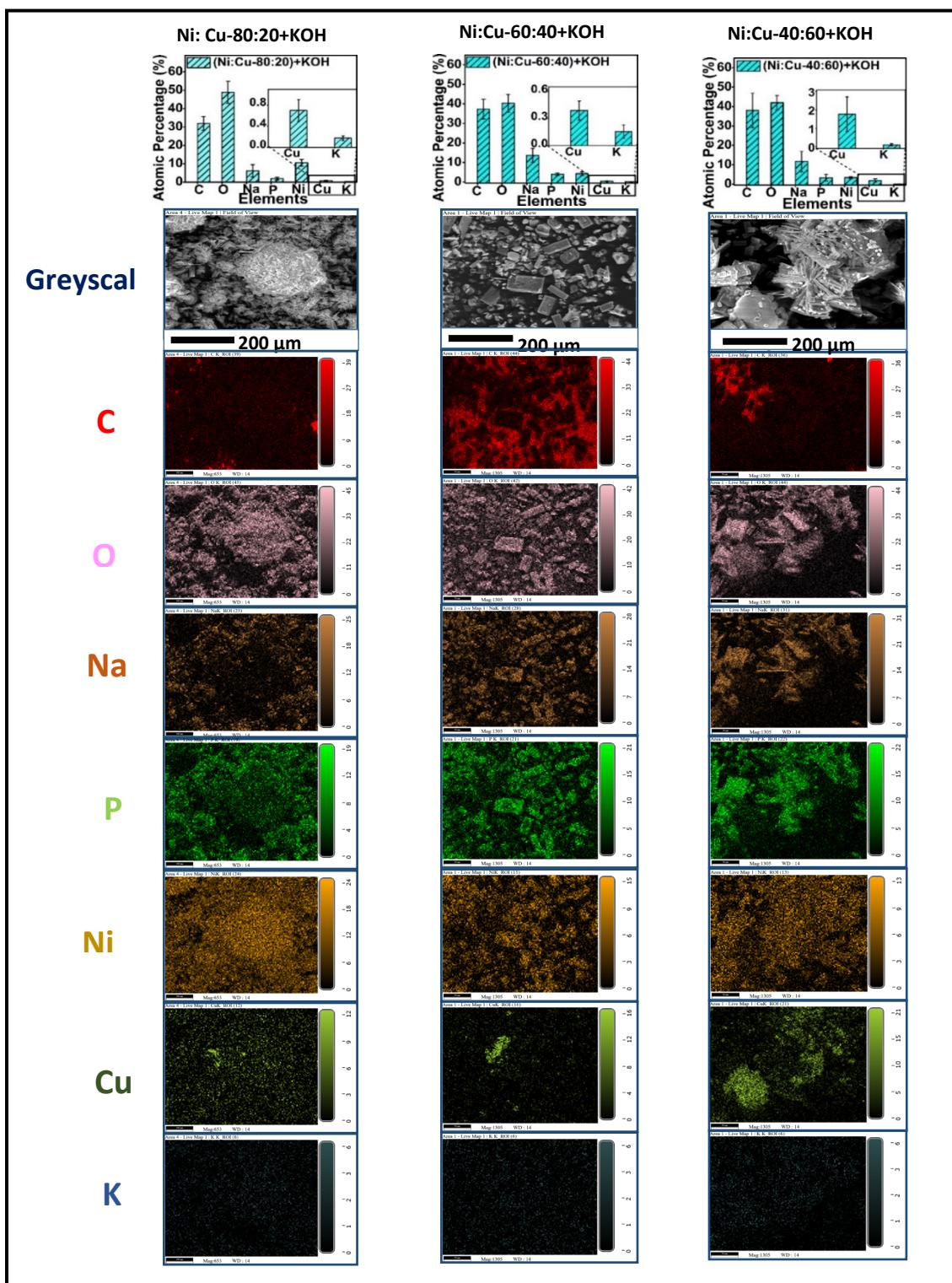


Fig. S4. FESEM elemental mapping of different elements at different electrochemical processing state.

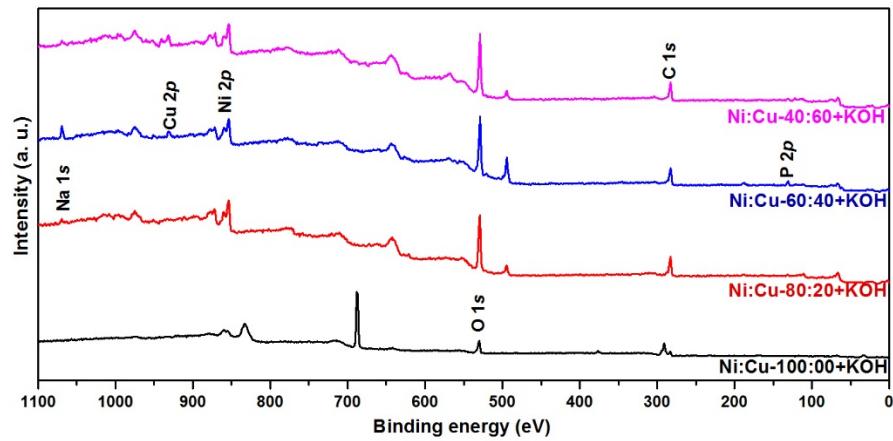


Fig. S5. The survey spectra acquired for $\text{Na}_3\text{NiCuCO}_3\text{PO}_4$ samples after KOH etching.

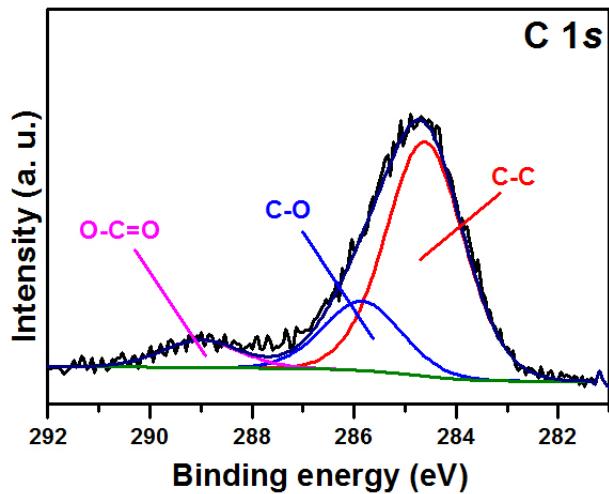


Fig. S6. High resolution C 1S spectrum of a Ni:Cu-80:20+KOH sample.

Table S3. XPS analysis data of various elements present in the KOH etched samples.

Elements (in at. %)	1 M KOH etched samples			
	Ni:Cu-100:00+KOH	Ni:Cu-80:20+KOH	Ni:Cu-60:40+KOH	Ni:Cu-40:60+KOH
Na 1s	-	0.85	3.21	0.98
Ni 2p	12.02	5.25	7.45	7.51
Cu 2p	-	0.31	1.00	2.98
C 1s	19.63	44.84	37.26	39.16
P 2p	-	2.47	6.42	3.52
O 1s	37.73	46.28	44.66	45.87

Table S4. Spectral fitting parameters for Ni $2p_{3/2}$: Relative peak positions, FWHM and % contributions for Ni⁰ and Ni²⁺ GS envelopes for Ni:Cu-80:20+KOH sample.

Species	Charged State			
	Relative peak positions (in eV)	FWHM (in eV)	% contributions	Total %
Ni ⁰	852.5	1.0	0.27	
	856.2	2.5	4.06	5.6
	858.6	1.8	1.27	
NiO	853.7	1.5	1.01	
	855.4	3.2	1.33	
	860.8	3.9	2.30	5.86
	863.9	2.0	1.22	
Ni(OH) ₂	854.8	1.1	2.69	
	855.7	2.3	22.32	
	857.6	1.6	3.69	88.54
	860.3	3.0	0.68	
	861.5	4.6	22.01	
	866.3	3.0	37.15	

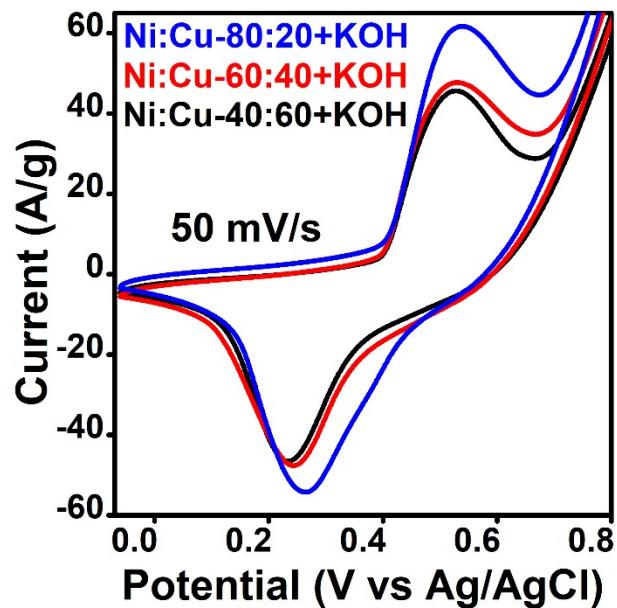


Fig. S7. CV profiles of KOH etched Na₃NiCuCO₃PO₄ samples in 1 M KOH solution obtained at 50 mV/s scan rate.

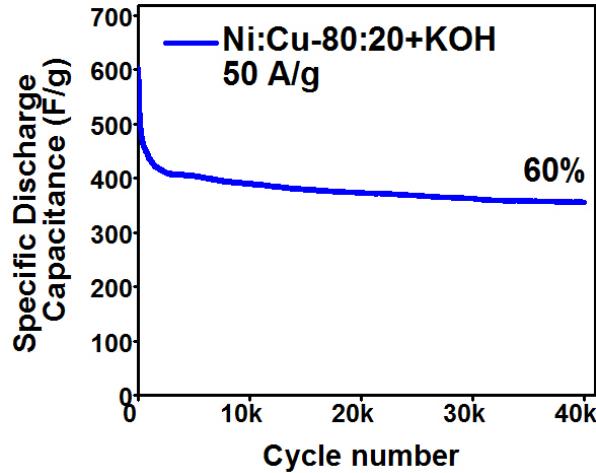


Fig. S8. The cycling stability of Ni:Cu-80:20+KOH in 1 M KOH electrolyte at 50 A g^{-1} for 40000 cycles.

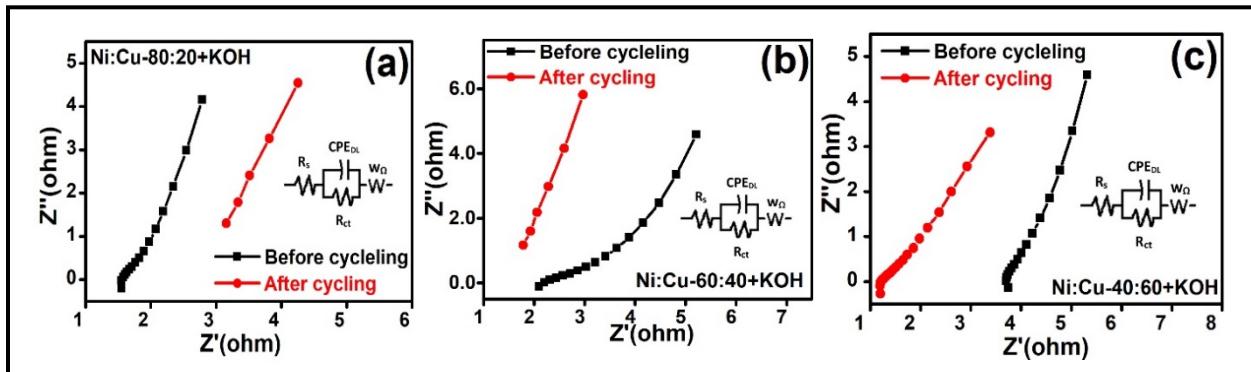


Fig. S9. (a) The Nyquist plots for the KOH etched samples before and after 15000 cycles at 10 A g^{-1} .

Table S5. EIS fitting results for different KOH etched $\text{Na}_3\text{NiCuCO}_3\text{PO}_4$ samples in 1 M KOH solution before charge-discharge cycling.

Materials	R_s (Ωcm^2)	R_{ct} (Ωcm^2)	W_Ω (Ωcm^2)	CPE_{DL} ($\mu\text{F cm}^{-2}$)
Ni:Cu-80:20+KOH	1.50	3.85	0.01037	94.85
Ni:Cu-60:40+KOH	2.32	12.11	0.003379	153.9
Ni:Cu-40:60+KOH	3.59	35.99	0.007009	98.81

Table S6. Comparison of electrochemical performance of Ni-Cu composite materials based asymmetric supercapacitors

Electrode Materials	Electrolyte	Specific Capacitance (F/g) at 1 A/g	Cycles (5 A/g)	Retention (%)	Energy Density of SCs (Wh/Kg)	Power Density of SCs (W/Kg)	References
NiCu(OH) ₂ CO ₃	6 M KOH	476	2000	88	48.55	541	¹
Ni-Cu oxides rGO	1 M KOH	197 (0.5 A/g)			49	1816	²
(Ni _{0.89} Cu _{0.11}) ₂ (OH) ₂ CO ₃ AC	2 M KOH	96.06	4000	70.8	21.7	8407.4	³
NiCu- hybrid AC	1 M KOH	2420 mC/cm ² (2 mA/cm ²)			420 µWh/cm ²	2297 µW/cm ²	⁴
NiCu(OH) ₂ CO ₃ AC	2 M KOH	163.7 (0.6 A/g)	5000 (2 A/g)	88.8	19.5	3789.5	⁵
NiCu(CO ₃)(OH) ₂ graphene	1 M KOH	758.9 mA h g ⁻¹ (3 A/g)	5000 (3 A/g)	87.2	26.7	2534	⁶
MoS ₂ /NiCo(OH) ₂ C O ₃ AC	2 M KOH	1296	2000 (1 A/g)		16.4	375	⁷
Co/Ni hydroxide/CNT paper	6 M KOH	1497 (0.5 A/g)	5,000	--	-	-	⁸
PAN@NiCu(CO ₃) (OH) ₂ graphene	2 M KOH	870 mAh g ⁻¹ (3 A/g)	5000 (1 A/g)	90.1	90	835	⁹
core/shell Na ₃ NiCuCO ₃ PO ₄	1 M KOH	2647.9	40000	79	30.6	1555	This work

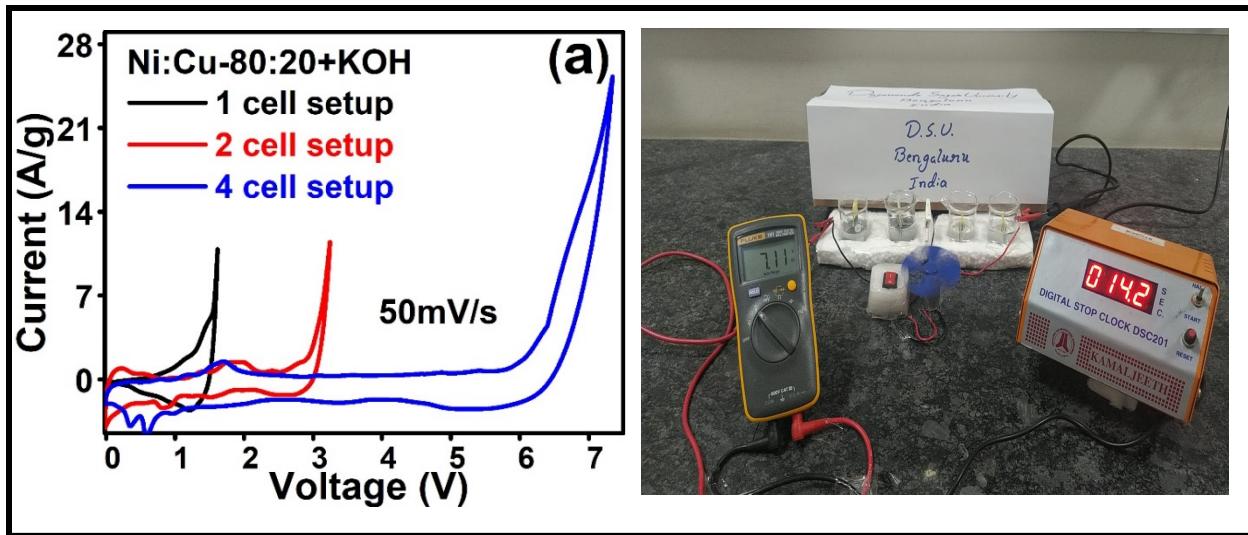


Fig. S10. (a) GCD curves of single, two and four SSCs in series at current density 1 A/g (b) photograph of tandem (four cells in series) SC powering the 6V DC motor fan.

REFERENCES

1. X. Zheng, Y. Ye, Q. Yang, B. Geng and X. Zhang, Ultrafine nickel–copper carbonate hydroxide hierarchical nanowire networks for high-performance supercapacitor electrodes, *Chemical Engineering Journal*, 2016, **290**, 353-360.
2. L. Zhang and H. Gong, Unravelling the correlation between nickel to copper ratio of binary oxides and their superior supercapacitor performance, *Electrochimica Acta*, 2017, **234**, 82-92.
3. P. W. Yuan, S. H. Guo, S. Q. Gao, J. Wang, W. Q. Chen, M. Li, K. Y. Ma, N. Wang, F. Liu and J. P. Cheng, Influence of Ni/Cu ratio in nickel copper carbonate hydroxide on the phase and electrochemical properties, *Journal of Alloys and Compounds*, 2019, **780**, 147-155.
4. J. Zhu, L. Wei, Q. Liu and X. Kong, Room-temperature preparation of amorphous CuNi-hybrid nanorod array as a fast battery-type electrode for high performance supercapacitor, *Materials Chemistry and Physics*, 2020, **247**, 122786.

5. A. Bera, A. Kumar Das, A. Maitra, R. Bera, S. Kumar Karan, S. Paria, L. Halder, S. Kumar Si and B. Bhushan Khatua, Temperature dependent substrate-free facile synthesis for hierarchical sunflower-like nickel–copper carbonate hydroxide with superior electrochemical performance for solid state asymmetric supercapacitor, *Chemical Engineering Journal*, 2018, **343**, 44-53.
6. D. Lee, H. W. Lee, N. M. Shinde, J. M. Yun, S. Mathur and K. H. Kim, Synthesis of nickel–copper composite with controllable nanostructure through facile solvent control as positive electrode for high-performance supercapacitors, *Dalton Transactions*, 2020, **49**, 13123-13133.
7. A. Y. Chen, H. H. Liu, P. Qi, X. F. Xie, M. T. Wang and X. Y. Wang, Nanosheet-assembled 3D flower-like MoS₂/NiCo(OH)₂CO₃ composite for enhanced supercapacitor performance, *Journal of Alloys and Compounds*, 2021, **864**, 158144.
8. F. Tan, H. Chen, R. Yuan, X. Zhang and D. Chen, Co-Ni Basic Carbonate Nanowire/Carbon Nanotube Network With High Electrochemical Capacitive Performance via Electrochemical Conversion, 2021, **9**.
9. D. Lee, A. Verma, K. Lê, T. Fischer, K. H. Kim and S. Mathur, Hybrid nanostructured PAN@ NiCu (CO₃)(OH) ₂ composite for flexible high-performance supercapacitors, *Journal of Materials Research*, 2021, 1-15.