Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

Two-dimensional layered nickel-based coordination polymer for supercapacitive performance

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Physical measurements

All the chemicals and solvents were procured from Sigma Aldrich and Merck, respectively. The Single crystal data was collected by using Bruker D8 Quest Single Crystal - XRD at 150(2) K using graphite monochromated Mo Kα radiation (λα = 0.71073 Å). For Thermogravimetric analysis (TGA), Mettler Toledo (TGA/DSC 1) analyzer with STARe software was used and heated up to 800 °C using a rate of 10 °C/min under a N_2 flow. For the Powder X-ray diffraction (PXRD) analysis Cu Kα (0.154 nm) monochromatic radiation was used with Rigaku Smart Lab X-ray diffractometer. Brunauer−Emmett−Teller (BET) surface area and Barrett−Joyner−Halenda (BJH) distribution determinations were conducted on an Autosorb iQ (Quantachrome Instruments, version 1.11). FT-IR experiment was performed by using Perkin Elmer-Spectrum Two with ATR mode. FE-SEM images were recorded by JOEL-7610 F plus. X-ray photoelectron spectroscopy (XPS) was performed on an XPS spectrometer (PHI 5000 VersaProbe III spectrophotometer (ULVAC-PHI INC) using Al K_α as the X-ray source). For the electrochemical study Autolab PGSTAT 204N instrument is utilized with platinum electrode as counter electrode and Ag/AgCl as reference electrode. Graphitic electrode (GE) are used as working electrode along with NOVA (2.1) software for the electrochemical measurement.

X-Ray structural analysis

The single crystal of **Ni-CP** produced with Agilent Technologies' SUPERNOVA diffractometer with CCD and standard scan technique employing graphite-monochromated Mo Kα (λα= 0.71073 Å) at room temperature (293 K) with standard φ−ω scan technique. CrysAlisPro CCD software was used to estimate the data, while CrysAlisPro RED was used to accomplish the necessary reduction and refining. Direct methods were used to clarify the crystal structure, which was further improved using a SHELXL-97 by F^2 utilizing the full-matrix least-squares method.[1] All non-H atoms were discriminated anisotropically, and H atoms were deployed in geometrically and refined using isotropic temperature factors, generally 1.2 × U_{eq} of their corresponding atoms. The Diamond programmed was used to draw the molecular structure, interactions, and mean-plane evaluations (ver. 3.1d).[2] The Alert A and B in checkcif is due to some unresolved disorder over C6 atom and for additional space group, respectively. The addional symmetry is found to be of C m m 2 but being lower symmetry, this was ignored and also structure solution better fits well with existing space group.

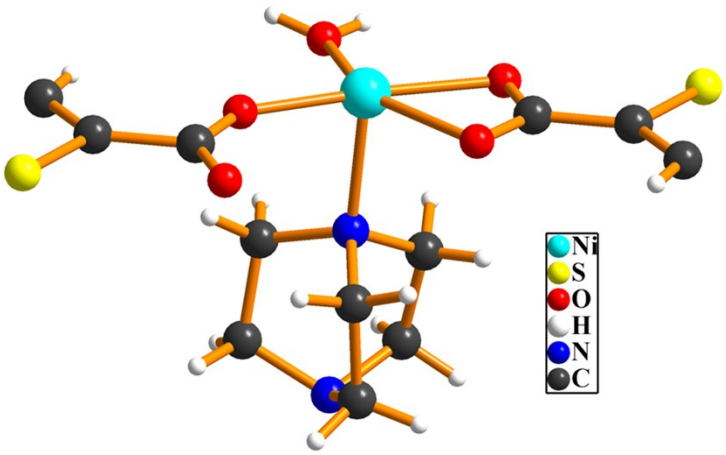

Fig. S1 Asymmetric unit of **Ni-CP**

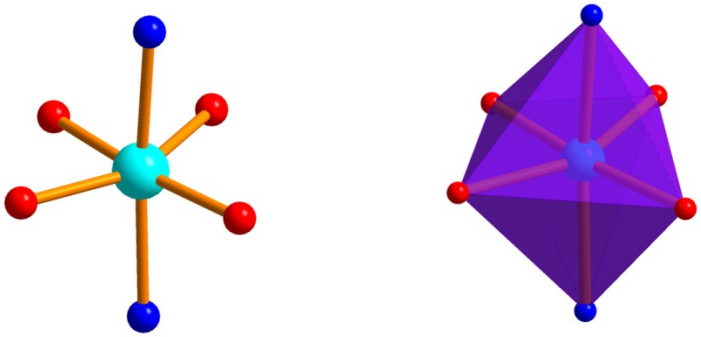

Fig. S2 Distorted octahedral coordination of Ni(II) ion of **Ni-CP**.

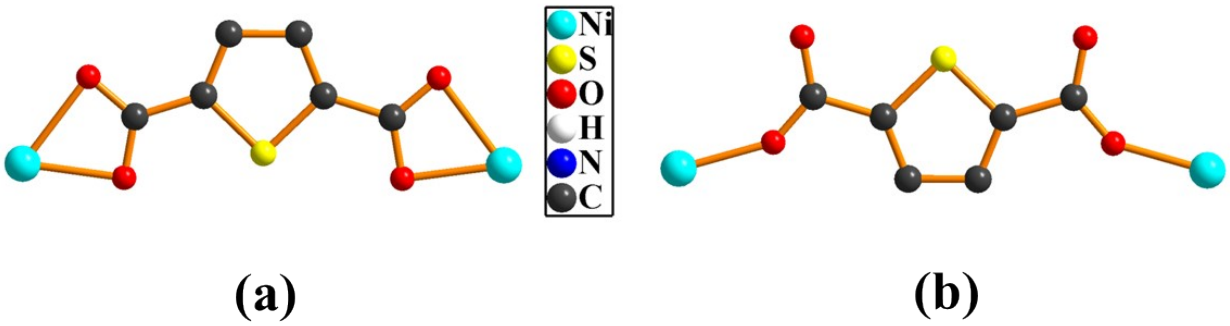

Fig. S3 Coordination modes of TDA (a) $((\kappa^1)\text{-}(\kappa^1))\text{-}\mu_2$, (b) $((\kappa^1\text{-}\kappa^0)\text{-}(\kappa^1\text{-}\kappa^0))\text{-}\mu_2$.

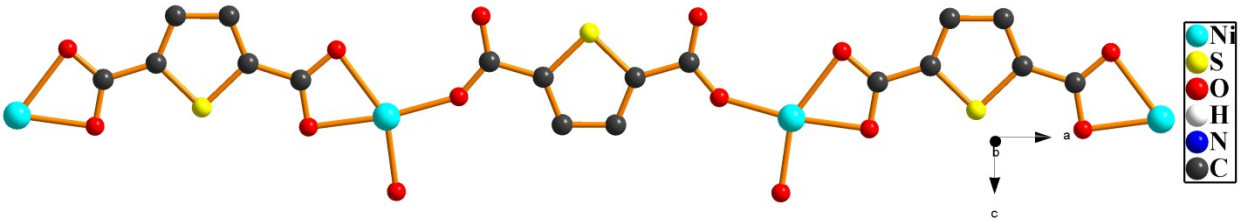

Fig. S4 Ball and stick model showing one-dimensional chain along *b*-axis.

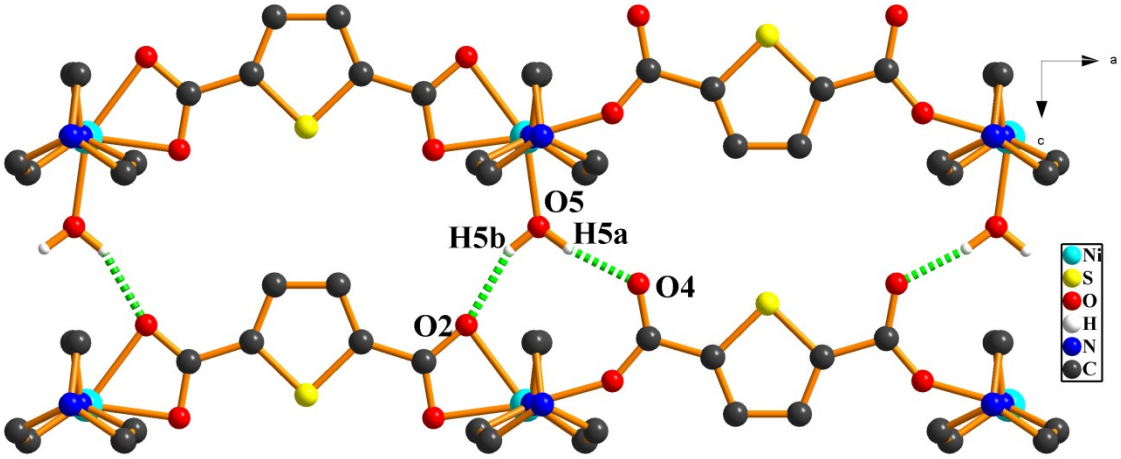

Fig. S5 Ball and stick model showing the Hydrogen bonding interaction between the two 2D structure along the *b*-axis.

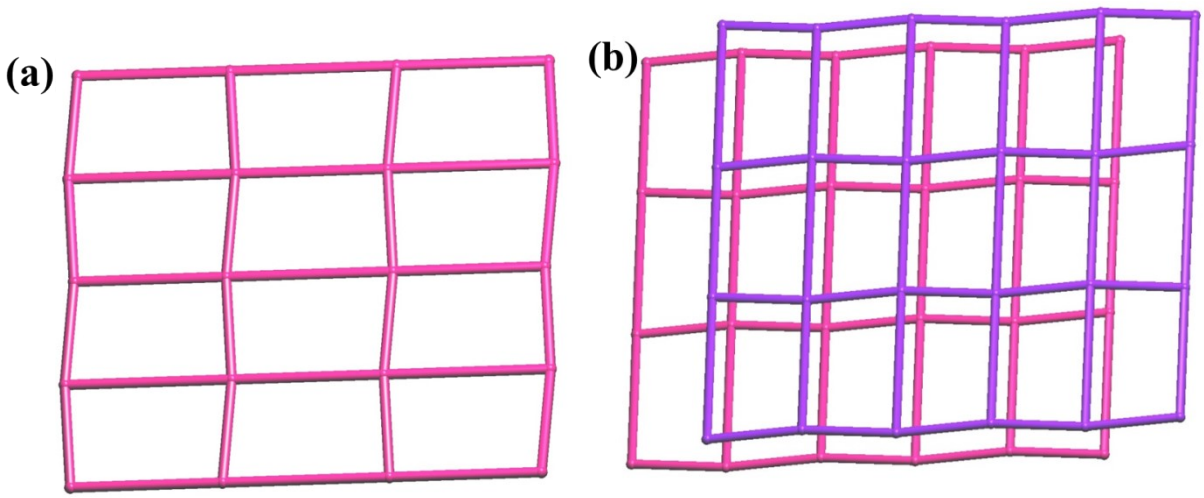

Fig. S6 Topological investigation of **Ni-CP** (a) 4-c unimodal net, (b) 2D layered framework having *sql* topology.

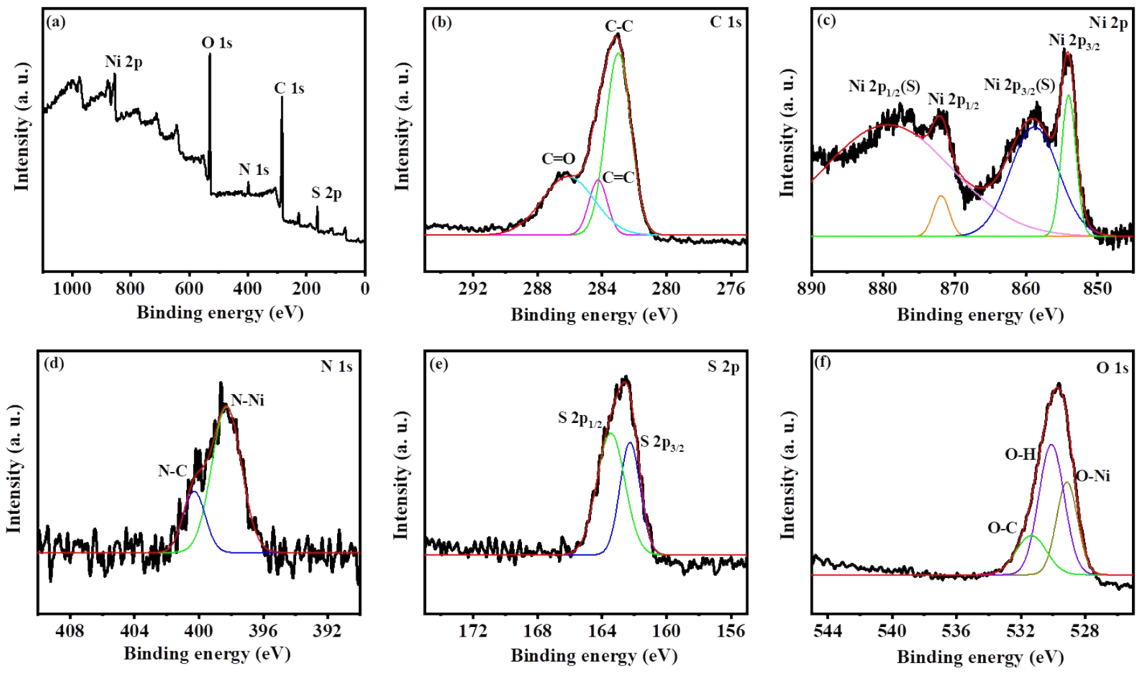

Fig. S7 (a) XPS survey spectrum (b-f) corresponding high resolution spectra of C 1S, Ni 2P, N 1S, S 2P and O 1S of **Ni-CP**.

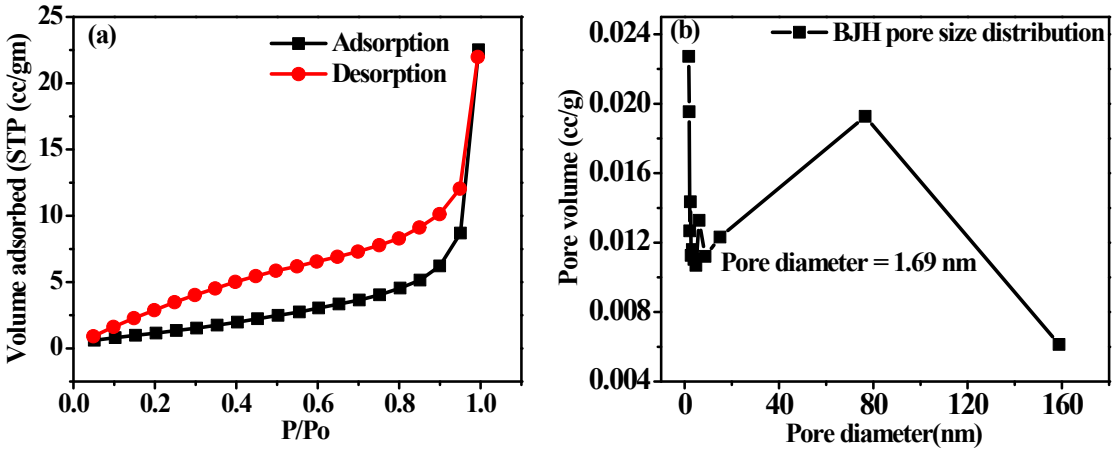

Fig. S8 (a) Nitrogen adsorption and desorption isotherms and (b) the corresponding microporous analysis of **Ni-CP**.

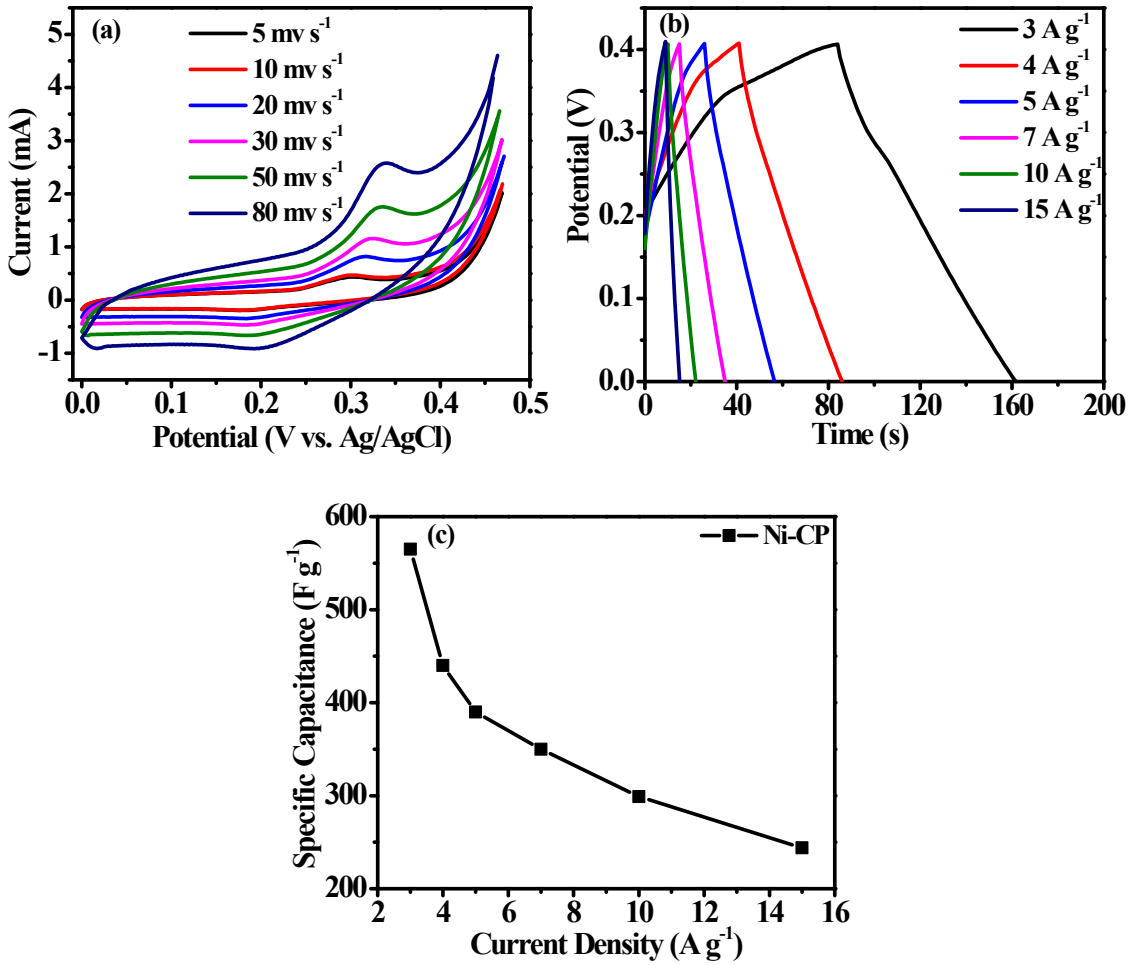

Fig. S9 (a) CV curves at various scan rate from 5 to 80 mV s^{-1} (b) GCD curves at different current density from 3 to 15 A g^{-1} (c) Specific capacitance of **Ni-CP** (5M KOH).

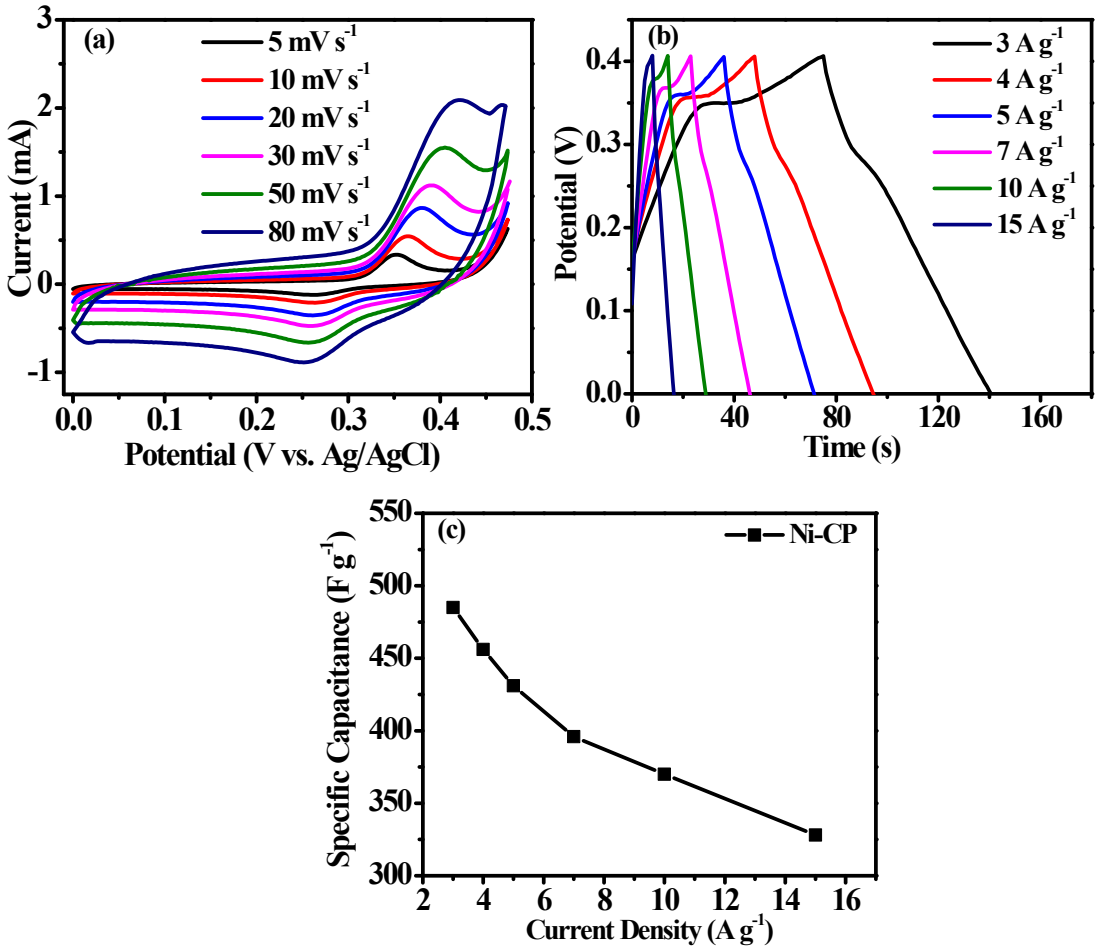

Fig. S10 (a) CV curves at various scan rate from 5 to 80 mV s^{-1} (b) GCD curves at different current density from 3 to 15 A g^{-1} (c) Specific capacitance of **Ni-CP** (3M KOH).

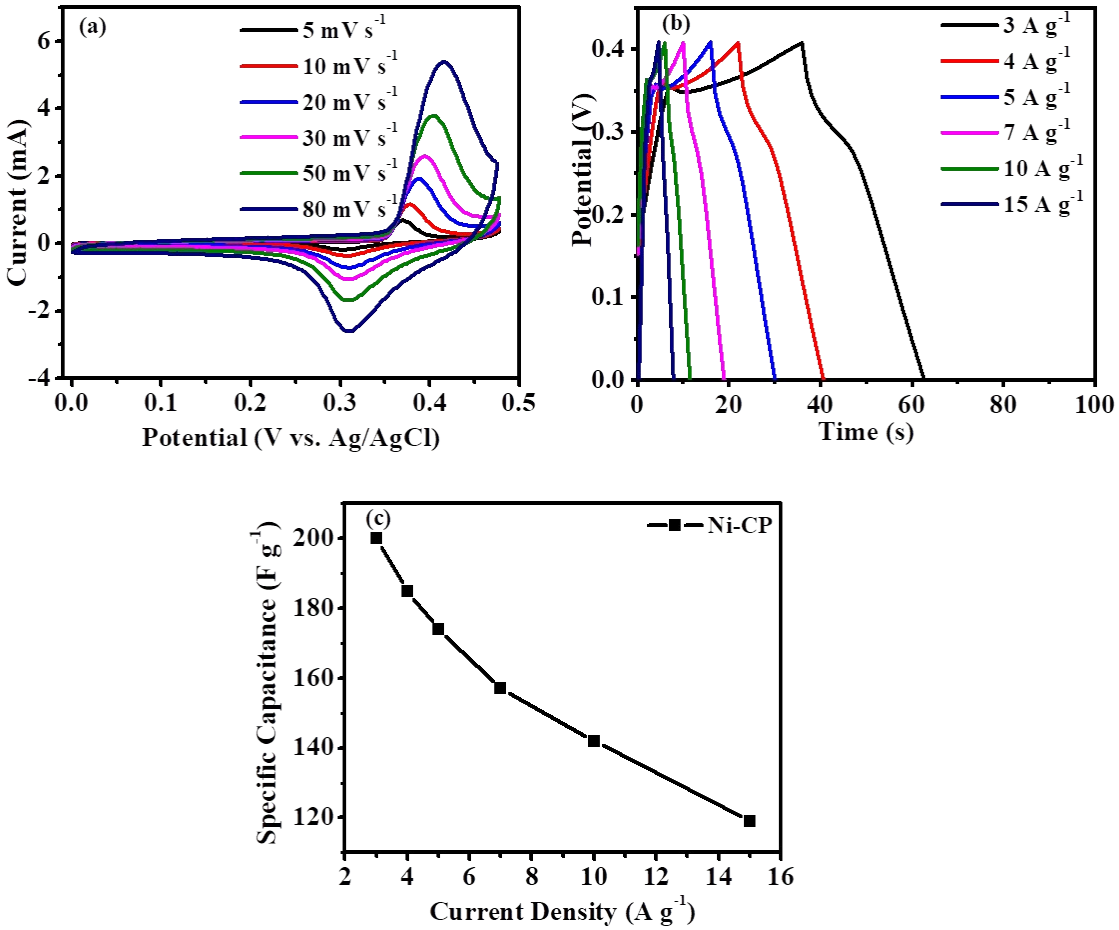

Fig. S11 (a) CV curves at various scan rate from 5 to 80 mV s^{-1} (b) GCD curves at different current density from 3 to 15 A g^{-1} (c) Specific capacitance of **Ni-CP** (1M KOH).

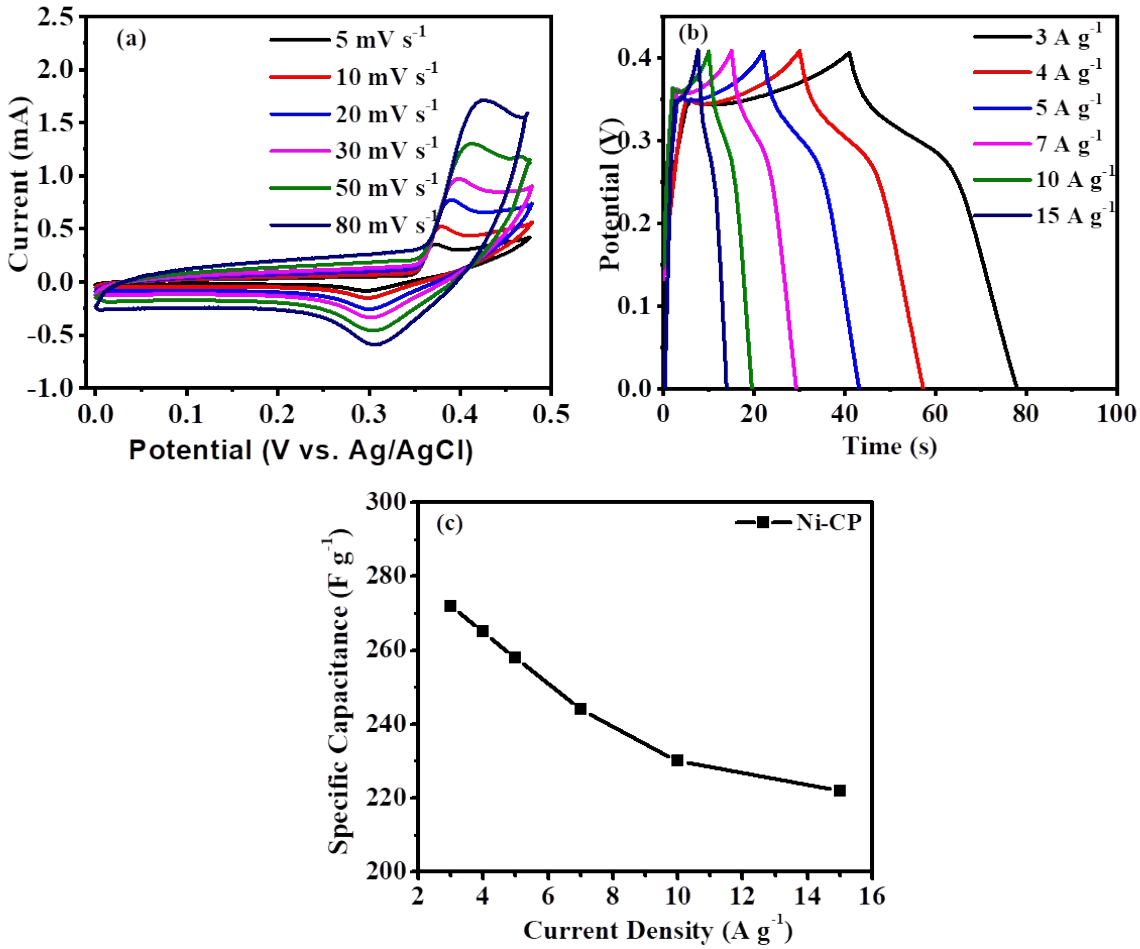

Fig. S12 (a) CV curves at various scan rate from 5 to 80 mV s^{-1} (b) GCD curves at different current density from 3 to 15 A g^{-1} (c) Specific capacitance of **Ni-CP** (1M NaOH).

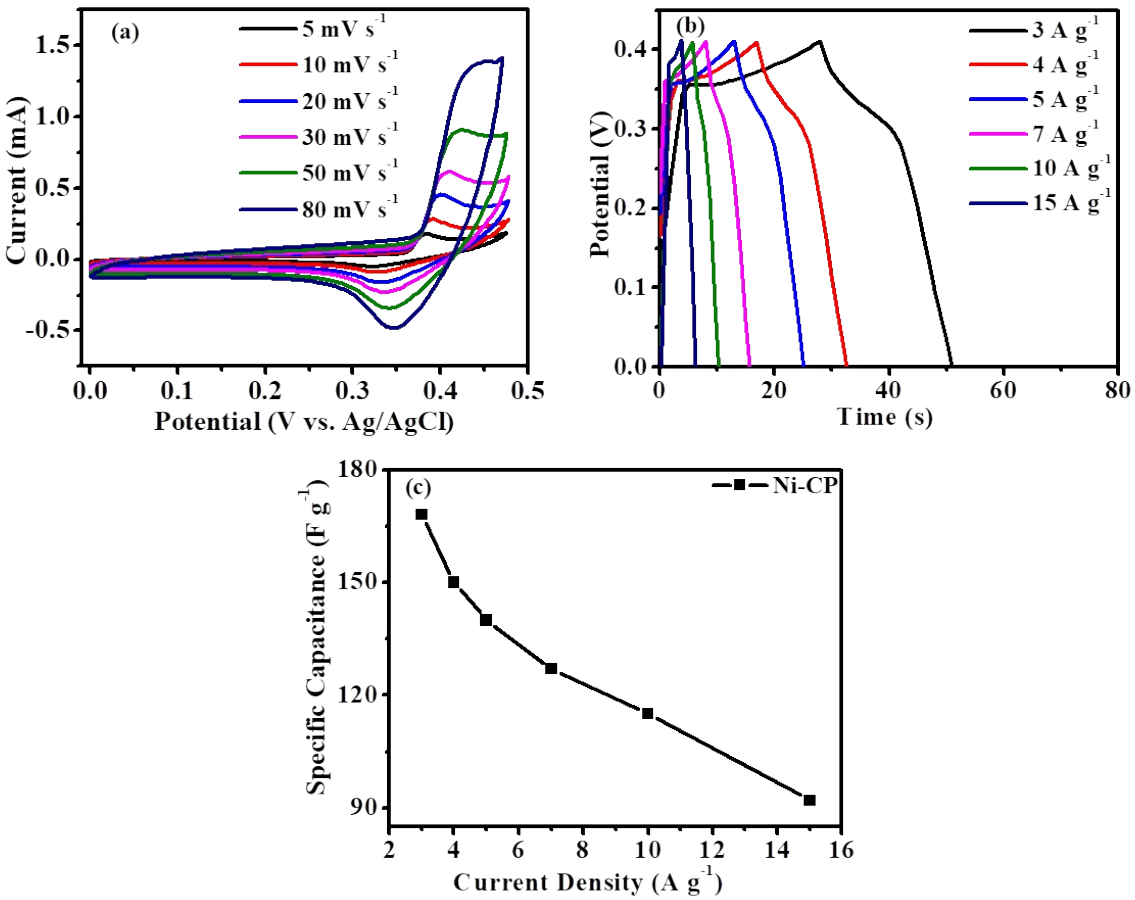

Fig. S13 (a) CV curves at various scan rate from 5 to 80 mV s^{-1} (b) GCD curves at different current density from 3 to 15 A g^{-1} (c) Specific capacitance of **Ni-CP** (1M LiOH).

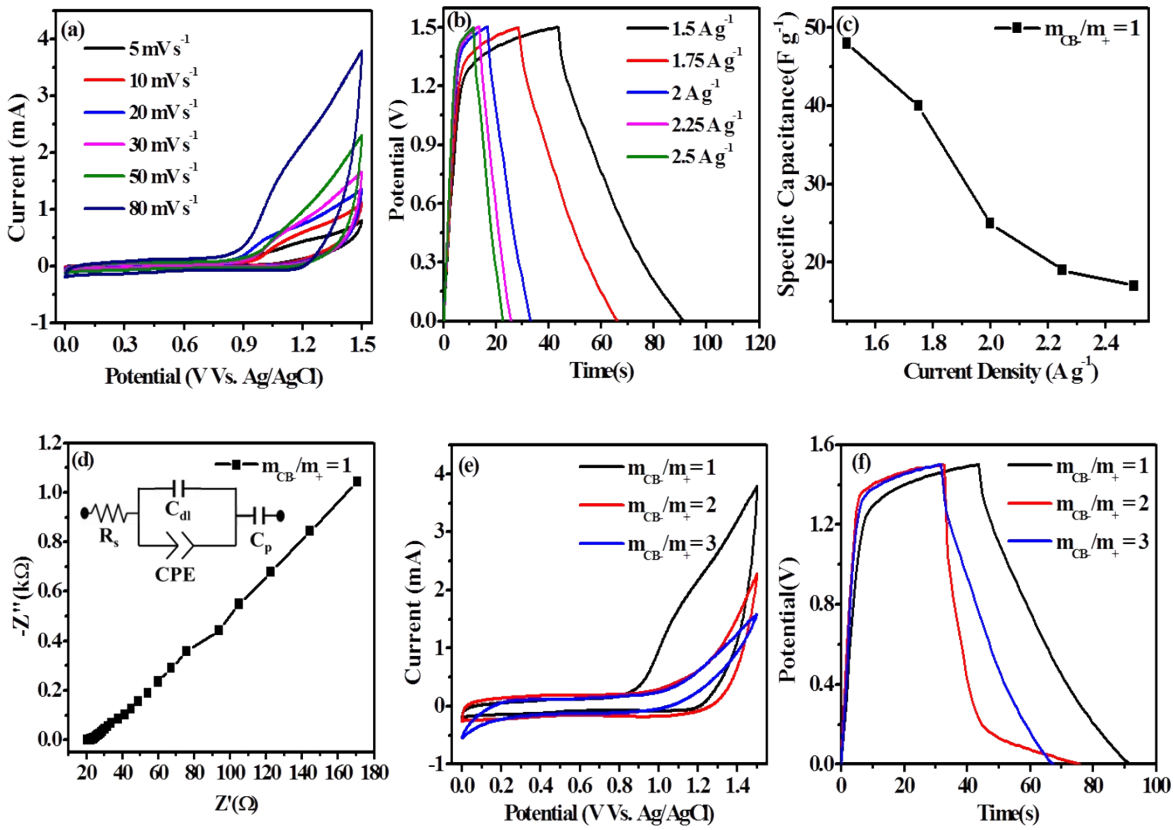

Fig. S14 (a) CV curves at various scan rate from 5 to 80 mV s^{-1} (b) GCD curves at different current density from 1.5 to 2.5 A g^{-1} (c) Specific capacitance, (d) EIS of ASC device of Ni-CP of m_{CB-}/m_{+} = 1, (e) and (d) Comparison of CV (at 80 mV s^{-1}) and GCD (at 1.5 A g^{-1}) curve of different mass loading of positive and negative electrode materials (m_{CB-}/m_{+} = 1, m_{CB-}/m_{+} = 2, m_{CB-}/m_{+} = 3)

Table S1 EIS circuit fitting parameter of ASC device of **Ni-CP** ($m_{CB}/m_{+} = 1$).

Element	**Parameter**	**ASC device**
R_S	R(Ω)	20.728
C_{dl}	C(fF)	900
C_p	C(mF)	1.76
CPE	Y0(mMho*S^N)	7.77
	N	0.642

Table S2 Bond lengths (Å) and bond angles (°) details of **Ni-CP**

Bond lengths	
Ni(1)-O(3)	2.004(2)
Ni(1)-O(5)	2.022(2)
Ni(1)-O(1)	2.099(2)
Ni(1)-N(1)	2.165(2)
Ni(1)-N(2)	2.166(2)
Ni(1)-O(2)	2.239(3)
Ni(1)-C(1)	2.498(3)
S(1)-C(2)#1	1.709(3)
S(1)-C(2)	1.709(3)
S(2)-C(5)#2	1.716(3)
S(2)-C(5)	1.716(3)
O(1)-C(1)	1.276(5)
O(2)-C(1)	1.260(4)
O(3)-C(4)	1.255(4)
O(4)-C(4)	1.246(4)
O(5)-H(5A)	0.8502
O(5)-H(5B)	0.8498
N(1)-C(9)	1.482(4)
N(1)-C(7)	1.489(3)
N(1)-C(11)	1.523(4)
N(2)-C(10)	1.487(4)
N(2)-C(12)	1.494(3)
N(2)-C(8)	1.502(4)
C(1)-C(2)	1.477(4)
C(2)-C(3)	1.373(5)
C(3)-C(3)#1	1.427(6)
C(3)-H(3)	0.9300
C(4)-C(5)	1.499(4)
C(5)-C(6)	1.374(4)
C(6)-C(6)#2	1.426(6)
C(6)-H(6)	0.9300
C(7)-C(8)#3	1.548(4)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)#3	1.540(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9700

C(10)-H(10B)	0.9700
C(11)-C(12)#3	1.532(4)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
Bond angles	
O(3)-Ni(1)-O(5)	97.83(11)
O(3)-Ni(1)-O(1)	171.98(11)
O(5)-Ni(1)-O(1)	90.19(10)
O(3)-Ni(1)-N(1)	86.72(8)
O(5)-Ni(1)-N(1)	89.47(11)
O(1)-Ni(1)-N(1)	93.68(7)
O(3)-Ni(1)-N(2)	86.28(8)
O(5)-Ni(1)-N(2)	90.87(11)
O(1)-Ni(1)-N(2)	93.34(7)
N(1)-Ni(1)-N(2)	172.97(9)
O(3)-Ni(1)-O(2)	111.08(11)
O(5)-Ni(1)-O(2)	151.09(10)
O(1)-Ni(1)-O(2)	60.91(9)
N(1)-Ni(1)-O(2)	91.36(10)
N(2)-Ni(1)-O(2)	91.74(9)
O(3)-Ni(1)-C(1)	141.30(12)
O(5)-Ni(1)-C(1)	120.88(11)
O(1)-Ni(1)-C(1)	30.69(11)
N(1)-Ni(1)-C(1)	93.13(9)
N(2)-Ni(1)-C(1)	92.72(9)
O(2)-Ni(1)-C(1)	30.23(11)
C(2)#1-S(1)-C(2)	91.9(2)
C(5)#2-S(2)-C(5)	91.6(2)
C(1)-O(1)-Ni(1)	92.2(2)
C(1)-O(2)-Ni(1)	86.3(2)
C(4)-O(3)-Ni(1)	146.3(3)
Ni(1)-O(5)-H(5A)	132.3
Ni(1)-O(5)-H(5B)	121.0
H(5A)-O(5)-H(5B)	104.5
C(9)-N(1)-C(7)	107.5(2)
C(9)-N(1)-C(11)	107.8(2)
C(7)-N(1)-C(11)	106.6(2)
C(9)-N(1)-Ni(1)	112.56(19)
C(7)-N(1)-Ni(1)	111.78(16)
C(11)-N(1)-Ni(1)	110.35(17)
C(10)-N(2)-C(12)	107.6(2)
C(10)-N(2)-C(8)	107.5(2)
C(12)-N(2)-C(8)	106.5(3)

C(10)-N(2)-Ni(1)	112.01(19)
C(12)-N(2)-Ni(1)	112.74(17)
C(8)-N(2)-Ni(1)	110.23(16)
O(2)-C(1)-O(1)	120.5(3)
O(2)-C(1)-C(2)	122.1(3)
O(1)-C(1)-C(2)	117.3(3)
O(2)-C(1)-Ni(1)	63.43(18)
O(1)-C(1)-Ni(1)	57.11(17)
C(2)-C(1)-Ni(1)	174.4(3)
C(3)-C(2)-C(1)	129.5(3)
C(3)-C(2)-S(1)	112.0(2)
C(1)-C(2)-S(1)	118.5(3)
C(2)-C(3)-C(3)#1	112.04(18)
C(2)-C(3)-H(3)	124.0
C(3)#1-C(3)-H(3)	124.0
O(4)-C(4)-O(3)	128.9(3)
O(4)-C(4)-C(5)	116.7(3)
O(3)-C(4)-C(5)	114.5(3)
C(6)-C(5)-C(4)	128.3(3)
C(6)-C(5)-S(2)	112.1(2)
C(4)-C(5)-S(2)	119.7(2)
C(5)-C(6)-C(6)#2	112.11(17)
C(5)-C(6)-H(6)	123.9
C(6)#2-C(6)-H(6)	123.9
N(1)-C(7)-C(8)#3	110.5(2)
N(1)-C(7)-H(7A)	109.6
C(8)#3-C(7)-H(7A)	109.6
N(1)-C(7)-H(7B)	109.6
C(8)#3-C(7)-H(7B)	109.6
H(7A)-C(7)-H(7B)	108.1
N(2)-C(8)-C(7)#4	110.3(2)
N(2)-C(8)-H(8A)	109.6
C(7)#4-C(8)-H(8A)	109.6
N(2)-C(8)-H(8B)	109.6
C(7)#4-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
N(1)-C(9)-C(10)#3	110.7(2)
N(1)-C(9)-H(9A)	109.5
C(10)#3-C(9)-H(9A)	109.5
N(1)-C(9)-H(9B)	109.5
C(10)#3-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	108.1
N(2)-C(10)-C(9)#4	110.8(2)
N(2)-C(10)-H(10A)	109.5
C(9)#4-C(10)-H(10A)	109.5

N(2)-C(10)-H(10B)	109.5
C(9)#4-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	108.1
N(1)-C(11)-C(12)#3	109.8(2)
N(1)-C(11)-H(11A)	109.7
C(12)#3-C(11)-H(11A)	109.7
N(1)-C(11)-H(11B)	109.7
C(12)#3-C(11)-H(11B)	109.7
H(11A)-C(11)-H(11B)	108.2
N(2)-C(12)-C(11)#4	111.2(2)
N(2)-C(12)-H(12A)	109.4
C(11)#4-C(12)-H(12A)	109.4
N(2)-C(12)-H(12B)	109.4
C(11)#4-C(12)-H(12B)	109.4
H(12A)-C(12)-H(12B)	108.0

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, z #2 –x, y, z #3 -x+1/2, y+1/2 #4 -x+1/2, y-1/2, z

References

1. G. M. Sheldrick, A short history of SHELX. *Acta Crystallogr.*, *Sect. A: Found. Crystallogr.*, 2008, **64**, 112−122.

2. G. Bergerhoff, M. Berndt, and K. Brandenburg, Evaluation of Crystallographic Data with the Program DIAMOND. *J. Res. Natl. Inst. Stand. Technol.*, 1996, **101**, 221−225.