

Supporting Information

Analyzing the charge contributions of metal-organic framework derived nanosized Cobalt Nitride/Carbon composites in asymmetrical supercapacitors

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S1. Characterization

A Renishaw (Invia) system with a 532 nm laser source was used to record Raman spectra. A QuantachromeAsiQwin instrument monitored N₂ adsorption-desorption isotherm. X-ray diffractometer (XRD) of model Bruker, D8 Advance, CuK α source 1.54Å was used to capture XRD patterns. Thermal analyses were performed in open α -Al₂O₃ crucibles with a Netzsch STA 449C Jupiter instrument at a heating rate of 5 °C min⁻¹, under Ar flow in the sample compartment. Hitachi SU8010 based Field emission scanning electron microscopy (FESEM)

with applied voltage of 2-5 kV has been used to record morphological images of the samples, Energy-dispersive X-ray spectroscopy (EDS) and elemental mapping. X-ray photoelectron spectroscopy is performed to determine different bonding with respect to different binding energies.

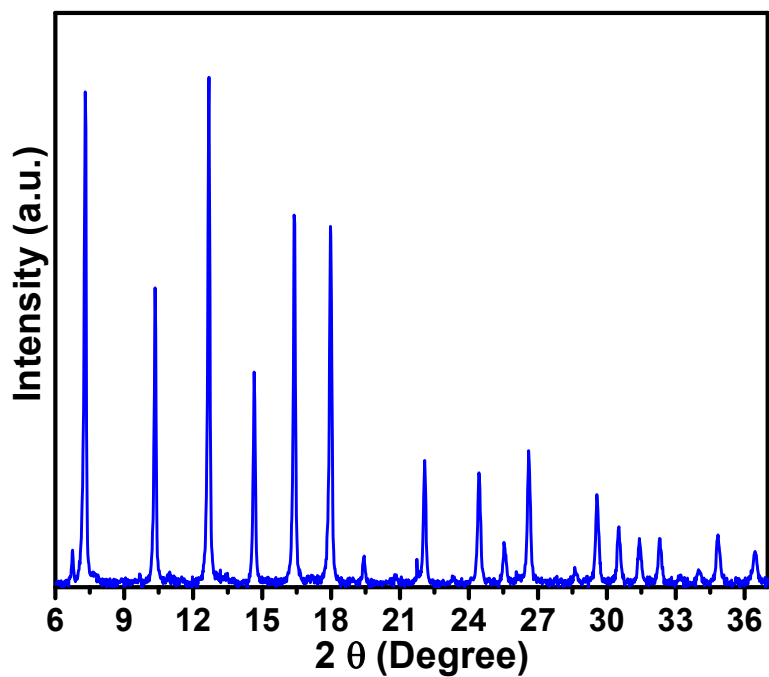


Figure S1. XRD pattern of ZIF-67.

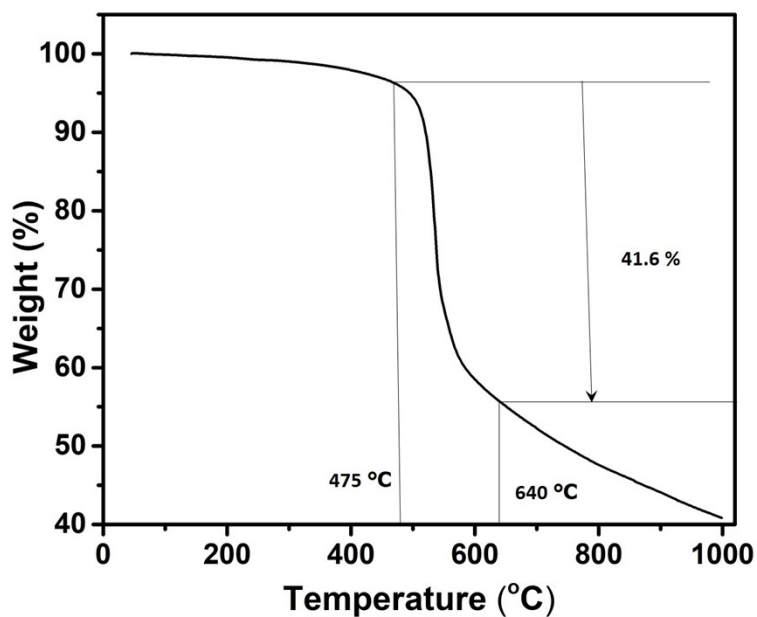


Figure S2. TGA of ZIF-67 from room temperature to 1000 °C under Ar atmosphere.

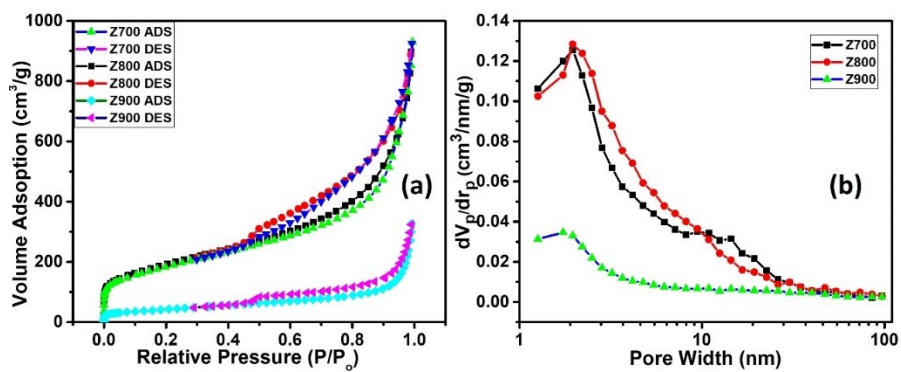


Figure S3. N₂ adsorption desorption isotherm and pore size distribution of Z-700, Z-800, and Z-900.

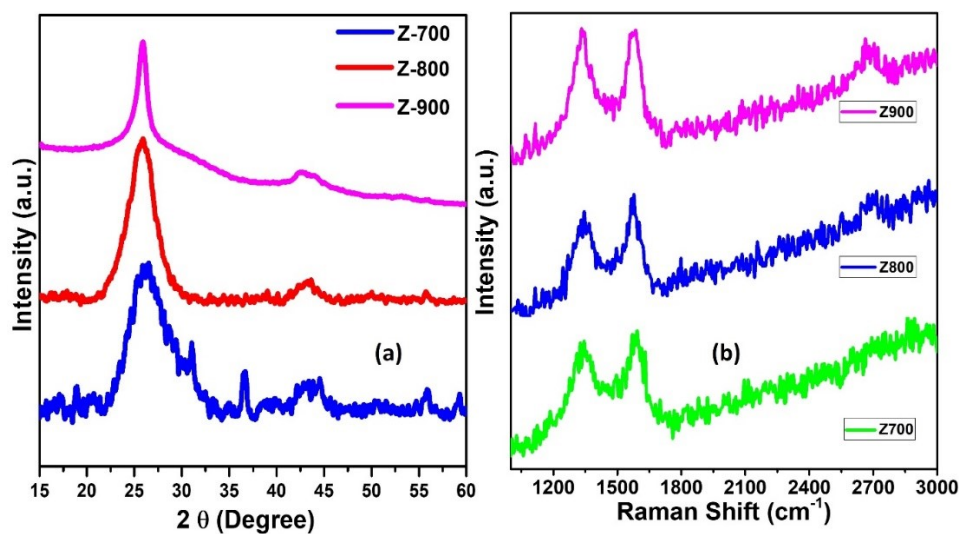


Figure S4. (a) XRD and (b) Raman spectra of Z-700, Z-800, and Z-900.

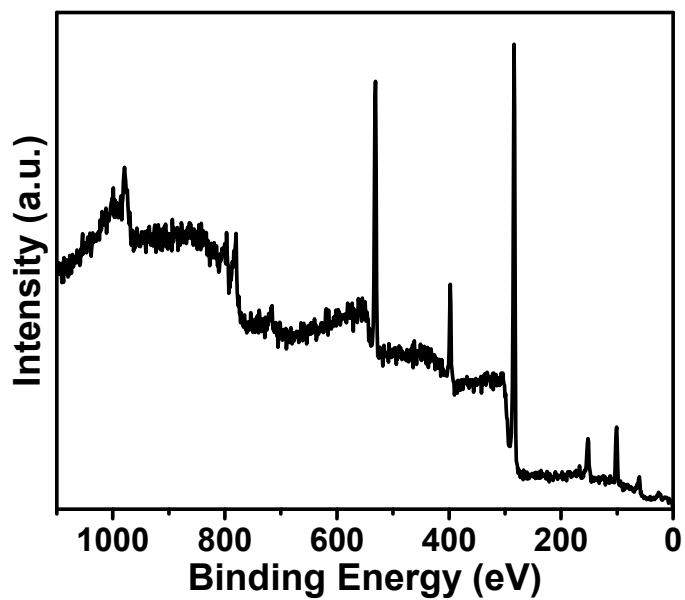


Figure S5. Survey scan of Co₄N/carbon.

S2. Calculations of electrochemical parameters

The calculation for specific capacitance from CV and GCD has been calculated using the following equations-

(i) Three-electrode system

For CV calculation [2],

$$C_s = \frac{1}{2ms\Delta V} \int_{V_i}^{V_f} I(V) dV \quad (S1)$$

where ($\int IdV$) is the integral area of the CV curve, m is the mass of the active material, ΔV is the potential window of the material and s is the scan rate under which CV has been performed.

For GCD calculation

$$C_s = \frac{\Delta t \times I_d}{m \times \Delta V} \quad (S2)$$

Where, Δt is the discharging time, I_d is the discharge current density, m is the mass of active materials on the electrode in g, and ΔV is the voltage window.

(ii) Asymmetric Supercapacitor Device Calculation (two-electrode system)

For GCD calculation

$$C_s = \frac{\Delta t \times I_d}{mt \times \Delta V} \quad (S3)$$

Where, Δt is the discharging time, I_d is the discharge current density, mt is the total mass of positive and negative electrode materials in g, and ΔV is the voltage window of the device.

The energy density and power density is calculated using the following formulae¹,

$$E_s = \frac{C_s \times \Delta V_D^2}{2 \times 3.6} \quad (\text{S4})$$

$$P_s = \frac{E_s \times 3600}{\Delta t} \quad (\text{S5})$$

where, C_s = specific capacitance, Δt = discharging time, ΔV = total potential deviation of the voltage window

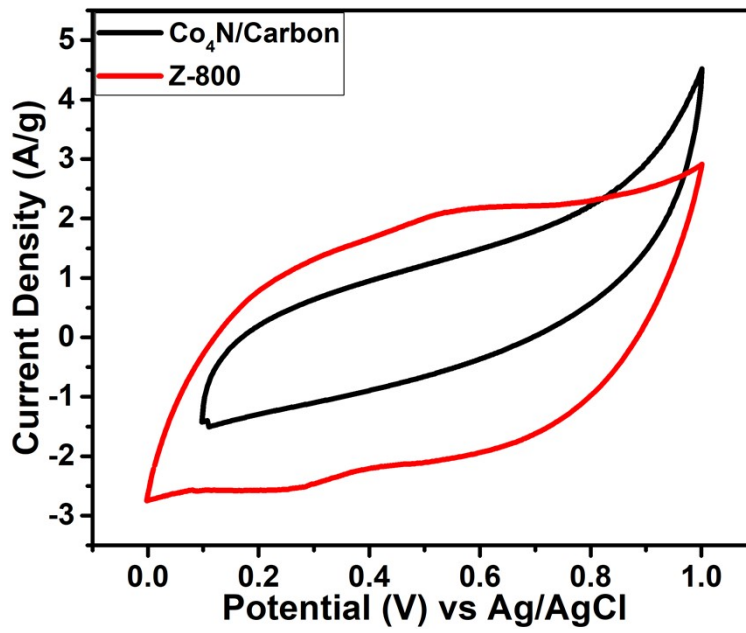


Figure S6. CV comparison of Co₄N/carbon and Z8-800 in positive voltage range.

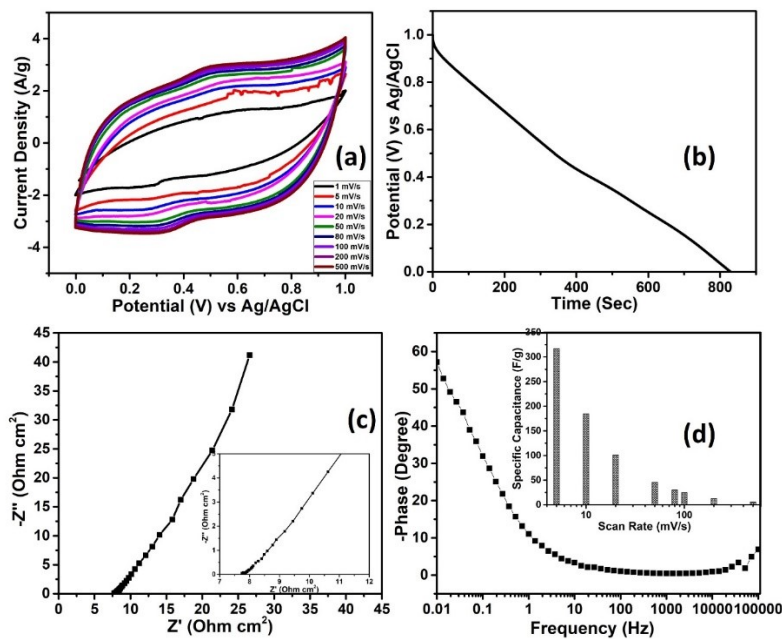


Figure S7. Electrochemical characterization of Z-800 electrode: (a) CV, (b) discharge curve, (c) Nyquist plot, and (d) Phase vs frequency plot (inset: capacitance vs scan rate).

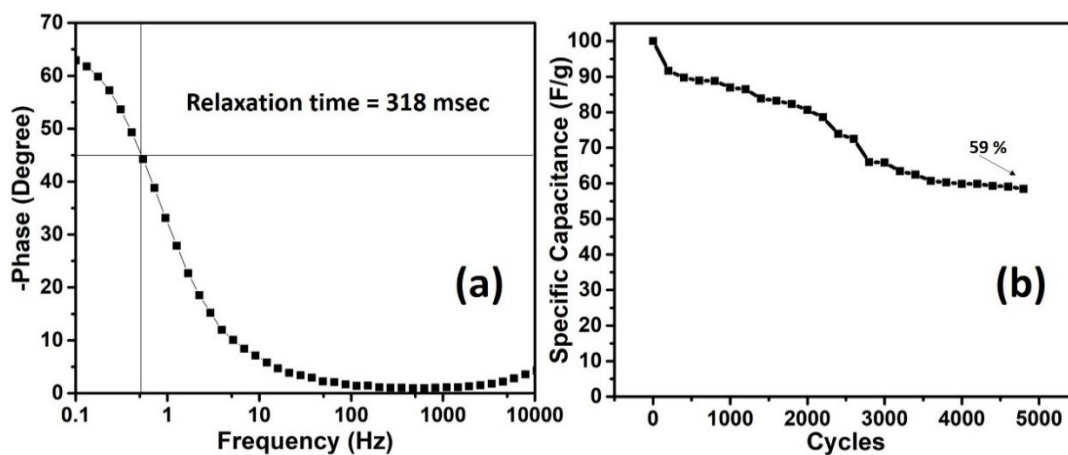


Figure S8. (a) Relaxation time of the Co_4N /carbon electrode from the phase vs frequency plot and (b) cyclic stability test of the Co_4N /carbon electrode.

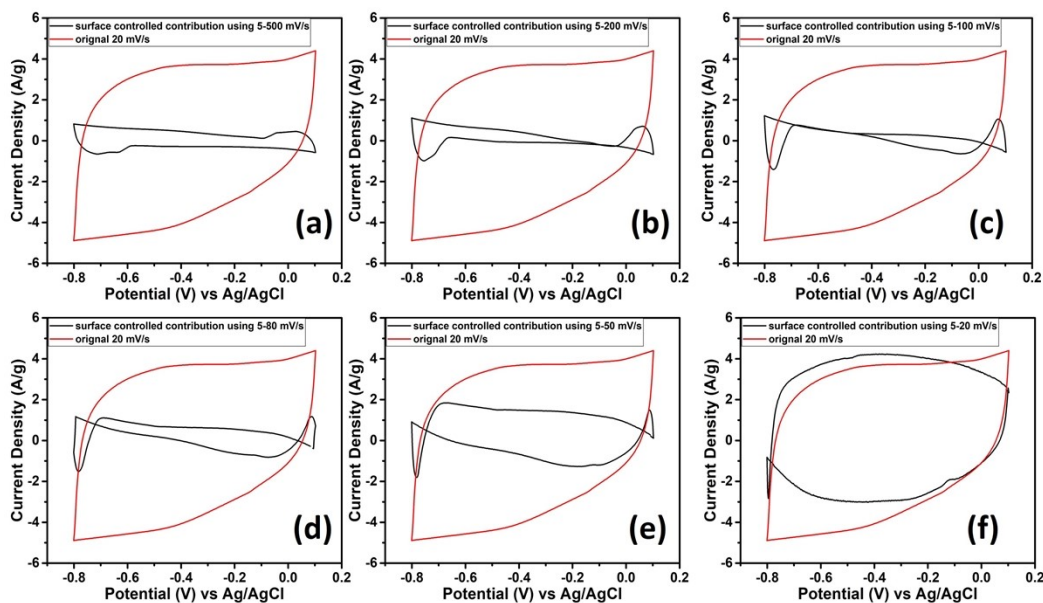


Figure S9. Comparison of original CV area of $\text{Co}_4\text{N}/\text{carbon}$ and the area contributing surface-controlled reaction at 20 mV/s using different slope values using Dunn's method (a) using slope 5-500 mV/s, (b) using slope 5-200 mV/s, (c) using slope 5-100 mV/s, (d) using slope 5-80 mV/s, (e) using slope 5-50 mV/s, and (f) using slope 5-20 mV/s.

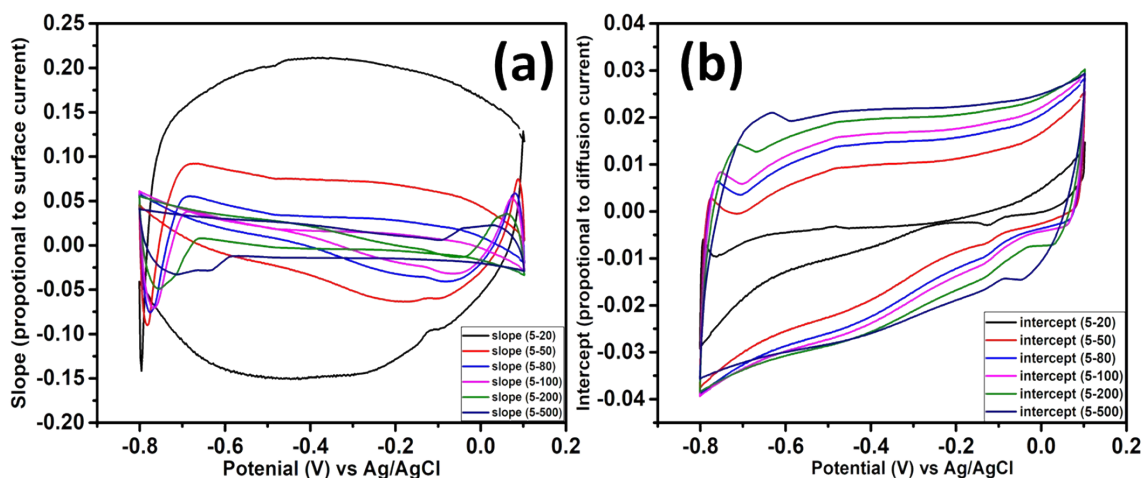


Figure S10. (a) Different slope (proportional to the surface contribution) calculated from different data sets, and (b) different intercept (proportional to the diffusion contribution).

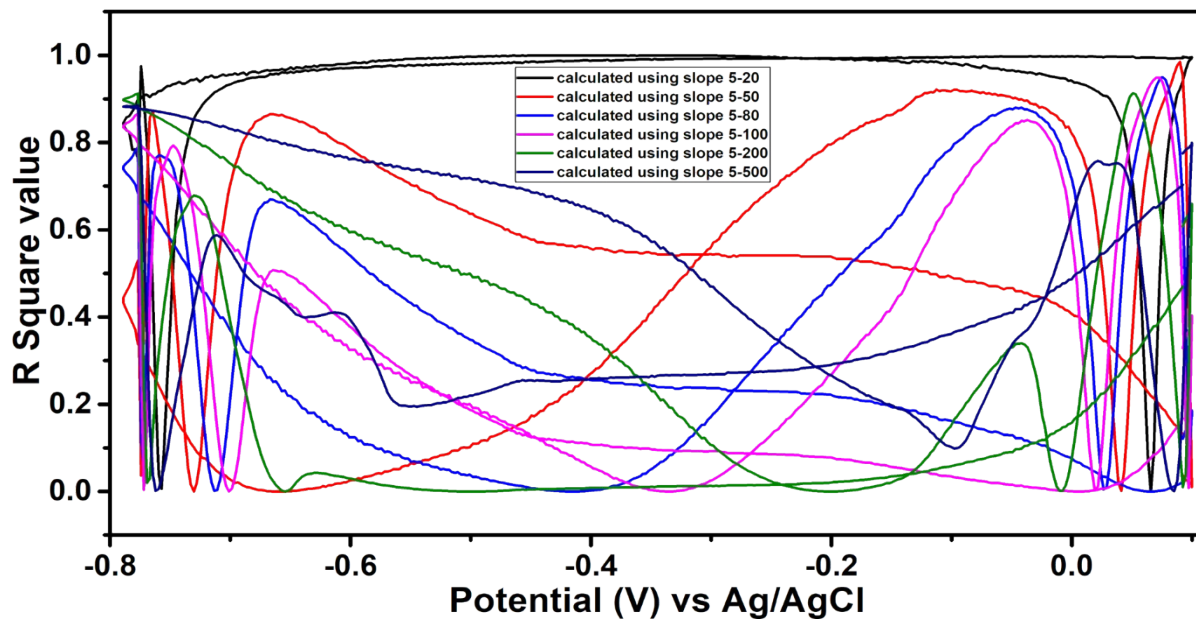


Figure S11. R^2 value of the linear fitting using different scan rate ranges.

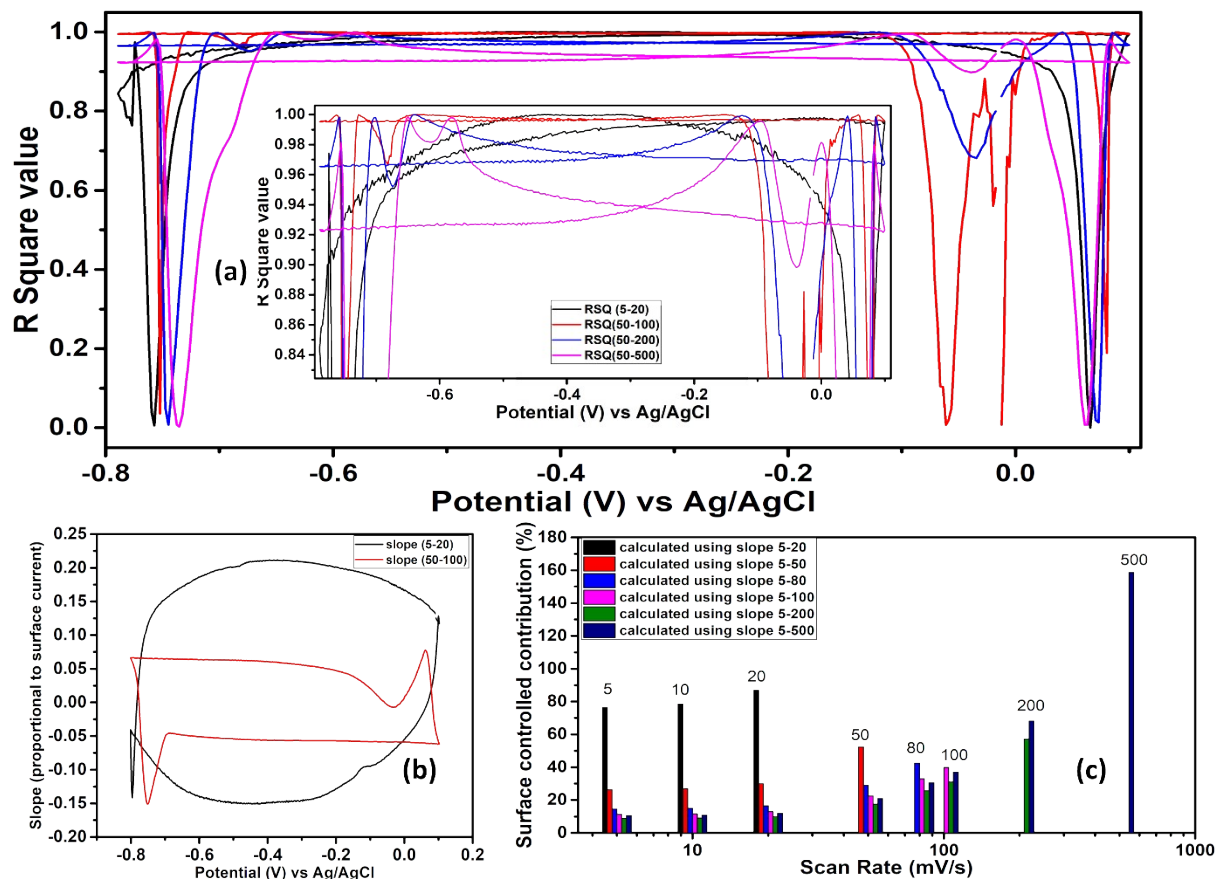


Figure S12. (a) R^2 value of the linear fitting using 5-20, 50-100, 50-200, and 50-500 mV/s of CV data, (b) slope (proportional to the surface contribution) calculated for 5-20 and 50-100 mV/s of CV data set, and (c) surface contribution value calculated from slope of different data sets of CV.

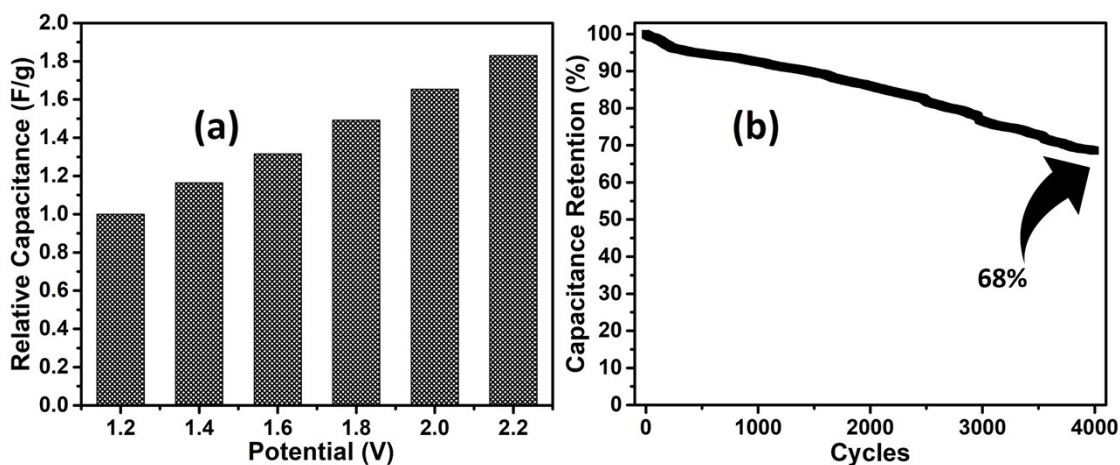


Figure S13. (a) Relative capacitance of the device in different voltage window range, and (b) cyclic stability.

Table S1. Comparison of different material's supercapacitor performance with this work.

Supercapacitor Device	Electrolyte	Energy Density (Wh/kg)	Power Density (kW/kg)	Ref
MOF-derived Co(OH) ₂ //AC	6 M KOH	13.6	0.14	2
MIL-100 (Fe) derived Fe ₃ O ₄ /Fe/C//MIL-100 (Al) derived NPC	6 M KOH	17.49	0.388	3
Ni ₃ S ₂ /MWCNT-NC//AC	2 M KOH	19.8	0.798	4
ZIF-8/PANI	1 M H ₂ SO ₄	21	0.1	5
MOF derived NiO@400//AC	3 M KOH	21.4	0.375	6
ZIF-8 derived AQ functionalized Carbon// NQ and TCNQ functionalized Carbon	1 M H ₂ SO ₄	23.5	0.7	7
ZIF-8 derived ZnO QDs/carbon/CNTs// N-doped carbon/CNTs	1 M Na ₂ SO ₄	26.8	0.847	8
Ni-Zn-BDC derived NiS ₂ /ZnS	3 M KOH	28	0.748	9
ZIF-67/PEDOT//ZIF-67/PEDOT	PVA/1M H ₂ SO ₄	11	0.2	10
ZIF-8 derived NPC// ZIF-8 derived NPC	1M H ₂ SO ₄	10.8	0.22	11
Fe-MOF derived NPC/CNT// Fe-MOF derived NPC/CNT	1M H ₂ SO ₄	18.8	0.3	12
CNTs@Mn-MOF//CNTs@Mn-MOF	1M Na ₂ SO ₄	6.9	0.122	13

Cu-CAT/NWA// Cu-CAT/NWA	PVA/KCl	2.6	0.2	14
CNT@NiO//PCP derived from Zn-MOFs	1 M KOH	25.4	0.4	15
Ni doped MOF-5/rGO//Ni doped MOF-5/rGO	1M KOH	37.8	0.227	16
ZIF-67 derived Co ₄ N/carbon//Z-800	1 M H ₂ SO ₄	26.6	0.36	This work

*AQ= Anthraquinone, NQ= 1, 4-naphthoquinone, TCBQ= tetrachlorobenzoquinone

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