Supporting Information

Assembling a High-Performance Asymmetric Supercapacitor Based on Pseudocapacitive S doped VSe_2/CNT Hybrid and 2D Borocarbonitride Nanosheets

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S1. Experimental

S1.1 Materials

Ammonium metavanadate (NH_4VO_3, SDFCL AR), Selenium dioxide (SeO_2, Himedia), Formic acid (SDFCL AR), Sulphur powder (Himedia), Multi walled carbon nanotube (<5% impurty, 1-10μm length and 3-15 number of walls, Plasma Chem GmbH, Berlin), Boric acid (SDFCL AR), Activated charcoal (Avra), Urea (SDFCL AR) and DI water.

S1.2 Synthesis of S-VSe_2/CNT

117 mg of NH_4VO_3 and 220 mg of SeO_2 is dispersed in 15 mL DI water. Then 5 mL of formic acid is added drop wise into this dispersion. 16 wt % of S powder is dispersed in 10 mL DI water through vigorous 1 hr ultra-sonication. This solution is thoroughly mixed along with the initial dispersion and the solution volume is raised to 40 mL by adding DI water. Further, 50 mg of functionalized (using H_2SO_4 and HNO_3) multiwalled carbon nanotube is added to the mixture under ultra-sonication. The mixture is then transferred into a 50 mL Teflon lined stainless steel autoclave and is kept under 200° C for 24 hrs. After the reaction, the product is

collected and washed several times using DI water and ethanol then dried in vacuum at 60° C.

S1.3 Synthesis of BCN

To synthesize BCN, boric acid (60 mg), activated charcoal (500 mg) and urea (2.4 g) are added into DI water under vigorous stirring and kept at 80° C till a slurry is obtained. The obtained slurry is then transferred into a quartz boat, transferred to a tubular furnace and heated at 900° C under N_2 atmosphere. The obtained black powder is kept in air-tight container to utilize for further analysis.

S1.4 Material Characterization

Structural and morphological characterizations of the samples are carried using X-Ray diffraction (XRD, Rigaku Ultima IV X-ray diffractometer with Ni-filter (Cu Kα, λ = 0.1541 nm) and field emission scanning microscope (FESEM, JEOL JSM-7100F, JEOL Ltd., Singapore). Raman spectroscopy is carried out in LABRAM HR (Horiba Jobin Yvon, 488 λ =nm). X-ray photo electron spectroscopy (XPS) measurements are performed in Thermo K-alpha spectrometer using micro focused and monochromated Al Kα radiation with an energy of 1486.6 eV.

S1.5 Electrochemical Characterization

Electrochemical assessments of all the samples are carried in a Wuhan Corrtest electrochemical work station. The three-electrode analysis are performed in a conventional three electrode cell with Ag/AgCl as reference electrode, Pt wire as counter electrode, a typical glassy carbon electrode with an area of 0.071 cm^2 as working electrode and 0.5M K_2SO_4 as electrolyte. The working electrode is prepared by drop casting 5 µL of active material solution; this is prepared by dissolving 1 mg of active material in a solution containing 95 µL of propanol and 5 µL

Nafion binder. The asymmetric supercapacitor is assembled in a typical Swagelok set up with the working electrodes prepared by drop casting active material solution on a circular Ni foam conducting substrate and Whatman filter paper as a separator. Electrochemical impedance spectroscopy (EIS) measurements are obtained in the frequency range of 0.01 Hz – 10 kHz. The mass loading in both positrode and negatrode are 1 mg and 1.56 mg respectively.

S2. Calculations

In three-electrode configuration;

Areal capacitance (C_A) from cyclic voltammetry;

$$C_A = \frac{\int I\,(V)\,dV}{2 * A * \vartheta * \Delta V} \qquad \text{(S1)}$$

Where, A is the active area of the electrode, ν is the scan rate and ΔV is the potential window.

Areal capacitance (C_A) from galvanostatic charge discharge;

$$C_A = \frac{i * \Delta t}{A * \Delta V} \qquad \text{(S2)}$$

Where, i is the applied current, Δt is the discharge time.

Areal capacitance (C_A) from galvanostatic charge discharge for non-linear curves;

$$C_A = \frac{2 * i * \int V\,dt}{A * (Vf^2 - Vi^2)} \qquad \text{(S3)}$$

Areal capacitance (C_A) of ASC from galvanostatic charge discharge;

$$C_A = \frac{i * \Delta t}{A * \Delta V} \qquad \text{(S4)}$$

Charge balance equation

$$\frac{m_+}{m_-} = \frac{C_- * \Delta V_-}{C_+ * \Delta V_+} \qquad \text{(S5)}$$

Energy density of ASC;

$$E_D = \frac{1}{2}CV^2 \quad \text{(S6)}$$

Where, C is areal capacitance of ASC, V is the working window of ASC.

Power density of ASC;

$$P_D = \frac{E_D}{\Delta t} \quad \text{(S7)}$$

S3. Supporting Figures

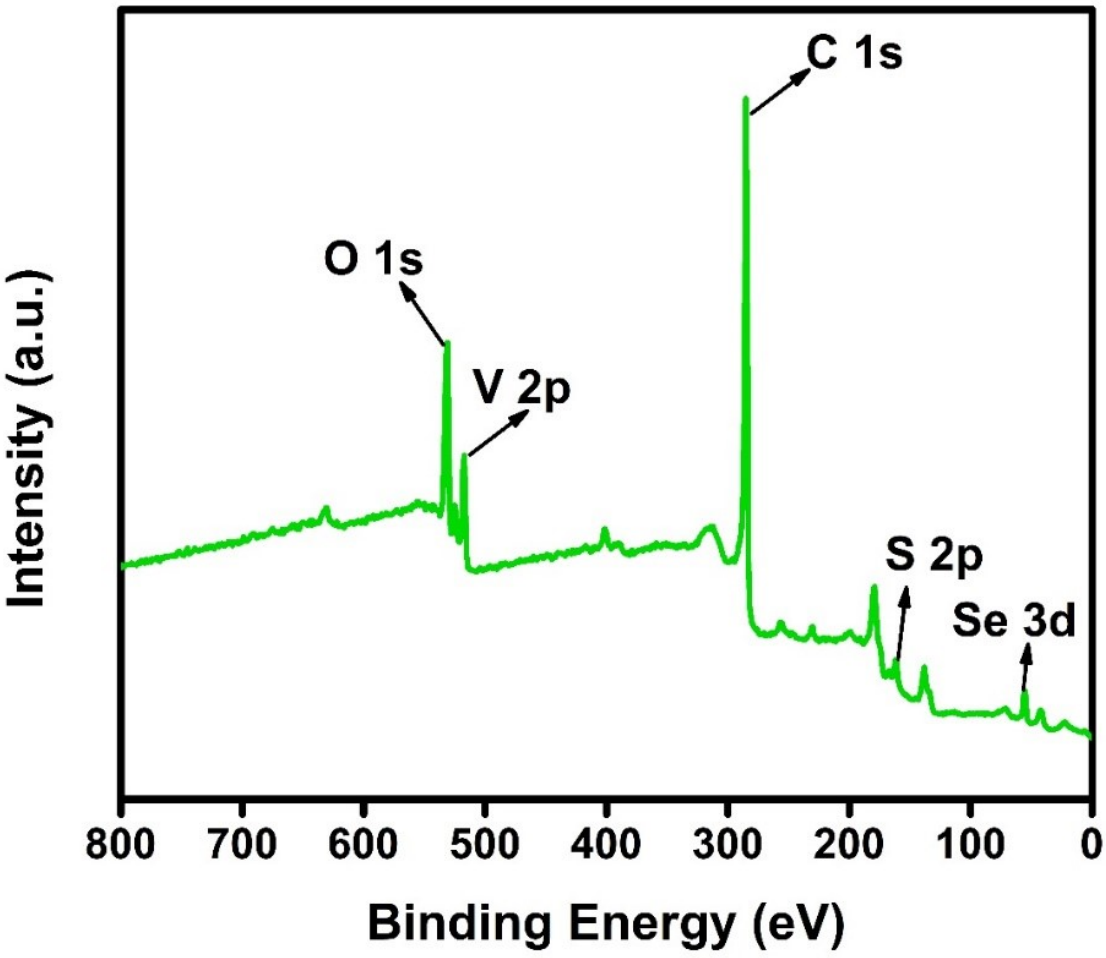

Figure S1: XPS survey spectrum of S-VSe_2/CNT.

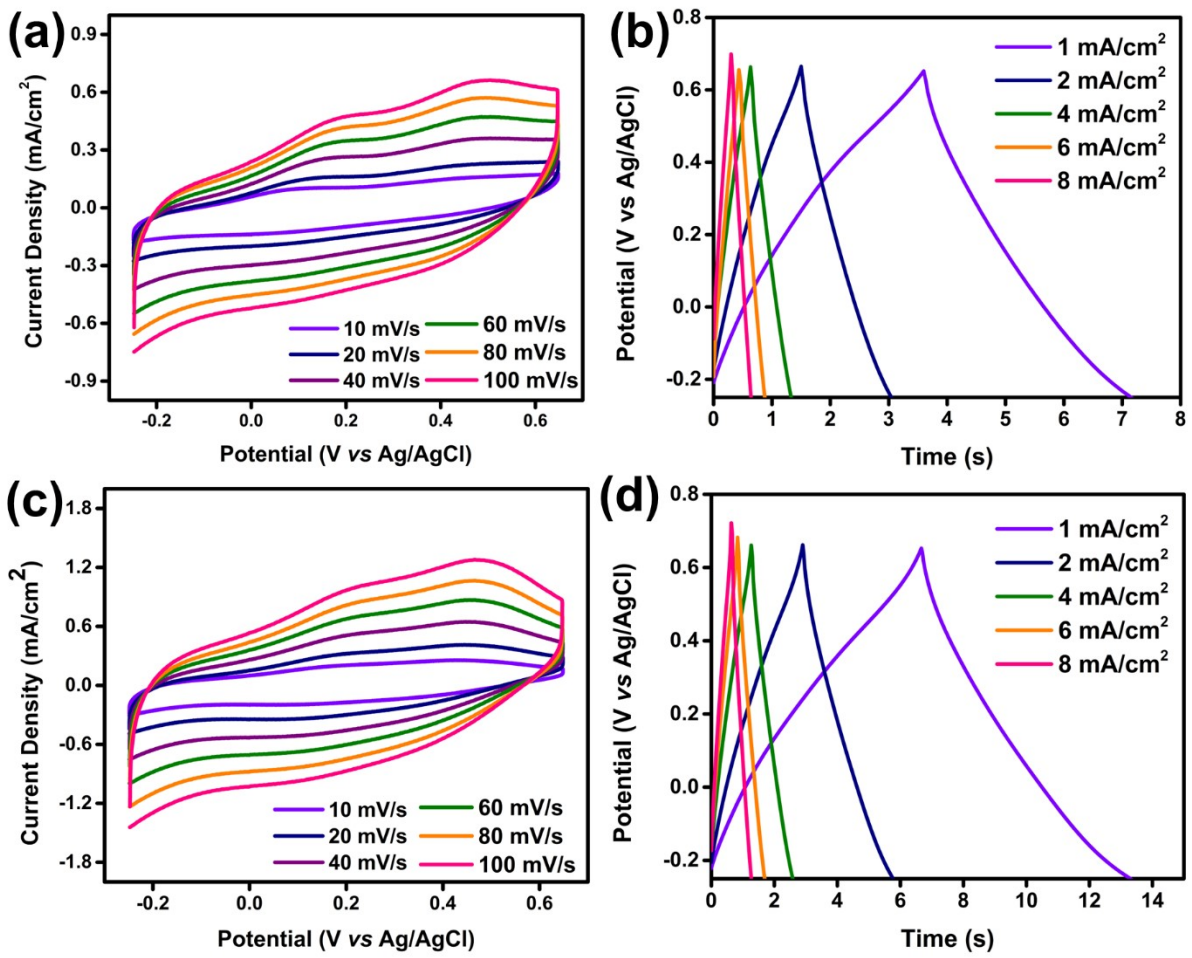

Figure S2: (a) CV and (b) GCD profiles of pristine VSe_2 in various scan rates and current densities respectively, (c) CV and (d) GCD profiles of pristine S-VSe_2 in various scan rates and current densities respectively.

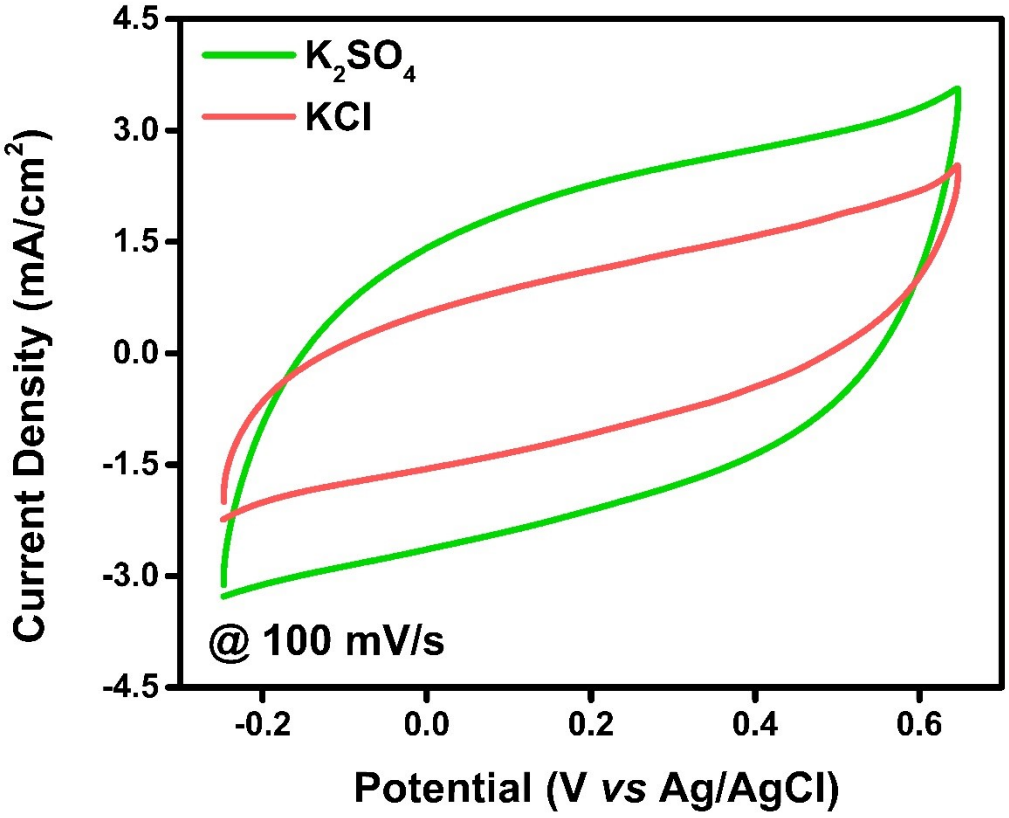

Figure S3: CV curves of S-VSe_2/CNT electrode in both K_2SO_4 and KCl electrolytes.

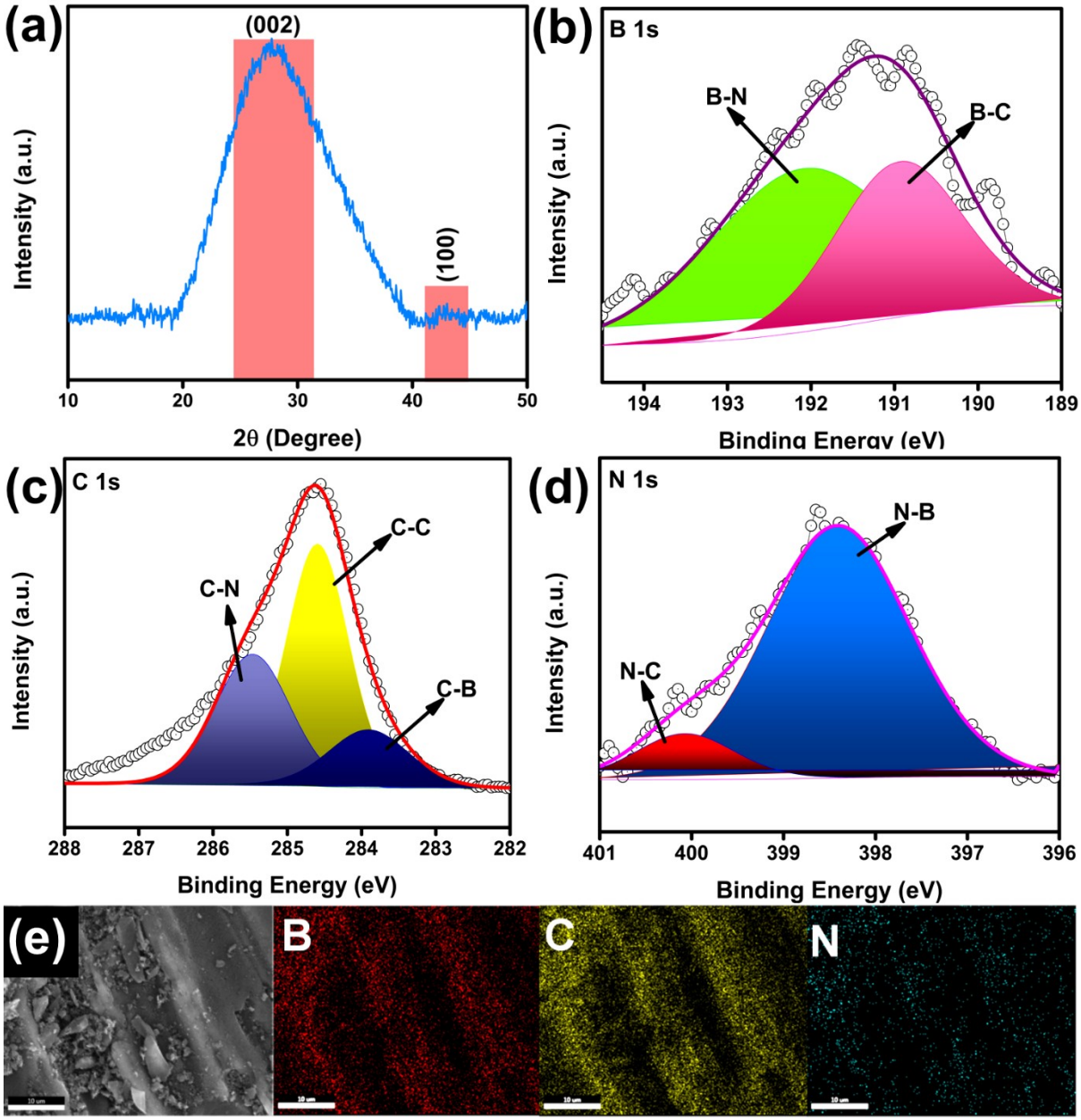

Figure S4: (a) XRD of BCN, High-resolution XPS spectra of (b) B 1s, (c) C 1s and (d) N 1s of BCN and (e) EDS elemental mapping of BCN sheets showing the uniform distribution of B, C and N.

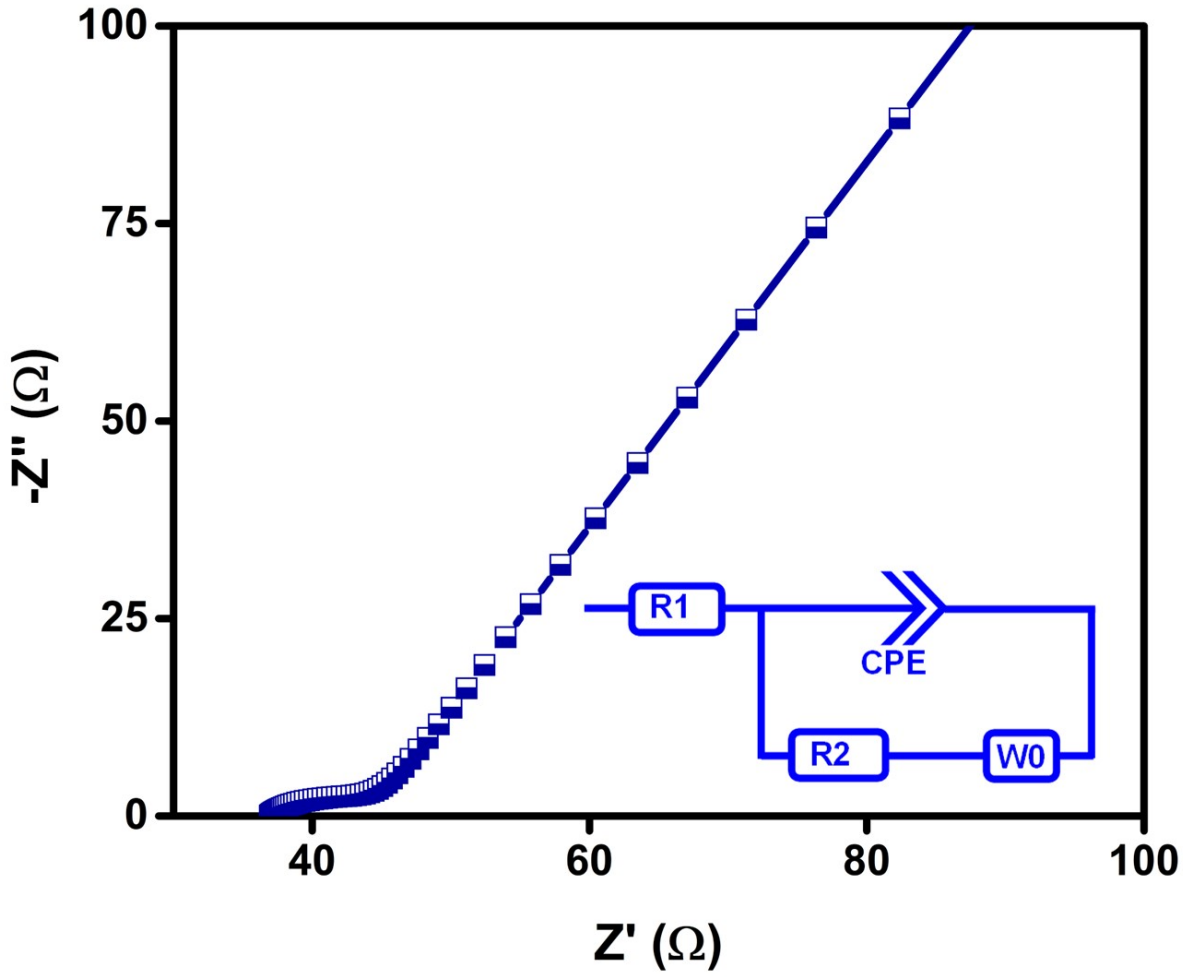

Figure S5: Nyquist plot of BCN electrode; inset showing the equivalent circuit.

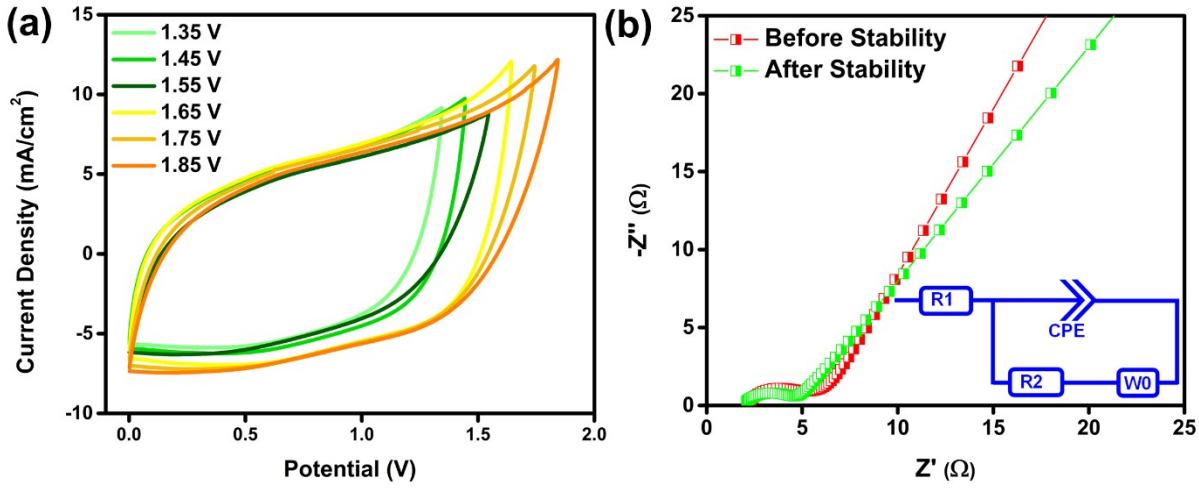

Figure S6: (a) S-VSe_2/CNT//BCN ASC in various working potentials and (b) Nyquist plots of the ASC before and after stability test.

S4. Tables

Table S1: EIS details of VSe_2, S-VSe_2 and S-VSe_2/CNT

Sample	R_s (Ω)	R_{ct} (Ω)
VSe_2	13.9	44.3
S-VSe_2	31.7	20.5
S-VSe_2/CNT	14.4	14.8

Table S2: Comparison of electrochemical performance of S-VSe_2/CNT//BCN ASC with other relevant ASCs.

ASC	Electrolyte	Working Window (V)	Energy Density	Cyclic stability	Ref
$Co(OH)_2$//erGO (CG-ASC)	PVA-KOH	1.4	11.85 μWh/cm^2 at 0.57 mW/cm^2		[52]
RuO_2//Ti_3C_2 in plane	PVA-H_2SO_4	1.5	19 μWh/cm^2 at 1.5 mW/cm^2		[44]
Ni−Co DHs/pen ink/nickel/CF// ink-coated nickel/CF	PVA-KOH	1.55	9.75 μWh/cm^2 at 0.49 mWh/cm^2	86% (5000 cycles)	[53]
$Ni(OH)_2$//AC	PVA-KOH	1.4	11.9 μWh/cm^2 at 0.169 mWh/cm^2	92.7% (7000 cycles)	[54]
MnO_2//Carbon paper	PVA-LiCl	1.8	5.4 μWh/cm^2 at	90%	[55]

			0.28 mWh/cm^2	(2000 cycles)	
CuCHF//PC	PVA-KCl	2.0	37.8 μWh/cm^2 at 0.18 mWh/cm^2	84% (2000 cycles)	[56]
CNT@ZnO-NW@MnO_2//CNT	PVA-H_2SO_4	1.5	13.25 μWh/cm^2 at 0.21 mWh/cm^2	96.7% (1000 cycles)	[57]
d-Ti_3C_2/CF//Ti_3C_2	6M KOH	1.6	18.1 Wh/kg at 397.8 W/kg	80.6% (5000 cycles)	[58]
CuS/ Ti_3C_2//Ti_3C_2	1M KOH	1.5	15.4 Wh/kg at 750.2 W/kg	82.4% (5000 cycles)	[59]
S-VSe_2/CNT//BCN	**0.5M K_2SO_4**	**1.65**	**36.3 μWh/cm^2 at 3.2 mW/cm^2**	**87.3% (5000 cycles)**	**This Work**