Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

High Performance of In-situ Annealed Partial Pressurized Pulsed Laser Deposited (PLD) WO_3 & V_2O_5 Thin Film Electrodes for Flexible all Solid State Supercapbatteries

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Experimental Section:

All the films were prepared using PLD process; the experimental conditions used for the thin film preparation are listed in Table S1.

Table S1: Experimental parameters of PLD

Experimental parameter	value
Wavelength of KrF Eximer	248 nm
Laser Eximer Energy	400 mJ
Pulse reprate rate	5 Hz
Pulse duration	10 ns
Target dimensions	2 inches × 5 mm
Chamber pressure	2×10^{-6} Torr
Film thickness	1 to 1.5 µm
Deposition temperature	RT-650 °C

Capacitance Calculations:

The Areal capacitances of the three electrodes configuration was estimated from CV and GCD curves, respectively

$$C_S(Areal) = \frac{\oint i\,dV}{2A\vartheta\Delta V}\left(\frac{F}{cm^2}\right) \qquad \text{-----------} \quad (1)$$

$Here\ \vartheta \rightarrow Scan\ Rate\ , A \rightarrow active\ area\ of\ the\ electrode, \Delta V - Potential\ window$

$\oint i\,dV - Area\ under\ the\ CV\ curve,$

$$C_{DS}(Areal) = \frac{J_p\Delta t}{\Delta V}\left(\frac{F}{cm^2}\right) \qquad \text{----------} \quad (2)$$

$Here\ J_p \rightarrow \frac{i}{A}\ Current\ density\left(\frac{A}{cm^2}\right)$

The Volumetric capacitances was calculated from CV and GCD curves along with the following equation

$$C_{Vol} = \frac{\oint i\,dV}{2V_{vol}\,\vartheta\Delta V}\left(\frac{F}{cm^3}\right) \qquad \text{---------} \quad (3)$$

$V_{total} = Volume\ of\ the\ device$

$$C_{Vol} = \frac{J_p\Delta t}{\Delta V}\left(\frac{F}{cm^3}\right) \qquad \text{-----------} \quad (4)$$

$J_p \rightarrow \frac{i}{V_{vol}}\ Current\ density\left(\frac{A}{cm^3}\right)$

The specific area and volumetric capacitance of the symmetric devices were calculated from CV and GCD curves by using following equation

$$C_{spec} = 2C_S \qquad \text{-----------} \quad (5)$$

The specific area and volumetric capacitances of the HSC device were investigated from GCD curves by using following relation

$$C_{spec} = 4C_S \qquad \text{-----------} \quad (6)$$

To construct an HSC, the charges stored on the electrodes are balanced using the below relation, The calculated specific capacitances (C) of single electrode, the voltage range for the HSC device by using GCD method (ΔV), and the active mass of the thin film electrodes (m), succeeding the equation:

$$\frac{m_+}{m_-} = \frac{C_{S-}\Delta V}{C_{S+}\Delta V} \qquad ------------ \qquad (7)$$

m+ mass of the positive electrode, m- mass of the negative electrodes; Cs- specific capacitance of the negative electrode and Cs+ specific capacitance of the positive electrode obtained from the three electrode testing's.

The coulombic efficiency of the each GCD curve were calculated following the equation

$$\eta(\%) = \frac{\Delta t_d}{\Delta t_c} \times 100 \qquad ----------- \qquad (8)$$

$Here\ \Delta t_d \rightarrow discharging\ time, \Delta t_c \rightarrow charging\ time$

The volumetric specific energy density (E) and volumetric specific power density (P) alongside symmetric and HSC devices were estimated with the following equations

$$E = \frac{C_{cell}V^2}{3600} \quad \left(\frac{mWh}{cm^3}\right) \qquad ----------- \qquad (9)$$

$$P = \frac{E}{\Delta t_d} \times 3600 \quad \left(\frac{mW}{cm^3}\right) \qquad --------------- \qquad (10)$$

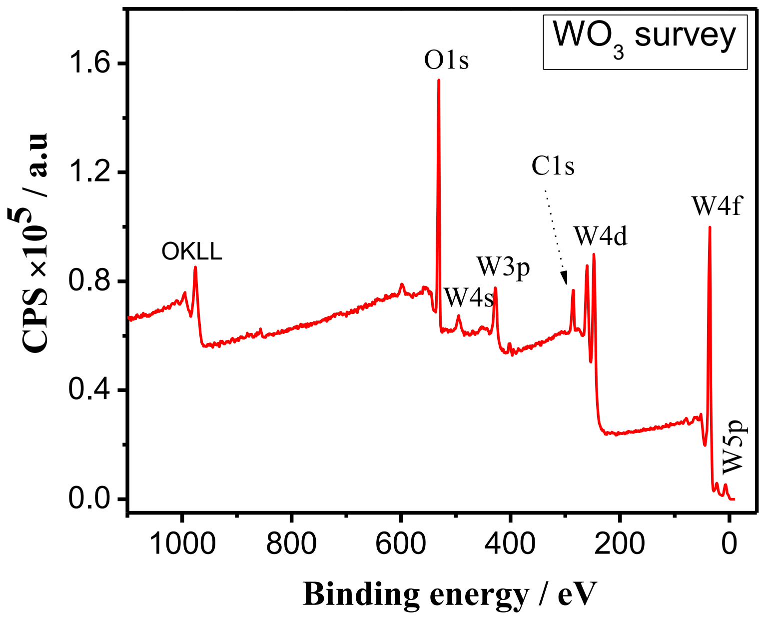

Figure S1: (a) XPS survey spectra of WO_3 thin film.

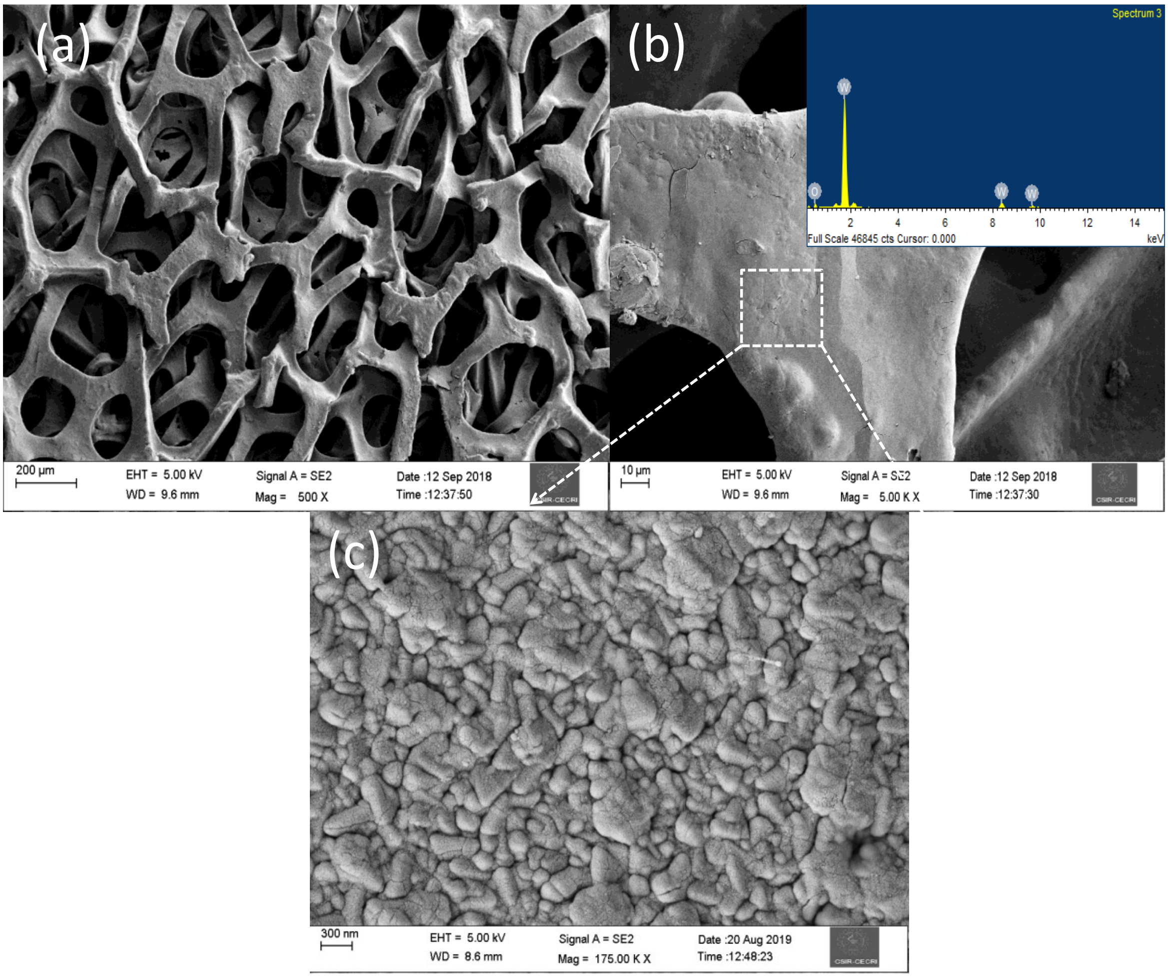

Figure S2: FESEM image of WO_3 annealed sample at different magnification coated on Ni-foam substrate: a) x 500; b) X 5k (inset view –EDAX spectrum) ; c) X 175k.

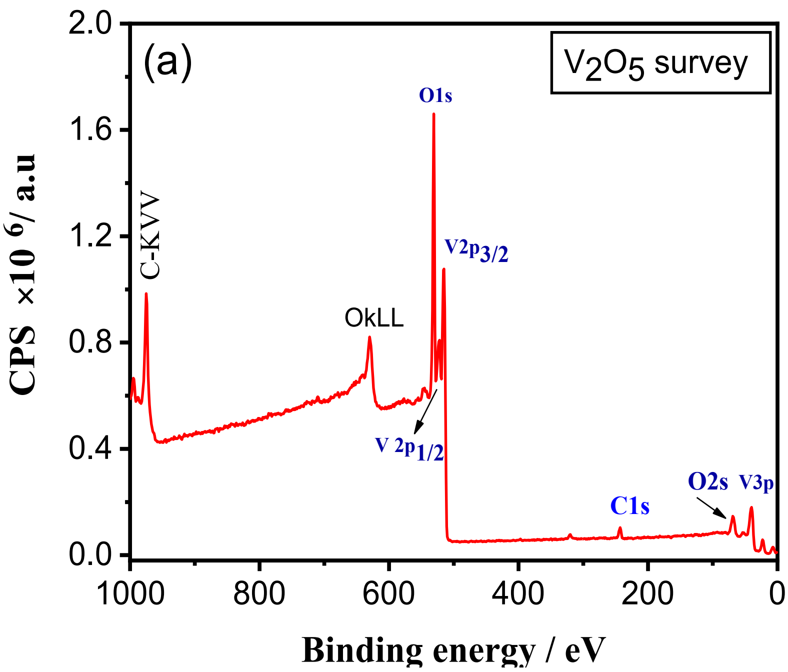

Figure S3: (a) XPS survey spectra of V_2O_5 thin film

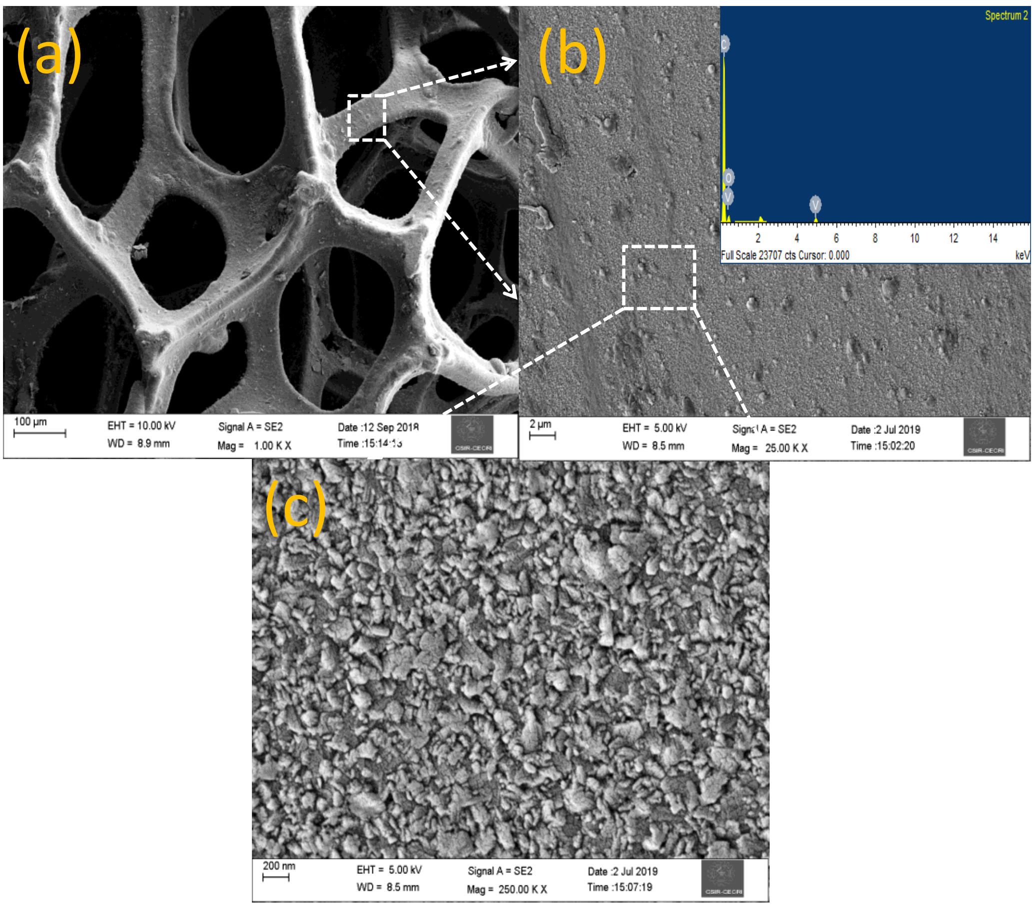

Figure S4: FESEM image of V_2O_5 annealed sample at different magnification coated on Ni-foam substrate: a) x 500; b) X 5k (inset view –EDAX spectrum) ; c) X 175k.

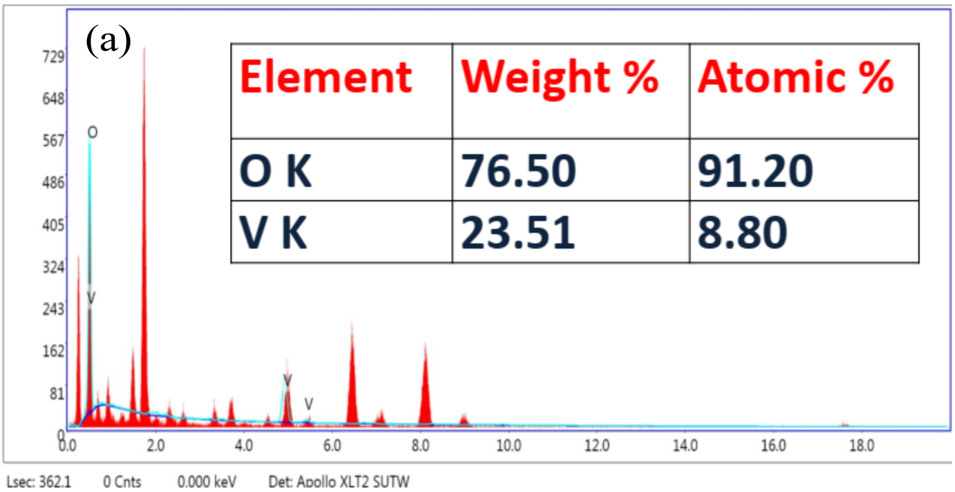

Figure S5; TEM EDAX spectrum of V_2O_5 thin film as prepared

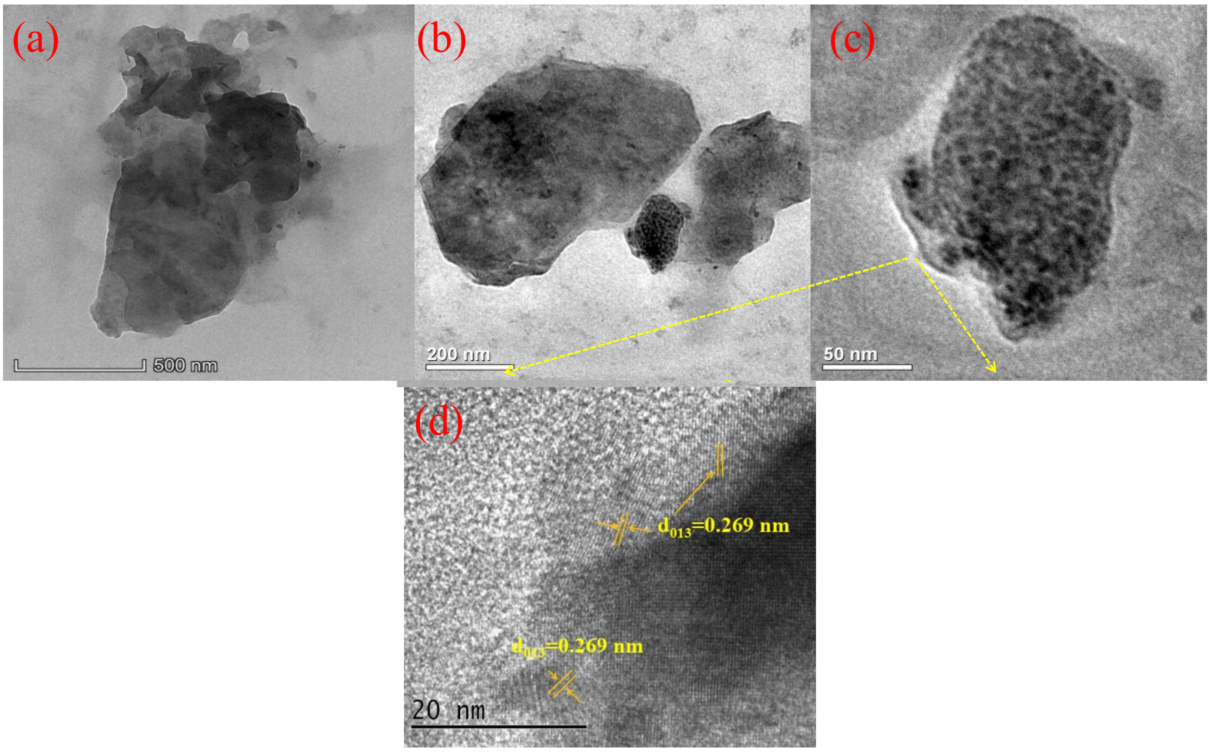

Figure S6: V_2O_5 thin film as prepared sample; **(a-c)** TEM images of the low and high magnifications; d) HR-TEM images with lattice planes;

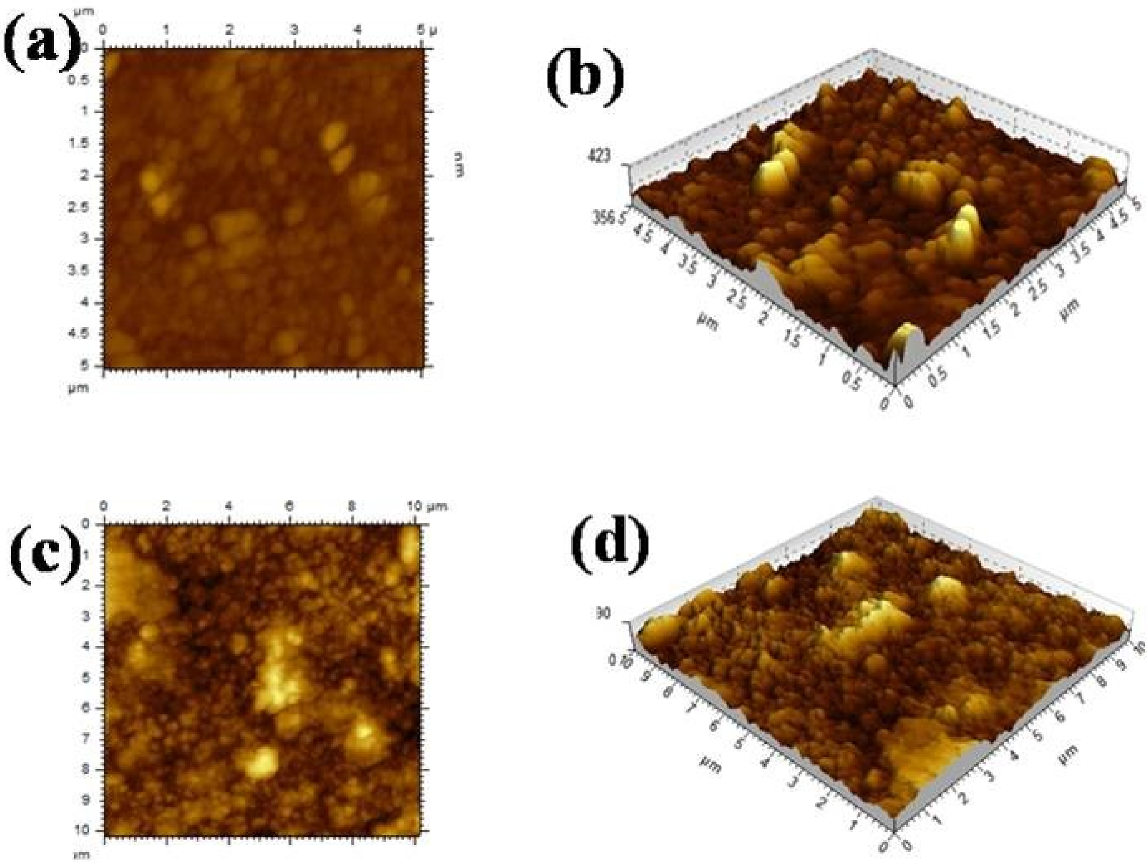

Figure S7; a-b) AFM 2D and 3D topographic images of V_2O_5 thin film; **(c-d)** AFM 2D and 3D topographic images of WO_3 thin film;

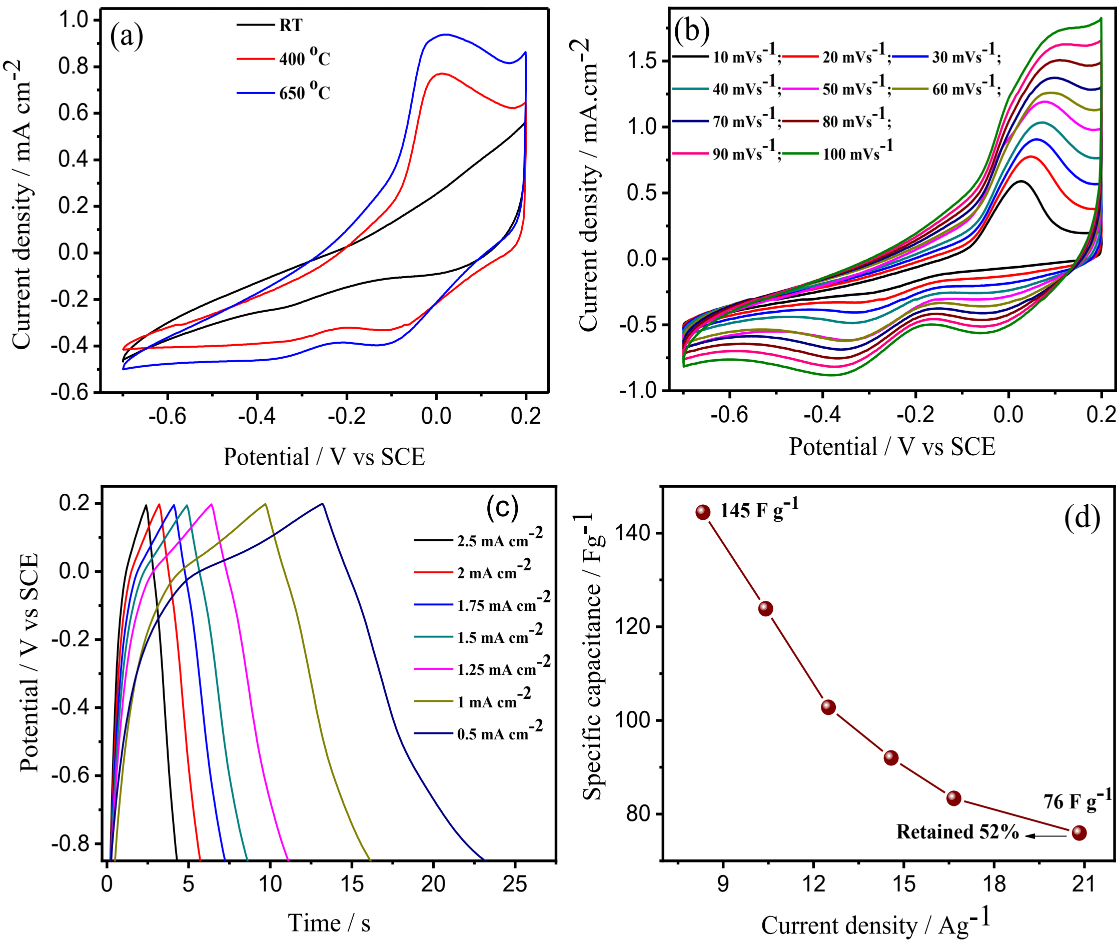

Figure S8; a) CV curve comparisons of the different WO_3 thin film electrodes annealed at different temperature in a three electrode configuration at scan rate of 50 mV. s^{-1}. **;** (b) CV curves of the WO_3 thin film electrode different scan rates annealed at 650 °C tested at three electrode systems; (c) GCD profile curves of the sample annealed at 650 °C at different current density tested at three electrode systems; (d) Discharge capacitance vs. current density.

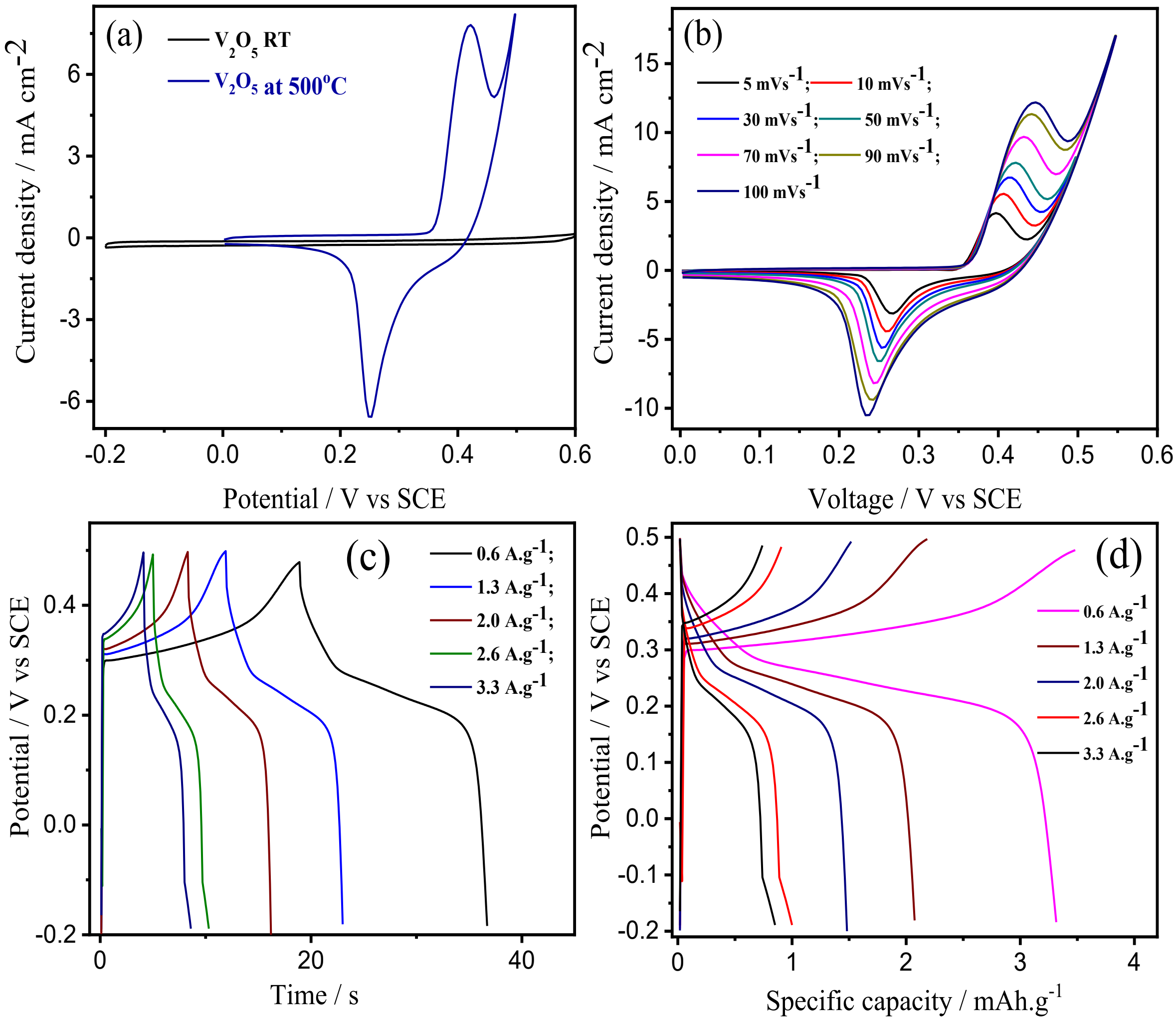

Figure S9: a) CV curve of as prepared and annealed at 500 °C V_2O_5 coated carbon paper in a three electrode configuration at scan rate of 100 mV.s^{-1};((b) CV curves of the V_2O_5thin film electrode different scan rates annealed at 500 °C tested in a three electrode systems; (b) GCD curves of the sample annealed at 500 °C at different current density tested at three electrode systems; (b) Specific capacity vs potential of the sample annealed at 500 °C

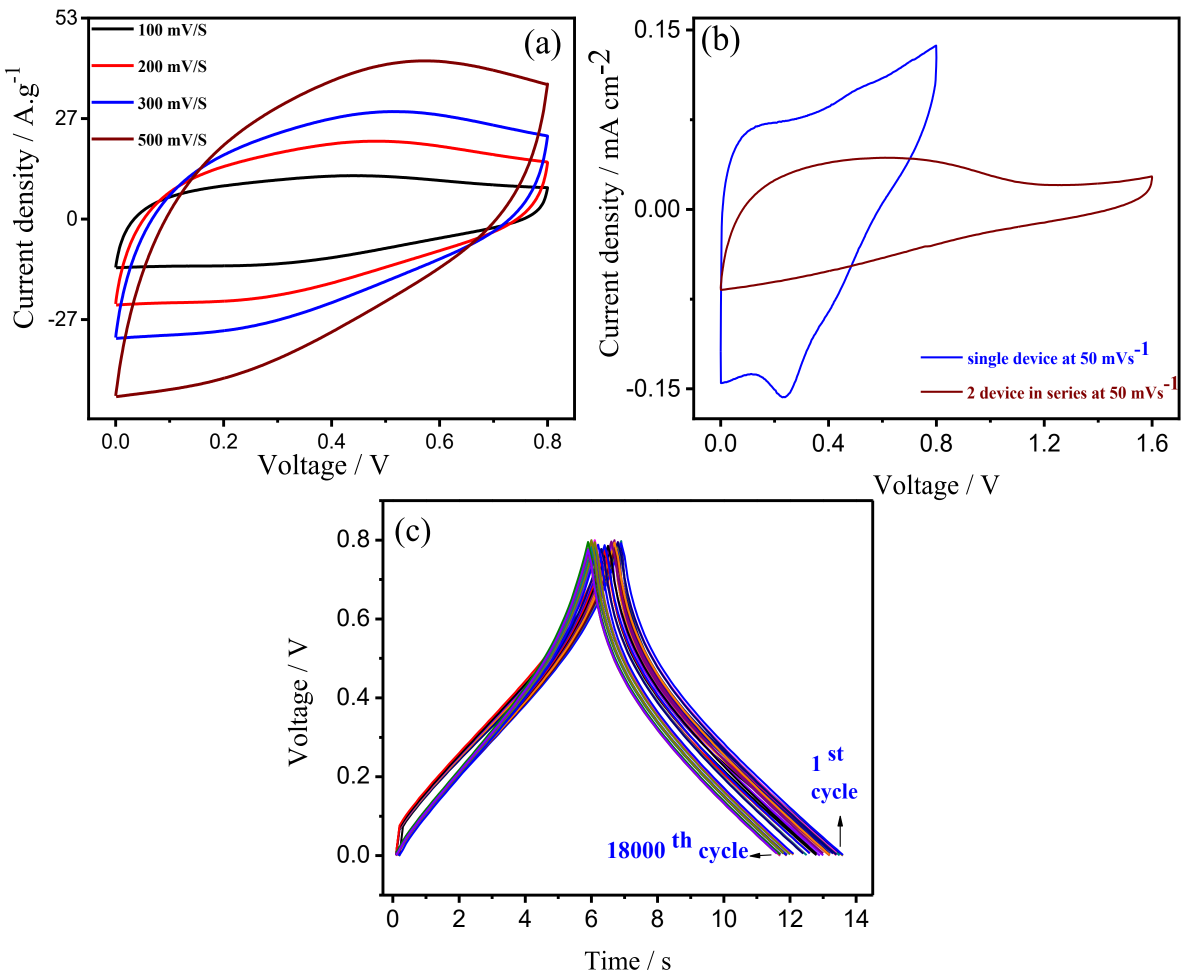

Figure S10; (a)CV curves performance of the WO_3 symmetric device at high scan rates ;(b) CV curves of WO_3 symmetric two devices in series; (c) GDC profile of WO_3 symmetric device stability curve for every 500th cycle up to 18k are compared.

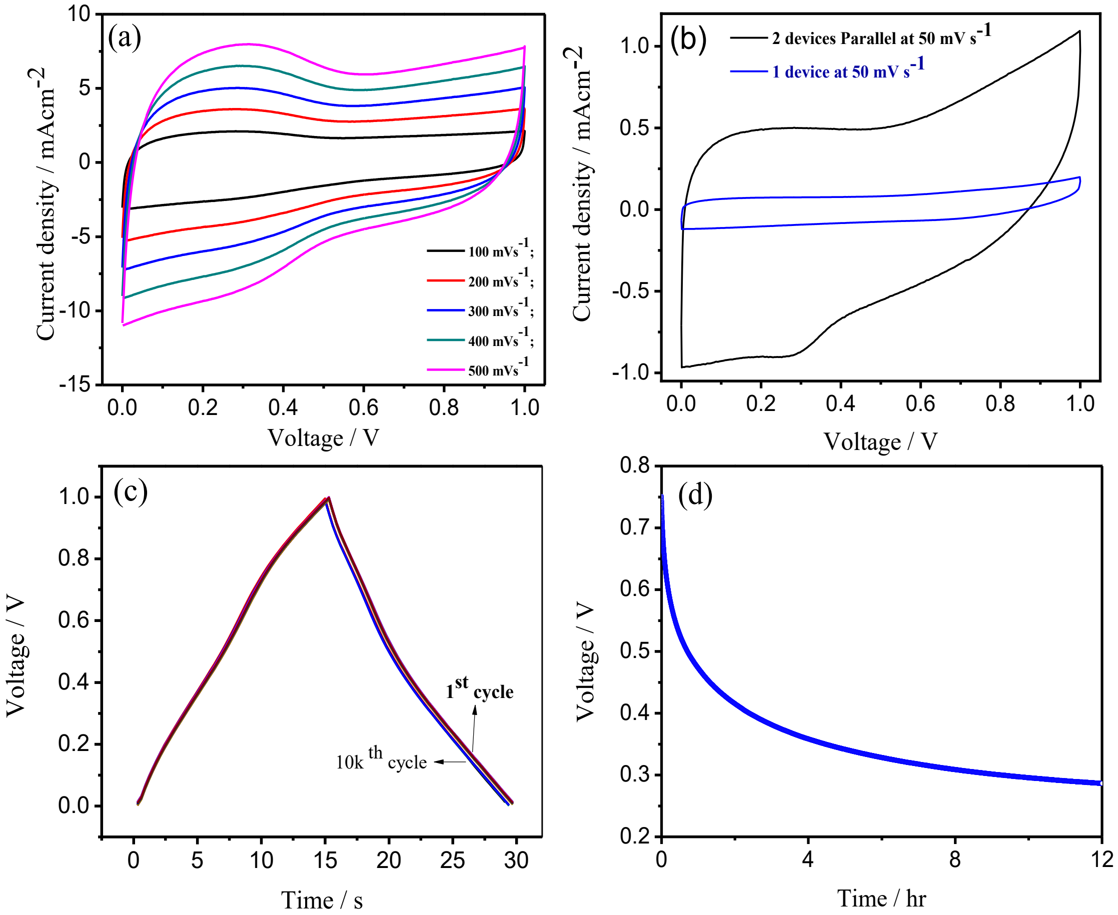

Figure S11 : (a)CV curves performance of the V_2O_5 symmetric device at high scan rates ;(b) CV curves of two devices in parallel at scan rate 50 mVs^{-1};(c) GCD profile comparisons of the V_2O_5 symmetric device stability every 1k cycles; (d) Self-discharge study of the V_2O_5 symmetric supercapacitor.

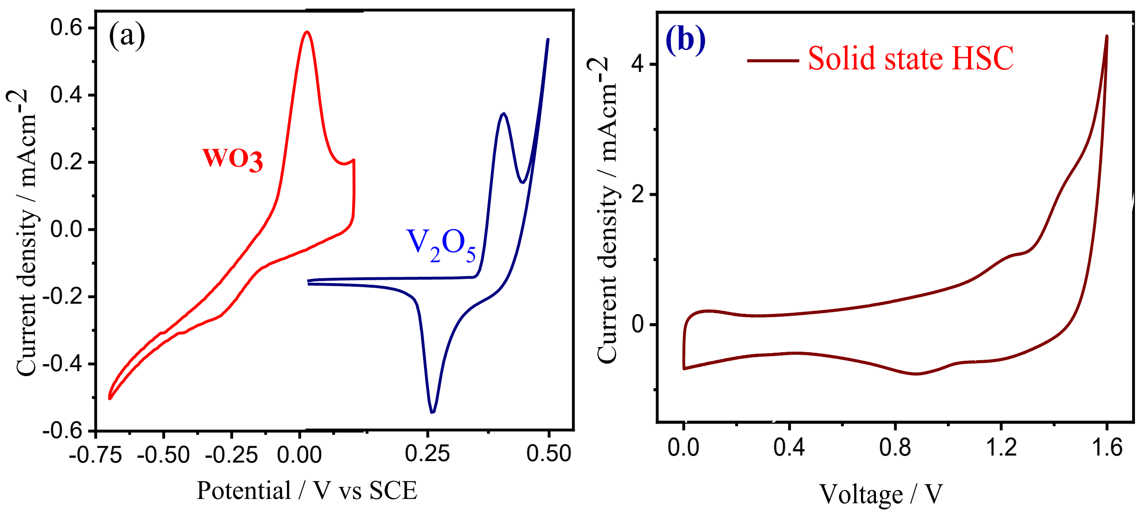

Figure S12; a) CV curve combination of positive and negative electrodes in a three electrode configurations at scan rate of 50 $mV.s^{-1}$; b) CV curve of HSC device at scan rate of 50 $mV\ s^{-1}$.

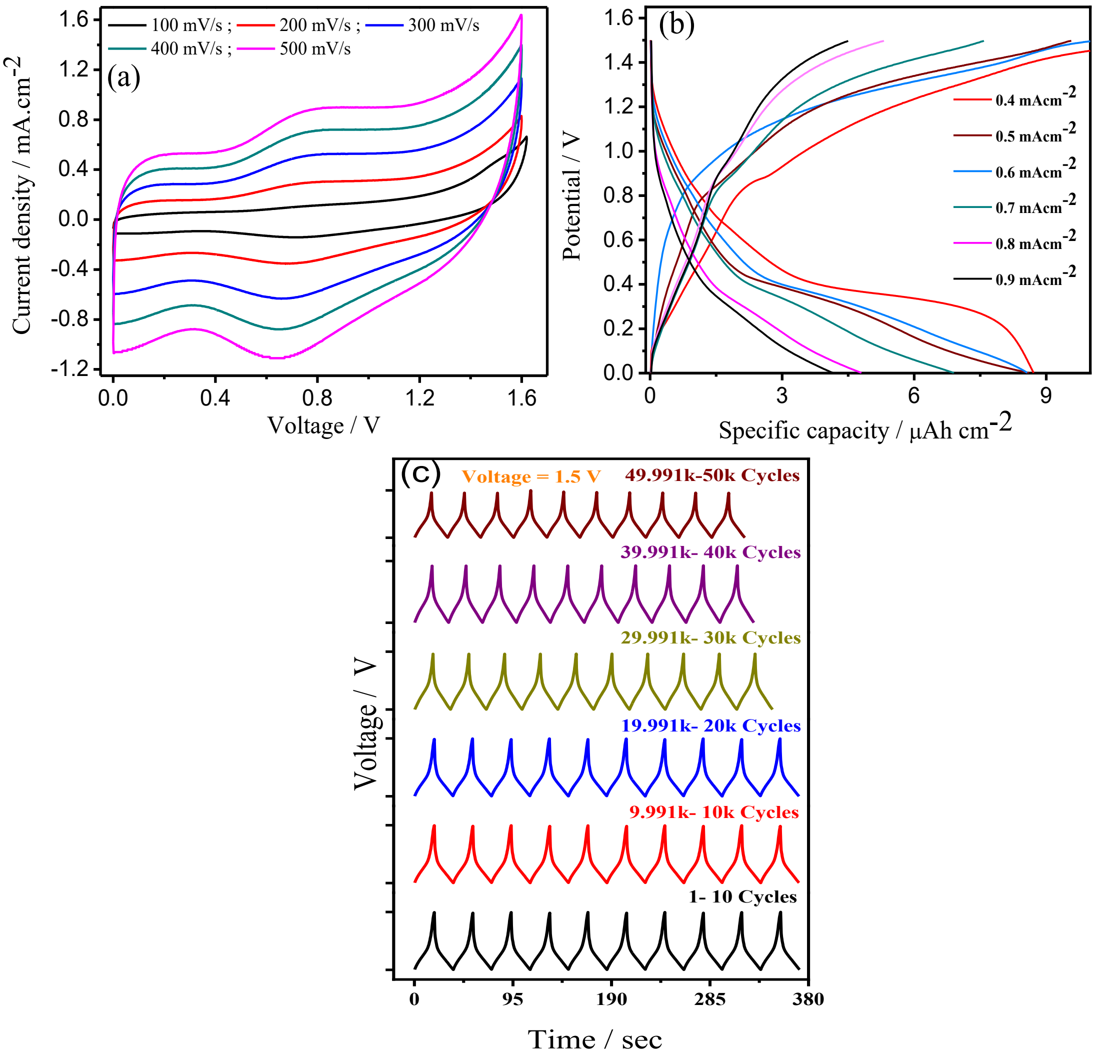

Figure S13; a) CV curves of solid state HSC device at high scan rates; (b) specific capacity curve at different current density; (c) GCD profile comparison of an HSC device at different cycle range.

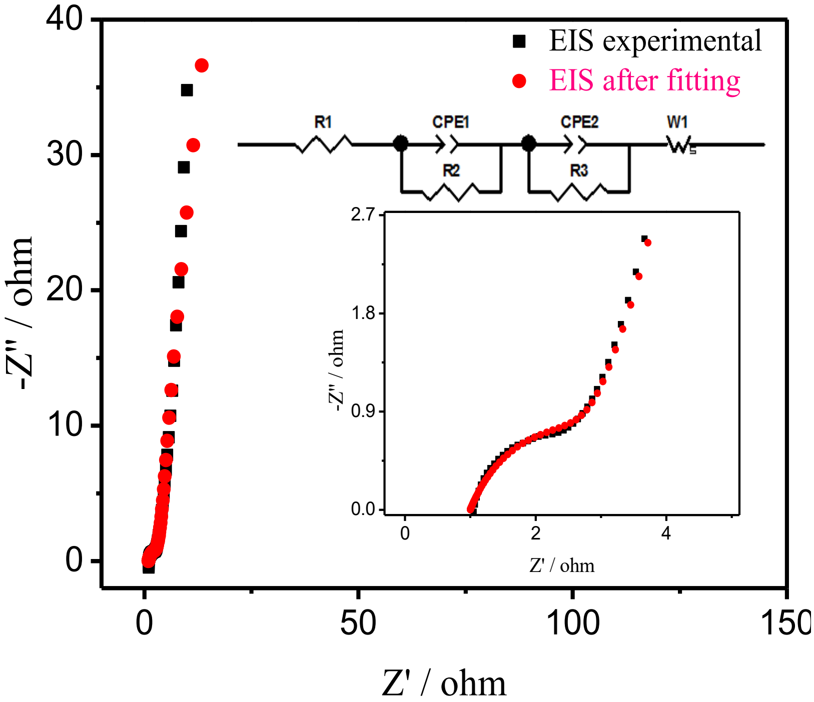

Figure S14; EIS analysis comparisons of the pristine solid state HSC device and after fitting EIS curve with equivalent circuit.

Table S2: EIS model fitting parameters

Element	**Value**	**Error**	**Error%**
R1	1	N/A	N/A
CPE1-T	0.21	N/A	N/A
CPE1-P	0.88	N/A	N/A
CPE2-T	0.03	N/A	N/A
CPE2-P	0.63	N/A	N/A
W1-R	0.627	N/A	N/A
W1-T	0.7	N/A	N/A
W1-P	0.5	N/A	N/A

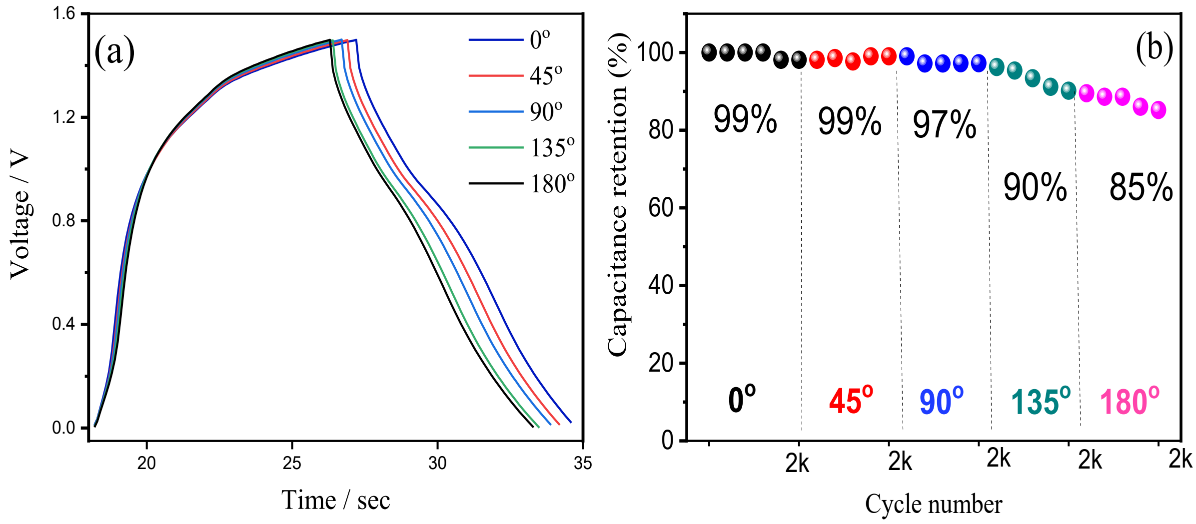

Figure S15; (a) GCD characteristics of solid state HSC device in various bending positions such as 0 to 180 deg; (b) capacitance retention curve at different bending angles such as 0 to 180 deg.

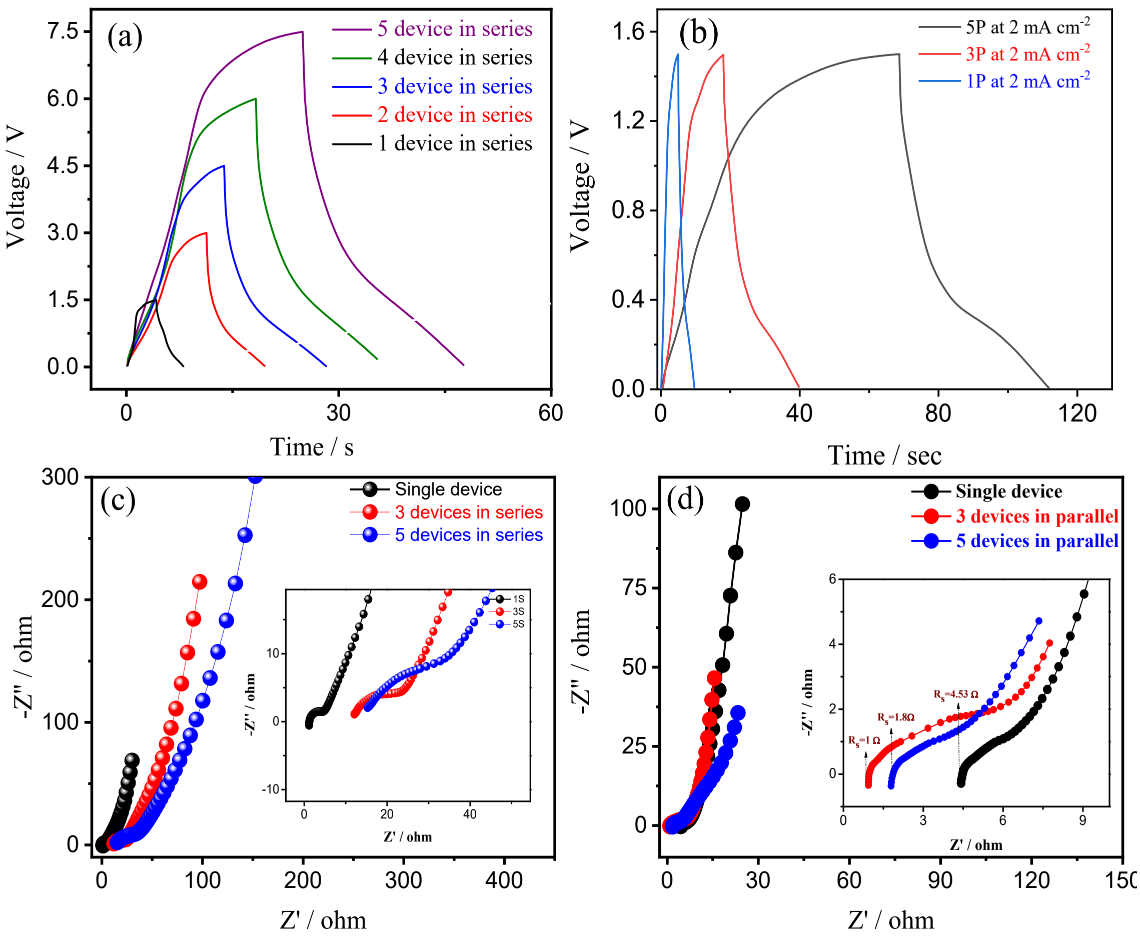

Figure S16; :(a)GCD profile comparison solid state HSC devices in series combination at a current density of 5 mA.cm^{-2}; (b)GCD profile comparison solid state HSC devices in parallel combination at a current density of 2 mA.cm^{-2}; (c) EIS comparison solid state HSC devices in series combination; (d) EIS comparison solid state HSC devices in parallel combination.

Table S3: The electrochemical stability of the WO_3 thin film based supercapacitor comparison study with the reported literature

Reported Materials	**Method**	**Electrolyte**	**Voltage Window [V]**	**Specific capacitance**	**Ref**
WO_3	SILAR	1 M Na_2SO_4	0.8V	266 Fg^{-1}	[1]
WO_3	Wet chemical method	1 M H_2SO_4	-0.2 to -0.7	246 $F g^{-1}$	[2]
WO_3 Polymorphs	Hydrothermal	1M H_2SO_4	-0.6 to 0.2V	377.5 Fg^{-1}	[3]
WO_3	RF Magnetron sputtering	1M $LiClO_4$ + PC	−0.9 and 0.5 V	228 $F g^{-1}$	[4]
Pd-WO_3	Hydrothermal	1M Na_2SO_4	−0.7 to 0.1V	33.3 Fg^{-1}	[5]
WO_3	Electrodeposition	1M H_2SO_4	-0.5 to 0.2 V	138.2 $F g^{-1}$	[6]
$WO_3@W_{18}O_{49}$-CNF	Electro-spinning	4 M KOH	−0.85-0.05 V	333.92 $F g^{-1}$	[7]
MWCNTs-WO_3	ZnNPs	1M H_2SO_4	2.0 V	103 $F g^{-1}$	[8]
WO_3	**PLD**	**2M KOH**	**-0.2 to 0.7V**	**145 $F g^{-1}$**	**This work**

Table S4: The electrochemical stability of the V_2O_5 thin film based supercapacitor comparison study with the reported literature

Reported Material /Symmetric Devices	Method	Electrolyte	Potential Window [V]	Specific capacitance	Ref
V_2O_5/MWCNT	Hydrothermal Method	H_2SO_4–HNO_3	-0.2 to 0.8 v	410 F g^{-1}	[9]
V_2O_5/ PPY	Slurry	5 M $LiNO_3$	0 to 1 V	448 F g^{-1}	[10]
V_2O_5/ Graphene	Atomic Layer Deposition	1M Na_2SO_4	0 to 1 V	189 F g^{-1}	[11]
V_2O_5	Thermal treatment	0.5 M K_2SO_4	-0.1 to 0.8 V	417 F g^{-1}	[12]
V_2O_5	Hydrothermal reduction	1M $LiClO_4$	-0.3 to 1.1V	405 F g^{-1}	[13]
V_2O_5	Spray pyrolysis	1M KCl	-1.35 to 0.05V	307.3 F g^{-1}	[14]
V_2O_5	Hydrothermal	1M Na_2SO_4	0 to 0.8V	177 Fg^{-1}	[15]
Graphene /V_2O_5	Hydrothermal	1M Na_2SO_4	0 to 0.6 V	457 Fg^{-1}	[16]
V_2O_5	Thermal evaporation	PVA-KOH	0 to1V	10 Fg^{-1}	[17]
V_2O_5	**PLD**	**2M KOH**	**0 to 0.6 V**	**433 Fg^{-1}**	**This work**

Table S5: State of art of the thin film based electrode materials and their performance characteristics with other metal oxide symmetric supercapacitor

Reported SC Devices	Method	Electrolyte	Potential Window [V]	Specific Capacitance	Energy Density [Wh/ kg]	Power Density [kW/ kg]	Stability [Cycles]	Retention	Ref
MnO_2	Pulsed Electrochemical Deposition	BMIBF4	1V	39.68 mF/ cm^2	---	----	--	---	[18]
α -MoO_3	Hydrothermal	1 M H_2SO_4	0.26–0.43 V	64 μF/ cm^2	---	----	720	----	[19]
MoO_2	Magnetron Sputtering	0.5 M Li_2SO_4	-0.8 to 0.2V	31 mF/ cm^2	----	---	12000	89%	[20]
$(Fe,Cr)_2O_3$	Thermal Oxidization	2 M KOH	0 to -1 V	45.92 mF/cm^2	0.57 mWh/ cm^2	200 mW/ cm^2	10000	90%	[21]
$NiCo_2O_4$ Symmetric	Electrospinning	PVA-KOH	1 V	42.6 mF/cm^2	----	----	5000	100%	[22]
MnO_2	Electrodeposition	1.0 M Na_2SO_4	0.8 V	52.55 mF/ cm^2	----	-----	5000	90%	[23]
$NiCo_2O_4$	Sol–Gel	2MKOH	-0.2 to 0.5 V	40.6 mF/cm^2	---	---	10,000	(96.5%	[24]
TiO_2	Atomic Layer Deposition	PVA/ H_3PO_4	0.8 V	8.6 mF/cm^2	----	---	5000	95%	[25]
WO_3	**PLD**	**PVA-KOH**	**0 to - 0.8V**	**5.31mF/cm^2 49.4 F/cm^3**	**1.87 mWh/ cm^3**	**0.54 W/ cm^3**	**18000**	**88.8 %**	**This work**
V_2O_5	**PLD**	**PVA-KOH**	**0 to 1.0V**	**6.5 mF/cm^2 44.21 F/cm^3**	**1.71 mWh/ cm^3**	**0.68 W/ cm^3**	**10000**	**90.2 %**	**This work**

Table S6: HSC device comparative study of electrochemical performance of volumetric capacitance with the reported literature.

Reported ASC Devices	Potential Window [V]	Volumetric Capacitance	Energy Density	Power Density	Stability [Cycles]	Retention	Ref
α-MnO_2 NW/ Fe_2O_3 NT	1.6V	1.5F cm^{-3}	0.55 mW h cm^{-3}	139.1 mW/cm^3	6000	90%	[26]
CNT–WO_3	1.4 V	2.6 F cm^{-3}	0.59 mW h cm^{-3}	30.6 mW/cm^3	50 000	75.8%	[27]
V_2O_5 / MWCNT	1.8 V	31 F cm^{-3}	2.1mW h cm^{-3}	1.5 W/cm^3	5000	100%	[28]
α-Fe_2O_3/MnO_x NR	1 V	1.28 F cm^{-3}	0.64 mW h cm^{-3}	155 mW/cm^3	4000	78%	[29]
Co_9S_8NR// RuO_2NS	1.6 V	4.3 F cm^{-3}	1.21 mW h cm^{-3}	13.29 W/cm^3	2000	90%	[30]
$NiCo_2O_4$ NS	1V	10.3 F cm^{-3}	1.44 mW h cm^{-3}	17W/cm^3	500	92%	[31]
RuO_2-WO_3	1.6 V	3.52 F cm^{-3}	1.25 mW h cm^{-3}	40 mW/cm^3	6500	100%	[32]
WO_3/MnO_2	1.8 V	7.22 F cm^{-3}	3.25 mW h cm^{-3}	411 mW/cm^3	6000	89%	[33]
Fe_2O_3 /MnO_2	1.2 V	60 F·cm^{-3}	12 mWh cm^{-3}	14.8 Wcm^{-3}	2,500	80%	[34]
WO_3/ G/PT	1.6	167.6 mF cm^{-3}	60 µWh cm^{-3}	2320 µWcm^{-3}	3000	99%	[35]
rGO/H-Fe_2O_3	1.5	37.88 mF cm^{-2}	0.14 mW h cm^{-3}	12.30 W cm^{-3}	10 000	97%	[36]
WO_3-V_2O_5	**1.5 V**	**40.28 Fcm^{-3}**	**12.6 mW h cm^{-3}**	**1.42 W cm^{-3}**	**50000**	**95%**	**This work**

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