

Enhancing Supercapacitor Performance with Zero-dimensional Tin-Niobium Oxide Heterostructure Composite Spheres: Electrochemical Insights

Vediyappan Thirumal †, Bathula Babu †, Palanisamy Rajkumar, Jin-Ho Kim * and Kisoo Yoo*

School of Mechanical Engineering, Yeungnam University, Gyeongsan 38541, South Korea

*Correspondence: jinho@ynu.ac.kr (J.H.K); kisooyoo@ynu.ac.kr (K.Y)

† These authors contributed equally to this work.

Supplementary Information (SI)

Diffusion Coefficient using EIS measurement and Warburg diffusion fitting:

The Warburg impedance, also known as the Warburg diffusion element (W_{Ω}), serves as the most basic circuit element for modeling diffusion behavior. It represents semi-infinite linear diffusion, wherein diffusion occurs in one dimension, bounded only by a large planar electrode. The Warburg element (W_{ohm}) is characterized by the Warburg coefficient 'W', measured in units of $\Omega s^{-1/2}$. In Nyquist plots, the Warburg impedance manifests as a straight line at a 45° phase angle, making it easily identifiable in electrochemical impedance spectroscopy (EIS) [1-2]. The presence of a 45° line in the Nyquist plot typically indicates diffusion phenomena. The three set of samples linear fitted using Origin 8.5 version software. Figures S1, S2, S3 shows the linear fitting low frequency region, each electrodes observed the inserted value for fitted for B-line slope data value 6.78913, 4.3821 and 3.50496 corresponding to SnO_2 , Nb_2O_5 and $SnNb_2O_5$ electrode respectively.

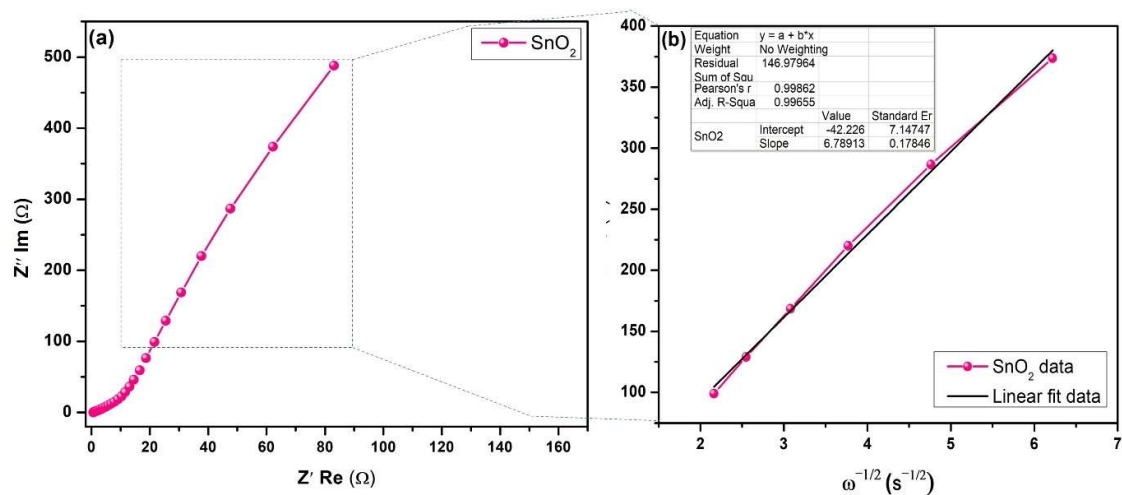


Figure S1. Nyquist impedance plot for SnO_2 and the, the Warburg impedance with the diffusion coefficient using Nyquist plot a linear line fitting SnO_2 data.

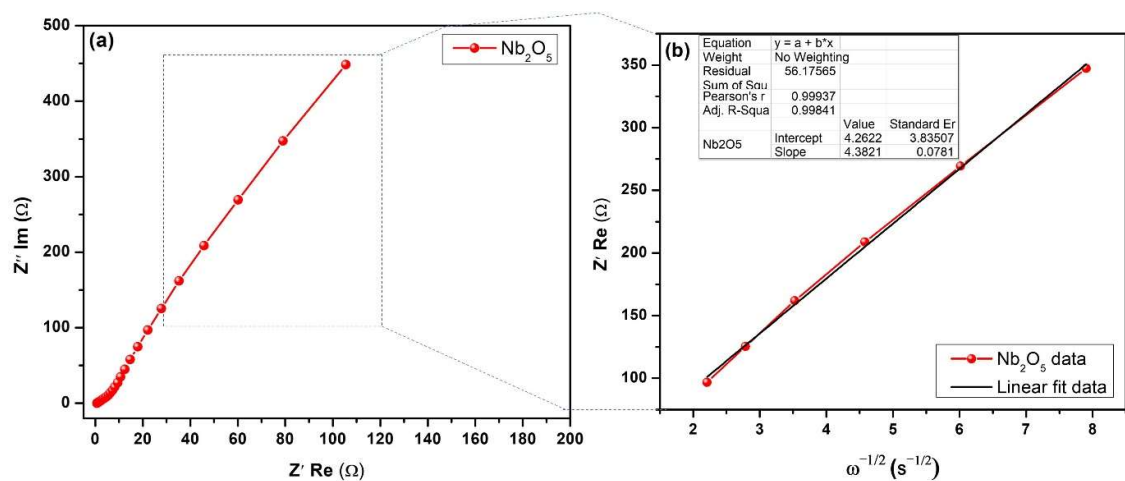


Figure S2. Nyquist impedance plot for Nb_2O_5 and the, the Warburg impedance with the diffusion coefficient using Nyquist plot a linear line fitting Nb_2O_5 data.

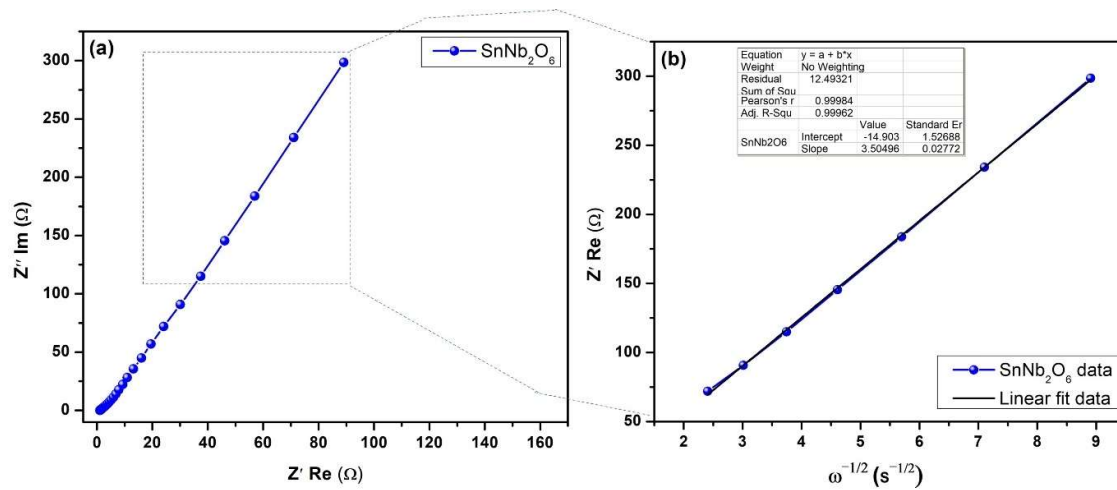


Figure S3. Nyquist impedance plot for SnNb_2O_6 and the Warburg impedance with the diffusion coefficient using Nyquist plot a linear line fitting SnO_2 data.

The diffusion coefficient of the K^+ ions in the electrochemical EIS Nyquist plot for the diffusion coefficient is finding through the use of Eqn (1)

$$D_{\text{K}^+} = \frac{R^2 T^2}{2A^2 n^4 F^2 C^2 \sigma^2} \quad \text{Eqn-1}$$

Where,

R is the molar gas constant ($R = 8.3144598 \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1} \text{ mol}^{-1}$),

T is the absolute temperature (298.15 K)

A is the working area of the working electrode active area ($1 \times 1 \text{ cm}^2$)

n is the number of electrons transferred in during redox process (1)

F is the Faraday constant ($96485.33 \text{ A s mol}^{-1}$)

C is the molar density of K^+ -ion in an electrode (1 mol/L), its derived in 3M KOH aqueous ionic (K^+ , OH^-) electrolyte solution.

σ is the slope on the diffusion state of EIS measurement Warburg factor, which is measured from EIS Nyquist plot linear fitting B-slope value [3-4].

In addition, the diffusion coefficient calculated by Equ-1, from liner fit different electrode active materials techniques and are shown in Arrhenius plots [5-7] shown in Figures S1(b), S2(b), S3 (b). Further, diffusion coefficient moderate value of D values in $1.370 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, $2.284 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and $8.571 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ corresponds to the electrode active materials SnO_2 , Nb_2O_5 and SnNb_2O_6 respectively. Hence, Electrochemical impedance spectroscopy (EIS) reveals higher diffusion coefficients in bimetallic oxide supercapacitor electrodes SnNb_2O_6 compared to their pristine electrode materials SnO_2 , Nb_2O_5 due to enhanced ion transport pathways facilitated by the synergistic effects of the metal dopants SnNb_2O_6 spherical composite. The advantageous bimetallic oxide spherical nanostructures promote faster ion diffusion through the porous electrode structure, reducing charge transfer resistance and enhancing electrochemical performance. Introducing tin oxide dopants into the Nb oxide lattice structure alters the electronic properties and surface chemistry of the oxide, optimizing ion adsorption-desorption kinetics and facilitating rapid charge transport within the electrode-electrolyte interface.

BET surface area analysis

The specific BET surface area and pore size of photocatalysts are crucial characteristics used to evaluate active sites, with higher specific surface areas being favorable for electrical energy storage applications. In the BET surface area analysis shown in Figure S4, S5, S6, significant variations were observed among the materials studied. The SnO_2 material exhibited a specific surface area of 4.16

m²/g, reflecting its inherent characteristics. In addition, Nb₂O₅ demonstrated a slightly lower specific surface area of 5.40 m²/g, although it presented the largest surface area compared to the pure materials. Remarkably, the bimetallic SnNb₂O₆ spherical composite displayed an exceptionally high specific surface area of 23.97 m²/g, surpassing that of the individual components. This notable increase underscores the synergistic effects of combining SnO₂ and Nb₂O₅, leading to enhanced surface activity and porosity in the composite material. Further investigations are warranted to understand the mechanisms behind this enhancement. The findings suggest the potential of SnNb₂O₆ as a promising candidate for applications requiring high surface area materials, with the notable increase in surface area facilitating a greater number of surface-active sites for energy storage.

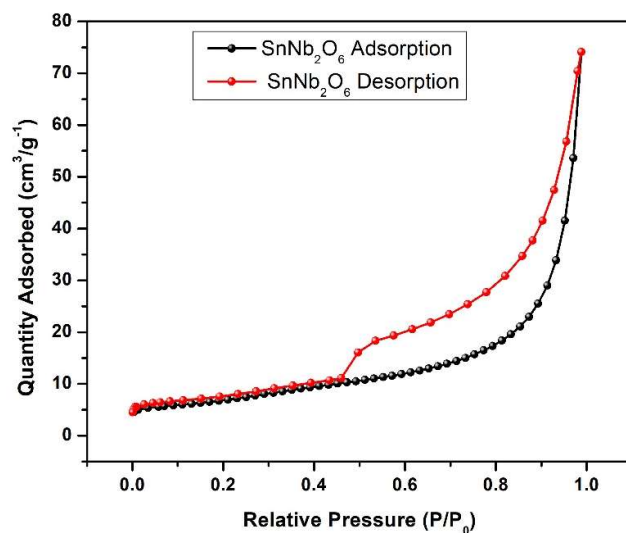


Figure S4. BET isotherm graph of specific surface area analysis of SnNb_2O_6 composite material with quantitative volumetric adsorbed (cm^3/g) versus relative pressure isotherm in terms of P/P_0 .

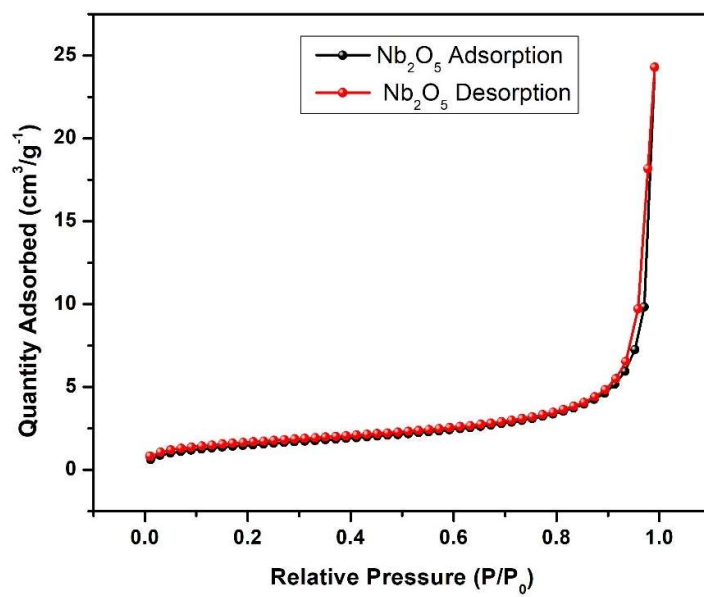


Figure S5. BET surface area analysis with N_2 adsorption/desorption isotherms linear curves of Nb_2O_5 material.

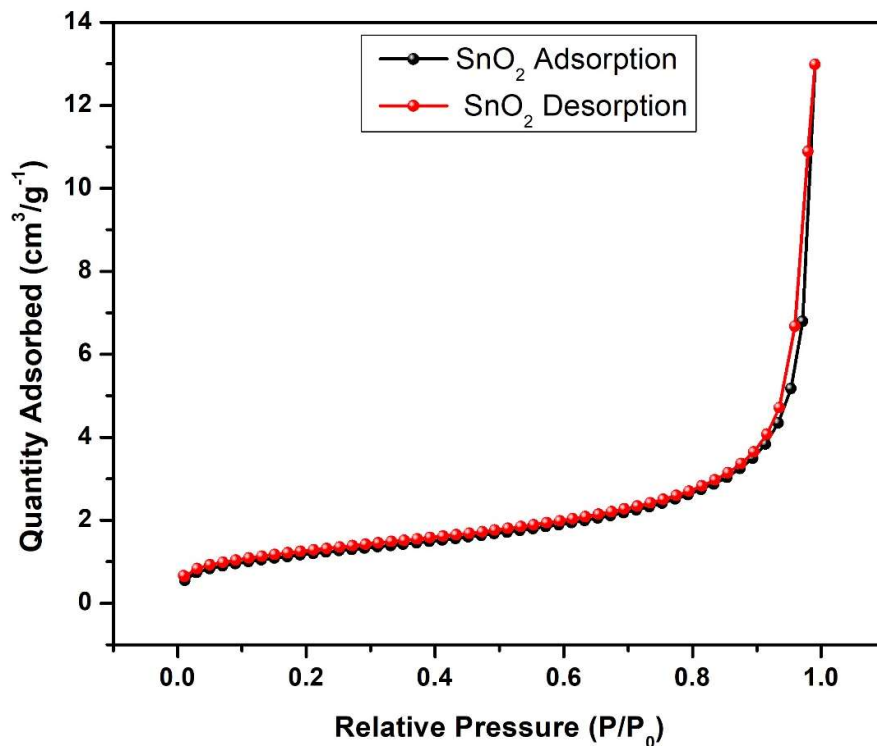


Figure S6. BET surface area analysis with N₂ adsorption/desorption isotherms linear curves of SnO₂ material.

XRD analysis: After cycling performance

The XRD analysis of the electrodes composed of SnO₂, Nb₂O₅, and SnNb₂O₆, following 5000 cycles shown in (figure S7, S8, S9) revealed remarkable stability in the inner structural characteristics. Despite the extensive electrochemical testing, there was no discernible alteration observed in the phase and structure of the electrode active materials. This robust structural integrity suggests the resilience of the materials to cycling-induced degradation. The consistent phase and structure retention indicate the suitability of SnO₂, Nb₂O₅, and SnNb₂O₆ for long-term electrochemical applications. These findings X-ray diffraction with

matched JCPDS card number and PDF#2 finding in “X-Pert High score plus software”, After cycling XRD data with Ni-foam electrode (*) combined active materials underscore the potential of these materials for use in high-performance energy storage devices, where durability and stability are critical factors. Further studies are warranted to elucidate the underlying mechanisms responsible for the observed phase/structural stability, paving the way for the optimization of electrode materials for enhanced performance and longevity in electrochemical systems.

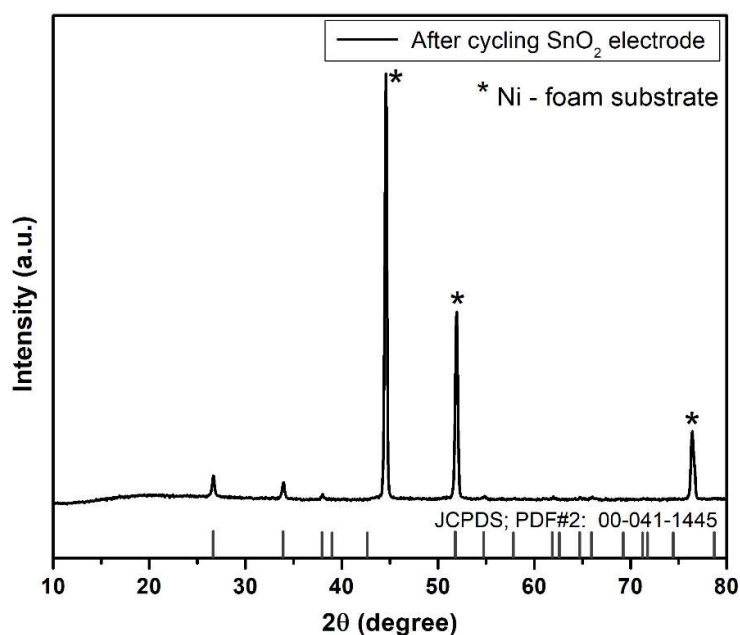


Figure S7. X-ray diffraction (XRD) patterns of SnO₂ electrode for after cycling data.

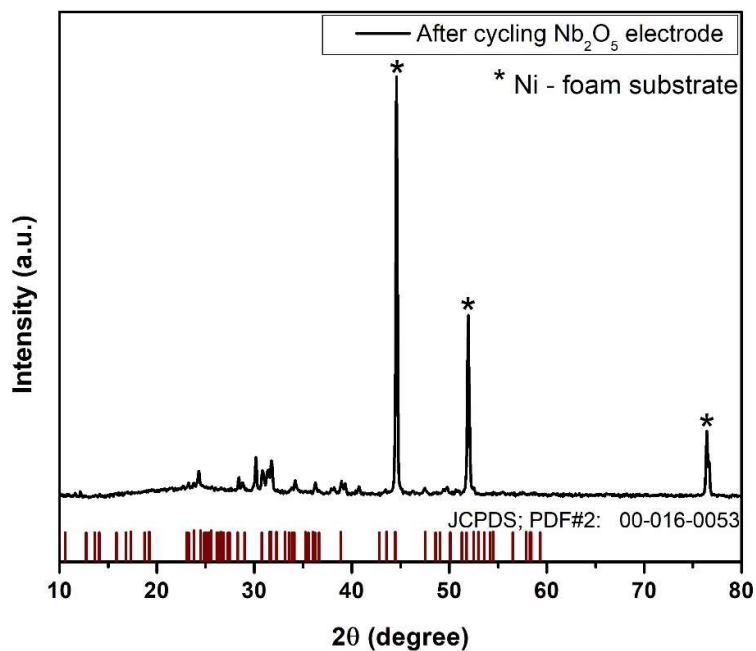


Figure S8. X-ray diffraction (XRD) patterns of Nb_2O_5 electrode for after cycling data.

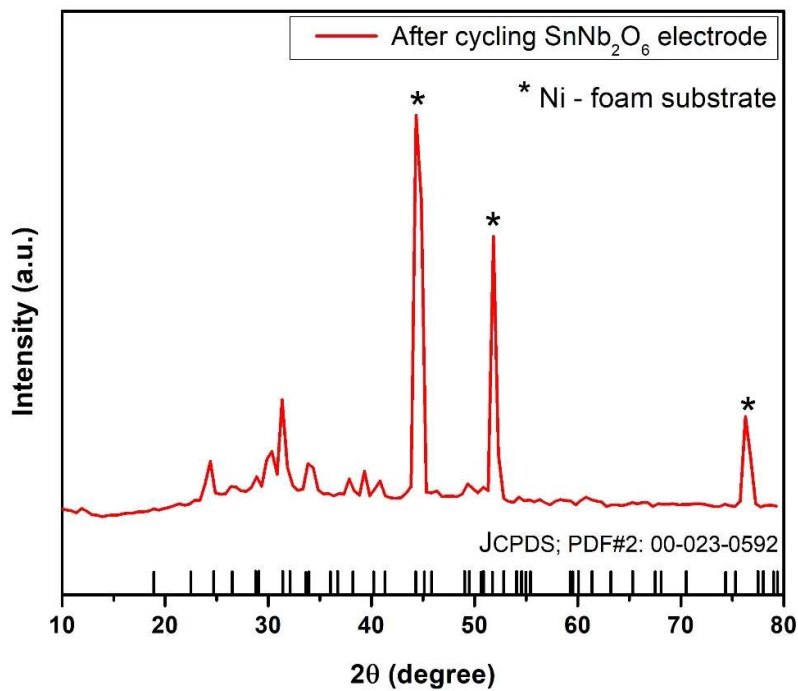


Figure S9. X-ray diffraction (XRD) patterns of SnNb_2O_6 electrode for after cycling data.

Table S1. Electrochemical impedance spectroscopy (EIS) is a Nyquist plot with measured by z-fit software fitting to an equivalent electrical circuit model.

	Randal's Circuit: $R1+Q1/(R2+W1)+Q2$
1.	SnO₂
	$R1 = 0.6873 \text{ Ohm}$
	$Q1 = 0.0054099 \text{ F.s}^{(a-1)}$
	$R2 = 7.64 \text{ Ohm}$
	$Q2 = 0.0024232 \text{ F.s}^{(a-1)}$
	$s1(W) = s3 = 8.817\text{e-}9 \text{ Ohm.s}^{-1/2}$
2.	Nb₂O₅
	$R1 = 0.7251 \text{ Ohm}$
	$Q1 = 0.009832 \text{ F.s}^{(a-1)}$
	$R2 = 3.35 \text{ Ohm}$
	$Q2 = 0.003361 \text{ F.s}^{(a-1)}$
	$s1(W) = 1.805\text{e-}9 \text{ Ohm.s}^{-1/2}$
3.	SnNb₂O₆
	$R1 = 1.0951 \text{ Ohm}$
	$Q1 = 0.01821 \text{ F.s}^{(a-1)}$
	$R2 = 2.25 \text{ Ohm}$
	$Q2 = 0.004759 \text{ F.s}^{(a-1)}$
	$s1(W) = 1.1482\text{e-}10 \text{ Ohm.s}^{-1/2}$

Table 2. Comparison of previous reported supercapacitor composite electrode materials for energy storage applications.

S.No	Materials/applications	Method of preparation	Electrolyte	Specific capacitance	Ref.
1.	GNs/SnO ₂ –MWCNTs Supercapacitor application	Chemical method	30 wt% KOH aqueous electrolyte	224 F/g @ 5 mV/s	[8]
2.	MWCNT/SnO ₂ Supercapacitor	Sonochemically synthesized	1M Na ₂ SO ₄ electrolyte	133.33 F/g @ 0.5 mA/cm.	[9]
3.	1D T-Nb ₂ O ₅ nanowires growth on carbon cloth Li-ion supercapacitor electrode	Single step – annealing method	1M LiPF ₆ (EC/DEC)	Specific gravimetric capacitance 220 mAh/g at current density of 0.5 C rate	[10]
4.	Nb ₂ O ₅ /graphene-supercapacitors	Hydrothermal technique	non-aqueous electrolyte (1 M LiPF ₆ in 1:1 v/v EC–DMC)	192 mAh/g @ 0.1C rate	[11]
5.	Ti doped T-Nb ₂ O ₅ , non-aqueous supercapacitors	Hydrothermal technique and thermal annealing 600 °C	1 M LiClO ₄ dissolved in propylene carbonate as the electrolyte	pseudocapacitive Li ⁺ storage capacity of 204.3 mAh/g @ 0.5C rate	[12]
6.	Nb ₂ O ₅ /MoS ₂ nanocomposite electrode material - supercapacitors	Microwave radiation method	3 M KOH	Nb ₂ O ₅ nanoparticles (183 F/g) and MoS ₂ at a current density of 1 A/g (125 F/g)	[13]
7.	SnNb₂O₆ spherical nanocomposite	Facile Hydrothermal preparation	3 M KOH	294.02 F/g @ 1A/g	Present work

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