PREPARATION OF PEROVSKITE-TYPE ZnSnO₃
NANOPARTICLES AND ENHANCING THEIR BEHAVIOR AS A
POSITIVE ELECTRODE FOR SUPERCAPACITOR
APPLICATIONS.

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ABSTRACT
This work aims to prepare perovskite zinc stannate (ZnSnO₃) by the sol-gel method and
to study the electrochemical properties. This performance improves by adding different
percentages of naturally prepared activated carbon from pomegranate peels. ZnSnO₃ is
considered an attractive cathode material for energy storage, which shows a specific
capacitance of 115 F g⁻¹ at 1 A g⁻¹, while the optimum added percentage of the activated
carbon is 5%AC+95%ZnSnO₃, which exhibits 312.5 F g⁻¹ at the same current density,
which considered about three times more than that of the ZnSnO₃, with capacitance
retention of 66% after 2000 cycles at the current density of 10 A g⁻¹. The practical
hybrid device shows a specific capacitance value of 61.6 F g⁻¹ at 1 A g⁻¹, the specific
energy of 22 Wh kg⁻¹, and specific power of 1077 W kg⁻¹ with capacitance retention of
50% of the initial capacitance after 2000 cycles at a current density of 10 A g⁻¹. As a
result, ZnSnO₃ and its composite with cheap and natural materials are considered
promising supercapacitor electrodes.

Keywords
Perovskite ZnSnO₃; Activated carbon; Sol-gel method; hybrid device; supercapacitor
electrode.

1. INTRODUCTION
Great efforts of green energy devices and researchers have been made to overcome the
ever-growing energy crisis and environmental pollution by converting environmental
waste into useful material for energy storage systems such as supercapacitors [1-6].
Electrochemical energy storage devices are classified into electrochemical double-layer
capacitors (EDLCs), Pseudocapacitors, and hybrid capacitors [7-9]. Currently, most of
the research focuses on supercapacitors to obtain advanced electrode materials with
higher specific capacitance and more extended cycling stability, as an essential ternary
semiconducting oxide, mostly ABO₃ type (ZnSnO₃), has been attracting most of the
studies due to its different applications in various fields, such as gas sensor [10, 11],
photo-catalyst [12], and lithium-ion batteries [13]. A few studies have reported ZnSnO₃
as a supercapacitor due to their low thermal stability than Zn₂SnO₄; with a focus on
charge storage applications, it is undeniable that stannate has proved very effective in
sensor and charge storage technologies [14-22]. The main reasons are phase
stabilization in ZnSnO₃ and structural complexities in Zn₂SnO₄ [23, 24]. In the ZnO:SnO₂ system at normal pressure, two phases exist; stable Zn₂SnO₄ and metastable ZnSnO₃ [25, 26]. Zn₂SnO₄ has a spinal structure and can be easily synthesized by a simple solid-state reaction method or another method. It has high thermal stability and has been chemically and structurally characterized [27]. Comparatively, reports on ZnSnO₃ are sparse and ambiguous, owing to its low thermal stability and challenging synthesis methods [15].

Lower thermal stability of ZnSnO₃ also results in its decomposition into Zn₂SnO₄, ZnO, and SnO₂ at higher temperatures. Therefore, low-temperature synthesis techniques like co-precipitation and hydrothermal synthesis were employed to overcome the problems mentioned above. However, these techniques have low sample output to input ratio and are less industry-friendly. Consequently, the sol–gel method can overcome this problem, giving the appropriate amount of the ZnSnO₃ required. During the past decades, perovskite oxides (ABO₃), such as SrRuO₃ [28], BiFeO₃ [29], etc., have been reported as potential electrode materials for supercapacitors. However, most of the reported perovskite oxides exhibit unsatisfactory electrochemical properties, limiting their further applications. Therefore, exploring new-type of perovskite candidates becomes highly valuable for high-performance supercapacitors like ZnSnO₃ as well as carbon-based materials [30], metal oxides [31], metal sulfides [32], and conducting polymers [33] are used as supercapacitor electrode materials [34-36]. Carbon materials have been used from the beginning of supercapacitor fabrication due to their high surface area. Metal oxides offer attractive options as electrode material due to high specific capacitance and low resistance, making it easier to construct high-energy and power supercapacitors. Few studies reported the usage of zinc stannate for supercapacitors application; Sim et al. [37, 38] reported the synthesis and supercapacitive behavior of ZnSnO₃@carbon composite and ZnSnO₃/mesoporous carbon composite, which showed only specific capacitance of 104 and 94 F g⁻¹, respectively, at a low current density of 0.3 A g⁻¹.

This work investigated perovskite zinc stannate's electrochemical performance and improved performance by mixing it with different percentages of naturally prepared activated carbon from waste material with a higher surface area. The morphological and surface area properties were studied as they play a critical role in the ions' adsorption and diffusion during the electrochemical process. Detailed electrochemical studies were conducted on a single electrode and a practical symmetrical device. ZnSnO₃ was obtained with a surface area of 4.064 m² g⁻¹ with a microporous characteristic. 5%AC+95%ZnSnO₃ exhibited an excellent electrochemical feature with a remarkable specific capacitance of 312.5 F g⁻¹ at 1 A g⁻¹ with good cycling stability of 66% capacitance retention after 2000 cycles at a current density of 10 A g⁻¹, which improved energy storage life.

2. EXPERIMENTAL METHODS

2.1. Preparation of ZnSnO₃ Nanoparticles
Polycrystalline perovskite-type ZnSnO₃ nanoparticles were synthesized by sol-gel method at atmospheric pressure using stoichiometric amounts of high purity Zinc Acetate (Zn(CH₂COOH)₂), Tin (IV) Chloride (SnCl₄.5H₂O), and fuel (EDTA). The
starting materials were dissolved in 50 ml of distilled water to form transparent homogenous precursors. The precursors were magnetically stirred for 3 h (condensation time) at 300°C and were immediately mixed to form a milky white solution. Mixing was followed by adding 5 ml of Ethylene Glycol and a few drops of NH₃ until pH control of the solution (pH~7). The grayish-brown powder obtained after drying the solution in the air was ground, and the obtained powder was calcined for 3 h at 400°C.

2.2. Materials Characterization
The as-prepared materials were characterized by powder X-ray diffraction (XRD, Bruker D8 diffractometer) using the Cu-Kα (λ=1.5406A0) radiation and secondary monochromator in the range 20 from 10 to 70° and a scan rate of 20 min⁻¹. The morphologies were characterized by a field emission scanning electron microscope (FSEM) using a JEOL instrument (JSM –5410, Japan). The chemical compositions and the valence states of the elements were determined by X-ray photoelectron spectroscopy (XPS, thermos scientific) using Al Kα monochromatized radiation. The specific surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Quanta chrome NovaWin - Data Acquisition and Reduction for NOVA instruments ©1994-2013, Quanta chrome Instruments version 11.03.

2.3. Electrochemical Measurements
To evaluate the electrochemical properties of the prepared samples using a 3-electrode configuration in 6 M KOH solution as electrolyte. The working electrode was fabricated by adding the prepared active material with carbon black (conductive additive) and Nafion as a binder in a weight ratio of 80:10:10, respectively. Then 0.5 ml of ethanol was added to the mixture to produce a suspended solution. The working electrode was fabricated by the drop-casting method, and the suspended solution was dropped into nickel foam substrate (NF) with the dimensions of 1 cm (width), 2 cm (length), and 1.6 mm (thickness). The prepared film was then dried at 70°C overnight. The electrochemical behavior of the prepared material was tested by a three-electrode system using an electrochemical testing station (Volta lab 40 PGZ 301, Radiometer Analytical, France) at room temperature, with a platinum wire as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The electrochemical measurements were performed in a 6 M KOH aqueous solution electrolyte. For practical application, an asymmetric hybrid device (ASHD) was assembled, in which the perovskite zinc stannate was used as a positive electrode and the activated carbon (AC) as a negative electrode. According to the previous report, [39]. The ASHD was denoted as (95% ZnSnO₃ + 5% AC)//AC). The electrochemical measurements were performed using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements. The CV measurements were carried out within a potential window of -0.1 to 0.6V (vs. SCE) at different scan rates from 10 to 200 mV s⁻¹. GCD measurements were tested at different current densities from 1 to 10 A g⁻¹ within a potential window of 0 to 0.4 V (vs. SCE). The EIS measurements were performed using Nyquist plots in the frequency range of 100 kHz to 0.01 Hz. The stability test was carried out at a current density of 10 A g⁻¹. The specific capacitance (Csp) F g⁻¹ was then calculated from the GCD results according to the following equation: [40, 41]

\[
C_{sp} = \frac{2}{m} \int \frac{V}{\Delta V^2} \, dt
\]
Where I is the applied current (A), ∆t is the discharging time (s), ∆V is the potential window (V), and m is the mass of active material (g). For fabrication of battery-like ASHD, the (95% ZnSnO₃ - 5% AC) was used as a positive electrode and AC as a negative electrode. The following equation can calculate the mass ratio of positive and negative electrodes (m⁺/ m⁻)[42].

\[
m^{+}/m^{-} = \frac{C_{sp-} \Delta V^{-}}{C_{sp+} \Delta V^{+}}
\]

Where \(C_{sp} (-)\) and \(C_{sp} (+)\) are the capacitances of the negative and positive electrode, respectively, and \(\Delta V^{-}\) and \(\Delta V^{+}\) are the potential windows of the negative and positive electrode, respectively. The CV measurements of the device were carried out within a voltage window of 0 to 1.6 V at different scan rates from 10 to 200 mV s⁻¹. GCD measurements were tested at different current densities from 1 to 10 Ag⁻¹ between voltage windows of 0 to 1.6 V. The energy density (Ed) and power density (Pd) of the device were calculated according to the equations, respectively. [43, 44]

\[
Ed = I \int V \, dt/3.6m
\]

\[
Pd = 3600 \frac{Ed}{td}
\]

Where Ed is the energy density (Wh kg⁻¹), dt is discharge time (s), Pd is the power density (W kg⁻¹), and (V) is the operating voltage window of the device.

3. RESULTS AND DISCUSSION

3.1. Structural and Morphological of the Synthesized ZnSnO₃ Nanoparticles
The X-ray diffraction patterns of samples shown in Figure 1a indicate that sample calcined at 400°C for 3 h with EDTA as fuel yields a pure phase with no detectable secondary phase. All the peaks were ascribed to ilmenite type ZnSnO₃ (JCPDS card no. 28-1486). The crystal structure of ZnSnO₃ can be regarded as a cubic phase. Crystallite size was automatically calculated from X-ray diffraction data using Debye-Scherrer equation; \(WF' = 0.9 \lambda \cos \theta D\) Where \(WF'\) is the width at half–maximum intensity of Bragg reflection excluding instrumental broadening, \(\lambda\) the wavelength of the X-ray radiation, D the average crystallite size, \(\theta D\) the Bragg angle. Considering the major peaks in the XRD pattern, the average crystallite size was calculated as 95.6 nm. Figure1b shows XPS spectra of O1s, with a mean peak with a small shoulder at a high binding energy side. The O1 is attributed to lattice oxygen O₂ is ascribed to surface O₂, O, OH groups, and oxygen vacancies [45]. As shown in Figure 1c, we can clearly find the peaks at 1021.5 eV and 1044.5 ev, consistent with the binding energy of Zn 2p3/2 and Zn 2p1/2. The splitting energy of 23 eV between Zn 2p3/2 and Zn 2p1/2 is a typical value for Zn in the ZnSnO₃. Meanwhile, the high-resolution XPS spectra of Sn 3d5/2 and Sn3d3/2 in Figure 1d are obviously observed at 486.9 eV and 495.5eV, respectively, which correspond to the Sn⁴⁺ [46]. Figures 2a and b reveal the nitrogen adsorption isotherm of the prepared oxide. The BET surface area was calculated from the nitrogen adsorption isotherm in the P/P0 range from 0.01 to 0.1 at room temperature; the obtained BET surface area is 4.064 m² g⁻¹. The BET curve exhibits the typical type I isotherms according to the IUPAC classification [48], indicating the microporous feature of this sample, the average pore diameter is 2.8 nm. Figures 3a and
b show the FESEM image of the ZnSnO$_3$ nanoparticles, which revealed the formation of cubic shaped and some irregular shaped nanoparticles. From the FESEM image, it is visible that prepared ZnSnO$_3$ nanoparticles were pure with no impurities.

![Image of XRD pattern, XPS spectra, and FESEM images](image_url)

**Fig. 1:** (a) XRD pattern, and (b, c, d) High-resolution XPS spectra of ZnSnO$_3$.

![Image of N$_2$ adsorption-desorption isotherms and pore size distributions](image_url)

**Fig. 2:** (a) N$_2$ adsorption-desorption isotherms and (b) pore size distributions of ZnSnO$_3$.

![Image of FE-SEM images](image_url)

**Fig. 3:** (a, b) FE-SEM images of the as-prepared Zn$_2$SnO$_4$ with different magnifications.
3.2. Electrochemical Performance of the Supercapacitor Electrodes

To examine the electrochemical properties, CV, GCD, and EIS were measured in 6 M KOH, of the as-prepared ZnSnO and different ratios (3,5,10) % of natural prepared activated carbon mixed with prepared ZnSnO to form other composites as an active electrode materials for SCs. It can be seen from figure 4a that, CV profiles of different ratios of ZnSnO + AC composite and blank ZnSnO operated at 50 mV s⁻¹ and potential range of -0.1 to 0.6V which illustrate the oxidation and reduction peaks as a result of the faradic reactions between Sn(II)- Sn(III) -Sn(IV), as a result of CV profiles 5% AC + 95% ZnSnO composite was considered to be the best ratio with high capacitance more than the blank ZnSnO. In order to evaluate the effect of scan rate on the electrochemical performance, the CV profiles of 5% AC + 95% ZnSnO composite were performed at different scan rates, as illustrated in figure 4b. At low scan rates, the redox peaks are symmetrical, indicating the excellent reversibility of redox reaction at the surface of 5% AC + 95% ZnSnO composite. With the increasing scan rate, it is observed that the shifting of anodic peaks towards the more positive position and the corresponding cathodic peaks towards a more negative position due to the electrode polarization as well as the sluggish diffusion rate of the electrolyte at high scan rates that is required to fulfill the electrochemical reactions of the electrode material [41]. However, the redox reaction peaks of the CV curves maintained their well-defined and sharp behavior, implying that these materials are suitable for fast redox reactions and possess better reversibility, which is significantly essential for power systems [47]. For an in-depth evaluation of the actual value of capacitance, we tested the charge-discharge profiles of the prepared 5% AC + 95% ZnSnO hybrid composite at different current densities ranges from 1- 10 A g⁻¹ in the potential range of 0 to 0.4V. As shown in Figure 3c, it is clear that the GCD curves exhibit apparent voltage plateaus, indicating that the supercapacitive performance is a Faradic-type. The presence of plateaus in the curves further confirms the existence of redox reaction, which is consistent with the results obtained from the CV curves. Csp was calculated from GCD measurements. Figure 4c also illustrates the effect of different current densities on performance; it is clear that all GCD curves exhibit apparent voltage plateaus, further demonstrating the Faradic-type supercapacitive performance. As a result of the comparison between values of the calculated capacitance of 5% AC + 95% ZnSnO hybrid composite and ZnSnO electrodes, as shown in figure 4d, which are 312.5 and 115 F g⁻¹ at the current density of 1 A g⁻¹, respectively, presenting the capacitance of the 5% AC + 95% ZnSnO hybrid composite electrode is about three times more than that of the ZnSnO. This result indicates a superior enhancement of the electrochemical performance of perovskite ZnSnO as supercapacitor electrode by adding to the activated carbon from a natural source. For measuring cycle life stability of 5%AC+95%ZnSnO hybrid composite and ZnSnO electrodes, GCD measurements were operated at 10 A g⁻¹ for 2000 cycles. The percentage of capacitance retention of 5% AC + 95% ZnSnO hybrid composite and ZnSnO electrodes were 66 and 53%, respectively, as shown in figure 4e. EIS was obtained at the open-circuit voltage, and the corresponding Nyquist plots are displayed in figure 4f. At the high-frequency region, the intersection of the curve at the real part (Zr) represents the equivalent series resistance (ESR), which is related to ionic resistance of the electrolyte, internal resistance of the electrode active material, and the contact resistance between the electrode and the current collector [48]. From the plots, the blank ZnSnO electrode shows more value of ESR (2.43 ohm) than the 5% AC +
95% ZnSnO₃ hybrid composite (1.48 ohm) after the stability test, indicating the absence of the ohmic loss upon cycling due to high conductivity of activated carbon and opening more active site on the surface of composite electrode which improves EIS. The Nyquist plots show a semicircle in the high-frequency region and a near-vertical line at low frequency. The near-vertical line in the low-frequency region indicates the good capacitive of the composite electrode.

Fig. 4: (a) CV curves at scan rate from 50 mV s⁻¹ (b) CV Curves of 5% composite at different scan rate from 10 to 200 mV s⁻¹ (C) GCD curves at different current density from 1 to 10 Ag⁻¹ for 5% composite (d) GCD curves of blank ZnSnO₃ and 5% Composite at 1 Ag⁻¹ .(e) Cycling stability of at a current density of 10 A g⁻¹ of blank ZnSnO₃ and 5% Composite, and (f) EIS profile of blank ZnSnO₃ and 5% Composite electrodes.

3.3. Asymmetric Supercapacitor Device
For real simulation, a battery type of asymmetric device was fabricated in 6 M KOH electrolyte using two electrodes, 5% AC + 95% ZnSnO₃ hybrid composite as anode and naturally prepared AC as the cathode to evaluate the energy storage capacity of this hybrid composite in the complete supercapacitor cell. According to the mass balance equation, the mass ratio of the positive and negative electrode materials is 2, Eq. 2 (Csp(-) was calculated from the GCD profile Figure 4d). The operation potential of the prepared device can be calculated as the sum of the potential windows of 5% AC + 95% ZnSnO₃ (-0.1 to 0.6 V) and AC (-1 to 0 V). Therefore, a potential operation window of 0 to 1.6 V. The CV curves recorded at different scan rates from 10 mV s⁻¹ to 200 mV s⁻¹ for asymmetric supercapacitor in the potential range of 0 to 1.6 V is shown in figure 5a. As shown in Figure 5a, in all CV curves of the asymmetrical supercapacitor, the redox peaks were still noticeable in all CV curves, indicating the Faradic-type (battery-like) behavior of the 5% AC + 95% ZnSnO₃ composite/AC hybrid device. For more evidence, GCD measurements of the device, figure 5b, were performed at different current densities of 1, 2, 3, 4, 5, 10 Ag⁻¹, which show a nonlinear battery type charge-discharge profile. The hybrid device offers a specific capacitance value of 61.6 F g⁻¹ at 1
A g$^{-1}$, Ed of 22 Wh kg$^{-1}$, and Pd of 1077 W kg$^{-1}$. The capacitance retention of the as-fabricated hybrid asymmetric device was operated at a current density of 4 Ag$^{-1}$ within 0 to 1.6 V by the GCD test. As shown in Figure 5c, the hybrid device of 5% AC + 95% ZnSnO$_3$ composite//AC exhibits stability of 50% capacitance retention of the initial capacitance after 2000 cycles. EIS was also tested as in Figure 5d, which showed an ESR value of 2.5 ohm for fresh device electrode and 1.73 Ohm after the stability test, revealing that, after stability, EIS improved due to the absence of the ohmic loss upon cycling due to high conductivity of activated carbon and opening more active site on the surface of the composite electrode. Finally, electrochemical results indicate that the 5% AC + 95% ZnSnO$_3$ composite//AC hybrid device works as a battery-type capacitor and has excellent potential as an energy storage material.

Fig. 5: Electrochemical performance of the 5% AC + 95% ZnSnO$_3$ composite//AC hybrid device (a) CV curves at different scan rates, (b) GCD curves at different current densities, (c) cycling performance at a current density of 4 A g$^{-1}$, and (d) EIS for the fresh device and after 2K cycles.

4. CONCLUSIONS
In summary, a sol-gel method was used as a facile method to prepare ZnSnO$_3$, which overcame the lack of quantity and produced low time and temperature are used, giving the appropriate amount of the ZnSnO$_3$ required. Due to the excellent conductivity of activated carbon and high capacitive ZnSnO$_3$, a different percentage of ZnSnO$_3$/AC composites are successfully obtained by well mixing. The value of specific capacitance obtained for ZnSnO$_3$ and 5% AC + 95% ZnSnO$_3$ hybrid composite is 115 and 312.5 F g$^{-1}$ at 1 A g$^{-1}$, respectively, improving the electrochemical behavior of perovskite ZnSnO$_3$.
with capacitance retention of 66% after 2000 cycles at a current density of 10 A g$^{-1}$. Meanwhile, the practical simulation of the asymmetrical hybrid device shows a specific capacitance value of 61.6 F g$^{-1}$ at 1 A g$^{-1}$, Ed of 22 Wh kg$^{-1}$, and Pd of 1077 W kg$^{-1}$. With capacitance retention of 50% of the initial capacitance after 2000 cycles at a current density of 10 A g$^{-1}$, from this result we reached to the main goal by improving electrochemical properties by mixing with cheap and natural materials which used anode material for supercapacitor applications.

Declaration of interests
All authors declare that they have no conflicts of interest.

5. REFERENCES


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