Synthesis and Characterization of Strontium Titanate ($SrTiO_3$) Nanoparticles Doped with Azadirachta Indica Leaf Extract and Coconut Water by Sol-gel Method

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Abstract:

In the present work, Strontium titanate ($SrTiO_3$), Azardirachta indica leaf extract, and coconut water doped Strontium titanate ($SrTiO_3$) nanoparticles were successfully synthesized by the sol-gel technique. Strontium titanate has been used in various areas of applications, such as flat panel displays, tunable microwave capacitors, radioisotope power systems, tunable multilayer capacitors, semi-conductive ceramics, microwave solitons, varistors, and pyroelectric far-infrared detectors, etc. The synthesized samples were analyzed by X-Ray Diffraction (XRD), Fourier-Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray spectroscopy (EDX), Cyclic Voltammetry (CV), and Electrochemical Impedance Spectroscopy (EIS). From the XRD analysis, it was found that the structures of the prepared samples were, cubic and their size decreased with doping. FTIR band at 513 cm^{-1} was observed due to Sr-Ti-O stretching vibration. EDX analysis reveals the elemental compositions of the samples. Cyclic voltammetry results revealed that the prepared strontium titanate exhibited pseudocapacitive behavior. The EIS studies, suggest that strontium nanoparticles synthesized has a higher charge transfer resistance than Azadirachta indica, and coconut water doped Strontium titanate ($SrTiO_3$) nanoparticles.

Keywords: Strontium titanate, Sol-gel method, Electrochemical Impedance Spectroscopy, Cyclic voltammetry

Introduction:

Energy storage has drawn the attention of experts due to its importance on a worldwide scale. There are various energy storage technologies being used, including rechargeable batteries, fuel cells, and electrochemical super capacitors.[1,2] Because of their properties, such as high power density, energy storage mechanism, stability, fabrication methods, long life cycle, etc., Supercapacitors are further divided into three categories: electric double-layer capacitors (EDLC), pseudo capacitors, and hybrid capacitors. In the first kind, electric double-layer capacitors (EDLC), the energy is stored electrostatically by means of absorption and desorption; there is no charge transfer; a non-faradaic mechanism takes place; and activated carbon-based materials are frequently utilized.[3] Second, the pseudocapacitor stores the energy by a faradaic process that involves the oxidation, reduction, and intercalation of metal-based components (oxides, sulfides, nitrides, and hydroxides) and conducting polymer materials. The third type (hybrid capacitor) combines the EDLC and pseudocapacitor principles .[4,5-7] Consequently, the pseudocapacitor attracts high attention due to its faradaic mechanism, which causes high capacitance, a low voltage rating, etc. Further, the choice of the material characteristics advances the research on pseudo capacitors as a higher priority in this field of energy storage research.[8] Conventionally, the ABO_3 general group of composite materials (ABO_3 = A^{2+} B^{4+} O_3 $^{2-}$ (A^{2+}= (Sr^{2+}, Pb^{2+}, Ca^{2+}, and B^{4+} =Ti^{4+}, Mn^{4+}, La^{4+}) has notable physical and chemical properties due to its perovskite structure, such as thermal and electrical response, catalytic performance, stability, conductivity characteristics, etc.[9,10,11] Further, these kinds of combinational composites are focused on various research areas such as photocatalytic analysis, energy storage, solar cells, etc. and are applied to industrial and commercial appliances.[12,13,14] There are many material research avenues that are explored for the synthesis of ABO_3 group nanoparticles for a variety of applications. In contrast, strontium titanate (called STO) (n-type semiconductor, band gap is 3.2 eV, ferroelectric phase with a large dielectric constant, non-toxicity, excellent stability) is pointed out in various research areas because of its properties such as perovskite structure with oxide (ABO_3), thermal, dielectric, and optical nonlinearity characteristics, etc. Thus, strontium titanate nanoparticles are pointed in various fields, including likely photovoltaic technology,[15] photocatalytics,[16] structural analysis, etc.[17] Different methodologies are employed for synthesis of strontium titanate nanoparticles, such as the sol-gel process,[18] rapid sol-precipitation,[19] microwave-aided,[20] sol-gel combustion[21] and the solid state reaction method, etc.

The sol-gel method is a well-known technique for synthesizing different nanomaterials, particularly metal oxides. Commonly, the precursors are dissolved in a suitable solvent, which causes them to gel. They are then dried properly, using suitable methods, and applied for the application. In recent years, a various sources (simple chemicals, leaf extracts, coconut water) have been used for reasons such as simplicity, eco-friendliness, cost effectiveness, etc. [22, 23]

An intriguing aspect of research is the potential use of plant elements such as leaves, stems, roots, and others in the creation of nanoparticles.[24] Silver, gold, iron, zinc oxide, and other nanoparticles have all been created using Azadirachta indica leaf extract.[25] Moreover, using Azardirachta indica leaf extract as a starting material, Kiran K.S. et al. synthesized strontium titanate nanoparticles for photocatalytic applications.[26] Phytochemicals (Terpenoids and flavanones), which act as reducing and capping agents in Azardirachta indica, also aid in stabilizing the nanoparticles.[27] Coconut water has been employed in environmentally friendly nanoparticles production. Sugars (sucrose, glucose) are used in the process to produce metal and metal oxides by acting as chelating agents as well as fuel.[29,28] Using coconut water, Maria de Andrade Gomes et al. synthesized $BaTiO_3$ nanoparticles (ABO_3 group), with an average crystallite size of 31 nm.[30] The present study is focused on the synthesis of strontium titanate nanoparticles, doped with Azardirachta indica leaf extract and coconut water. The prepared samples are analyzed through X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS).

Materials and methods

Materials

Titanium tetraisopropoxide (TTIP, 97% purity, Sigma-Aldrich), Strontium nitrate ($Sr(NO_3)_2$; 99.9% purity, Sigma-Aldrich), Sodium hydroxide (NaOH),Ethanol , deionized water, acetone, and Glass ware, such as beakers, conical flasks, burette, etc., were procured from Mercury Scientific Chemicals Industries, Salem. Coconut water, Fresh leaves of Azadirachta Indica (Neem) was collected in and around Namakkal, Tamilnadu.

Preparation of Azadirachta Indica Leaf Extract:

Fresh leaves of Azadirachta indica (Neem) were collected, properly cleaned with fresh water and deionized water to remove any contaminants, and then dried with a hot air gun at room temperature. Around 50 g of leaf shreds were placed in a 250 mL beaker with 100 mL of deionized water, and the mixture was heated at 100 ºC for two hours while being constantly stirred. The resulting greenish solution is cooled to room temperature and filtered using Whatman filter paper.

Synthesis of Strontium Titanate Nanoparticles Doped with Azadirachta Indica Leaf Extract and Coconut Water:

Titanium tetraisopropoxide and strontium nitrate were used as precursors for the synthesis of strontium titanate nanoparticles. Titanium tetraisopropoxide was added to ethanol (contained in a reaction beaker), which was being stirred at 400 rpm. Further, acetylacetone solution was drop wise added to the mixture solution and stirred for 2 hrs, Strontium nitrate was further added to titanium tetraisopropoxide solution while being continuously stirring; the reaction was carried out using the optimal molar ratios: titanium tetraisopropoxide, strontium nitrate, acetylacetone, ethanol, and water (1:1:1:20:3). The samples were dried at 80 ºC overnight and calcined in a muffle furnace at 900 ºC for 5 h. Similar procedure is followed for the preparation of strontium titanate doped with *Azadirachta indica* leaf extract (1:1) and coconut water (1:1).The obtained sample is performed to characteristic analysis.[31]

Results and discussion

X-Ray Diffraction Analysis

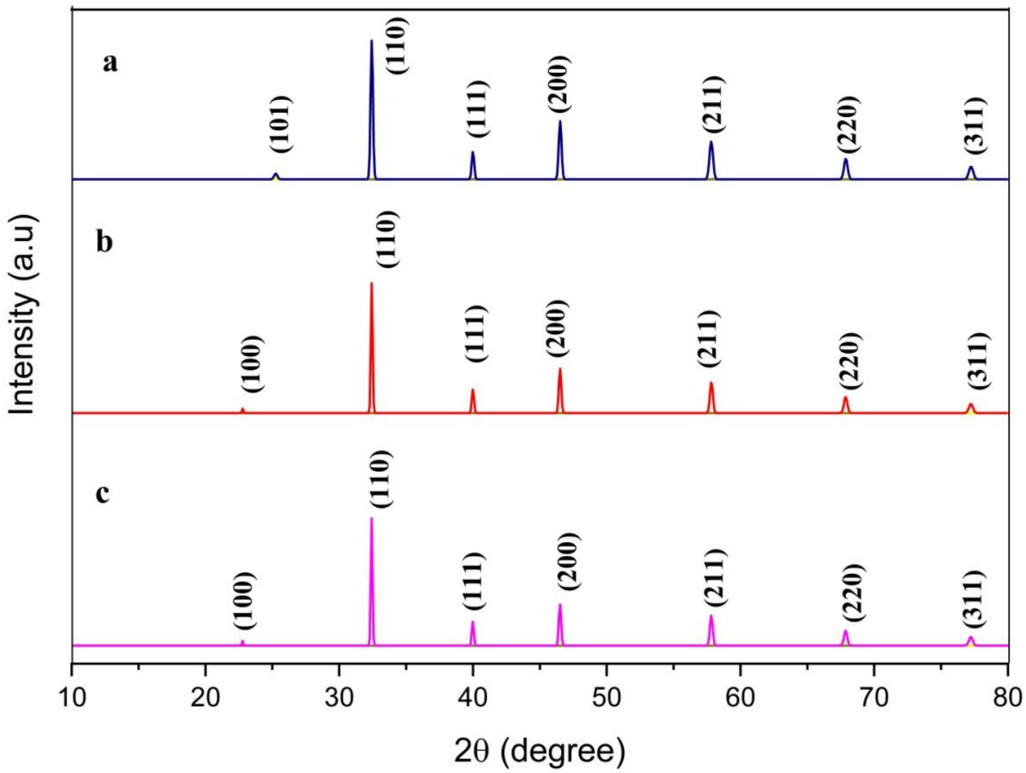


Figure 1. XRD patterns of $SrTiO_3$ nanoparticles (a), $SrTiO_3$ nanoparticles doped with Azardirachta indica leaf extract (b), and coconut water (c).

The XRD analysis of synthesized, strontium titanate nanoparticles, doped with Azardirachta indica leaf extract and coconut water are shown in **Figure 1**. (a), (b), and (c). From the analysis, it reveals that all the patterns of the samples existing in cubic structure, according to JCPDS data (JCPDS file No. 89-4934), at 22.7°,25.2°, 32.4°, 39.99°, 46.5°, 57.8°, 67.8°, and 77.2°, which correspond to crystal planes of (1 0 0),(101), (1 1 0), (1 1 1), (2 00), (2 1 1), (2 2 0), and (3 1 1), respectively, confirm the presence of strontium titanate nanoparticles, and the lattice parameters are, a = b = c = 3.907 Å and $\alpha = \beta = \gamma = 90°$. It indicates the synthesized strontium titanate nanoparticles are highly crystalline, and the average crystallite size is in the range of 46.2 nm, 43.2 nm, and 32.7 nm for pure strontium titanate, doped with Azardirachta indica leaf extract and coconut water respectively.[32, 33]

Fourier Transforms Infrared spectroscopy (FTIR) Analysis

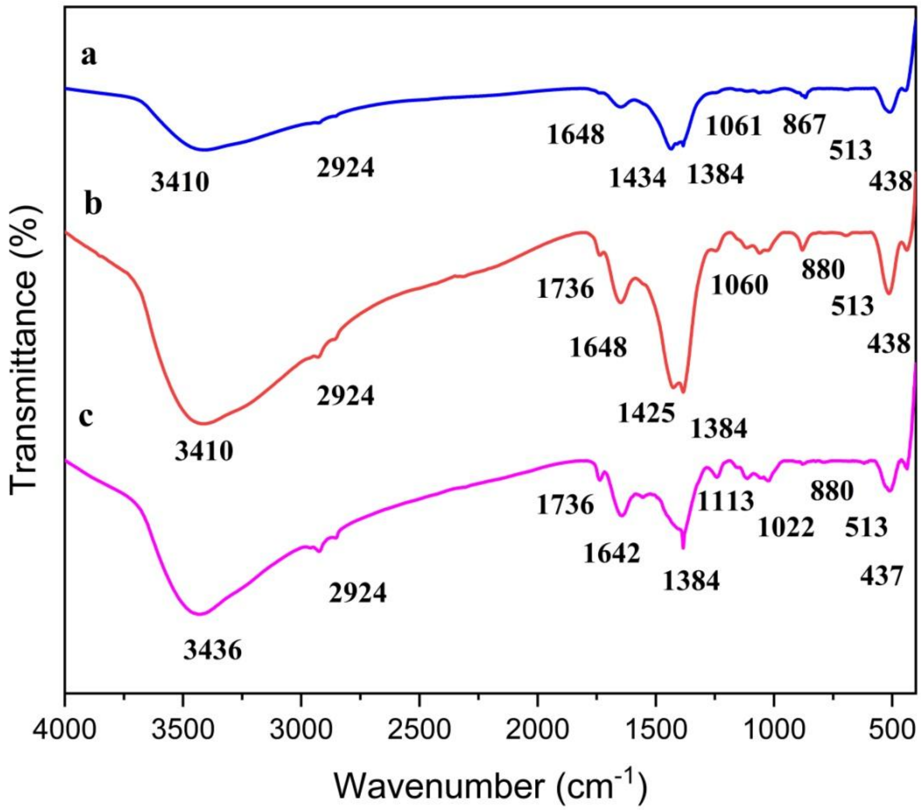


Figure 2. FTIR spectra of $SrTiO_3$ nanoparticles (a), $SrTiO_3$ nanoparticles doped with Azardirachta indica leaf extract (b), and coconut water (c).

The FTIR analysis of the prepared strontium titanate nanoparticles, doped with Azardirachta indica leaf extract, and coconut water by sol-gel method is shown **Figure 2.** a, b, and c respectively. From the analysis, the peaks at 3410 cm^{-1}, 3436 cm-1, and 1736 cm^{-1} are assigned to stretching vibrations of OH- groups. The peaks located at 2924 cm^{-1}, 1113 cm^{-1} , is attributed to C-H stretching vibration, and the peaks at 1648 cm^{-1}, and 1642 cm^{-1} are assigned to C=O and carbonyl group stretching vibration. CH_2 and CH_3 groups are noted at 1425 cm^{-1}, 1434 cm^{-1} peaks and peak at 1384 cm^{-1} is assigned to C-N Stretching vibration. The absorption for C-O at 1060 cm^{-1} and 1061 cm^{-1}, C-H bending mode at 1022 cm^{-1}, Ti-O-Ti stretching vibration at 867 cm^{-1}, 880 cm^{-1} was observed. The characteristic peaks at 513 cm^{-1} can be assigned to Sr-Ti-O stretching vibration and the peak at 437 cm^{-1}, 438 cm^{-1} can be attributed to the stretching vibration of Sr-O.[34, 35]

Scanning Electron Microscopy (SEM) Analysis

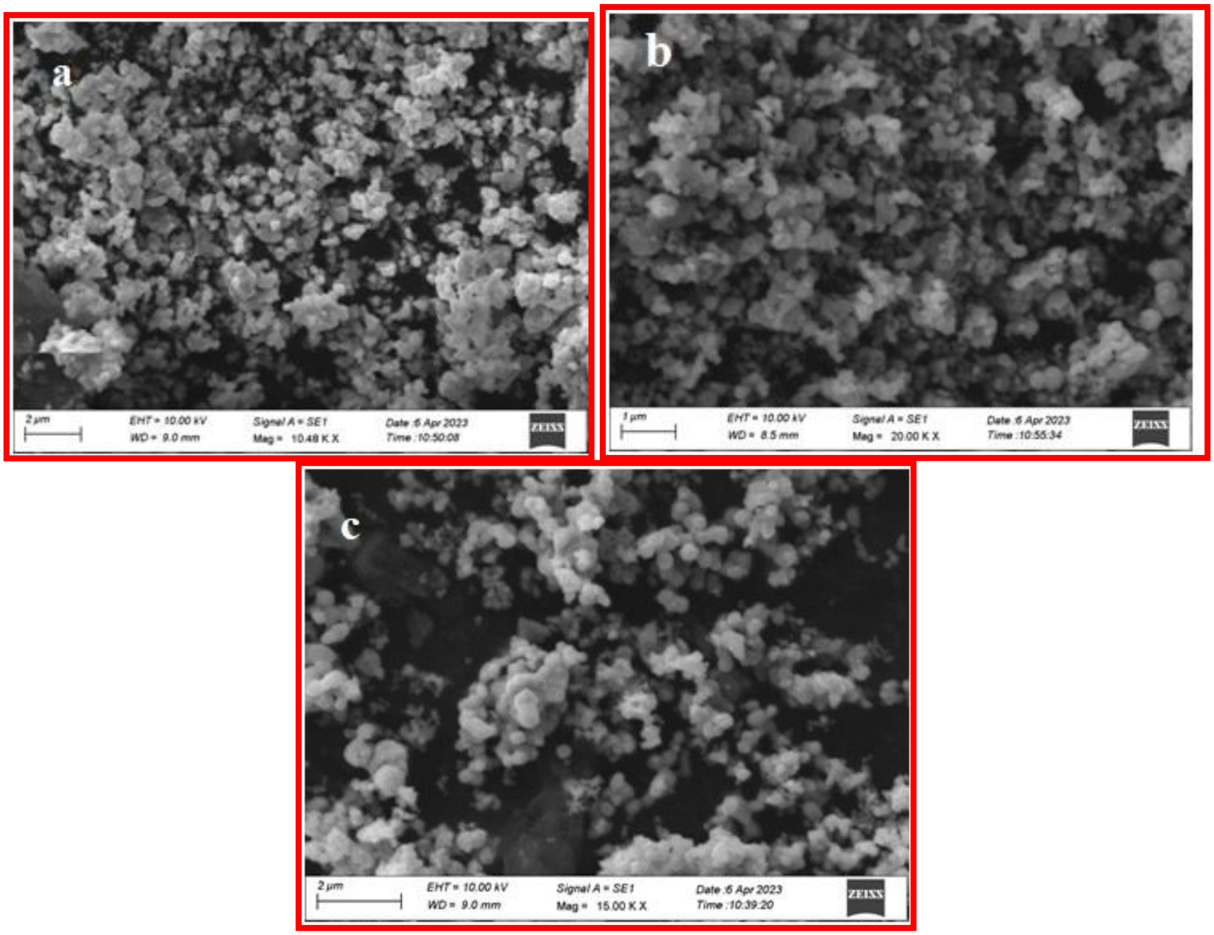


Figure 3. SEM images of $SrTiO_3$nanoparticles (a), $SrTiO_3$ nanoparticles doped with Azardirachta indica leaf extract (b), and coconut water (c).

The morphology images of the prepared strontium titanate nanoparticles, doped with Azardirachta indica leaf extract, and coconut water by sol-gel method is shown **Figure 3**. a, b, and c respectively. From the analysis, the synthesized strontium titanate nanoparticles (**Figure 3. a**) has a regular morphology, a uniform size distribution, and a cubic structure was observed. Furthermore, with Azardirachta indica leaf extract doped strontium titanate nanoparticles confirms the structure is to be spherical as shown in **Figure 3. b** and irregular agglomerations are noted in **Figure 3.c** due to the presence of compositions of coconut water presence in strontium titanate.[36]

Energy Dispersive X-ray spectroscopy (EDX) Analysis:

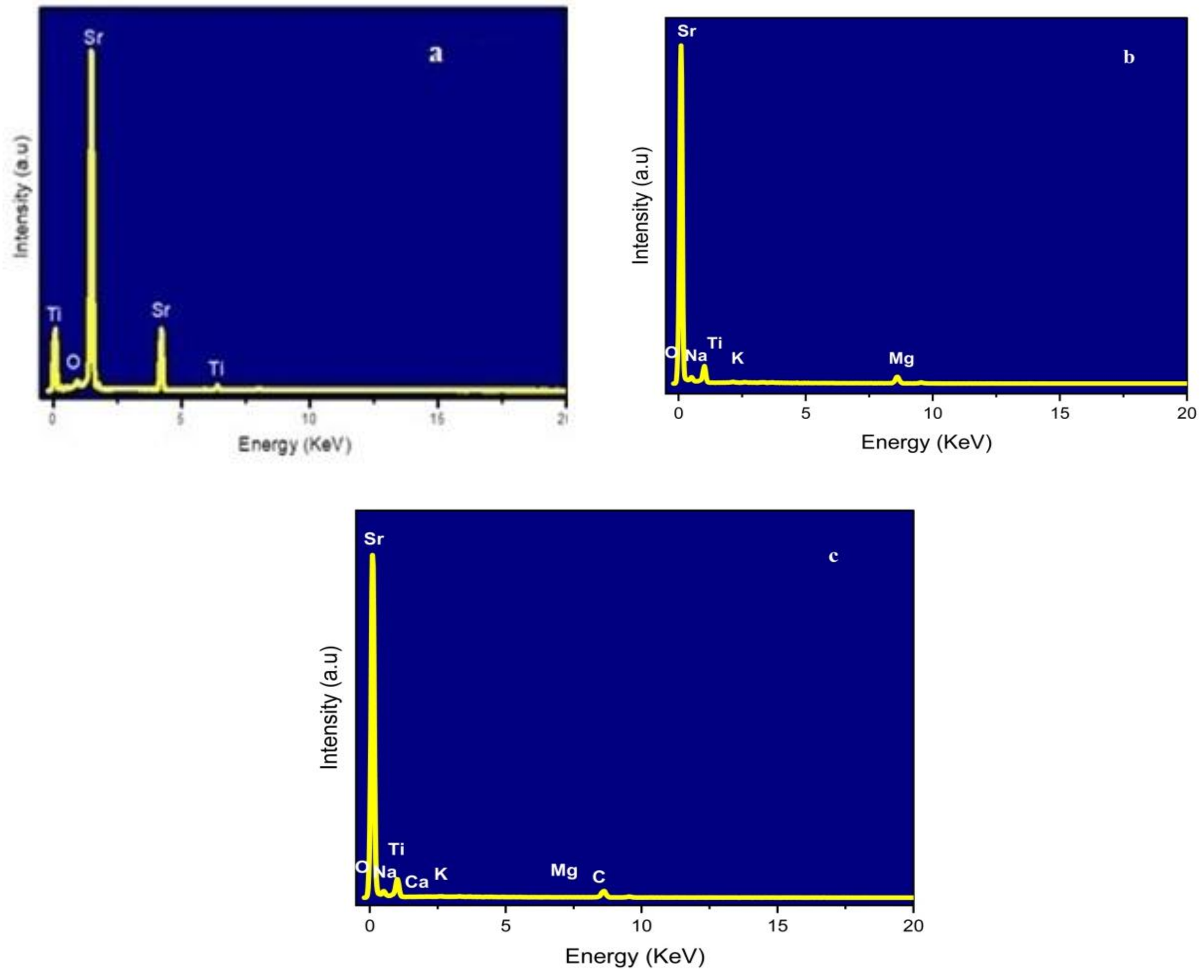


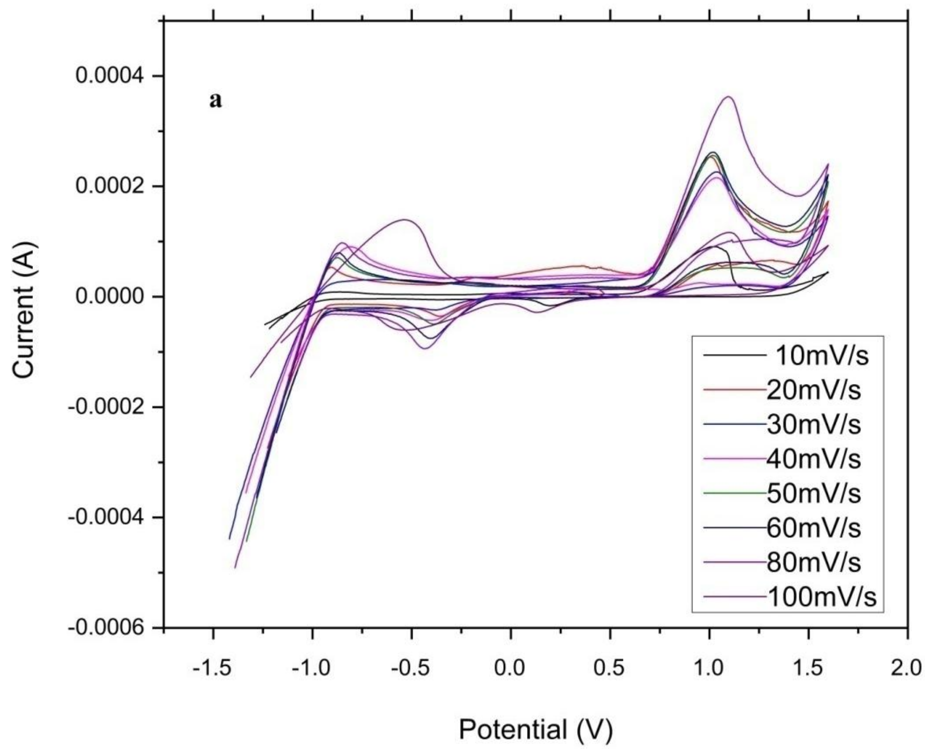
Figure 4. EDX images of $SrTiO_3$nanoparticles (a), $SrTiO_3$ nanoparticles doped with Azardirachta indica leaf extract (b), and coconut water (c).

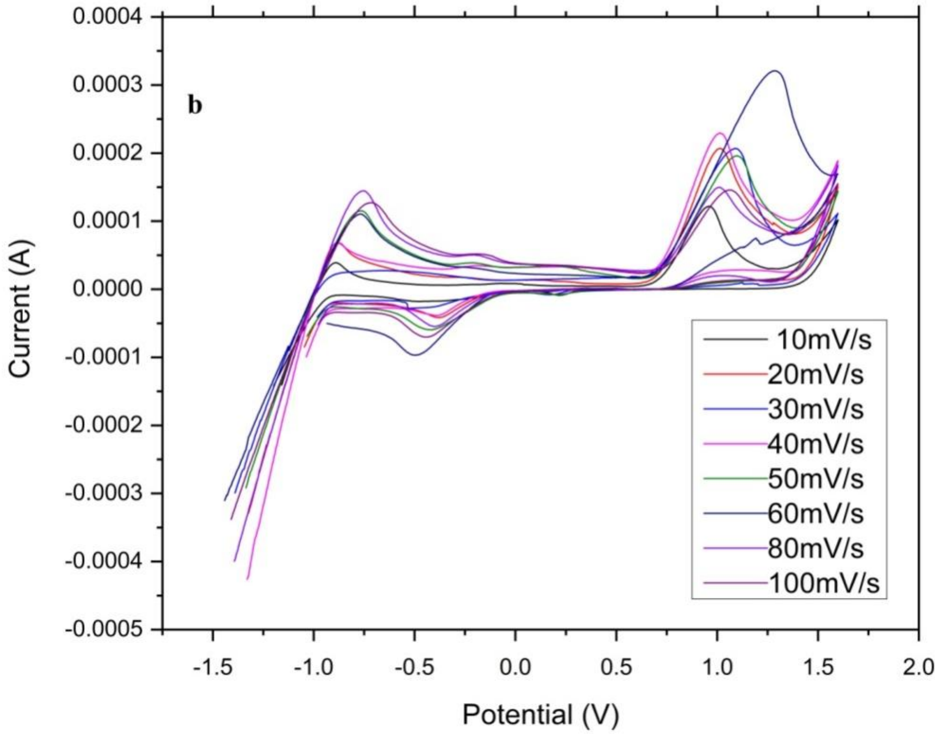
EDX analysis spectrum of the synthesized strontium titanate nanoparticles, doped with Azardirachta indica leaf extract, and coconut water by sol-gel method is shown **Figure 4**. a, b, and c respectively. EDX analysis confirms that the elemental percentage of strontium (Sr) 35.25%, titanium (Ti) 34.24%, and oxygen (O) 30.51 % was exhibit in the pure strontium titanate nanoparticles, and the weight percentage Azardirachta indica leaf extract doped strontium titanate reveals the compositional presence (Sr-42.25 %, Ti-28.15 %, O-19.25 %, potassium (K)- 1.15 %, sodium (Na) – 4.10 %, Magnesium (Mg) – 5.10 %) was observed. and coconut water doped strontium titanate with the compositional weight percentage of Sr-27.82 %, Ti-25.15 %, O-26.24 %, carbon (C) – 6.94 %, potassium (K)- 2.17 %, sodium (Na) – 5.29 %) calcium (Ca)- 4.14 %, Magnesium (Mg) – 2.25 % were studied. The results are tabulated as shown in **Table 1**. It clearly revealed that the Sr, Ti and O elemental percentage is reduced due to the compositions present in the extracts and coconut water. From the analysis, it reveals that there were the absences of other impurities.[37]

Table 1. Elemental compositions of strontium titanate doped with azardirachta indica leaf extract and coconut water

S.No.	Samples	Element (Weight (%))
1	$SrTiO_3$	Sr-35.25,Ti-34.24,O-30.514
2	Azardirachta indica leaf extract + $SrTiO_3$	Sr-32.58, Ti-28.35, O-29.42,N-4.15, P-2.13, K-2.17, S-1.20%
3	Coconut water +$SrTiO_3$	Sr-27.82,Ti-25.14,O-26.24,K -5.94, Na-4.21, Mg-5.41,Ca-4.14,Fe-1.10

Cyclic Voltammetry (CV) analysis:




b
Current (A)
Potential (V)
10mV/s
20mV/s
30mV/s
40mV/s
50mV/s
60mV/s
80mV/s
100mV/s

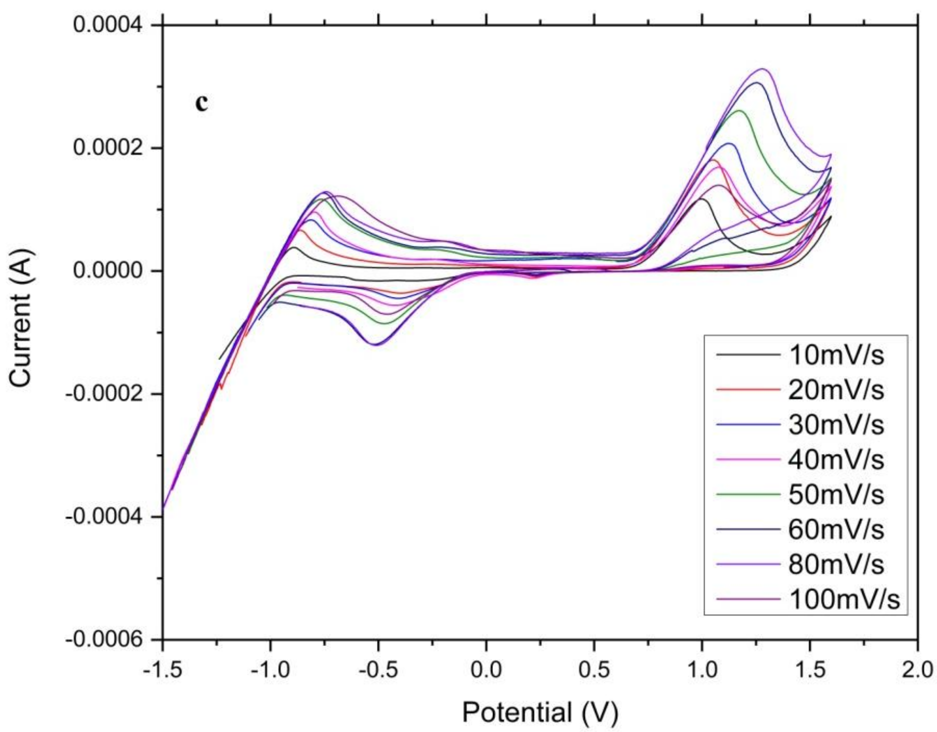

c
Current (A)
Potential (V)
10mV/s
20mV/s
30mV/s
40mV/s
50mV/s
60mV/s
80mV/s
100mV/s

Figure 5. CV graph of $SrTiO_3$nanoparticles (a), $SrTiO_3$ nanoparticles doped with *Azardirachta indica* leaf extract (b), and coconut water (c).

The electrochemical behaviour of synthesized strontium titanate nanoparticles, doped with Azadirachta indica leaf extract, and coconut water, by sol-gel method was examined by cyclic voltammetry (CV) analysis in three electrode systems, such as a reference electrode (Ag/AgCl), a counter electrode (Platinum electrode), and a working electrode fabricated using strontium titanate, the results are represented in **Figure 5**. The analysis was done with the consideration of different scan rates ranging from 10 mV/s to 100 mV/s , a potential range of 0 V to 2 V, 3M KOH as the electrolyte solution ; From the curves, redox peaks are observed for all scan rates ranging from 10mV/s to100 mV/s. The anodic peaks are observed in the range of 0.69 V-1.55 V, 0.70 V-1.50 V, 0.68 V -1.45 V, and the cathode peaks are noted in the range of 0.98 V-0.71 V, 0.94 V- 0.72 V, and 0.91 V- 0.68 for the prepared strontium titanate nanoparticles, doped with Azadirachta indica leaf extract and coconut water by sol-gel method, respectively.

The specific capacitance (C_p (F/g)) is calculated by using the formula,

$$Specific\ capacitance, (C_p) = \frac{A}{2km\Delta V} \quad - (1)$$

Where A, k, m and ΔV are an area, scan rate, mass of the working sample, and potential window of the cyclic voltammetry curve, respectively. The high values of the specific capacitance of the samples were found to be 245.5 F/g, 268.2 F/g, and 315.9 F/g for pure strontium titanate nanoparticles, doped with Azardirachta indica leaf extract, and coconut water, respectively and the corresponding graph of scan rate with respect to the specific capacitance graph is drawn and shown in the **Figure 6**.

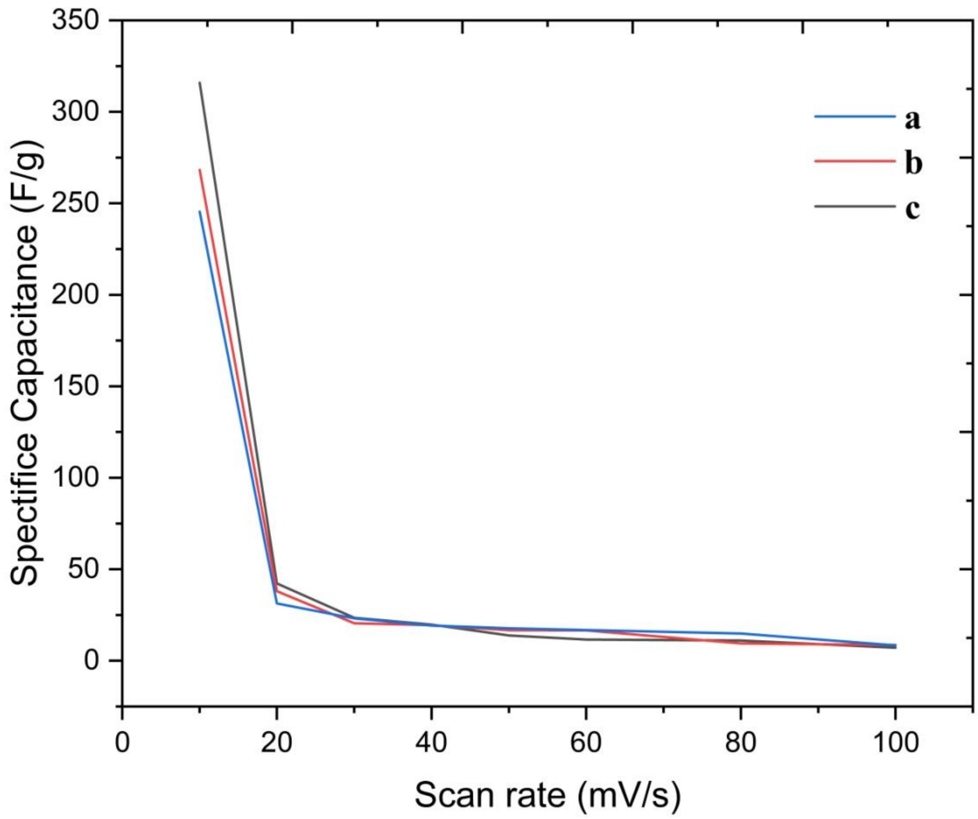


Figure 6. Scan rate vs specific capacitance

From the analysis, pseudocapacitive characteristics were observed for prepared strontium titanate nanoparticles, doped with Azardirachta indica leaf extract and coconut water. Further coconut water doped strontium titanate nanoparticles possesses high capacitive behaviour compared with pure strontium titanate nanoparticles and doped with Azardirachta indica leaf extract.[38, 39]

Electrochemical impedance spectroscopy (EIS) analysis

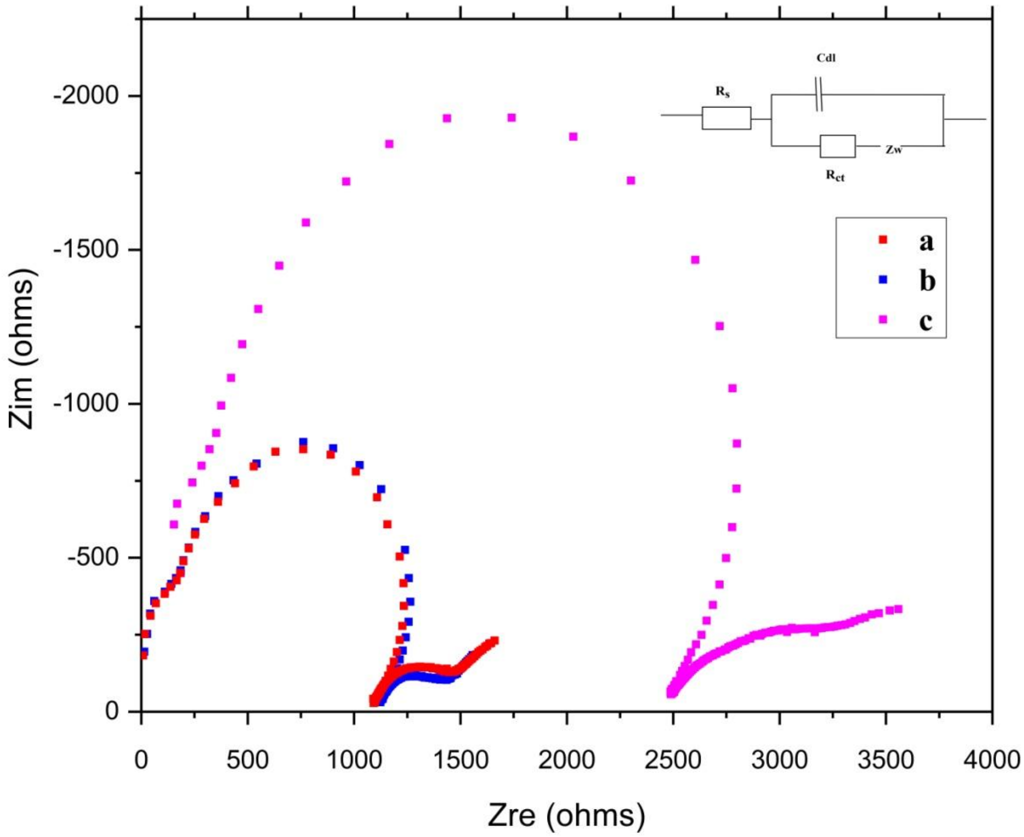


Figure 7. EIS analysis of $SrTiO_3$ nanoparticles (a), $SrTiO_3$ nanoparticles doped with Azardirachta indica leaf extract (b), and coconut water (c).

Electrochemical impedance spectroscopy (EIS) is used to analyze the prepared pure strontium titanate nanoparticles, doped with Azadirachta indica leaf extract and coconut water. The corresponding Nyquist plot is plotted between the real component impedance (Z_{re}) and imaginary component impedance (Z_{im}), with the frequency ranges of 1Hz to 10^6 Hz, the equivalent circuit is also shown in the **Figure 7**. At higher frequencies, the graph shows a semicircle, while at lower frequencies, it shows a straight line. The equivalent series resistance, which combines ionic resistance, intrinsic resistance (electrode, electrolyte), and charge transfer resistance, is responsible for the semicircle's intercept (Rct). According to the Nyquist plot, the high-frequency region is attributed to the solution resistance (Rs) of the electrode and electrolyte interface, the semicircle is caused by interfacial charge transfer, and the low-frequency region corresponds to the Warburg element (Z_w). The findings imply that the coconut water doped strontium titanate nanoparticles has a higher charge transfer resistance, resulting in a greater increase in capacitance than pure strontium titanate nanoparticles and doped with Azadirachta indica leaf extract. [40, 41, 42]

Conclusion

In the present describes that the strontium titanate ($SrTiO_3$) nanoparticles, doped with Azardirachta indica (Neem) leaf extract and coconut water. Further, the synthesized samples were analyzed by X-Ray Diffraction (XRD), Fourier Transforms Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS).The results of X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) indicate that the prepared strontium titanate nanoparticles have a cubic structure and some spherical while doped with Azardirachta indica leaf extract and coconut water. The characteristic peak 513 cm^{-1} for Sr-Ti-O stretching vibration was observed in the FTIR analysis. The SEM analysis confirms that the regular morphology is regular and uniform in size distribution. Energy-Dispersive X-ray spectroscopy (EDX) analysis reveals the weight percentage of prepared strontium titanate nanoparticles, doped with Azardirachta indica (Neem) leaf extract and coconut water. Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis suggest that the prepared samples exhibit pseudocapacitive behaviour and the coconut water doped strontium titanate nanoparticles have a higher discharge rate than pure strontium titanate nanoparticles and doped with Azardirachta indica (Neem) leaf extract. As a result, the coconut water doped strontium titanate nanoparticles might be considered a promising approach for applications involving super capacitors.

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