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RESEARCH ARTICLE

The electrochemical activity of Titanium dioxide nanostructures using the *Ocimum tenuiflorum* Plant Leaves Extract

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Abstract

Objectives: To investigate the electrochemical performance of TiO_2 (Titanium dioxide) nanoparticles prepared from *Ocimum tenuiflorum* Plant (OTP) Leaves extract. **Methods :** cost-effective and eco-friendly green synthesis approach is used to synthesize the TiO_2 nanoparticles. XRD (X-ray diffraction) and FESEM (Field Emission Scanning Electron Microscopy) techniques are used to analyse microstructural details. Raman and EDX (Energy Dispersive X-ray spectroscopy) are used to analyse the phase and the chemical composition of the synthesized TiO_2 nanoparticles. The nature of chemical bonding as well as the functional groups that the sample contains is identified by using FITR (Fourier Transform Infrared spectroscopy) investigation. The optical band gap of the prepared nanoparticles is estimated by UV-Vis spectroscopic analysis. Finally, Cyclic Voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) are used to investigate the electrochemical performance of the produced TiO_2 nanoparticles. **Findings:** The XRD data exhibited that the prepared TiO_2 nanoparticles are in a tetragonal structure with an anatase phase and have a crystallite size of 18.6 nm. FESEM images of the TiO_2 nanoparticles confirm the smooth surface morphology of spherical grains having an average grain size of 92 nm. The formation of the anatase phase is confirmed by the Raman spectroscopic analysis. The Ti-O-Ti bonds are identified in the sample through the FTIR absorption spectra. The optical band gap of green TiO_2 nanoparticles is found to be 3.07 eV and indexed to the anatase phase. Moreover, the better electrochemical performance of the prepared TiO_2 nanoparticles is identified from both CV and CP studies in Na_2SO_4 aqueous electrolyte. At last, the capacitive retention attains up to 65% even after 5000 cycles for the sample prepared from OTP. **Novelty:** A significant component of this study is the creation of the 3D nanostructured morphology of TiO_2 nanoparticles using the green synthesis method which follows

the green chemistry principles. This type of research provides assurance for the protection of rights of the future generations and ecosystems. This type of 3D nanostructure demonstrates superior performance as a supercapacitor electrode, photocatalyst, antibacterial agent, UV-resistant material and solar-powered H_2 fuel producer.

Keywords: TiO 2 nanoparticles; Green synthesis; Ocimum tenuiflorum Plant (OTP); Optical band gap; Specific capacitance

1 Introduction

Renewable energy is the only way to keep the rights of future generations and environmental ecosystems[(1)]. Scientists in the modern era have been very interested in developing more efficient forms of energy storage technology such as batteries, capacitors and fuel cells in order to accommodate the intermittent nature of renewable energy sources. Due to their high power density, quick charge-discharge and long cycle life without performance degradation, supercapacitors addressed these problems and met the needs of hybrid electric vehicles, portable devices and gadgets. Supercapacitors, in contrast to batteries, have drawbacks such as a high cost per watt, rapid self-discharge and poor specific energy. These issues in supercapacitors may be solved by using 3D nanostructured metal oxide electrodes[(2)]. TiO_2 is particularly versatile among the various metal oxides, with applications ranging from photocatalysis and antibacterial goods to lithium-ion battery electrode materials and supercapacitors[(3)]. Moreover, its low cost, non-toxicity, corrosive resistance and high availability make researchers glance at this material[(4)].

The above-mentioned complex challenges prompted and guided the selection of scientific goals in the present work. This work explains the mentioned concerns and prepared the 3D nanostructure electrodes for supercapacitor application through a simple and environment-friendly green approach. Table 1 shows the various parts of different medicinal plants that are used to synthesize the TiO_2 nanoparticles.

The majority of plants included in Table 1 belong to the group of medicinal Asclepiadaceous plants, which are native to Asia, including India, Indonesia, Malaysia, Thailand, Sri Lanka and China[(5)]. These plants contain several bioactive compounds with therapeutic characteristics[(6)]. These are generally referred to as milkweed or swallow-wort and they generate copious quantities of latex. In the current work, TiO_2 nanoparticles were effectively synthesized utilizing the leaf extract of the medicinal herb *Ocimum tenuiflorum* (OTP) in accordance with green chemistry principles. These leaf extracts include a variety of bioactive compounds, including glycosides, tannins, alkaloids, flavonoids, saponins, sterols, triterpenes and many proteins[(7)], which contribute to the reduction of Ti^{4+} ions to create TiO_2 nanoparticles and also aid in their stability and capping. Furthermore, the obtained powders were carefully analyzed and also studied their electrochemical properties. This analysis proved that the green synthesis method is a low-cost, low-temperature and environmentally friendly method to synthesize high surface area 3D nanostructures[(8–11)].

Table 1. List of different medicinal plants used to synthesize the TiO_2 nanoparticles

S.no	Name of the plant extract	Part utilized	Shape	Size (nm)
1	*Azadirachta indica A.Juss.*	Leaves	Spherical	124
2	*Aloe vera (L.) Burm.f.*	Leaves	Irregular	60
		WP	Irregular	60-80
3	*Jatropha curcas L.*	Latex	Spherical	25-100
4	*Trigonella foenum-graecum L.*	Leaves	Spherical	20-90
5	*Euphorbia prostrate Aiton*	Leaves	Polydisperse	83
6	*Solanum trilobatum L.*	Leaves	Spherical	70
7	*Eclipta prostrate (L.) L.*	Leaves	Spherical	36-68
8	*Ocimum basilicum L.*	Leaves	Spherical	50
9	*Psidium guajava L.*	Leaves	Spherical	32

2 Methodology

2.1 Materials

TiO_2 nano metal oxides were manufactured using a simple green synthesis approach. In this approach, $TiCl_4$ with 99.0% purity (employed without any additional purification) was taken as a precursor material with OTP leaf extract as a catalyst.

2.2 *Ocimum tenuiflorum* plant leaf extract preparation

During the preparation procedure, firstly, the healthy leaves of the *Ocimum tenuiflorum* plant were taken and washed several times using RO purified, distilled and double distilled (DD) water to clear the dust particles and other unwanted substances present on the leaves. 25 g of OTP leaves were chopped into very small pieces and placed directly into a single-neck, round-bottom boiling flask containing DD water of 100 ml. The flask was heated at 90 °C for about two hours using a heating mantle. After 5 hours, OTP leaves solution was filtered using a filter paper having pores of 2.5 μm size. This final solution was used as a reducing agent to create TiO_2 nanoparticles.

2.3 TiO_2 nanoparticles preparation

Finally, 1.0 N Titanium tetra chloride ($TiCl_4$) solution was prepared using 100 ml of DD water and OTP leaf extract (25 ml) was added to it dropwise under continual stirring conditions at room temperature. The final solution pH was found to be 2.0 - 2.4, after 24 hours of stirring[12]. Plant leaf extracts typically contain significant levels of secondary metabolites such as alkaloids, polyphenols, terpenoids, flavonoids and peptides, which have hydroxyl and ketonic groups that aid in the reduction of Ti^{4+} ions to TiO_2 and also stabilizing and capping of those nanoparticles. The TiO_2 nanoparticles obtained were cleaned many times with DD and ethanol until the solution's pH level reached 7. After then, the obtained white TiO_2 nanoparticles were dried overnight at 90 °C. Lastly, the sample was calcined for 5 hours at 200 °C to eliminate any evaporable contaminants and produce pure TiO_2 nanoparticles. The collected nanoparticles were used to investigate various material characterizations towards the supercapacitor applications. The following is the reaction process for the synthesis of TiO_2 from $TiCl_4$[13].

$$TiCl_4 + xH_2O \rightarrow Ti(OH)_xCl_{4-x} + xHCl$$

$$Ti(OH)_xCl_{4-x} \rightarrow TiO_2 + (4 - x)HCl + (x - 2)H_2O.$$

2.4 Material Characterization

TiO_2 nanoparticles' structural characteristics were investigated using a Seifert X-ray diffractometer using CuK_α radiation (λ = 0.154 nm) and a Horiba Jobin Yvon Lab RAM HR800UV Raman Spectrometer (λ = 532 nm). In a high vacuum, a Carl ZEISS-EVO MA15 FESEM (Field Emission Scanning Electron Microscope) was used to study surface morphology. The Thermo Nicolet IR-200 FTIR spectrophotometer was used to study the atomic bonding. The elements in the sample were identified using a BRUKER EDS (Energy Dispersive spectrometer). A UV-Vis spectrometer with a range of 200-1100 nm was utilized to record the absorption spectrum of the TiO_2 sample at room temperature. Utilizing the CHI 608C electrochemical workstations, the

electrochemical performance of green synthesized TiO_2 nanoparticles was investigated.

2.5 Construction of working electrode and three electrode glass cells

The active working electrode is made up of 80% of the synthesized TiO_2 nanoparticles, 10% of the carbon black and 10% of the Poly Vinylidene Fluoride. This mixture was grinded for one and a half hours in an agate motor. The aforesaid mixture was homogenized by the addition of the needed amount of N-methyl-2-pyrrolidone. The mixture was evenly coated onto the chemically washed nickel foam after which it was dried for 2 hours at 100 °C.

2.6 Preparation of electrochemical work station

Utilizing a glass cell with three electrodes, the electrochemical behaviours of TiO_2 nanoparticles was observed. Three electrode glass cells typically have an electrolyte as well as the counter, working, and reference electrodes.

Counter electrode - Pt (platinum) foil.
Working electrode - Ni (nickel) foam coated with TiO_2.
Reference electrode - Ag/AgCl (Silver/Silver Chloride).
Electrolyte - 1M Na_2SO_4 aqueous electrolyte.

3 Results and Discussion

3.1 X-ray diffraction

Figure 1 depicts the XRD spectrum of TiO_2 nanoparticles prepared with OTP leaf extract in between the 2θ range of 20°-70°. This XRD pattern displayed a (101) predominant orientation peak at 2θ = 25.76°, along with the other characteristic peaks of (004), (200), (105), (211), (204) and (116) at 38.36°, 48.61°, 54.44°, 58.38°, 63.11° and 69.09° sequentially. All the obtained diffraction peaks were matched with the tetragonal structured anatase phase TiO_2 with $I4_1/amd$ space group (JCPDS card No. 21-1272). The calculated lattice constants were a=b=3.779 Å and c = 9.521 Å, which were in close agreement with prior reports[14]. The sample's crystallite size (D) was estimated by using Scherrer's formula and found to be 18.6 nm.

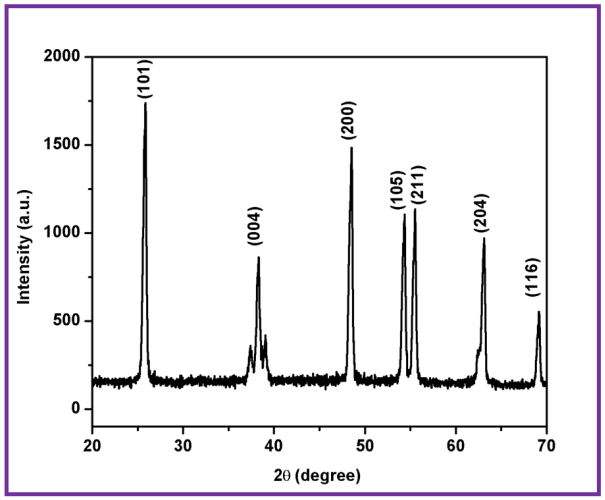

Fig 1. XRD Spectrum of TiO_2 nanoparticles synthesized using OTP extract

3.2 Raman Spectroscopy

The structure and phase of TiO_2 samples have been verified using Raman spectroscopy over the range of 200-1000 cm^{-1}. Figure 2 depicts the micro-Raman spectrum of the synthesized TiO_2 nanoparticles using OTP extract and exhibits Raman-active modes of B_{1g}, A_{1g} and E_g at frequencies of 392, 514 and 636 cm^{-1} respectively, corresponding to the anatase phase[15].

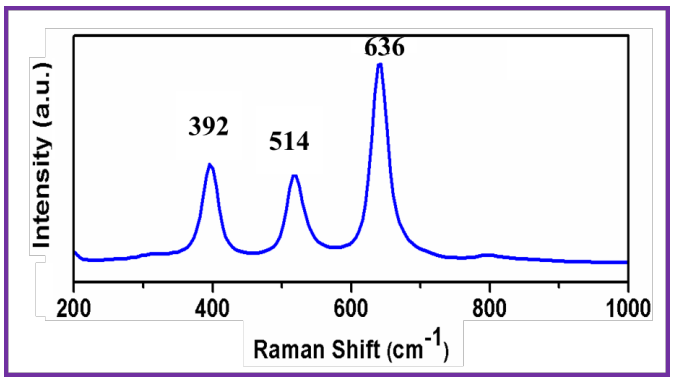

Fig 2. Raman Spectrum of TiO_2 nanoparticles synthesized using OTP extract

3.3 Fourier Transform Infrared spectroscopy (FTIR)

The vibrational studies of OTP extracted TiO_2 nanoparticles were done using the FTIR technique to understand the chemical bonds and also the functional groups present in the compound over the 400 - 4000 cm^{-1} wavenumber range which was shown in Figure 3. The presence of titanium oxide in the sample was confirmed by the existence of a significant absorption peak between 400 and 1000 cm^{-1}, which corresponds to Ti-O-Ti bonding[16]. In this OTP sample, the O-H stretching vibrational bonds signified at 3029 cm^{-1} because of the presence of H_2O molecules. At 2092, 1881 and 1612 cm^{-1}, absorption peaks were identified that represent the C-H stretching vibrations and C-C bonds, respectively.

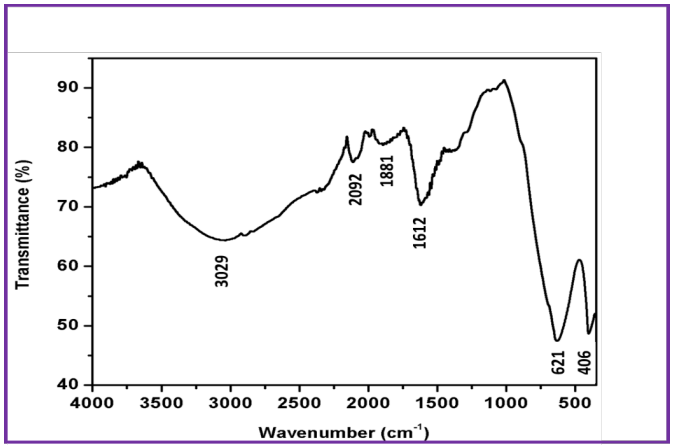

Fig 3. FTIR Spectrum of TiO_2 nanoparticles synthesized using OTP extract

3.4 Field Emission Scanning Electron Microscopy (FESEM)

The electrode material with a greater surface area improves the electrochemical properties of supercapacitors. As illustrated in Figure 4, the surface morphology of the synthesized TiO_2 nanoparticles was captured by the FESEM technique. The FESEM pictures (Figure 4 a-d)] demonstrated that the OTP extracted sample consists of nano-size spherical grains with an average grain size of 92 nm. This type of morphology will provide a better surface area and also provide more active sites for the electrolyte ions[17].

3.5 Energy dispersive spectroscopic analysis (EDS)

The compositional analysis of the synthesized TiO_2 nanoparticles was provided by EDS analysis. The EDS spectrum of the sample was shown in Figure 5 . The binding energy peaks in the obtained spectrum qualitatively validated the existence of Ti and O elements, indicating satisfactory stoichiometry in the samples[18].

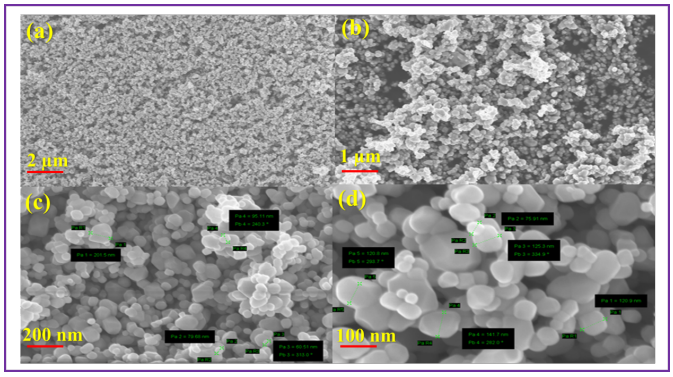

Fig 4. FESEM micrographs of TiO_2 nanoparticles synthesized using OTP extract

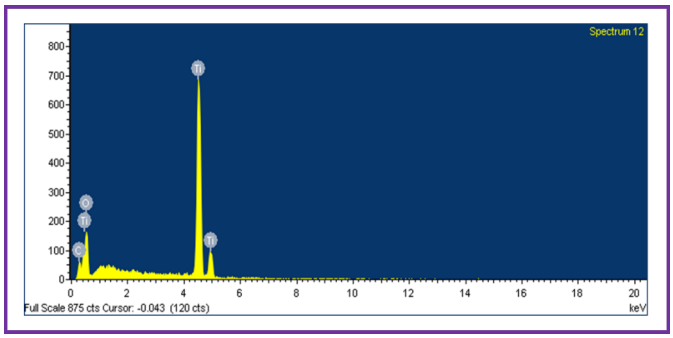

Fig 5. EDS spectrum of TiO_2 nanoparticles synthesized using OTP extract

3.6 Optical spectroscopy

The optical absorption characteristics of TiO_2 samples synthesized through OTP extract were studied by UV-visible spectroscopic study. The anatase phase TiO_2 shows a significant absorption peak in the UV range at 344 nm (Figure 6) and exhibited an optical band gap of 3.07 eV as illustrated in Figure 6 [19].

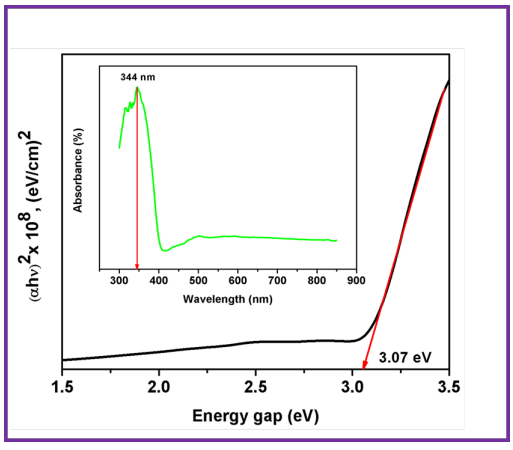

Fig 6. UV vis and absorption spectra (inset) of TiO_2 synthesized using OTP extract

3.7 Electrochemical Properties

The electrochemical characteristics of the OTP sample were examined at at a scan rate of 10 mV s^{-1} under different working potential windows utilizing 1M Na_2SO_4 aqueous electrolyte to study its electrochemical reversibility property. Cyclic Voltammetry (CV) curves exhibit capacitive-like characteristics due to the rapid reversal of currents during a change in potential direction. Furthermore, it was found that the specific capacitance value was higher in the 0.8 V to -0.2 V working potential window. However, the reduction curve in the working potential window of 0.8 V to -0.2 V looks exactly like the oxidation curve in Figure 7 (a). Also, the supercapacitive performance of the OTP sample was investigated in the range of -0.2 V to 0.8 V.

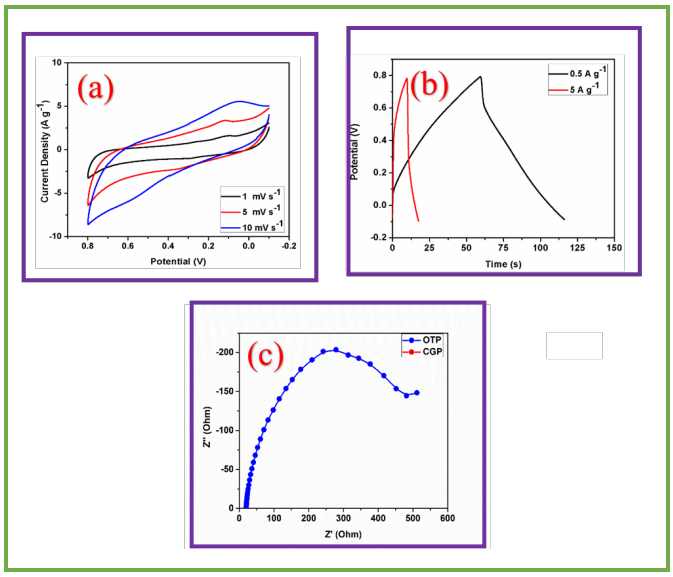

Fig 7. (a) CV curves of TiO_2 derived from OTP extract (b) CP curves of TiO_2 derived from OTP extract (c) Nyquist plots of TiO_2 using OTP extracts

OTP extracted samples' electrochemical properties were studied by Cyclic Voltammetry (CV) in a three-electrode glass cell. TiO_2 nanoparticles formed with OTP extract as the working electrode, the platinum foil and Ag/AgCl were used as the counter and the reference electrode respectively in a 1M Na_2SO_4 liquid electrolyte. Figure 7 (b). demonstrates the CV curves of the OTP sample at scan rates of 1, 5, and 10 mV s^{-1} in between -0.2 V and +0.8 V vs. Pt. All of the CV curves seem to be rectangular, indicating that Faraday redox reactions are reversible and that the sample possesses perfect capacitive performance. The sample specific capacitance value was determined using the following formula [20].

$$C = \frac{\int I(V)\,dV}{(2m\Delta V\,(V_2 - V_1))}$$

Here the terms C, I(V), $\int I(V)\,dV$, m, ΔV and (V_2 - V_1) signifies specific capacitance value measured in F g^{-1}, the instantaneous current value measured in A, total voltametric charge value measured in C, the mass of active material measured in gram, the scan rate is measured in V s^{-1} and the potential window range is measured in V respectively.

The specific capacitance values for OTP extracted samples are 167, 138 and 112 F g^{-1} at 1, 5 and 10 mV s^{-1} scan rates respectively. Because electrolyte ions don't respond quickly enough to use all of the electrode's active sites, specific capacitance decreases as the scan rate increases [21].

Chronopotentiometry (CP) investigations were performed to understand more about the electrochemical behaviour of OTP samples. A sharp potential drop at the start of the discharge curve in Figure 7 (c) indicated the presence of internal resistance within samples. The double-layer capacitive behaviour resulting from electrolyte ion separation near the electrode-electrolyte interface was detected from the potential line that did not deviate with time. The determination of the samples' discharge specific capacitance was done by using the following formula [22].

$$C = \frac{I\triangle t}{\triangle V m}$$

Here, C, I, △t, △V and m stand for specific capacitance in F g^{-1}, galvanostatic discharge current in A, discharge time in seconds, voltage range in V and active material mass in grams.

For OTP-extracted samples, the calculated specific capacitances were 159 and 126 F g^{-1} at 0.5 and 2 A g^{-1} respectively. Because of the increase of internal resistance value with the increase of current density, specific capacitance decreased. Furthermore, to study the capacitive retention of the OTP extracted samples, charge-discharge cycles were performed up to 5000 cycles at a current density of 0.5 A g^{-1}, as depicted in Figure 8. For the OTP samples, capacitive retention is 65% up to 5000 cycles. Because the active sites of the electrode were covered by electrolyte ions during prior charge-discharge cycles, the specific capacitance value decreases with the cycle number.

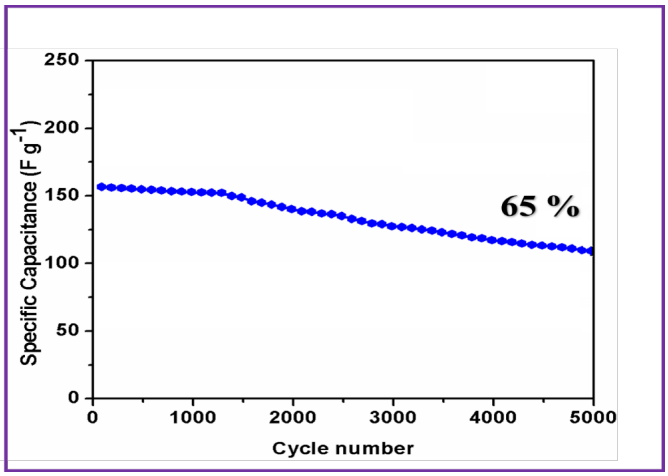

Fig 8. Specific capacitance with cycle number of TiO_2 synthesized using OTP extract

The OTP extracted sample showed good electrochemical performance, which was confirmed by an Electrochemical Impedance Spectroscopy (EIS) study performed in the frequency range of 1Hz to 1MHz. Figure 7 (d) depicts the samples' typical Nyquist curves. It is obvious from Figure 7(d) that the solution resistance (Rs) and charge transfer resistance (Rct) of the OTP sample are 18 Ω and 620 Ω respectively and support CV results.

The current study findings were compared with those obtained earlier by Li Zhang et al. [23] and Yan Zhao et al. [24]. Li Zhang et al. synthesized the TiO_2 nanoflakes with 91% of capacitive retention and a specific capacitance of 34.79 Mf/cm^2 at 5 mVs^{-1} scan rate in a 1M Na_2SO_4 aqueous electrolyte. Yan Zhao et al. established that TiO_2/C_3N_4 hybrid materials exhibit 95% of capacitive retention and have a specific capacitance of 125 Fg^{-1} at 1 Ag^{-1} current density in a 2M KOH aqueous electrolyte. Finally, these comparison findings showed that green TiO_2 nanoparticles were alternate electrode materials for electrochemical energy storage devices.

4 Conclusion

TiO_2 3D nanoparticles were successfully synthesised at room temperature using *Ocimum tenuiflorum* plant leaf (OTP) extracts using a simple eco-friendly green synthesis approach. Both the XRD and Raman spectra showed that the TiO_2 nanoparticles produced by OTP extracts were in the anatase phase. FESEM analysis of OTP samples showed that the grains were round and averaged 92 nm in size. The presence of elements inside the samples was qualitatively confirmed by the EDS spectra. The FTIR analysis showed that the material included TiO_2 bonds. Electrochemical tests showed that TiO_2 nanoparticles made from OTP extracts had a capacitance of 167 F g^{-1} and remarkable cyclic stability. This type of research provides faith in an environmentally friendly synthesis process. Further, it is suggested that the green synthesis method will aid researchers of the twenty-first century in creating high surface area porous 3D nanostructured metal oxide nanoparticles for supercapacitors.

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