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RESEARCH ARTICLE

Electrochemical Activity of TiO_2 Nanoparticles in NaOH Electrolyte via Green Synthesis Using *Calotropis gigantea* Plant Leaf Extract

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Abstract

Objectives: Green synthesis of Titanium dioxide (TiO_2) nanoparticles using *Calotropis gigantea* (CG) plant leaf extract. **Methods:** Environmental eco-friendly green approach is used to synthesize nanostructured TiO_2 nanoparticles by using $TiCl_4$ as a precursor and *C. gigantea* plant leaf extract as a catalyst. The secondary metabolites in the CG plant leaf extract help to transform the Ti^{4+} ions to TiO_2 nanoparticles. The detailed structural properties are studied using X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM), and high-resolution transmission electron microscopy (HRTEM). The phase formation and chemical state of the prepared samples are examined by Raman and Energy Dispersive X-ray spectroscopy (EDX). The vibrational frequencies between the bonds of atoms are studied with Fourier Transform Infra-Red spectroscopy (FTIR). The electrochemical properties of green synthesized nanoparticles using cyclic voltammetry (CV) technique in aqueous electrolyte. **Findings:** XRD data conform to the tetragonal structure of TiO_2 in the rutile phase with P42/mnm space group and crystallite size is also found to be 9.84 nm. The SEM and TEM images show that the non-uniform spherical and flower-like shape of grains with an average grains size of 100 nm. The specific capacitance of the sample is estimated to be 238 F g^{-1} at a scan rate of 1 mV s^{-1} with good reversibility. **Novelty:** The novelty of this research lies in the fabrication of the electrode material with TiO_2 3D nanostructures for supercapacitor applications. This kind of morphology certainly enhances the surface area and leads to achieving better electrochemical performance.

Keywords: Titanium tetra chloride; TiO 2 nanoparticles; Green synthesis; Calotropis gigantea (CG) Plant; 3D nanostructure; specific capacitance

1 Introduction

Synthesis of high surface area 3D nanostructures is an important task to improve the electrochemical performance of an energy storage devices [1,2]. The high surface area 3D nanostructures have more active cites compared to normal 2D nanomaterials. Now the 21st century researchers have planned various processes for the synthesis of 3D nanostructure metal oxides (NMOs) which have contributed in the development of energy storage devices [3]. Synthesis of NMOs using plant leaf extract is compatible with the green chemistry principles. Green synthesis of NMOs makes use of environmental friendly, non-toxic and safe reagents. NMOs synthesized using biological techniques or green technology have diverse natures, with greater stability and appropriate dimensions since they are synthesized using a one-step procedure. NMOs can be synthesized using a variety of methods including chemical, physical, biological, and hybrid techniques. Physical methods including plasma arching, ball milling, thermal evaporate, spray pyrolysis, ultrathin film, pulsed laser desorption, lithographic techniques, sputter deposition, layer by layer growth, molecular beam epitasis, and diffusion flame synthesis of NMOs. Similarly, chemical methods are used to synthesize NPs by electrodeposition, sol–gel process, chemical solution deposition, chemical vapour deposition soft chemical method, Langmuir Blodgett method, catalytic route, hydrolysis co-precipitation method, and wet chemical method [4–7]. Chemical and Physical methods have been using high radiation and highly concentrated reductants and stabilizing agents that are harmful for the environmental and to human health. Hence, biological synthesis of NMOs is a single-step bio-reduction method and less energy is used to synthesize eco-friendly.

So far, various transition metal oxides have been used as the electrode materials for supercapacitors, such as RuO_2, Co_3O_4, NiO, CuO, SnO_2, and manganese based oxides like MnO, Mn_3O_4, Mn_2O_3, and MnO_2 [8–11]. Among these transition metal oxides, RuO_2 was the most widely studied metal oxide due to its high conductivity and high specific capacitance as well as its excellent chemical stability. However, due to its less abundance and high cost regarding the usage of Ruthenium, there were major limitations to its practical applications. Titanium Dioxide (TiO_2) become alternate and promising electrode materials for supercapacitors due to their extraordinary properties like hydrophobic nature, non-wet ability, high energy bandgap, thermally stable, outstanding structure stability, chemical stability, potential oxidation strength; hence it can be used in different types of applications such as self-cleaning, gas sensors, solar cell, photo catalysis, charge spreading devices, chemical sensors, microelectronics, electrochemistry, anti-bacterial products, textiles and promising electrode material for lithium-ion batteries and Supercapacitors [12–16]. Moreover, TiO_2 has attractive advantages like high relative abundance and resistance to corrosion, low cost, better safety, and environmental friendliness due to non-flammable and non-toxicity.

Quite a few reports are available on the green synthesis of TiO_2 nanoparticles using various plant extracts like Nyctanthes arbor-tristis, *Solanum trilobatum, Annona squamosa, Catharanthus roseus, Jatropha curcas, Cucurbita pepo, Eclipta prostrata*, *C. gigantea*, and *Ocimum basilicum* (Ocimum tenuiflorum) [17–28]. *C. gigantea* is a well-known medicinal plant belongs to the Asclepiadaceous family, this plant is widely used as a scent through which it netted its title Queen (basileus) of aromatic herbs [29]. The present study focused on the preparation of Titanium dioxide (TiO_2) nanoparticles with CG plant leaf extract using the green synthesis method. This plants leaf extract is the source of various biologically active compounds, including glycosides, tannins, alkaloids, flavanols, saponins, sterols and triterpenoids and many proteins among others contain which helps to reducing Ti^{4+} ions to TiO_2 nanoparticles and at the same time which stabilize and capping those nanoparticles [30]. Further, the powders were systematically characterized and their electrochemical properties were studied.

2 Experimental method and materials

To synthesize TiO_2 NMOs, a simple green approach is used. In this method $TiCl_4$ which is bought from the organization Merck co. with $\geq$99.0% purity (used without further purification) used as precursor and CG plant leaf extract as catalyst. In the synthesis process first, the good and healthy leaves of the CG plant were collected and cleaned thoroughly with RO purified water, distilled water, and double-distilled (DD) water a few times to remove the dust particles and other unnecessary materials on the leaves. A 100 g of CGP leaves were cut into tiny pieces and directly taken into the single neck round base boiling flask contains 500 ml of DD water and heated for 2 hours at 90 °C with the help of heating mantle. After three hours, the solutions of CGP leaf extricate was filtered using filter paper with pore size 2.5 μm. The final solution is directly utilized as a reducing agent to obtain TiO_2 nanoparticles at various reaction times.

Finally, in the round bottom flask, 1.0 N Titanium tetrachloride solution was prepared using 100 ml of DD water and 25 ml of CGP leaf extract was included dropwise under continuous stirring at room temperature. After being stirred for 24 hours, the pH of the final solution was recorded in the range of 2.0-2.4. The plant leaf extract usually contains a high level of secondary metabolites like polyphenols, flavonoids, alkaloids, terpenoids, and peptides has hydroxyl and ketonic groups which helps in reducing Ti^{4+} ions to TiO_2 state and at the same time which stabilize and capping those nanoparticles. The obtained TiO_2 nanoparticles were washed several times with double distilled water and ethanol up to the pH of the solution reached to 7. The

white TiO_2 nanoparticles was dried at 100 °C for overnight. Finally, the product was calcined at 200 °C for 5 hours to remove any evaporable impurities and obtain pure TiO_2nanoparticles. The collected nanoparticles were utilized to study different material characterization for supercapacitor applications.

2.1 Material Characterization

X-ray diffraction data and Raman scattering data of TiO_2 nanoparticles were recorded by Seifert X-ray diffractometer using CuK_α radiation (λ=0.154 nm) and Horiba Jobin Yvon Lab RAM HR800UV Raman Spectrometer using 532 nm wavelength He-Ne laser source to study the structural properties. The Scanning electron microscope (Carl ZEISS-Model EVO MA15) was used to investigate the surface morphology and elemental composition of TiO_2 nanoparticles in high vacuum condition. The High Resolution Transmission Electron Microscope (HR-TEM) images were captured by Tecnai. G2 20 Twin. The Energy Dispersive Analysis of X-ray (EDAX) spectrum was recorded using BRUKER instrument. The electrochemical properties of TiO_2 nanoparticles were studied using CHI 608C electrochemical workstation.

2.2 Preparation of electrode

The working electrode was prepared using 80% of TiO_2 nanoparticles, 10% of carbon black and 10% of Poly Vinylidene Fluoride (PVdF). The combination was grinded for one and half an hour and N-methyl-2-pyrrolidone was added to obtain homogeneous slurry. Finally, the slurry was coated uniformly on a chemically cleaned nickel foam and dried at 100 °C for 2h.

2.3 Preparation of electrochemical work station

The electrochemical work station was prepared using TiO_2 as working electrode, Ag/AgCl as reference electrode, platinum foil as counter electrode and 1M Na_2SO_4 as aqueous electrolyte to record Cyclic voltammetry (CV) data of TiO_2 nanoparticles.

3 Results and discussion

X-ray powder diffraction spectrum of TiO_2 nanoparticles synthesized with CG plant extract was recorded in the 2θ range of 20^o-$70^o$is as shown in Figure 1a. The XRD pattern exhibited (110) predominant orientation peak at 2θ = 27.52° with other different characterization peaks (101), (200), (111), (210), (211), (220), (002), (310) and (301) at 36.21°, 39.24°, 41.28°, 44.03°, 54.45°, 56.77°, 62.99°, 63.86°, and 69.21° respectively. All the diffraction peaks were indexed to the tetragonal structure of rutile phase TiO_2 with $P4_2/mnm$, density = 4.25 g/cm^2 space group (JCPDS card No. 88-1172)[31]. The estimated lattice parameters are a=b=4.566 Å and c = 2.948 Å which are good agreement with previous literature reports. The broad and high intensity of diffraction peaks indicate the smaller crystallite size and high crystallinity. The coherent length (Lc) which corresponds to the crystallite size of the sample was calculated and found to be 9.84 nm from the predominant (110) diffraction peak using Debye-Scherrer's formula[3]

$$D = \frac{k\lambda}{\beta cos\ \theta}$$

The obtained powder was characterized by Raman spectroscopy, which is a very sensitive technique to atomic arrangements and vibrations. The Raman spectra of TiO_2 nanoparticles synthesized with CG plant extract were recorded in the range 200-1000 cm^{-1}and the results are shown in Figure 1b. The Raman spectroscopy allows clear identification of the different TiO_2 crystalline phases rutile exhibits four Raman-active modes, namely the B_{1g}, E_g and A_{1g}. The Raman frequencies for rutile structures are 250 (B_{1g}), 443 (E_g) and 608 (A_{1g}) cm^{-1} [32]. The vibrational studies of TiO_2 nanoparticles synthesized CG plant extract sample has been studied by FTIR within the wave number range of 4000–400 cm^{-1}in order to know the chemical bonds present in the TiO_2 sample as shown in Figure 1c. The observed transmittance bands of the samples in the range 800–400 cm^{-1} are accredited to Ti–O/Ti–O–Ti stretching bonds. The spectroscopic band is observed at around 3034 cm^{-1}is due to the O-H stretching vibration bonds. The absorption peaks identified at 2098, 1886 and 1617 cm^{-1} corresponds to the C-H stretching vibrations, C=O and C=C bonds respectively[33].

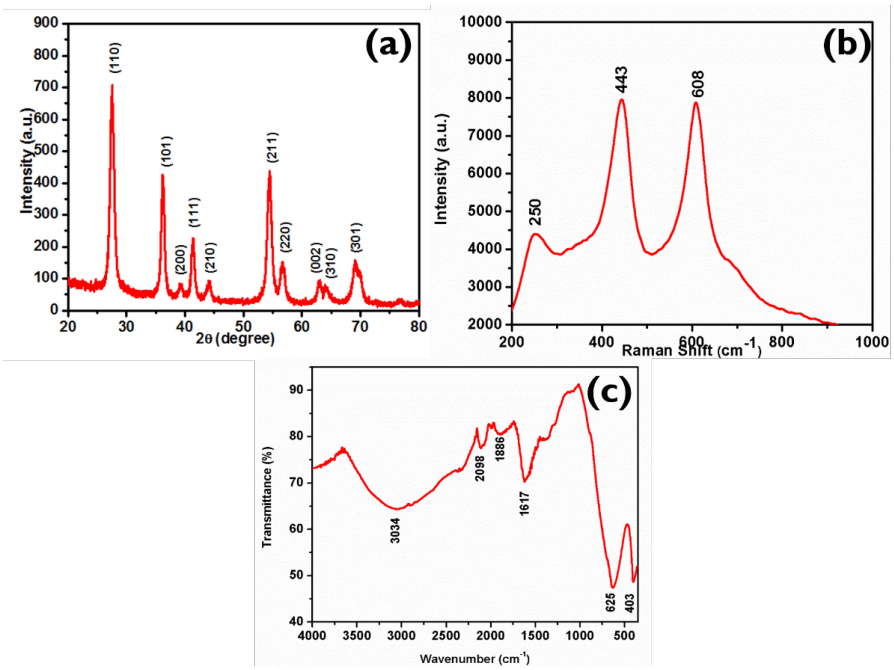

Fig 1. XRD (b) Raman (c) FTIR Spectrum of TiO_2 nanoparticles

The effective surface area of the materials mainly depends on the size and shape of the nanoparticles which is very important for supercapacitor applications[34]. The TiO_2 nanoparticles synthesized with CG plant extracts sample morphology recorded from SEM is shown in Figure 2a. The SEM images showed that the non-uniform spherical and flower-like shape of grains with an average grains size of 100 nm and crystallite size around 11 nm. Figure 2b shows the SEM image at different magnification. The TEM image from Figure 2c shows the flower-like morphology with an average grains size of 100 nm and crystallite size around 10 nm which is a coincidence with SEM results. Finally the SEM and TEM results are good agreement with XRD results. The EDS spectrum of TiO_2 nanoparticles is displayed in the Figure 2d which clearly indicates the presence of Ti and O binding energy peaks indicate the chemical purity of the sample.

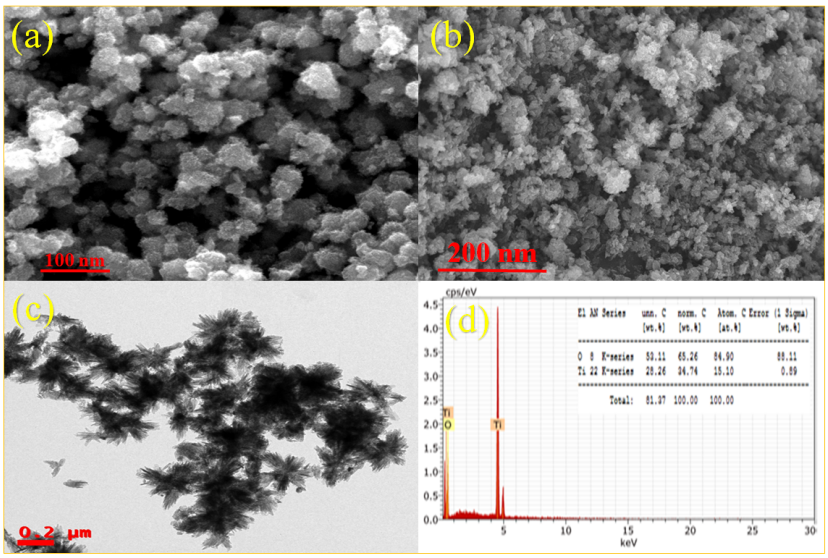

Fig 2. (a, b) SEM micrographs (c) HRTEM images (d) EDS spectrumof TiO_2 nanoparticles

Electrochemical Properties

The electrochemical properties of TiO_2 nanoparticles was studied using a three-electrode system includes working, reference, and counter electrode in 1M NaOH aqueous electrolyte. The cyclic voltametric (CV) curves of the TiO_2 at different reaction times were measured in the potential window of -0.4 to 0.4 V (vs. Ag/AgCl) at different scan rates from 1 to 100 mVs^{-1}. As revealed in Figure 3a, the TiO_2 show redox peaks at about 0.2 V, and thus their capacitance mainly results from pseudo capacitance of Ti ions. In Figure 3a, the CV curves of the sample showed similar profiles under different scan rates, indicate good reversibility with minor shirt in the redox peaks. It can be seen that the current under curve increases with an increase in scan rate and in turn results in a decrease in capacitance. It is well known that the voltametric current is always directly proportional to the scan rate [7]. The specific capacitance of the sample was measured using the following formula

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

Where, C is the specific capacitance in Fg^{-1}, I(V) is the instantaneous current in A, $\int I(V)\,dV$ is total voltametric charge in C, ΔV is the scan rate in Vs^{-1}, and (V_2 - V_1) is the potential window range in V. The value of specific capacitance decrease from 238 F g^{-1} to 92 F g^{-1} with increase in scan rate form 1 to 100 mV s^{-1}. The decrease in specific capacitance with scan rate is due the electrolyte ions do not find sufficient time to avail all active sites of the electrode [35]. At a low scan rate, the ions from the electrolyte can utilize all the available sites in the active electrode material. The rich in specific capacitance of the sample is owing to the beautiful flower-like structure with the clear formation of petals. The Charge-discharge curves of TiO_2 nanoparticles were shown in Figure 3b. The figure shows the slight bump in the charge and discharge at around 0.2 V, indicate the redox reactions which further supports the CV results. The obtained specific capacitance results are compared with the previous reports listed in Table 1. The cycling stability of the 3D TiO_2 nanostructures was evaluated under GCD conditions at 2 A g^{-1} current density [Figure 3c]. The sample showed 85% of specific capacitive retention even after 1000 cycles. The greater performance of the TiO_2 sample is due to outstanding dispersion and formation of 3D nanostructure demonstrates that the electrolyte ions can easily diffuse through the active electrode material.

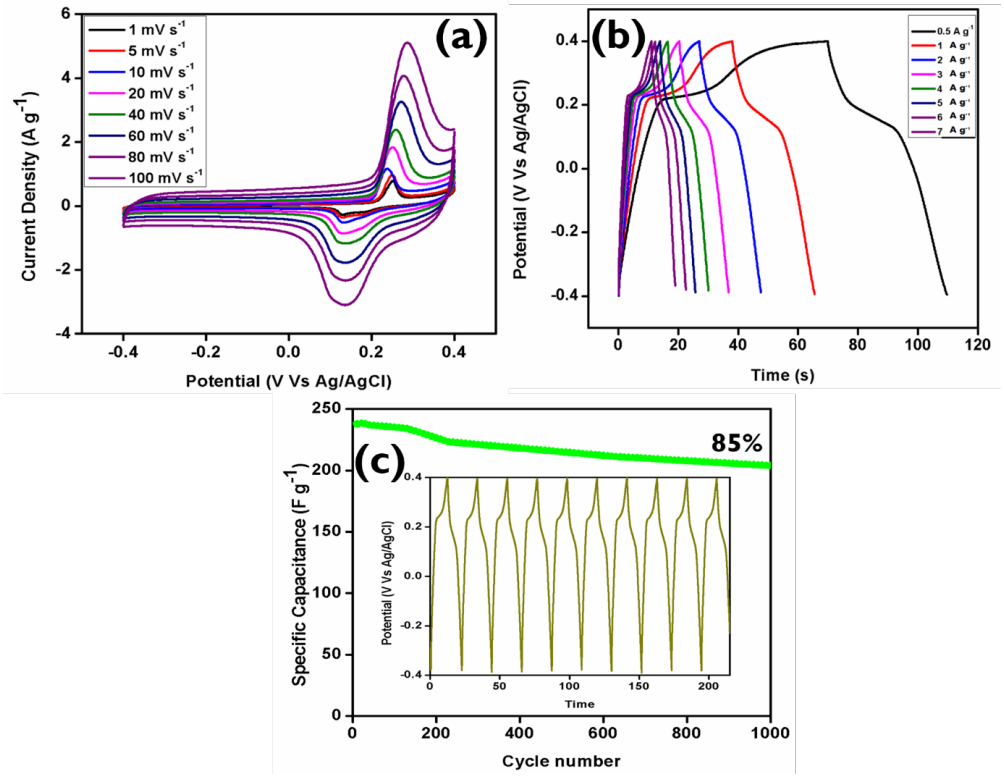

Fig 3. (a). CV (b) Charge-discharge curves of TiO_2 nanoparticles (c) Specific capacitance with cycle number

Table 1. Comparative study of specific capacitance of TiO_2.

Sl. No.	Material	Preparation Method	Electrolyte	Specific Capacitance	Scan rate/ Current density	Reference
1	The porous anatase TiO_2 nanoparticles	Hydrothermal method	1 M $LiPF_6$	48.6 F g^{-1}	100 mA g^{-1}	(36)
2	TiO_2/rGO/TiO_2	Sol preparation	1 M KOH	83.7 F g^{-1}	5 mV s^{-1}	(37)
3	TiO_2/Cu_2O	Electrochemical doping approach using a facile cyclic voltammetry method	0.5 M Na_2SO_4	98.7 F g^{-1}	100 mV s^{-1}	(38)
4	TiO_2/C_3N_4	–	2 M KOH	125.1 F g^{-1}	1 A g^{-1}	(39)
5	TiO_2/reduced graphene oxide	Sol-gel method	1 M $LiPF_6$	150 F g^{-1}	20 mV s^{-1}	(40)
6	TiO_2 Nanoflakes	Sol-gel method	1 M Na_2SO_4	164 F g^{-1}	5 mV s^{-1}	(41)
7	Flower like TiO_2	Green Synthesis	1 M Na_2SO_4	224 F g^{-1}	0.5 A g^{-1}	(42)
8	TiO_2 3D Nanostructures	Green Synthesis	1 M NaOH	238 F g^{-1}	1 mV s^{-1}	This work

4 Conclusion

3D nanostructure TiO_2 particles have been successfully synthesized by a simple green synthesis method using *Calotropis gigantea* plant (CGP) extract at room temperature. XRD and Raman data was confirmed the tetragonal structure of TiO_2 in the rutile phase with $P4_2/mnm$ space group and crystallite size was found to be 9.84 nm. The SEM and TEM images showed that the non-uniform spherical and flower-like shape of grains with an average grains size of 100 nm. The EDS spectra confirmed the high purity of the samples. The vibrational modes of the samples were studied using FTIR. The electrochemical studies of TiO_2 exhibited a specific capacitance of 238 F g^{-1} at a scan rate of 1 mV s^{-1} with good reversibility.

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