ENHANCED CAPACITIVE CHARACTERISTICS OF TiO_2 NANOFLAKES BASED ELECTRODE MATERIAL FOR SUPERCAPACITOR

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Abstract

This paper presents an experimental investigation of the enhanced capacitive characteristics of newly fabricated TiO_2 based electrode material for supercapacitor. TiO_2 particles have been synthesized by means of sol-gel method. The size, morphology and structural properties of TiO_2 particles have been studied with the help of high resolution transmission electron microscope, field emission scanning electron microscopy and X-ray diffraction, respectively. The electrochemical properties of the TiO_2 based electrode were determined by using cyclic voltammetry and galvanostatic charge-discharge tests. The results obtained from cyclic voltammetry test show that maximum specific capacitance for TiO_2 based electrodes has been evaluated as 164 F g^{-1} at the scan rate of 5 mV s^{-1} in 1M Na_2SO_4 electrolyte. The cycle stability of the TiO_2 based electrodes has been probed with the help of the cyclic voltammetry and galvanostatic charge-discharge measurements.

Keywords: *nanoflakes, electrode material, Specific capacitance, charge-discharge, cycle stability.*

1. Introduction

In last two decades, Supercapacitors (also called as electric double layer capacitor or ultracapacitor) have been drawing more attention from the researchers and engineers as they have some significant features such as higher power density, longer life cycle, short response time and high durability [1]. Due to these salient features, a new concept of the hybrid charge storage devices where in, supercapacitor integrated with a fuel cell or a battery has been developed [2, 3]. Some of their applications can be found in portable electronic devices, backup power supply, low-emission hybrid cars, instant switches, regenerative braking system, motor starter, industrial power and renewable energy systems [4-9]. An immense potential of the supercapacitor can be explored further in many power source sectors provided the energy density is increased to a desired level [10, 11]. Therefore, more research works are currently carried out to address this low energy density issue through by enhancing the specific capacitance values to a greater extent.

Based on the past literatures, they are reported that if the transition metal oxides are used as active materials for the electrodes, the electro sorption or redox processes would increase the specific capacitance values [12-15]. Metal oxides including ruthenium oxide (RuO_2), manganese oxides (MnO_2), nickel oxide (NiO), tin oxide (SnO_2), vanadium oxide (V_2O_5), iron oxide (Fe_3O_4), etc., were investigated in the past for supercapacitor applications. Amongst transition metal oxides, RuO_2 is reckoned to be a most attractive electrode material due to significant features like, greatly reversible redox reactions, broad potential window, good thermal stability, proton-electron mixed conductive behavior, high rate capability and high theoretical specific capacitance (up to 2200 F g^{-1}) [16]. In spite of these significant features, applications of RuO_2 are limited due to toxicity and high cost.

Manganese oxides (MnO_2) are environmentally friendly feature, abundance, non-toxicity, low cost and have high theoretical specific capacitance. From the past literatures, it is observed that MnO_2 based electrodes have moderate cycle stability up to 1000 charge-discharge cyclic operations and if number of charge-discharge cycles are increased more than 1000 then, specific capacitance values of MnO_2 based electrodes would be expected to be retain less than 80% while comparing to that of initial value [7]. To improve the cycle stability and conductivity, metals, metal oxides or carbon based nanomaterials like graphene oxide (GO), single wall carbon nanotube (SWCNT) and multiwall nanotube (MWCNT) are doped with MnO_2. NiO can be preferred for pseudocapacitor electrode applications due to low cost, and high chemical and thermal stability and the capacitive behavior of NiO nanomaterials relies on their morphology solely. Wu and Wang (2010) reported that nanoflakes structure could be preferred as they can enhance the diffusion of electrolyte and offer more paths for diffusion of ions and as a result, performance of the electrode material could be improved for supercapacitor applications [17].

Tin oxide (SnO_2) synthesized via sol-gel method was investigated as active material for electrode of the supercapacitor [18]. The test results divulge that at a high scan rate of 200 mV s^{-1}, specific capacitance of the electrode using SnO_2 was able to attain the value of 101 F g^{-1} exhibiting the high power characteristics of the material. Furthermore, SnO_2 based electrode could retain the specific capacitance value of about 97% after 1000 charge-discharge cyclic operations and while increasing the mass of the SnO_2, the capacitive characteristics of the electrode could be expected to be better owing to high conductivity, formation of nanostructured and microporous material [19, 20]. Efforts were made on vanadium oxides (V_2O_5) for studying the electrochemical characteristics for electrode material. Owing to the layered structure of V_2O_5, it would help to intercalate the electrolyte ions into electrode [21]. Due to poor electrical conductivity and cyclic stability, applications of V_2O_5 for supercapacitor are restricted [22]. Of late, carbon based nanomaterials are embedded with V_2O_5 so as to improve the electrode performance in terms of electrical conductivity and cycle stability. Thangappan et al (2014) accomplished a research work on the graphene oxide/vanadium pentoxide nanofibers for supercapacitor applications [23] and from the test results, authors inferred that nanofibers prepared by electrospinning technique exhibited the better electrochemical characteristics for supercapacitor.

Studies on the electrochemical performance of iron oxide for electrode materials were carried out [24-26]. Depending on the crystalline structures, it can be recognized as Fe_2O_3 and Fe_3O_4 and also, these two iron oxides could be expected to fetch the different electrochemical performance. Between these iron oxides, the specific capacitance of Fe_3O_4 can achieve a higher value than Fe_2O_3 due to the dynamic faradic redox reaction occurred on the surface [24]. Albeit there are many research works accomplished on the various transition metal oxides for investigating the electrochemical performances for supercapacitor applications in the past, it is yet to be studied as active material for electrode extensively but, several literatures reported on the composite materials containing TiO_2 as electrode materials. TiO_2 has significant advantages such as chemically stable, low cost, low toxicity, natural abundance, environmentally friendly nature [27, 28] and with these features it can be investigated to assess its potential applications for supercapacitor. The aim of this work is to prepare TiO_2 via sol-gel method and their sizes, morphology and structural properties were studied. In addition to this, electrochemical performances of TiO_2 based electrode were ascertained. The CV and galvanostatic charge-discharge tests were conducted to determine the enhanced specific capacitance value and improved cycle stability.

2. Materials and Method

2.1 Materials

Ethanol and titanium butoxide were procured from SRL, India. Sodium hydroxide (NaOH) pellets were obtained from Lobha Chemie Private Limited, India. 2D water (two times deionised water) was used throughout the experiment. Chemicals utilized for the synthesis of TiO_2 particles were analytical reagent grade and they were not purified further.

2.2 Synthesis of TiO_2 nanoflakes

For preparing TiO_2 particles, titanium butoxide and NaOH were taken as precursor and reducing agent, respectively. Titanium butoxide and ethanol were considered as 1:4 volume ratio and they were blended together for synthesis of TiO_2 nanoparticles by using sol-gel method [29]. The mixed solution was placed on the magnetic stirring for 15 min at a speed of 750 rpm. During stirring action, NaOH pellets were added drop by drop into the above solution until the pH value of the solution reached at 7. Besides, the addition of NaOH during the reaction would make an important effect on size and shape of the particles. Afterwards, the large amount of TiO_2 white precipitation was found. Then, it was centrifuged and washed with 2D water for 3 times to derive the purified nanoparticles. It was dried in hot air oven at 100°C for 24 h and then, grinded by agate mortar, to obtain powder.

2.3 Electrode preparation

The as synthesized flake-like TiO_2 nanoparticles was used as electrode material for supercapacitors. The working electrode was prepared by adding the active material (TiO_2), acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10. The mass of the active materials in the prepared electrodes was estimated to be 3 mg. Electrochemical measurements were performed in an electrochemical work station (Biologic Instruments, India) with a three electrode arrangement in 1 M Na_2SO_4 aqueous solution saturated with N_2 gas. In the measurements, Pt electrode was used as counter electrode and the saturated calomel electrode as reference electrode. Cyclic voltammetry (CV) and galvanostatic charge - discharge analyses were conducted with respect to the scan rate and current density.

2.4 Analysis methods

High resolution transmission electron microscope (HRTEM) (model - Philips) was recommended for determining the size of the TiO_2 particles. Samples were obtained by spreading drops of colloid on the copper grid, surrounded with the carbon film and the solvent was dried. The morphology of the TiO_2 nanoflakes was studied by field emission scanning electron microscope (FESEM, LEO 1530, Zeiss, Germany). For determining the crystal sizes of TiO_2 particles, X-ray diffraction analysis (XRD) was performed on a Shimatzu diffractometer X-ray 6000 model using CuK_α radiation. The scattering angle (2θ) covered was from 20 to 80°. The average crystallite size (D) has been calculated from the line broadening using Debye-Scherrer's relation of $D = 0.9\lambda / W\cos\theta$, where λ is the wavelength of X-ray and W is full width of half maximum (FWHM).

3. Results and Discussion

3.1 Characterization of TiO_2 nanoflakes

The HRTEM images as seen in Fig. 1 ascertain the size of the as synthesized TiO_2 particles and the sizes of the particles are varied in the range between 13 nm and 76 nm. The FESEM images shown in Fig. 2 are appeared to be flake-like structure. The flake-like structure of the particles could offer larger surface area for ions transfer process and it would be beneficial for achieving the higher values of the specific capacitance. The XRD pattern of TiO_2 particles as synthesized is shown in Fig. 3.

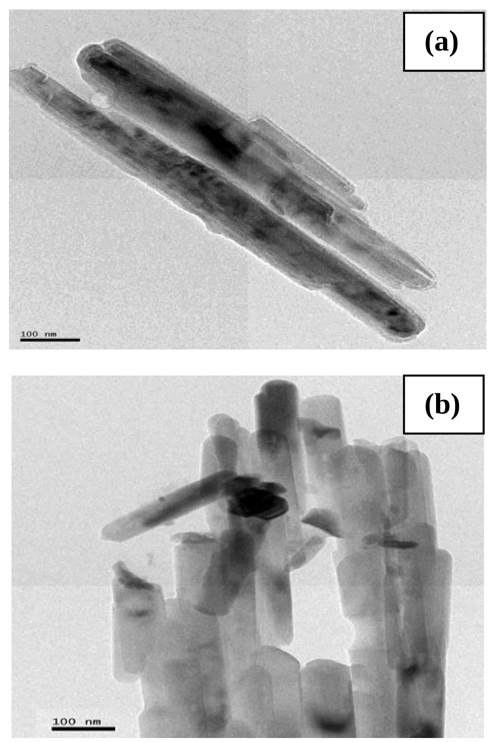

Fig. 1. HRTEM images of TiO_2 nanoflakes (a) the size of the individual nanoflakes, (b) the sizes of the agglomerated nanoflakes.

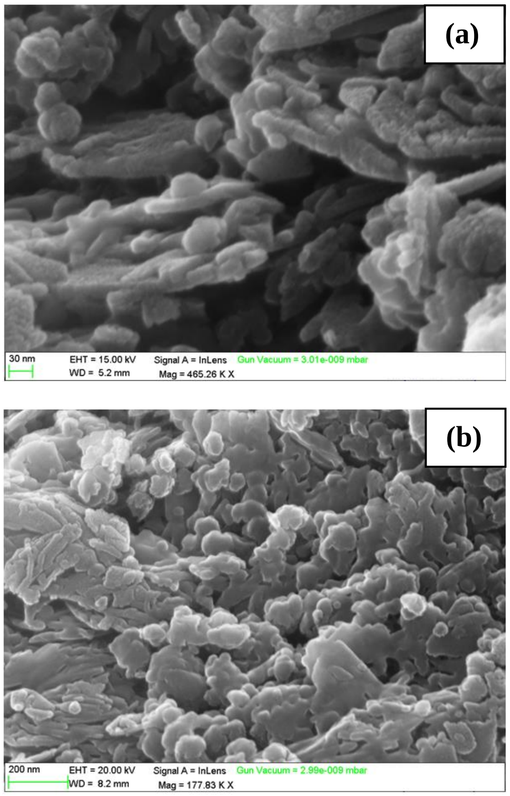

Fig. 2. FESEM images of TiO_2 nanoflakes (a) the morphology of the nanoflakes at 30 nm magnification, (b) the morphology of the nanoflakes at 200 nm magnification.

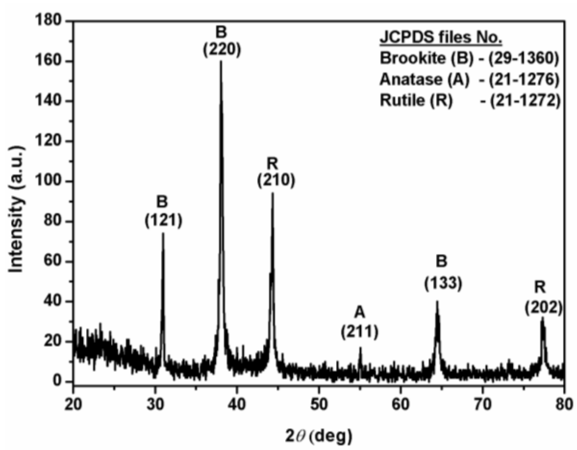

Fig. 3. XRD Pattern of TiO_2 nanoflakes

The XRD result divulges the three phases of TiO_2 particles namely, brookite, anatase and rutile. The presence of these three phases is attributed to the annealing temperature of 600°C [27]. Using Debye-Scherrer's formula, the average crystallite sizes were determined as 29 nm. Also, it was understood that no impurity peaks were present in the XRD pattern. The Brookite, Anatase and Rutile of TiO_2 nanoparticles were in good agreement with JCPDS files Nos. of 29-1360, 21-1276 and 21-1272, respectively.

3.2 Cyclic voltammetry (CV) tests of TiO_2 nanoflakes

The cyclic voltammetric (CV) curves for TiO_2 electrode at different scan rates (5 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1} and 100 mV s^{-1}) within the voltage range of 0 to 0.8 V are seen in Fig. 4. From Fig. 4, it is observed that as scan rate increases the area of the potential window also increases. Also, the current density is directly proportional to the scan rate, which exhibits a capacitive behavior. The specific capacitance of TiO_2 nanoflakes can be determined by using the following equation [30].

$$Cs = \frac{i}{V \times M} = \frac{1}{V \times M \times \Delta V} \int_{V0}^{V0+\Delta V} i dV = \frac{S}{2 \times V \times M \times \Delta V} \quad (1)$$

where, Cs is the specific capacitance, S is the area of CV curve, V is the CV scan rate, M is the loading mass of active material and ΔV is the potential window.

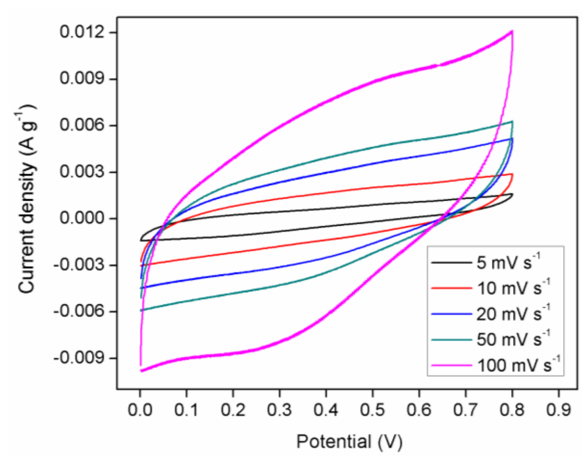

Fig. 4. Cyclic voltammetry curves of TiO_2 nanoflakes

The relationship between specific capacitance and scan rate are represented in Fig. 5. The specific capacitance values obtained for 5 mV s^{-1} and 100 mV s^{-1} were evaluated as 165 F g^{-1} and 53 F g^{-1}, respectively. At lower scan rates, the value of specific capacitance was found to be higher than that of the value at higher scan rates. This is mainly attributed to the intercalation of ions into the interior of the electrode. Also, the specific capacitance achieved at lower scan rate is the maximum utilization of the electrode material surface [27].

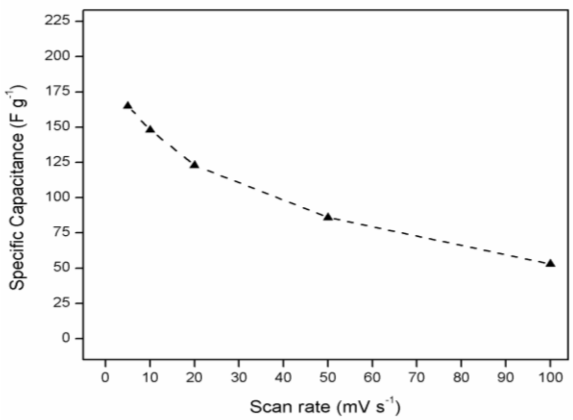

Fig. 5. Variation of specific capacitance with scan rate

At higher scan rate, electron transfer process is hindered because of depletion or saturation of the electrons in the electrolyte inside the electrode. This slow process of electron transfer inherently causes increase in resistivity and results in drop in the specific capacitance of the electrode. Furthermore, this fall in specific capacitance implies that surface of the electrode material is not completely utilized for electron transfer at higher scan rates.

3.3 Galvanostatic charge-discharge tests of TiO_2 nanoflakes

Galvanostatic charge-discharge is indeed reliable and acceptable method to determine the specific capacitance of electrodes as it achieves almost exact value of the practical application of a supercapacitor. The charge - discharge tests were performed at current densities of 1 mA g^{-1} with potential window of 0 to 0.8 V in 1 M Na_2SO_4 electrolyte. The relationship between the charge - discharge time and potential is shown in Fig. 6. The charge/discharge results are clear evident for reversible characteristics without noticeable deviation in each cycle.

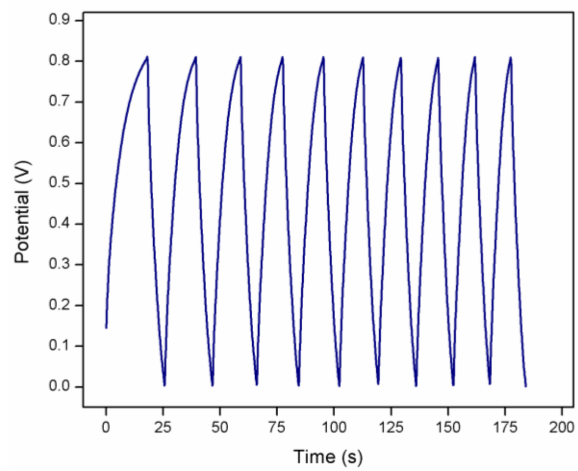

Fig. 6. Charge-discharge characteristics of TiO_2 nanoflakes

It is found that all the charge and discharge curves are similar and the IR drop is less. It implies that the charge-discharge characteristics of TiO_2 electrode would be expected to be better at high charge–discharge rate. The specific capacitance (C_s) of TiO_2 based supercapacitor can be determined based on the following equation [31]:

$$Cs = \frac{Q}{\Delta V \times M} = \frac{I \times \Delta t}{\Delta V \times M} \qquad (2)$$

where, Cs is the specific capacitance, I is the current during discharge process, Δt is the discharge time, ΔV is the potential window and M is the mass of the active material. The specific capacitance values were found to be 173 Fg^{-1}. The specific capacitance of TiO_2 based supercapacitor relies on certain parameters, such as the mass of the active material, the morphology of the active material and the conductivity of the active electrode.

3.4 Cycle stability of TiO_2 nanoflakes

In order to ascertain the reliability of the supercapacitor for long run utility, cycle stability of the TiO_2 nanoflakes was investigated. The CV test for TiO_2 samples were carried out at the scan rate of 5 mV/s in 0.1 M Na_2SO_4 aqueous solution with a voltage window of 0 to 0.80 V. The values of specific capacitance for several cycles obtained from the CV test are furnished in Fig. 7. From Fig.7, it is found that the specific capacitance for first cycle was observed as 164 F g^{-1}. The specific capacitance of TiO_2 nanoflakes was reduced considerably in the 200 cycles and it was determined to be 158 F g^{-1}.

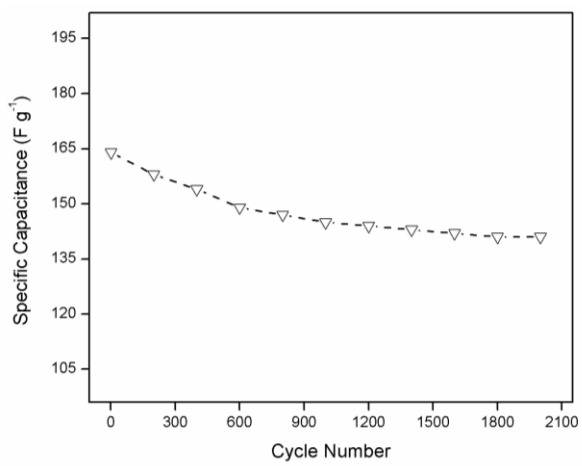

Fig. 7. Variation of specific capacitance with cycle number

In the 1000 cycles, the specific capacitance reached about 145 F g^{-1}. After 1000 cycles, the decrease in specific capacitance was delayed and in the 2000 cycles, the specific capacitance was found to be 141 F g^{-1}. Then, the retention of specific capacitance value was estimated to be 86% of that of the initial value. It might be due to the fact that dispersed TiO_2 nanoflakes on the electrode of the supercapacitor could act as thermal retardant for increase in temperature due to more number of cyclic operations. By considering the fact, the nanoflake-like structure of TiO_2 could be considered to be a stable and efficient electrode material for supercapacitor.

4. Conclusions

In this research work, TiO_2 based electrode material was fabricated and its capacitive characteristics were investigated for supercapacitor application. TiO_2 nanoflakes were synthesized successfully by using sol-gel method. Based on the test results, following conclusions are made.

1. The average size and morphology of TiO_2 nanoflakes were found to be 27 nm and flake-like structure by using HRTEM and FESEM, respectively.
2. The XRD analysis divulges that the TiO_2 nanoflakes synthesized through sol-gel method are cubic phase.
3. The CV test results show that the specific capacitance for supercapacitor using TiO_2 based electrode was able to achieve the values of 165 F g^{-1} and 53 F g^{-1} at the scan rates of 5 mV s^{-1} and 100 mV s^{-1}, respectively.
4. The galvanostatic charge-discharge tests prove that newly fabricated electrode materials achieved the symmetric charge-discharge profile and good cycle stability.
5. The cycle stability test reveals that after 2000 charge-discharge cycles, TiO2 based electrode has lost only 14% capacitance value of that of the initial value.
6. Thus, the as synthesized TiO_2 nanoflakes could be suggested to be the potential candidate as the electrode material for supercapacitor.

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