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Electrospun TiO₂ nanofiber electrodes for high performance supercapacitors

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Abstract

Nanofibers are one dimensional (1D) nanoarchitecture materials having high surface-to-volume ratio which provides improved ion diffusion and high mechanical strength to prevent volume expansion during electrochemical process and enhance the cycle stability. In the present study, TiO₂ nanofibers (TNFs) were successfully synthesized on an aluminum collector with a polymer concentration of 9 wt % by cost-effective electrosprining technique followed by annealing at a temperature 500 °C. The XRD spectrum of electrospun TNFs exhibited predominant (101) orientation corresponding to anatase TiO₂ with I4₁/amd symmetry. The estimated average crystallite size is 18 nm. The strongest Raman vibrational mode at 143 cm⁻¹ confirms the phase purity of TNFs. The surface morphological feature depicts interconnected network fibers with a variation in the fiber diameter and the estimated average diameter is ~150 ± 20 nm. Very smooth surface and homogeneously distributed ultra long nanofibers are observed from TEM analysis. The newly fabricated TNF electrode delivered a specific capacitance of 75 Fg⁻¹ and retained 95% capacitance even after 5000 cycles. Moreover, it exhibited energy density and power density values of 24 Whkg⁻¹ and 22.08 Wkg⁻¹ respectively. The large capacitance, high coulombic efficiency and good structural stability demonstrate that TNFs should open up new opportunities for the next-generation high performance supercapacitors.

1. Introduction

One dimensional (1D) nanoarchitectures have attracted intense interest because of its superior applications compared to their bulk counterparts owing to their unique and fascinating properties towards potential applications in hydrogen generation by photolysis, DSSC (Dye sensitized solar cells), photo catalysis and energy conversion and storage devices [1–3]. Among various electrochemical energy storage devises, supercapacitors are an ideal option for storing high energy rapidly due to their high power density (> 10 kW Kg⁻¹), long calendar life (>10⁵), wide operating voltage range and safety concern [4, 5]. The both high specific power and specific energy of supercapacitors dominated the conventional energy storage rechargeable batteries and di-electric capacitors [6]. According to the charge storage mechanism supercapacitors can be classified into two categories (1) Electric double layer capacitor (EDLC) which store charge through electrostatic diffusion and the charge accumulation is at the electrode/electrolyte interface. (2) Pseudocapacitors are dominated by faradaic reactions at the surface of the electrode materials [7–9]. The carbon based materials such as activated carbons, graphene, carbon nano tubes (CNTs), carbon nano fibers, porous carbon, mesoporous carbon, carbide derived carbons are commonly used as electrode materials for EDLCs because of their high conductivity and long-term electrochemical stability [10–14]. However, the limited charge accumulation of EDLCs restricts their capacitance between the ranges 90–250 Fg⁻¹. In contrary, pseudocapacitors have performed substantially higher capacitance of 300–1200 Fg⁻¹ through faradaic storage mechanism [15]. The transition metal oxides such as RuO₂ [16], MnO₂ [17], NiO₂ [18], Co₃O₄ [19], CuO₂ [20], Fe₂O₃ [21], MoO₃ [22], V₂O₅ [23], Li₂TiO₃ [24] and TiO₂ [25] etc, conductive polymers and polyaniline are commercially used pseudocapacitor compounds.
Among them TiO2 is ubiquitous material for the supercapacitor applications. TiO2 can be described into three crystallographic polymorphs such as anatase, rutile and brookite. In which anatase TiO2 has thermodynamically stable, high work function (>0.2 eV) wide band gap of ~3.2 eV semiconductor material and suitable potential electrode with higher working voltage, excellent chemical stability material for supercapacitor applications [29–31]. Moreover, the commercial viability, non-toxicity to the environment and human, abundance makes it efficient alternative material for supercapacitors. However, its relatively poor electrical conductivity and poor electrochemical activity results low specific capacitance in the practical applications [32,33]. The electrochemical properties of TiO2 have been defined by its morphology, crystal phase and particle size [34,35]. The one-dimensional (1D) nano architectures such as nanowires, nanotubes, nanosheets, and nano fibers have been utilized to reduce the diffusional length and improve the conductivity as well as capacitance. Among them, TiO2 nanofibers have exhibited enhanced supercapacitor properties due to their high surface-to-volume ratio, high thermal stability, excellent mechanical strength, light weight and increased electro active sites with in a small footprint [36,37]. Several approaches have been proposed to prepare the 1D-nanoarchitectures TiO2 nano fibers (TNFs) such as sol-gel template synthesis, metal organic chemical vapour deposition (MOCVD), electrochemical synthesis etc, among them the electrospinning technique is a simple and cost effective, versatile technique to fabricate ultrafine fibers of polymeric and inorganic materials with diameter ranging from tens of nanometers to sub-microns, tunable composition, low density and high porosity along with high surface-to-volume ratio according to the process of parameters [38–42].

There are few reports on synthesis of nano fibers by electrospinning method for energy storage applications. In the present work, 1D-TNFs have been successfully synthesized by simple and cost effective electrosprinning method followed by annealing treatment and studied their microstructural and optical properties. The electrochemical properties of electrospun TNFs are studied through cyclicvoltammetry (CV), chronopotentiometry (CP), electrochemical impedance spectroscopy (EIS) and cycliability test for supercapacitor applications and demonstrated high specific capacitance with excellent electrochemical performance.

2. Experimental

2.1. Synthesis procedure of TNFs

Polyvinylpyrrolidone (PVP – Mw ~ 1300 000), Ethanol, Titanium (IV) isopropoxide (TIP) and acetic acid were used as starting materials to synthesis TNF. In a typical synthesis, 1.5 g of TIP and 3 ml of acetic acid were dissolved in pre-prepared 9 wt% PVP-ethanol solution and stirred continuously for 3 h at room temperature. Then this precursor solution loaded into 10 ml plastic syringe having stainless steel needle with a diameter of 500 µm. The electrode of high voltage source (0–30 KV) was connected to the needle and aluminum collector was connected to the ground. The distance between the collector and the needle was kept as 10 cm and 10 KV DC potential difference was applied between them. A solution flow rate of 1 ml h−1 was maintained using precise (0.1 ml h−1) syringe pump. The resultant TNFs were collected on an aluminum collector and subjected to annealing at 500 °C for 2 h in air.

2.2. Structural and electrochemical characterization

The morphological and microstructural features of electro spun TNFs were characterized by scanning electron microscopy (SEM - Carl Zeiss) and transmission electron microscope (TEM) images were collected with a TEM-FEI microscope (TECHNAI G2—30 S-twin D905). The x-ray diffraction (XRD) measurements were performed with an x-ray diffractometer (Siefert, Model 3003 TT) using a CuKα radiation (λ = 0.154 06 nm). The elemental composition of the sample was analyzed by energy dispersive spectroscopy (EDS) using an EDAX spectrometer (Oxford instruments). The Raman scattering (RS) spectrum was collected with Raman spectrometer (Model Lab Ram HR800) to analyze the vibrational modes of TNFs in the spectral range of 200–800 cm−1. The electrochemical tests were carried out using three electrode aqueous type cell. The electro spun TNFs prepared at 500 °C, platinum strip and Ag/AgCl were used as working, counter and reference electrodes. The working electrode was prepared with through mixing of active material (TNF - 80%), conductive agent (carbon black—10%) and binder (polyvinylidene fluoride (PVDF)—10%) then added N-methyl pyrrolidone (NMP) to form a slurry. This slurry was coated on the nickel (Ni) substrate (active area 1 cm2 and mass loading of the active material is 20 µgm) and it was dried at 100 °C for 2 h. The aqueous 1 mol l−1 Li2SO4 solution was used as electrolyte due to its high lithium concentration. The electrochemical measurements were conducted with electrochemical work station (CHI 608C) in the range from 0 to 0.8 V for capacitance measurements. Cyclic voltammetry data was gathered at various scan rates from 1–200 mVs−1. All the tests were conducted at 25 °C.
3. Results and discussion

3.1. Surface morphological and compositional analysis
Morphological features of the as-spun (30 °C) and annealed (500 °C) TNFs are analyzed by SEM and displayed in figures 1(a) and (b). Smooth and uniform nanofibers without any bead formation were observed at 9 wt% of PVP with an average diameter of 200 ± 20 nm (figure 1(a)). The as-spun TNFs annealed at 500 °C demonstrated nanofiber diameter of 150 ± 20 nm (figure 1(b)). At high temperature, the organic contents such as PVP, acetic acid and ethanol are removed off from the TNFs. This leads to decrease the fiber diameter morphology [43]. The difference in the diameters is caused for different nucleation growths and different crystallization rates during annealing in the formation of TiO2 nanofibers [44].

The randomness is a common character in the formation of nanofibers which can be attributed to the bending instabilities of TNFs during electrospinning [45,46]. The elemental composition of as-spun and annealed TNFs were carried out by EDS and shown in figures 1(c) and (d). Figure 1(c) illustrates the presence of organic compounds in the form of carbon in TNFs at room temperature. The observed characteristic peaks of pure Ti and oxygen without any residuals in EDS spectrum shown in figure 1(d) confirms the phase purity of TNFs when annealed at 500 °C.

3.2. Microstructural properties
The low magnification TEM image depicts that the as-spun TNFs have very smooth surface and could become porous, high surface-volume ratio along with high densification after annealing process at 500 °C (figure 2). The calculated average diameter of TNF from the TEM observation is about 100 nm.

The observed uniform nanofibers morphology in TiO2 can provide an adjustable geometry that serves as an easy and fast Li-ion and electron diffusion resulting improved conductivity and pseudocapacitive behavior. The selected area electron diffraction (SAED) pattern of annealed TNFs (figure 2(b)) displays concentric diffraction rings indicating the polycrystalline structure with no preferential orientation. Figure 2(c) displays the HRTEM image which confirms the well-resolved lattice of TNFs with fringes at inter planar distance ~0.35 nm corresponding to the (101) plane.
3.3. XRD and Raman studies

The crystalline structure and crystal phase of the TNFs prepared at 500°C were shown in figures 3(a), (b). The XRD spectrum of TNFs (figure 3(a)) exhibited predominant (101) orientation at 2θ = 25.4° along with (004), (200), (105) and (204) other characteristics Bragg’s planes at 2θ of 37.9°, 48.2°, 54.0° and 62.9° corresponding to anatase TiO2 phase with tetragonal structure and I41/amd symmetry (JCPDS card No: 21–1272). The XRD spectrum evidenced the formation of phase pure TNFs structure without any impurity traces. The crystallite size of the anatase TNFs at (101) plane can be calculated from the Scherer’s formula \( D = \frac{0.9 \lambda}{\beta \cos \theta} \) and the estimated average crystallite size is about 18 nm. The lattice parameters calculated by least-square fitting using six Bragg lines and found to be \( a = 11.518 \text{ Å}, b = 4.380 \text{ Å}, c = 3.567 \text{ Å} \), these values are consistent with the reported values [47].

It can be noticed that the widened diffraction peaks confirms the nano range distribution of TNFs which can short the Li-ion diffusion path and store high energy due to their high surface-volume ratio. The Raman spectrum (RS) was recorded in the frequency range 100–800 cm\(^{-1}\) to further confirm the crystal phase and formation of chemical bonds in TNFs prepared at 500 °C and is shown in figure 3(b). The RS of TNFs showed totally four characteristic peaks confirming the formation of phase pure anatase TiO2. The dominant sharp characteristic peak at 143 cm\(^{-1}\) and small intense band at 396 cm\(^{-1}\) are corresponding to \( E_1g, B_{1g} \) vibration modes of anatase TNFs and are attributed to bending vibrational modes of O-Ti-O. The Raman bands at 515 cm\(^{-1}\) and 638 cm\(^{-1}\) are finger prints of \( A_{1g} \) and \( E_g \) modes and assigned to stretching vibrational modes of Ti-O. The obtained Raman characteristic peak values are well indexed to the reported values for TiO2 anatase phase prepared at 500 °C [48]. The appearance of no extra peaks in the spectrum indicating that the phase purity of the TNFs.

![Figure 2](image-url) Figure 2. Microstructural properties of TNFs prepared at 500 °C (a) Low magnification TEM image, (b) selected area diffraction pattern (SAED), (c) HRTEM image.

![Figure 3](image-url) Figure 3. Crystallography and vibration studies of TNFs prepared at 500 °C (a) XRD pattern (b) Raman spectrum of TNFs recorded in the spectral range 100–800 cm\(^{-1}\) at 1 cm\(^{-1}\) spectral resolution.
3.4. Optical properties

Figure 4. shows the optical energy band gaps of as-spun and annealed TNFs calculated by the Kubelka-Munk function $(\alpha h \nu)^{1/2}$ (where $\alpha$ is the absorption coefficient) as a function of photon energy ($h \nu$). The absorption edge lies in the region of photon energies 3.0–3.3 eV confirming the indirect band gap of semiconductor TiO$_2$ [49]. The optical energy band gap is recognized by plotting the intercept of tangent to the x-axis in a graph. The annealed TNFs demonstrated an absorption peak shift from 325 nm to 335 nm [50, 51]. The calculated optical band gap from $(\alpha h \nu)^{1/2}$ versus $h \nu$ plot for as-spun and annealed TNFs are 3.18 eV and 3.08 eV. The band gap of a semiconductor in generally decreases as the crystallite size increases [52]. Here it is clearly observed that the TNF band gap decreases due to the increase in crystallite size at higher annealing temperatures.

The optical properties of TNFs depends on its morphology and compaction, the smooth surface. The random compaction of the TNFs causes the high scattering coefficient and leads to red shift of band gap value. The optical properties of TNFs were examined through UV-visible DRS spectra and are shown in the inset of figure 4 in which the absorption edge is observed between 380–400 nm indicating the excitation of electron from valance band to the conduction band of the TNFs matrix [53]. The red shifting of the absorption edge has been observed for TNFs leads to absorption capability of TNFs in visible region leads to ability of high harvesting of light to the photo anode material [54].

3.5. Electrochemical properties

Cyclicvoltammogram (CV) is a suitable tool to analyse the electrochemical properties of the electrode material for supercapacitor applications. Figure 5(a) shows the CV profile of the TNFs prepared at 500 °C, in the potential cutoff 0.0 to 0.8 V using 1 mol Li$_2$SO$_4$ aqueous electrolyte. As depicted in the figure, the CV signature of TNFs prepared at 500 °C shows almost rectangular shape at different sweep rates from 1–200 mVs$^{-1}$. The almost rectangular and symmetrical image is appeared without conspicuous redox peaks at all scan rates indicating that the electrochemical process is involved both faradaic and double layer capacitance, an evidence of TNFs capacitive behavior [55]. The pseudocapacitive behavior arises from the reversible redox reactions involving the exchange of protons and/or Li-ions with the electrolyte [56]. It can be seen that with increasing sweep rate the integral area and current densities are increased infer good rate capability of the TNFs electrode. Moreover, the CV profile retain the rectangular shape even at high sweep rates implies good dissipation of charge at the electrode surface provided by large double layer interface resulting improved supercapacitive performance [57]. The similar behavior can also be observed for Li$_2$TiO$_3$, Ni(OH)$_2$, and V$_2$O$_5$/polyaniline. [27, 55, 58]. The specific capacitance of the TNFs electrode prepared at 500 °C are further evaluated by galvonostatic charge-discharge (GCD) measurements at different current densities ranging 1–100 mA g$^{-1}$ in the potential window 0.0–0.8 V and shown in figure 5(b). The non-linear shaped GCD curves are observed at various current densities, indicates pseudocapacitive behavior of the electrode. The insertion and extraction of proton/Li-ion is occurred from/to the surface of the electrode to electrolyte which causes the capacitive behavior.
The specific capacitance can be estimated by the relation:

\[
C_{sp} = \frac{I}{\frac{dv}{dt}m}
\]  

(1)

Where \(C_{sp}\) is the specific capacitance (in \(\text{Fg}^{-1}\)), \(I\) is the charge/discharge current, \(t\) is the time of discharge, \(V\) is the voltage difference between the upper and lower potential limits, and \(m\) is the mass of the active material [59]. TNFs electrode demonstrates the \(C_{sp}\) values of the 75, 50, 35.7 and 22.7 \(\text{Fg}^{-1}\) respectively at current densities of 1, 5, 10, and 100 \(\text{mAg}^{-1}\). The obtained \(C_{sp}\) value at 1 \(\text{mAg}^{-1}\) is greater than the reported values 6.4 \(\text{Fg}^{-1}\) [60], 28.94 \(\text{Fg}^{-1}\) [61], 45.3 \(\text{Fg}^{-1}\) [62], 48.6 \(\text{Fg}^{-1}\) [63] and 59.69 \(\text{Fg}^{-1}\) [64]. The high \(C_{sp}\) of the electrode is due to morphology of nano fibers in particular nano range scale fiber shortens the Li\(^+\)-ion diffusion paths resulting improved conductivity and high ratio area/volume of the electrode which facilitate high charge storage. In addition to that the high mechanical strength and flexibility of the fibers hold the structure at high rates also. The decreasing trend of the capacitance at high current densities suggests slow proton kinetics, therefore it results either depletion or saturation of the proton/Li-ion in the electrolyte inside the TNFs electrode [57].

Electrochemical impedance spectroscopy (EIS) is a powerful tool to evaluate electrode performance in the frequency domain. Figure 5(c) shows the EIS of TNFs electrode prepared at 500 °C, before and after cycling test and corresponding nyquist plots are depicted as in set (in which the EIS curves are drawn in the high frequency zone). In the figure 5(c) a semicircle followed by an inclined lines are originated in the high and low frequency regions. The semicircle’s left crossover point at the real axis equals to the Equivalent Series Resistance (ESR), which is assigned as solution resistance generated by the electrolyte solution and termed as \(R_s\). The radius of the semicircle at high to medium frequency determines the value of the charge transfer resistance (Rct) at the solid-electrolyte interface. The inclined line in the low frequency region is originated from the lithium ion diffusion process called Warburg diffusion (\(Z_w\)) [65]. The impedance values of TNFs electrode is slightly increased from 17 \(\Omega\) to 18 \(\Omega\) after 5000 cycles infer that the electrochemical process in the electrode is diffusion controlled and highly reversible. The \(R_s\) value is \(~13\ \Omega\), same for the both plots indicates no change is occurred in the solution
resistance during the cycling process evidenced the structural stability of the electrode. Moreover, the height of the semicircle is very small signifies that the electrode has large capacity and this could be attributed to fibrous morphology of good conductive TNFs electrode, which not only provide high surface area but also facilitate fast charge transfer and electrolyte ion diffusion [61]. The slight change in the Warburg impedance after 5000 cycles implies that the diffusion control process is highly reversible and consistence with previous reports [61]. The reliability of the supercapacitor electrode is mainly determined by cycle life test. The specific capacitance versus cycle number of the TNFs prepared at 500 °C is shown in figure 5(d). The cycling test of TNFs electrode for 5000 cycles is conducted at a current density of 1 mAg⁻¹. The TNFs electrode is delivered an initial capacitance of 75 Fg⁻¹ and retained 95% of capacitance (71 Fg⁻¹) even after 5000 cycles demonstrates excellent cycliability with good structural stability. Furthermore, the coulombic efficiency of the electrode can be determined by the following relation [66]
\[
\eta = \frac{t_d}{t_c} \times 100
\]
Where \(t_d\) and \(t_c\) are the discharging and charging times notably the calculated coulombic efficiency is about 95%.

The power density and energy density are major parameters to determine the complete electrochemical performance of the supercapacitor. The energy density and power density of the TNFs electrode can be calculated the following relations:
\[
E = \frac{1}{2} C_m (\Delta V)^2
\]
\[
P = \frac{E}{\Delta t}
\]
Where \(E\) is Energy density (Wh Kg⁻¹), \(C_m\) is the specific capacitance (Fg⁻¹), \(\Delta V\) is voltage window (V), \(P\) is the power density (W Kg⁻¹) and \(\Delta t\) is the discharge time in hours. The electrospun TNFs prepared at 500 °C demonstrated energy density of 24 Wh Kg⁻¹, and power density of 22.08 W Kg⁻¹ respectively.

4. Conclusions
Titanium dioxide nanofibers (TNFs) have been successfully synthesized via electrospinning technique. The as prepared nanofibers were annealed at 500 °C and studied their crystallography and phase by XRD and Raman spectroscopy. The high intense (101) Braggs plane from XRD and 141 cm⁻¹ Raman vibration mode confirmed that the obtained TNFs were corresponding to anatase TiO₂ phase with I4₁/amd symmetry. Ultra long, high aspect-ratio smooth surface nanofibers with diameter of ~100 nm in a random network structure was derived from TEM analysis which composed of TiO₂ nanoscopic particulates. The surface morphology of the TNFs shows interconnected network fibers with an estimated average diameter of ~150 ± 20 nm. The optical absorption band showed a red shift towards visible region with an evaluated optical band gap of 3.08 eV for annealed TNFs. The TNFs electrode demonstrated an excellent specific capacitance of 75 Fg⁻¹, and retained 95% capacitance even after 5000 cycles with good structural stability. Moreover, the TNF electrode exhibit energy density of 24 WhKg⁻¹ and power density of 22.08 WKg⁻¹. These results concluded that high surface-to-volume ratio, high mechanical strength nano architecture TNFs could open up new paths to construct high performance supercapacitors for energy storage devices.

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