This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Yellow bristle grass

TiO$_2$ nanostructure

254x190mm (96 x 96 DPI)
TiO₂ nanofibers resembling ‘yellow bristle grass’ in morphology by a soft chemical transformation†

Sandeep Nandan, T. G. Deepak, Shantikumar V Nair and A. Sreekumaran Nair*

We synthesized a uniquely shaped one-dimensional (1-D) TiO₂ nanostructure having the morphology of yellow bristle grass with high surface area by titanate route under soft reaction conditions. The electrospun TiO₂-SiO₂ composite nanofibers upon treatment with concentrated NaOH at 80 °C under ambient pressure for 24 h resulted in sodium titanate (Na₂Ti₃O₇) nanostructures. The Na₂Ti₃O₇ nanostructures have an overall 1-D fibrous morphology but the highly porous fiber surfaces were decorated with layered thorn-like features (a morphology resembling that of yellow bristle grass) resulting in high surface area (113 m²/g) and porosity. The Na₂Ti₃O₇ nanostructures were converted into TiO₂ nanostructures of the same morphology by acidification (0.1 N HCl) followed by low temperature sintering (110 °C) processes. Dye-sensitized solar cells (DSCs) constructed out of the material (cells of area 0.20 cm² and thickness of 12 μm) showed a power conversion efficiency (η) of 8.02 % in comparison to commercial P-25 TiO₂ (η = 6.1 %).

Introduction

TiO₂ is a versatile material having applications in various fields such as renewable energy harvesting (especially dye- and perovskite-sensitized solar cells (DSCs/PSSCs)),1,5 energy storage (Li-ion batteries, supercapacitors, etc.),6,8 photocatalysis (water splitting),9,12 environmental remediation,13-15 photonic crystals,16 self-cleaning coatings,17 etc. For most of the applications mentioned above, TiO₂ with a high surface area (and porosity) is preferred. There are two ways to increase the surface area of TiO₂ in a TiO₂ nanostructure: one is to reduce the size of the particles in the nanoarchitecture and the other is to increase its porosity. One-dimensional TiO₂ nanostructures such as nanofibers, nanowires and nanotubes find renewed interests for the above mentioned applications because of guided/semi-guided electron transport, scattering of solar photons corresponding to the red part of the solar spectrum, etc.18-20 However, the TiO₂ nanofibers inherently have a low internal surface area which is particularly true for the electrospun TiO₂ nanofibers (~ 44 m²/g).21-22 The fabrication of electrospun TiO₂ nanofibers involves a high

temperature sintering at 450 °C and during the process the sizes of the particles in the nanofiber architecture increase which results in loss of surface area for the fibers.21-22 Further, the nanofibers are formed out of fusion of particles which results in loss of internal surface area for the former.21-22 Thus increasing the surface area of the electrospun TiO₂ nanofibers through size reduction of constituting particles in the fibers is not a feasible approach. The second approach of roughening the surface through chemical means is a facile one. Previously we have shown that etching ZnO from rice-shaped TiO₂-ZnO composite leads to coral reef-shaped TiO₂ nanostructures with good photovoltaic and photocatalytic properties.23 In the present paper we show that a soft etching of SiO₂ from electrospun TiO₂-SiO₂ composite nanofibers with the in-situ chemical transformation of the TiO₂ using the sodium titanate process produces a fascinating morphology for the TiO₂, which is yellow bristle grass-like. The TiO₂ had a surface area of 113 m²/g which when tested for a DSC showed a conversion efficiency of 8.02% for a cell of area 0.2 cm² and thickness ~ 12 μm. It must be noted that the present morphology appears only under soft reaction conditions (treatment with
concentrated NaOH at 80 °C, ambient pressure) and under rigorous conditions (such as the hydrothermal reaction with concentrated NaOH, 180 °C in a typical steel-lined autoclave) the product was always 2-D (such as leaf) and 3-D (such as flowers) morphologies of TiO₂.²⁴-²⁶

Experimental

a) Chemicals needed

PVP (polyvinylpyrrolidone, Mw=1.3×10⁶, mp. 300 °C, Aldrich, Steinhein, Germany), methanol (Aldrich, Steinhein, Germany), acetic acid (LR, Nice Chemicals, India), titanium (IV) isoproxide (TiP, 97%, Aldrich, Germany), tetraethoxysilane (TES, 98% GC grade, Alfa Aesar, UK), sodium hydroxide pellets (A.R, Nice Chemicals, India), hydrochloric acid (ACS, ISO Reag. Merk KGaA, Germany), and N719 dye (Solaronix SA) were used as received. Fluorine-doped tin oxide plates (FTO, sheet resistance of 6-8 Ω/sq) were fabricated in-house by spray-pyrolysis deposition method. The precursors of the FTO solution were made of dibutyltin diacetate (DBTDA) in 2-propanol (0.2 M) and ammonium fluoride (NH₄F) in water (9 M).

b) Fabrication of TiO₂-SiO₂ Composite nanofibers

The TiO₂-SiO₂ composite nanofibers (NFs) were fabricated by electrospinning technique.²⁴a Typically; about 1 g of PVP was dissolved in 14 mL of methanol followed by the addition of 4 mL of acetic acid, 1.75 mL of TiP and 0.25 mL of TES, respectively. The polymeric solution containing the precursors was subjected to continuous magnetic stirring for 5 h at room temperature to get sufficient viscosity and homogeneity for electrospinning. Electrospinning was done using a humidity-controlled electrospinning set-up (IME Technologies, The Netherlands) under the optimized conditions of 30 kV and with a flow rate of 1 mL h⁻¹. The humidity level inside the electrospinning chamber was maintained at ~ 50%. The as-spun composite fibers were collected on an Al foil which is wrapped to a static metallic collector. The distance between the needle tip and the collector was kept at 10 cm. The as-pun fibers were collected in the form of white sheet on the Al foil and which was peeled-off and sintered at 450 °C for 3 h for removing the polymer and crystallizing the TiO₂-SiO₂ composite. The as-spun composite (TiO₂-SiO₂-PVP) was characterized by scanning electron microscopy (SEM) and the sintered (TiO₂-SiO₂) nanofibers were analysed by spectroscopy and microscopy, respectively, as detailed below in the manuscript.

c) Synthesis of titaneate-derived yellow bristle grass-like TiO₃ from the titaneate fibers

The fluffy white titaneate was suspended in dil. HCl (0.1 M HCl) at room temperature for 24 h. The resulted protonated titaneate (H₂Ti₃O₇) was then washed several times with deionized water and finally with methanol and dried in an oven at 110 °C for 24 h. During the heat treatment, the H₂Ti₃O₇ gets converted into TiO₂ (the titaneate-derived TiO₂) with thorn-like features on the nanofiber backbone. The TiO₂ was characterized by spectroscopy, microscopy and BET surface area analysis.

d) Fabrication of dye-sensitized solar cells (DSCs)

Dye-sensitized solar cells (DSCs) were fabricated with the thorn-like TiO₂ fibers by doctor-blading technique. The polymer used for making the TiO₂ paste was polyester which was prepared by the polycondensation of citric acid and ethylene glycol as reported before.²⁵e About 100 mg of the TiO₂ fibers was mixed with 100 μL of polyester and sonicated for 10 h to get a unique paste for doctor-blading. The TiO₂ paste was doctor-bladed onto the Fluorine-doped tin oxide (FTO) plates which had a prior thin TiO₂ coating (of ~ 100 nm thickness) by spray pyrolysis deposition method.²⁵b The doctor-bladed films had a thickness of around 15 μm. We also made similar films from the commercially available P-25 for a comparison. The doctor-bladed FTO plates were sintered at 450 °C for 1 h during which the polymer got degraded and removed resulting in an optimum electrode thickness of ~11 to 12 μm for the TiO₂. The porous TiO₂ films were subsequently immersed in aq. TiCl₄ solution (30 mM, 70 °C) for 30 min and again sintered at 450 °C for 1 h. The sintered electrodes were soaked in 0.5 mM N719 dye solution in 1:1 acetonitrile-tert-butanol mixture for 24 h at room temperature and washed with absolute methanol for removing the loosely bound dyes. The electrodes having an active area of 0.25 cm² were placed against platinum (Pt sputter-coated) counter-electrodes in the presence of a parafilm spacer and I₂/I⁻ electrolyte for DSC fabrication.

Characterization

The initial TiO₂-SiO₂ composite, the sodium titaneate and the final titaneate-derived TiO₂ were characterized by spectroscopy and microscopy. The scanning electron microscopy (SEM) was performed using a JSM 6490 LA (JEOL-Tokyo, Japan) machine at an operating voltage of 15 kV. The samples spread on glass were coated with a thin film of gold before SEM measurements. High-resolution transmission electron microscopy (HR-TEM) was done with the JEOL 3010 machine.
at an operating voltage of 300 kV. A suspension of the samples was made in methanol under sonication and a drop of the solution was cast on a carbon-coated TEM grid which was subsequently dried in ambience and in vacuum, respectively. The surface area of the materials was analyzed by the BET (Brunauer-Emmett-Teller) N₂ adsorption method using a BET Analyzer ((Model No. Nova 1200 series from Quantachrome (USA)). Pore size distribution and average pore volume were estimated from the BET measurement using the manufacturer’s software. The powder XRD measurements were performed on each sample by an X'pert pro PAN Analytical operated at 30 mA current and with a voltage 40 kV. X-ray photo electron spectroscopy (XPS) was performed with a machine from Kratos Analytical, UK. The materials were characterized by Raman spectroscopy as well using a Witec confocal Raman-300 AR instrument (with an excitation laser of 488 nm and power of 0.6 mW). Current-voltage (I–V) characteristics of the DSCs were probed by a solar simulator under AM 1.5G condition (Newport Oriel class A-Solar simulator, USA). The electron lifetime and recombination resistance of the DSCs were analyzed using electrochemical impedance spectroscopy (EIS) in dark under an applied bias voltage of 0.69 V by using an Autolab (Metrohm, Newport model, The Netherlands).

Results and discussion

a) Characterization of TiO₂-SiO₂ composite nanofibers, the intermediate sodium titannate and the final titanate-derived TiO₂

Fig. 1 shows the SEM images of as-spun TiO₂-SiO₂-PVP composite nanofibers and the sintered TiO₂-SiO₂ nanofibers. Fibers were smooth and nearly continuous with an average diameter ranging from 200-250 nm (Fig. 1A and 1B). Upon sintering at 450 ⁰C for 3 h, the polymer degradation (reduction in the fiber diameter) and crystallization of the metal oxide grains occurred which results in continuous composite fibers of TiO₂-SiO₂ of 100-150 nm diameter range. Fig. 1(C and D) gives the details of TiO₂–SiO₂ composites after sintering. Fig. 2A shows the large area TEM image of TiO₂–SiO₂ nanofibers. Fig. 2B and 2C shows the magnified image of a single nanofiber. Fig. 2D shows the high-resolution TEM image which indicates the amorphous nature of the SiO₂ in the TiO₂–SiO₂ composite. The lattice spacing of 0.35 nm corresponds to the (101) lattice and this indicates the anatase phase of the TiO₂ in the TiO₂–SiO₂ composites. Lattice spacing corresponding to the SiO₂ was absent in the lattice-resolved image implying that SiO₂ is in amorphous phase. The TiO₂–SiO₂ nanofibers were further analyzed by powder XRD, Raman spectroscopy, BET surface area and XPS measurements. The peaks in XRD spectrum (Fig. 3A) further confirm the anatase phase of the TiO₂ and the amorphous nature of SiO₂ in the composite (i.e. the absence of peaks corresponding to the SiO₂). From the Raman spectra (Fig. 3B) the bands at 152 cm⁻¹, 430 cm⁻¹ and 517 cm⁻¹ show anatase phase of the TiO₂ while the other peaks (612 cm⁻¹ and 253 cm⁻¹) indicate the amorphous SiO₂. The BET surface area of the TiO₂–SiO₂ composites was 53 m²/g. Fig. 4a shows the XPS wide spectrum of the TiO₂–SiO₂ composite and the high-resolution spectra of the elements are shown in Fig. 4b-d. The binding energies of Ti 2p3/2 and Ti 2p1/2 were centered at 458.46 eV and 464.16 eV, respectively, which corresponds to a spin-orbit coupling of 5.7 eV. The O 1s peak shown in the Fig. 4c was de-convoluted into two peaks at 529.7 eV and 531 eV, respectively, corresponding to the presence of Ti-O-Ti and Si-O-Si bonds.

![Fig. 1. SEM images of (A and B) as-spun TiO₂-SiO₂-PVP composite nanofibers and (C and D) TiO₂-SiO₂ composite nanofibers after sintering at 450 ⁰C.](Image)

![Fig. 2. TEM analysis (A) large area TEM image of TiO₂-SiO₂ nanofibers, (B) and (C) respectively show magnified images of a few nanofibers and a single nanofiber and (D) shows a lattice-resolved TEM image of a single TiO₂-SiO₂ nanofiber where red circled area indicates the regions of amorphous SiO₂ and the lattice spacing of 0.35 nm shows anatase TiO₂.](Image)
This confirms the SiO$_2$ incorporation into the TiO$_2$ matrix through Ti-O-Si bonds.$^{31}$ The peak for Si was centered at a binding energy of 102.01 eV as evident from Fig. 4d.

On alkali treatment (i.e. by NaOH treatment), the TiO$_2$-SiO$_2$ composite was converted into sodium titanate (Na$_2$Ti$_3$O$_7$) with the in-situ leaching of the SiO$_2$. The fiber morphology was well retained but the fibers became highly anisotropic and porous with thorn-like features all-over the fiber backbone. Fig. 5A shows the EDS spectrum of the TiO$_2$-SiO$_2$ composites. The peaks for Si, O and Ti were clear from the spectrum. Fig. 5B shows the EDS spectrum of the Na$_2$Ti$_3$O$_7$ showing the absence of Si implying the near complete etching of SiO$_2$ from the TiO$_2$-SiO$_2$ composite.

Fig. 6 shows the SEM images of the titanate showing the thorn-like features randomly decorating the fiber backbone. The TEM images of the titanate are shown in Fig. 7. Fig. 7A shows the large area image of the fiber titanate and Fig. 7B-D gives the resolved images of respective fibers. Fig. C and D show the HR-TEM images of the thorn-like features. Fig. 7E shows the layered nature of the Na$_2$Ti$_3$O$_7$ and the layer spacing was found to be 0.8 nm; typical for sodium titanate materials.$^{33,34(a)}$ The SAED pattern in Fig. 7F shows the amorphous nature of the sodium titanate. Fig. 8 A&B shows the powder XRD and Raman spectra of the titanate. The diffraction peak at 2θ=9.7$^\circ$ (which is characteristic of the (200) peak of the titanate)$^{33,34a}$ and the absence the TiO$_2$ peaks in the XRD spectrum show that the conversion of TiO$_2$-SiO$_2$ composite into the titanate was complete. From the Raman analysis we clearly observe the bands at 295 cm$^{-1}$, 722 cm$^{-1}$, and 911 cm$^{-1}$, respectively, and they confirm the material to be sodium titanate, Na$_2$Ti$_3$O$_7$. 

Fig. 5. EDS spectrum of (5A) TiO$_2$-SiO$_2$ composite and (5B) the sodium titanate. A small hump seen around 2 eV (in Fig. B) could be due to the Si impurity (may be from incomplete washing).
Fig. 6. SEM results of titanates showing thorn like figures originate from the fiber backbone.

Fig. 7. TEM images of sodium titanates. Fig 7A gives the large area TEM image while resolved images showed by Fig 7B-D. SAED pattern shown by 7F.

The peak 295 cm\(^{-1}\) corresponds to the Na–O–Ti bond and peak at 911 cm\(^{-1}\) can be attributed to the Ti–O stretching vibration in distorted TiO\(_6\) octahedra.\(^{33c}\) The Raman band at 722 cm\(^{-1}\) represents the Ti–O–Ti stretch vibrational bond in edge-shared TiO\(_6\).\(^{33c}\) The XPS spectrum of the titanate is given in Fig. 9 (A-D). The wide spectrum of the titanate shown in Fig. 9A implies the absence of the Si peak which further confirms the complete etching of Si during the formation of the titanate. The high-resolution spectrum of Ti shows the binding energies of Ti 2p3/2 and Ti 2p1/2 centered at 458.4 eV and 464.1 eV, respectively. The O 1s peak (Fig. 9C) showed only a single peak at 530.07 eV corresponding to Ti-O-Ti bonds present in the material.\(^{34}\) Fig. 9D indicates the presence of Na 1s peak at 1070.4 eV which shows the formation of Ti-O-Na bonds in the Na\(_2\)Ti\(_3\)O\(_7\). The BET surface area of the Na\(_2\)Ti\(_3\)O\(_7\) was measured as 200 m\(^2\)/g. A control Na\(_2\)Ti\(_3\)O\(_7\) was also made from electrospun TiO\(_2\) nanofibers (that is without the incorporation of SiO\(_2\)) by treatment with NaOH under similar conditions and the resulting Na\(_2\)Ti\(_3\)O\(_7\) showed a BET surface area of 166 m\(^2\)/g. This highlights the role of SiO\(_2\) in the chemical transformation process. SiO\(_2\) is an acidic oxide which can be easily etched using NaOH. Thus the TiO\(_2\)-SiO\(_2\) composite fibers when treated with NaOH, the chemical transformation of TiO\(_2\) to Na\(_2\)Ti\(_3\)O\(_7\) occurs with the in-situ etching of SiO\(_2\). This is the
reason for the high surface area of the Na₂Ti₃O₇ obtained from TiO₂-SiO₂ composite fibers than that from TiO₂ fibers.

The Na₂Ti₃O₇ upon acid treatment (0.1 N HCl for 12 h) followed by washing (with water and ethanol several times) and then sintering (110 °C) resulted in the conversion of the Na₂Ti₃O₇ into TiO₂ (denoted as the titanate-derived TiO₂ hereafter) with the same morphology as that of the Na₂Ti₃O₇, that is fiber architecture with thorn-like features on the fiber backbone. The BET surface area of the TiO₂ (113 m²/g) was lower than that of the Na₂Ti₃O₇ (200 m²/g) but nearly double than that of the TiO₂-SiO₂ composite (53 m²/g) and 2.5 times than that of commercial P-25 TiO₂. The average pore sizes and pore volumes of the Na₂Ti₃O₇ and the TiO₂ were (5.6 nm and 5.8 nm) and (0.28 cc/g and 0.16 cc/g), respectively. A comparison of the BET isotherms of the P-25 and the titanate-derived TiO₂ is given in Electronic Supplementary Information (ESI) 1.

The TiO₂ fibers were analyzed by microscopy. Fig. 10 and Fig. 11, respectively, show the SEM and TEM images. Low- and high-resolution SEM images (Fig. 10 A&B) show the nearly similar morphology of the Na₂Ti₃O₇ for TiO₂ as well, i.e. thorn-like features on the fiber architecture resulting in a completely anisotropic morphology. The large area and resolved TEM images (Fig. 11A & 11B) also show the thorn-like morphology of the TiO₂ fibers. Fig. 11C gives the lattice-resolved TEM image of the TiO₂ which confirms its anatase structure with the lattice spacing of 0.35 nm corresponding to the (101) orientation of the anatase TiO₂. The SAED pattern shown by Fig. 11D indicates its polycrystalline nature. The TiO₂ was further characterized by powder XRD and Raman spectra (Fig. 12), respectively. The XRD pattern of TiO₂ further

![Fig. 10. SEM analysis of TiO₂ in various resolutions further confirms its anisotropic morphology.](image1)

![Fig. 11. TEM analysis of TiO₂ nanofibers (11A and 11B gives the large area and resolved TEM images). The lattice spacing (0.35 nm of 101 orientations) had shown by 11C and 11D gives the SAED pattern of the same.](image2)

![Fig. 12. (A) Powder XRD and (B) Raman spectrum of titane derived TiO₂ nanofibers](image3)

![Fig. 13. XPS wide spectrum of TiO₂ (A) and the high-resolution spectra of Ti (B) and O (13C), respectively.](image4)
(A_{1g}, B_{1g} and 3E_g) corresponds to anatase phase. The peaks at 640 cm\(^{-1}\), 200 cm\(^{-1}\), and 156 cm\(^{-1}\) show the three \(E_g\) vibrational modes and the peaks at 398 cm\(^{-1}\), 515 cm\(^{-1}\) represent the \(B_{1g}\) and \(A_{1g}\) vibrational modes, respectively. XPS analysis was done to confirm the elemental composition and phase purity of TiO\(_2\) (Fig. 13). The binding energies of Ti 2p\(_{3/2}\) and Ti 2p\(_{1/2}\) were centered at 458.43 eV and 464.13 eV, respectively, corresponding to a spin-orbit coupling of 5.7 eV. The single peak for O 1s at 530.11 eV corresponds to Ti-O-Ti bonds in the TiO\(_2\) which further confirms the absence of oxygen related impurities in the TiO\(_2\).

(b) Photovoltaic property of the titanate-derived TiO\(_2\)

We fabricated DSCs out of commercial P-25 TiO\(_2\) the TiO\(_2\) nanofibers and the titanate-derived TiO\(_2\) for comparing their photovoltaic performance (Fig. 14A). The photovoltaic parameters of the DSC using P-25 were conversion efficiency (\(\eta\)) of 6.04 % with a current density (\(J_{sc}\)) of 10.78 mA cm\(^{-2}\), fill-factor (FF) of 73.55% and an open-circuit voltage (\(V_{oc}\)) of 761 mV. The TiO\(_2\) nanofiber (electrospun TiO\(_2\))\(^{25}\) DSC achieved a \(\eta\) of 5.51 % with a \(J_{sc}\) of 10.25 mA cm\(^{-2}\), a FF of 71.27% and a \(V_{oc}\) of 753 mV. The DSC using titanate-derived TiO\(_2\) gave a pretty decent performance than the above two. It gave a \(\eta\) of 8.02 % with a \(J_{sc}\) of 14.48 mA cm\(^{-2}\), FF of about 73.55% and a \(V_{oc}\) of 770 mV. The incident photon-to-current conversion efficiency (IPCE) of the device was ~78% whereas the same was ~58% for the P-25-based DSC.

![Image](image1.png)

**Fig. 14.** (A) I–V characteristics DSCs of film using titanate-derived TiO\(_2\) and P-25, (B) the IPCE (%) of DSCs using titanate-derived TiO\(_2\) and the P-25.

We have analyzed the reasons for the superior performance of the titanate-derived TiO\(_2\) in comparison to the P-25. A comparison of the photovoltaic parameters reveals that high \(J_{sc}\) and \(V_{oc}\) of the DSC from titanate-derived TiO\(_2\) are the reasons for its high efficiency. The BET surface area of the titanate-derived TiO\(_2\) was measured to be 113 m\(^2\)/g which was ~2.5 times higher than that of the commercial P-25 (~44 m\(^2\)/g) (ESI 1). We have quantified the amount of dyes in the DSCs (cells having same thickness and area, respectively) by de-loading them using 0.1 N NaOH. A comparison of the dye-loading data is given in Fig. 15A which shows enhanced dye adsorption on the titanate-derived TiO\(_2\) than that in the P-25 (owing to the high surface area of the former). Thus high dye loading partly contributed to the increased photocurrent density (\(J_{sc}\)). The TiO\(_2\) nanofibers had an average diameter of ~250 nm, tens of micron length and have highly roughened surface with thorn-like features projecting out from the fiber backbone. The dimensions and surface features of the fibers were also apt for good light scattering especially at the red part of the solar spectrum. We measured the reflectance of the electrodes from titanate-derived TiO\(_2\) fibers and the P-25 (Fig. 15B). It can be seen that the titanate TiO\(_2\) fibers scattered more photons at the red part of the spectrum than the P-25 implying more photon confinement within the TiO\(_2\) fiber electrode. This also might have contributed to the increased \(J_{sc}\) value.

Electrochemical impedance spectra (EIS) of the DSCs were measured under dark condition under an applied forward bias of 0.7 V to find the recombination resistance values. EIS result is depicted in the Nyquist plot (Fig. 15C). The Nyquist plot for an ideal DSC device will show three semicircles corresponding to charge transfer at the counter electrode-electrolyte interface (appears in high frequency range), charge transfer at the oxide-electrolyte interface (\(R_{ct}\)) (appears in medium frequency range) and ion diffusion through the electrolyte (appears in lower frequency range). The recombination resistance (middle frequency) is more for the titanate-derived TiO\(_2\) (larger semicircle) than for the P-25 (smaller semicircle) implying reduced electron recombination for the former. This is further evident from the lifetime of the electrons in the respective DSCs measured from the Bode phase plots (Fig. 15 D). The lifetime of the electrons is related to the peak of the Bode phase plot by the relation: \(T_e = 1/2\pi f_{peak}\) where \(f_{peak}\) corresponds to the frequency maximum. The respective electron lifetimes were calculated to be 13 ms and 16 ms for P-25 and the titanate-derived TiO\(_2\). Increased lifetime of electrons in the fiber DSC implies reduced electron recombination which is reflected in the increased \(V_{oc}\) and \(J_{sc}\) of the DSC made from the titanate derived TiO\(_2\). While reduced recombination is one of the reasons for the observed high \(V_{oc}\) yet another reason can be the chemical composition of the TiO\(_2\). The titanate TiO\(_2\) nanofiber...
is phase pure (anatase), the P-25 is a mixture of ~ 75% anatase (band-gap of 3.2 eV) and ~ 25% rutile (band-gap of 3.0 eV). Thus the apparent Fermi level of P-25 will be slightly lower than that of the titanate TiO$_2$ and hence the observed variations in the $V_{oc}$. Thus it can be summarized that the high $J_{sc}$ and $V_{oc}$ are the primary reasons for the enhanced performance of the titanate-derived TiO$_2$ in comparison to the P-25 TiO$_2$.

Conclusions

TiO$_2$ nanofibers resembling the morphology of yellow bristle grass were fabricated from TiO$_2$-SiO$_2$ composite nanofibers by a soft chemical transformation and etching process. The soft etching process also involved chemically transforming the TiO$_2$ with the in-situ etching of SiO$_2$ by concentrated NaOH under room temperature and ambient pressure. The initial TiO$_2$-SiO$_2$ composite fibers, the chemically transformed Na$_2$Ti$_3$O$_7$ fibers and the titanate-derived TiO$_2$ fibers with the morphology of yellow bristle grass were characterized by spectroscopy and microscopy. A comparison of the dye-sensitized solar cell performance of the commercially available P-25, the TiO$_2$ nanofibers and the present TiO$_2$ with the yellow bristle grass morphology showed a superior performance for the final one (an efficiency of 8.02 % vs. that for the commercial P-25 TiO$_2$, 6.039 %). We anticipate many promising applications for the titanate-derived TiO$_2$ in anti-reflecting coatings, Li-ion battery, environmental remediation, etc.

Acknowledgements

The authors acknowledge financial support from Ministry of New and Renewable Energy (MNRE) and Solar Energy Research Initiative (SERI), Dept. of Science and Technology (DST), respectively, of Govt. of India.

Notes and references

* Amrita Centre for Nanoscience and Molecular Medicine, Amrita Institute of Medical Sciences, Amrita Vishwa Vidyapeetham, AIMS PO, Kochi 682041, Kerala, India. Email: sreekumaranmair@aims.amrita.edu.
† Electronic Supplementary Information (ESI) available [a comparison of the BET surface area of P-25 TiO$_2$ and titanate-derived TiO$_2$]. See DOI: 10.1039/b000000x.


