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Novel Hollow Mesoporous 1D TiO₂ Nanofibers as Photovoltaic and Photocatalytic Materials

Xiang Zhang a b, Velmuragan Thavasi c, S G Mhaisalkar b and Seeram Ramakrishna * a d

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Hollow mesoporous one dimensional (1D) TiO₂ nanofibers are successfully prepared by co-axial electrospinning of titanium tetraisopropoxide (TTIP) solution with two immiscible polymers; polyethylene oxide (PEO) and polyvinylpyrrolidone (PVP) using core-shell spinneret, followed by annealing at 450°C. The annealed mesoporous TiO₂ nanofibers are found to be hollow structure with an average diameter of 130 nm. Measurements using Brunauer–Emmett–Teller (BET) method reveals that hollow mesoporous TiO₂ nanofibers possess high surface area of 118 m²/g with two types of mesopores; 3.2 nm and 5.4 nm that resulted from gaseous removal of PEO and PVP respectively during annealing. With hollow mesoporous TiO₂ nanofibers as photoelectrode in dye sensitized solar cells (DSSC), the solar-to-current conversion efficiency (η) and short circuit current (Jsc) are measured as 5.6 % and 10.38 mA/cm² respectively, which are higher than that of DSSC made using regular TiO₂ nanofibers under identical conditions (η = 4.2 %, Jsc = 8.99 mA/cm²). The improvement on the conversion efficiency is mainly attributed to higher surface area and mesoporous TiO₂ nanostructure. It facilitates the adsorption of more dye molecules and also promotes the incident photon to electron conversion. Hollow mesoporous TiO₂ nanofibers with closely packing of grains and crystals intergrowth with each other demonstrates faster electron diffusion, and longer electron recombination time than that of regular TiO₂ nanofibers as well as P25 nanoparticles. The surface effect of hollow mesoporous TiO₂ nanofibers as photocatalyst on the degradation of rhodamine dye was also investigated. The kinetic study shows that the hollow mesoporous surface of the TiO₂ nanofibers influenced its interactions with the dye, and resulted in an increased catalytic activity over P25 TiO₂ nanocatalysts.

Introduction

Electrospinning has been popular in producing one dimensional (1D) metal oxides fibers or polymer fibers for energy based applications include as electrode in photovoltaic, fuel cells, energy storage devices and as photo catalysts.1-3 High molecular weight polymers as structure directing agents, blended with metal oxide precursor and were drawn into composite fibers through a spinneret by applying a high voltage. Besides its application in energy, electronspun fibers could be also be used in other areas including wetting material, etc. Besnbacher et al produced the responsive biodegradable polycaprolactone nanofibers by functionalizing its surface with photoresponsive azobenzene and shown a reversiable light-driven wettability changes. 4 Nanofibers may be preferred over nanoparticles in energy for the following reasons: faster electrons diffusion than in nanoparticles; fibers of diameter lesser than 150 nm provides an additional energetic barrier to recombination due to the formation of a space-charge region; 1D nanofibers ensure for the rapid collection of carriers generated by reducing surface.

A standard dye sensitized solar cell (DSSC) consists of TiO₂ nanoparticulate film as photoelectrode on transparent conducting oxide glass (fluorine doped tin oxide, FTO), a photosensitizer (dye), a platinum-coated FTO as counter electrode and an iodide/triiodide redox couple electrolyte.5-8 Upon illumination, the sensitized dye injects electron into the conduction band of the TiO₂, which transports through the nanoparticulate matrix to FTO.9 The electron-deficient dye is subsequently regenerated by the redox electrolyte. The performance of DSSCs was more closely related to the surface area of TiO₂ films.10 More dye molecules could be anchored efficiently if the metal oxide is

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.
provided with larger surface area, leading to stronger absorption of solar irradiation from the adsorbed dye.\textsuperscript{11} There also has been a strong motivation to increase the active surface area of TiO\textsubscript{2} and also produce novel morphology because of its excellent catalytic activity. TiO\textsubscript{2} as photocatalyst has many advantages including UV absorption range, excellent chemical stability and relatively available in abundant.

Much research activities have been directed to develop the methodologies that produce metal oxide nanostructures with higher surface area as it facilitates for the adsorption of more dye molecules in photovoltaic and greater catalytic activity. Methods such as electrodeposition, hydrothermal, potentiostatic anodization, chemical and bio-based templates were employed to obtain higher surface area. Meng et al.\textsuperscript{12} and Grimes et al.\textsuperscript{13,14} prepared hollow hemispherical nano-TiO\textsubscript{2} and TiO\textsubscript{2} nanotube arrays respectively using radio frequency (RF) sputtering method. There are few drawbacks associated with the synthesis of TiO\textsubscript{2} nanotube arrays directly on FTO for energy applications. For example, loose packing of TiO\textsubscript{2} nanotubes on FTO is common using synthetic method that results in recombination loss, reduces the conversion efficiency in solar cells. For the improvement of adhesion of TiO\textsubscript{2} nanotubes onto FTO, a thin layer of TiO\textsubscript{2} nanoparticulate film has been employed that however could render more free-contact space, increase ohmic loss and the dark current in solar cells.

Using electrospinning, well defined hollow structured materials were achieved either by using polymer as additive or volatile solvents or soluble oils as additives, or process temperature.\textsuperscript{15} Xia et al.\textsuperscript{16} demonstrated the formation of hollow TiO\textsubscript{2} nanowires using polystyrene (PS) in the electrospinning blend. However, no data about the surface area and also no specific applications were reported by these authors. Another group led by Kim\textsuperscript{17,18} produced fine TiO\textsubscript{2} nanorods with higher surface area of 138 m\textsuperscript{2}/g by electrospinning the blend with their lab-synthesized polymer PVAc (polyvinyl acetate, m.wt 10\textsuperscript{6}). Nanorods morphology is relatively inferior for energy applications because the number of contact points in between the rods is quite more, hence electron trap is expected to be considerably significant in nanorods.\textsuperscript{19}

The formation of porous structure enhances the interfacial surface area that is beneficial for energy devices. For instance, larger interfacial area between TiO\textsubscript{2} and dye in solar cells leads to high visible-light absorbance from the numerous successive monolayers of adsorbed dye, and also improves the accessibility of electrolyte to electrode.\textsuperscript{45} Lofton et al.\textsuperscript{20} produced porous TiO\textsubscript{2} fibers by electrospinning the sol gel precursor with sodium chloride/calcium carbonate, and subsequent removal of salt through leaching. This approach however also led to the formation of micro-size pores, which are undesirable for the application in solar cells. The electrons transport would be affected within the porous structure of TiO\textsubscript{2}, in turn causes electron-hole recombination. The higher surface area of the porous TiO\textsubscript{2} film with the smaller pore size (< 5 nm) is critical for efficient device performance.

Considering the advantages of higher surface area and larger interfacial area by hollow and mesoporous structures respectively, an electrospinning method that is capable of generating both hollow and mesoporous structures within each fiber using cost-effective polymers has been developed. TiO\textsubscript{2} fibrous mat that possesses both hollow and mesoporous structures in each fiber was produced using co-axial electrospinning of precursors with polyethylene oxide (PEO) in the core, and polyvinylpyrrolidone (PVP) solution alone in shell part of the spinneret, followed by annealing to 450°C at ramp rate of 2°C/min. DSSCs were constructed using the as-prepared hollow mesoporous TiO\textsubscript{2} nanofibers as photoelectrode, and their performances were evaluated in comparison to regular and smooth TiO\textsubscript{2} nanofibers. It was found that DSSCs based on hollow mesoporous TiO\textsubscript{2} nanofibers exhibited a significant increase of 33 % in solar-to-current conversion efficiency over regular TiO\textsubscript{2} fibers.

As-obtained hollow mesoporous TiO\textsubscript{2} nanofibers mat was also investigated for its catalytic performance against the degradation of organic dye (rhodamine B) and compared with the P25 TiO\textsubscript{2} nanoparticles (NPs). The study revealed that the higher surface area resulted out of hollow mesoporous structure appears to be a promising morphology for TiO\textsubscript{2} to be as more effective photocatalyst.

**Experimental**

**a. Materials**

Titanium tetraisopropoxide [Ti(O\textsubscript{2}Pr)	extsubscript{4}; 97%], solvents N,N-dimethylformamide (DMF, 99.8 %), ethanol (100 %) and acetic acid (99.7 %) were purchased from Sigma-Aldrich (Singapore). All chemicals were used as received without further purification. Cis-di(thiocyanato)-bis(2,20-bipyridyl-4-carboxylate-40-carboxylic acid)-ruthenium(II) (N719) dye was purchased from

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\textsuperscript{11} Cis-di(thiocyanato)-bis(2,20-bipyridyl-4-carboxylate-40-carboxylic acid)-ruthenium(II) (N719) dye was purchased from...
Solaronix and used as sensitizer to harvest the solar radiation. All chemicals were used as received without further purification.

b. Core-shell electrospinning
Core-shell spinneret (Scheme 1) was set up with two needles of size of 27G (core) and 21G (shell) fixed coaxially. Two precursor gels were chosen such that they were immiscible in nature, one for the core liquid and another for the shell liquid.

For this study, the precursor solution for the shell side was prepared by dissolving 0.9 g of polyvinyl pyrrolidone (PVP, $M_W = 100,000$, Aldrich) in 10 ml of ethanol followed by the addition of 3 ml acetic acid. Titanium tetraisopropoxide (1.5 g) was then added into PVP solution under vigorous stirring for 12h. The precursor for core fluid was prepared by dissolving $0.9 g$ of polyethylene oxide (PEO, $M_W = 900,000$, Sigma-Aldrich) in 5 ml of DMF under heating at 50°C. As-prepared two precursor gels were loaded into two plastic syringes (5 ml) and connected to a coaxial core-shell spinneret (Scheme 1). A high-voltage power was applied to the needle tip. The flow rate for core and shell fluids was set to 0.2 ml/h and 0.6 ml/h respectively. The electric field strength was 15 kV and an aluminum foil wrapped plate collector was placed at 12 cm below the needle tip for the collection of fibers.

A compound (core and shell) droplet formed at the edge of spinneret nozzles and transformed into a Taylor cone with a compound jet co-electrospun from its tip. The core-shell electrospun fibers were produced as in the simple electrospinning, the jet was pulled by the electric field, and stretched by the bending instability. The solvents from core and shell solution were evaporated rapidly due to set-humidity of 50% and concentrated core and shell solutions in the traveling path. The compound Taylor cone was subsequently formed with a shell droplet surrounded core solution droplet at the core-shell spinneret tip. PEO and PVP-TiO$_2$ were obtained as core and shell nanofibers respectively (Scheme 1). The electrospun core-shell nanofibers were calcined at 450°C for 1 h at a heating rate of 2°C/min to remove polymers, obtained hollow mesoporous nanofibers.

For performance comparison with regular TiO$_2$ nanofibers, the precursor gel consisting of titanium (IV) isopropoxide (1.5 g), 0.9 g polyvinyl pyrrolidone (PVP, $M_W = 100,000$, Aldrich), 10 ml ethanol and 3 ml acetic acid was loaded into a plastic syringe and a 15 kV DC voltage was applied to the single nozzle spinneret. The flow rate was set to 1 ml/h. The collector was grounded and placed at a distance of 10 cm below the spinneret.

c. Characterizations
The morphology of the samples was examined by field emission scanning electron microscope (SEM, JEOL-6701F, Japan) operated at voltage of 10kV after platinum coating (20 mA/30s).

The energy dispersive X-ray spectroscopy (EDS) is attached with the SEM machine. The average diameter of the TiO$_2$ nanofibers was measured using the software. Further examination on the calcined TiO$_2$ nanofibers were done using transmission electron microscopy (TEM, JEOL 3010, Japan) and selected area electron diffraction (SAED) operated at 200 kV. The samples were prepared by ultrasonic bath to disperse the TiO$_2$ nanofibers in ethanol followed by dropping the suspension on a carbon-coating copper grid. X-ray diffraction (XRD) was measured with Cu-Ka X-ray radiation at $\lambda = 1.54056\text{Å}$ with diffract grams recorded for 20 between 10° and 70°. The surface area and pore volume were determined by nitrogen adsorption/desorption using Brunauer-Emmett-Teller (BET, Micromeretics Tristar 2000, surface area and pore size analyzer). The samples were degassed under inert nitrogen ($N_2$) at 300°C for 12 h prior to BET measurements (under standard protocols at 77 K).

UV-Vis spectra were measured using Shimadzu UV-3600 UV-Vis-NIR spectrophotometer with a spectral resolution of 1 nm.

d. Photoelectric measurements
The fluorine-doped tin oxide (FTO) substrates were ultrasonically cleaned with DI water, acetone, and $\alpha$-propanol. The paste was
made by adding 3.75 g hollow mesoporous nanofibers and 18.7 g ethyl cellulose (Aldrich) into 15.2 g α-terpineol (Aldrich). The paste was then sonicated for 2 h until a homogenous suspension without aggregate was obtained. After that, the TiO₂ paste was bladed on a FTO glass to a thickness of 12 ± 2 μm using a doctor-blading technique. The TiO₂ electrode was dried in air at 90°C for 30 min and calcined at 450°C for 1 h to completely remove ethyl cellulose and α-terpineol. Anchoring of the dye molecules on the hollow mesoporous TiO₂ nanofibers electrode surface was done by soaking the electrode in a 1:1 volume mixture of acetonitrile and tert-butanol of N719 dye (0.5 mM) for 24 h at room temperature. The TiO₂ photoelectrode was then washed with DI water to remove unanchored dye molecules and dried in desiccator. A 50 μm space was covered the TiO₂ electrode. A DSSC was assembled by sandwiching TiO₂ photo anode, counter electrode and filling with electrolyte solution which containing 0.1 M lithium iodide, 0.03 M iodine, 0.5 M 4-tert-butylpyrididine, 0.6 M 1-propyl-2,3-imethylimidazoliumiodide (acetonitrile as solvent).

The performance of DSSC was obtained by photocurrent measurements of the assembled DSSC under irradiation of a 100 mWcm⁻² xenon lamp (Thermo Oriel Xenon Lamp 150 W: Model 66902) with AM 1.5 G, 1 sun condition. I-V curve was obtained via a potentiostat (Autolab PGSTAT30, Eco Chemie B.V, and The Netherlands). The amount of chemisorbed dye was performed by measuring the concentration of dye which was desorbed into a equal volume (20 mL) of diluted NaOH solution (0.1M). The relative difference of absorbance is translated to the relative difference of dye loading of TiO₂ electrode. The Incident phot-to-current conversion efficiency (IPCE) was measured by using a monochromator and a 300 W Xenon lamp with a spectral resolution of 5 nm. Electrochemical impedance spectroscopy (EIS) measurements were performed using AutoLab PSTAT30 with a frequency range of 0.05 Hz - 30 kHz in the dark. The amplitude of ac signal was set to be 10 mV.

e. Photocatalytic measurements

Rhodamine B was chosen as model pollutant to evaluate the photocatalytic performance of the samples. 0.05 g of TiO₂ sample was added into a 50mL rhodamine B solution with the concentration of 20 mg/L in quartz photoreactor. The mixed solution was stirred for 30 min in dark to achieve adsorption-desorption equilibrium. Then the reaction solution was irradiated in visible light using 200 W lamp. A glass filter was used as cutoff for short-wavelength components of light. A water-cooling system was performed to maintain the reaction solution at room temperature. The mixture solution was centrifuged and filtered through 0.22-µm Millipore membrane filter to filter out catalysts. Then the concentration of rhodamine B was measured by a UV-vis spectrophotometer with an acceptable error of ± 3%. The absorbance peak of rhodamine B was at 552 nm.

Results and Discussion

a. Morphology Characterization

The morphology of the TiO₂ nanofibers obtained by coaxial electrospinning using PEO as core and PVP mixed with titanium tetraisopropoxide as shell material were investigated. As-spun core-shell (PEO/TiO₂-PVP) composite nanofibers were found to be continuous as shown in Fig 1 (a). The inset is the as-spun core-shell (PEO/TiO₂-PVP) composite nanofibers deposited on aluminum foil. The fibers diameter varied between approximately 40 nm and 190 nm. A high magnified SEM image the core-shell (PEO/TiO₂-PVP) composite nanofibers are shown in Fig 1 (b). The surface of the composite nanofibers is relatively smooth. Fig 1 (c) illustrates the TEM image of these composite nanofibers. There is a thin layer of TiO₂-PVP composite shell uniformly covering the entire length of the core nanofibers (PEO). However, the shell layer is slightly unsymmetrical.

Upon sintering at 450 °C in the air for 1 h, the core-shell (PEO/TiO₂-PVP) nanofibers were converted to hollow mesoporous TiO₂ nanofibers. Figure 1 (e) shows the SEM micrographs of hollow mesoporous TiO₂ nanofibers. The average diameter of synthesized hollow mesoporous TiO₂ nanofibers was measured to be 130 ± 80 nm. PEO which was used as the core material found to be decomposed and removed during sintering, yielding the hollow structure in the core. Meanwhile, the PVP phase present in the shell layer was also found to be decomposed during sintering and produced ceramic TiO₂ with uniform mesoporous in the shell structure. SEM figures 1 (f) and (g) confirmed the formation of hollow nanostructures in the core and also mesoporous surface in the shell. The wall thickness of hollow mesoporous TiO₂ nanofibers was measured to be 28 ± 18 nm with slightly asymmetrical. Cross-sectional view of elliptical tubular tip is illustrated in Fig 1(h). As shown in Fig 1 (d), only Ti and O peaks are seen in the EDX spectrum and the molar ratio of Ti to O is around 1:2, which well agrees with the
stoichiometric ratio of TiO$_2$. The inset is the optical image of hollow mesoporous TiO$_2$ nanofibers after sintering.

The microstructure of the hollow mesoporous TiO$_2$ fibers after sintering was further examined by transmission electron microscopy (TEM). Figure 1 shows typical microstructure of a bundle of hollow mesoporous TiO$_2$ nanofibers. A single hollow mesoporous TiO$_2$ nanofiber is illustrated in Fig 1 (j). The tubular shape and the pores on the surface of hollow mesoporous TiO$_2$ nanofibers were clearly observed. The corresponding crystalline diffraction rings of (101), (004), (200), (105) and (204) in the selected area electron diffraction (SAED) patterns (Fig 1 (k)) confirming that anatase phase of TiO$_2$ nanofibers was formed. It also demonstrates that the hollow mesoporous TiO$_2$ nanofibers were polycrystalline.

As shown in Fig 1 (l), high resolution TEM image revealed the hollow mesoporous TiO$_2$ nanofibers possessed well-crystallized structure and lattice fringes having interplanar spacing of 0.352 nm corresponding to TiO$_2$ anatase (101) plane.

The crystal structures of hollow mesoporous TiO$_2$ fibers were investigated by X-ray diffraction (XRD) (Figure 2). All diffraction peaks at 25.3° (101), 37.8° (004), 48.2° (200) and 54.1° (105) were assigned to pure anatase phase and no crystalline products. The peaks were rather sharp and in excellent agreement with the results from SAED analysis, indicating that the fibers were highly crystalline. There are no additional peaks
observed in the XRD spectrum indicating no detectable impurities.

The average grain size of annealed hollow mesoporous TiO$_2$ nanofibers from the corresponding XRD peaks were determined by Scherrer equation:

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

where $D$ is the crystallite size, $K$ is shape factor and taken as 0.94 for a small cubic crystal of uniform size, $\lambda$ is X-ray wavelength, $\beta$ is full width at half the maximum intensity (FWHM) in radians and $\theta$ is the Bragg angle. The average crystallite size was calculated to be 9.6 nm.

The morphology of regular TiO$_2$ nanofibers was first investigated using SEM. Regular TiO$_2$ nanofibrous mat obtained after annealing at 450°C in the air for 1 h were found to be continuous (Figure 3 (a)). The average diameter of synthesized regular TiO$_2$ nanofibers was measured to be 100 ± 63 nm. The highly crystallinity was observed on the surface of regular TiO$_2$ nanofibers (Figure 3 (b)).

b. Texture property

Figure 4 (a) shows the N$_2$ adsorption-desorption isotherms of the hollow mesoporous TiO$_2$ nanofibers and regular TiO$_2$ nanofibers. All the fibers exhibit the type IV isotherm curves with well-defined characteristic condensation step at P/P$_0$ ~ 0.3–0.5. It clearly indicates that TiO$_2$ possessed mesoporous structure. The point of inflection of P/P$_0$ ~ 0.4 (hollow mesoporous nanofibers) is characteristic of capillary condensation within the uniform mesopores.

The intersection point in N$_2$ adsorption and desorption curves of

| Table 1: Texture properties of Electrospun TiO$_2$ nanofibers |
|---------------------------------|--------|------------|----------------|-------|
| Morphology                     | BET    | Avg Pore   | Total Pore     | Dimensions |
|                                 | Surface area (m$^2$/g) | diameter (nm) | volume (cm$^3$/g) |             |
| Hollow Mesoporous Nanofibers   | 118    | 8.6        | 0.281          | d = 130 ± 180 nm |
| Regular Nanofibers             | 59     | 11.3       | 0.168          | d = 100 ± 63 nm |

$d_w$ is the thickness of mesoporous wall.
hollow mesoporous TiO$_2$ nanofibers demonstrate that there were mainly two sizes of pores on the surface. The two types of mesopores; 3.2 nm and 5.4 nm in hollow mesoporous TiO$_2$ nanofibers were observed in the pore size distribution curve (Figure 4 (b)). This effect is ascribed to the evaporation of two polymers; PEO and PVP that were removed during sintering from core and shell components of the nanofibers respectively. These polymers have different thermal degradation temperature and different size and shape. The evaporation of the polymers from the solution will leave void space/pores inside the structure. The pore size distribution was calculated based on Barrett-Joyner-Halenda (BJH) method. Narrow pore-size distribution with pore diameter of 5.8 nm was observed for regular TiO$_2$ nanofibers. The Brunauer-Emmett-Teller (BET) surface area, average pore diameter and total pore volume are summarized in Table 1. BET study revealed that the hollow mesoporous TiO$_2$ nanofibers had surface area of 118 m$^2$/g, which is about 2 times higher than that of regular TiO$_2$ nanofibers (59 m$^2$/g). The average pore diameter further confirmed the mesoporous structure of hollow mesoporous TiO$_2$ nanofibers. The total pore volumes of hollow mesoporous TiO$_2$ nanofibers and regular TiO$_2$ nanofibers were found to be 0.281 and 0.168 cm$^3$/g respectively, indicating the hollow mesoporous structure improve the porosity of one dimension nanofibers.

The surface area of the commercial P25 (Degussa AG, Frankfurt, Germany) was measured to be 53 m$^2$/g and the comparison of P25 and hollow mesoporous TiO$_2$ nanofibers on the electrochemical properties and photocatalytic activities were also discussed in this report.

c. Photovoltaic performance

Photovoltaic properties of as-prepared TiO$_2$ architectures were evaluated by constructing DSSCs and the overall light-to-electrical energy conversion efficiency was evaluated using the equation $\eta = FF \cdot J_{SC} \cdot V_{OC}/P_{in}$, where FF is the fill factor, J$_{SC}$ is the short circuit current density, V$_{OC}$ is the open circuit voltage, and P$_{in}$ is the incident light power density. Figure 5 shows the photocurrent density vs. voltage (J-V) characteristics of DSSCs based on the hollow mesoporous and regular TiO$_2$ nanofibers.

Fig 6 compares the absorption spectrum of the N719 dye anchored on hollow mesoporous TiO$_2$ nanofibers and regular TiO$_2$ nanofibers. It showed that hollow mesoporous TiO$_2$ nanofibers with high surface area (118 m$^2$/g) absorbed more dye than regular TiO$_2$ nanofibers (59 m$^2$/g). The amount of chemisorbed ruthenium dye (N719) was determined by Beer law, $A = \varepsilon \cdot C \cdot L$ (2)

where A is the light absorbance, $\varepsilon$ is the molar absorptivity, L is the distance the light travels through the material and C is the concentration of absorbing dye molecules. The dye loading of hollow mesoporous TiO$_2$ nanofibers and regular TiO$_2$ nanofibers electrodes were calculated to be 3.86 and 1.68 $\times$ 10$^{-6}$ mol/cm$^2$, respectively. This result revealed that the absorption intensity of dye molecules on the hollow mesoporous TiO$_2$ nanofibers electrode is 2 times more than that of regular TiO$_2$ nanofibers electrode of same thickness, indicating the enhancement of incident light absorption.

The calculated solar cell parameters were given in Table 2.
The short circuit current (Jsc), open circuit voltage (Voc) and fill factor (FF) of the DSSC using the hollow mesoporous fibers were found to be 10.38 mA/cm², 0.758 V and 0.72 respectively. For regular TiO₂ nanofibers based DSSC, Jsc of 8.99 mA/cm², Voc of 0.738 and FF of 0.64, and power conversion efficiency of 4.17±0.08% were obtained. The reduced current density obtained with regular TiO₂ nanofibers was due to insufficient light harvesting by TiO₂ films. Lower surface area of regular TiO₂ nanofibers limited the anchoring of more dye molecules on the surface of TiO₂ films, thus leading to poor optical absorbance. The conversion efficiency of DSSC using hollow mesoporous TiO₂ nanofibers was about 1.4 times higher than that of DSSC using regular TiO₂ nanofibers. The improved energy conversion efficiency was mainly from the increase in Jsc compared to that for regular nanofibers based DSSCs, indicating hollow mesoporous structure facilitates the electron injection density with large interface between dye molecules and nanofibers. The higher surface area is related to the larger amount of adsorbed dyes. Voc is related to the energy gap between Fermi level of semiconductor and Nernst potential of redox couple. For the same film thickness, it is influenced by the electron affinity of semiconductor, ionization potential of dye and the dark current. Raising the conduction band of semiconductor can reduce the recombination loss, which results in higher open circuit voltage. The Voc was found to be improved for the hollow mesoporous TiO₂ nanofibers based DSSC, attributes to better penetration of electrolyte into TiO₂ electrode, which suppressed back electron transfer and enhanced the redox process between dye molecules and electrolyte. The presence of mesoporous structure promotes better contact with electrolyte and more adsorption of the dye in the hollow nanofibers. The retardation of surface recombination between conduction band electrons and I₃⁻ species in the Nernst potential of electrolyte in hollow mesoporous nanofibers should be able to offset the adverse shift of the band edge toward positive potential and produce a net Voc gain of about 20 mV. In literature, TiO₂ nanorods/nanofibers based DSSCs was reported to have the efficiency η up to 7.2%, which was however achieved using the C101 dye. C101 dye possesses heteroleptic polypyridyl ruthenium(II) complex structure, is characterized by a high molecular extinction coefficient that facilitated for conversion efficiency of 7.2%. Efforts aiming at decreasing the diameter of nanofibers and thus increasing the roughness factor of fibrous photoelectrode are currently pursued by us.

Incident photo-to-current conversion efficiency (IPCE) of device fabricated by hollow mesoporous TiO₂ nanofibers and regular TiO₂ nanofibers are showed in Figure 7. The IPCE value was determined by IPCE (λ) = LHE (λ) \( \phi_{\text{inj}} \eta_c \), where LHE (λ) is the light harvesting efficiency for photons of the wavelength λ, \( \phi_{\text{inj}} \) is the quantum yield for electron injection and \( \eta_c \) is the electron collection efficiency. The maximum IPCE was increased from 58.6% to 67% at 520 nm by hollow mesoporous TiO₂ nanofibers based cells. The improvement of ∼15% suggests that the devices based on hollow mesoporous TiO₂ nanofibers have more electrons injection and better electron transportation behaviour than that of regular TiO₂ nanofibers. Although the electron transportation obtained with the single-crystal electrode is theoretically higher than that obtained from polycrystalline form due to the lack of domain boundaries and defect in the single crystal, Gratzel et al. demonstrated that the IPCE value obtained with the single-crystal TiO₂ anatase electrode was much smaller than that of polycrystalline TiO₂ anatase electrode. This dramatic improvement is mainly due to the better light harvesting of the dye-sensitized polycrystalline. A. J. Frank et al. further
proved that anatase film was 25% and 14% higher of rutile film in the overall energy conversion efficiencies and incident photon-to-current conversion efficiency respectively, which is mainly due to difference in their surface area (i.e. the amount of dye adsorbed). The 1-D hollow dimensional anatase film having high surface area synthesized by electron-spinning method could be one possible solution to the high efficiency electron conductor in the DSSCs.

d. Electronic transport analysis

To investigate the transport characteristic of injected electron in hollow mesoporous TiO₂ nanofibers film and the electron recombination between quasi Fermi level and redox potential, the electrochemical impedance spectroscopy (EIS) technique was carried out. Figure 8 shows a general transmission line model which was developed by Bisquert et al. Various interfaces in DSSC were modeled by parallel RC circuit. Resistance element models charge exchange and constant phase element (CPE) denotes charge accumulation at double layer interface. The constant phase element was modeled by a finite Warburg element. By fitting the impedance spectra, the electron recombination lifetime (τₙ) and collection lifetime (τₜ) were calculated using the correlation τₙ= (RₑQₑ)⁻¹β and τₜ=(RₑQₑ)⁻¹β, where β is the CPE exponent. The effective electron diffusion coefficient was measured as follows: Dₑffective = L²/τₙ.

Figures 9 (a) and (b) illustrate electron diffusion coefficient (Dₑffective) and recombination lifetime (τₑ) in transmission line model, compared to the data of regular TiO₂ nanofibers based DSSC from our previous research work and P25 TiO₂ nanoparticles based DSSC (Jsc = 10.07 mA/cm², Voc = 0.748 V, FF = 0.65, η = 5.02 ± 0.13 %). The fitting results of electron transport resistance Rₑ, electron recombination resistance Rₑffective, chemical capacitance Qₑ are shown in the supporting information. The electron effective diffusion coefficient of hollow mesoporous TiO₂ nanofibers, P25 nanoparticles and regular TiO₂ nanofibers based DSSCs showed a decrease in the following order; hollow mesoporous TiO₂ nanofibers > P25 nanoparticles > regular TiO₂ nanofibers. It suggests that one dimensional (1D) hollow mesoporous TiO₂ nanofibers with closely packing of grains and crystals intergrowth with each other has better directivity. Higher surface area of the hollow mesoporous morphology allowed for anchoring of more dye molecules and better electrolyte penetration which resulted in
faster electron diffusion and shortened the electron collection time. In the electron recombination between Femi level and Nernst potential, the electron recombination resistance of hollow mesoporous TiO₂ nanofibers based DSSCs were found to be higher than that of P25 nanoparticles, and also regular TiO₂ nanofibers based DSSCs. The chemical capacitance of hollow mesoporous TiO₂ nanofibers was slightly lower than that of P25 nanoparticles, which reveals relatively lower charge accumulated in the space charge region of 1D nanostructure. The electron recombination life time was found to be decreased in the following order; hollow mesoporous TiO₂ nanofibers > P25 nanoparticles > regular TiO₂ nanofibers, indicating electron recombination rate is slower in hollow mesoporous TiO₂ nanofibers. It may be ascribed to the higher surface area of hollow mesoporous TiO₂ nanofibers that increase the effective contact point between TiO₂ grains and triiodide in electrolyte. Higher surface area of nanofibers showed a positive effect of electron trapping and de-trapping on the surface of nanofibers and suppresses the electron back reaction. Gratzel et al. demonstrated that the trapping of carrier reduced in TiO₂ fibers and electron transfer rate to the dye oxidized state was higher than that of the TiO₂ nanoparticulate. This accelerating effect is attributed to the particular morphology of pores surrounding the oxide fibers. Triiodide ions in the electrolyte have the possibility to escape faster and farer and to diffuse more freely to the counter electrode in the one dimensional (1D) nanofibers mat.

Although high surface area give rise to defect states in the bandgap that perform as trap centers for the free carriers, this slow down effect was overcome by the large promotional effect of 1D nanofiber structure.

e. Photocatalytic activities

The photocatalytic performance of hollow mesoporous TiO₂ nanofibers was evaluated by carrying out the degradation study on rhodamine B dye. Commercial P-25 (Degussa AG, Frankfurt, Germany) was also adopted for a comparison purpose. The photodegradation profiles (concentration change) of rhodamine B in the presence of hollow mesoporous TiO₂ nanofibers and P25 TiO₂ NPs under visible light irradiation are shown in Fig 10 (a). Rhodamine B was clearly seen stable in the absence of catalysts. The decomposition rate (C/C₀) of hollow mesoporous TiO₂ nanofibers was observed to be higher than that of P25. Using Langmuir-Hinshelwood model, the degradation profile of
Conclusions

Electrospinning has so far been used for producing anatase 1D TiO$_2$ in either hollow form or mesoporous structure. Herein we demonstrated for the first time that the individual anatase TiO$_2$ fiber was possessed with both hollow and mesoporous structures by selecting suitable polymers, optimising the polymer/precursor ratio and post-process condition. Annealing of core-shell nanofibers prepared using PEO/TiO$_2$-PVP at 450°C for 1 h at a heating rate of 2°C /min yielded hollow mesoporous structure in TiO$_2$ nanofibers. The method presented in this study is the undoubtedly cost-effective approach in making high surface area TiO$_2$ nanofibers by electrospinning, and also potential alternative to the currently available methods like hydrothermal synthesis, conventional electrospinning and template assisted fabrication.

Compare to regular TiO$_2$ nanofibers based DSSCs, the enhancement of power conversion efficiency was observed in hollow mesoporous nanostructured TiO$_2$ fibers, due to more dye loading and faster electron transport. The characteristics of transient photocurrent/photovoltage measurements on hollow mesoporous TiO$_2$ nanofibers are under further investigation. Hollow mesoporous TiO$_2$ nanofibers should offer obvious advantages that would inspire for new developments in the design of high efficient heterojunction structures in DSSCs and hybrid solar cells applications. The hollow mesoporous TiO$_2$ nanofibers also showed higher catalytic activity than that of TiO$_2$ nanoparticles, which is attributed to its higher surface area that enabled the strong interactions between the TiO$_2$ and dye. Studies of the catalytic mechanism of TiO$_2$ nanofibers on the various organic pollutants and relation between materials morphology and surface structure verses organic molecular structures are currently under investigation.

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Notes and references