Erbia-modified electrospun titania nanofibres for selective infrared emitters

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Abstract
Tetraisopropyl titanate (TPT) was mixed with a solution of polyvinylpyrroli-
done (PVP) and the solution electrospun into nanofibres. Thermal annealing at
900 °C was used to pyrolyse the PVP, leaving nanofibres of rutile-phase titania.
Erbium (III) oxide particles were also added into the solution before electrospin-
ning, and selectively modified the near-infrared optical properties of the titania
nanofibres as verified by both absorption and emission spectra. We thereby
demonstrate the production of high-temperature optically functionalized nanos-
tructures that can be used in a thermophotovoltaic energy conversion system.

1. Introduction

Electrospun nanofibres have potential for use as biomaterials, sensors, photovoltaic cells,
filtration media, and mechanical supports for other materials [1]. Surface modifications of
electrospun nanofibres have been demonstrated [2–6], and the incorporation of particles within
electrospun nanofibres has also been reported [7, 8]. Recently the electrospinning process has
been used to make hybrid polymer, ceramic, and metal oxide nanofibres and tubes [9–15].
The emphasis here is on the production of titania nanofibres with selectively modified optical
properties for use in energy conversion and utilization systems.

One of these potential applications, thermophotovoltaics (TPV), is a promising energy
conversion technology for the direct production of electricity from the infrared (IR) light
radiated by a hot emitter [16–25]. The salient features of an idealized TPV system are a
source of thermal energy, an emitter, and an IR photovoltaic cell which serves as the collector.
The origin of the thermal energy is unrestricted, and can range from industrial waste streams

and automotive exhaust gases to concentrated sunlight and radioisotope sources. There are no moving parts, implying low maintenance costs, and little noise or pollution beyond that intrinsic to the source of the thermal energy. This technology is ideally suited for power generation in space, in remote locations on the Earth, and in co-generation systems. Ideally, emitters should be isothermal and efficient at producing light that can be absorbed and converted to electricity by the photovoltaic collectors. The thermal properties and spectral distribution of light from the emitters play key roles in enabling this technology to advance.

Our approach is based on the use of nanofibres with spectral outputs tuned to emit near the bandgap of GaSb and other commercially available IR photovoltaic cells. 'Selective emitters' are superior to black-body-like (grey-body) emitters which emit much of their light in the wrong regions of the spectrum for efficient energy conversion by the collectors. Grey-body TPV system designs rely on spectral control devices such as optical filters placed between the emitter and collector to reflect the low- and high-wavelength light which cannot be utilized by the collector. These optical filters and their ancillary structures add more components and kinds of materials to the TPV system making it more complex and harder to manufacture, and potentially limiting its lifetime. We are investigating a conceptually simpler approach that utilizes nanofibre selective emitters that do not require optical filters since they already emit a narrow-band spectrum.

An additional benefit with nanofibres is that the selective emitter is in a form where the surface area (responsible for net emission to the collector) is maximized while the volume (responsible for re-absorption of light and thereby preventing it from reaching the collector) is minimized. An isothermal emitter is advantageous in that cooler regions do not re-absorb the light from hotter parts of the structure. A nanofibre is essentially an isothermal surface with very little volume. Isothermal nanofibre-based selective emitter structures with high ratios of surface area to volume should significantly increase TPV system performance. The final major benefit of using nanofibres for this application is that they are self-supporting. This eliminates the need for a substrate, and therefore the associated spectral 'shine through', that has hampered previous selective emitter schemes for TPV.

In this work, continuous nanofibres of titania and of titania modified with erbium oxide were fabricated by electrospinning followed by thermal pyrolysis. Erbia is a candidate selective emitter for GaSb TPV collectors. Titania is transparent in the near-IR regions where erbia emits, which is one of the reasons it was selected for this study. It is also thermally stable at the temperatures of interest here. The goal of this work is to demonstrate the synthesis and characterization of high-temperature nanoscale materials with optical properties tailored for TPV applications.

2. Synthesis

Tetraisopropyl titanate (TPT) (TYZOR® TPT, from Dupont) was mixed with a 10% solution of polyvinylpyrrolidone (PVP) (average MW 360 000 from PolySciences, Inc.) in absolute ethanol. The mixture ratio of TPT to the PVP solution was varied from 0.008 to 1.38 by weight. The mixtures were then placed in a vertical pipette and electrospun into nanofibres using an electric field of $1 \, \text{kV cm}^{-1}$. Metal washers, with inside diameter 13.5 mm and outside diameter 31 mm, or aluminium foils were used as substrates onto which the nanofibres were spun. The fibres were allowed to hydrolyse in air for 12 h and were then heated in air to pyrolyse the PVP, leaving fibres of titania.

The major factor studied for controlling the nanofibre size and shape is the TPT:PVP ratio. We therefore kept the other parameters constant (voltage, geometry, etc). Solvent evaporation is very important in determining how the electrospinning process behaves, and is not completely
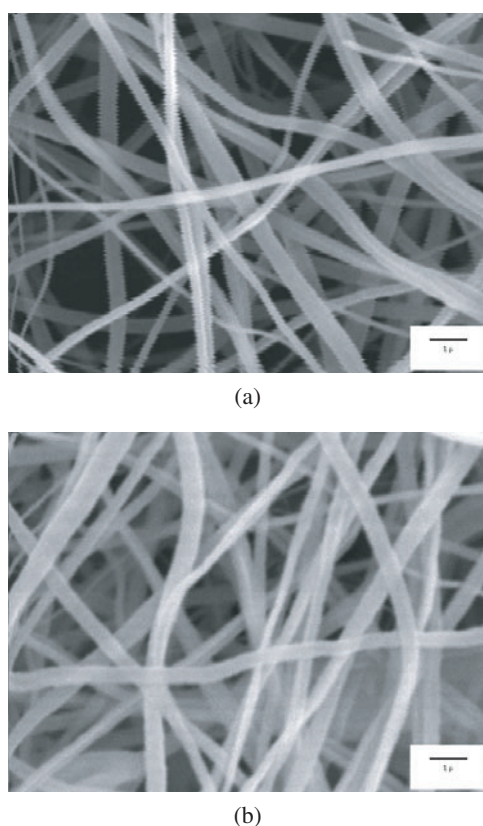
(a)

(b)

Figure 1. Scanning electron microscope images of self-supporting and continuous titania nanofibres after pyrolysis. These structures result from electrospinning TPT/PVP solutions with ratios of (a) 0.2 and (b) 0.4 by weight. The scale bar in both panels is 1 μm.

understood. In the present case, we chose a convenient solvent that would solvate the PVP and held this solution constant. We then subsequently varied the amount of TPT in a controlled way to arrive at titania nanofibres. For erbia-doped titania nanofibres, a 0.4 TPT/PVP weight ratio was used and erbium (III) oxide powder (Strem Chemical, Inc.) was added to the mixture before electrospinning. Fibres made with an erbia/TPT ratio of 1.0 by weight were used for the experiments described below.

3. Characterization

A Nicolet Fourier transform infrared bench (FTIR, Nexus 670) was used in both the near- and mid-IR regions. Thermogravimetric analysis (TGA, TA Instruments 2950) using a temperature ramp of 10 °C min^{-1} from 25 to 1000 °C was performed in air. TGA data (not shown) indicate that after pyrolysis, neither the titania nor the erbia-doped titania nanofibres show significant weight loss (<6%) up to 1000 °C in air. It is important that these materials maintain their thermal integrity in nanofibre form for TPV applications. Structural information on the fibres was provided by scanning electron microscopy (SEM, JEOL JEM-5310) and x-ray diffraction (XRD, Philips PW 1710). Compositional studies of the nanofibres were performed with x-ray photoelectron spectroscopy (XPS, Kratos ES 300). It should be noted that before pyrolysis,
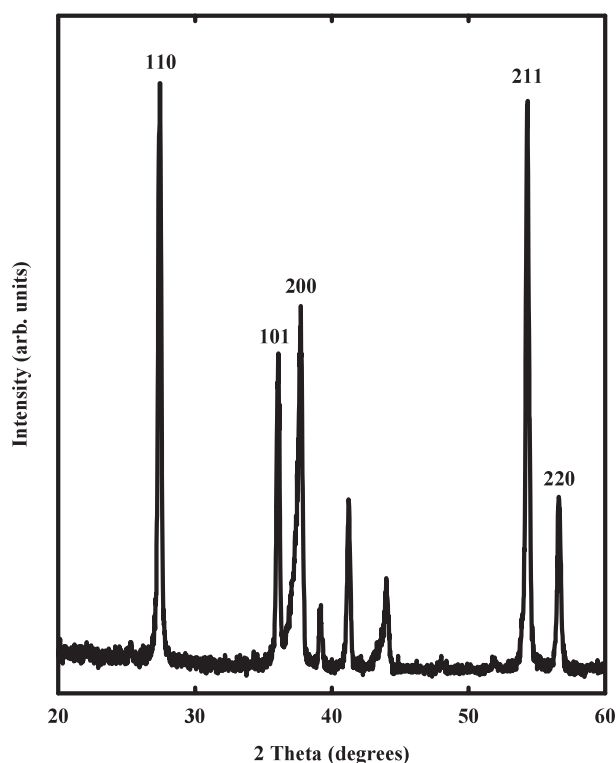
Figure 2. The x-ray diffraction pattern from titania nanofibres after 900 °C pyrolysis. The major assigned features correspond to the rutile form of titania.

the fibres contain the polymer and are not useful for TPV applications (which require heating). Therefore, we did not study the fibres in detail before pyrolysis.

Scanning electron microscope images of the titania fibres after pyrolysis are shown in figure 1 for two TPT/PVP weight ratios. This ratio plays an important role in determining the nominal diameters of the resulting fibres. At a TPT/PVP ratio of 0.008 (not shown), continuous titania fibres cannot be produced by electrospinning. By increasing the TPT/PVP ratio to 0.02, we can form titania nanofibres with diameters less than 100 nm with relatively rough surfaces (not shown). We find that 0.02 is the critical TPT/PVP ratio for forming titania nanofibres after pyrolysis under the conditions used in this work. Increasing the TPT/PVP ratio further leads to an increase in the diameter and morphological homogeneity of the titania nanofibres as seen in figure 1 for (a) 0.2 and (b) 0.4 weight ratios. Increasing the TPT content above a weight ratio of 0.8 leads to fibres with diameters approaching or exceeding the micron range. The segments of titania nanofibres shown in figure 1 extend outside the images and have very large length-to-diameter ratios. These nanofibres are also self-supporting. For producing rare-earth-modified nanofibres, a TPT/PVP ratio of 0.4 is chosen. It should be noted that the erbia particle sizes are not well controlled (we use the powders as received), but this does not appear to be an issue for our intended TPV application.

Titania has three crystalline phases: brookite, anatase and rutile. The titanium atoms occupy sites inside deformed oxygen octahedra, and it is the number of shared edges of these octahedra that defines the crystal structure. We expect the rutile phase to be predominant in our nanofibres after 900 °C pyrolysis, and this was verified by XRD. As shown in figure 2,
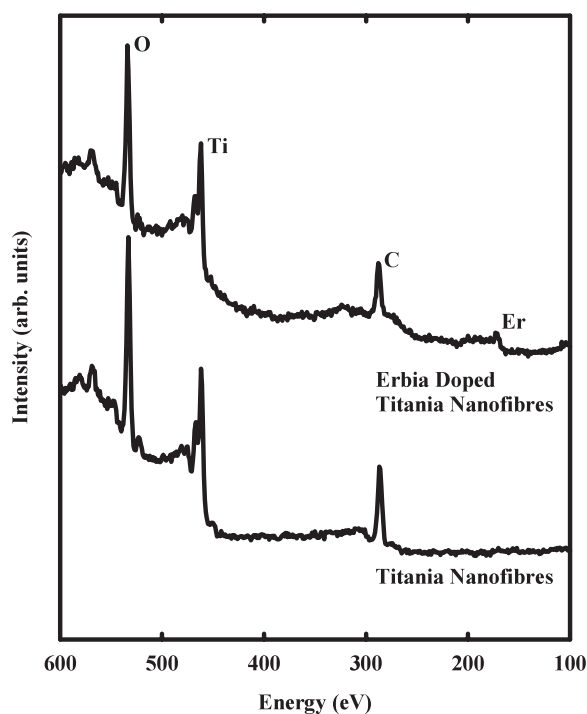
Figure 3. X-ray photoelectron survey scans of titania nanofibres and of those incorporating erbia particles after pyrolysis. Adventitious carbon could not be removed by ion sputtering without damaging the nanofibres.

the resulting diffraction maxima are intense. The main diffraction peaks labelled in figure 2 correspond to rutile-phase titania, which is presumably polycrystalline.

XPS was used to investigate the chemical composition of the nanofibres. Survey spectra of pyrolysed titania nanofibres and those incorporating erbia particles are presented in figure 3. These spectra have been vertically displaced for clarity without other background corrections. It is clear that the fibres contain Ti, O, C, and Er (the latter only in the case of the doped nanofibres). The low intensity of the Er signature is attributed to the small amount of erbium present near the surface of these nanofibres (XPS can only probe a few nanometres deep). Higher-resolution scans of the regions containing these features were also collected and analysed. After smoothing and background fitting, the spectral features were integrated and corrected for atomic sensitivity factors. This process yielded the following percentage composition for the surfaces of these erbia-doped nanofibres: O: 44%; C: 39%; Ti: 15%; Er: 2%. Removing the adventitious carbon with argon ion sputtering without damaging the nanofibre structures proved to be impossible.

To demonstrate that we can modify the optical properties of electrospun nanofibres by changing the precursor solution, erbia-doped fibres are analysed by the FTIR method. The near-IR absorption spectrum of titania nanofibres is essentially featureless, whereas erbia powder has strong absorption features as shown in figure 4. It is also clear that the strong absorption features of erbia-doped nanofibres after pyrolysis are essentially identical to those of erbia powder. These spectra have been shifted vertically for clarity, but no background fitting has been performed. The incorporation of rare-earth particles into nanofibres is therefore an effective way of tailoring the IR signature of the resulting non-woven mats. It should be noted
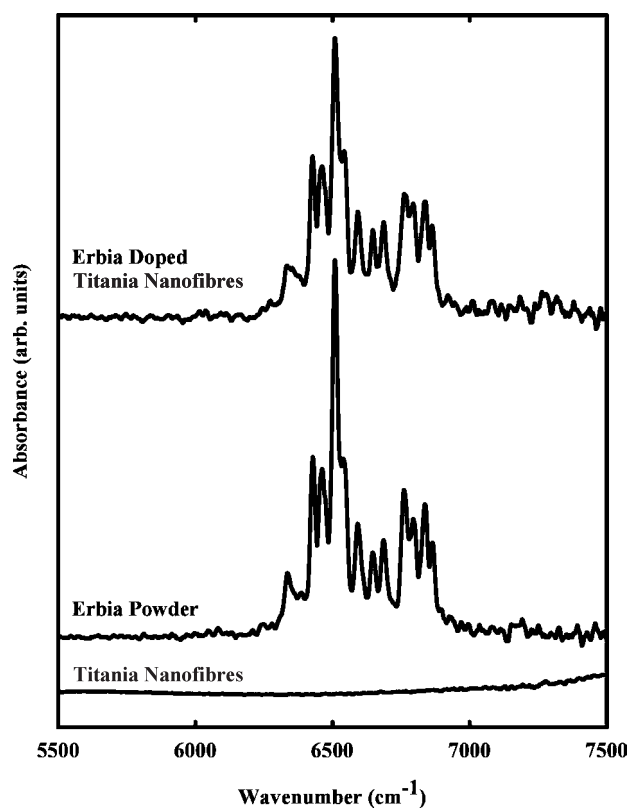
Figure 4. Near-IR absorption spectra of pyrolysed titania nanofibres, erbium oxide powder, and
nanofibres pyrolysed from an electrospun mixture of PVP, TPT, and erbia. Note how closely the
spectrum of titania nanofibres containing erbia particles matches the spectrum from erbium oxide
powder, with no interference from the transparent nanofibre support.

that these IR data do not imply erbia concentration, since we did not control the amount of
material sampled in each case (powders versus nanofibres).

Transmission/absorption spectra such as those of figure 4 are insufficient if we are going
to achieve nanofibre-based selective emitters for thermophotovoltaics. We must measure the
emission spectra of erbia-doped nanofibres while they are heated in air in order to verify that
they emit selectively as expected. To accomplish this, the emitted IR light is collected using
the optics from a Raman system and sent into our FTIR bench through an external port. The
nanofibres reside in a quartz tube and are heated convectively by hot off-gases from a propane
flame. Estimates of the nanofibre temperature are made with a type-K thermocouple (0.005
inch diameter wires) inserted through a small hole in the wall of the tube and fixed with high-
temperature cement. The highest temperature that we can achieve with this proof-of-concept
apparatus is around 800 °C, with temperature stability good to about 5 °C.

We present IR emission spectra in figure 5. Note the *very low temperatures* as compared
to those for standard TPV designs (>1000 °C operating temperatures). It is our hypothesis
that dispersing the rare-earth species in a nanofibre mat will significantly improve selectively
emitted power density by increasing the surface-to-volume ratio and achieving isothermal
conditions. This, in turn, should allow TPV systems to operate at lower temperatures than
those for the current state-of-the-art designs in thermophotovoltaics. It is obvious in figure 5
that our initial attempts at performing emission spectroscopy on self-supporting nanofibres are
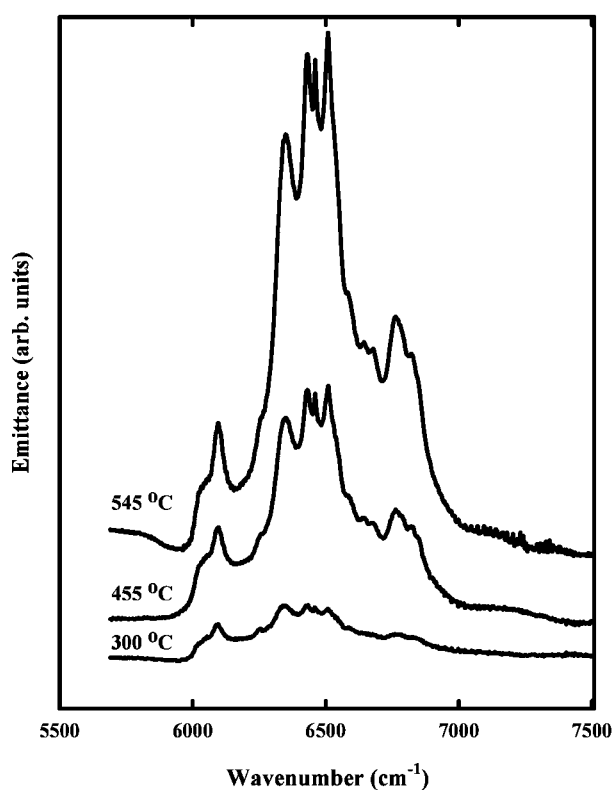
Figure 5. Near-IR emission spectra from erbia-doped titania nanofibres at different temperatures. The fibres are in the form of a self-supporting mesh situated in a quartz tube and heated convectively by hot gases from a remote propane flame. The temperature of the region containing the nanofibres is measured with a small thermocouple.

successful. It is interesting that the relative intensities and linewidths of the emission peaks in figure 5 differ from the absorption spectra of figure 4. The emission spectra of figure 5 cut off at the low-energy end due to the limited throughput of the external optics that we use for this experiment. The spectra of figure 5 have been shifted vertically for clarity and backgrounds have been subtracted. These backgrounds are due to unavoidable heating of components of the spectrometer by the hot gases from the flame, which in turn behave as grey-body emitters.

4. Summary discussion

Thermophotovoltaic systems are simplest and most efficient when the emitters produce light in the range of wavelengths that the collectors can absorb to produce electrical energy; i.e., the emitters are spectrally selective. The nanofibre approach described here has the potential to provide significant advances in thermophotovoltaic technology. Although the physics of the selective emission process is not completely understood, there are some common features in the case of rare-earth systems. The main requirement is that the rare-earth elements reside in an environment in which they have strong ionic character. The electronic structure of erbium, for example ([Xe]$4f^{12}5d^{0}6s^{2}$), is dominated by high-angular-momentum configurations when ionized as Er^{+3}. Electronic transitions within the 4f levels are possible, resulting in the

emission of light. However, structures currently made from these oxide materials suffer from mechanical instability and low thermal conductivity, making them incompatible with standard TPV designs.

We are in the process of improving the mechanical stability, thermal conductivity, and overall emission efficiency of rare-earth selective emitters using nanofibres. The major advantages of nanofibres for these applications are their large surface/volume ratio, their large aspect ratio (length/diameter) which enables us to incorporate them into structures, their self-supporting nature, and the overall simplicity of the electrospinning process. Nanofibre electrospinning technology provides the key to more efficient low-temperature thermophotovoltaic systems using existing selective emitter materials. Here we have presented the synthesis of erbia-doped electrospun titania nanofibres and their characterization by several techniques, including novel near-IR emission spectroscopy. These material development efforts may lead to significant advances in TPV energy conversion technologies by eliminating the reliance on spectral control filters and other energy recuperation strategies.

Acknowledgments

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