Supplementary Information (SI) for Nanoscale.

Supporting Information

Ecofriendly Fabrication of Organic-Inorganic Fibers as Template for Hollow Titanium Oxide Structures via Electrospinning and Magnetron Sputtering

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Experimental section

Materials. Pullulan (η= 15.0 ÷ 180.0 mPa s, 10% in H_2O at 30 °C, TCI Europe); Polyamide 6,6 (Zytel® E53 NC010, DuPont); hexafluoroisopropanol (HFIP) (99 %, Fluorochem); phosphorus pentoxide (P_2O_5) (99 %, SigmaAldrich) were all used as received.

Fabrication of pullulan electrospun mats.

Electrospun mats were produced from a 19 % w/v solution of pullulan in MilliQ water. The electrospinning process utilized an in-house apparatus consisting of a high-voltage power supply (Spellman, SL 50 P 10/CE/230), a syringe pump (KDScientific 200 series, Massachusetts, USA), a glass syringe, a stainless-steel blunt-ended needle (inner diameter of 0.5 mm) connected to the power supply electrode, and a grounded steel plate collector (6.5 × 6.5 cm^2). The entire system was housed within a glove box (Iteco Eng., Ravenna, Italy, 100 × 75 × 100 cm^3) equipped with a temperature and humidity control system. The electrospinning process was conducted at a temperature of 23 °C and a relative humidity of 43 %. The solution was fed at a flow rate of 15 µL min^{-1}, with an applied voltage of 20 kV and a 20 cm gap between the needle outlet and the collector. Mats comprising randomly arranged nanofibers with a thickness of 200 µm were collected and cut into square pieces measuring 2x2 cm^2. Each piece was inserted into an aluminum frame to ensure the presence of a conductive border, necessary for the subsequent magnetron sputtering process.

Magnetron sputtering of Ti on electrospun mats.

The sputtering of Ti on the surface of as-spun pullulan nanofibers was performed by means of DC magnetron sputtering system manufactured by Microsplav OOO (Tomsk, Russia). The system is equipped with three sputtering sources (placed at 120 degrees to each other and at the same time directed towards the sample) and the Ti targets (> 99,1 c.p. grade 1 Ti) with a diameter of 75 mm were used for the deposition. The process was performed by applying a 1.5 A direct current and an argon pressure of 0.267 Pa for a deposition time of 12.30 min. The mat was mounted on a rotable metal platform for a more homogeneous deposition of the coating. The deposition was performed on a single face or on both faces (2 steps: first deposition, rotation of the sample at atmospheric pressure, second deposition) of the electrospun mats.

Characterization of Ti sputtered electrospun mats.

Scanning electron microscopy (SEM) was carried out by a FEG-SEM Tescan Mira 3 at an accelerating voltage of 15 kV. Samples were gold-sputtered for 45 s before the analysis. The distribution of fiber diameters was determined by measuring around 150 fibers using ImageJ software, and the results were given as the average diameter ± standard deviation. The Energy Dispersion X-ray Spectroscopy (EDS) was performed on the surface of as-spun, one-side, and two-side coated mats as well as along the thickness of one-side and two-side coated mats using a Bruker XFlash 630M at low vacuum conditions. For the analysis of the thickness, the mats were vertically fixed on the stub. No gold sputter-coating was performed before the analysis.

Atomic Force Microscopy (AFM) analyses on as-spun and one-side Ti sputtered mats were performed using a Park NX10 system, Korea, in noncontact mode.

Thermogravimetric analysis (TGA) was carried out using a TGA Q500 thermogravimetric analyzer (TA Instruments, New Castle). Samples were subjected to an isothermal step at 60 °C for 150 min, followed by a heating ramp up to 700 °C with a heating rate of 10 °C/min in a N_2 atmosphere.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on two-side sputtered mats by means of a VG Microtech Ltd. (Uckfield, UK) with a CLAMII analyzer, using an Mg $K_{\alpha1,2}$ X-ray source (1253,6 eV). The X-ray source in the standard conditions had been working at 200 W, 10 kV, and 20 mA. The base pressure of the instrument was $5 \cdot 10^{-10}$ Torr, and an operating pressure of $2 \cdot 10^{-8}$ Torr was adopted. For acquiring the spectra, a take-off angle of 45° was used with a pass energy of 100 eV for widescans and pass energy of 50 eV for narrowscans. Binding energies were referenced to the C—H level at 285.0 eV of the so-called adventitious carbon.

X-ray diffractograms were collected on two-side sputtered mats using an X'PERT diffractometer pro with PIXcell 1D as a detector. The 2θ range was from 5° to 70°, with a step size of 0.06° and a time of 30 s per step. A CuKα (40 mA, 40 kV) radiation with a wavelength of 0.154 nm was used; the X'Pert HighScore Plus software was used for the integration of the most relevant peaks.

The electrical resistance on the surface of the sputtered samples was measured as a function of temperature (from 20 °C to 80 °C) using a four-probe method and placing them inside a Binder WTB heating chamber.

Development of hollow structures and their characterization.

Hollow structures from two-side sputtered mats were created using two distinct procedures: thermal degradation and the solubilization of sacrificial pullulan fibers. In the thermal degradation process, the mat was heated in air up to 700 °C with a heating rate of 10 °C/min in a TGA furnace. For the pullulan solubilization procedure, 2x2 cm samples were immersed in 2.5 mL of distilled water in a 4 mL Eppendorf, vortexed (VELP Scientifica VX-2500) at 240 rpm for 6 hours to induce polymer solubilization. The supernatant was removed, replaced with 2.5 mL of clean distilled water, vortexed for 30 minutes at 100 rpm, and the supernatant remove. This process was repeated nine times, and the collected inorganic sample was dried overnight at room conditions and then desiccated under P_2O_5 for two days. The structures obtained from both procedures were morphologically characterized by means of SEM-FEG and of a Philips CM 100 transmission electron microscope operating at 80 kV. ImageJ software was employed for the measurement of the wall thickness of hollow nanotubes.

Embedding of two-sides coated electrospun mats in a polyamide matrix.

Mats were coated with polyamide 6,6 through a process consisting of inducing the passage of a 2% w/v polyamide 6,6 solution in HFIP through the pores of the mat in order to favour the formation of a thin and homogenous coating around the fibers. The surface of the resulting samples was characterized by means of FEG-SEM imaging. The samples were cut under liquid nitrogen to investigate their cross-section morphology. The imaging was carried out both before and after 30 minutes of water immersion to enable the solubilization of pullulan.

Results of TGA characterization of as-spun Pullulan mat

The Pullulan electrospun mat was characterized by TGA to evaluate the thermal resistance and the applicability of the material in the desired temperature range. TGA analysis (Figure S1) shows a weight loss of about 10% before 100°C, ascribable to the evaporation of absorbed water, and a single step of thermal degradation starting around 250°C with a temperature of maximum degradation rate at 330°C.

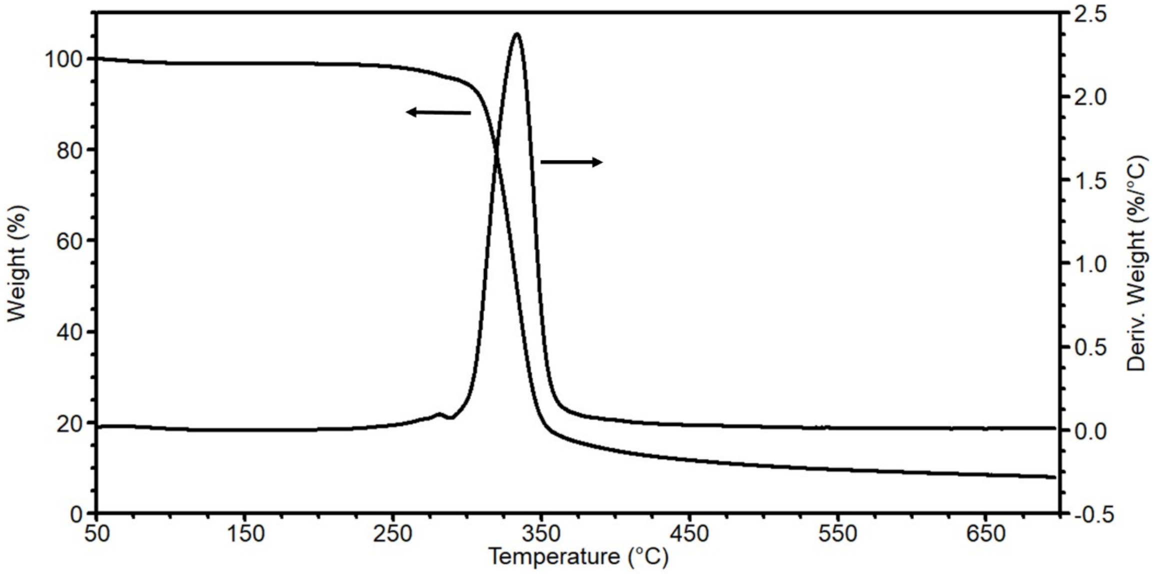

Figure S1. TGA curve and first derivative of as-spun pullulan mat. The analysis is performed in N_2 after drying the samples for 150 min at 60 °C

Fiber diameter distribution

The fiber diameter distribution of the as-spun mats and the sputtered mats were analyzed as described in the experimental section, and results are reported in Figure S2.

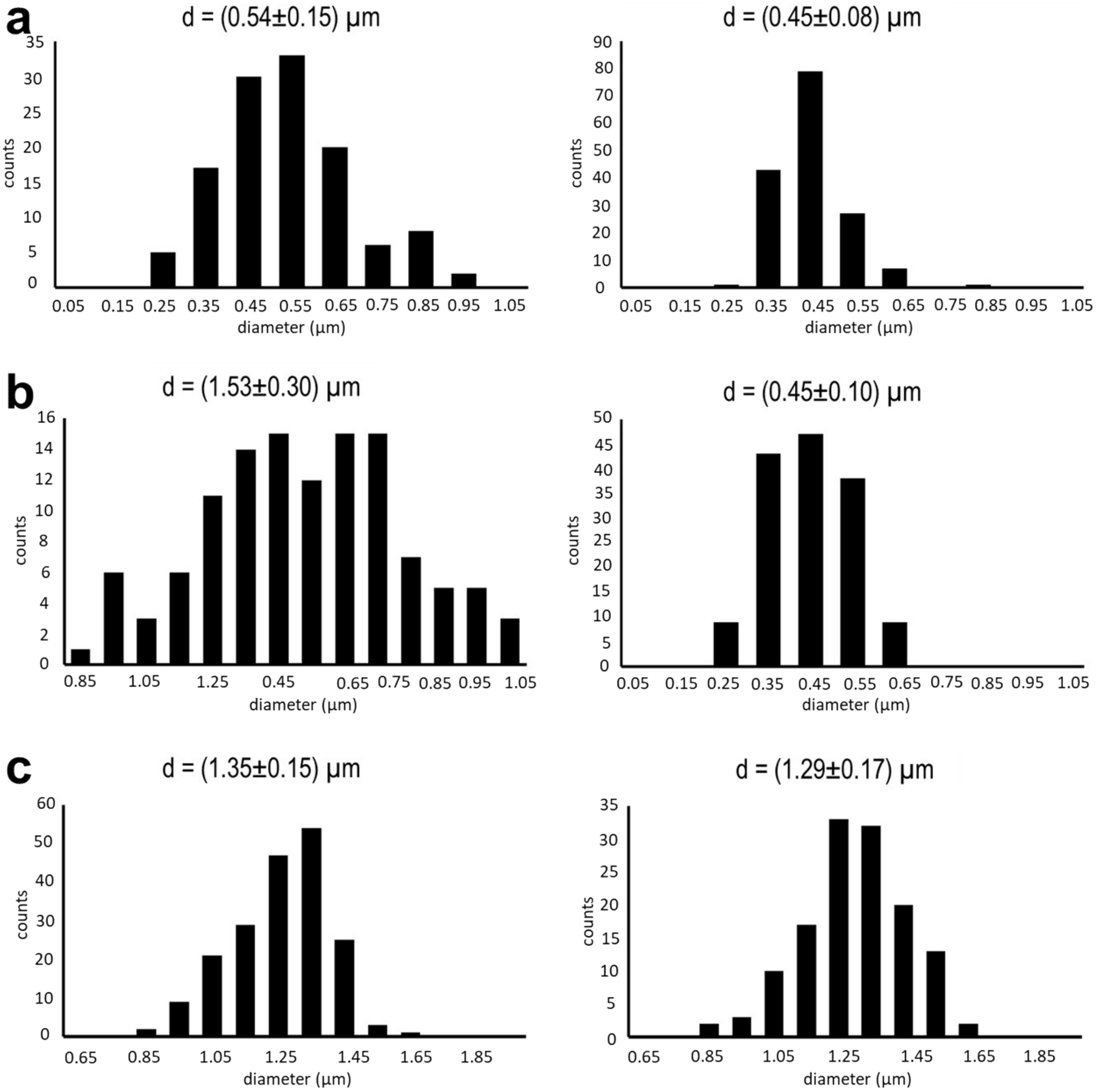

Figure S2. Fiber diameter distributions on the two faces of the as-spun mat (a), one-side sputtered mat (b), and two-side sputtered mat (c).

EDS analysis

Table 1. Percentage atomic contents of elements detected with EDS analysis on as-spun and Ti-sputtered mats.

	C	O	Ti
As-spun mat	55.7±6.0	44.3±6.6	n.d.
Sputtered face of one-side sputtered mat	5.3±0.5	23.4±2.0	71.4±2.6
Not-sputtered face of one-side sputtered mat	53.2±6.0	46.6±7.2	0.19±0.1
Two-sides sputtered mat	11.8±0.9	27.2±2.5	61.0±2.2

Thermogravimetric analysis of the hollow structures obtained from pullulan water solubilisation

To confirm the complete removal of pullulan after its solubilisation in water, the hollow structures were characterized by means of TGA analysis in N2 atmosphere. The comparison between the TGA curves of two-sides sputtered mat before and after the water solubilisation procedure is reported below. The pullulan characteristic degradation step at 250°C, observed for the two-sides sputtered mat, was not detected in the TGA curve of the hollow fibres, confirming the successful removal of the polymer and the formation of fully inorganic structures.

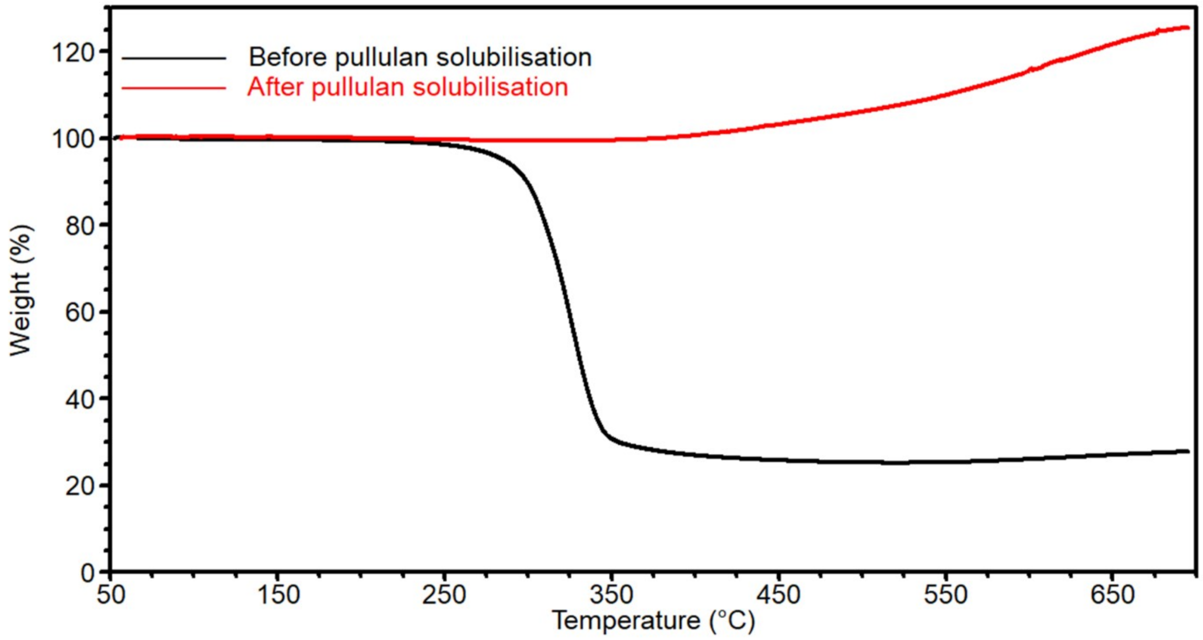

Figure S3. TGA curves in N_2 of two-sides sputtered mat before and after the solubilisation in water of pullulan.

Estimation of overall environmental impact

A preliminary assessment of the overall environmental impact has been carried out considering the experimental procedures applied in this work. It was considered that the energy consumption for a TGA (TA Instrument, Q500) operating from room temperature to 700°C, which is the temperature needed to remove the pullulan, with a heating rate of 10°C/min is estimated to be around 1.35 kWh. On the other hand, the energy consumption of a vortex mixer (VELP Scientifica VX-2500) operating at 240 rpm for 6 hours with a power rating of 80 W is 0.48 kWh. Including the washing of the supernatants in fresh distilled water, the total energy consumption of the water solubilization procedure is estimated to be around 0.84 kWh. The solubilization procedure is therefore characterized by an energy consumption which is the 38% lower than the energy consumed by a thermal procedure performed in TGA.

It is also worth noting that the calcination process required to remove the organic component is typically not performed using TGA. Instead, it generally requires an oven to be maintained at a high temperature (around 700°C) for several hours (i.e. from 4 to 6). Consequently, the energy consumption in this case may be higher than that recorded in TGA.

Regarding the waste generation, the water employed in the solubilization procedure for the washing of the supernatants could represent the only waste of this process and it might be reused after purification. The thermal treatment generates products deriving from the thermal degradation of pullulan, including water vapor, CO_2, CO, and additional volatile carbon-based products.

Considering the lower energy consumption of the water solubilization protocol as well as the lower amount of waste, this approach was assumed to have a lower environmental impact than the thermal treatment performed in this work.