

Electronic Supplementary Information

Single step elaboration of size-tuned Pt loaded titania nanofibres

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Experimental

Synthesis of TiO₂-Nb/Pt nanofibres

The precursor solution was prepared by adding 0.23 g of polyvinyl pyrrolidone (average $M_w \sim 1,300,000$, Aldrich) and 0.04 g of Pt(II) 2,4-pentanedionate (48,0% min., Alfa Aesar) to 3.3 ml of absolute ethanol (puriss., Sigma-Aldrich) and stirring until complete dissolution. A second solution was prepared by mixing 0.52 mL of titanium(IV)isopropoxide (97%, Aldrich), 0.040 ml of niobium ethoxide (99.95%, Aldrich) (10 at% doping) (stored in a glove box) and 1 mL of acetic acid (Sigma-Aldrich). The solutions were degassed by ultrasonication for 15 min, mixed together and stirred for 1 hour and finally poured into the syringe. Electrospinning was carried out in air at 40/50 °C with a standard syringe and a grounded collector plate configuration¹. The distance between the needle tip and the collector plate was 8-12 cm, the applied voltage 10-15 kV and the flow rate 0.5 mL h⁻¹.

The as-prepared fibres were calcined in air at 500 °C for 6h in order to decompose and remove the carrier polymer and allow the Pt nanoparticle growth. The heating rate was modulated from 2 to 10 °C/min in order to tune the platinum size from 3.5 to 10 nm.

Characterisation of Pt/TiO₂-Nb nanofibres

The nanofibre morphology was identified by using a scanning electron microscope (SEM) FEI Quanta FEG 200 equipped with energy-dispersive spectroscopy analysis (EDS) and a JEOL 1200 EXII transmission electron microscope (TEM) operating at 120 kV equipped with a CCD camera SIS Olympus Quemesa (11 million pixels). The samples were

¹ D. Li, Y.L. Wang, Y.N. Xia, *Nano Lett.*, 2003, **3**, 1167.

suspended in ethanol and ultrasonicated before deposition onto carbon coated copper grids for TEM analyses.

Structural characterisation was performed by X-ray diffraction on a PANalytical X'pert powder diffractometer equipped with CuK α radiation ($\lambda = 1.541 \text{ \AA}$). Full profile matching and Scherrer analysis were performed using the FullProf Suite sets of software.

The nanofibres were analysed by X-Ray fluorescence. The samples were pellets of grounded fibres in a H₃BO₃ matrix. The analyses were performed with a PANalytical Axios Max spectrometer fitted with a Rh (4kW) tube. Omnia software and eight analyser crystals (LIF200, LIF220, Ge111, PE002, PX1, PX5, PX4A, PX7) have been used for characterisation and analysis.

Nitrogen adsorption/desorption isotherms were determined at 77 K by means of a Micromeritics ASAP 2020 apparatus after outgassing overnight at 5 $\mu\text{m Hg}$. The specific surface area was calculated using the BET equation and taking 0.162 nm² as the cross-sectional area of one N₂ molecule. The average pore diameter was calculated using the BJH model (desorption branch).

The surface composition of the Pt/TiO₂-Nb fibres was monitored by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 (Thermo Electron). The X-ray excitation was provided by a monochromatic Al K α (1486.6 eV) source. Analysed surface was 400 μm^2 . A constant analyser energy mode was used for the electron detection (20 eV pass energy). The detection of the emitted photoelectrons was performed perpendicularly to the surface sample. Data quantification was performed on the Avantage program. The background signal was removed using the Shirley method. The surface atomic concentrations were determined from photoelectron peaks areas using the atomic sensitivity factors reported by Scofield. Binding energies (BE) of all core levels were referred to the C–C bond of C1s at 284.8 eV.

Raman analysis was performed on a LabRAM Aramis IR² Horiba Jobin Yvon equipped with a He/Ne laser ($\lambda = 633 \text{ nm}$, 17 mW on sample) and an objective $\times 50$ long wide distance.

Figures

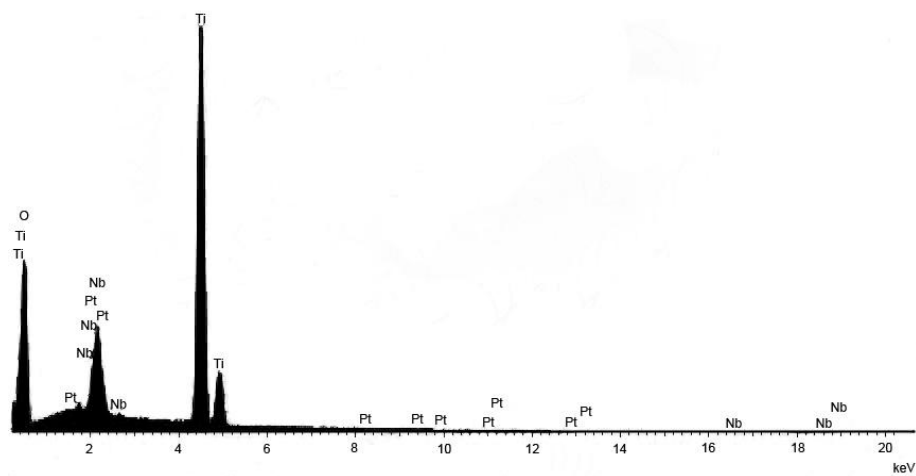


Figure S1. EDS spectrum of Pt/TiO₂-Nb nanofibres.

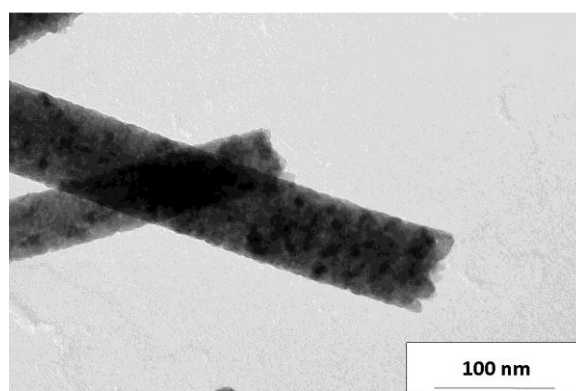


Figure S2. TEM micrograph of TiO₂-Nb nanofibres.

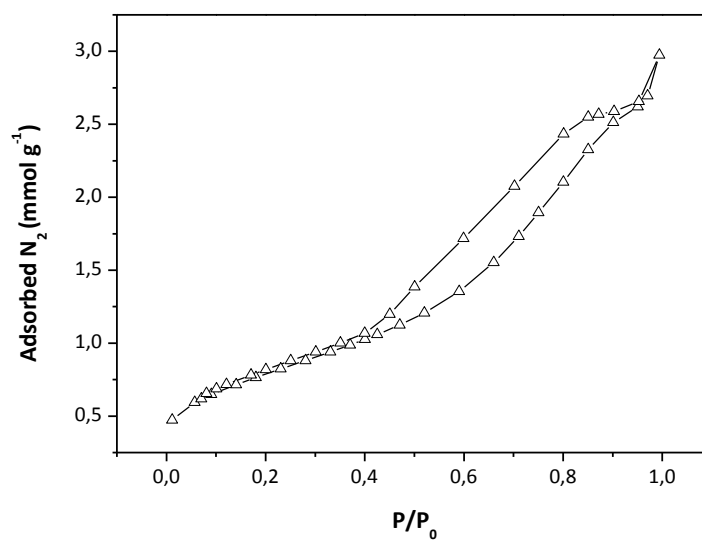


Figure S3. Nitrogen adsorption-desorption isotherms at 77K of Pt/TiO₂-Nb nanofibres.

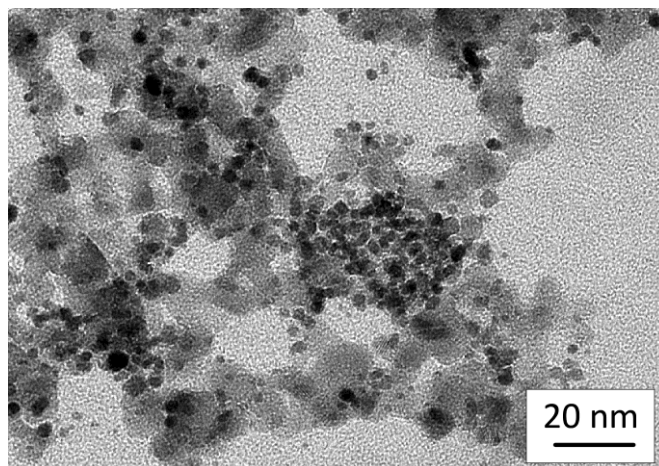


Figure S4. TEM micrograph of Pt/TiO₂-Nb nanofibres after support dissolution in H₂SO₄ 30% at 90 °C for 24 h².

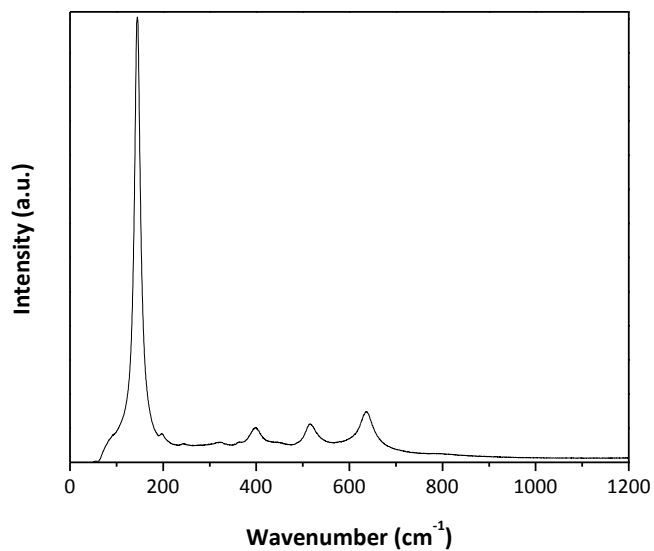


Figure S5. Raman spectrum of Pt/TiO₂-Nb nanofibres.

² Q.-H. Zhang, L. Gao, *Acta Chim. Sinica*, 2005, **63**, 65.

Tables

Table S1. Chemical composition of the Pt/TiO₂-Nb nanofibres obtained by XRF.

Element	wt %
Pt	5.1
Ti	40.0
Nb	5.1
O	49.8

Table S2. Unit cell parameters (in pm) of undoped electrospun TiO₂ nanofibres and Pt/TiO₂-Nb calculated from XRD data.

TiO ₂	a	b	c
anatase	378.81(2)	378.81(2)	950.95(4)
rutile	458.75(12)	458.75(12)	294.77(8)
brookite*	921(3)	539(2)	523(2)
Pt/TiO₂-Nb			
anatase	380.08(5)	380.08(5)	948.07(11)
rutile*	459(1)	459(1)	327(5)
brookite	917.6(4)	546.6(3)	516.9(2)
Pt	389.5(5)	389.5(5)	389.5(5)

*Due to the very low intensity of the reflections of these phases, the calculations could not achieve higher precision.

Table S3. Chemical composition of the Pt/TiO₂-Nb nanofibre surface obtained by XPS.

Name	Peak BE	FWHM eV	at %
Pt4f _{7/2} A	70.7	0.9	1.5
Pt4f _{7/2} B	72.2	2.0	0.4
Pt4f _{5/2} A	74.0	0.9	0.0
Pt4f _{5/2} B	75.5	2.1	0.0
Nb3d _{5/2}	207.2	1.2	4.5
Nb3d _{3/2}	210.0	1.2	0.0
Ti2p _{3/2}	458.8	1.2	27.6
Ti2p _{1/2}	464.5	2.2	0.0
O1s	530.1	1.2	66.0

Table S4. Chemical composition of the TiO₂ undoped nanofibre surface obtained by XPS.

Name	Peak BE	FWHM eV	at %
Ti2p _{3/2}	458.7	1.0	27.8
Ti2p _{1/2}	464.4	2.1	0.0
O1s	529.9	1.2	72.2