

Electronic Supplementary Information

The ability of a fibrous titanium oxophosphate for nitrogen-adsorption above room temperature

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1. Synthesis

All chemicals used were of reagent grade and were employed without further purification. Hydrothermal synthesis of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**1**) was carried out in a Teflon-lined stainless steel vessel (100 mL) under autogenous pressure. Details about its preparation procedure are previously reported (I. Bortun, S. A. Khainakov, L. N. Bortun, D. M. Poojary, J. Rodríguez, J. R. García, A. Clearfield, *Chem. Mater.*, **1997**, 9, 1805).

2. Powder thermodiffraction studies.

Thermal evolution of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**1**) to $\text{Ti}_2\text{O}(\text{PO}_4)_2$ (**2**) in vacuum was monitored by X-ray powder diffraction. The sample was placed in an Anton Paar HTK 1200N oven-chamber on a Panalytical X'Pert Pro diffractometer. Each powder pattern was recorded in the $10 - 40^\circ$ range (2θ) at intervals of ca. 50°C up to 400°C and cooling down to RT. The measurements were done in continuous mode with an effective step and a counting time of 0.013° and 1 s/step , respectively. The temperature ramp between two consecutive temperatures was 5°C/min .

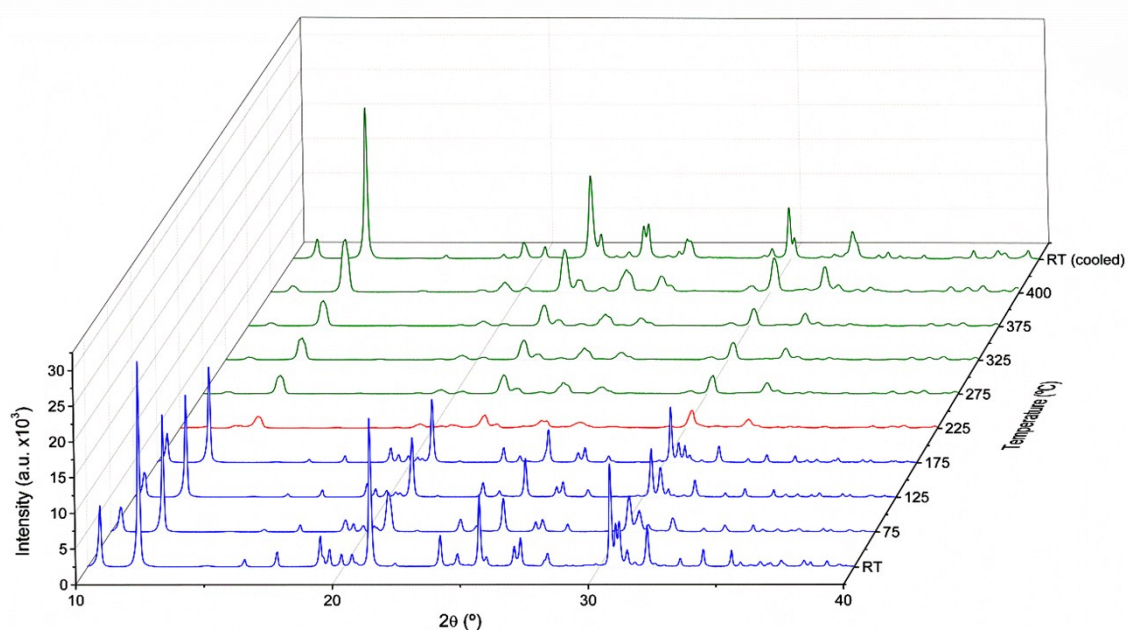


Figure S1. X-ray thermodiffraction patterns recorded in vacuum, heating up from RT to 400°C and cooling down to RT. Colour code corresponding to the structural changes. Blue: compound **1**, red: phase transition of **1** into compound **2**, green: compound **2**.

3. Structural data for $\text{Ti}_2\text{O}(\text{PO}_4)_2$ (**2**)

The X-ray powder diffraction pattern was recorded in vacuum using a Panalytical X'Pert Pro diffractometer with $\text{CuK}\alpha_1$ radiation (1.540596 Å). The sample was finely powdered in an agate mortar. Room-temperature data was collected over the angular 2θ range 5 – 120° in continuous mode, with an effective step and a counting time of 0.013° and 2 s/step, respectively. The structure of compound **2** was solved *ab initio* by using EXPO2014 program (A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio. *J. Appl. Cryst.* 2013, **46**, 1231-1235) and refined using Rietveld method with Topas Academic 5 program (<http://www.topas-academic.net/>). The refinement cycles were carried out with Topas on the free atom coordinates, without using constraints for Ti-O and P-O bonds or O-P-O angles. The final Rietveld plot is given in [Figure S2](#). Crystallographic parameters are summarized in [Table S1](#).

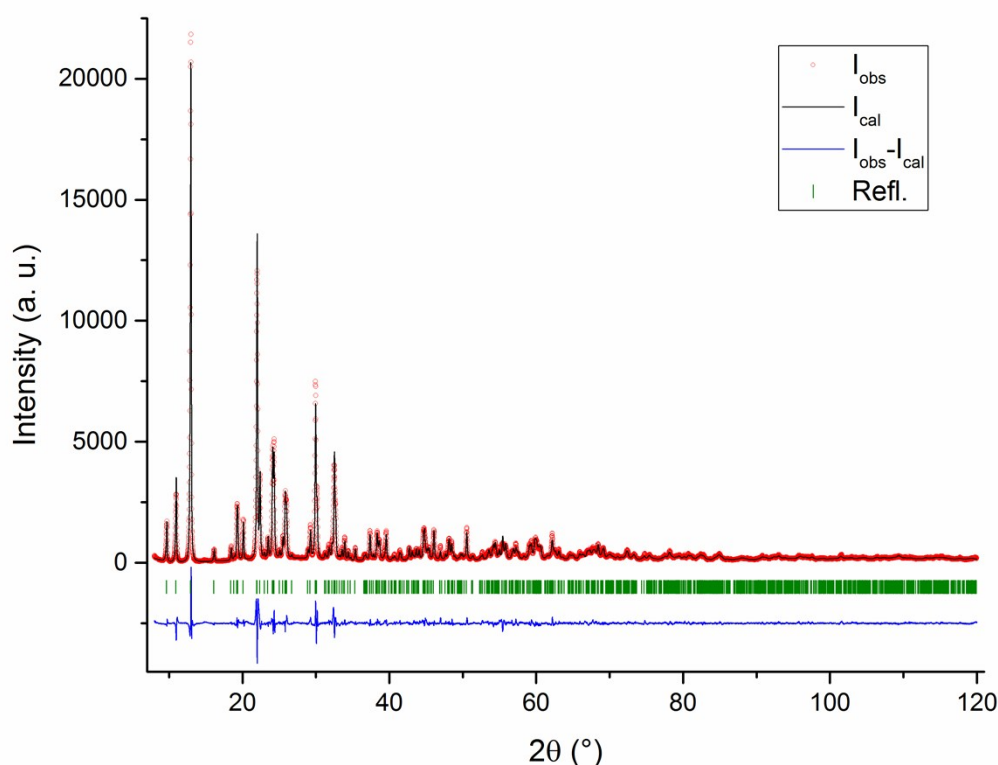


Figure S2. Final Rietveld refinement plot for $\text{Ti}_2\text{O}(\text{PO}_4)_2$ (**2**), showing the experimental (red circles), calculated (black line) and difference profiles (blue line); green marks indicate reflection positions.

Table S1. Crystallographic data and Rietveld refinement summary for compound $\text{Ti}_2\text{O}(\text{PO}_4)_2$ (**2**).

CCDC nos.	1496186
Formula	$\text{Ti}_2\text{O}(\text{PO}_4)_2$
Formula weight (g/mol)	301.68
Crystal system	Triclinic
Space group	<i>P</i> -1
a (Å)	5.0843(1)
b (Å)	8.6121(2)
c (Å)	9.6766(2)
α (°)	74.501(2)
β (°)	76.146(2)
γ (°)	74.488(3)
V (Å³)	386.93(2)
Z	2
R_p (%)	8.91
R_w (%)	11.57
R_B (%)	2.65
GoF	2.32

4. TEM studies.

Transmission electron microscopy (TEM) studies were performed on a JEOL JEM-2100F microscope operated at an accelerating voltage of 200 kV, equipped with a field emission gun (FEG) and an ultra-high resolution pole-piece that provided a point-resolution better than 0.19 nm. The samples for TEM were dispersed in ethanol, sonicated and sprayed on a carbon-coated copper grid and then allowed to air-dry, finally, *Gatan SOLARUS 950* was used before observation.

5. Gas Adsorption experiments.

High resolution N₂ adsorption–desorption isotherms (between 10⁻⁶ and 1 bar) were measured using a volumetric analyzer (ASAP 2020 HD, Micromeritics) equipped with a turbo molecular drag vacuum pump and three pressure transducers (ca. 0.1, 10, 1000 mmHg, uncertainty within 0.15% of reading), allowing high sensitivity in the low pressure range. The samples were previously outgassed under a dynamic vacuum (ca. 10⁻⁵ mbar) at 673 K (1K min⁻¹) for 12 hours to remove moisture. The isotherms were measured at 77 K for textural characterization and above ambient temperature (between 373-573 K) for the evaluation of the nitrogen uptake. The warm and cold free-space correction measurements were performed by using ultrahigh purity He gas (grade 5.0, 99.999% purity). The temperature of the isotherms was controlled using a liquid nitrogen bath (77 K) and an air-assisted oven (373-573 K). Ultrahigh purity N₂ (99.992%) was supplied by Air Products. The Brunauer-Emmett-Teller (BET) theory was used to calculate the specific surface area from the N₂ adsorption isotherms at 77 K (see [Figure S3](#) and [Table S2](#)).

The gas adsorption of the studied sample (i.e., non-porous material) at such high temperatures (ca. 100-300 °C) is quite low, which makes the accurate experimental measurement of the adsorption a delicate and time-consuming process. In order to guarantee the accuracy of the recorded data, all the adsorption isotherms were performed in triplicate. Most importantly, the corrections of the dead volume (free space) of the tubes were performed at each temperature using the helium density of the sample (measured by helium pycnometry), the volume of the empty tube and the mass of the sample, to correct the measurements of the gas adsorbed by the sample at each temperature (measurements of the free space were also recorded in triplicate). This protocol allows us to assure the accuracy of the experimental data.

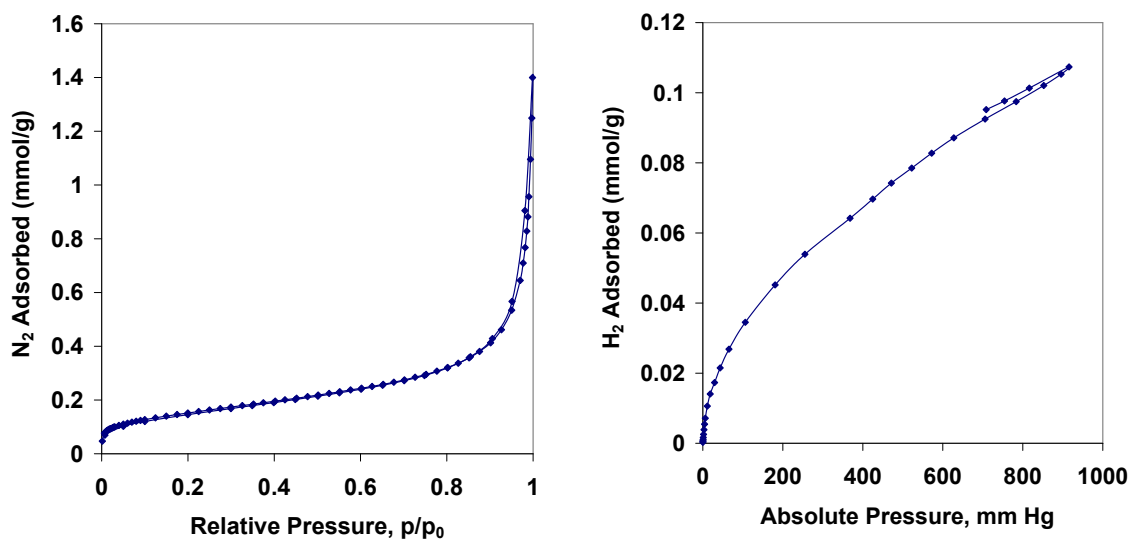


Figure S3. High resolution N₂ (left) and H₂ (right) adsorption-desorption isotherms at 77 K for compound **2**.

Table S2. Main textural parameters obtained from the equilibrium nitrogen adsorption isotherm at 77 K.

He density [cm ³ g ⁻¹]	S _{BET} [m ² g ⁻¹]	V _{TOTAL PORES} ^A [cm ³ g ⁻¹]	Wo N ₂ ^B [cm ³ g ⁻¹]
2.59	13	0.032	0.003

^A Total pore volume evaluated at 77 K at p/p₀ ~ 0.99.
^B Micropore volume evaluated from the Dubinin-Radushkevich equation