

Nanocrystalline NaTaO₃ thin film materials with ordered 3D mesoporous and nanopillar-like structures through PIB-*b*-PEO polymer templating: Towards high-performance UV-light photocatalysts†

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Electronic Supplementary Information

Experimental procedure

Materials

Ta(OBut)₅ (98%), NaOAc (99.99%), glacial acetic acid (99.99%), ethanol, and 2-methoxyethanol were purchased from Sigma-Aldrich. H[C(CH₃)₂CH₂]₅₃C₆H₄(OCH₂CH₂)₄₅OH, referred to as PIB₅₃-*b*-PEO₄₅, was obtained from BASF SE and used as the structure-directing agent.

Synthesis of mesoporous NaTaO₃ thin films

In a water-free container, 40 mg of PIB₅₃-*b*-PEO₄₅ dissolved in a mixture of 1.6 mL of ethanol, 0.4 mL of 2-methoxyethanol, and 0.1 mL of glacial acetic acid are combined with both 232.1 mg of Ta(OBut)₅ and 34.8 mg of NaOAc. Once the solution is homogeneous, films can be produced *via* dip-coating on polar substrates, including quartz and Si(100). Optimal conditions include relative humidities of ~20% and constant withdrawal rates of 1-5 mm/s. For best results, the films are first aged at 300 °C for 12 h and then heated in air using a 40 min ramp to 700 °C.

Characterization

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were taken with a CM30-ST from Philips and a MERLIN from Carl Zeiss, respectively. Wide-angle X-ray diffraction (WAXD) measurements were carried out on an X'Pert PRO diffractometer

from PANalytical instruments. Grazing incidence small-angle X-ray scattering (GISAXS) data were collected at the German synchrotron radiation facility HASYLAB at DESY on beamline BW4 using a MarCCD area detector and a sample-detector distance of ~1820 mm. X-ray photoelectron spectroscopy (XPS) spectra were acquired on a VersaProbe PHI 5000 Scanning ESCA Microprobe from Physical Electronics with monochromatic Al-K α X-ray source and a hemispherical electron energy analyzer. The electron takeoff angle to the sample surface was adjusted to 54°. The C1s signal from adventitious hydrocarbon at 284.8 eV was used as the energy reference to correct for charging. N₂-physisorption experiments were conducted at 77 K using the Autosorb-1-MP automated gas adsorption station from Quantachrome Corporation. Optical absorption measurements were carried out on a Perkin Elmer Lambda 900 UV-vis-NIR spectrophotometer. A substrate made from fused silica and an aluminium mirror served as the reference for transmission and reflection measurements, respectively. The film thickness was determined with an Alpha Step IQ Surface Profiler from KLA Tencor. For crystal structure visualization, the software Crystal Impact Diamond version 3.2h was used.

For photodegradation experiments, 10 mL of an aqueous solution of 15 $\mu\text{mol/L}$ methylene blue (MB) was irradiated with 254 nm light ($P = 8 \text{ W}$) in the presence of either ~170 nm thick PIB₅₃-*b*-PEO₄₅-templated films or nontemplated films with a total area of ~4 cm².

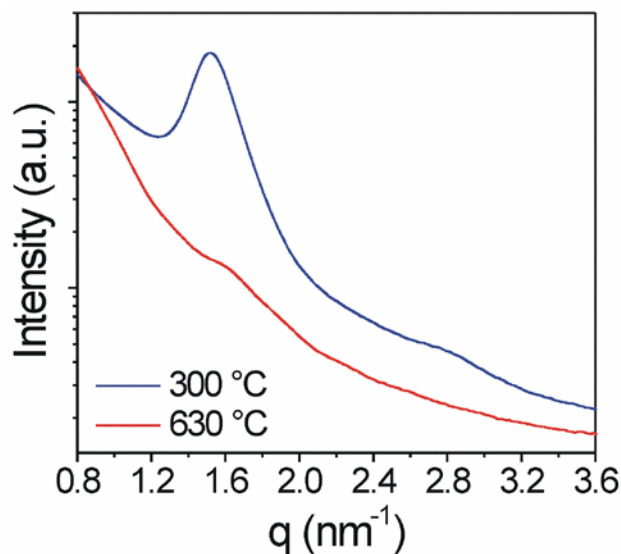


Figure S1. SAXS patterns collected on a PIB₅₃-*b*-PEO₄₅-templated NaTaO₃ thin film heated to different annealing temperatures of 300 °C and 630 °C. Unlike GISAXS, these Bragg-Brentano scans provide only information about the periodicity in the direction normal to the plane of the substrate. The fact that even a weak second order reflection can be observed after 12 h at 300 °C verifies good out-of-plane order. In addition, it can be seen that higher temperatures do not lead to further contraction, because the various sodium and tantalum species that are formed during thermal annealing are virtually fully converted to glassy NaTaO₃ at 300 °C.

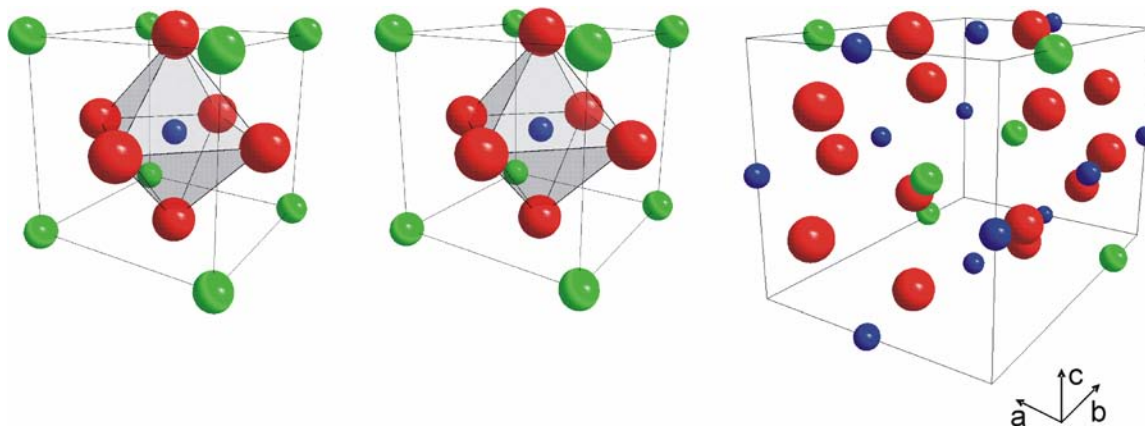


Figure S2. Schemes of the monoclinic (left), cubic (middle), and orthorhombic (right) unit cells of perovskite-type NaTaO_3 . Sodium atoms are shown in green, tantalum atoms in blue, and oxygen atoms in red.

Table S1. Crystallographic data of the monoclinic, cubic, and orthorhombic NaTaO_3 phases according to Joint Committee on Powder Diffraction Standards (JCPDS).

Phase	JCPDS card no.	Space group	a	b	c	α	β	γ
monoclinic	74-2479	$P2/m$	3.8995	3.8965	3.8995	90	90.15	90
cubic	74-2488	$Pm\bar{3}m$	3.9290	3.9290	3.9290	90	90	90
orthorhombic	25-0863	$Pcmm$	5.5130	7.7508	5.4941	90	90	90

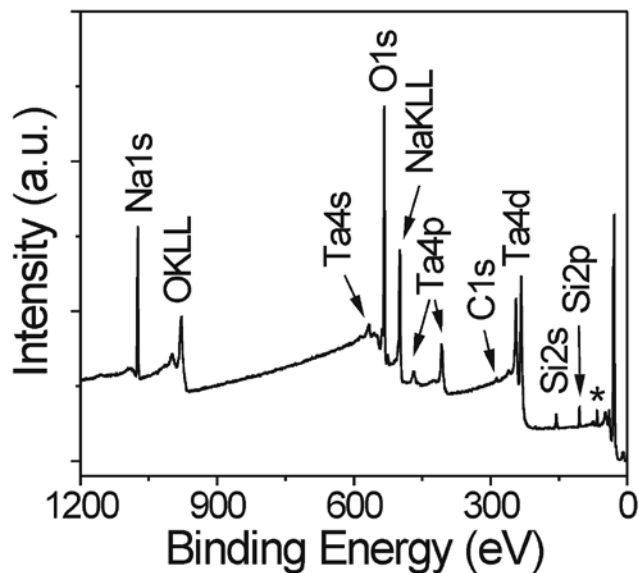


Figure S3. Typical XPS survey spectrum of PIB₅₃-*b*-PEO₄₅-templated NaTaO₃ thin films heated to 650 °C in air. The Ta5s and Na2s regions are indicated by an asterisk. The peaks at lower binding energies can be attributed to the Ta5p, Na2p, Ta4f, and O2s core level regions. Apart from a very weak carbon C1s peak, which we associate with adventitious hydrocarbon at the top surface, only sodium, tantalum, oxygen, and silicon core levels are observed. The appearance of Si-lines is presumably associated with diffusion of silicon across the interior of the films at elevated temperatures; mobile species are always enriched at interfaces due to surface energy minimization reasons.