

Supporting information

Unexpected Adsorption of Oxygen on TiO₂ Nanotube Arrays – Influence of Crystal Structure

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Synthesis of the TiO₂ nanotube arrays used.

TiO₂ nanotube layers were produced by anodization of titanium foils (99.6 % purity) with a thickness of 0.1 mm. Before any electrochemical treatment, the foils were sonicated in acetone, isopropanol, and methanol successively followed by rinsing with deionized water (DI) and drying in a N₂ stream. A three-electrode cell with a Haber-Luggin capillary, a Ag/AgCl (1M KCl) reference electrode, and platinum gauze as a counter electrode was used for electrochemical anodization by means of and a high-voltage potentiostat Jaissle (IMP 88 PC). The electrolyte was 1M (NaH₂PO₄) + 0.5% w.t. HF (pH 4.5) and anodization was carried out at room temperature by ramping the potential from open circuit potential (OCP) to 20 V (500 mV/s) and holding the potential at 20 V for 2 h. Afterwards, the samples were rinsed with DI and dried in a N₂ stream. Thermal treatments (temperature ramping from RT to 450⁰ C at a heating/cooling rate of 30⁰ C/min) of the initially amorphous anatase TiO₂ nanotube layers were carried out using a Rapid Thermal Annealer (Jipelec JetFirst 100). After the ramp-up the temperature of 450⁰ C was hold for 1 h. This procedure leads to the formation of polycrystalline anatase TiO₂ nanotubes. Further annealing treatments result in mixed anatase-rutile TiO₂ nanotubes.

Very brief literature survey about TiO₂ nanotubes.

The literature about TiO₂ nanotubes is dominated by studies devoted to characterize their morphology and by material science applications such as sensor design and photovoltaics.¹⁻⁵ We are not aware of ultra-high vacuum surface chemistry studies. However, the great potential of planar TiO₂ for surface science and catalysis applications⁶ promises fascinating potential for applications in surface chemistry and heterogeneous catalysis on TiO₂ nanotubes. TiO₂ nanotubes were synthesized 10-years after the first observation of C-nanotubes.⁷ Thus, there is an urgent need to keep up with basic research which will open the door for industrial applications. TiO₂ nanotubes obtained by anodized titania supports are open end and intrinsically amorphous. Depending on the annealing temperatures polycrystalline anatase tubes or mixed polycrystalline rutile/anatase tubes can be obtained without damaging the tubular structure. The size of typical crystallites amounts to 40 nm.¹ The large variety of the TiO₂ nanotube morphologies makes them a perfect model system for surface science studies and allows tuning of the catalytic performance towards a given reaction of commercial interest.

Thermal desorption spectroscopy.

The kinetics experiments have been conducted in a standard ultra-high vacuum system equipped with a mass spectrometer.⁸ TDS measurements can be experimentally critical in regard to contributions from the sample holder, etc. Therefore, a number of precautions have been taken.

The mass filter used for TDS is equipped with an 8 mm (O.D.) aperture and the sample (10 x 10 mm) to detector distance amounts to less than one mm.

The sample holder consists of a 4-pin ceramics feed-through with the air side connected to a stainless steel rod which acts as the reservoir for IN₂. The TiNT samples were either mounted on a tantalum plate or directly spot welded on Ta wires. Both versions allow for radiative as well as electron-beam heating of the sample by means of a W-filament mounted behind the sample which is biased by means of a

high-voltage power supply. No significant differences in TDS curves have been observed for the two different sample mounting versions used.

No bulky parts have been used in designing the sample holder, and the metal pins on which the sample is mounted stick directly into the LN_2 reservoir. Furthermore, He gas is fluxed through the LN_2 reservoir which reduced the temperature by $\sim 10\text{-}15\text{ K}^9$ as compared with LN_2 cooling.

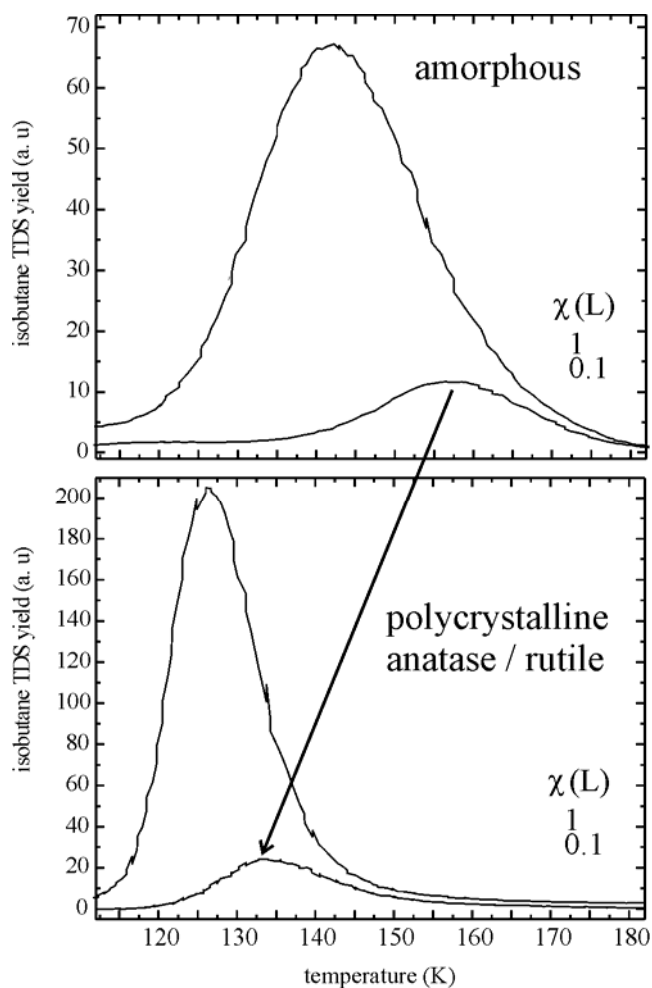
No molecular oxygen desorption traces have been observed from the back side of the samples.

The reading of the thermocouple has been calibrated *in situ* by TDS measurements using the known heat of condensation of the alkanes. Research grade oxygen, CO_2 , and CO are purchased from PraxAir (ND). The research grade alkanes are obtained from Alfa Aesar (Massachusetts). A series of freeze-pump-thaw cycles has been used to purify the alkanes.

Sample cleaning in ultra-high vacuum.

Typically the desorption of CO_2 , CO, CH_4 , and H_2 from a TiO_2 nanotube sample has been detected during the first flashing (cleaning) cycle of a sample in vacuum. The detected gases evolve from the solvents used in the electrochemical sample synthesis process. Similar desorption traces have been observed for all samples studied. Note that no signals have been detected for $m/e = 19$ (F), 32 (O_2), and 43 (alkane fragment). Outgassing the samples reduces the desorption of these contaminations mostly below the detection limit.

The effect of sample cleaning on thermal desorption spectroscopy (TDS) curves obtained for the alkanes was the detection of a single structure at 105 K (alkane physisorption on solvent layer) independent of the tube polymorph. The shape and position of the TDS traces changed significantly after the flashing (cleaning) cycles.



Alkanes

The figure above depicts iso-butane TDS data obtained for the cleaned amorphous and mixed polycrystalline anatase/rutile system for 0.1 L and 1.0 L exposures. The binding energy clearly depends on the nanotube polymorph.

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