Polymer-Templated Ordered Large-Pore Mesoporous Anatase-Rutile TiO₂:Ta Nanocomposite Films: Microstructure, Electrical Conductivity, and Photocatalytic and Photoelectrochemical Properties

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Abstract

We describe the polymer templating of inorganic sol-gel precursors for making thermally stable mesoporous anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films with high surface area ($S_{\text{BET}} \geq 150 \text{ m}^2\cdot\text{g}^{-1}$). Mesostructured films with cubic pore symmetry and pore sizes ranging from 17-26 nm in diameter were prepared from different diblock copolymers such as polyisobutylene-*block*-poly(ethylene oxide) and were characterized by various microscopy techniques, grazing incidence small-angle X-ray scattering, X-ray diffraction and Rietveld refinement, X-ray photoelectron spectroscopy, and impedance spectroscopy. Here, we specifically focus on the material with the smaller pores. Our research data establish that (1) the nanoscale structure can be preserved up to 900 °C, (2) anatase is the primary phase, (3) the phase composition remains constant over a broad temperature range, (4) anatase-to-rutile transformation and formation of $L\text{-Ta}_2\text{O}_5$ do not occur below 800 °C, and that (5) the films contain a non-negligible fraction of Ti^{3+} species. The latter results in a room-temperature electrical conductivity ($\sim 2.4 \text{ mS}\cdot\text{cm}^{-1}$) much higher than that reported for stoichiometric TiO_2 . Compositionally, the material can be described by the chemical formula $\text{Ta}_{0.24}\text{Ti}_{0.75}\text{O}_{2\pm\delta}$. The mesoporous nanocomposite films ($E_g \sim 3.4 \text{ eV}$) also display interesting photocatalytic properties and photoelectrochemical activity which makes them interesting for different applications such as wastewater detoxification.

Keywords

anatase, rutile, mesoporous, electrical conductivity, photocatalysis, water splitting

1. Introduction

The wide-bandgap semiconductor titanium dioxide (TiO_2) has attracted much attention since the discovery of its high photocatalytic activity in the 1970s [1-3]. Since then, a plethora of papers has appeared on the use of TiO_2 materials with different morphologies in applications such as heterogeneous (environmental) catalysis [4, 5], including water detoxification [6, 7] and water splitting [8, 9], solar energy conversion [10-12], sensing [13, 14], functional coatings [15-17] with antifogging, antibacterial, and other properties etc. Many of these have been described in detail in excellent reviews elsewhere [18-21]. TiO_2 is also very interesting from an industrial point of view. This is due, in part, to the fact that it is considered a safe substance, chemically and thermally quite stable, and is an abundant, low cost material with optical and electronic properties that can be tailored to some extent through control of both chemical composition and defect structure [22-25].

Titanium dioxide has four naturally occurring polymorphs, namely anatase, rutile, brookite, and $\text{TiO}_2(\text{B})$. Anatase with an optical band gap at approx. 3.2 eV is the most stable polymorph at the nanoscale and transformation to the thermodynamically stable rutile phase typically occurs when heated at temperatures above 600 °C [26, 27]. However, in recent years it has been shown that this transformation is not only strongly dependent on grain size, but also on microstructure, impurities, and other parameters [28]. For photocatalytic applications, nonetheless, the presence of a mixed phase with anatase as the predominant component (like in the commercial TiO_2 catalyst Degussa P25) can be beneficial due to synergistic effects [29]. The increased photocatalytic activity of Degussa P25, which contains approx. 30% rutile and 70% anatase, is most likely a result of interfacial electron transfer from rutile to anatase which decreases the recombination rate of electron-hole pairs [30, 31].

In the present work, we specifically focus on photoactive anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films, materials that as we show here, can be produced with a thermally stable pore-solid architecture, high specific surface area, and increased electrical conductivity.

Research over the past decade has clearly shown that, in particular, soft-templating methods lend themselves to the preparation of nanoscale oxides with different pore structures such as cubic and 2D-hexagonal [32-36]. Their formation relies essentially on the solution-phase coassembly of molecular or nanocrystal building blocks with a polymer structure-directing agent (SDA) to achieve periodicities reminiscent of lyotropic liquid crystal phases [35-40]. Thin films of such materials can be produced by the same coassembly methods but using an evaporation-induced self-assembly (EISA) process [41-43]. Although many different materials have been made by means of EISA, the synthesis of metal oxides with both an ordered pore structure and highly crystalline walls from molecular (sol-gel) precursors is still challenging. Part of the reason for this is the lack of appropriate polymer SDAs [44-46]. The majority of the amphiphilic polymers described in the literature have been shown to produce materials with rather small repeat distances – in other words – with wall structures that are not sufficiently thick to allow for uniform crystallization with retention of porosity.

Here, we describe the facile (swelling agent-free) polymer templating of sol-gel precursors for making truly large-pore mesoporous anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films with both tailorable pore and grain sizes and with high thermal stability. We use the material with an ordered cubic network of open 17 nm diameter pores as model system to study (1) the phase composition as a function of calcination temperature, (2) the electrical conductivity, and (3) the photocatalytic and photoelectrochemical properties. Overall, we believe that the unique

combination of high surface area and photoactivity with high thermal stability and electronic conductivity might be beneficial to broaden the scope of mesoporous TiO₂ materials.

2. Experimental section

2.1. Materials

Ta(OC₄H₉)₅ (95%), TiCl₄ (99.9%), absolute ethanol, and 2-methoxyethanol were purchased from Sigma-Aldrich. H[(CH₂CH₂)_{0.67}(CH₂CHCH₂CH₃)_{0.33}]₈₉(OCH₂CH₂)₇₉OH, referred to as KLE [34, 40, 47, 48], and H[C(CH₃)₂CH₂]_xC₆H₄(OCH₂CH₂)_yOH, referred to as PIB_x-*b*-PEO_y, were obtained from BASF SE and used as polymer SDAs [46, 49-51].

2.2. Film synthesis

First, a 50 mg portion of KLE or PIB_x-*b*-PEO_y is dissolved in a mixed solvent of 1.5 mL of absolute ethanol, 0.6 mL of 2-methoxyethanol, and 0.2 mL of H₂O. This solution is then combined with both 132 mg of Ta(OC₄H₉)₅ and 138 mg of TiCl₄. Thereafter, films with thicknesses in the sub-micrometer to nanometer range can be produced *via* dip-coating on polar substrates, including quartz glass slides as well as bare and platinum-coated Si(100) wafers. Optimal conditions include a relative humidity of 25%. After drying the as-made films for 3 min at room-temperature, the samples are transferred to an oven at 140 °C for 15 min and then heated to 300 °C using a 90 min ramp followed by aging for 12 h. To remove the polymer SDA and to achieve crystallization, the films are heated to temperatures above 600 °C at a rate of 10 °C·min⁻¹ followed by aging for 5 min and subsequent quenching to room-temperature.

2.3. Methods

Bright-field 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. Contact mode atomic force microscopy (AFM) images were collected on an Omicron VT-UHV AFM/STM at a constant force of 10 nN. X-ray diffraction (XRD) measurements were carried out on an X'Pert PRO diffractometer from PANalytical instruments. Grazing incidence small-angle X-ray scattering (GISAXS) patterns were collected at the German synchrotron radiation facility HASYLAB at DESY on beamline BW4. The sample-to-detector distance was approx. 1820 mm. X-ray photoelectron spectroscopy (XPS) data 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 at 50° electron takeoff angle. The C 1s signal from adventitious hydrocarbon at 284.8 eV was used as the energy reference to correct for charging. Optical absorption measurements were carried out on a Perkin Elmer Lambda 900 UV-vis-NIR spectrophotometer. A substrate made from quartz glass and an aluminum mirror served as a reference for transmission and reflection measurements, respectively. N₂-physisorption measurements were conducted at 77 K using the Autosorb-6 automated gas adsorption station from Quantachrome Corporation. The film thickness was determined with an Alpha Step IQ Surface Profiler from KLA Tencor. For Rietveld refinement, the software FullProf was used. In the refinement, the half-width parameters V , W , and X were kept constant at instrumental values determined using LaB₆. The electrical conductivity was determined by two-electrode ac impedance measurements using the SP-300 potentiostat from BioLogic in the frequency range from 7 MHz to 1 Hz. The voltage amplitude was 40 mV. Prior to measurements, the approx. 250 nm thick films were first vacuum dried at 120 °C and then mounted in gas-tight argon filled pouch bags with electrical contacts. For photodegradation

experiments, 10 mL of an aqueous solution of 15 μ M methylene blue was exposed to 254 nm light in the presence of an approx. $250 \text{ nm} \times 4 \text{ cm}^2$ KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite film. An 8 W lamp (Benda NU-8 KL) was used as the light source. Photoelectrochemical experiments were carried out in a rectangular PMMA reactor ($\sim 3 \times 5 \times 10 \text{ cm}^3$) equipped with quartz glass window using the SP-150 potentiostat from BioLogic. A two-electrode system was used, consisting of an approx. 300 mm^2 platinum foil as the counter electrode and an approx. $19.6 \text{ mm}^2 \times 250 \text{ nm}$ KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite film on platinum-coated Si(100) wafer as the photoanode, both immersed in 0.1 M NaOH(aq) electrolyte. A 150 W Xe arc lamp (Lot-Oriel) was used as the light source. The light intensity was measured using a power meter (OPHIR, Nova-Oriel) and a thermopile (OPHIR).

3. Results and discussion

In this work, we take advantage of the superior templating properties of poly(ethylene-*co*-butylene)-*block*-poly(ethylene oxide) [referred to as KLE] and polyisobutylene-*block*-poly(ethylene oxide) [referred to as $\text{PIB}_x\text{-}b\text{-PEO}_y$] diblock copolymers to achieve thermally stable mesoporous anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films. KLE has proven in the past to be very efficient for making mesostructured non-silicate oxides with cubic pore symmetry and highly crystalline walls [34, 44, 46, 52-55]. This is due, in part, to the fact that KLE produces materials that are capable of accommodating sub-20 nm crystallites while retaining nanoscale structure. Although we focus here on KLE-derived films, we also show that the different $\text{PIB}_x\text{-}b\text{-PEO}_y$ diblock copolymers used lend themselves well to the synthesis of mesoporous metal oxides with large repeat distances [46, 49-51]. Overall, both types of polymer SDAs are found to

produce materials with sufficiently thick walls that can be fully crystallized with retention of porosity.

In short, in a typical synthesis both the inorganic sol-gel precursors and the polymer SDA are dissolved in a mixed solvent of ethanol, water, and 2-methoxyethanol. After stirring the solution for a couple of minutes, films with thicknesses in the sub-micrometer to nanometer range can be readily produced *via* dip-coating on polar substrates. A multistep thermal treatment is then used to stabilize the framework by driving condensation, combust the diblock copolymer to make the material porous, and to crystallize the amorphous (glassy) walls.

3.1. Nanoscale morphology and microstructure

The pore structure of the KLE-, PIB₁₀₇-*b*-PEO₁₅₀-, and PIB₅₃-*b*-PEO₇₅-templated anatase-rutile TiO₂:Ta nanocomposite films calcined at 700 °C was analyzed by a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Panels (a–c) of **Figure 1** show high-magnification top view SEM images which indicate that the pore cavities at the solid-air interface (top surface) are open and that the average in-plane pore size can be tailored from 17 nm for KLE to 26 nm for PIB₁₀₇-*b*-PEO₁₅₀ (see also low-magnification SEM images in **Figure S1** in the Supporting Information [SI]). The latter dimension is among the largest reported so far for polymer-templated mesoporous TiO₂ materials produced from molecular precursors without using swelling agents. While the network of pores seems to be disordered for both PIB_{*x*}-*b*-PEO_{*y*}-templated samples, KLE-derived films reveal a highly ordered hexagonal top surface. These observed trends in terms of pore ordering and repeat distance (*d*-spacing) are further supported by small-angle X-ray scattering (SAXS) in Bragg-Brentano geometry (see SAXS patterns in **Figure S2** in the SI). In addition, SEM shows

that the different samples are crack-free on the micrometer level. From cross-sectional SEM in panels (d) and (e) of **Figure 1** it can be clearly seen that the pore cavities are highly anisotropic in shape due to unidirectional volume contraction during thermal treatment and that the nanoscale structure persists throughout the bulk of the films. Panels (f–i) of **Figure 1** show results from TEM and AFM imaging as well as from selected-area electron diffraction (SAED). These data were obtained on the KLE-templated $\text{TiO}_2\text{:Ta}$ films and establish that (1) the samples are flat (contrast range 0–8 nm) with a root-mean-square roughness of less than 1.5 nm, (2) the pores are uniform in size and shape, (3) the crystallization of the initially amorphous walls comes at little cost to the ordering of the mesostructure, and that (4) anatase is the primary phase.

Taken together, the microscopy results lead us to conclude that the pore structure at the top surface and in the interior of the polymer-templated $\text{TiO}_2\text{:Ta}$ nanocomposite films is well developed after calcination at 700 °C. Furthermore, they indicate that the material is not single phase, unlike pure mesoporous TiO_2 materials that were treated similarly [50, 52, 53].

Figure 1. Microstructure of PIB₁₀₇-*b*-PEO₁₅₀-templated (a, d), PIB₅₃-*b*-PEO₇₅-templated (b), and KLE-templated (c, e–i) anatase-rutile TiO₂:Ta nanocomposite films calcined at 700 °C. (a–c) High-magnification top view SEM images. (d, e) Cross-sectional SEM images at a tilt of 80°. (f) Contact mode AFM height image. The contrast covers height variations in the 0–8 nm range.

(g) Bright-field TEM image. (h) HRTEM image. (i) SAED pattern showing typical Debye-Scherrer rings for anatase and weak reflections for rutile TiO₂.

As mentioned above, in the following we specifically focus on the KLE-templated TiO₂:Ta films. To probe the thermal stability of the nanoscale structure, *ex situ* grazing incidence small-angle X-ray scattering (GISAXS) measurements were carried out. **Figure 2** shows GISAXS patterns obtained on a sample calcined at 300 °C (a) for 12 h and 600 °C (b), 800 °C (c), and 900 °C (d) for 5 min, respectively. Material with a glassy – fully amorphous – wall structure produces patterns with distinct scattering maxima that can be indexed in terms of a face-centered cubic (fcc) mesostructure with (111) orientation. Such structure is often found for polymer-templated thin films and is further consistent with the hexagonal symmetry of the top surface (see also SEM and AFM images in **Figure 1**). Both fundamental and higher order maxima can be clearly observed, which emphasizes the ordered nature of the porosity. The fact that the reflections appear as lines, rather than spots, is likely due to stacking faults. The elliptical shape of the GISAXS patterns indicates large lattice contraction of more than 80% in the out-of-plane direction. This is not very surprising considering that the samples were produced from molecular precursors *via* sol-gel methods. It also provides an explanation for the presence of oblate pores, as is evident from cross-sectional SEM. It can be seen, nonetheless, that the unidirectional volume contraction is practically completed after aging at 300 °C. Furthermore, it is apparent that the nanoscale structure is indeed only affected to a limited extent throughout the crystallization process ($T_{\text{onset}} \geq 600$ °C). Even the out-of-plane scattering, which is typically lost first as a result of the morphological anisotropy of the films, is still visible after calcination at

800 °C. This finding emphasizes the exceptional thermal stability of the ordered large-pore mesoporous TiO₂:Ta films employed in this work.

In summary, GISAXS corroborates the microscopy data and confirms that the nanoscale structure is of high quality, similar to that reported in the literature for polymer-templated silicate materials, and that the pore-solid architecture can be preserved up to temperatures as high as 900 °C.

Figure 2. GISAXS patterns at an angle of incidence $\beta = 0.2^\circ$ obtained on a KLE-templated TiO₂:Ta film calcined at different temperatures of 300 °C (a) for 12 h, and 600 °C (b), 800 °C (c), and 900 °C (d) for 5 min, respectively. Scattering vector $\mathbf{q}$ components are given in nm⁻¹.

The porous properties of the KLE-templated anatase-rutile TiO₂:Ta nanocomposite films calcined at 700 °C and 800 °C were also examined by N₂-physisorption measurements at 77 K.

For these experiments, the films were deposited onto 300 micron thick, double side polished silicon wafers, cut into small pieces, and then transferred to a cylindrical sorption cell. The measured BET surface areas were always larger than 1 m², which is regarded as sufficient to make the results reliable and representative. Panels (a) and (b) of **Figure 3** show typical adsorption/desorption isotherms of type-IV, as expected for mesoporous materials. Data analysis provides Brunauer-Emmett-Teller (BET) surface areas of 295 m²·cm⁻³ and 245 m²·cm⁻³ and pore volumes of 1.94·10⁻³ cm³ and 1.91·10⁻³ cm³ (equivalent to ~57% porosity), respectively. Assuming densities of 3.87 g·cm⁻³ and 4.13 g·cm⁻³ for anatase and rutile, respectively, and a relative anatase-to-rutile ratio of 0.82:0.18 (see Rietveld refinement results in **Table 1**) in the films calcined at 700 °C, the BET-value of 295 m²·cm⁻³ corresponds to 175 m²·g⁻¹ (146 m²·g⁻¹ @800 °C). We estimate the error margin as being ±10%. Lastly, we note that the shift of the lower hysteresis closure point to larger p/p_0 values is likely caused by slight changes in pore geometry during grain growth.

Figure 3. N₂-adsorption/desorption isotherms for approx. 640 nm × 52 cm² KLE-templated anatase-rutile TiO₂:Ta nanocomposite films calcined at 700 °C (a) and 800 °C (b).

3.2. Phase composition and bonding configuration

In order to better understand the effect of tantalum on the crystallization behavior and to obtain insight into the overall chemical composition and the oxidation states, a series of X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements was carried out. Panel (a) of **Figure 4** shows XRD patterns obtained on a KLE-templated $\text{TiO}_2\text{:Ta}$ film calcined at 650 °C, 750 °C, and 850 °C. The onset of crystallization is found at $T \geq 600$ °C and polycrystalline anatase-rutile mixed phases are achieved for all temperatures. The XRD data were also analyzed using Rietveld analysis to obtain microstructural information, including unit-cell parameters, average crystallite size, and phase composition (according to procedure of Hill and Howard) [56]. The refinement was carried out using a Thompson-Cox-Hastings pseudo-Voigt profile function assuming that line broadening of the deconvoluted profile results from the small crystallite size and microstrain in the lattice. The quality of the refinement was assessed by the magnitude of the discrepancy factor (R_{wp}) and the goodness-of-fit (χ^2). **Table 1** summarizes the main results from Rietveld refinement and panels (b) and (c) of **Figure 4** display the changes in crystallite size and phase composition with calcination temperature. From the latter data it can be clearly seen that anatase is in fact the primary phase and that the anatase-to-rutile ratio (based on weight fractions) remains virtually constant over a broad temperature range from 650 °C to 800 °C. In contrast, the average crystallite sizes increase rapidly above 700 °C but tend to level off at $T \geq 800$ °C. Interestingly, both polymorphs reveal a similar trend in grain growth. Partial anatase-to-rutile transformation and formation of $L\text{-Ta}_2\text{O}_5$ due to nanoscale phase separation are observed after calcination at 850 °C. This result helps explain the grain growth behavior and further indicates that films calcined at temperatures less than or equal to 800 °C not only have a well retained pore structure, but are also more defined in terms of phase composition.

Figure 4. (a) XRD patterns obtained on a KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite film calcined at 650 °C (A), 750 °C (B), and 850 °C (C). The solid-line curves are simulated patterns by Rietveld refinement. The region between $2\theta = 32.0^\circ$ and 34.0° (containing a strong peak from the Si(100) wafer used as substrate) was excluded in the refinement. Anatase peaks are indexed in blue and those for rutile in black. (b, c) Average crystallite size and relative weight fraction ($\pm 1.54\%$) for both polymorphs as a function of calcination temperature. Solid lines are for eye guidance only.

Table 1. Refined structural parameters by Rietveld analysis.

Phase	Anatase					Rutile				
Space group	$I4_1/amd$ (141)					$P4_2/mnm$ (136)				
Lattice parameter [$\text{\AA}$]	$a = b = 3.805(4)$ $c = 9.483(5)$					$a = b = 4.629(6)$ $c = 2.983(1)$				
Unit-cell volume [$\text{\AA}^3$]	137.37(4)					64.06(3)				
Calcination temperature [$^\circ\text{C}$]	650	700	750	800	850	650	700	750	800	850
Average crystallite size	10.7	11.2	15.4	17.0	17.5	6.5	6.7	8.6	11.3	11.8

[nm]										
Relative weight fraction [%]	82.8	81.8	83.3	83.0	80.2	17.2	18.2	16.7	17.0	19.8
R_{wp} [%]	4.67	4.82	5.05	4.91	5.03	4.67	4.82	5.05	4.91	5.03
Goodness of fit, χ^2	1.92	1.96	2.02	2.00	2.72	1.92	1.96	2.02	2.00	2.72

Both the chemical composition and the oxidation state of titanium and tantalum in KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films calcined at 700 °C was examined in detail using XPS. Panels (a–c) of **Figure 5** display detail spectra of the O 1s, Ti 2p, and Ta 4f levels. A survey spectrum is shown in **Figure S3** in the SI. The O 1s spectrum in panel (a) reveals two different oxygen bonding states. The main peak centered at (530.67 ± 0.05) eV can be attributed to lattice oxygen while the minor one at (531.60 ± 0.05) eV can be associated with OH-groups at the top surface. The Ti 2p spectrum in panel (b) is more complex and was fitted using spin-orbit splitting parameters with relative area ratios of 1:2 for the different $2p_{1/2}$ and $2p_{3/2}$ component peaks, peak-to-peak separations of 5.88 eV (for Ti^{4+}) and 5.80 eV (for Ti^{3+}), and with different full width at half maximum (FWHM) values. The reason for the different FWHM is due to Coster-Kronig broadening effects [57]. The main peaks at (465.20 ± 0.05) eV and (459.32 ± 0.05) eV for the $2p_{1/2}$ and $2p_{3/2}$ lines, respectively, are characteristic of Ti^{4+} and those at binding energies of (463.28 ± 0.05) eV and (457.48 ± 0.05) eV can be attributed to Ti^{3+} [58, 59]. The presence of Ti^{3+} ions is not surprising and can be explained by the aliovalent ionic substitution of Ta^{5+} (64 pm) for Ti^{4+} (61 pm). Quantitative analysis of the peak areas provides a Ti^{3+} content of approx. 11% relative to the total titanium content. At first glance, this value seems too low. However, charge compensation is not necessarily only achieved by Ti^{3+} species ($\text{Ti}_{\text{Ti}}^{3+}$), but also by incorporation of interstitial oxygen (O_i'') and formation of titanium vacancies

(V_{Ti}^{III}) [60]. Furthermore, we note that the Ti 2p spectrum also contains the Ta 3p_{1/2} line at (464.80 ± 0.05) eV. In contrast, the Ta 4f spectrum shows a single doublet due to spin-orbit splitting with symmetric peaks with an area ratio of 3:4 at (28.55 ± 0.05) eV and (26.65 ± 0.05) eV for the 4f_{5/2} and 4f_{7/2} lines, respectively, thereby indicating the 5+ oxidation state [61]. The atomic titanium-to-tantalum ratio is found to be 3.14 consistent with the precursor ratio used in the synthesis. In summary, XPS establishes that the mesoporous thin films are well-defined at the atomic level and contain a non-negligible fraction of Ti³⁺ ions – they can be described by the chemical formula Ta_{0.24}Ti_{0.75}O_{2±δ}.

Figure 5. Typical XPS detail spectra for the O 1s (a), Ti 2p (b), and Ta 4f (c) levels of KLE-templated anatase-rutile TiO₂:Ta nanocomposite films calcined at 700 °C in air. Solid-line curves in black, red, and blue represent fits to the data assuming Gaussian-Lorentzian peak shape while those in green correspond to the sum of the peak fits. In panel (b), the Ta 4p_{1/2} line is shown in black and spin-orbit peaks for Ti³⁺ and Ti⁴⁺ in red and blue, respectively. The Shirley method was applied to subtract backgrounds.

3.3. Electrical conductivity

The electrical conductivity of approx. 250 nm thick KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films calcined at 700 °C was determined by two-electrode ac impedance measurements. A schematic of the setup used is shown in the inset of **Figure 6**. To keep the impact of water and oxygen on the conductivity at a minimum, the films were first vacuum dried at 120 °C and then sealed in argon filled pouch bags. The conductivity – electronic in nature – was determined to be $2.4 \text{ mS}\cdot\text{cm}^{-1}$ at 25 °C. This value is in the range reported for stabilized TiO_2 materials with nanocrystalline grain structures. In contrast, highly stoichiometric TiO_2 typically has a conductivity five to six orders of magnitude smaller [62, 63]. The significant increase in room-temperature conductivity can be explained by (partial) incorporation of Ta^{5+} ions into the TiO_2 lattice and formation of Ti^{3+} species, as mentioned in the section on XPS above [64, 65]. However, we note that the location of “dopants” in nanoscale materials is largely unclear, although it is believed that cationic dopants are most stable in lattice positions. The activation energy for charge transfer was determined by temperature-dependent impedance measurements from the linear slope of $\ln(\sigma T)$ versus $1/T$ and calculated to be $\sim 0.11 \text{ eV}$ consistent with previous studies. For reasons of readability, however, $\lg(\sigma)$ is plotted against $1000/T$ in **Figure 6**. The increase in conductivity with increasing temperature clearly indicates the semiconducting behavior of the mesoporous material. The room-temperature impedance spectrum in the inset of **Figure 6** can be fitted well using a parallel RQ -circuit (R – ohmic resistance, Q – constant phase element with exponent equal to 0.973). Since the material is nanocrystalline, the contribution of grain boundaries to the overall impedance is significant [66]. This might also be the reason why only one semicircle is observed. A constant phase element (non-ideal capacitor) was used in the equivalent circuit instead of a pure capacitor because of the

slightly oblate shape of the semicircle. Furthermore, we note that a possible contribution from the gold electrodes (on the top surface) in the frequency range investigated can be largely ruled out.

Figure 6. Arrhenius-type plot for the temperature-dependent electrical conductivity of approx. 250 nm thick KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films calcined at 700 °C. The activation energy for charge transfer is ~ 0.11 eV. Inset: (bottom) Nyquist representation (Cole-Cole plot) of impedance data measured at 25 °C. The diameter of the semicircle equals to $\sim 1.6 \cdot 10^6$ Ohm. (top) Schematic of the setup used. The quartz glass substrate is shown in green, the mesoporous film in blue, and the gold electrodes on the top surface in yellow. The distance between the $2.5 \cdot 10^{-5} \text{ cm}^2$ ($a \cdot b$) electrodes was 0.1 cm (l).

3.4. Optical, photocatalytic, and photoelectrochemical properties

For photocatalytic and photoelectrochemical applications, knowledge of optical properties is critical. In semiconductors, the relationship between the photon energy of incident light ($h \cdot \nu$) and the absorption coefficient, α , is given by the following equation: $\alpha \propto (h \cdot \nu - E_g)^n$ – with $h \cdot \nu \geq E_g$ –

where E_g is the band gap energy and the exponent, n , represents the type of transition. As reported in the literature, bulk TiO_2 is considered to be an indirect band gap material with E_g values close to 3.2 eV and 3.0 eV for anatase and rutile, respectively [67, 68]. However, in recent years it has been shown that both the direct and the indirect transition may occur at similar energy in nanocrystalline TiO_2 and that a blue shift in the absorption spectrum may be expected when the grain size enters the sub-20 nm regime due to finite size (quantum confinement) effects [69, 70]. From **Figure 7** we estimate the indirect and direct band gap energies as being (3.45 ± 0.10) eV and (3.50 ± 0.10) eV, respectively, for the KLE-templated $\text{TiO}_2\text{:Ta}$ nanocomposite films calcined at 700 °C. Furthermore, there is a much less-intense indirect transition at (3.05 ± 0.10) eV, which we hypothesize might be the band gap of the rutile component.

Figure 7. Direct (○) and indirect (□) optical transitions in KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films calcined at 700 °C. The intersections of the dashed lines with the x -axis yield the band gap energies.

The photocatalytic activity of the KLE-templated anatase-rutile TiO₂:Ta nanocomposite films calcined at 700 °C and 800 °C was examined by photobleaching experiments using methylene blue (MB) as the model pollutant. The performance data in **Figures 8** and **S5** in the SI show that (1) MB is rather stable in the absence of any catalyst under UV-light irradiation, but undergoes rapid degradation in the presence of a mesoporous TiO₂:Ta catalyst, (2) the shift of the absorption maxima (indication of only partial cleavage of chromophores) during irradiation is negligible, and that (3) the degradation kinetics are pseudo-first-order. We note that the aqueous MB solution was not irradiated over the first 15 min to ensure adsorption/desorption equilibrium of MB between solution and catalyst. The degradation rates were determined by linear regression of $\ln(c/c_0)$ versus time (green lines in panel (b) in **Figure 8**) and ranged from $(1.8 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$ to $(1.9 \pm 0.1) \times 10^{-2} \text{ min}^{-1}$ consistent with literature values for pure and stabilized porous TiO₂ materials [71-74]. However, direct comparison is rather difficult due to differences in material morphologies. Nonetheless, the results suggest that the anatase-rutile TiO₂:Ta nanocomposite films studied here display interesting photocatalytic properties and therefore show promise for applications such as wastewater treatment (i.e., photocatalytic mineralization of organic pollutants). This is further supported by the finding that the mesoporous samples are capable of maintaining stable photocatalytic performance over several cycles since there was no notable decline in activity, e.g., due to photocorrosion (see also SEM images after photobleaching experiments in **Figure S4** in the SI). As is evident from the data in **Figures 8b** and **S5** in the SI, films calcined at 800 °C exhibit slightly higher activity. The reason for this is not fully understood. However, considering the fact that the BET surface is lower by approx. 30 m²·g⁻¹, this result might be associated with the reduced number of grain boundaries because the

crystallite size is the only major difference among the samples (see also SEM and TEM images of films calcined at 800 °C in **Figure S6** in the SI).

Figure 8. Degradation of methylene blue without ($\triangle$) and with approx. $250 \text{ nm} \times 4 \text{ cm}^2$ KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite film catalysts calcined at 700 °C ($\square$) and 800 °C ($\circ$) under irradiation with 254 nm light. It should be noted that the aqueous dye solution was not irradiated during the course of the first 15 min. Green lines are linear fits to the data.

Lastly, the photoelectrochemical properties were analyzed by water splitting experiments ($\text{H}_2\text{O} \xrightarrow{h\nu} 1/2\text{O}_2 + \text{H}_2$). **Figure 9** shows typical current-voltage (I - V) profiles for approx. 250 nm thick KLE-templated anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite film photoanodes calcined at 700 °C both under illumination ($\sim 200 \text{ mW}\cdot\text{cm}^{-2}$) and in the dark. For these experiments, linear potential sweeps were performed at $2 \text{ mV}\cdot\text{s}^{-1}$. The open circuit voltage (V_{oc}) is found to be approx. -0.55 V when exposed to illumination. At anodic voltages (i.e., $V > V_{\text{oc}}$) a significant increase in current response is observed until a plateau is reached with an average current density of approx. $0.25 \text{ mA}\cdot\text{cm}^{-1}$ for the voltage range from -0.2 V to $+0.7 \text{ V}$. Voltages above $+0.7 \text{ V}$ result in a

steep increase in current response. A similar trend is also observed for the cell in the dark, except for the fact that the measured current densities at voltages equal to or smaller than +0.6 V are negligible. This finding indicates that the response below +0.6 V can be associated with the photoelectrochemical decomposition of water. Using the following equation:

$$\eta_{CE} = I_{ph} \cdot (1.229V - V_{bias}) \cdot P_{irr}^{-1}$$

where I_{ph} is the photocurrent, P_{irr} is the irradiation power (~40

mW), and V_{bias} represents the applied bias voltage, we can calculate the conversion efficiency (η_{CE}) for the water splitting reaction. The highest conversion efficiency of approx. 0.16% is obtained without external bias. This value is significantly lower than the theoretical efficiency of 0.8% [75] for a semiconductor with an optical band gap at 3.4 eV, but is comparable to previous results report by Hartmann *et al.* for polymer-templated mesoporous TiO₂ thin films [50].

Figure 9. *I-V*-characteristics for approx. 250 nm thick KLE-templated anatase-rutile TiO₂:Ta nanocomposite film photoanodes calcined at 700 °C under illumination (○) and in the dark (□).

Linear potential sweeps were carried out at a rate of 2 mV·s⁻¹.

Overall, the data shown in this section demonstrate that the mesoporous anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films have interesting material properties which make them, for example, attractive for application in environmental catalysis. However, considering both the comparably high electrical conductivity and the nanoscale porosity, they might also serve as photochemically-active transparent conductive oxide (TCO) layers (e.g., in dye-sensitized solar cells and gas sensors). Future work will be dedicated to obtaining a better understanding of the relationships among photocatalytic performance, grain size, BET surface area, and phase composition, as well as to finding out if any of the two polymorphs can be stabilized at high temperature by selective incorporation of different aliovalent dopants into the TiO_2 lattice [76] and if the electrical conductivity can be tailored (and if so, to what extent).

4. Conclusion

Thermally stable ordered large-pore mesoporous thin films of anatase-rutile $\text{TiO}_2\text{:Ta}$ have been successfully synthesized by facile solution-phase coassembly of inorganic sol-gel precursors with different amphiphilic diblock copolymers. Our research data indicate that all films are mesostructured with cubic pore symmetry and that pore size can be effectively tailored from 17 nm to 26 nm. In the present work, we specifically focus on the material with the smaller pores which, compositionally, can be described by the chemical formula $\text{Ta}_{0.24}\text{Ti}_{0.75}\text{O}_{2\pm\delta}$. We find that (1) the pore structure is only affected to a limited extent up to calcination temperatures as high as 800 °C, (2) the phase composition (~20% rutile and 80% anatase) remains rather constant, (3) the BET surface area is in the range $150 \text{ m}^2\cdot\text{g}^{-1} - 180 \text{ m}^2\cdot\text{g}^{-1}$, and that (4) the room-temperature electrical conductivity is significantly increased compared to bulk forms of highly stoichiometric TiO_2 due to the presence of Ti^{3+} in the lattice. Photoactivity studies further establish the high

quality of the mesoporous anatase-rutile $\text{TiO}_2\text{:Ta}$ nanocomposite films and indicate their potential for use in the forefront field of environmental catalysis.

Appendix A. Supplementary data

Additional data from (1) TEM and SEM imaging, (2) photodegradation experiments, and (3) SAXS and (4) XPS measurements can be found in the online version of the manuscript.

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